Seymour/Carraher's

Polymer Chemistry

Sixth Edition
Revised and Expanded

Charles E. Carraher, Jr.

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Boca Raton, and
Florida Center for Environmental Studies
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To Raymond Seymour—educator, scientist,
pioneer, prophet, historian, family man,
and friend—we miss you

Foreword

Polymer science and technology has developed tremendously over the last few decades, and the production of polymers and plastics products has increased at a remarkable pace. By the end of 2000, nearly 200 million tons per year of plastic materials were produced worldwide (about 2% of the wood used, and nearly 5% of the oil harvested) to fulfill the ever-growing needs of the *plastic age*; in the industrialized world plastic materials are used at a rate of nearly 100 kg per person per year. Plastic materials with over $250 billion dollars per year contribute about 4% to the gross domestic product in the United States. Plastics have no counterpart in other materials in terms of weight, ease of fabrication, efficient utilization, and economics.

It is no wonder that the demand and the need for teaching in polymer science and technology have increased rapidly. To teach polymer science, a readable and up-to-date introductory textbook is required that covers the entire field of polymer science, engineering, technology, and the commercial aspect of the field. This goal has been achieved in Carraher's textbook. It is eminently useful for teaching polymer science in departments of chemistry, chemical engineering, and material science, and also for teaching polymer science and technology in polymer science institutes, which concentrate entirely on the science and technologies of polymers.

This sixth edition addresses the important subject of polymer science and technology, with emphasis on making it understandable to students. The book is ideally suited not only for graduate courses but also for an undergraduate curriculum. It has not become more voluminous simply by the addition of information—in each edition less important subjects have been removed and more important issues introduced.

Polymer science and technology is not only a fundamental science but also important from the industrial and commercial point of view. The author has interwoven discussion of these subjects with the basics in polymer science and technology. Testimony to the high acceptance of this book is that early demand required reprinting and updating of each of the previous editions. We see the result in this new significantly changed and improved edition.

Otto Vogl
Herman F. Mark Professor Emeritus
Department of Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts

Preface

An explosive scientific and technological revolution is underway and at its center are polymers. This revolution is the result of a number of factors that complement one another. These factors include a better understanding of the science of materials and availability of new and refined materials, synthetic techniques, and analytical tools. Much of this revolution is of a fundamental nature and it is explored in the latest edition of this text. These advances are often based on new and extended understanding and application of basic principles initially presented in the core chemistry courses (organic, physical, inorganic, analytical, and biological).

Polymer Chemistry complies with the advanced course definition given by the American Chemical Society Committee on Professional Training, building on the foundations laid in general, organic, physical, analytical/instrumentation, and inorganic chemistry. It also includes all the major and optional topics recommended in the syllabus adopted by the joint polymer education committee of the American Chemical Society (Appendix D: Syllabus). The text integrates and interweaves the important core topic areas. The core topics are interrelated with information that focuses on polymer topics. This assists students in integrating their chemical knowledge and illustrates the connection between theoretical and applied chemical information. Also, industrial practices and testing procedures and results are integrated with the theoretical treatment of the various topics, allowing the reader to bridge the gap between industrial practice and the classroom. It is written so that chapters can be taken out of order and not all the chapters need to be covered to gain an adequate appreciation of the science of polymers. Many of the chapters begin with theory, followed by application. Some readers will elect to read the more descriptive chapters dealing with polymer types before looking at the analytical/analysis/properties chapters.

This book is user friendly—it is appropriate as an advanced undergraduate text or an introductory-level graduate-level course text. It can serve as the text for the initial course in a series taken by a student, or it can be the lone polymer text read by a student in the study of polymers. Students of chemistry, materials, engineering, medicine, biochemistry, physics, and geology will benefit from an understanding of the material found in this text.

The application and theory of polymers continues to expand. This new edition reflects this growth and the continually expanding role of polymers. There is an increased emphasis on pictorializing, reinforcing, integrating, and interweaving the basic concepts.

The first chapter is shorter in order to allow time for student orientation. However, the other chapters should not require more than a week's time each. Each chapter is essentially self-contained, but each relates to the other chapters. Whenever possible, difficult concepts are distributed and reinforced over several chapters. A glossary, biography, suggested questions (and answers), and learning objectives/summary are included at the end of each chapter.

Application and theory are integrated so that they reinforce one another. This is true for all the various important and critical types of polymers including synthetic, biological, organometallic, and inorganic polymers. The principle that the basic concepts that apply to one grouping of polymers apply to all the other types of polymers is emphasized.

The updating of analytical, physical, and spectral characterization techniques continues, including expanded coverage of the theory and results arising from atomic force microscopy and scanning probe microscopy. Special sections dealing with industrially important polymers are included, and the section dealing with soluble stereoregulating catalysis has been expanded.

There is still an emphasis on naturally occurring polymers, and discussions of supercoiling, replication, and compacting are included. As before, the interplay between natural and synthetic polymers is emphasized.

A number of miscellaneous topics have been drawn together in one chapter, which includes sections on conductive polymers, smart materials, protomics, human genome, optical fibers, material selection charts, carbon nanotubes, and liquid crystals.

Emphasis on nanotechnology and nanomaterials remains with added or expanded sections dealing with zeolites, nanotubes, nanocomposites, molecular wires, dendrites, and self assembly. The chapter on polymer technology and processing has been rewritten and expanded. The section listing Web sites has been updated.

The nomenclature section has been enlarged, and a new appendix on the stereogeometry of polymers has been added.

Additional aids and appendixes are included: how to study, nomenclature, over 1500 trade names, about 400 citations to appropriate *Journal of Chemical Education* and *Polymer News* articles, Web sites dealing with polymer topics, and over 100 structures of common polymers.

Charles E. Carraher, Jr.

Acknowledgments

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I also thank the following for their special contributions to the book: Charles Gebelein, Les Sperling, Anglo Volpe, Stam Israel, Carl Wooten, Rita Blumstein, Eckhard Hellmuth, Frank Millich, Norman Miller, Rudy Deanin, Guy Donaruma, Leo Mandelkem, R. V. Subramanian, Charles Pittman, Brian Currell, C. Bamford, Roger Epton, Paul Flory, Charles Overberger, William Bailey, Jim O’Donnell, Rob Burford, Edgar Hardy, John H. Coates, Don Napper, Frank Harris, G. Allan Stahl, John Westerman, William A. Field, Nan-Loh Yang, Sheldon Clare, E. N. Ipiotis, D. H. Richards, G. Kirshenbaum, A. M. Sarquis, Lon Mathias, Sukumar Maiti, S. Temin, Yoshinobu Naoshima, Eberhard Neuse, John Sheats, George Hess, David Emerson, Kenneth Bixgorin, Thomas Miranda, M. B. Hocking, Marsha Colbert, Joseph Lagowski, Dorothy Sterling, Amanda Murphy, John Kloss, Qingmao Zhang, Bhoomin Pandya, Ernest Randolph, Alberto Rivalta, and Fengchen He.

This book could not have been written without the long-time efforts of Professor Herman Mark, who was one of the fathers of polymer science.

For the fourth edition, a special thanks for the assistance of Colleen Carraher.

I acknowledge the kind permission of Gerry Kirshenbaum and *Polymer News* for allowing us to use portions of articles that have appeared in *Polymer News*.

Finally, I thank Edward S. Wilks for his help with the section on “Chemical Abstracts–Based Polymer Nomenclature.”

Polymer Nomenclature

As with most areas of science, names associated with reactions, particular chemical and physical tests, etc., were historically derived with few overall guiding principles. Further, the wide diversity of polymer science permitted a wide diversity in naming polymers. Even though the International Union of Pure and Applied Chemistry (IUPAC) has a long-standing commission associated with the nomenclature of polymers [reports include "Report on nomenclature in the field of macromolecules," *Journal of Polymer Science, 8*, 257 (1952); "Report on nomenclature dealing with steric regularity in high polymers," *Pure and Applied Chemistry, 12*, 645 (1966); "Basic definitions of terms relating to polymers," *IUPAC Information Bull*. App., *13*, 1 (1971); and "Nomenclature of regular single-strand organic polymers," *Macromolecules, 6*(2), 149 (1973)], most of these suggestions for naming of simple polymers have not yet been accepted by many in the polymer science community.

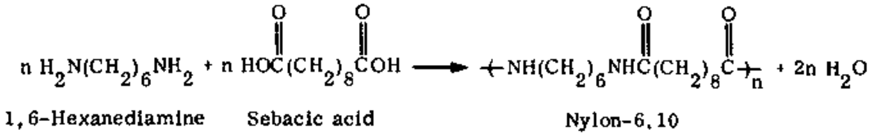
Although there is wide diversity in the practice of naming polymers, we will concentrate on the most utilized systems.

COMMON NAMES

Little rhyme or reason is associated with the common names of polymers. Some names are derived from the place of origin of the material, such as *Hevea brasiliensis*—literally "rubber from Brazil"—for natural rubber. Other polymers are named after their discoverer, as is Bakelite, the three-dimensional polymer produced by condensation of phenol and formaldehyde, which was commercialized by Leo Baekeland in 1905.

Portions adapted from C. Carraher, G. Hess, and L. Sperling, *J. Chem. Ed., 64*(1), 36 (1987) and L. H. Sperling W. V. Metanomski, and C. Carraher, *Appl Polym Science* (C. Craver and C. Carraher, eds.), Elsevier, New York, 2000.

For some important groups of polymers, special names and systems of nomenclature were invented. For example, the nylons were named according to the number of carbons in the diamine and carboxylic acid reactants (monomers) used in their syntheses. The nylon produced by the condensation of 1,6-hexanediamine (6 carbons) and sebacic acid (10 carbons) is called nylon-6,10.

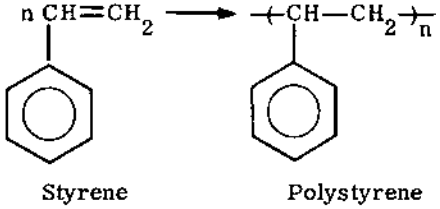


$$n\,H_2N(CH_2)_6NH_2 + n\,HO\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OH \longrightarrow -\!\!\left(NH(CH_2)_6NH\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}\right)_{\!n}\!\!- + 2n\,H_2O$$

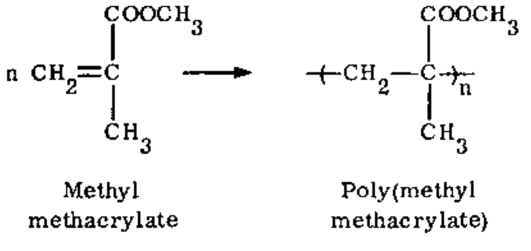
Similarly, the polymer from 1,6-hexanediamine and adipic acid (each with 6 carbons) is called nylon-6,6 or nylon-66, and the nylon from the single reactant caprolactam (6 carbons) is called nylon-6.

SOURCE-BASED NAMES

Most polymer names used by polymer scientists are source-based; i.e., they are based on the common name of the reactant monomer, preceded by the prefix "poly." For example, polystyrene is the most frequently used name for the polymer derived from the monomer 1-phenylethene, which has the common name styrene.

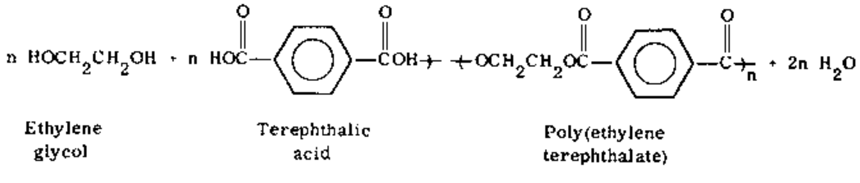


The vast majority of polymers based on the vinyl group ($CH_2{=}CHX$) or the vinylidene group ($CH_2{=}CX_2$) as the repeat unit are known by their source-based names. For example, polyethylene is derived from the monomer ethylene, poly(vinyl chloride) from the monomer vinyl chloride, and poly(methyl methacrylate) from methyl methacrylate:



$$n\,CH_2{=}\overset{\overset{COOCH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} \longrightarrow -\!\!\left(CH_2-\overset{\overset{COOCH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\right)_{\!n}\!\!-$$

Many condensation polymers are also named in this manner. In the case of poly(ethylene terephthalate), the glycol portion of the name of the monomer, ethylene glycol, is used in constructing the polymer name, so that the name is actually a hybrid of a source-based and a structure-based name.



This polymer is well known by trade names, such as Dacron, or its common grouping, polyester.

Although it is often suggested that parentheses be used in naming polymers of more than one word [like poly(vinylidene chloride)] but not for single-word polymers (like polyethylene), many authors omit entirely the use of parentheses for either case (like polyvinylidene chloride). Thus there exists a variety of practices with respect to even source-based names.

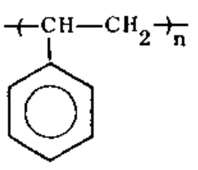
Copolymers are composed of two or more monomer units. Source-based names are conveniently used to describe copolymers by using an appropriate term between the names of the monomers. Any of a half dozen or so connecting terms may be used, depending on what is known about the structure of the copolymer. When no information is specified about the sequence of monomer units in the copolymer, the connective term *co* is used in the general format poly(A-*co*-B), where A and B are the names of the two monomers. An unspecified copolymer of styrene and methyl methacrylate would be called poly[styrene-*co*-(methyl methacrylate)].

Kraton, the yellow rubber-like material on the bottom of many running shoes, is an example of a copolymer about which structural information is available. It is formed from a group of styrene units, i.e., a "block" of polystyrene, attached to a group of butadiene units, or a block of polybutadiene, which is attached to another block of polystyrene forming a triblock copolymer. The general representation of such a block copolymer is —AAAAABBBBBAAAAA—, where each A or B represents an individual monomer unit. The proper source-based name for Kraton is polystyrene-*block*-polybutadiene-*block*-polystyrene, with the prefix "poly" being retained for each block.

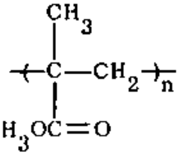
STRUCTURE-BASED NAMES

Although source-based names are generally employed for simple polymers, the international body responsible for systematic nomenclature of chemicals, IUPAC, has published a number of reports for the naming of polymers, now being accepted for more complex polymers. The IUPAC system names the components of the repeat unit, arranged in a prescribed order. The rules for selecting the order of the components to be used as the repeat unit are found elsewhere [*Macromolecules, 6*(2), 149 (1973); *Pure and Applied Chemistry, 48*, 373 (1976), *57*, 149 (1985), and *57*, 1427 (1985)]. However, once the order is selected, the naming is straightforward for simple linear molecules, as indicated in the following examples:

Polystyrene



Poly(1-phenylethylene)



$$\left(\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3OC{=}O}{C}} - CH_2 \right)_n$$

Poly[1-(methoxycarbonyl)-1-methylethylene]

A listing of source- and structure-based names for some common polymers is given in Table 1.

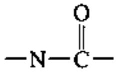
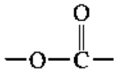
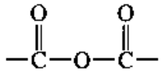
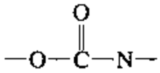
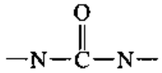
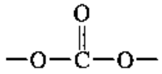
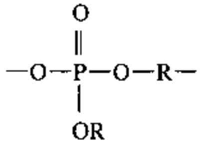
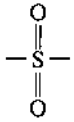
LINKAGE-BASED NAMES

Many polymer "families" are referred to by the name of the particular linkage that connects the polymers (Table 2). The family name is "poly" followed by the linkage name. Thus,

Table 1 Source- and Structure-Based Names

Source-based names	Structure-based names
Polyacrylonitrile	Poly(1-cyanoethylene)
Poly(ethylene oxide)	Polyoxyethylene
Poly(ethylene terephthalate)	Polyoxyethyleneoxyterephthaloyl
Polyisobutylene	Poly(1,1-dimethylethylene)
Poly(methyl methacrylate)	Poly[(1-methoxycarbonyl)-1-methylethylene]
Polypropylene	Poly(1-methylethylene)
Polystyrene	Poly(1-phenylethylene)
Polytetrafluoroethylene	Polydifluoromethylene
Poly(vinyl acetate)	Poly(1-acetoxyethylene)
Poly(vinyl alcohol)	Poly(1-hydroxyethylene)
Poly(vinyl chloride)	Poly(1-chloroethylene)
Poly(vinyl butyral)	Poly[(2-propyl-1,3-dioxane-4,6-diyl)methylene]

Table 2 Linkage-Based Names

Family name	Linkage	Family name	Linkage
Polyamide	 $-\mathrm{N}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$	Polyvinyl	$-\mathrm{C}-\mathrm{C}-$
Polyester	 $-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$	Polyanhydride	 $-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$
Polyurethane	 $-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{N}-$	Polyurea	 $-\mathrm{N}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{N}-$
Polyether	$-\mathrm{O}-$	Polycarbonate	 $-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-$
		Polyphosphate ester	 $-\mathrm{O}-\underset{\mathrm{OR}}{\underset{\|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}-\mathrm{O}-\mathrm{R}-$
Polysiloxane	$-\mathrm{O}-\mathrm{Si}-$		
Polysulfide	$-\mathrm{S}-\mathrm{R}-$	Polysulfones	 $-\underset{\mathrm{O}}{\underset{\|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}}}-$

those polymers that contain the carbonate linkage are known as polycarbonates; those containing the ether linkage are called polyethers, etc.

CHEMICAL ABSTRACTS–BASED POLYMER NOMENCLATURE

The most complete indexing of any scientific discipline is done in chemistry and is provided by Chemical Abstracts (CA). Almost all of the modern searching tools for chemicals and chemical information depend on CA for at least some of their information base. It is critical for polymer chemists to have some grasp of how CA names chemical compounds. The full description of the guidelines governing the naming of chemical compounds and related properties is given in Appendix IV at the end of the CA *Index Guide*. This description is about 200 pages. While small changes are made with each new edition, the main part has remained largely unchanged since 1972.

CA organizes the naming of materials into twelve major arrangements that tie together about 200 subtopics. These main topic headings are

A. Nomenclature systems and general principles
B. Molecular skeletons
C. Principal chemical groups
D. Compound classes
E. Stereochemistry and stereoparents
F. Specialized substances
G. Chemical substance names for retrospective searches
H. Illustrative list of substituent prefixes
J. Selective bibliography of nomenclature of chemical substances
K. Chemical prefixes
L. Chemical structural diagrams from CA Index Names
M. Index

The section dealing with polymers is subtopic *222: Polymers*. The subsection on polymers builds on the foundations given before. Some of the guidelines appear to be confusing and counterproductive to the naming of polymers, but the rules were developed for the naming of small molecules. Following is a description of the guidelines that are most important to polymer chemists. Additional descriptions are found in the CA Appendix IV itself and in articles listed in the readings. Appendix IV concentrates on linear polymers. A discussion of other more complex polymeric materials is also found in articles cited in the readings section.

General Rules

In the chemical literature—in particular, systems based on Chemical Abstracts—searches for particular polymers can be conducted using the Chemical Abstracts Service number, (CAS #) (where known) or the repeat unit. The International Union of Pure and Applied Chemistry (IUPAC) and CAS have agreed on a set of guidelines for the identification, orientation, and naming of polymers based on the structural repeat unit (SRU). IUPAC refers to polymers as "poly(constitutional repeat unit)" while CAS utilizes a "poly(structural repeating unit)." These two approaches typically give similar results.

Here we will practice using the sequence "identification, orientation, and naming," first by giving some general principles and finally by using specific examples.

In the *identification* step, the structure is drawn, usually employing at least two repeat units. Next, in the *orientation* step, the guidelines are applied. Here we concentrate on basic guidelines. Within these guidelines are subsets of guidelines that are beyond our scope.

Structures will generally be drawn in the order, from left to right, in which they are to be named.

Seniority

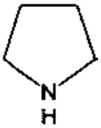
The starting point for the naming of a polymer unit involves determining seniority among the subunits.

A. This order is

Heterocyclic rings>
Greatest number of most preferred acyclic heteroatoms>
Carbocyclic rings>
Greatest number of multiple bonds>
Shortest path or route (or lowest locant) to these substituents
Chains containing only carbon atoms.

with the symbol ">" indicating "is senior to."
This is illustrated below.

Heterocyclic ring > Acyclic hetero atoms > Carbocyclic rings



$> \text{—O—CH}_2\text{—} >$

> Multiple bonds > Lowest locant > Only carbon chains

$> \text{—CH=CH—} \quad > \text{—CF}_2\text{—CHF} > \text{—CHF—CF}_2\text{—} \quad > \text{—CH}_2\text{—CH}_2\text{—}$

This order is partially derived from guidelines found in other sections such as Section 133, Compound Radicals, where the ordering is given as

Greatest number of acyclic hetero atoms>
Greatest number of skeletal atoms>
Greatest number of most preferred acyclic hetero atoms>
Greatest number of multiple bonds>
Lowest locants or shortest distance to nonsaturated carbons.

The lowest locant or shortest distance refers to the number of atoms from one senior subunit to the next most senior subunit when there is only one occurrence of the senior subunit.

This order refers to the backbone and not substitutions. Thus, polystyrene and poly(vinyl chloride) are contained within the "chains containing only carbon atoms" grouping.

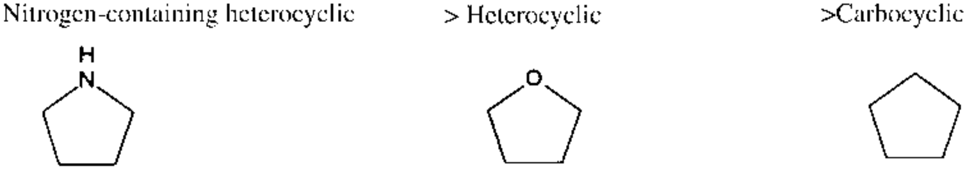
B. For ring systems the overall seniority is

Heterocyclic>
Carbocyclic

but within the rings there is also an ordering (Section 138) that is

Nitrogenous heterocyclic>
Heterocyclic>
Largest number of rings>
Cyclic system occurring earliest in the following list of systems
  spiro, bridged fused,
  bridges nonfused, fused>
Largest individual ring (applies to fused carbocyclic systems)>
Greatest number of ring atoms

For example,



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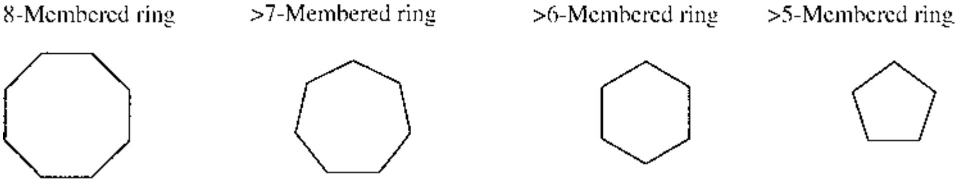
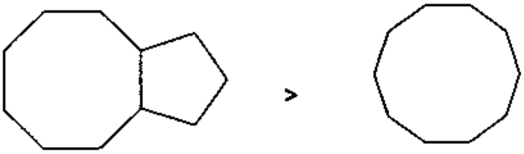


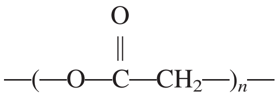
and



C. For hetero-atomed linear chains or cyclic rings, the order of seniority is O > S > Se > Te > N > P > As > Sb > Bi > Si > Ge > Sn > Pb > B > Hg.

Thus, because —O— CH_2—is senior to —S—CH_2—, it would be named first in a polymer that contained both —O—CH_2— and —S—CH_2 —segments. Further, a polymer containing these alternating units would *not* be poly(thiomethyleneoxymethylene) but would be named poly(oxymethylenethiomethylene).

Another example,



$$—(—O—\overset{\overset{O}{\|}}{C}—CH_2—)_n—$$

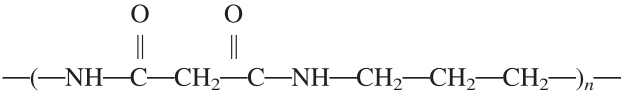
is named poly[oxy(1-oxy-1,2-ethanediyl)] or less preferred poly[oxy(1-oxoethylene)] but not poly[(2-oxo-1,2-ethanediyl)oxy] or poly[(2-oxoethylene)oxy].

D. In rings, unsaturation is senior to saturation. The more unsaturated, the more senior with all other items being equal. Thus 1,4-phenylene is senior to 2,5-cyclohexadiene-1,4-diyl, which in turn is senior to 2-cyclohexene-1,4-diyl, which is senior to 1,4-cyclohexanediyl. For linear chains —CH=CH—CH=CH— is senior to $\text{—CH=CH—CH}_2\text{—CH}_2\text{—}$, which is in turn senior to the totally saturated chain segment.

Route

A. From the senior subunit determined from “Seniority” take the shortest path (smallest number of atoms) to another like or identical unit or to the next most preferred subunit. Thus for the homopolymer poly(oxymethylene) it is simply going from one oxygen to the next oxygen and recognizing that this is the repeat unit. For a more complex ether this means going until the chain begins to repeat itself going in the shortest direction from the senior unit or atom to the next most senior unit or atom. Thus, —O—C—C-—O—C—C—C— is named “oxy-1,2-ethanediyloxy-1,3-propanediyl” rather than “oxy-1,3-propanediyloxy-1,2-ethanediyl.

B. Where path lengths are equal, such as in some nylons, the repeat unit is named so that the heteroatom “N” is first named and then the more highly substituted (carbonyl) unit appears next. Thus, nylon 3,3, with the structure



$$\text{—(—NH—}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{—CH}_2\text{—}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{—NH—CH}_2\text{—CH}_2\text{—CH}_2\text{—)}_n\text{—}$$

is named poly[imino(1,3-dioxo-1,3-propanediyl)imino-1,3-propanediyl].

C. In otherwise identical subunits, there are three items to be considered in decreasing order of importance:

1. Maximum substitution: thus, 2,3,5-trichloro-*p*-phenylene is senior to 2,5-dichloro-*p*-phenylene which in turn is senior to 2-chloro-*p*-phenylene,
2. Lowest locants: thus, 2,3-dichloro-*p*-phenylene is senior to 2,5-dichloro-*p*-phenylene,
3. Earliest alphabetical order: thus, 2-bromo-*p*-phenylene is senior to 2-chloro-*p*-phenylene that is senior to 2-iodo-*p*-phenylene.

D. Where there is no conflict with other guidelines, multiple bonds should be assigned the lowest locants; in rings, double bonds are senior to single bonds; in acyclic carbon chains, double bonds are senior to triple bonds, which are in turn senior to single bonds. Thus, the polymer from 1,3-butanediene polymerized in the so-called “1,4—” mode is usually drawn as —(—C—C=C—C—)— but it is named as drawn as —(—C=C—C—C—)— and named poly(1-butene-1,4-diyl) with the appropriate “cis-” or “trans-” designation. Polyisoprene, typically drawn as

$$\text{—(—CH}_2\text{—C(CH}_3\text{)=CH—CH}_2\text{—)}_n\text{—}$$

is frequently named poly(2-methyl-1,3-butadiene) but it is named as though its structure is

$$\text{—(C(CH}_3\text{)=CH—CH}_2\text{—CH}_2\text{—)}_n\text{—}$$

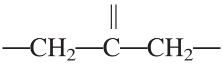
with the name poly(1-methyl-1-butene-1,4-diyl).

Substituents are named as one of several classes. The most important ones are dealt with here. For monoatomic radicals from borane, methane, silane (and other Group IVA elements) they are named by replacing the “ane” ending with “yl,” “ylene,” and “ylidyne” to denote the loss of one, two, or three hydrogen atoms, respectively.

H_2B- boryl H_3C- methyl $H_2C=$ methylene $HC\equiv$ methylidyne

Acyclic hydrocarbon radicals are named from the skeletons by replacing "ane," "ene," and "yne" suffixes by "yl," "enyl," and "ynyl," respectively.

CH_3-CH_2- ethyl $CH_3-CH_2-CH_2-$ propyl $-CH_2-CH_2-$ 1,2-ethanediyl
$-CH=CH-$ 1,2-ethenediyl $H_2C=CH-CH=$2-propenylidene


$-CH_2-\overset{\|}{C}-CH_2-$ 1,3-propanediyl-2-ylidene

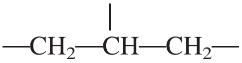

$-CH_2-\overset{|}{CH}-CH_2-$ 1,2,3-propanetriyl

Table 3 contains the names of selected bivalent radicals that may be of use to polymer chemists.

Searching

Polymers from a single monomer are indexed at the monomer name with the term "homopolymer" cited in the modification. Thus, polymers of 1-pentene are listed under the monomer

1-Pentene
    homopolymer

Polymers formed from two or more monomers such as condensation polymers and copolymers, and homopolymers are indexed at each inverted monomer name with the modifying term "polymer with" followed by the other monomer names in uninverted alphabetical order. The preferential listing for identical heading parents is in the order: (a) maximum number of substituents, (b) lowest locants for substituents, (c) maximum number of occurrences of index heading parent, and (d) earliest index position of the index heading. Examples are

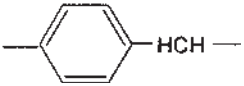
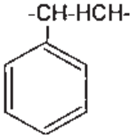
1-Petene
    polymer with 1-hexene
2,5-Furandione
    polymer with 1,4-butanedisulfonic acid
Silane, dichlorodiethyl-
    polymer with dichlorodiphenylsilane

Although the percentage composition of copolymers (i.e., the ratio of comonomers) is not given, copolymers with architecture other than random or statistical are identified as "alternating, block, graft, etc." Random or statistical copolymer are not so identified in the CA index. Oligomers with definite structure are noted as dimer, trimer, tetramer, . . .

Often, similar information is found at several sites. For instance, for copolymers of 1-butene and 1-hexene, information will be listed under both 1-butene and 1-hexene, but because the listings are not necessarily complementary both entries should be consulted for completeness.

CA's policy for naming acetylenic, acrylic, methacrylic, ethylenic, and vinyl polymers is to use the source-based method, and source-based representation is used to depict the polymers graphically; thus, a synonym for polyethene is polyethylene and not poly(1,2-

Table 3 Names of Selected Bivalent Radicals

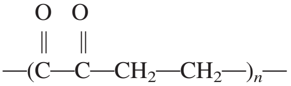
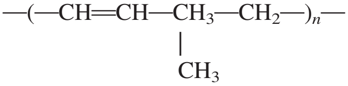
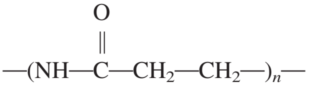
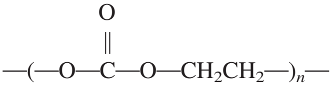
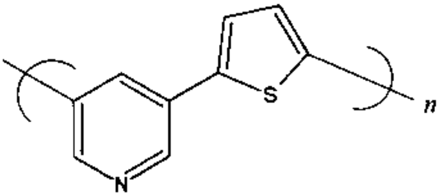
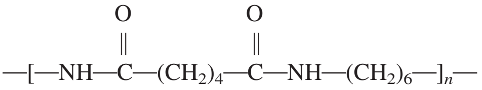
"Common" or "trivial" name	CAS name	Structure
Adipyl, adipoyl	1,6-Dioxo-1,6-hexanediyl	$—CO—(CH_2)_4—CO—$
1,4-Butanediyl	1,4-Butanediyl	$—(CH_2)_4—$
Carbonyl	Carbonyl	$—CO—$
Diglycoloyl	Oxybis (1-oxo-2,1-ethanediyl)	$—CO—CH_2—O—CH_2\text{-}CO—$
Ethylene	1,2-Ethanediyl	$—CH_2—CH_2—$
Imino	Imino	$—NH—$
Iminodisulfonyl	Iminobis(sulfonyl)	$—SO_2—NH—SO_2—$
Methene, methylene	Methylene	$—CH_2—$
Oxybis(methylenecarbonylimino)	Oxybis[(1-oxo-2,1-ethanediyl)imino)]	$—NHCO—CH_2—O—CH_2—CO—NH—$
Pentamethylene	1,5-Pentanediyl	$—(CH_2)_5—$
p-Phenylene	1,4-Phenylene	
Phenylenedimethylene	1,4-Phenylenebis(methylene)	
Phenylenedioxy	1,4-Phenylenebis(oxy)	
Sebacoyl	1,10-Dioxo-1,10-decanediyl	$—CO—(CH_2)_8CO—$
Styrenyl	1-Phenyl-1,2-ethanediyl	
Sulfonyl, sulfuryl	Sulfonyl	$—SO_2—$
Tartaroyl	2,3-Dihydroxy-1,4-dioxo-1,4-butanediyl	$—CO—CH(OH)—CH(OH)—CO—$
Terephthaloyl	1,4-Phenylenedicarbonyl	
Thio	Thio	$—S—$
Thionyl	Sulfinyl	$—SO—$
Ureylene	Carbonyldiimino	$—NH—CO—NH—$
Vinylene	1,2-Ethenediyl	$—CH{=}CH—$

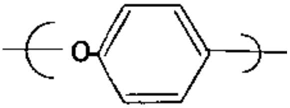
In this text we typically employ the more "common" (semisystematic or trivial) names of polymers, but it is important in searching the literature using any CA-driven search engine that you be familiar with CA naming for both monomers and polymers.

ethanediyl); a synonym for poly-1-propylene is polypropylene, and poly(vinyl alcohol) is named ethenol, homopolymer although ethenol does not exist. Thus, these polymers are named and represented structurally by the source-based method, not the structure-based method.

Examples

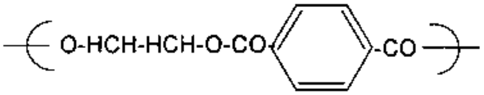
Following are examples that illustrate CAS guidelines for naming.

$-(\mathrm{CH_2}-)_n-$	Poly(methylene) (to locate poly(methylene) in the Registry file by name, search for "Ethane, homopolymer")
$-(\mathrm{CH_2}-\mathrm{CH_2}-)_n-$	Poly(ethylene) (to search for poly(ethylene) search for "Ethane, homopolymer")
$-(\mathrm{CH}{=}\mathrm{CH}-)_n-$	Poly(1,2-ethenediyl)
 $-(\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{CH_2}-)_n-$	Poly1,2-dioxo-1,4-butanediyl
 $-(-\mathrm{CH}{=}\mathrm{CH}-\underset{\underset{\mathrm{CH_3}}{\vert}}{\mathrm{CH_3}}-\mathrm{CH_2}-)_n-$	Poly(3-methyl-1-butene-1,4-diyl
 $-(\mathrm{NH}-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{CH_2}-)_n-$	Poly[imino(1-oxo-1,3-propanediyl)]
 $-(-\mathrm{O}-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-\mathrm{O}-\mathrm{CH_2CH_2}-)_n-$	Poly[oxocarbonyloxy(1,2-ethanediyl)]
$-(-\mathrm{O}-\mathrm{CH_2}-\mathrm{S}-\mathrm{CH_2}-\mathrm{NH}-\mathrm{CH_2}-\mathrm{CH_2}$ $-\mathrm{S}-\mathrm{NH}-\mathrm{CH_2}-\mathrm{CH_2}-)_n-$	Poly(oxymethylenethiomethyleneimino-1,2-ethanediylthioimino-1,2-ethanediyl)
$-(-\mathrm{CFH}-\mathrm{CH_2}-)_n-$	Poly(1-fluoro-1,2ethanediyl) search for under "Ethene, fluoro-homopolymer")
$-(-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-)_n-$	Poly(oxy-1,2-ethanediyl)
$-(-\mathrm{O}-\mathrm{CH_2}-)_n-$	Poly(oxymethylene)
	Poly(3,5-pyridinediyl-2,5-thiophenediyl)
 $-[-\mathrm{NH}-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-(\mathrm{CH_2})_4-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-\mathrm{NH}-(\mathrm{CH_2})_6-]_n-$	Poly[imino(1,6-dioxo-1,6hexanediyl)imino-1,6-hexanediyl]

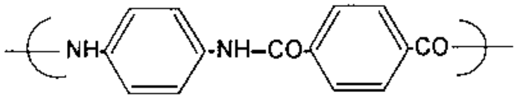


Poly(oxy-1,4-phenylene)

Poly(thio-1,4-phenylene)



Poly(oxy1,2-ethanediyloxycarbonyl-1,4-phenylenecarbonyl)



Poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl)

TRADE NAMES, BRAND NAMES, AND ABBREVIATIONS

Trade (and/or brand) names and abbreviations are often used to describe materials. They may be used to identify the product of a manufacturer, processor or fabricator and may be associated with a particular product or with a material or modified material. Trade names are used to describe specific groups of materials that are produced by a specific company or under licence of that company. Bakelite is the trade name given for the phenol-formaldehyde condensation polymer developed by Baekeland. A sweater whose contents are described as containing Orlon contains polyacrylonitrile fibers that are “protected” under the Orlon trademark and produced or licenced to be produced by the holder of the Orlon trademark. Also, Carina, Cobex, Dacovin, Darvic, Elvic, Geon, Koroseal, Marvinol, Mipolam, Opalon, Plioflex, Rucon, Solvic, Trulon, Velon, Vinoflex, Vygen, and Vyram are all trade names for poly(vinyl chlorides) manufactured by different companies. Some polymers are better known by their trade name than their generic name. For instance, polytetrafluoroethylene is better known as Teflon, the trade name held by DuPont. An extensive listing of trade names is given in Appendix B of this text.

Abbreviations, generally initials in capital letters, are also employed to describe materials. Table 4 contains a listing of some of the more widely employed abbreviations and the polymer associated with the abbreviation.

COPOLYMERS

Generally, copolymers are defined as polymeric materials containing two or more kinds of mers. It is important to distinguish between two kinds of copolymers—those with statistical distributions of mers or at most short sequences of mers (Table 5), and those containing long sequences of mers connected in some fashion (Table 6).

ACKNOWLEDGMENTS

The author thanks William Work, Les Sperling, and W. V. (Val) Metanomski for their assistance with polymer nomenclature. The author also acknowledges the assistance of Edward S. Wilks for his help in preparing the section on ‘‘Chemical Abstracts Based Polymer Nomenclature.’’

Table 4 Abbreviations for Selected Polymeric Materials

Abbreviation	Polymer	Abbreviation	Polymer
ABS	Acrylonitrile-butadiene-styrene copolymer	CA	Cellulose acetate
EP	Epoxy	HIPS	High-impact polystyrene
MF	Melamine-formaldehyde polymer	PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile	SBR, PBS	Butadiene-styrene copolymer
PBT	Poly(butylene terephthalate)	PC	Polycarbonate
PE	Polyethylene	PET	Poly(ethylene terephthalate)
PF	Phenol-formaldehyde polymer	PMMA	Poly(methyl methacrylate)
PP	Polypropylene	PPO	Poly(phenylene oxide)
PS	Polystyrene	PTFE	Polytetrafluoroethylene
PU	Polyurethane	PVA, PVAc	Poly(vinyl acetate)
PVA, PVAI	Poly(vinyl alcohol)	PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)	SAN	Styrene-acrylonitrile copolymer
UF	Urea-formaldehyde polymer		

Table 5 Short Sequence Copolymer Nomenclature

Type	Connective	Example
Homopolymer	None	PolyA
Unspecified	*-co-*	*Poly*(A-*co*-B)
Statistical	*-stat-*	Poly(A-*stat*-B)
Random	*-ran-*	Poly(A-*ran*-B)
Periodic	*-per-*	Poly(A-*per*-B-*per*...)
Alternating	*-alt-*	Poly(A-*alt*-B)
Network	*net-*	*net*-PolyA

Table 6 Long Sequence Copolymer Nomenclature

Type	Connective	Example
Block copolymer	*-block-*	PolyA-*block*-polyB
Graft copolymer	*-graft-*	PolyA-*graft*-polyB
AB-crosslinked	*-net-*	PolyA-*net*-polyB
Polymer blend	*-blend-*	PolyA-*blend*-polyB
Interpenetrating network polymer	*-ipn-* or *-inter-*	*net*-PolyA-*ipn-net*-polyB
Starblock	*star-*	*star*-(PolyA-*block*-polyB)

SUMMARY

While there are several important approaches to the naming of polymers, in this book we utilize common and source-based names because these are the names that are most commonly utilized by polymer chemists and the general public and these names, in particular the source-based names, allow a better understanding of the basics of polymers as a function of polymer—structure relationships based on starting materials. Even so, those wishing to do further work in polymers must become proficient in the use of the guidelines used by Chemical Abstracts and IUPAC.

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Contents

Studying Polymer Chemistry

Studying polymer chemistry is similar to studying any chemistry. Following are some ideas that may assist you as you study polymer chemistry.

Much of chemistry is abstract. While much of polymer chemistry is abstract, it is easier to conceptualize—i.e., make mind pictures of what a polymer is and how it should behave—than many other areas of chemistry. For linear polymers, think of a string or rope. Long ropes get entangled with themselves and other ropes. In the same way, polymers entangle with themselves and with other polymer chains that are brought into contact with them. *Thus, create mental pictures of the polymers as you study them.*

Polymers are real and all around us. We can look at polymers on a microscopic or atomic level or on a macroscopic level. The PET bottles we have are composed of long chains of poly(ethylene terephthalate) chains. The aramid tire cord is composed of aromatic polyamide chains. Our hair is made up of complex bundles of fibrous proteins, again polyamides. *The chemistry you study is related to the real world in which we live. We experience this "chemistry" at the macroscopic level every day of our lives and this macroscopic behavior is a direct consequence of the atomic level structure and behavior.* Make pictures in your mind that allow you to relate the atomic and macroscopic worlds.

At the introductory level we often examine only the primary factors that may cause particular polymer behavior. Other factors may become important under particular conditions. *The polymer chemistry you study at times examines only the primary factors that impact polymer behavior and structure. Nevertheless, it does form the basis for both complex and simple structure–property behavior.*

The structure–property relationships you will be studying are based on well-known basic chemistry and physical relationships. *Because such relationships build on one another you need to study in an ongoing manner. Understand as you go along. Read the material BEFORE you go to class.*

This course is an introductory-level course that builds on firm foundations in all of the core areas of chemistry. Each chapter or topic emphasizes knowledge from one or more of these areas. *Polymer chemistry also has its own language. It is a language that requires you to memorize it.* Our memory can be short-term or long-term. Short-term memory may be considered as that used by an actor or actress for a TV drama. It really does not need to be totally understood or retained after the final “take.” *Long-term memory is required in studying polymer chemistry since it will be called on repeatedly and is used to understand other concepts.*

In memorizing, learn how you do this best—at what time of day, in what setting, etc. Use as many senses as necessary—*be active*—read your assignment, write out what you need to learn, say it, listen to yourself say it. Also, look for patterns, create mnemonic devices, avoid cramming too much into too little time, practice associations in all directions, and test yourself. *Memorization is hard work.*

While knowledge involves recalling memorized material, to really *know* something involves more than simple recall. It involves comprehension, application, evaluation, and integration of the knowledge. Comprehension is the interpretation of this knowledge, i.e., making predictions, applying it to different situations. Analysis involves evaluation of the information and comparison with other information. Synthesis has to do with integration of the information with other information.

In studying polymer chemistry, consider doing the following:

Skim the text *before* the lecture.
Attend the lecture and take notes.
Organize your notes and relate information.
Read and study the assigned material.
Study your notes and the assigned material.
Review and self-test.

Learning takes time and effort. Study daily, skimming the text and other study material; think about it, visualize key points and concepts, write down important material, make outlines, take notes, study sample problems, etc. All of this helps, but some approaches may help you more than others, so focus on these modes of learning—but not to the exclusion of the other aspects.

In preparing for an exam, consider doing the following:

Accomplish the above. Do not wait until the day before the exam to begin studying. Develop good study habits.
Study wisely. Study how *you* study best, i.e., time of day, surroundings, etc.
Take care of yourself. Get plenty of sleep the night before the exam.
Attend to last-minute details. Is your calculator working? Is it the right kind? Do you have the needed pencils? Review the material once again.
Know what kind of test it will be (if possible).
Get copies of old exams (if possible). Talk to others who have already taken the course.

During the test,

Stay cool; do not panic.
Read the directions; try to understand what is being asked.
In an essay or similar exam work for partial credit, plan your answers ahead of time.
In a multiple-choice or true/false exam, eliminate obviously wrong choices.
Look over the entire exam. Work on questions that you are sure of, then go to less obvious questions. Check answers if time permits.

Polymer chemistry comprises a variety of chemical content:

Facts. The term *polymer* means “many” (poly) “units” (mers).

Concepts. Linear polymers are long molecules like a string.

Rules. Solutions containing polymer chains are more viscous, slower flowing, than solutions that do not contain polymers; the relationship between the resistance to flow, viscosity, and molecular weight is given by the Mark-Houwink equation $LVN = KM^a$, where LVN is the viscosity number, K and a are constants, and M is molecular weight.

Problems. Given an LVN of 0.2 dL/g, $a = 0.55$, and $K = 6 \times 10^{-5}$dL/g, determine the molecular weight of the sample.

Although these categories are often integrated within any topic, in this introduction to polymer chemistry the emphasis is often on concepts. However, all aspects are important.

1

Introduction to Polymer Science

1.1 HISTORY OF POLYMERS

Since most chemists and chemical engineers are now involved in some phase of polymer science or technology, some have called this the polymer age. Actually, we have always lived in a polymer age.

The ancient Greeks classified all matter as animal, vegetable, and mineral. Minerals were emphasized by the alchemists, but medieval artisans emphasized animal and vegetable matter. All are largely polymers and are important to life as we know it.

The word *polymer* is derived from the Greek *poly* and *meros*, meaning many and parts, respectively. Some scientists prefer to use the word *macromolecule*, or large molecule, instead of polymer. Others maintain that naturally occurring polymers, or *biopolymers*, and synthetic polymers should be studied in different courses. However, the same principles apply to all polymers. If one discounts the end uses, the differences between all polymers, including plastics, fibers, and elastomers or rubbers, are determined primarily by the intermolecular and intramolecular forces between the molecules and within the individual molecule, respectively, and by the functional groups present.

In addition to being the basis of life itself, protein is used as a source of amino acids and energy. The ancients degraded or depolymerized the protein in tough meat by aging and cooking, and they denatured egg albumin by heating or adding vinegar to the eggs.

Early humans learned how to process, dye, and weave the natural proteinaceous fibers of wool and silk and the carbohydrate fibers of flax and cotton. Early South American civilizations such as the Aztecs used natural rubber (*Hevea brasiliensis*) for making elastic articles and for waterproofing fabrics.

There has always been an abundance of natural fibers and elastomers but few plastics. Of course, early humans employed a crude plastic art in tanning the protein in animal skins to make leather and in heat-formed tortoise shells. They also used naturally occurring tars as caulking materials and extracted shellac from the excrement of small coccid insects (*Coccus lacca*).

Until Wöhler synthesized urea from inorganic compounds in 1828, there had been little progress in organic chemistry since the alchemists emphasized the transmutation of base metals to gold and believed in a vital force theory. Despite this essential breakthrough, little progress was made in understanding organic chemistry until the 1850s, when Kekulé developed the presently accepted technique for writing structural formulas. However, polymer scientists displayed a talent for making empirical discoveries before the science was developed.

Charles Goodyear grew up in poverty. He was a Connecticut Yankee born in 1800. He began work in his father's farm implement business. Later he moved to Philadelphia where he opened a retail hardware store that soon went bankrupt. He then turned to being an inventor. As a child he had noticed the magic material that formed a rubber bottle he had found. He visited the Roxbury India Rubber Company to try and interest them in his efforts to improve the properties of rubber, but they assured him that there was no need to do so.

He started his experiments with a malodorous gum from South America in debtor's prison. In a small cottage on the grounds of the prison, he blended the gum, the raw rubber called hevea rubber, with anything he could find, e.g., ink, soup, caster oil. While rubber-based products were available, they were either sticky or became sticky in the summer heat. He found that treatment of the raw rubber with nitric acid allowed the material to resist heat and not to adhere to itself. This success attracted backers who helped form a rubber company. After some effort he obtained a contract to supply the U.S. Post Office with 150 rubber mailbags. He made the bags and stored them in a hot room while he and his family went away. When they returned they found the bags in a corner of the room, joined together as a mass. The nitric acid treatment was sufficient to prevent surface stickiness, but the internal rubber remained tacky and susceptible to heat.

While doing experiments in 1839 at a Massachusetts rubber factory he accidently dropped a lump of rubber mixed with sulfur on the hot stove. The rubber did not melt but rather charred. He had discovered vulcanization, the secret that was to make rubber a commercial success. While he had discovered vulcanization, it would take several years of ongoing experimentation before the process was really commercially useful. During this time he and his family were nearly penniless. Although he patented the process, it was too easily copied and pirated, so that he was not able to profit fully from his invention and years of hard work. Even so, he was able to develop a number of items.

Charles Goodyear and his brother Nelson transformed natural rubber, hevea rubber, from a heat-"softenable" thermoplastic to a less heat-sensitive product through the creation of crosslinks between the individual polyisoprene chain-like molecules using sulfur as the crosslinking agent. *Thermoplastics* are two-dimensional molecules that may be softened by heating. *Thermosets* are materials that are three-dimensional networks that cannot be reshaped by heating. Rather than melting, thermosets degrade. As the amount of sulfur was increased, the rubber became harder becoming a hard rubber-like (ebonite) material.

The spring of 1851 found the construction of a remarkable building on the lawns of London's Hyde Park. The building was designed by a maker of greenhouses so it was not unexpected that it had a greenhouse look. This Crystal Palace was to house almost 14,000 exhibitors from all over the world. It was the chance for exhibitors to show their wares. Charles Goodyear, then 50 years old, used this opportunity to show off his over two decades worth of rubber-related products. He decorated his Vulcanite Court with rubber walls, roof, furniture, buttons, toys, carpet, combs, etc. Above it hung a six-foot rubber raft and assorted balloons. The European public was introduced to the world of new man-made materials.

Within little more than a decade Charles Goodyear was dead. Within a year of his death, the American Civil War broke out. The Union military used about $27 million worth of rubber products by 1865 helping launch the U.S. rubber industry.

In 1862 Queen Victoria, while in mourning for her recently departed husband Albert, opened the World's Fair in London. One of the exhibitors was Alexander Parks. He was displeased with the limited colors available for rubber products (generally dull and dark). In his workshop in Birmingham, England he was working with nitrocellulose, a material made from the treatment of cotton and nitric and sulfuric acids. Nitrocellulose solutions were made from dissolving the nitrocellulose in organic liquids such as ethanol and ether. Thin films and coatings were made by simply pouring the nitrocellulose solutions onto the desired item or surface and allowing the solvent to evaporate. He wanted to make solid objects from nitrocellulose. After years of work he developed a material he called Parkensine from which he made buttons, combs, and many of the items that were made of rubber, except that his materials could be brightly colored, clear, or made to shine like mother-of-pearl. At the London World's Fair he advertised "Patent Parkesine of various colours: hard elastic, transparent, opaque, and waterproof." Even with his work he had not developed a material that could be "worked" or was stable, and even with his hype the material never caught on except in exhibition halls.

About this time, John Wesley Hyatt, a printer from Albany, New York who was seeking a $10,000 prize for anyone who could come up with a material that was a substitute for ivory billiard balls, developed a material that was stable and could be "worked" from shellac and wood pulp. He then turned to nitrocellulose discovering that shredded nitrocellulose could be mixed with camphor and heated under pressure to produce a tough white mass that retained its shape. This material, dubbed celluloid, could be made into the usual rubber-like products, but also solid pieces like boxes, wipe-clean linen, collars, cuffs, and ping-pong balls. Celluloid could also, like the shellac–wood pulp mixture, be cut, drilled, and sawed. But celluloid was flammable and did not stand up well in hot water. The wearers of celluloid dentures truly could have their "teeth curled" when drinking a hot cup of coffee. One of its best qualities was that it could be made to look like other materials—it could be dyed to look like marble, swirled to mimic tortoiseshell and mother-of-pearl, and even look and feel like ivory. It did not make good billiard balls. One account has billiard balls hitting and exploding like a shot that caused cowboys to draw their guns.

Both cellulose and cellulose nitrate are linear, or two-dimensional, polymers, but the former cannot be softened because of the presence of multitudinous hydrogen bonds between the chain-like molecules. When used as an explosive the cellulose nitrate is essentially completely nitrated, but the material used by Parks and Hyatt was a dinitrate, still potentially explosive but less so. Parks added caster oil and Hyatt added camphor to plasticize-reduce the effect of the hydrogen bonding—the cellulose nitrate.

Worldwide, rubber gained in importance with the invention of the air-filled or pneumatic tires by a Scotsman, John Dunlop in 1888. He had a successful veterinary practice in Belfast. In his off time he worked to improve the ride of his son's tricycle. His invention happened at the right time. The automobile was emerging and air-filled tires offered a more gentle ride. Thus was begun the tire industry.

All of these inventions utilized natural materials as at least one ingredient. After years of work in his chemistry labs in Yonkers, New York, Leo Baekeland in 1907 announced in an American Chemical Society meeting the synthesis of the first truly synthetic polymeric material, later dubbed Bakelite.

Baekeland was born in Belgium in 1863, the son of an illiterate shoe repairman and a maid. He was bright and received his doctorate with highest honors at the age of 20. He could have spent the remaining part of his life in academics in Europe, but heeding the words of Benjamin Franklin, he sailed to America. In the 1890s he developed the first photographic paper, called Velox, that could be developed in synthetic light rather than sunlight. George Eastman saw the importance of this discovery and paid Bakeland $750,000 for the rights to this invention.

It was generally recognized by the leading organic chemists of the nineteenth century that phenol would condense with formaldehyde. Since they did not recognize the concept of functionality, Baeyer, Michael, and Kleeberg produced useless crosslinked goos, gunks, and messes and then returned to their research on reactions of monofunctional reactants. However, by the use of a large excess of phenol, Smith, Luft; and Blumer were able to obtain a hard yet meltable thermoplastic material.

With his $750,000 Baekeland set up a lab next to his home. He then sought to solve the problem of making the hard material made from phenol and formaldehyde soluble. After many failures, he thought about circumventing the problem by placing the reactants in a mold of the desired shape and allowing them to form the intractable solid material. After much effort he found the conditions under which a hard, clear solid could be made—Bakelite was discovered. Bakelite could be worked, was resistant to acids and organic liquids, stood up well to heat and electrical charge, and could be dyed to give colorful products. It was used to make bowling balls, phonograph records, telephone housings, gears, and cookware. His materials also made excellent billiard balls.

Bakelite also acted as a binder for sawdust, textiles, and paper, forming a wide range of composites including Formica laminates, many of which are still used. It was also used as an adhesive giving us plywood.

While there is no evidence that Baekeland recognized what polymers were, he appeared to have a grasp on functionality and how to "use" functionality to produce thermoplastic materials that could later be converted to thermosets. Through control of the ratio of phenol to formaldehyde he was able to form a material that was a thermoplastic. He coined the term *A-stage resole resin* to describe this thermoplastic. This A-stage resole resin was converted to a thermoset crosslink, *C-stage Bakelite*, by additional heating. Baekeland also prepared thermoplastic resins called *novolacs* by the condensation of phenol with a lesser amount of formaldehyde under acidic conditions. The thermoplastic novolacs were converted to thermosets by addition of more formaldehyde. While other polymers had been synthesized in the laboratory, Bakelite was the first truly synthetic plastic. The "recipes" used today differ little from the ones developed by Baekeland, showing his ingenuity and knowledge of the chemistry of the condensation of the trifunctional phenol and difunctional formaldehyde.

While poly(vinyl chloride) was initially formed by Baumann in 1872, it awaited interest until 1926 when B. F. Goodrich discovered how to make sheets and adhesives from poly(vinyl chloride)—and the "vinyl age" began. While polystyrene was probably first formed by Simon in 1839, it was almost 100 years latter, in 1930, that the giant German company I. G. Farben placed polystyrene on the market. Polystyrene molded parts have became common place. Rohm and Haas bought out Plexiglas from a British firm in 1935 and began the production of clear plastic parts and goods, including replacements for glass as camera lenses, aircraft windows, clock faces, and car tail lights.

Polymer science was largely empirical, instinctive, and intuitive. Prior to World War I, celluloid, shellac, Galalith (casein), Bakelite, and cellulose acetate plastics; hevea rubber, cotton, wool, silk rayon fibers; Glyptal polyester coatings; bitumen or asphalt; and coumarone-indene and petroleum resins were all commercially available. However, as evidenced by the chronological data shown in Table 1.1, there was little additional development in polymers prior to World War II because of a general lack of fundamental knowledge of polymers. But the theoretical basis was being built. Only a few of the many giants of the industry will be mentioned.

Over a century ago, Graham coined the term *colloid* for aggregates with dimensions in the range of 10^{-9} to 10^{-7} m. Unfortunately, the size of many macromolecules is in this range, but it is important to remember that unlike colloids, whose connective forces are ionic and/or secondary forces, polymers are individual molecules whose size cannot be reduced without breaking the covalent bonds that hold the atoms together. In 1860 an oligomer, a small polymer, was prepared from ethylene glycol and its structure correctly given as $H—(—OCH_2CH_2—)_n—OH$. But when poly(methacrylic acid) was made by Fittig and Engelhorn in 1880 it was incorrectly assigned a cyclic structure. Polymers were thought of as being colloids, or cyclic compounds like cyclohexane. By use of the Raoult and van't Hoff concepts, several scientists obtained high molecular weight values for these materials and for a number of other polymeric materials. But since the idea of large molecules was not yet accepted they concluded that these techniques were not applicable to these molecules rather than accepting the presence of giant molecules.

Hermann Staudinger studied the polymerization of isoprene as early as 1910. Intrigued by the difference between this synthetic material and natural rubber, he began to develop his studies toward such materials. His turn to these questionable materials, of interest to industry but not academically important, was viewed unkindly by his fellow academics. He was told by one of his fellow scientists "Dear Colleague, Leave the concept of large molecules well alone. . . . There can be no such thing as a macromolecule." But Staudinger systematically synthesized a variety of polymers. In the 1920 paper "Uber Polymerization" he summarized his findings and correctly proposed linear structures for such important polymers as polyoxymethylene and polystyrene. X-ray studies of many natural and synthetic materials were used as structural proof that polymers existed. Foremost in these efforts were Herman Mark and Linus Pauling. Both of these giants contributed to other important areas of science. Pauling contributed to the fundamental understanding of bonding and the importance of vitamins. Mark helped found the academic and communication (journals, short courses, workshops) basis that would allow polymer science to grow from its very diverse roots.

Wallace Hume Carothers is the father of synthetic polymer science. History is often measured by the change in the flow of grains of sand in the hour glass of existence. Carothers is a granite boulder in this hour glass. Carothers was born, raised, and educated in the U.S. midwest. In 1920 he left Tarkio College with his BS degree and entered the University of Illinois where he received his MA in 1921. He then taught at the University of South Dakota where he published his first paper. He returned to receive his PhD under Roger Adams in 1924. In 1926 he became an instructor in organic chemistry at Harvard.

In 1927 the DuPont Company decided to begin a program of fundamental research "without any regard or reference to commercial objectives." This was a radical departure since the bottom line was previously products marketed and not papers published. Charles Stine, director of DuPont's chemical department, was interested in pursuing fundamental research in the areas of colloid chemistry, catalysis, organic synthesis, and polymer forma-

Table 1.1 Chronological Development of Commercial Polymers (to 1971)

Date	Material
Before 1800	Cotton, flax, wool, and silk fibers; bitumen caulking materials; glass and hydraulic cements; leather and cellulose sheet (paper); natural rubber (*Hevea brasiliensis*), gutta percha, balata, and shellac
1839	Vulcanization of rubber (Charles Goodyear)
1845	Cellulose esters (Schönbein)
1846	Nitration of cellulose (Schönbein)
1851	Ebonite (hard rubber; Nelson Goodyear)
1860	Molding of shellac and gutta percha
1868	Celluloid (plasticized cellulose nitrate; Hyatt)
1889	Regenerated cellulosic fibers (Chardonnet)
1889	Cellulose nitrate photographic films (Reichenbach)
1890	Cuprammonia rayon fibers (Despeisses)
1892	Viscose rayon fibers (Cross, Bevan, and Beadle)
1897	Poly(phenylene sulfide)
1907	Phenol-formaldehyde resins (Bakelite; Baekeland)
1907	Cellulose acetate solutions (dope; Doerfinger)
1908	Cellulose acetate photographic fibers
1912	Regenerated cellulose sheet (cellophane)
1913	Poly(vinyl acetate)
1914	Simultaneous interpenetrating network (SIN)
1920	Urea-formaldehyde resins
1923	Cellulose nitrate automobile lacquers
1924	Cellulose acetate fibers
1926	Alkyd polyester (Kienle)
1927	Poly(vinyl chloride) (PVC) wall covering
1927	Cellulose acetate sheet and rods
1927	Graft copolymers
1928	Nylon (Carothers, Dupont)
1929	Polysulfide synthetic elastomer (Thiokol; Patrick)
1929	Urea-formaldehyde resins
1931	Poly(methyl methacrylate) (PMMA) plastics
1931	Polychloroprene elastomer (Neoprene, Carothers)
1934	Epoxy resins (Schlack)
1935	Ethylcellulose
1936	Poly(vinyl acetate)
1936	Poly(vinyl butyral) safety glass
1937	Polystyrene
1937	Styrene-butadiene (Buna-S) and styrene-acrylonitrile (Buna-N) copolymer elastomers
1939	Melamine-formaldehyde resins
1939	Nylon 6 (Schlack)
1939	Nitrile rubber (NR)
1940	Isobutylene-isoprene elastomer (butyl rubber; Sparks and Thomas)
1941	Low-density polyethylene (LDPE)
1941	Poly(ethylene terephthalate) (PET)
1942	Butyl rubber
1942	Unsaturated polyesters (Ellis and Rust)

Table 1.1 Continued

Date	Material
1943	Fluorocarbon resins (Teflon; Plunkett)
1943	Silicones
1943	Polyurethanes (Baeyer)
1945	SBR
1946	Poly(sulfide) rubber (Thiokol)
1948	Copolymers of acrylonitrile, butadiene, and styrene (ABS)
1949	Cyanoacrylate (Goodrich)
1950	Polyester fibers (Whinfield and Dickson)
1950	Polyacrylonitrile fibers
1952	Block copolymers
1953	High impact polystyrene (HIPS)
1953	Polycarbonates (Whinfield and Dickson)
1956	Poly(phenylene ether); Poly(phenylene oxide) (GE)
1956	Polyoxymethylene (acetals)
1957	High-density (linear) polyethylene (HDPE)
1957	Polypropylene
1957	Polycarbonate
1958	Poly(dihydroxymethylcyclohexyl terephthate) (Kodel, Eastman Kodak)
1959	cis-Polybutadiene and cis-polyisoprene elastomers
1960	Ethylene-propylene copolymer elastomers
1961	Aromatic nylons (Aramids, Nomex, Dupont)
1962	Polyimide resins
1964	Poly(phenylene oxide)
1964	Ionomers
1965	Polysulfone
1965	Styrene-butadiene block copolymers
1966	Liquid crystals
1970	Poly(butylene terephthalate)
1974	Polyacetylene
1982	Polyetherimide (GE)

tion and convinced the board to hire the best chemists in each field to lead this research. Stine visited with many in the academic community, including the then president of Harvard (one of my distant uncles) J. B. Conant, an outstanding chemist himself, who told him about Carothers. Carothers was persuaded to join the DuPont group attracted with a generous research budget and an approximate doubling of his academic salary to $6,000. This was the birth of the Experimental Station at Wilmington, Delaware.

Up to this point, it was considered that universities were where discoveries were made and industry was where they were put to some practical use. This separation between basic and applied work was quite prominent at this juncture and continues in many areas even today in some fields of work though the difference has decreased. But in polymers, most of the basic research was done in industry having as its inception the decision of DuPont to bridge this “unnatural” gap between fundamental knowledge and application. In truth, they can be considered as the two hands of an individual and in order to do manual work both hands are important.

Staudinger believed that large molecules were based on the joining, through covalent bonding, of large numbers of atoms. Essentially, he and fellow scientists like Karl Freudenberg, Herman Mark, Michael Polanyi, and Kurt Myer looked at already existing natural polymers. Carothers however looked at the construction of these giant molecules from small molecules forming synthetic polymers. His intention was to prepare molecules of known structure through the use of known organic chemistry and to "investigate how the properties of these substances depended on constitution." Early work included the study of polyester formation through reaction of diacids with diols forming polyesters. But he could not achieve molecular weights greater than about 4,000 below the size where many of the interesting so-called polymeric properties appear.

DuPont was looking for a synthetic rubber. Carothers assigned Arnold Collins to this task. Collin's initial task was to produce pure divinylacetylene. While performing the distillation of an acetylene reaction in 1930, he obtained a small amount of an unknown liquid that he set aside in a test tube. After several days the liquid turned to a solid. The solid bounced and eventually was shown to be a synthetic rubber polychloroprene whose properties were similar to those of vulcanized rubber, but it was superior in its resistance to ozone, ordinary oxidation, and to most organic liquids. It was sold under its generic name "neoprene" and the trade name "Duprene."

Also in 1930 Carothers and Julian Hill designed a process to remove water that was formed during the esterification reaction. Essentially, they simply froze the water as it was removed using another recent invention called a molecular still (basically a heating plate coupled to vacuum) allowing the formation longer chains. In April, Hill synthesized a polyester using this approach and touched a glass stirring rod to the hot mass and then pulled the rod away effectively forming strong fibers, the pulling helping reorient the mobile polyester chains. The polyester had a molecular weight of about 12,000. Additional strength was achieved by again pulling the cooled fibers. Further reorienting occurred. This process of drawing or pulling to produce stronger fibers is now known as *cold drawing* and is widely used in the formation of fibers today. The process of cold drawing was discovered by Carother's group. While interesting, the fibers were not considered to be of commercial use. Carothers and his group then moved to look at the reaction of diacids with diamines instead of diols. Again, fibers were formed but these initial materials were deemed not to be particularly interesting.

In 1934, Paul Flory was hired to work with Carothers to help gain a mathematical understanding of the polymerization process and relationships. Thus, there was an early association between theory and practice or structure–property relationships.

The polyamide fiber project began again. One promising candidate was formed from the reaction of adipic acid with hexamethylenediamine, called *fiber 66* because each carbon-containing unit had six carbons. It formed a strong, elastic, largely insoluble fiber with a relatively high melt temperature. DuPont chose this material for production. These polyamides were given the name "nylons." Thus was born nylon-6,6. It was the first synthetic material whose properties equaled or exceeded the natural analog, namely silk. (In reality, this may not be the truth, but at the time it was believed to be true.)

As women's hemlines rose in the 1930s, silk stockings were in great demand but were very expensive. Nylon changed this. Nylon could be woven into sheer hosiery. The initial presentation of nylon hose to the public was by Stine at a forum of women's club members in New York City on October 24, 1938. Nearly 800,000 pairs were sold on May 15, 1940 alone—the first day they were on the market. By 1941 nylon hosiery held 30% of the market, but by December 1941 most nylon manufactured was diverted to make parachutes and other items for the war effort.

From these studies Carothers established several concepts. First, polymers could be formed by employing already known organic reactions but with reactants that had more than one reactive group per molecule. Second, the forces that bring together the individual polymer units are the same as those that hold together the starting materials, namely, primary covalent bonds. Much of the polymer chemistry names and ideas that permeate polymer science were standardized through his efforts.

Representing the true multidisciplinary nature of polymers, early important contributions were also made by physicists, engineers, and those from biology, medicine, and mathematics including W. H. Bragg, Peter Debye, Albert Einstein, and R. Simha.

World War II helped shape the future of polymers. Wartime demands and shortages encouraged scientists to seek substitutes and materials that even exceeded currently available materials. A polycarbonate (Kevlar) that could stop a speeding bullet was developed as was polytetrafluoroethylene (Teflon), which was superslick. New materials were developed spurred on by the needs of the military, electronics industry, food industry, etc. The creation of new materials continues at an accelerated pace brought on by the need for materials with specific properties and the growing ability to tailor-make giant molecules—macromolecules—polymers.

The leading polymer scientists of the 1930s agreed that polymers were chain-like molecules and that the viscosities of solution of these macromolecules were dependent on the size and shape of the molecules in the solution. While it is true that the large-scale production of many polymers was accelerated by World War II, it must be recognized that the production of these essential products was dependent on the concepts developed by Staudinger, Carothers, Mark, and other leading polymer scientists.

The development of polymer technology since the 1940s has been extremely rapid (Table 1.1). In some instances, such as polymerization in aqueous emulsion systems, the art has preceded the science, but much theory has been developed, so that polymer science today is relevant, based on sound science, and no longer largely empirical.

1.2 TODAY'S MARKETPLACE

Polymers are all around us. The soil we grow our foods from is largely polymeric as are the foods we eat. The plants about us are largely polymeric. We are walking exhibits as to the widespread nature of polymers—from our hair and fingernails, our skin, bones, tendons and muscles; our socks, shoes, glasses, undergarments; the morning newspaper; major portions of our automobiles, airplanes, trucks, boats, space craft; our chairs, waste paper baskets, pencils, tables, pictures, coaches, curtains, glass windows; the roads we drive on, the houses we live in, and the buildings we work in; the tapes and CDs we listen to; packaging—all are either totally polymeric or contain a large amount of polymeric materials. Table 1.2 lists some general groupings of important polymers.

As shown in Tables 1.3 to 1.6, almost 90 billion pounds (45 million tons) of synthetic polymers is produced annually in the United States, and the growth of the industry is continuing at a faster rate than that of any other industry. There is every reason to believe that this polymer age will continue as long as petroleum and other feedstocks are available and as long as consumers continue to enjoy the comfort, protection, and health benefits provided by elastomers, fibers, plastics, adhesives, and coatings. The 90 billion pounds translates to over 200 pounds of synthetic polymers for every man, woman, and child in the United States. This does not include paper- and wood-related products, natural polymers, such as cotton and wool, or inorganic polymers.

Table 1.2 Polymer Classes: Natural and Synthetic

Inorganic			Organic	
Natural	Synthetic	Organic/inorganic	Natural	Synthetic
Clays	Fibrous glass	Siloxanes	Proteins	Polyethylene
Cement	Poly(sulfur nitride)	Polyphosphazenes	Nucleic acids	Polystyrene
Pottery	Poly(boron nitride)	Polyphosphate esters	Lignins	Nylons
Bricks	Silicon carbide	Polysilanes	Polysaccharides	Polyesters
Sands		Sol-gel networks	Melanins	Polyurethanes
Glasses			Polyisoprenes	Poly(methyl methacrylate)
Rock-like				Polytetrafluoroethyler
Agate				Polyurethane
Talc				Poly(vinyl chloride)
Zirconia				Polycarbonate
Mica				Polypropylene
Asbestos				Poly(vinyl alcohol)
Quartz				
Ceramics				
Graphite/diamond				
Silicas				

Table 1.3 U.S. Production of Plastics (Millions of Pounds)

Plastic	1975	1980	1985	1990	1995	2000
Thermosetting resins						
Epoxies	200	320	390	510	630	660
Polyesters	800	950	1200	1300	1460	2400
Ureas	690	1200	1200	1500	1890	2580
Melamines	120	170	200	220	290	290
Phenolics	1100	1500	2600	2900	3210	3940
Thermoplastics						
Polyethylene—low density[a]	4700	7300	8900	9700	12,900	17,900
Polyethylene—high density	2500	4400	6700	8100	11,200	15,400
Polypropylene	1900	3600	5100	7200	10,900	15,460
Styrene-acrylonitrile	110	100	70	135	130	124
Polystyrene	2700	3500	4100	5000	5600	6600
Acrylonitrile-butadiene-styrene	1200	1700	2000	2300	2900	3100
Polyamides	140	270	400	560	1000	1400
Poly(vinyl chloride) and copolymers	3600	5500	6800	9100	12,300	14,300
Polyester	—	—	1300	1880	3200	4400

[a] Includes low density and linear low density.

Source: American Plastics Council.

Table 1.4 U.S. Production of Man-made Fibers (Millions of Pounds)

Fiber	1975	1980	1984	1990	1995	2000
Noncellulosic						
Acrylics	500	780	670	510	430	340
Nylons	1800	780	2400	2700	2700	2610
Olefins	500	750	1000	1800	2390	3180
Polyesters	3000	4000	3400	3200	3890	3870
Cellulosic						
Acetate	310	320	200	210	230	—
Rayon	440	490	420	300	270	—
Glass	550	870	1400	—	—	—

Source: Fiber Economics Bureau.

Table 1.5 U.S. Production of Paints and Coatings (Millions of Gallons)

Paint/coating	1987	1990	1995	2000
Architectural	530	560	621	668
Product	340	340	376	449
Special	150	200	195	189

Source: Department of Commerce.

Polymers are often divided according to whether they can be melted and reshaped through application of heat and pressure, called *thermoplastics*, or whether they decompose before they can be melted or reshaped, called *thermosets* (Table 1.3). While both thermoset polymers and thermoplastics can be recycled, because thermoplastics can be reshaped simply through the application of heat and pressure, recycling of thermoplastics is easier.

The number of professional chemists directly involved with polymers is estimated to be between 40% and 60% of all of the chemists employed. The number of chemical industrial employees involved with synthetic polymers is reported by the U.S. Department of Labor to be over one million, or almost 60% of the chemical industrial work force

Table 1.6 U.S. Production of Synthetic Rubber (Millions of Pounds)

Rubber	1975	1980	1985	1990	1995	2000
Styrene-butadiene	2400	2200	1600	1580	1760	1750
Polybutadiene	580	620	660	890	1040	1210
Nitrile	120	120	120	120	160	180
Ethylene-propylene	160	280	400	420	540	700
Other	660	840	920	760	1000	1100

Source: International Institute of Synthetic Rubber Producers.

Table 1.7 U.S. Chemical Industrial Employment (in Thousands)

Sector	1975	1985	1994	2000
Industrial inorganic	149	143	131	98
Drugs	167	205	264	305
Soaps, cleaners, etc.	142	148	152	158
Industrial organics	150	164	144	121
Agricultural	65	60	56	53
Synthetic polymers	888	1026	1150	1206

Source: U.S. Department of Labor.

(Table 1.7). There are almost another million employed as production workers in the synthetic polymer sector (Table 1.8).

Polymeric materials, along with the majority of the chemical industrial products, contribute positively to the balance of trade (Table 1.9). In fact, plastics and resins show the greatest value increase of exports minus imports.

Table 1.10 contains a listing of the major chemical producers. All of these producers are involved directly and/or indirectly with polymers.

Table 1.8 U.S. Production Workers (in Thousands), 2000

Sector	Number
Inorganic chemicals	55
Drugs	140
Soap, cleaners, etc.	97
Organic chemicals	73
Agricultural	32
Synthetic polymers	909

Source: U.S. Department of Labor.

Table 1.9 U.S. Chemical Trade—Imports and Exports, 1994 and 2000 (Millions of Dollars)

Chemical	Exports (1994)	Exports (2000)	Imports (1994)	Imports (2000)
Organic chemicals	12,800	18,900	10,800	28,600
Inorganic chemicals	4100	5500	4100	6100
Oils and perfumes	3500	5000	2000	3200
Dyes, colorants	2300	4200	1900	2700
Medicinals and pharmaceuticals	6100	13,100	4700	14,700
Fertilizers	2700	2500	1300	1700
Plastics and resins	8500	20,100	3300	10,600
Others	7600	12,700	2700	5700
Total chemicals[a]	51,600	82,500	33,400	73,600
Total	502,800	780,400	669,100	1,024,800

[a] Includes nonlisted chemicals.

Table 1.10 Major Chemical Producers Based on Sales (in Millions of U.S. Dollars)

Producer	1985	1990	1994	2000
United States				
DuPont	11,300	15,600	16,800	28,400
Dow Chemical	9500	14,700	14,100	23,000
Exxon (now Exxon-Mobile)	6700	11,200	11,000	21,500
Monsanto	5200	5700	5900	3900
Union Carbide	4000	7600	4900	6500
Shell Oil	3300	3700	4100	6300
Celanese (now Hoechst Celanese)	3300	5500	7000	2800
W. R. Grace	2900	3600	3200	1600
Chevron (now Chevron Phillips)	2600	3300	3100	7600
BASF	2600	4400	4300	7800
Eastman Kodak (now Eastman Chemical)	2300	3600	4300	5300
General Electric	2300	5200	5700	7800
Phillips Petroleum (now Chevron Phillips)	2300	2100	2800	
Mobil (now Exxon-Mobil)	2300	4100	4200	
Rohm & Haas	2000	2800	3500	6000
Air Products	1700	2600	3200	5200
Occidental Petroleum	1600	5000	4700	3800
Ciba	1500	2000	2800	2000
Ashland Oil	1500	2200	2900	1300
B. F. Goodrich	1400	1900	1100	1200
FMC	1300	1600	1900	2100
ICI Americas	—	—	4000	3,300
Praxair				5000
IMC Global				2100
Solutia				3200
Dow Corning				2800
Potash Corp. of Sask.				2200
Hercules				3200
Huntsman Chemical	—	—	3400	8000
Akzo-Nobel	—	—	3000	3300
Equistar				7500
Totalfina Elf				4800
Lyondell				4000
Nova				3900
PPG				6300
BP				5100
Europe				
Bayer (Germany)	15,600		26,800	28,500
BASF (Germany)	15,100		28,700	33,100
Imperial Chemical Inds. (U.K.)	13,900		15,400	11,700
DSM (Netherlands)	7300		4900	7500
Akzo (Netherlands)	5400		12,200	12,900
Norsk Hydro (Norway)	4900		10,100	17,800
Solvay (Belgium)	3800		7800	8200
Roche (Switzerland)	3600		10,800	17000
Ciba (Switzerland)	—		16,100	4700

(*continued*)

Table 1.10 Continued

Producer	1985	1990	1994	2000
Europe				
Degussa (Germany)	—		8500	18,700
EniChem (Italy)	—		7100	5500
Aventis (France)				20,500
Air Liquid (France)				7500
Syngenta (Switzerland)				7200
Rhodia (France)				6800
Clairant (Switzerland)				6300
Merch (Germany)				6200
Japan				
Mitsubishi Chemical Industries	3960		8500	16,200
Asahi Chemical Industries	3910		9600	11,800
Sumitomo Chemical	3220		5500	9700
Toray Industries	3200		5100	10,000
Mitsui Toatsu Chemicals	2100		3700	8700
Teijin	2100		3200	7100
Showa Denko	2100		4400	6900
Dainippon				9100
Shin-Etsu				7500
Canada				
DuPont Canada	870		1230	1500
Nova Corp.	—		2700	3900
Methanex	—		1500	1100
Potash Corp.				2200
Agrium				1900

Thus, polymers play a critical role in our everyday lives, actually forming the basis for both plant and animal life, and represent an area where chemists continue to make important contributions.

SUMMARY

After reading this chapter, you should understand the following concepts.

1. Polymers or macromolecules are giant molecules with molecular weights at least 100 times greater than those of smaller molecules such as water or methanol.
2. If we disregard metals and inorganic compounds, we observe that practically everything else in this world is polymeric. This includes the protein and nucleic acid in our bodies, the fibers we use for clothing, the protein and starch we eat, the elastomers in our automobile tires, and the paint, plastic wall and floor coverings, foam insulation, dishes, furniture, pipes, and so forth in our homes.
3. In spite of the many varieties of fibers, elastomers, and plastic, they all have a similar structure and are governed by the same theories. Linear polymers, such as high-density polyethylene (HDPE), consist of long chains made up of thousands of covalently bonded carbon atoms. The repeating unit for HDPE is represented as $[CH_2CH_2]_n$, where n is the number of repeating units.

4. Most linear polymers such as HDPE are thermoplastic, i.e., they may be softened by heat and hardened by cooling in a reversible physical process. However, linear polymers like cellulose, which have very strong intermolecular forces (hydrogen bonds), cannot be softened by heating below the decomposition temperature.
5. Thermoset polymers are crosslinked and cannot be softened by heating. Thermoplastics such as natural rubber and A-stage resole Bakelite resins can be transformed to thermosetting polymers by the introduction of crosslinks between the polymer chains.
6. Early developments in polymer technology were empirical because of a lack of knowledge of polymer science. Advancements in polymer technology were rapid in the 1930s and 1940s because of the theories developed by Staudinger, Carothers, Mark, and other polymer scientists.
7. Thermoplastic resole resins that may be thermoset by heating are obtained by heating phenol and formaldehyde on the alkaline side. Novolacs are obtained when an insufficient amount of formaldehyde is reacted in acid solution. Novolacs are converted to infusible plastics by heating with hexamethylenetetramine.

GLOSSARY

ABS: A polymer produced by the copolymerization of acrylonitrile, butadiene, and styrene.
acetal: A polymer produced by the polymerization of formaldehyde.
alkyd: A polyester produced by the condensation of a dihydric alcohol, such as ethylene glycol, and a dicarboxylic acid, such as phthalic acid, in the presence of controlled amounts of an unsaturated monofunctional organic acid, such as oleic acid.
A-stage: A linear resole resin.
Bakelite: A polymer produced by the condensation of phenol and formaldehyde.
biopolymer: A naturally occurring polymer, such as protein.
buna: Copolymer of butadiene and styrene or acrylonitrile.
butyl rubber: A copolymer of isobutylene and isoprene.
cellulose: A naturally occurring carbohydrate polymer consisting of repeating glucose units.
cellulose acetate: The ester of cellulose and acetic acid.
cellulose nitrate: The product obtained by the reaction of nitric acid and sulfuric acid with cellulose; erroneously called nitrocellulose. The product is classified as primary, secondary, or tertiary according to how many groups in each repeating anhydroglucose unit in cellulose are nitrated.
cis: A geometric isomer with both groups on the same side of the ethylenic double bond.
collodion: A solution of cellulose nitrate in an equimolar mixture of ethanol and ethyl ether.
colloid: An aggregate 10^{-9} to 10^{-7} m long; an aggregate of smaller particles.
coumarone-indene resins: Polymers produced by the polymerization of distillation residues.
covalent bond: Chemical bonds formed by the sharing of electrons of the bonded atoms such as the carbon atoms in graphite or diamonds.
cross-links: Covalent bonds between two or more linear polymeric chains.
crystallites: Aggregates of polymers in crystalline form.
C-stage: A crosslinked resole resin.

cuprammonia rayon: Rayon produced from a solution of cellulose in a copper ammonia hydroxide solution.

denaturation: The change in properties of a protein resulting from the application of heat or the addition of a foreign agent, such as ethanol.

ebonite: Hard rubber; highly crosslinked natural rubber (NR).

elastomer: A rubber.

filament: The individual extrudate emerging from the holes in a spinneret.

functionality: The number of reactive groups in a molecule.

Galalith: A plastic produced by molding casein.

glyptal: A polyester produced by the condensation of glycerol and phthalic anhydride.

hydrogen bonds: Very strong forces resulting from the attraction of hydrogen atoms in one molecule with an oxygen or nitrogen atom in another molecule. These forces may also be present as intramolecular forces in macromolecules.

intermolecular forces: Secondary valence forces between molecules.

intramolecular forces: Secondary valence forces within a molecule.

linear: A continuous chain, such as HDPE.

macromolecule: A polymer.

natural rubber, or NR (*Hevea brasiliensis*): Polyisoprene obtained from rubber plants.

novolac: A thermoplastic phenol-formaldehyde resin prepared by the condensation of phenol and a small amount of formaldehyde on the acid side. Novolacs may be advanced to thermoset by heating with formaldehyde, which is usually obtained by the thermal decomposition of hexamethylenetetramine.

NR: Natural rubber.

nylon-66 (or nylon-6,6): A polyamide produced by the condensation of adipic acid [$HOOC(CH_2)_4COOH$] and hexamethylenediamine [$H_2N(CH_2)_6NH_2$].

oligomer: A very low molecular weight polymer in which the number of repeating units (n) equals 2 to 10 (*oligos* is the Greek term for few).

plasticizer: An additive that reduces intermolecular forces in polymers.

polymer: A giant molecule (or macromolecule) made up of multiple repeating units, such as polyethylene, in which at least 1000 ethylene units ($—CH_2CH_2—$) are joined together by covalent bonds. The word is derived from the Greek words meaning many parts.

polymer age: An age when the use of polymers is emphasized, as in the twentieth century.

protein: A polymer made up of many amino acid repeating units, i.e., a polyamide.

Raoult's law: A law that states that colligative properties of solutions, such as osmotic pressure and changes in vapor pressure, are related to the number of solute molecules present.

rayon: Regenerated cellulose in the form of filaments.

resole: A condensation product produced by the reaction of phenol and formaldehyde under alkaline conditions.

shellac: A resin secreted by small coccid insects.

spinneret: Small holes through which a solution or molten polymer is extruded in order to form filaments for fibers.

tanning: Crosslinking of proteins by the reaction with crosslinking agents such as tannic acid.

thermoplastic: A linear polymer that may be softened by heat and cooled in a reversible physical process.

thermoset plastic: A network polymer usually obtained by crosslinking a linear polymer.

Thiokol: A polyethylene sulfide elastomer.

viscose: A solution of cellulose xanthate produced by the reaction of alkali cellulose and carbon disulfide.

viscosity: The resistance to flow as applied to a solution or a molten solid.

vital force concept: A hypothesis that stated that organic compounds could be produced only by natural processes and not in the laboratory.

vulcanization: The process in which natural rubber is crosslinked by heating with sulfur.

EXERCISES

1. Name six polymers that you encounter daily.
2. Which would be more likely to be softened by heat?
    (a) (1) unvulcanized rubber, or (2) ebonite.
    (b) (1) A-stage, or (2) C-stage resole
    (c) (1) cellulose, or (2) cellulose acetate.
3. Name a polymer having the following repeating units:
    (a) ethylene ($—CH_2CH_2—$)
    (b) phenol and formaldehyde residual units.
    (c) amino acid residual units
4. In which of the following polymers will hydrogen bonding predominate?
    (a) natural rubber (NR).
    (b) linear polyethylene (HDPE)
    (c) cellulose.
    (d) cellulose nitrate
5. Which of the following products are polymeric?
    (a) water
    (b) wood
    (c) meat
    (d) cotton
    (e) rubber tires
    (f) paint
6. Which of the following is a thermoset or cross-linked polymer?
    (a) cellulose
    (b) unvulcanized rubber
    (c) A-stage resole
    (d) cellulose nitrate
    (e) molded Bakelite
    (f) ebonite
7. Which of the items in question 6 are thermoplastic?
8. If you were Staudiner, how would you answer your critical colleagues?
9. Why are so many outstanding polymer scientists alive today?
10. What percentage of polymer science students receive job offers after graduation?
11. What is the molecular weight of $H(CH_2CH_2)_{1000}H$?
12. What is the principal difference between rayon and cellophane?
13. Which is the more heat stable, a resole or a novolac phenolic (Bakelite) resin?

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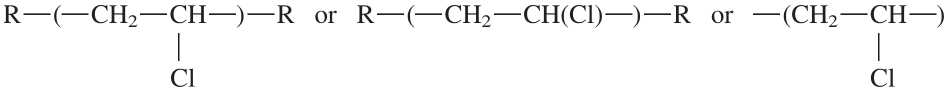
2

Polymer Structure (Morphology)

The size and shape of polymers are intimately connected to their properties. The shape of polymers is also intimately connected to the size of the various units that make up the macromolecules and the various primary and secondary bonding forces that are present within the chain and between chains. This chapter covers the basic components that influence polymer shape or morphology.

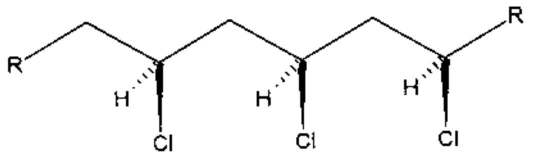
We generally describe the structure of both synthetic and natural polymers in terms of four levels of structure. The primary structure describes the precise sequence of the individual atoms that compose the polymer chain. For polymers where there is only an average structure, such as proteins, polysaccharides, and nucleic acids, a representative chain structure is often given.

The structure can be given as a single repeat unit such that the full polymer structure can be obtained by simply repeating the repeat unit 100, 500, or 1,000 times, depending on the precise number of repeat units in the polymer chain. For poly(vinyl chloride), PVC, this is

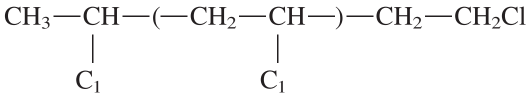


$$R\text{—}(\text{—}CH_2\text{—}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{—})\text{—}R \quad \text{or} \quad R\text{—}(\text{—}CH_2\text{—}CH(Cl)\text{—})\text{—}R \quad \text{or} \quad \text{—}(CH_2\text{—}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{—})$$

Or some fuller description of the primary structure may be given such as that below for three repeat units of PVC where the particular geometry about each chiral carbon is given.

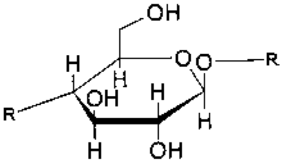


The ends may or may not be given depending on whether they are important to the particular point being made. Thus, for the single PVC repeat unit given above the end groups may given as follows:



$$CH_3—\underset{\overset{|}{C_1}}{CH}—(—CH_2—\underset{\overset{|}{C_1}}{CH}—)—CH_2—CH_2Cl$$

The repeat unit for cellulose is



The secondary structure describes the molecular shape or conformation of the polymer chain. For most linear polymers this shape approaches a helical or "pleated skirt" (or sheet) arrangement depending on the nature of the polymer, treatment, and function. Examples of secondary structures appear in Figs. 2.15 and 2.20.

The tertiary structure describes the shaping or folding of the polymer. Examples of this are found in Figs. 2.9, 2.16, and 2.21–2.22.

Finally, the quaternary structure represents the overall shape of groups of the tertiary structures where the tertiary structures may be similar or different. Examples are found in Figs. 2.21–2.22.

2.1 STEREOCHEMISTRY OF POLYMERS

The terms "memory" and "to remember" are similar and used by polymer chemists in similar, but different, ways. The first use of the terms "memory" and "to remember" involves reversible changes in the polymer structure usually associated with stress–strain deformation of a rubber material where the dislodged, moved polymer segments are connected to one another through chemical and physical crosslinks, so that once the particular stress/strain is removed the polymer returns to its original, prestress–strain arrangement of the particular polymer segments. Thus, the polymer "remembers" its initial segmental arrangement and returns to it through the guiding of the crosslinks.

The second use involves nonreversible changes of polymer segments and whole chain movements also brought about through stress–strain actions. These changes include any synthetic chain and segmental orientations as well as postsynthesis changes including fabrications effects. These changes involve "permanent" changes in chain and segmental orientation and in some ways these changes represent the total history of the polymer materials from inception (synthesis) through the moment when a particular property or behavior is measured. These irreversible or nonreversible changes occur with both crosslinked and noncrosslinked materials and are largely responsible for the change in polymer property as the material moves from being synthesized, processed, fabricated, and used in what ever capacity it finds itself. Thus, the polymeric material "remembers" its history with respect to changes and forces that influence chain and segmental chain changes. The ability of polymers to remember and have a memory are a direct consequence of their size.

We can get an idea of the influence of size in looking at the series of methylene hydrocarbons as the number of carbon atoms increases. For low numbers of carbons,

Table 2.1 Typical Properties of Straight Chain Hydrocarbons

Average number of carbon atoms	Boiling range,°C	Name	Physical state at room temp.	Typical uses
1–4	<30	Gas	Gas	Heating
5–10	30–180	Gasoline	Liquid	Automotive fuel
11–12	180–230	Kerosene	Liquid	Jet fuel, heating
13–17	230–300	Light gas oil	Liquid	Diesel fuel, heating
18–25	305–400	Heavy gas oil	Viscous liquid	Heating
26–50	Decomposes	Wax	Waxy	Wax candles
50–1000	Decomposes		Tough waxy to solid	Wax coatings of food containers
1000–5000	Decomposes	Polyethylene	Solid	Bottles, containers, films
>5000	Decomposes	Polyethylene	Solid	Waste bags, ballistic wear, fibers, automotive parts, truck liners

methane, ethane, propane, butane, the materials are gases at room temperature. For the next groupings (Table 2.1) the materials are liquids. The individual hydrocarbon chains are held together by dispersion forces that are a sum of the individual methylene and end group forces. There is a gradual increase in boiling point and total dispersion forces for the individual chains until the materials become waxy solids such as found in bees' waxes and finally where the total dispersion forces are sufficient to be greater than individual carbon–carbon bond strengths, so that the chains decompose prior to their evaporation. Finally, the chain lengths are sufficient to give the tough and brittle solids we call polyethylene. It is interesting to note that these long chain straight chain hydrocarbons become very strong but brittle. They are crystalline—and as with most other crystalline materials, such as rocks and diamonds, they are strong but brittle. Fortunately, synthetic polyethylene contains both crystalline regions where the polymer chains are arranged in ordered lines and regions where the chains are not arranged in ordered lines. These latter arrangements are imposed on the polyethylene because of the presence of branching in the linear polymer backbone. They are referred to as amorphous regions and are responsible for allowing the polyethylene to have some flexibility. Thus, many polymers contain both amorphous and crystalline regions that provide both flexibility and strength.

The polyethylene chains described in Table 2.1 exhibit irreversible and, when appropriate crosslinking is present, reversible memory.

As a side note, low-molecular-weight polyethylene with appreciable side branching has a melting range generally below 100°C, whereas high-molecular-weight polyethylene with few branches has a melting range approaching the theoretical value of about 145°C.

High-density polyethylene (HDPE), formerly called low-pressure polyethylene $[H(CH_2CH_2)_nH]$, like other alkanes $[H(CH_2)_nH]$, may be used to illustrate a lot of polymer structure. As in introductory organic chemistry, we can comprehend almost all of the complex organic compounds if we understand the basic chemistry and geometry.

High-density polyethylene, like decane $[H(CH_2)_{10}H]$ or paraffin $[H(CH_2)_{\sim 50}H]$, is a largely linear chain-like molecule consisting of catenated carbon atoms bonded covalently. The carbon atoms in all alkanes, including HDPE, are joined at characteristic tetrahedral bond angles of approximately 109.5°. While decane consists of 10 methylene groups (CH_2), HDPE may contain more than 1000 of these groups. While we use the term normal straight chain or linear for alkanes, we know that because of the characteristic bond angles the chains are zigzag-shaped.

The distance between the carbon atoms is 1.54 angstroms (Å) or 0.154 nanometers (nm). The apparent zigzag distance between carbon atoms in a chain of many carbon atoms is 1.26 Å, or 0.126 nm. Therefore, the length of an extended nonane chain would be 8 (1.26 Å), or 10.08 Å, or 1.008 nm. Likewise, the length of an extended chain of HDPE having 1000 repeat ethylene units or structural elements [$H(CH_2CH_2)_{1000}H$ or $H(CH_2)_{2000}H$] would be 2520 Å or 252 nm. However, as shown by the magnified simulated structure in the diagram for HDPE (Fig. 2.1, top) because of rotation of the carbon–carbon

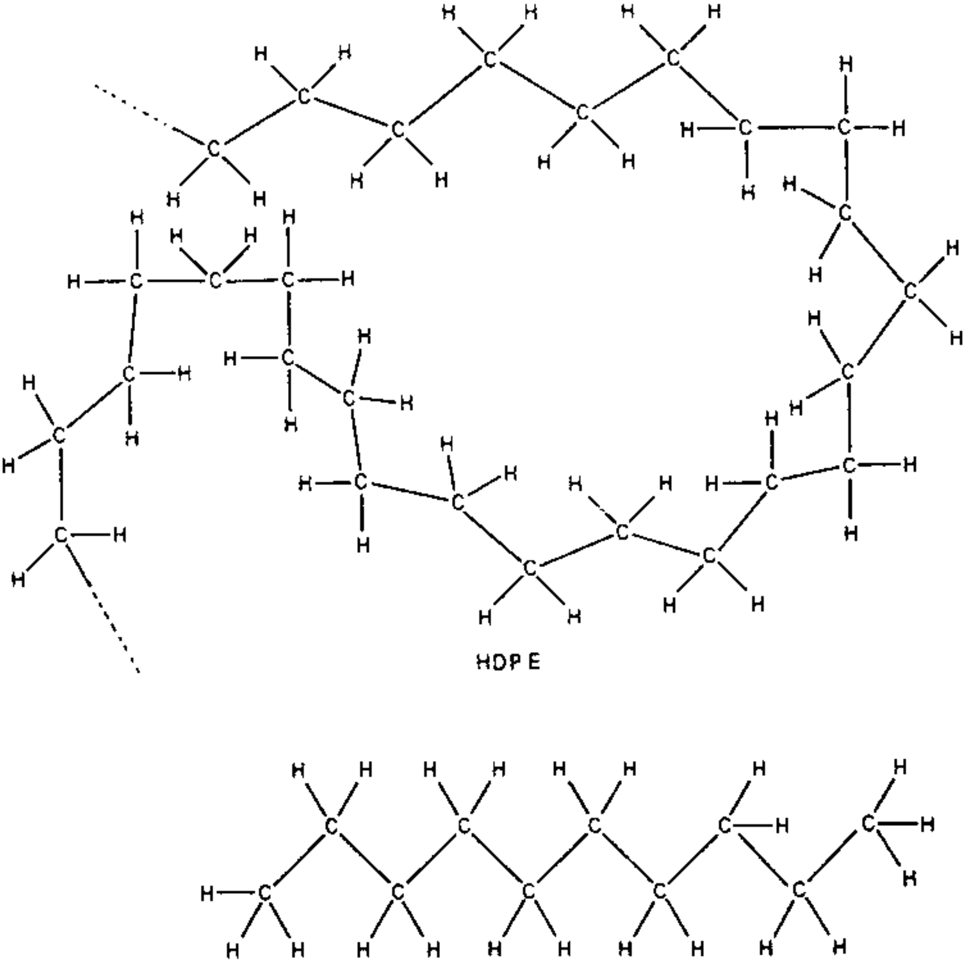


Figure 2.1 Magnified simulated structure of high-density polyethylene (HDPE), contrasted with the structural formula of decane.

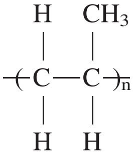
bonds, these chains are seldom extended to their full contour length but are present in many different shapes, or *conformations*.

Problem

Determine the contour length of a polyethylene chain 1300 ethylene units long given the average zigzag distance between carbon atoms of 0.126 nm. There are two carbon atoms within the polymer chain backbone per repeat unit. Thus, per unit the average contour length is $2 \times 0.126\ \text{nm} = 0.252\ \text{nm}$. The contour length is then $0.252\ \text{nm/unit} \times 1300$ units $\simeq 330$ nm.

Each specific protein molecule has a specific molecular weight, like the classic small molecules, and is said to be monodisperse with respect to molecular weight. However, commercial synthetic polymers, such as HDPE, are made up of molecules of different molecular weights. Thus, the numerical value for n, or the degree of polymerization (DP), should be considered as an average DP and designated with an overbar, i.e., $\overline{\text{DP}}$. Accordingly, the average molecular weight ($\overline{\text{M}}$) of a polydisperse polymer will equal the product of the (average) $\overline{\text{DP}}$ and the molecular weight of the repeating unit or mer.

In classic organic chemistry, it is customary to call a nonlinear molecule, like isobutane, a branched chain. However, the polymer chemist uses the term *pendant group* to label any group present on the repeating units. Thus, polypropylene



$$-\!\!\left(\begin{array}{cc} \text{H} & \text{CH}_3 \\ | & | \\ \text{C} - & \text{C} \\ | & | \\ \text{H} & \text{H} \end{array}\right)_{\!n}\!\!-$$

has a pendant methyl group but is designated as a linear polymer. In contrast, low-density polyethylene (LDPE), which was formerly called high-pressure polyethylene, is a branched polymer because chain extensions or branches of polyethylene sequences are present on branch points, irregularly spaced along the polymer chain, as shown in Fig. 2.2. The number of branches in nonlinear polyethylene (LDPE) may vary from 1.5 per 20 methylene groups to 1 per 2000 methylene groups. This branching, like branching in simple alkanes like isobutane, increases the specific volume and thus reduces the density of the polymer.

Recently, low-pressure processes have been developed that produce linear low-density polyethylene (LLDPE). LLDPE is largely linear but does have some branching. The linearity provides strength while the branching provides toughness (Table 2.2).

Problem

Determine the approximate number of repeat units (degree of polymerization) for a polypropylene chain with a molecular weight of 5.4×10^4. The formula weight of a polypropylene unit is 42 atomic mass units (amu). The number of repeat units $= 54{,}000$ amu/42 amu/unit $\simeq 1300$ units.

Both linear and branched polymers are thermoplastics. However, crosslinked three-dimensional, or network, polymers are thermoset polymers. As shown in Fig. 2.3,, the crosslinked density may vary from the low crosslinked density in vulcanized rubber to the high crosslinked density observed in ebonite.

While there is only one possible arrangement for the repeat units in HDPE, these units in polypropylene (PP) and many other polymers may be arranged in a head-to-tail

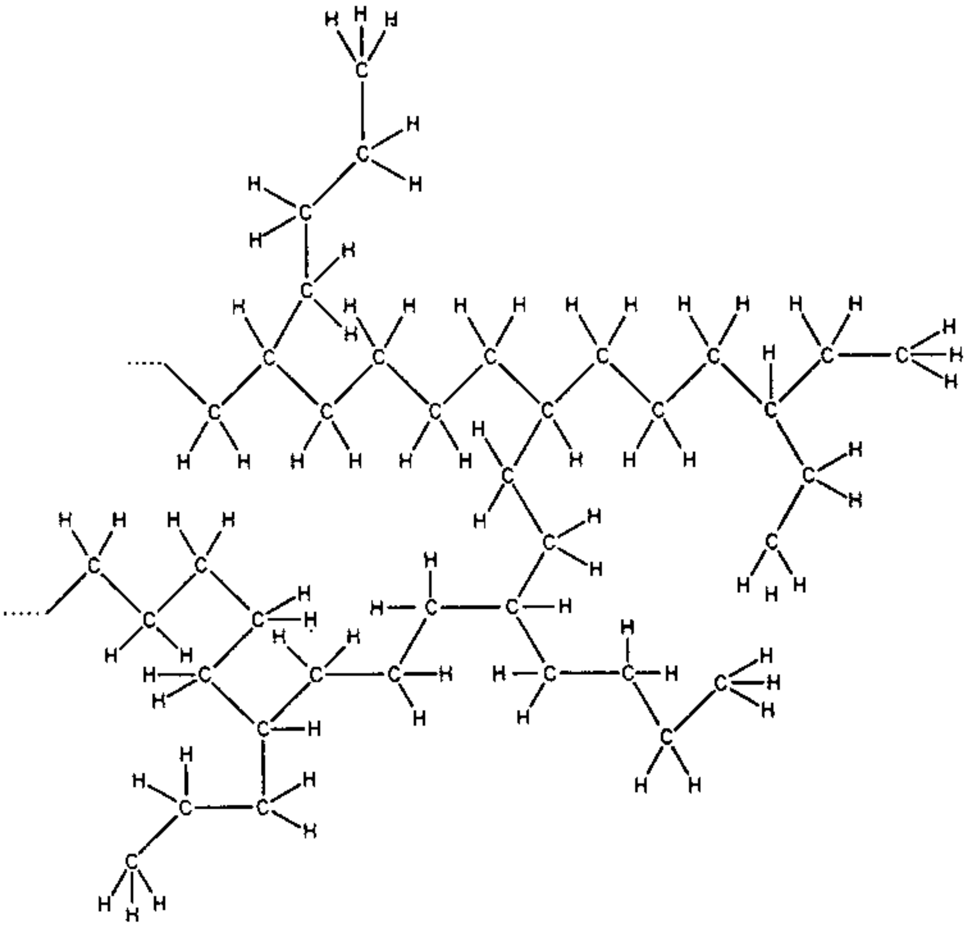


Figure 2.2 Simulated structural formula of branched low-density polyethylene (LDPE; compare to Fig. 2.1. HDPE).

Table 2.2 Types of Commercial Polyethylene

	General structure	Crystallinity (%)	Density (g/cc)
LDPE	Linear with branching	50	0.92–0.94
LLDPE	Linear with less branching	50	0.92–0.94
HDPE	Linear with little branching	90	0.95

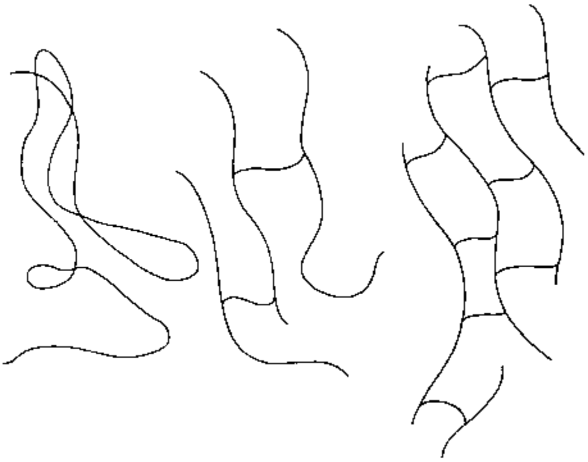


Figure 2.3 Simulated skeletal structural formulas of a linear polymer (left) and network polymers with low (middle) and high (right) crosslinked density.

or a head-to-head configuration, as shown in Fig. 2.4. The usual arrangement is head to tail, so that the pendant groups are usually on every other carbon atom in the chain.

The polymerization of monosubstituted vinyl compounds give polymers like polystyrene and polypropylene polymer chains that possess chiral sites on every other carbon in the polymer backbone. (A review of chiral sites and other related topics is given in Appendix L.) The number of possible arrangements within a polymer chain is staggering, since the number of possible isomers is 2^n where "n" is the number of chiral sites. Thus, for a relatively short chain containing 50 propylene units, the number of isomers is about 1 times 10^{15}. While the presence of such sites in smaller molecules can be the cause of optical activity, these polymers are not optically active since the combined interactions

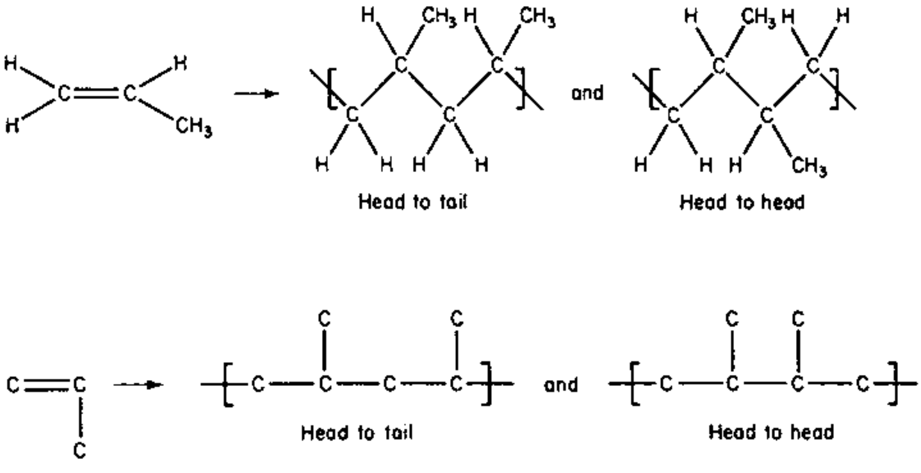


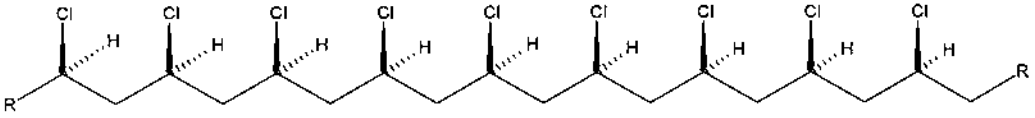
Figure 2.4 Simulated structural (top) and skeletal (bottom) formulas showing the usual head-to-tail and the less usual head-to-head configurations of polypropylene.

with light are negated by similar, but not identical, other sites contained on the particular and other polymer chains. Further, it is quite possible that no two polymer chains made during a polymerization will be exactly identical.

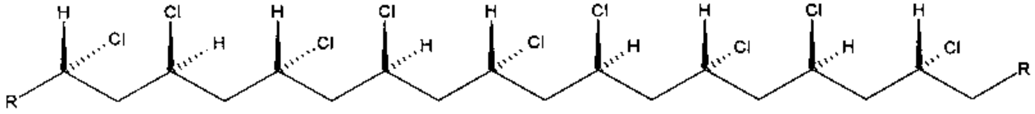
The particular combinations of like and mirror image units within a polymer chain influences the polymer properties on a molecular level. On the bulk level, the average individual chain structure influences properties.

In the early 1950s, Nobel laureate Giulio Natta used stereospecific coordination catalysts to produce stereospecific isomers of polypropylene. Natta used the term *tacticity* to describe the different possible structures. As shown in Figs. 2.5 and 2.6 the isomer corresponding to the arrangement DDDD or LLLL is called isotactic. The isomer corresponding to the arrangement DLDL is called syndiotactic, and a polymer having a random arrangement of building units corresponding to DDLDDLD, etc., is called atactic. Isotactic PP, which is available commercially, is a highly crystalline polymer with a melting point of 160°C, while the atactic isomer is an amorphous (noncrystalline) soft polymer with a melting point of 75°C. The term *eutactic* is used to describe either an isotactic polymer, a syndiotactic polymer, or a mixture of both.

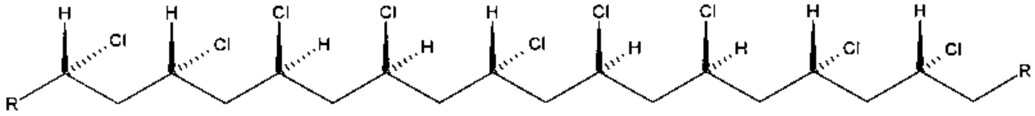
While most polymers contain only one chiral or asymmetrical center in the repeating units, it is possible to have diisotacticity when two different substituents (R and R′) are present at the chiral centers. These isomers are labeled erythro- and threodiisotactic and erythro- and threosyndiotactic isomers, as shown in Fig. 2.7.



Syndiotactic

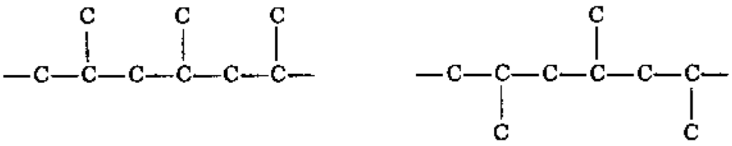


Isotactic



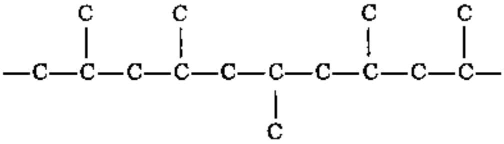
Atactic

Figure 2.5 Skeletal formulas of isotactic, syndiotactic, and atactic poly(vinyl chloride) (PVC).



Isotactic PP

Syndiotactic PP

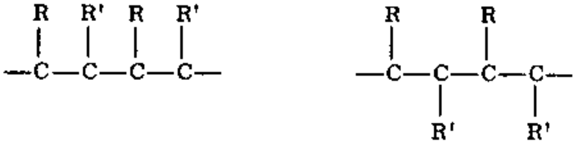


Atactic PP

Figure 2.6 Skeletal formulas of isotactic, syndiotactic, and atactic polypropylene (PP).

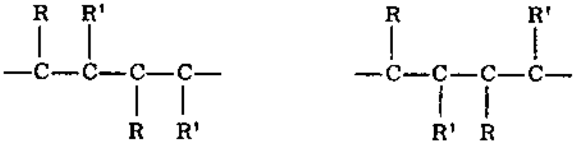
The many different conformers resulting from rotation about the carbon–carbon bond in a simple molecule like n-butane [$H(CH_2)_4H$] may be shown by Newman projections. As shown in Fig. 2.8, the most stable form is the anti or trans (t) conformer in which the two methyl groups (Me) are as far apart as possible. The difference in energy between the anti and eclipsed conformer is at least 3 kcal, and, of course, there are numerous conformations between these two extremes (0 and 180°). Among these are the two mirror image gauche (g) conformers in which the methyl groups are 60° apart.

In a polymer such as HDPE, the methyl groups shown in Fig. 2.8 would be replaced by methylene groups in the chain. The flexibility in a polymer would be related to the ease of conversion from t to g. This ease is dependent on the lack of hindering groups



Erythrodiisotactic

Threodiisotactic



Erythrodisyndiotactic

Threodisyndiotactic

Figure 2.7 Skeletal formulas of ditactic isomers.

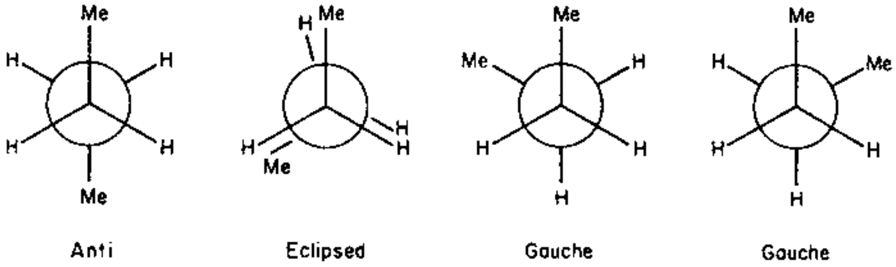


Figure 2.8 Newman projections of designated conformers of n-butane.

and increased temperature. Thus, poly(methyl methacrylate) (PMMA) is hard at room temperature because of the polar ester groups that restrict rotation. In contrast, polyisobutylene is flexible at room temperature. The flexibility of both polymers will be increased as the temperature is increased.

2.2 MOLECULAR INTERACTIONS

The forces present in nature are often divided into primary forces (typically greater than 50 kcal/mol [200 kJ/mol] of interactions) and secondary forces (typically less than 10 kcal/mol [40 kJ/mol] of interactions). Primary bonding forces can be further subdivided into ionic (characterized by a lack of directional bonding; between atoms of largely differing electronegativities; not typically present within polymer backbones), metallic (the number of outer, valence electrons is too small to provide complete outer shells; often considered as charged atoms surrounded by a potentially fluid sea of electrons; lack of bonding direction; not typically found in polymers), and covalent (including coordinate and dative) bonding (which are the major means of bonding within polymers; directional). The bonding lengths of primary bonds are usually about 0.90–2.0 Å (0.09–0.2 nm) with the carbon–carbon bond length being about 1.5–1.6 Å (0.15–0.16 nm).

Atoms in individual polymer molecules are joined to each other by relatively strong covalent bonds. The bond energies of the carbon–carbon bonds are on the order of 80–90 kcal/mol (320–370 kJ/mol). Further more polymer molecules, like all other molecules, are attracted to each other (and for long-chain polymer chains even between segments of the same chain) by intermolecular, secondary forces.

Secondary forces, frequently called van der Waals forces because they are the forces responsible for the van der Waals corrections to the ideal gas relationships, are of longer distance in interaction, in comparison to primary bond lengths, generally having significant interaction between 2.5 and 5 Å (0.25–0.5 nm). The force of these interactions is inversely proportional to some power of r, generally 2 or greater [force $\propto 1/(\text{distance})^r$] and thus is quite dependent on the distance between the interacting molecules. Thus, many physical properties of polymers are indeed quite dependent on both the conformation (arrangements related to rotation about single bonds) and configuration (arrangements related to the actual chemical bonding about a given atom), since both affect the proximity one chain can have relative to another. Thus, amorphous polypropylene is more flexible than crystalline polypropylene (compare linear polymers a (left) and b of Fig. 2.9).

These intermolecular forces are also responsible for the increase in boiling points within a homologous series such as the alkanes, for the higher-than-expected boiling points

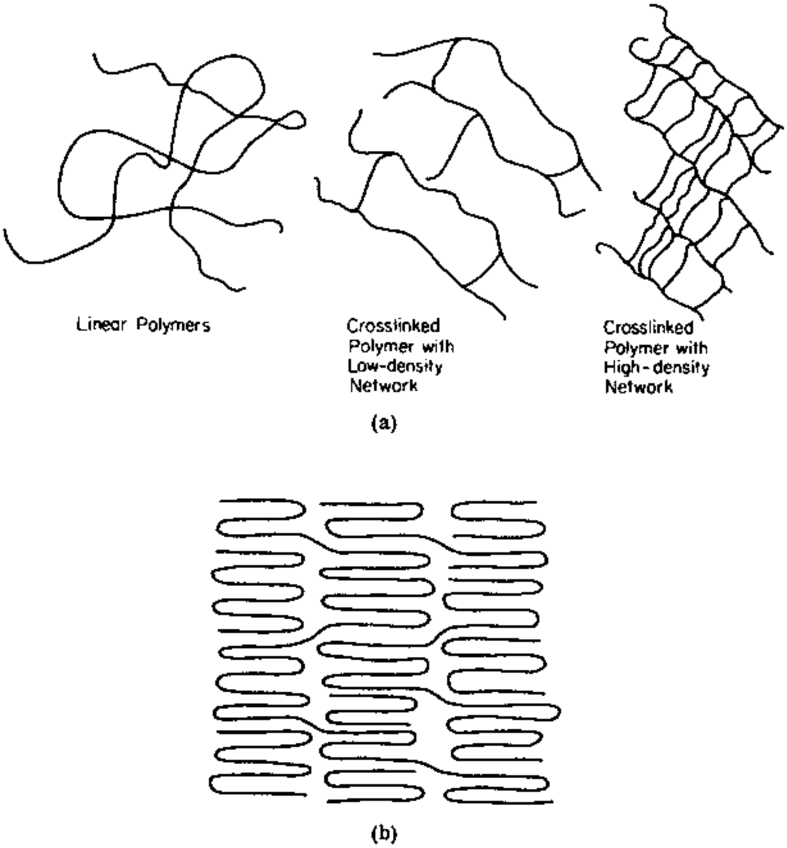


Figure 2.9 Representation of an amorphous polymer and representation of folded polymer chains in polymer crystals. (From *Modern Plastics Technology* by R. Seymour, 1975, Reston Publishing Company, Reston, Virginia. Used with permission.)

of polar organic molecules such as alkyl chlorides, and for the abnormally high boiling points of alcohols, amines, and amides. While the forces responsible for these increases in boiling points are all called van der Waals forces, these are subclassified in accordance with their source and intensity. Secondary, intermolecular forces include London dispersion forces, induced permanent forces, and dipolar forces including hydrogen bonding.

Nonpolar molecules such as ethane [$H(CH_2)_2H$] and polyethylene are attracted to each other by weak London or dispersion forces resulting from induced dipole–dipole interaction. The temporary or transient dipoles in ethane or along the polyethylene chain are due to instantaneous fluctuations in the density of the electron clouds. The energy range of these forces is about 2 kcal/mol (8 kJ/mol) unit in nonpolar and polar polymers alike, and this force is independent of temperature. These London forces are typically the major forces present between chains in largely nonpolar polymers present in elastomers and soft plastics.

It is of interest to note that methane, ethane, and ethylene are all gases; hexane, octane, and nonane are all liquids (at room conditions); while polyethylene is a waxy solid. This trend is primarily due to both an increase in mass per molecule and to an increase in the London forces per molecule as the chain length increases. Assuming that the attraction between methylene or methyl units is 2 kcal/mol (8 kJ/mol), we calculate an interaction between methane to be 2 kcal/mol, hexane to be 12 kcal/mol, and for a mole of polyethylene chains of 1000 units to be 4000 kcal (16000 kJ).

Problem

Determine the approximate interaction present for a single polyethylene chain of 1500 repeat units within a liquid hexane solution assuming that the interactions are about 2 kcal/mol repeat methylene unit. There are 6×10^{23} units per mol; thus the interactive energy per methylene moiety is $2000\ \text{cal/mol}/6 \times 10^{23}\ \text{units/mol} = 3.3 \times 10^{-21}$ cal/unit. There are two methylene units per repeat unit, so there are 2×1500 or 3000 methylene units. The interaction present in the polyethylene is then about $3000\ \text{units} \times 3.3 \times 10^{-21}\ \text{cal/unit} \simeq 1 \times 10^{-17}$ cal (4×10^{-17} J).

Polar molecules such as ethyl chloride ($H_3C—CH_2CI$) and poly(vinyl chloride) [$(—CH_2—CHCl—)_n$, PVC, see Fig. 2.10] are attracted to each other by dipole–dipole interactions resulting from the electrostatic attraction of a chlorine atom in one molecule to a hydrogen atom in another molecule. Since this dipole–dipole interaction, which ranges from 2 to 6 kcal/mol (8–25 kj/mol) repeat unit in the molecule, is temperature-dependent, these forces are reduced as the temperature is increased. While the London forces are typically weaker than the dipole–dipole forces, the former are also present in polar compounds, such as ethyl chloride and PVC. These dipole–dipole forces are characteristic of many plastics.

Strong polar molecules such as ethanol, poly(vinyl alcohol), and cellulose are attracted to each other by a special type of dipole–dipole interaction called hydrogen bonding, in which the oxygen or nitrogen atoms in one molecule are attracted to the hydrogen atoms attached to a highly electronegative atom in another molecule. These are the strongest of the intermolecular forces and may have energies as high as 10 kcal/mol (40 kJ/mol) repeat unit. Intermolecular hydrogen bonds are usually present in fibers, such as cotton, wool, silk, nylon, polyacrylonitrile, polyesters, and polyurethanes. Intramolecular hydrogen bonds are responsible for the helices observed in starch and globular proteins.

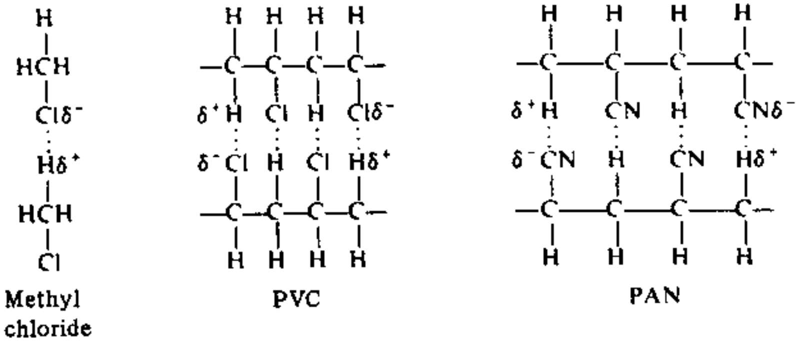


Figure 2.10 Typical dipole–dipole interaction between molecules of methyl chloride and segments of chains of poly(vinyl chloride) (PVC) and polyacrylonitrile (PAN). (From *Modern Plastics Technology* by R. Seymour, 1975, Reston Publishing Company, Reston, Virginia. Used with permission.)

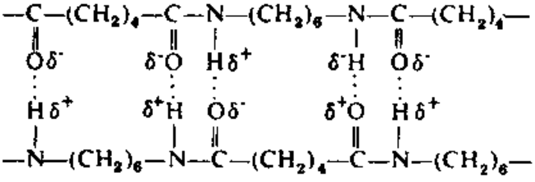


Figure 2.11 Typical hydrogen bonding between hydrogen and oxygen or nitrogen atoms in nylon-66. (From *Modern Plastics Technology*, by R. Seymour, 1975, Reston Publishing Company, Reston, Virginia. Used with permission.)

It is important to note that the high melting point of nylon-66 (265°C, Fig. 2.11) is the result of a combination of London, dipole–dipole, and hydrogen bonding forces between the polyamide chains. The hydrogen bonds are decreased when the hydrogen atoms in the amide groups in nylon are replaced by methyl groups and when the hydroxyl groups in cellulose are esterified.

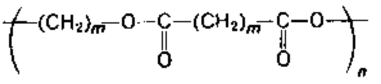
In addition to the contribution of intermolecular forces, chain entanglement is also an important contributory factor to the physical properties of polymers. While paraffin wax and HDPE are homologs with relatively high molecular weights, the chain length of paraffin is too short to permit entanglement and hence it lacks the strength and other characteristic properties of HDPE.

The critical chain length (z) required for the onset of entanglement is dependent on the polarity and shape of the polymer. The number of atoms in the critical chain lengths of PMMA, polystyrene (PS), and polyisobutylene are 208, 730, and 610, respectively. The melt viscosity (η) of a polymer is often found to be proportional to the 3.4 power of the critical chain length as related in Eq. (2.1), regardless of the structure of the polymer. The constant K is temperature-dependent.

$$\log \eta = 3.4 \log z + \log K \tag{2.1}$$

Viscosity is a measure of the resistance to flow. The latter, which is the result of cooperative movement of the polymer segments from hole to hole in a melt, is impeded by chain entanglement, high intermolecular forces, the presence of reinforcing agents, and crosslinks.

The *flexibility* of amorphous polymers above the glassy state is governed by the same forces as melt viscosity and is dependent on a wriggling type of segment motion in the polymer chains. This flexibility is increased when many methylene groups (CH_2) or oxygen atoms are present between stiffening groups in the chain. Thus, the flexibility of aliphatic polyesters usually increases as m is increased.



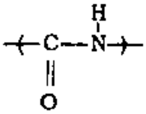
$$\left((CH_2)_m - O - \overset{O}{\overset{\|}{C}} - (CH_2)_m - \overset{O}{\overset{\|}{C}} - O \right)_n$$

Aliphatic polyester

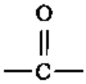
Flexibilizing groups include methylene and ethylene oxides, dimethylsiloxanes, and methylene groups.

In contrast, the flexibility of amorphous polymers above the glassy state is decreased when stiffening groups such as

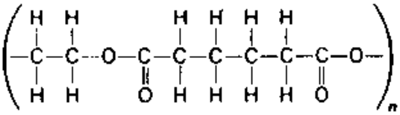

p-phenylene

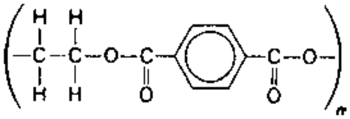

amide


sulfone


carbonyl

are present in the polymer backbone. Thus, poly(ethylene terephthalate) (PET) is stiffer and higher melting than poly(ethylene adipate), and the former is stiffer than poly(butylene terephthalate) because of the presence of fewer methylene groups between the stiffening groups.


Poly(ethylene adipate)


Poly(ethylene terephthalate)

The flexibility of amorphous polymers is reduced drastically when they are cooled below a characteristic transition temperature called the *glass transition temperature* (T_g). At temperatures below T_g, there is no segmental motion and any dimensional changes in the polymer chain are the result of temporary distortions of the primary valence bonds. Amorphous plastics perform best below T_g, but elastomers must be used above the brittle point, or T_g.

The melting point is the temperature range where total or whole polymer chain mobility occurs. The *melting point* (T_m) is called a first-order transition temperature, and T_g is sometimes called a second-order transition temperature. The values for T_m are usually 33–100% greater than T_g, and symmetrical polymers like HDPE exhibit the greatest difference between T_m and T_g. As shown by the data in Table 2.3, the T_g values are low for elastomers and flexible polymers such as PE and dimethylsiloxane, and relatively high for hard amorphous plastics, such as polyacrylonitrile and PET.

As shown in Table 2.3, the T_g value of isotactic polypropylene (PP) is 373 K or 100°C, yet because of its high degree of crystallinity it does not flow to any great extent below its melting point of 438 K (165°C). In contrast, the highly amorphous polyisobutylene, which has a T_g value of 203 K (-70°C), flows at room temperature. Also, as shown in Table 2.3, T_g decreases as the size of the ester groups increases in polyacrylates and polymethacrylates. The effect of the phenylene stiffening group is also demonstrated by the T_g of poly(ethylene terephthalate), which is 119 K higher than that of poly(ethylene adipate).

Since the specific volume of polymers increases at T_g in order to accommodate the increased segmental chain motion, T_g values may be estimated from plots of the change in specific volume with temperature. Other properties, such as stiffness (modulus), refractive index, dielectric properties, gas permeability, X-ray adsorption, and heat capacity, all change at T_g. Thus, T_g may be estimated by noting the change in any of these values, such as the increase in gas permeability. Since the change in the slope of the specific volume–temperature or index of refraction–temperature curves is not always obvious, it is best to extrapolate the curves linearly and designate the intersection of these curves at T_g, as shown in Fig. 2.12.

As shown in Fig. 2.13, values for both T_g and T_m are observed as endothermic transitions in calorimetric measurements, such as differential thermal analysis (DTA) or

Table 2.3 Approximate Glass Transition Temperatures (T_g) for Selected Polymers

Polymer	T_g (K)
Cellulose acetate butyrate	323
Cellulose triacetate	430
Polyethylene (LDPE)	148
Polypropylene (atactic)	253
Polypropylene (isotactic)	373
Polytetrafluoroethylene	160, 400[a]
Poly(ethyl acrylate)	249
Poly(methyl acrylate)	279
Poly(butyl methacrylate) (atactic)	339
Poly(methyl methacrylate) (atactic)	378
Polyacrylonitrile	378
Poly(vinyl acetate)	301
Poly(vinyl alcohol)	358
Poly(vinyl chloride)	354
Cis-poly-1, 3-butadiene	165
Trans-poly-1, 3-butadiene	255
Poly(hexamethylene adipamide) (nylon-66)	330
Poly(ethylene adipate)	223
Poly(ethylene terephthalate (PET)	342
Polydimethylsiloxane (silicone)	150
Polystyrene	373

[a] Two major transitions observed.

differential scanning calorimetry (DSC). It is important to note that since the values observed for T_g are dependent on the test method and on time, the values obtained by different techniques may vary by a few degrees. While the T_g value reported in the literature is related to the onset of segmental motion in the principal chain of polymer backbone, separate values, called α, β, . . . or secondary, tertiary T_g, may be observed for the onset of motion of large pendant groups or branches on the polymer chain.

While no motion exists, except for the stretching or distortion of covalent bonds, at temperatures below T_g, the onset of segmental motion leads to many different conformations. Thus, the full contour length (nl) of a polymer chain obtained by multiplying the length of each mer, or repeat unit (1), by the number of units in the chain (n) provides a value of the length of only one of the many possible conformers present.

It is not always possible or generally useful to calculate the length of other conformers, but it is important to know the average end-to-end distance of polymer chains. The statistical method for this determination, called the random flight technique, was developed by Lord Raleigh in 1919. The classic statistical approach may be used to show the distance traveled by a blindfolded person taking n number of steps of length 1 in a random walk or the distance flown by a confused moth or bird.

The distance traveled from start to finish is not the straight-line path measured as nl but the root-mean-square distance ($\sqrt{\bar{r}^2}$), which is equal to 1 $\sqrt{n}$. Nobel laureate Paul Flory and others have introduced several corrections so that this random flight technique could be applied to polymer chains approaching a full contour length of 1n.

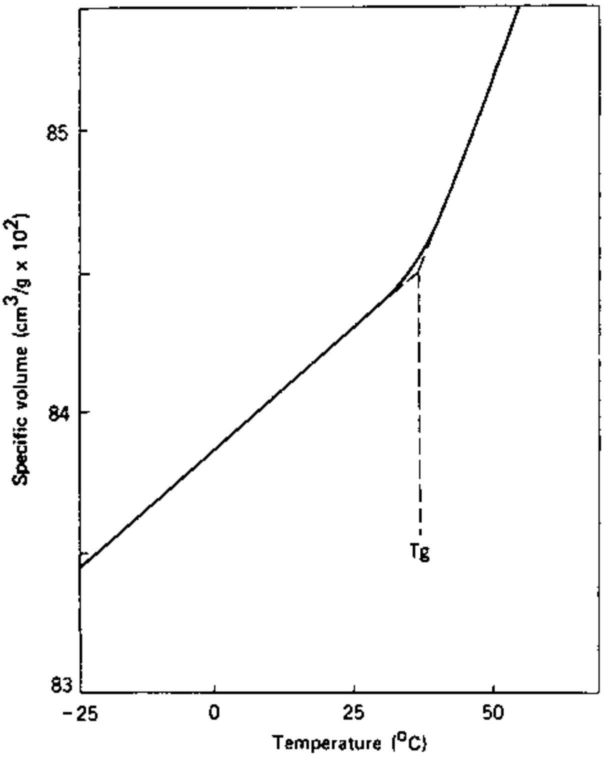


Figure 2.12 Determination of T_g by noting abrupt change in specific volume. Please remember that values such as those appearing here for specific volume are 1/100 of the values shown as designated by the multiplier 10^2. For example, the value where the break in the curve occurs is not 84.5 or 8450, but is 0.845. (From *Introduction to Polymer Chemistry* by R. Seymour, 1971, McGraw-Hill, Hill, New York. Used with permission.)

When we calculate the distance values for HDPE [$H(CH_2CH_2)_nH$], where DP or n equals 1000 using a C—C bond length of 1.26 Å or 0.126 nm, we will find approximate values of ln of 252 nm, i.e., [0.126(2)(1000)], and of $1\sqrt{n}$ of 8.1 nm, i.e., ($0.256\sqrt{1000}$). Thus, the calculated root-mean-square distance $\sqrt{\bar{r}^2}$, where r is the vector distance from end to end, is only about 3% of the full-contour end-to-end distance.

Since there are restrictions in polymer chain motions that do not apply to the blindfolded walker, corrections must be made that increase the value found by the Raleigh technique. Thus, the value of ($\sqrt{\bar{r}^2}$), increases from 8.1 to 9.8 nm when one corrects for the fixed tetrahedral angles in the polymer chain.

A still higher value of 12.2 nm is obtained for the root-mean-square end-to-end distance when one corrects for the hindrance to motion caused by the hydrogen atoms. Since the hydrogen atoms of the first and fifth carbon atom overlap when the methylene groups assume a cyclopentane-like shape, another correction must be made for this so-called pentane interference. The corrected value for $\sqrt{\bar{r}^2}$ is 18.0 nm for the pentane interference correction.

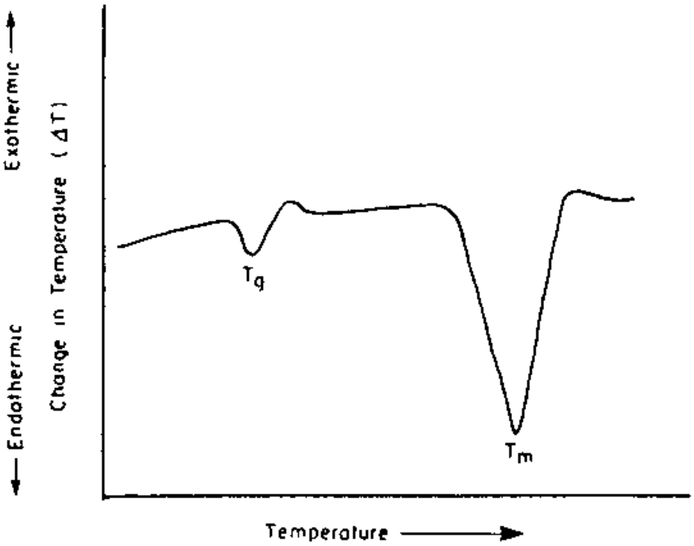


Figure 2.13 Typical DTA thermogram of a polymer.

Problem

Determine the average (root-mean-square average) distance for polypropylene chains with DP = 1300. The end-to-end distance between carbon atoms is 0.126 nm or (2) (0.126 nm) for each ethylene unit. The relationship between the root-mean-square distance, $\sqrt{\bar{r}^2}$ and number of carbon–carbon distances, n, is $\sqrt{\bar{r}^2} = 1.\sqrt{n}$.

$$\sqrt{\bar{r}^2} = 0.256\sqrt{1300} \approx 9.2 \text{ nm} \tag{2.2}$$

This is much less than the contour length of 330 nm (see problem, page 24).

While corrections should also be made for the excluded volume, the approximate value of 18.0 nm can be used for the root-mean-square, end-to-end distance. The excluded volume results from the fact that in contrast to the blindfolded walker who may backtrack without interference, only one atom of a three-dimensional carbon–carbon chain may occupy any specific volume at any specified time, and thus the space occupied by all other atoms must be excluded from the walker's available path.

The number of possible conformers increases with chain length and can be shown statistically to equal 2^{2n}. Thus, when n = 1000, the number of possible conformers of HDPE is 2^{2000}, or 10^{600}. As shown in Fig. 2.14, the end-to-end distance (r) of a linear molecule such as HDPE may be readily visualized and must be viewed statistically as an average value.

However, since there are many ends in a branched polymer, it is customary to use the radius of gyration (S) instead of r for such polymers. The radius of gyration is actually the root-mean-square distance of a chain end from the polymer's center of gravity. S is less than the end-to-end distance (r), and for linear polymers, $\bar{r}^2$ is equal to 6 $\overline{S}^2$.

In addition to the restrictions to free rotation noted for HDPE, free rotation of polymer chains will be hindered when the hydrogen atoms in polyethylene are replaced by bulky groups. Because the energy barrier (E) restricting the rotation from trans to gauche con-

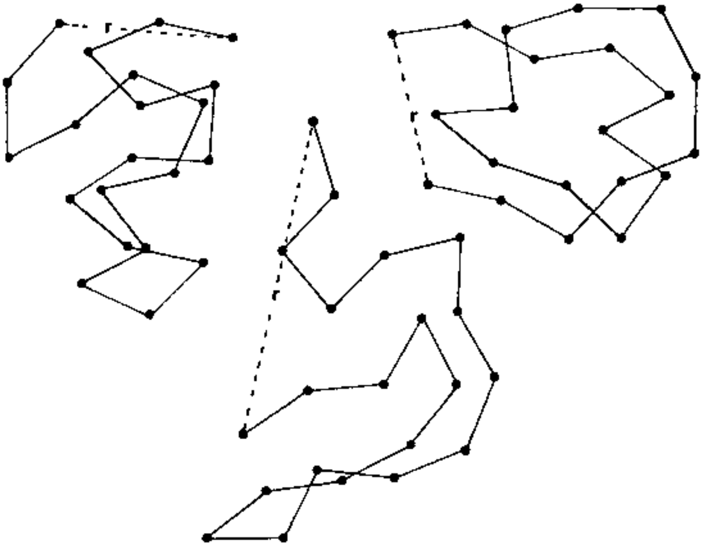


Figure 2.14 End-to-end distances (r) of linear polymer chains containing the same number of units.

formers is low (3 kcal per mer) in HDPE, these polymers are flexible, and this flexibility increases with temperature (T) in accordance with the Arrhenius equation shown in Eq. (2.3). The flexibility is related to the orientation time (τ_m), which is a measure of the ease of uncoiling of polymer coils. The constant A is related to the polymer structure, and R is the ideal gas constant.

$$\tau_m = A\, e^{E/RT} \text{ or } \log \tau_m = \log A + \frac{E}{2.3RT} \tag{2.3}$$

The bulky phenyl group in polystyrene (PS) restricts rotation, and hence its T_g and τ_m are higher than the values for HDPE. When substituents such as chlorine atoms are present in polystyrene, T_g and τ_m values are even higher. Likewise, aromatic nylons, called aramids, have greater T_g and τ_m values than aliphatic nylons.

In general, polymers (both natural and synthetic) "emphasize" two general shapes—helical and pleated (Figs. 2.11, 2.15). The intermolecular bonds in many polyamides and some fibers, including β-keratin, produce strong pleated sheets. Hair, fingernails and toenails, feathers, and horns have a β-keratin structure. Polyurethanes, polyacrylonitrile, and polyesters are characterized by the presence of strong hydrogen bonds. In contrast, isotactic polypropylene, which has no hydrogen bonds, is also a strong fiber as a result of the good fit of the regularly spaced methyl pendant groups on the chain. Since this molecular geometry is not present in atactic polypropylene (A-PP), it is not a fiber.

α-Keratin (composed of parallel polypeptide α-helices) and most globular proteins are characterized by intramolecular bonds. These and many other polymers, including nucleic acids, may form helices. Ribonucleic acid (RNA) exists as a single helix, whereas deoxyribonucleic acid (DNA) exists as a double helix.

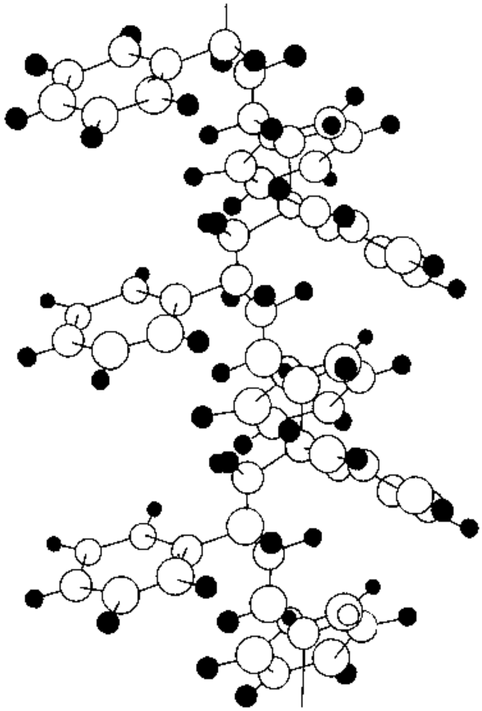


Figure 2.15 Ball-and-stick structure of polystyrene in the helical conformation.

2.3 POLYMER CRYSTALS

Introduction

Polymers typically contain combinations of ordered (crystalline) regions and structures and less ordered (amorphous) regions and structures. These different structures profoundly influence the chemical and physical properties of the material and products derived from them. Chains can be connected to one another through physical entanglement similar to what happens when a kitten gets a hold of a ball of yarn. Chains can be connected through formation of chemical linkages that chemically hold one chain to another chain. Some polymers, such as the traditional rubbers of our automobile tires, are highly interconnected (Sec. 10.8) through chemical bonds, whereas other polymers have only a small amount of chemical interconnections, such as are often present in so-called "permanent press" dress shirts. These two types of interconnections, physical and chemical, are referred to as *crosslinks*, and the extent of crosslinking referred to as the *crosslink density*. Crosslinking helps "lock-in" a particular structure. Thus, the formation of crosslinks in our hair can lock in curly or straight hair. The locked-in structure can be an ordered structure such as the locking in of a specific shape for a protein (Sec. 10.7), or the locked-in structure can be a general or average shape such as is present in the ebonite rubber head of a hammer (Sec. 10.8). Further, some structures are composed of a maze of crosslinking and have a high crosslink density, forming a complex interlocking structure that offers only an average overall structure such as the melamine-formaldehyde dishes (sec. 6.15) and silicon dioxide

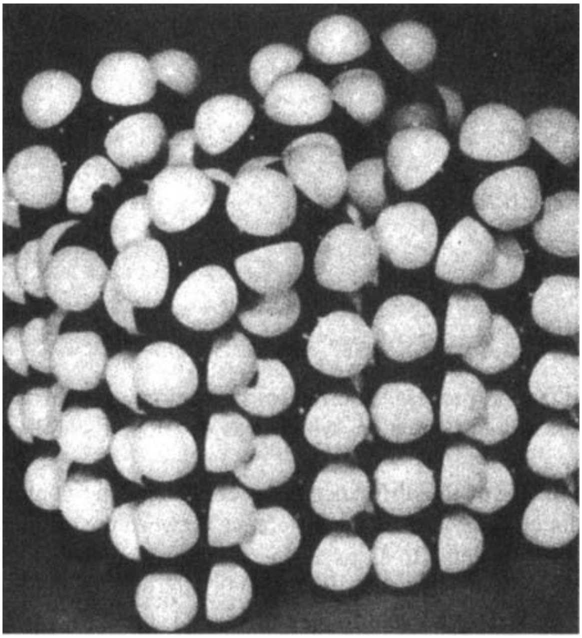


Figure 2.16 Model representation of a folded chain lamellar crystal for polyethylene at the surface of a single crystal. (From P. Geil and D. Reneker, J. Appl. Phys. *31*:1921 (1960). With permission from the American Institute of Physics.)

glass (Sec. 12.5), while other highly crosslinked structures have ordered structures such as in silicon dioxide quartz (sec. 12.6).

Sections 2.3 and 2.4 briefly introduce topics related to ordered and less ordered polymer structures of largely linear polymers. Crystalline portions are represented by structures such as Figs. 2.16, 2.17 while historically important amorphous-crystalline representations are given in Figs. 2.18, 2.19 with both structures building upon helical and pleated structures (Figs. 2.11, 2.17, 2.20).

Polymer Crystals

Prior to 1920, leading chemistry researchers not only stated that macromolecules were nonexistent, but they also believed that the products called macromolecules, i.e., proteins, hevea elastomer, and cellulose, could not exist in the crystalline form. However, in the early 1920s, Haworth used X-ray diffraction techniques to show that elongated cellulose was a crystalline polymer consisting of repeat units of cellobiose. In 1925, Katz in jest placed a stretched natural rubber band in an X-ray spectrometer and to his surprise observed an interference pattern typical of a crystalline substance.

This phenomenon may also be shown qualitatively by the development of opacity when a rubber band is stretched and by the abnormal stiffening and whitening of unvulcanized rubber when it is stored for several days at 0°C. The opacity noted in stretched rubber and cold rubber is the result of the formation of crystallites, or regions of crystallinity. The latter were first explained by a fringed micelle model.

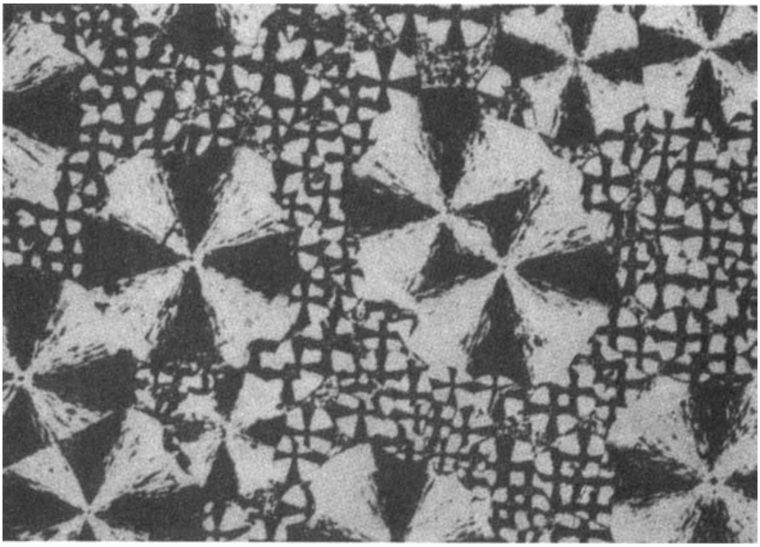


Figure 2.17 Maltese cross–like pattern for spherulites viewed under a polarizing microscope with crossed Nicol prisms in a silicone-like polymer. The large and small spherulites are the result of crystallization occurring at different temperatures. [From F. Price, in *Growth and Perfection of Crystals* (R. Doremus, B. Roberts, and D. Turnbull, eds)]. John Wiley, New York, 1958, p. 466. With permission.]

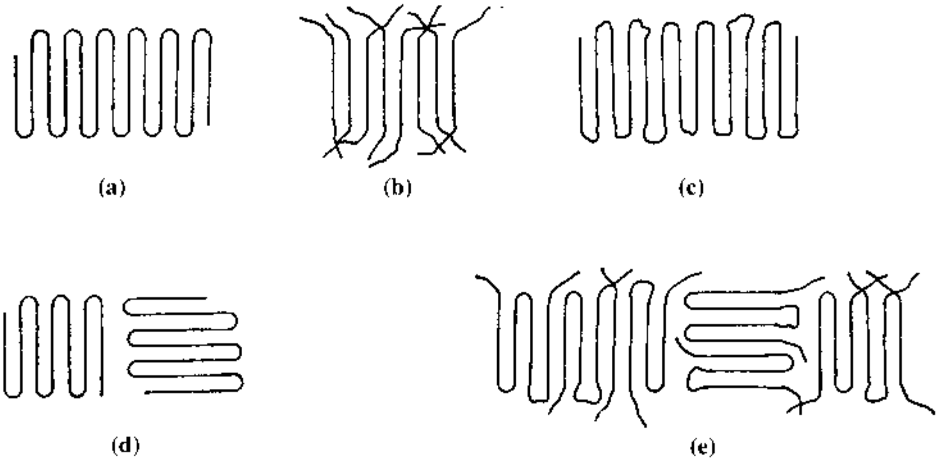


Figure 2.18 Schematic two-dimensional representations of models of the fold surface in polymer lamellae: (a) sharp folds, (b) switchboard model, (c) loops with loose folds, (d) buttressed loops, and (e) a combination of these features.

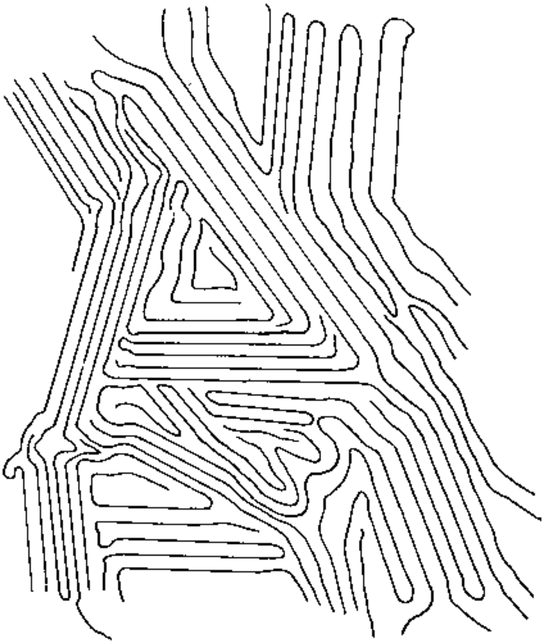


Figure 2.19 Schematic two-dimensional representation of a modified micelle model of the crystalline amorphous structure of polymers incorporating features from Fig. 2.18.

In contrast to the transparent films of amorphous polymers, relatively thick films of LDPE are translucent because of the presence of crystals. This opacity is readily eliminated when the film is heated above 100°C. It is of interest to note that Sauter produced single crystals of polymers in 1932, and Bunn produced single crystals of LDPE in 1939, but the existence of single crystals was not generally recognized until the 1950s, when three experimenters—Fischer, Keller, and Till—reproduced Bunn's work independently.

Amorphous polymers with irregular bulky groups are seldom crystallizable, and unless special techniques are used, ordered polymers are seldom 100% crystalline. The rate of crystallization may be monitored by X-ray diffraction techniques or by dilatometry (measurement of change in volume).

Historically, the various folded surfaces as shown in fringed micelle models similar to those given in Figs. 2.18 and 2.19 were important to explain many of the physical properties of polymers, but the actual structures of the amorphous and crystalline regions are complex and still undergoing clarification. Such fringed micelle models are not consistent with much of the current experimental findings.

The particular structure and combinations of amorphous and crystalline regions and structures vary with the structure of the polymer chain and the precise conditions that have been imposed on the material. For instance, rapid cooling often decreases the amount of crystallinity because there is not sufficient time to allow the long chains to organize themselves into more ordered structures. The reason linear ordered polymers fail to be almost totally crystalline is kinetic, resulting from an inability of the long chains to totally disentangle and perfectly align themselves during the time the polymer chain is mobile.

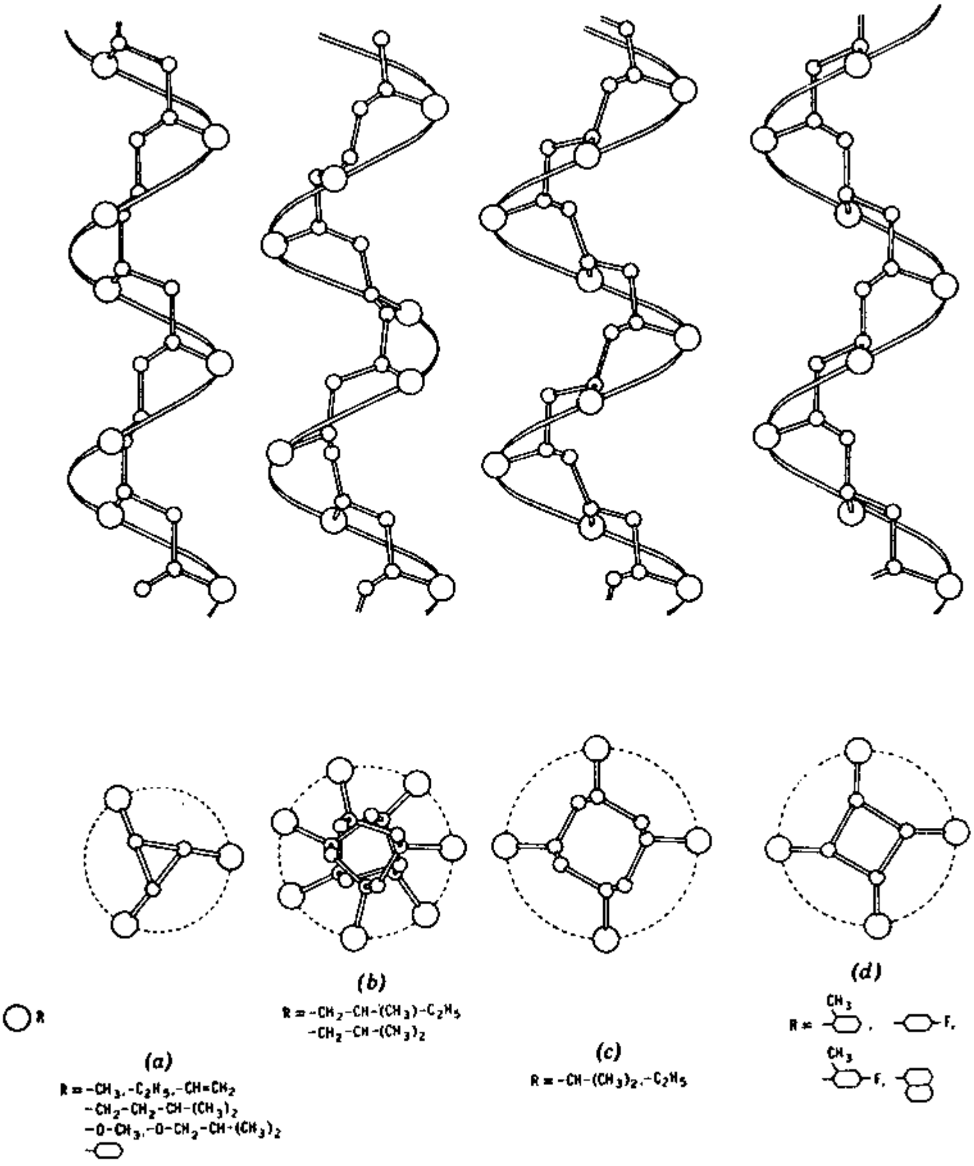


Figure 2.20 Helical conformations of isotactic vinyl polymers. [From N. Gaylord, in *Linear and Stereoregular Addition Polymers* (N. Gaylord and H. Mark, eds.), Wiley Interscience, New York, 1959. With permission from the Interscience Division of John Wiley and Sons, Publishers.]

Mixtures of amorphous and mini-crystalline structures or regions may consist of somewhat random chains containing some chains that are parallel to one another forming short range mini-crystalline regions. Crystalline regions may be formed from large range ordered platelet-like structures, including polymer single crystals, or they may form even larger organizations such as spherulites as shown in Figs. 2.21 and 2.22. Short and longer range ordered structures can act as physical crosslinks.

In general, linear polymers form a variety of single crystals when crystalized from very dilute solutions. For instance, highly linear polyethylene (7.6) can form diamond-shaped single crystals with a thickness on the order of 11 to 14 nm when crystallized from dilute solution. The surface consists of "hairpin turned" methylene units as depicted in Fig. 2.16. The polymer chain axes is perpendicular to the large flat crystal faces. A single polymer chain with 1,000 ethylene (2,000 methylene) units might undergo on the order of 50 of these hairpin turns on the top surface and another 50 turns on the bottom face with about 20 ethylene units between the two surfaces.

Many polymers form more complex single crystals when crystallized from dilute solution including hollow pyramids that often collapse on drying. As the polymer concentration increases, other structures occur, including twins, spirals, and multilayer dendritic structures with the main structure being spherulites.

When polymers are produced from their melt, the most common structures are these spherulites. These spherulites can be seen by the naked eye and viewed as Maltese cross-like structures with polarized light and crossed Nicol prisms in a microscope as shown in Fig. 2.17.

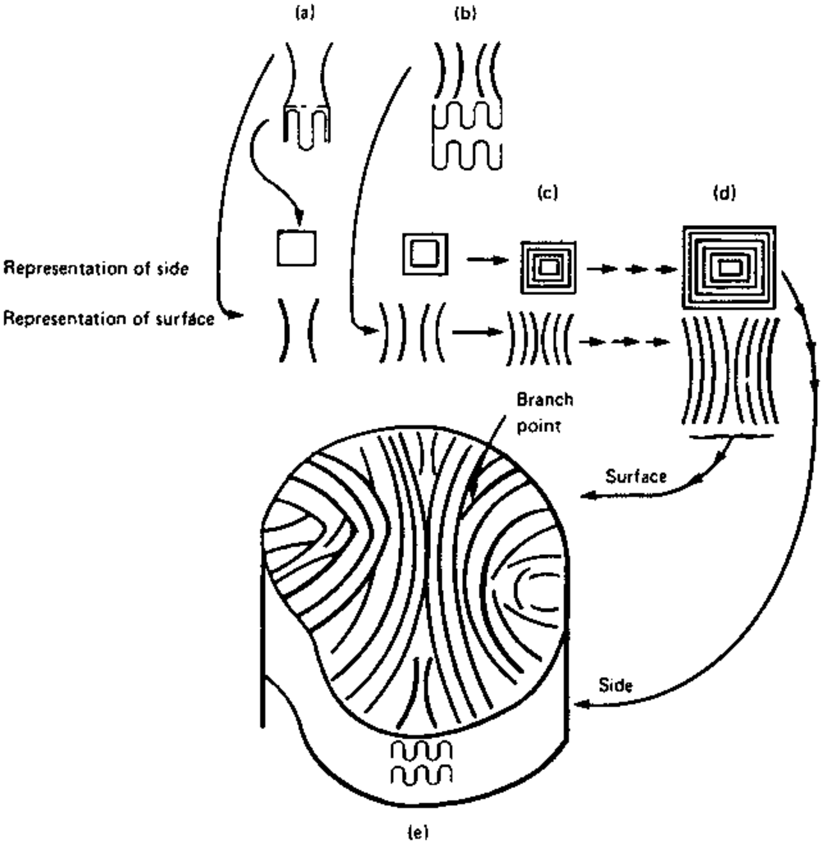


Figure 2.21 Steps in the formation of a spherulite from the bulk.

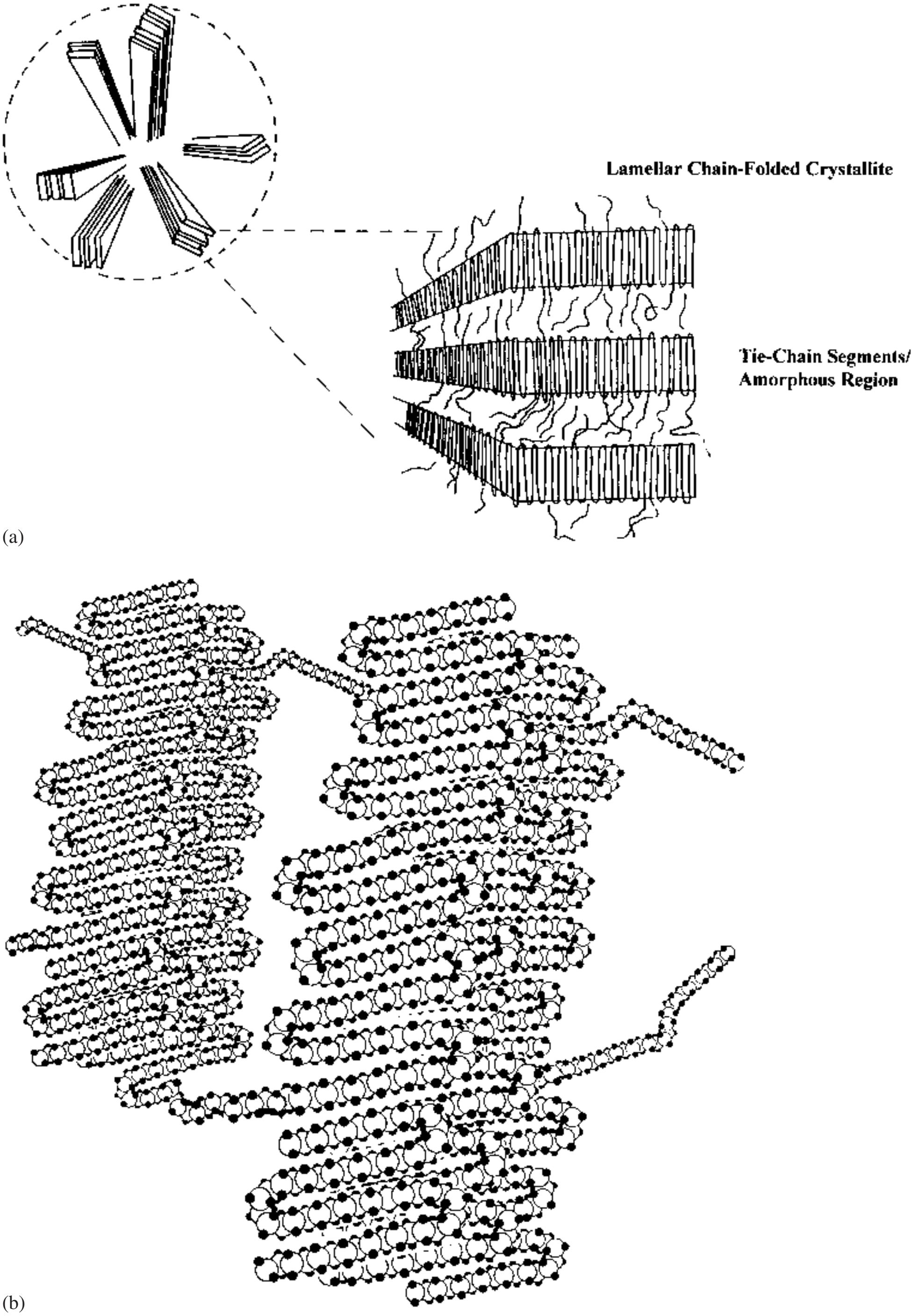


Figure 2.22 (a) Spherulite structure showing the molecular-level lamellar chain-folded platelets and tie and frayed chain arrangements. (b) A more complete description of two sets of three lamellar chain-folded platelets formed from polyethylene. Each platelet contains about 850 ethylene units as pictured here.

For linear polyethylene, the initial structure formed is a single crystal with folded chain lamellae as shown in Fig. 2.16 and depicted in Fig. 2.21a. These quickly lead to the formation of sheaf-like structures (Fig. 2.21d) called *axialites* or *hedrites*. As growth proceeds, the lamellae develop on either side of a central reference plane. The lamellae continue to fan out, occupying increasing volume sections through the formation of additional lamellae at appropriate branch points. The result is the formation of spherulites as pictured in Figs. 2.17, 2.21, and 2.22.

While the lamellar structures present in spherulites are similar to those present in polymer single crystals, the folding of chains in spherulites is less organized. Further, the structures that exist between these lamellar structures are generally occupied by amorphous structures including atactic chain segments, low molecular material, and impurities.

The individual spherulite lamellae are bound together by “tie” molecules that are present in both spherulites. Sometimes these tie segments form intercrystalline links which are threadlike structures that are important in developing the characteristic good toughness found in semicryatalline polymers. They act to tie together the entire assembly of spherulites into a more or less coherent “package.”

Depending upon the particular conditions of crystallization, a number of secondary and tertiary structures can be formed. In most cases, crystalline polymers attempt to form crystalline platelets. Under little or no externally applied stress, these platelets organize themselves into spherulites as pictured in Figs. 2.21 and 2.22. As noted above, formation of spherulites starts by a nucleating process with polymer crystallization radiating outward from the central nucleating site. Amorphous chain segments get trapped between the forming crystalline platelet combinations giving kind of a fuzzy or frayed exterior. These platelets are generally either planar, as shown in Fig. 2.22, or they can be helical or twisted. The platelets continue to grow until they butt up against other spherulites.

When nucleation occurs at about the same time the boundaries of the spherulites appear to be somewhat straight. When nucleation occurs at different times the spherulites are different sizes and the boundaries hyperbolas as seen in Fig. 2.17. Rapid cooling decreases the amount of spherulite formation presumably because of a lack of time to allow the chains to organize into spherulite structures.

Under externally applied stress, including simple melt flow, the tertiary structure can approach a “shish kebab” arrangement, where there are planes of platelets separated by areas where there exist both crystalline and amorphous regions as pictured in Fig. 2.23. These “shish kebab” structures often organize into quaternary structures consisting of bundles of “shish kebab” single-strand filaments forming fibrils.

Interestingly, the amorphous regions within the spherulite confer onto the material some flexibility while to crystalline platelets give the material strength, just as in the case with largely amorphous materials. This theme of amorphous flexibility and crystalline strength (and brittleness) is a central idea in polymer structure–property relationships.

It must be remembered that the secondary structure of both the amorphous and crystalline regions typically tend toward a helical arrangement of the backbone.

The rate of crystalline growth can be followed by dilatometry using the Avrami equation [Eq. (2.4)], which was developed to follow the rate of crystallization of metals.

As shown by Eq. (2.4), the quotient of the difference between the specific volume V_t at time t and the final specific volume V_f divided by the difference between the original specific volume V_o and the final volume is equal to an experimental expression in which K is kinetic constant related to the rate of nucleation and growth and n is an integer related to nucleation and growth of crystals. The value of n can vary (Table 2.4).

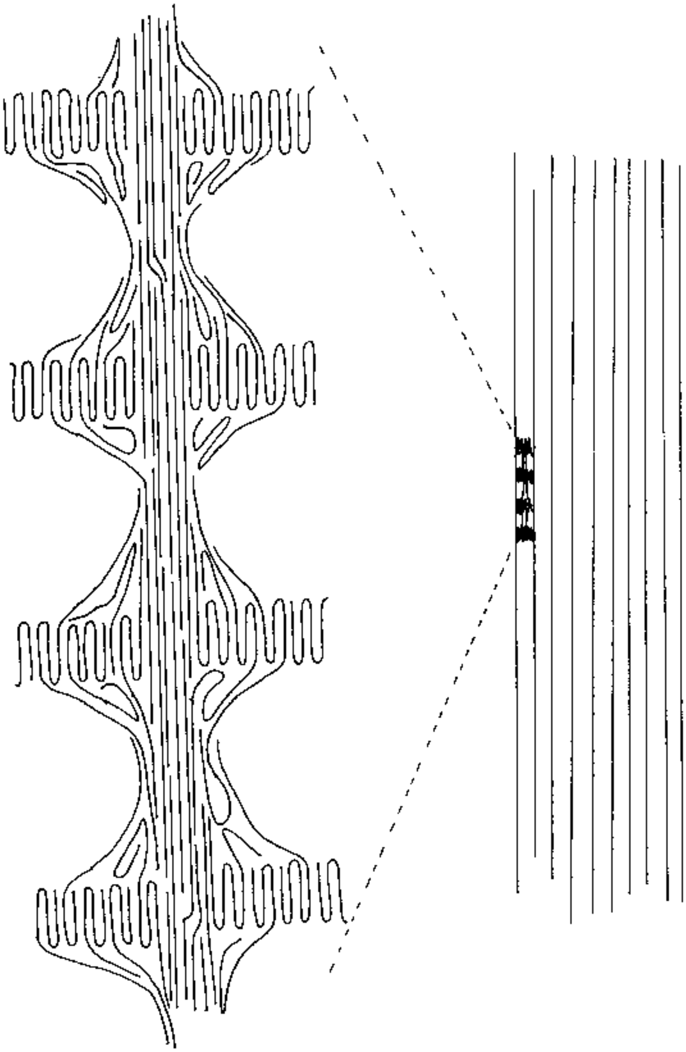


Figure 2.23 Crystalline polymer structures formed under applied tension including flow conditions. (Left) The tertiary mono-fibrilar structure including platelets and (right) these mono-fibrilar structures bundled together forming a quaternary structure fibril.

Table 2.4 Avrami Values for Particular Crystallization Growth for Sporadic and Ordered or Predetermined Nucleation

Crystallization growth pattern	Sporadic nucleation	Ordered nucleation	Overall dimensionality
Fibril/Rod	2	1	One
Disc	3	2	Two
Spherulite	4	3	Three
Sheaf	6		

$$\frac{V_t - V_f}{V_o - V_f} = e^{-Kt^n} \tag{2.4}$$

The particular value of n has been calculated based on possible resulting structures and on two nucleating scenarios. These values appear in Table 2.4 and are valid for only the initial stages of crystallization.

Noninteger values for n have been reported. As noted before, depending on the particular conditions, several crystalline formations are possible and actually found for the same polymer. Sperling has collected a number of Avrami values for common polymers and gives literature values for polyethylene of 2.6–4.0; polypropylene values of 2.8–4.1; poly(ethylene oxide), 2.0–4.0; poly(decamethylene terephthalate), 2.7–4.0; and isotactic-polystyrene, 2.0–4.0.

The kind, amount, and distribution of polymer chain order/disorder (amorphous/crystalline) is driven by the processing (including pre- and post-) conditions and thus it is possible to vary the polymer properties through a knowledge of and ability to control the molecular-level structures.

The crystalline regions may be disrupted by processing techniques such as thermoforming and extrusion of plastics and biaxial orientation and cold drawing of fibers. In the last process, which is descriptive of the others, the crystallites are ordered in the direction of the stress, the filament shrinks in diameter (necks down), and heat is evolved and reabsorbed as a result of additional orientation and crystallization.

In addition to crystallization of the backbone of polymers, crystallization may also occur in regularly spaced bulky groups even when an amorphous structure is maintained in the backbone. In general, the pendant group must contain at least 10 carbon atoms in order for this side chain crystallization to occur. Rapid crystallization to produce films with good transparency may be brought about by the addition of a crystalline nucleating agent, such as benzoic acid, and by cooling rapidly.

Ordered polymers with small pendant groups crystallize more readily than those with bulky groups, such as poly(vinyl acetate), ($—CH_2CHOOCCH_3$). Thus, the hydrolytic product of the latter [poly(vinyl alcohol), $—CH_2—CHOH$] crystallizes readily. Crystallization also occurs when different groups with similar size, like CH_2 and CH_3, are present (see Fig. 2.20).

While polymeric hydrocarbons have been used as illustrations for simplicity, it is important to note that the principles discussed apply to all polymers, organic as well as inorganic and natural as well as synthetic, and to elastomers, plastics, and fibers. The principal differences among the last are related to T_g, which is governed by the groups present in the chain and by pendant groups and the relative strength of the intermolecular bonds.

2.4 AMORPHOUS BULK STATE

An amorphous bulk polymer contains chains that are arranged in something less than a well-ordered, crystalline manner. Physically, amorphous polymers exhibit a glass transition temperature but not a melting temperature, and do not give a clear X-ray diffraction pattern. Amorphous polymer chains have been likened to spaghetti strands in a pot of spaghetti, but in actuality the true extent of disorder that results in an amorphous polymer is still not well understood.

Section 5.11 contains a discussion of a number of techniques employed in the search for the real structure of the amorphous bulk state. Briefly, there is evidence to suggest that little order exists in the amorphous state, the order being similar to that observed with low molecular weight hydrocarbons in the case of vinyl polymers for short-range interactions. For long-range interactions, there is evidence that the chains approximate a random coil with some portions paralleling one another.

In 1953, Flory and Mark suggested a random coil model whereby the chains had conformations similar to those present if the polymer were in a theta solvent (similar to Fig. 2.9a, left). In 1957, Kargin suggested that amorphous polymer chains exist as aggregates in parallel alignment. Models continue to be developed, but all contain the elements of disorder suggested by Flory and Mark and the elements of order suggested by Kargin.

2.5 POLYMER STRUCTURE–PROPERTY RELATIONSHIPS

Throughout the text we will relate polymer structure to the properties of the polymer. Polymer properties are related not only to the chemical nature of the polymer but also to such factors as extent and distribution of crystallinity, distribution of polymer chain lengths, and nature and amount of additives, such as fillers, reinforcing agents, and plasticizers, to mention only a few. These factors influence essentially all the polymeric properties to some extent, such as hardness, flammability, weatherability, chemical resistance, biological responses, comfort, appearance, dyeability, softening point, electrical properties, stiffness, flex life, moisture retention, etc. Chapters 1 and 12 concentrate on the chemical nature of the polymer itself, whereas Chapters 13 and 14 deal with the nature and effect on polymer properties by addition of plasticizers, fillers, stabilizers, etc. Chapter 17 deals with the application of both the polymers themselves and suitable additives aimed at producing polymers exhibiting desired properties.

Materials must be varied to perform the many tasks required of them in today's society. Often they must perform them repeatedly and in a "special" manner. We get an idea of what materials can do by looking at some of the behavior of the giant molecules that compose the human body. While a plastic hinge must be able to work thousands of times, the human heart, a complex muscle largely composed of protein polymers (Sec. 10.7), provides about 2.5 billion beats within a lifetime moving oxygen (Sec. 15.10) throughout the approximately 144,000 km of the circulatory system with (some) blood vessels the thickness of hair and delivering about 8000 L of blood every day with little deterioration of the cell walls. The master design allows nerve impulses to travel within the body at a rate of about 300 m/min; again polymers are the "enabling" material that allows this rapid and precise transfer of nerve impulses. Human bones, again largely composed of polymers, have a strength about five times that of steel. Genes, again polymers, appear to be about 99.9% the same, with the 0.1% functioning to give individuals the variety of size, abilities, etc., that confer uniqueness. In the synthetic realm, we are beginning to understand and mimic the complexities, strength, and flexibility that are already present in nature (Chapter 10).

Here we will deal briefly with the chemical and physical nature of polymeric materials that permits their division into three broad divisions—elastomers or rubbers, fibers, and plastics.

Elastomers are high polymers possessing chemical and/or physical crosslinks. For industrial application the "use" temperature must be above T_g (to allow for "chain" mobility), and its normal state (unextended) must be amorphous. The restoring force, after elongation, is largely due to entropy. As the material is elongated, the random chains are forced to occupy more ordered positions. On release of the applied force the chains tend to return to a more random state. Gross, actual mobility of chains must be low. The cohesive energy forces between chains should be low to permit rapid, easy expansion. In its extended state a chain should exhibit a high tensile strength, whereas at low extensions it should have a low tensile strength. Crosslinked vinyl polymers often meet the desired property requirements. The material, after deformation, should return to its original shape because of the crosslinking. This property is often referred to as an elastic "memory." Figure 2.24 illustrates force vs. elongation for a typical elastomer. As the elastomer is pulled, the largely random chain segments become "stretched out" forming microcrystalline domains. Eventually, most of the chains are part of these microcrystalline domains resulting in further elongation requiring much increased force (stress). This microcrystallization also confers to the elastomer a greater brittleness, eventually resulting in the rubber breaking as additional stress is applied.

Fiber properties include high tensile strength and high modulus (high stress for small strains). These can be obtained from high molecular symmetry and high cohesive energies between chains, both requiring a fairly high degree of polymer crystallinity. Fibers are normally linear and drawn (oriented) in one direction, producing high mechanical properties in that direction. Typical condensation polymers, such as polyester and nylon, often exhibit these properties. If the fiber is to be ironed, its T_g should be above 200°C, and if it is to be drawn from the melt, its T_g should be below 300°C. Branching and crosslinking are undesirable since they disrupt crystalline formation, even though a small amount of crosslinking may increase some physical properties, if effected after the material is drawn and processed.

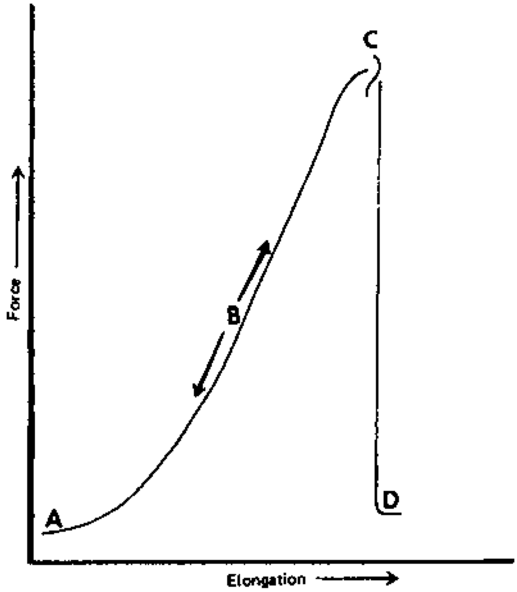


Figure 2.24 Elongation of an elastomer as a function of applied force where A is the original "relaxed" state, B represents movement to full extension, C is point at which the elastomer "breaks," and D represents force necessary to pull two separate pieces of rubber (elastomer) apart.

Table 2.5 Selected Property–Structure Relationships

Glass transition temperature

- Increases with presence of bulky pendant groups
  - Stiffening groups as 1,4-phenylene
  - Chain symmetry
  - Polar groups
  - Crosslinking
- Decreases with presence of additives like plasticizers
  - Flexible pendant groups
  - Nonpolar groups
  - Dissymmetry

Solubility

- Favored by lower chain lengths
  - Increased amorphous content
  - Low interchain force
  - Disorder and dissymmetry
  - Increased temperature
  - Compatible solvent

Crystallinity

- Favored by high interchain forces
  - Regular structure; high symmetry
  - Decrease in volume
  - Increased stress
  - Slow cooling from melt
  - Homogeneous chain lengths

Products with properties intermediate between elastomers and fibers are grouped together under the heading “plastics.”

Some polymers can be classified in two categories, with properties being greatly varied by varying molecular weight, end groups, processing, crosslinking, plasticizer, and so on. Nylon in its more crystalline from behaves as a fiber, whereas less crystalline forms are generally classified as plastics. Selected property–structure relationships are summarized in Tables 2.5 and 2.6.

Many polymers can be treated to express more than one behavior. Thus, nylon-66 provides a good fibrous material when aligned and behaves as a plastic if it is not subjected to orientation. Polyesters also exhibit the same tendencies. Other materials, such as PVC and siloxanes, can be processed to act as plastics or elastomers.

2.6 CRYSTALLINE AND AMORPHOUS COMBINATIONS

Most polymers consist of a combination of crystalline and amorphous regions. Even within polymer crystals such as spherulites (Figs. 2.21 and 2.22), the regions between the ordered folded crystalline lamellae are less ordered, approximating amorphous regions. This combination of crystalline and amorphous regions is important for the formation of materials that have both good strength (contributed to largely by the crystalline portions) and some flexibility or “softness” (derived from the amorphous portions). Figure 2.25 contains a space-filled model for polyethylene chains (a total of about 400 units with 5 branches, one longer and four shorter).

Table 2.6 General Property Performance–Structure Relationships[a]

	Increased crystallinity	Increased crosslinking	Increased mol. wt.	Increased mol. wt. distribution	Addition of polar backbone units	Addition of backbone stiffening groups
Abrasion resistance	+	+	+	−	+	−
Brittleness	−	M	+	+	+	+
Chemical resistance	+	V	+	−	−	+
Hardness	+	+	+	+	+	+
T_g	+	+	+	−	+	+
Solubility	−	−	−	0	−	−
Tensile strength	+	M	+	−	+	+
Toughness	−	−	+	−	+	−
Yield	+	+	+	+	+	+

[a] +, increase in property; 0, little or no effect; −, decrease in property; M, property passes through a maximum; V, variable results dependent on particular sample and temperature.

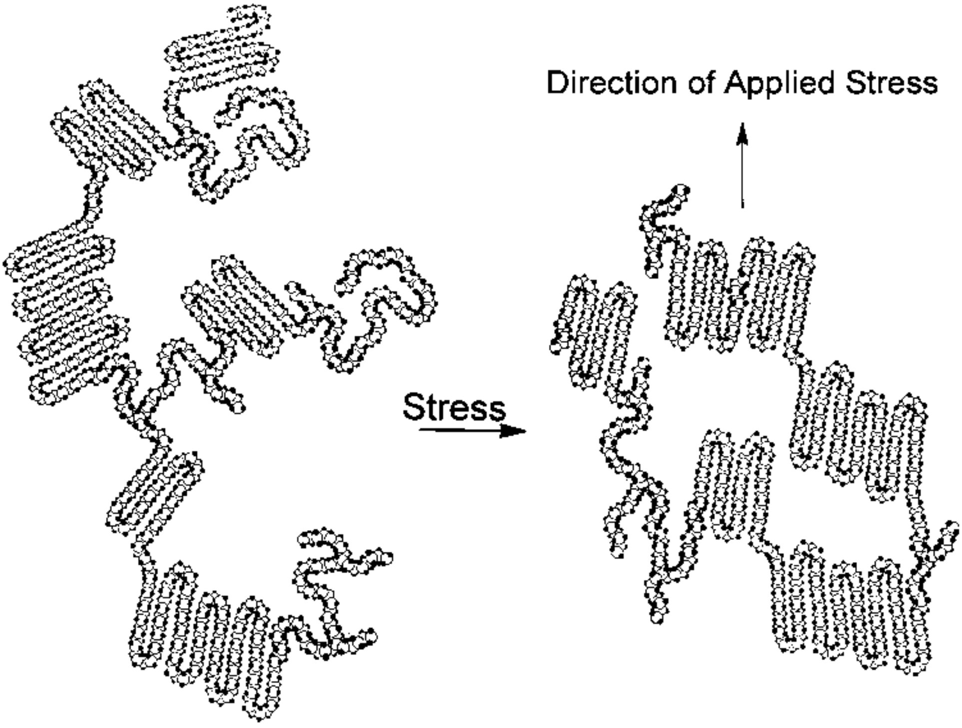


Figure 2.25 Idealized structure illustrating crystalline (ordered) and amorphous (nonordered) regions of lightly branched polyethylene chains for a prestressed and stressed orientation.

This model of polyethylene (Fig. 2.25) contains a mixture of amorphous and crystalline regions. Note the cavities within the amorphous regions with materials containing a majority of amorphous regions having a greater porosity and consequently a greater diffusion and greater susceptibility to chemical and natural attack. As noted before, materials that contain high amounts of crystalline regions are referred to as being crystalline and are less flexible and stronger—and offer better stability to natural attack by acids and bases, oils, etc. Also as noted before, the amorphous regions give the material flexibility, while the crystalline regions give the material strength. Thus, many materials contain both crystalline and amorphous regions giving the material a balance between strength and flexibility. The final properties of a material are then dependent on the molecular structure of that material.

Through the use of specific treatment(s) the crystalline/amorphous regions can vary from being largely random to being preferentially oriented in one direction with a greater degree of "crystalline-type" structure when unidirectional stress is applied (Fig. 2.25). Here the amount of free space or volume is less, the overall order is greater and properties associated with these changes are changed. The material will be stronger, have a greater ability to resist attack by acids, bases, oils, and other external agents, and the diffusion of gases and other agents through it is less.

Figure 2.26 shows the general relationship between material "hardness/softness" and the proportion that is crystalline for largely linear polymers.

Through the use of specific treatment(s) the crystalline/amorphous regions can vary from being largely random to being preferentially oriented in one direction (Fig. 2.25) and in the proportion of crystalline/amorphous regions. Thus, polymers can be oriented through the unidirectional "pulling" of the bulk material either during the initial synthesis (such as the pulling of fibers as they exit a spinneret) or during the processing phase where preferential application of stress (pulling) in one direction results in the preferential orientation of the chains, including both crystalline and amorphous regions. This preferential orientation results in fibers or bulk material with anisotropic properties, with the

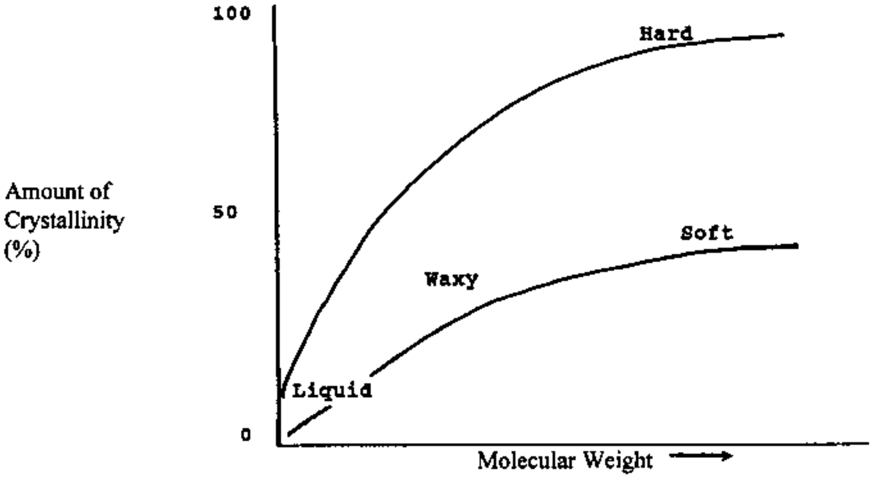


Figure 2.26 General physical nature of materials as a function of the amount of crystallinity and molecular weight.

material generally showing greater strength along the axis of applied stress (in the direction of the pull). These crystalline sites may be on a somewhat molecular level involving only a few chains (Fig. 2.25) or they may exist as larger units such as spherulites (Figs. 2.17 and 2.21).

The amount of orientation is dependent on a number of factors. Increased mobility of the crystalline and amorphous regions typically results in greater reorientation for a specified applied stress. Thus, materials with little or no crosslinking, materials with lowered inter- and intramolecular attraction, and materials that are near (or above) their glass transition temperature will respond with greater reorientation (per unit of stress) in comparison to materials where mobility is more limited. Application of increased stress will eventually lead to distortion of both the crystalline (including spherulites) and amorphous regions and finally breakage of primary chains.

SUMMARY

1. Polymers, or macromolecules, are high molecular weight compounds with chain lengths greater than the critical length required for the entanglement of these chains. There is an abrupt change in melt viscosity and other physical properties of high molecular weight compounds when the chain length exceeds the critical chain length.
2. While some naturally occurring polymers, such as proteins, are monodisperse, i.e., all have the same molecular weight, other natural and synthetic polymers, such as cellulose and polyethylene, are polydisperse, i.e., they consist of a mixture of polymer chains with different molecular weights. Hence, one uses the term $\overline{\mathrm{DP}}$ to indicate an average degree of polymerization, where $\overline{\mathrm{DP}}$ is equal to the number of mers (repeating units) in the polymer chain.
3. Many polymers, such as cellulose and HDPE, are linear polymers consisting of long, continuous, covalently bonded atoms. Others, such as amylodextrin and LDPE, have branches or chain extensions from the polymer backbone and hence have greater volume and lower density than linear polymers. Both linear polymers and those with branches are *thermoplastics*. In contrast, network polymers such as ebonite, in which individual chains are joined to each other by covalently bonded crosslinks, are infusible *thermoset* polymers.
4. Functional groups in the polymer backbone, such as the methyl group in polypropylene and hevea rubber, are called *pendant groups*.
5. Many rubber-like polymers are flexible because the free rotation of carbon–carbon single bonds allows the formation of many different shapes, or conformations. This segmental motion is restricted by bulky pendant groups, by stiffening groups in the polymer chains, and by strong intermolecular forces. Hydrogen bonding, which is the strongest of these intermolecular forces, is essential for most strong fibers.
6. Free rotation of covalently bonded atoms is also prevented by the presence of double bonds. Thus, stable trans and cis configurations are possible for polymers such as polyisoprene. The cis and trans isomeric forms of polyisoprene are known as flexible hevea rubber and hard plastic gutta percha, respectively.
7. When a chiral center is present in a polymer such as polypropylene, many different configurations or optical isomers are possible. The principal configurations with ordered arrangements of the pendant groups are high-melting,

strong molecules known as isotactic and syndiotactic isomers. Lower melting isomers in which the pendant groups are randomly oriented in space are known as atactic polymers.

8. The temperature at which segmental motion occurs because of free rotation of the covalent bonds is a characteristic temperature called the glass transition temperature. To be useful as plastics and elastomers, the polymers must be at a temperature below and above the glass transition temperature, respectively.
9. Since the specific volume, index of refraction, gas permeability, and heat capacity increase because of the onset of segmental motion at T_g, abrupt changes in these properties may be used to determine T_g.
10. The first-order transition, or melting point (T_m), is 33–100% greater than T_g, which is sometimes called the second-order transition. The greatest difference between T_m and T_g is demonstrated by symmetrical polymers like HDPE.
11. A polymer chain stretched out to its full contour length represents only one of the myriad of conformations present in a polymer at temperatures above T_g. Hence, the chain length is expressed statistically as the root-mean-square distance $\sqrt{\bar{r}^2}$, which is about 7% of the full contour length of the polymer chain.
12. Since branched chains like LDPE have many chain ends, it is customary to use the radius of gyration (S), which is the distance of a chain end from the polymer's center of gravity, instead of r.
13. The flexibility, which is related inversely to the orientation time (τ_m), increases as the temperature increases and may be calculated from the Arrhenius equation:

$$\tau_m = Ae^{E/RT}$$

14. Fibers and stretched elastomers are translucent because of the presence of spherulites consisting of organized crystallites or regions of crystallinity.
15. Since single-lamellar crystals consisting of folded chains of symmetrical polymers can be prepared, it is now assumed that crystalline polymers may be represented by a switchboard model consisting of crystalline and amorphous domains.
16. Additional orientation of crystalline polymers occurs and physical properties are improved when films are biaxially oriented or when fibers are stretched.
17. The principal differences between elastomers, plastics, and fibers are the presence and absence of stiffening groups in the chain, the size of the pendant groups on the chain, and the strength of the intermolecular forces. Elastomers are usually characterized by the absence of stiffening groups in the polymer backbone, the presence of bulky pendant groups, and the absence of strong intermolecular forces. In contrast, fibers are characterized by the presence of stiffening groups in the polymer backbone and of intermolecular hydrogen bonds and the absence of branching or irregularly spaced pendant groups. The structure and properties of plastics are between these two extremes.

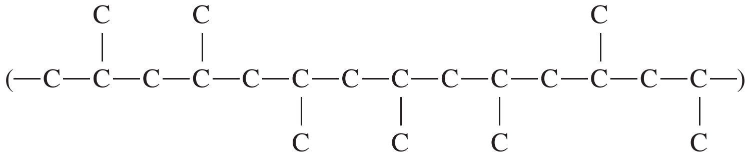
GLOSSARY

amorphous: Noncrystalline polymer or noncrystalline areas in a polymer.
anti form: Trans (t) or low-energy conformer.

aramides: Aromatic nylons.

Arrhenius equation: An equation showing the exponential effect of temperature on a process.

atactic: A polymer in which there is a random arrangement of pendant groups on each side of the chain, as in atactic PP:



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Avrami equation: An equation used to describe the crystallization rate.

backbone: The principal chain in a polymer molecule.

biaxially oriented film: A strong film prepared by stretching the film in two directions at right angles to each other. This strong film will shrink to its original dimensions when heated.

branched polymer: A polymer having extensions of the polymer chain attached to the polymer backbone, such as LDPE. Polymers having pendant groups, such as the methyl groups in polypropylene, are not considered to be branched polymers.

bulky groups: Large pendant groups on a polymer chain.

cellulose: A polymer in which cellobiose is the repeating unit.

chiral center: An asymmetric center such as a carbon atom with four different groups.

cold drawing: The stretching of a fiber or fibers to obtain products with high tensile strength.

configurations: Related chemical structures produced by the breaking and making of primary valence bonds.

conformations: Various shapes of polymers resulting from the rotation of single bonds in the polymer chain.

conformer: A shape produced by a change in the conformation of a polymer.

contour length: The fully extended length of a polymer chain, equal to the product of the length of each repeating unit (1) times the number of units, or mers (n), i.e., nl is the full contour length.

critical chain length (z): The minimum chain length required for entanglement of the polymer chains.

crosslinked density: A measure of the relative degree of crosslinking in a network polymer.

crystalline polymer: A polymer with ordered structure that has been allowed to disentangle and form crystals such as HDPE. Thus, isotactic polypropylene, cellulose, and stretched rubber are crystalline polymers.

crystallites: Regions of crystallinity.

differential scanning calorimetry (DSC): An instrumental thermal analytical technique in which the difference in the amount of heat absorbed by a polymer sample and a standard is measured by the power consumed as the temperature is increased.

differential thermal analysis (DTA): A thermal instrumental analytical technique in which the rate of absorption of heat by a polymer is compared with that of a standard such as glass or alumina.

dilatometry: A technique in which changes in specific volume are measured.

dipole-dipole interactions: Moderate secondary valence forces between polar groups in different molecules or in different locations in the same molecule.

dispersion forces: Same as London forces.

DNA: Deoxyribonucleic acid.

DP: Degree of polymerization or the number of repeating units (mers) in a polymer chain.

$\overline{\text{DP}}$: Average degree of polymerization in a polydisperse polymer.

η: Viscosity or coefficient of viscosity.

end-to-end distance (r): The shortest distance between chain ends in a polymer.

endothermic: A process in which energy is absorbed.

eutactic: An isotactic or syndiotactic polymer.

excluded volume: The volume that must be disregarded because only one atom of a chain may occupy any specific space at any specified time.

fiber: A polymer with strong intermolecular hydrogen bonding.

flexibilizing groups: Those groups in the polymer backbone that increase the segmental motion of polymers, e.g., oxygen atoms or multiple methylene groups.

fringed micelle model: An outmoded model showing amorphous and crystalline domains in a polymer.

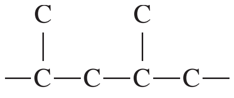
gauche forms (g): Conformers in which the methylene groups in the polymer chain are 60° apart relative to rotation about a C–C bond.

glass transition temperature (T_g): A characteristic temperature at which glassy amorphous polymers become flexible or rubber-like because of the onset of segmental motion.

glassy state: Hard, brittle state.

gutta percha: naturally occurring trans isomer of polyisoprene.

head-to-tail configuration: The normal sequence of mers in which the pendant groups are regularly spaced like the methyl groups in polypropylene, i.e., high-density polyethylene (HDPE): Formerly called low-pressure polyethylene, a linear polymer produced by the polymerization of ethylene in the presence of Ziegler-Natta or Phillips catalysts.



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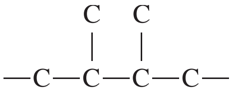

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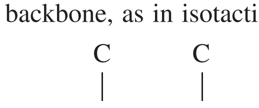
hydrogen bonding: Strong secondary valence forces between a hydrogen atom in one molecule and an oxygen, nitrogen, or fluorine atom in another molecule. These forces may also exist between hydrogen atoms in one location and oxygen, nitrogen, or fluorine atoms in another location in the same molecule. Intermolecular hydrogen bonds are responsible for the high strength of fibers. Helices are the result of intramolecular hydrogen bonds.

intermolecular forces: Secondary valence, or van der Waals, forces between different molecules.

intramolecular forces: Secondary valence, or van der Waals, forces within the same molecule.

isotactic: A polymer in which the pendant groups are all on the same side of the polymer backbone, as in isotactic PP:



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lamellar: Plate-like in shape.

linear polymer: A polymer like HDPE that consists of a linear chain without chain-extending branches.

London forces: Weak transitory dispersion forces resulting from induced dipole-induced dipole interaction.

low-density polyethylene (LDPE): Formerly called high-pressure polyethylene, a branched polymer produced by the free radical-initiated polymerization of ethylene at high pressure.

Maltese cross: A cross with arms like arrowheads pointing inward.

melting point (T_m): The first-order transition when the solid and liquid phases are in equilibrium.

mer: The repeating unit in a polymer chain.

methylene: —CH_2—.

modulus: The ratio of stress to strain, as of strength to elongation, which is a measure of stiffness of a polymer.

monodisperse: A polymer made up of molecules of one specific molecular weight, such as a protein.

n: Symbol for the number of mers (repeating units) in a polymer.

nanometer (nm): 10^{-9} m.

nylon: A synthetic polyamide.

pendant groups: Groups attached to the main polymer chain or backbone, like the methyl groups in polypropylene.

pentane interference: The interference with free motion caused by the overlap of the hydrogen atoms on the terminal carbon atoms in pentane.

polydisperse: A polymer consisting of molecules of many different molecular weights, such as commercial HDPE.

r: Symbol for end-to-end distance.

radius of gyration (S): The root-mean-square distance of a chain end to a polymer's center of gravity.

random flight technique: A statistical approach used to measure the shortest distance between the start and finish of a random flight.

RNA: Ribonucleic acid.

root-mean-square distance: $\sqrt{\bar{r}^2} = 1\sqrt{n}$, the average end-to-end distance of polymer chains.

S: The radius of gyration.

side chain crystallization: Crystallization related to that of regularly spaced long pendant groups.

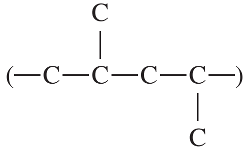
single polymer crystals: A lamellar structure consisting of folded chains of a linear polymer, such as polyethylene.

spherulites: Aggregates of polymer crystallites.

stiffening groups: Those groups in the polymer backbone that decrease the segmental motion of polymers, e.g., phenylene, amide, carbonyl, and sulfonyl groups.

switchboard model: A model resembling a switchboard used to depict crystalline and amorphous domains in a polymer.

syndiotactic: A polymer in which the pendant groups are arranged alternately on each side of the polymer backbone, as in syndiotactic PP:



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τ_m: The orientation time, a measure of the ease of uncoiling.

tacticity: The arrangement of the pendant groups in space. Examples are isotactic or syndiotactic polymers.

van der Waals forces: Forces based on attractions between groups in different molecules or in different locations in the same molecule.

viscosity: A measure of the resistance of a polymer to flow, either as a melt or as a solution.

EXERCISES

1. Make crude sketches or diagrams showing (a) a linear polymer, (b) a polymer with pendant groups, (c) a polymer with short branches, (d) a polymer with long branches, and crosslinked polymers with (e) low and (f) high crosslinked density.
2. Which has (a) the greater volume and (b) the lower softening point: HDPE or LDPE?
3. What is the approximate bond angle of the carbon atoms in (a) a linear and (b) a crosslinked polymer?
4. What is the approximate length of an HDPE chain when $n = 2000$ of a PVC chain of the same number of repeating units?
5. Which of the following is a monodisperse polymer: (a) hevea rubber, (b) corn starch, (c) cellulose from cotton, (d) casein from milk, (e) HDPE, (f) PVC, (g) β-keratin, (h) nylon-66, (i) DNA?
6. What is the degree of polymerization ($\overline{DP}$) of LDPE having an average molecular weight ($\overline{M}$) of 27,974?
7. What is the structure of the repeating unit (mer) in (a) polypropylene, (b) poly(vinyl chloride), (c) hevea rubber?
8. Which of the following is a branched chain polymer: (a) HDPE, (b) isotactic PP, (c) LDPE, (d) amylose starch?
9. Which of the following is a thermoplastic: (a) ebonite, (b) Bakelite, (c) vulcanized rubber, (d) HDPE, (e) celluloid, (f) PVC, (g) LDPE?
10. Which has the higher crosslinked density, (a) ebonite or (b) soft vulcanized rubber?
11. Do HDPE and LDPE differ in (a) configuration or (b) conformation?
12. Which is a trans isomer: (a) gutta percha or (b) hevea rubber?
13. Which will have the higher softening point: (a) gutta percha or (b) hevea rubber?
14. Show (a) a head-to-tail, and (b) a head-to-head configuration for poly(vinyl alcohol).
15. Show the structure of a typical portion of the chain of (a) syndiotactic PVC, (b) isotactic PVC.
16. Show Newman projections of the gauche forms of HDPE.
17. Name polymers whose intermolecular forces are principally (a) London forces, (b) dipole-dipole forces, (c) hydrogen bonding.
18. Which will be more flexible: (a) poly(ethylene terephthalate), or (b) poly(butylene terephthalate)?
19. Which will have the higher glass transition temperature (T_g): (a) poly(methyl methacrylate) or (b) poly(butyl methacrylate)?
20. Which will have the higher T_g: (a) isotactic polypropylene or (b) atactic polypropylene?
21. Which will be more permeable to a gas at room temperature: (a) isotactic polypropylene or (b) atactic polypropylene?

22. Which will have the greater difference between T_m and T_g values: (a) HDPE or (b) LDPE?
23. What is the full contour length of a molecule of HDPE with a DP of 1500?
24. Which would be more flexible: (a) poly(methyl acrylate) or (b) poly(methyl methacrylate)?
25. Would you expect the orientation time of HDPE to increase by approximately 5% or 50% when it is cooled from 90°C to 80°C?
26. Which would have the higher melting point: (a) nylon-66 or (b) an aramide?
27. What type of hydrogen bonds are present in a globular protein?
28. Which would have the greater tendency to cold flow at room temperature: (a) poly(vinyl acetate) ($T_g = 301$ K) or (b) polystyrene ($T_g = 375$ K)?
29. Which would be more transparent: (a) polystyrene or (b) isotactic polypropylene?
30. Which would be more apt to produce crystallites: (a) HDPE or (b) poly(butyl methacrylate)?
31. How would you cast a nearly transparent film of LDPE?
32. Which would tend to be more crystalline when stretched: (a) unvulcanized rubber or (b) ebonite?
33. Which would be more apt to exhibit side chain crystallization (a) poly(methyl methacrylate) or (b) poly(dodecyl methacrylate)?

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3

Molecular Weight of Polymers

3.1 INTRODUCTION

It is the size of macromolecules that gives them their unique and useful properties. Size allows polymer chains to act as a group so that when one part of the chain moves the other parts are affected, and so that when one polymer chain moves, surrounding chains are affected by that movement. Size allows memory to be imparted, retained, and used. Size allows cumulative effects of secondary bonding to become dominant factors in some behavior. Thus, the determination of a polymer's size adds an important factor in understanding its behavior.

Generally, the higher the molecular weight, the larger the polymer. The average molecule weight ($\overline{M}$) of a polymer is the product of the average number of repeat units or mers expressed as $\bar{n}$ or $\overline{DP}$ times the molecular weight of these repeating units. $\overline{M}$ for a group of chains of average formula $(CH_2\ CH_2)_{1000}$ is $1000(28) = 28{,}000$.

Polymerization reactions, both synthetic and natural, lead to polymers with heterogeneous molecular weights, i.e., polymer chains with a different number of units. Molecular weight distributions may be relatively broad (Fig. 3.1), as is the case for most synthetic polymers and many naturally occurring polymers. It may be relatively narrow for certain natural polymers (because of the imposed steric and electronic constraints), or may be mono-, bi-, tri-, or polymodal. A bimodal curve is often characteristic of a polymerization occurring under two distinct pathways or environments. Most synthetic polymers and many naturally occurring polymers consist of molecules with different molecular weights and are said to be polydisperse. In contrast, specific proteins and nucleic acids, like typical small molecules, consist of molecules with a specific molecular weight (M) and are said to be monodisperse.

Since typical small molecules and large molecules with molecular weights less than a critical value (Z) required for chain entanglement are weak and are readily attacked by appropriate reactants, it is apparent that the following properties are related to molecular

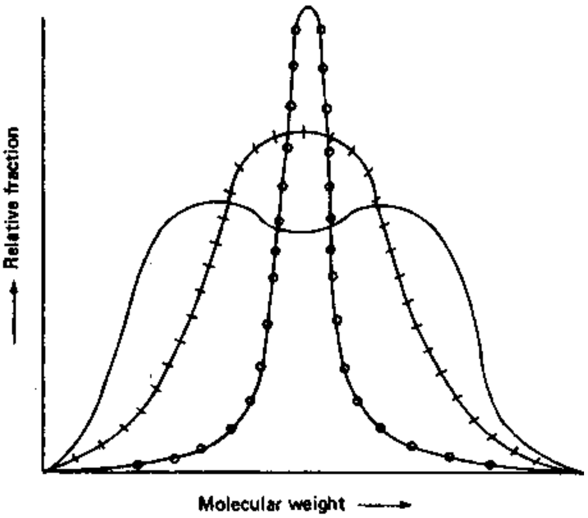


Figure 3.1 Representative differential weight distribution curves: (├┼┼┼┼┼) relatively broad distribution curve; (-o-o-o-o-) relatively narrow distribution curve; (————) bimodal distribution curve.

weight. Thus, melt viscosity, tensile strength, modulus, impact strength or toughness, and resistance to heat and corrosives are dependent on the molecular weight of amorphous polymers and their molecular weight distribution (MWD). In contrast, density, specific heat capacity, and refractive index are essentially independent of the molecular weight at molecular weight values above the critical molecular weight.

The melt viscosity is usually proportional to the 3.4 power of the average molecular weight at values above the critical molecular weight required for chain entanglement, i.e., $\eta \; \alpha \; \overline{M}^{3,4}$. Thus, the melt viscosity increases rapidly as the molecular weight increases and more energy is required for the processing and fabrication of these large molecules. However, as shown in Fig. 3.2, the strength of polymers increases as the molecular weight increases and then tends to level off.

Thus, while a value above the threshold molecular weight value (TMWV; lowest molecular weight where the desired property value is achieved) is essential for most practical applications, the additional cost of energy required for processing extremely high molecular weight polymers is seldom justified. Accordingly, it is customary to establish a commercial polymer range above the TMWV but below the extremely high molecular weight range. However, it should be noted that since toughness increases with molecular weight, extremely high molecular weight polymers, such as ultrahigh molecular weight polyethylene (UHMPE), are used for the production of tough articles such as trash barrels.

Oligomers and other low molecular weight polymers are not useful for applications where high strength is required. The word oligomer is derived from the Greek word *oligos*, meaning "a few." The value for TMWV will be dependent on T_g, the cohesive energy density (CED) of amorphous polymers (Sec. 3.2), the extent of crystallinity in crystalline polymers, and the effect of reinforcements in polymeric composites. Thus, while a low molecular weight amorphous polymer may be satisfactory for use as a coating or adhesive,

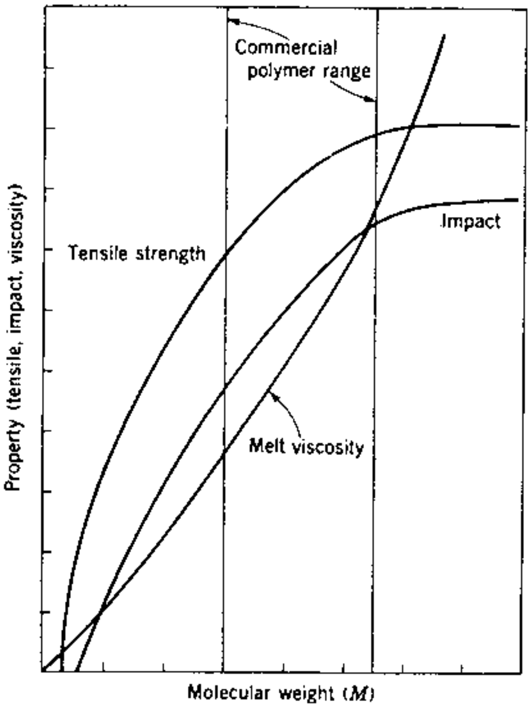


Figure 3.2 Relationship of polymer properties to molecular weight. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

a $\overline{\mathrm{DP}}$ value of at least 1000 may be required if the polymer is used as an elastomer or plastic. With the exception of polymers with highly regular structures, such as isotactic polypropylene, strong hydrogen intermolecular bonds are required for fibers. Because of their higher CED values, lower $\overline{\mathrm{DP}}$ values are satisfactory for polar polymers used as fibers.

3.2 SOLUBILITY

Polymer mobility is an important aspect helping determine a polymer's physical, chemical, and biological behavior. Lack of mobility, either because of interactions that are too swift to allow the units within the polymer chain some mobility or because there is not enough energy (often a high enough temperature) available to create mobility, results in a brittle material. Many processing techniques require the polymer to have some mobility. This mobility can be achieved through application of heat and/or pressure, or by having the polymer in solution. Because of its size, the usual driving force for the mixing and dissolving of materials is much smaller for polymers in comparison with smaller molecules. Here we will look at some of the factors that affect polymer solubility.

The physical properties of polymers, including T_g values, are related to the strength of the covalent bonds, the stiffness of the segments in the polymer backbone, and the strength of the intermolecular forces between the polymer molecules. The strength of the intermolecular forces is equal to the CED, which is the molar energy of vaporization per unit volume. Since intermolecular attractions of solvent and solute must be overcome when a solute dissolves, CED values may be used to predict solubility.

When a polymer dissolves, the first step is a slow swelling process called solvation in which the polymer molecule swells by a factor δ, which is related to CED. Linear and branched polymers dissolve in a second step, but network polymers remain in a swollen condition.

In order for solution to take place, it is essential that the free energy G, which is the driving force in the solution process, decrease as shown in the Gibbs free energy equation for constant temperature [Eq. (3.1)]. ΔH and ΔS are equal to the change in enthalpy and the change in entropy in this equation.

$$\Delta G = \Delta H - T\Delta S \tag{3.1}$$

By assuming that the sizes of polymer segments were similar to those of solvent molecules, Flory and Huggins obtained an expression for the partial molar Gibbs free energy of dilution, which included the dimensionless Flory-Huggins interaction parameter, $\chi_1 = Z\Delta H/RT$ in which $Z =$ a lattice coordination number. It is now recognized that χ_1 is composed of enthalpic and entropic contributions.

While the Flory-Huggins theory has its limitations, it may be used to predict the equilibrium behavior between liquid phases containing an amorphous polymer. The theory may also be used to predict the cloud point, which is just below the critical solution temperature T_c at which the two phases coalesce. The Flory-Huggins interaction parameter may be used as a measure of solvent power. The value of χ_1 for poor solvents is 0.5 and decreases for good solvents.

Some limitations of the Flory-Huggins lattice theory were overcome by Flory and Krigbaum, who assumed the presence of an excluded volume—the volume occupied by a polymer chain that exhibited long-range intramolecular interactions. These interactions were described in terms of free energy by introducing the enthalpy and entropy terms K_i and Ψ_i. These terms are equal when ΔG equals zero. The temperature at which these conditions prevail is the thedn, θ, temperature at which the effects of the excluded volume are eliminated and the polymer molecule assumes an unperturbed conformation in dilute solutions. The θ temperature is the lowest temperature at which a polymer of infinite molecular weight is completely miscible with a specific solvent. The coil expands above the θ temperature and contracts at lower temperatures.

As early as 1926, Hildebrand showed a relationship between solubility and the internal pressure of the solvent, and in 1931 Scatchard incorporated the CED concept into Hildebrand's equation. This led to the concept of a solubility parameter which is the square root of CED. Thus, as shown below, the solubility parameter δ for nonpolar solvents is equal to the square root of the heat of vaporization per unit volume:

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} \tag{3.2}$$

According to Hildebrand, the heat of mixing a solute and a solvent is proportional to the square of the difference in solubility parameters, as shown by the following equation in which ϕ is the partial volume of each component, namely, solvent γ_1 and solute ϕ_2. Since typically the entropy term favors solution and the enthalpy term acts counter to solution, the general objective is to match solvent and solute so that the difference between their δ values is small.

$$\Delta H_m = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \tag{3.3}$$

The solubility parameter concept predicts the heat of mixing liquids and amorphous polymers. Hence, any nonpolar amorphous polymer will dissolve in a liquid or a mixture of liquids having a solubility parameter that does not differ by more than ± 1.8 $(\text{cal cm}^{-3})^{0.5}$. The Hildebrand (H) is preferred over these complex units.

The solubility parameters concept, like Flory's θ temperature, is based on Gibbs' free energy. Thus, as the term ΔH in the expression ($\Delta G = \Delta H - T\,\Delta S$) approaches zero, ΔG will have the negative value required for solution to occur. The entropy (S) increases in the solution process and hence the emphasis is on negative or low values of ΔH_m.

For nonpolar solvents, which have been called regular solvents by Hildebrand, the solubility parameter δ is equal to the square root of the difference between the enthalpy of evaporation (ΔH_v) and the product of the ideal gas constant (R) and the Kelvin temperature (T) all divided by the molar volume (V), as shown below:

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} = \left(\frac{\Delta H_v - RT}{V}\right)^{1/2} \tag{3.4}$$

Since it is difficult to measure the molar volume, its equivalent, namely, the molecular weight M divided by density D, is substituted for V as shown below:

$$\delta = \left[D\,\frac{(\Delta H_v - RT)}{M}\right]^{1/2} \text{ or } \left[\frac{D(\Delta H_v - RT)}{M}\right]^{1/2} \tag{3.5}$$

As shown by the following illustration, this expression may be used to calculate the solubility parameter δ for any nonpolar solvent such as n-heptane at 298 K. n-Heptane has a molar heat of vaporization of 8700 cal, a density of 0.68 g cm^{-3}, and a molecular weight of 100.

$$\delta = \left\{\frac{0.68[8700 - 2(298)]}{100}\right\}^{1/2} = (55.1\ \text{cal cm}^{-3})^{1/2} = 7.4\ \text{H} \tag{3.6}$$

The solubility parameter $(\text{CED})^{1/2}$ is also related to the intrinsic viscosity of solutions ([η]) as shown by the following expression:

$$[\eta] = \eta_0\, e^{-v(\delta - \delta_0)^2} \tag{3.7}$$

The term intrinsic viscosity or limiting viscosity number is defined later in this chapter.

Since the heat of vaporization of solid polymers is not readily obtained, Small has supplied values for molar attraction constants (G) which are additive and can be used in the following equation for the estimation of the solubility parameter of nonpolar polymers:

$$\delta = \frac{D\sum G}{M} \tag{3.8}$$

Typical values for G at 25°C are shown in Table 3.1.

The use of Small's equation may be illustrated by calculating the solubility parameter of amorphous polypropylene ($D = 0.905$), which consists of the units CH, CH_2, and CH_3 in each mer. Polypropylene has a mer weight of 42.

Table 3.1 Small's Molar Attraction Constants (at 25 °C)

Group	$G[(\mathrm{cal/cm^3})^{1/2}\ \mathrm{mol^{-1}}]$
$-CH_3$	214
$>CH_2$	133
$\geqslant CH$	28
$-\overset{\vert}{\underset{\vert}{C}}-$	−93
$=CH_2$	190
$=CH-$	111
$=C<$	19
$HC\equiv C-$	285
Phenyl	735
Phenylene	658
$-H$	80–100
$-C\equiv N$	410
F or Cl	250–270
Br	340
$>CF_2$	150
$-S-$	225

$$\delta = \frac{0.905(28 + 133 + 214)}{42} = 8.1\ \mathrm{H} \tag{3.9}$$

Since CED is related to intermolecular attractions and chain stiffness, Hayes has derived an expression relating δ, T_g, and a chain stiffness constant M as shown below:

$$\delta = [M(T_g - 25)]^{1/2} \tag{3.10}$$

Since the polarity of most solvents except the hydrocarbons decreases as the molecular weight increases in a homologous series, δ values also decrease, as shown in Fig. 3.3.

Since "like dissolves like" is not a quantitative expression, paint technologists attempted to develop more quantitative empirical parameters before the Hildebrand solubility parameter had been developed. The Kauri–butanol and aniline points are still in use and are considered standard tests by the American Society for Testing and Materials (ASTM).

The Kauri–butanol value is equal to the minimum volume of test solvent that produces turbidity when added to a standard solution of Kauri–Copal resin in 1-butanol. The aniline point is the lowest temperature at which equal volumes of aniline and the test solvent are completely miscible. Both tests are measurements of the relative aromaticity of the test solvent, and their values may be converted to δ values.

Since the law of mixtures applies to the solubility parameter, it is possible to blend nonsolvents to form a mixture which will serve as a good solvent. For example, an equimolar mixture of n-pentane ($\delta = 7.1$ H) and n-octane ($\delta = 7.6$ H) will have a solubility parameter value of 7.35 H.

The solubility parameter of a polymer may be readily determined by noting the extent of swelling or actual solution of small amounts of polymer in a series of solvents having different δ values. Providing the polymer is in solution, its δ value may be deter-

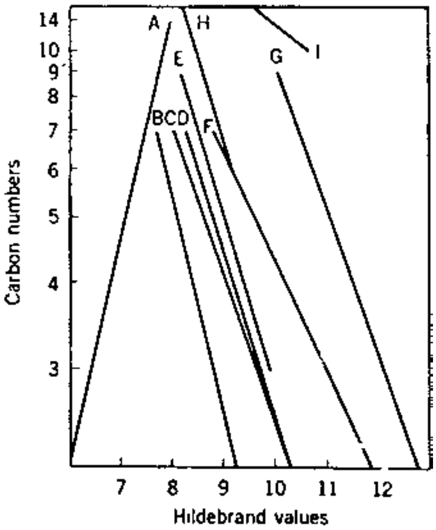


Figure 3.3 Spectrum of solubility parameter values for polymers ($\delta = 6.2$–15.4). A = Normal alkanes, B = normal chloroalkanes, C = methyl esters, D = other alkyl formates and acetates, E = methyl ketones, F = alkyl nitriles, G = normal alkanols H = alkyl benzenes and I = dialkyl phthalates. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

mined by turbidimetric titration using as titrants two different nonsolvents, one that is more polar and one that is less polar than the solvent present in the solution.

Since dipole–dipole forces are present in polar solvents and polar molecules, these must be taken into account when estimating solubilities with such “nonregular solvents.” A third factor must be considered for hydrogen-bonded solvents or polymers. Domains of solubility for nonregular solvents or solutes may be shown on three-dimensional plots showing the relationships between the “regular solvents,” dipolar and “H”-bonding contributions, and the solubility parameter values.

Plasticizers are typically nonvolatile solvents with $\Delta\delta$ values between the polymer and the plasticizer of less than 1.8 H. Plasticizers reduce the intermolecular attractions (CED and δ) of polymers such as cellulose nitrate (CN) and PVC and make processing less difficult. While camphor and tricresyl phosphate, which are plasticizers for CN and PVC, were discovered empirically, it is now possible to use δ values to screen potential plasticizers.

Complete data for solubility parameters may be found in the *Polymer Handbook* (Burrell, 1974). Typical data are tabulated in Tables 3.2 and 3.3.

3.3 AVERAGE MOLECULAR WEIGHT VALUES

Small molecules such as benzene, ethylene, and glucose have precise structures such that each molecule of benzene will have 6 atoms of carbon and 6 atoms of hydrogen, each molecule of ethylene will have 2 atoms of carbon and 4 atoms of hydrogen, and each molecule of glucose will have 12 atoms of hydrogen, 6 atoms of carbon, and 6 atoms of

Table 3.2 Solubility Parameters (δ) for Typical Solvents

Poorly hydrogen-bonded solvents (δ_p)		Moderately hydrogen-bonded solvents (δ_m)		Strongly hydrogen-bonded solvents (δ_s)	
Hydrogen	3.0	Diisopropyl ether	6.9	Diethylamine	8.0
Dimethylsiloxane	5.5	Diethyl ether	7.4	n-Amylamine	8.7
Difluorodichloromethane	5.5	Isoamyl acetate	7.8	2-Ethylhexanol	9.5
Ethane	6.0	Diisobutyl ketone	7.8	Isoamyl alcohol	10.0
Neopentane	6.3	Di-n-propyl ether	7.8	Acetic acid	10.1
Amylene	6.9	sec-Butyl acetate	8.2	m-Cresol	10.2
Nitro-n-octane	7.0	Isopropyl acetate	8.4	Aniline	10.3
n-Pentane	7.0	Methyl amyl ketone	8.5	n-Octyl alcohol	10.3
n-Octane	7.6	Butyraidehyde	9.0	tert-Butyl alcohol	10.6
Turpentine	8.1	Ethyl acetate	9.0	n-Amyl alcohol	10.9
Cyclohexane	8.2	Methyl ethyl ketone	9.3	n-Butyl alcohol	11.4
Cymene	8.2	Butyl cellosolve	9.5	Isopropyl alcohol	11.5
Monofluorodichloromethane	8.3	Methyl acetate	9.6	Diethylene glycol	12.1
Dipentene	8.5	Dichloroethyl ether	9.8	Furfuryl alcohol	12.5
Carbon tetrachloride	8.6	Acetone	9.9	Ethyl alcohol	12.7
n-Propylbenzene	8.6	Dioxane	10.0	N-Ethylformamide	13.9
p-Chlorotoluene	8.8	Cyclopentanone	10.4	Methanol	14.5
Decalin	8.8	Cellosolve	10.5	Ethylene glycol	14.6
Xylene	8.8	N,N-Dimethylacetamide	10.8	Glycerol	16.5
Benzene	9.2	Furfural	11.2	Water	23.4
Styrene	9.3	N,N-Dimethylformamide	12.1		
Tetralin	9.4	1,2-Propylene carbonate	13.3		
Chlorobenzene	9.5	Ethylene carbonate	14.7		
Ethylene dichloride	9.8				
p-Dichlorobenzene	10.0				
Nitroethane	11.1				
Acetonitrile	11.9				
Nitroethane	12.7				

oxygen. By comparison, each molecule of poly-1,4-phenylene may have a differing number of benzene-derived moieties, while single molecules (single chains) of polyethylene may vary in the number of ethylene units, the extent and frequency of branching, the distribution of branching, and the length of branching. Finally, glucose acts as a basic unit in a whole host of naturally available materials including cellulose, lactose, maltose, starch, and sucrose (some polymeric and others oligomeric). While a few polymers, such as enzymes and nucleic acids, must have very specific structures, most polymeric materials consist of molecules, individual polymer chains, that can vary in a number of features. Here we will concentrate on the variation in the number of units composing the individual polymer chains.

While there are several statistically described averages, we will concentrate on the two that are most germane to polymers: number average and weight average. These are averages based on statistical approaches that can be described mathematically and which correspond to measurements of specific factors.

The number average value, corresponding to a measure of chain length of polymer chains, is called the *number-average molecular weight*. Physically, the number-average

Table 3.3 Approximate Solubility Parameter Values for Polymers

Polymer	δ_p	δ_m	δ_s
Polytetrafluoroethylene	5.8–6.4		
Ester gum	7.0–10.6	7.4–10.8	9.5–10.9
Alkyd 45% soy oil	7.0–11.1	7.4–10.8	9.5–11.8
Silicone DC-1107	7.0–9.5	9.3–10.8	9.5–11.5
Poly(vinyl ethyl ether)	7.0–11.0	7.4–10.8	9.5–14.0
Poly(butyl acrylate)	7.0–12.5	7.4–11.5	
Poly(butyl methacrylate)	7.4–11.0	7.4–10.0	9.5–11.2
Silicone DC-23	7.5–8.5	7.5–8.0	9.5–10.0
Polyisobutylene	7.5–8.0	—	—
Polyethylene	7.7–8.2	—	—
Gilsonite	7.9–9.5	7.8–8.5	—
Poly(vinyl butyl ether)	7.8–10.6	7.5–10.0	9.5–11.2
Natural rubber	8.1–8.5	—	—
Hypalon 20 (sulfochlorinated LDPE)	8.1–9.8	8.4–8.8	—
Ethylcellulose N-22	8.1–11.1	7.4–10.8	9.5–14.5
Chlorinated rubber	8.5–10.6	7.8–10.8	—
Dammar gum	8.5–10.6	7.8–10.0	9.5–10.9
Versamid 100	8.5–10.6	8.5–8.9	9.5–11.4
Polystyrene	8.5–10.6	9.1–9.4	—
Poly(vinyl acetate)	8.5–9.5	—	—
Poly(vinyl chloride)	8.5–11.0	7.8–10.5	—
Phenolic resins	8.5–11.5	7.8–13.2	9.5–13.6
Buna N (butadiene-acrylonitrile copolymer)	8.7–9.3	—	—
Poly(methyl methacrylate)	8.9–12.7	8.5–13.3	—
Carbowax 4000 [poly(ethylene oxide)]	8.9–12.7	8.5–14.5	9.5–14.5
Thiokol [poly(ethylene sulfide)]	9.0–10.0	—	—
Polycarbonate	9.5–10.6	9.5–10.0	—
Pliolite P-1230 (cyclized rubber)	9.5–10.6	—	—
Mylar [poly(ethylene terephthalate)]	9.5–10.8	9.3–9.9	—
Vinyl chloride-acetate copolymer	9.5–11.0	7.8–13.0	—
Polyurethane	9.8–10.3	—	—
Styrene acrylonitrile copolymer	10.6–11.1	9.4–9.8	—
Vinsol (rosin derivative)	10.6–11.8	7.7–13.0	9.5–12.5
Epon 1001 (epoxy)	10.6–11.1	8.5–13.3	—
Shellac	—	10.0–11.0	9.5–14.0
Polymethacrylonitrile	—	10.6–11.0	—
Cellulose acetate	11.1–12.5	10.0–14.5	—
Nitrocellulose	11.1–12.5	8.0–14.5	12.5–14.5
Polyacrylonitrile	—	12.0–14.0	—
Poly(vinyl alcohol)	—	—	12.0–13.0
Nylon-66 [poly(hexamethylene adipamide)]	—	—	13.5–15.0
Cellulose	—	—	14.5–16.5

molecular weight can be measured by any technique that "counts" the molecules. These techniques include vapor phase and membrane osmometry, freezing point lowering, boiling point elevation, and end-group analysis.

We can describe the number average using a jar filled with plastic capsules such as those that contain tiny prizes (Fig. 3.4). Here, each capsule contains one polymer chain. All of the capsules are the same size, regardless of the size of the polymer chain contained therein. Capsules are then withdrawn, opened, and the individual chain length determined and recorded. The probability of drawing a capsule containing a chain with a specific length is dependent on the fraction of capsules containing such a chain and independent of the length of the chain. (In point of fact, this is an exercise in fantasy since the molecular size of single molecules is not easily measured.) After a sufficient number of capsules have been withdrawn and the chain size recorded, a graph like the one shown in Fig. 3.5 is constructed. The most probable value is the number-average molecular weight or number-average chain length. It should be apparent that the probability of drawing out a chain of a particular length is independent of the length or size of the polymer chain, but the probability is dependent on the number of chains of various lengths.

The *weight-average molecular weight* is similarly described, except that the capsules correspond in size to the size of the polymer chain (Fig. 3.6). Thus, a capsule containing a long polymer chain will be larger than one containing a smaller chain, and the probability of drawing a capsule containing a long polymer chain will be greater because of its greater size. Again, a graph can be constructed and the maximum value is the weight-average molecular weight.

Several mathematical moments (about a mean) can be described using the differential or frequency distribution curve, and can be described by equations. The first moment is the number-average molecular weight, $\overline{M}_n$. Any measurement that leads to the number of molecules, functional groups, or particles that are present in a given weight of sample allows the calculation of $\overline{M}_n$. The number-average molecular weight $\overline{M}_n$ is calculated like

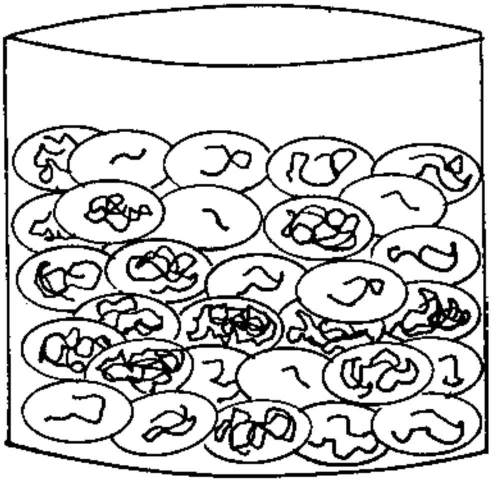


Figure 3.4 Jar with capsules, each of which contains a single polymer chain where the capsule size is the same and independent of the chain size, illustrating the number-average dependence on molecular weight.

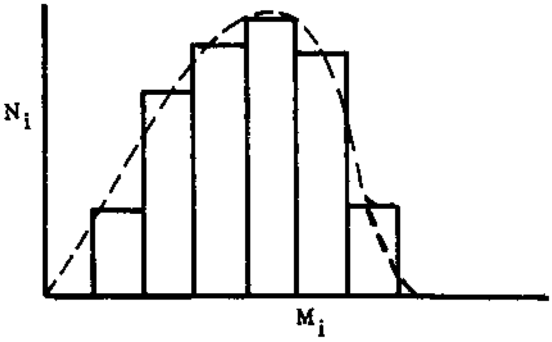


Figure 3.5 Molecular weight distribution for a polydisperse polymeric sample constructed from "capsule-derived" data.

any other numerical average by dividing the sum of the individual molecular weight values by the number of molecules. Thus, $\overline{M}_n$ for three molecules having molecular weights of 1.00×10^5, 2.0×10^5, and 3.00×10^5 would be $(6.00 \times 10^5)/3 = 2.00 \times 10^5$. This solution is shown mathematically:

$$\overline{M}_n = \frac{\text{total weight of sample}}{\text{no. of molecules of } N_i} = \frac{W}{\sum_{i=1}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i} \tag{3.11}$$

Most thermodynamic properties are related to the number of particles present and thus are dependent on $\overline{M}_n$.

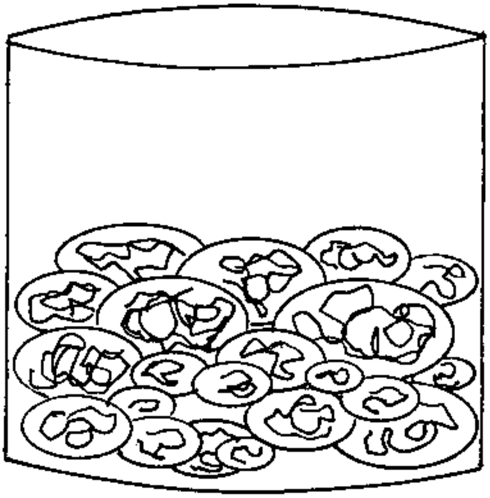


Figure 3.6 Jar with capsules, each of which contains a single polymer chain where the capsule size is directly related to the size of the polymer chain contained within the capsule.

Colligative properties are dependent on the number of particles present and are obviously related to $\overline{M}_n$. $\overline{M}_n$ values are independent of molecular size and are highly sensitive to small molecules present in the mixture. Values for $\overline{M}_n$ are determined by Raoult's techniques that are dependent on colligative properties such as ebulliometry (boiling point elevation), cryometry (freezing point depression), osmometry, and end-group analysis.

Weight-average molecular weight, $\overline{M}_w$, is determined from experiments in which each molecule or chain makes a contribution to the measured result relative to its size. This average is more dependent on the number of heavier molecules than is the number-average molecule weight, which is dependent simply on the total number of particles.

The weight-average molecular weight $\overline{M}_w$ is the second moment or second power average and is shown mathematically as

$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} M_i^2 N_i}{\sum_{i=1}^{\infty} M_i N_i} \tag{3.12}$$

Thus, the weight-average molecular weight for the example used in calculating $\overline{M}_n$ would be 2.33×10^5:

$$\frac{(1.00 \times 10^{10}) + (4.00 \times 10^{10}) + 9 \times 10^{10})}{6.00 \times 10^5} = 2.33 \times 10^5$$

Bulk properties associated with large deformations, such as viscosity and toughness, are particularly affected by $\overline{M}_w$ values. $\overline{M}_w$ values are determined by light scattering and ultracentrifugation techniques.

However, melt elasticity is more closely dependent on $\overline{M}_z$—the z-average molecular weight which can also be obtained by ultracentrifugation techniques. M_z is the third moment or third power average and is shown mathematically as

$$\overline{M}_z = \frac{\sum_{i=1}^{\infty} M_i^3 N_i}{\sum_{i=1}^{\infty} M_i^2 N_i} \tag{3.13}$$

Thus, the $\overline{M}_z$ average molecular weight for the example used in calculating $\overline{M}_n$ and $\overline{M}_w$ would be 2.57×10^5:

$$\frac{(1 \times 10^{15} + (8 \times 10^{15}) + (27 \times 10^{15})}{(1 \times 10^{10}) + (4 + 10^{10}) + (9 \times 10^{10})} = 2.57 \times 10^5$$

While z + 1 and higher average molecular weights may be calculated, the major interests are in $\overline{M}_n$, $\overline{M}_v$, $\overline{M}_w$, and $\overline{M}_z$, which as shown in Fig. 3.7 are listed in order of increasing size. For heterogeneous molecular weight systems, $\overline{M}_z$ is always greater than $\overline{M}_w$ and $\overline{M}_w$ is always greater than $\overline{M}_n$. The ratio of $\overline{M}_w/\overline{M}_n$ is a measure of polydispersity and is called the polydispersity index. The most probable distribution for polydisperse polymers produced by condensation techniques is a polydispersity index of 2.0. Thus, for a polymer mixture which is heterogeneous with respect to molecular weight, $\overline{M}_z > \overline{M}_w > \overline{M}_n$. As the heterogeneity decreases, the various molecular weight values converge until for homogeneous mixtures $\overline{M}_z = \overline{M}_w = \overline{M}_n$. The ratios of such molecular weight values are often used to describe the molecular weight heterogeneity of polymer samples.

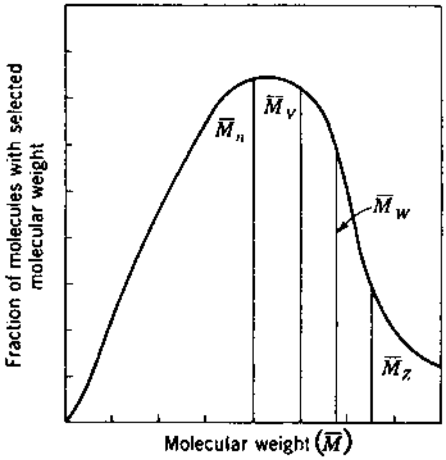


Figure 3.7 Molecular weight distributions. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

Typical techniques for molecular weight determination are given in Table 3.4. The most popular techniques will be considered briefly.

All classic molecular weight determination methods require the polymer to be in solution. To minimize polymer–polymer interactions, solutions equal to and less than 1 g of polymer to 100 mL of solution are utilized. To further minimize solute interactions, extrapolation of the measurements to infinite dilution is normally practiced.

When the exponent a in the Mark-Houwink equation is equal to 1, the average molecular weight obtained by viscosity measurements ($\overline{M}_v$) is equal to $\overline{M}_w$. However, since typical values of a are 0.5 to 0.8, the value $\overline{M}_w$ is usually greater than $\overline{M}_v$. Since viscometry does not yield absolute values of $\overline{M}$ as is the case with other techniques, one must plot [η] against known values of $\overline{M}$ and determine the constants K and a in the Mark-Houwink equation. Some of these values are available in the *Polymer Handbook* (Burrell, 1974), and simple comparative effluent times or melt indices are often sufficient for comparative purposes and quality control where K and a are known.

For polydisperse polymer samples, molecular weight values determined from colligative properties (3.6–3.8), light scattering photometry (3.10), and the appropriate data treatment of ultracentrifugation (3.11) are referred to as "absolute molecular weights," while those determined from gel permeation chromatography (GPC) (3.5) and viscometry (3.13) are referred to as relative molecular weights. An absolute molecular weight is one that can be determined experimentally and where the molecular weight can be related, through basic equations, to the parameter(s) measured. GPC and viscometry require calibration employing polymers of known molecular weight determined from an absolute molecular weight technique.

3.4 FRACTIONATION OF POLYDISPERSE SYSTEMS

The data plotted in Fig. 3.7 were obtained by the fractionation of a polydisperse polymer. Prior to the introduction of GPC, polydisperse polymers were fractionated by the addition

Table 3.4 Typical Molecular Weight Determination Methods[a]

Method	Type of mol. wt. average	Applicable wt. range	Other information
Light scattering	$\overline{M}_w$	To ∞	Can also give shape
Membrane osmometry	$\overline{M}_n$	2×10^4 to 2×10^6	
Vapor phase osmometry	$\overline{M}_n$	To 40,000	
Electron and X-ray microscopy	$\overline{M}_{n,w,z}$	10^2 to ∞	Shape, distribution
Isopiestic method (isothermal distillation)	$\overline{M}_n$	To 20,000	
Ebulliometry (boiling point elevation)	$\overline{M}_n$	To 40,000	
Cryoscopy (melting point depression)	$\overline{M}_n$	To 50,000	
End-group analysis	$\overline{M}_n$	To 20,000	
Osmodialysis	$\overline{M}_n$	500–25,000	
Centrifugation			
Sedimentation equilibrium	$\overline{M}_z$	To ∞	
Archibald modification	$\overline{M}_{z,w}$	To ∞	
Trautman's method	$\overline{M}_w$	To ∞	
Sedimentation velocity	Gives a real M only for monodisperse systems	To ∞	
Chromatography	Calibrated	To ∞	Mol. wt. distribution
SAXS	M_w		
Mass spectroscopy		To 10^6	
Viscometry	Calibrated	To ∞	
Coupled chromatography-LS		To ∞	Mol. wt. distribution, shape, M_w, M_n

[a] "To ∞" means that the molecular weight of the largest particles soluble in a suitable solvent can be determined in theory.

of a nonsolvent to a polymer solution, by cooling a solution of polymer, solvent evaporation, zone melting, extraction, diffusion, or centrifugation. The molecular weight of the fractions may be determined by any of the classic techniques previously mentioned and discussed subsequently in this chapter.

The least sophisticated but most convenient technique is fractional precipitation, which is dependent on the slight change in the solubility parameter with molecular weight. Thus, when a small amount of miscible nonsolvent is added to a polymer solution at a constant temperature, the product with the highest molecular weight precipitates. This procedure may be repeated after the precipitate is removed. These fractions may also be redissolved and again fractionally precipitated.

For example, isopropyl alcohol or methanol may be added dropwise to a solution of polystyrene in benzene until the solution becomes turbid. It is preferable to heat this solution and allow it to cool before removing the first and subsequent fractions. Extraction of a polymer in a Soxhlet-type apparatus in which fractions are removed at specific time intervals may also be used as a fractionation procedure.

3.5 CHROMATOGRAPHY

As will be noted shortly, certain techniques such as colligative methods (Secs. 3.6–3.8), light scattering photometry, special mass spectral techniques, and ultracentrifugation allow the calculation of specific or absolute molecular weights. Under certain conditions some of these allow allow the calculation of the molecular weight distribution (MWD).

These are a wide variety of chromatography techniques including paper and column techniques. Chromatographic techniques involve passing a solution containing the to-be-tested sample through a medium that shows selective absorption for the different components in the solution. Ion exchange chromatography separates molecules on the basis of their electrical charge. Ion exchange resins are either polyanions or polycations. For a polycation resin, those particles that are least attracted to the resin will flow more rapidly through the column and be emitted from the column first. This technique is most useful for polymers that contain changed moieties.

In affinity chromatography, the resin contains molecules that are especially selected that will interact with the particular polymer(s) under study. Thus, for a particular protein, the resin may be modified to contain a molecule that interacts with that protein type. The solution containing the mixture is passed through the column and the modified resin preferentially associates with the desired protein allowing it to be preferentially removed from the solution. Later, the protein is washed through the column by addition of a salt solution and collected for further evaluation.

In high-performance liquid chromatography (HPLC), pressure is applied to the column that causes the solution to rapidly pass through the column allowing procedures to be completed in a fraction of the time in comparison to regular chromatography.

When an electric field is applied to a solution, polymers containing a charge will move toward either the cathode (positively charged species) or the anode (negatively charged species). This migration is called *electrophoresis*. The velocity at which molecules move is mainly dependent on the electric field and change on the polymer driving the molecule toward one of the electrodes, and a frictional force dependent on the size and structure of the macromolecules that opposes the movement. In general, the larger and more bulky the macromolecule, the greater the resistance to movement, and the greater the applied field and charge on the molecule the more rapid the movement. While electrophoresis can be conducted on solutions it is customary to use a supporting medium of a paper or gel. For a given system, it is possible to calibrate the rate of flow with the molecular weight and/or size of the molecule. Here the flow characteristics of the calibration material must be similar to those of the unknown.

Generally though, electrophoresis is often employed in the separation of complex molecules such as proteins where the primary factor in the separation is the charge on the species. Some amino acids such as aspartic acid and glutamic acid contain an “additional” acid functional group, while amino acids such as lysine, arginine, and histidine contain “additional” basic groups. The presence of these units will confer to the protein tendencies to move towards the anode or cathode. The rate of movement is dependent on a number of factors including the relative abundance and accessability of these acid and base functional groups.

Figure 3.8 contains an illustration of the basic components of a typical electrophoresis apparatus. The troughs at either and contain an electrolyte buffer solution. The sample to be separated is placed in the approximate center of the electrophoresis strip.

Gel permeation chromatography (GPC) is a form of chromatography that is based on separation by molecular size rather than chemical properties. GPC or size exclusion

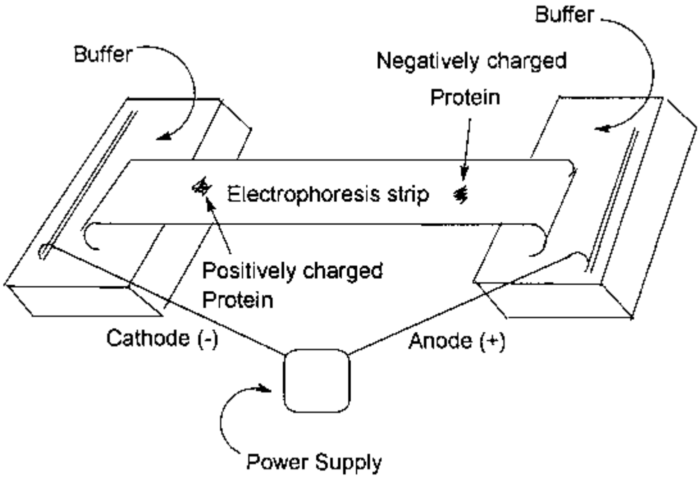


Figure 3.8 Basic components of an electrophoresis apparatus.

chromatography (SEC) is widely used for molecular weight and MWD determination. In itself, SEC does not give an absolute molecular weight and must be calibrated against polymer samples whose molecular weight has been determined by a technique that does give an absolute molecular weight.

Size exclusion chromatography is an HPLC technique whereby the polymer chains are separated according to differences in hydrodynamic volume. This separation is made possible by use of special packing material in the column. The packing material is usually polymeric porous spheres, often composed of polystyrene crosslinked by addition of varying amounts of divinylbenzene. Retension in the column is mainly governed by the partitioning (or exchanging) of polymer chains between the mobile (or eluent) phase flowing through the column and the stagnate liquid phase that is present in the interior of the packing material.

Through control of the amount of crosslinking, nature of the packing material and specific processing procedures, spheres of widely varying porosity are available. The motion in and out of the stationary phase is dependent on a number of factors including Brownian motion, chain size, and conformation. The latter two are related to the polymer chain's hydrodynamic volume—the real, excluded volume occupied by the polymer chain. Since smaller chains preferentially permeate the gel particles, the largest chains are eluted first. As noted above, the fractions are separated on the basis of size.

The resulting chromatogram is then a molecular size distribution (MSD). The relationship between molecular size and molecular weight is dependent on the conformation of the polymer in solution. As long as the polymer conformation remains constant, which is generally the case, molecular size increases with increase in molecular weight. The precise relationship between molecular size and molecular weight is conformation-dependent. For random coils, molecular size as measured by the polymer's radius of gyration, R, and molecular weight, M, is proportional to M^b, where b is a constant dependent on the solvent, polymer concentration, and temperature. Such values are known and appear in the literature for many polymers, allowing the ready conversion of molecular size data collected by SEC into molecular weight and MWD.

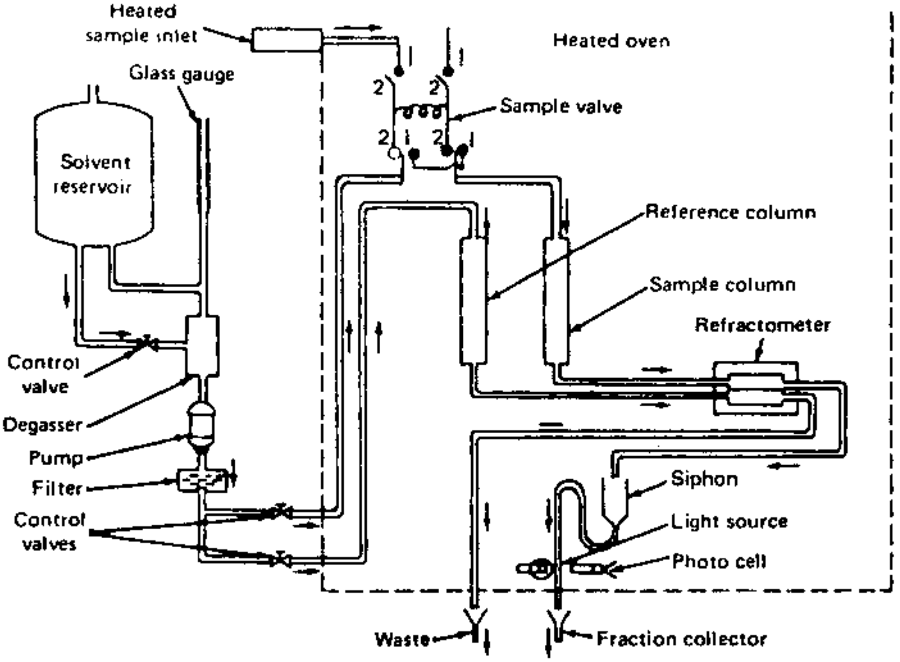


Figure 3.9 Sketch showing flow of solution and solvent in gel permeation chromatograph. (With permission of Waters Associates.)

There is a wide variety of instrumentation ranging from simple manually operated devices to completely automated systems. Figure 3.9 contains a brief sketch of one system. Briefly, the polymer-containing solution and solvent alone are introduced into the system and pumped through separate columns at a specific rate. The differences in refractive index between the solvent itself and polymer solution are determined using a differential refractometer. This allows calculation of the amount of polymer present as the solution passes out of the column.

The unautomated procedure was used first to separate protein oligomers (polypeptides) by use of Sephadex gels. Silica gels are also used as the GPC sieves. The efficiency of these packed columns may be determined by calculating the height in feet equivalent to a theoretical plate (HETP) which is the reciprocal of the plate count per feet (P). As shown by the expression in Eq. (3.14), P is directly proportional to the square of the elution volume (V_c) and inversely proportional to the height of the column in feet and the square of the baseline (d).

$$p = \frac{16}{f}\left(\frac{V_e}{d}\right)^2 \tag{3.14}$$

Conversion of retention volume for a given column to molecular weight can be accomplished using several approaches including peak position, universal calibration, broad standard and actual molecular weight determination by coupling the SEC to an instrument that gives absolute molecular weight.

In the peak position approach, well-characterized narrow fraction samples of known molecular weight are used to calibrate the column and retention times determined. A plot of log M vs. retention is made and used for the determination of samples of unknown molecular weight. Unless properly treated, such molecular weights are subject to error. The best results are obtained when the structures of the samples used in the calibration and those of the test polymers are the same.

The universal calibration approach is based on the product of the limiting viscosity number (LVN) and molecular weight being proportional to the hydrodynamic volume. Benoit showed that for different polymers elution volume plotted against the log LVN times molecular weight gave a common line. In one approach molecular weight is determined by constructing a "universal calibration line" through plotting the product of log LVN for polymer fractions with narrow MWDs as a function of the retention of these standard polymer samples for a given column. Molecular weight is then found from retention time of the polymer sample using the calibration line.

Probably the most accurate approach is to directly connect, or couple, the SEC to a device, such as a light scattering photometer, that directly measures the molecular weight for each elution fraction. Here both molecular weight and MWD are accurately determined.

3.6 OSMOMETRY

A measurement of any of the colligative properties of a polymer solution involves a counting of solute (polymer) molecules in a given amount of solvent and yields a number-average. The most common colligative property that is conveniently measured for high polymers is osmotic pressure. This is based on the use of a semipermeable membrane through which solvent molecules pass freely but through which polymer molecules are unable to pass. Existing membranes only approximate ideal semipermeability, the chief limitation being the passage of low molecular weight polymer chains through the membrane.

There is a thermodynamic drive toward dilution of the polymer-containing solution with a net flow of solvent toward the cell containing the polymer. This results in an increase in liquid in that cell causing a rise in the liquid level in the corresponding measuring tube. The rise in liquid level is opposed and balanced by a hydrostatic pressure resulting in a difference in the liquid levels of the two measuring tubes—the difference is directly related to the osmotic pressure of the polymer-containing solution. Thus, solvent molecules tend to pass through a semipermeable membrane to reach a "static" equilibrium, as illustrated in Fig. 3.10.

Since osmotic pressure is dependent on colligative properties, i.e., the number of particles present, the measurement of this pressure (osmometry) may be applied to the determination of the osmotic pressure of solvents vs. polymer solutions. The difference in height (Δh) of the liquids in the columns may be converted to osmotic pressure (π) by multiplying the gravity (g) and the density of the solution (ρ), i.e., $\pi = \Delta h \rho g$.

In an automatic membrane osmometer, such as the one shown in Fig. 3.11, the unrestricted capillary rise in a dilute solution is measured in accordance with the modified van't Hoff equation:

$$\pi = \frac{RT}{\overline{M}_n} C + BC^2 \tag{3.15}$$

As shown in Fig. 3.11, the reciprocal of the number average molecular weight ($\overline{M}_n^{-1}$) is the intercept when data for π/RTC vs. C are extrapolated to zero concentration.

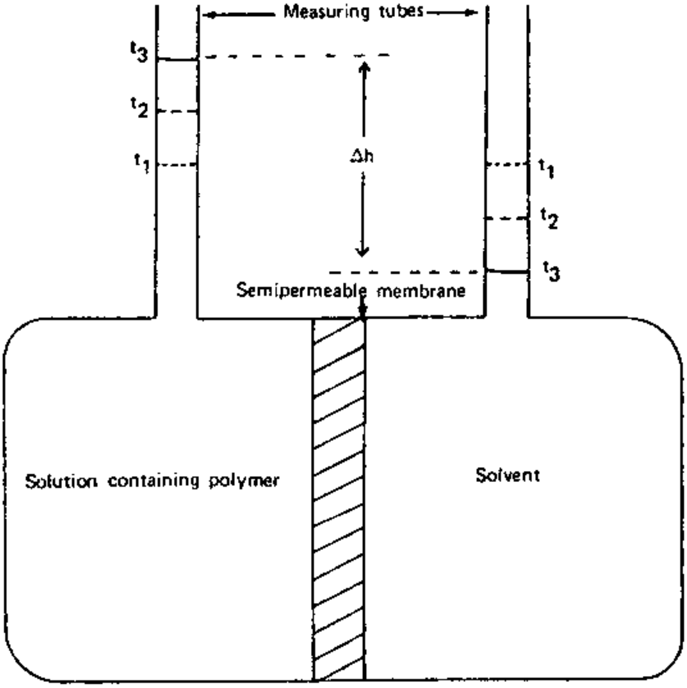


Figure 3.10 Schematic diagram showing the effect of pressure exerted by a solvent separated by a semipermeable membrane from a solution containing a nontransportable material (polymer) as a function of time, where t_1 represents the initial measuring tube levels, t_2, the levels after an elapsed time, and t_3 the levels when the "static" equilibrium occurs.

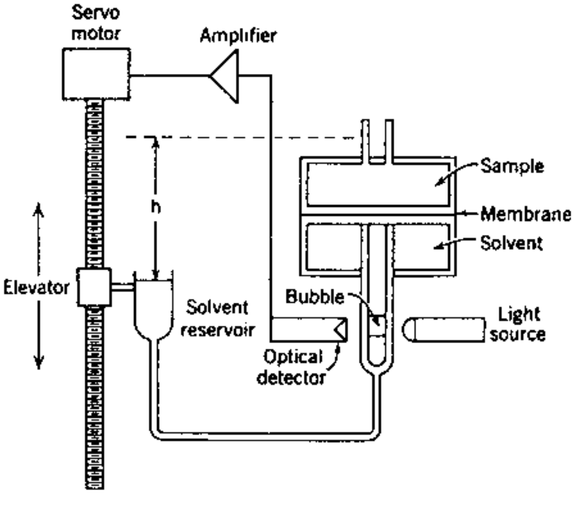


Figure 3.11 Automatic membrane osmometer. (Courtesy of Hewlett-Packard Company.)

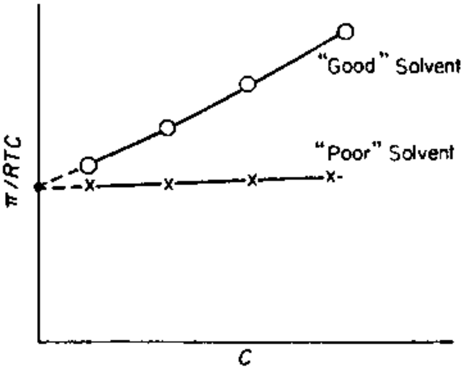


Figure 3.12 Plot of π/RTC vs. C used to determine $1/\overline{M}_n$ in osmometry. (From *Modern Plastics Technology* by R. Seymour, Reston Publishing Company, Reston, Virginia, 1975. Used with permission.)

The slope of the line in Fig. 3.12, i.e., the virial constant B, is related to CED. The value for B would be 0 at the θ temperature. Since this slope increases as the solvency increases, it is advantageous to use a dilute solution consisting of a polymer and a poor solvent. Semipermeable membranes may be constructed from hevea rubber, poly(vinyl alcohol), or cellulose nitrate.

The static head (Δh) developed in the static equilibrium method is eliminated in the dynamic equilibrium method in which a counterpressure is applied to prevent the rise of solvent in the measuring tubes, as shown in Fig. 3.11. Since osmotic pressure is large (1 atm for a 1 M solution), osmometry is useful for the determination of the molecular weight of large molecules.

Static osmotic pressure measurements generally require several days to weeks before a suitable equilibrium is established to permit a meaningful measurement of osmotic pressure. The time required to achieve equilibrium is shortened to several minutes to an hour in most commercial instruments utilizing dynamic techniques.

Classic osmometry is useful and widely used for the determination of a range of M_n values from 5×10^4 to 2×10^6. New dynamic osmometers expand the lower limit to 2×10^4. The molecular weight of polymers with lower molecular weights which may pass through a membrane may be determined by vapor pressure osmometry (VPO) or isothermal distillation. Both techniques provide absolute values for $\overline{M}_n$.

In the VPO technique, drops of solvent and solution are placed in an insulated chamber in proximity to thermistor probes. Since the solvent molecules evaporate more rapidly from the solvent than from the solution, a difference in temperature (ΔT) is recorded. Thus, the molarity (M) may be determined by use of Eq. (3.16) if the heat of vaporization per gram of solvent (λ) is known.

$$\Delta T = \left(\frac{RT^2}{\lambda 100}\right) \underline{M} \tag{3.16}$$

A sketch of a vapor pressure osmometer is shown in Fig. 3.13

Problem

Insulin, a hormone that regulates carbohydrate metabolism in the blood, was isolated from a pig. A 0.200-g sample of insulin was dissolved in 25.0 mL of water, and at 30°C the

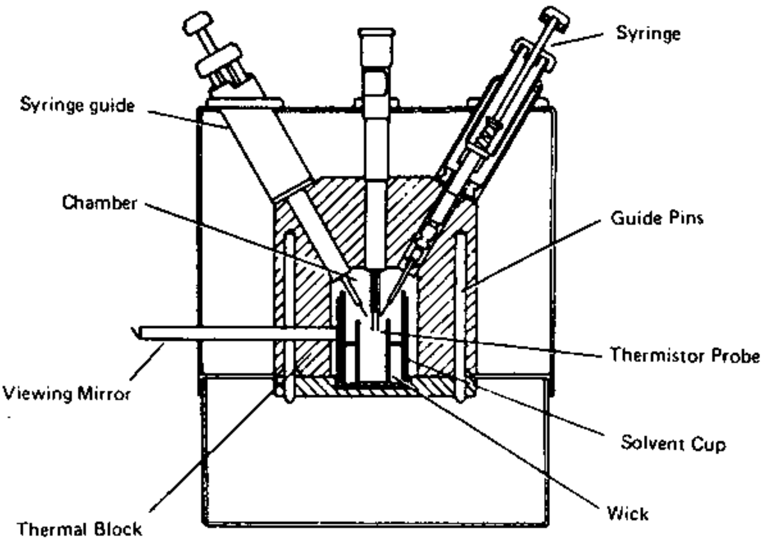


Figure 3.13 A sketch of a vapor pressure osmometer. (Courtesy of Hewlett-Packard Company.)

osmotic pressure of the solution was found to be 26.1 torr. What is the molecular weight of the insulin?

Rearrangement of the first terms of Eq. (3.15) gives $M = RTC/\pi$. Appropriate units of concentration, osmotic pressure, and R need to be chosen. The following units of grams per liter, atmospheres, and liter atmosphere per mol K are employed, giving

$$M = \frac{(0.08206\ 1\ \text{atm mol}^{-1}\ \text{K}^{-1})(303°\text{K})(8.0\ \text{g L}^{-1})}{\left(\dfrac{26.1\ \text{torr}}{760\ \text{torr/atm}}\right)} = 5800$$

This is an “apparent” molecular weight since it is for a single concentration and is not extrapolated to zero concentration.

Additional colligative approaches that are applicable to molecular weight determination for oligomeric and low molecular weight polymers are end-group analysis, ebulliometry, and cryometry.

3.7 END-GROUP ANALYSIS

While early experiments were unable to detect the end groups present in polymers, appropriate techniques are now available for detecting and analyzing quantitatively functional end-groups of linear polymers, such as those in nylon. The amino end-groups of nylon dissolved in m-cresol are readily determined by titration with a methanolic perchloric acid solution. The sensitivity of this method decreases as the molecular weight increases. Thus, this technique is limited to the determination of polymers with a molecular weight of less than about 20,000. Other titratable end groups are the hydroxyl and carboxyl groups in polyesters and the epoxy end groups in epoxy resins.

3.8 EBULLIOMETRY AND CRYOMETRY

These techniques, based on Raoult's law, are similar to those used for classic low molecular weight compounds and are dependent on the sensitivity of the thermometry available. The number-average molecular weight $\overline{M}_n$ in both cases is based on the Clausius-Clapeyron equation using boiling point elevation and freezing point depression (ΔT), as shown:

$$\overline{M}_n = \frac{RT^2V}{\Delta H}\left(\frac{C}{\Delta T}\right)_{C\to O} \tag{3.17}$$

Results obtained using the Clausius-Clapeyron equation, in which T is the Kelvin temperature and ΔH is the heat of transition, must be extrapolated to zero concentration. This technique, like end-group analysis, is limited to low molecular weight polymers. By use of thermistors sensitive to 1×10^{-4}°C, it is possible to measure molecular weight values up to 40,000–50,000, although the typical limits are about 5000.

3.9 REFRACTOMETRY

The index of refraction decreases slightly as the molecular weight increases and, as demonstrated by the techniques used in GPC, this change has been used for the determination of molecular weight after calibration, using samples of known molecular weight distribution.

3.10 LIGHT SCATTERING MEASUREMENTS

Ever watch a dog or young child chase moonbeams? The illumination of dust particles is an illustration of light scattering, not of reflection. Reflection is the deviation of incident light through one particular angle such that the angle of incidence is equal to the angle of reflection. Scattering is the radiation of light in all directions. Thus, in observing the moonbeam, the dust particle directs a beam toward you regardless of your angle in relation to the scattering particle. The energy scattered per second (scattered flux) is related to the size and shape of the scattering particle and to the scattering angle.

Scattering of light is all about us—the fact that the sky above us appears blue, the clouds white, and the sunset shades of reds and oranges is a consequence of preferential scattering of light from air molecules, water droplets, and dust particles. This scattered light caries messages about the scattering objects.

The measurement of light scattering by polymer molecules in solution is a widely used technique for the determination of absolute values of $\overline{M}_w$. This technique, which is based on the optical heterogeneity of polymer solutions, was developed by Nobel Laureate Peter Debye in 1944.

Today, modern instruments utilize lasers as the radiation source because they provide a monochromatic, intense, and well-defined light source. Depending upon the size of the scattering object, the intensity of light can be essentially the same or vary greatly with respect to the direction of the oncoming radiation. For small particles the light is scattered equally independent of the angle the observer is to the incoming light. For larger particles the intensity of scattered light varies with respect to the angle of the observer to the incoming light. For small molecules at low concentrations this scattering is described in terms of the Raleigh ratio.

In 1871, Rayleigh showed that induced oscillatory dipoles were developed when light passed through gases and that the amount (intensity) of scattered light (τ) was inversely proportional to the fourth power of the wavelength of light. This investigation was extended to liquids by Einstein and Smoluchowski in 1908. These oscillations reradiate the light energy to produce turbidity, i.e., the Tyndall effect. Other sources of energy, such as X-rays or laser beams, may be used in place of visible light waves.

For light scattering measurements, the total amount of the scattered light is deduced from the decrease in intensity of the incident beam, I_0, as it passes through a polymer sample. This can be described in terms of Beer's law for the absorption of light as follows:

$$\frac{I}{I_0} = e^{-\tau l} \tag{3.18}$$

where τ is the measure of the decrease of the incident beam intensity per unit length 1 of a given solution and is called the turbidity.

The intensity of scattered light or turbidity (τ) is proportional to the square of the difference between the index of refraction (n) of the polymer solution and of the solvent n_0, to the molecular weight of the polymer ($\overline{M}$), and to the inverse fourth power of the wavelength of light used (λ). Thus,

$$\frac{Hc}{\tau} = \frac{1}{\overline{M}_w P_\theta}(1 + 2Bc + Cc^2 + \ldots) \tag{3.19}$$

where the expression for the constant H is as follows:

$$H = \frac{32\pi^2}{3}\frac{n_0^2(dn/dc)^2}{\lambda^4 N} \text{ and } \tau \cdot = K'n^2\left(\frac{i_{90}}{i_0}\right) \tag{3.19a}$$

where n_0 = index of refraction of the solvent, n = index of refraction of the solution, c = concentration, the virial constants B, C, etc., are related to the interaction of the solvent, P_θ is the particle scattering factor, and N is Avogadro's number. The expression dn/dc is the specific refractive increment and is determined by taking the slope of the refractive index readings as a function of polymer concentration.

In the determination of the weight-average molecular weight of polymer molecules in dust-free solutions, one measures the intensity of scattered light from a mercury arc lamp or laser at different concentrations and at different angles (θ), typically 0, 90, 45, and 135° (Fig. 3.14). The incident light sends out a scattering envelope that has four equivalent quadrants. The ratio of scattering at 45° compared with that for 135° is called the dissymmetry factor or dissymmetry ratio Z. The reduced dissymmetry factor Z_0 is the intercept of the plot of Z as a function of concentration extrapolated to zero concentration.

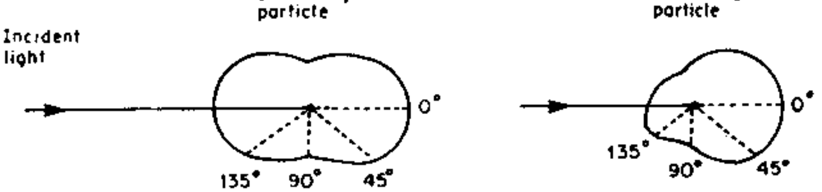


Figure 3.14 Light-scattering envelopes. Distance from the scattering particle to the boundaries of the envelope represents the magnitude of scattered light as a function of angle.

For polymer solutions containing polymers of moderate to low molecular weight, P_θ is 1 and Eq. (3.19) reduces to

$$\frac{Hc}{\tau} = \frac{1}{\overline{M}_w}(1 + 2Bc + Cc^2 + \ldots) \tag{3.20}$$

Several expressions are generally used in describing the relationship between values measured by light scattering photometry and molecular weight. One is given in Eq. (3.20) and the others, such as Eq. (3.21), are exactly analogous except that constants have been rearranged.

$$Kc/R = 1/M_w\,(1 + 2Bc + Cc^2 + \ldots \tag{3.21}$$

At low concentrations of polymer in solution, Eq. (3.21) reduces to an equation of a straight line ($y = b + mx$):

$$\frac{Hc}{\tau} = \frac{1}{\overline{M}_w} + \frac{2Bc}{\overline{M}_w} \tag{3.22}$$

When the ratio of the concentration c to the turbidity τ (related to the intensity of scattering at 0 and 90°) multiplied by the constant H is plotted against concentration, the intercept of the extrapolated curve, is the reciprocal of $\overline{M}_w$ and the slope contains the virial constant B, as shown in Fig. 3.15. Z_0 is directly related to P_θ, and both are related to both the size and shape of the scattering particle. As the size of the polymer chain approaches about one-twentieth the wavelength of incident light, scattering interference occurs giving a

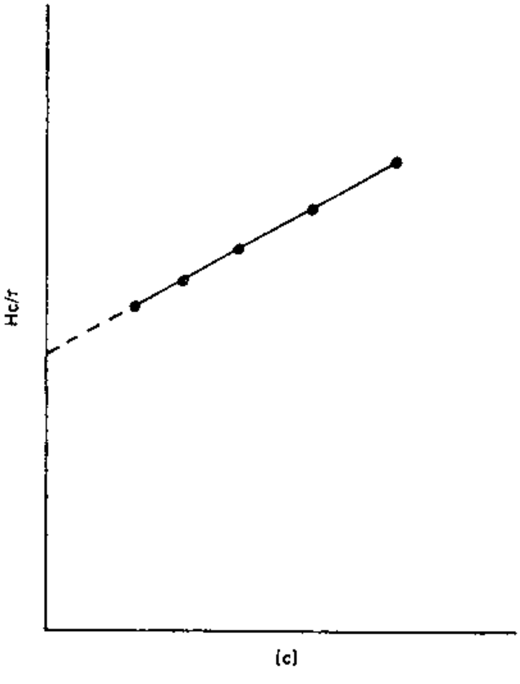


Figure 3.15 Typical plot used to determine $\overline{M}_w^{-1}$ from light scattering data.

scattering envelope that is no longer symmetrical. Here the scattering dependency on molecular weight reverts back to the relationship given in Eq. (3.19), thus, a plot of Hc/τ vs. c extrapolated to zero polymer concentration gives as the intercept $1/\overline{M}_w P_\theta$, not $1/\overline{M}_w$. The molecular weight for such situations is typically found using one of two techniques.

Problem

Determine the apparent weight-average molecular weight for a polymer sample where the intensity of scattering at 0° is 1000 and the intensity of scattering at 90° is 10 for a polymer (0.14 g) dissolved in DMSO (100 mL) that had a dn/dc of 1.0.

Most of the terms employed to describe H and τ are equipment constants, and their values are typically supplied with the light-scattering photometer and redetermined periodically. For the sake of calculation we will use the following constant values: $K' = 0.100$ and $\lambda = 546$ nm. DMSO has a measured refractive index of 1.475 at 21°C.

$$\tau = K' n^2 \frac{i_{90}}{i_0} = (0.100)\,(1.475)^2 \left(\frac{10}{1000}\right) \simeq 2.18 \times 10^{-3}$$

At 546 nm $H = 6.18 \times 10^{-5} n_0^2\,(dn/dc)^2 = 6.18 \times 10^{-5}\,(1.475)^2(1.0)^2 = 1.34 \times 10^{-4}$.

Typically, concentration units of g/mL or g/cc are employed for light-scattering photometry. For the present solution the concentration is 0.14 g/100 mL = 0.0014 g/mL.

$$\frac{Hc}{\tau} = \frac{1.34 \times 10^{-4} \times 1.4 \times 10^{-3}}{2.18 \times 10^{-3}} \simeq 8.6 \times 10^{-5}$$

The apparent molecular weight is then the inverse of 8.6×10^{-5} or 1.2×10^4. This is called "apparent" since it is for a single point and not extrapolated to zero.

The first of the techniques is called the dissymmetrical method or approach because it utilizes the determination of Z_0 vs. P_θ as a function of polymer shape. $\overline{M}_w$ is determined from the intercept $1/\overline{M}_w P_\theta$ through substitution of the determined P_θ. The weakness in this approach is the necessity of having to assume a shape for the polymer in a particular solution. For small Z_o values, choosing an incorrect polymer shape results in a small error, but for larger Z_0 values, the error may become significant, i.e., greater than 30%.

The second approach uses a double extrapolation to zero concentration and zero angle with the data forming what is called a Zimm plot (Figs. 3.15 and 3.16). The extrapolation to zero angle corrects for finite particle size effects. The radius of gyration, related to polymer shape and size, can also be determined from this plot.

The second extrapolation to zero concentration corrects for concentration factors. The intercepts of both plots is equal to $1/M_w$.

The Zimm plot approach does not require knowing or having to assume a particular shape for the polymer in solution.

Related to the Zimm plot is the Debye plot. In the Zimm approach, different concentrations of the polymer solution are used. In the Debye, one low concentration sample is used with $1/M_w$ plotted against $\sin^2(\theta/2)$, essentially one-half of the Zimm plot.

Low-angle laser light-scattering photometry (LALLS) and multiangle low-angle laser light scattering photometry (MALS) take advantage of the fact that at low or small angles the form factor, P_θ, becomes 1, reducing Equation 3.19 to 3.20 and at low concentrations to 3.22.

A number of automated systems exist with varying capabilities. Some internally carry out dilutions and refractive index measurements, allowing molecular weight to be

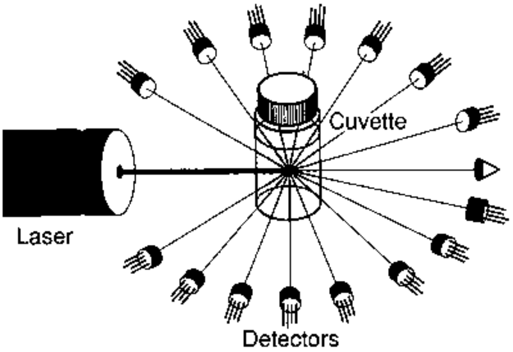


Figure 3.16 Detector arrangement showing a sample surrounded by an array of detectors that collect scattered laser light by the sample. (Used with permission of Wyatt Technology Corporation.)

directly determined without additional sample treatment. The correct determination of dn/dc is very important since any error in its determination is magnified because it appears as the squared value in the expression relating light scattering and molecular weight.

Low-angle and multiangle light-scattering photometers are available that allow not only the determination of the weight-average molecular weight but also additional values under appropriate conditions. For instance, the new multiangle instrument obtains data using a series of detectors as shown in Fig. 3.16. From data obtained from this instrument a typical Zimm plot is constructed as shown in Fig. 3.17 that gives both the weight-average molecular weight and the mean radius independent of the molecular conformation and branching. The actual shape of the Zimm plot shown in Fig. 3.17 is dependent on various "fit" constants such as the 1000 used as the multiplier for "c" in Fig. 3.17. Obtaining "good" plots can be routine through the use of special computer programs. These systems may also allow the determination of molecular conformation matching the radius and

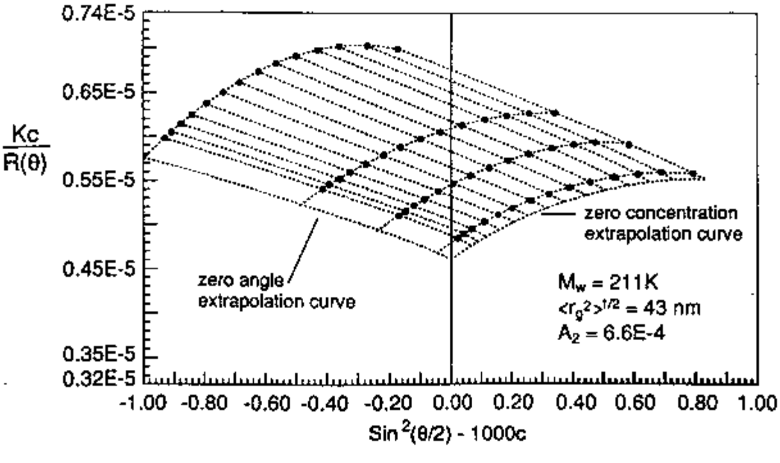


Figure 3.17 Zimm plot for a polymer scaled with a negative-concentration coefficient to improve data aesthetics and accessibility. (Used with permission of Wyatt Technology Corporation.)

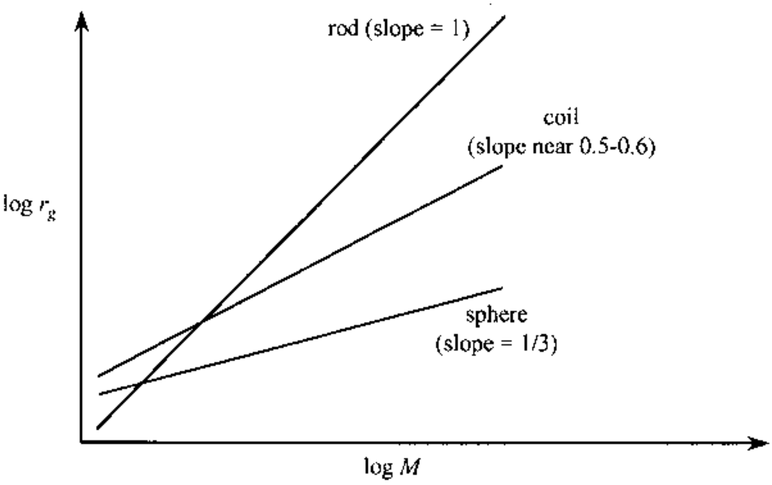


Figure 3.18 Standard plot of the log of the mean radium of gyration vs. log molecular weight for differently shaped macromolecules. Essentially, for a sphere the radius is proportion to the root-mean-square radius (rms radius) and $M^{1/3}$ with a slope in the log r_g vs. log M of 1/3; for rod-shaped polymers, length is proportional to rms radius and M with a slope of 1; and for random coils the end-to-end distance is proportional to the rms radius and $M^{1/2}$ with a slope of about 0.5–0.6. (Used with permission of Wyatt Technology Corporation.)

molecular weight to graphs showing the change in the root-mean-square radius of gyration and molecular weight for differently shaped molecules (Fig. 3.18). The expression for the mean square radius of gyration is given as

$$r_g^2 = \sum r_i^2 m_i / \sum m_i \tag{3.22a}$$

One of the most important advances in polymer molecular weight determination is the "coupling" of SEC and light-scattering photometry, specifically LALLS or MALS. As noted in Sec. 3.5, SEC allows the determination of the MWD. It does not itself allow the calculation of an absolute molecular weight but relies on calibration with polymers of known molecular weight. By coupling HPLC and light scattering, the molecular weight of each fraction is determined, giving an MWD where the molecular weight distribution and various molecular weight (weight-average, number-average, Z-average) values can be calculated (since it can be assumed that the fractionated samples approach a single molecular weight so that the weight-average molecular weight is equal to the number-average molecular weight is equal to the Z-average molecular weight, etc.).

The LALLS or MALS detector measures τ-related values; a differential refractive index (DRI) detector is used to measure concentration; and the SEC supplies samples containing "fractionated" polymer solutions allowing both molecular weight and MWD to be determined. Further, polymer shape can be determined. This combination represents the most powerful, based on ease of operation, variety of samples readily used, and cost, means to determine polymer size, shape, and MWD available today.

A general assembly for a SEC-MALS instrument is given in Fig. 3.19. A typical three-dimensional plot obtained from such an assembly is shown as Fig. 3.20.

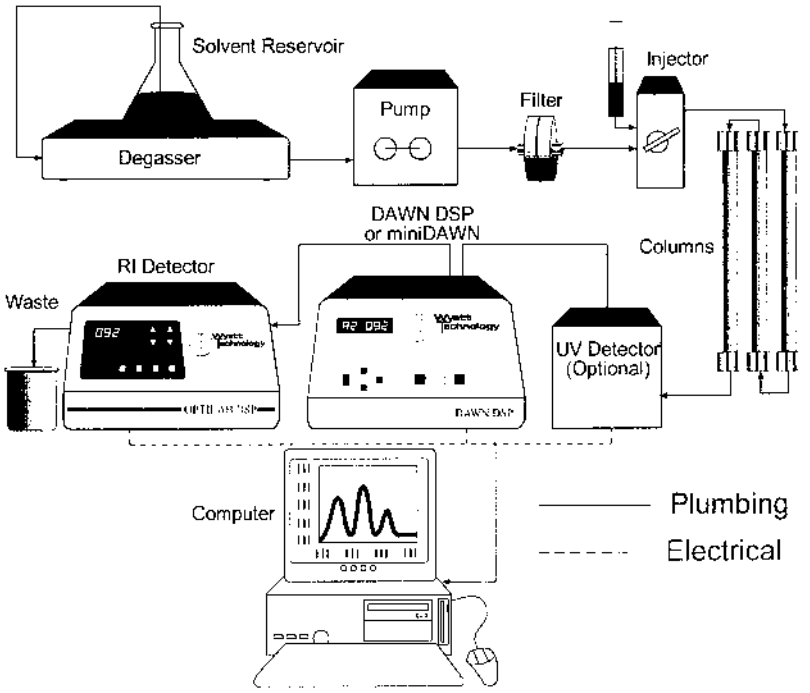


Figure 3.19 Typical SEC-MALS setup including refractive index refractometer. (Used with permission of Wyatt Technology Corporation.)

Dynamic light scattering is similar in principle to typical light scattering. When several particles are hit by oncoming laser light, a spotted pattern appears. The spots originate from the interference between the scattered light from each particle, giving a collection of dark (from destructive interference) and light (from constructive interference) spots. This pattern of spots varies with time because of the Brownian motion of the individual scattering particles. The rate of change in the pattern of spots is dependent on a number of features, including particle size. The larger the particle, the slower the Brownian motion and consequently the slower the change in the pattern. Measurement of these intensity fluctuations with time allows the calculation of the translational diffusion constant of the scattering particles. The technique for making these measurements is given several names, including: dynamic light scattering (DLS), emphasizing the fact that it is the difference in the scattered light with time that is being measured; photon correlation spectroscopy (PCS), with the name emphasizing the particular mathematical technique employed to analyze the light scattering data; and quasielastic light scattering (QELS), with the name emphasizing the fact that no energy is lost between the collision between the particle and the light photon.

In an experiment, the sample is exposed to light and the amount of light scattered, generally at 90°, is measured as a function of time intervals called *delay times*. The scattering function G(τ) can be described, for Brownian motion, to be

$$G(\tau) = 1 + e^{(-2Dq2\ \tau)} \tag{3.23}$$

Where q is the wave vector ($q = 4\pi\ n\ \sin(\theta/2)/\lambda$) that is dependent on the scattering

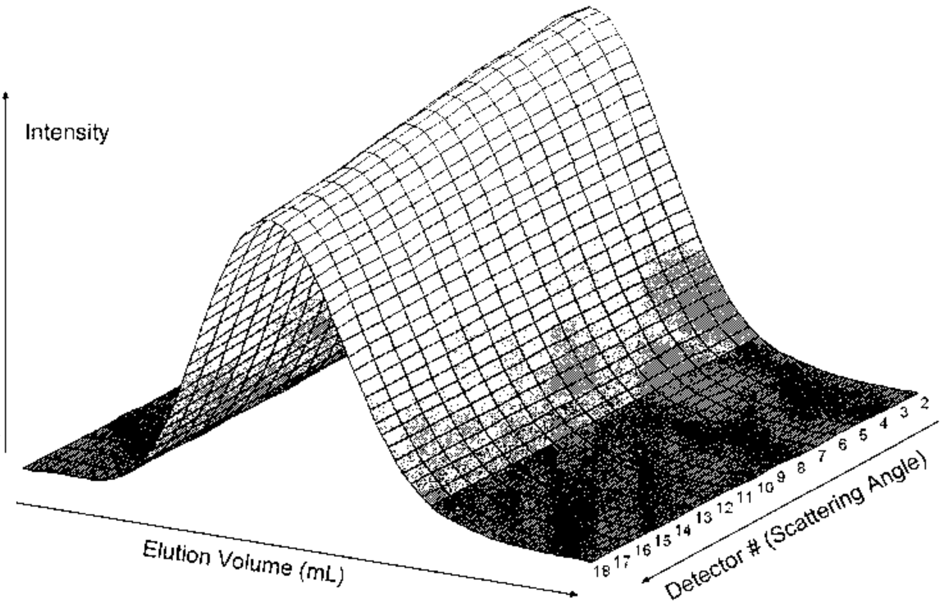


Figure 3.20 Three-dimensional plot of scattering intensity as a function of scattering angle and elution volume for a broad molecular weight distribution polystyrene (NITS standard reference 706). (Used with permission of Wyatt Technology Corporation.)

angle θ, the index of refraction of the solvent, n, and the wavelength of the scattered light, λ.

The diffusion constant, D, is given by the Stokes-Einstein relationship.

$$D = kT/6\pi\ \eta\ R \tag{3.24}$$

where k = Boltzmann constant, R is the (average) hydrodynamic radius, η is the solvent viscosity, and T is the Kelvin temperature.

The decay time is a measure of the time taken for a particle to move some distance, say 1/q, which gives an optical phase change of π radians at the detector. Because the decay time τ is related to the product of the wave vector squared and the translational diffusion coefficient as follows

$$\tau = 1/Dq^2 \tag{3.25}$$

the differences in size can be calculated using the Stokes-Einstein equation. One caution is that this is possible because of the assumption that the particle is a hard sphere and this assumption is not valid for many polymers. Even so, valuable information can be obtained through making appropriate adjustments in the results. Molecular weight and shape can also be estimated using this approach. Further, analysis of the correlation function can be combined with a Gaussian size distribution function and from this distribution of particle sizes. Also, changes in aggregation size, folding/unfolding, and conformation can also be monitored.

The effect of subtle particle changes as a function of temperature, sample preparation, time, solvent, and other changes can be measured using DLS. Such changes can then be related to performance variations eventually interrelating structure shape and biological/physical property.

Another variation that is useful employing coupled light scattering is referred to as a *triple detection set*. The set consists of three detectors—a light scattering detector, a differential refractometer detector, and a capillary differential viscometer. It functions in concert with a GPC and light scattering source. The GPC separates the polymer mixture into molecular weight fractions. According to the Einstein equation, the intrinsic viscosity times the molecular weight is equal to the hydrodynamic volume or size of polymers in solution. Thus, the molecular weight is determined using light scattering photometry, viscometry gives the intrinsic viscosity, and the equation is solved for size.

Generally, light scattering photometry has a limit to determining molecular size with the lower limit being about 10 nm. The addition of the viscometer allows molecular sizes to be determined for oligomeric materials to about 1 nm. The assembly allows an independent measure of size and molecular weight as well as additional conformational and aggregation information including small conformational changes. The assembly also allows good molecular determination to occur even when there are small dn/dc values, low molecular weight fractions, absorbing and fluorescent polymers, copolymers with varying dn/dc values, and chiral polymers that depolarize the incident beam.

Figure 3.21 contains data on myoglobin (see Fig. 15.5 for a representative structure of myoglobin) obtained using a triple detection setup. A molecular weight of 21,100 is found with a viscosity of 0.0247 dl/g and from this a hydrodynamic radius of 2.06 nm, which is essentially the same as the Stokes value of 2.0 nm reported for myoglobin.

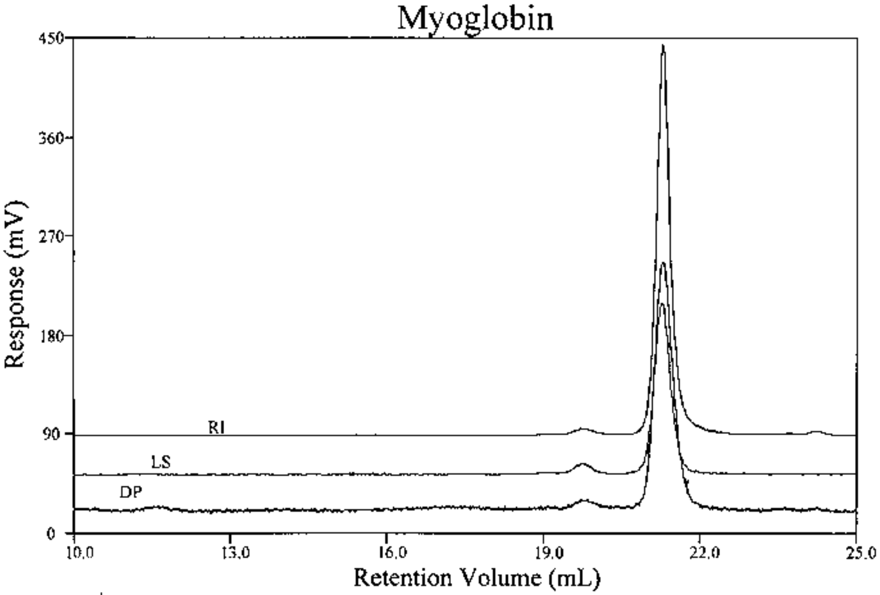


Figure 3.21 Response to selected detectors as a function of retention volume for myoglobin (dissolved in PBS buffer at a pH of 6.9). The three detectors are the RI, refractive index signal, LS, light scattering signal, and DP, differential pressure transducer (viscosity signal). (Used with permission of Viscotek, Houston, TX.)

3.11 ULTRACENTRIFUGATION

Since the kinetic energy of solvent molecules is much greater than the sedimentation force of gravity, polymer molecules remain suspended in solution. However, this traditional gravitation field, which permits Brownian motion, may be overcome by increasing this force by use of high centrifugal forces, such as the ultracentrifugal forces developed by Nobel Laureate The Svedberg in 1925.

Both $\overline{M}_w$ and $\overline{M}_z$ may be determined by subjecting dilute solutions of polymers in appropriate solvents to ultracentrifugal forces at high speeds. Solvents with densities and indices of refraction different from the polymers are chosen to ensure polymer motion and optical detection of this motion.

In the sedimentation velocity experiments, the ultracentrifuge is operated at extremely high speeds up to 70,000 rpm in order to transport the denser polymer molecules through the less dense solvent to the cell bottom or to the top if the density of the solvent is greater than the density of the polymer. The boundary movement during ultracentrifugation can be followed by using optical measurements to monitor the sharp change in index of refraction (n) between solvent and solution.

The rate of sedimentation is defined by the sedimentation constant s, which is directly proportional to the mass m, solution density ρ, and specific volume of the polymer $\overline{V}$, and inversely proportional to the square of the angular velocity of rotation ω, the distance from the center of rotation to the point of observation in the cell r, and the frictional coefficient f, which is inversely related to the diffusion coefficient D extrapolated to infinite dilution. These relationships are shown in the following equations in which $(1 - \overline{V}\rho)$ is called the buoyancy factor since it determines the direction of macromolecular transport in the cell.

$$s = \frac{1}{\omega^2 r}\frac{dr}{dt} = \frac{m(1 - \overline{V}\rho)}{f} \tag{3.26}$$

$$D = \frac{RT}{Nf} \text{ and } mN = M \tag{3.27}$$

$$\frac{D}{s} = \frac{RT}{\overline{M}_\omega(1 - \overline{V}\rho)} \tag{3.28}$$

The sedimentation velocity determination is dynamic and can be completed in a short period of time. It is particularly useful for monodisperse systems and provides qualitative data and some information on molecular weight distribution for polydisperse systems.

The sedimentation equilibrium method yields quantitative results, but long periods of time are required for centrifugation at relatively low velocities to establish equilibrium between sedimentation and diffusion.

As shown in the following equation, the weight-average molecular weight $\overline{M}_w$ is directly proportional to the temperature T and the In of the ratio of concentration c_2/c_1 at distances r_1 and r_2 from the center of rotation and the point of observation in the cell and inversely proportional to the buoyancy factor, the square of the angular velocity of rotation and the difference between the squares of the distances r_1 and r_2.

$$\overline{M} = \frac{2RT \text{ In } c_2/c_1}{(1 - \overline{V}\rho)\omega^2(r_2^2 - r_1^2)} \tag{3.29}$$

3.12 SMALL-ANGLE X-RAY SCATTERING

The theoretical basis for light-scattering photometry applies to all radiation. X-ray scattering or diffraction techniques are typically divided into two categories: wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS). Typically, SAXS gives information on a scale of 1 nm and smaller, while SAXS gives information on a scale of about 1–1000 nm. While both employ X-ray scattering, the instrumentation is generally very different. WAXS is employed to measure crystal structure and related parameters, including percentage crystallinity.

Atoms are of the order of 0.1 nm while an extended polyethylene (PE) chain (typically PE exists as a modified random coil in solution) with a molecular weight of 50,000 (and a degree of polymerization of about 1800) would have an end-to-end distance of about 150 nm, well within the range typically employed for SAXS. Thus, SAXS can be utilized to determine weight-average molecular weights because the scattering distance is dependent on the molecular size of the polymer.

3.13 MASS SPECTROMETRY

Certain mass spectral (MS) procedures allow the determination of the molecular weight or molecular mass of oligomeric to polymeric materials (Table 3.5). In matrix-assisted laser desorption/ionization (MALDI), the polymer is dissolved, along with a "matrix chemical," and the solution deposited onto a sample probe. The solution is dried. MALDI depends on the sample having a strong UV absorption at the wavelength of the laser used. This helps minimize fragmentation since it is the matrix UV-absorbing material that absorbs most of the laser energy. Often employed UV matrix materials are 2,5-dihydroxybenzoic acid, sinnapinic acid, picplinic acids, and cyano-4-hydroxycinnamic acid. The high energy of the laser allows both the matrix material and the test sample to be volatilized. Such techniques are referred to as "soft" since the test sample is not subjected to (much) ionizing radiation and hence little fragmentation occurs.

Mass accuracy on the order of a few parts per million are obtained. Thus, chain content can be determined for copolymers and other chains with unlike repeat units. Polymer molecular weight distributions can also be determined using MALDI and related MS techniques.

Recently, MS combinations have become available including the TG-MS combination developed by Carraher that allows the continuous characterization of evolved materials as a polymer undergoes controlled thermal degradation.

3.14 VISCOMETRY

Viscosity is a measure of the resistance to flow of a material, mixture, or solution. Here we will consider the viscosity of solutions containing small, generally 1 g/cc and less,

Table 3.5 Mass Spectrometry Approaches Used in Determination of Molecular Weights of Oligomeric and Polymeric Materials

MS type	(Typical) upper molecular weight range (Da)
(Usual) electron impact (EI)	To 2000
Fast atom bombardment (FAB)	To 2000
Direct laser desorption (direct LD)	To 10^4
Matrix-assisted laser desorption/ionization (MALDI)	To 10^6

amounts of polymer. The study of such dilute polymer solutions allows a determination of a "relative" molecular weight. The molecular weight is referred to as relative since viscosity measurements have not been directly related, through rigorous mathematical relationships, to a specific molecular weight. By comparison, measurements made using light-scattering photometry and "some of" the other methods covered before are relatable to specific molecular weight values and these techniques are said to give us "absolute" molecular weights.

In looking at the relationship between the force, f, necessary to move a plane of area A relative to another plane a distance d from the initial plane, it is found that the force is proportional to the area of the plane and inversely proportional to the distance, or

$$f \propto A/d \tag{3.30}$$

In order to make this a direct relationship, a *proportionality factor* is introduced. This factor is called the *coefficient of shear viscosity* or, simply, *viscosity*:

$$f = \eta(A/d) \tag{3.31}$$

Viscosity can be considered as a measure of the resistance of a material to flow. In fact, the inverse of viscosity is given the name *fluidicity*. As a material's resistance to flow increases, its viscosity increases.

Viscosities have been reported using a number of units. The CGS (centigrams, grams, seconds) unit of viscosity is called the poise, which is dyne seconds per square centimeter. Another widely employed unit is pascal (or Pas), which is Newton seconds per square centimeter. The relationship is 10 poise = 1 Pas.

Table 3.6 gives the (general) viscosity for some common materials. It is important to note the wide variety of viscosities of materials from gases such as air to viscoelastic solids such as glass.

In polymer science, we typically do not utilize direct measures of viscosity, but rather employ relative measures—measuring the flow rate of one material relative to that of a second material.

Viscometry is one of the most widely utilized methods for the characterization of polymer molecular weight since it provides the easiest and most rapid means of obtaining molecular weight–related data and requires minimal instrumentation. A most obvious

Table 3.6 Viscosities of Selected Common Materials

Substance	General viscosity (MPas)
Air	0.00001
Water	0.001
Polymer latexes/paints	0.01
PVC plastisols	0.1
Glycerol	10.0
Polymer resins and "pancake" syrups	100.0
Liquid polyurethanes	1,000.0
Polymer "melts"	10,000.0
Pitch	100,000,000.0
Glass	1,000,000,000,000,000,000,000.0

Table 3.7 Commonly Used Viscometry Terms

Common name	Recommended name (IUPAC)	Definition	Symbol
Relative viscosity	Viscosity ratio	η/η_0	$\eta_{rel} = \eta_r$
Specific viscosity	—	$(\eta/\eta_0) - 1$ or $(\eta - \eta_0)/\eta_0$	η_{sp}
Reduced viscosity	Viscosity number	η_{sp}/c	η_{red} or η_{sp}/c
Inherent viscosity	Logarithmic viscosity number	$\ln(\eta_r)/c$	η_{inh} or $\ln(\eta_r)/c$
Intrinsic viscosity	Limiting viscosity number	$\lim(\eta_{sp}/c)_{c\to 0}$ or $\lim(\ln \eta_r/c)_{c\to 0}$	$[\eta]$ or LVN

characteristic of polymer solutions is their high viscosity, even when the amount of added polymer is small.

The ratio of the viscosity of a polymer solution to that of the solvent is called relative viscosity (η_r). This value minus 1 is called the specific viscosity (η_{sp}), and the reduced viscosity (η_{red}), or viscosity number, is obtained by dividing η_{sp} by the concentration of the solution (c). The intrinsic viscosity, or limiting viscosity number, is obtained by extrapolating η_{red} to zero concentration. These relationships are given in Table 3.7, and a typical plot of η_{sp}/c and $\ln \eta_r/c$ as a function of concentration is given in Fig. 3.22.

Staudinger showed that the intrinsic viscosity of a solution ($[\eta]$), like the viscosity of a melt (η), was related to the average molecular weight of the polymer (M). The present form of this relationship is expressed by the Mark-Houwink equation [Eq. (3.32)], in which the proportionality constant K is characteristic of the polymer and solvent and the exponential a is a function of the shape of the polymer coil in a solution. In a θ solvent, the a value for the ideal statistical coil is 0.5. This value, which is actually a measure of the interaction of the solvent and polymer, increases as the coil expands in good solvents, and the value is between 1.8 and 2.0 for a rigid polymer chain extended to its full contour length and 0 for spheres. When a equals 1.0, the Mark-Houwink equation becomes the

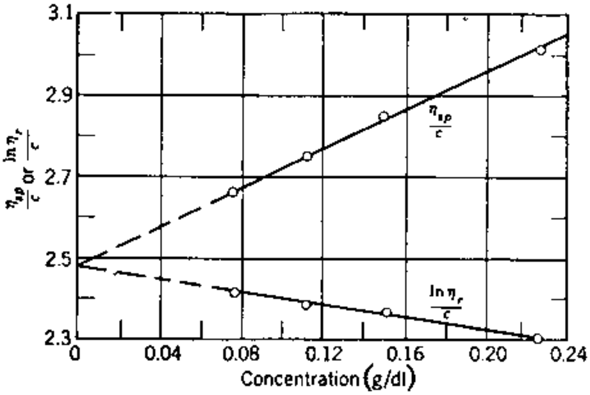


Figure 3.22 Reduced and inherent viscosity–concentration curves for a polystyrene in benzene. (From R. Ewart, in *Advances in Colloid Science*, Vol. II [H. Mark and G. Whitby, eds.]. Wiley Interscience, New York, 1946. With permission from the Interscience Division of John Wiley and Sons, Publishers.)

Table 3.8 Typical K Values for the Mark-Houwink Equation

Polymer	Solvent	Temp. (K)	$K \times 10^5$ dL g^{-1}
LDPE (low-density polyethylene)	Decalin	343	39
HDPE (high-density polyethylene)	Decalin	408	68
Polypropylene (isotactic)	Decalin	408	11
Polystyrene	Decalin	373	16
Poly(vinyl chloride)	Chlorobenzene	303	71
Poly(vinyl acetate)	Acetone	298	11
Poly(methyl acrylate)	Acetone	298	6
Polyacrylonitrile	Dimethylformamide	298	17
Poly(methyl methacrylate)	Acetone	298	10
Poly(ethylene terephthalate)	m-Cresol	298	1
Nylon-66	90% aqueous formic acid	298	110

Staudinger viscosity equation. However, the value of a is usually 0.5–0.8 in polymer solutions. K generally has values in the range of 10^{-2} to 10^{-4} ml/g. Sample values are given in Table 3.8. A more complete collection of K and a values can be found in the *Polymer Handbook* (Burrell, 1974).

Since the relative viscosity η_{rel} is a ratio of viscosities, it is dimensionless, as is the specific viscosity. However, since the value for reduced viscosity is obtained by dividing η_{sp} by the concentration, η_{red} is expressed in reciprocal concentration units, such as milliliters per gram. The intrinsic viscosity will have the same units.

$$[\eta] = K\overline{M}^a \tag{3.32}$$

Unlike most of the methods discussed in this chapter, viscometry does not yield absolute molecular weight values but rather is only a relative measure of a polymer's molecular weight. The reason may be stated in several ways. First, an exact theory of polymer solution viscosity as related to chain size is still in the formulation stage. Second, an expression, such as Eq. (3.32), cannot be directly used to relate (absolute) polymer viscosity and polymer molecular weight using only viscometry measurements since two additional unknowns, K and a, must be determined.

Thus, viscometry measurements must be correlated with an "absolute molecular weight method" such as light scattering. Taking the log of Eq. (3.32) yields Eq. (3.33).

$$\log[\eta] = a \log \overline{M} + \log K \tag{3.33}$$

This predicts a linear relationship between log $[\eta]$ and log $\overline{M}$ with a slope of a and intercept log K. Experimentally the viscosity is determined for several polymer samples varying only in molecular weight. Then the molecular weight of each sample is determined using an absolute method. A plot of log $[\eta]$ v. log $\overline{M}$ is constructed enabling the determination of a and K. Often K is determined by inserting a known $[\eta]$ and $\overline{M}$ value along with the calculated a value and solving for K. It is customery to distinguish the type of a and K value determined. For instance, if light scattering were employed to determine molecular weights, then the a and K values and subsequent $\overline{M}$ values are designated as weight-average values.

After calculation of a and K values for a given polymer–solvent pair, $\overline{M}$ can be easily calculated using a determined $[\eta]$ and Eq. (3.32).

Flory, Debye, and Kirkwood have shown that $[\eta]$ is directly proportional to the effective hydrodynamic volume of the polymer in solution and inversely proportional to the molecular weight (M). The effective hydrodynamic volume is the cube of the root-mean-square end-to-end distance $(\sqrt{\bar{r}^2})^3$. The proportionality constant (ϕ) in the Flory equation for hydrodynamic volume [Eq. (3.34)] has been considered to be a universal constant independent of solvent, polymer, temperature, and molecular weight.

$$[\eta] = \phi(\bar{r}^2)^{3/2}M^{-1} \tag{3.34}$$

The actual average end-to-end distance, $\bar{r}$, is related to the nonsolvent expanded average end-to-end distance, $\bar{r}_0$, using the Flory expansion factor, α, as follows:

$$\bar{r} = \bar{r}_0\alpha \tag{3.35}$$

Substitution of Eq. (3.35) into Eq. (3.34) and rearrangement gives

$$[\eta]M = \phi(\bar{r}_0^2)^{3/2}\alpha^2 \tag{3.36}$$

Values of α range from 1 for Flory θ solvents to about 3 for high polymers in good solvents.

In Eq. (3.32) it is found that for random coils, “a” ranges from 0.5 for θ solvents to 0.8 for good solvents, 0 for hard spheres, about 1 for semicoils, and 2 for rigid rods.

The θ temperature corresponds to the Boyle point in an imperfect gas and is the range in which the virial coefficient B in the expanded gas law becomes zero. This same concept applies to the modification of the gas law ($PV = nRT$) used to determine the osmotic pressure (π) of a polymer solution as shown below:

$$\pi = \frac{RT}{\overline{M}}C + BC^2 + \ldots \tag{3.37}$$

where R is the universal gas constant, T is the temperature in Kelvin, $\overline{M}$ is the number-average molecular weight, and C is the concentration of polymer in solution.

For linear chains at their θ temperature, i.e., the temperature at which the chain attains its unperturbed dimensions, the Flory equation resembles the Mark-Houwink equation in which α is equal to 1.0, as shown below:

$$[\eta] = KM^{1/2}\alpha^3 = KM^{1/2} \tag{3.38}$$

The intrinsic viscosity of a solution, like the melt viscosity, is temperature-dependent and will decrease as the temperature increases as shown by the following Arrhenius equation:

$$[\eta] = Ae^{E/RT} \tag{3.39}$$

However, if the original temperature is below the θ temperature, the viscosity will increase when the mixture of polymer and solvent is heated to a temperature slightly above the θ temperature.

Provided the temperature is held constant, the viscosity of a solution may be measured in any simple viscometer such as an Ubbelohde viscometer, a falling-ball viscometer, or a rotational viscometer, such as a Brookfield viscometer. It is customary to describe the viscosity of a solid plastic in terms of the melt index, which is the weight in grams of a polymer extruded through an orifice in a specified time.

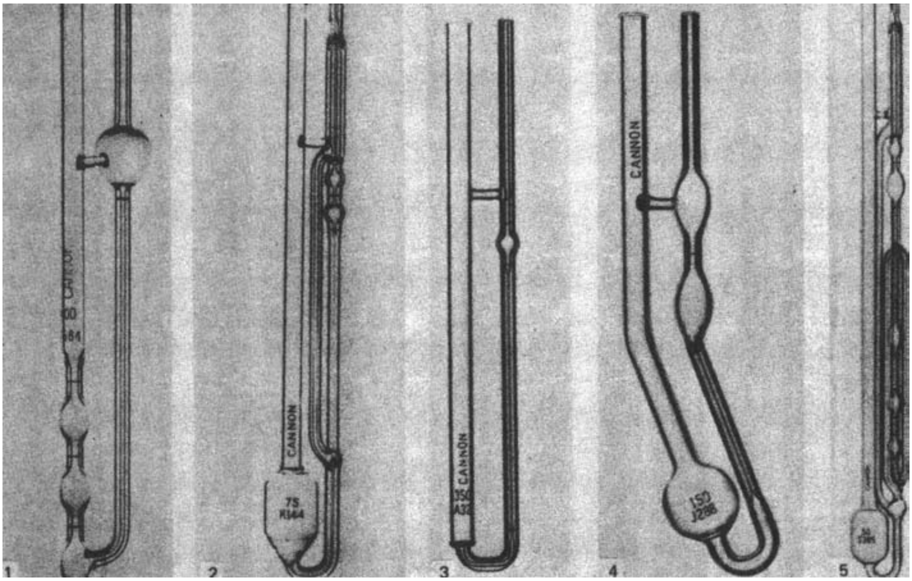


Figure 3.23 Common solution viscometers: (1) Cannon-Fenske Opaque, (2) Cannon-Ubbelohde Semi-Micro Dilution, (3) Cannon-Manning Semi-Micro, (4) Cannon-Fenske Routine, (5) Cannon-Ubbelohde Shear Dilution. (With permission Cannon Instrument Co.)

Viscosity measurements of polymer solutions are carried out using a viscometer, such as any of those pictured in Fig. 3.23 placed in a constant temperature bath with temperature controlled to ±0.1°C. The most commonly used viscometer is the Ubbelohde viscometer, which, because of the side arm, gives flow times independent of the volume of liquid in the reservoir bulb.

The following relationship exists for a given viscometer:

$$\frac{\eta}{\eta_o} = \frac{\rho t}{\rho_0 t_0} = \eta_r \tag{3.40}$$

where t and t_0 are the flow times for the polymer solution and solvent, respectively, and ρ is the density of the polymer solution.

Viscometry measurements are generally made on solutions that contain 0.01–0.001 g of polymer per milliliter of solution. For such dilute solutions, $\rho \simeq \rho_0$, giving

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} = \eta_r \tag{3.41}$$

Thus, η_r is simply a ratio of flow times for equal volumes of polymer solution and solvent. Reduced viscosity is related to $[\eta]$ by a virial equation as follows:

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2 c + k'[\eta]^3 c^2 + \ldots \tag{3.42}$$

For most systems, Eq. (3.42) reduces to the Huggins viscosity relationship:

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2 c \tag{3.43}$$

which allows $[\eta]$ to be determined from the intercept of a plot of η_{sp}/c vs. c and is the basis for the top plot given in Fig. 3.22.

Another relationship often used in determining $[\eta]$ is called the inherent viscosity equation and is as follows:

$$\frac{\text{In } \eta_r}{c} = [\eta] - k_2[\eta]^2 c \tag{3.44}$$

Again, in a plot of ln η_r/c vs. c, an extrapolation to c equals zero and allows the calculation of $[\eta]$. Plotting using Eq. (3.43) is more common than plotting using Eq. (3.44), even though the latter probably yields more precise values of η since k_1 is generally larger than k_2.

While k_1 and k_2 are mathematically related by

$$k_1 + k_2 = 0.5 \tag{3.45}$$

many systems appear not to follow this relationship.

Problem

Calculate the relative viscosity, specific viscosity, reduced viscosity, and inherent viscosity of a 0.5% (made by dissolving 0.25 g of polymer in 50 mL of solvent) solution where the time for solvent flow between the two appropriate marks was 60 s and the time of flow for the solution was 80 s. Using the relationship $t/t_0 = \eta/\eta_0 = \eta_r$, a value of η is calculated as follows: 80 s/60 s $= 1.3 = \eta_r$. The specific viscosity is determined employing any of the following three relationships.

$$\frac{\eta}{\eta_0} - 1 = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$$

Selecting the first one yields

$$\frac{\eta}{\eta_0} - 1 = \frac{t}{t_0} - 1 = \frac{80}{60} - 1 = 1.3 - 1 = 0.3$$

To determine the reduced viscosity, an appropriate concentration unit must be selected. The most widely employed concentrations in viscosity determinations are g/mL (g/cc) and g/dL or %. The units g/cc are recommended by IUPAC, while the units of % or g/dL are the most commonly used units. Since the problem gives the units in %, this unit will be employed.

Reduced viscosity is then calculated as follows:

$$\frac{\eta_{sp}}{c} = \frac{0.3}{0.5} = 0.06\%^{-1} \text{ or } 0.6\,\frac{\text{dL}}{\text{g}}$$

Problem

Determine the molecular weight of a polystyrene sample which has an a value of 0.60, a K value of 1.6×10^{-4} dL/g, and a limiting viscosity number or intrinsic viscosity of 0.04 dL/g. The molecular weight can be found by the relationship:

$$[\eta] = K\overline{M}^a$$

$$\log [\eta] = a \log M + \log K$$

$$\log M\ [= \log[\eta] - \log K]/a = [\log (0.04) - \log (1.6 \times 10^{-4}]/0.060 \simeq 4$$

$$\therefore M = 1 \times 10^4$$

We will now turn our attention from the viscosity of dilute solutions and look at the viscosity of melted polymers. The viscosity of melted polymers is important in transferring resins and in polymer processing, such as for determining the correct conditions to have a specific flow rate for injection processing and for determining the optimum conditions to get the necessary dimensions of extruded shapes. Fillers, plasticizers, temperature, solvents, and molecular weight are just some of the variables that influence the viscosity of polymer melts. Here we will look at the dependence of melt viscosity on polymer molecular weight. Polymer melts have viscosities on the order of 10,000 M Pas (1 centiposes is equal to 0.001 Pas/s).

For largely linear polymers, such as polystyrene, where particularly bulky side chains are not present the viscosity or flow is mainly dependent on the chain length. In most polymers, the melt viscosity–chain length relationship has two distinct regions. The region division occurs when the chain length reaches the *critical entanglement chain length*, Z, where intermolecular entanglement occurs. This intermolecular entanglement causes the individual chains in the melt to act as if they are much more massive because of the entanglement. Thus, the resistance to flow is a combination of the friction and entanglement between chains as they slide past one another. Below the critical entanglement length, where only the friction part is important, the melt viscosity, η, is related to the weight-average molecular weight by

$$\eta = K_1 M_w^{1.0} \tag{3.46}$$

And above the critical chain length, where both the friction and entanglement are important, the relationship is

$$\eta = K_h M_w^{3.4} \tag{3.47}$$

where K_1 is a constant for the pre-critical entanglement chain length and K_h is for the situation above Z and where both K values are temperature dependant. The first power dependence is due to the simple increase in molecular weight as chain length increases, but the 3.4 power relationship is due to a complex relationship between chain movement as related to entanglement and diffusion and chain length.

The critical chain length is often the onset of “strength” related properties and is often considered the lower end for useful mechanical properties. The Z-value for polymers vary but are generally between about 200 to 1000 units in length. For instance, the Z-value for polystyrene is about 700, for polyisobutylene about 600, for poly(decamethylene sebacate) about 300, for poly(methyl methacrylate) about 200, and for poly(dimethyl siloxane) about 1000.

A number of techniques have been developed to measure melt viscosity. Some of these are listed in Table 3.9. Rotational viscometers are of varied structures. The Couette

Table 3.9 Viscosity Measuring Techniques and Their Usual Range

Technique	Typical range, poise
Capillary pipette	0.01–1000
Falling sphere	1–100,000
Parallel plate	$10{,}000–10^9$
Falling coaxial cylinder	$100{,}000–10^{11}$
Stress relaxation	$1000–10^{10}$
Rotating cylinder	$1–10^{12}$
Tensile creep	100,000—greater than 10^{12}

cup-and-bob viscometer consists of a stationary inner cylinder, the bob, and an outer cylinder, cup, that is rotated. Shear stress is measured in terms of the required torque needed to achieve a fixed rotation rate for a specific radius differential between the radius of the bob and cup. The Brookfield viscometer is a bob-and-cup viscometer. The Mooney viscometer, often used in the rubber industry, measures the torque needed to revolve a rotor at a specified rate. In cone and plate assembly, the melt is sheared between a flat plat and a broad cone whose apex contacts the plate containing the melt.

A number of capillary viscometers or rheometers have been employed to measure melt viscosity. In some sense, these operate on a principle similar to the simple observation of a trapped bubble moving from the bottom of a shampoo bottle when it is turned upside down. The more viscous the shampoo, the longer it takes for the bubble to move through the shampoo.

SUMMARY

1. Some naturally occurring polymers such as proteins consist of molecules with a specific molecular weight and are called monodisperse. However, cellulose, natural rubber, and most synthetic polymers consist of molecules with different molecular weights and are called polydisperse. Many properties of polymers are dependent on their molecular weight above that required for entanglement. Since the melt viscosity increases exponentially with molecular weight, the high energy costs of processing high molecular weight polymers are not usually justified.
2. The distribution of molecular weights in a polydisperse system may be represented on a typical probability curve. The number-average molecular weight $\overline{M}_r$, which is smallest in magnitude, and a simple arithmetic mean may be determined by techniques based on colligative properties, such as osmotic pressure, boiling point increase, and freezing point depression. The weight-average molecular weight ($\overline{M}_w$), which is larger than $\overline{M}_n$ for polydisperse systems, is the second-power average. This value may be determined by light scattering which, like techniques based on colligative properties, yields absolute values for molecular weights.
3. Since $\overline{M}_w = \overline{M}_n$ for a monodisperse system, the polydispersity index $\overline{M}_w/\overline{M}_n$ is a measure of polydispersity. The most probable value for this index for polymers synthesized by condensation techniques is 2.0. The viscosity average $\overline{M}_v$ which is not an absolute value, is usually between $\overline{M}_n$ and $\overline{M}_w$, but when the exponent a in the Mark-Houwink equation is equal to 1, $\overline{M}_w = \overline{M}_v$.
4. Various molecular weight distributions may be obtained by special analytical techniques—centrifugation, gel permeation chromatography, and solvent fractionation. In the last technique one adds a small amount of nonsolvent to precipitate the highest molecular weight polymer from solution. In (GPC) smaller crosslinked polymers in a column act as a sieve and allow the larger molecules to elute first. After calibration, the molecular weight of the eluted polymer is determined automatically by measuring the difference in index of refraction of the solution and solvent.
5. The use of boiling point increase and freezing point lowering is limited to the determination of the molecular weights of relatively small polymers. However, since the osmotic pressure of a 1 M solution is large (1 atm), osmometry is

readily used for characterizing large molecules. The possibility of oligomers and other small polymers passing through the semipermeable membrane is avoided by use of vapor pressure osmometry for characterization of polymers having molecular weights less than 40,000. This technique utilizes the difference in temperatures noted during the evaporation of a solvent from a solution and the pure solvent.

6. Absolute molecular weight values reported as weight-average molecular weights are obtained by light scattering techniques. $\overline{M}_w$ values for nonpolar polymers with molecular weights less than 100,000 are determined by extrapolating the plot of the product of the ratio of the concentration and the turbidity and a constant H vs. concentration, the intercept is $\overline{M}_w^{-1}$.
7. Since the gravitational force present in the ultracentrifuge is sufficient to precipitate polymer molecules in accordance with their size, ultracentrifugation is used as a technique for the determination of molecular weight, especially for monodisperse systems such as proteins.
8. A polymer dissolves by a swelling process followed by a dispersion process or disintegration of the swollen particles. This process may occur if there is a decrease in free energy. Since the second step in the solution process involves an increase in entropy, it is essential that the change in enthalpy be negligible or negative to assure a negative value for the change in free energy.
9. Flory and Huggins developed an interaction parameter (χ_1) that may be used as a measure of the solvent power of solvents for amorphous polymers. Flory and Krigbaum introduced the term θ temperature at which a polymer of infinite molecular weight exists as a statistical coil in a solvent.
10. Hildebrand used solubility parameters which are the square root of CED to predict the solubility of nonpolar polymers in nonpolar solvents. This concept is also applicable to mixtures of solvents. For polar solvents it is also necessary to consider dipole–dipole interactions and hydrogen bonding in predicting solubility.
11. The molecular weight of a polymer is proportional to the intrinsic viscosity of its solution ($[\eta]$) when the polymer chain is extended to its full contour length. The value $[\eta]$, or limiting viscosity number, is proportional to the square root of the molecular weight M when the polymer is in a θ solvent. In general, $[\eta] = K\,\overline{M}^a$ where a, which is a measure of the shape of the polymer chain, is usually 0.5–0.8. The constant K is dependent on the polymer and solvent studied.
12. The intrinsic viscosity is the limiting reduced viscosity (η_{red}) at zero concentration. The reduced viscosity of viscosity number is equal to the specific viscosity (η_{sp}) divided by concentration. The value η_{sp} is obtained by subtracting 1 from the relative viscosity (η_r), which is the ratio of the viscosities of the solution and the solvent. Plasticizers are nonvolatile good solvents that reduce the CED and T_g of a polymer.

GLOSSARY

a: Exponent in Mark-Houwink equation, usually 0.6–0.8.

affinity chromatography: Chromatography in which the resin is designed to contains moieties that interact with the particular molecules being studied.

B: second virial constant.
a_T: Constant in the WLF equation related to holes or free volume of a polymer.
a_T: Shift factor relative to a reference temperature.
alpha (α): The linear expansion ratio of a polymer molecule in a Flory θ solvent.
aniline point: A measure of the aromaticity of a solvent.
Arrhenius equation for viscosity: $\eta = Ae^{E/RT}$.
Bingham, E. C. The father of rheology.
Bingham equation:

$$s - s_0 = \eta \frac{d\gamma}{dt}$$

Bingham plastic: A plastic that does not flow until the external stress exceeds a critical threshold value (S_0).
Brownian motion: movement or large particles in a liquid as a result of bombardment by smaller molecules. This phenomenon was named after the botanist Robert Brown, who observed it in 1827.
buoyancy factor: $(1 - \overline{V}\rho)$ or 1 − the specific volume × density of a polymer. This term, used in ultracentrifugal experiments, determines the direction of polymer transport under the effect of centrifugal forces in the cell.
CED: Cohesive energy density.
chi (χ): Flory-Huggins interaction parameter.
chromatography: Separation technique based on use of a medium that shows selective absorption.
Clausius-Clapeyron equation: For small changes in pressure, the unintegrated expression $dT/dp = RT^2/Lp$ may be used where L is the molar heat of vaporization. The form used for molecular weight determination is as follows:

$$\overline{M}_n = \frac{RT^2V}{\Delta H}\left(\frac{C}{\Delta T}\right)_{c \to 0}$$

colligative properties: Properties of a solution that are dependent on the number of solute molecules present and are usually related to the effect of these molecules on vapor pressure lowering.
cloud point: The temperature at which a polymer starts to precipitate when the temperature is lowered.
cohesive energy density (CED): The heat of vaporization per unit volume $\Delta E(V^{-1})$.
commercial polymer range: A molecular weight range high enough to have good physical properties but not too high for economical processing.
critical molecular weight: The threshold value of molecular weight required for chain entanglement.
cryometry: Measurement of $\overline{M}_n$ from freezing point depression.
d: The width of the baseline of idealized peaks in a gel permeation chromatogram.
delta (δ): Symbol for solubility parameter.
e: Symbol for base of Napierian logarithms ($e = 2.718$).
E: Energy of activation.
ebulliometry: Measurement of $\overline{M}_n$ from boiling point elevation of a solution.
effective hydrodynamic volume $[(\sqrt{\bar{r}^2})^3]$: The cube of the root-mean-square end-to-end distance of a polymer chain.

electrophoresis: A form of chromatography that uses an electric field to separate molecules.
end group analysis: The determination of molecular weight by counting of end groups.
end groups: The functional groups at chain ends such as the carboxyl groups (COOH) in polyesters.
eta (η) Symbol for viscosity.
f: Symbol for frictional coefficient in ultracentrifugal experiments.
Flory-Huggins theory A theory used to predict the equilibrium behavior between liquid phases containing an amorphous polymer.
fractional precipitation: Fractionation of polydisperse systems by adding small amounts of a nonsolvent to a solution of the polymer and separating the precipitate.
fractionation of polymers: Separation of a polydisperse polymer into fractions of similar molecular weights.
gel permeation chromatography: A type of liquid-solid elution chromatography which automatically separates solutions of polydisperse polymers into fractions by means of the sieving action of a swollen crosslinked polymeric gel. Also called size exclusion chromatography.
Gibbs equation: The relationship between free energy (ΔG), enthalpy (ΔH), and entropy (ΔS); $\Delta G = \Delta H - T\,\Delta S$ at constant T.
GPC: Gel permeation chromatography.
H: Symbol for enthalpy or heat content and for Hildebrand units.
H: Symbol for the proportionality constant in a light-scattering equation.
HETP: Height equivalent to a theoretical plate (in feet).
high-performance liquid chromatography (HPLC): Chromatography in which pressure is applied that causes the solution to pass more rapidly through the column.
Hildebrand (H): Unit used in place of $(\text{cal cm}^{-3})^{0.5}$ for solubility parameter values.
ion exchange chromatography: Chromatography that separates molecules on the basis of their electrical charge; employs polyanionic or polycationic resins.
isothermal distillation: Same as vapor pressure osmometry.
K: Symbol for Kelvin or absolute temperature scale.
Kauri-Butanol values: A measure of the aromaticity of a solvent.
lambda (λ): Symbol for the wavelength of light.
In: Symbol for natural or naperian logarithm.
log: Common logarithm based on the number 10.
low-angle laser light-scattering photometry, (LALLS): Light scattering that employs low-angle measurements minimizing the effect of polymer shape on the scattering.
M: Symbol for molecular weight.
$\overline{M}$: Symbol for average molecular weight.
Mark-Houwink equation: $[\eta] = K\,\overline{M}^a$, where a is 0.5 for a statistical coil in a θ solvent and 2.0 for a rigid rod.
matrix-assisted laser desorption/ionization mass spectrometry (MALDI): Mass spectrometry in which the sample, containing a strong UV absorber chosen to match the UV absorption to the wavelength of the laser, is exposed to the laser radiation; this combination allows the molecule to be volatilized with little fragmentation.
melt index: A measure of flow related inversely to melt viscosity, the time for 10 g of a polymer, such as a polyolefin, to pass through a standard orifice at a specified time and temperature.
$\overline{M}_n$: Number-average molecular weight.
monodisperse: A system consisting of molecules of one molecular weight only.

$\overline{M}_w$: Weight-average molecular weight.

$\overline{M}_z$: z-Average molecular weight.

multiangle low-angle laser light-scattering photometry (MALS): Similar to LALLS except where the necessary angle ratios are made together; employs low-angle measurements minimizing the effect of polymer shape on the scattered light.

MWD: Molecular weight distribution.

n: Index of refraction.

N: Symbol for Avogadro's number, 6.23×10^{23}.

number-average molecular weight: The arithmetical mean value obtained by dividing the sum of the molecular weights by the number of molecules.

oligomer: Very low molecular weight polymer usually with DP less than 10 (the Greek *oligos* means "few").

omega (ω): Symbol for the angular velocity of rotation.

osmometry: The determination of molecular weight $\overline{M}_n$ from measurement of osmotic pressure.

osmotic pressure: The pressure a solute would exert in solution if it were an ideal gas at the same volume.

P: Symbol for plate count in GPC.

phi (ϕ): Proportionality constant in Flory equation $= 2.5 \times 10^{23}$ mol^{-1}.

pi (π): Symbol for osmotic pressure.

plate count (P): The reciprocal of HETP.

polydisperse: A mixture containing polymer molecules of different molecular weights polydispersity index: $\overline{M}_w/\overline{M}_n$.

polypeptides: A term used to describe oligomers of proteins, which of course are also polypeptides or polyamino acids.

Raoult's law: The vapor pressure of a solvent in equilibrium with a solution is equal to the product of the mole fraction of the solvent and the vapor pressure of the pure solvent at any specified temperature. Osmotic pressure, boiling point elevation, and freezing point depression are related to this decrease in vapor pressure.

rho (ρ): Symbol for density.

SEC-MALS and SEC-LALLS: Coupled chromatography and light-scattering photometry that allows the direct determination of molecular weight and molecular weight distribution along with other important values.

sedimentation equilibrium experiment: An ultracentrifugal technique that provides quantitative information on molecular weights. Long times are required for the attainment of equilibrium in this method.

sedimentation velocity experiment: A dynamic experiment with the ultracentrifuge which provides qualitative information on molecular weight in a short period of time.

semipermeable membranes: Those membranes that will permit the diffusion of solvent molecules but not large molecules such as polymers.

size exclusion chromatography (SEC): Chromatography in which separation is by molecular size or differences in hydrodynamic volume; also called gel permeation chromatography (GPC); can use the universal calibration approach to obtain molecular weight.

solubility parameter (δ): A numerical value equal to $\sqrt{\text{CED}}$ which can be used to predict solubility.

tau (τ): Symbol for turbidity.

theta (θ): Symbol for the angle of the incident beam in light scattering experiments.

theta (θ) solvent: A solvent in which the polymer exists as a statistical coil and where the second virial constant B equals zero at the θ temperature.

theta temperature: The temperature at which a polymer of infinite molecular weight starts to precipitate from a solution.

turbidimetric titration: A technique in which a poor solvent is added slowly to a solution of a polymer and the point of incipient turbidity is observed.

ultracentrifuge: A centrifuge which by increasing the force of gravity by as much as 100,000 times causes solutes to settle from solutions in accordance with their molecular weights.

$\overline{V}$: Symbol for specific volume.

V: Hydrodynamic volume in GPC; V: Symbol for molar volume.

V_e: Elution volume in GPC.

velocity gradient: $d\gamma/dt$, γ, or flow rate.

van't Hoff's law: Osmotic pressure

$$\pi = \frac{C}{M}\frac{RT}{V} = \frac{RTC}{M}.$$

vapor pressure osmometry: A technique for determining the molecular weight of relatively small polymeric molecules by measuring the relative heats of evaporation of a solvent from a solution and pure solvent.

viscosity: Resistance to flow.

viscosity, intrinsic $[\eta]$: The limiting viscosity number obtained by extrapolation of the reduced viscosity to zero concentration.

viscosity, reduced: The specific viscosity divided by the concentration.

viscosity, relative: The ratio of the viscosities of a solution and its solvent.

viscosity, specific: The difference between the relative viscosity and 1.

weight-average molecular weight: The second-power average of molecular weights in a polydisperse polymer.

z-average molecular weight: The third-power average of molecular weights in a polydisperse polymer.

Zimm plot: A type of double extrapolation used to determine $\overline{M}_w$ in light scattering experiments Both the concentration of the solution and the angle of the incident beam of light are extrapolated to zero on one plot.

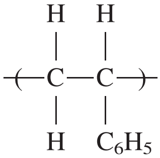
zone melting: The fractionation of polydisperse systems by heating over long periods of time.

EXERCISES

1. Which of the following is polydisperse: (a) casein, (b) commercial polystyrene, (c) paraffin wax, (d) cellulose or (e) *Hevea brasiliensis*?
2. If $\overline{M}_n$ for LDPE is 1.4 million, what is the value of $\overline{DP}$?
3. What are the $\overline{M}_n$ and $\overline{M}_w$ values for a mixture of five molecules each having the following molecular weights: 1.25×10^6, 1.35×10^6, 1.50×10^6, 1.75×10^6, 2.00×10^6?
4. What is the most probable value for the polydispersity index for (a) a monodisperse polymer and (b) a polydisperse polymer synthesized by condensation techniques?
5. List in order of increasing values: $\overline{M}_z$, $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_w$.

6. Which of the following provides an absolute measure of the molecular weight of polymers: (a) viscometry, (b) cryometry, (c) osmometry, (d) light scattering, (e) GPC?
7. What is the relationship between the intrinsic viscosity or limiting viscosity number $[\eta]$ and average molecular weight $\overline{M}$?
8. What molecular weight determination techniques can be used to fractionate polydisperse polymers?
9. Which of the following techniques yields a number-average molecular weight, $\overline{M}_n$: (a) viscometry, (b) light scattering, (c) ultracentrifugation, (d) osmometry, (e) ebulliometry, (f) cryometry?
10. What is the relationship of HETP and plate count per foot in GPC?
11. What is the value of the exponent a in the Mark-Houwink equation for polymers in θ solvents?
12. How many amino groups are present in each molecule of nylon-66 made with an excess of hexamethylenediamine?
13. What is the value of the exponent a in the Mark-Houwink equation for a rigid rod?
14. If the value of K and a in the Mark-Houwink equation are 1×10^{-2} cm^3 g^{-1} and 0.5, respectively, what is the average molecular weight of a polymer whose solution has an intrinsic viscosity of 150 cc/g?
15. Which polymer of ethylene will have the highest molecular weight: (a) a trimer, (b) an oligomer, or (c) UHMWPE?
16. What is a Zimm plot?
17. What type of molecular weight average, $\overline{M}_w$ or $\overline{M}_n$, is based on colligative properties?
18. What principle is used in the determination of molecular weight by vapor pressure osmometry?
19. What does the melt viscosity increase faster with molecular weight increase than other properties such as tensile strength?
20. In spite of the high costs of processing, ultrahigh molecular weight polyethylene is used for making trash cans and other durable goods. Why?
21. Under what conditions are $\overline{M}_n$ and $\overline{M}_w$ equal for a polydisperse system?
22. What nonsolvent would you use to fractionate a polydisperse polymer in a solution?
23. Which colligative property technique would you use to determine the molecular weight of a polymer having a molecular weight of (a) 40,000, (b) 80,000?
24. What is the advantage of vapor pressure osmometry when measuring relatively low molecular weight polymers?
25. Which will yield the higher apparent molecular weight values in the light scattering method: (a) a dust-free system or (b) one in which dust particles are present?
26. Which is the more rapid ultracentrifugation technique for the determination of molecular weight of polymers: (a) sedimentation velocity method or (b) sedimentation equilibrium method?
27. Which ultracentrifugation technique is more accurate: (a) sedimentation velocity or (b) sedimentation equilibrium method?
28. What is the significance of the virial constant B in osmometry and light scattering equations?
29. According to Hildebrand, what is a regular solvent?
30. Which of the two steps that occur in the solution process, (a) swelling and (b) dispersion of the polymer particles, can be accelerated by agitation?
31. Define CED.

32. For solution to occur ΔG must be. (a) 0, (b) <0, or (c) >0.
33. Will a polymer swollen by a solvent have higher or lower entropy than the solid polymer?
34. Define the change in entropy in the Gibbs free energy equation.
35. Is a liquid that has a value of 0.3 for its interaction parameter (χ_i) a good or a poor solvent?
36. What is the value of ΔG at the θ temperature?
37. What term is used to describe the temperature at which a polymer of infinite molecular weight precipitates from a dilute solution?
38. At which temperature will the polymer coil be larger in a poor solvent: (a) at the θ temperature, (b) above the θ temperature, or (c) below the θ temperature?
39. If δ for water is equal to 23.4 H, what is the CED for water?
40. What is the heat of mixing of two solvents having identical δ values?
41. If the density (D) is 0.85 g/cc and the molar volume (V) is 1,176,470 cc, what is the molecular weight?
42. Use Small's molar attraction constants to calculate δ for polystyrene.



$$-\!\!\left(\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}-\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{C_6H_5}\end{array}\right)\!\!-$$

43. Calculate M for a polymer having a δ value of 10 H and a T_g value of 325K (M = chain stiffness).
44. Why do δ values decrease as the molecular weight increases in a homologous series of aliphatic polar solvents?
45. Which would be the better solvent for polystyrene: (a) n-pentane, (b) benzene, or (c) acetonitrile?
46. Which will have the higher slope when its reduced viscosity or viscosity number is plotted against concentration: a solution of polystyrene (a) in benzene or (b) in noctane?
47. What is the value of the virial constant B in Eq. (3.32) at the θ temperature?
48. When is the Flory equation [Eq. (3.31)] similar to the Mark-Houwink equation?
49. What is the term used for the cube root of the hydrodynamic volume?
50. Explain why the viscosity of a polymer solution decreases as the temperature increases.
51. Which sample of LDPE has the higher average molecular weight: (a) one with a melt index of 10 or (b) one with a melt index of 8?

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4

Testing and Spectrometric Characterization of Polymers

Public acceptance of polymers is usually associated with an assurance of quality based on a knowledge of successful long-term and reliable tests. In contrast, much of the dissatisfaction with synthetic polymers is related to failures that might have been prevented by proper testing, design, and quality control. The American Society for Testing and Materials (ASTM), through its committees D-1 on paint and D-20 on plastics, has developed many standard tests, which may be referred to by all producers and consumers of polymeric materials. There are also cooperating groups in many other technical societies: the American National Standards Institute (ANSI), the International Standards Organization (ISO), and standards societies such as the British Standards Institution (BSI) in England, Deutsche Normenausschuss (DNA) in Germany, and comparable groups in every nation with developed polymer technology throughout the entire world.

Testing is done by industry to satisfy product specifications and for public protection using standardized tests for stress–strain relationships, flex life, tensile strength, etc. In the United States tests are overseen by the ASTM through a committee arrangement. For instance, Committee D-1 oversees tests related to coatings while Committee D-20 oversees tests on plastic. New tests are continuously being developed, submitted to the appropriate ASTM committee, and after adequate verification through "round-robin" testing, finally accepted by concensus, as standard tests. These tests are published by the ASTM. Each ASTM test is specified by a unique combination of letters and numbers, along with exacting specifications regarding data gathering, instrument design, and test conditions making it possible for laboratories throughout the world to reproduce the test and hopefully the test results if requested to do so. The Izod test, a common impact test, has the ASTM number D-256-56 (1961). The latter number, 1961, is the year the test was first accepted. The ASTM publication gives instructions for the Izod test specifying test material shape and size, exact specifications for the test equipment, detailed description of the test procedure, and how results should be reported. Most tests developed by one testing society have analogous tests or more often utilize the same tests so that they may have both ASTM, ISO, and other standardized society identification symbols.

A number of physical tests emphasizing stress–strain behavior will be covered in Chapter 5. Here we will concentrate on other areas of testing, emphasizing thermal and electrical properties, and on the characterization of polymers by spectral means. Spectroscopic characterization generally concentrates on the structural identification of materials. Most of these techniques, and those given in Chapter 5, can be directly applied to nonpolymeric materials such as small organic molecules, inorganic compounds, and metals.

The testing of materials can be based on whether the tested material is chemically changed or is left unchanged. Nondestructive tests are those that result in no chemical change in the material. Nondestructive tests include many electrical property determinations, infrared and ultraviolet spectroanalysis, simple melting point determinations, density and color determinations, and most mechanical property determinations.

Destructive tests are those where there is a change in the chemical structure of at least a portion of the tested material. Examples include flammability property determination and chemical resistance tests where the test material is not resistant to the tested material.

What constitutes destructive and nondestructive tests may differ depending on the test, material, and definition. Thus, mechanical properties of solid polymers and viscosity test results of polymer melts may vary depending on the past history of the polymer. Prior stirring or chain orientation will influence most subsequent mechanical and viscosity test results for polymeric materials but will have little effect on the test results for small molecules. If destruction includes changes in polymer property, then melt viscosity and mechanical tests that influence chain location will be included in destructive testing for polymers, whereas if only chemical change is implied in destructive tests, then such tests will normally fall within nondestructive tests.

4.1 ELECTRIC PROPERTIES: THEORY

Some important dielectric properties are dielectric loss, loss factor, dielectric constant (or specific inductive capacity), direct current (DC) conductivity, alternating current (AC) conductivity, and electric breakdown strength. The term "dielectric behavior" usually refers to the variation of these properties within materials as a function of frequency, composition, voltage, pressure, and temperature.

The dielectric behavior of materials is often studied by employing charging or polarization currents. Since polarization currents depend on the applied voltage and the dimensions of the condenser, it is customary to eliminate this dependence by dividing the charge Q by the voltage V to obtain a parameter C, called the capacitance (capacity):

$$C = \frac{Q}{V} \tag{4.1}$$

and then using the dielectrical constant ϵ, which is defined as

$$\epsilon = \frac{C}{C_0} \tag{4.2}$$

where C is the capacity of the condenser when the dielectric material is placed between its plates in a vacuum and C_0 is the empty condenser capacity.

Dielectric polarization is the polarized condition in a dielectric resulting from an applied AC or DC field. The polarizability is the electric dipole moment per unit volume induced by an applied field or unit effective intensity. The molar polarizability is a measure of the polarizability per molar volume; thus it is related to the polarizability of the individual molecules or polymer repeat unit.

Conductivity is a measure of the number of ions per unit volume and their average velocity in the direction of a unit applied field. Polarizability is a measure of the number of bound charged particles per cubic unit and their average displacement in the direction of the applied field.

There are two types of charging currents and condenser charges, which may be described as rapidly forming or instantaneous polarizations, and slowly forming or absorptive polarizations. The total polarizability of the dielectric is the sum of contributions due to several types of displacement of charge produced in the material by the applied field. The relaxation time is the time required for polarization to form or disappear. The magnitude of the polarizability, k, of a dielectric is related to the dielectric constant ϵ as follows:

$$k = \frac{3(\epsilon - 1)}{4\pi(\epsilon + 2)} \tag{4.3}$$

The terms "polarizability constant" and "dielectric constant" have been used interchangeably in the qualitative discussion of the magnitude of the dielectric constant. The k values obtained utilizing DC and low-frequency measurements are a summation of electronic (E), atomic (A), dipole (P), and interracial (I) polarizations as shown in Fig. 4.1. Only the contribution by electronic polarizations is evident at high frequencies. The contributions to dielectric constant at low frequencies for a material having interfacial, dipole, atomic, and electronic polarization contributions are additive.

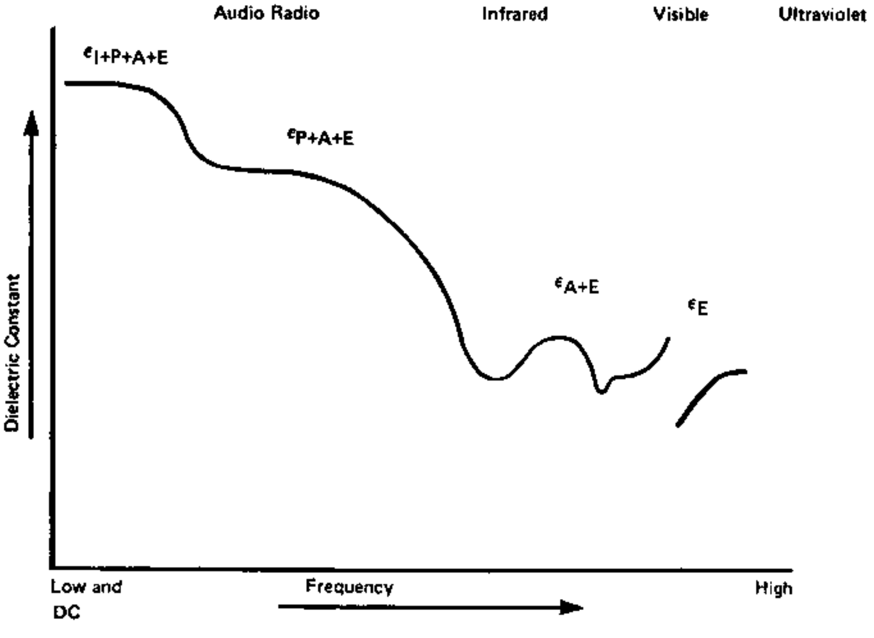


Figure 4.1 Relationship of dielectric constant with frequency emphasizing interfacial (I), dipole (P), atomic (A), and electronic (E) polarization contributions.

Instantaneous polarization occurs when rapid (less than 10^{-10}s) transitions take place, i.e., at frequencies greater than 10^{10} Hz or at wavelengths less than 1 cm. Electronic polarization falls within this category and is due to the displacement of charges within the atoms. Electronic polarization is directly proportional to the number of bound electrons in a unit volume and inversely proportional to the forces binding these electrons to the nuclei of the atoms.

Electronic polarization occurs so rapidly that there is no observable effect of time or frequency on the dielectric constant until frequencies are reached that correspond to the visible and UV spectra. For convenience, the frequency range of the infrared through the UV region is called the optical frequency range, and the radio and the audio range is called the electric frequency range.

Electronic polarization is an additive property dependent on the atomic bonds. Thus the electronic polarizations and related properties per unit volume are similar for both small molecules and polymers.

Accordingly, values obtained for small molecules can be appropriately applied to analogous polymeric materials. This does not apply in cases where the polymeric nature of the material plays an additional role in the conductance of electric charges, as is the case for whole chain resonance electric conductance.

Atomic polarization is attributed to the relative motion of atoms in the molecule effected by perturbation by the applied field of the vibrations of atoms and ions having a characteristic resonance frequency in the infrared region. The atomic polarization is large in inorganic materials which contain low-energy-conductive bonds and approaches zero for nonpolar organic polymers.

The atomic polarization is rapid, and this as well as the electronic polarizations constitutes the instantaneous polarization components. The remaining types of polarization are absorptive types with characteristic relaxation times corresponding to relaxation frequencies.

In 1912, Debye suggested that the high dielectric constants of water, ethanol, and other highly polar molecules are due to the presence of permanent dipoles within each individual molecule. There is a tendency for the molecules to align themselves with their dipole axes in the direction of the applied electric field.

The major contributions to dipole polarizations are additive and are similar whether the moiety is within a small or a large (polymeric) molecule. Even so, the secondary contributions to the overall dipole polarization of a sample are dependent on both the chemical and the physical environment of the specific dipole unit and on the size and the mobility of that unit. Thus dipole contributions can be utilized to measure glass transition temperature (T_g) and melting point (T_m).

These polarizations are the major types found in homogeneous materials. Other types of polarization, called *interfacial polarizations*, are the result of heterogeneity. Ceramics, polymers containing additives, and paper are considered to be electrically heterogeneous.

Table 4.1 contains often used electrical units.

4.2 ELECTRIC MEASUREMENTS

Material response is typically studied by utilizing either direct (constant) applied voltage (DC) or alternating applied voltage (AC). The AC response as a function of frequency is characteristic of the material. In the future these “electric spectra” may be utilized as a product identification tool, much like infrared spectroscopy. Factors such as current

Table 4.1 Selected Electrical Primary and Derived Units

Electrical value	Symbol	SI units: Primary	SI units: Derived
Capacitance	C	s^2-C^2/kg-m^2	Farad
Conductivity	σ	s-C^2/kg-m^3	1/Ohm-meter
Dielectric constant	ϵ, ϵ_r	Simple ratio with no units	
Dielectric displacement	D	C/m^2	Farad-volt/m^2
Electric charge	Q	C	Coulomb
Electrical current	I	C/s	Ampere
Electric polarization	P	C/m^2	Farad-volt/m^2
Electric potential	V	kg-m^2/s^2-C	Volt
Permittivity	ϵ	s^2C^2/kg-m^3	Farad/meter
Resistance	R	kg-m^2/s-C^2	Ohm
Resistivity	ρ	kg-m^3/s-C^2	Ohm-meter

strength, duration of measurements, specimen shape, temperature, and applied pressure typically affect the electric responses of materials.

The electric properties of a material vary with the frequency of the applied current. The response of a polymer to an applied current may be delayed because of a number of factors including the interaction between polymer chains, the presence within the chain of specific molecular groupings, and effects related to interactions in the specific atoms themselves. A number of parameters, such as relaxation time, power loss, dissipation factor, and power factor, are employed as measures of this lag.

The movement of dipoles (related to the dipole polarization, P) within a polymer can be divided into two types: an orientation polarization (P′) and a dislocating or induced polarization.

The relaxation time required for the charge movement of electronic polarization E to reach equilibrium is extremely short ($\simeq 10^{-15}$s), and this type of polarization is related to the square of the index of refraction, n^2. The relaxation time for atomic polarization A is about 10^{-3}s. The relaxation time for induced orientation polarization P′ is dependent on molecular structure and is temperature-dependent.

The electric properties of polymers are related to their mechanical behavior. The dielectric constant and dielectric loss factor are analogous to the elastic compliance and mechanical loss factor. Electric resistivity is analogous to viscosity.

Polar polymers, such as ionomers, possess permanent dipole moments. Polar molecules are capable of storing more electric energy than nonpolar polymers. Nonpolar polymers are dependent almost entirely on induced dipoles for electric energy storage. Thus, orientation polarization is produced in addition to the induced polarization, when the polar polymers are placed in an electric field.

The induced dipole moment of a polymer in an electric field is proportional to the strength of the field, and the proportionality constant is related to the polarizability of the atoms in the polymer. The dielectric properties of polymers are affected adversely by the presence of moisture, and this effect is greater in hydrophilic than in hydrophobic polymers.

As shown by the Clausius-Mossotti equation,

$$P = \left(\frac{\epsilon - 1}{\epsilon + 2}\right)\frac{M}{\rho} \qquad (4.4)$$

the polarization P of a polymer in an electric field is related to the dielectric constant ϵ, the molecular weight M, and the density ρ.

At low frequencies, the dipole moments of polymers are able to keep in phase with changes in a strong electric field, and the power losses are low. However, as the frequency is increased, the dipole moment orientation may not occur rapidly enough to maintain the dipole in phase with the electric field.

Dielectric Constant

As noted before, the dielectric constant (ASTM D-150–74) is the ratio of the capacity of a condenser made with or containing the test material to the capacity of the same condenser with air as the dielectric. Materials to be employed as insulators in electrical applications should have low dielectric constants, whereas those to be employed as conductors or semiconductors should exhibit high dielectric constants.

The dielectric constant is independent of the frequency at low to moderate frequencies but is dependent on the frequency at high frequencies. The dielectric constant is approximately equal to the square of the index of refraction and to one-third the solubility parameter.

Electrical Resistance

There are a number of electrical properties related to electrical resistance (ASTM D-257). These include insulation resistance, volume resistivity, surface resistivity, volume resistance, and surface resistance.

The bulk (or volume)—specific resistance is one of the most useful electrical properties. Specific resistance is a physical quantity that may differ by more than 10^{23} in readily available materials. This unusually wide range of conductivity is basic to the wide use of electricity and many electrical devices. Conductive materials, such as copper, have specific resistance values of about 10^{-6} ohm cm, whereas good insulators, such as polytetrafluoroethylene (PTFE) and low-density polyethylene (LDPE), have values of about 10^{17} ohm cm.

Specific resistance is calculated from Eq. (4.5), in which R is the resistance in ohms, a is the pellet area in cm^2, t is the pellet thickness in cm, and p is the specific resistance in ohm cm.

$$p = R(a/t) \qquad (4.5)$$

Dissipation Factor and Power Factor

The dissipation factor (ASTM D-150) can be defined in several ways, including the following:

1. Ratio of the real (in phase) power to the reactive (90° out of phase) power
2. Measure of the conversion of the reactive power to real power or heat
3. Tangent of the loss angle and the cotangent of the phase angle
4. Ratio of the conductance of a capacitor (in which the material is the dielectric) to its susceptibility

Both the dielectric constant and dissipation factor are measured by comparison or substitution in a classical electric bridge.

The power factor is the energy required for the rotation of the dipoles of a polymer in an applied electrostatic field of increasing frequency. These values, which typically range from 1.5×10^4 for polystyrene to 5×10^{-2} for plasticized cellulose acetate, increase at T_g because of increased chain mobility. The loss factor is the product of the power factor and the dielectric constant, and is a measure of the total electric loss in a dielectric material.

Arc Resistance

The are resistance is a measure of the resistance of a material to the action of an arc of high voltage and low current close to the surface of the sample to form a conducting path on this surface. Arc resistance values are of use in surface quality control since small surface changes will affect the arc resistance value.

Dielectric Strength

No steady current flows in a perfect insulator in a static electric field, but energy is “stored” in the sample as a result of dielectric polarization. Thus the insulator acts as a device to store energy. In actuality, some leakage of current does occur even for the best insulators.

The insulating property of materials breaks down in strong fields. This breakdown strength, called the electric or dielectric strength (DS), i.e., the voltage required for failure, is inversely related to the thickness L of the material as shown in Eq. (5.15).

$$\mathrm{DS} \alpha \mathrm{L}^{-0.4} \tag{4.6a}$$

Breakdown may occur below the measured DS as a result of an accumulation of energy through inexact dissipation of the current; this leads to an increase in temperature and thermal breakdown. Breakdown means sudden passage of excessive current through the material, which often results in visible damage to the specimen.

The DS is high for many insulating polymers and may be as high as 10^3 MV/m. The upper limit of the DS of a material is dependent on the ionization energy present in the material. Electric or intrinsic decomposition (breakdown) occurs when electrons are removed from their associated nuclei; this causes secondary ionization and accelerated breakdown. The DS is reduced by mechanical loading of the specimen and by increasing the temperature.

Typically dielectric strength (ASTM D-149) is an indication of the electrical strength of an insulating material. DS is dependent on test conditions.

For conductive polymers, and other materials, conductivity is defined by Ohm’s law that says

$$\mathrm{U} = \mathrm{R\,I} \tag{4.6b}$$

where I is the current in amperes through a resistor, U is the drop in potential in volts, and the relationship between I and U is called the resistance generally measured in ohms. Resistance, R, is measured by applying a known voltage across the material and measuring the current that passes though it. The reciprocal of resistance (1/R) is called conductance. Ohm’s law is an empirical law related in irreversible thermodynamics to the flow of the current, I, as a result of a potential gradient that leads to energy being dissipated (RI^2-Joule/second). (Not all materials obey Ohms law.) Gas discharges, semiconductors, and vacuum tubes are what are called one-dimensional conductors and generally deviate from Ohm's law.

For materials that obey Ohm's law, the resistance is proportional to the length, L, of a sample and inversely proportional to the material cross section, A.

$$R = \rho L/A \tag{4.6c}$$

where ρ is the resistivity measured in ohm-meters.

The inverse of ρ is called conductivity and is generally given in Siemens, S (S = 1/ohms). The unit of conductivity is S/meters. A graph of conductivity for many materials is given in Sec. 18.1.

Conductivity depends on a number of factors including the number density of charge carriers (number of electrons, n) and how rapidly they can move in the sample called mobility μ.

$$\text{Conductivity} = n\mu e \tag{4.6d}$$

where e is the electron charge.

Conductivity also varies with temperature generally decreasing for "metallic" materials such as silver and copper but increasing as temperature is increased for semiconductive materials such as insulator, semiconductive, and conductive polymers (Sec. 18.1).

4.3 WEATHERABILITY

Polymers are used in almost every conceivable environment. They are tested for their interactions with radiation, weather, and microorganisms. Weathering includes the ability to resist attacks by freezing and heating cycles, resistance to frictional damage caused by rain and air, and influence of high and low temperatures as the polymeric material is used.

Outdoor exposure of polymer samples, mounted at a 45° angle and facing south (in the Northern Hemisphere), has been used to measure the resistance of polymers to outdoor weathering (ASTM D-1345). Since these tests are expensive and time consuming, tests such as ASTM G-S23 have been developed in an attempt to gain "accelerated" test results. Tests related to the accelerated exposure to light are described in ASTM-625 and 645.

There are several accelerated tests that differ in the selection of light source and cyclic exposure to varying degrees of humidity. Some accelerated tests include salt spray, heat, cold, and other weather factors. The environmental stress cracking (ESCR) test described in Fig. 5.19 can also give a measure of weatherability.

Moisture is an important factor for some polymers, especially condensation polymers where hydrolysis, and subsequent degradation, can bring about drastic changes in chain length. Such attack can occur on the surface and is indicated, as can many chemical attacks, by a discoloration generally followed by crazing and cracking. Other attack can occur within the matrix with the polymer absorbing moisture. Absorbing of large amounts of water can be measured by weighing a dried sample, exposing it to moisture under specified conditions, and reweighing. As expected, largely nonpolar polymers such as polyethylene have low water absorption whereas more polar polymers such as polycarbonates, nylons, and polysaccharides have relatively greater moisture retention.

Resistance to biological attack is important for many polymer applications including almost all of the biomedical applications, food storage and protection, and coatings where microorganism destruction is important. Most synthetic polymers are resistant to destruction by microorganisms. This is particularly true for nonpolar polymers, but less so for condensation polymers such as nylons and polyesters. Various preservatives and antimicroorganism additives are added, when appropriate, to protect the material against these microorganisms. Tests include destructive degradation and simple growth of the microorganism on the material.

4.4 OPTICAL PROPERTY TESTS

Since polymers are often used as clear plastics or coatings and have many applications in which transparency is an important property, a knowledge of the optical properties of specific polymers is essential. The radiation scale, of course, includes microwave, infrared, ultraviolet, and visible regions.

It is important to recognize the difference between refraction (associated with properties such as refractive index) and reflection (associated with properties such as haze). This difference is illustrated in Fig. 4.2.

Index of Refraction

Optical properties are related to both the degree of crystallinity and the actual polymer structure. Most polymers are transparent and colorless, but some, such as phenolic resins and polyacetylenes, are colored, translucent, or opaque. Polymers that are transparent to visible light may be colored by the addition of colorants, and some become opaque as the result of the presence of additives such as fillers, stabilizers, flame retardants, moisture, and gases.

Many of the optical properties of a polymer are related to the refractive index n, which is a measure of the ability of the polymer to refract or bend light as it passess through the polymer. The refractive index n is equal to the ratio of the sine of the angles of incidence, i, and refraction, r, of light passing through the polymer:

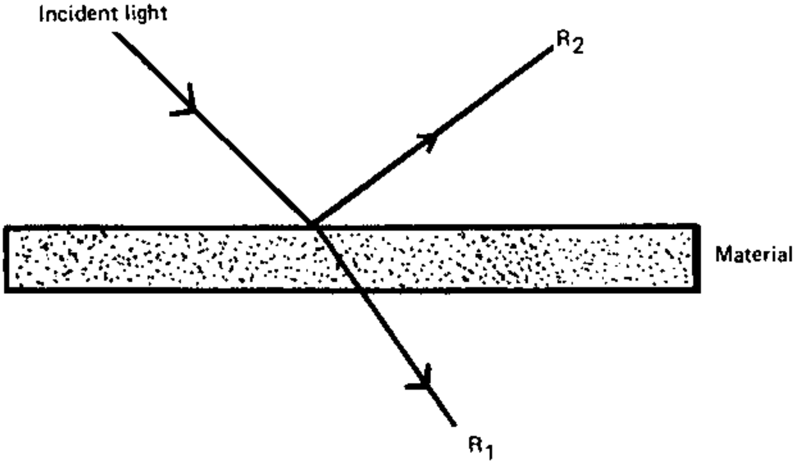


Figure 4.2 Refraction and reflection of incident light at the surface of a solid. The path of refracted light is indicated by R_1 and that of reflected light by R_2.

$$n = \frac{\sin i}{\sin r} \tag{4.7}$$

The magnitude of n is related to the density of the substance and varies from 1.000 and 1.333 for air and water, respectively, to about 1.5 for many polymers and 2.5 for the white pigment titanium dioxide. The value of n is often high for crystals and is dependent on the wavelength of the incident light and on the temperature; it is usually reported for the wavelength of the transparent sodium D line at 298 K. Typical refractive indices for polymers range from 1.35 for polytetrafluoroethylene to 1.67 for polyarylsulfone.

The velocity of light passing through a polymer is affected by the polarity of the bonds in the molecule. Polarizability P is related to the molecular weight per unit volume, M, and density ρ as follows (the Lorenz-Lorenz relationship):

$$P = \left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{M}{\rho} \tag{4.8}$$

The polarizability P of a polymer is related to the number of molecules present per unit volume, and the polarizability of each molecule is related to the number and mobility of the electrons present in the molecule. The P value of carbon is much greater than that of hydrogen, and the value of the latter is usually ignored in calculating the polarizability of organic polymers.

Heterogeneity of n values is related to a number of factors, including end groups, differences in density between amorphous and crystalline regions, anisotropic behavior of crystalline portions, incorporation of additives, and the presence of voids.

The index of refraction of transparent plastics may be determined by placing a drop of a specified liquid on the surface of the polymer before measuring the index with a refractometer. An optical microscope is used to measure the index of refraction in an alternative method (ASTM D-542).

Optical Clarity

Optical clarity or the fraction of illumination transmitted through a material is related by the Beer-Lambert relationship:

$$\log\frac{I}{I_0} = -AL \qquad \text{and} \qquad \frac{I}{I_0} = e^{-AL} \tag{4.9}$$

where the fraction of illumination transmitted through a polymer, I/I_0, is dependent on the path length of the light, L, and the absorptivity of the polymer at that wavelength of light, A [see Eq. (4.9)].

Clarity is typical for light passing through a homogeneous material, such as a crystalline ordered polymer or a completely amorphous polymer. Interference occurs when the light beam passes through a heterogeneous material in which the polarizability of the individual units varies, such as a polymer containing both crystalline and amorphous regions.

Absorption and Reflectance

Colorless materials range from almost totally transparent to opaque. The opacity is related to the light scattering process occurring within the material.

Incident radiation passes through nonabsorbing, isotropic, and optically homogeneous samples with essentially little loss of radiation intensity. Actually, all materials scatter some light. The angular distribution of the scattered light is complex because of the scattering due to micromolecular differences in values.

Transparency is defined as the state permitting perception of objects through a sample. Transmission is the light transmitted. In more specific terms; transparency is the amount of undeviated light, i.e., the original intensity minus all light absorbed, scattered, or lost through any other means.

The ratio of reflected light to the incidental light is called the reflectance coefficient, and the ratio of the scattered light to the incident light is called the absorption coefficient. The attenuation coefficient is the term associated with the amount of light lost. The transmission factor is the ratio of the amount of transmitted light to the amount of incident light. The transmission factor for weakly scattering colorless materials decreases exponentially with the sample thickness 1 and the scattering coefficient S as follows:

$$\text{In (transmission factor)} = -S1 \tag{4.10}$$

Light scattering reduces the contrast between light, dark, and other colored parts of objects viewed through the material and produces a milkiness or haze in the transmitted image. Haze is a measure of the amount of light deviating from the direction of transmittancy of the light by at least 2.5°.

The visual appearance and optical properties of a material depend on its color and additives, as well as on the nature of its surface. Gloss is a term employed to describe the surface character of a material responsible for luster or shine, i.e., surface reflection.

A perfect mirror-like surface reflects all incident light, and this represents one extreme. At the other extreme is a highly scattering surface that reflects light equally in all directions at all angles of incidence. The direct reflection factor is the ratio of the light reflected at the specular angle to the incident light for angles of incidence from 0 to 90°.

Total reflectance is observed at angle θ (Brewster's angle), which is related to the ratio of the n values of the polymer, n_1, and air, n_2.

$$\tan B = \frac{n_1}{n_2} \tag{4.11}$$

Absorption of light or loss of intensity I of light passing through a path of distance 1 may be calculated from the Lambert relationship

$$I = I_0 e^{-4\pi Nkl/\lambda} \tag{4.12}$$

where k is the absorption index, λ is the wavelength of the light, I_0 is the original intensity, and N is Avogadro's number.

Luminous reflectance, transmittance, and color can be obtained experimentally as follows. Samples are generally prepared as films, sheets, or molded specimens that have parallel plane surfaces. The sample is mounted as noted in Fig. 4.3 along with a comparison surface, typically white chalk. The sample and comparison surface are exposed to light of varying wavelength. Reflected or transmitted light is then measured. The precise requirements are described in ASTM E-308.

A Hardy-type spectrophotometer may also be used for determining luminous reflectance, transmittance, and color of polymers (ASTM 791). The transmittance of plastic films is measured by ASTM D-1746.

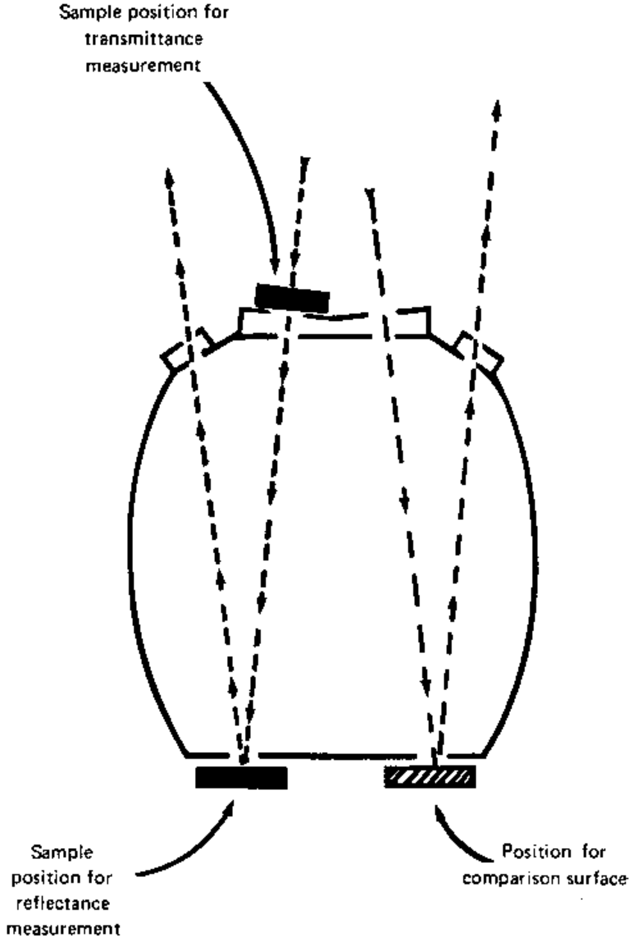


Figure 4.3 Instrument for measuring reflectance and transmittance.

4.5 CHEMICAL RESISTANCE

A fuller discussion of the chemical reactions that polymers undergo is given in Chapter 15.

The classic test for chemical resistance (ASTM D-543) measures the percentage weight change (PWC) of test samples after immersion in many different liquid systems. Tests for chemical resistance have been extended to include changes in mechanical properties of the polymer test sample after immersion. Although there is no single standard test of changes in mechanical properties of the samples, changes in the following have been investigated: hardness, tensile strength, stress relaxation, stress rupture, impact strength, compressive strength, flexural strength, and flexural modulus. Since chemical attack involves changes in chemical structure, it can be readily observed by many instrumental methods that measure chemical structure.

Other related ASTM tests include those under accelerated service conditions [ASTM D-756–78 (1971)], water absorption [ASTM D-570–63 (1972)], and ESCR of ethylene plastics (ASTM D-1693–70).

Table 4.2 Stability of Various Polymers to Various Conditions[a]

Polymer	Nonoxidizing acid, 20% sulfuric	Oxidizing acid, 10% nitric	Aqueous salt sol., NaCl	Aqueous base, NaOH	Polar liquids, ethanol	Nonpolar liquids, Benzene	Water
Nylon 6,6	U	U	S	S	M	S	S
Polytetrafluoroethylene	S	S	S	S	S	S	S
Polycarbonate	M	U	S	M	S	U	S
Polyester	M	M	S	M	M	U	S
Polyetheretherketone	S	S	S	S	S	S	S
LDPE	S	M	S	—	S	M	S
HDPE	S	S	S	—	S	S	S
Poly(phenylene oxide)	S	M	S	S	S	U	S
Polypropylene	S	M	S	S	S	M	S
Polystyrene	S	M	S	S	S	U	S
Polyurethane	M	U	S	M	U	M	S
Epoxy	S	U	S	S	S	S	S
Silicone	M	U	S	S	S	M	S

[a] S = satisfactory, M = moderately to poor, U = unsatisfactory.

Tables 4.2 and 4.3 contain a summary of typical stability values for a number of polymers and elastomers against typical chemical agents. As expected, condensation polymers generally exhibit good stability to nonpolar liquids while they are generally only (relatively) moderately or unstable toward polar agents and acids and bases. This is because of the polarity of the connective “condensation” linkages within the polymer backbone. By comparison, vinyl type of polymers exhibit moderate to good stability toward both polar and nonpolar liquids and acids and bases. This is because the carbon–carbon backbone is not particularly susceptible to attack by polar agents, and nonpolar liquids, at best, will simply solubilize the polymer. All of the materials show good stability to water alone because all of the polymers have sufficient hydrophobic character to repeal the water.

4.6 SPECTRONIC CHARACTERIZATION OF POLYMERS

Index of Refraction

The index of refraction (n), which is the ratio of the velocity of light in a vacuum to the velocity of light in a transparent medium, e.g., polymer, is characteristic for each polymer.

Table 4.3 Stability to Various Elemental Conditions of Selected Elastomeric Materials[a]

Polymers	Weather, sunlight aging	Oxidation	Ozone cracking	NaOH, Dil/Con	Acid, Dil/Con	Degreasers, chlorinated, hydrocarbons	Aliphatic hydrocarbons
Butadiene	P	G	B	F/F	F/F	P	P
Neoprene	G	G	G	G/G	G/G	P	F
Nitrile	P	G	F	G/G	G/G	G	G
Polyisoprene (natural)	P	G	B	G/F	G/F	B	B
Polyisoprene (synthetic)	B	G	B	F/F	F/F	B	B
Styrene-butadiene	P	G	B	F/F	F/F	B	B
Silicone	G	G	G	G/G	G/F	B	F–P

[a] G = good, F = fair, P = poor, B = bad.

This value, which is also a function of molecular weight, may be determined by use of an Abbe refractometer [ASTM D-542–50 (1970)].

Differences in indices of refraction may be measured by phase-contrast microscopy, and the structure of spherulites may be studied using crossed polarizers in a polarized light microscope. Melting points may be determined when the latter is equipped with a hot stage. Thickness may be measured in nanometers using interference microscopy.

Infrared Spectroscopy

The infrared (IR) range spans the region bound by the red end of the visible region to the microwave region at the lower frequencies. Molecular interactions that involve vibrational modes correspond to this energy region. Infrared spectroscopy is one of the most common spectronic techniques used today to identify polymer structure. Briefly, when the frequency of incident radiation of a specific vibration is equal to the frequency of a specific molecular vibration the molecule absorbs the radiation. Today most IR machines are rapid scan where the spectra are Fourier-transformed.

Most monomers and polymers may be identified by IR spectroscopy in which the energy, in the wavelength range 1–50 nm, is associated with molecular vibration and vibration–rotation spectra of polymer molecules. These motions are comparable to those of small molecules of similar structure (model compounds).

For example, as shown in Fig. 4.4, the IR spectrum of polystyrene is sufficiently characteristic that it is used as a standard for checking instrumental operation. The repeating unit in polystyrene (C_8H_8) has 16 atoms, and since it has no symmetry, all vibrations are active, i.e., 3° each of rotational and translational freedom and 42° of vibrational freedom (3n−6).

The bands in the range of 8.7–9.7 μm are characteristic wavelengths, but not identified as to origin, and are said to be in the “fingerprint” region. Typical C—H stretching vibrations are at 3.8, 3.4, and 3.g μm, and out-of-plane bending of aromatic C—H bonds occurs at 11.0 and 14.3 μm. Characteristic C—C stretching vibrations are at 6.2 and 6.7 μm. Characteristic bands for other typical groups in polymers are shown in Table 4.4.. Following are brief discussions of some of the more important techniques used in polymer analysis.

Attenuated Total Reflectance IR

ATR-IR is used to study films, coatings, threads, powders, interfaces, and solutions. (It also serves as the basis of much of the communications systems based on fiberoptics).

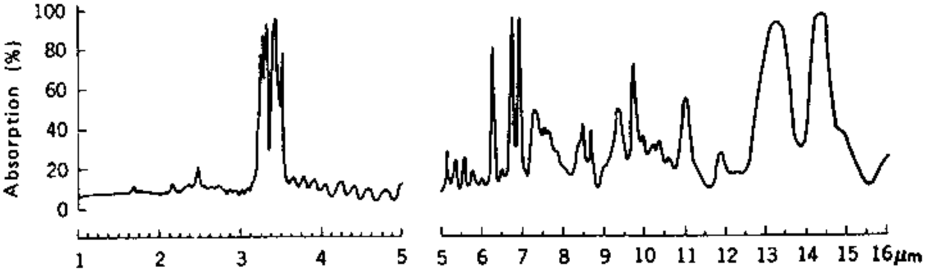


Figure 4.4 Infrared spectrum of a polystyrene film. (From *Introduction to Polymer Chemistry* by R. Seymour. McGraw-Hill, New York, 1971. Used with permission.)

Table 4.4 Absorption Bands for Typical Groups in Polymers

Group	Type of vibration	Wavelength (λ, μm)	Wave number (V, cm^{-1})
CH_2	Stretch	3.38–3.51	2850–2960
	Bend	6.82	1465
	Rock	13.00–13.80	725–890
CH_3	Stretch	3.38–3.48	2860–2870
	Bend	6.9	1450
H R	C — H stretch	3.25–3.30	3030–3085
| |	C — H bend in plane	7.10–7.68	1300–1410
C=C	C — H bend out of plane	10.10–11.00	910–990
| |	C — C stretch	6.08	1643
H=H	C — H stretch	3.24	3080
H R	C — H bend in plane	7.10	1410
| |	C — H bend out of plane	11.27	888
C=C	C — C stretch	6.06	1650
| |			
H R			
Benzene	C — H bend out of plane	14.50	690
OH	Stretch	2.7–3.2	3150–3700
SH	Stretch	3.9	2550
Aliphatic acid	C=O stretch	5.85	1710
Aromatic acid	C=O stretch	5.92	1690
CCI	Stretch	12–16	620–830
CN	Stretch	4.8	2200

ATR occurs when radiation enters from a more dense (i.e., a material with a higher refractive index) into a material that is less dense (i.e., with a lower refractive index). The fraction of the incident radiation reflected increases when the angle of incidence increases. The incident radiation is reflected at the interface when the angle of incidence is greater than the critical angle. The radiation penetrates a short depth into the interface before complete reflection occurs. This penetration is called the *evanescent wave*. Its intensity is reduced by the sample where the sample absorbs.

Specular Reflectance IR

Specular reflectance IR involves a mirror-like reflection producing measurements of a reflective material or a reflection–absorption spectrum of a film on a reflective surface. This technique is used to look at thin (from nanometers to micrometers thick) films.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

DRIFTS is used to obtain spectra of powders and rough polymeric surfaces such as textiles and paper. IR radiation is focused onto the surface of the sample in a cup resulting in both specular reflectance (which directly reflects off the surface having equal angles of incidence and reflectance) and diffuse reflectance (which penetrates into the sample subsequently scattering in all angles). Special mirrors allow the specular reflectance to be minimized.

Photoacoustic Spectroscopy IR

Photoacoustic Spectroscopy IR (PAS) is used for highly absorbing materials. Generally, modulated IR radiation is focused onto a sample in a cup inside a chamber containing an IR-transparent gas such as nitrogen or helium. The IR radiation absorbed by the sample is converted to heat inside the sample. The heat travels to the sample surface and then into the surrounding gas causing expansion of the boundary layer of gas next to the sample surface. The modulated IR radiation thus produces intermittent thermal expansion of the boundary layer creating pressure waves that are detected as photoacoustic signals.

The PAS spectra are similar to those obtained using ordinary Fourier transform infrared (FTIR) except truncation of strong absorption bands because of photoacoustic signal saturation often occurs. PAS allows the structure to be studied at different thicknesses because the slower the frequency of modulation, the deeper the penetration of IR radiation.

Emission Infrared Spectroscopy

Emission infrared spectroscopy is used for thin films and opaque polymers. The sample is heated so that energy is emitted. The sample acts as the radiation source and the emitted radiation is recorded giving spectra similar to those of classical FTIR. In some cases, IR frequencies vary because of differences in the structures at different depths and interactions between surface and interior emissions.

Infrared Microscopy

IR microscopy allows the characterization of minute amounts of a material or trace contaminants or additives. Samples as small as 10 μm can be studied. The microscope, often using fiberoptics, allows IR radiation to be pinpointed.

Today there are many so-called hyphenated methods with IR acting to illustrate this. Hyphenated methods involving IR include GC-IR where the IR spectra are taken of materials as they are evolved through the column. Related to this are HPLC-IR, TG-IR, and MS-IR.

Raman Spectroscopy

Raman spectroscopy is similar to IR spectroscopy in that it investigates polymer structure focusing on the vibrational modes. Whereas IR is a result of energy being absorbed by a molecule from the ground state to an excited state, Raman spectroscopy is a scattering phenomenon where the energy of photons is much larger than the vibrational transition energies. Most of these photons are scattered without change (so-called Rayleigh scattering). Even so, some are scattered from molecular sites with less energy than they had before the interaction resulting in Raman-Stokes lines. Another small fraction of photons have energies that are now greater than they originally had, leading to the formation of anti-Stokes lines. Only the Raman-Stokes photons are important in Raman spectroscopy. While many chemical sites on a polymer are both IR- and Raman-active, i.e., they give rise to bands, some are less active or even nonactive because of the difference between groups that can absorb and those that scatter. These differences are generally described in terms of symmetry of vibration. Briefly, IR absorption occurs only if there is a change in the dipole moment during the vibration where as a change in polarizability is required for Roman scattering to occur. Even so, the spectra are generally similar and a comparison of the two allows for additional structural characterization beyond that obtained from either technique alone.

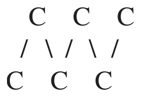
As in the case with IR spectrometers, there exists a wide variety of speciality techniques especially applicable to polymer analysis.

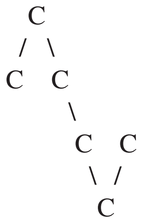
In surface-enhanced Raman spectroscopy (SERS), samples are adsorbed onto microscopically roughened metal surfaces. Spectra are the intensities and frequencies of scattered radiation originating from a sample that has been irradiated with a monochromatic source such as a laser. SERS spectra are of molecules that are less than 50 Å from the surface.

Carraher and Williams and many others showed that for many polymers, differences in symmetry and band production was similar for small molecules as they were for the same groups found in polymers. Thus, observations from the literature and in model compound studies are generally applicable to similar moieties present in polymeric systems for both Raman and IR spectral analyses.

Vibrational Spectra Applications

Vibrational (IR and Raman) spectra are important not only for describing the individual groupings of atoms but also for looking at finer points of structure. Within a polymer chain rotation about a single backbone bonds give different configurations. The proportions of these conformations change with temperature, processing, stress/strain, etc. Taking a simple six carbon segment of polyethylene, we can look at a simple bond rotation that occurs as below. In the segment on the left the chain exists in a zig-zag conformation where the bond angle between the two planes is zero. This conformation is referred to as the trans state, t. The conformation about the rotated bond (right structure) gives an angle between the two planes that is 120° (see Fig. 2.8). This conformation is called the gauche state, g.





Units of poly(ethylene oxide) can exist in a number of conformations. The O—C bond can be t or g; the C—C bond can be t or g; and finally the C—O bond can be either t or g. In the polymer melt all forms exist as indicated by various vibrational spectral bands. Bands associated with the C—O, C—C grouping have been assigned as being t, g and g, t. For instance, there are present bands at (for CH_2 scissoring) 1485 (all bands given in cm^{-1}; IR) assigned to the t form, 1460 (IR and 1470 (Raman) assigned to the g form and 1448 (Raman) for the g form. Such band assignments are made using model compounds and by comparison to the spectra of other related materials. In the solid state, only one structure predominates; that is the t,g,t structure with the O—C in the t conformation, the C—C in the g state, and the C—O in the t state. As stress/strain is applied the ratios of the various bands change intensities allowing a better understanding of the conformational changes that occur when the material is exposed to external changes in the stress/strain.

Ultraviolet Spectroscopy

Ultraviolet spectroscopy has less applicability to the characterization of polymers than IR, but it is useful in detecting aromatics, such as polystyrene, and appropriate additives, such

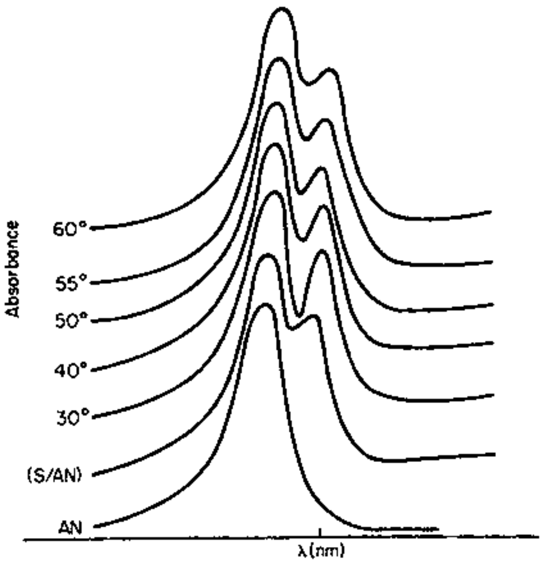


Figure 4.5 Ultraviolet spectra of styrene-acrylonitrile (SAN) $ZnCl_2$ in t-butanol at 25, 30, 40, 50, 55, and 60°C, and styrene at 25°C. [From R. Seymour, G. Stahl, D. Garner, and R. Knapp, Polymer Preprints, *17*(1):219 (1976). With permission from the Division of Polymer Chemistry, ACS.]

as antioxidants, which exhibit characteristic absorption in the UV region. The absorption of the charge transfer constant of styrene-acrylonitrile-$ZnCl_2$ at different temperatures is shown in Fig. 4.5.

The relative amounts of styrene and acrylonitrile in the copolymer in the UV spectrogram in Fig. 4.5 may be determined from the relative areas of absorption bands for styrene and acrylonitrile at wave numbers 1600 and 2240 cm^{-1}, respectively.

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) is a powerful tool for polymer structure characterization. Certain isotopes have two or more energy states available when exposed to a magnetic field. The transitions between these energy states is the basis for NMR. These magnetically active nuclei have a property called *spin*. As a consequence of this spin, these nuclei have an angular momentum and magnetic moment. The ratio of these two properties is called the magnetogyric ratio. Each isotope has a distinct magnetogyric ratio that varies a little with the particular chemical environment in which they are placed.

While NMR has been a strong characterization tool for polymers for many years, it has increased in its usefulness because of continually improved instrumentation and techniques. When a nucleus is subjected to a magnetic field, two phenomenon are observed: Zeeman splitting and nuclear precession. Zeeman splitting creates $2I + 1$ magnetic energy states where I is the spin quantum number. When the atomic mass and atomic number are even numbers, $I = 0$, so that these nuclei are unable to have multiple energy levels when exposed to a magnetic field. Thus ^{12}C, which has both an even atomic number and atomic mass, is NMR-inactive, whereas ^{13}C, which has an uneven atomic mass, is NMR-active. Nuclear precession is the motion of a spinning body whose axis of rotation changes orientation. The precessional frequency is equal to the magnetic field strength times the magnetogyric ratio.

In a magnetic field, NMR-active nuclei can be aligned with the magnetic field (low-energy state) or aligned against the field (high-energy state). At room temperature, there are slightly more nuclei in the lower energy state than the higher energy state. As magnetic energy is supplied that corresponds to the energy gap, i.e., quantum level, between the low and high energy states, some nuclei in the low energy state move to the high-energy state resulting in an absorption of energy which is recorded as a NMR spectra. The difference between the two energy states is related to the strength of the external magnet. Better spectra are obtained when instruments with larger magnetic fields are employed.

NMR spectra of maleic anhydride, vinyl acetate, and the charge-transfer complex of these two monomers have different characteristic spectra (Fig. 4.6). Tetramethylsilane is generally used as a standard.

The characteristic spectra and structures of polyolefins are shown in Fig. 4.7 and Table 4.5. As shown in Fig. 4.7, the ratio of the area of the pmr peaks may be used to determine molecular structure based on the ratios of methyl to methylene groups present.

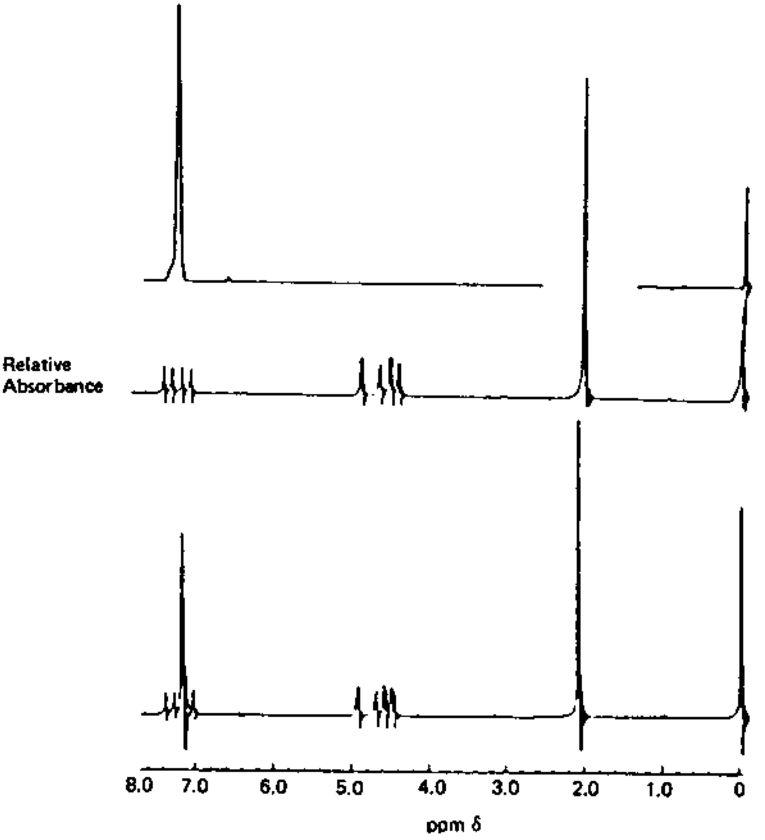
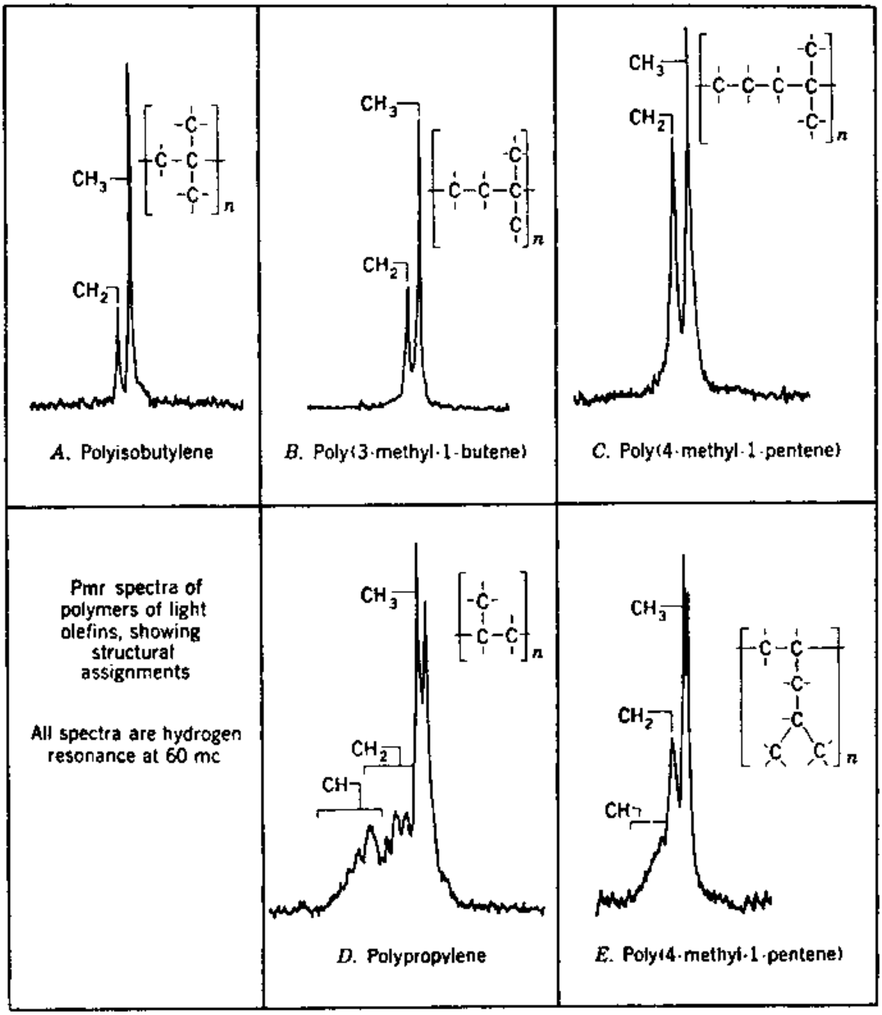


Figure 4.6 PMR spectra of maleic anhydride and vinyl acetate and the charge transfer complex of these two monomers at 25°C. [From R. Seymour, D. Garner, G. Stahl, and L. Sanders, Polymer Preprints, *17*(2):663 (1976). With permission from the Division of Polymer Chemistry, ACS.]


A. Polyisobutylene

B. Poly(3-methyl-1-butene)

C. Poly(4-methyl-1-pentene)

D. Polypropylene

E. Poly(4-methyl-1-pentene)

Figure 4.7 PMR peaks for hydrocarbon polymers. (With permission of N. Chamberlain, F. Stehling, K. Bartz, and J. Reed, Esso Research and Engineering Co.)

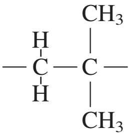
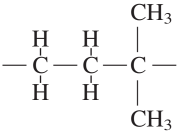
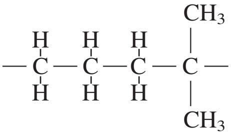
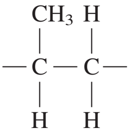
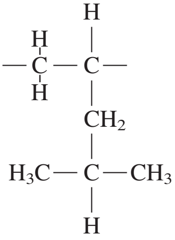
Because of the small but consistent concentrations of carbon-13 present in all organic compounds, it is necessary to use more sophisticated NMR spectroscopy (^{13}C-NMR) for determining the effect of neighboring electrons on these nuclei. However, ^{13}C-NMR spectroscopy is an extremely valuable tool for the investigation of polymer structure. A representative ^{13}C-NMR spectrum of the alternating copolymer of styrene and acrylonitrile is shown in Fig. 4.8.

Following are short descriptions of some of the newer advances.

Nuclear Overhauser Effect

The nuclear Overhauser effect (NOE) only occurs between nuclei that share a dipole coupling, i.e., their nuclei are so close that their magnetic dipoles interact. Techniques that use NOE enhance ^{13}C spectra and allow special relationships of protons to be determined.

Table 4.5 Relationships of Methyl and Methylene Groups in Polymers in Fig. 4.7

Polymer	Structure	CH_3/CH_2
Polyisobutylene	 $-CH_2-C(CH_3)_2-$	2 : 1
Poly(3-methyl-1-butene)[a]	 $-CH_2-CH_2-C(CH_3)_2-$	1 : 1
Poly(4-methyl-1-pentene)	 $-CH_2-CH_2-CH_2-C(CH_3)_2-$	2 : 3
Polypropylene	 $-CH(CH_3)-CH_2-$	1 : 1
Poly(4-methyl-1-pentene)[a]	 $-CH_2-CH(CH_2-CH(CH_3)_2)-$	2 : 2

[a] According to Chamberlain, the PMR-measurements were used to show an unexpected structure for poly(3-methyl-1-butene) and two different structures for poly(4-methyl-1-pentene).

Two-Dimensional NMR

Basically, the two-dimensional NMR techniques of nuclear Overhauser effect spectroscopy (NOESY) and correlation spectroscopy (COSY) depend on the observation that spins on different protons interact with one another. Protons that are attached to adjacent atoms can be directly spin-coupled and thus can be studied using the COSY method. This technique allows assignment of certain NMR frequencies by tracking from one atom to another. The NOESY approach is based on the observation that two protons closer than about 0.5 nm perturb one another's spins even if they are not closely coupled in the primary structure. This allows special geometry to be determined for certain molecules.

The use of actively shielded magnetic field gradients has made the use of pulsed field gradients possible. The use of pulsed field gradients reduces experiment time, minimizes artifacts, and allows for further solvent suppression.

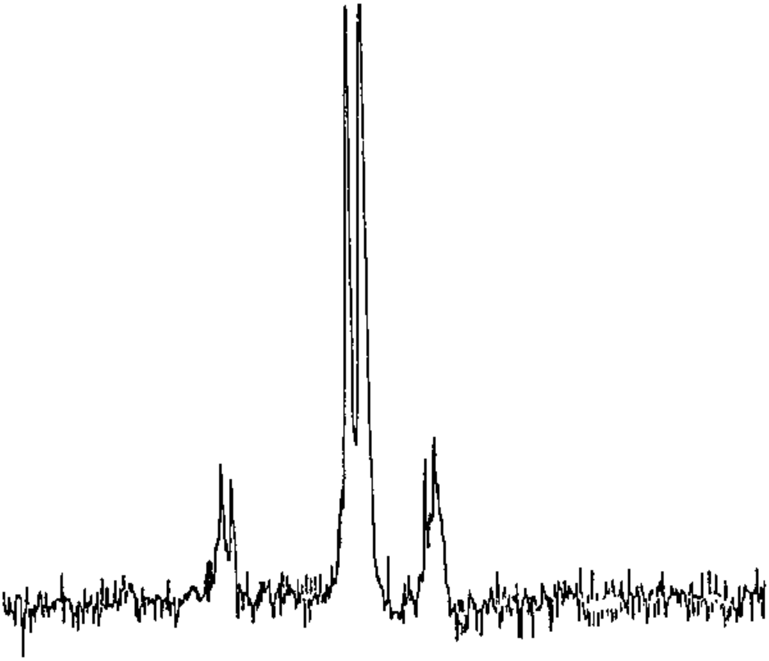


Figure 4.8 Representative ^{13}C-NMR spectra of styrene-acrylonitrile (SAN) alternating copolymer. [From R. Seymour, G. Stahl, D. Garner, and R. Knapp, Polymer Preprints, *17*(1):220 (1976). With permission from the Division of Polymer Chemistry, ACS.]

In pulsed NMR the magnetic field is turned on for the time necessary to rotate the magnetization vector into a plane called the 90° rotation or 90° pulse. The field is turned off and the magnetization vector rotates at a nuclear presession frequency relative to the coil. This induces a NMR signal that decays with time as the system returns to equilibrium. This signal is called the free induction decay (FID).

After a sample is excited, the spin loses excess energy through interactions with the surroundings, eventually returning to its equilibrium state. This process is exponential and is called spin-lattice relaxation. The decay is characterized by an exponential time constant.

Two-dimensional experiments allow the more precise determination of coupling relationships. Such experiments are carried out by collecting a series of FID spectra. The time between the pulses is called the evolution time. The evolution time is systematically increased as each successive FID is obtained. Each new FID shows a continued change in the couplings in the polymer. The FID spectra are treated using Fourier transformation. A new series of FID spectra are now created by connecting points for each spectra and these new FIDs are again treated by Fourier transformation producing two-dimensional spectra that are often presented as contour plots. Nuclei that share J coupling produce a correlation peak. Such approaches allow better interpretation of dipole couplings, molecular diffusion, J coupling, and chemical exchange.

Solids

Many polymers are either difficultly soluble or insoluble. NMR of solids generally gave broad lines because of the effects of dipolar coupling between nuclei and the effect of chemical shift anisotropy (CSA). Both of these effects are greatly reduced for polymers in solution and allow for decent spectra of soluble polymers in solution.

CSA effects are large for solids and are the result of the directional dependence of electronic shielding. CSA effects are overcome through rapidly spinning the sample at an angle to the magnetic field known as the magic angle. Solids probes use spinning rotors to hold and spin the sample. The sample is rotated at the magic angle and spun fast enough to remove CSA effects. High-power decouplers or multiple pulse line narrowing allow the decoupling between protons and carbon by using a series of pulses to average the dipolar interactions through spin reorienting. Cross-polarization uses dipolar coupling to increase the sensitivity of less sensitive nuclei. The combination of cross-polarization and magic angle spinning (CPMAS) allows good spectra to be obtained for solid polymers.

NMR Applications

The various types of spectroscopes complement one another, sometimes giving "new" information and other times giving similar information. The amount of crystallinity and preference for syndiotactic, isotactic, and atactic structure has been determined employing a number of techniques including X-ray. This information can be correlated to information that can be readily obtained from IR and NMR so that product control can be readily achieved. For instance, NMR spectra of poly(methyl methacrylate), PMMA, made by different synthetic routes give different proton shifts that allow the determination of the amounts of isotactic, syndiotactic, and atactic material. Briefly, production of PMMA via so-called high-temperature free radical polymerization gives a largely atactic material. The proton chemical shifts for the alpha methyl appear at about 8.8, 8.9, and 9.1 (chemical shifts are based on the tetramethylsilane peak having a value of 10.0 ppm). Largely isotactic PMMA produced using anionic polymerization shows an enhanced peak at about 8.8 that is assigned to the configuration where the alpha methyl group in the PMMA repeat unit is flanked on both sides by units of the same configuration. It is the major peak in the 8.8–9.1 triad. PMMA produced employing low-temperature free radical polymerization gives largely syndiotactic product. The peak at 8.9 is assigned to the alpha methyl present in a heteroatctic configuration so that the units on either side of it are unlike the central mer since it now becomes the major peak. The 9.1 peak is the largest for the higher temperature product produced via free radical polymerization and is due to the triad central unit being flanked by a like and unlike mer.

Today's NMR capability allows the determination of additional structural features in solution and solid state including the identification of end groups, branches, and defects.

Combinations of solid-state NMR and IR allow the molecular description of the affect of stress/strain, exposure to various conditions including chemical treatments, radiation, and heat on materials.

Electron Paramagnetic Resonance Spectroscopy

Electron paramagnetic resonance (EPR), or electron spin resonance (ESR), spectroscopy is a valuable tool for measuring the relative abundance of unpaired electrons present in macroradicals. For example, as shown in Fig. 4.9, macroradicals are formed by the homogeneous cleavage of nylon chains when these filaments are broken, and the concentration of macroradicals increases as the stress is increased.

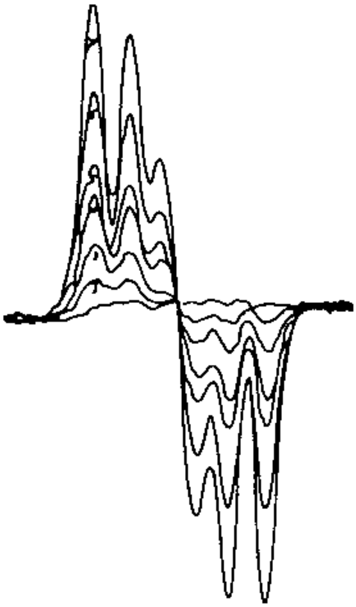


Figure 4.9 EPR spectra for nylon-66 fibers taken under increasing stress.

X-Ray Spectroscopy

X-ray diffraction is a widely used tool for structural identification for almost all solids under the right conditions. X-ray diffractometers are generally either single crystal or powder.

Single-crystal studies allow the absolute configurational determination of polymeric materials that have high degrees of crystallinity. Such determinations are costly with respect to time because of the complexity of polymeric materials.

Powder X-ray spectroscopy can employ smaller crystalline samples from 1 to several hundred nanometers. These crystalites have broadened peak profiles as a result of incomplete destructive interference at angles near the Bragg angle defined as

$$n\lambda = 2d \sin \theta \tag{4.13}$$

where n is the order of a reflection, λ the wavelength, d the distance between parallel lattice planes, and θ the angle between the incident beam and a lattice plane known as the Bragg angle. This broadening allows determination of crystallite size and size distribution. (Note that this is not particle size.)

X-ray analysis of proteins and nucleic acids is especially important as the absolute structure is needed for many advances in the fields of medicine and biochemistry.

4.7 THERMAL ANALYSIS

Major instrumentation involved with the generation of thermal property behavior of materials includes thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), differential thermal analysis (DTA), torsional braid analysis (TBA), thermomechanical analysis (TMA), and pyrolysis gas chromatography (PGC).

One of the simplest techniques is PGC, in which the gases, resulting from the pyrolysis of a polymer, are analyzed by gas chromatography. This technique may be used for qualitative and quantitative analysis. The latter requires calibration with known amounts of a standard polymer pyrolyzed under the same conditions as the unknown. Representative PGC pyrograms of poly(vinyl acetate), alternating and random copolymers of vinyl acetate and maleic anhydride and the copolymer of styrene and acrylonitrile are shown in Figs. 4.10 and 4.11.

There are several different modes of thermal analysis described as DSC. DSC is a technique of nonequilibrium calorimetry in which the heat flow into or away from the polymer is measured as a function of temperature or time. This is different from DTA where the temperature difference between a reference and a sample is measured as a function of temperature or time. Presently available DSC equipment measures the heat flow by maintaining a thermal balance between the reference and sample by changing a current passing through the heaters under the two chambers. For instance, the heating of a sample and reference proceeds at a predetermined rate until heat is emitted or consumed by the sample. If an endothermic occurrence takes place, the temperature of the sample will be less than that of the reference. The circuitry is programmed to give a constant temperature for both the reference and the sample compartments. Excess current is fed

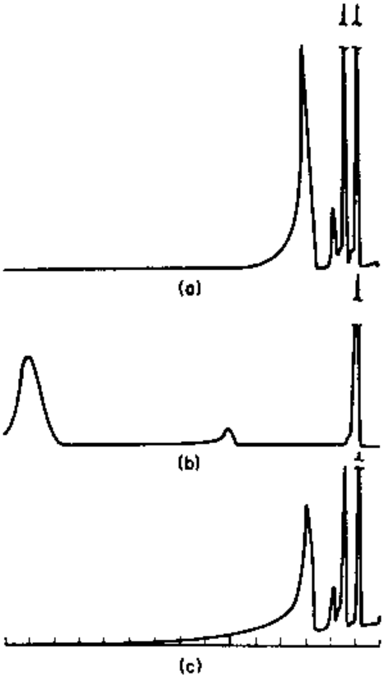


Figure 4.10 Gas chromatography programs of the homopolymer of vinyl acetate (a) and the alternating (b) and random copolymers (c) of vinyl acetate and maleic anhydride. [From R. Seymour, D. Garner, G. Stahl, and L. Sanders, Polymer Preprints, *17*(2):665 (1976). With permission from the Division of Polymer Chemistry, ACS.]

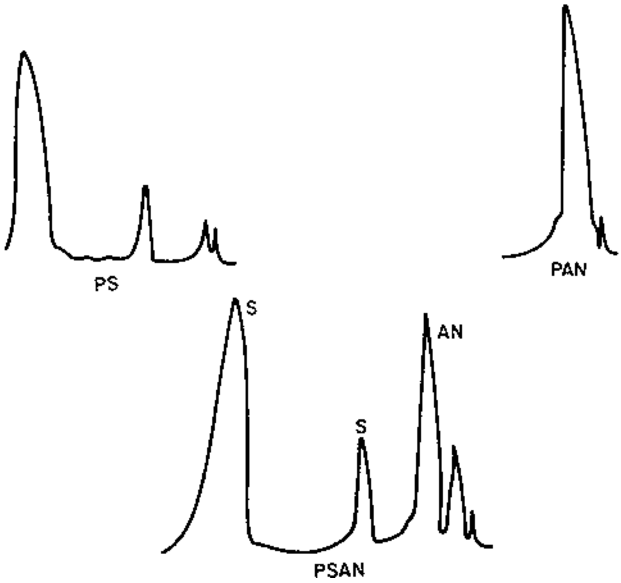


Figure 4.11 Representative PGC programs of polystyrene (PS), polyacrylonitrile (PAN), and poly(styrene-co-acrylonitrile) (PSAN). [From R. Seymour, G. Stahl, D. Garner, and R. Knapp, Polymer Preprints, *17*(1):221 (1976). With permission from the Division of Polymer Chemistry, ACS.]

into the sample compartment to raise the temperature to that of the reference. The current necessary to maintain a constant temperature between the sample and reference is recorded. The area under the resulting curve is a direct measure of the heat of transition.

The advantages of DSC and DTA over a good adiabatic calorimeter include speed, low cost, and the ability to use small samples. Sample size can range from 0.5 mg to 10 g. A resultant plot of ΔT as a function of time or temperature is known as a thermogram. Since the temperature difference is indirectly proportional to the heat capacity, the curves resemble inverted specific heat curves. A typical DSC thermogram of a block copolymer of vinyl acetate and acrylic acid is shown in Fig. 4.12. The distinctions between DSC and DTA are becoming less clear with the advent of new instrumentation which uses components of both DSC and DTA.

Possible determinations from DSC and DTA measurements include the following: (1) heat of transition, (2) heat of reaction, (3) sample purity, (4) phase diagram, (5) specific heat, (6) sample identification, (7) percentage incorporation of a substance, (8) reaction rate, (9) rate of crystallization or melting, (10) solvent retention, and (11) activation energy. Thus, thermocalorimetric analysis can be a quite useful tool in describing the chemical and physical relationship of a polymer with respect to temperature.

In TGA, a sensitive balance is used to follow the weight change of a polymer as a function of time or temperature. Usual sample sizes for commercial instruments are in the range of 0.1 mg to 10 g with heating rates of 0.1 to 50°C/min. The most commonly employed heating rates are 10, 15, 20, 25, and 30°C/min. In making both TGA and thermocalorimetric measurements, the same heating rate and flow of gas should be employed to give the most comparable thermograms. TGA can be used to determine the following: (1)

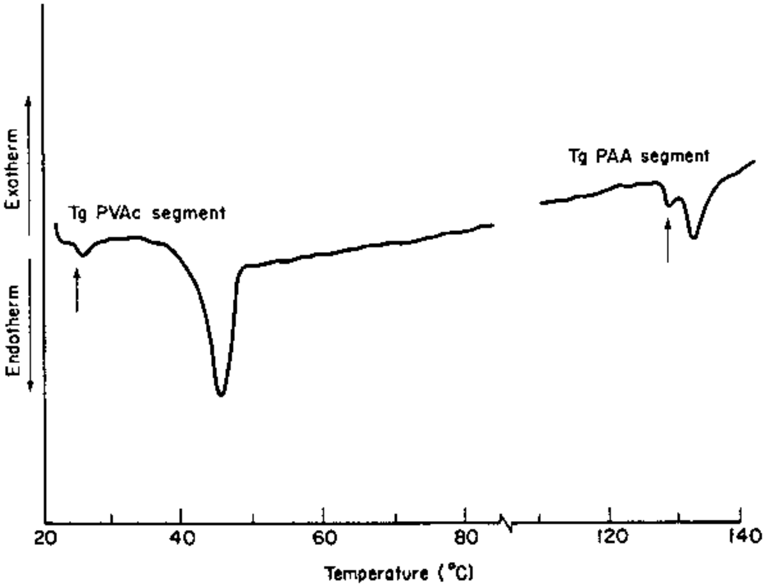


Figure 4.12 Typical DSC thermogram of a block copolymer of vinyl acetate and acrylic acid [P(V Ac-*b*-AA)].

sample purity, (2) identification, (3) solvent retention, (4) reaction rate, (5) activation energy, and (6) heat of reaction.

Thermomechanical analysis measures the mechanical response of a polymer as a function of temperature. Typical measurements as a function of temperature include the following: (1) expansion properties, i.e., expansion of a material leading to the calculation of the linear expansion coefficient; (2) tension properties, i.e., the measurement of shrinkage and expansion of a material under tensile stress, e.g., elastic modulus; (3) dilatometry, i.e., volumetric expansion within a confirming medium, e.g., specific volume; (4) single-fiber properties, i.e., tensile response of single fibers under a specific load, e.g., single-fiber modulus; and (5) compression properties, such as measuring the softening or the penetration under load.

Compressive, tensile, and single-fiber properties are usually measured under some load, yielding information about softening points, modulus changes, phase transitions, and creep properties. For compressive measurements, a probe is positioned on the sample and loaded with a given stress. A record of the penetration of the probe into the polymer is obtained as a function of temperature. Tensile properties can be measured by attaching the fiber to two fused quartz hooks. One hook is loaded with a given stress. Elastic modulus changes are recorded by monitoring of a probe displacement.

In torsional braid analysis, the changes in tensile strength as the polymer undergoes thermal transition is measured as a function of temperature and sometimes also as a function of the applied frequency of vibration of the sample. As thermal transitions are measured, irreversible changes such as thermal decomposition or crosslinking are observed, if present. In general, a change in T_g or change in the shape of the curve (shear modulus vs. temperature) during repeated sweeps through the region, such as a region containing the T_g is evidence of irreversible change. The name TBA is derived from the fact that measurements are made on fibers that are "braided" together to give test samples connected between or onto vice-like attachments or hooks.

DSC, DTA, TMA, and TBA analyses are all interrelated, all signaling changes in thermal behavior as a function of heating rate or time. TGA is also related to the others in the assignment of phase changes to observed weight changes.

Recent trends include increased emphasis on coupling thermal techniques and on coupling thermal techniques with other analysis techniques, such as mass spectrometry (MS) of the off-gases produced by thermolysis or pyrolysis of polymers. Useful combinations include TG-MS, GC-MS, TG-GC-MS, and PGC-MS, with intercorrelation of data from IR, NMR, GPC, and electron microscopy of analyzed samples at different heating times and temperatures.

Reading and co-workers have pioneered in the adaptation of nano-associated atomic force microscopy (AFM) for thermal analyses. The tip of the AFM is replaced with a miniature resistive heater that is used to heat or measure temperature differences on a nano scale. This allows differentiation between phases and (at times) individual polymer chains and segments (such as block and graft segments of copolymers), T_g and T_m, and melting based on differences in thermal conductivity and diffusivity. This technique using the microthermal sensor (MTDSC) is called calorimetric analysis with scanning microscopy (CASM). The probe can also be used to measure certain mechanical properties performing a microthermal mechanical analysis with scanning microscopy (MASH).

The polymer softening range, while not a specific thermodynamic property, is a valuable "use" property. It is normally a simple and readily obtainable property. Softening ranges generally lie between the polymers' T_g and T_m. Some polymers do not exhibit a softening range but rather undergo a solid state decomposition before softening.

Softening ranges are dependent on the technique and procedure used to determine them. Thus, listings of softening ranges should be accompanied by the specific technique and procedure employed for the determination. The following are techniques often used for the determination of polymer softening range.

The capillary technique is analogous to the technique employed to determine melting points of typical organic compounds. The sample is placed in a capillary tube and heated with the temperature recorded from beginning to end of melting. Control of the heating rate lends more importance to the measurements. Instruments such as the Fisher-Johns Melting Point Apparatus are useful in this respect.

Another technique calls for a plug of film (or other suitable form) of the polymer to be stroked along a heated surface whose temperature is being increased until the polymer sticks to the surface. A modification of this utilizes a heated surface containing a temperature gradient between the ends of the surface.

The Vicat needle method (Fig. 4.13) consists of determining the temperature at which a 1-mm penetration of a needle (having a point with an area of 1 mm) occurs on a standard sample (1/8 in. thick, minimum width 3/4 in.) at a specified heating rate (often 50°C/h) under specific stress (generally less than 1 kg). This is also referred to as the heat deflection point.

In the ring-and-ball method the softening range of a sample is determined by noting the temperature at which the sample, held within a horizontal ring, is forced downward by the weight of a standard steel ball supported by the sample. The ball and ring are generally heated by inserting them in a bath.

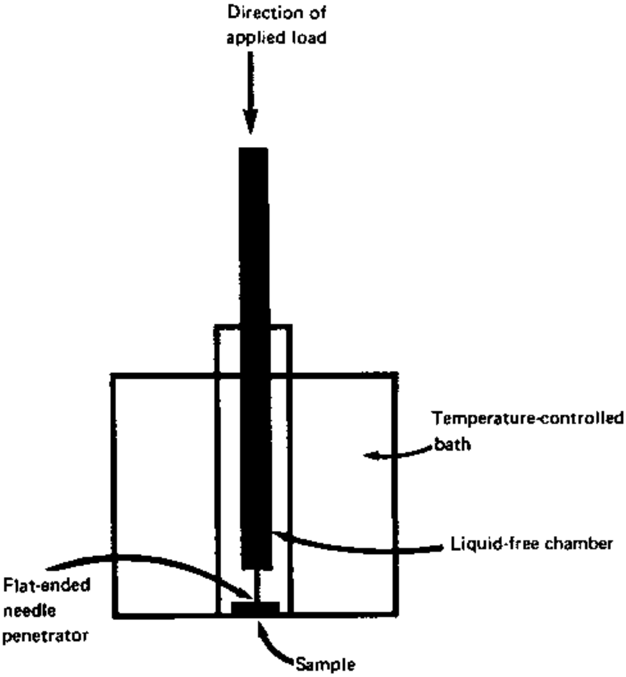


Figure 4.13 Vicat apparatus for softening point determination.

It is important that softening range data can serve as guides to proper temperatures for melt fabrication, such as melt pressing, melt extruding, and molding. It is also an indication of the product's thermal stability.

4.8 THERMAL PROPERTY TESTS

Thermal Conductivity

As energy—heat, magnetic, or electric—is applied to one side of a material, the energy is transmitted to other areas of the sample. Heat energy is largely transmitted through the increased amplitude of molecular vibrations. The heat flow Q from any point in a solid is related to the temperature gradient dt/dl through the thermal conductivity λ as follows:

$$Q = -\lambda(dt/dl) \tag{4.14}$$

The transmission of heat is favored by the presence of ordered lattices and covalently bonded atoms. Thus graphite, quartz, and diamond are good thermal conductors, while less ordered forms of quartz such as glass have lower thermal conductivities. Most polymeric materials have λ values between 0.1 and 1.0 W/m K, while metals typically have values near and above 100 W/m K.

Practically, thermal conductivity, or K factor (ASTM C-177–71), is the time rate of heat flow Q required to attain a steady state in the temperature of a sample having a thickness L and an area A. Change in T is the difference in temperature between a hot plate and a cooling plate above and below the test sample. The thermal conductivity K is calculated from the following equation:

$$K = \frac{QL}{A\ \Delta T} \tag{4.15}$$

Thermal Expansion

Coefficients of thermal expansion can refer to differences in length, area, or volume as a function of temperature. Relative to metals such as steel, polymers have large coefficients of thermal expansion (Table 4.6). Polymers also have quite varied coefficients of thermal expansion. Both of these factors are troublesome when different materials are bound together and exposed to wide temperature ranges. Such wide temperature ranges regularly occur in the aerospace industry (aircraft), within computer chips (and many other electrical and visual areas), engines and motors, etc. Thus, it is critical to match the coefficients of thermal expansions of materials that are to be bound through mechanical (such as screws and bolts) and chemical (polymer alloys, blends, adhered through use of adhesives) means, or stress will develop between the various materials, possibly resulting in fracture or separation.

For polymeric materials, aspects that restrict gross movement, such as crosslinking, typically result in lowered coefficients of expansion. Thus, the typical range for coefficients of linear expansion for (crosslinked) thermosets is lower than the typical range found for (largely noncrosslinked) thermoplastics. Further, such highly crosslinked polymeric

Table 4.6 Typical Coefficients of Linear Expansion (Multiplied by 1 Million to Nearest 5)

Material	K range or value (mm/mm)
Ferrous metals	5–20
Iron	10
Steel	10
Nonferrous metals	5–30
Aluminum	25
Copper	15
Thermosets	Near zero to 120
Melamine/formaldehyde	20–60
Phenol/formaldehyde	30–45
Thermoplastics	20–320
(Aromatic) nylons	90–110
Polyethylene	100–250
Poly(vinyl chloride)	185–200
Poly(methyl methacrylate)	50–110
Polystyrene	60–80
Polytetrafluoroethylene	50–100
Glass (window)	10
Wood	5
Concrete	15
Granite	10

materials such as glass, granite, and concrete (see Chapter 12) also exhibit low coefficients of expansion for the same reason.

Heat Capacity

The thermal conductivity is also related to the specific heat capacity C_p as described in Eq. (4.16), where d is the density of the material and TD is the thermal diffusivity:

$$\lambda = (TD)C_p d \tag{4.16}$$

The amount of heat required to raise the temperature of a material is related to the vibrational and rotational motions thermally excited within the sample. Polymers typically have relatively (compared with metals) large specific heats, with most falling within the range of 1–2 kJ kg^{-1} K^{-1}. The values change as materials undergo phase changes (such as that at the T_m) but remain constant between such transitions.

DSC and DTA instruments are able to rapidly give C_p values.

Vicat Softening Point

The softening point of relatively soft polymers (ASTM D-1525) is the temperature at which a flat-ended Vicat needle with a cross-section of 1 mm penetrates a test specimen to a depth of 1 mm under a specified load, which is usually 1 kg. The needle with a specific load is placed on the sample as shown in Fig. 4.13. The temperature of the bath is raised at a specified rate, and the temperature at which the needle penetrates 1 mm is the Vicat softening point.

Heat Deflection Temperature

The heat deflection temperature (ASTM D-648) is determined by noting the temperature at which a simple beam under load deflects a specified amount, typically 0.01 inch (0.25 mm) (Fig. 4.14). It is not intended to be a direct measure of high-temperature applications but is generally employed as a general use indicator.

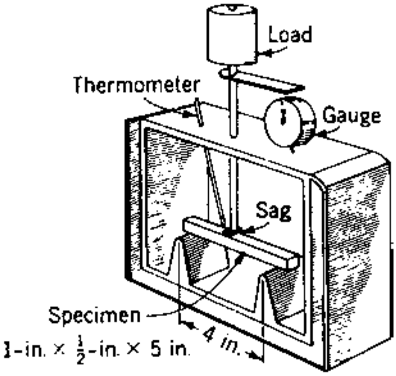


Figure 4.14 Deflection temperature test. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

Glass Transition Temperature

Qualitatively, the glass transition temperature corresponds to the onset of short-range (typically 1–5 chain atoms) coordinated motion. Actually, many more (often 10–100) chain atoms may attain sufficient thermal energy to move in a coordinated manner at T_g.

The glass transition temperature (T_g; ASTM D-3418) is the temperature at which there is an absorption or release of energy as the temperature is raised or lowered. The T_g may be determined from DTA, DSC, TBA, (FTIR), NMR, dynamic mechanical spectroscopy (DMS), modulus-dependent techniques, dilatometry (and other associated techniques that measure area, volume, or length), dielectric loss, and TMA.

DMS refers to a group of dynamic techniques where the sample is subjected to repeated small-amplitude strains in a cyclic fashion. The polymer molecules store some of this imparted energy and dissipate a portion in the form of heat. Since the amount of energy stored and converted to heat is related to molecular motion, changes in the ratios of energy stored to energy converted to heat can be employed to measure T_g.

The coefficient of linear thermal expansion (α) (ASTM D-696) is equal to the change in length of a sample (ΔL) divided by its length (L) and the change in temperature (ΔT) during the test, i.e., $\alpha = \Delta L/L\,\Delta T$. The thermal linear expansivity of polymers is usually higher than that of ceramics and metals; polymers have values ranging from 4 to $20 \times 10^{-5}\,K^{-1}$, whereas metals have values of about 1 to $3 \times 10^{-5}\,K^{-1}$. Further, the expansion of polymeric materials, unlike the expansion of metals, is usually not a linear function of temperature.

It must be emphasized that the actual T_g of a sample is dependent on many factors including pretreatment of the sample and the method and conditions of determination. For instance, the T_g for linear polyethylene has been reported to be from about 140 to above 300 K. Calorimetric values centralize about two values—145 and 240 K; thermal expansion values are quite variable within the range of 140–270 K; nmr values occur between 220 and 270 K; and mechanical determinations range from 150 to above 280 K. If nothing else, the method of determination and end-property use should be related. Thus, if the area of concern is electrical, then determinations involving dielectric loss are appropriate.

Whether a material is above or below its T_g is important in describing the material's properties and potential end use. Fibers are composed of generally crystalline polymers that contain polar groups. The polymers composing the fibers are generally near their T_g to allow flexibility. Crosslinks are often added to prevent wholesale, gross chain movement. An elastomer is crosslinked and composed of essentially nonpolar chains. The use temperature is above its T_g. Largely crystalline plastics may be used above or below their T_g. Coatings or paints must be used near their T_g so that they have some flexibility but are not rubbery. In fact, many coatings behave as "leather" (see Fig. 5.5). Adhesives are generally mixtures where the polymeric portion is above its T_g. Thus the T_g is one of the most important physical properties of an amorphous polymer.

4.9 FLAMMABILITY

Small-scale horizontal flame tests have been used to estimate the flammability of solid (ASTM D-635), cellular (ASTM D-1692–74), and foamed polymers (ASTM D-1992), but these tests are useful for comparative purposes only. Large-scale tunnel tests (ASTM E-84) and corner wall tests are more significant, but they are also more expensive than laboratory tests.

One of the most useful laboratory flammability tests is the oxygen index (OI) test (ASTM D-2043 and ASTM D-2863). In this test, the specimen is burned by a candle in controlled mixtures of oxygen and nitrogen. The minimum oxygen concentration that produces downward flame propagation is considered the OI or ignitability of the polymer.

4.10 SURFACE CHARACTERIZATION

Everything has a surface or an interface. These surfaces have their own kinetic and thermodynamic features that affect their formation and behavior. Sperling notes that for most polymers, the end groups reside perpendicular to the bulk of the polymers probably because the end is less hydrophobic to the bulk and the polymer surfaces generally are "faced" with an air atmosphere that is more hydrophillic. When a polymer solution is deposited on a surface to "dry" the concentration has an influence on the orientation of the polymer chains at the surface in the dried solid. Thus when the amount of polymer is small, the polymer chain lays parallel to the surface in a so-called "pancake" form. As the concentration increases, the surface is not able to accommodate the entire polymer chain and it begins to form an inner tangled chain with only the end and some of the chain segments facing the surface forming a "mushroom" shape. Finally, as the concentration of polymer increases, only the ends of the polymer chains occupy the surface with the polymer ends forming "brushes."

There is no exact, universally accepted definition of a surface. Here, the surface will be defined as the outermost atomic layers, including absorbed foreign atoms. The chemical and physical composition, orientation, and properties of surfaces differ from the interior bulk solid.

Current surface characterization techniques fall into two broad categories—those that focus on the outermost few layers and those whose focus includes components present to several thousand angstroms into the solid.

Attenuated total reflectance (ATF) typically employs special cells fitted onto traditional IR, FTIR, or UV. While some outer surface aspects are gleaned from such techniques, the techniques focus on the bulk surface to several thousand angstroms in depth.

Techniques that analyze the first few atomic layers generally involve low-energy electrons or ions since the incident radiation should penetrate only the top few layers. Normally a combination of techniques is employed to clearly define the outer surface. Special precautions are employed to minimize sample surface contamination. Auger electron spectroscopy (AES) allows the detection of only carbon, oxygen, nitrogen, and heavier atoms. The material surface can be changed by the action of the applied electron beam, often resulting in chemical bonding information being uncertain.

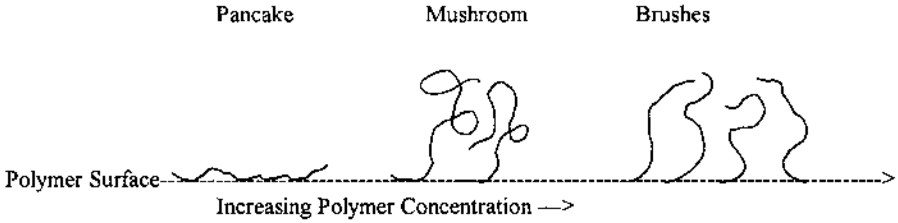


Figure 4.15 General surface structure as a function of polymer concentration.

Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy

AES and X-ray photoelectron spectroscopy (XPS) are two principal surface analysis techniques. They are employed to identify the elemental composition, to determine the amount and nature of species present at the surface, and to elucidate the properties of the outermost atomic layers (1 nm) of a solid.

In the Auger transition, incident electrons interact with the inner shell electrons (E_i) of the sample. The vacancy created by an ejected inner shell electron is filled by an outer shell electron (E_{o1}), and a second outer shell electron (E_{o2}) is ejected leaving the atom in a doubly ionized state. The electrons ejected from the outer shells are the Auger electrons, named after the Frenchman Pierre Auger, who discovered this effect. Thus, AES is a technique that measures the energies of Auger electrons (E_A) emitted from the first 10 Å of a sample surface. The energy equation can be expressed in the following way:

$$E_A = E_{o1} - E_i + E_{o2} \tag{4.17}$$

AES instrumentation in its simplest form involves a vacuum system, an electron gun for target excitation, and an electron spectrometer for energy analysis of the emitted secondary electrons. Additionally, most AES systems presently in use employ an ion gun for in-depth profiling measurements, a manipulator for positioning the sample, a means for precisely locating the area for analysis, and frequently an attachment for performing in situ fracture or cleavage of specimens.

For XPS, a sample is bombarded by a beam of X-rays with energy hv and core electrons are ejected with a kinetic energy (E_k), overcoming the binding energy (E_B) and work function (ϕ). These core electrons are called the X-ray photoelectrons. The energy equation can be expressed as follows:

$$E_k = h\nu - E_B - \phi \tag{4.18}$$

The kinetic energies of these ejected electrons originating within the first 30 Å of the sample surface are measured by XPS.

The functions of an X-ray photoelectron spectrometer are to produce intense X irradiation, to irradiate the sample to photoeject core electrons, to introduce the ejected electrons into an energy analyzer, to detect the energy-analyzed electrons, and to provide a suitable output of signal intensity as a function of electron binding energy.

Both techniques are equally well applied to determine the nature of solid surfaces of polymeric materials, ceramics, metals, metallic alloys, and solid small-molecule samples.

Because of the critical nature of solid surfaces and because the nature of the surface may be quite different from the bulk chemical structure, determination of the nature of surfaces is an important endeavor.

Major surface problems addressed by surface analysis techniques include metal–polymer adhesion, gas–polymer interactions, wear, friction, corrosion, sites of deformation, catalysis structure, water content, effect of processing aids and additives, composite structure, and sites of environment and chemical action.

Electron Microscopy

The upper limit of magnification for optical microscopes is about 2,000 times. Thus, additional forms of microscopy have been developed that allow near to actual atomic observation of polymer surfaces. Electron microscopy utilizes an electron beam to act as the sensing radiation in place of light. High energy electrons take on wave character as they approach the speed of light. The wavelength is inversely proportional to the electron speed or velocity. When accelerated over large voltages, electrons can be made to travel at speeds to permit wavelengths on the order of 0.003 nm. The electron beam is focused and the image formed using magnetic lenses. The two most common forms of electron microscopy are transmission electron microscopy and scanning electron microscopy.

In scanning electron microscopy (SEM), the surface of the polymeric surface is scanned using an electron beam with the reflected or back-scattered beam of electrons collected and displayed on a cathode-ray tube screen. The image represents the surface contour of the scanned material. Because the surface must be conductive, most polymer surfaces must be overlaid with a conductive coating. Magnification up to about 50,000 are carried out.

Transmission electron microscopy (TEM) utilizes an image formed by an electron beam that passes through the sample. This allows internal microstructures to be determined. Structural details of materials can be observed on an atomic level by looking at contrasts in the image caused by various concentrations of different elements. Very thin films are employed. Under good conditions magnifications up to one million are possible.

Scanning Probe Microscopy

Scanning probe microscopy (SPM) encompasses a group of surface-detection techniques that include atomic force microscopy (AFM) and scanning tunneling microscopy (STM) that allow the topographic profiling of surfaces. SPM techniques investigate only the outermost few atomic layers of the surface with nanometer resolutions and at times atomic level resolution.

STM is generally used with electrically conductive materials applied to polymeric materials giving overlays consisting of conducting material layered over the surface of the sample. STM experiments typically require extremely low pressures less than 1×10^{-10} mbar. By comparison, AFM can be run under room conditions and does not require the use of electrically conductive material. In STM the metallic tip is held close (about 0.5–1 nm) to the surface. A voltage, applied between the tip and sample surface, drives a tunneling current. The conductive surface reconstructs the atomic positions via minimizing the surface free energy. This gives topographic superstructures with specific electronic states that are recorded as surface contours or images.

AFM can be run under room conditions. AFM can be performed in either of two forms—a contact mode and a noncontact mode. It does not require the use of electrically conductive material since (in the contact mode) the tip actually “touches” the surface rather than residing immediately above it, as is the case in STM, and in both the contact and the noncontact mode light is used as the sensing source rather than an applied voltage. In contact AFM a cantilever with as sharp a point as possible is laid onto the sample surface with a small loading force in the range of 10^{-7}–10^{-10} Ns. Tips of differing size and shape are tailor-made. Data are obtained optically by bouncing an incident laser beam onto the cantilever toward a quadrant detector on or into an interferometer. In the noncontact mode the attractive force is important and the experiment must be carried out under low pressures similar to those employed in STM.

In the contact mode the tip acts as a low-load, high-resolution profiler. Along with structure determination, the AFM is also used to “move” atoms about allowing the construction of images at the atomic level. The AFM is an important tool in the nanotechnology revolution.

Nanotubes have been used as the points in scanning probe microscopy (Sec. 15.11). The ends of these nanotubes can be closed or functionalized offering even “finer” tips and tips with variable functionality to sense and interact with specific surfaces allowing manipulation on an atom-by-atom basis. These nanotube tips are typically smaller than silicon tips and are generally more robust.

AFM is useful in identifying the nature and amount of surface objects. AFM, or any of its variations, also allow studies of polymer phase changes, especially thermal phase changes, and results of stress/strain experiments. In fact, any physical or chemical change that brings about a variation in the surface structure can, in theory, be examined and identified using AFM.

Today there exists a wide variety of AFMs that are modifications or extensions of traditional AFM. Following is a brief summary of some of these techniques.

Contact mode AFM is the so-called traditional mode of AFM. Topography contours of solids can be obtained in air and fluids. *Tapping mode AFM* measures contours by “tapping” the surface with an oscillating probe tip thereby minimizing shear forces that may damage soft surfaces. This allows increased surface resolution. This is currently the most widely employed AFM mode.

There are several modes that employ an expected difference in the adhesion and physical property (such as flexibility) as the chemical nature is varied. *Phase imaging* experiments can be carried out that rely on differences in surface adhesion and viscoelasticity. *Lateral force microscopy* (LFM) measures frictional forces between the probe tip and sample surface. *Force modulation* measures differences between the stiffness and/or elasticity of surface features. *Nanoindenting/scratching* measures mechanical properties by “nanoindenting” to study hardness, scratching, or wear, including film adhesion and coating durability. LEM identifies and maps relative differences in surface frictional characteristics. Polymer applications include identifying transitions between different components in polymer blends, composites, and other mixtures, identifying contaminants on surfaces, and looking at surface coatings.

Non-contact AFM measures the contour through sensing van der Waals attractive forces between the surface and the probe tip held above the sample. It provides less resolution than tapping mode AFM and contact mode AFM.

There are several modes that employ differences in a materials surface electronic and/or magnetic character as the chemical nature of the surface varies. *Magnetic force microscopy* (MFM) measures the force gradient distribution above the sample. *Electric force microscopy*, (EFM) measures the electric field gradient distribution above a sample surface. EFM maps the gradient of the electric field between the tip and the sample surface. Due to trapped charges on or beneath the surface, the field is often enough to generate contrast in an EFM image. The voltage can be induced by applying a voltage between the tip and the surface. The voltage can be applied from the microscopes electronics under AFM control or from and external power supply. EFM is performed in one of three modes—phase detection, frequency modulation (FM), or amplitude detection. Three-dimensional plots are formed by plotting the cantilever’s phase or amplitude as a function of surface location.

Surface potential microscopy (SP) measures differences in the local surface potential across the sample surface. SP imaging is a nulling technique. As the tip travels above the surface, the tip and the cantilever experience a force whenever the surface potential differs from that of the tip. The force is nullified by varying the voltage of the tip so that the tip remains at the same potential as the immediate surface. The voltage applied to the tip to maintain this constant potential as the tip surveys the surface is plotted as a function of the surface coordinates creating a surface potential image. For best results, SP and EFM do the best job with conductive materials. *Force volume* measurements involve producing two-dimensional arrays of force-distance values allowing a mapping of the force variation and surface topology with individual force curves.

Force-distance microscopy measures repulsive, attractive, and adhesion forces between the time and surface during approach, contact, and separation. This techniques, in some manner, combines electrical with adhesion/physical property as a means to study sample surfaces.

Scanning thermal microscopy (SThM) measures two-dimensional temperature distribution across a sample surface. This is a special thermal technique.

The number of varieties of STM are less. In *electochemical microscopy* (ECSTM and ECAFM), the material is immersed in electrolyte solution and the surface and properties of conductive materials studied. Information derived from several of these techniques go together to give a clearer idea of the nature of the surface.

AFM results can be used in conjunction with other techniques. While some techniques, such as SAXS and SANS, allow structural information to be inferred, AFM gives real space results. While some of the polymeric structural designs may not be unambiguously determined, many can be determined employing ATM. The major limitation concerns whether the structures observed at or near the surface are similar to those in the interior. We are well aware that surface composition differs from the interior composition. For instance, surfaces may be less organized being enriched in chain ends, loops, and switchboard chain segments. Further, for "sliced" samples, does the "slicing" disturb the fine structure along the "cut" surface? For instance, the structure of linear polymers such as polyethylene has been suggested to consist of ordered or sharp folds (Fig. 2.18a), switchboard-like (Fig. 2.18b), loops with loose folds (Fig. 2.18c), buttressed loops (Fig. 2.18d) and combinations of these features (such as Fig. 2.18e and 2.19). Magonov and Godovsky and others recently investigated the surface structures of a number of polymers employing ATM. For single crystals of PE, ordered grains 10–12 nm in size are found. For meltcrystallized LLDPE, spherulites of several microns are the major morphological features. Edge-on standing lamellae and lamellar sheets are found. Dark areas are assigned as amorphous regions. The lamellar edges are on the order of 25–40 nm while the strands are several microns in length. By comparison, melt-crystallized LDPE, which is only about 30% crystalline, shows only spherulitic patterns with ill-defined ring patterns. The grain sizes are about 15–25 nm with fibrillar structures visible. A sample of melt-crystalized ULDPE with low crystalinity (about 15%) gives largely an ill-defined surface consistent of the surface being largely amporphous. As higher force is applied to press through the surface layer, grains of 0–10 nm and finally 9–11 nm become visible, with some grains up to about 100–150 nm visible.

Other polymers have been studied. For instance isotactic-polypropylene, i-PP, shows well-defined spherulites with grains (15–20 nm) embedded in an amorphous material. The grains are assembled in the circles and in some cases along the radial direction giving an ordered texture. PVDF shows numerous spherulites with fibrils 12–15 nm in width. The granular nanostructure of spherulites has also been found for polyesters and polyurethanes. ATM and other studies (including WAXS and SAXS) suggest that the nanoscale grains are elementary building blocks of the crystalline architecture in most polymers. These grains or blocks can have more or less structure within them. The overall crystalline structure may be developed as a one-dimensional assembling of grains into fibrils and the two-dimensional structures being an assembling of grains into lamella. A correlation between grain size and the size of molecular coils has not yet been answered using ATM.

Spin-cast films of poly(ethylene oxide) (PEO) show a flat crystalline morphology with lamellar sheets of different shapes. When melted and then cooled, PEO crystallizes with a similar morphology except the lamellar sheets are smaller. When it is again melted and cooled, crystallization proceeds more slowly and the PEO morphology is dominated by spiral crystallites formed via a screw dislocation mechanism. In all cases, the thickness of the lamellar sheets is about 12 nm indicating multiple folding of the PEO chains. The lamellar sheets disappear at about 60°, though the melting point is listed to be 70°C. The lamellar structures reappear at about 50°C.

The morphology of spin-cast film, thickness of 180 nm, from polycaprolactone shows many spherulitic structures with fibrillar nanostructures formed of lamellae lying edge on (about 10 nm thick) and areas with lamellar sheets lying flat on. Different crystalline structures are found when the sample is melted and crystallized as a function of temperature. These two studies reinforce the complex inner relationship between physical treatment and nanostructure.

While some structures show seemingly independent spherulitic structures on the surface, we know from other studies that the structures are connected to one another and to the more amorphous regions overall, giving a material with a characteristic flexibility and strength. In general, chains are shared with adjacent areas, allowing a sharing of stress/strain factors.

AFM is important for biological as well as synthetic macromolecules. Several examples are given to illustrate applications. Collagen is an important natural protein that is present in many tissues including bones, skin, tendons, and the cornea. It is also employed in medical devices such as artificial skin, tendons, cardiac valves, ligaments, hemostatic sponges, and blood vessels. There are at least 13 different types of collagen. ATF can image collagen molecules and fibers and their organization allowing identification of the different kinds of collagen and at least surface interactions.

AFM allows the study of cell membranes. The precise organization of such cell membranes is important since they play a role in cell communication, replication, and regulation. It is possible to study real time interactions of such biologically important surfaces. Further, bilayers, modeled or containing naturally produced bilayers, are used as biosensors. Again, interactions of these biomembranes can be studied employing AFM. For instance, the degradation of bilayers by phospholipases, attachment of DNA, etc., can be studied on a molecular level. In another application, antibody–antigen interactions have been studied employing AFM. One application of this is the creation of biosensors to detect specific interactions between antigens and antibodies.

Secondary Ion Mass Spectroscopy

Secondary ion mass spectroscopy (SIMS) is a sensitive surface analysis tool. Here the mass analysis of negative and positive ions sputtered from the polymer surface through ion bombardment are analyzed. The sputtering ion beam is called the primary ion beam. This beam causes erosion of the polymer surface removing atomic and molecular ions. These newly created ions, composing what is called the secondary ion beam, are then analyzed as a function of mass and intensity. Depth of detection for SIMS is of the order of 20–50 Å. Because it is the ions in the secondary ion beam that are detected, the mass spectra obtained from SIMS are different from those obtained using simple electron impact methods. The extent of particular ion fragments observed is dependent on a number of factors including the ionization efficiency of the particular atoms and molecules composing the polymer surface.

SIMS can detect species that are present on surfaces of the order of parts per million to parts per billion.

4.11 AMORPHOUS REGION DETERMINATIONS

Experimental tools that have been employed in an attempt to characterize amorphous regions are given in Table 4.7. Techniques such as birefringence and Raman scattering give information related to the short-range (less than 20 Å) nature of the amorphous domains, while techniques such as neutron scattering, electron diffraction, and electron microscopy yield information concerning the lower range nature of these regions.

Birefringence measures order in the axial, backbone direction. The birefringence of a sample can be defined as the difference between the refractive indices for light polarized in two directions 90° apart, i.e.,

$$\Delta n = n_{\theta} - n_{\theta-90} \tag{4.19}$$

Thus, a polymer sample containing polymer chains oriented in a preferential direction by stretching or some other method will exhibit a different refractive index along the direction of preferred chain alignment compared to that obtained at right angles to this. This change in birefringence as an amorphous material, such as a melt of rubber, is deformed and gives information concerning the amount of order.

The results of utilizing techniques for short-range interactions for vinyl polymers are consistent with at least some amorphous regions consisting of only limited (5–10 Å and 1–2 units) areas with orientation similar to that observed for typical low molecular weight hydrocarbons.

Small-angle neutron scattering (SANS) results indicate that vinyl polymers exist in random coils in the amorphous state. Results from electron and X-ray diffraction studies show diffuse halos, meaning that the nearest-neighbor spacings are somewhat irregular. The diffuse halos could result from situations where short-range order is present but long-range disorder exists. This is a situation believed to be present in liquid water and may be the result of both short-range order and long-range disorder.

The smooth changes observed with relaxation and annealing studies suggest little order for amorphous polymers. However, the density of an amorphous polymer is generally

Table 4.7 Techniques Employed to Study the Amorphous Regions of Polymers

Short-range interactions	Long-range interactions
Magnetic birefringence	Electron diffraction
Raman scattering	Wide-angle X-ray scattering
Depolarized light scattering	Electron microscopy
Rayleigh scattering	Density
Bruillouin scattering	Small-angle neutron scattering
NMR relaxation	
Small-angle X-ray scattering	

85–90% of that of the analogous crystalline polymer, and density-related calculations suggest that there may be some short, organized parallel arrangements of vinyl chain segments. The interpretations of such studies are still unclear.

4.12 PARTICLE SIZE

Particle size is important in many polymer applications including coatings applications, creation of suspensions, and a number of quality control procedures such as the determination of contaminates.

There are many analytical techniques that allow the determination of particle size (Table 4.8). Before a technique is chosen, one needs to determine the relative particle size to be determined and the type of size information needed. Refractive index values are generally needed for size measurements based on light scattering. Densities are often needed for techniques based on acoustics and sedimentation. Simple microscopy generally allows the determination of the general range of size and shape. Most particle size determinations are dependent on particle shape with most techniques and related equations based on spherically shaped particles. Thus, the greater the deviation in particle shape from spherical, generally the greater the error. Particles that differ greatly in particle shape from spherical, such as needles and rods, are best analyzed using some form of microscopy. Properties of the particle in the suspending fluid are also important because some liquids may bring about changes in particle shape or encourage clustering of the particles. The suspending liquid should not dissolve or appreciably influence particle shape.

Light obscuration (LO) is one of the major techniques used to determine particle size. LO is based on the observation that particles whose refractive index is different from the suspending solvent scatter light. This scattering is the same as that employed in molecular weight determinations using light-scattering photometry. In fact, light-scattering photometry can also be used to determine particle size. Even so, LO instruments have been developed for the main purpose of determining particle size. Stirring is often required to maintain a somewhat homogeneous suspension. Wetting of the particles by the suspending liquid, often achieved by addition of a wetting agent, is also generally required. Dispersion of the particles is assisted by sonication for situations where a single particle size is needed. Sonication is not recommended if particle aggregation sizes are important.

Sedimentation techniques are also used to determine particle size distributions of the order of 0.1–50 μm. Capillary hydrodynamic chromatography (HDC) gives particle size distributions for particles of about 0.005 to 0.7 μm.

4.13 MEASUREMENT OF ADHESION

Adhesion is the binding of two surfaces where they are held together by primary and/or secondary bonding forces. A discussion of the types of adhesives is given in Sec. 17.11.

Table 4.8 Particle Size and Particle Size Distribution Determination Techniques

Sedimentation	Capillary hydrodynamic chromatography
Microscopy	Light obscuration
Fraunhofer diffraction	Field flow fractionation
Phase Doppler anemometry	Ultrasonic spectroscopy

A discussion of surface analysis is given in Sec. 4.10. Here we will look at the mechanical measurement of adhesion. As with all of polymer testing, the conditions of testing are important and experiments and experimental conditions should be chosen to reflect the particular conditions and operating conditions under which the material may subjected to. During the fracture of adhered surfaces, the bonded surfaces and adhesive are both deformed.

Failure can be effected through a variety of mechanisms. The major mechanisms are through peeling, shearing, and detachment. In peel separation, the adhesive simply "peels" away from the surface. Lap shear occurs when the adhered material is subjected to a force that is applied parallel to the bonding plane. Here the bond becomes deformed and stretched after initial rupture of some portion of the bond. It is a "sliding" type of failure. In tensile detachment, bond disruption occurs as force is applied at right angles to the bonding surface. Tensile detachment is a "ripping" type of bond disruption.

Scratch testing. Often some type of "scratch" testing can be used to measure adhesion of thin films. Fingernail and pencil tip results are often used as a first measure of adhesion. Thus, a person presses their fingernail against the adhered surface watching to see if the adhesive is removed from the surface. Even in more complex scratch tests, such tests create both elastic and plastic deformations around the probe tip. The critical load for adhesion failure depends on the interfacial adhesion and on the mechanical properties of the adhesive. Today, there exists techniques that give better measures of adhesion. In the microimpact test, the test probe continuously impacts the adhesive along the wear track. This allows the effects of impacts adjacent to prior impacts to be studied allowing the influence of large area damage near the impact to be studied.

Peel testing. Peel angle is important with 180° and 90° peel angles being the most common. In general, a small amount of the adhesive is "peeled" away and the force necessary to continue the peel measured.

Tensile detachment testing. A simple description of tensile tests involves attaching two thick microscope slides to one another so the slides are at right angles to one another (Fig. 4.16). After the bond is allowed to set-up a desired amount, the ends of the top microscope are attached to the measuring device and the ends of the second, bottom, slide are attached to a load-bearing segment of the apparatus. Eventually, deformation and bond breakage occurs as the load is increased.

Lap shear testing. Shear can be applied in a number of ways—cyclic, intermittent, static (or constant), or increasing. A simple overlap shear test is described in ASTM-D-

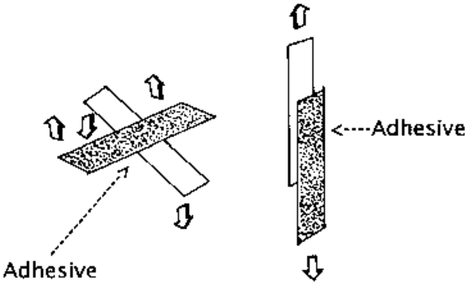


Figure 4.16 Illustrations of simple tensile detachment (left) and simple lap shear (right) assemblies for testing adhesion.

1002. This can be illustrated again using two strong microscope slides. Here, the microscope slides are adhered in parallel to one another except off-set (Fig. 4.16). After the appropriate set-up time, the top and bottom of the slide combination are attached to the shear tensile measuring device and the experiment is carried out.

SUMMARY

1. The American Society for Testing and Materials (ASTM) and comparable organizations throughout the world have established meaningful standards for the testing of polymers.
2. The electrical properties of materials is important for many of the higher technology applications. Measurements can be made using variable alternating current and/or direct current. The electrical properties are dependent on voltage frequency. Important electrical properties include dielectric loss, loss factor, dielectric constant, conductivity, relaxation time, induced dipole moment, electrical resistance, power factor, dissipation factor, and electrical breakdown.
3. Electrical properties are related to polymer structure. While most polymers are nonconductors, some are semiconductors whereas others are conductors.
4. Important physical properties of polymers include weatherability, optical properties, absorption, and reflectance.
5. Most polymers show moderate to good chemical resistance when compared to nonpolymers and metals.
6. With some particular and important differences the spectronic properties of polymers are similar to and can be determined similar to small molecules. Important spectronic results can be obtained from infrared, Raman, and microwave spectroscopy, UV spectroscopy, NMR, EPR/ESR, and X-ray diffraction. These techniques can be used to determine polymer structures.
7. Thermal analysis measures particular polymer properties as a function of temperature including heating rate, recycling sequences, temperature program, atmosphere, and technique. DSC/DTA measures changes in temperature with varying temperature changes and allows the determination of phase transitions including glass transition range and melting range. TGA measures weight changes as a function of temperature.
8. Surface properties are important to the physical and chemical behavior of polymers. Similar to smaller molecules, polymer surface structures can be determined using a variety of techniques including Auger electron spectroscopy and X-ray photoelectron spectroscopy.

GLOSSARY

Abbe refractometer: An instrument used for measuring the index of refraction.
ASTM: American Society for Testing and Materials.
ASTM D-20: Committee responsible for standards for plastics.
AES: Auger electron spectroscopy.
ATM: atomic force microscopy attenuated total reflectance infrared spectroscopy (ATR-IR) Infrared spectroscopy used to study surfaces.
BSI: British Standards Institution.
BTU: British thermal unit.

chemical shifts: Peaks in proton magnetic resonance spectroscopy.

^{13}C NMR: Nuclear magnetic resonance spectroscopy based on the effect of neighboring electrons on carbon-13 nuclei.

COSY: Correlation spectroscopy.

CPMAS: CASS-polarization/magic angle spinning.

CSA: Chemical shift anisotropy.

dielectric constant: Ratio of the capacitance of a polymer to that of air or a vacuum.

dielectric strength: Maximum applied voltage that a polymer can withstand.

differential scanning calorimetry: Measurement of the differences in changes in enthalpy of a heated polymer and a reference standard based on power input.

differential thermal analysis: Measurement of the difference in the temperature of a polymer and a reference standard when heated.

DMS: Dynamic mechanical spectroscopy.

DNA: Deutsche Normenausschuss (German standard tests).

DSC: Differential scanning calorimetry.

DTA: Differential thermal analysis.

environmental stress cracking. Cracking of polyolefins in liquid media such as liquid detergents.

EPR: Electron paramagnetic resonance.

ESCR: Environmental stress cracking.

ESR: Electron spin resonance.

FID: Free induction decay.

glass transition temperature (t_3): Lowest temperature at which segmental motion of polymer chains exists.

heat deflection temperature: The temperature at which a simple loaded beam undergoes a definite deflection.

index of refraction: The ratio of the velocity of light in a vacuum to that in a transparent polymer.

infrared spectroscopy: A technique used for the characterization of polymers based on their molecular vibration and vibration–rotation spectra.

IR: Infrared.

ISO: International Standards Organization.

K factor: A measure of thermal conductivity.

LO: Light obscuration.

loss factor: Power factor multiplied by dielectric constant.

Moh’s scale: A hardness scale ranging from 1 for talc to 10 for diamond.

NMR: Nuclear magnetic resonance spectroscopy.

NOE: Nuclear Overhauser effect.

NOESY: Nuclear Overhauser effect spectroscopy.

nuclear magnetic resonance spectroscopy (NMR): Based on the absorption of magnetic energy by nuclei that have an uneven number of protons or neutrons; this absorption is dependent on the particular chemical structure and environment of the molecule.

OI: Oxygen index.

oxygen index: A test for the minimum oxygen concentration in a mixture of oxygen and nitrogen that will support a candle-like flame of a burning polymer.

PGC: Pyrolysis gas chromatography.

phase contrast microscopy: Measurement of differences in indices of index of refraction.

PMR: Spectroscopy based on proton or hydrogen magnetic resonance.

power factor: Electrical energy required to rotate the dipoles in a polymer while in an electrostatic field.
Q: Rate of heat flow.
Raman spectroscopy: Based on the interaction of vibrational modes of molecules with relatively high energy where absorption is based on the chemical moieties that undergo changes in polarization.
SANS: Small-angle neutron scattering.
scanning probe microscopy (SPM): A group of surface detection techniques that includes atomic force microscopy (AFM) and scanning tunneling microscopy (STM).
secondary ion mass spectroscopy (SIMS): Mass spectroscopy that looks at the ion fragments generated from the bombardment of surfaces with an ion beam.
SEM: Scanning electron microscopy.
SPM: Scanning probe microscopy.
STM: Scanning tunneling microscopy.
T_g: Glass transition temperature.
thermogravimetric analysis (TGA): Measurement of the loss in weight when a polymer is heated.
TMA: Thermomechanical analysis.
UV: Ultraviolet.
volume resistivity: Electrical resistance between opposite forces of a 1-in. cube.
XPS: X-ray photoelectron spectroscopy

EXERCISES

1. Why are electrical tests for polymers important?
2. Which is the better insulator: a polymer with (a) a low or (b) a high K factor?
3. Why are the specific heats of polymers higher than those of metals?
4. What are the standard heat deflection loads in metric units?
5. Why is the use of the term flameproof plastics incorrect?
6. Which plastic will be more resistant when immersed in 25% sulfuric acid at 50°C (a) HDPE, (b) PMMA, or (c) PVAc?
7. What happens to indices of refraction values at T_g?
8. How does the index of refraction change when the molecular weight of a polymer is increased?
9. How many degrees of vibrational freedom are present in polypropylene?
10. What is the UV region of the spectrum?
11. Which would absorb in the UV region: (a) polystyrene, (b) hevea rubber, or (c) PVC?
12. What technique would you use to determine crystallinity in a polymer?
13. What thermal instrumental technique would you use to determine T_g?

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5

Rheology and Physical Tests

Polymers are viscoelastic materials, meaning that they can act as liquids, the “visco” portion, and as solids, the “elastic” portion. Description of the viscoelastic properties of materials generally falls within the area called rheology. Determination of the viscoelastic behavior of materials generally occurs through stress/strain and related measurements. Whether a material behaves as a viscous or an elastic material depends on temperature, the particular polymer and its prior treatment, polymer structure, and the particular measurement or conditions applied to the material. The particular property demonstrated by a material under given conditions allows polymers to act as solid or viscous liquids, as plastics, elastomers, or fibers, etc. This chapter deals with the viscoelastic properties of polymers.

5.1 RHEOLOGY

The branch of science related to the study of deformation and flow of materials was given the name rheology by Bingham, whom some have called the father of modern rheology. The prefix *rheo* is derived from the Greek term *rheos*, meaning current or flow. The study of rheology includes two vastly different branches of mechanics called fluid and solid mechanics. The polymer chemist is usually concerned with viscoelastic materials that act as both solids and fluids.

The elastic component is dominant in solids, hence their mechanical properties may be described by Hooke’s law [Eq. (5.1)], which states that the applied stress (s) is proportional to the resultant strain (γ) but is independent of the rate of this strain ($d\gamma/dt$).

$$s = E\gamma \tag{5.1}$$

Stress is equal to force per unit area, and strain or elongation is the extension per unit length. For an isotropic solid, i.e., one having the same properties regardless of direction, the strain is defined by Poisson's ratio, $V = \gamma_l/\gamma_w$, the percentage change in longitudinal strain, γ_l, to the percentage change in lateral strain, γ_w.

When there is no volume change, as when an elastomer is stretched, Poisson's ratio is 0.5. This value decreases as the T_g of the substance increases and approaches 0.3 for rigid poly(vinyl chloride) (PVC) and ebonite. For simplicity, the polymers will be considered to be isotropic viscoelastic solids with a Poisson's ratio of 0.5, and only deformations in tension and shear will be considered. Thus, a shear modulus (G) will usually be used in place of Young's modulus of elasticity (E) [refer to Eq. (5.2), Hooke's law for shear], where $E \simeq 2.6G$ at temperatures below T_g. The moduli (G) for steel, HDPE, and hevea rubber (NR) are 86, 0.087, and 0.0006 m^{-2}, respectively.

$$s = G\gamma \qquad \text{and} \qquad ds = G d\gamma \tag{5.2}$$

The viscous component is dominant in liquids, hence their flow properties may be described by Newton's law [Eq. (5.3)] (where η is viscosity), which states that the applied stress s is proportional to the rate of strain $d\gamma/dt$, but is independent of the strain γ or applied velocity gradient. The symbol $\dot{\gamma}$ is sometimes used for strain rate.

$$s = \eta \frac{d\gamma}{dt} \tag{5.3}$$

Both Hooke's and Newton's laws are valid for small changes in strain or rate of strain, and both are useful in studying the effect of stress on viscoelastic materials. The initial elongation of a stressed polymer below T_g is the reversible elongation due to a stretching of covalent bonds and distortion of the bond angles. Some of the very early stages of elongation by disentanglement of chains may also be reversible.

However, the rate of flow, which is related to slower disentanglement and slippage of polymer chains past each other, is irreversible and increases (and η decreases) as the temperature increases in accordance with the following Arrhenius equation (5.4) in which E is the activation energy for viscous flow.

$$\eta = A\ E^{E/RT} \tag{5.4}$$

It is convenient to use a simple weightless Hookean, or ideal, elastic spring with a modulus of G and a simple Newtonian (fluid) dash pot or shock absorber having a liquid with a viscosity of η as models to demonstrate the deformation of an elastic solid and an ideal liquid. The stress-strain curves for these models are shown in Fig. 5.1.

In general terms, the Hookean spring represents bond flexing while the Newtonian dash pot represents chain and local segmental movement. It is customary to attempt to relate stress-strain behavior to combinations of dash pots and springs as indicators of the relative importance of bond flexing and segmental movement.

Again, in general terms, below their T_g polymers can be modeled as having a behavior where the spring portion is more important. Above their T_g where segmental mobility occurs, the dashpot portion is more important.

The relative importance of these two modeling parts, the spring and the dash pot, is also dependent on the rate at which an experiment is carried out. Rapid interaction, such as striking a polymer with a hammer, is more apt to result in a behavior where bond flexibility is more important, while slow interactions are more apt to allow for segmental mobility to occur.

Since polymers are viscoelastic solids, combinations of these models are used to demonstrate the deformation resulting from the application of stress to an isotropic solid

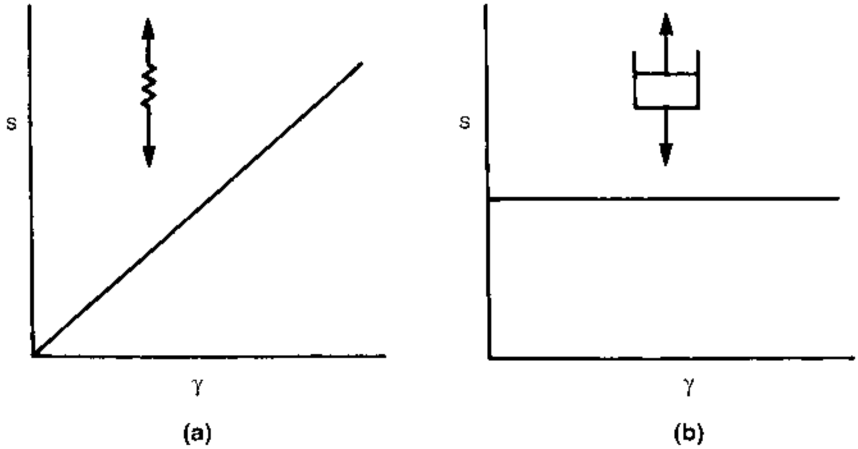


Figure 5.1 Stress–strain plots for (a) a Hookean spring where E [Eq. (5.1)] is the slope, and (b) a Newtonian dash pot where s is constant [Eq. (5.3)].

polymer. Maxwell joined the two models in series to explain the mechanical properties of pitch and tar (Fig. 5.2). He assumed that the contributions of both the spring and dash pot to strain were additive and that the application of stress would cause an instantaneous elongation of the spring, followed by a slow response of the piston in the dash pot. Thus, the relaxation time (τ), when the stress and elongation have reached equilibrium, is equal to η/G.

In the Maxwell model for viscoelastic deformation, it is assumed that $\gamma_{\text{total}} = \gamma_{\text{elastic}} + \gamma_{\text{viscous}}$. This may be expressed in the form of the following differential equation from Eqs. (5.2) and (5.3).

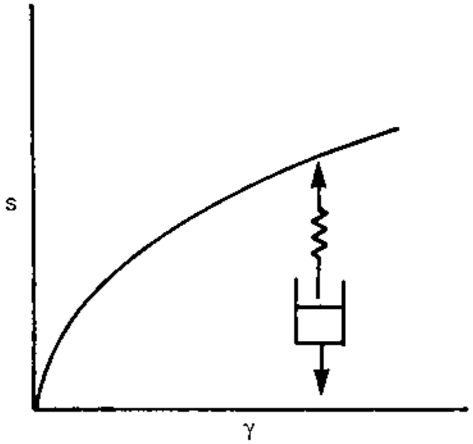


Figure 5.2 Stress–time plot for stress relaxation in the Maxwell model.

$$\frac{d\gamma}{dt} = \frac{s}{\eta} + \frac{ds}{dt}\frac{1}{G} \tag{5.5}$$

The rate of strain dγ/dt is equal to zero under conditions of constant stress (s), i.e.,

$$\frac{s}{\eta} + \frac{ds}{dt}\frac{1}{G} = 0 \tag{5.6}$$

Then, assuming that $s = s_0$ at zero time, we set

$$s = s_0 e^{-tG/\eta} \tag{5.7}$$

And, since the relaxation time $\tau = \eta/G$, then

$$s = s_0 e^{-t/\tau} \tag{5.8}$$

Thus, according to Eq. (5.8) for the Maxwell model or element, under conditions of constant strain, the stress will decrease exponentially with time and at the relaxation time $t = \tau$, s will be equal to $1/e = 1/2.7$, or 0.37 of its original value (s_0).

As shown in Fig. 5.3, the spring and dash pot are parallel in the Voigt-Kelvin model. In this model or element, the applied stress is shared between the spring and the dash pot, and thus the elastic response is retarded by the viscous resistance of the liquid in the dash pot. In this model, the vertical movement of the spring is essentially equal to that of the piston in the dash pot. Thus, if G is much larger than η, the retardation time (η/G) or τ is small, and τ is large if η is much larger than G.

In the Voigt-Kelvin model for viscoelastic deformation, it is assumed that the total stress is equal to the sum of the viscous and elastic stress $s_v + s_0$, as shown in Eq. (5.9).

$$s = \eta\frac{d\gamma}{dt} + G\gamma \tag{5.9}$$

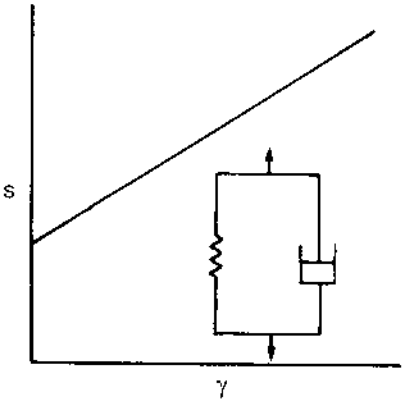


Figure 5.3 Stress–time plot for a Voigt-Kelvin model.

On integration one obtains

$$\gamma = \frac{s}{G}(1 - e^{-tG/\eta}) = \frac{s}{G}(1 - e^{-t/\tau}) \tag{5.10}$$

The retardation time τ is the time for the strain to decrease to $1 - (1/e)$ or $1 - (1/2.7) = 0.63$ of the original value. The viscoelastic flow of polymers is explained by appropriate combinations of the Maxwell and Voigt-Kelvin models.

Rheology and Physical Tests

While polymer melts and elastomers flow readily when stress is applied, structural plastics must resist irreversible deformation and behave as elastic solids when relatively small stresses are applied. These plastics are called ideal or Bingham plastics as described by

$$s - s_0 = \eta \frac{d\gamma}{dt} \tag{5.11}$$

As shown in Fig. 5.4, a Bingham plastic exhibits Newtonian flow above the stress yield or stress value (s_0). The curves for shear thickening (dilatant) and shear thinning (pseudoplastic) materials are also shown in Fig. 5.4.

Liquids that undergo a decrease in viscosity with time are called thixotropic, or false-bodied. Those that undergo an increase in viscosity with time are called rheopectic (shear thickening). The term *creep* is used to describe the slow slippage of polymer chains over a long period of time. The Herschel-Buckley equation [Eq. (5.12)] is a general equation which reduces to the Bingham equation when $\eta = 1$ and to the Newtonian equation when $\eta = 1$ and $s_0 = 0$:

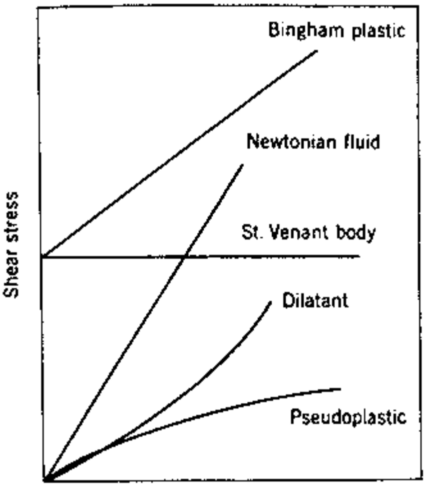


Figure 5.4 Various types of polymer flow. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

$$(s - s_0)\eta = \phi\frac{d\gamma}{dt} \tag{5.12}$$

where ϕ is related to viscosity.

Eyring has explained liquid flow using a random hole–filling model in which the holes account for about 15% of the volume at room temperature. The size of these holes is similar to that of small molecules, and hole filling is restrained by an energy barrier which is about one-third the value of the heat of evaporation. The number of holes increases as the temperature increases, and thus flow or hole filling is temperature-dependent.

Small molecules jump into the holes and leave empty holes when their energy exceeds the activation energy (E_a). This last value is smaller for linear polymers which fill the holes by successive correlated jumps of chain segments along the polymer chain. The jump frequency ϕ is governed by a segmental factor (f_0), and both ϕ and f_0 are related to molecular structure and temperature.

For convenience and simplicity, polymers have been considered to be isotropic in which the principal force is shear stress. While such assumptions are acceptable for polymers at low shear rates, they fail to account for stresses perpendicular to the plane of the shear stress, which are encountered at high shear rates. Thus, an extrudate such as a pipe or filament expands when it emerges from the die in what is called the Barus or Weissenberg effect, or die swell.

As illustrated later in Fig. 5.8, viscoelasticity can be subclassified into five types: (1) viscous glass, Hookean elastic, or Hookean glass region, where chain segmental motion is quite restricted and involves mainly only bond bending and bond angle deformation; the material behaves as a glass like a glass window; while flow occurs it is detectable only with delicate, exacting instruments; stained-glass windows in the old churches in Europe are typically thicker at the bottom of each segment due to the slow flow; (2) glassy transition and (3) the rubbery flow region are both related to what is often referred to as the viscoelastic region where polymer deformation is reversible but time-dependent and associated with both side chain and main chain rotation; (4) rubbery, highly elastic rubbery, or rubber-like elasticity, where local segmental mobility occurs but total chain flow is restricted by physical and/or chemical network matrix structure; and (5) rubbery flow or viscous flow region where irreversible bulk deformation and slippage of chains past one another occur. Each of these viscoelastic types is time-dependent. Thus, given a short interaction time, window glass acts as a Hookean glass or like a solid, yet observation of glass over many years would permit the visual observation of flow, with the window glass giving a viscous flow response and thus acting as a fluid. In fact, most polymers give a response as noted, for example, in Fig. 5.5 if a rubber ball were dropped onto the material either as the temperature of the sample increases or the interaction time increases. Commercial Silly Putty or Nutty Putty easily illustrates three of these regions. When struck rapidly it shatters as a solid, when dropped at a moderate rate it acts as a rubber, and when allowed to reside in its container it flows to occupy the container contour, acting as a liquid. The exact response (illustrated in Fig. 5.5) varies from material to material.

The study of these types of viscoelasticity may be simplified by application of the Boltzman time–temperature superposition principle which provides master curves. This transposition for amorphous polymers is readily accomplished by use of a shift factor a_T calculated relative to a reference temperature T_R, which may be equal to T_g.

The relationship of the shift factor a_T to the reference temperature T_R and some other temperature T, which is between T_g and $T_g + 50K$, may be approximated by the Arrhenius equation:

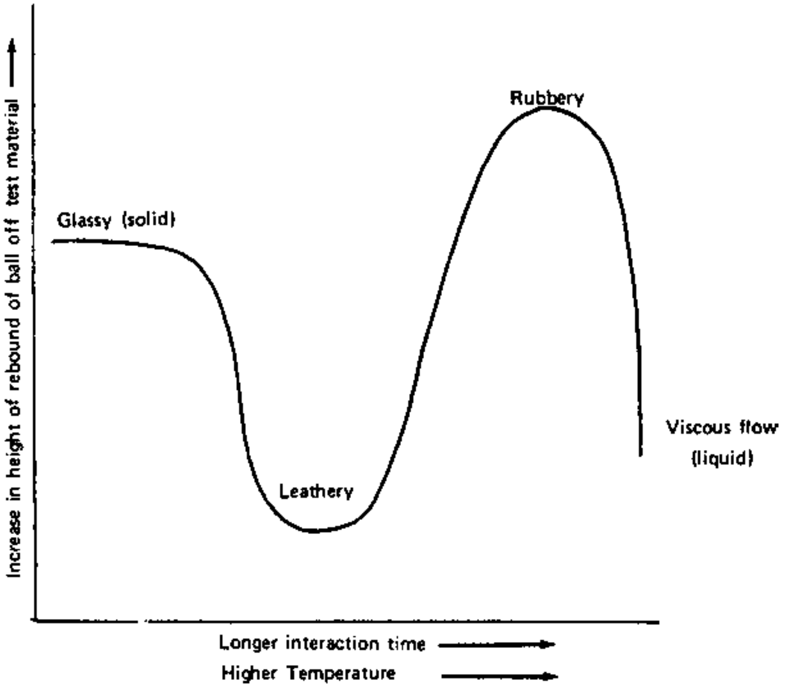


Figure 5.5 Regions of material response as a function of interaction (reaction) time and temperature.

$$\log a_T = -\frac{b}{2.3TT_g}(T - T_g) \tag{5.13}$$

According to the more widely used empirical Williams, Landel, and Ferry (WLF) equations, all linear, amorphous polymers have similar viscoelastic properties at T_g and at specified temperatures above T_g such as $T_g + 25°C$; and the constants C_1 and C_2 are related to holes or free volume. When T_g is the reference temperature, $C_1 = 17.44$ and $C_2 = 51.6$.

$$\log a_T = -\frac{C_1 (T - T_g)}{C_2 + (T - T_g)} \tag{5.14a}$$

Equations such as (5.13) and (5.14a) have been used to predict the long-range (long-time) behavior of materials from short-range (short-time) measurements. While this can be done under certain conditions with some success, such approaches have been employed in attempts to predict "long-term" failure of materials. One of the arguments employed to justify this involves the relationship between such equations and properties such as the flow of materials so that it can be argued that there is some relationship between long-range properties dependent on properties such as the flow of the material and its subsequent failure. Such arguments might be valid where failure is approached in some orderly fashion, but most failures are catastrophic dependent on the "weak link within the chain" rather than overall structure. Thus, care should be employed when utilizing such time–temperature superposition approaches to predict failure.

Response Time

We can get a first approximation of the physical nature of a material from its response time. For a Maxwell element, the relaxation time is the time required for the stress in a stress–strain experiment to decay to 1/e or 0.37 of its initial value. A material with a low relaxation time flows easily so it shows a relatively rapid stress decay. Thus, whether a viscoelastic material behaves as a solid or fluid is indicated by its response time and the experimental time scale or observation time. This observation was first made by Marcus Reiner who defined the ratio of the material response time to the experimental time scale as the Deborah number, D_n. Presumably, the name was derived by Reiner from the Biblical quote in Judges 5, Song of Deborah, where it says "The mountains flowed before the Lord."

$$D_n = \frac{\text{response time}}{\text{experimental time scale}} \tag{5.14b}$$

A high Deborah number designates the solid behavior of a viscoelastic material while a low Deborah number corresponds to a viscoelastic material behaving as a fluid. Thus, window glass has a high relaxation time at room temperature. Application of a stress to produce a little strain and looking for it to return to its approximate prestressed state will take a long time as we count our observation time in hours, days, and weeks. Thus, it would have a relatively high Deborah number under this observation time scale and be acting as a solid. Yet, if were to have as our observation scale millions of years, the return to the prestressed state would be rapid with the glass acting as a viscous liquid and having a low Deborah number. Again, this represents only a first approximation measure of the behavior of a material.

5.2 TYPICAL STRESS–STRAIN BEHAVIOR

Most physical tests involve nondestructive evaluations. For our purposes, there types of mechanical stress measurements can be described as pictured in Fig. 5.6. The ratio of stress to strain is called Young's modulus. This ratio is also called the modulus of elasticity and tensile modulus. It is calculated by dividing the stress by the strain:

$$\text{Young's modulus} = \frac{\text{stress (Pa)}}{\text{strain (mm/mm)}} \tag{5.15}$$

Large values for Young's modulus indicate that the material is rigid and resistant to elongation and stretching. Many synthetic organic polymers have a Young's modulus in the general range of about 10^5 psi; fused quartz has a Young's modulus of about 10^6, cast iron, tungsten, and copper have values in the range of 10^7; and diamond has a value of about 10^8.

Carswell and Nason assigned five classifications to polymers (Fig. 5.7). The soft and weak class (a) of polymers, including polyisobutylene, is characterized by a low modulus of elasticity, low yield (stress) point, and moderate time-dependent elongation. The Poisson ratio, i.e., the ratio of contraction to elongation, for class (a) polymers is 0.5, which is similar to that of liquids.

In contrast, the Poisson ratio of hard and brittle class (b) polymers, such as polystyrene, approaches 0.3. Class (b) polymers are characterized by a high modulus of elasticity, a poorly defined yield point, and little elongation before failure. However, class (c) poly-

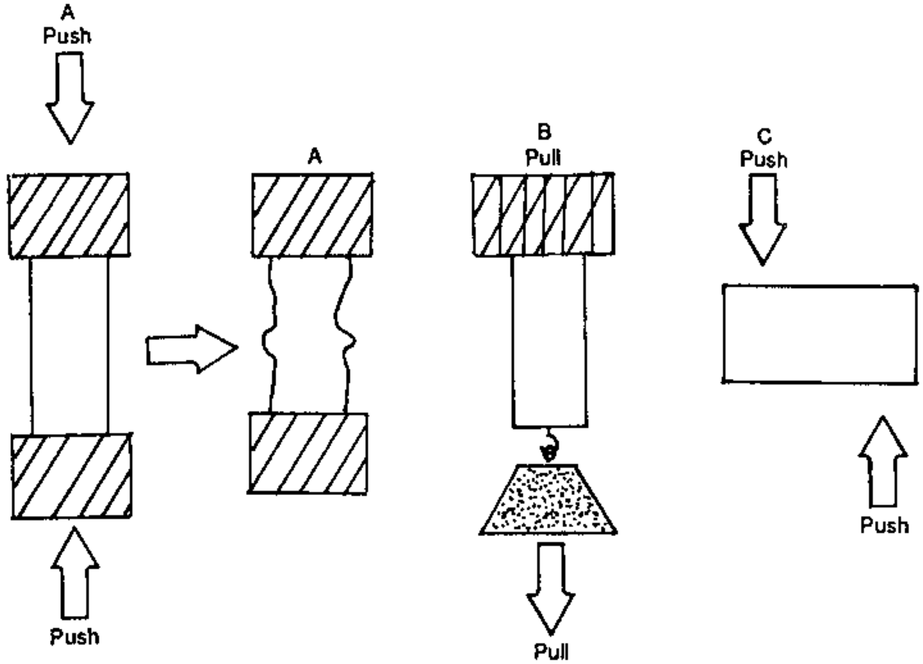


Figure 5.6 Major types of stress tests. (A) Compressive start and end. (B) Pulling stress or tensile strength. (C) Shear stress.

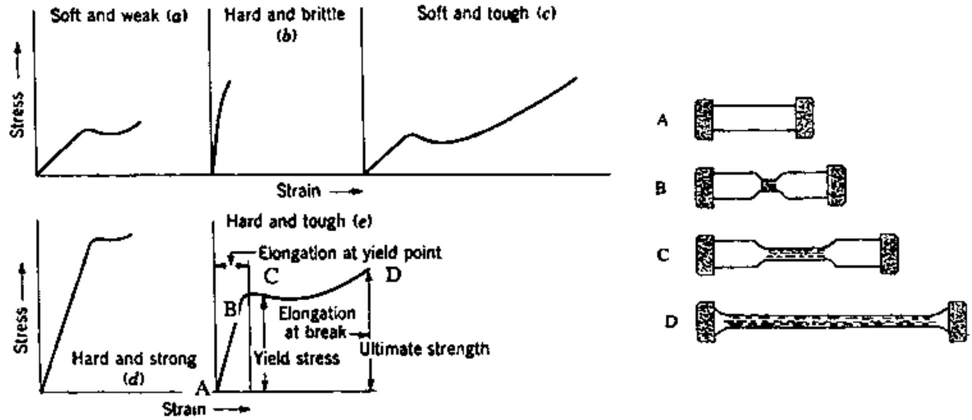


Figure 5.7 Typical stress–strain curves for plastics. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

mers, such as plasticized PVC, have a low modulus of elasticity, high elongation, a Poisson ratio of about 0.5–0.6, and a well-defined yield point. Since class (c) polymers stretch after the yield point, the area under the entire curve, which represents toughness, is greater than that in class (b).

Rigid PVC is representative of hard and strong class (d) polymers. These polymers have a high modulus of elasticity and high yield strength. The curve for hard and tough class (e) polymers, such as ABS copolymers, shows moderate elongation prior to the yield point followed by nonrecoverable elongation. In general, the behavior of all classes is Hookean prior to the yield point. The reversible recoverable elongation prior to the yield point, called the elastic range, is primarily the result of bending and stretching covalent bonds in the polymer backbone. This useful portion of the stress–strain curve may also include some recoverable uncoiling of polymer chains. Irreversible slippage of polymer chains is the predominant mechanism after the yield point.

Since these properties are time-dependent, class (a) polymers may resemble class (d) polymers if the stress is applied rapidly, and vice versa. These properties are also temperature-dependent. Hence, the properties of class (c) polymers may resemble class (b) polymers when the temperature is decreased. The effects of temperature and the mechanisms of elongation are summarized in Fig. 5.8.

As noted in Fig. 5.6, the major modes for applying stress are axial (compression or tension), flexural (bending or shear), and torsional (twisting—not shown). Superimposed on these can be any number of cyclic arrangements. Several common fluctuating stress–time modes are typically employed. In the regular and sinusoidal time-dependent mode the stress is applied, as both compressional and tensional, in a regular manner with respect to both time and amount. In a second cyclic arrangement stress, again both

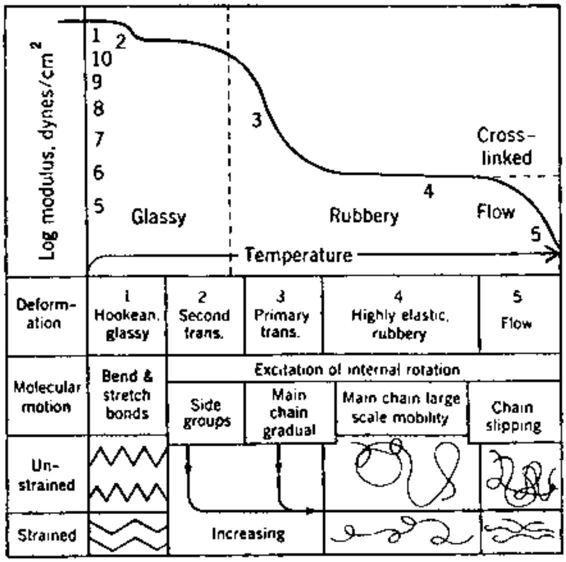


Figure 5.8 Characteristic effects of temperature on the properties of a typical polymer. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

compressional and torsional (pulling), is applied in an uneven manner with respect to amount and time so that the maxima and minima are asymmetrical relative to the zero-stress level.

Associated with such cyclic application of stress is the term *fatigue* to describe the failure that occurs after repeated application of stresses. The fatigue values are almost always less than measurements, such as tensile strength, obtained under static load. Thus, it is important that both static and cyclic measurements be made.

Data is often plotted as stress versus the logarithm of the number of cycles, N, to failure for each sample. Generally tests are taken using about two-thirds of the static parameter value. There is some limiting stress level below which fatigue does not occur (over some reasonably extended time). This value is called the *fatigue* or *endurance limit*. The *fatigue strength* is defined as the stress at which failure will occur for some specified number of cycles. *Fatigue life* is the number of cycles that are needed to cause failure.

Polymeric materials are dissimilar to metals in a number of respects. For instance, the range of strain–strain behavior is more complex and varied for polymers. Highly elastic polymers can exhibit a modulus as low as 7 M Pa or as high as 4 G Pa for stiff polymeric materials. The modulus values for metals are higher (50 to 400 M Pa) but not as varied. Tensile strengths for polymers are on the order of 100 M Pa for polymers and for some metal alloys 4000 M Pa. By comparison, polymers are more deformable with elastic polymers having elongations in excess of 1,000%, while even “moldable” metals having elongations not exceeding 100%. Further, stress–strain behavior for polymers is more temperature dependent in comparison to metals. For instance, Fig. 5.9 contains the

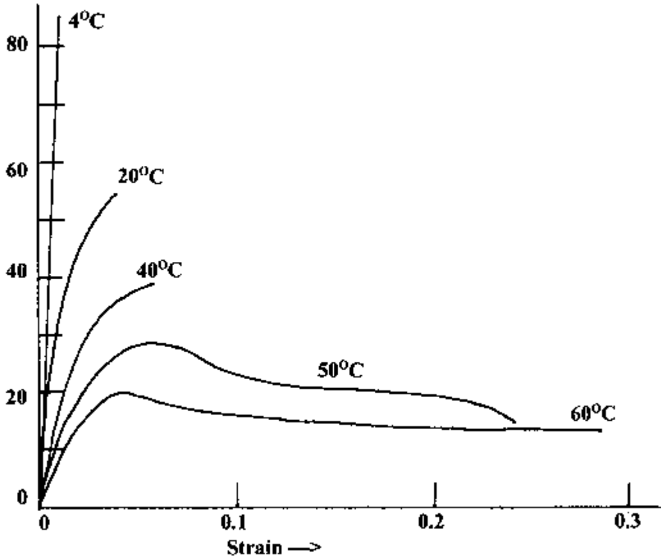


Figure 5.9 Influence of temperature on the stress–strain behavior of a sample of poly(methyl methacrylate). (From T. S. Carswell and H. K. Nason, “Effects of Environmental Conditions on the Mechanical Properties of Organic Plastics,” Symposium on Plastics, American Society for Testing Materials, Philadelphia, PA., 1944; Copyright, ASTM, 1916 Race Street, Philadelphia, PA, 19103. Reprinted by permission.)

stress–strain behavior for a poly(methyl methacrylate) (PMMA) material. Below the T_g the material behaves as a stiff, brittle solid similar to the behavior shown in Fig. 5.7b. As the temperature increases, the PMMA gains enough thermal energy to allow for some segmental mobility. The T_g varies greatly for PMMA depending upon the tacticity with isotactic PMMA having a T_g of about 45°C, and for syndiotactic the T_g is about 130°C. The material in Fig. 5.9 is presumably largely isotactic or atactic with a T_g of about 50–60°C. By 50°C, the material behaves as a soft and tough material (see Fig. 5.7c).

5.3 STRESS–STRAIN RELATIONSHIPS

Mechanical testing involves a complex of measurements including creep and shear strength, impact strengths, etc. Stress–strain testing is typically carried out using holders where one member is movable contained within a load frame. Studies typically vary with either the stress or strain fixed and the result response measured. In a variable-stress experiment a sample of given geometry is connected to the grips. Stress, or load, is applied, generally by movement of the grip heads either toward one another (compression) or away from one another (elongation). This causes deformation, or strain, of the sample. The deformation is recorded as is the force necessary to achieve this deformation. The applied load deformation is recorded and translated into stress–strain curves such as those given in Figs. 5.10 and 5.11.

The stress–strain behavior of materials is dependent on how the precise test is performed and the physical state of the material, such as whether the material is above or below its T_g.

Elastic solids under a constant rate of strain give responses as pictured in Fig. 5.10A. The overall input is shown on the left and the response on the right. Thus, constant strain begins at a and continues to b, where strain remains constant. The increase in strain produces analogous increases in stress (below the point of fracture) as shown in the corresponding graph on the right. The ordinates of such plots are scaleless, emphasizing the relative nature of the responses. The second set of plots in Fig 5.10B and C describes what occurs when a stress is applied rapidly from a to b, followed by release of this stress at c and returning to a. For materials below their T_g, the response is shown in B, where the strain response is immediate and the compliance is constant. The response shown in C is for materials between their T_g and T_m. There is some rapid response with strain from a to b (right side, C) at which point creep begins. Over the period of b to c, the creep is time (t)–dependent and can be described as follows:

$$\text{Compliance (t)} = \frac{\text{strain (t)}}{\text{stress}} \qquad (5.16)$$

Creep behavior is similar to viscous liquid flow, and materials exhibiting creep are described as viscoelastic materials. The linear behavior shown by Eq. (5.16) describes a linear time-dependent response, i.e., compliance and strain are linearly related to strain through inverse stress. This linear behavior is typical of most amorphous polymers for small strains over short periods of time. Further, the over-all effect of a number of such imposed stresses are additive.

Recovery occurs when the applied stress is relieved. Thus, amorphous polymers and polymers containing amorphous portions act both as elastic solids and viscous liquids above their T_g.

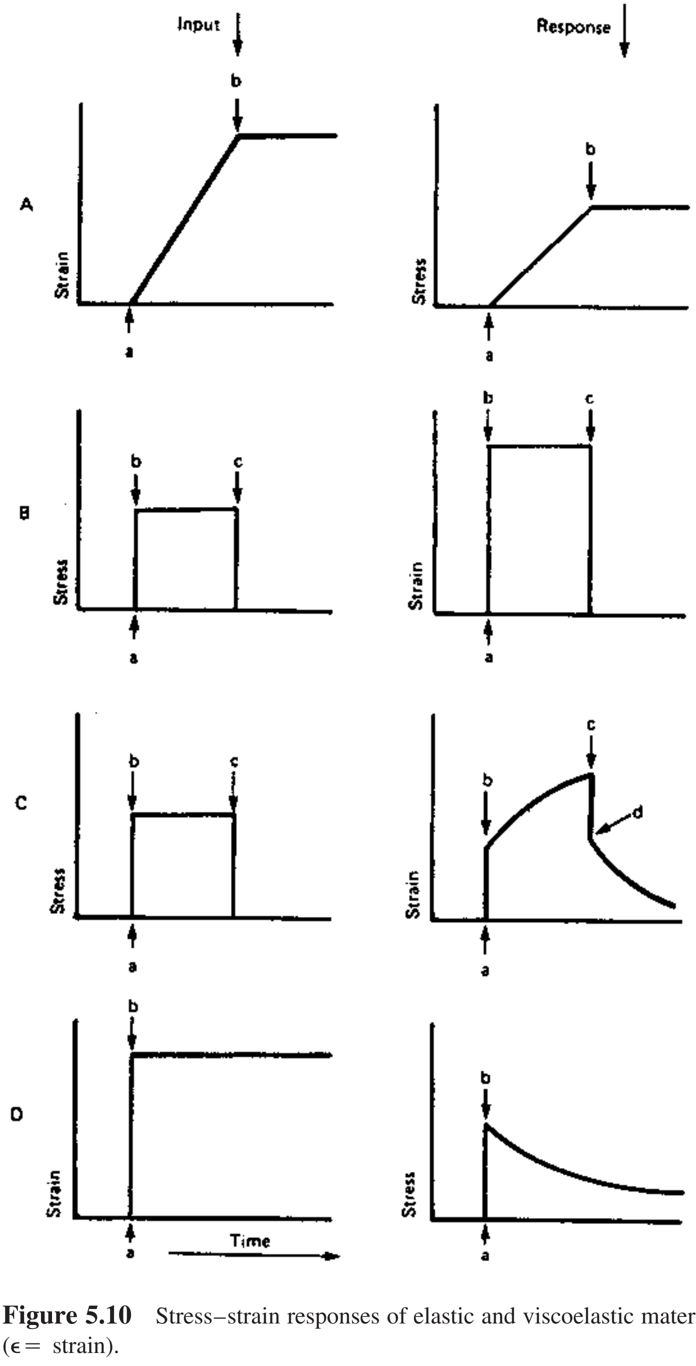
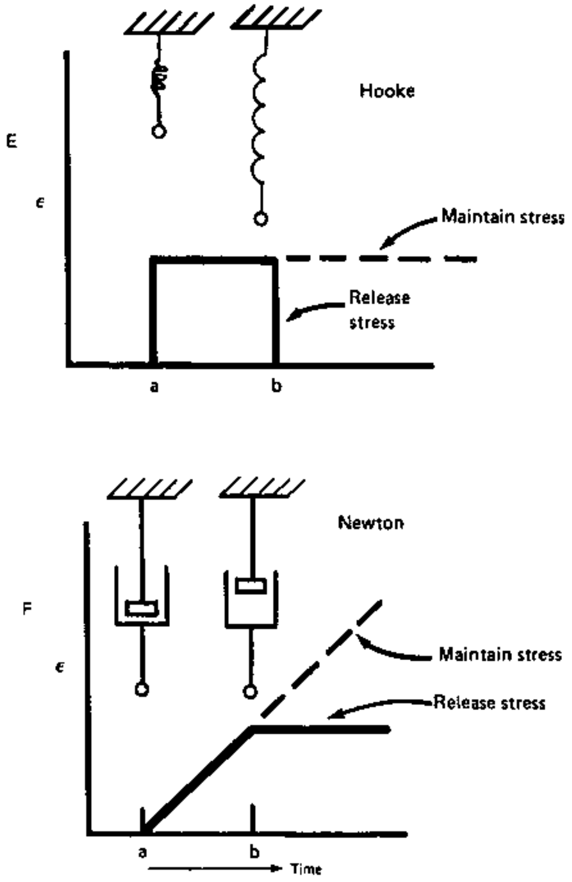


Figure 5.10 Stress–strain responses of elastic and viscoelastic materials and for various models ($\epsilon =$ strain).



The plots in Fig. 5.10D show the response where fixed strain is rapidly applied to a specimen. This stress is time dependent, and a decrease in stress, known as stress relaxation, occurs. This stress relaxation is also time-related and linearly related to stress as follows:

$$\text{Stress relaxation} = \frac{\text{stress (t)}}{\text{strain}} = \text{S(t)}/\gamma \tag{5.17}$$

As noted in Sec. 5.1, models have been developed in an attempt to illustrate stress–strain behavior. Plots for the stress–strain–time behavior of two of these models are shown in Fig. 5.11. The Maxwell model (Fig. 5.2) consists of a combination of a spring and a dash pot in series. The response of a constant stress by the Maxwell model given in Fig. 5.11A is described as follows:

$$\text{Strain} = (\text{compliance} + t/\eta)\ \text{stress} \tag{5.18}$$

Thus the strain increases linearly with time from b to d.

The response on a Maxwell model to application of rapid strain is illustrated in Fig. 5.11B and is described by

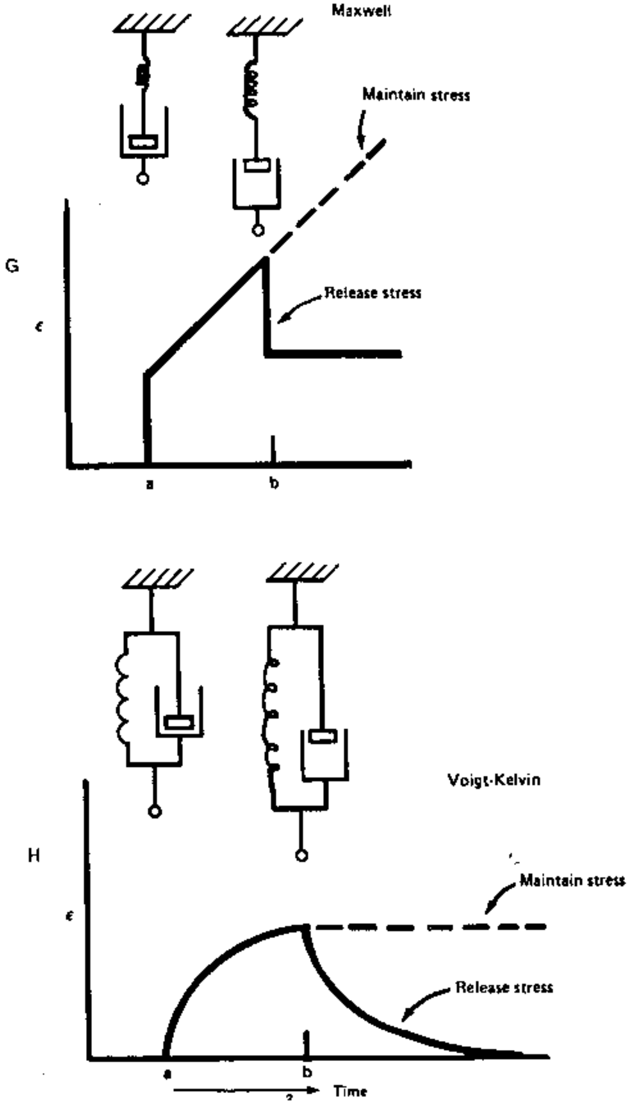


Figure 5.10 Continued.

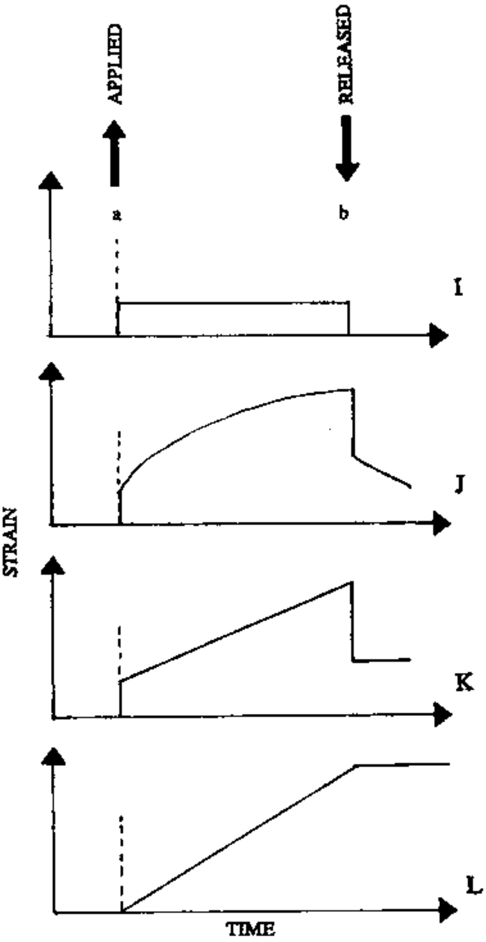
$$\text{Stress} = \text{strain}\ e^{-(t/\eta\ \text{compliance})/\text{compliance}} = \text{strain}\ e^{-t/\eta(\text{compliance})^2} \qquad (5.19)$$

A slow relaxation time, t, is a result of a weak spring or high viscosity.

The Voigt-Kelvin model (Fig. 5.3) contains the dash pot and spring in parallel. This combination prevents creep from occurring at a constant rate under a constant load. The response of the Voigt model to rapid stress is shown in Fig. 5.11C and described mathematically as follows:

$$\text{Strain} = \text{stress} \cdot \text{compliance}[1 - e^{-(t/\eta\ \text{compliance})}] \qquad (5.20)$$

For long periods of time, strain approaches η. Compliance and the ultimate strain



at d approach the strain developed in an elastic solid (Fig. 5.11C) of the same compliance. The strain response is retarded and not instantaneous. The product of η and compliance is characteristic of a retardation time for the system.

Additional models have been developed to attempt to illustrate the real behavior of materials and attempt to determine the particular critical structural parameters which determine physical properties.

Phase transition refers to a change of state. Most low molecular weight materials exist as solids, liquids, and gases. The transitions that separate these states are melting (or freezing) and boiling (or condensing). By contrast, polymers do not vaporize “intact” to a gaseous state, nor do they boil. The state of a polymer, i.e., its physical response character, depends on the time allotted for interaction and the temperature as well as the molecular organization (crystalline, amorphous, mix). The term *relaxation* refers to the time required for response to a change in pressure, temperature, or other applied parameter. The term *dispersion* refers to the absorption or emission of energy at a transition. In practice, the terms relaxation and dispersion are often employed interchangeably.

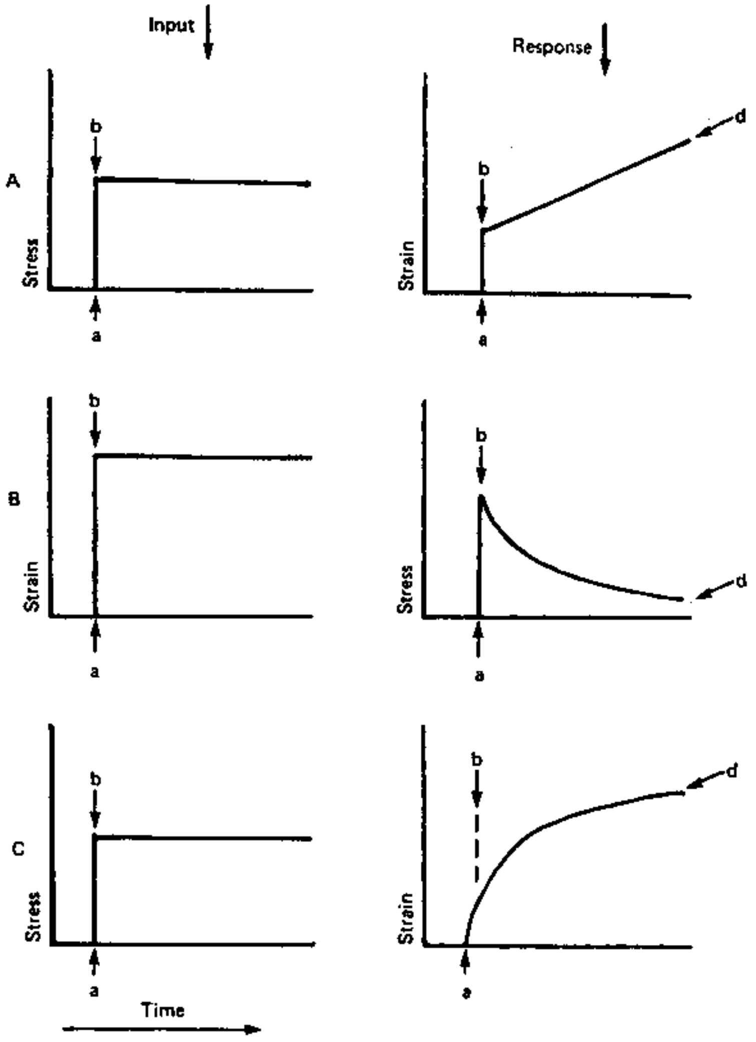


Figure 5.11 Stress–strain relationships for the Maxwell model (A and B) and the Voigt-Kelvin model (C).

Stress–strain plots can also be given for the various regions shown in Fig. 5.8. It is important to understand that many polymers with amorphous and crystalline regions will give a relationship such as pictured in Fig. 5.8. The region between 1 and 2 (Fig. 5.8) is called the Hookean glassy region or simply the glassy region (see also Fig. 5.5). Here there is a direct and relatively rapid response as stress is applied (a) and as stress is released (b) (Fig. 5.10I). The primary response to an applied stress is the “flexing” of bonds. The region between 2 and 3 (Fig. 5.8) is referred to as the leathery region, where there is both movement of side chains and the beginnings of main chain movement. Here the stress–strain behavior (Fig. 5.10J) can be considered to be sluggish and incomplete with respect to the application and release of the stress. The third and fourth regions (Fig.

5.8, from 3 to 4) are referred to as the rubbery regions and involve main chain movement. In region 3, from the area marked 3 to the plateau, the chain movement is more gradual, while the movement along the plateau is larger in scale. The stress–strain response is given in Fig. 5.10K and shows a rapid initial response followed by a more gradual response due to continued chain slippage. Some of this chain slippage is reversible, while some is not recoverable, resulting in a more or less permanent deformation of the material, often referred to as "creep." The fifth region, between 4 and 5 (Fig. 5.8), is referred to as the viscous or "flow" region where both "local" and "wholesale" chain movement (slippage) occurs in a largely nonreversible fashion (Fig. 5.10L).

These five regions (Fig. 5.8) make up the typical viscoelastic behavior of materials. It must be stated again that for a material to behave as a viscoelastic material it must be *above* the glass transition temperature, but not at the melting point. Thus, viscoelastic behavior occurs between the glass transition temperature (or range) and the melting temperature (or range). As noted in Sec. 5.1 and Fig. 5.5, these responses are time-dependent. Thus, an amorphous material or a material with both amorphous and crystalline regions above the glass transition temperature can behave as a glassy solid if the interaction is rapid, such as striking the material with a hammer, or it can act as a liquid-like material if a constant pull is exerted over a long time.

It must be remembered when dealing with a plot such as shown in Fig. 5.8, considering only the temperature aspect, that the glass transition temperature or range occurs around the transition from the "glassy" to the "rubbery" region and that the melting point occurs around the transition to the melt or "flow" region. Further, a material that is largely crystalline will act like a glass throughout the temperature region until reaching the melting temperature, at which juncture it will flow.

Finally, for Figs. 5.5 and 5.8, the thermodynamic driving forces for a deformed material to return to its original shape within the glassy region are mainly derived from enthalpy or energy, while the driving forces within the rubbery regions are largely entropy- or order-derived forces.

As seen in Eqs, (5.13), (5.18), and (5.19), the viscoelastic behavior of a material is both temperature- and time-dependent. One measure of the tendency to deform and rebound is to look at the stress relaxation of materials. Stress relaxation measurements are carried out by rapidly straining a material by tension to a predetermined but low strain level and measuring the stress needed to maintain this strain as a function of time. The stress needed to maintain the strain decreases with time due to a molecular relaxation processes with the various bond flexing and chain and segmental movements influencing this time. Figure 5.12 contains an idealized plot of the logarithm of the relaxation modulus as a function of temperature for a typical vinyl (largely) crystalline polymer, curve a, a lightly crosslinked vinyl amorphous polymer, curve b, and an amorphous vinyl polymer, line c. The T_g for the polymer is about 100°C and the T_m is about 200°C for this illustration.

Four general behavior patterns emerge and correspond to the same regions given in Fig. 5.5. The first region is called the glassy region. The Young's modulus for glassy polymers is somewhat constant over a wide range of vinyl polymers having a value of about 3×10^9 Pa. Here the molecular motions are restricted to vibrational and short-range rotational movement, often the former sometimes referred to as bond flexing. Two diverse approaches are often used to describe molecular motion in this range. The cohesive energy density (see Sec. 3.2) approach measures the energy theoretically required to move a detached segment into the vapor state per unit volume. Using polystyrene as an example, a value of about 3×10^9 Pa is calculated for the modulus. For largely hydrocarbon

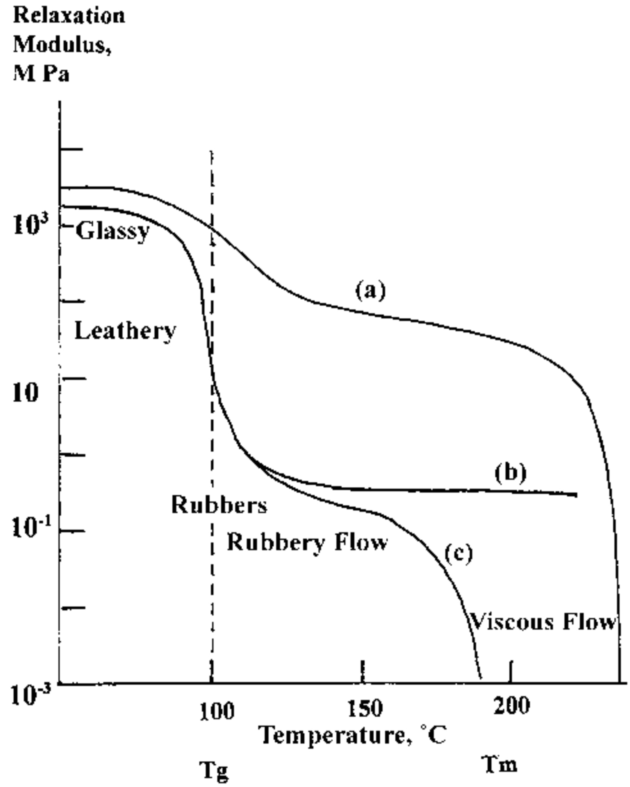


Figure 5.12 Logarithm of the relaxation modulus as a function of temperature for three polymer samples. Sample (a) is a (largely) crystalline vinyl polymer, sample (b) is an amorphous vinyl polymer that contains light crosslinking, and sample (c) is an amorphous vinyl polymer. The T_g for the amorphous polymer is about 100°C and the T_m for the crystalline polymer is about 200°C.

polymers, the cohesive energy density is typically similar to that of polystyrene and similar theoretical modulus values are found. The second approach is based on the carbon–carbon bonding forces as seen using vibrational frequencies. Again, values on the order of 3×10^9 Pa are found. Thus, in the glassy or solid region, below the T_g, only bond flexing and short range rotational movement occurs and the response time is fast for all three samples.

After the precipitous drop that occurs near the T_g, the modulus again is about constant, often on the order of 2×10^6 Pa, until the melting point is achieved. Over this rubbery range moderate segmental chain mobility is possible when stress/strain, is applied but wholesale mobility does not occur. Thus, somewhat elastic behavior occurs where segmental mobility allows the material to be stretched often to beyond 100% with an approximate return to the prestretched structure after release of the stress/strain. The rubbery region is particularly “interaction-time” sensitive. For instance, if applied stress/strain is maintained chain slippage will occur for noncrosslinked materials limiting return to the original molecular conformation after release of the stress/strain. For the same polymer the width of this plateau is somewhat molecular weight dependant such that the longer the polymer chains the broader the plateau.

As the temperature is increased, there is available sufficient energy to melt the crystalline polymer, the T_m, and prior to this for the amorphous polymer sufficient energy so that in both cases ready wholesale movement of polymer chains occurs. The entire polymer now behaves as a viscous liquid such as molasses. For the crosslinked material, wholesale mobility is not possible so it remains in the rubbery region until the temperature is sufficient to degrade the material.

The crystalline material does not exhibit a T_g and only a T_m so the leathery and rubbery areas are muted since only bond flexing is largely possible until the T_m is reached. The crystalline polymer is not totally crystalline so it exhibits "amorphous" polymer behavior corresponding to the amount of amorphous regions present. The lightly crosslinked material behaves similarly to the amorphous material through the first three regions but crosslinking prevents ready wholesale movement of the polymer chains preventing it to flow freely. Finally, the amorphous material, curve c, shows all four behaviors. Here, above the T_g, segmental movement occurs and the time required for the chains to return to a relaxed state is considerably greater than that required for simple return of bond flexing. Finally, as the temperature approaches the T_m, wholesale movement of the polymer chains becomes possible and the material behaves as a viscous liquid.

With dynamic mechanical analysis, (DMA), a sinusoidal applied stress or strain is applied. Application of the sinusoidal signal to an ideal viscous liquid gives a response that is 90° out of phase while application of the signal to a perfectly elastic material gives a response that is proportional to and in phase with the applied signal. Since plastics are viscoelastic with both liquid and elastic properties, the responses of materials to application of sinusoidal applied stresses and strains is generally between the two. The degree of response that is out of phase is called the phase angle, which in turn is a measure of the viscoelastic behavior of the material.

5.4 SPECIFIC PHYSICAL TESTS

Tensile Strength

Tensile strength can be determined by applying force to the test material until it breaks. It is defined by the following relationship:

$$\text{Tensile strength (Pascals)} = \frac{\text{force required to break sample (N)}}{\text{cross-sectional area (m}^2\text{)}} \tag{5.21}$$

Tensile strength, which is a measure of the ability of a polymer to withstand pulling stresses, is usually measured by pulling a dumbbell specimen, such as the one shown in Fig. 5.13, in accordance with ASTM D-638–72. These test specimens, like all others, must be conditioned under standard conditions of humidity (50%) and temperature (23°C) before testing.

The behavior of materials under applied stress and strains is given in Eq. (5.16) and Eq. (5.17). For typical tensile strength measurements, both ends of the specimen are clamped in the jaws of the test apparatus pictured in Fig. 5.13. One jaw is fixed and the other moves at specific increments. The stress and applied force is plotted against strain and elongation.

The elastic modulus (also called tensile modulus or modulus of elasticity) is the ratio of the applied stress to the strain it produces within the region where the relationship between stress and strain is linear. The ultimate tensile strength is equal to the force required to cause failure divided by the minimum cross-sectional area of the test sample.

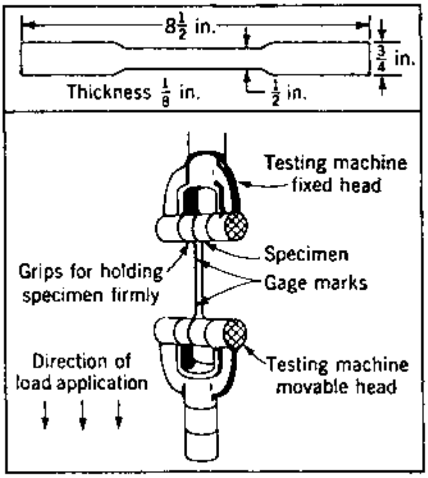


Figure 5.13 Typical tensile test. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

When rubbery elasticity is required for ample sample performance, a high ultimate elongation is desirable. When rigidity is required, it is desirable that the material exhibit a lower ultimate elongation. Some elongation is desirable since it allows the material to absorb rapid impact and shock. The total area under a stress–strain curve is indicative of overall toughness.

Pulling stress is the deformation of a test sample caused by application of specific loads. It is specifically the change in length of the test sample divided by the original length. Recoverable strain or elongation is called elastic strain. Here, stressed molecules return to their original relative locations after release of the applied force. Elongation may also be a consequence of wholesale movement of chains past one another. The wholesale movement of polymer chains is called creep or plastic strain. Here the strain is nonreversible with an end result of permanent deformation, i.e., elongation of the test material. Many samples undergo both reversible and irreversible strain.

As noted above, creep is the irreversible elongation caused by the application of force (such as a weight) over a specified time. If the change in length occurs at room temperature, it is called cold creep.

Elongation is measured by the tensile test shown in Fig. 5.13. The percentage of elongation is equal to the change in length divided by the original length of the specimen multiplied by 100, i.e.,

$$\%\ \mathrm{E1} = \frac{\Delta 1}{1} \cdot 100 \tag{5.22}$$

Problem

Determine the percentage elongation of a 10.0-cm polystyrene sample that increases in length to 10.2 cm when subjected to a tensile stress. The percentage elongation is determined employing $\%\ \mathrm{El} = (\Delta 1/1) \times 100 = [(10.2 - 10.0)/10.0] \times 100 = 2\%$.

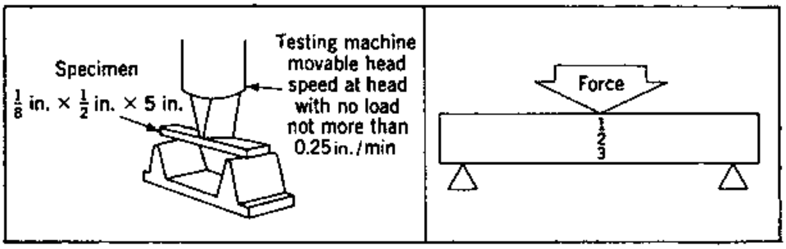


Figure 5.14 Typical flexural strength test. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

Flexural strength, or cross-breaking strength, is a measure of the bending strength or stiffness of a bar test specimen used as a simple beam in accordance with ASTM D-790.

The specimen is placed on the supports as pictured in Fig. 5.14. A load is applied in the center at a specified rate, and the loading at failure is called the flexural strength. However, since many materials do not break even after being greatly deflected, the actual flexural strength cannot be calculated. Instead, by agreement, the modulus at 5% strain is used for these specimens as a measure of flexural strength, i.e., the ratio of stress to strain when the strain is 5%.

Tensile Strength of Inorganic and Metallic Fibers and Whiskers

The tensile strength of materials is dependent on the treatment and form of the material. Thus, the tensile strength of isotropic bulk nylon-6,6 is less than that of anisotropic oriented nylon-6,6 fiber. Inorganics (Chapter 12) and metals also form fibers and whiskers with varying tensile strengths (Table 5.1). Fibers are generally less crystalline and larger than whiskers.

Many of these inorganic fibers and whiskers are polymeric including many of the oxides (including the so-called ceramic fibers), carbon and graphite materials, and silicon carbide. Carbon and graphite materials are similar but differ in the starting materials and the percentage carbon. Carbon fibers, typically derived from polyacrylonitrile (PAN), are about 95% carbon, while graphite fibers are formed at higher temperatures yielding a material with about 99% carbon.

Table 5.1 Tensile Strengths of Inorganic and Metallic Materials as a Function of Form

Material	Form	Tensile strength (MPa)
Graphite	Bulk	1000
	Fiber	2800
	Whisker	15,000
Glass	Bulk	1000
	Fiber	4000
Steel	Bulk	2000
	Fiber	4000
	Whisker	10,000

Table 5.2 Ultimate Tensile Strength of Representative Organic, Inorganic, and Metallic Fibers

Material	Tensile strength (MPa)	Tensile strength/density
Aluminum silica	4100	1060
Aramid	280	200
Beryllium carbide	1000	400
Beryllium oxide	500	170
Boron-tungsten boride	3450	1500
Carbon	2800	1800
Graphite	2800	1800
Polyethylene terephthalate	690	500
Quartz	900	400
Steel	4000	500
Titanium	1900	400
Tungsten	4300	220

These specialty fibers and whiskers exhibit some of the highest tensile strengths recorded (Table 5.2). They are employed in applications where light weight and high strength are required. Organics offer weight advantages, typically being less dense than most inorganic and metallic fibers (Table 5.2). Uses include in dental fillings, the aircraft industry, production of lightweight fishing poles, automotive antennas, bicycles, turbine blades, heat-resistant reentry vessels, golf club shafts, etc.

Many of these inorganic fibers and whiskers are utilized as reinforcing agents in composites.

Compressive Strength

Compressive strength is defined as the pressure required to crush a material. Compressive strength is defined by the relationship

$$\text{Compressive strength (Pa)} = \frac{\text{force (Newtons)}}{\text{cross-sectional area (m}^2\text{)}} \tag{5.23}$$

Compressive strength can be calculated by dividing the maximum compressive force in Newtons divided by the material's area in meters squared giving the compressive strength in units of Pascals.

Problem

Calculate the compressive strength for a material with a cross-section of 2 mm squared where the force required to crush the test sample is 200 kg.

$$\text{Force} = \text{mass times acceleration} = 200\text{ kg} \times 9.8\text{ m/s}^2$$

Since 9.8 m/s^2 is the gravity constant,

$$\text{Compressive strength} = \frac{200\text{ kg} \times 9.8\text{ m/s}^2}{2\text{ mm}^2 \times 10^{-6}\text{ m}^2/\text{mm}^2} = 9.8 \times 10^8\text{ Pa}$$

Compressive strength, or the ability of a specimen to resist crushing force, is measured by crushing a cylindrical specimen in accordance with ASTM D-695.

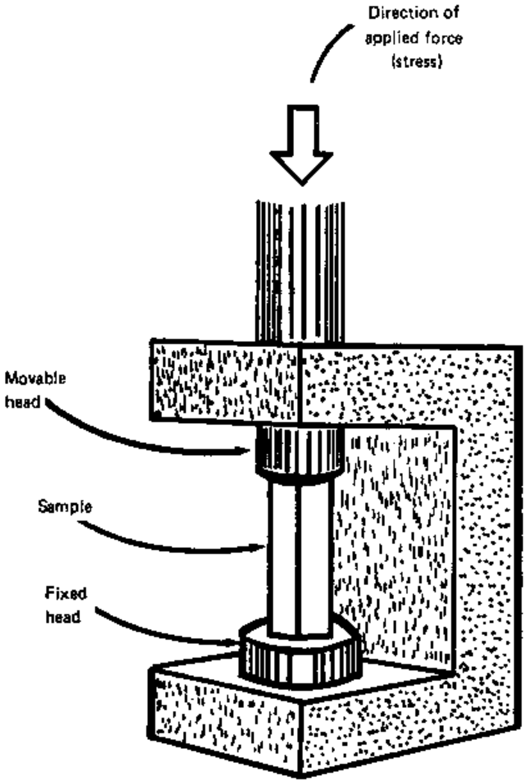


Figure 5.15 Representation of test apparatus for measurement of compression-related properties.

The test material is mounted in a compression tool as shown in Fig. 5.15. One of the plungers advances at a constant rate. The ultimate compression strength is equal to the load that causes failure divided by the minimum cross-sectional area. Since many materials do not fail in compression, strengths reflective of specified deformation are often reported.

Impact Strength

Impact strength is a measure of the energy needed to break a sample—it is not a measure of the stress needed to break the material. The term toughness is typically employed in describing the impact strength of a material. Toughness is a measure of the energy required (or absorbed) to break a sample. Toughness does not have a precise definition but is often described as the area under stress—strain curves such as shown in Fig. 5.7.

Impact strength tests fall within two main categories: (1) falling-mass tests and (2) pendulum tests. Figure 5.16 Illustrates two common falling-mass tests. The falling-mass assembly is typically employed for bulk specimens, whereas the dart test is used for films.

Izod and Charpy Impact Resistance

The Izod impact test (ASTM D-256) is a measure of the energy required to break a notched sample under standard conditions. A sample is clamped in the base of a pendulum testing

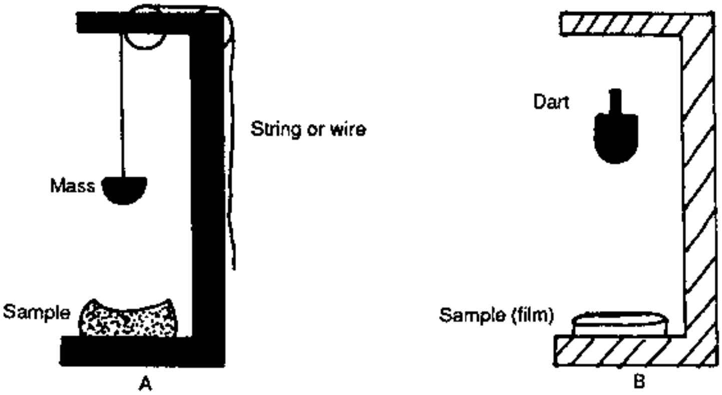


Figure 5.16 Assemblies used to measure the impact strength of (A) solids and (B) films.

apparatus so that it is cantilevered upward with the notch facing the direction of impact. The pendulum is released from a specified height. The procedure is repeated until the sample is broken. The force needed to break the sample is then calculated from the height and weight of the pendulum required to break the specimen. The Izod value is useful when comparing samples of the same polymer but is not a reliable indicator of toughness, impact strength, or abrasive resistance. The Izod test may indicate the need to avoid sharp corners in some manufactured products. Thus, nylon is notch-sensitive, gives relatively low Izod impact values, but is considered a tough material.

An unnotched or oppositely notched specimen (Fig. 5.17) is employed in the Charpy test (ASTM D-256).

Overall, impact strength tests are measures of toughness or the ability of a specimen to withstand a sharp blow, such as being dropped from a specific height or, as already noted, determined by the energy required to break a specimen.

Hardness

The term *hardness* is a relative term. Hardness is the resistance to local deformation that is often measured as the ease or difficulty for a material to be scratched, indented, marred, cut, drilled, or abraded. It involves a number of interrelated properties such as yield strength and elastic modulus. Because polymers present such a range of behavior—they are viscoelastic materials—the test conditions must be carefully described. For instance, elastomeric materials can be easily deformed, but this deformation may be elastic with the indentation disappearing once the force is removed. While many polymeric materials deform in a truly elastic manner returning to the initial state once the load is removed, the range of total elasticity is often small resulting in limited plastic or permanent deformation. Thus, care must be taken in measuring and in drawing conclusions from results of hardness measurements.

Hardness is related to abrasion resistance—resistance to the process of wearing away the surface of a material. The major test for abrasion resistance involves rubbing an abrader against the surface of the material under specified conditions (ASTM D-1044).

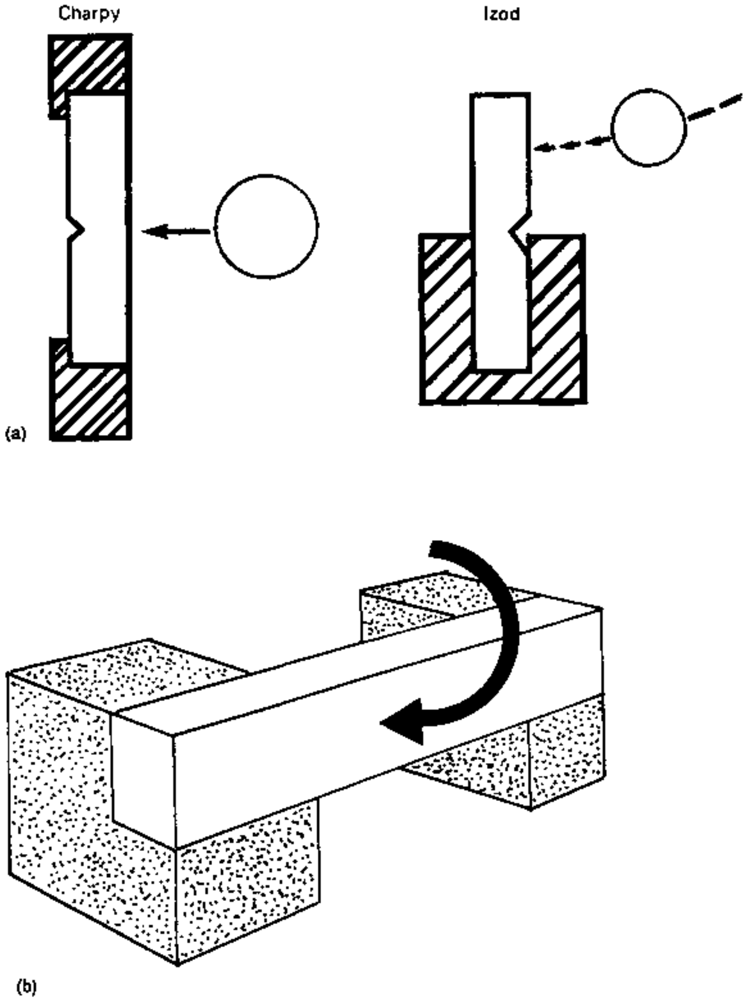


Figure 5.17 Pictorial description of (a) Izod- and Charpy-type pendulum impact tests, and (b) Charpy assembly using an unnotched sample.

Static indentation is most widely employed as a measure of hardness. Here, permanent deformation is measured. Hardness is often computed by dividing the peak contact load by the projected area of impression. The indention stresses, while concentrated within a concentrated area, are generally more widely distributed to surrounding areas. Because of the presence of a combination of elastic and plastic or permanent deformation, the amount of recovery is also determined. The combination of plastic and elastic deformation is dependent on the size, distribution and amount of various crystalline and amorphous regions as well as physical and chemical crosslinks and polymer structure. For a pyramidal shaped indenter, the pressure is nearly independent of depth of penetration. Here, the hardness value is approximately three times the yield stress for a material acting as a plastic. Following is a brief description of several of the more important test methods.

Brinell Hardness

Here, a steel ball is pushed against the flat surface of the test specimen. The standard test uses a ball of specific size pushed against the test surface with a given force.

Rockwell Hardness

Rockwell hardness tests [ASTM-D785–65 (1970)], depicted in Fig. 5.18, measure hardness in progressive numbers on different scales corresponding to the size of the ball indenter and force of the load.

The distance RB (Fig. 5.16) is used to calculate the Rockwell hardness values. While Rockwell hardness allows differentiation between materials, factors such as creep and elastic recovery are involved in determining the overall Rockwell hardness. Rockwell hardness may not be a good measure of wear qualities or abrasion resistance. For instance, polystyrene has a relatively high Rockwell hardness value, yet it is easily scratched.

In the most used Rockwell tests, the hardness number does not measure total indentation but only the irreversible portion after a heavy load is applied for a given time and reduced to a minor load for a given time. In Table 5.3, the "M" value is for a major load of 980 N (100 kgf) and a minor load of 98 N (10 kgf) using an indenter with a 6.25 mm diameter. The values given in the R column are for a lower initial load of 588 N (60 kgf) and a minor load of 98 N employing a larger indenter with a diameter of 12.5 mm.

Hardness may also be measured by the number of bounces of a ball or the extent of rocking by a Sward Hardness Rocker. Abrasion resistance may be measured by the loss in weight caused by the rubbing of the wheels of a Tabor-abrader (ASTM-D-1044).

The shore durometer is a simple instrument used to measure the resistance of a material to the penetration of a blunt needle. The values given in Table 5.3 are for one specific set of conditions and needle area.

Scratch hardness may be measured on the Mohs scale, which ranges from 1 for talc to 10 for diamond, or by scratching with pencils of specified hardness (ASTM-D-3363).

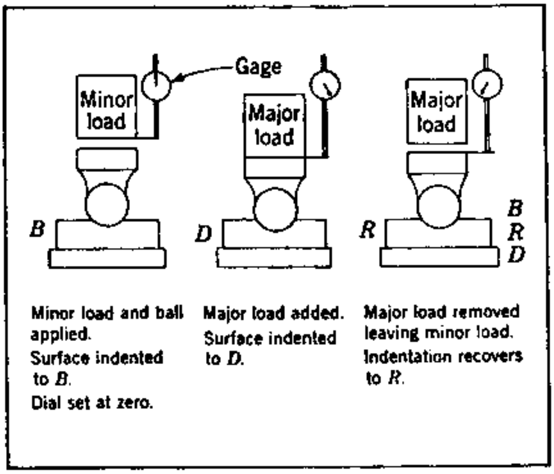


Figure 5.18 Rockwell hardness test. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

Table 5.3 Comparative Hardness Scales

Hardness scale					
		Rockwell			Type of material
Mohs	Brindell	M	R	Shore	
2 (Gypsum)	25	100			Hard plastics
	16	80			
	12	70	100	90	
	10	65	97	86	
	8	60	93	80	
	6	54	88	74	
1 (Talc)	5	50	85	70	
	2	32	ca50	89	Soft plastics
	1	23		42	
	0.8	20		38	Rubbery
	0.5	15		30	

Shear Strength

This test utilizes a punch-type shear fixture for testing flat specimens. The shear strength is equal to the load divided by the area. Thus, the sample is mounted in a punch-type shear fixture and punch-pushed down at a specified rate until shear occurs. This test is important for sheets and films but is not typically employed for extruded or molded products (Fig. 5.19).

Deformation Underload

The specimen, usually a 1/2-in. (12.7-mm) cube, is subjected to a specific pressure, typically 1000 psi. The deflection is measured shortly after the load is applied and again 24

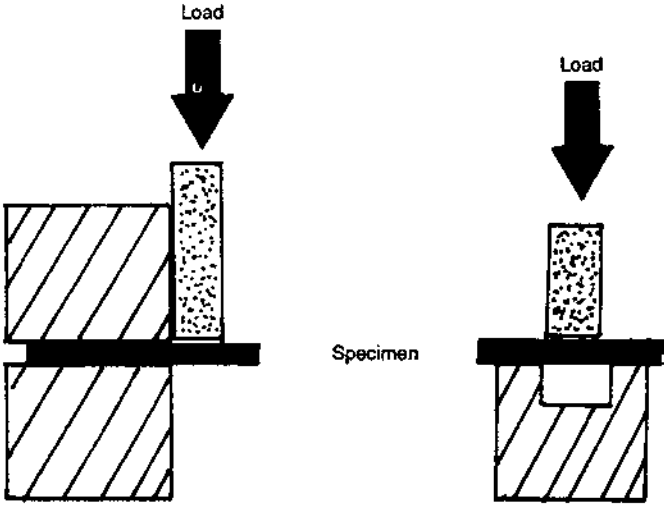


Figure 5.19 Two assemblies employed to measure shear strength.

h later. The deformation is calculated as the difference in sample height divided by the original height. This is a good measure of a material's ability to withstand constant, short-term compression but is not a satisfactory measure of long-term creep resistance.

Indentation Hardness

An indenter is pressed into the specimen, typically 1/4 in. (6.35 mm) thick. The indenter is applied to the face of the sample under different loading and the amount of indentation is measured. Many of the hardness tests, including the indentation hardness test (ASTM D2240) and the Rockwell hardness test, are time-dependent due to creep. The indentation hardness test is preferred for softer materials where creep is significant when measurements are taken shortly after the indenter has been applied to the sample.

Hardness is a general term which describes a combination of properties, such as the resistance to penetration, abrasion, and scratching. Indentation hardness of thermosets may be measured by a Barcol Impresser as described in ASTM D-2583–67. A shore durometer is used to measure the penetration hardness of elastomers and soft thermoplastics (ASTM D-2240) (Fig. 5.20).

The tests for change in dimensions of a polymer under long-term stress, called creep or cold flow (ASTM D-674), are no longer recommended by ASTM. ASTM D-671 describes suggested tests for fatigue or endurance of plastics under repeated flexure.

Additional Physical Tests

The brittleness temperature of plastics (ASTM D-746) and plastic film (ASTM D-1790–62) is the temperature at which 50% of test samples fail an impact test.

The environmental stress cracking (ESR) test pictured in Fig. 5.21 measures the time of failure of scored test samples that are bent 180° and inserted in a solution of standard detergent. Many failures of polymers are the result of molecular changes which can be detected by the use of appropriate instrumentation and testing.

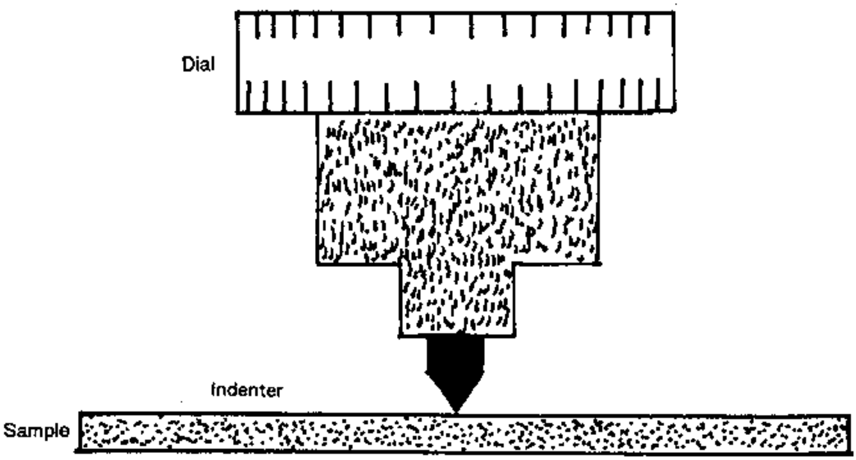


Figure 5.20 Sharp-pointed indenter employed in the measure of indentation hardness [Barcol instrument (ASTM D-2583-67)].

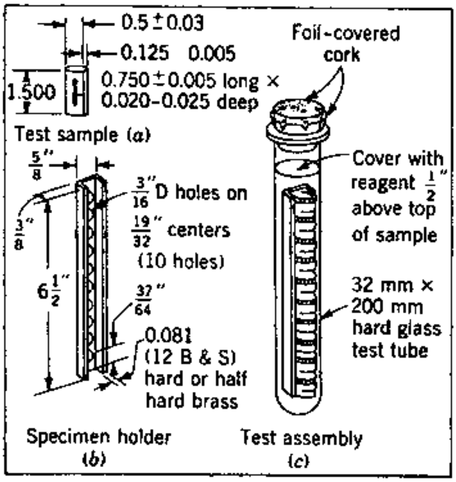


Figure 5.21 Environmental stress cracking test. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

Failure

The failure of materials can be associated with a number of parameters. Two major causes of failure are creep and fracture. The tensile strength is the nominal stress at the failure of the material. Toughness is related to ductility and, for stress–strain curves, toughness is measured by the area under a stress—strain curve taken to failure. For a material to be tough, it typically has a combination of stiffness and give. The shape of stress–strain curves and, subsequently, the toughness that will control the usefulness of the material where toughness is the important feature is due to many factors, including the interaction time or speed of the test. The Charpy and Izod impact tests interact with the test material rapidly, so that features related to brittleness are important relative to slower interactive tests, such as load creep tests, where factors associated with deformation play a more important role.

Calculations have been made to determine the theoretical upper limits with respect to the strength of polymeric materials. Real materials show behaviors near to those predicted by the theoretical calculation during the initial stress–strain determinations but vary greatly near the failure of the material. It is believed that the major reasons for the actual tensile strength at failure being smaller than calculated are related to imperfections, the nonhomogeneity of the polymeric structure. These flaws—molecular irregularities—act as the weak link in the polymer's behavior. These irregularities can be, for example, dislocations, voids, physical cracks, and energy concentrations.

Even with polymeric materials performing strengthwise below the theoretical limits, they have high strength-to-mass ratios. For instance, steel has a tensile strength of about 2000 MPa and density of 7800 kg/m^3, giving a strength-to-mass ratio of 0.26. Ultrahigh molecular weight polyethylene has a tensile strength of about 380 MPa and a density of 940 kg/m^3, giving a strength-to-mass ratio of 0.40—about double that of steel.

The fracture strengths of polymers are generally lower than those of metals and ceramics. The mode of failure for thermosets is generally referred to as brittle. Cracks, related to bond breakage, occur at points of excess stress. These create weak spots and may lead to fracture if the applied stress, appropriate to create bond breakage, continues. Fracture of thermoplastics can occur by either a ductile or brittle fashion, or some combination. Rapid application of stress (short reaction time), lower temperatures, application of the stress by a pointed or sharpened object all increase the chances that failure will occur by a brittle mechanism as expected. For instance, below the T_g thermoplastics behave as solids and above T_g polymer fracture increasingly moves to a ductile mode. Above the T_g they display some plastic deformation before fracture. For some thermoplastics, crazing occurs prior to fracture. These crazes are a form of defect and are associated with some yielding or void formation either through migration or elimination of some part of the polymer mix or because of chain migration through chain alignment or other mechanism. Fibrillar connections, from aligned chains, often form between void sides. If sufficient stress is continued, these fibrillar bridges are broken and the microvoids enlarge eventually leading to crack formation. Crazes can begin from scratches, flaws, molecular inhomogeneities, and molecular-level voids formed from chain migration (such as through crystallization) or small molecule migration from a site as well as application of stress.

SUMMARY

1. Rheology is the study of deformation and flow of materials. Polymers are viscoelastic materials, meaning they can act both as liquids and as solids.
2. Many of the rheological properties of materials is determined using stress–strain measurements.
3. Models are used to describe the behavior of materials. The fluid or liquid part of the behavior is described in terms of a Newtonian dash pot or shock absorber while the elastic or solid part of the behavior is described in terms of a Hookean or ideal elastic spring. The Hookean spring represents bond flexing, while the Newtonian dash pot represents chain and local segmental movement.
4. In general, the spring-like behavior is more important for polymers below their T_g whereas the dash pot behavior is more important for polymers above their T_g.
5. Mathematical relationships have been developed to relate models composed to varying degrees of these two aspects of behavior to real materials.
6. Stress—strain behavior is closely dependent on the particular conditions under which the experiment is carried out.
7. There are a number of specific tests that are used to measure various physical properties of materials. Many of these tests are described in detail by the various governing bodies that specify testing procedures and conditions.

GLOSSARY

A: area

alpha (α): Coefficient of expansion.

Barcol impressor: An instrument used to measure the resistance of a polymer to penetration or indentation.

biaxially stretching: Stretching of a film in two directions perpendicular to each other.

Bingham, E. C.: The father of rheology.

Bingham equation: $s - s_0 = \eta d\gamma/dt$.

Bingham plastic: A plastic that does not flow until the external stress exceeds a critical threshold value (s_0).

Charpy test: An impact resistance test.

CN: Symbol for cellulose nitrate.

coefficient of expansion: Change in dimensions per degree Celsius.

compressive strength: Resistance to crushing forces.

creep: Cold flow of a polymer.

dash pot: A model for Newtonian fluids consisting of a piston and a cylinder containing a viscous liquid.

ΔT: Difference in temperature.

dilatant: Shear thickening agent; describes a system where the shear rate does not increase as rapidly as the applied stress.

e: Symbol for base of Napierian logarithms ($e = 2.718$).

E: Energy of activation.

E: Symbol for Young's modulus of elasticity.

elastic range: The range on a stress—strain curve below the yield point.

ESCR: Environmental stress cracking.

flexural strength: Resistance to bending.

G: Symbol for shear modulus.

G: Symbol for Small's molar attraction constants.

gamma (γ): Symbol for strain.

Herschel-Buckley equation: $(s - s_0)^n = \phi(d\gamma/dt)$.

Hookean: Obeys Hooke's law.

Hooke's law: $s = E\gamma$.

impact strength: Measure of toughness.

isotropic: Having similar properties in all directions.

Izod: An impact resistance test.

K: Symbol for Kelvin or absolute temperature scale.

1: Length of a sample.

L: Thickness of test specimen in thermal conductivity test.

log: Common logarithm based on the number 10.

M: Symbol for Hayes chain stiffening constant.

Maxwell element or model: A model in which an ideal spring and dash pot are connected in series, used to study the stress relaxation of polymers.

modulus: Stress per unit strain. A high-modulus plastic is stiff and has very low elongation. Stiffness of a polymer.

Newtonian fluid: A fluid whose viscosity (η) is proportional to the applied viscosity gradient $d\gamma/dt$.

Newton's law: Stress is proportional to flow; $s = \eta(d\gamma/dt)$.

plasticizer: A nonvolatile solvent that is compatible with a hard plastic and reduces its T_g.

Poisson's ratio:The ratio of the percentage change in length of a specimen under tension to its percentage change in width.

pseudoplastic: Shear thinning agent; system where the shear rate increases faster than the applied stress.

relaxation time (τ): Time for stress of a polymer under constant strain to decrease to 1/e or 0.37 of its original value.

retardation time (τ): Time for the stress in a deformed polymer to decrease to 63% of the original value.
rheology: The science of flow.
rheopectic: A rheopectic liquid is one whose viscosity increases with time.
Rockwell hardness: A measure of indentation resistance.
s: Symbol for applied stress.
S: Symbol for entropy or measure of disorder.
shear: Stress caused by planes sliding by each other, as in a pair of shears or the greasing or polishing of a flat surface.
shear strength: Resistance to shearing forces.
shore durometer: A simple instrument used to measure resistance of a polymer to penetration of a blunt needle.
standard testing conditions: 23°C, 50% humidity.
stress (s): Force per unit area.
stress relaxation: The relaxation of a stressed specimen with time after the load is removed.
Sward hardness rocker: A rocking device used as a measure of hardness.
Tabor abrader: A mechanical rotator used to test abrasion resistance.
tensile strength: Resistance to pulling stresses.
thixotropic: A thixotropic liquid is one whose viscosity decreases with time.
V: Symbol for molar volume.
velocity gradient: $d\gamma/dt$, $\dot{\gamma}$, or flow rate.
viscoelastic: Having the properties of a liquid and a solid.
Voigt-Kelvin element or model: A model consisting of an ideal spring and dash pot in parallel in which the elastic response is retarded by viscous resistance of the fluid in the cylinder.
WLF: Williams, Landel, and Ferry equation for predicting viscoelastic properties at temperatures above T_g when these properties are known for one specific temperature such as T_g.
yield point: The point on a stress–strain curve below which there is reversible recovery.

EXERCISES

1. What is the difference between morphology and rheology?
2. Which of the following is viscoelastic: (a) steel, (b) polystyrene, (c) diamond, or (d) neoprene?
3. Define G in Hooke's law.
4. Which would be isotropic: (a) a nylon filament, (b) an extruded pipe, or (c) ebonite?
5. Would Poisson's ratio increase or decrease when (a) a plasticizer is added to rigid PVC and (b) the amount of sulfur used in the vulcanization of rubber is increased?
6. How would the slopes in Fig. 5.1a differ for polyisobutylene and polystyrene?
7. Which will have the higher relaxation time (τ): (a) unvulcanized rubber or (b) ebonite?
8. Which would be more readily extruded through a die: (a) a pseudoplastic or (b) a dilatant substance?
9. Which would increase in volume when stretched: (a) plasticized PVC or (b) rigid PVC?
10. According to the Eyring theory, which would have the higher percentage of holes: (a) polystyrene at its T_g or (b) have a rubber at its T_g?

11. In designing a die for a pipe with an outside diameter of 5 cm, would you choose inside dimensions of (a) less than 5 cm, (b) 5 cm, or (c) greater than 5 cm for the die?
12. At what temperature would the properties of polystyrene resemble those of hevea rubber at 35K above its T_g?
13. What is the significance of the constants in the WLF equation?
14. Define the proportionality constant in Newton's law.
15. What term is used to describe the decrease of stress at constant length with time?
16. In which element or model for a viscoelastic body, (a) Maxwell or (b) Voigt-Kelvin, will the elastic response be retarded by viscous resistance?
17. What is the most important standards organization in the United States?
18. What is the tensile strength (TS) of a test sample of PMMA 1.25 cm^2 with a thickness of 0.32 cm, if failure occurs at 282 kg?
19. What is the tensile strength (TS) of a test sample of PMMA which is 1.27 cm^2 with a thickness of 0.32 cm, if failure occurs at 282 kg?
20. What is the compressive strength (CS) of a 10-cm-long plastic rod with a cross section of 1.27 cm × 1.27 cm which fails under a load of 3500 kg?
21. If a sample of polypropylene measuring 5 cm elongates to 12 cm, what is the percentage of elongation?
22. If the tensile strength is 705 kg cm^{-2} and the elongation is 0.026 cm, what is the tensile modulus?
23. Define creep.
24. What is the value of Poisson's ratio for hevea rubber at (a) 25°C and (b) -65°C?
25. What changes occur in a polymer under stress before the yield point?
26. What changes occur in a stressed polymer after the yield point?
27. How can you estimate relative toughness of polymer samples from stress–strain curves?
28. What effect will a decrease in testing temperature have on tensile strength?
29. What effect will an increase in the time of testing have on tensile strength?
30. Is the statement correct that a polymer with a notched impact strength of 2 ft-lb per inch of notch is twice as tough as one with a value of 1 ft-lb per inch of notch?

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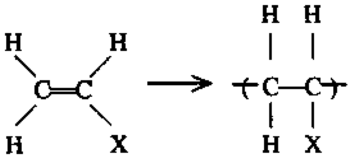
6

Step-Reaction Polymerization or Polycondensation Reactions

6.1 COMPARISON BETWEEN POLYMER TYPE AND KINETICS OF POLYMERIZATION

There is a large but not total overlap between the terms condensation polymers and stepwise kinetics and the terms addition (or sometimes the term vinyl) polymers and chain kinetics. In this section we will describe briefly each of these four terms and illustrate their similarities and differences.

The terms addition and condensation polymers were first proposed by Carothers and are based on whether the repeat unit of the polymer contains the same atoms as the monomer. An addition polymer has the same atoms as the monomer in its repeat unit.

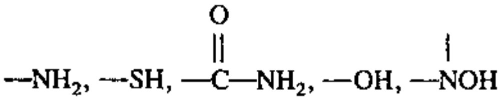


(6.1)

The atoms in the polymer backbone are usually carbon atoms. Condensation polymers contain fewer atoms within the polymer repeat unit than the reactants because of the formation of byproducts during the polymerization process, and the polymer backbone usually contains atoms of more than one element.

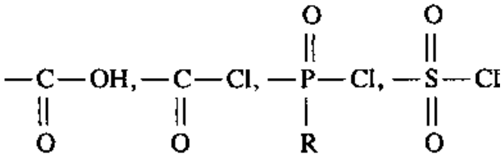
$$\text{X—A—R—A—X} + \text{Y—B—R}'\text{—B—Y} \rightarrow (\text{A—R—A—B—R}'\text{—B})_n \qquad (6.2)$$

where A—X can be



$$\text{—NH}_2,\ \text{—SH},\ \text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—NH}_2,\ \text{—OH},\ \text{—}\overset{|}{\text{N}}\text{OH}$$

and Y—B can be

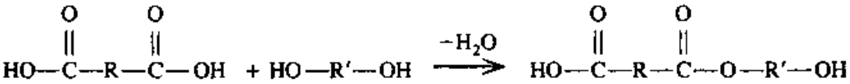


$$-\mathrm{C}(=\mathrm{O})-\mathrm{OH},\ -\mathrm{C}(=\mathrm{O})-\mathrm{Cl},\ -\mathrm{P}(=\mathrm{O})(\mathrm{R})-\mathrm{Cl},\ -\mathrm{S}(=\mathrm{O})_2-\mathrm{Cl}$$

The corresponding reactions can then be called addition polymerizations and condensation polymerizations.

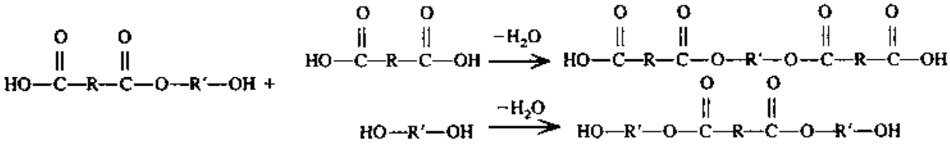
The term stepwise kinetics, or step-growth kinetics, refers to polymerizations in which the polymer's molecular weight increases in a slow, step-like manner as reaction time increases.

Polyesterification in a bulk polymerization process will be utilized to illustrate stepwise growth. Polymer formation begins with one dialcohol (diol) molecule reacting with one diacid molecule, forming what we will call one repeat unit of the eventual polyester.



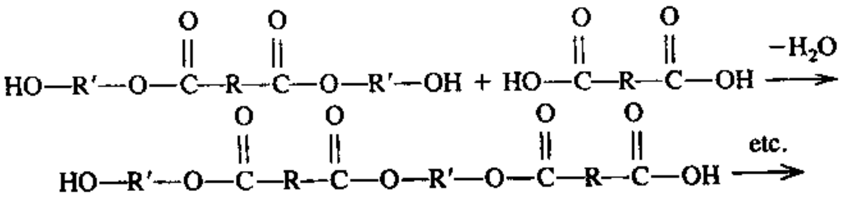
$$\mathrm{HO{-}C({=}O){-}R{-}C({=}O){-}OH} + \mathrm{HO{-}R'{-}OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{HO{-}C({=}O){-}R{-}C({=}O){-}O{-}R'{-}OH} \qquad (6.3)$$

This ester unit can now react with either an alcohol or acid group producing chains ending with either two active alcohol functional groups or two active acid groups.

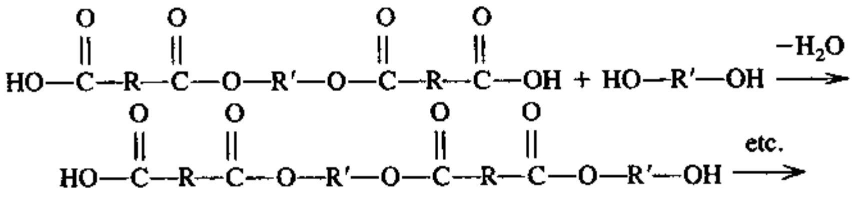


$$\mathrm{HO{-}C({=}O){-}R{-}C({=}O){-}O{-}R'{-}OH} + \begin{cases} \mathrm{HO{-}C({=}O){-}R{-}C({=}O){-}OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{HO{-}C({=}O){-}R{-}C({=}O){-}O{-}R'{-}O{-}C({=}O){-}R{-}C({=}O){-}OH} \\ \mathrm{HO{-}R'{-}OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{HO{-}R'{-}O{-}C({=}O){-}R{-}C({=}O){-}O{-}R'{-}OH} \end{cases} \qquad (6.4)$$

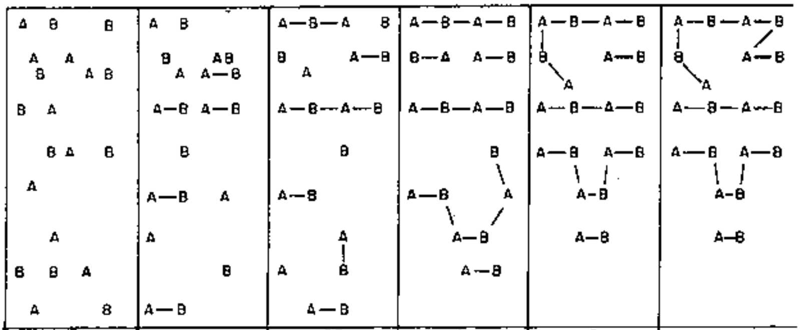
The chain with the two alcohol end groups can now condense with a molecule containing an acid end group, while the molecule with two acid end groups can react with a molecule containing an alcohol functional group. This reaction continues through the monomer matrix wherever molecules of the correct functionality having the necessary energy of activation and correct geometry collide. The net effect is that dimer, trimer, tetramer, etc., molecules are formed as the reaction progresses.



$$\mathrm{HO{-}R'{-}O{-}C({=}O){-}R{-}C({=}O){-}O{-}R'{-}OH} + \mathrm{HO{-}C({=}O){-}R{-}C({=}O){-}OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{HO{-}R'{-}O{-}C({=}O){-}R{-}C({=}O){-}O{-}R'{-}O{-}C({=}O){-}R{-}C({=}O){-}OH} \xrightarrow{\text{etc.}} \qquad (6.5)$$



$$\mathrm{HO{-}C({=}O){-}R{-}C({=}O){-}O{-}R'{-}O{-}C({=}O){-}R{-}C({=}O){-}OH} + \mathrm{HO{-}R'{-}OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{HO{-}C({=}O){-}R{-}C({=}O){-}O{-}R'{-}O{-}C({=}O){-}R{-}C({=}O){-}O{-}R'{-}OH} \xrightarrow{\text{etc.}} \qquad (6.6)$$



% Monomer Unreacted	100	50	25	0	0	0
% Functional Groups Unreacted	100	75	55	30	25	20
System Average DP*	0	1	1.25	1.67	2	2.5
Highest DP	0	1	2	3	3	4

Figure 6.1 Chain length dependency on reaction time and extent of monomer reaction for a stepwise kinetic model. Since DP refers to reacted units that compose a polymer and since each repeat unit is composed of one A and one B, the repeat unit is AB. By comparison, Fig. 6.4 represents the homopolymerization of vinyl units, and here each repeat unit is represented by one reacted A unit. *Includes only reacted portion.

Thus the reactants are consumed with very few long chains being formed throughout the system until the reaction progresses toward total reaction of the chains with themselves. The molecular weight of the total system increases slowly in a stepwise manner. Considering A molecules to be diacid molecules and B to represent dialcohol molecules (diols), we can construct a system containing 10 each of A and B, and assuming a random number of condensations of unlike functional groups, we can calculate changes in degree of polymerization (DP), maximum DP, and the percentage of unreacted monomer (Fig. 6.1). The maximum DP for this system is 10 AB units. For this system, while the percentage of reacted monomer increases rapidly, both system $\overline{\text{DP}}$ and highest DP increase slowly. Figures 6.1 and 6.3 graphically show this stepwise growth as a function of both reaction time and reaction temperature T. It should be noted that the actual plot of molecular

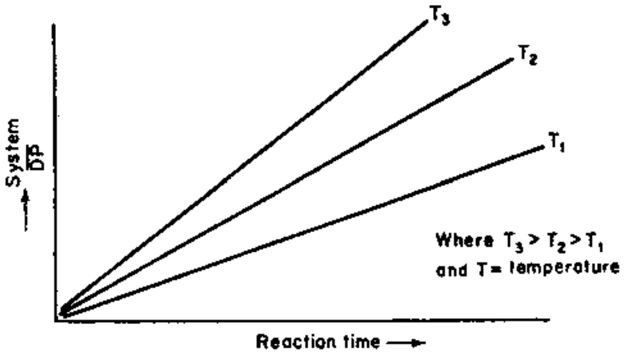


Figure 6.2 System molecular weight for stepwise kinetics as a function of reaction time and reaction temperature.

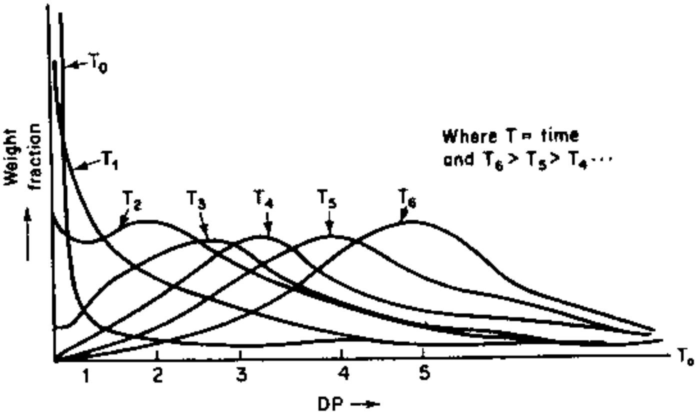
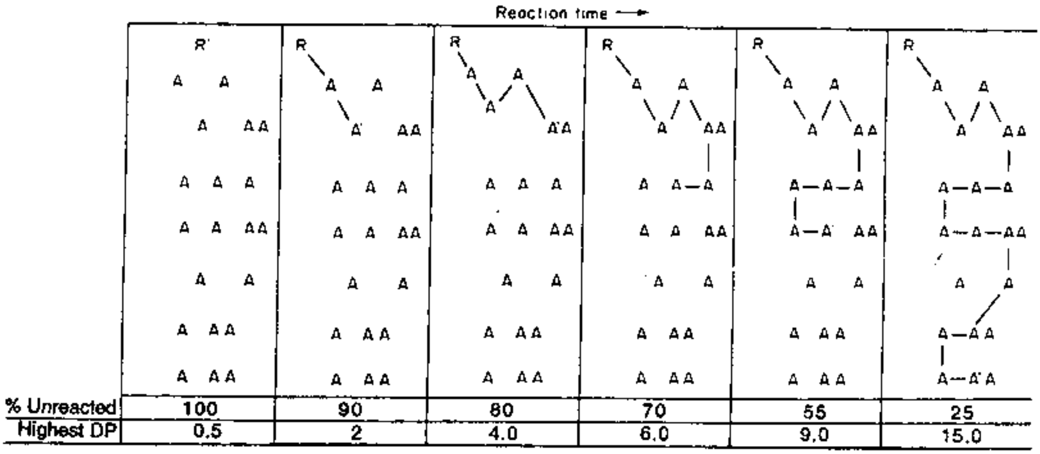


Figure 6.3 Molecular weight distribution for stepwise kinetics as a function of extent of reaction.

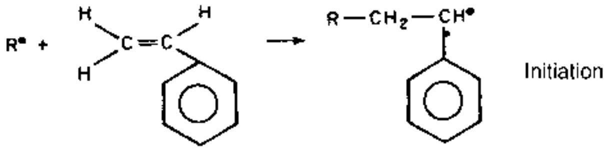
weight as a function of reaction time depends on the particular kinetic dependency for the particular system in question and need not be linear (Fig. 6.2).

Chain growth reactions require initiation to begin chain growth. Here, the initiation of a styrene molecule in a bulk reaction system occurs by means of a free radical initiator R′. This free radical quickly adds to a styrene monomer, shifting the unpaired free electron away from the adding free radical. This new active chain, which contains an unpaired electron, adds to another styrene monomer, with the unpaired electron shifting toward the chain end. This continues again and again, eventually forming a long polystyrene chain.

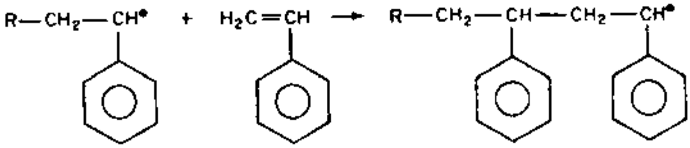


% Unreacted	100	90	80	70	55	25
Highest DP	0.5	2	4.0	6.0	9.0	15.0

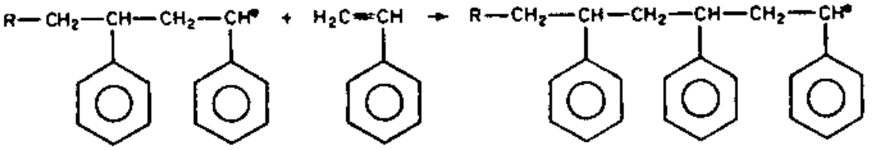
Figure 6.4 Molecular weight for chain-growth kinetics as a function of reaction time and extent of reaction. Please note that each repeat unit is represented by one reacted A unit. R is not included in the calculations since it represents the initiator radical in this system.



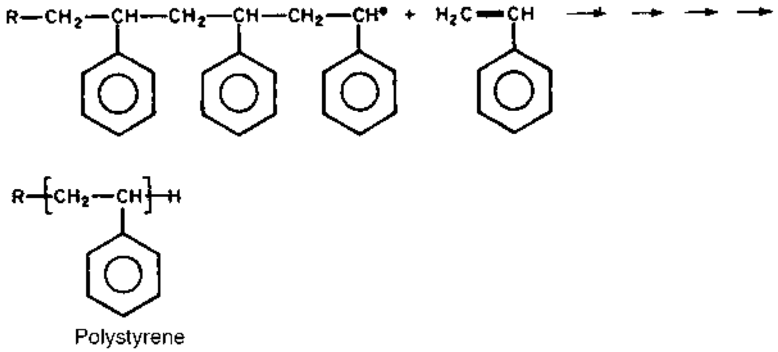
(6.7)



(6.8)



(6.9)



(6.10)

This growth continues until some termination reaction renders the chain inactive. Since polymerization occurs only with active chains (i.e., chains containing an unpaired electron), since the activation energy for chain growth is low, and since the concentration of growing chains is maintained at a low concentration at any given time, long chains are formed rapidly, and most of the styrene monomer remains unreacted. Again, we can construct a system illustrating the dependency of chain length on reaction extent and reaction time. Let us consider a system containing 20 styrene molecules (since styrene can react with itself the system can be constructed using only styrene molecules) (Fig. 6.4). While the $\overline{DP}$ for the entire system does not increase at a markedly different rate than for the stepwise kinetic model, the DP for the longest chain increases rapidly. Furthermore, the number of unreacted monomers remains high throughout the system, and in actual bulk and solution polymerizations of styrene, the number of unreacted styrene monomers far exceeds the number of polymer chains until very high conversion. For chain-growth polymerizations it is usual to plot molecular weight only of materials that had become free radicals as a function of reaction time, giving plots such as those in Figs. 6.5 and 6.6. Both average chain length and molecular weight distribution remain approximately constant throughout much of the polymerization.

Most addition polymers are formed from polymerizations exhibiting chain-growth kinetics. This includes the typical polymerizations of the vast majority of vinyl monomers,

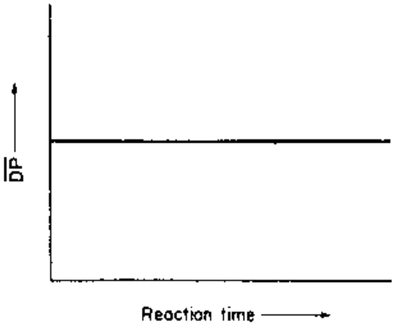
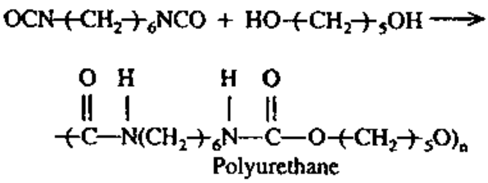


Figure 6.5 Idealized average molecular weight of formed polymers as a function of reaction time for chain-growth kinetics.

such as ethylene, styrene, vinyl chloride, propylene, methyl acrylate, and vinyl acetate. Furthermore, most condensation polymers are formed from systems exhibiting stepwise kinetics. Industrially this includes the formation of polyesters and polyamides. Thus, there is a large overlap between the terms addition polymers and chain-growth kinetics and the terms condensation polymers and stepwise kinetics (Table 6.1). The following are examples illustrating the lack of adherence to the above.

1. The formation of polyurethanes and polyureas typically occurs in the bulk solution through kinetics that are clearly stepwise, and the polymer backbone is heteroatomed, yet there is not byproduct released through the condensation of the isocyanate with the diol or diamine because condensation occurs through internal rearrangement and shift of the hydrogen—neither necessitating expulsion of a byproduct.



$$\mathrm{OCN{\leftarrow}CH_2{\rightarrow}_6NCO + HO{\leftarrow}CH_2{\rightarrow}_5OH \longrightarrow}$$
$$\mathrm{{\leftarrow}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}(CH_2{\rightarrow}_6\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}O{\leftarrow}CH_2{\rightarrow}_5O)_n} \tag{6.11}$$

Polyurethane

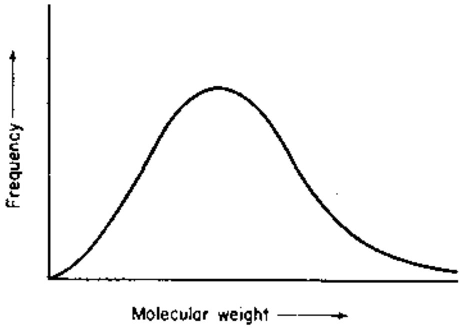
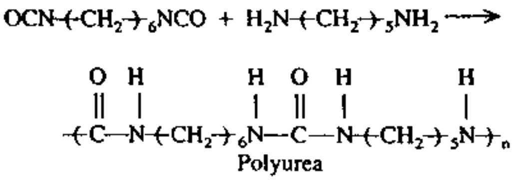


Figure 6.6 Molecular weight distribution for chain-growth kinetics.

Table 6.1 Comparison of Stepwise and Chainwise Polymerizations

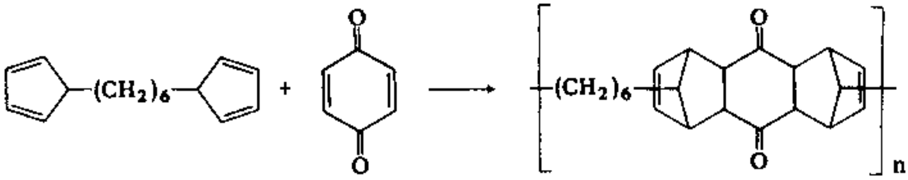
Chain	Step
Growth occurs by addition of one unit at a time	Any two molecular units can react
Monomer concentrations decrease steadily throughout the polymerization	Monomer disappears early in the reaction
Polymer chains are formed from the beginning of the polymerization and throughout the process	Polymer chain length increases steadily during the polymerization
Average chain length for reacted species remains approximately constant throughout the polymerization	Average molecular weight for the reaction (for the reacted species) increases throughout the polymerization
As reaction time is increased, polymer yield increases but molecular weight remains about the same	High “extents” of reaction are required to obtain high chain lengths
Reaction mixture contains almost only unreacted monomer, polymer, and very little growing polymer chain	Reaction system contains various stages, chain lengths, of product present in a calculable distribution



$$OCN-(CH_2)_6-NCO + H_2N-(CH_2)_5-NH_2 \longrightarrow -\!\!\left[\overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} -(CH_2)_6- \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} -(CH_2)_5- \overset{H}{\overset{|}{N}} \right]_n \quad (6.12)$$

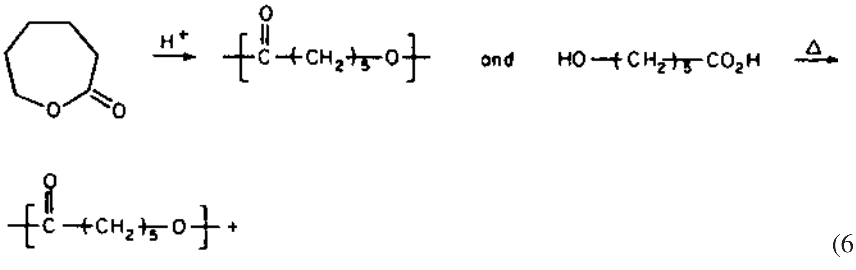
Polyurea

2. The Diels-Alder condensation of a bisdiene and benzoquinone forms an addition polymer, i.e., one possessing only carbon atoms in its backbone and where no byproduct is produced. Yet the polymer is formed through a stepwise kinetic process.



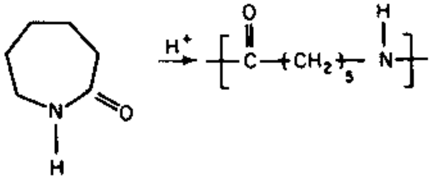
(6.13)

3. Internal esters (lactones) are readily polymerized by chainwise, acid-catalyzed ring openings without expulsion of a byproduct, yet the resulting polyester is a condensation polymer exhibiting a heteroatomed polymeric backbone. Furthermore, the six-carbon polyester is also formed using typical stepwise polycondensation of ω-hydroxycarboxylic acid



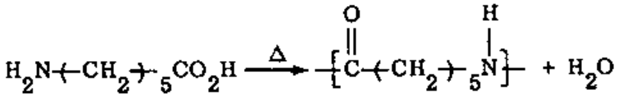
(6.14)

4. Nylon-6, a condensation polymer, is readily formed from either the internal amide (lactam) through a chainwise kinetic polymerization, or from the stepwise reaction of the ω-amino acid.



(6.15)

and



$$H_2N{+}CH_2{+}_5CO_2H \xrightarrow{\Delta} {+}\overset{O}{\overset{\|}{C}}{+}CH_2{+}_5\overset{H}{\overset{|}{N}}{+} + H_2O \qquad (6.16)$$

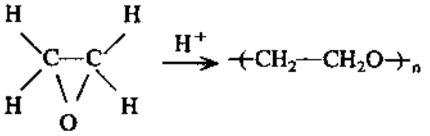
5. A hydrocarbon polymer can be made using the typical chainwise polymerization of ethylene, through a steplike polymerization of 1,8-dibromooctane utilizing the Wurtz reaction, or through the chain-growth boron trifluoride-catalyzed polymerization of diazomethane.

$$CH_2{=}CH_2 \longrightarrow {+}CH_2{-}CH_2{+}_n \qquad (6.17)$$

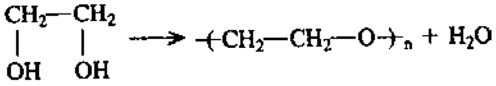
$$BrH_2C{+}CH_2{+}_6CH_2\,Br \xrightarrow{2Na} {+}CH_2{+}_n + 2NaBr \qquad (6.18)$$

$$CH_2N_2 \xrightarrow{BF_3} {+}CH_2{+}_n + N_2 \qquad (6.19)$$

6. Polyethylene oxide can be formed from either the usual catalyzed chain polymerization of ethylene oxide or the less usual condensation polymerization by means of a stepwise reaction of ethylene glycol.



(6.20)



$$\underset{OH}{\underset{|}{CH_2}}{-}\underset{OH}{\underset{|}{CH_2}} \longrightarrow {+}CH_2{-}CH_2{-}O{+}_n + H_2O \qquad (6.21)$$

7. Further interfacially formed condensation polymers, such as polyurethanes, polyesters, polyamides, and polyureas, typically are formed on a microscopic level in a chain-growth manner due to comonomer migration limits and the highly reactive nature of the reactants employed for such interfacial polycondensations.

Thus, a number of examples illustrate the lack of total overlap associated with describing the nature of the polymer backbone and the kinetics of formation for that polymer.

6.2 INTRODUCTION

While condensation polymers account for only a small percentage of all synthetic polymers, most natural polymers are of the condensation type. The first all-synthetic polymer, Bakelite, was produced by the stepwise condensation of phenol and formaldehyde, and many of the other synthetic polymers available before World War II were produced using stepwise polycondensations of appropriate reactants.

As shown by Carothers in the 1930s, the chemistry of condensation polymerizations is essentially the same as classic condensation reactions leading to the formation of monomeric esters, amides, and so on. The principal difference is that the reactants used for polymer formation are bifunctional instead of monofunctional.

The kinetics for stepwise polycondensation reactions and the kinetics for monofunctional aminations and esterifications, for example, are similar. Experimentally, both kinetic approaches are found to be essentially identical. Usual activation energies (30–60 kcal/mol) require only about one collision in 10^{12}–10^{15} to be effective in producing product at 100°C, whereas for the vinyl reactions between R′ and a vinyl-monomer, activation energies are small (2–5 kcal/mol), with most collisions of proper orientation being effective in lengthening the chain. This is in agreement with the slowness of stepwise processes compared with radical chain processes. The rate constant of individual polycondensation steps is essentially independent of chain length, being similar to that of the "small-molecule" condensation. This is responsible for the stepwise growth pattern of polycondensations, since addition of a unit does not greatly increase the reactivity of the growing end, whereas for radical and ionic vinyl polymerizations the active radical and ionic site is transmitted to the growing chain end, giving a reactive end group. Table 6.2 contains a listing of a number of industrially important condensation polymers.

6.3 STEPWISE KINETICS

While more complicated situations can occur, we will consider only the kinetics of simple polyesterification. The kinetics of most other common condensations follows an analogous pathway.

For uncatalyzed reactions where the diacid and diol are present in equimolar amounts, one diacid is experimentally found to act as a catalyst. The experimental rate expression dependencies are described in the usual manner as follows:

$$\text{Rate of polycondensation} = -\frac{d[A]}{dt} = k[A]^2\,[D] \qquad (6.22)$$

where [A] represents the diacid concentration and [D] the diol concentration. Where [A] = [D], we can write

$$-\frac{d[A]}{dt} = k[A]^3 \qquad (6.23)$$

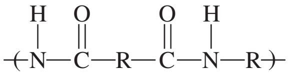
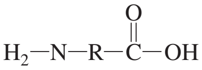
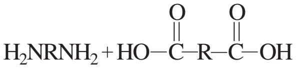
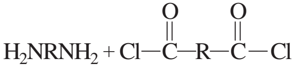
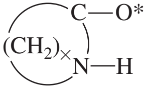
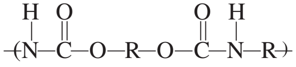
Rearrangement gives

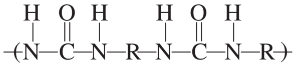
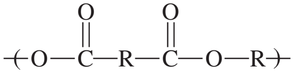
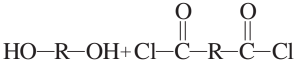
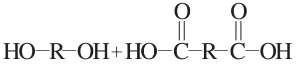
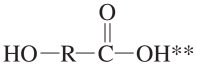
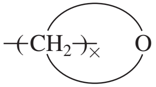
$$-\frac{d[A]}{[A]^3} = kdt \qquad (6.24)$$

Integration of the above over the limits of $A = A_0$ to $A = A_t$ and $t = 0$ to $t = t$ gives

$$2kt = \frac{1}{[A_t]^2} - \frac{1}{[A_0]^2} = \frac{2}{[A_t]^2} + \text{constant} \qquad (6.25)$$

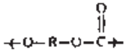
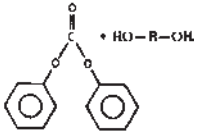
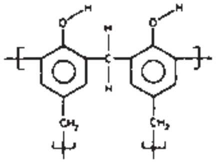
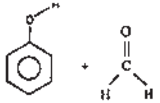
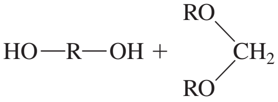
Table 6.2 Structures, Properties, and Uses of Some Synthetic Condensation-Type Polymers

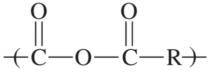
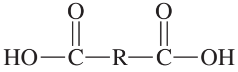
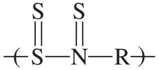
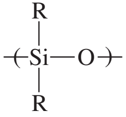
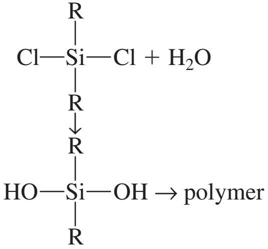
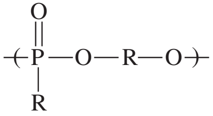
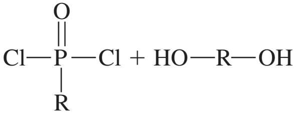
Type (common name)	Characteristic repeating unit	Typical reactants	Typical properties	Typical uses
Polyamide (nylon)	 $-\!\left(\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{O}}{\overset{\Vert}{\text{C}}}-\text{R}-\overset{\text{O}}{\overset{\Vert}{\text{C}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\text{R}\right)\!-$	 $H_2-N-R-\overset{\text{O}}{\overset{\Vert}{\text{C}}}-OH$  $H_2NRNH_2 + HO-\overset{\text{O}}{\overset{\Vert}{\text{C}}}-R-\overset{\text{O}}{\overset{\Vert}{\text{C}}}-OH$  $H_2NRNH_2 + Cl-\overset{\text{O}}{\overset{\Vert}{\text{C}}}-R-\overset{\text{O}}{\overset{\Vert}{\text{C}}}-Cl$ 	Good balance of properties, high strength, good elasticity and abrasion resistance, good toughness, favorable solvent resistance, only fair outdoor weathering properties, fair moisture resistance	Fibers—about 1/2 of all nylon fiber produced goes into tire cord (tire replacement); rope, cord, belting and fiber cloths, thread, hose, undergarments, dresses; plastics—use as an engineering material, substitute for metal in bearings, cams, gears rollers: jackets on electrical wire
Polyurethane	 $-\!\left(\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{O}}{\overset{\Vert}{\text{C}}}-O-R-O-\overset{\text{O}}{\overset{\Vert}{\text{C}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\text{R}\right)\!-$	OCN—R—NCO + HO—R—OH	Elastomers—good abrasion resistance, hardness, good resistance to grease and good elasticity; fibers—high elasticity, excellent rebound; coatings—good resistance to solvent attack and abrasion, good flexibility and impact resistance; foams—good strength per weight, good rebound, high impact strength	Four major forms utilized—fibers, elastomers, coatings cross-linked foams; elastomers—small industrial wheels, heel lifts; fibers—swimsuits and foundation garments; coatings—floors where high impact and abrasion resistance are required, such as dance floors; bowling pins; foams—pillows, cushions

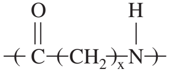
Polyurea	 $-\!\left(\overset{\overset{H}{\vert}}{N}-\overset{\overset{O}{\Vert}}{C}-\overset{\overset{H}{\vert}}{N}-R-\overset{\overset{H}{\vert}}{N}-\overset{\overset{O}{\Vert}}{C}-\overset{\overset{H}{\vert}}{N}-R\right)\!-$	$OCN-R-NCO+H_2N-R-NH_2$	High T_g, fair resistance to greases, oils, solvents	Not widely utilized
Polyester	 $-\!\left(O-\overset{\overset{O}{\Vert}}{C}-R-\overset{\overset{O}{\Vert}}{C}-O-R\right)\!-$	 $HO-R-OH+Cl-\overset{\overset{O}{\Vert}}{C}-R-\overset{\overset{O}{\Vert}}{C}-Cl$  $HO-R-OH+HO-\overset{\overset{O}{\Vert}}{C}-R-\overset{\overset{O}{\Vert}}{C}-OH$  $HO-R-\overset{\overset{O}{\Vert}}{C}-OH$**	High T_g, high T_m, good mechanical properties to about 175 °C, good resistance to solvent and chemicals; fibers—good crease resistance and rebound, low moisture absorption, high modulus, good resistance to abrasion; film—high tensile strength (almost equal to that of some steel), stiff, high resistance to failure on repeated flexing, fair tear strength, high impact strength	Fibers—garments, permanent press and “wash and wear” garments, felts, tire cord; film—magnetic recording tape, high grade films
Polyether	$-\!\left(O-R\right)\!-$		Good thermoplastic behavior, water solubility, generally good mechanical properties, moderate strength and stiffness (similar to polyethylene)	Sizing for cotton and synthetic fibers; stabilizers for adhesives, binders, and film-formers in pharmaceuticals; thickeners; production of films

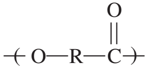
(*continued*)

Table 6.2 Continued

Type (common name)	Characteristic repeating unit	Typical reactants	Typical properties	Typical uses
Polycarbonate	 $-\!\!(O-R-O-\overset{\overset{O}{\|}}{C})\!\!-$	$COCl_2$ + HO—R—OH 	Crystalline thermoplastic with good mechanical properties, high impact strength, good thermal and oxidative stability, transparent, self-extinguishing, low moisture absorption	Machinery and business
Phenol-formaldehyde resins			Good heat resistance, dimensional stability and resistance to cold flow; good resistance to most solvents; good dielectric properties	Used in molding applications; phonograph records; electrical, radio, televisions, appliance, and automotive parts where their good dielectric properties are of use; filler; missile nose cones; impregnating paper; varnishes; decorative laminates for wall coverings; electrical parts, such as printed circuits; countertops, toilet seats; coatings for electrical wire; adhesive for plywood, sandpaper, brake linings and abrasive wheels
Polyacetal	$-\!\!(O—R—O—CH_2)\!\!-$	 $HO—R—OH + (RO)_2CH_2$		No large industrial application

Polyanhydride	 $-\!(C(=O)-O-C(=O)-R)\!-$	 $HO-C(=O)-R-C(=O)-OH$	Intermediate physical properties Medium to poor T_g and T_m, medium physical properties	No large industrial application
Polysulfides	$-\!(S_x-R)\!-$  $-\!(S(=S)-N(=S)-R)\!-$ $-\!(S-S-R)\!-$	$Cl-R-Cl + Na_2S_x$ $Cl-R-Cl + Na_2S_4$ $Cl-R-Cl$ (oxidation)	Outstanding oil and solvent resistance, good gas impermeability, good resistance to aging and ozone, bad odors, low tensile strength, poor heat resistance	Solvent resistant and gas resistant elastomer—such as gasoline hoses and tanks, gaskets, diaphragms
Polysiloxane	 $-\!(SiR_2-O)\!-$	 $Cl-SiR_2-Cl + H_2O \rightarrow HO-SiR_2-OH \rightarrow$ polymer	Available in a wide range of physical states—from liquids to greases, to waxes to to resins to rubbers; excellent high and moderate low temperature physical properties; resistant to weathering and lubricating oils	Fluids—cooling and dielectric fluids, in waxes and polishes, as antifoam and release agents, for paper and textile treatment; elastomers—gaskets, seals, cable and wire insultation, hot liquids and gas condults, surgical and prosthetic devices, sealing compounds; resins—varnishes, industrial paints, encapsulating and impregnating agents
Polyphosphate and polyphosphonate esters	 $-\!(P(=O)(R)-O-R-O)\!-$	 $Cl-P(=O)(R)-Cl + HO-R-OH$	Good fire resistance, fair adhesion, moderate moisture stability, fair temperature stability	Additive to promote flame retardance, adhesive for glass (since refractive index of some esters is about the same as that of glass), certain pharmaceutical applications, surfactant

*repeat unit  $-\!(C(=O)-(CH_2)_x-N(H))\!-$

**repeat unit  $-\!(O-R-C(=O))\!-$

It is convenient to express Eq. (6.25) in terms of extent of reaction p, where p is defined as the fraction of functional groups that have reacted at time t. Thus $1 - p$ is the fraction of groups unreacted. A_t is in turn $A_0 \times (1 - p)$, i.e.,

$$A_t = A_0(1 - p) \tag{6.26}$$

Substitution of the expression for A_t from Eq. (6.26) into Eq. (6.25) and re-arrangement gives

$$2A_0^2kt = \frac{1}{(1 - p)^2} + \text{constant} \tag{6.27}$$

A plot of $1/(1 - p)^2$ as a function of time should then be linear with the slope $2A_0^2\,k$ from which k is determinable. Determination of k at different temperatures enables the calculation of activation energy.

The number-average degree of polymerization $\overline{DP}_N$ can be expressed as

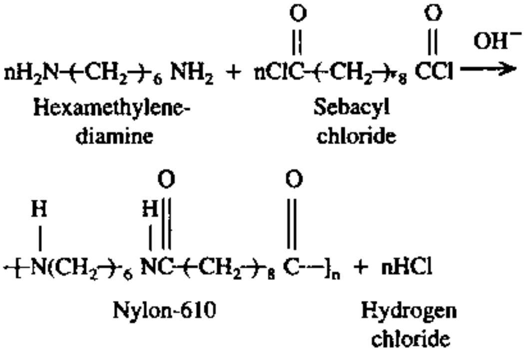
$$\overline{DP}_N = \frac{\text{number of original molecules}}{\text{number of molecules at a specific time t}} = \frac{N_0}{N} = \frac{A_0}{A_t} \tag{6.28}$$

Thus,

$$\overline{DP}_N = \frac{A_0}{A_t} = \frac{A_0}{A_0(1 - p)} = \frac{1}{1 - p} \tag{6.29}$$

The relationship given in Eq. (6.29) is called the Carothers equation because it was first found by Carothers while working with the synthesis of nylons (polyamides). For an essentially quantitative synthesis of polyamides where p is 0.9999, the $\overline{DP}$ was found to be approximately equal to 10,000, the value calculated using Eq. (6.29).

$$\overline{DP}_N = \frac{1}{1 - p} = \frac{1}{1 - 0.9999} = \frac{1}{0.0001} = 10{,}000 \tag{6.30}$$



$$n\text{H}_2\text{N}\text{+}(\text{CH}_2)_6\text{NH}_2 + n\text{Cl}\overset{\text{O}}{\overset{\|}{\text{C}}}(\text{CH}_2)_8\overset{\text{O}}{\overset{\|}{\text{C}}}\text{Cl} \xrightarrow{\text{OH}^-} \left[\overset{\text{H}}{\overset{|}{\text{N}}}(\text{CH}_2)_6\overset{\text{H}}{\overset{|}{\text{N}}}\overset{\text{O}}{\overset{\|}{\text{C}}}(\text{CH}_2)_8\overset{\text{O}}{\overset{\|}{\text{C}}}\right]_n + n\text{HCl} \tag{6.31}$$

The $\overline{DP}$ of 10,000 calculated above for nylon-610 is more than adequate for a strong fiber. Actually, it would be difficult to force such a high molecular weight polymer through the small holes in the spinneret in the melt extrusion process used for fiber production.

The many possible nylons are coded to show the number of carbon atoms in the amine and acid repeat units, respectively. The most widely used nylon fiber is nylon-66.

The high value of p would be decreased and the value of $\overline{DP}$ also decreased accordingly if a competing cyclization reaction occurred.

Since the values of k at any temperature may be determined from the slope ($2kA_0$) of the line when $1/(1 - p)^2$ is plotted against t, one may determine $\overline{DP}_N$ at any time t from the expression

$$(\overline{DP}_N)^2 = 2kt[A_0]^2 + \text{constant} \tag{6.32}$$

Returning again to consider the synthesis of polyesters, generally much longer reaction times are required to effect formation of high polymer in uncatalyzed esterifications than for acid- or base-catalyzed systems. For catalyzed systems since the added acid or base is a catalyst, its apparent concentration does not change with time; thus it need not be included in the kinetic rate expression. In such cases the reaction follows the rate expression

$$\text{Rate of polycondensation} = -\frac{d[A]}{dt} = k[A][B] \tag{6.33}$$

For [A] = [B] we have

$$-\frac{d[A]}{dt} = k[A]^2 \tag{6.34}$$

which gives on integration and subsequent substitution

$$kt = \frac{1}{A_t} - \frac{1}{A_0} = \frac{1}{A_0(1 - p)} - \frac{1}{A_0} \tag{6.35}$$

Rearrangement gives

$$A_0kt = \frac{1}{1 - p} - 1 = \overline{DN}_N - 1 \tag{6.36}$$

which predicts a linear relationship of $1/(1 - p)$ with reaction time. This is shown in Fig. 6.7.

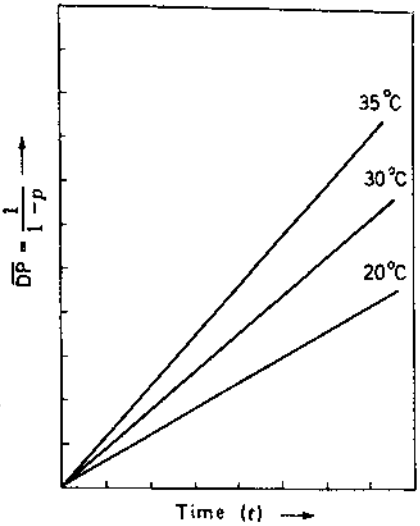


Figure 6.7 Plot of chain length as a function of reaction time for the acid-catalyzed condensation of ethylene glycol with terephthalic acid. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

For such second-order reactions, $\overline{DP}_N = [A_0]\,kt + 1$. The effect of time on $\overline{DP}$ can be demonstrated using $A_0 = 2$ mol/L and $k = 10^{-2}$ L/mol-s at the reaction times of 1800, 3600, 5400 s. Thus, $\overline{DP}$ increases from 37 to 73 to 109.

$$\begin{aligned}\overline{DP} &= 1 + (10^{-2})\,(2)\,(1800) = 37\\ \overline{DP} &= 1 + (10^{-2}\,(2)\,(3600) = 73\\ \overline{DP} &= 1 + (10^{-2})\,(2)\,(5400) = 109\end{aligned} \tag{6.37}$$

Useful high molecular weight linear polymers are not obtained unless the value for the fractional conversion p is at least 0.990, i.e., a $\overline{DP}$ greater than 100.

It is important to note that the rate constant k for reactions of monofunctional compounds is essentially the same as that for difunctional compounds, and hence these k values, which are essentially unchanged during the reaction, can be used for polycondensation reactions. Likewise, as is the case with reactions of small molecules, the rate constant k increases with temperature in accordance with the Arrhenius equation shown below. The energies of activation (E_a) are also comparable to those for monofunctional reactants.

$$k = Ae^{-E_a/RT} \tag{6.38}$$

6.4 GENERAL STEP-REACTION POLYMERIZATION

From an equation such as (6.36), it is possible to derive expressions describing the molecular weight distribution of such a stepwise polymerization at any degree of polymerization. The same relationship is more easily derived from statistical considerations. The following statistical treatment assumes the reaction rate to be independent of chain length.

One may write a general equation for the formation of a linear polymer by the step reaction of bifunctional reactants A and B as follows:

$$nA + nB \rightarrow A(BA)_{n-1}B \tag{6.39}$$

The probability of finding a repeating unit AB in the polymer is p, and the probability of finding $n - 1$ of these repeating units in the polymer chain is p^{n-1}. Likewise, the probability of finding an unreacted molecule of A or B is $1 - p$. Thus, the probability (p_n) of finding a chain with n repeating units $(BA)_n$ is

$$p_n = (1 - p)\,p^{n-1} \tag{6.40}$$

Hence, N_n, the probability of choosing (at random) a molecule with $(BA)_n$ repeating units, where N is equal to the total number of molecules, is

$$N_n = N(1 - p)\,p^{n-1} \tag{6.41}$$

Since

$$\frac{N_0}{N} = \frac{1}{1-p} \qquad \text{or} \qquad N = N_0(1 - p) \tag{6.42}$$

where N_0 is the total number of structural units present,

$$N_n = N_0(1 - p)^2\,p^{n-1} \tag{6.43}$$

The corresponding weight-average molecule weight distribution W_a may be calculated from the relationship $W_n = nN_n/N_0$ as follows:

$$W_n = \frac{nN_0(1 - p)^2 p^{n-1}}{N_0} = n(1 - p)^2 p^{n-1} \qquad (6.44)$$

The relationships shown in Eqs. (6.43) and (6.44) demonstrate that high values of p (>0.99) are essential in order to produce either high N_n or high W_n values. The number-average molecular weight M_n and weight-average molecular weight M_w calculated from Eqs. (6.41) and (6.42) are as follows:

$$M_n = \frac{mN_0}{N} = \frac{m}{1 - p} \qquad (6.45)$$

where m = the molecular weight of the mer and

$$M_w = \frac{m(1 + p)}{1 - p} = M_n(1 + p) \qquad (6.46)$$

Thus, the index of polydispersity M_w/M_n for the most probable molecular weight distribution becomes 1 + p, as shown below:

$$\frac{M_w}{M_n} = \frac{m(1 + p)/(1 - p)}{m/(1 - p)} = 1 + p \qquad (6.47)$$

Thus, when p is equal to 1, the index of polydispersibility for the most probable distribution for step-reaction polymers is 2.

Because the value of p is essentially 1 in some step-reaction polymerizations, the products obtained under normal conditions have very high molecular weights and are difficult to process. It is obvious that the value of p may be reduced by using a slight excess of one of the reactants or by quenching the reaction before completion. Thus, if a reaction is quenched when the fractional conversion p is 0.995, $\overline{DP}$ will be equal to 200.

If more than 1 mol of B is used with 1 mol of A, the ratio of A/B, or r, may be substituted in the modified Carothers equation as shown below:

$$\overline{DP} = \frac{\text{total nA at p}}{\text{total nA at rp}} = \frac{n[(1 + 1/r)]/2}{n[1 - p + (1 - rp/r)]/2} = \frac{1 + (1/r)}{1 - p + [(1 - rp)/r]} \qquad (6.48)$$

Therefore, multiplying top and bottom by r gives

$$\overline{DP} = \frac{r + 1}{r(1 - p) + (1 - rp)} = \frac{1 + r}{(1 + r) - 2rp} \qquad (6.49)$$

Thus, if r = 0.97 and $p \simeq 1$, $\overline{DP}$ is equal to

$$\overline{DP} = \frac{1 + r}{(1 + r) - 2rp} = \frac{1 + 0.97}{1 + 0.97 - 2(0.97)} = \frac{1.97}{0.03} = 66 \qquad (6.50)$$

The $\overline{DP}$ value of 66 is above the threshold limit of 50 required for nylon-66 fibers.

Since quenching the reaction or adding a stoichiometric excess of one reactant is not economical, the commercial practice is to add a calculated amount of a monofunctional reactant. Acetic acid is used as the monofunctional reactant in the synthesis of polyamides and polyesters. In this case, one may employ a functionality factor (f) which is equal to the average number of functional groups present per reactive molecule. While the value of f in the preceding examples has been 2.0, it may be reduced to lower values and used in the following modified Carothers equation:

$$\overline{\mathrm{DP}} = \frac{A_0}{A_0[1 - (pf/2)]} = \frac{2}{2 - pf} \tag{6.51}$$

Thus, if 0.01 mol of acetic acid is used with 0.99 mol of two difunctional reactants, the average functionality or functional factor, f, is calculated as follows.

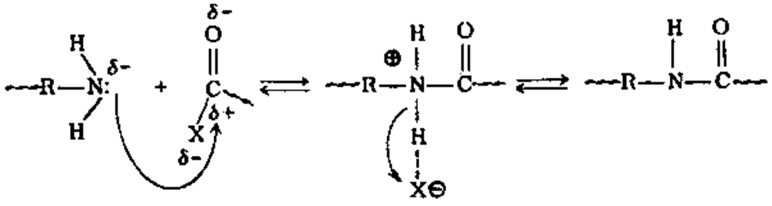
$$\begin{aligned} f &= \frac{\text{mol of each reactant} \times \text{functionality}}{\text{total number of moles}} \\ &= 0.99\ \text{mol} \times 2 + 0.99\ \text{mol} \times 2 + 0.01\ \text{mol} \times \frac{1}{1.99\ \text{mol}} = 1.99 \end{aligned}$$

Substitution of $f = 1.99$ and $p = 1.00$ in Eq. (6.51) gives an average $\overline{\mathrm{DP}}$ of 200, representing an upper limit for this situation. The same calculation, but employing $p = 0.95$, gives an average $\overline{\mathrm{DP}}$ of only 20.

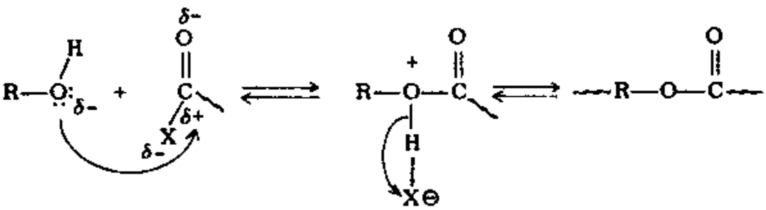
Since the average molecular weight increases with conversion, useful high molecular weight linear polymers may be obtained by step-reaction polymerization when the fractional conversion (p) is high (>0.99). The concentration of reactants decreases rapidly in the early stages of polymerization, and polymers with many different molecular weights will be present in the final product. The requirement for a linear polymer is a functionality of 2. Network polymers are usually produced when the functionality is greater than 2. The original reactants and all products resulting from their condensation may react to produce higher molecular weight species. The rate constant k is similar to that of corresponding condensation reactions with monofunctional groups and remains essentially unchanged with higher molecular weight species.

6.5 POLYCONDENSATION MECHANISMS

Proposed mechanisms for polycondensations are essentially the same as those proposed in the organic chemistry of smaller molecules. Here we will briefly consider several examples to illustrate this similarity between proposed mechanisms for reactions involving smaller molecules and those that eventually produce polymers. For instance, the synthesis of polyamides (nylons) can often be envisioned as a simple S_N2 type of Lewis acid–base reaction with the Lewis base nucleophilic amine attacking the electron-poor, electrophilic carbonyl site followed by loss of a proton. A similar mechanism can be proposed for most polyesterifications.

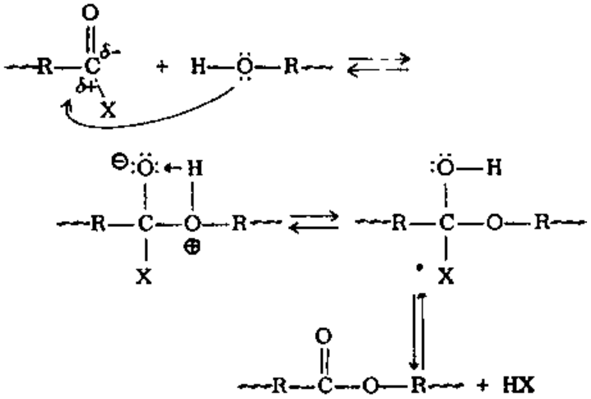


(6.52)



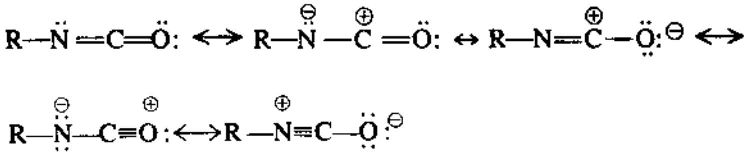
(6.53)

and a related pathway



(6.54)

Below are a number of resonance forms for the isocyanate moiety illustrating the overall electrophilic nature of the carbon atom, giving overall

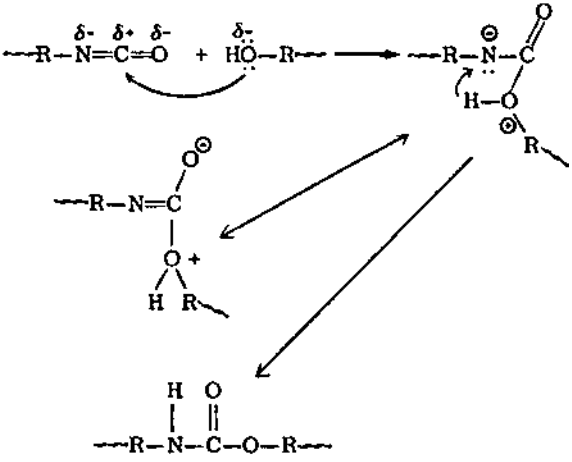


(6.55)

an electron arrangement which can be described by

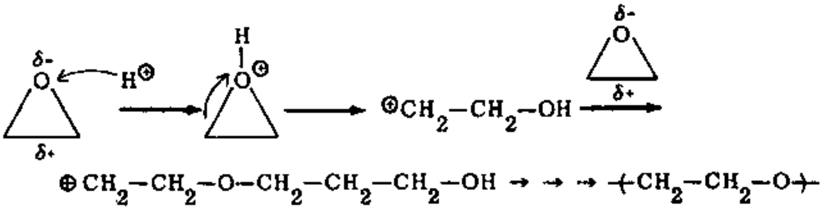
$$\mathrm{R{-}\overset{\delta-}{N}{=}\overset{\delta+}{C}{=}\overset{\delta-}{O}}$$

Polyurethene formation occurs with attack of the nucleophilic alcohol at the electron-poor isocyanate carbon with a proton shift followed by a rearrangement to the urethane linkage.

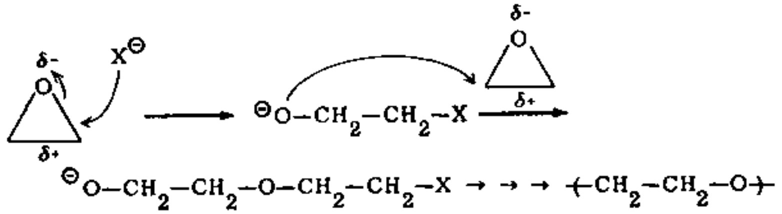


(6.55a)

Polyether formations, such as the formation of poly(ethylene oxide) from ethylene oxide, can occur either through acid or base catalysis as depicted below.



(6.56)



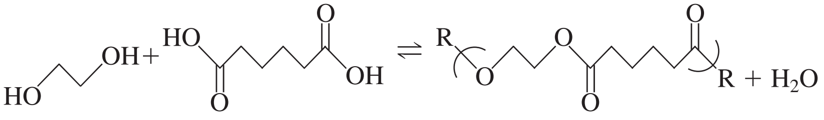
(6.57)

where X = −OH, −OR. The topic of polyether formation is discussed in Sec. 6.12.

Again, the mechanistic pathways suggested for condensations involving smaller molecules can generally be directly applied to polycondensation processes.

6.6 POLYESTERS AND POLYCARBONATES

Carothers and his research group at Dupont began to investigate the formation of polymers from the reaction of aliphatic diacids with diols, generally adipic acid and ethylene glycol (derived from the reaction of ethylene oxide with water, it is the major ingredient in most antifreezes), in search of materials that would give them fibers. They were only able to form syrupy mixtures. This is because unlike reactions with diamines (Sec. 6.7), the equilibrium reaction greatly disfavors ester formation. Further, the ability to have almost equal amounts of functional groups is easily achieved with the amines through formation of salts with the amines as shown in (6.59) but diols do not form such salts. The critical need to have the reactants present in equal molar amounts for equilibrium determined reactions is clearly seen in Eq. (6.29). Carothers' group understood the principle of "driving" an equilibrium reaction so sought to remove water thus forcing the reaction toward ester formation. For this they developed a so-called "molecular still," which was simply heating the mixture and applying a vacuum coupled with a "cold-finger" that allowed evacuated water to condense and be removed from the reaction system. Since the fractional conversion (p) was only 0.95 the average chain length of these polyesters was less than 20.



Ethylene glycol Adipic acid Poly(ethylene adipate) Water

(6.58)

The Dupont research turned from the synthesis of polyesters to tackle, more successfully, the synthesis of the first synthetic fiber material, nylon, which approached, and in some cases exceeded, the physical properties of natural analogs (see the next section).

The initial experience with polyesters was put to use in the nylon venture. Today, we know that Carothers would of had greater success in producing high molecular weight material had his group employed transesterification, ring opening (of the "diol" derived moiety), or the reaction of diols with acyl dichlorides (Schotten-Baumann reaction) or anhydrides. These techniques then compose the major techniques employed in the synthesis of polyesters. Each of these reactions involve the nuclophilic addition to the carbonyl group as shown in Sec. 6.5 and are illustrated in reactions (6.59)–(6.63). Focusing on the carbonyl-containing reactant, polyester formation employing direct esterification (reaction between an acid and alcohol) and transesterification is relatively slow with each mechanistic step reversible. Reaction rates are increased through the use of acid catalysts that coordinate the carbonyl oxygen enhancing the electrophilic nature of the carbonyl carbon. Weakly basic catalysts are often employed in transesterification reactions probably to increase the nucleophilicity of the alcohol through formation of an alkoxide ion. Reaction with anhydrides and acid chlorides are more rapid and can occur in an essentially nonreversible fashion. But anhydrides and acid chlorides are considered so-called "high energy" reactants, since they often involve additional energy requiring steps in their production and thus are less suitable for large scale production of materials. The activity energies for direct esterification and transesterification are on the order of 30 kcal/mole (120 kJ/mole), while the activation energies for anhydride and acid chloride reaction with alcohols are on the order of 15–20 kcal/mole (60 to 80 kJ/mole).

The initial polyester formation actually occurred much earlier and is attributed to Gay Lussac and Pelouze in 1833 and Berzelius in 1847. These polyesters are called glyptals and alkyds, and they are useful as coatings materials and not for fiber production. While these reactions had low fractional conversions, they formed high molecular weight materials because they had functionalities (that is number of reactive groups on a single reactant) greater than 2 resulting in crosslinking.

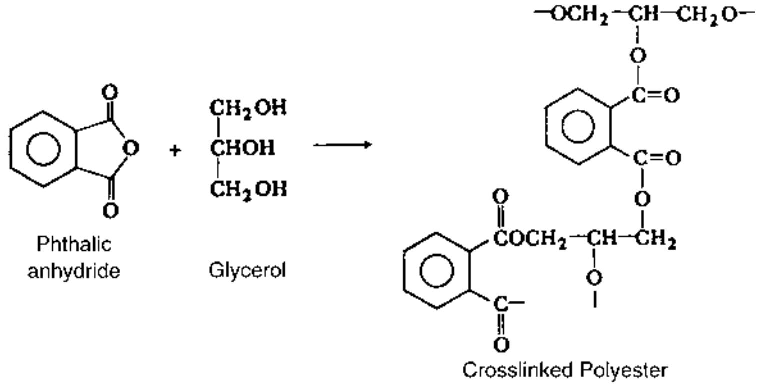
When the average functionality is greater than 2 crosslinking occurs. Utilization of the modified Carothers equation (6.51) gives large numbers approaching infinity for the average DP as the product of p and f approaches 2. Thus, for the reaction of 0.99 mol of difunctional phthalic anhydride with 0.99 mol of ethylene glycol and 0.01 mol of trifunctional glycerol,

$$f = \frac{0.99 \text{ mol} \times 2 + 0.99 \text{ mol} \times 2 + 0.01 \text{ mol} \times 3}{1.99 \text{ mol}} = 2.02$$

Substitution of $r = 2.02$ and $p = 0.95$ into Eq. (6.51) gives an average DP of 25. For $p = 0.97$, the average DP is 50; for $p = 0.99$, the average DP increases to 10,000. This march toward infinity as the product of pf approaches 2 is consistent with the formation of high molecular weight crosslinked products.

In the statistical approach to the requirements for incipient gelation, one introduces a branching coefficient α, which is defined as the probability that a reactant with a value for f of greater than 2.0 is connected to a linear chain segment or to another multifunctional reactant or branch point. The critical value for incipient gelation (α_c) is the probability that one or more of the $f - 1$ chain segments on the branch unit will be connected to another branch unit, i.e., $\alpha_c = (f - 1)^{-1}$ or $1/(f - 1)$. Thus, when $f = 2.2$, $\alpha_c = 0.83$.

Glyptal polyesters were produced in 1901 by heating glycerol and phthalic anhydride. Since the secondary hydroxyl is less active than the terminal primary hydroxyls in glycerol, the first product formed at conversions of less than about 70% is a linear polymer. A crosslinked product is produced by further heating:



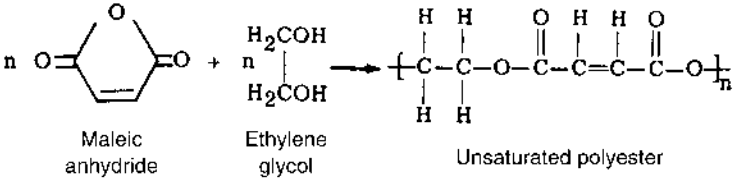
(6.59)

Alkyds were synthesized by Kienle in the 1920s from trifunctional alcohols and dicarboxylic acids. Unsaturated oils called drying oils were transesterified with the phthalic anhydride in the reaction so that an unsaturated polyester was obtained.

The extent of crosslinking or “drying” of these alkyds in the presence of a soluble lead or cobalt catalyst or drier was dependent on the amount of unsaturated oil present. The terms short oil, medium oil, and long oil alkyd are used to signify the “oil length” obtained by use of 30–50%, 50–65%, and 65–80% of unsaturated oil, respectively.

The term alkyd is sometimes used to describe all polyesters produced from the condensation of a polybasic acid and a polyhydric alcohol. Thus, the terms nonoil and oil-free alkyds have been used to distinguish between the principal types of polyesters. The terms saturated and unsaturated polyesters are also widely used. The chain reaction mechanism of the curing of these unsaturated polymers will be discussed in Chapter 15.

Another type of unsaturated polyester is produced by the condensation of ethylene glycol with phthalic anhydride and maleic anhydride [Eq. (6.60)]. These polyesters may be dissolved in styrene and used as crosslinking resins for the production of fibrous glass–reinforced plastics.

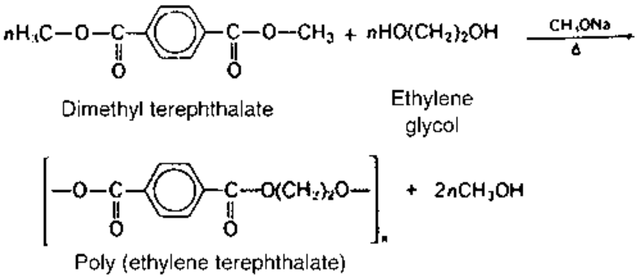


(6.60)

Aromatic polyesters had been successfully synthesized from reaction of ethylene glycol and various aromatic diacids but commercialization awaited a ready inexpensive source of aromatic diacids. An inexpensive process was discovered for the separation of the various xylene isomers by crystalization. The availability of inexpensive xylene isomers allowed the formation of terephthalic acid through the air oxidation of the p-xylene isomer. In 1953, Dupont produced polyester fibers from melt spinning, but it was not until the 1970s that Dupont’s polyester fibers became commercially available.

Expanding on the work of Carothers and Hill on polyesters, in England Whinfield and Dickson overcame the problems of Carothers and coworkers by employing an ester interchange reaction between ethylene glycol and the methyl ester of terephthalic acid forming the polyester poly(ethylene terephthalate) with the first plant coming on line in

1953. This classic reaction producing Dacron, Kodel, and Terylene fibers and Dacron fibers is shown below.



(6.61)

Polyester fibers [poly(ethylene terephthalate), PET, Fig. 6.8], which are now the world’s leading synthetic fibers, are produced at an annual rate of over 1.5 million tons in the United States. Thicker oriented films or sheets are used in the manufacture of containers for carbonated drinks.

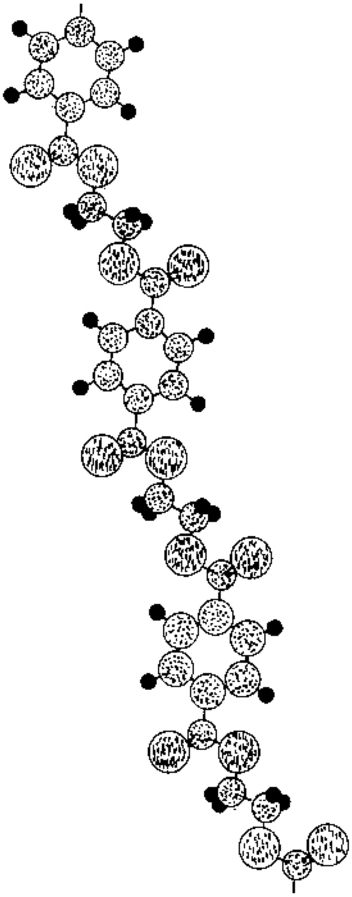


Figure 6.8 Ball-and-stick model of poly(ethylene terephthalate).

PET is generally produced using a two-step process. Dimethyl terephthalate is heated with ethylene glycol giving a mixture of oligomers including dihydroxyethyl terephthalate. The mixture is then heated to over 250°C under vacuum in the presence of a catalyst to give the final product.

Fibers are produced if the product is pushed through a small hole. As the polyester emerges from the hole, tension is applied assisting the polymer chains to align, giving a material with added strength. Crystallization of polyester resin can be achieved through heating to about 190°C followed by slow cooling. Rapid cooling, called *quenching*, produces more amorphous material from which transparent film can be produced.

Film strength is increased through application of heat and pulling of the film. Biaxially oriented PET film is one of the strongest films available. It is used as magnetic film in X-ray and other photographic applications, and in such food applications as food packaging including the boil-in-a-bag foods. Thicker films are used in the manufacture of many of the carbonated single-drink bottles because PET can be injection-molded and because it has low carbon dioxide permeability.

The addition of antinucleating agents permits the injection molding of PET (Rynite). Injection-moldable glycol-modified polyesters (PETG, Kodar) have been produced by partial replacement of the ethylene glycol by cyclohexanol dimethylol.

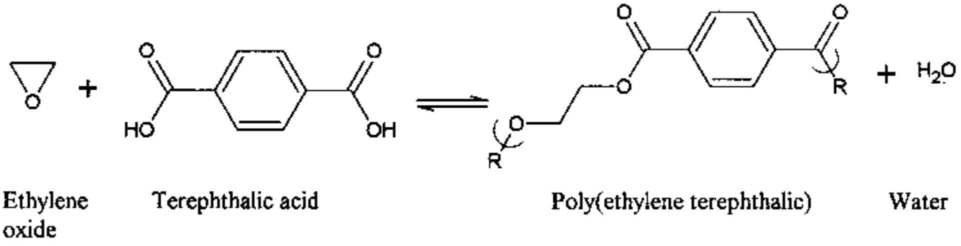
Moldability of aryl polyesters has also been improved by the use of poly(butylene terephthalate) (PBT) instead of PET or by the use of blends of PET and PBT. PBT under the trade names Celanex, Valox, Gafite, and Versel is being produced at an annual rate of 25 thousand tons. Copolymers of carbonate and aryl esters, acrylics and aryl esters, and imide and aryl esters as well as physical blends of polyesters and other polymers are available. These aryl polyesters are being used for bicycle wheels, springs, and blow-molded containers.

A new high-impact blend of PBT and polybutene (Valox CT) is also available. The melt viscosity of blends of PET and nylon-66 has been reduced by the addition of poly(vinyl alcohol). Self-reinforcing PET has been produced by the addition of p-hydroxybenzoic acid, which forms liquid crystals in the composite.

Since PET has a melting point of 240°C, it is difficult to mold. However, PBT produced from butylene glycol has a melting point of 170°C and is more readily molded. It is a strong, highly crystalline engineering plastic.

Floppy disks and hard drives use magnetic material laid on thin flexible sheets made of PET or on stiffer sheets made from glass or aluminum. These sheets can be made quite thin, less than 10 nm.

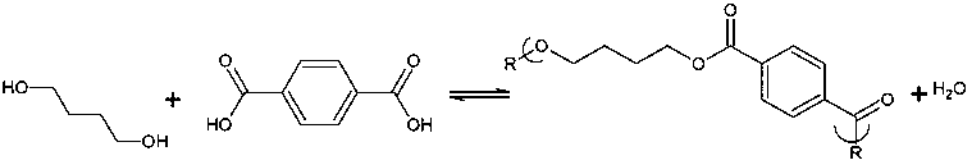
While PET is normally made as described in Eq. (6.61), it can also be made from the ring-opening reaction with ethylene glycol as shown below.



(6.62)

PET is difficult to mold because of its high melting point (T_m 240°C). PBT, because of the addition of two methylene units in the diol-derived portion, is lower melting with a T_g of about 170°C. PET also crystalizes relatively slowly so that extra care must be exercised to insure that the PET-molded products are fully crystallized or the partial crystalized portions will be preferred sites for cracking, crazing, shrinkage, etc. Thus, nucleating agents and crystallization accelerators have been used to improve the crystallization rate. Postannealing has been used where appropriate.

PET is now extensively used as bottling material for soft drinks because of its low carbon dioxide permeability. Carbon dioxide permeability decreases with increasing film thickness and crystallinity. To achieve the necessary crystallinity, partially crystalline PET is employed in the stretch blow molding process with the molding process carried out to promote further crystalline formation.

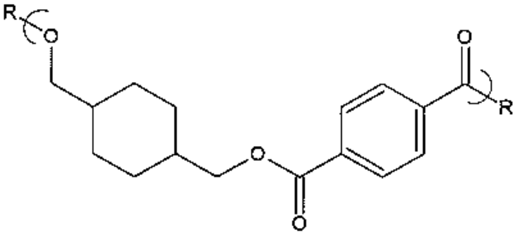


Poly(butylene terephthalate), PBT

(6.63)

By comparison, PBT melts at a lower temperature and crystallizes more rapidly and is often employed as a molding compound. PBT offers a balance of properties between nylons and acetals with low moisture absorption, good fatigue resistance, good solvent resistance, extremely good self-lubrication, and good maintenance of physical properties even at relatively high use temperatures. Fiber-reinforced PBT molding compound is sold under the tradename Celanex. A PBT molding compound was first sold under the tradename Valox. Today, there are many PBT molding compounds available.

Poly(dihydroxymethylcyclohexyl terephthalate) was introduced by Eastman Kodak as Kodel in 1958. In comparison to PET and PBT, the insertion of the cyclohexyl moiety gives a more hydrophobic material as well as a more moldable product that can be injected molded. The sole raw material is again dimethyl terephthalate. Reduction of the dimethyl terephthalate gives the dialcohol cyclohexanedimethanol. (Notice the reoccurring theme of reusing or using in a modified form the same readily available and inexpensive materials.) This material, along with blends and mixtures, is often extruded into film and sheeting for packaging. Kodel-type materials are used to package hardware and other heavy items as well as blow molded to produce packaging for shampoos, liquid detergents, etc.



(6.64)

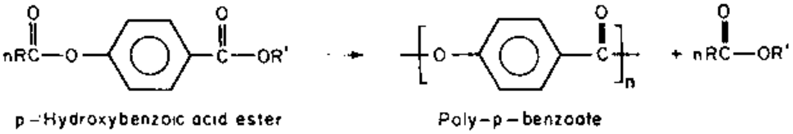
Poly(dihydroxymethylcyclohexyl terephthalate)

The hard-soft block copolymer approach (Sec. 9.4) employed to produce segmental polyurethanes has also been used with polyesters with the hard block formed from 1,4-

butadienediol and terephthalic acid while the soft block is provided from oligomeric (approximate molecular weight of 2000 Daltons) poly(tetramethylene glycol) and is sold under the trade name of Hytrel.

Along with nylons, polyester fibers approach and exceed common natural fibers such as cotton and wool in heat stability, wash-and-wear properties, and wrinkle resistance. Blended textiles from polyester and cotton and wool also can be made to be permanent press and wrinkle resistant. The fibers are typically formed from melt or solvent spinning (Chapter 17). Chemical and physical modification are often employed to produce differing fiber appearances from the same basic fiber material. Self-crimping textiles are made by combining materials with differing shrinkage properties. Different shaped dyes produce materials with varying contours and properties, including hollow fibers.

Several "wholly" aromatic polyesters are available. As expected, they are more difficult to process, stiffer, and less soluble, but are employed because of their good high thermal performance. Ekonol is the homopolymer formed from p-hydroxybenzoic acid. Ekonol has a T_g in excess of 500°C. It is highly crystalline and offers good strength.



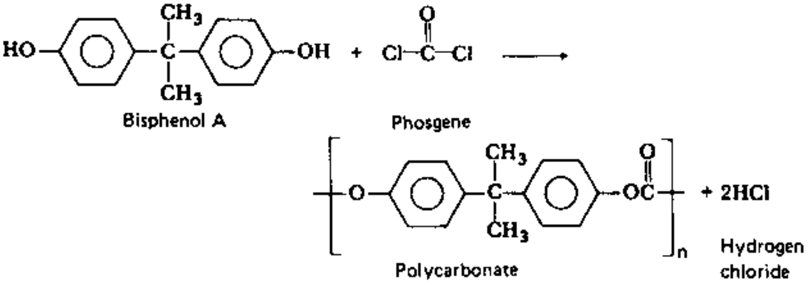
(6.65)

It is not unexpected that such aromatic polyesters have properties similar to polycarbonates because of their structural similarities.

Polycarbonates (PCs), which are polyesters of unstable carbonic acid, are relatively stable polymers that were originally produced by the reaction of phosgene with bisphenol A [2,2-bis(4-hydroxyphenyl) propane] [Eq. (6.66)]. This unusually tough transparent plastic is available under the trade names of Lexan (General Electric) and Merlon (Mobay). Most polycarbonates are produced by the interfacial polymerization of the diol with phosgene. Polycarbonates may also be produced by ester interchange between diphenyl carbonate and bisphenol A.

The melting point of polycarbonates is decreased from 225°C to 195°C when the methyl pendant groups are replaced by propyl groups. The polycarbonate prepared from bis(4-hydroxyphenyl)ether also has a lower melting point and lower glass transition temperature.

Polycarbonates and polycarbonate-polyester copolymers are used for glazing, sealed beam headlights, door seals, popcorn cookers, solar heat collectors, and appliances. Polycarbonate tends to stress-crack in the presence of gasoline, but a 50–50 blend (Xenoy) is unusually resistant to gasoline.



(6.66)

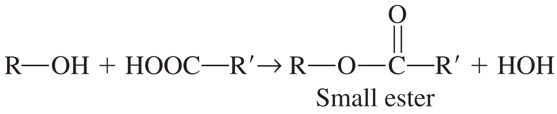
Nonrecordable compact disks (CDs) are made of rigid, transparent polycarbonates such as those given in 6.66 with a reflective metal coating on top of the polycarbonate. A laser is used to encode information through creation of physical features sometimes referred to as “pits and lands” of different reflectivity at the polycarbonate–metal interface.

Recordable CDs contain an organic dye between the polycarbonate and metal film. Here, a laser creates areas of differing reflectiveness in the dye layer through photochemical reactions.

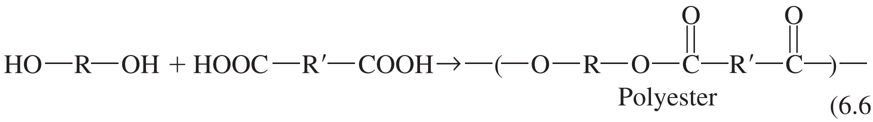
A beam from a semiconductor diode laser “interrogates” the undersides of both types of CDs seeking out areas of reflected, corresponding to the binary “one”, and unreflected, corresponding to the binary “zero,” light. The ability to “read” information is dependent on the wavelength of the laser. Today most of the CD players use a near-infrared laser because of the stability of such lasers. Efforts are underway to develop stable and inexpensive lasers of shorter wavelengths that will allow the holding of more information within the same space.

6.7 SYNTHETIC POLYAMIDES

Wallace Hume Carothers was brought to Dupont because his fellow researchers at Harvard and the University of Illinois called him the best synthetic chemist they knew. He started a program aimed at understanding the composition of natural polymers such as silk, cellulose, and rubber. Many of his efforts related to condensation polymers was based on his belief that if a monofunctional reactant reacted in a certain manner forming a small molecule, similar reactions except employing reactants with two reactive groups would form polymers.



$$\mathrm{R{-}OH + HOOC{-}R' \rightarrow \underset{\text{Small ester}}{R{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'} + HOH} \tag{6.67}$$

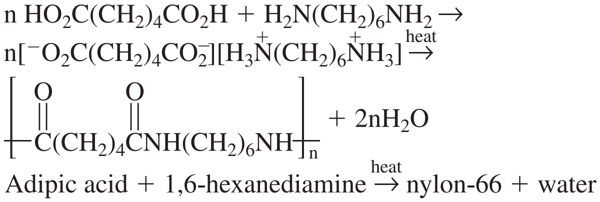


$$\mathrm{HO{-}R{-}OH + HOOC{-}R'{-}COOH \rightarrow \underset{\text{Polyester}}{{-}({-}O{-}R{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}){-}}} \tag{6.68}$$

While the Carothers group had made both polyesters and polyamides, they initially emphasized work on the polyesters since they were more soluble and easier to work with. One of Carothers’ co-workers, Julian Hill, noticed that he could form fibers if he took a soft polyester material on a glass stirring rod and pulled some of it away from the clump. Because the polyesters had too low softening points for use as textiles, the group returned to work with the polyamides. They found that fibers could also be formed by the polyamides similar to those formed by the polyesters. These fibers allowed the formation of fibers that approached, and in some cases surpassed, the strength of natural fibers. This new miracle fiber was introduced at the 1939 New York World’s Fair in an exhibit that announced the synthesis of this wonder fiber from “coal, air, and water”—an exaggeration—but nevertheless eye catching. When the polyamides—nylons—were first offered for sale in New York City, on May 15, 1940, over 4 million pairs were sold in the first few hours. Nylon sales took a large drop when it was noted that nylon was needed to produce the parachute material so critical to World War II.

The first polyesters, produced by Carothers, had relatively low molecular weights because of low fractional conversions. Carothers was successful in producing higher molecular weight polymers by shifting the equilibrium by removing the water produced. However, these aliphatic polyesters, which he called “superpolymers,” lacked stiffening groups in the chain and thus had melting points that were too low for laundering and ironing.

Carothers’ next step was to increase the fractional conversion (p) by making salts by the reaction of hexamethylenediamine and adipic acid. These were recrystallizable from ethanol. Thus, a high molecular weight polyamide known generally as nylon, which had a melting point of 265°C, could be produced by the thermal decomposition of this pure, equimolar nylon-66 salt, as shown by



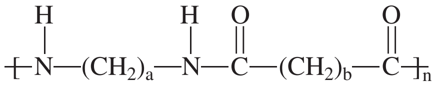
$$\begin{gathered}\text{n } HO_2C(CH_2)_4CO_2H + H_2N(CH_2)_6NH_2 \rightarrow \\ \text{n}[{}^{-}O_2C(CH_2)_4CO_2^{-}][H_3\overset{+}{N}(CH_2)_6\overset{+}{N}H_3] \xrightarrow{\text{heat}} \\ \left[\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_4\overset{\overset{\displaystyle O}{\|}}{C}NH(CH_2)_6NH \right]_n + 2nH_2O \\ \text{Adipic acid} + \text{1,6-hexanediamine} \xrightarrow{\text{heat}} \text{nylon-66} + \text{water}\end{gathered} \tag{6.69}$$

Since the molecular weight of the original nylon-66 produced by Carothers in 1938 was higher than he desired, he added 1% of acetic acid to the reactants in order to reduce the $\overline{DP}$ value. Because of the stiffening effect of the amide groups, the melting point of nylon-66 is 200°C greater than that of the corresponding polyester. The melting point of nylons (PA) increases as the number of methylene groups between amide groups in the chain are reduced.

In the early 1950s George deMestral was walking in the Swiss countryside. When he got home he noticed that his jacket had a lot of cockleburs on them. For some reason he examined the cockleburs and noticed that they had a lot of tiny “hooks.” His cotton jacket had loops that “held” the cockleburs. He began putting into practice his observations, making combinations of materials with rigid hooks and flexible loops or eyes. The initial hook-and-eye for commercial use was made in France. Today, Velcro, the name given to the hook-and-eye combination, is based on nylon as both the hook and eye material. Remember that nylon can be made to behave as both a fiber and a plastic. Polyester is blended with the nylon to make it stronger. Polyesters have also been employed to make hook-and-eye material. The hook-and-eye material is used to fasten shoes, close space suits, and in many other applications.

Molded nylon-66 is used for lawnmower blades, bicycle wheels, tractor hood extensions, skis for snowmobiles, skate wheels, motorcycle crank cases, bearings, and electrical connections. The radiator in the 1982 model Ford Escort was molded from nylon-66. Mono- and biaxially oriented nylon film is available.

The structure of nylons (e.g., nylon-ab) is



$$\left[\overset{\overset{\displaystyle H}{|}}{N} - (CH_2)_a - \overset{\overset{\displaystyle H}{|}}{N} - \overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_b - \overset{\overset{\displaystyle O}{\|}}{C} \right]_n \tag{6.70}$$

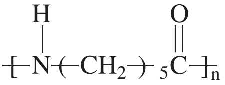
where a and b are equal to the number of carbon atoms in the repeating units of the diamine and dicarboxylic acid.

Nylon-610 and nylon-612 produced by the condensation of hexamethylenediamine and sebacic or dodecanoic acid, respectively, are more resistant to moisture and more ductile than nylon-66. The properties of these polyamides may be improved by the formation of polyether blocks (NBC) and by blending with thermoplastics, such as EPDM, PET, PBT, and TPE.

NBC (Nyrim) is more expensive than RIM polyurethane, but it may be heated to 200°C without softening. NBC moldings are produced by the reaction injection molding (RIM) of poly(propylene glycol) and caprolactam in the presence of a catalyst. The tendency for this copolymer to swell in the presence of water is reduced by reinforcing with glass fibers.

Since the chains of nylons having an even number of carbon atoms between the amide groups pack better, their melting points are higher than comparable nylons with odd numbers of carbon atoms. The melting points decrease and the water resistance increases as the number of methylene groups between amide groups is increased.

Nylon-6, which has a heat deflection temperature of 80°C, was produced by the ring-opening polymerization of caprolactam in Germany in the 1940s. Molded articles made of these polymers may be produced in situ in the RIM process. Nylon-11 and nylon-12, produced by the anionic polymerization of 11 and 12 amino acids, are also characterized by good resistance to moisture and superior ductility. The structure of the repeating unit in monadic nylons, such as nylon-6, is:



$$\left[\overset{H}{\overset{|}{N}} \left(CH_2 \right)_5 \overset{O}{\overset{\|}{C}} \right]_n \qquad (6.71)$$

Nylon-6

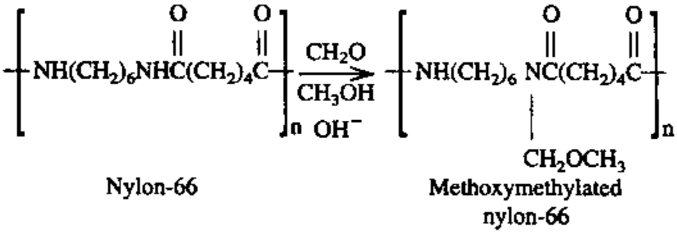
The copolymer of nylon-6 and nylon-66 is tougher and has a smoother surface than either of the homopolymers.

Injection-moldable, yellow, transparent polyamide (PA7030) is also available.

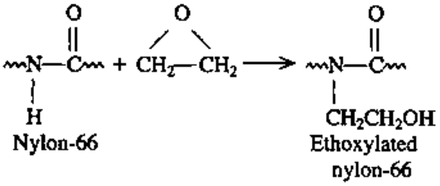
The aromatic polyamides (aramids) have been produced by the interfacial condensation of aromatic diamines, such as 1,3-phenylenediamine and isophthaloyl chloride in chloroform. Amorphous transparent aramids with heat deflection temperatures of 160°C have been produced from 2,2-bis-4-(aminocyclohexyl)propane.

Aromatic nylons prepared from terephthalic acid (Kevlar) have very high melting points and are called aramids. The solubility and ease of fabrication of aramids is improved by the preparation of ordered copolyamides. For example, a copolymer consisting of metabenzamide and isophthalamide units is more readily processed than poly(orthophenylene phthalamide).

Because of the presence of the bulky methoxymethyl pendant group, the hydrogen-bonding forces are reduced, the melting point is reduced, and the flexibility is increased in methoxymethylated nylon-66. Comparable results are observed when nylon-66 is condensed with ethylene oxide. The equations for these reactions are shown below.



$$\left[NH(CH_2)_6NH\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}} \right]_n \xrightarrow[CH_3OH \quad OH^-]{CH_2O} \left[NH(CH_2)_6\,\underset{\underset{CH_2OCH_3}{|}}{N}\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}} \right]_n \qquad (6.72)$$



(6.73)

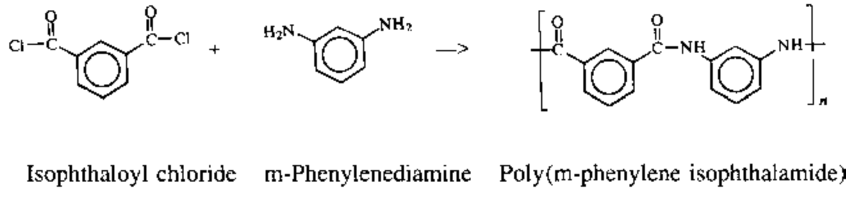
Comparable changes in physical properties are observed when branched dicarboxylic acids and branched diamines are used as the reactants for producing nylons. Thus, nylons produced from α-methyladipic acid and hexamethylenediamine and from adipic acid and 3-methylhexamethylenediamine have melting points that are at least 80°C less than that of nylon-66. These nylons are not suitable for fiber use because of the presence of branches on the chain.

Nylon-6,6 is the dominant (sales-wise) nylon in the United States while nylon-6 is the dominant nylon in Europe.

While aliphatic-containing polyamides are given the name nylons, those in which at least 85% of the amide groups are attached to an aromatic are called aramids. Aramids are stronger and tougher than nylons but they are also more difficult to solubilize and fabricate. Because the presence of the aromatic groups causes the aramids to be stiff, they often form liquid crystals that are present in a nematic liquid crystal state in concentrated solution.

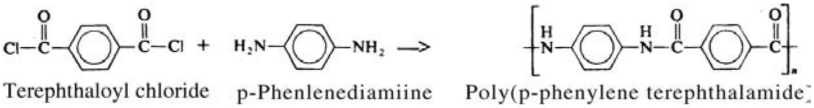
Aramids are generally prepared by the solution or interfacial polycondensation of meta- and para-substituted diacid chlorides and/or diamines. In some systems, synthesis is achieved under rapid stirring conditions where the polymer is quasi-soluble in the system. The polymer mixture is forced through a small opening into a nonsolvent forming a fiber without the need to dissolve the polymer before fiber formation.

Poly(m-phenylene isophthalamide), sold under the trade name Nomex, exhibits good thermal stability, decomposing above 370°C. It is used in flame-resistant clothing. It is also used in the form of thin pads to protect sintered silica-fiber mats from stress and vibrations during the flight of the space shuttle.



(6.74)

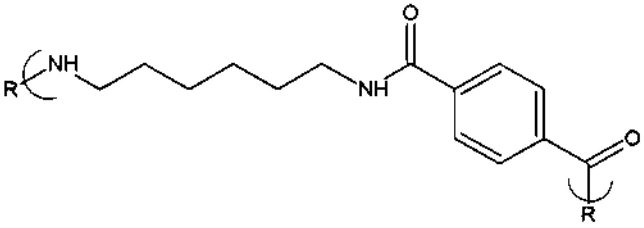
The corresponding aramid produced using the para reactant in place of the meta gives poly(p-phenylene terephthalamide) (PPT), produced under the tradename Kevlor. It also exhibits good thermal stability decomposing above about 500°C. By weight it has a higher strength and modulus than steel and is used in the manufacture of so-called bullet-proof clothing. Because of its outstanding strength, it was used as the skin covering of the Gossamer Albatross which was flown, using only human power, across the English Channel.



(6.75)

Aramids are also used as fiber reenforcement in composites and as tire cord.

Several so-called semiaromatic nylons have been produced. Nylon 6, T is produced from condensation of terephthalic acid and 1,6-hexanediamine (below). Both reactants are readily available and inexpensive and the resulting materials offer greater strength than simply wholly aliphatic nylons such as nylon 6,6. Nylon 6,T has a very high T_m of 370°C and a T_g of 180°C. The high T_m results in the need for a high temperature to be employed in processing so that a third reactant is often introduced to lower the T_m and the needed processing temperature. "Third reactants" often used are adipic acid, caprolactam, isophthalic acid, and 1,5-hexyl diamine. These materials are sold under the tradenames of Zytel HTN, Ultramid T, and Amodel R.



(6.76)

Nylon 6, T

Nylons offered new challenges to the chemical industry. Because of the presence of polar groups the attractive forces between chains was high in comparison to vinyl polymers. Nylons are generally semicrystalline, meaning they have a good amount of order. Thus, while they have a T_g, the main physical transition is the T_m so that they undergo a sharper transition from solid to melt in comparison to many of the vinyl polymers discussed in the next three chapters. Thus, the processing temperature window is more narrow. If melt flow is required for processing, then the temperature must be high enough to allow for ready flow but low enough so as not to break primary bonds within the processed material. Even so, processing techniques have been developed that allow nylons to be readily processed using most of the standard techniques.

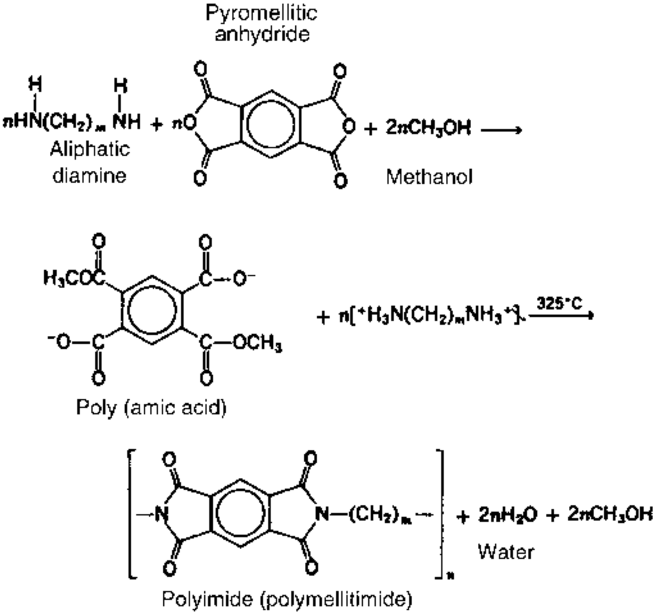
The presence of the polar groups result in materials with relatively high T_g and T_m values so that unlike many vinyl polymers that must be above their T_g to allow needed flexibility, nylons, and many condensation polymers function best where strength, and not flexibility, is the desired behavior.

Because of the presence of these polar groups that also allow for hydrogen bonding, nylons and most condensation polymers are stronger, more rigid and brittle, and tougher in comparison to most vinyl polymers. Nylons are also "lubrication-free" meaning they do not need a lubricant for easy mobility so that they can be used as mechanical bearings and gears without need for periodic lubrication.

In general, more crystalline nylons are fibrous while less crystalline nylon materials are more plastic in behavior. The amount of crystallinity is controlled through a variety of means including introduction of bulky groups and asymmetric units, rapid cooling of nonalined melts, and introduction of plasticizing materials. The theme of using asymmetric units was used by Grace and Company in developing Trogamid T, an amorphous transparent nylon, from the condensation of terephthalic acid with a mixture of 2,2,4- and 2,4,4-trimethylhexamethylene diamines.

6.8 POLYIMIDES

Polyimides (PIs) with melting points greater than 600°C are produced by the condensation of an aliphatic diamine and a dianhydride, such as pyromellitic anhydride [Eq. (6.77)]. It is customary to carry out this reaction stepwise to produce a soluble prepolymer (polyamic acid) that is insolubilized when heated. However, the product of the first step is insoluble when aromatic diamines are used. (Again, decomposition may occur prior to 600°C.)



(6.77)

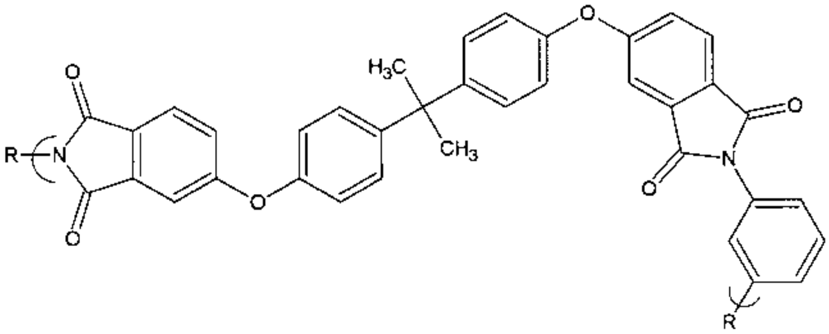
Heat-resistant intractable thermoset polyimides (Vespel, Kinel, Kapton) have been supplemented by injection-moldable polyamide-imides (Torlon) and modified polyimides (Kanox, Toramid). Thermoplastic polyimide adhesives were cited as one of the top 100 inventions of 1981. Polyimide foam does not ignite at temperatures below 430°C and is being considered as a cushioning material in public conveyances.

The processing properties are improved when polyimides are produced from meta-substituted diamines. A new amorphous polyether-imide (Ultem) with a high heat deflection temperature has been introduced by General Electric.

The ether linkages in polyether-imide (PEI) improve the ease of processing and increase the ductility of these high-performance plastics. PEI reinforced with 30% fiberglass has a heat deflection temperature of 210°C.

The polyamide-imide (PAI) Torlon has a heat deflection temperature of 285°C. A Ford automobile prototype engine has been built from PAI.

The initial announcement for the commercial preparation of polyetherimides, PEIs, was made by General Electric in 1982 under the tradename of Ultem. As in the case of other polyimides the final reaction involves the imidization of a diacid anhydride through reaction with a diamine, here m-phenylenediamine (below). The “ether” portion of the polymer backbone results from the presence of ether linkages within the diacid anhydride. These products are high melting, offer good stiffness, transparency, impact and mechanical strength, high flame resistance, low smoke generation, and broad chemical resistance. Some of these properties are expected. The high flame resistance is at least in part derived from the presence of already partially or largely oxidized atoms in the product. The low smoke generation is partially derived from the largely cyclic structure with other cyclic structures predictable from the product structure if exposed to sufficient heat. These cyclic



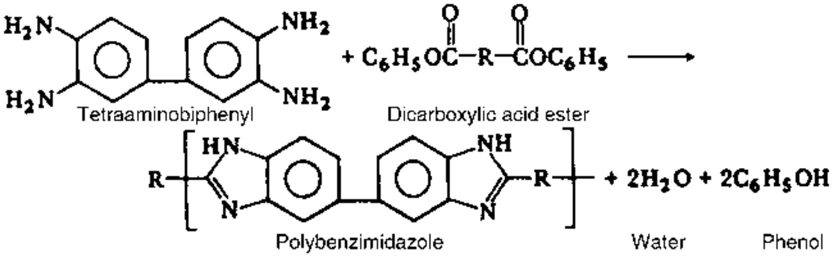
Polyetherimide

(6.78)

structures often give products that are not evolved resulting in good char formation when the material is exposed to ordinary flame conditions. The general good mechanical properties are a result of the presence of strong double bonds present within polycyclic structures composing the polymer backbone plus the presence of strongly polar bonding units that allow the formation of good interactions between chains. Further, the structure is largely rigid with good dimensional stability along the polymer backbone. Any flexibility is gained largely from the presence of the ether linkages for the polyetherimides and the presence of methylene units for the polyimides shown in (6.77). These products offer good stable melt viscosities even after recycling several times. They can be processed using a variety of techniques including formation of sections as thin as 5 mil.

6.9 POLYBENZIMIDAZOLES AND RELATED POLYMERS

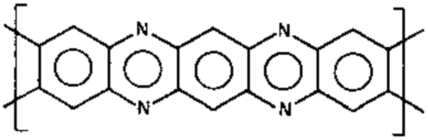
Many heterocyclic polymers have been produced in an attempt to develop high-temperature-resistant polymers for aerospace applications. Among these are the polybenzimidazoles (PBIs), which, as shown by the following equation, are prepared from aromatic tetramines and esters of dicarboxylic aromatic acids. In the standardized procedure, the reactants are heated at temperatures below 300°C in order to form a soluble prepolymer, which is converted to the final insoluble polymer by heating at higher temperatures.



(6.79)

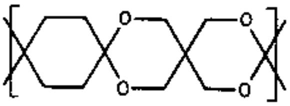
Polymers such as PBI have a weak link in the single covalent bond connecting the phenyl rings in biphenyl. This weakness is overcome by the synthesis of a ladder polymer, which, as shown by the formula for polyquinoxaline, has two covalent bonds throughout the chain. Thus, the integrity of the polymer is maintained even if one bond is broken.

This requirement is also met by spiropolymers, such as the intractable spiroketal polymers produced by the condensation of 1,4-cyclohexanedione and pentaerythritol, as shown below.



Polyquinoxaline
(a ladder polymer)

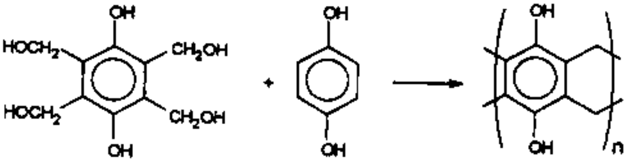
(6.80)



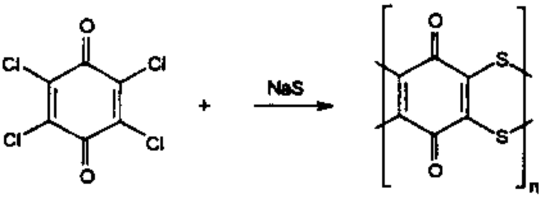
Spiroketal polymer
(a spiropolymer)

(6.81)

This property of maintaining “connectiveness,” even when one of the bonds in the main chain of a ladder polymer is broken, is important in many areas including thermal stabilities where rupture of both bonds is required for permanent bond breakage. Furthermore, for normal volatilization simple linear polymers require breakage of two “near” bonds within the backbone. For ladder polymers, rupture of a minimum of four bonds is required. A large number of ladder polymers have been synthesized using the condensation process. These include polydioxines and polydithiones,

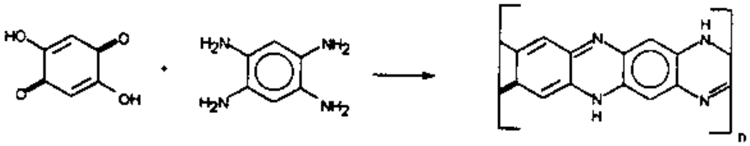


(6.82)



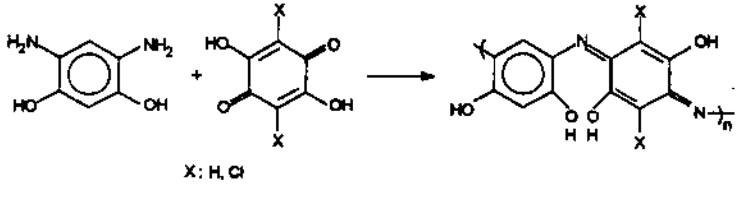
(6.83)

polyquinoxalines,



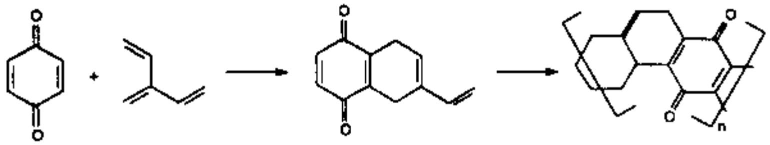
(6.84)

polyphenoxazines, and many others.



(6.85)

Some ladder polymers have been formed using other reactions, such as the Diels-Alder addition of quinones with vinyl-containing compounds, to form ladder polymers.



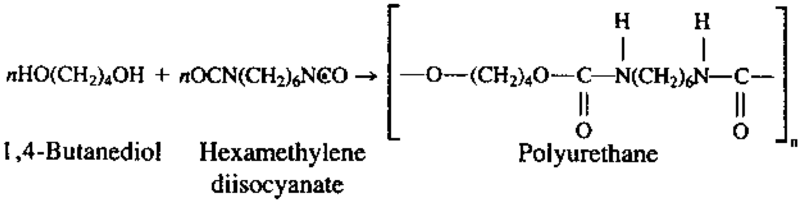
(6.86)

These ladder polymers are stiff and often difficulty solubilized. The latter is the result of a decrease in the already small entropy term that is a driving force for solubility to occur. The former is a result of the restricted bond rotation of π bonds.

For some polymers, formation of a ladder structure is an important intermediate in the thermal degradation of the polymers. For polyacrylonitrile, the tendency to form ladder polymers is an important step in the formation of carbon fibers (Sec. 15.11)

6.10 POLYURETHANES AND POLYUREAS

Urethanes, or carbamates, are well-known organic compounds that were formerly used for the characterization of alcohols. Since the fractional conversion (p) of the reaction is relatively high, Bayer was able to prepare numerous useful polyurethanes (PUs) by the reaction of dihydric alcohols and diisocyanates. For example, a crystalline polymeric fiber (Perlon U) may be prepared by the reaction of 1,4-butanediol and hexamethylene diisocyanate as shown in the following equation.

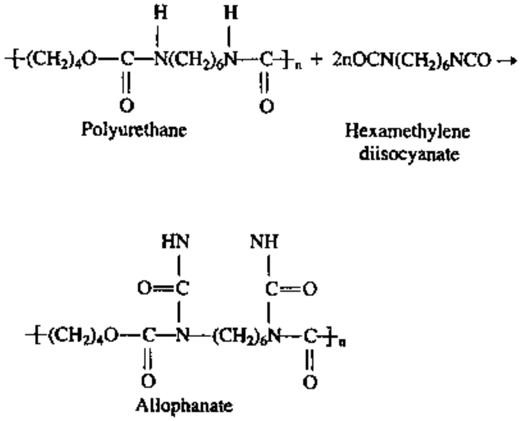


$$nHO(CH_2)_4OH + nOCN(CH_2)_6NCO \rightarrow \left[-O-(CH_2)_4O-\underset{\underset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}(CH_2)_6\overset{\overset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}- \right]_n \qquad (6.87)$$

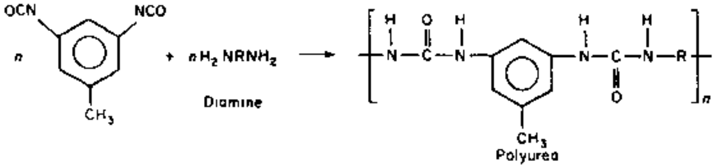
Reactants with an even number of carbon atoms as used in Eq. (6.87) produce higher melting polymers than those with an odd number of carbon atoms. The melting point is decreased as the number of methylene groups is increased, and increased by the incorporation of stiffening groups such as phenylene groups.

Isocyanates react with water to produce unstable carbamic acids, which decompose to form diamines and carbon dioxide, which acts as a blowing agent. Hence, polymeric foams are produced when traces of moisture are present in the reactants. Since many of these forms are formed in situ and isocyanates are toxic, it is preferable to use isocyanate-terminated prepolymers. The latter are prepared from flexible or rigid hydroxyl-terminated polyesters or polyethers.

Crosslinked PU coatings, elastomers, or foams may be produced by using an excess of the diisocyanate, which reacts with the urethane hydrogen to produce an allophanate, or by incorporating polyols such as glycerol or pentaery-thritol in the reactant mixture. The diamines produced by the decomposition of carbamic acids react with diisocyanates to produce polyureas. Equations for the formation of an allophanate and a polyurea are shown below.



(6.88)



(6.89)

Many polyurethanes are produced from diisocyanates and macroglycols, also called polyols. The most widely used diisocyanates are tolylene diisocyanate (TDI), methylene isocyanate (MDI), and polymeric isocyanate (PMDI). Mixtures of these can be obtained from the acid-catalyzed condensation of aniline and formaldehyde. MDI and PMDI are coproducts with the MDI separated using distillation.

Analine, in turn, is produced from the nitration of benzene followed by hydrogenation of the resulting nitrobenzene. The 2,4- and 2,6-toluene diisocyanates (TDIs) are produced from the analogous nitration of toluene followed by the hydrogenation of the resulting dinitrotoluenes.

The polyols are generally either polyether- or polyester-based. Polyether diols are formed from the ring-opening polymerization of alkylene oxides.

Foams

Flexible foams are formed from reaction of the diisocyanates and polyether triols with the trifunctionality producing a three-dimensional network. The foams are generally formed from the introduction of water into the system, which in turn reacts with unreacted isocyanate groups producing carbon dioxide gas giving an open-celled structure used in bedding, furniture, automotive seating, and carpet backing.

More rigid foams are generally formed from the reaction between PMDI and difunctional polyether diols. The multifunctionality is controlled by the use of PMDIs with differing numbers of unreacted isocyanate groups and use of polyols with a functionality greater than 2. The increased crosslinking results in a more rigid product. These materials are used in refrigeration, building and construction, insulation, and storage.

Elastomers

Polyurethane elastomers are segmented block copolymers containing so-called hard (less flexible) and soft segments. The hard segments consist of a stiffer, more rigid polyurethane portion derived from reaction of the diisocyanate with a short-chained glycol such as ethylene glycol. The soft or flexible portion is derived from the polyester diols with degrees of polymerization generally above 15. The hard segments often aggregate in domains held together by hydrogen bonding mainly between the urethane segments. These polyurethanes can be either thermoset or thermoplastic depending on whether or not crosslinking is introduced.

Reaction injection molding (RIM) is an increasingly important technology that emphasizes the production of thermoset polyurethanes. Here liquid monomers are mixed together under high pressure prior to injection into the mold. Polymerization occurs within the mold.

Polyurethane elastomers are used in the automotive industry. Most automotive dash panels are RIM-produced. Polyurethane elastomeric materials exhibit good abrasion resistance, chemical resistance, and good tear strength with a wide variation of flexibility available. These polyurethanes are also used in fabrics and sporting goods.

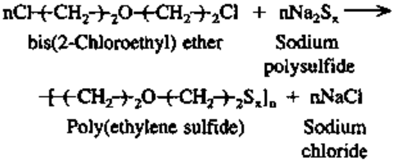
Such polymers are also referred to as segmented polyurethanes and are described in greater detail in Chapter 9.

Coatings

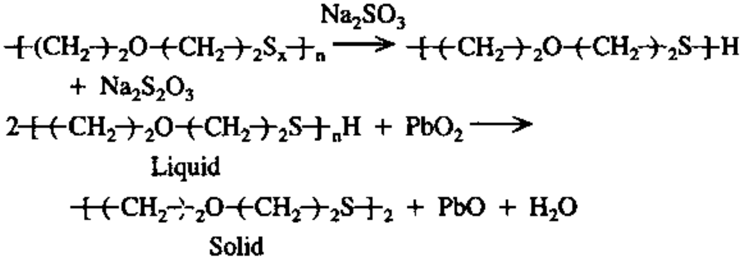
Polyurethanes are also widely used as coating materials sold as finished polymers, two-part systems, and prepolymer systems. Water-based systems are now available allowing easy home use. Aromatic diisocyanate–derived coatings generally offer poor external light stability while aliphatic-derived systems offer good light stability.

6.11 POLYSULFIDES

Thiokol, which was the first synthetic elastomer, was synthesized by Patrick by the condensation of alkylene dichlorides and sodium polysulfides in the 1920s. These solvent-resistant elastomers have limited use because of their foul odor. They may be reduced to liquid polymers (LP-2), which may be reoxidized to solid elastomers in caulking material and in some rocket propellant formulations. The equations for the production of these alkylene polysulfides are shown below.



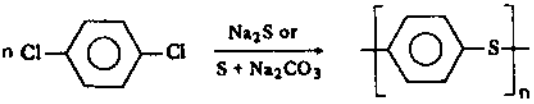
$$\underset{\text{bis(2-Chloroethyl) ether}}{n\mathrm{Cl}\!-\!(\mathrm{CH_2})_2\mathrm{O}(\mathrm{CH_2})_2\mathrm{Cl}} + \underset{\text{Sodium polysulfide}}{n\mathrm{Na_2S_x}} \longrightarrow \underset{\text{Poly(ethylene sulfide)}}{[(\mathrm{CH_2})_2\mathrm{O}(\mathrm{CH_2})_2\mathrm{S_x}]_n} + \underset{\text{Sodium chloride}}{n\mathrm{NaCl}} \quad (6.90)$$



$$[(\mathrm{CH_2})_2\mathrm{O}(\mathrm{CH_2})_2\mathrm{S_x}]_n \xrightarrow{\mathrm{Na_2SO_3}} [(\mathrm{CH_2})_2\mathrm{O}(\mathrm{CH_2})_2\mathrm{S}]\mathrm{H} + \mathrm{Na_2S_2O_3}$$

$$2\underset{\text{Liquid}}{[(\mathrm{CH_2})_2\mathrm{O}(\mathrm{CH_2})_2\mathrm{S}]_n\mathrm{H}} + \mathrm{PbO_2} \longrightarrow \underset{\text{Solid}}{[(\mathrm{CH_2})_2\mathrm{O}(\mathrm{CH_2})_2\mathrm{S}]_2} + \mathrm{PbO} + \mathrm{H_2O} \quad (6.91)$$

Poly(phenylene sulfide) (PPS; Ryton) is a solvent-resistant plastic that is useful in high-temperature service. This crystalline polymer is synthesized from p-dichlorobenzene as shown by the following equation:

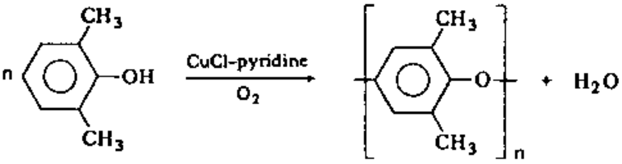


(6.92)

PPS is used for pumps, sleeve bearings, cookware, quartz halogen lamp parts, and electrical appliances.

6.12 POLYETHERS

In 1956, Hay discovered an oxidative coupling catalyst that allowed the production of polymeric aromatic ethers. The hope was to make polymers from readily starting materials, mainly phenol. The main aromatic polyether today is derived not from phenol but rather from the catalytic coupling of 2,6-dimethylphenol. The resulting poly(phenylene ether), PPE, or poly(phenylene oxide), PPO, was given the name Noryl by General Electric. PPO is made by a room temperature oxidation brought about by bubbling oxygen through a solution of the phenol in the presence of copper (I) chloride and pyridine. Initially, there was not a ready, inexpensive source of 2,6-dimethylphenol but because of early found positive properties of PPO, an inexpensive source of 2,6-dimethylphenol was found and both the monomer and polymer became commercial in 1964.

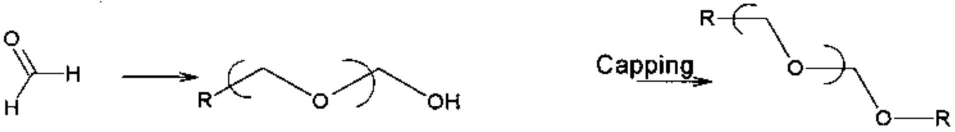


(6.93)

PPO has a very high T_g of 215°C, a T_m of about 270°C, exhibited good hydrolytic stability, but it has a very high melt viscosity and a tendency to oxidize and gel at processing temperatures. In spite of these negative processing features, PPO showed good compatibility with polystyrene While the methyl groups discouraged good interactions between PPO chains, the aromatic character positively interacts with the phenyl group on the polystyrene and the methyl groups interact positively with the aliphatic polystyrene backbone. The Noryl tradename covers a variety of related PPOs. PPO resins are the most important materials for forming blends and alloys with polystyrene and styrene derivatives. These blends and alloys with polystyrene raise the heat distortion to over 100°C allowing production of materials that can be boiled. Combinations with PS are more easily processed and the PPO imparts needed flame resistance. The combinations also offer good hydrolytic stabilities and electrical properties, and they are relatively light weight. They can also be modified by addition to glass and other mineral fillers and are especially adaptable to metallizing.

PPO-extruded sheet is being used for solar energy collectors, lifeguards on broadcasting towers, airline beverage cases, and window frames.

Aliphatic polyethers are also referred to as polyacetals. Polyoxymethylene, POM, precipitates spontaneously from uninhibited aqueous solutions of formaldehyde and was isolated by Butlerov in 1859. Staudinger, in the 1920s and 1930s, experimented with the polymerization of formaldehyde but failed to produce chains of sufficient length to be useful. While pure formaldehyde readily polymerized, it also spontaneously depolymerizes, unzippers. In 1947 Dupont began a program to make useful polymers from formaldehyde since formaldehyde is inexpensive and readily available. After twelve years they announced the commercialization of the polymer from formaldehyde, polyoxymethylene, under the tradename of Delrin. The "secret" was capping the end groups by acetylation of the hydroxyl end groups, thus preventing the ready unzipping of the polymer chain. POM has a T_g of $-75°C$ and a T_m of 180°C.



(6.94)

Celanese came out a year latter with a similar product under the trademark of Celcon. Celanese circumvented Dupont's patent on the basis of employing a copolymer variation that allowed enhanced stabilization against thermal depolymerization. The copolymer has a T_m of 170°C.

(6.95)

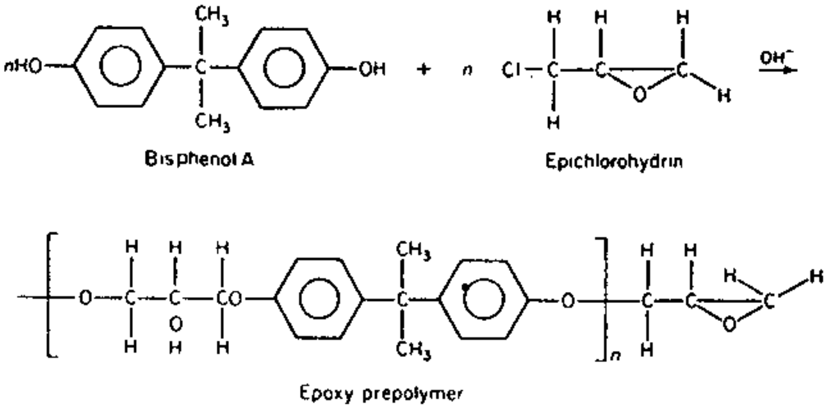
The selling price of polyacetal and other engineering plastics is about one-half that of cast metals. Polyacetals have been approved by the Food and Drug Administration for contact with foods. Some of the uses for molded polyacetals are as follows: valves, faucets, bearings, appliance parts, springs, automobile window brackets, hose clamps, hinges, gears, shower heads, pipe fittings, video cassettes, tea kettles, chains, flush toilet float arms, pasta machines, desktop staplers, and air gun parts.

POMs are also employed in plumbing and irrigation because they resist scale accumulation, have good thread strength, torque retention, and creep resistance.

These unique polymers are resistant to many solvents, aqueous salt and alkaline solutions, and weak acids at a pH greater than 4.5. More complete data on physical properties and resistance to hostile environments of these and other polymers are available.

Epoxy resins (ethoxyline resins), under the trade names of Araldite and Epon, were synthesized in the 1940s by a step-reaction polymerization between epichlorohydrin and bisphenol A. The $\overline{DP}$ of the prepolymer produced in this reaction is dependent on the ratio of the reactants. The low molecular weight liquid prepolymer is cured, or crosslinked, at room temperature by the addition of alkylene polyamines and at high temperatures by the addition of cyclic carboxylic anhydrides. The equations for the production and curing of these widely used molding, laminating, and surface-coating resins are shown below.

The high molecular weight thermoplastics called phenoxy resins are produced by the hydrolysis of high molecular weight linear epoxy resins. These transparent resins, whose structures resemble epoxy resins, do not contain epoxide groups. They may be molded as such, or crosslinked through the hydroxyl pendant groups by diisocyanates or cyclic anhydrides.



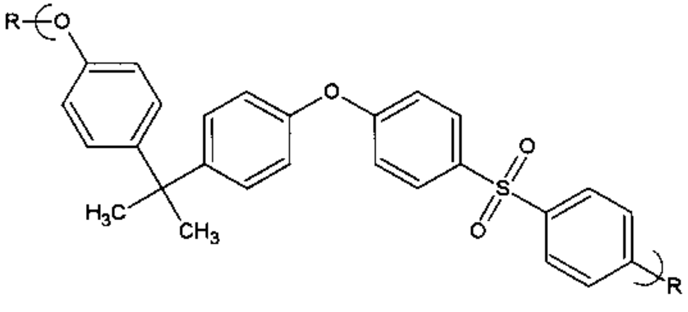
(6.96)

$$\text{Epoxy prepolymer} + \begin{matrix}\text{alkylene polyamine}\\ \text{or}\\ \text{cyclic anhydride}\end{matrix} \longrightarrow \text{cured epoxy resin} \qquad (6.97)$$

Furan resins are produced by the acid-catalyzed polymerization of furfuryl alcohol or the products obtained by the condensation of this chemurgic product or furfural with acetone or maleic anhydride. The dark resins produced from these unsaturated compounds are characterized by excellent resistance to alkalis, solvents, and nonoxidizing acids.

6.13 POLYSULFONES

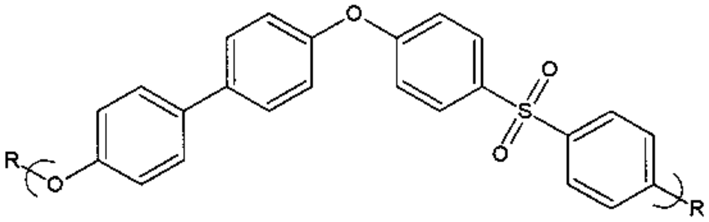
Polysulfones exhibit excellent thermal oxidative resistance, and resistance to hydrolysis and other industrial solvents, and creep. The initial commercial polysulfones were synthesized by the nucleophillic replacement of the chloride on bis(p-chlorophenyl) sulfone by the anhydrous sodium salt of bisphenol A. It became commercially available in 1966 under the tradename Udel. It exhibits a reasonably high T_g of 190°C.



(6.98)

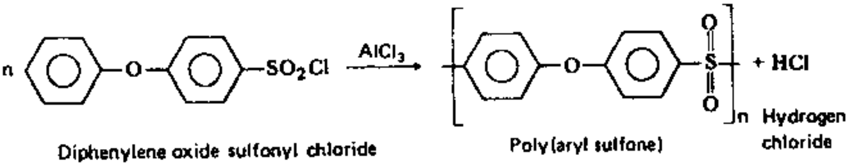
Udel

Union Carbide, in 1976 made available a second generation polysulfone under the tradename of Radel. Radel was formed from the reaction of a bisphenol and bis(p-chlorophenyl) sulfone. This polysulfone exhibited greater chemical/solvent resistance, a greater T_g of 220°C, greater oxidative stability, and good toughness.



(6.99)

Polysulfones can also be made from the Friedal-Crafts condensation of sulfonyl chlorides as shown below.



(6.100)

Another polysulfone (Astrel) is produced by the Friedel-Crafts condensation of biphenyl with oxybis(benzene sulfonyl chloride). Another polysulfone (Victrex) is produced by the alkaline condensation of bis(chlorophenyl)sulfone. Blends of polysulfones with ABS (Arylon, Mindel) and SAN (Ucardel) are available.

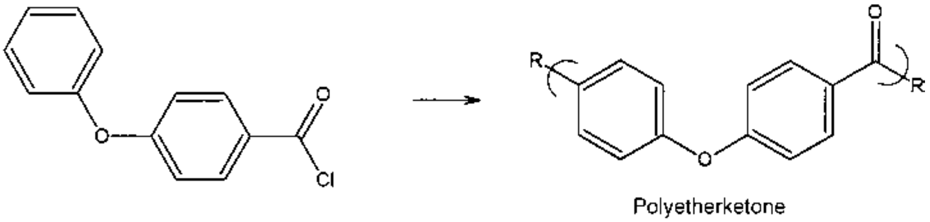
Polysulfones are used for ignition components, hair dryers, cook ware, and structural foams. Because of their good hydrolytic stability, good mechanical properties, and high thermal endurance they are good candidate materials for hot water and food handling equipment, alkaline battery cases, surgical and laboratory equipment, life support parts, autoclavable trays, tissue culture bottles, and surgical hollow shapes, and film for hot transparencies. Their low flammability and smoke production, again because of their tendency for polycyclic formation on thermolysis and presence of moieties that are partially oxidized, makes them useful as materials for aircraft and the automotive industry.

Grumman has developed an automated triangular truss-type beam builder using graphite-reinforced polyethersulfone. This beam can be formed in outer space at the rate of 1.5 m/min from flat stock which is heated and forced continuously around a die. The sections are induction welded and may be protected from deterioration by the application of a coating of poly(ether ether ketone).

6.14 POLY(ETHER ETHER KETONE) AND POLYKETONES

Aromatic polyketones are semicrystalline materials that contain both ketone groups generally flanked by aromatic units. Many also have included within them ether moieties that allow for some flexibility and better processing. They have good thermal stabilities, also well as offering good mechanical properties, flame resistance, impact resistance, and resistance to the environment.

Polyetherketone, PEK, was introduced by Raychem in the 1970s. It is made by the Friedel-Crafts reaction requiring good solvents or an excess of aluminum chloride to keep the polymer in solution allowing polymer growth to occur. Most polymerizations require that the reactants remain mobile, through solution or being melted, so that the individual units involved in the reaction can get together. Rapid precipitation of growing polymer chains often results in the formation of only oligomeric to small chains.

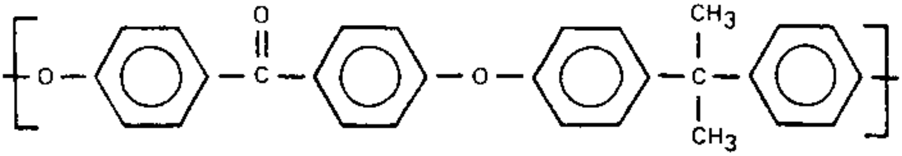


Polyetherketone

(6.101)

ICI has introduced a new crystalline poly(ether ether ketone) (PEEK), which has a glass transition of 145°C and a heat deflection temperature for reinforced PEEK of 300°C. PEEK is being considered for use as blow-molded containers for nuclear wastes, jet engine components, printed circuits, electrical applications, and wire coatings.

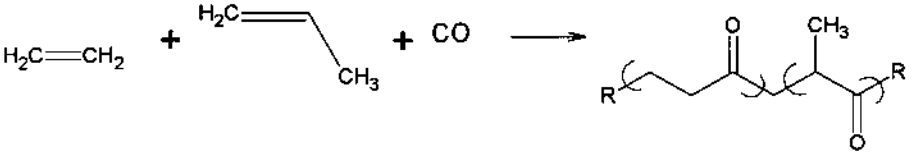
The structure of the repeat unit in PEEK is



(6.102)

Applications in the chemical industry include as compressor plates, valve seats, thrust washers, bearing cages, and pump impellers. In the aerospace industry they are employed as aircraft fairings, fuel valves, and ducting. They are also used in the electrical industry as wire coating and semiconductor wafer carriers.

Aliphatic polyketones are made from the reaction of olefin monomers and carbon monoxide using a variety of catalysts. Shell commercialized a terpolymer of carbon monoxide, ethylene, and a small amount of propylene in 1996 under the tradename of Carilon. They have a useful range of T_g (15°C) and T_m (200°C) that corresponds to the general useful range of use temperatures for most industrial applications. The presence of polar groups cause the materials to be tough with the starting materials readily available.

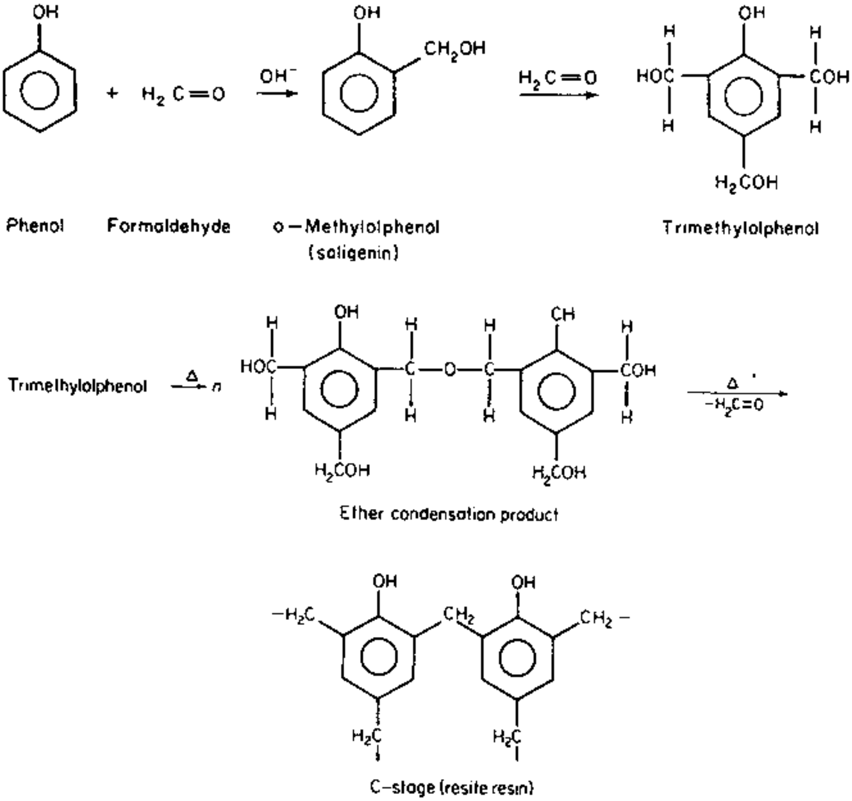


Aromatic Polyketone

(6.103)

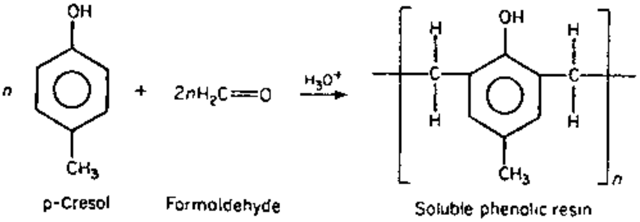
6.15 PHENOLIC AND AMINO PLASTICS

Baekeland showed that a relatively stable resole prepolymer could be obtained by the controlled condensation of phenol and formaldehyde under alkaline conditions. These linear polymers (PF) may be readily converted to infusible crosslinked polymers called resites by heating or by the addition of mineral acids. As shown by the following equation, the first products produced when formaldehyde is condensed with phenol are hydroxybenzyl alcohols. The linear resole polymer is called an A-stage resin, and the crosslinked resite is called a C-stage resin.



(6.104)

Baekeland recognized that the trifunctional phenol would produce network polymers and hence used difunctional ortho- or para-substituted phenols to produce soluble linear paint resins. As shown by the following equation, linear thermoplastic polymers may be produced by alkaline or acid condensation of formaldehyde with phenolic derivatives such as paracresol.



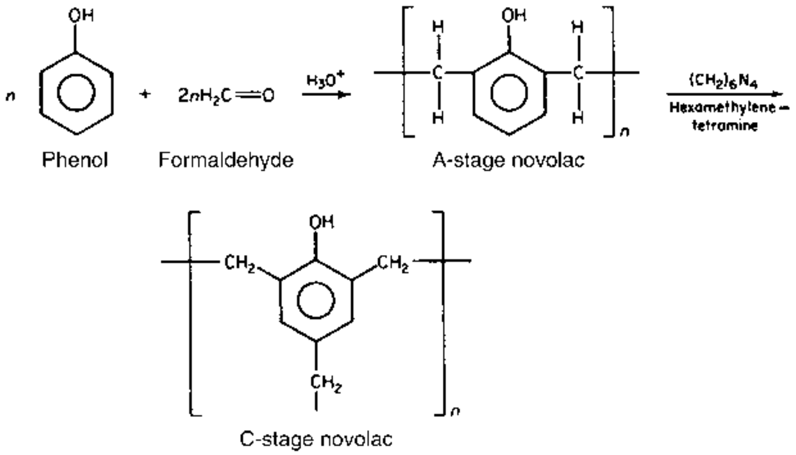
(6.105)

Since the acid condensation of 1 mol of phenol with 1.5 mol of formaldehyde produced infusible C-stage products, Baekeland reduced the relative amount of formaldehyde used and made useful novolac resins in a two-step process. Thus, a stable A-stage novolac resin is produced by heating 1 mol of phenol with 0.8 mol of formaldehyde in the presence of sulfuric acid.

The A-stage resin thus produced, after the removal of water by vacuum distillation, is cooled to yield a solid, which is then pulverized. The additional formaldehyde required to convert this linear polymer to an infusible thermoset resin is supplied by hexamethylenetetramine. The latter, which is admixed with the pulverized A-stage resin, is produced by the condensation of formaldehyde and ammonia.

Other essential ingredients, such as attrition ground wood (wood flour) filler, pigments, and lubricants, are also admixed with the resin and hexamethylenetetramine. The A-stage resin in this mixture is advanced, or further polymerized, by passing it through heavy heated rolls, through an extruder or a heated heavy-duty mixer. The term phenolic molding compound is applied to the granulated product containing the B-stage novolac resin.

The phenolic molding compound is converted to the infusible C stage by heating under pressure in cavities in a compression or transfer molding press. Plywood and other laminates are produced by heating and pressing a series of sheets coated with liquid resole resin. Articles such as automobile distributor heads are molded from novolac molding compounds. The equation for making and curing novolac resins is shown below.

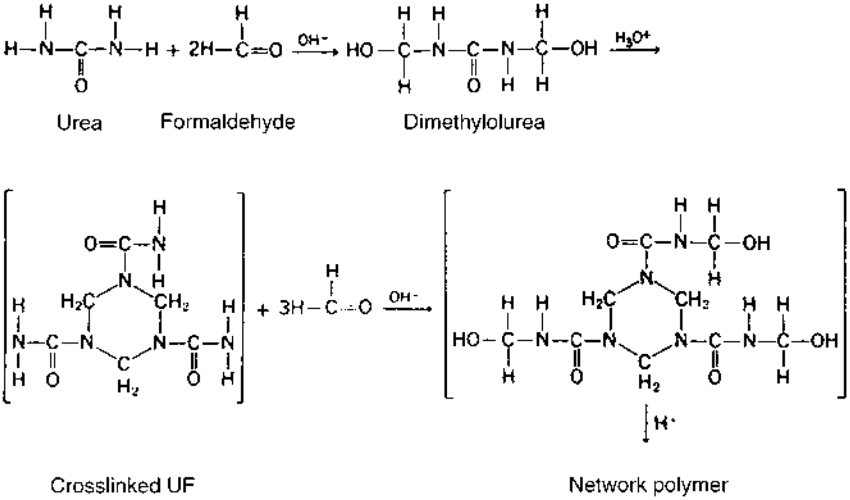


(6.106)

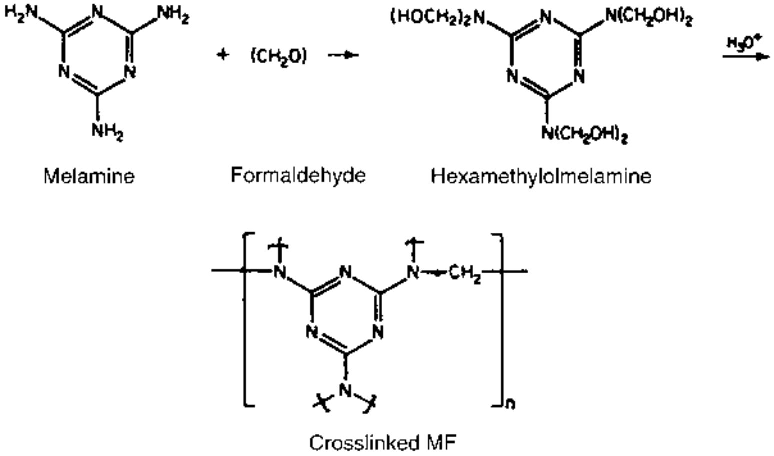
While the condensation of urea and formaldehyde had been described in 1884, ureaformaldehyde (UF) resins were not patented until 1918. Comparable products based on the condensation of formaldehyde and melamine (2,4,6-triamino-1,3,5-triazine) were not patented until 1939. The term amino resins is now used to describe both urea and melamine-formaldehyde (MF) resins.

Urea and melamine are tetra- and hexafunctional molecules, respectively. However, the formation of network polymers is prevented by adding alcohols such as n-butanol and by condensing with formaldehyde at low temperature under alkaline conditions. While phenolic resins have better moisture and weather resistance than urea resins, the latter are preferred for light-colored objects.

For example, the interior layers of laminated countertops are bonded together by phenolic resins, but either urea or melamine resins are used for the decorative surface. Melamine plastics are more resistant to heat and moisture than UF and hence are used for the decorative surface and for the manufacture of plastic dinnerware. As shown by the following equations, the intermediate reaction products are methylol derivatives. Also, cyclization occurs when UF resins are cured in the presence of acids.



(6.107)



(6.108)

As shown in Table 6.3, amino resins, phenolic resins, epoxy resins, saturated and unsaturated polyester resins, nylons, and polyurethanes are produced on a relatively large scale by step-reaction polymerization. Synthetic fibers, thermoplastics, thermosetting plastics, adhesives, coatings, and plastic foams are produced by this technique. However, few synthetic elastomers are produced by step-reaction polymerization, and actually most synthetic polymers are produced by chain-reaction polymerization, which is discussed in the next chapters.

6.16 SYNTHETIC ROUTES

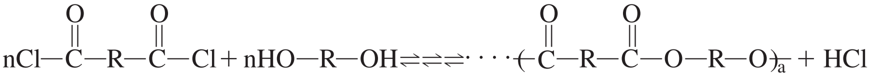
The previous sections contain the general synthesis for a number of important condensation polymers. Here we will consider briefly the three main synthetic techniques utilized in

Table 6.3 Production of Polymers in the United States by Step-Reaction Polymerization (Millions of lb 1995)

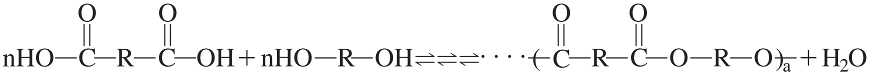
Synthetic fibers (1995)	
Nylon	2,750
Polyester	3,900
Total	6,650
Thermosetting plastics (1995)	
Phenolics	3,230
Polyesters	1,470
Ureas	1,910
Epoxies	600
Melamines	300
Total	7,510
Coatings	
Alkyds	~750
Total for principal synthetic step-reaction polymers	14,810

the synthesis of condensation polymers. This will be followed by a discussion of some considerations that must be taken into account when choosing a given synthetic procedure utilizing specific examples to illustrate the points.

The *melt* technique is also referred to by other names to describe the same or similar processes. These names include high melt, bulk melt, and simply bulk or neat. The melt process is an equilibrium-controlled process in which polymer is formed by driving the reaction toward completion, usually by removal of the by product. For polyesterifications involving the formation of water or HCl, the driving force is the elimination, generally by a combination of reduced pressure and applied heat, of the water or HCl.



$$n\mathrm{Cl{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Cl} + n\mathrm{HO{-}R{-}OH} \rightleftharpoons\rightleftharpoons\rightleftharpoons \cdots \!\left(\mathrm{\overset{\displaystyle O}{\overset{\|}{C}}{-}R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R{-}O}\right)_{a} + \mathrm{HCl} \tag{6.109}$$



$$n\mathrm{HO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH} + n\mathrm{HO{-}R{-}OH} \rightleftharpoons\rightleftharpoons\rightleftharpoons \cdots \!\left(\mathrm{\overset{\displaystyle O}{\overset{\|}{C}}{-}R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R{-}O}\right)_{a} + \mathrm{H_2O} \tag{6.110}$$

Reactants are introduced along with any added catalyst to the reaction vessel. Heat is applied to melt the reactants, permitting their necessary intimate contact. Heating can be maintained at the reaction melt temperature or increased above it. Pressure is reduced. Typical melt polycondensations take several hours to several days before the desired polymeric product is achieved. Yields are necessarily high.

Solution condensations are also equilibrium processes, with the reaction often driven by removal of the byproduct by distillation or by salt formation with added base. Reactants generally must be more reactive in comparison with the melt technique, since lower temperatures are employed, with a number of solution processes occurring near room temperature. Solvent entrapment is a problem, but since a reaction may occur under considerably reduced temperatures compared to the melt technique, thermally induced side reactions are minimized. Side reactions with the solvent have been a problem in some cases. Because the reactants must be quite energetic, many condensations are not suitable for the solution technique.

The *interfacial* technique, while old, only gained popularity with the work of Morgan and Carraher in the 1960s and 1970s. Many of the reactions can be carried out under essentially nonequilibrium conditions. The technique is heterophasic, with two fast-reacting reactants dissolved in a pair of immiscible liquids, one of which is usually water. The aqueous phase typically contains the Lewis base—a diol, diamine, or dithiol—along with any added base or other additive. The organic phase consists of a Lewis acid, such as an acid chloride, dissolved in a suitable organic solvent, such as toluene, octane, or pentane. Reaction occurs near the interface (hence the name). The technique offers the ability to synthesize a wide variety of polymers ranging from modification of cotton, polyester synthesis, synthesis of nucleic acids, and synthesis of polycarbonates, the last being the only polymer produced on a large industrial scale using the interfacial technique. Figure 6.9 describes a simple assembly that can be put together rapidly to form nylon with the interfacial technique. (A note of caution: diamine, carbon tetrachloride, and acid chloride are harmful, and the reaction should be carried out with adequate ventilation and other necessary safety procedures, including rubber gloves.) A few drops of phenolphthalein added to the aqueous phase will give a more colorful nylon material. While aqueous organic solvent systems are the rule, there are a number of other interfacial liquid–gas and nonaqueous liquid systems. With all the potential that the interfacial system offers, it has not attracted wide industrial use because of the high cost of the necessarily reactive monomers and the added expense of trying to cope with solvent removal and recovery.

In principle, any dibasic acid will condense with any diol or diamine. In practice, few such condensations have been utilized on an industrial scale for a variety of reasons,

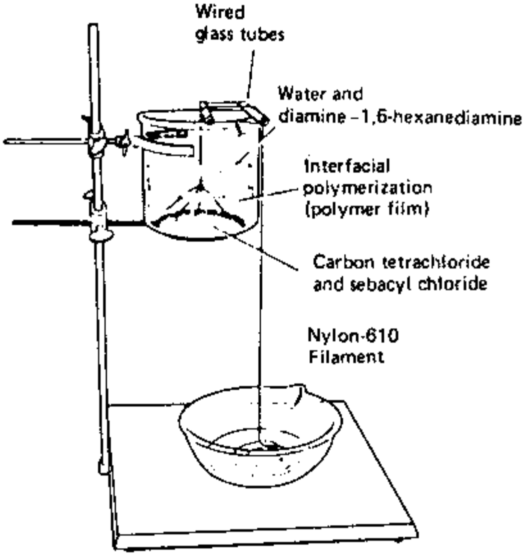
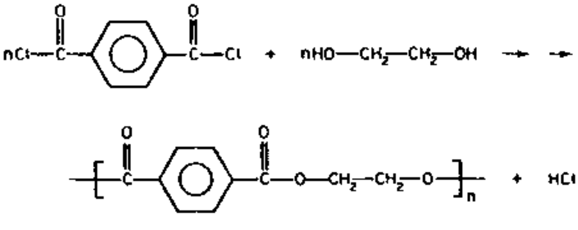


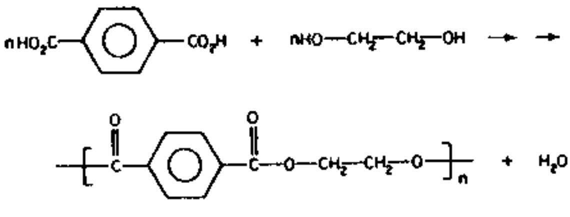
Figure 6.9 Self-propelled interfacial spinning of nylon-610 in the “nylon rope trick.” (From R. Seymour and J. Higgins, *Experimental Organic Chemistry*, Barnes and Noble, New York, 1971. Used with permission.)

including availability of inexpensive comonomers in large quantity and undesirable chemical and physical properties of the synthesized polymer. For instance, several companies were interested in the synthesis of aromatic amines for commercial use. Aromatic amines offered much greater tear resistance and strength compared with an aliphatic nylon such as nylon-66. While aromatic amines could be synthesized using several routes, each produced a solid nylon which was only with difficulty soluble in a limited number of undesirable solvents. Solution of the nylon was necessary for fabrication of the polymer. Morgan and others noted that some polymers formed with rapid stirring would remain in solution for different periods of time. Today aromatic amides, under the name aramids, are synthesized using rapidly stirred systems which permit the aromatic nylon to remain in solution long enough to permit fabrication.

Poly(ethylene terephthalate) is the best known polyester being used as a film (Mylar) and as a fiber (Dacron and Terylene). It can be produced using any of the three major polycondensation procedures. It can be prepared rapidly from the acid chloride using the aqueous interfacial system, giving poor to good yield and short to long chain lengths. Due to the excessive cost of acid chlorides, the interfacial technique of synthesis is presently ruled out industrially. In solution and bulk, the polymerization rate is slow, so excess ethylene glycol is employed to increase the esterification rate. The use of excess diol, while producing the polyester at an acceptable rate, effectively decreases molecular weight. This is overcome by subsequent removal of the excess ethylene glycol. The necessity of using two steps in the production of high molecular weight polyester is undesirable in terms of both time and material.

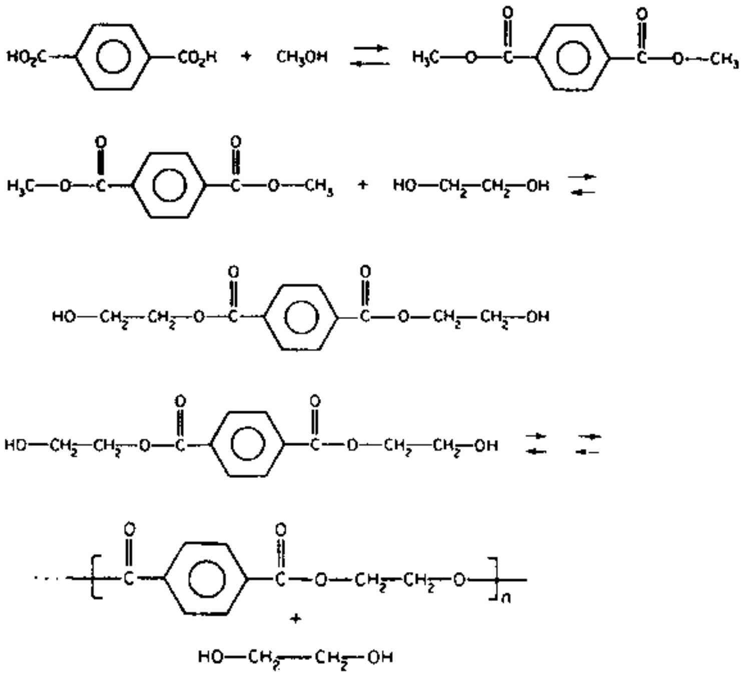


(6.111)



(6.112)

Terephthalic acid is insoluble in most common organic solvents and is also high melting (>300°C), compounding the problem of utilizing it directly for bulk and solution syntheses. Thus, the transesterification reaction utilizing the dimethyl ester of terephthalic acid with removal of methanol and subsequent removal of the “excess” glycol offers an attractive alternative. Yet because the necessary technology, including facilities, is already present to handle terephthalic acid itself, this alternative will probably not become a major part in the industrial synthesis of poly(ethylene terephthalate). Thus, consideration of previous investment of time and facilities is important in deciding on the particular polycondensation technique to be utilized.



(6.113)

Table 6.4 contains a comparison of the three systems. Other often-noted liabilities, strengths, and comparisons of the systems include the following. A characteristic of melt polycondensations is that they are slow and require that conversion be high before high polymer is formed. Most melt systems utilize less reactive reactants than called for in solution and interfacial systems. Thus, higher temperatures are necessary to achieve a reasonable reaction rate. Undesirable side reactions, depolymerization, and degradation of thermally unstable reactants and products can occur at such elevated temperatures. On

Table 6.4 Comparison of Requirements for Different Polycondensation Techniques

Requirement	Melt	Solution	Interfacial
Temperature	High	Limited only by MP and BP of solvents utilized—generally about room temperature	
Stability to heat	Necessary	Unnecessary	Unnecessary
Kinetics	Equilibrium, stepwise	Equilibrium, stepwise	Often nonequilibrium; chain-like on a macroscopic level
Reaction time	1 h to several days	Several minutes to 1 h	Several minutes to 1 h
Yield	Necessarily high	Low to high	Low to high
Stoichiometric equivalence	Necessary	Less necessary	Often unnecessary
Purity of reactants	Necessary	Less necessary	Less necessary
Equipment	Specialized, often sealed	Simple, open	Simple, open
Pressure	High, low	Atmospheric	Atmospheric

the other hand, the less reactive reactants are generally less expensive than those called for in solution and interfacial syntheses. The need for near-equivalence of reactants to achieve high polymers is much greater for the melt process than for the other two processes. Solution and interfacial systems have the added expense of solvent utilized in the reaction system and subsequent solvent removal and recovery from the polymer. The solution and interfacial systems are often collectively known as the low-temperature methods. Assets of the low-temperature methods often cited include use of cis, trans, or optically active structures without rearrangement; direct polymerization to polymer coatings, fibrous particles, small articles, wires, fibers, and films; and the possible synthesis of thermally unstable products and use of thermally unstable reactants. Most industrial processes utilize the melt and solution techniques, although the interfacial technique is gaining limited use.

SUMMARY

1. Many naturally occurring and some synthetic polymers are produced by condensation reactions which are described kinetically by the term step-reaction polymerization. Since a high fractional conversion (p) is required, only a relatively few useful linear polymers, such as polyesters, polycarbonates, polyamides, polyurethanes, polyureas, polysulfides, polyoxides, and polysulfones, may be synthesized by step reactions. However, this technique may be used to produce network polymers even when the fractional conversion is relatively low. Phenolic, epoxy, urea, and melamine resins are produced by step-reaction polymerization.
2. Since the fractional conversions are very high, useful polymers may be produced by the stepwise condensation of a bifunctional acyl or sulfonyl chloride with a diamine or glycol. The rate constant k for these second- and third-order reactions is similar to corresponding reactions of monofunctional reactants and is essentially unchanged as the reactions proceed through dimers, tetramers, octamers, oligometers, and higher molecular weight polymers. This rate constant increases with temperature in accordance with the Arrhenius equation.
3. The degree of polymerization $\overline{DP}$ of a reaction of bifunctional reactants may be calculated from the Carothers equation, $\overline{DP} = 1/(1 - p)$. However, this value will be changed if cyclization occurs to form “wasted loops.” Since this is a step reaction, DP increases with time.
4. The index of polydispersity $\overline{M_w}/\overline{M_n}$ for the most probable molecular weight distribution is $1 + p$ for the certain stepwise kinetics. When the value of p is very high, the $\overline{DP}$ may be lowered by the inclusion of a small amount of a monofunctional reactant so that the functionality (f) is reduced to below 2.
5. High molecular weight linear polyesters may be produced by ester interchange or by interfacial condensation (Schotten-Baumann reaction). When the functionality of one of the reactants is greater than 2, branching may occur and incipient gelation (α_c) or crosslinking may take place. The critical value for α_c is $1/(f - 1)$.
6. The crosslinking of polyesters produced from phthalic anhydride and glycerol may be controlled using relatively low-temperature conditions under which the secondary hydroxyl group is not esterified until the temperature is increased. The crosslinking of unsaturated polyesters such as alkyds occurs by

so-called drying reactions in which crosslinking occurs in the presence of oxygen and a heavy metal catalyst.

7. High molecular weight polyamides, such as nylon-66, may be produced by the thermal decomposition of pure salts of the diamine and dicarboxylic acid reactants. The melting point of these polyamides is decreased as the number of methylene groups in the reactants is increased or if pendant groups are present. The introduction of stiffening groups such as phenylene groups increases the melting point. Polyamides, polybenzimidazoles, polyquinoxaline, and spiroketal polymers have many stiffening groups in the chains and are useful at high temperatures.
8. Polyurethanes and polyureas are produced by the room temperature reaction of a diisocyanate with a dihydric alcohol or a diamine, respectively. When water is present in the reactants, unstable carbamic acids are produced, there decompose to form carbon dioxide, which serves as a blowing agent for foam production.
9. Flexible and rigid polysulfides are produced by a Williamson condensation of aliphatic reactants and a Wurtz condensation of aromatic reactants, respectively. Rigid polyoxides are produced by the low-temperature oxidative coupling of hindered phenols. Stable rigid aromatic polysulfones are produced by the Friedel-Crafts condensation of phenyl sulfonyl chlorides.
10. Low molecular weight epoxy resins are produced by the condensation of epichlorohydrin and dihydroxy compounds such as bisphenol A. These prepolymers, which contain hydroxyl pendant groups and epoxy end groups, may be cured at room temperature by the reaction of polyamines and at elevated temperature by the reaction with cyclic anhydrides.
11. Linear phenolic and amino resins may be produced by the condensation of formaldehyde with phenol, urea, or melamine under alkaline conditions at moderate temperatures. These A-stage resole resins may be advanced almost to incipient gelation (B stage) by heating and cured to the C stage by heating at higher temperatures or by the addition of acids. Novolac resins may be produced under acid conditions by condensing formaldehyde with an excess of phenol. These A-stage linear resins are advanced to the B stage by heating with hexamethylenetetramine under moderate conditions and cured to the C stage in a mold at higher temperatures.
12. When the functionality of phenol, urea, or melamine is reduced to 2 by the incorporation of substituents, the condensation with formaldehyde yields soluble thermoplastics.

GLOSSARY

advancing: Polymerizing further.
alkyds: Originally used to describe oil-modified polyesters, but now used for many polyester plastics and coatings.
allophanates: The reaction product of a urethane and an isocyanate.
α: Symbol for branching coefficient.
α_c: Critical value for incipient gelation.
amino resins: A term used to describe urea and melamine-formaldehyde resins.
Araldite: Trade name for an epoxy resin.

aramids: Aromatic polyamides.

A stage: A linear prepolymer of phenol and formaldehyde.

Baekeland, Leo: The inventor of phenol-formaldehyde resins.

Bakelite: A polymer produced by the condensation of phenol and formaldehyde.

bifunctional: A molecule with two active functional groups.

bisphenol A: 2,2′-Bis(4-hydroxyphenyl)propane.

B stage: An advanced A-stage resin.

C: Concentration at a temperature (T).

C, A: Concentration at a time t.

C_0, A_0: Original concentration.

carbamate: A urethane.

carbamic acids: Unstable compounds which decompose spontaneously to produce amines and carbon dioxide.

Carothers equation: $1/(1 - p)$.

Carothers, W. H.: The inventor of nylon who also developed the kinetic equations for the step-reaction polymerization.

compression molding press: A press that uses external pressure to force a heat-softened molding compound into a die to produce a molded article.

condensation reaction: A reaction in which two molecules react to produce a third molecule and a byproduct such as water.

cyclization: Ring formation.

Dacron: Trade name for a polyester fiber.

drier: A catalyst for crosslinking by oxygen. Driers are soluble heavy metal salts such as cobalt naphthenate.

drying: Crosslinking of an unsaturated polymer in the presence of oxygen.

drying oil: An unsaturated oil like tung oil.

E_a: Energy of activation.

Ekanol: Trade name for poly(p-benzoate).

engineering plastics: Those with physical properties good enough for use as structural materials.

Epon: Trade name for an epoxy resin.

epoxy resin: A polymer produced by the condensation of epichlorohydrin and a dihydric alcohol or by the epoxidation of an unsaturated compound.

ester interchange: The reaction between an ester of a volatile alcohol and a less volatile alcohol in which the lower boiling alcohol is removed by distillation.

filament: The extrudate when a polymer melt is forced through a hole in a spinneret.

functionality: The number of active functional groups in a molecule.

functionality factor: The average number of functional groups present per reactive molecule in a mixture of reactants.

furan esin: Resin produced from furfuryl alcohol or furfural.

gel point: The point at which crosslinking begins.

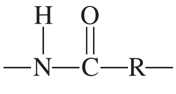
glyptals: Polyesters, usually crosslinked by heating at elevated temperatures.

hexamethylenetetramine: A crystalline solid obtained by the condensation of formaldehyde and ammonia.

incipient gelation: The point at which $\overline{DP}$ equals infinity.

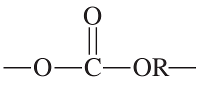
interfacial polymerization: One in which the polymerization reaction takes place at the interface of two immiscible liquids.

k: Symbol for rate constant.
Kodel: Trade name for a polyester fiber.
ladder polymer: A double-chained, temperature-resistant polymer.
laminate: Layers of sheets of paper or wood adhered by resins and pressed together like plywood.
long oil alkyd: One obtained in the presence of 65–80% of an unsaturated oil.
MF: Melamine-formaldehyde resin.
medium oil alkyd: An alkyd obtained in the presence of 50–65% of an unsaturated oil.
melamine-formaldehyde resin: A resin produced by the condensation of melamine and formaldehyde.
methylol: $—CH_2OH$.
molding compound: A name used to describe a mixture of a resin and essential additives.
N: Number of molecules.
network polymer: Infusible crosslinked polymer.
nonoil alkyd: An oil-free alkyd containing no unsaturated oils.
novolac: Polymers prepared by the condensation of phenol and formaldehyde under acidic conditions.
nucleophilic substitution: A reaction in which a nucleophilic reagent displaces a weaker nucleophile or base and the latter becomes the leaving group.
nylon: A synthetic polyamide.
nylon-610 (PA): A polyamide synthesized from a 6-carbon diamine and a 10-carbon dicarboxylic acid.
nylon rope trick: The preparation of a polyamide by the Schotten-Baumann reaction of a diacyl chloride and a diamine.
nylon salt: A salt of a diamine and a dicarboxylic acid used as the precursor of nylon.
oil length: A term used to indicate the relative percentage of unsaturated oils used in the production of alkyds.
ordered copolyamides: Polymers produced from a mixture of diamine and dicarboxylic acid reactants of different types.
p: Fractional conversion or fractional yield.
PA: Symbol for polyamide.
PBI: Symbol for polybenzimidazole.
Perlon U: A trade name for polyurethane.
PF: A phenolic resin.
phenoxy resin: A polymer with hydroxyl pendant groups resembling an epoxy resin without epoxy groups.
PI: Polyimide.
polyamide: A polymer with repeat units of



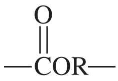
$$—\overset{\displaystyle H}{\overset{|}{N}}—\overset{\displaystyle O}{\overset{\|}{C}}—R—$$

polybenzimidazole (PBI): A temperature-resistant heterocyclic polymer.
polycarbonate (PC): A polymer with the repeat unit of



$$—O—\overset{\displaystyle O}{\overset{\|}{C}}—OR—$$

polyester: A polymer with the repeat unit of

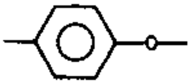


$$-\overset{\overset{\displaystyle O}{\|}}{C}OR-$$

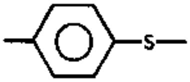
poly(ethylene terephthalate) (PET): A linear polyester used for fibers and for blow-molding soft drink bottles.

polyimide (PI): A temperature-resistant heterocyclic polymer.

poly(phenylene oxide): A polymer with the repeat unit



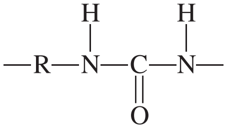
poly(phenylene sulfide): A polymer with the repeat unit



polysulfide: A polymer with the repeat unit $-(RS)_x-$.

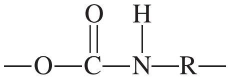
polysulfone: A polymer with sulfone groups (SO_2) in its backbone.

polyurea: A polymer with the repeat unit of



$$-R-\overset{\overset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-$$

polyurethane (PU): A polymer with the repeat unit of



$$-O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-R-$$

prepolymer: A low molecular weight material (oligomer) capable of further polymerization produced by step-reaction polymerization.

PU: Polyurethane.

r: Molar ratio of reactants.

resite: A crosslinked resole.

resole: A linear polymer prepared by the condensation of phenol and formaldehyde under alkaline conditions.

Ryton: Trade name for poly(phenylene sulfide).

Schotten-Baumann reaction: A reaction between an acryl chloride and an alcohol or amine in the presence of sodium hydroxide or pyridine.

second-order reaction: A reaction in which the rate of proportional to the concentration of one reactant to the second power or to the product of two reactants to the first power.

short oil alkyd: An alkyd obtained in the presence of 30–50% of an unsaturated oil.

spiropolymer: Polymer having a structure resembling a spiral and thus consisting of a double chain.

step-reaction polymerization: Polymerization in which polyfunctional reactants react to produce larger units in a continuous stepwise manner.

t: Time in seconds.

T: Temperature (K).

TDI: 2,4-Tolylene diisocyanate.

Thiokol: Trade name for a polysulfide elastomer.

UF: Symbol for urea-formaldehyde resin.

unsaturated polyester: A term used to describe alkyds with unsaturated chains, particularly those produced by the condensation of maleic anhydride with ethylene glycol.

urea-formaldehyde resin: A resin produced by the condensation of urea and formaldehyde.

wasted loops: The formation of cyclic compounds instead of polymers.

wood flour: A filler produced by the attrition grinding of wood.

EXERCISES

1. Which of the following will yield a polymer when condensed with adipic acid: (a) ethanol, (b) ethylene glycol, (c) glycerol, (d) aniline, or (e) ethylenediamine?
2. Could Carothers have produced strong polyester fibers by ester interchange or Schotten-Baumann reactions using aliphatic reactants?
3. Which would be more useful as a fiber: (a) poly(ethylene terephthalate) or (b) poly (hexylene terephthalate)?
4. If the fractional conversion in an ester interchange reaction is 0.99999, what would be the $\overline{\text{DP}}$ of the polyester produced?
5. Use the logarithmic form of the Arrhenius equation to show that the value of the rate constant k increases as the temperature increases.
6. What is the first product produced when a molecule of sebacyl chloride reacts with a molecule of ethylene glycol?
7. What is the next product formed in exercise 6?
8. How would you improve the strength of the filament produced in the nylon rope trick without changing the reactants?
9. Name the product produced by the condensation of adipic acid and tetramethylenediamine.
10. In which reaction would you expect the more “wasted loops”: the reaction of oxalyl chloride with (a) ethylenediamine or (b) hexamethylenediamine?
11. Which system would be more apt to produce “wasted loops”: (a) a dilute solution or (b) a concentrated solution?
12. If the values of A_0 and k are 10 mol L^{-1} and 10^{-3} L mol s^{-1}, respectively, how long would it take to obtain a $\overline{\text{DP}}$ of 37?
13. Which will yield the lower index of polydispersity: (a) $p = 0.999$ or (b) $p = 0.90$?
14. If you used a 2% molar excess of bisphenol A with TDI, what would be the maximum $\overline{\text{DP}}$ obtainable assuming $p = 1$?
15. Why would the product obtained in question 14 be a useful fiber assuming $\overline{\text{DP}} = 100$?
16. Assuming a value of 0.999 for p, what would be the $\overline{\text{DP}}$ of a polyester prepared from equimolar quantities of difunctional reactants in the presence of 1.5 mol% of acetic acid? Let the mol% difunctional reactants both be 98.5.
17. What is the functionality of a mixture consisting of 0.7 mol ethylene glycol, 0.05 mol ethanol, and 0.25 mol of glycerol?

18. What is the critical value of f for incipient gelation in the mixture described in exercise 17?
19. What is the functionality of a mixture consisting of 0.4 mol of pentaerythritol and 0.6 mol of diethylene glycol?
20. Which would be the better or stronger fiber: one made from an ester of (a) terephthalic acid or (b) phthalic acid?
21. What would be the deficiency of a nylon film that was stretched in one direction only?
22. Which would be more flexible: (a) poly(butylene terephthalate) or (b) poly(hexylene terephthalate)?
23. Which would be more apt to deteriorate in the presence of moisture: (a) Lexan molding powder or (b) Lexan sheet?
24. How could you flexibilize Ekanol?
25. How would you prepare a nylon with greater moisture resistance than nylon-66?
26. How would you prepare a nylon that would be less “clammy” when used as clothing?
27. Which would be higher melting: (a) a polyamide or (b) a polyester with similar numbers of methylene groups in the repeat units?
28. Why is a methoxymethylated nylon more flexible than nylon?
29. Which would perform better at high temperatures: (a) a polyimide or (b) polyquinoxaline?
30. Isn’t it wasteful to decompose a diisocyanate by hydrolysis to produce foams?
31. How would you prepare a hydroxyl-terminated polyester?
32. How would you prepare a more flexible polyalkylene sulfide than the one shown in Sec. 7.10?
33. Why is Ryton stiffer than Thiokol?
34. Why do polyurethanes and epoxy resins have good adhesive properties?
35. Why are furan resins relatively inexpensive?
36. Why it is necessary to add hexamethylenetetramine to a novolac molding compound?
37. Could you produce a soluble novolac resin from resorcinol?
38. Can you explain why there are so many terms used, such as novolac, resole, etc., in phenolic resin technology?
39. Why isn’t Bakelite used for dinnerware?
40. Which of the following could be a nonpetrochemical plastic: (a) Bakelite, (b) urea plastics, or (c) melamine plastics?
41. Which would produce the better fiber: the reaction product of phthalic acid and (a) 1,4-butanediol, or (b) 2-hydroxybutanol?

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7

Ionic Chain-Reaction and Complex Coordinative Polymerization (Addition Polymerization)

In contrast to the slow step-reaction polymerization discussed in Chapter 6, chain-reaction polymerization is usually rapid, and the initiated species continue to propagate until termination. Thus, in the extreme case, one initiating species could be produced which would produce one high molecular weight polymer molecule, leaving all of the other monomer molecules unchanged. In any case, the concentration of the monomer, which is usually a derivative of ethylene, decreases continuously throughout the reaction. In contrast to stepwise polymerization, the first species produced is a high molecular weight polymer.

A kinetic chain reaction usually consists of at least three steps, namely, initiation, propagation, and termination. The initiator may be an anion, a cation, a free radical, or a coordination catalyst. While coordination catalysts are the most important commercially, the ionic initiators will be discussed first in an attempt to simplify the discussion of chain-reaction polymerization.

While most vinyl monomers undergo free radical polymerization (Chapter 8), a smaller number undergo ionic polymerization. Cationic polymerizations require monomers that have electron-releasing groups such as an alkoxy, a phenyl, or a vinyl group. Anionic polymerization occurs with monomers containing electron-withdrawing groups such as carboxyl, nitrile, or halide. This selectivity is due to the strict requirements for stabilization of anionic and cationic species.

Compared with free radical polymerizations, ionic polymerizations are not as well defined. Reactions can use heterogeneous initiators and they are usually quite sensitive to the presence of impurities. Thus, kinetic studies are difficult and the results sensitive to the particular reaction conditions. Furthermore, the rates of polymer formation are more rapid.

Cationic and anionic polymerizations are similar. Both involve the formation and propagation of ionic species. While high-energy, low-stability ions would be expected to react with most double bonds, ionic species that are stable enough to propagate are difficult

Table 7.1 Major Techniques Used in the Production of Important Vinyl Polymers

Free radical	Low-density polyethylene (LDPE)
	Poly(vinyl chloride)
	Poly(vinyl acetate)
	Polyacrylonitrile and acrylic fibers
	Poly(methyl methacrylate)
	Polyacrylamide
	Polychloroprene
	Poly(vinyl pyridine)
	Styrene-acrylonitrile copolymers, (SAN)
	Polytetrafluoroethylene
	Poly(vinylene fluoride)
	Acrylonitrile-butadiene-styrene copolymers (ABS)
	Ethylene-methacrylic acid copolymers
	Styrene-butadiene copolymers (SBR)
	Nitrile rubber (NBR)
	Polystyrene
Cationic	Polyisobutylene
	Butyl rubber
	Polyacetal
Anionic	Thermoplastic olefin elastomers (copolymers of butadiene, isoprene, and styrene)
	Polyacetal
Complex	High-density polyethylene (HDPE)
	Polypropylene
	Polybutadiene
	Polyisoprene
	Ethylene-propylene elastomers

to form and are easily destroyed. The "energenic window" that allows the formation of such charged species is narrow. While polar solvents might be desirable to solvate the ions and hence help stabilize them, they often cannot be used. Some polar solvents, such as water and alcohols, react with and destroy most ionic initiators. Other polar solvents, such as ketones, prevent initiation because of the formation of stable complexes with the initiators. Ionic polymerizations are therefore conducted in low or moderately polar solvents, such as hexane and ethylene dichloride.

By bulk, almost all vinyl polymers are made by four processes: free radical (>50%), complex coordinate (12–15%), anionic (10–15%), and cationic (8–12%); Table 7.1. Three of these techniques are covered in this chapter.

Chain Growth Polymerization—General

The next three chapters will deal with polymers formed from chain growth polymerization. Chain growth polymerization is also called addition polymerization and is based on free radical, cationic, anionic, and coordination reactions where a single initiating species causes the growth of a polymer chain.

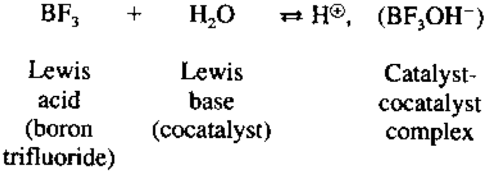
The kinetic chain reaction typically consists of three steps: initiation, propagation, and termination. The initiators for free radical, anionic and cationic polymerizations are organic radicals, carbanions, and carboniums. Chain growth is exothermic with the polymerization is mainly controlled by steric and resonance factors of the monomer. Generally, the less resonance stabilization the more exothermic the reaction and the greater the steric factors, the less exothermic the polymerization.

For high polymer to be formed, the activated monomer and growing polymer chain must be stable and growth rapid enough to allow long chains to be formed. Stability of the activated monomer or growing end is primarily dependant on resonance, polar, and inductive effects. Thus, a vinyl monomer with electron donating groups is more apt to polymerize through a cationic route because the active carbonium site is stabilized inductively and through resonance. Styrene can be polymerized by either cationic, anionic, or free radical polymerization because all three active forms are resonance stabilized.

7.1 CATIONIC POLYMERIZATION

The art of cationic polymerization, like that of many other types of polymerization, is at least a century old. However, the mechanisms for the early reactions were not understood, and, of course, the early scientists did not grasp the modern concept of macromolecules. Nevertheless, it is of interest to note that turpentine, styrene, isobutylene, and ethyl vinyl ether were polymerized over a century ago by the use of cationic initiators such as sulfuric acid, tin(IV) chloride, boron trifluoride, and iodine.

The first species produced in these reactions are carbocations, and these were unknown as such prior to World War II. It is now known that pure Lewis acids, such as boron trifluoride or aluminum chloride, are not effective as initiators. A trace of a proton-containing Lewis base, such as water, is also required. As shown in Eq. (7.1), the Lewis base coordinates with the electrophilic Lewis acid, and the proton is the actual initiator. Since cations cannot exist alone, they are always accompanied by a *counterion*, also called a *gegenion*.

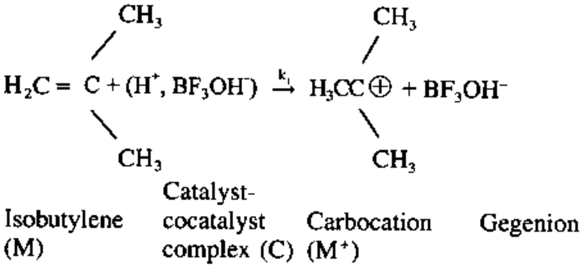


$$\underset{\substack{\text{Lewis}\\\text{acid}\\\text{(boron}\\\text{trifluoride)}}}{BF_3} + \underset{\substack{\text{Lewis}\\\text{base}\\\text{(cocatalyst)}}}{H_2O} \rightleftarrows H^{\oplus},\ \underset{\substack{\text{Catalyst-}\\\text{cocatalyst}\\\text{complex}}}{(BF_3OH^-)} \tag{7.1}$$

Since the required activation energy for ionic polymerization is small, these reactions may occur at very low temperatures. The carbocations, including the macrocarbocations, repel each other, hence, chain termination cannot take place by combination but is usually the result of reaction with impurities.

Both the initiation step and the propagation step are dependent on the stability of the carbocations. Isobutylene (the first monomer to be polymerized commercially by ionic initiators), vinyl ethers, and styrene may be polymerized by this technique. The order of activity for olefins is $(CH_3)_2\ C = CH_2 > CH_3\ (CH = CH_2) > CH_2 = CH_2$, and for para-substituted styrenes, the order for the substituents is $OCH_3 > CH_3 > H > Cl$. The mechanism is also dependent on the solvent as well as the electrophilicity of the monomer and the nucleophilicity of the gegenion. Rearrangements may occur in ionic polymerizations.

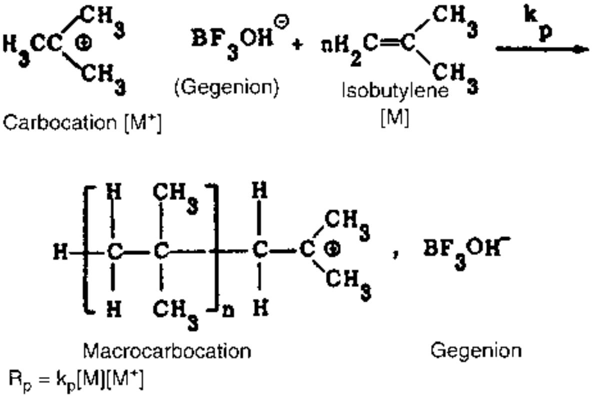
The rate of initiation (R_i) for typical reactions, as shown in the following equation, is proportional to the concentration of the monomer [M] and the concentration of the catalyst–cocatalyst complex [C].



(7.2)

$R_i = k_i[C][M]$

Propagation, or chain growth, takes place in a head-to-tail configuration as a result of carbocation (M^+) addition to another monomer molecule. The rate constant (k_p) is essentially the same for all propagation steps and is affected by the dielectric constant of the solvent. The rate is fastest in solvents with high dielectric constants, promoting separation of the carbocation-gegenion pairs. The chemical and kinetic equations for propagation are as follows:



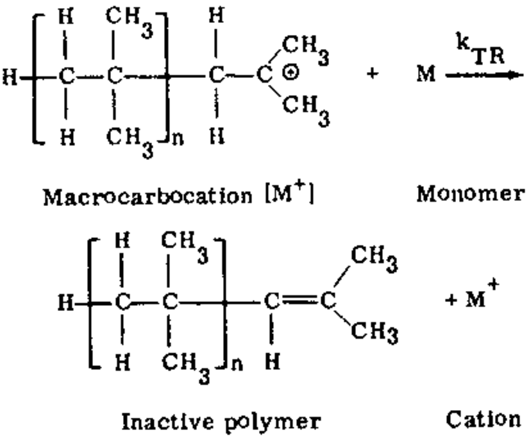
(7.3)

$R_p = k_p[M][M^+]$

The termination rate R_T, assumed to be a first-order process, is simply the dissociation of the macrocarbocation–gegenion complex forming BF_3 and H_2O and the now neutral polymer chain. This may be expressed as follows:

$$R_T = k_T[M^+] \tag{7.4}$$

Termination may take place by chain transfer, in which a proton is transferred to a monomer molecule [M], leaving a cation which may serve as an initiator. The $\overline{DP}$ is equal to the kinetic chain length (v) when chain transfer occurs. The chemical and kinetic equations for chain transfer are shown below.



(7.5)

$$R_{Tr} = k_{Tr}[M][M^+]$$

Since it is difficult to determine values for members of these equations, which include $[M^+]$, one assumes a steady state in which the rate of initiation equals the rate of termination, giving $R_i = R_T$, and solves for $[M^+]$ as shown below:

$$k_i[C][M] = k_T[M^+], \text{ therefore, } [M^+] = \frac{k_i[C][M]}{k_T} \tag{7.6}$$

This expression for $[M^+]$ may then be substituted in the propagation rate equation [Eq. (7.3)] and the overall rate for cationic polymerization:

$$R_p = k_p[M][M^+] = \frac{k_p k_i [M][M]^2}{k_T} = k'[C][M]^2 \tag{7.7}$$

We may also determine the value for $\overline{DP}$ when termination, via internal dissociation [Eq. (7.4)], is the dominant step, as follows:

$$\overline{DP} = \frac{R_p}{R_T} = \frac{k_p[M][M^+]}{k_T[M^+]} = \frac{k_p}{k_T}[M] = k''[M] \tag{7.8}$$

However, if chain transfer is the dominant step in the termination of a growing chain,

$$\overline{DP} = \frac{R_p}{R_{Tr}} = \frac{k_p[M][M^+]}{k_{Tr}[M][M^+]} = \frac{k_p}{k_{Tr}} = k'' \tag{7.9}$$

It is important to note that regardless of how termination takes place, the molecular weight of a polymer synthesized by the cationic process is independent of the concentration of the initiator. However, the rate of ionic chain polymerization is dependent on the dielectric constant of the solvent, the resonance stability of the carbonium ion, the stability of the gegenion, and the electropositivity of the initiator.

The rates of all single-step reactions increase as the temperature increases. This may not be true for multistep reactions such as those involved with the cationic polymerization. For cationic polymerizations the activation energies are generally of the order $E_{Tr} > E_i > E_p$. Remembering that the description of the specific rate constant is

$$k = Ae^{-Ea/RT} \tag{7.10}$$

the overall or "net" activation energy is

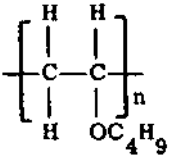
$$E_{(\text{overall})} = E_{Tr} + E_i + E_p \tag{7.11}$$

For many cationic polymerization, the net activation is negative, using the relationships given in (7.7), so that the overall rate of polymerization decreases, for these cases, as the temperature is increased. Further, using (7.9) and since $E_{Tr} > E_p$, the overall degree of polymerization does decrease as the temperature is increased.

Polyisobutylene (Vistanex, IM) is a tacky polymer with a very low T_g (-70°C) used as an adhesive, a caulking compound, a chewing gum base, and an oil additive. Its use as an oil additive is related to its change in shape with increasing temperature. Since lubricating oil is not a good solvent for polyisobutylene, polyisobutylene is present as a coil at room temperature when mixed with an oil. However, the chain tends to uncoil as the temperature increases and as the oil becomes a better solvent. This effect tends to counteract the decrease in viscosity of the oil as the temperature is increased.

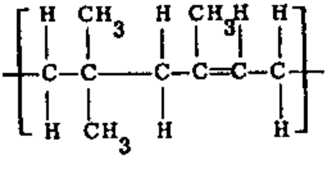
Butyl rubber (IIR), widely used for inner tubes and as a sealant, is produced by the cationic low-temperature copolymerization of isobutylene in the presence of a small amount of isoprene (10%), as shown in Scheme 7.1. Thus, the random copolymer chain contains a low concentration of widely isolated double bonds which assume a low cross-linked density as a result of the formation of large “principal sections” when the butyl rubber is vulcanized or cured. (Copolymers are discussed in Chapter 9.)

When the gegenion and the carbocation present in the polymerization of vinyl isobutyl ether form an ion pair in propane at -40°C, stereoregular polymers are produced. The carbocations of vinyl alkyl ethers are stabilized by the delocalization of p electrons in the oxygen atom, and thus these monomers are readily polymerized by cationic initiators. Poly(vinyl isobutyl ether) has a low T_g and is used as an adhesive and as an impregnating resin.


$$\left[\begin{array}{cc} H & H \\ | & | \\ -C- & C- \\ | & | \\ H & OC_4H_9 \end{array} \right]_n$$

The value of the propagation rate constant (k_p) for vinyl isobutyl either is 6.5 L $\text{mol}^{-1}\ \text{sec}^{-1}$. This value decreases as one goes from vinyl ethers to isoprene, isobutylene, butadiene, and styrene. The k_p value for styrene in 1,1-dicholoroethane is 0.0037 L $\text{mol}^{-1}\ \text{sec}^{-1}$.

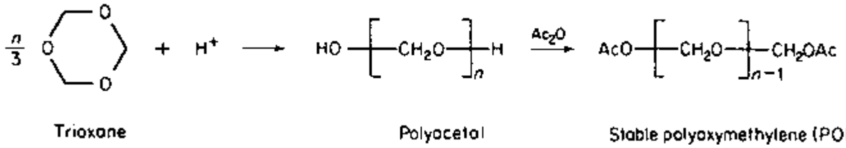
Commercial polymers of formaldehyde may also be produced by cationic polymerization using boron trifluoride etherate as the initiator. As shown in Eq. (7.12), the polymer is produced by ring opening of trioxane. Since the polyacetal is not thermally stable, the



Scheme 7.1 A typical repeat unit in the butyl rubber chain.

hydroxyl end groups are esterified (capped) by acetic anhydride. The commercial polymer is a strong engineering thermoplastic. Engineering plastics usually have higher modulus and higher heat resistance than general purpose polymers. The commercial polymer Delrin is produced by anionic polymerization.

Another stable polyacetal [polyoxymethylene (POM); Celcon] is produced commercially by the cationic copolymerization of a mixture of trioxane and dioxolane.



(7.12)

As shown in Scheme 7.2, this copolymer contains repeat units from both reactants in the polymer chain. It is believed that the irregularities in the composition of the copolymer hinder the "unzipping" degradation pathway of the polymeric chain.

Polychloral is a flame-resistant strong polymer that can be produced by cationic polymerization the uncapped polymer decomposes at a ceiling temperature of 58°C. The polymer does not exist above this temperature, which is called the ceiling temperature, T_c. Thus, one may produce solid castings by pouring a hot mixture of trichloroacetaldehyde and initiator into a mold and allowing the polymerization to take place in situ as the mixture cools below the ceiling temperature.

In addition to the production of polyacetals by the ring-opening polymerization of trioxane, this technique was also investigated by Staudinger for the synthesis of ethers and is still used for the production of polymers of ethylene oxide (oxirane). Other homologous, cyclic ethers, such as oxetane and tetrahydrofuran, may be polymerized by cationic ring-opening polymerization techniques. Since the tendency for ring cleavage decreases as the size of the ring increases, it is customary to include some oxirane with the reactants as a promotor. The six-membered ring oxacyclohexane is so stable that it does not polymerize even in the presence of a promotor.

As shown in the following equations, an initiator such as sulfuric acid produces an oxonium ion and a gegenion. The oxonium ion then adds to the oxirane, and the macrooxonium ion produced by propagation may then be terminated by chain transfer with water.

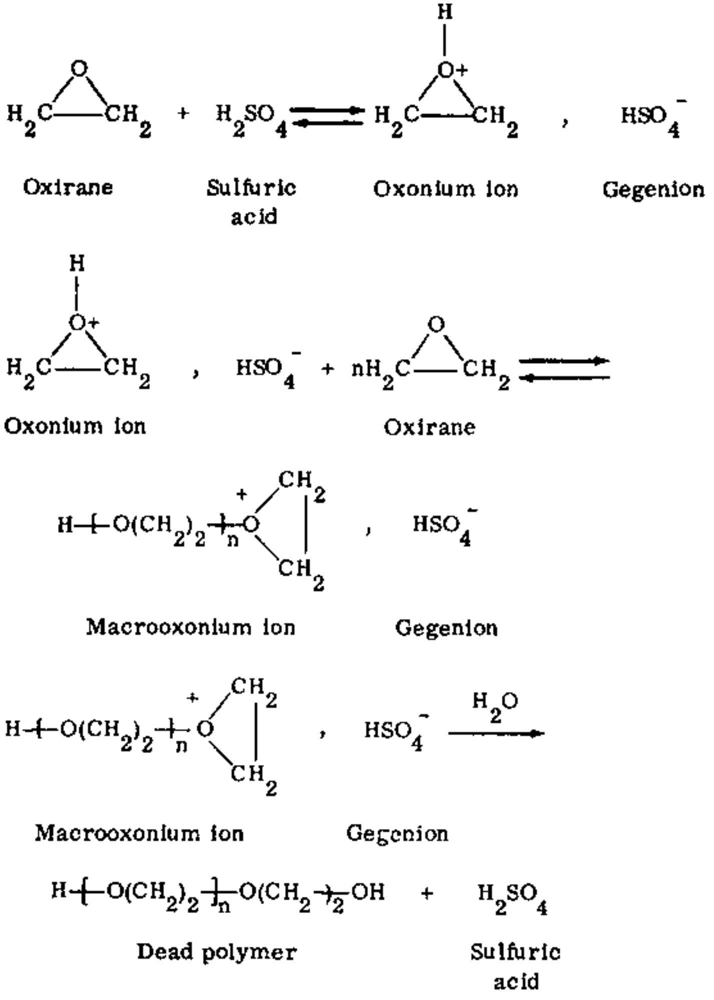
As indicated by the double arrow, the propagation is an equilibrium reaction that tends to hinder the production of high molecular weight polymers. The highest molecular weight products are obtained in polar solvents, such as methylene chloride, at low temperatures (−20 to −100°C).

These water-soluble polymers, which may also be produced by anionic polymerization techniques, are available commercially in several molecular weight ranges under the trade names of Carbowax and Polyox. In addition to their use as water-soluble bases for

$$\mathrm{HO{+}CH_2OCH_2O(CH_2)_2OCH_2O{+}_nH}$$

Scheme 7.2 A segment of a copolymer chain produced from the cationic copolymerization of trioxane and dioxolane.

cosmetics and pharmaceuticals, these polymers may be added to water to increase its flow rate.

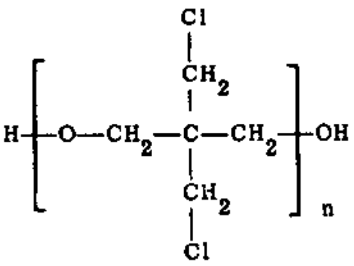


(7.13)

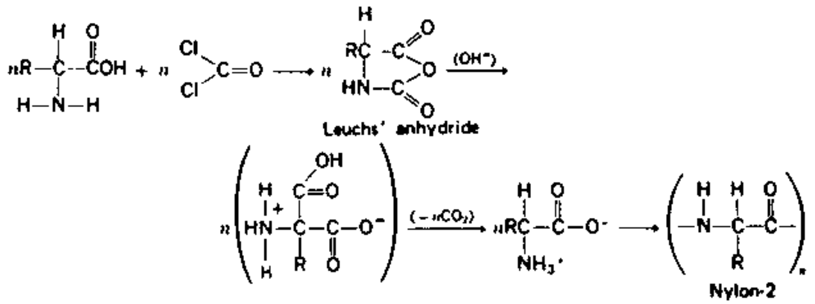
The oxacyclobutane derivative, 3,3-bischloromethyloxacyclobutane, may be polymerized by cationic ring-opening polymerization techniques to yield a water-insoluble, crystalline, corrosion-resistant polymer. As shown in Scheme 7.3, this polymer (Penton) has two regularly spaced chloromethylene pendant groups on the polymer chain.

An acid-soluble polymer, Montrek, has also been produced by the ring-opening polymerization of ethyleneimine (aziridine). This monomer has been classified as a carcinogen and should be used with extreme caution.

While lactams are usually polymerized by anionic ring-opening reactions, N-carboxyl-α-amino acid anhydrides (NCA) may be polymerized by either cationic or anionic techniques. These polypeptide products, which are now called nylon-2, were first produced by Leuchs in 1908 and are called Leuchs' anhydrides. The synthesis may be used to produce homopolypeptides that can be used as model compounds for proteins. As shown in the following equation, carbon dioxide is eliminated in each step of the propagation reaction.



Scheme 7.3 Poly(3,3-bis-chloromethyloxybutylene).



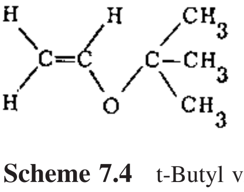
(7.14)

Polyterpenes, coumarone-indene resins, and the so-called petroleum resins are produced commercially in relatively large quantities by the cationic polymerization of unsaturated cyclic compounds. These inexpensive resinous products are used as additives for rubber, coatings, floor coverings, and adhesives.

It has been known for some time that cationic polymerizations can produce polymers with stereoregular structures. While a number of vinyl monomers have been evaluated in this regard, much of the work has centered about vinyl ethers. Several general observations have been noted, namely: (1) the amount of stereoregularity is dependent on the nature of the initiator; (2) stereoregularity increases with a decrease in temperature; and (3) the amount and type of polymer (isotactic or syndiotactic) is dependent on the polarity of the solvent. For instance, polymerization of t-butyl vinyl ether (Scheme 7.4) has the isotactic form preferred in nonpolar solvents, but the syndiotactic form is preferred in polar solvents.

7.2 ANIONIC POLYMERIZATION

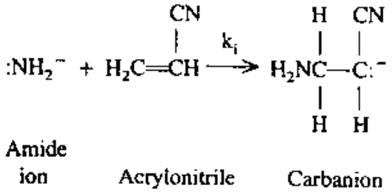
Anionic polymerization was used to produce synthetic elastomers from butadiene at the beginning of the twentieth century. Early investigators used alkali metals in liquid ammonia



Scheme 7.4 t-Butyl vinyl ether.

as initiators, but these were replaced in the 1940s by metal alkyls such as n-butyllithium. In contrast to vinyl monomers with electron-donating groups polymerized by cationic initiators, vinyl monomers with electron-withdrawing groups are more readily polymerized by anionic initiators. Accordingly, acrylonitrile is readily polymerized by anionic techniques, and the order of activity with an amide ion initiator is as follows: acrylonitrile > methyl methacrylate > styrene > butadiene. As might be expected, methyl groups on the α carbon decrease the rate of anionic polymerization, and chlorine atoms on the α carbon increase that activity.

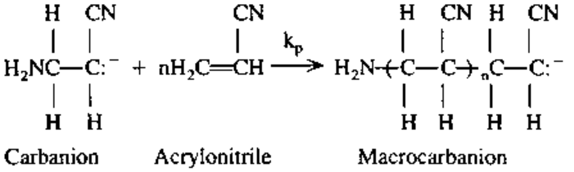
As shown by the following chemical and kinetic equations, potassium amide may be used to initiate the polymerization of acrylonitrile. The propagating species in anionic polymerization are carbanions instead of carbonium ions, but the initiation, propagation, and chain transfer termination steps in anionic polymerization are similar to those described for cationic polymerization:



$$:NH_2^- + H_2C{=}\overset{CN}{\overset{|}{C}}H \xrightarrow{k_i} H_2N\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{CN}{\overset{|}{C}}}}:^- \qquad (7.15)$$

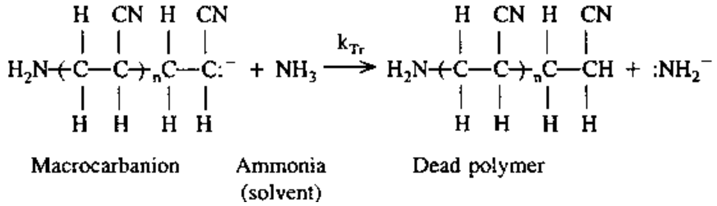
$$R_i = k_i\, C[M]$$

where C is equal to [:NH_2^-].



$$H_2N\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{CN}{\overset{|}{C}}}}:^- + nH_2C{=}\overset{CN}{\overset{|}{C}}H \xrightarrow{k_p} H_2N\left(\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{CN}{\overset{|}{C}}}}\right)_n\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{CN}{\overset{|}{C}}}}:^- \qquad (7.16)$$

$$R_p = k_p[M][M^{-}]$$



$$H_2N\left(\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{CN}{\overset{|}{C}}}}\right)_n\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{CN}{\overset{|}{C}}}}:^- + NH_3 \xrightarrow{k_{Tr}} H_2N\left(\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{CN}{\overset{|}{C}}}}\right)_n\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{CN}{\overset{|}{C}}}}H + :NH_2^- \qquad (7.17)$$

$$R_{Tr} = k_{Tr}[NH_3][M^-]$$

Since it is difficult to determine the concentration of carbanion [M^-], one assumes a steady state in which $R_i = R_{Tr}$ and solves for [M^-], as shown below.

$$k_i[C][M] = k_{Tr}[NH_3][M^-] \text{ therefore, } [M^-] = \frac{k_i[C][M]}{k_{Tr}[NH_3]} \qquad (7.18)$$

Thus,

$$R_p = k_p[M][M^-] = [M]\frac{k_p k_i C[M]}{k_{Tr}[NH_3]} = \frac{[M]^2C}{[NH_3]}\frac{k_i k_p}{k_{Tr}} = k'\frac{[M]^2C}{[NH_3]} \qquad (7.19)$$

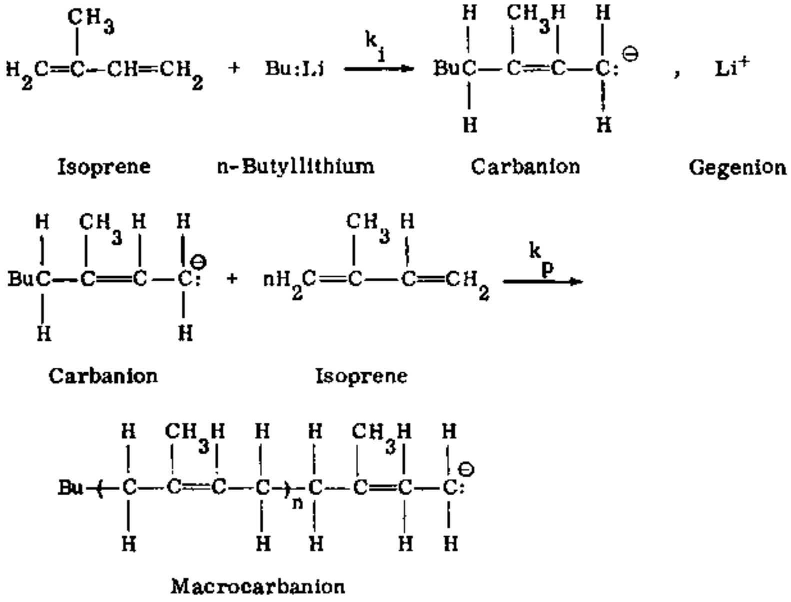
Therefore,

$$\overline{DP} = \frac{R_p}{R_{Tr}} = \frac{k_p[M][M^-]}{k_{Tr}[M^-][NH_3]} = \frac{k_p[M]}{k_{Tr}[NH_3]} = k'' \frac{[M]}{[NH_3]} \tag{7.20}$$

Thus, the rate of propagation and the molecular weight are both inversely related to the concentration of ammonia. The activation energy for chain transfer is larger than the activation energy for propagation. The overall activation energy is approximately +38 kcal mol^{-1}. The reaction rate increases and molecular weight decreases as the temperature is increased.

The reaction rate is dependent on the dielectric constant of the solvent, the electronegativity of the initiator, the resonance stability of the carbanion, and the degree of solvation of the gegenion. Weakly polar initiators such as Grignard's reagent may be used when strong electron-withdrawing groups are present on the monomer, but monomers with weak electron-withdrawing groups require more highly polar initiators, such as n-butyllithium.

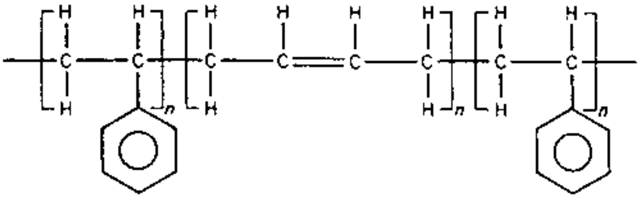
Synthetic cis-1,4-polyisoprene is produced at an annual rate of about 76,000 tons by the polymerization of isoprene in a low dielectric solvent, such as hexane, using n-butyllithium as the initiator. It is assumed that an intermediate cisoid conformation assures the formation of a cis elastomer.



(7.21)

When isoprene is polymerized in a stronger dielectric solvent, such as ethyl ether using butyllithium or sodium, equal amounts of trans-1,4-polyisoprene and cis-3,4-polyisoprene are produced.

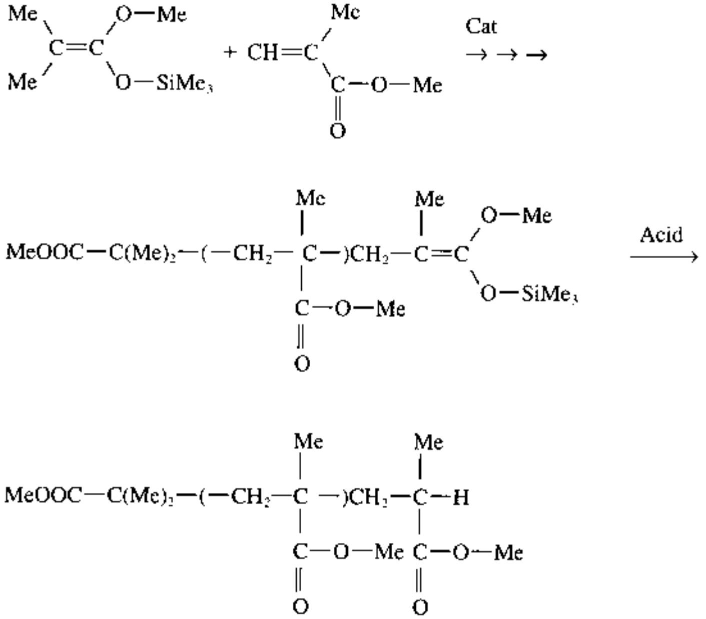
No formal termination step was shown in the previous equations, since in the absence of contaminants the product is a stable macroanion. Szwarc has used the term "living polymers" to describe these active species. Thus, these macroanions or macrocarbanions may be used to produce a block copolymer, in which, as shown in Scheme 7.5, there are long sequences of similar repeat units. Kraton is an ABA block copolymer of styrene (A) and butadiene (B). Termination may be brought about by the addition of water, ethanol, carbon dioxide, or oxygen.



Scheme 7.5 An ABA block copolymer of styrene and butadiene.

Living polymers are generally characterized by (1) an initiation rate that is much larger than the polymerization rate; (2) polymer molecular weight is related to [monomer]/[initiator]; (3) linear molecular weight conversion relationship; (4) narrow molecular weight range; and (5) stabilization of the living end groups allowing the formation of telechelics, macromers, block copolymers, and star polymers.

Group transfer polymerizations make use of a silicon-mediated Michael addition reaction. They allow the synthesis of isolatable, well-characterized living polymers whose reactive end groups can be converted into other functional groups. It allows the polymerization of α,β-unsaturated esters, ketones, amides, or nitriles through the use of silyl ketenes in the presence of suitable nucleophilic catalysts such as soluble Lewis acids, fluorides, cyanides, azides, and bifluorides, $HF_2{}^-$.



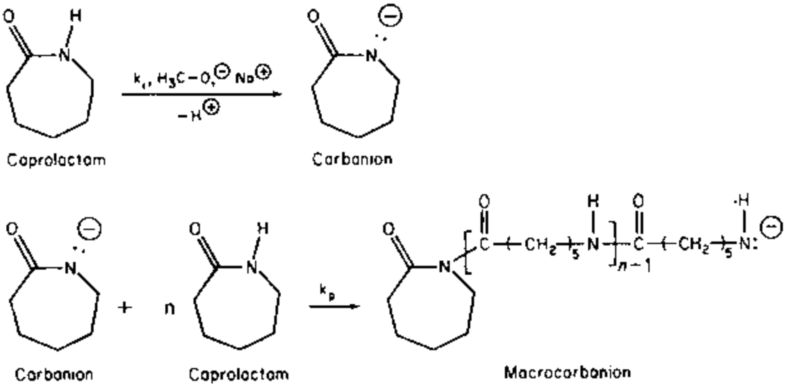
$$\mathrm{Me_2C{=}C(O{-}Me)(O{-}SiMe_3)} + \mathrm{CH{=}C(Me)(C({=}O){-}O{-}Me)} \xrightarrow{\text{Cat}} \to \to$$

$$\mathrm{MeOOC{-}C(Me)_2{-}(-CH_2{-}C(Me)(C({=}O){-}O{-}Me){-})CH_2{-}C(Me){=}C(O{-}Me)(O{-}SiMe_3)} \xrightarrow{\text{Acid}} \qquad (7.22)$$

$$\mathrm{MeOOC{-}C(Me)_2{-}(-CH_2{-}C(Me)(C({=}O){-}O{-}Me){-})CH_2{-}C(Me)(C({=}O){-}O{-}Me){-}H}$$

As the polymerization occurs, the reactive ketene silyl acetal group is transfered to the head of each new monomer as it is added to the growing chain. Similar to anionic polymerization, the molecular weight is controlled by the ratio of the concentration of monomer to initiator. Reactions are generally carried out at low temperatures (about 0–50°C) in organic liquids such as tetrahydrofuran. Compounds with "active" hydrogens such as water and alcohols will stop the polymerization and their presence will curtain polymer chain length. Under the right conditions, polymerization will continue until all of the monomer has been used up. The trimethylsiloxy end group is a “living” end that continues to add units as long as monomer is available or until it is neutralized.

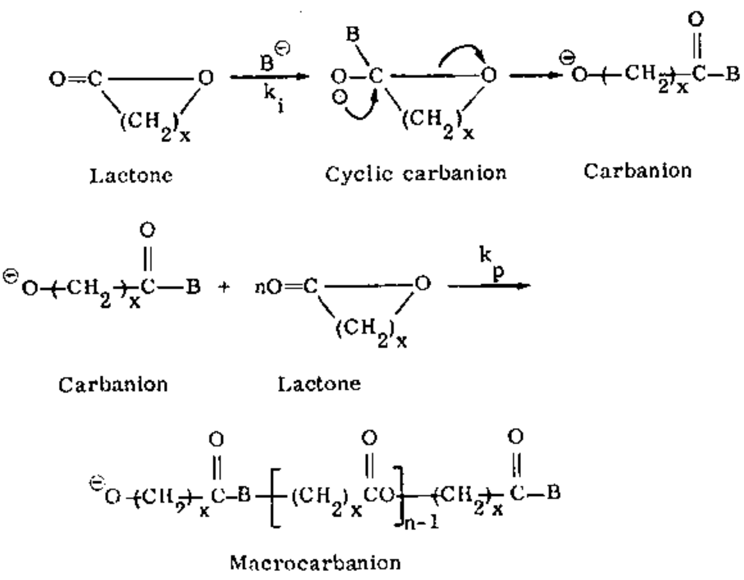
In addition to the thermal dehydration of ammonium salts, nylons may also be produced by the anionic ring-opening polymerization of lactams. As shown in Eq. (7.23), the polymerization of caprolactam may be initiated by sodium methoxide. This polymer contains six carbon atoms in each repeating unit and is called nylon-6. The term *monadic* is used to describe nylons such as nylon-6 that have been produced from one reactant. The term *diadic* is used to describe nylons such as nylon-66 that have been produced from two reactants.



(7.23)

The induction period in lactam ring-opening polymerization may be shortened by the addition of an activator, such as acetyl chloride. Nylon-4, nylon-8, and nylon-12 are commercially available and are used as fibers and coatings.

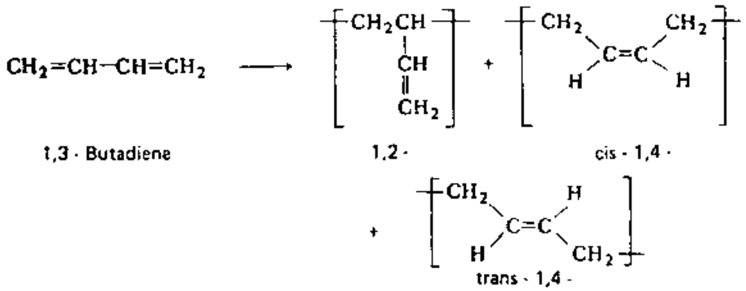
Lactones may also be polymerized by ring-opening anionic polymerization techniques. While the five-membered ring (γ-butyrolactone) is not readily cleaved, the smaller rings polymerize readily to produce linear polyesters. These polymers are used commercially as biodegradable plastics and in polyurethane foams. A proposed general reaction for the ring-opening polymerization of lactones is shown below:



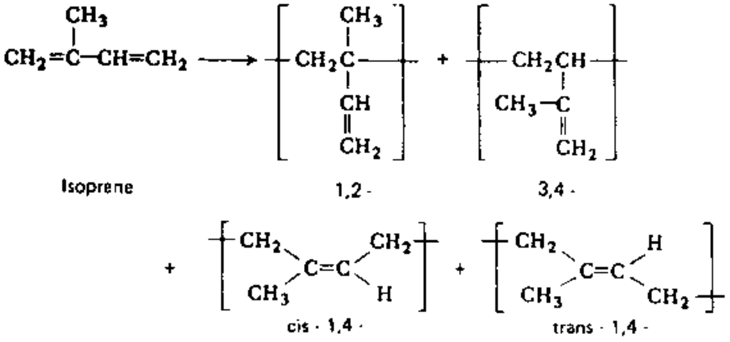
(7.24)

The sterochemistry associated with anionic polymerization is similar to that observed with cationic polymerization. For soluble anionic initiators at low temperatures, syndiotactic formation is favored in polar solvents, whereas isotactic formation is favored in nonpolar solvents. Thus, the stereochemistry of anionic polymerization appears to be largely dependent on the amount of association the growing chain has with the counterion—as it does for cationic polymerizations.

The stereochemistry of diene polymerization is also affected by solvent polarity. For instance, the proportion of cis-1,4 units is increased by using organolithium or lithium itself as the initiator in the polymerization of isoprene or 1,3-butadiene in nonpolar solvents. One can obtain a polymer similar to natural hevea rubber using the anionic polymerization of isoprene. With sodium and potassium initiators the amount of cis-1,4 units decreases and trans-1,4- and trans-3,4 units predominate.



(7.25)



(7.26)

7.3 STEREOREGULARITY

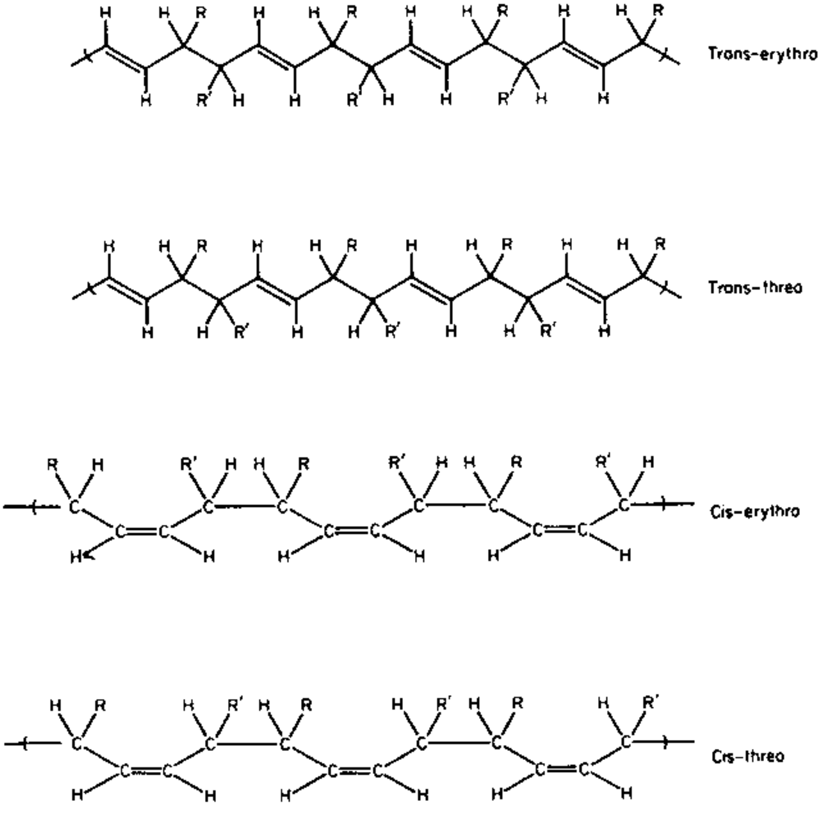
One of the more outstanding areas of research involves the synthesis and characterization of stereoregular polymers. Polymers differing in stereoregularity (tacticity) generally vary with respect to such properties as infrared spectra, X-ray diffraction patterns, solubilities, rate and extent of solubility, density, and thermal and mechanical transitions, among others. For instance, the T_g for poly(methyl methacrylate) is about 105°C for atactic forms, 150°C for isotactic forms, and 115°C for syndiotactic forms. Many of these physical differences are due to the ability, or possibility, of more ordered materials to achieve crystalline orientations.

The stereogeometry of 1- and 1,1-disubstiuted vinyl addition polymers has been divided into the three conformations illustrated in Eq. (7.27). The isotactic (7.27) form features a configuration whereby all substituents of one kind would lie on one side, if the molecule were arranged in a linear chain and viewing were done by looking down the "barrel." The syndiotactic form features an alternating arrangement of substituents, whereas a random sequence of substitutent placement leads to the atactic configuration. These arrangements assume an adherence to the head-to-tail addition of monomers.

Generally, each substituted vinyl carbon represents a site of asymmetry; it is, in fact, a site of potential optical activity, when included in a polymer chain. Thus, the number of optically active carbons is 2n, where n is the number of asymmetrical carbons. Since a polymerizing system can introduce a variety of chain lengths, the total possible number of geometrical and chain length combinations is extremely large. It is quite possible that each polymerization of even common monomers such as styrene might produce many chains previously not synthesized.

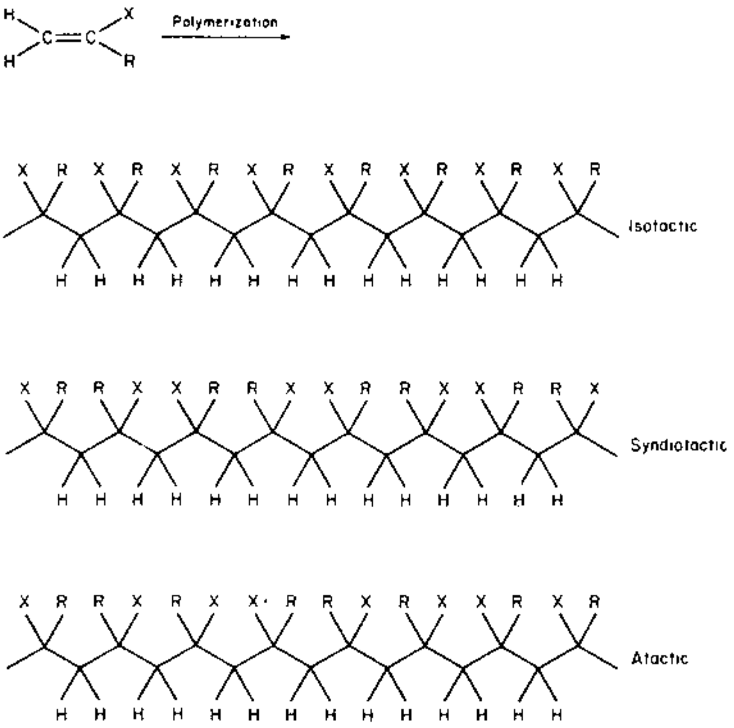
Other geometrical possibilities exist for situations involving conjugated double-vinyl compounds. For instance, 1,3-dienes, containing one residual double bond per repeating unit after polymerization, can contain different configurations [Eq. (7.28)].

Those derivatives of butadiene that are 1- and 4-disubstituted can be polymerized to produce a polymer having two asymmetrical carbon atoms and one double bond per repeating unit. Possible geometrical forms are illustrated in Scheme 7.6.

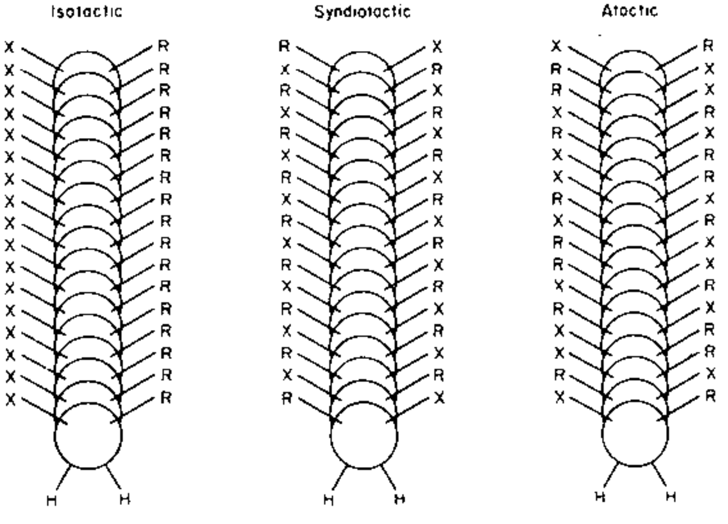


Scheme 7.6 Possible butadiene-derived polymers.

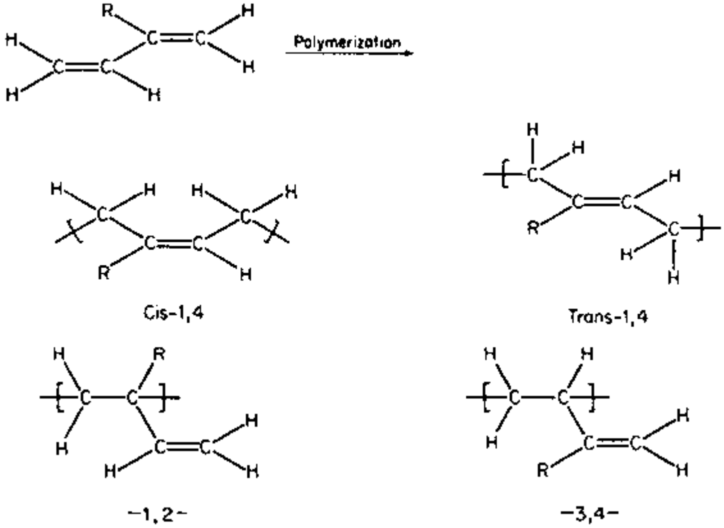
The requirements for obtaining measurable optical activity in polymers are still items of active debate. It is known that whole-chain conformations can contribute to the overall optical activity of polymers. For instance, helical conformations offer a major source of optical rotatory power. In addition to the direct use of stereoregular polymers, such products are currently being used (and further investigated) as "templates" to form other products, some of these possessing stereoregularity.



(7.27)



It is important to realize that the configuration and conformation of polymers are related. Thus, there is a great tendency for isotactic polymers (configuration) to form helical structures (conformation) in an effort to minimize steric constraints brought about because of the isotactic geometry.



(7.28)

Since R = H for 1,3-butadiene, only three structures are possibles cis-1,4, trans-1,4, and 1,2.

7.4 POLYMERIZATION WITH COMPLEX COORDINATION CATALYSTS

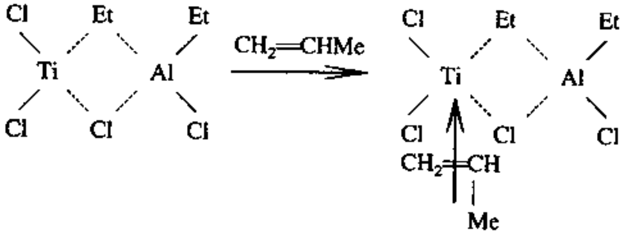
Prior to 1950, the only commercial polymer of ethylene was a highly branched polymer called high-pressure polyethylene (extremely high pressures were used in the polymerization process). The technique for making a linear polyethylene was discovered by Marvel and Hogan and Banks in the 1940s and by Nobel Laureate Karl Ziegler in the early 1950s. Ziegler prepared high-density polyethylene by polymerizing ethylene at low pressure and ambient temperatures using mixtures of triethylaluminum and titanium tetrachloride. Another Nobel Laureate, Giulio Natta, used Ziegler's complex coordination catalyst to produce crystalline polypropylene. These catalysts are now known as Ziegler-Natta catalysts. Hogan and Banks also produced crystalline polyethylene in the 1950s.

In general, a Ziegler-Natta catalyst may be described as a combination of a transition metal compound from groups IV to VIII and an organometallic compound of a metal from groups I to III of the periodic table. It is customary to refer to the transition metal compounds, such as $TiCl_4$, as the catalyst, and the organometallic compound, such as diethylaluminum chloride, as the cocatalyst.

Several exchange reactions between catalyst and cocatalyst take place, and some of the Ti(IV) is reduced to Ti(III). It is customary to use either the α, γ, or δ form, but not the β crystalline form, of $TiCl_3$ as the catalyst for the production of stereoregular polymers. Both the extent of stereoregularity and the rate of polymerization are increased by the addition of triethylamine and Lewis acids. At least 98% of the isotactic polymer is produced when propylene is polymerized in the presence of triethylamine, γ-titanium(III) chloride, and diethylaluminum chloride.

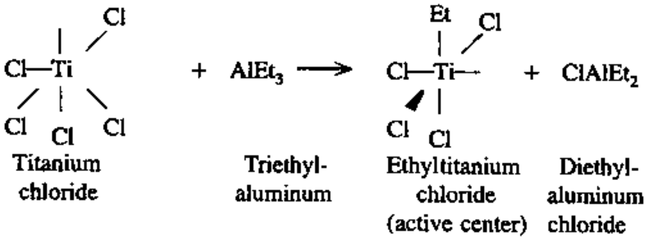
It is generally agreed that a monomer molecule ($H_2C = CHCH_3$) is inserted between the titanium atom and the terminal carbon atom in the growing chain and that this propagation reaction takes place on the catalyst surface at sites activated by the ethyl groups of the cocatalyst. The monomer molecule is always the terminal group on the chain.

The formation of a π complex is assumed in both the mono- and bimetallic mechanisms. The latter, favored by Natta, involves a cyclic electron-deficient transition complex as shown below:



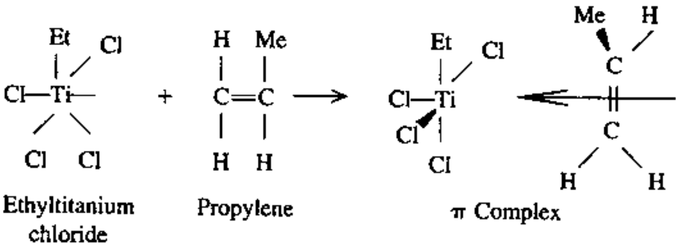
(7.29)

In the more generally accepted monometallic mechanism, shown in the following equation, triethylaluminum reacts to produce ethyltitanium chloride as the active site for polymerization of a nonpolar vinyl monomer such as propylene.



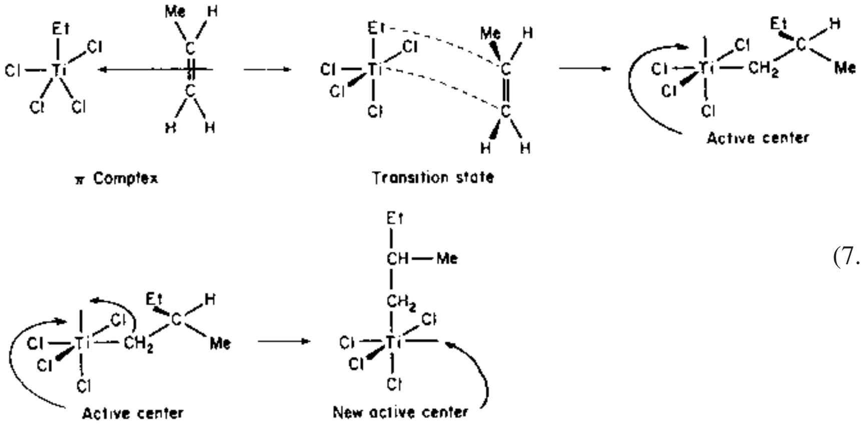
(7.30)

Then, as shown by Eq. (7.31), propylene forms a π complex with the titanium at the vacant d orbital.



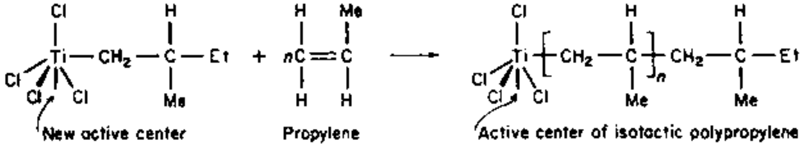
(7.31)

Insertion of the monomer takes place with the formation of a transition state complex, insertion of the monomer, and reformation of an active center in which the ethyl group is now at the end of a propylene group, as shown in the following equation.



(7.32)

As shown in Eq. (7.33), the process outlined for initiation is repeated for propagation, and stereoregularity is maintained.



(7.33)

For most vinyl monomers, Ziegler-Natta catalysts polymerize to give polymers emphasizing the isotactic form. The degree of stereoregulation appears to be dependent on the amount of exposure of the active site—which is probably a combination of the solid surface and the corners. Typically, the more exposed the catalytic site, the less the isotactic fraction in the resulting chains.

The potential versatility is clearly demonstrated in the polymerization of conjugated dienes, such as 1,3-butadiene, where any of the four possible forms—isotactic 1,2; syndiotactic 1,2; trans-1,4; and cis-1,4—can be synthesized in relatively pure form using different Ziegler-Natta catalysis systems.

Molecular weight is regulated to some degree by chain transfer with monomer and with the cocatalyst, plus internal hydride transfer. However, hydrogen is added in the commercial process to terminate the reaction. Low temperatures, at which the alkyl shift and migration are retarded, favor the formation of syndiotactic polypropylene. Commercial isotactic polymer is produced at ambient temperatures. The percentage of polymer insoluble in n-hexane is called the isotactic index.

High-density polyethylene (HDPE) is produced at an annual rate of 5.7 million tons, but most of this is produced using a chromia catalyst supported on silica, i.e., a Phillips catalyst. Some HDPE and polypropylene are produced commercially using a Ziegler-Natta catalyst. This initiator is also used for the production of polybutene and poly(-4-methylpentene-1) (TPX). Because of their regular structure, both of these polymers are useful at relatively high temperatures. TPX has a melting point of 300°C and because of its large bulky groups has a low specific gravity of 0.83.

Polypropylene, TPX, and LDPE are less resistant to oxidation than HDPE because of the tertiary carbon atoms present in the chain. Their deterioration by weathering and other factors is retarded by incorporation of antioxidants (discussed in Chapter 14).

7.5 SOLUBLE STEREOREGULATING CATALYSIS

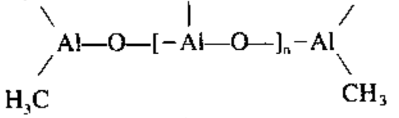
The 1940s was a time of studying the kinetics and mechanisms of production of the vinyl polymers that would take center stage in the 1950s. The 1950s produced the solid state stereoregulating catalysis described in Sec. 7.3, which spawned a chemical revolution with the synthesis of stereoregular vinyl polymers in the 1960s. The 1990s witnessed the introduction of soluble stereoregulating catalysis, spawning another revolution related to the production of vinyl polymers with enhanced properties.

The solid state stereoregulating catalysts suffered from at least three problems. First, while stereoregular polymers were formed with good control of the stereogeometry, polymer properties still fell short of predicted (upper limit) values. This was probably due to the presence of the associated solid catalyst structure that accompanied the active catalytic site. This "excess baggage" restricted the motion of the growing chains. Second, in many cases the solid state catalysts were incorporated, as contaminants, within the growing polymer, making an additional purification step necessary in the polymer processing to rid the polymer of this undesired material. Third, many solid state catalysts offered several active polymerization sites due to differences in the precise structure at and about the active sites.

The new soluble catalysts offer a solution to these three problems. First, the smaller size of the active site and associated molecules allows the growing chains to take advantage of a natural tendency to form a regular helical structure (in comparison to polymers formed from solid state catalysts). Second, the soluble catalysts allow the synthesis of polymers that contain little or no catalytic agents, allowing the elimination of the typical additional clean-up steps necessary for polymers produced from solid state catalysts. Third, the newer soluble catalytic sites are homogeneous, offering the same electronic and stereo structure and allowing the synthesis of more homogeneous polymers.

The new soluble stereoregulating polymerization catalysts require three features: a metal atom (active) site, a cocatalyst or counterion, and a ligand system. While the major metal site is zirconium, other metals have been successfully used, including Ti, Hf, Sc, Th, and rare earths (such as Nd, Yb, Y, Lu, and Sm). Cyclopentadienyls (Cp) have been the most commonly used ligands, although a number of others have been successfully employed including substituted Cp and bridged Cp. The most widely used metal-ligand grouping is zirconocene dichloride.

Methylalumoxane (MAO) is the most widely utilized counterion. MAO is an oligomeric material with the following approximate structure:



Methylalumoxane

(7.34)

where n = 4–20.

It is believed that MAO plays several roles. It maintains the catalyst complex as a cation, but without strongly coordinating to the active site. It also alkylates the metallocene chloride, replacing one of the chloride atoms with an alkyl group and removing the second chlorine, thus creating a coordinately unsaturated cation complex, $Cp_2\,MR^+$.

It is believed that as an olefin approaches the ion pair containing the active metal, a metallocene–alkyl–olefin complex forms. This complex is the intermediate stage for the insertion of the monomeric olefin into a growing polymer chain.

The structure of the catalyst complex controls activity, stereoselectivity, and selectivity toward monomers. The catalyst structure is sensitive to Lewis bases such as water and alcohols encouraging the use of strongly oxyphilic molecules, such as MAO, to discourage the inactivation (poisoning) of the catalyst.

These soluble catalysts are able to give vinyl polymers that have increased stereogeometry with respect to tacticity as well as allowing the growing chains to form more precise helical structures. Further, the homogeneity of the catalytic sites also allows for the production of polymers with narrow molecular weight spreads.

The summation of these effects is the production of polymers with increased strength and tensile properties. For polyethylene, the use of these soluble catalysts allows the synthesis of PE chains with less branching compared to those produced using solid state catalysts such as the Ziegler-Natta catalysts. Table 7.2 gives some comparisons of polyethylenes produced using Ziegler-Natta catalysts with those produced with soluble catalysts.

The active site is a cationic metallocene-alkyl generated by reaction of a netural metallocene formed from reaction with excess MAO or other suitable co-catalysts such as a borane Lewis acid. This sequence is shown below employing MAO with ethylene to form polyethylene. Initiation and propagation occur through pre-coordination and insertion of the ethylene into the alkyl group-polymer chain. Here termination occurs through beta-hydride elimination producing a zirconium hydride and a long-chain alpha-olefin. These long-chain alpha-olefins can form linear high-density polyethylene or be used as comonomers with monomers such as 1-propylene, 1-hexene, or 1,5-hexadiene to give a variety of branched and linear products. These Group IV B metallocene catalysts are very active producing yields in excess of one ton of polyethylene per gram of catalyst per hour with a total efficiency on the order of 25 tons of PE per gram of catalyst.

These catalysis systems are also used to form other hydrocarbon polymers such as a variety of polypropylenes.

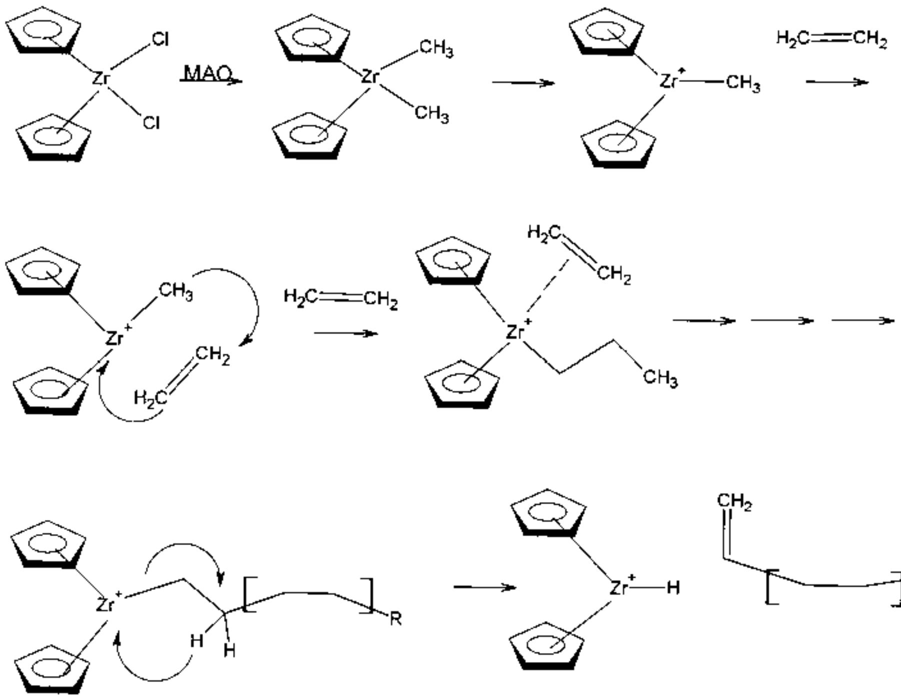
A major limitation of such Group IV B metallocene catalysts is that they are very air and moisture sensitive and not tolerant of heteroatom-containing monomers. In the

Table 7.2 Comparison of Properties of Polyethylene Using Solid (Ziegler-Natta) Catalysts and Soluble Catalysts

Property	Unit	Soluble	ZNC
Density	g/cm^3	0.967	0.964
Melt index		1.3	1.1
Haze		4.2	10.5
Tensile yield	psi	800	750
Tensile brake	psi	9400	7300
Elongation break	%	630	670

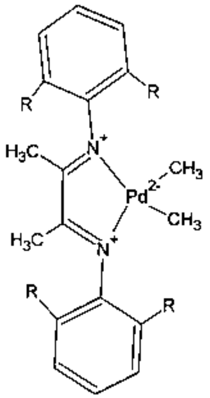
Values of M_ψ/M_η of 2 or less are common for the soluble catalyst systems, whereas values of 4–8 are usual for ZNC systems. The soluble catalyst systems also are able to polymerize a larger number and greater variety of vinyl monomers to form homogeneous polymers and copolymers than solid catalyst systems.

Source: From C. F. Pain, *Proceedings Worldwide Metallocene Conference*, May 26–28. 1993, Catalyst Consultant Inc., Houston, Texas.

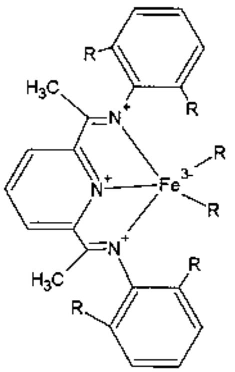


Scheme 7.7

case of heteroatom-containing monomers the unbonded electron pairs on the heteroatom, such as oxygen, preferentially coordinate to the Lewis acid metal center in place of the carbon-carbon double bond. Some so-called middle and late transition metal organometallics are more tolerant to the presence of such heteroatoms and can be used as effective co-catalysts. These include some palladium, iron, cobalt, and nickel initiators. Two of these structures are given below.



(7.35)



(7.36)

The use of transition and selected main group metal catalysis is increasing with the ability to design special catalytic systems for special polymer architecture and property production. These catalysis systems involve the transition metal as a site for active polymer growth. The new soluble stereoregulating catalysts are one example these systems. These growing sites may be more or less ionic/covalent depending upon the catalyst used and such sites are not generally appreciably dissociated as is the case in classical cationic and anionic systems. The metal's ligands can provide both electronic and steric structural control and are generally more robust in comparison to the anionic/cationic systems. Along with many advantages, there are some challenges. Because of their vary nature transition metal initiators can be very complex requiring several synthetic steps, they may be expensive and/or require costly co-catalysts, and control of the particular reaction conditions is very important since small, seemingly subtle changes can be magnified into larger polymer structural changes.

There is an increasingly large number of metal-catalyzed polymerizations including olefin metathesis reactions (Sec. 7.9) including ring-opening metathesis polymerizations (ROMPs), formation of polyketones from the copolymerization of carbon monoxide, group transfer polymerizations, and step-growth addition/elimination (coupling) polymerizations. The study of metal catalytic sites is a vigorous area of ongoing research.

Polymers produced form single-site catalysts are increasingly being used in the marketplace. As noted above, the strength of the materials is increased because of the greater order in the individual polymer chains. For polyethylene this means the number of branches is less and for substituted polymers such as polyproplyene this means that the order about the substituted-carbon is increased allowing for a more dense, tighter fit of the individual polymer chain segments resulting in increased overall polymer strengths and less permeability for materials.

Use of materials produced from single-site catalysts in areas employing thin films is increasing. For instance, bananas are generally produced at one location and shipped and stored to other locations for sale. Even when picked green, they ripen rapidly when exposed to oxygen. Regular LLDPE is generally employed as a thin film to protect bananas for shipment and storage. Regular LLDPE permits some transfer of oxygen and because of the somewhat pointed nature of bananas may be punctured. Single-site metallocene-based LLDPE is less permeable and less apt to tear and is now replacing regular LLDPE in this use. It's use is also increasing in the containment of heavier materials such as topsoil and water-purification salt utilizing thicker films. In both cases, thinner films, and consequently less film material is necessary to give an equal or better job performance. Single-site produced materials also offer better clarity, toughness, and easy sealability.

7.6 POLYETHYLENES

Tupperware was the idea of Earl Silas Tupper, a New Hampshire tree surgeon and plastics innovator. He began experimenting with polyethylene during the early part of WW II. In 1947 he designed and patented the famous “Tupper seal” that “sealed in” freshness. In order to close the container it had to be “burped” to remove air. Tupperware was also bug proof, spill proof, did not rot or rust, and did not break when dropped. Even with all of these advantages, few were sold. Enter Brownie Wise, a divorced single mother from Detroit who desperately needed to supplement her income as a secretary. Her idea: “Tupperware Parties.” By 1951 he had withdrawn all of the Tupperware from the stores and turned over their sales to Brownie Wise with the only source of the ware being through the Tupperware Parties.

Polyethylene was probably initially synthesized by M. E. P. Friedrich while a graduate student working for Carl S. Marvel in 1930 when it was an unwanted byproduct of the reaction of ethylene and a lithium alkyl compound. In 1932 British scientists at the Imperial Chemical Industries (ICI) accidentally made polyethylene while investigating what products could be produced from the high-pressure reaction of ethylene with various compounds. On March 1933, they found the formation of a white solid when they combined ethylene and benzaldehyde under high pressure (about 1400 atm). They correctly identified the solid as polyethylene. They attempted the reaction again but with ethylene alone. Instead of again getting the waxy white solid, they got a violent reaction and the decomposition of the ethylene. They delayed their work until December 1935 when they had better high-pressure equipment. At 180°C, the pressure inside of the reaction vessel containing the ethylene decreased consistent with the formation of a solid. Because they wanted to retain the high pressure, they pumped in more ethylene. The observed pressure drop could not be totally due to the formation of polyethylene, but something else was contributing to the pressure loss. Eventually they found that the pressure loss was also due to the presence of a small leak that allowed small amounts of oxygen to enter into the reaction vessel. The small amounts of oxygen turned out to be the right amount needed to catalyze the reaction of the additional ethylene that was pumped in subsequent to the initial pressure loss. The ICI scientists saw no real use for the new material. By chance, J. N. Dean of the British Telegraph Construction and Maintenance Company heard about the new polymer. He had needed a material to encompass underwater cables. He reasoned that polyethylene would be water-resistant and suitable to coat the wire protecting it from the corrosion caused by the salt water in the ocean. In July 1939, enough polyethylene was made to coat one nautical mile of cable. Before it could be widely used, Germany invaded Poland and polyethylene production was diverted to making flexible high-frequency insulated cable for ground and airborne radar equipment. Polyethylene was produced, at this time, by ICI and by Dupont and Union Carbide for the United States.

Polyethylene did not receive much commercial use until after the war when it was used in the manufacture of film and molded objects. Polyethylene film displaced cellophane in many applications being used for packaging produce, textiles, and frozen and perishable foods, etc. This polyethylene was branched and had a relatively low softening temperature, below 100°C, preventing its use for materials where boiling water was needed for sterilization.

Karl Ziegler, director of the Max Planck Institute for Coal Research in Muelheim, Germany, was extending early work attempting to get ethylene to form polyethylene at lower pressures and temperatures. His group found that certain organometallics prevented the polymerization of ethylene. He then experimented with a number of other organometallic materials that inhibited polyethylene formation. Along with finding compounds that inhibited polyethylene formation, they found compounds that allowed the formation of polyethylene under much lower pressures and temperatures. Furthermore, these compounds produced a polyethylene that had fewer branches and higher softening temperatures.

The branched polyethylene is called low-density, high-pressure polyethylene because of the high pressures usually employed for its production and because of the presence of the branches. The chains are not able to pack closely, leaving voids and subsequently producing a material with a lower density than low branched polyethylene.

Giulio Natta, a consultant for the Montecatini company of Milan, applied the Zeigler catalysts to other vinyl monomers such as propylene and found that the polymers were higher density, higher melting, and more linear than those produced by the then-classical techniques such as free radical–initiated polymerization. Ziegler and Natta shared the Nobel Prize in 1963 for their efforts in the production of vinyl polymers using what we know today as solid state steroregulating catalysts.

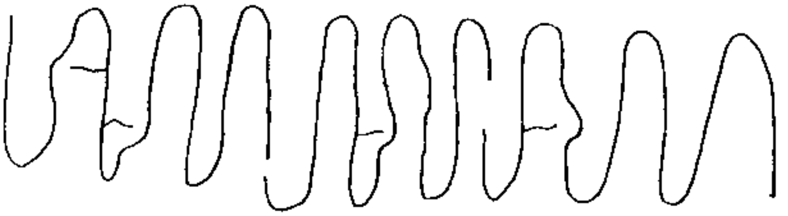
While many credit Natta and Ziegler as first having produced so-called high density PE and stereoregular polyolefins, Phillips' scientists first developed the conditions for producing stereospecific olefin polymers and high density PE. In 1952 J. Paul Hogan and Robert Bands discovered that ethylene and propylene polymerized into what we today know as high density PE and stereoregular PP. As with many other advancements their initial studies involved other efforts, here to improve fuel yields by investigating catalysts that converted ethylene and propylene to higher molecular weight products. They found that chromium trioxide supported on a silica-alumina catalyst produced a hard solid rather than the usual waxy-like PE. They quickly looked at other olefins and soon discovered a crystalline PP, namely a stereoregular PP.

Today there exist a number of polyethylenes that vary in the extent and length of branching as well as molecular weight and molecular weight distribution and amount of crystallinity. Some of these are pictured in Figs. 7.1 to 7.3. Commercial LDPE typically has between 40 and 150 short alkyl branches for every 1000 ethylene units. It is produced employing high pressure (15,000 to 50,000 psi and temperatures to 350°C). It has a density of about 0.912 to 0.935. Because of the branching, LDPE is amorphous (about 50%) and sheets can allow the flow-through of liquids and gases. Because of the branching and low amount of crystallinity, LDPE has a low melting point of about 100°C, making it unsuitable for use with materials requiring sterilization through the use of boiling water. LDPE has a ratio of about 10 short branches to every long branch.

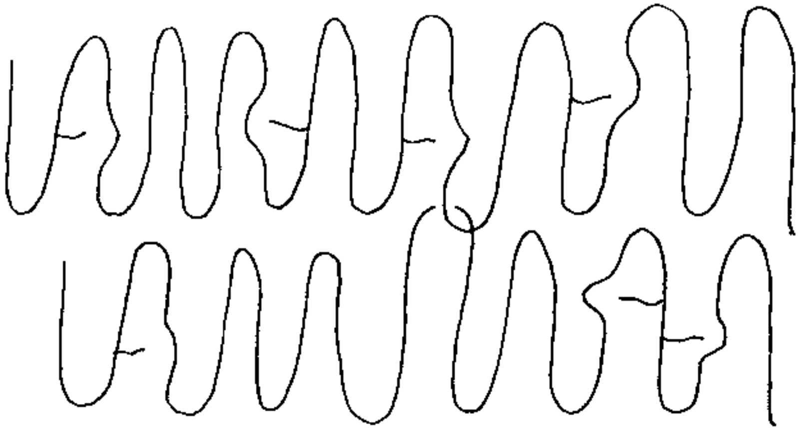
HDPE produced using organometallic catalysts, such as the Ziegler-Natta or Phillips catalysts, have less than 15 (normally within the range of 1–6) short alkyl branches (and essentially no long branches) per 1000 ethylene units. Because of the regular structure of the ethylene units themselves and the low extent of branching, HDPE chains can pack more efficiently, resulting in a material with greater crystallinity (generally up to 90%), higher density (0.96), with increased chemical resistance, hardness, stiffness, barrier properties, melting point (about 130°C), and tensile strength. Low molecular weight (chain lengths in the hundreds) HDPE is a wax, while typical HDPE is a tough plastic.

Linear low-density polyethylene (LLDPE) can be produced with less than 300 psi and at about 100°C. It is actually a copolymer of ethylene with about 8–10% of an α-olefin such as 1-butene, 1-pentene, 1-hexene, or 1-octene produced by solution or gas phase polymerization. Through control of the nature and amount of α-olefin, it is possible to produce materials with densities and properties between those of LDPE and HDPE. LLDPE does not contain the long branches found in LDPE.

Ultrahigh molecular weight polyethylene (UHMWPE) is a high-density polyethylene with chain lengths of over 100,000 ethylene units. Because of the long chain lengths, they "intertangle" causing physical crosslinks, increasing the tensile strength and related properties of these materials. (By comparison, HDPE rarely is longer than 2000 ethylene units.) UHMWPE is about 45% crystalline and offers outstanding resistance to corrosion and environmental stress cracking, outstanding abrasion resistance and impact toughness, and good resistance to cyclic fatigue and radiation failure with a low surface friction. It is produced utilizing catalyst systems similar to those employed for the production of HDPE (i.e., Ziegler-Natta and Phillips catalysts). It has a density of about 0.93.



HDPE



UHMWPE

Figure 7.1 Simulated skeletal structural formulas for various commercially available forms of polyethylene.

Ultralinear polyethylene (ULPE) has recently become available through the use of soluble stereoregulating catalysts described in Sec. 7.5. Along with a decreased amount of short-chain alkyl branching, ULPE has a narrower molecular weight spread.

Polymethylene can be produced through several routes including the use of diazomethane or a mixture of carbon monoxide and hydrogen. This polymer has only a little branching.

It is well accepted that the history of a polymer influences polymer behavior including polymer processing. Some of these influences are just becoming known. Interestingly, as in much of science, once the critical parameters are known on a macro-level, we are able to better understand them on a molecular and conceptual level. An example that illustrates this involves the processing of annealed polyethylene. In general, for much linear polyethylene, when it is melted and cooled slowly micelles and associated spherulites are formed. If no force is applied during the annealing process (simple melt crystallization), a high amount of force and large deformation is required to breakdown the initial spherulite structures with reformation occurring along the axis of the pull when high-strength polyethylene rod, film, and sheet is produced. However, if the polyethylene is crystallized under pressure applied in one direction, less energy and lower deformation is required to align

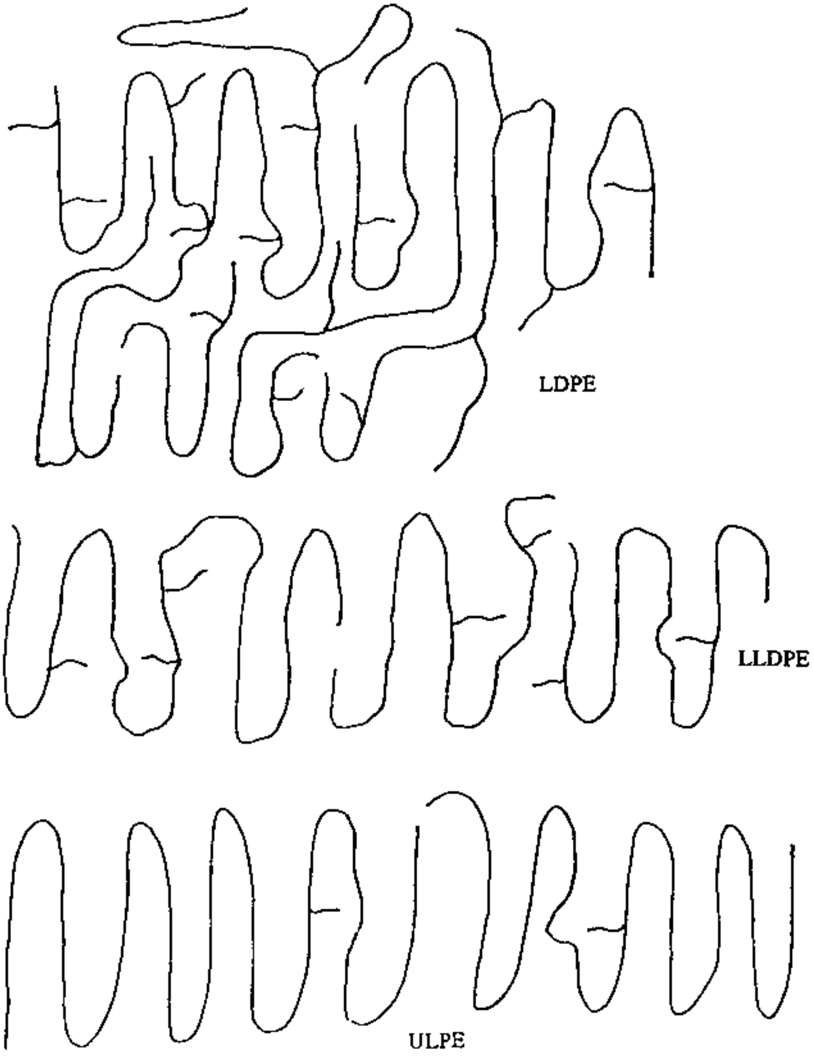


Figure 7.1 Continued.

the polyethylene spherulites since the spherulites are already partly aligned. In both cases, stretching of the molecular network is required. For the simple melt crystallized polyethylene, the original spherulite structure is destroyed during the deformation followed by the formation of new fibrillar structures. For the pressure-associated annealing process, elongated micelles are formed that largely remain after the deformation process.

LDPE films are nearly clear even though they contain a mixture of crystalline and amorphous regions. This is because the crystalline portions are space filling and not isolated spherulites allowing a largely homogeneous structure with respect to refractive index that results in the material being transparent. In fact, the major reason LDPE films appear hazy or not completely transparent is because of the roughness of the surface and is not due to the light scattering of the interior material.

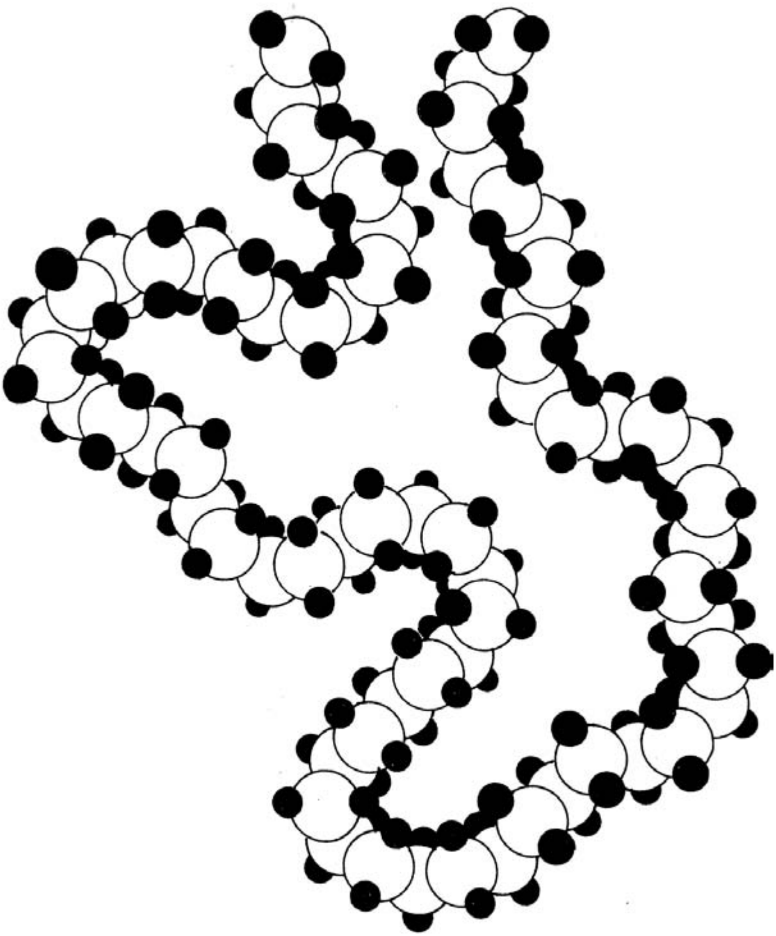


Figure 7.2 Space-filling structure of a portion of a linear amorphous polyethylene region.

Types of applications for the various polyethylenes include:

1. UHMWPE: battery separators, lightweight fibers, permanent solid lubricant materials in rail car manufacture, automobile parts, truck liners; liners to hoppers, bins, and chutes; farm machinery such as sprockets, idlers, wear plates, and wear shoes; sewage treatment bearings, sprockets, wear shoes; lumbering chute, sluice, and chain-drag liners; neutron shields
2. “Typical” HDPE: blow-molded products—bottles, cans, trays, drums, tanks, and pails; injection-molded products—housewares, toys, food containers, cases, pails, and crates; films, pipes, bags, conduit, wire and cable coating, foam, insulation for coaxial and communication cables
3. Low molecular weight HDPE: spray coatings, emulsions, printing inks, wax polishes and crayons
4. LDPE: packaging products, bags, industrial sheeting, piping and tubing, films, garbage cans, industrial containers, household items

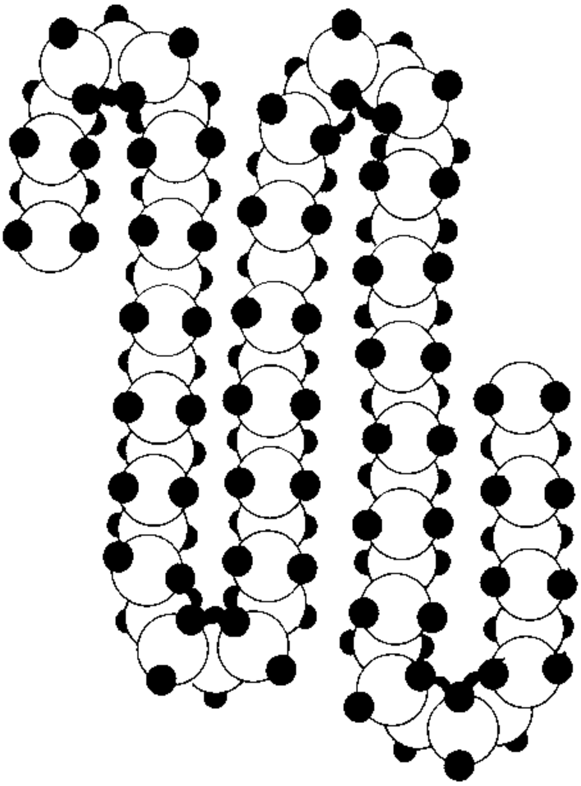


Figure 7.3 Space-filling structure of a portion of a linear crystalline polyethylene region.

5. LLDPE: telephone jacketing, wire and cable insulation, piping and tubing, drum liners, bottles, films

Plastomers is the name given to copolymers of ethylene that have a little crystallinity, but are largely amorphous. They are also called very low density polyethylene, VLDPE. They are more elastic than LLDPE but less stiff. They are used as a sealing layer in film applications and controlled permeation packaging for vegetables and fruits.

7.7 POLYPROPYLENE

Polypropylene, PP, is one of the three most heavily produced polymers (Sec. 1.2). The abundance of PP is called for because of its variety and versatility being employed today in such diverse applications as a film in disposable diapers and hospital gowns to geotextile liners, plastic applications as disposable food containers and automotive components, and fiber applications such as carpets, furniture fabrics, and twine.

While PP was produced for some time, it only became commercially available in the late 1950s with the production by Natta and coworkers at Phillips of somewhat isotactic PP, iPP. The first PP was not highly crystalline because the tacticity was only approximate but with the use of the Natta-Zeigler catalysts iPP was produced that contained greater amounts of stereoregular material with a corresponding increase in crystallinity and associated properties such as an increased stiffness, better clarity, and a higher distortion temperature. Today, with better catalysts, including the soluble metallocene catalysts, the tacticity has been increased so that 99% isotactic material can be readily produced. The more traditional Zeigler-Natta catalysts systems today have activities as high as producing 100 kg iPP per gram of catalysts eliminating the need for catalyst removal. Most iPP is made using bulk propylene, either as a gas or liquid.

While it was possible to produce syndiotactic PP, sPP, employing the Zeigler-Natta solid systems, commercial sPP has only recently become commercial through the use of the soluble metallocene catalysts (Fig. 7.4). These materials have a similar T_g as iPP but they have a different balance between stiffness and toughness (total area under the stress-strain curve; Fig. 5.7).

Atactic or amorphous forms of PP are also used. Initially atactic PP, aPP, was obtained as a byproduct of the production of iPP. As an inexpensive byproduct it is used as a modifier for asphalt for roofing and in adhesives. As the effectiveness of catalyst systems becomes better less aPP is available so that today some aPP is intentionally made for these applications.

Isotactic PP exists in three important crystalline forms. The crystalline forms are mostly controlled through the use of pressure and nucleating agents. The alpha form is the most common and most stable thermodynamically at room temperature with a number of nucleating agents available to achieve the alpha form of iPP. The beta form is obtained

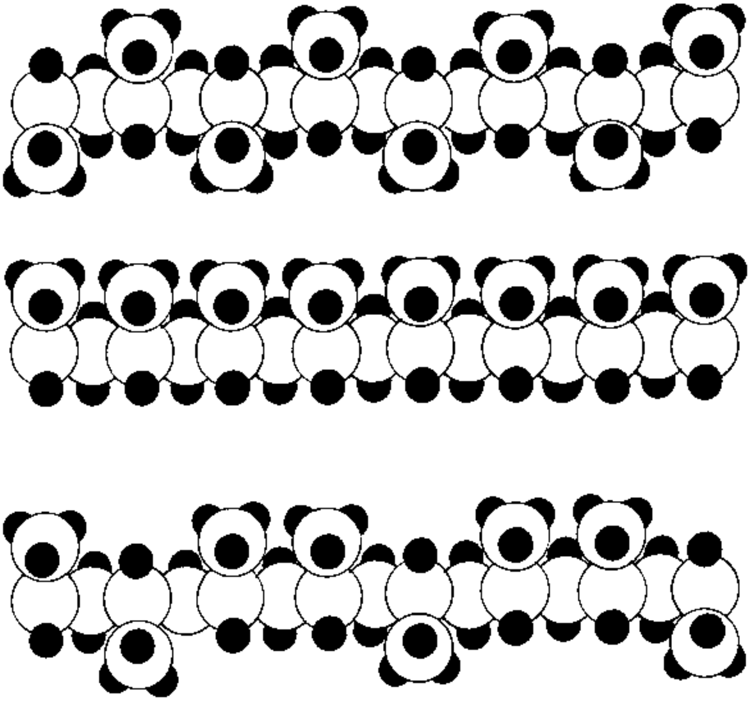


Figure 7.4 Space-filled models of syndiotactic (top), isotactic (middle), and atactic (bottom) forms of polypropylene. (My children and now grandchildren believe that the isotactic polypropylene is really a chorus-line of dancing teddy bears.)

through the use of special nucleating agents. The gamma form is only dominant under high pressure. Since the properties of the iPP vary somewhat according to the particular mix of crystalline forms, polymer properties are manipulated through a conscious effort to achieve a particular mix of these crystalline forms.

Because iPP is stiff and has a relatively high T_g (about 0°C) some effort has involved the lowering of the T_g and to achieve greater toughness. One approach is to employ a little ethylene in the polymerizing mixture thus creating a copolymer that is largely i-PP but with enough polyethylene, PE, to effectively lower the amount of crystallinity. Such copolymers are called reactor copolymers, RCPs. Another approach is to blend iPP with rubber. These materials form the important class of ethylene–propylene copolymers. Today, such blending can be done in situ.

The use of metallocene catalyst systems allows the formation of an important group of copolymers from the use of alpha-olefins as comonomers with propylene. These catalysts also allow the production of wholly PP block copolymer elastomers that contain blocks of aPP and iPP. The aPP blocks act as the soft and/or noncrosslinked portion while the iPP blocks act as the hard and/or physically crosslinked portion.

7.8 POLYMERS FROM 1,4-DIENES

There are three commercially important monomeric 1,4-dienes. Two are primarily produced using steroregulating catalyst systems. These monomers possess a conjugated pi-bond sequence of -C = C-C = C- that readily forms polymers with an average energy release of about 20 kcal/mol (80 kJ/mol) with the conversion of one of the double bonds into lower (potential energy wise; generally more stable) energy single bonds. For all of these products, crosslinking and grafting sites are available through the remaining double bond.

1,4-Butadiene can form three repeat units as described in (7.25), the 1,2; cis-1,4; and trans-1,4. Commercial polybutadiene is mainly composed of the 1,4-cis isomer and is known as butadiene rubber, BR. As noted before, polybutadiene is made from the use of stereoregulating catalysts. The composition of the resulting polybutadiene is quite dependent on the nature of the catalyst such that almost total trans-1,4 units, or cis-1,4 units, or 1,2 units can be formed as well as almost any combination of these units. The most important single application of polybutadiene polymers is its use in automotive tires where over 10^7 tons are used yearly in the US manufacture of automobile tires. BR is usually blended with natural rubber, NR, or styrene-butadiene rubber, SBR, to improve tire tread performance, particularly wear resistance.

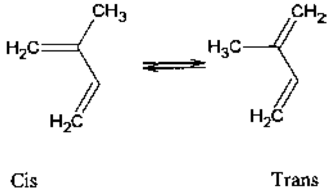
A second use is in the manufacture of ABS copolymers where the stereogeometry is also important. A polybutadiene composition of about 60% trans-1,4; 20% cis-1,4; and 20% 1,2 configuration is generally employed in the production of ABS. The good low temperature impact strength is achieved in part because of the low T_g values for the compositions. For instance, the T_g for trans-1,4-polybutadiene is about -14°C while the Tg for cis-1,4-polybutadiene is about -108°C. Most of the ABS rubber is made employing an emulsion process where the butadiene is initially polymerized forming sub micron particles. The styrene–acrylonitrile copolymer is then grafted onto the outside of the BR rubber particles. ABS rubbers are generally tougher than HIPS rubbers but are more difficult to process. ABS rubbers are used in a number of appliances including luggage, power tool housings, vacuum cleaner housings, toys, household piping, and automotive components such as interior trim.

Another major use of butadiene polymer is in the manufacture of high impact polystyrene, HIPS. Most HIPS has about 4 to 12% polybutadiene in it so that HIPS is mainly a polystyrene intense material. Here the polybutadiene polymer is dissolved in a liquid along with styrene monomer.

The polymerization process is unusual in that both a matrix composition of polystyrene and polybutadieneis is formed as well as a graft between the growing polystyrene onto the polybutadiene being formed. The grafting provides the needed compatibility between the matrix phase and the rubber phase. The grafting is also important in determining the structure and size of rubber particles that are formed.

The grafting reaction occurs primarily by hydrogen abstraction from the polybutadiene backbone either by growing polystyrene chains or alkoxy radicals if peroxide initiators are employed.

Interestingly isoprene, 2-methyl-1,3-butadiene, exists as an equilibrium mixture of cis and trans isomers.



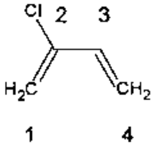
(7.37)

Polyisoprene is composed of four structures as shown in (7.26). As in the case of polybutadiene, it is the cis-1,4 structure that is emphasized commercially. The cis-1,4-polyisoprene is similar to the cis-1,4-polybutadiene material except it is lighter in color, more uniform, and less expensive to process. Polyisoprene is composition-wise analogous to natural rubber (Sec. 10.8). The complete cis-1,4 product has a T_g of about -71°C. Interestingly, isomer mixtures generally have higher T_g values. Thus an equal molar product containing cis-1,4; trans-1,4; and 3,4 units has a T_g of about -40°C.

As with many polymers, polyisoprene exhibits non-Newtonian flow behavior at shear rates normally used for processing. The double bond can undergo most of the typical reactions such as carbene additions, hydrogenation, epoxidation, ozonolysis, hydrohalogenation, and halogenation. As with the case of the other 1,4-diene monomers, many copolymers are derived from polyisoprene or isoprene itself.

Polyisoprene rubbers are used in the construction of passenger, truck, and bus tires and inner liners as well as sealants and caulking compounds, sporting goods, gaskets, hoses, rubber sheeting, gloves, belts, and footwear.

Polychloroprene was the first commercially successful synthetic elastomer introduced in 1932 under the tradenames of DuPrene and Neoprene by Dupont. It was discovered by Carothers and coworkers. Because of its early discovery good synthetic routes were worked out prior to the advent of good steroregulating catalytic systems. Thus, polychloroprene is largely manufactured by emulsion polymerization using both batch and continuous systems. Free radical products contain mainly 1,4-trans units. Along with the four “main” structural units analogous to those of polyisoprene, sequence distributions are available for both polyisoprene and polychloroprene similar to those given in Sec. 10.8. Polymerization can occur with the growing end being the 4 end or the 1 end. Generally the 1,4-polymerization sequence is favored with the growing end being carbon 4.



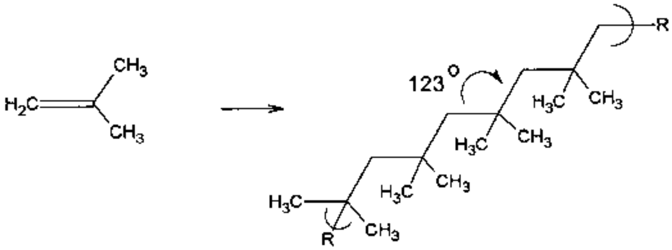
(7.38)

Structural regularity for inclusion of the 1,4-trans unit is inversely proportional to temperature. Thus, at 90°C the product contains about 85% of the trans-1,4 units while this increases to almost 100% at -150°C. Both uncured and cured polychloroprene exists as largely crystalline materials because of the high degree of stereoregularity. Cured polychloroprene has good high tensile strength because of this and application of stress to the material, either before or after curing increases the tensile strength. The trans-1,4-polychloroprene has a T_g of about -49°C while 1,4-cis-polychloroprene has a T_g of about -20°C.

Compounding of polychloroprene is similar to that of natural rubber. Vulcanizing is achieved using a variety of agents including accelerators. Because of its durability, polychloroprene rubber is often used where deteriorating effects are present. It offers good resistance to oils, ozone, heat, oxygen, and flame (the latter because of the presence of the chlorine atom). Automotive uses include as hoses, V-belts, and weatherstripping. Rubber goods include gaskets, diaphragms, hoses, seals, conveyer belts, and gaskets. It is also used in construction for highway joint seals, bridge mounts and expansion joints, and for soil-pipe gaskets. It is also used for wet-laminating and contact-bond adhesives, in coatings and dipped goods, as modifiers in elasticized bitumens and cements, and in fiber binders.

7.9 POLYISOBUTYLENE

Polyisobutylene, PIB, was initially synthesized in the 1920s. It is one of the few examples of the use of cationic catalysis to produce commercial scale polymers. Low molecular weight (about 5,000 Daltons) PIB can be produced at room temperature but large chains (over 1,000,000 Daltons) are made at low temperatures where transfer reactions are suppressed.



(7.39)

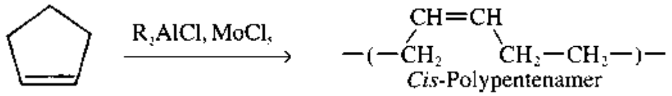
PIB and various copolymers are called butyl rubber. Butyl rubbers have lower permeability and higher damping than other elastomers making them ideal materials for tire innerliners and engine mounts.

Because of the symmetry of the monomer, it might be expected that the materials would be quite crystalline like linear polyethylene. While PIB does crystallize under stress is does not under non-stressed conditions. This is because the geminal dimethyl groups on alternating carbons in the backbone cause the bond angles to be distorted from about the usual tetrahedral bond angle of 109.5° to 123° forcing the chain to be straightened out. As a consequence of this the chains pack efficiently giving a relatively high density material (density of 0.917 g/cc compared to densities of about 0.85 g/cc for many amorphous polymers) even when amorphous. This close packing reduces the incentive for crystallization, accounts for its low permeability, and produces an usually low T_g of $-60°C$ for such a dense material.

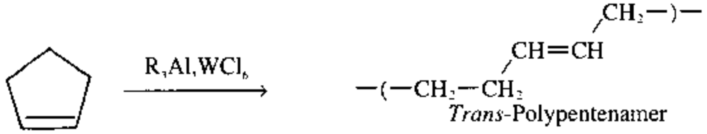
Because PIB is fully saturated, it is cured as a thermoset elastomer through inclusion of about 1 to 2% isoprene that supplies the needed double bonds used in the curing process. Other materials including brominated paramethyl styrene are replacing isoprene for this use. PIB is also used in sealing applications and medical closures and sealants.

7.10 METATHESIS REACTIONS

Olefin metathesis is a catalytically induced reaction wherein olefins, such as cyclobutene and cyclopentene, undergo bond reorganization resulting in the formation of so-called polyalkenamers. Because the resulting polymers contain double bonds that can be subsequently used to introduce crosslinking, these materials have been used to produce elastomeric materials as well as plastics. Transition metal catalysts are required for these reactions. Catalysts include typical Natta-Ziegler types and other similar catalyst–cocatalyst combinations. The reactions can be run at room temperature and the stereoregularity controlled through choice of reaction conditions and catalysts. For instance, the use of a molybdenum-based catalyst with cyclopentene gives the cis product whereas the use of a tungsten-based catalyst gives the trans product.



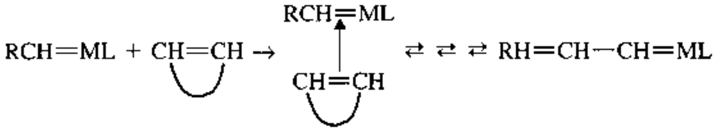
(7.40)



(7.41)

As expected, the metathesis polymerization of more strained cycloalkenes such as cyclobutene occurs more rapidly than less strained structures such as cyclopentene.

It is believed that polymerization occurs via a chain polymerization where ring opening occurs via complete scission of the carbon–carbon double bond through the reaction with metal carbene precursors giving an active carbene species.



(7.42)

where L is the ligand attached to the metal.

7.11 ZWITTERIONIC POLYMERIZATION

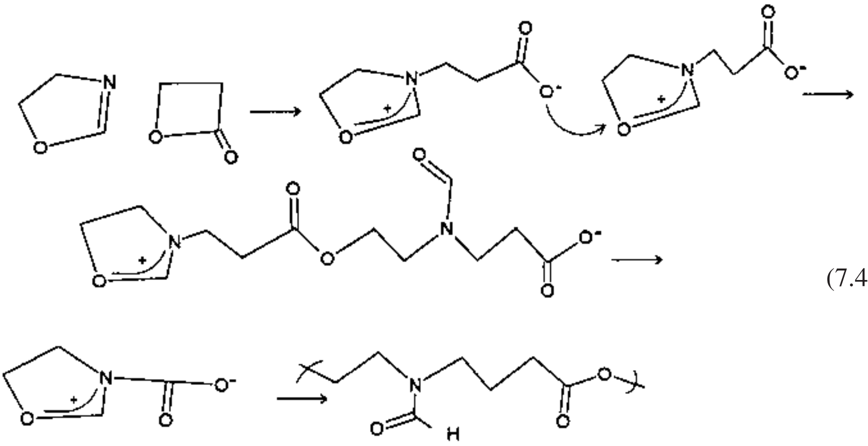
While most polymerizations require an initiator, catalyst, or some other form of activation, zwitterionic copolymerizations do not. These copolymerizations require a specific combination of one monomer that is nucleophilic and a second that is electrophilic. The interaction of these two comonomers gives a zwitterion that is responsible for both initiation and propagation.

$$\text{Initiation } MN + ME \rightarrow {}^{+}MN{-}ME^{-}$$

$$\text{Propagation } {}^{+}MN - ME^{-} + {}^{+}MN - ME^{-} \rightarrow\rightarrow {}^{+}MN - ME - MN - ME^{-} \rightarrow\rightarrow\rightarrow\rightarrow {}^{+}MN - (- ME - MN -) - ME^{-} \quad (7.43)$$

If growth involves only addition and condensation reactions, then an alternating copolymer is formed. Sometimes a lateral reaction occurs where the zwitterion interacts with one of the monomers giving a product that is a statistical copolymer.

The zwitterionic copolymerization is illustrated by the reaction of 2-oxazoline with β-propiolactone below (7.44).



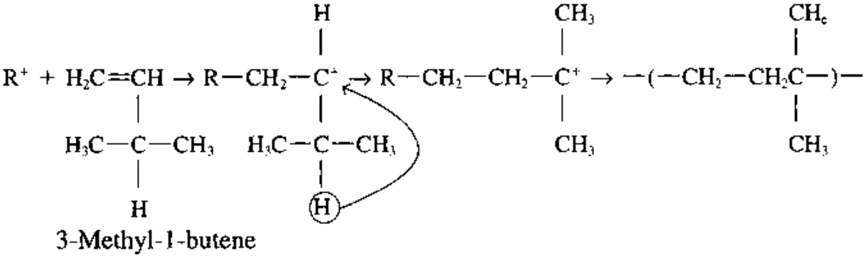
(7.44)

7.12 ISOMERIZATION POLYMERIZATION

Isomerization polymerizations are polyaddition reactions whereby the propagating species rearranges to energetically preferred structures prior to subsequent chain growth.

$$nA \rightarrow -(-B-)_n- \quad (7.45)$$

In 1962 Kennedy reported the first isomerization polymerization using 3-methyl-1-butene to give a 1,1-dimethyl polypropylene as shown below.



$$R^+ + \underset{\substack{|\\ H_3C-C-CH_3\\ |\\ H}}{H_2C{=}CH} \rightarrow R-CH_2-\overset{\substack{H\\|}}{\underset{\substack{|\\ H_3C-C-CH_3\\ |\\ H}}{C^+}} \rightarrow R-CH_2-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\ CH_3}}{C^+}} \rightarrow -(-CH_2-CH_2\overset{\substack{CH_3\\|}}{\underset{\substack{|\\ CH_3}}{C}}-)- \quad (7.46)$$

3-Methyl-1-butene

Isomerization polymerizations can be associated with coordination catalyst systems, ionic catalyst systems, and free radical systems. The cationic isomerization polymerization of

4-methyl-1-pentene is of interest because the product can be viewed as an alternating copolymer of ethylene and isobutylene. This structure cannot be obtained by conventional approaches.

In the presence of certain Zeigler catalysts, an equilibrium exists between cis- and trans-1,3-pentadiene. Here the cis-1,4-polypentadiene is formed from trans-1,3-pentadiene or from a mixture of cis and trans isomers.

Such isomerizations are sometimes desired and sometimes are the cause of or explanation for unwanted structures. In the cationic polymerization forming poly(1-butene), nine different structural units have been found. Classical 1,2-hydride and 1,2-methide shifts, hydride transfer, and proton elimination account for these structures.

Unwanted branching of many polymers probably occurs through such isomerizations. Polypropylene, formed using cationic polymerization, has methyl, ethyl, n-propyl, n-butyl, isopropyl, gem-dimethyl, isobutyl, and t-butyl groups connected to the main chain.

7.13 PRECIPITATION POLYMERIZATION

Precipitation polymerization, also called slurry polymerization, is a variety of solution polymerization where the monomer is soluble but the polymer precipitates as a fine floc. The formation of olefin polymers via coordination polymerization occurs by a slurry process. Here, the catalyst is prepared and polymerization is carried out under pressure and at low temperatures, generally less than 100°C. The polymer forms a viscous slurry. Care is taken so that the polymer does not cake up on the sides and stirrer.

SUMMARY

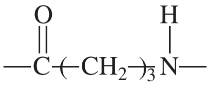
1. Chain reactions, including ionic chain polymerization reactions, consist of at least three steps: initiation, propagation, and termination. Because of the repulsion of similarly charged species, termination by coupling seldom occurs. Instead, termination may take place by chain transfer to produce a new ion and a dead polymer. The $\overline{\mathrm{DP}}$ of the latter is equal to the kinetic chain length.
2. Sulfuric acid and Lewis acids with a cocatalyst of water or ether serve as possible initiators in cationic polymerizations, producing a carbonation and a gegenion. Monomers with electron-donating groups, such as isobutylene and vinyl alkyl ethers, may be polymerized at low temperatures in solvents with high dielectric constants.
3. The degree of polymerization is proportional to the concentration of monomer in cationic polymerization, and the overall rate of polymerization is proportional to the square of the concentration of monomers.
4. In general, the rate of cationic polymerization is dependent on the dielectric constant of the solvent, the resonance stability of the carbocation, the degree of salvation of the gegenion, and the electropositivity of the initiator.
5. Stereoregular polymers are produced at low temperatures in solvents that favor the formation of ion pairs between the carbocation and the gegenion.
6. The stability of formaldehyde polymers is improved by capping the hydroxyl end groups or by copolymerizing with other monomers, such as dioxolane.
7. Water-soluble polymers of ethylene oxide are formed readily, but those of more stable cyclic ethers require a promotor, such as ethylene oxide, for this formation.

8. Nylon-2, a polyamide with a wide variety of pendant groups, may be prepared from N-carbosyl amino acid anhydrides.
9. Monomers with electron-withdrawing groups, such as acrylonitrile, may be polymerized in the presence of anionic initiators, such as butyllithium.
10. The rate of anionic polymerization is dependent on the dielectric constant of the solvent, the stability of the carbanion, the electronegativity of the initiator, the degree of solvation of the gegenion, and the strength of the electron-withdrawing groups in the monomer.
11. Monadic nylons are produced by the anionic ring opening of lactams, such as caprolactam, yielding nylon-6.
12. Stereospecific polymers of nonpolar monomers may be produced by polymerization with a Ziegler-Natta catalyst. The most widely used system consists of a titanium trichloride catalyst and an alkylaluminum cocatalyst.
13. This mechanism (cf. 12) involves a reaction on the surface of $TiCl_3$, activated by the addition of the ethyl group from the cocatalyst. The monomer adds to this active site to produce a π complex, which forms a new active center by insertion of the monomer between the titanium and carbon atoms. This step is repeated in the propagation reactions, in which the alkyl group from the cocatalyst is always the terminal group.
14. Stereospecific polymers are also produced using alfin and chromia on silica initiators. The former, which consists of allyl sodium, sodium isopropoxide, and sodium chloride, yields high molecular weight transpolydienes.
15. The production of cis- and trans-polydienes, as well as stereospecific poly-1,2-dienes, is influenced by the proper choice of Ziegler-Natta catalysts and the polymerization temperature.

GLOSSARY

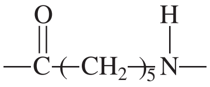
alfin: A complex catalyst system consisting of allyl sodium, sodium isopropoxide, and sodium chloride.
anionic polymerization: A polymerization initiated by an anion.
aziridine: Ethyleneimine.
block copolymer: A macromolecule consisting of long sequences of different repeat units ($A_nB_nA_n$).
butyl rubber (IIR): A copolymer of isobutylene and isoprene.
C: Catalyst–cocatalyst complex.
capping: Reacting the end groups to produce a stable polymer.
carbanion: A negatively charged organic ion.
carbocation: A positively charged organic ion, i.e., one lacking an electron pair on a carbon atom.
cationic polymerization: Polymerization initiated by a cation and propagated by a carbonium ion.
ceiling temperature: A threshold temperature above which a specific polymer cannot exist.
Celcon: A trade name for a copolymer of formaldehyde and dioxolane.
chain-reaction polymerization: A rapid polymerization based on initiation, propagation, and termination steps.
chain transfer: A process in which a growing chain becomes a dead polymer by abstracting a group from some other compound, thereby generating another active site.

cocatalyst: The alkylaluminum compound in the Ziegler-Natta catalyst system.
copolymer: A polymer chain containing repeat units from more than one monomer.
copolymerization: A polymerization of a mixture of monomers.
coupling: Joining of two active species.
Delrin: Trade name for a polyacetal.
diadic: A polyamide produced from more than one reactant.
dioxolane: A five-membered cyclic ether containing three carbon and two oxygen atoms in the ring.
electrophilic: Electron seeking.
EP: Ethylene-propylene copolymer.
gegenion: A counterion.
IIR: Butyl rubber.
initiation: The start of a chain reaction.
isomerization polymerization: Polyaddition reactions in which the propagating species rearranges to energetically preferred structures prior to chain growth.
it: Isotactic.
k: Rate constant.
Kraton: A trade name for an ABA block copolymer of styrene-butadiene-styrene.
lactam: A heterocyclic amide with one nitrogen atom in the ring.
lactone: A heterocyclic ester with one oxygen atom in the ring.
Leuchs' anhydride: A cyclic anhydride that decomposes to carbon dioxide and an amino acid.
living polymers: Macroanions or macrocarbanions.
[M]: Monomer concentration.
[M^+]: Carbonium ion concentration.
macroions: Charged polymer molecules.
Metathesis reaction: Catalytically induced reaction wherein olefins undergo bond reorganization resulting in the formation of polyalkenamers.
monadic: A polyamide produced from one reactant.
Natta, Giulio: The discoverer of stereospecific polymers.
nylon-4: A polymer with the following repeat unit:



$$-\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_3\!-\!\overset{H}{\overset{|}{N}}-$$

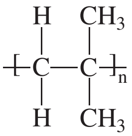
nylon-6: A polymer with the following repeat unit:



$$-\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_5\!-\!\overset{H}{\overset{|}{N}}-$$

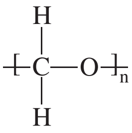
oxacycloalkane: A cyclic compound containing an oxygen atom in the ring.
oxirane: Ethylene oxide.
Penton: A trade name for a polychloroether.
π complex: A complex formed by a metal with an empty orbital, such as titanium, overlapping with the p orbitals in an alkene.
polyacetal: Polyoxymethylene.
polychloral: A polymer of trichloroacetaldehyde.

polyisobutylene: A polymer with the following repeat units:



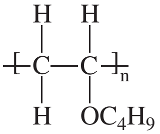
$$\left[\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{CH_3}{C}}\right]_n$$

polyoxymethylene: A polymer with the following repeat units:



$$\left[\underset{H}{\overset{H}{C}}-O\right]_n$$

poly(vinyl isobutyl ether): A polymer with the following repeat units:



$$\left[\underset{H}{\overset{H}{C}}-\underset{OC_4H_9}{\overset{H}{C}}\right]_n$$

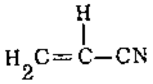
POM: Polyoxymethylene.
PP: Polypropylene.
promoter: A term used for strained cyclic ethers that are readily cleaved.
propagation: The continuous successive chain extension in a chain reaction.
R: Rate.
soluble stereoregulating catalysts: Soluble catalysts requiring a metal active site, cocatalyst or counterion, and a ligand system; capable of producing polymers with high stereoregularity and a minimum of branching.
st: Syndiotactic.
termination: The destruction of active species in a chain reaction.
TPX: Poly-4-methylpentene.
trioxane: A trimer of formaldehyde.
Ziegler, Karl: The discoverer of complex coordination catalysts.
Ziegler-Natta catalyst: $TiCl_3$-AIR_3.
Zwitterionic polymerization: Copolymerizations between nucleophilic and electrophilic comonomers.

EXERCISES

1. Describe the contents of the reaction flask 10 min after the polymerization of (a) reactants in step polymerization, such as dimethyl terephthalate and ethylene glycol, and (b) monomer in chain reaction, such as isobutylene.
2. What is the initiator in the polymerization of isobutylene?
3. What is the general name of the product produced by cationic initiation?
4. What reactant besides the monomer is present in cationic chain propagation reactions?

5. What name is used to describe the negatively charged counterion in cationic chain-reaction polymerization?
6. Is a Lewis acid (a) an electrophile or (b) a nucleophile?
7. Is a Lewis base (a) an electrophile or (b) a nucleophile?
8. Why isn't coupling a preferred termination step in the cationic chain polymerization of pure monomer?
9. Is the usual configuration of polymers produced by ionic chain polymerization (a) head to tail or (b) head to head?
10. Which condition would be more apt to produce stereoregular polymers in ionic chain polymerizations: (a) high temperatures or (b) low temperatures?
11. Name (a) a thermoplastic, (b) an elastomer and (c) a fiber that is produced commercially by ionic chain polymerization.
12. Which technique would you choose for producing a polymer of isobutyl vinyl ether: (a) cationic or (b) anionic?
13. Which technique would you choose for producing a polymer of acrylonitrile: (a) cationic or (b) anionic?
14. Which of the following could be used to initiate the polymerization of isobutylene: (a) sulfuric acid, (b) boron trifluoride etherate, (c) water, or (d) butyllithium?
15. Which of the following could be polymerized by cationic chain polymerization?

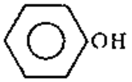
(a)



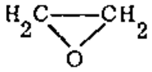
$H_2C{=}CH{-}CN$

(b) $H_2C{=}C(CH_3)_2$

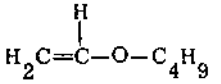
(c)



(d)



(e)



$H_2C{=}CH{-}O{-}C_4H_9$

16. Which polymer is more susceptible to oxidation: (a) HDPE or (b) PP?
17. When termination is by chain transfer, what is the relationship of $\overline{DP}$ and the kinetic chain length?
18. What would be the composition of the product obtained by the cationic low-temperature polymerization of a solution of isobutylene in ethylene?
19. What is the relationship of the rate of initiation (R_i) to the monomer concentration [M] in ionic chain polymerization?
20. What effect will the use of a solvent with a higher dielectric constant have on the rate of propagation (R_p) in ionic chain polymerization?
21. How does the rate constant k_p change as the yield of polymer increases?
22. Which will have the higher T_g value: (a) polystyrene or (b) polyisobutylene?
23. Which of the following could serve as an initiator for an anionic chain polymerization (a) $AlCl_3$ — H_2O, (b) BF_3 — H_2O, (c) butyllithium, or (d) sodium metal?

24. What species, in addition to a dead polymer, is produced in a chain transfer reaction with a macrocarbocation in cationic chain polymerization?
25. What is the relationship of R_i and R_T under steady-state conditions?
26. What is the relationship of $\overline{DP}$ to R_p and R_T?
27. Which would yield the higher molecular weight aldehyde: ozonolysis of (a) natural rubber or (b) butyl rubber?
28. What percentage of polymer is usually found when a polymer produced by chain-reaction polymerization is heated above its ceiling temperature?
29. What is the relationship of $\overline{DP}$ to initiator concentration in cationic chain polymerization?
30. Can the polymers found in the bottom of a bottle of insolubilized formaldehyde solution be useful?
31. How would you prepare stable polymers from formaldehyde?
32. Why is the thermal decomposition of polymers of formaldehyde called unzipping?
33. Can chloral be polymerized at 60°C?
34. How would you promote the ring-opening polymerization of tetrahydrofuran?
35. How would you increase the rate of flow of water in a fire hose?
36. Why is poly-3,3-bischloromethyloxybutylene crystalline?
37. Why must care be used in the polymerization of aziridine?
38. What byproduct is produced when Leuchs' anhydride is polymerized?
39. How could you remove unsaturated hydrocarbons from petroleum or coal tar distillates?
40. What species is produced by the reaction of an anionic chain polymerization initiator and the monomer?
41. What are the propagating species in anionic chain polymerization?
42. Why are polymers produced by the anionic polymerization of pure monomers called "living polymers?"
43. Using the symbols A and B for repeating units in the polymer chain, which of the following is a block copolymer: (a) —ABABAB—, (b) AABABBA—, (c) —$(A)_nB_n$—?
44. What is the most widely used monadic nylon?
45. What is the repeating unit in nylon-4?
46. What is the catalyst and cocatalyst in the most widely used Ziegler-Natta catalyst?
47. Why is β-$TiCl_3$ not used as a polymerization catalyst?
48. What is the principal difference between propagation reactions with butyllithium and a Ziegler-Natta catalyst?
49. In addition to good strength, clarity, and good resistance to heat and corrosives, what is a unique feature of poly-4-methylpentene-1?
50. Show the skeletal structures of cis- and trans-polyisoprene.
51. Write formulas for repeating units in the chains of (a) poly-1,4-isoprene and (b) poly-1,2-isoprene.
52. What is the most widely used catalyst for the production of HDPE?
53. What elastomer is produced by anionic chain polymerization?
54. What elastomer is produced by use of a Ziegler-Natta catalyst?

APPENDIX

Production of polymers in the United States and Canada in 1978 by ionic chain reaction and complex coordination polymerization (thousands of metric tons) is listed below.

By cationic polymerization	
butyl rubber	146
By anionic polymerization	
polyisoprene	76
By coordination polymerization, including chromia on silica (Phillips catalyst)	
high-density polyethylene (HDPE)	1852
polypropylene plastics	1341
polybutadiene	444
ethylene-propylene copolymer	181
polypropylene fibers	332

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8

Free Radical Chain Polymerization (Addition Polymerization)

Since most synthetic plastics and elastomers and some fibers are prepared by free radical polymerization, this method is obviously most important from a commercial viewpoint. Table 8.1 contains a listing of a number of commercially important addition polymers. Many of the concepts discussed in Chapter 7 on ionic chain polymerization also apply to free radical polymerization. However, because of the versatility of this polymerization technique, several new concepts will be introduced in this chapter.

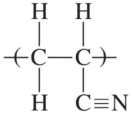
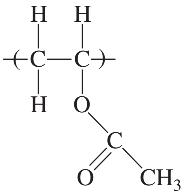
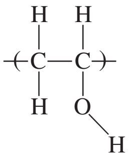
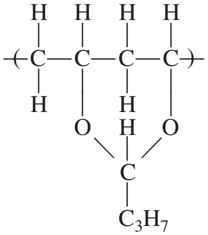
As is the case with other chain reactions, free radical polymerization is a rapid reaction which consists of the characteristic chain reaction steps, namely, initiation, propagation, and termination. Unlike the cationic and anionic initiators produced from the hetrolytic cleavage of ion pairs such as H^+, HSO_4^- and Bu^-, Li^+, respectively, free radical initiators are produced by homolytic cleavage of covalent bonds. The formation of free radicals is dependent on high-energy forces or the presence of weak covalent bonds.

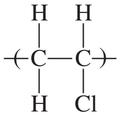
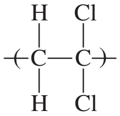
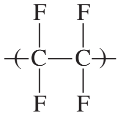
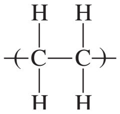
8.1 INITIATORS FOR FREE RADICAL CHAIN POLYMERIZATION

Free radical initiation can occur through application of heat (thermal), (ultraviolet and visible) light (photochemical), (ionizing) light, redox reagents, electricity (electrochemical), etc., that is any process that creates the essential free radicals.

While application of heat can rupture the pi bond in the vinyl monomer causing the formation of a two-headed free radical that can act as a free radical initiator, peroxides and dinitriles are generally employed. This is a consequence of the general bond dissociation energy trend of C—H>C—C>C—N>O—O. Dinitrile or azo compounds such as 2,2′-azo-bis-isobutyronitrile, AIBN, require temperatures of about 70–80°C to produce decomposition with free radical formation [Eq. (8.6)]. Peroxides such as benzoyl peroxide, BPO, require temperatures in the range of 60–140°C for decomposition and free radical formation [Eq. (8.7)]. While the dissociation bond energy for C—N is generally greater

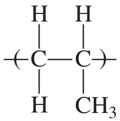
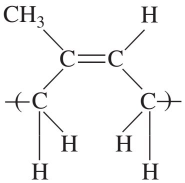
Table 8.1 Industrially Important Addition Polymers

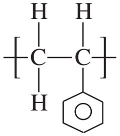
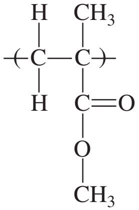
Name	Repeating unit	Typical properties	Typical uses
Polyacrylonitrile (including acrylic fibers)		High strength; good stiffness; tough; abrasion resistant; resilient; good flex life; relatively good resistance to moisture and stains, chemicals, insects, and fungi; good weatherability	Carpeting, sweaters, skirts, socks, slacks, baby garments
Poly(vinyl acetate)		Water sensitive with respect to physical properties such as adhesion and strength; generally good weatherability, fair adhesion	Lower molecular weight used in chewing gums, intermediate in production of poly(vinyl alcohol), water-based emulsion paints
Poly(vinyl alcohol)		Water soluble, unstable in acidic or basic aqueous systems; fair adhesion	Thickening agent for various suspension and emulsion systems, packaging film, wet-strength adhesive
Poly(vinyl butyral)		Good adhesion to glass; tough; good stability to sunlight; good clarity; insensitive to moisture	Automotive safety glass as the interlayer

Poly(vinyl chloride) and poly(vinylidene chloride) (called “the vinyls” or “viny! resins”)	 $-\!\left(\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}\right)\!-$  $-\!\left(\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{Cl}{C}}\right)\!-$	Relatively unstable to heat and light, fire resistant; resistant to chemicals, insects, fungi; resistant to moisture	Calendered products such as film sheets and floor coverings; shower curtains, food covers, rainwear, handbags, coated fabrics, insulation for electrical cable and wire, phonograph records
Polytetrafluoroethylene (Teflon)	 $-\!\left(\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}\right)\!-$	Insoluble in most solvents, chemically inert, low dielectric loss, high dielectric strength, uniquely nonadhesive, low friction properties, constant electrical and mechanical properties from 20 to about 250°C, high impact strength, not hard, outstanding mechanical properties	Coatings for frying pans, etc.; wire and cable insulation; insulation for motors, oils, transformers, generators; gaskets; pump and valve packings; nonlubricated bearings
Polyethylene (lowdensity, branched)	 $-\!\left(\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\right)\!-$	Dependent on molecular weight, branching, molecular weight distribution, etc.; good toughness and pliability over a wide temperature range, outstanding electrical properties, good transparency in thin films, inert chemically, resistant to acids and bases, ages on exposure to light and oxygen, low density, flexible without plasticizer, resilient, high tear strength, moisture resistant	Films; sheeting used in bags, pouchers, produce wrapping, textile materials, frozen foods, etc.; drapes, table cloths; covers for construction, ponds, greenhouses, trash can liners, etc.; electrical wire and cable insulator; coating of foils, papers, other films; squeeze bottles

(continued)

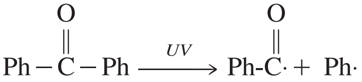
Table 8.1 Continued

Name	Repeating unit	Typical properties	Typical uses
Polyethylene (high-density, linear)		Most of the difference in properties between branched and linear concerns the high crystallinity of the latter; linear polyethylene has a high T_g, T_m, softening range, greater hardness and tensile strength.	Bottles, housewares, toys, films, sheets, extrusion coating, pipes, conduit, wire and cable insulation
Polypropylene	 $-\!\left(\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\right)\!-$	Lightest major plastic; its high crystallinity imparts to it high tensile strength, stiffness, and hardness, good gloss, high resistance to marring; high softening range permits polymer to be sterilized; good electrical properties, chemical inertness, moisture resistance	Filament—rope, webbing, cordage; carpeting; injection molding applications in appliance, small housewares, and automotive fields
Polyisoprene (cis-1, 4-polyisoprene)		Structure closely resembling that of natural rubber; properties similar to those of natural rubber	Replacement of natural rubber; often preferred because of its greater uniformity and cleanliness
SBR (styrene-butadiene rubber)	Random copolymer	Generally slightly poorer physical properties than those of natural rubber	Tire treads for cars, inferior to natural rubber with respect to heat buildup and resilience, thus not used for truck tires; belting; molded goods, gum, flooring, rubber shoe soles, electrical insulation, hoses

Butyl rubber (copolymer of isobutylene with small amounts of isoprene added to permit vulcanization)	Amorphous, isoprene—largely 1, 4 isomer	Good chemical inertness, low gas permeability, high viscoelastic response to stresses, less sensitive to oxidative aging than most other elastomers, better ozone resistance than natural rubber, good solvent resistance	About 70 to 60% used for inner tubes for tires
Polychloroprene (Neoprene)	Mostly 1, 4 isomer	Outstanding oil and chemical resistance; high tensile strength, outstanding resistance to oxidative degradation and aging; good ozone and weathering resistance; dynamic properties are equal or greater than those of most synthetic rubber and only slightly inferior to those of natural rubber	Can replace natural rubber in most applications; gloves, coated fabrics, cable and wire coatings, hoses, belts, shoe heels, solid tires
Polystyrene		Clear; easily colored; easily fabricated; transparent; fair mechanical and thermal properties; good resistance to acids, bases, oxidizing and reducing agents; readily attacked by many organic solvents; good electrical insulator	Used for the production of ion-exchange resins, heat- and impact-resistant copolymers, ABS resins, etc., foams, plastic optical components, lighting fixtures, housewares, toys, packaging, appliances, home furnishings
Poly(methylmethacrylate)		Clear, transparent, colorless, good weatherability, good impact strength, resistant to dilute basic and acidic solutions, easily colored, good mechanical and thermal properties, good fabricability, poor abrasion resistance compared to glass	Available in cast sheets, rods, tubes, and molding and extrusion compositions; applications where light transmission is needed, such as tail- and signal-light lenses, dials, medallions, brush backs, jewelry, signs, lenses, skylight "glass"

than for O—O, the formation of a stable N_2 molecule is the thermodynamic driving force due to an entropy effect allowing dissociation to occur at typically lower temperatures.

Light in the ultraviolet and visible range can disrupt selected bonds forming free radicals. Such disruption occurs as we are exposed to sunlight. Suntan treatments often contain certain compounds that can accept this damaging radiation. Related compounds are also used in foods to give them longer shelf life. They are generally known as antioxidants. Synthetic antioxidants include benzophenones, benzils, and certain organic ketones (Sec. 14.2, 14.4). Thus, diphenylketone decomposes on exposure of ultraviolet radiation of the appropriate wavelength forming two free radicals.



$$\mathrm{Ph}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Ph} \xrightarrow{UV} \mathrm{Ph\text{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\cdot + \mathrm{Ph}\cdot \tag{8.1}$$

The advantage of using such photochemical initiations is that polymerization can be carried out at room temperature.

When molecules are exposed to light of higher energy, shorter wavelength or higher frequency, electrons can be removed or added depending on the specific conditions. Usual forms of ionizing radiation employed industrially and experimentally include neutrons, X-rays, protons, and alpha and beta particles. A simplified scheme illustrating free radical formation is given following.

Electron removal

$$AB \xrightarrow{\text{Ionizing Radiation}} AB^{+}. + e^{-} \tag{8.2a}$$

$$AB^{+}. \longrightarrow A\cdot + B^{+} \ (\text{or}\cdot B^{+}.) \tag{8.2b}$$

$$B^{+} + e^{-} \longrightarrow \cdot B \tag{8.2c}$$

Electron Addition

$$AB + e^{-} \xrightarrow{\text{Ionizing Radiation}} AB^{-}. \tag{8.3a}$$

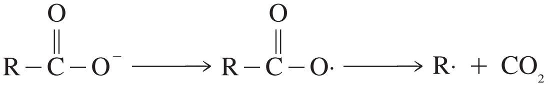
$$AB^{-}. \longrightarrow A\cdot + B^{-} \ (\text{or}\cdot B^{-}.) \tag{8.3b}$$

$$B^{-} \longrightarrow \cdot B + e^{-} \tag{8.3c}$$

In truth, the precise mechanism is generally more complex because various radicals, cations, and anions will be formed. Ionizing radiation induced polymerizations are generally carried out at room temperature and higher. Here, the reactants are selected so that the free radicals are more stable than the cations and anions allowing a largely free radical polymerization to occur.

Oxidation-reduction, redox, reactions are also often employed to initiate free radical polymerizations in solution or heterogeneous organic–aqueous systems.

Free radicals can be created by passing a current through a reaction system sufficient to initiate free radical polymerizations. Thus, solutions containing salts of carboxylic acids oxidize at the anode of an electrochemical cell forming free radicals when current is applied. Such free radicals can be used to initiate free radical polymerizations at, below, or above room temperature.



$$\mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}^{-} \longrightarrow \mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}\cdot \longrightarrow \mathrm{R}\cdot + \mathrm{CO_2} \tag{8.4}$$

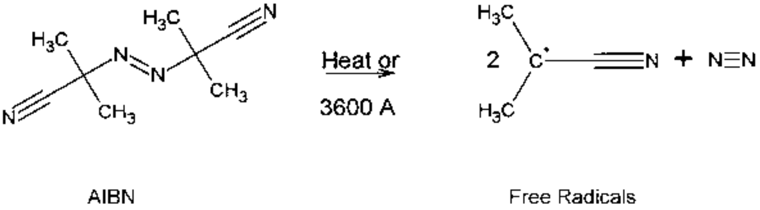
Here we will focus on the simple heat induced decomposition of classical free radical initiators.

The rate of decomposition of initiators usually follows first-order kinetics and is dependent on the solvent present and the temperature of polymerization. The rate is usually expressed as a half-life time ($t_{1/2}$) where $t_{1/2} = \text{In } 2/k_d = 0.693/k_d$. The rate constant ($k_d$) changes with temperature in accordance with the Arrhenius equation as shown below:

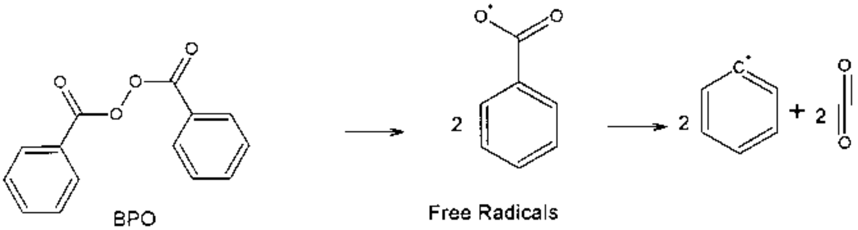
$$k_d = Ae^{-E_a/RT} \tag{8.5}$$

The rate constants for several common initiators are listed in Table 8.2. Typical equations for the dissociation of 2,2′-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) are shown below. It should be pointed out that because of recombination, which is solvent-dependent, and other side reactions of the free radicals (R·), the initiator efficiency is seldom 100%. Hence, an efficiency factor (f) is employed to show the percentage of effective free radicals produced.

The decomposition of AIBN and BPO to form radicals is given below.



(8.6)



(8.7)

The precise structure of the initiating agent and initial addition to the monomer varies according to the reaction conditions, monomer, and initiator. For illustration the peroxide bond in benzoyl peroxide, BPO, breaks forming two benzoyl free radicals. For styrene,

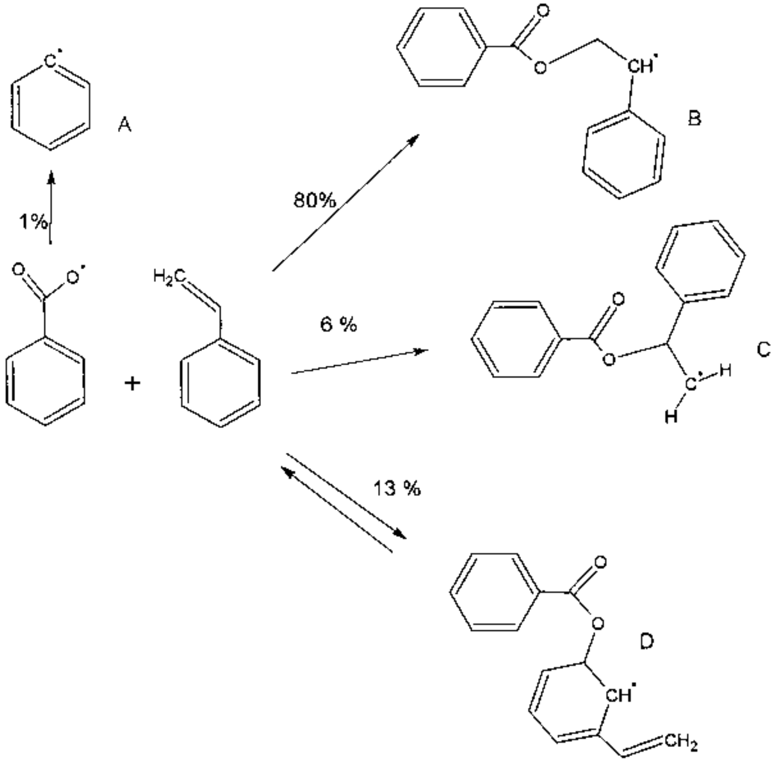
Table 8.2 Rate Constants for Common Initiators in Various Solvents[a]

Initiator	Solvent	Temp. (°C)	$k_d(s^{-1})$	E_a (kcal/mol^{-1})
2,2′-Azobisisobutyronitrile (AIBN)	Benzene	40	5.4×10^{-7}	30.7
Phenylazotriphenylmethane	Benzene	25	4.3×10^{-6}	26.8
tert-Butyl peroxide (TBP)	Benzene	80	7.8×10^{-8}	34
Cumyl peroxide	Benzene	115	1.6×10^{-5}	40.7
Acetyl peroxide	Benzene	35	9.5×10^{-5}	32.3
Benzoyl peroxide (BPO)	Benzene	30	4.8×10^{-8}	27.8
Lauroyl peroxide	Benzene	30	2.6×10^{-7}	30.4
tert-Butyl hydroperoxide	Benzene	154	4.3×10^{-6}	40.8
tert-Butyl perbenzoate	Benzene	100	1.1×10^{-5}	34.7

[a] All initiators are unstable compounds and should be handled with extreme caution!

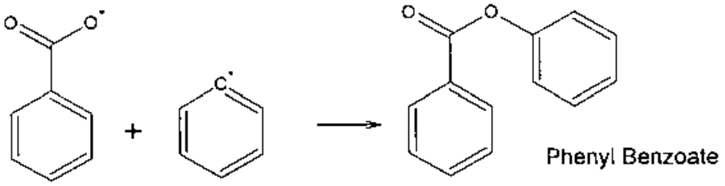
Source: Data from *Polymer Handbook* (Brandrup and Immergut, 1975).

the major reaction (8.8) involves direct addition of the benzoyl radical to the tail end of the styrene monomer creating a molecule where the radical resides at the head or more sterically demanding and more radical stabilizing site (structure B below). A lesser amount of the benzoyl radical adds to the head end (structure C). Some adds to the ring forming a variety of compounds (including structure D). A small amount decomposes forming the phenyl radical and carbon dioxide (structure A). For simplicity we will employ structure A as the initiating structure but all initiating structures give similar products only differing in the nature of the end group.



(8.8)

The benzoyl peroxide decomposes with a specific rate constant of about 10^{-8} $\sec^{-1}$, an Arrhenius constant, A, of about 10^{16}, and an activation energy of about 28 kcal/mole (about 115 kJ/mole). As noted before, not all radicals initiate new chains. Some terminate prior to initiation forming inactive products mainly phenyl benzoate (below). Thus an efficiency constant, f, is used that reflects the ratio of benzoyl peroxide that actually form chains.



(8.9)

The rate of decomposition of peroxides such as benzoyl peroxide may be increased by the addition of small amounts of tertiary amines such as N,N-dimethylaniline. The rate of decomposition of initiators may also be increased by exposure to ultraviolet (UV) radiation. For example, AIBN may be decomposed at low temperatures by UV radiation at a wavelength of 360 nm.

8.2 MECHANISM FOR FREE RADICAL CHAIN POLYMERIZATION

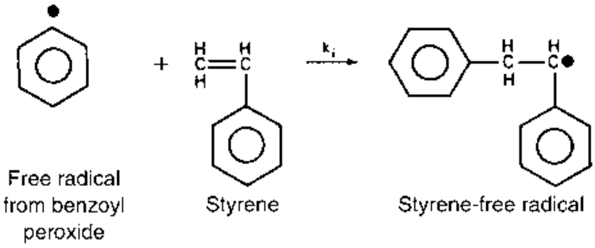
In general, the decomposition of the initiator (I) may be expressed by the following equations in which k_d is the rate or decay constant.

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}\cdot \tag{8.10}$$

$$R_d = \frac{-d[\mathrm{I}]}{dt} = k_d[\mathrm{I}] \tag{8.11}$$

where R_d is the rate of decomposition.

Initiation of a free radical chain takes place by addition of a free radical (R·) to a vinyl molecule. Polystyrene (PS) is produced by free radical polymerization at an annual rate of 2.9 million metric tons. The polymerization of styrene (S) will be used as an illustration. Styrene, like many other aromatic compounds, is toxic, and concentrations in the atmosphere should not exceed 10 ppm. It is important to note that that the free radical (R·) is a companion of all polymerizing species and hence should not be called a catalyst, even though it often is referred to as such.



(8.12)

$$\underset{\substack{\text{Free}\\\text{radical}}}{\mathrm{R}\cdot} + \underset{\text{Monomer}}{\mathrm{M}} \xrightarrow{k_i} \underset{\substack{\text{New free}\\\text{radical}}}{\mathrm{RM}\cdot} \tag{8.13}$$

$$R_i = \frac{d[\mathrm{RM}\cdot]}{dt} = k_i[\mathrm{R}\cdot][\mathrm{M}]$$

where R_i is the rate of initiation.

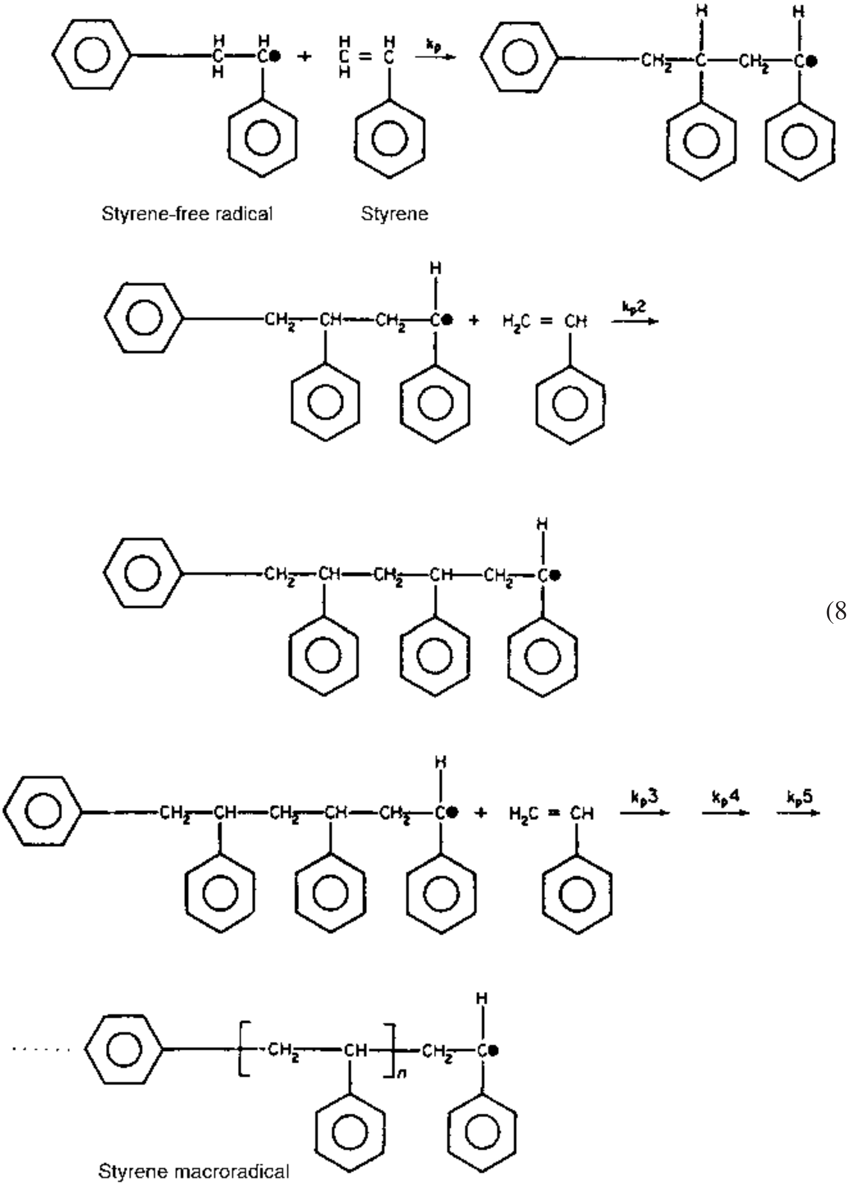
The rate of decomposition of I [Eq. (8.10)] is the rate-controlling step in the free radical polymerization. Thus, the overall expression describing the rate of initiation can be given as

$$R_i = 2k_d f[\mathrm{I}] \tag{8.14}$$

where f is the efficiency factor and is a measure of the fraction of initiator radicals that produce growing radical chains, i.e., are able to react with monomer.

A 2 is inserted in Eq. (8.14) because in this presentation, for each initiator molecule that decomposes, two radicals are formed. The 2 is omitted from Eq. (8.11) because this rate expression describes the rate of decomposition of the initiator, but not the rate of formation of free radicals (R·). [Similarly, in Eqs. (8.20) and (8.22), each termination results in the loss of two growing chains, thus a 2 appears in the descriptions.]

Propagation is a bimolecular reaction [Eq. (8.15)], which takes place by the addition of the new free radical (RM·) to another molecule of monomer (M), and by many repetitions of this step. While there may be slight changes in the propagation rate constant (k_p) in the first few steps, the rate constant is generally considered to be independent of chain length. Hence, the symbols M·, RM·, and RM_nM· may be considered equivalent in rate equations for free radical chain reaction polymerization.



(8.15)

Experimentally it is found that the specific rate constants associated with propagation are approximately independent of chain length; thus, the specific rate constants for each propagation step are considered to be the same, permitting all of the propagation steps to be described by a single specific rate constant k_p. Thus, Eq. (8.15) can be summed giving the overall propagation expression as

$$\sim\!\!\sim M\cdot + nM \xrightarrow{k_p} \sim\!\!\sim M - M_{n-1} - M\cdot$$

or simply

$$M\cdot + nM \xrightarrow{k_p} M - M_{n-1} - M\cdot \tag{8.16}$$

The rate of demise of monomer with time is described as:

$$-\frac{d[M]}{dt} = k_p[M\cdot][M] + k_i[R\cdot][M] \tag{8.17}$$

i.e., monomer consumption occurs only in steps 2 and 3 described by Eqs. (8.12) and (8.15).

For long chains the amount of monomer consumed by step 2 [Eq. (8.12)] is small compared with that consumed in step 3 [Eq. (8.15)], permitting Eq. (8.17) to be rewritten as:

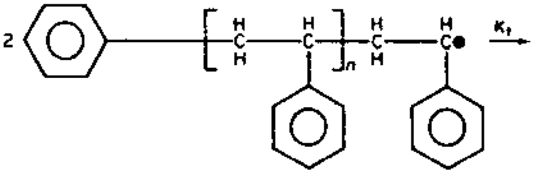
$$R_p = \frac{-d[M]}{dt} = k_p[M][M\cdot] \tag{8.18}$$

The polarity of the functional group in the monomers polymerized by free radical chain polymerization is between the positively inclined monomers, characteristic of undergoing cationic polymerization, and the negatively inclined monomers, characteristic of undergoing anionic polymerizations. However, as was true for the configuration of growing chains in ionic propagations, head-to-tail arrangement is the customary sequence in free radical propagation. The functional groups on the vinyl monomers are better stabilizers than the hydrogen atom that would be present as the macroradical end group in a head-to-head arrangement.

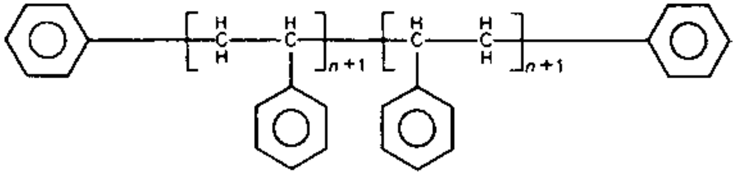
Unlike ionic polymerizations, the termination of the growing free radical chains usually takes place by coupling of two macroradicals. Thus, the kinetic chain length (v) is equal to DP/2. The chemical and kinetic equations for bimolecular termination are shown below.

$$\mathrm{RM}\bullet + \bullet\mathrm{MR} \xrightarrow{k_t} \mathrm{RMMR}$$

Macroradicals Dead polymer



Styrene macroradical



(8.19)

Dead polystyrene

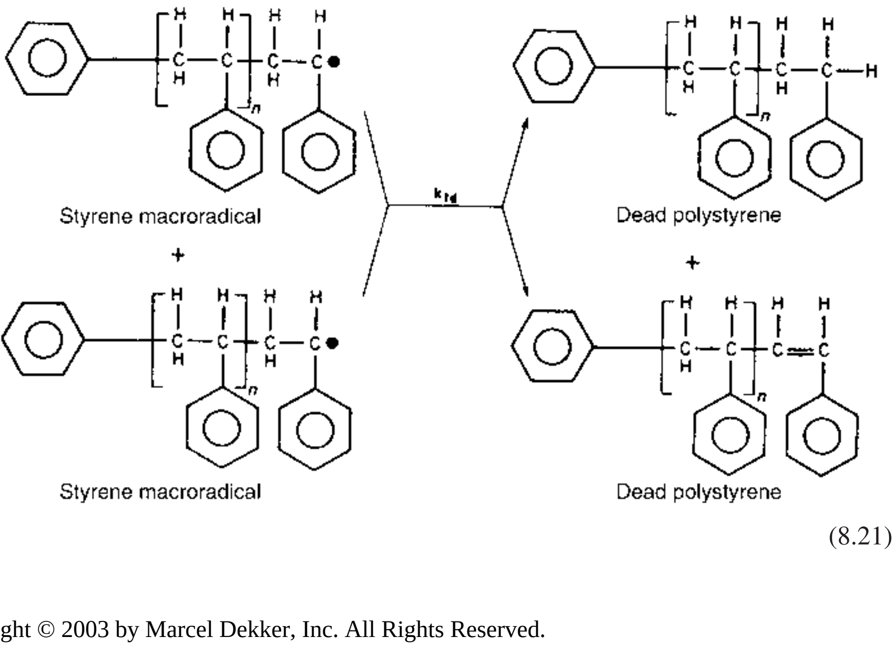
It should be noted that there is a head-to-head configuration at the juncture of the two macroradicals in the dead polymer. The kinetic equation for coupling termination is shown below.

$$R_t = \frac{-d[M\cdot]}{dt} = 2k_t[M\cdot][M\cdot] = 2k_t[M\cdot]^2 \qquad (8.20)$$

Termination of free radical chain polymerization may also take place by disproportionation. This termination process involves chain transfer of a hydrogen atom from one chain end to the free radical chain end of another growing chain, resulting in one of the "dead" polymers having an unsaturated chain end. Thus, the type and/or proportion of each type of chain termination can be obtained by determining the number of head-to-head configurations and number of end groups containing unsaturation. The kinetic description for chain termination by disproportionation is given in Eq. (8.22).

The kinetic chain length v is the number of monomer molecules consumed by each primary radical and is equal to the rate of propagation divided by the rate of initiation as described in Eq. (8.23) for termination by disproportionation. The kinetic chain length is independent of the type of termination, whereas the actual degree of polymerization or chain length depends on the mode of termination. For coupling, $\overline{DP} = 2v$ since the coupling acts to double the actual chain length. For disproportionation, $\overline{DP} = v$.

Styrene macroradicals are usually terminated by coupling. However, while methyl methacrylate macroradicals terminate by coupling at temperatures below 60°C, they tend to terminate by disproportionation at higher temperatures.



(8.21)

$$R_{td} = 2k_{td}[M\cdot]^2 \tag{8.22}$$

$$v_1 = \frac{R_p}{R_i} = \frac{R_p}{R_{td}} = \frac{k_p[M][M\cdot]}{2k_{td}[M\cdot]^2} = \frac{k_p}{2k_{td}}\frac{[M]}{[M\cdot]} = \overline{DP} = k'''\frac{[M]}{[M\cdot]} \tag{8.23}$$

However, while Eqs. (8.18), (8.22) and (8.23) are theoretically important, they contain [M·], which is difficult to experimentally determine and practically of little use. The following is an approach to render such equations more useful by generation of a description of [M·] involving more experimentally accessible terms.

The rate of monomer-radical change is described by:

$$\begin{aligned}\frac{d[M\cdot]}{dt} &= k_i[R\cdot][M] - 2k_t[M\cdot]^2 \\ &= (\text{monomer-radical formed}) - (\text{monomer radical utilized})\end{aligned} \tag{8.24}$$

It is experimentally found that the number of growing chains is approximately constant over a large extent of reaction. This situation is referred to as a “steady state.” For Eq. (8.24), this results in $d[M\cdot]/dt = 0$ and

$$k_i[R\cdot][M] = 2k_t[M\cdot]^2 \tag{8.25}$$

Additionally, a steady-state value for the concentration of R· exists, yielding

$$\frac{d[R\cdot]}{dt} = 2k_d f[I] - k_i[R\cdot][M] = 0 \tag{8.26}$$

Solving for [M·] from Eq. (8.25) and [R·] from Eq. (8.26) gives

$$[M\cdot] = \left(\frac{k_i[R\cdot][M]}{2k_t}\right)^{1/2} \tag{8.27}$$

and

$$[R\cdot] = \frac{2k_d f[I]}{k_i[M]} \tag{8.28}$$

Substituting into Eq. (8.27) the expression for [R·] from Eq. (8.28), we obtain an expression for [M·] [Eq. (8.29)], which contains readily determinable variables.

$$[M\cdot] = \left(\frac{k_d f[I]}{k_t}\right)^{1/2} \tag{8.29}$$

We then obtain useful rate and kinetic chain length equations by using the relationship shown above for [M·].

$$\begin{aligned}R_p &= k_p[M][M\cdot] = k_p[M]\left(\frac{k_d f[I]}{k_t}\right)^{1/2} \\ &= [M][I]^{1/2}\left(\frac{k_p{}^2 k_d f}{k_t}\right)^{1/2} = k'[M][I]^{1/2}\end{aligned} \tag{8.30}$$

where $k' = (k_p{}^2 k_d f/k_t)^{1/2}$

$$R_T = 2k_t[M\cdot]^2 = \frac{2k_t k_d f[I]}{k_t} = 2k_d f[I] \tag{8.31}$$

$$\overline{DP} = \frac{R_p}{R_i} = \frac{k_p[M](k_d f[I]/k_t)^{1/2}}{2k_d f[I]} = \frac{k_p[M]}{2(k_d k_t f[I])^{1/2}} \tag{8.32}$$

$$\overline{DP} = \frac{[M]}{[I]^{1/2}} \frac{k_p}{(2k_d k_t f)^{1/2}} = \frac{[M]}{[I]^{1/2}} K''$$

where $k'' = (k_p/(2k_d k_t f)^{1/2}$.

The Gibbs free energy relationship for a reversible process at constant temperature for polymerization is described by

$$\Delta G_p = \Delta H_p - T\Delta S_p \tag{8.33a}$$

where ΔH_p is the heat of polymerization defined by

$$\Delta H_p = E_p - E_{dp} \tag{8.33b}$$

where E_p is the activation energy for propagation and E_{dp} is the activation energy for depolymerization.

The entropy term is negative so that it is the enthalpy or energy term that “drives” the polymerization. At low temperatures the enthalpy term is larger than the $T\Delta S_p$ term, so that polymer growth occurs. At some temperature, called the ceiling temperature, the enthalpy term and entropy term are the same and $\Delta G_p = 0$. Above this temperature depolymerization occurs more rapidly than polymer formation, so that polymer formation does not occur. At the ceiling temperature depolymerization and polymerization rates are equal. The ceiling temperature is then defined as

$$T_c = \Delta H_p/\Delta S_p \tag{8.34}$$

since $\Delta G_p = 0$.

The ceiling temperature for styrene is about 310°C, for ethylene 400°C, for propylene 300°C, for methyl methacrylate 220°C, for tetrafluoroethylene 580°C, and for α-methylstyrene only 61°C.

Thus, one may make the following conclusions about free radical chain polymerizations using a chemical initiator:

1. The rate of propagation is proportional to the concentration of the monomer and the square root of the concentration of the initiator.
2. The rate of termination is proportional to the concentration of the initiator.
3. The average molecular weight is proportional to the concentration of the monomer and inversely proportional to the square root of the concentration of initiator.
4. The first chain that is initiated rapidly produces a high molecular weight polymer.
5. The monomer concentration decreases steadily throughout the reaction and approaches zero at the end.
6. The increases in rates of initiation, propagation, and termination with increases in temperature are in accord with the Arrhenius equation. The energies of activation of initiation, propagation, and termination are approximately 35, 5, and 3 kcal/mol, respectively. Data for typical energies of activation are given in Tables 8.3 and 8.4.
7. Increasing the temperature increases the concentration of free radicals and thus the rate of reactions, but it decreases the average molecular weight.
8. If the temperature exceeds the ceiling temperature (T_c), the polymer will decompose and no propagation will take place at temperatures above the ceiling temperature.

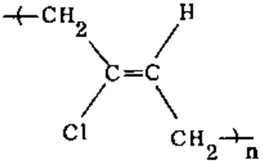
Table 8.3 Energies of Activation for Propagation (E_p) and Termination (E_t) in Free Radical Chain Polymerization

Monomer	E_p(kcal/mol)	E_t(kcal/mol)
Methyl acrylate	7.1	5.3
Acrylonitrile	4.1	5.4
Butadiene	9.3	—
Ethylene	8.2	—
Methyl methacrylate	6.3	2.8
Styrene	7.8	2.4
Vinyl acetate	7.3	5.2
Vinyl chloride	3.7	4.2

Source: Data from Brandrup and Immergut, 1975.

It is interesting to note that due to their great industrial importance, free radical polymerizations are the most studied reactions in all of chemistry. Furthermore, the kinetic approaches described in this chapter are experimentally verified for essentially all typical free radical vinyl polymerizations studied.

There is some tendency for the formation of stereoregular segments, particularly at low temperatures, but ionic and coordination catalyst techniques are preferred for the production of stereoregular polymers. For instance, the amount of trans-1,4 is increased from 71% at 100°C to 94% at −46°C for the free radical polymerization of the diene chloroprene. In fact, the trans-1,4 form (8.35) appears to be favored for most free radical polymerizations of dienes. For simple vinyl monomers, no clear trend with respect to stereoregular preference has yet emerged.



(8.35)

trans-1,4-Polychloroprene

Chapters 7 and 8 are concerned mainly with the polymerization of vinyl monomers. Experimentally, only a few vinyl monomers can undergo polymerization by way of anionic, cationic, and free radical pathways. As would be expected, anionic polymerizations occur mainly with vinyl monomers containing electron-withdrawing substituents, leaving the resulting vinyl portion electron-deficient, whereas cationic polymerizations occur mainly

Table 8.4 Typical Free Radical Kinetic Values

k_d	$10^{-3}\ s^{-1}$	E_{ad}	20–40 kcal/mol
k_i	10^3 L/mol s	E_{ai}	5–7 kcal/mol
k_p	10^3 L/mol s	E_{ap}	4–10 kcal/mol
k_t	10^7 L/mol s	E_{at}	≈ 0–6 kcal/mol

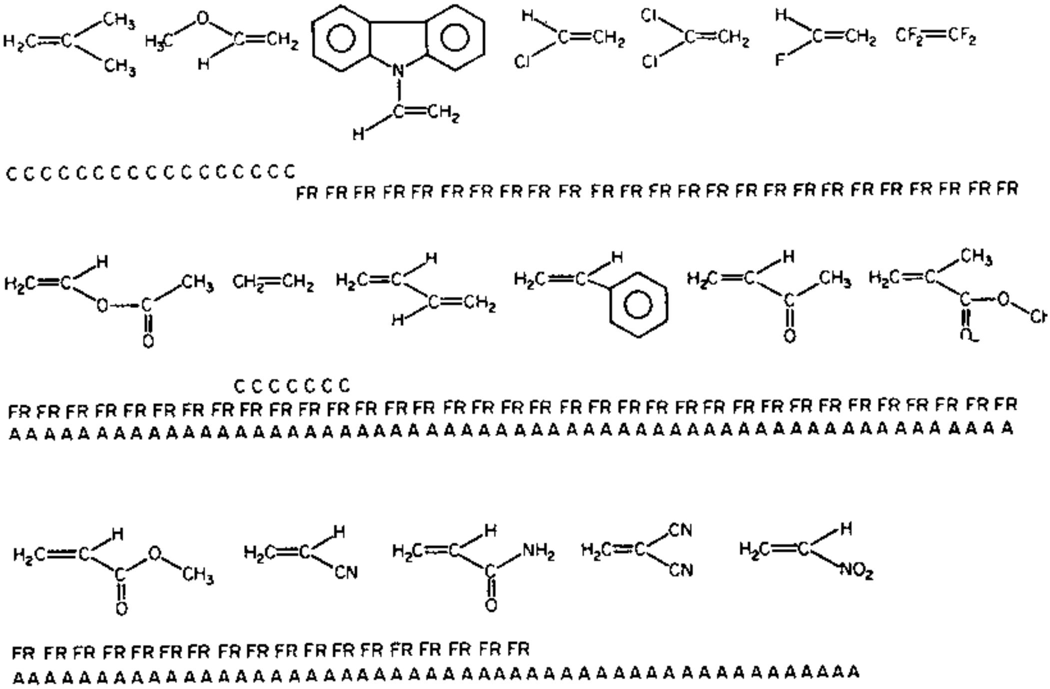


Figure 8.1 Type of chain initiation suitable for some common monomers in order of general decrease in electron density associated with the double bond: A, anionic; C, cationic; FR, free radical initiation possible.

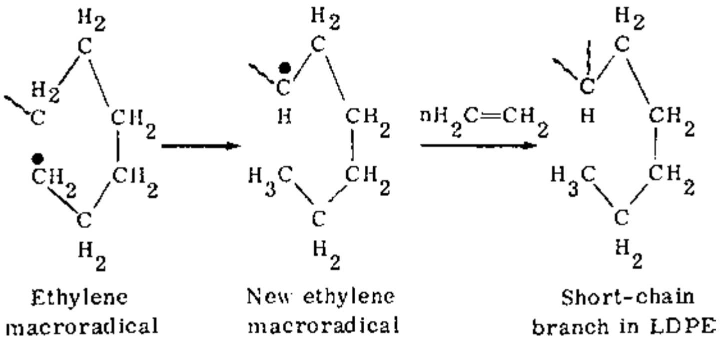
with vinyl monomers which contain electron-donating groups. Free radical polymerizations occur for vinyl monomers that are typically intermediate between electron-poor and electron-rich. It must be noted that these general tendencies are just that—general tendencies—and that variations do in fact occur. For instance, vinylidene chloride, which contains two chlorine atoms typically considered to be electron withdrawing, does not undergo homopolymerization by an anionic mechanism. Figure 8.1 contains a listing for some of the more common vinyl monomers as a function of type of chain initiation.

8.3 CHAIN TRANSFER

As shown in Eq. (8.21), two macroradicals may terminate by chain transfer of a hydrogen atom at one chain end to a free radical end of another chain in a chain transfer process called disproportionation. When the abstraction takes place intramolecularly or intermolecularly by a hydrogen atom some distance from the chain end, branching results. Thus, low-density polyethylene (LDPE), which is produced by a free radical chain polymerization at extremely high pressure, is highly branched because both types of chain transfer take place during the polymerization of ethylene at high pressure.

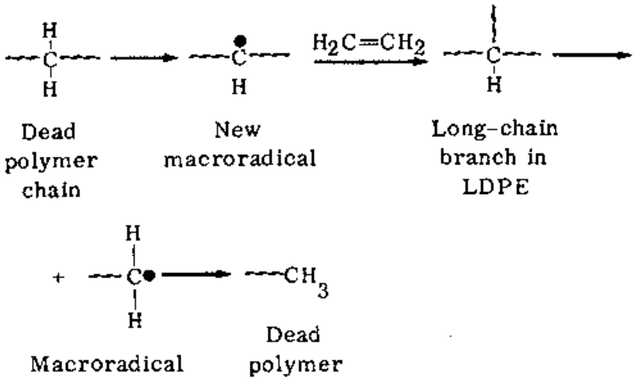
Each of these chain transfer processes causes termination of one macroradical and produces another macroradical. In either case, the unpaired electron is no longer on the terminal carbon atom. The new radical sites serve as branch points for additional chain extension or branching.

As shown by the following equation, short chain branching is the result of “back-biting” as the chain end assumes a preferred conformation resembling a stable hexagonal ring. The new active center, or branch point, is the result of an abstraction of a hydrogen atom on carbon 6 by the free radical on carbon 1.



(8.35a)

As shown in the following equation, long chain branching takes place as the result of the formation of a branch point by intermolecular chain transfer. Since it is more probable that the new active site will be at a considerable distance from the chain end, the result is a long branch.



(8.35b)

Chain transfer may also take place with monomer, initiator, solvent, or any other additives present in the polymerization system. Chain transfer to polymer is usually disregarded in the study of chain transfer reactions, and the emphasis is on chain transfer with solvents or other additives. Thus, while the average chain length is equal to R_p divided by the sum of all termination reactions, it is customary to control all termination reactions except the chain transfer reaction under investigation. The chain transfer to all other molecules, except solvent or additive, is typically negligible.

This chain transfer reaction decreases the average chain length in accordance with the concentration of chain transfer agent S. The resulting degree of polymerization ($\overline{DP}$) is equal to that which would have been obtained without the solvent or additive plus a factor related to the product of the ratio of the rate of propagation (R_p) to the rate of chain transfer (R_{tr}) and the ratio of the concentration of the monomer [M] to the concentration of chain transfer agent [S].

The Mayo equation, which yields positive slopes when the data are plotted, is the reciprocal relationship derived from the previously cited expression. The ratio of the rate of cessation or termination by transfer to the rate of propagation is called the chain transfer constant (C_s). The latter is related to relative bond strengths in the solvent or additive molecule and the stability of the new free radical produced. The Mayo equation is shown below.

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + C_s \frac{[S]}{[M]} \tag{8.36}$$

The chain transfer constant is then given as

$$C_s = k_{tr}/k_p \tag{8.37}$$

where k_{tr} is the chain transfer rate constant.

As shown in Fig. 8.2, the molecular weight of polystyrene is reduced when it is polymerized in solvents, and the reduction or increase in slope is related to the chain transfer efficiency of the solvent. The slopes in this graph are equal to C_s.

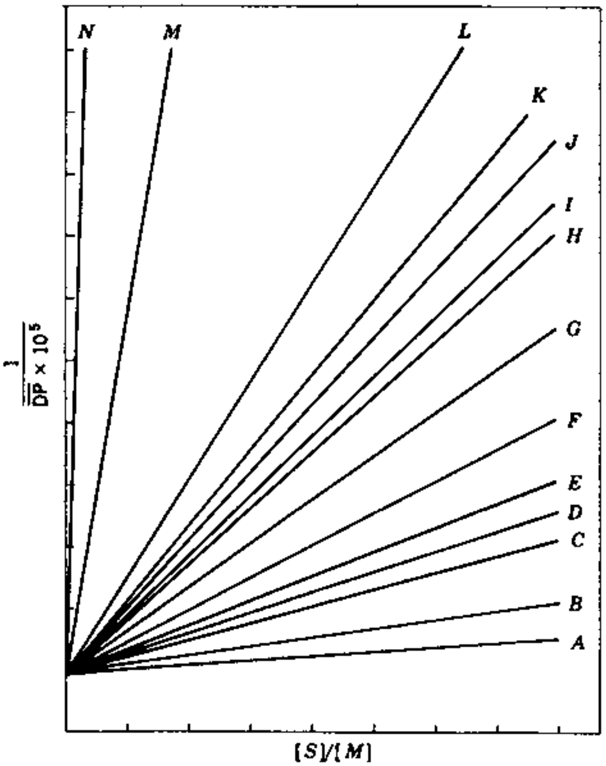


Figure 8.2 Molecular weight of polystyrene as a function of solvent and solvent concentration; A, benzene; B, toluene; C, n-heptane; D, chloroform; E, ethylbenzene; F, cumene; G, sec-butylbenzene; H, phenol; I, m-cresol, J, p-cresol; K, o-cresol; L, carbon tetrachloride; M, carbon tetrabromide; N, n-butylmercaptan; [S], concentration of chain transfer agent; [M], concentration of styrene monomer. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York. 1971. Used with permission.)

Table 8.5 Chain Transfer Constants of Solvents to Styrene in Free Radical Chain Polymerization at 60°C

Transfer agent	$C_s \times 10^4$
Acetic acid	2.0
Benzene	0.01
Butyl alcohol	0.06
tert-Butyl alcohol	6.7
Butyl disulfide	0.24
Carbon tetrabromide	18,000
Carbon tetrachloride	84
Chloroform	0.5
O-Chlorophenol	6.0
2,6-Ditert-butylphenol	49
1-Dodecanethiol	148,000
Hexane	0.9
N,N-Dimethylaniline	12
1-Naphthalenethiol	1500
1-Octanethiol	190,000
p-Methoxyphenol	260
Phenol	8.1
Triethylamine	1.4
Toluene	0.105
Water	0

Chain transfer agents have been called regulators (of molecular weight). When used in large proportions, they are called telogens, since they produce low molecular weight polymers (telomers) in these telomerization reactions. As shown in Table 8.5, alkyl mercaptans are effective chain transfer agents for the polymerization of styrene.

The hydrogen atom is abstracted from many telogens, including the phenolic hydrogen of phenol and the hydrogen of mercaptans. However, the hydrogen on the α-carbon atom is abstracted from carboxylic acids, and the hydroxyl group is abstracted from alcohols. Halogens are abstracted from many halogen compounds, such as carbon tetrabromide.

It is important to note that the new free radical produced by chain transfer may or may not initiate another polymer chain formation, depending on its activity. Retarders, chain stoppers, and many antioxidants produce new free radicals with low polymerization activity.

8.4 POLYMERIZATION TECHNIQUES

Many monomers such as styrene, acrylonitrile, and vinyl chloride are toxic, and the polymerization reaction is highly exothermic. Hence, precautions must be taken to minimize exposure to these compounds and to control the temperature of the polymerization reaction. The principal methods are bulk, solution, and emulsion polymerization (Table 8.6). Each has characteristic advantages and disadvantages (Tables 8.7 and 8).

Bulk Polymerization: Bulk polymerization of a liquid monomer such as methyl methacrylate is relatively simple in the absence of oxygen when small bottles or test tubes

Table 8.6 Types of Polymerization Systems

Monomer-polymer phase relationship	Monomer location	
	Continuous	Dispersed
Homogeneous (same phase)	Bulk, solid state solution	Suspension
Heterogeneous (different phases)	Bulk with polymer precipitating	Emulsion; suspension with polymer precipitating

Table 8.7 Comparison of Polymerization Systems

Type	Advantages	Disadvantages
Homogeneous		
Bulk-batch	Simple equipment	May require solution and subsequent precipitation for purification and/or fabrication; may require reduction to usable particle size; heat control important; broad molecular weight distribution
Bulk-continuous	Easier heat control; narrower molecular weight distribution	Requires reactant recycling; may require solution and subsequent ppt. for purification and/or fabrication; requires more complex equipment; may require reduction to usable particle size
Solution	Easy agitation; may allow longer chains to be formed; easy heat control	Requires some agitation; requires solvent removal and recycling; requires polymer recovery; solvent chain transfer may be harmful (i.e., reaction with solvent)
Heterogeneous		
Emulsion	Easy heat control; Easy agitation; latex may be directly usable; highly polymerization rates possible; molecular weight control possible; usable, small-particle size possible; usable in producing tacky, soft, and solid products	Polymer may require additional cleanup and purification; difficult to eliminate entrenched coagulants, emulsifiers, surfactants, etc., often requires rapid agitation
Precipitation	Molecular weight and molecular weight distribution controllable by control of polymerization environment	May require solution and reprecipitation of product to remove unwanted material; precipitation may act to limit molecular weight disallowing formation of ultra high molecular weight products
Suspension	Easy agitation; higher purity product when compared to emulsion	Sensitive to agitation; particle size difficult to control

Table 8.8 Summary of Popular Polymerization Techniques

Bulk

Simplest of the techniques requiring only monomer and monomer-soluble initiator, and perhaps a chain transfer agent for molecular weight control. Characterized on the positive side by high polymer yield per volume of reaction, easy polymer recovery. Difficulty of removing unreacted monomer and heat control are negative features. Examples of polymers produced by bulk polymerization include poly(methyl methacrylate), polystyrene, and low-density (high-pressure) polyethylene.

Solution

Monomer and initiator must be soluble in the liquid and the solvent must have the desired chain transfer characteristics, boiling point (above the temperature necessary to carry out the polymerization and low enough to allow for ready removal if the polymer is recovered by solvent evaporation). The presence of the solvent assists in heat removal and control (as it also does for suspension and emulsion polymerization systems). Polymer yield per reaction volume is lower than for bulk reactions. Also, solvent recovery and removal (from the polymer) is necessary. Many free radical and ionic polymerizations are carried out utilizing solution polymerization including water-soluble polymers prepared in aqueous solution [namely poly(acrylic acid), polyacrylamide, and poly(N-vinylpyrrolidinone)]. Polystyrene, poly(methyl methacrylate), poly(vinyl chloride), and polybutadiene are prepared from organic solution polymerizations.

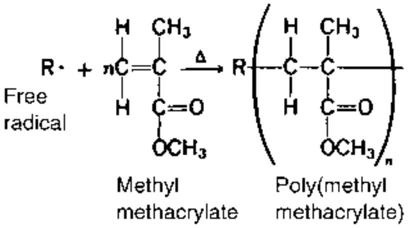
Suspension

A water-insoluble monomer and initiator are used. Again, a chain transfer agent may be used to control chain size. Stirring is usual. Droplets of monomer containing initiator and chain transfer agent are formed. A protective colloidal agent, often poly(vinyl alcohol), is added to prevent coalescence of the droplets. Near the end, the particles become hard and are recovered by filtration. Because the liquid is water-based, solvent recovery and treatment problems are minimal. The products may contain a number of impurities including any of the agents added to assist in the polymerization process. Polymers produced by suspension polymerization include poly(vinyl chloride), polystyrene resins, and copolymers such as poly(styrene-co-acrylonitrile), SAN, and poly(vinyl chloride-co-vinylidene chloride).

Emulsion

The system usually contains a water-soluble initiator (in contrast to the requirement that the initiator must not be water-soluble in suspension polymerizations), chain transfer agent, and a surfactant. The hydrophobic monomer forms large droplets that are stabilized by the surfactant. At a certain surfactant concentration, the surfactant molecules form micelles that contain 50–100 surfactant molecules. During the polymerization, the monomer, which has a small but real water solubility, migrates from the monomer droplets through the water and into these micelles. Polymerization begins when the water-soluble initiator enters into the monomer-containing micelle. Because the concentration of micelles (about 10^{21}/Liter) is high compared with the concentration of monomer droplets (about 10^{14}/Liter) the initiator is more likely to enter a micelle than a monomer droplet. As polymerization continues, monomer is transferred to the growing micelles. At about 50–80% conversion the monomer droplets disappear and the micelles become large polymer-containing droplets. This suspension is called a latex. The latex is stable and can be used as is or the polymer recovered by coagulation. In inverse emulsion polymerization, the monomer, which is hydrophilic, is dispersed in an organic liquid. Here the monomer is usually contained in an aqueous solution.

are used. One may heat this monomer in the presence of an initiator and obtain a clear plastic, shaped like the container but a little smaller because of shrinkage (8.38). Most monomers shrink during polymerization, and thus the density of the polymers is greater than that of the monomers. Poly(methyl methacrylate) (PMMA), as an atactic amorphous polymer, is sold under the trade names Lucite and Plexiglas.



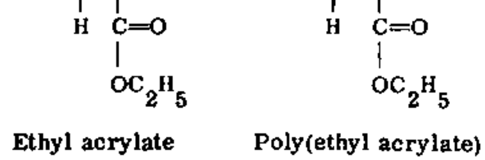
$$R\cdot + nCH_2=C(CH_3)COOCH_3 \xrightarrow{\Delta} R\text{-}\left(CH_2-C(CH_3)(COOCH_3)\right)_n \qquad (8.38)$$

The rate of polymerization of liquid monomers such as methyl methacrylate may be followed by monitoring the change in volume by dilatometry or the increase in viscosity. The latter has essentially no effect on rate of polymerization or molecular weight unless it is relatively high. When the viscosity is high, the termination reaction is hindered since the macroradicals are unable to diffuse readily in the viscous medium. In contrast, the monomer may diffuse quite readily and high molecular weight macroradicals are produced as the result of propagation in the absence of termination.

This autoacceleration, called the Norris-Trommsdorff, or gel, effect, causes the formation of unusually high molecular weight polymers. The additional heat of polymerization may be dissipated in a small test tube, but special design of equipment is necessary for large-scale bulk (mass) polymerizations. Fortunately, monomers such as methyl methacrylate may be polymerized without difficulty in sheets up to 5 cm in thickness either in static or continuous systems. The very high molecular weight product, produced because of increased viscosity that results in autoacceleration, is advantageous for cast plastics but not for those that must be molded or extruded.

It is standard practice to polymerize liquid monomers with agitation in appropriate vessels as long as the system is liquid. In some instances, the unreacted monomer is removed by distillation and recycled. In most cases, the polymerization is continued in special equipment in which the viscous material is forced through extruder-like equipment under controlled temperature conditions. The product is polydisperse, i.e., it consists of a polymer with a broad distribution of molecular weights.

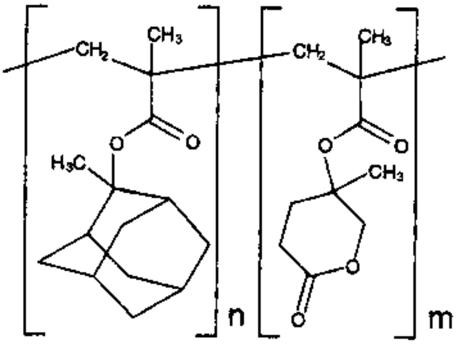
As shown in the following equation, ethyl acrylate may be polymerized by a free radical process. Poly(ethyl acrylate) does not have a pendant methyl group on the α-carbon atom like poly(methyl methacrylate), and it has a lower T_g and is flexible at room



$$R\cdot + nCH_2=CH(COOC_2H_5) \longrightarrow R\text{-}\left(CH_2-CH(COOC_2H_5)\right)_n \qquad (8.39)$$

temperature. Polyacrylates with larger alkyl groups have lower T_g values and are more soluble in hydrocarbon solvents. However, the value of T_g increases when more than 10 carbon atoms are present in the alkyl group because of side chain crystallization.

Polymers such as the methacrylates play an essential role as photoresists. To make a photoresist, the methacrylate polymer is deposited onto silicon dioxide. A mask that shields specific regions from subsequent exposure to light is placed over the methacrylate resist. The combination is exposed to light of such a strength to induce methacrylate polymer bond breakage producing a somewhat degraded methacrylate product that is more soluble in organic liquids, allowing the preferential removal of the exposed photoresist. These methacrylate polymers are especially designed to allow both easy degradation and subsequent easy removal. One of these is a copolymer with adamantane- and lactone-containing units.

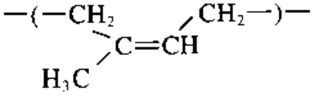


Modified Methacrylate Co-Polymer

(8.40)

This type of photoresist is called a "positive photoresist" since it is the exposed area that is removed.

Negative photoresists are formed from polymers that undergo reactions that decrease their solubility when exposed to radiation. Thus, polymers such as cis-1, 4-polyisoprene crosslink when exposed to the appropriate radiation giving insoluble products.



$$-(-CH_2\diagdown C{=}CH \diagup CH_2-)- \quad H_3C\diagup C$$

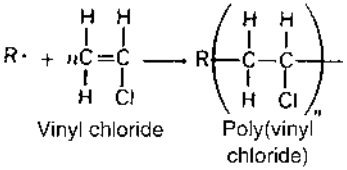
cis-1,4-Polyisoprene

(8.41)

Suspension Polymerization: Water-insoluble monomers such as vinyl chloride may be polymerized as suspended droplets (10–1000 nm in diameter) in a process called *suspension* (pearl) *polymerization*. Coalescence of droplets is prevented by the use of small amounts of water-soluble polymers, such as poly(vinyl alcohol) (PVA). The suspension process is characterized by good heat control and ease of removal of the discrete polymer particles.

Since poly(vinyl chloride) (PVC) is insoluble in its monomer (VCM), it precipitates as formed in the droplets. This is actually advantageous, since it permits ready removal of any residual carcinogenic monomer from the solid beads by stripping under reduced pressure.

PVC, which is produced at an annual rate of about 12 million tons, is characterized by good resistance to flame and corrosives. While the rigid product is used for some articles in which flexibility is not required, most PVC is plasticized or flexibilized by the addition of relatively large amounts of a compatible high-boiling liquid plasticizer such as dioctyl or didecyl phthalate. It has been recently reported that nonylphenols used sometimes in PVC are endocrine system disrupters. The equation for the polymerization of vinyl chloride is shown below:

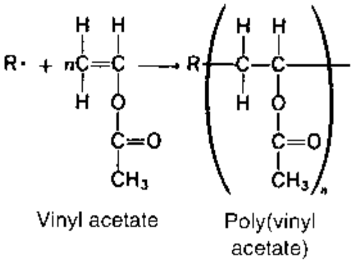


(8.42)

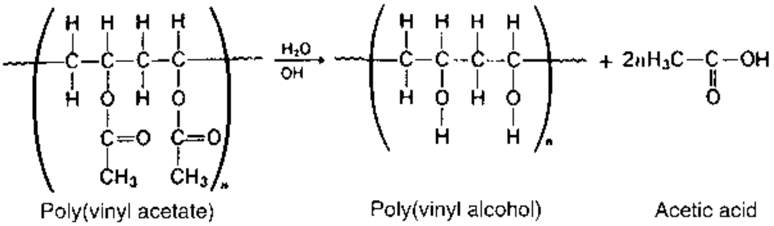
Solution Polymerization: Monomers may also be polymerized in solution using good or poor solvents for homogeneous and heterogeneous systems, respectively. In *solution polymerizations* solvents with low chain transfer constants should be used whenever possible to minimize reduction in molecular weight. While telogens decrease molecular weight, the molecular weight and the rate of polymerization are independent of the polarity of the solvent in homogeneous solution systems.

Poly(vinyl acetate) (PVAc) may be produced by the polymerization of vinyl acetate in the presence of an initiator in a solution such as benzene. The viscosity of the solution continues to increase until the reaction is complete, but the concentration of the solution is usually too dilute to exhibit autoacceleration because of the gel effect. The solution may be used as prepared, the solvent may be stripped off, or the polymer may be recovered by pouring the solution into an agitated poor solvent, such as ethanol.

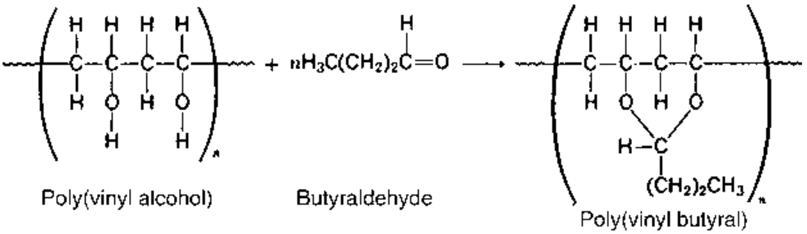
PVAc is used in adhesives and coatings and may be hydrolyzed to produce water-soluble PVA. The PVA, which is produced at an annual rate of about 100,000 tons, may be reacted with butyraldehyde to produce poly(vinyl butyral) (PVB) (used as the inner lining in safety glass). The equations for the production of these polymers are as follows:



(8.43)



(8.44)

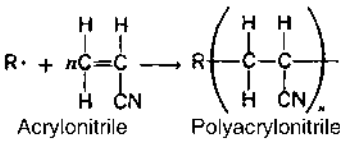


(8.45)

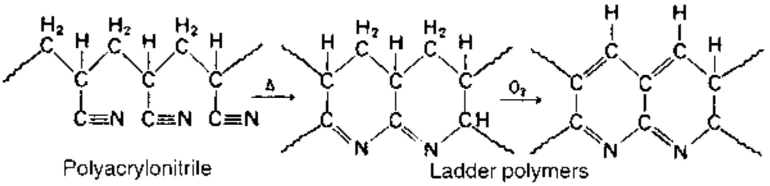
When a monomer such as acrylonitrile is polymerized in a poor solvent such as benzene, macroradicals precipitate as they are formed. Since these are "living polymers," the polymerization continues as more acrylonitrile diffuses into the precipitated particles. This heterogeneous solution type of polymerization has been called precipitation polymerization. Acrylic fibers (Acrilan; produced at an annual rate of 340 million lb) are based on polyacrylonitrile (PAN).

Pure PAN cannot be colored, so small amounts of a comonomer such as styrene, vinyl chloride, or vinylidene chloride are added to allow the fabrics and textiles to be colored. These copolymers are called modacrylics. The use of vinylidene chloride and vinyl chloride gives a product such as a carpet or wig that has increased flame resistance.

Since acrylonitrile is carcinogenic, precautions must be taken to avoid contact with this monomer. The monomer must not be present in high concentrations in acrylic fibers or plastics. It is of interest to note that polyacrylonitrile forms a heat-resistant ladder polymer when heated at elevated temperatures. The equations for these reactions are as follows:



(8.46)



(8.47)

The black ladder polymer produced by pyrolysis of PAN is sometimes called black orlon or fiber AF (see Sec. 15.11). PAN is a hydrogen-bonded polymer with a high solubility parameter value, on the order of 15 H, and hence is soluble only in polar solvents such as N,N-dimethyl formamide (DMF).

Emulsion Polymerization: Many water-insoluble vinyl monomers may also be polymerized by the *emulsion polymerization* technique. This technique, which differs from suspension polymerization in the size of the suspended particles and in the mechanism, is widely used for the production of many commercial plastics and elastomers. While the particles in the suspension range from 10 to 1000 nm, those in the emulsion process range from 0.05 to 5 nm. The small beads produced in the suspension process may be separated by filtering, but the latex produced in emulsion polymerization is a stable system in which the charged particles cannot be removed by ordinary separation procedures.

Since relatively stable macroradicals are produced in the emulsion process, the termination rate is decreased and a high molecular weight product is produced at a rapid rate. It is customary to use a water-soluble initiator such as potassium persulfate and an anionic surfactant such as sodium stearate, and to stir the aqueous mixture of monomer, initiator, and surfactant in the absence of oxygen at 40–70°C.

A typical recipe for emulsion polymerization includes 100 g of monomer, such as styrene, 180 g of water, 5 g of sodium stearate (a soap), and 0.5 g of potassium persulfate. When the concentration of soap exceeds the critical micelle concentration (CMC), these molecules are present as micelles in which the hydrophillic carboxylic acid ends are oriented toward the water–micelle interface, and the lyophilic hydrocarbon ends are oriented toward the center of the micelle. The micelles are present as spheres with a diameter of 5–10 nm when the soap concentration is less than 2%. However, with the higher concentrations customarily used, the micelles resemble aggregates of rods which are 100–300 nm in length.

As shown in Fig. 8.3, the water-insoluble monomer is attracted to the lyophilic ends in the micelles, causing the micelles to swell. The number of swollen micelles per milliliter of water is on the order of 10^{18}. However, at the initial stages of polymerization (phase

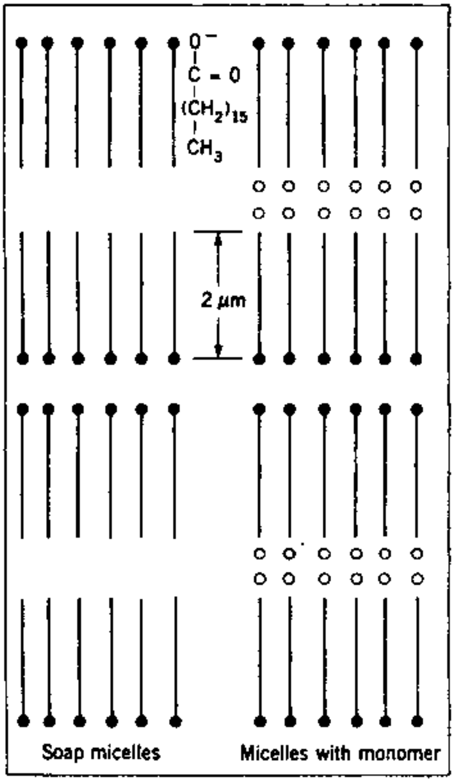
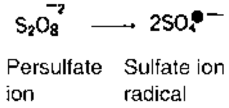


Figure 8.3 Micelles swollen with solubilized styrene monomer. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

I), most of the monomer is present at globules that resemble those observed in suspension polymerization.

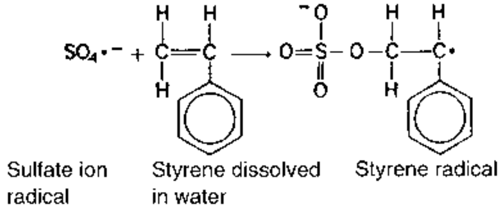
Since the initiation of polymerization takes place in the aqueous phase, essentially no polymerization takes place in the globules. Thus, they serve primarily as a reservoir of monomer supplied to the micelles to replace the monomer converted to polymer. The number of droplets per milliliter of water is on the order of 10^{11}. Hence, since there are 10 million times as many micelles as droplets, the chance of initiation of monomer in a droplet is very, very small.

As shown in the following equations, the persulfate ion undergoes homolytic cleavage to produce two sulfate ion radicals. These serve as initiators for the few water-soluble monomer molecules present in the aqueous phase.



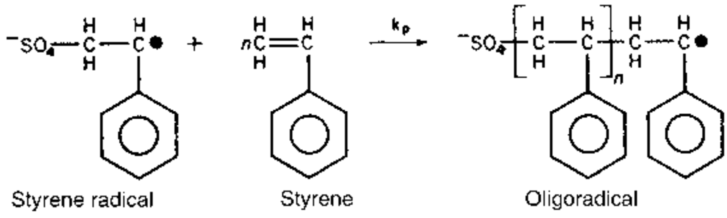
$$S_2O_8^{-2} \longrightarrow 2SO_4^{\bullet -}$$

(8.48)



(8.49)

According to a theory proposed by Harkins and refined by Smith and Ewart, the first stages of propagation in an emulsion system also take place in the aqueous phase to produce a more lyophilic surface-active oligoradical, as shown below.



(8.50)

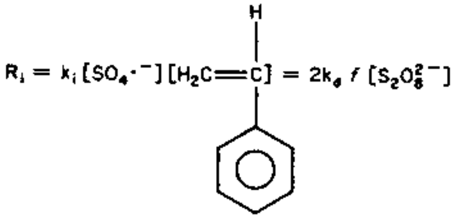
When the $\overline{DP}$ of the styrene oligoradical is 3–5, its solubility is much like that of styrene, and it migrates to the swollen micelle where propagation continues with the styrene molecules already present. According to accepted theories, each micelle can accommodate only one free radical, and until a second one enters and terminates the propagation reaction by coupling, propagation continues to take place in the micelles. From a statistical point of view, only one-half of the micelles (N/2) will contain growing chains at any one time. It should also be noted that since propagation occurs in the micelles, the rate of polymerization will be proportional to the number of micelles present, i.e., the rate is proportional to the soap concentration.

As the micelles grow by absorption of more monomer and formation of polymer, they become relatively large particles that absorb soap from micelles that have not been inoculated or stung by oligoradicals. Thus, in stage II, when about 20% of the monomer has been converted to polymer, the micelles disappear and are replaced by larger, but fewer, monomer-polymer particles.

Polymerization continues in stage II, and monomer continues to be supplied to the particles by the droplets in the aqueous phase. These droplets disappear when about 30% of the monomer has been converted to polymer. Polymerization continues in stage III after about a 60% conversion, but all monomer must now be supplied to the macroradicals by a diffusion process in the micelles.

As shown below, the rate of initiation in the aqueous phase of emulsion polymerization is the same as that described for other free radical chain initiations.

$$R_d = k_d[S_2O_8^{2-}] \qquad (8.51)$$



$$R_i = k_i[SO_4^{\cdot -}][H_2C{=}\overset{\displaystyle H}{\underset{\displaystyle C_6H_5}{C}}] = 2k_d f[S_2O_8^{2-}] \qquad (8.52)$$

The rate of propagation in the micelles is similar to that described for other free radical chain propagations, but since the free radical concentration is equal to the number of active micelles, the value of N/2 is used instead of [M·]. Thus, as shown by the following equation, the rate of propagation is dependent on the number of micelles present.

$$R_p = k_p[M][M\cdot] = k_p[M]\frac{N}{2} \qquad (8.53)$$

The rate of production of free radicals at 50°C is about 10^{13} radicals per mL per 1s. Thus, since there are 100,000 micelles for every free radical produced in 1s, inoculation of any of the 10^{18} micelles/mL is infrequent. Hence, since propagation is a very fast reaction, long chains are produced before termination by coupling, which takes place as the result of the entrance of a new oligoradical in the active micelle. As shown by the following equation, the degree of polymerization is also proportional to the number of active micelles (N/2).

$$\overline{DP} = \frac{R_p}{R_i} = \frac{k_p}{R_i}[M]\frac{N}{2} \qquad (8.54)$$

The rate of polymerization in emulsion systems may be increased by the addition of reducing agents such as iron(II) salts. The presence of high molecular weight polymers is advantageous when the latex is used directly as a coating, adhesive, or film. However, the high molecular weight solid polymer obtained when the emulsion is coagulated may make subsequent processing difficult. This difficulty is overcome by the addition of chain transfer agents, such as dodecyl mercaptan (1-dodecanethiol).

In addition to LDPE, PS, PVC, PMMA, PVAc, and PAN, many other commercial polymers are produced by free radical chain reaction polymerization (Table 8.9). Among these are the polyfluorocarbons, poly(vinylidene chloride), neoprene elastomer, and SBR rubber. The latter, which is a copolymer of butadiene (75%) and styrene (25%), will be discussed in Chapter 9.

Table 8.9 Production of Homopolymers in the United States by Free Radical Chain Polymerization in 1985 (Thousands of Metric Tons)

Thermoplastics	
Low-density polyethylene (LDPE)[a]	3825
Poly(vinyl chloride)	3551
Polystyrene	1798
Poly(vinyl alcohol), from PVAc	56
Total thermoplastics	9230
Elastomers	
Neoprene	126
Fibers	
Acrylic fibers (PAN)	339
Total polymers via free radical polymerization	9695

[a] Includes LLDPE, which is a copolymer of ethylene and α-olefins.

Production data for commercial polymers produced by free radical chain polymerizations are shown in Table 8.9.

8.5 FLUORINE-CONTAINING POLYMERS

Polytetrafluoroethylene, better know by the trade name Teflon, was accidently discovered by Roy J. Plunkett, a Dupont chemist who had just received his doctorate degree from Ohio State 2 years before. He was part of a group searching for nontoxic refrigerant gases. On April 6, 1938, he and his assistant, Jack Rebok, had filled a tank with tetrafluoroethylene. After some time, they opened the value but no gas came out. The tank weight indicated that there was no weight loss so what happened to the tetrafluoroethylene. Using a hacksaw, they cut the cylinder in half and found a waxy white powder. He correctly surmised that the tetrafluoroethylene had polymerized. The waxy white powder had some interesting properties. It was quite inert toward strong acids, bases, and heat, and was not soluble in any attempted liquid. It appeared to be quite "slippery."

Little was done with this new material until the military, working on the atomic bomb, needed a special material for gaskets that would resist the corrosive gas uranium hexafluoride that was one of the materials being used to make the atomic bomb. General Leslie Groves, responsible for the U.S. Army's part in the atomic bomb project, had learned of Dupont's new inert polymer and had Dupont manufacture it for them.

Teflon was introduced to the public in 1960 when the first Teflon-coated muffin pans and frying pans were sold. Like many new materials, problems were encountered. Bonding to the surfaces was uncertain at best. Eventually the bonding problem was solved. Teflon is now used for many other applications including as a biomedical material in artificial corneas; as substitute bones for nose, skull, hip, nose, and knees; in ear parts; in heart valves, tendons, sutures, dentures, and artificial tracheas. It has also been used in the nose cones and heat shield for space vehicles and for their fuel tanks.

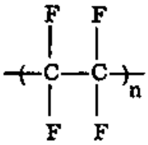
Polytetrafluoroethylene is produced by the free radical polymerization process. While it has outstanding thermal and corrosive resistance, it is a marginal engineering material because it is not easily machinable. It has low tensile strength, resistance to wear, and low creep resistance. Molding powders are processed by press and sinter methods used in powder metallurgy. It can also be extruded using ram extruder techniques.

Over one half million vascular graft replacements are performed yearly. Most of these grafts are made of poly(ethylene terephthalate) and PTFE. These relatively large diameter grafts work when blood flow is rapid, but they generally fail for smaller vessels.

As evident by its structural formula, PTFE contains no hydrogen atoms. Because of the stability of the carbon–fluorine bond, the closeness of the carbon atoms to each other, the crowding by the fluorine atoms, and the regularity in its structure, PTFE has outstanding resistance to heat. It is a crystalline polymer that does not melt below a temperature of 327°C. Teflon is one of the most expensive polymers with extensive commercial use. At least some of its high cost is due to difficulty in its processability.

The processability of this type of polyflurocarbon is improved by replacing one of the eight fluorine atoms by a trifluoromethyl group. The product, called FEP or Viton, is a copolymer of tetrafluoroethylene and hexafluoropropylene. Polytrifluoromonochloroethylene (CTFE, Kel F), in which one fluorine atom has been replaced by a chlorine atom, has a less regular structure than FEP and is also more easily processed.

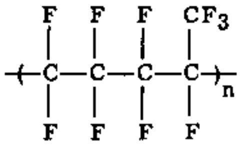
Poly(vinylidene fluoride) (Kynar) and poly(vinyl fluoride) (Tedlar) are also more readily processable and less resistant to solvents and corrosives than PTFE. The former has piezoelectric properties, i.e., it generates electric current when compressed.



$\left[\mathrm{CF_2-CF_2}\right]_n$

PTFE

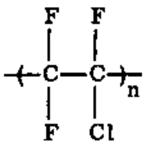
(8.55)



$\left[\mathrm{CF_2-CF_2-CF_2-CF(CF_3)}\right]_n$

FEP

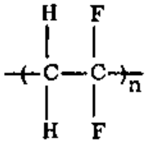
(8.56)



$\left[\mathrm{CF_2-CFCl}\right]_n$

CTFE

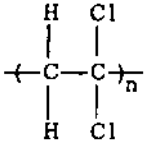
(8.57)



$\left[\mathrm{CH_2-CF_2}\right]_n$

Poly(vinylidene fluoride)

(8.58)



$\left[\mathrm{CH_2-CCl_2}\right]_n$

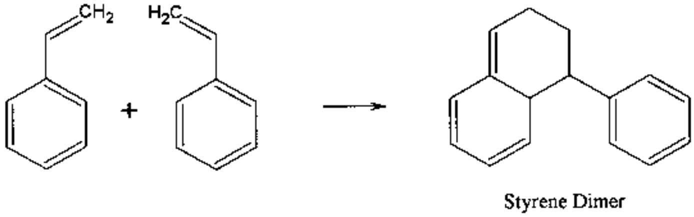
PVDC

(8.59)

8.6 POLYSTYRENE

Styrene monomer was discovered by Newman in 1786. The initial formation of polystyrene was by Simon in 1839. While polystyrene was formed almost 175 years ago, the mechanism of formation, described in Secs. 8.1–8.3, was not discovered until the early twentieth century. Staudinger, using styrene as the principle model, identified the general free radical polymerization process in 1920. Initially commercialization of polystyrene, as in many cases, awaited the ready availability of the monomer. While there was available ethyl benzene, it underwent thermal cracking rather than dehydrogenation until the appropriate conditions and catalysts were discovered. Dow first successfully commercialized polystyrene formation in 1938. While most commercial polystyrene, PS, has only a low degree of stereoregularity, it is rigid and brittle because of the resistance of easy movement of the more bulky phenyl-containing units in comparison, for example, to the methyl-containing units of polypropylene. This is reflected in a relatively high T_g of about 100°C for polystyrene. It is transparent because of the low degree of crystalline formation.

The description of its polymerization via a free radical mechanism employing typical catalysts is given in Secs. 8.1 and 8.2. It also undergoes “self-initiated” polymerization through the Diels-Alder reaction of two ethyl benzene molecules forming two stereo isomers of 1-phenyltetralin (below). The axial isomer is able to initiate styrene polymerization. Even so, initiators are generally employed in the formation of PS. Chain transfer agents, such as dodecyl mercaptans, are often employed to control chain growth. PS production is generally achieved employing either the Continuously Stirred Tube Reactor or stirred tube reactor. Since the polymerization is highly exothermic, the reaction systems are designed so that large amounts of heat can be readily removed. Conversely, as the conversion fraction increases, some temperature increase is allowed to encourage the decreasing amounts of monomer to react. After the desired conversion fraction is achieved, the reaction mixture is removed from the reaction system and exposed to high vacuum to remove unreacted monomer and other volatile materials. Unreacted monomer is recycled.



(8.60)

While PS is largely commercially produced using free radical polymerization, it can be produced by all four of the major techniques-anionic, cationic, free radical, and coordination-type systems. All of the tactic forms can be formed employing these systems. The most important of the tactic forms is syndiotactic PS, sPS. Metallocene-produced sPS is a semicrystalline material with a T_m of 270°C. It was initially produced by Dow in 1997 under the tradename of Questra. It has good chemical and solvent resistance in contrast with “regular” PS that has generally poor chemical and solvent resistance because of the presence of voids that are exploited by the solvents and chemicals.

Physical properties of PS are dependent on the molecular weight and presence of additives. While higher molecular weight PS offers better strength and toughness, it also offers poorer processability. Low molecular weight PS allows for good processability but poorer strength and toughness. Generally a balance is sought where intermediate chain lengths are used. Typically employed chain lengths are on the order of 1,500 to 3,500 with standard molecular weight distributions of about 2.2 to 3.5. Small amounts of plasticizers are often used to improve processability.

Styrene is employed in the formation of a number of co and terpolymers. The best known is the terpolymer ABS.

Because PS is brittle with little impact resistance under normal operating conditions, early work was done to impart impact resistance. The best known material from this work is called high-impact polystyrene or HIPS. HIPS is produced by dispersing small particles of butadiene rubber in with the styrene monomer. Bulk or mass polymerization of the styrene is begun achieving what is referred to as prepolymerization material. During the prepolymerization stage styrene begins to polymerize with itself forming droplets of polystyrene with phrase separation. When nearly equal phase volumes are obtained, phase inversion occurs and the droplets of polystyrene act as the continuous phase within which the butadiene rubber particles are dispersed. The completion of the polymerization generally occurs employing either bulk or aqueous suspension conditions.

The impact strength generally increases as the rubber concentration and particle size increases while gloss and rigidity decreases.

Major uses of PS are in packaging and containers, toys and recreational equipment, insulation, disposable food containers, electrical and electronics, housewares, and appliance parts. Expandable PS is used to package electronic equipment such as TVs, computers, and stereo equipment. Legislation was put in place in some states to insure the recycling of PS. Interestingly some of this legislation was written such that all PS had to be recycled within some period of time such as a year. This legislation was changed to reflect the real concern of fast food containers when it was pointed out that less than 10% PS is used in this manner and that well over twice as much used as house insulation that should not be recycled every year or so.

8.7 POLY(VINYL CHLORIDE)

Poly(vinyl chloride), PVC, is one of the three most abundantly produced synthetic polymers (section 1.2). PVC is one of the earliest produced polymers. In 1835 Justus von Liebig and his research student Victor Regnault reacted ethylene dichloride with alcoholic potash forming the monomer vinyl chloride. Latter Regnault believed he polymerized vinyl chloride but latter studies showed it to be poly(vinylidene chloride). In 1872 E. Baumann exposed vinyl chloride sealed in a tube to sunlight and produced a solid, PVC. Klasse, in Germany, found that vinyl chloride could be made by addition of hydrogen chloride to acetylene in a system that could be scaled up for commercial production. (Today most of the vinyl chloride is made from the oxychlorination reaction with ethylene.) By WWI Germany was producing a number of flexible and rigid PVC products. During WWI Germany used PVC as a replacement for corrosion-resistant metals.

Waldo Semon was responsible for bringing many of the poly(vinyl chloride) products to market. As a young scientist at BF Goodrich, he worked on ways to synthesize rubber and to bind the rubber to metal. In his spare time he discovered that PVC, when mixed with certain liquids, gave a elastic-like, pliable material that was rain proof, fire resistant, and that did not conduct electricity. Under the trade name Koroseal, the rubbery material came into the marketplace, beginning about 1926, as shower curtains, raincoats, and umbrellas. During WW II it became the material of choice to protest electrical wires for the Air Force and Navy. Another of his inventions was the synthetic rubber patented under the name Ameripol that was dubbed “liberty rubber” since it replaced natural rubber in the production of tires, gas masks and other military equipment. Ameripol was a butadiene-type material.

Because of its versatility, some unique performance characteristics, ready availability, and low cost PVC is now the second largest produced synthetic polymer behind polyethylene.

As a side note, there is today a debate concerning the use of chlorine-containing materials and their effect on the atmosphere. This is a real concern and one that is being addressed by industry. PVC, and other chloride-containing materials have in the past been simply disposed of through combustion that often created unwanted hydrogen chloride. This practice has largely been stopped but care should be continued to see that such materials are disposed of properly. Further, simply outlawing of all chloride-containing materials is not possible or practical. For instance we need common table salt for life and common table salt is sodium chloride. Chlorine is widely used as a water disinfectant both commercially (for our drinking water) as well as for pools. Further, PVC is an important material that is not easily replaced. Finally, the amounts of chloride-containing residue that is introduced into the atmosphere naturally is large in comparison to that introduced by PVC. Even so, we must exercise care as we want to leave a better world for our children and grandchildren so a knowledge-based approach must be taken.

PVC materials are often defined to contain 50% or more by weight vinyl chloride units. PVC is generally a mixture of a number of additives and often other units such as ethylene, propylene, vinylidene chloride, and vinyl acetate. Structurally similar products, but with differing properties, are made from the chlorination of polyethylene but almost all PVC is made from the polymerization of vinyl chloride. Typical homopolymers are about 400 to 1000 units long.

PVC is commercially produced by a number of techniques but mainly suspension, emulsion, bulk, and solution polymerization. Typically, product properties and form can be tailored through the use of a particular synthetic process and conditions. Particulate architecture is then controlled to achieve materials with specific sizes and distributions for specific uses and applications. Because of the tendency of PVC to split off hydrogen chloride, forming materials with high char at relatively low general processing temperatures, special care is taken with respect to temperature control and particulate architecture that allows ready processing of PVC by most of the common processing techniques (Chapter 17).

Tacticity of the PVC varies according to the particular reaction conditions but generally the materials favor a syndiotactic form with many PVC materials being about 50% sPVC. The reported amount of crystallinity is in the range of 5 to 10%. This allows for a material with some strength, but one with sufficient amorphous regions to retain good flexibility.

PVC, in comparison to many other polymers, employs an especially wide variety of additives. For instance, a sample recipe or formulation for common stiff PVC pipe such as used in housing and irrigation applications may contain in addition to the PVC resin, tin stabilizer, acrylic processing aid, acrylic lubricant-processing aid, acrylic impact modifier, calcium carbonate, titanium dioxide, calcium sterate, and paraffin wax. Such formulations vary according to the intended processing and end use. In such nonflexible PVC materials, the weight amount of additive is on the order of 5 to 10%.

As noted before, there is a tendency for PVC to undergo elimination of hydrogen chloride when heated. The most labile chlorine atoms are those at tertiary or terminal sites. Once the initial chloride is eliminated, continued unzipping occurs with the formation of unsaturated backbone sites and the evolution of hydrogen chloride. The purpose of the stabilizer is to cap unzipping sites by substitution of more stable groups for the evolved chloride as depicted below.

$$\text{——C—Cl} + \text{Sn—R} \rightarrow \text{—— C—R} + \text{Sn—Cl} \tag{8.61}$$

Some of the tin stabilizers are based on oligomeric materials first made by Carraher and co-workers. These oligomeric materials are essentially “non-migrational”.

A sample formula for a flexible upholstery fabric covering might contain PVC resin, medium molecular weight polymeric plasticizer, stearic acid lubricant, calcium carbonate, pigment, antimony oxide, linear phthalate ester, epoxidized soy bean oil, and linear phthalate ester. Here the weight amount of additive is in the range of 40 to 70% by weight with the plasticizer often being on the order of about 60%.

PVC has a built in advantage over many other polymers in that it is itself flame resistant. About 50% of PVC is used as rigid pipe. Other uses of rigid PVC are as pipe fittings, electrical outlet boxes, and automotive parts. Uses of flexible PVC include in gasoline-resistant hose, hospital sheeting, shoe soles, electrical tape, stretch film, pool liners, vinyl-coated fabrics, roof coatings, refrigerator gaskets, floor sheeting, and electrical insulation and jacketing. A wide number of vinyl chloride copolymers are commercially used. Many vinyl floor tiles are copolymers of PVC. Polymers and copolymers of vinylidene chloride (PVDC, Saran) are used as film (Saran Wrap).

8.8 SOLID STATE IRRADIATION POLYMERIZATION

There are numerous examples of solid state polymerizations. He we will briefly describe examples based on addition polymers. Generally the crystalline monomer is irradiated with electrons or some form of high-energy radiation such as γ or X-rays. Since many monomers are solids only below room temperature, it is customary to begin irradiation at lower temperatures with the temperature only raised after the initial polymerization occurs. (Some reactions are carried to completion at the lower temperature.) After polymerization, monomer is removed. Table 8.10 lists some of the common monomers that undergo solid state irradiation polymerization. This approach can offer several advantages. First, polymers can be formed from monomers that do not give polymer under more typical reaction conditions. Second, under some cases, the crystalline structure acts as a template giving order that might be difficult to otherwise achieve. Third, removal and interference by solvents or additives is eliminated since they are not present. Fourth, the polymers produced by this technique are often different from those formed from the same monomer except when produced using other reaction techniques.

8.9 PLASMA POLYMERIZATIONS

Organic and inorganic molecules can be placed in the vapor either through heating, low pressure, simple spraying, or some combination of these. These molecules are then subjected to some ionizing energy that forms active species that react with one another, eventually depositing themselves on a surface. Often the products are polymeric with complex structures. The term plasma polymerization is generally used to describe the process resulting in surface film formation, whereas the term deposition is generally used to describe the deposition of powdery particles formed in the gas phase. Others describe plasma polymerization as that polymerization that occurs at high rates in the gas phase resulting in powder formation and deposition as any sorption occurring on the surface. In

Table 8.10 Monomers That Undergo Solid State Irradiation Polymerization

Styrene
Acetaldehyde
Methacrylic acid (and salts)
1,3-Butadiene
Isoprene
Acrylamide
Diacetylenes
Formaldehyde
Acrylic acid (and salts)
Trioxane
3,3-Bischloromethylcyclooxabutane
Acrylonitrile
β-Propiolactone

truth, it is difficult to separate the two reaction sequences because active molecules can react both in the gaseous phase upon collision and on the surface.

Plasma environments are often created using plasma jets, ion beams, glow discharges, corona discharges, laser-induced plasmas, and electron beams. Low-temperature plasmas can also be created using radiofrequency, audiofrequency, microwave, or direct current energy sources. In general terms, the molecules enter the reactor as neutral species. They become reactive species as electronic energy is transferred to them. The reactive species can be ions, free radicals, or excited molecules. Reaction can occur in the gaseous phase and/or at the solid surface. Commercially, reactors often consist of a low-pressure glow discharge of reactive species. Because a small amount of electromagnetic radiation is emitted in the visible region, the term glow discharge was derived.

This approach allows the deposition of thin films at low temperatures. By comparison, polymer deposition generally requires very high temperatures. For instance, the chemical vapor deposition of silicon nitride requires a temperature of about 900°C whereas the plasma chemical deposition requires a temperature of only 350°C.

A number of typical polymer-forming monomers have been polymerized using plasma polymerization including tetrafluoroethylene, styrene, acrylic acid, methyl methacrylate, isoprene, and ethylene. Polymerization of many nontypical monomers has also occurred including toluene, benzene, and simple hydrocarbons.

Plasma films are usually highly crosslinked. They are resistant to higher temperatures, abrasion, and chemical attack, and adhesion to the surface is high. Adhesion to the surface is generally high both because the growing polymer complex can fit the surface contour and thus “lock itself in” (physical adhesion), and because in many instances the species are active enough to chemically react with the surface molecules to chemically bond to the surface. The surface can be prepared so that the chemical reaction is enhanced.

Plasma surface treatment of many polymers, including fabrics, plastics, and composites, often occurs. The production of ultrathin films via plasma deposition is important in microelectronics, biomaterials, corrosion protection, permeation control, and for adhesion control. Plasma coatings are often on the order of 1–100 nm thick.

SUMMARY

1. Peroxides, such as benzoyl peroxide, and diazo compounds, such as azobisisobutyronitrile, are readily homolytically cleaved by heat or ultraviolet light to produce free radicals, which serve as initiators for chain reaction polymerization. Each initiator has its characteristic half-life. Their decomposition into free radicals may be accelerated by heat or by reducing agents.
2. The rate of initiation of free radical chain polymerization, which is the rate-controlling step, is proportional to the product of the concentrations of the free radical (R·) and the monomer.
3. The rate of propagation is proportional to the concentrations of the monomer and the macroradicals. The additional stability of the macroradical with the functional group or the terminal carbon favors the head-to-tail configuration.
4. Termination of propagating macroradicals may take place by coupling or disproportionation. The kinetic chain length v is equal to $\overline{DP}$ for the latter and $\overline{DP}/2$ for the former. The rate of termination is proportional to the square of the concentration of macroradicals.

5. The degree of polymerization $\overline{DP}$ is inversely proportional to the square root of the concentration of initiator and decreases as temperature increases.
6. Since growing chains continue to propagate until a high molecular weight product is formed, the concentration of monomer decreases steadily and approaches zero at the end of the reaction. At all times prior to the end of the polymerization, the composition of the system consists of monomer and high molecular weight polymers.
7. Polymerization will not take place above the characteristic ceiling temperature.
8. Chain transfer, in which the macroradical abstracts a weakly bonded atom, causes branching when chain transfer with polymer occurs. Chain transfer with solvent or some other additive results in a dead polymer and a new free radical. If the latter does not serve as an initiator for further propagation, it is called a retarder or inhibitor.
9. The efficiency of a chain transfer agent (chain transfer constant) is the slope of the line with $1/\overline{DP}$ plotted against [S]/[M] when S is the solvent or telogen.
10. Vinyl monomers may be polymerized without other additives except free radicals in bulk polymerization. When the monomer is polymerized while suspended in a stirred aqueous medium, the process is called suspension, or pearl, polymerization. Polymerization may also take place in good or poor solvents. In the former case, the viscosity continues to increase, and in the latter, the macroradicals precipitate.
11. When the system is viscous, the termination step is hindered but propagation continues. Thus, this so-called Trommsdorff or gel effect produces high molecular weight polymers.
12. Monomers may also be polymerized by a water-soluble initiator while dispersed, by agitation, in a concentrated soap solution. In this emulsion polymerization process, initiation takes place in the aqueous phase and propagation takes place in the soap micelles. Since the growing macroradicals are not terminated until a new free radical enters the micelle, high molecular weight products are obtained in a relatively short time.
13. The rate of polymerization and the degree of polymerization in the emulsion process are proportional to the number of activated micelles.
14. The polyfluorocarbons are resistant to heat, solvents, and corrosives. The resistance is greatest in the regularly structured polytetrafluoroethylene and decreases as the geometry is upset by substitution of larger or smaller groups for the fluorine atoms.
15. Low-density polyethylene, poly(vinyl chloride), polystyrene, and neoprene are made in large quantities by free radical chain polymerization. Over 9 million tons of homopolymers is produced annually in the United States by this mechanism.

GLOSSARY

AIBN: Abbreviation for 2,2′-azobisisobutyronitrile.
Acrilan: Trade name for fibers based on polymers of acrylonitrile (PAN).
backbiting: the hydrogen atom abstraction that occurs when a chain end of a macroradical doubles back on itself to form a more stable hexagonal conformation.
bimolecular reaction: A reaction involving two reactants.

BPO: Abbreviation for benzoyl peroxide.

branch point: The point on the polymer chain where additional chain extension takes place to produce a branch.

bulk polymerization: The polymerization of monomer without added solvents or water.

[]: Concentration.

C_s: Chain transfer constant.

ceiling temperature (T_c): A characteristic temperature above which polymerization does to take place and polymers decompose.

chain stopper: A chain transfer agent that produces inactive free radicals.

chain transfer: A process in which a free radical abstracts an atom or group of atoms from a solvent, telogen, or polymer.

chain-transfer constant (C_s): The ratio of cessation or termination of transfer to the rate of propagation.

CMC: Critical micelle concentration.

critical micelle concentration: The minimum concentration of soap in water that will produce micelles.

dead polymer: A polymer in which chain growth has been terminated.

dilatometer: An instrument that measures changes in volume.

disproportionation: A process by which termination takes place as the result of chain transfer between two macroradicals to yield dead polymers, one of which has an ethylenic end group.

DMF: Abbreviation for N,N-dimethyl formamide.

E_a: Activation energy.

f: The efficiency factor in the decomposition of initiators.

FEP: A copolymer of tetrafluoroethylene and hexafluoropropylene.

first-order reaction: A reaction in which the rate is proportional to the concentration of the reactant to the first power.

half-life time ($t_{1/2}$): The time required for half the reactants to be consumed in a first-order reaction.

heterolytic cleavage: A cleavage of a covalent bond or ion pairs that leaves the two electrons on one of the atoms. The products are a carbonium ion and a carbanion, or a cation and an anion.

homogeneous cleavage: A cleavage of a covalent bond that leaves one of the two electrons on each atom. The products are free radicals.

homopolymer: A polymer made up of only one repeating unit, in contrast to a copolymer, which is made up of more than one repeat unit.

I: Initiator.

k_d: Decay constant or rate of decomposition constant.

Kel F: Trade name for polytrifluorochloroethylene (TFE).

kinetic chain length: The length of the polymer chain ($\overline{DP}$) initiated by one free radical, which can be described as follows:

$$v = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$

Kynar: Trade name for poly(vinylidene fluoride).

latex: A stable dispersion of a polymer in water.

M: Monomer.

M: A monomer radical or a macroradical.

macroradicals: Electron-deficient polymers, i.e., those having a free radical present on the chain.

Mayo equation:

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + C_s\frac{[S]}{[M]}$$

micelles: Ordered groups of soap molecules in water.

N: The number of active micelles present.

nm: Nanometers (1×10^{-9} m).

v: Symbol for the kinetic chain length.

Norris-Trommsdorff effect: Same as Trommsdorff effect.

oligoradical: A low molecular weight macroradical.

PAN: Polyacrylonitrile.

piezoelectric: The conversion of mechanical force such as pressure into electrical energy.

plasticizer: A high-boiling compatible liquid which lowers the T_g and flexibilizes a stiff polymer like PVC.

PMMA: Poly(methyl methyacrylate).

ppm: Parts per million.

PS: Polystyrene.

PTFE: Polytetrafluoroethylene.

PVA: Poly(vinyl alcohol).

PVAc: Poly(vinyl acetate).

PVB: Poly(vinyl butyral).

PVDC: Poly(vinylidene chloride).

R: Rate of reaction.

R: A free radical.

retarder: An additive which acts as a chain transfer agent to produce less active free radicals.

RM: A macroradical.

S: Solvent or telogen.

S: Styrene.

Saran: Trade name for polymers of vinylidene chloride.

SBR: A rubbery copolymer of styrene and butadiene.

stage I: The first stage in emulsion polymerization when up to 20% of the monomer is being polymerized.

stage II: The intermediate stage in emulsion polymerization when 20–60% of the monomer is being polymerized at a steady rate.

stage III: The last stage in emulsion polymerization when the last 40% of monomer is being polymerized.

suspension polymerization: A process in which liquid monomers are polymerized as liquid droplets suspended in water.

t: Time.

T_c: Ceiling temperature.

TBP: tert-Butyl peroxide.

Tedlar: Trade name for poly(vinyl fluoride).

telogen: An additive that readily undergoes chain transfer with a macroradical.

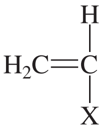
telomer: A low molecular weight polymer resulting from chain transfer of a macroradical with a telogen.

telomerization: The process in which telomers are produced by chain transfer reactions.

TFE: Polytrifluoromonochloroethyelene.

Trommsdorff effect: The decrease in termination rate in viscous media that results in higher molecular weight polymers.

vinyl groups:



$$H_2C{=}\overset{\displaystyle H \atop |}{\underset{\displaystyle | \atop X}{C}}$$

where X may be R, X, $\overset{O}{\overset{\|}{C}}{-}OR$, OR, etc.

Viton: Trade name for FEP.

EXERCISES

1. Use a slanted line to show the cleavage of (a) boron trifluoride–water, (b) sodamide, and (c) AIBN in cationic, anionic, and free radical initiations, respectively.
2. Which type of chain-reaction polymerization is most likely to terminate by coupling?
3. If an initiator has a half-life of 4 h, what percentage of this initiator will remain after 12 h?
4. If some head-to-head configuration is detected in a polymer chain known to propagate by head-to-tail addition, what type of termination has occurred?
5. Which is the better way to increase polymer production rates: (a) increasing the temperature or (b) increasing the initiator concentration?
6. Name three widely used thermoplastics produced by free radical chain polymerization.
7. What effect does the increase of polarity of the solvent have on free radical polymerization rates in solution?
8. Show the repeating units for (a) PS, (b) PVC, and (c) PMMA.
9. Can you think of any advantage of the Trommsdorff effect?
10. What is the limiting step in free radical chain polymerization?
11. In general, which is more rapid: (a) free radical chain reaction or (b) step reaction polymerization?
12. If one obtained a yield of 10% polymer after 10 min of polymerizing styrene by a free radical mechanism, what would be the composition of the other 90%?
13. Why is $t_{1/2}$ for all first-order reactions equal to $0.693/k_d$?
14. How could you follow the rate of decomposition of AIBN without measuring the rate of polymerization?
15. What is the usual value for the energy of activation of free radical initiator?
16. What is the advantage of producing free radicals by UV radiation?
17. Which is the better catalyst for the polymerization of styrene: (a) AIBN or (b) BPO?
18. If $[M\cdot]$ is equal to 1×10^{-11} mol/L under steady-state conditions, what will $[M\cdot]$ equal after (a) 30, (b) 60, and (c) 90 min?
19. In general, what is the activation energy in free radical chain propagation of polymer chains?
20. What is the relationship of the rate of propagation to the concentration of initiators [I]?

21. When chain transfer with solvent occurs, what effect does this have on $\overline{DP}$?
22. Name a plasticizer for PVC.
23. What monomer is used to produce PVA?
24. How can you reconcile the two different equations for R_i: $R_i \propto [R—]$ and $R_i \propto 2[I]$?
25. Does k_p increase or decrease when $\overline{DP}$ goes from 10 to 10^4?
26. Why is ethylene more readily polymerized by free radical chain polymerization than isobutylene?
27. What is the termination mechanism in free radical polymerization if $\overline{DP} = v$?
28. The value of v increases as the polymerization temperature of a specific monomer is increased. What does this tell you about the termination process?
29. In general, what is the activation energy of termination?
30. Why wouldn't you recommend the use of poly-α-methylstyrene for a handle of a cooking utensil?
31. When backbiting occurs, a long branch forms at the branch point. Why is this called "short-chain branching?"
32. Which would you expect to have the higher chain transfer constant: (a) carbon tetrafluoride or (b) carbon tetrachloride?
33. While the addition of dodecyl mercaptan to styrene causes a reduction in $\overline{DP}$, the rate of polymerization is essentially unchanged. Explain.
34. Would it be safe to polymerize styrene by bulk polymerization in a 55-gal drum?
35. How do the kinetics of polymerization differ in the bulk and suspension of polymerization methods?
36. Since the monomers are carcinogenic, should the polymerization of styrene, acrylonitrile, and vinyl chloride be banned?
37. What happens when a filament of polyacrylonitrile is pyrolyzed?
38. Why doesn't polymerization take place in the droplets instead of in the micelles in emulsion polymerization?
39. Why doesn't initiation occur in the micelles in emulsion polymerization?
40. What would happen if one added a small amount of an inhibitor to styrene before bulk polymerization?
41. What would be the effect on the rate of polymerization if one used AIBN as the initiator and an amount of soap that was less than CMC in emulsion polymerization?
42. Why is the T_g of PTFE higher than that of FEP?
43. Why does an increase in soap concentration increase the $\overline{DP}$ and R_p of emulsion polymerization?
44. Which will have the higher specific gravity: (a) PVC or (b) PVDC?

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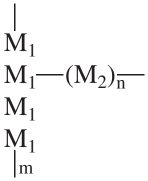
9

Copolymerization

While the mechanism of copolymerization is similar to that discussed for the polymerization of one reactant (homopolymerization), the reactivities of monomers may differ when more than one is present in the feed, i.e., reaction mixture. Copolymers may be produced by step reaction or by chain reaction polymerization. It is important to note that if the reactant species are M_1 and M_2, the composition of the copolymer is not a mixture or blend $[M_1]_n + [M_2]_n$.

Most naturally occurring polymers are largely homopolymers, but both proteins and nucleic acids are copolymers. While many synthetic polymers are homopolymers, the most widely used synthetic rubber (SBR) is a copolymer of styrene (S) and butadiene (B). A widely used plastic (ABS) is a copolymer or blend of polymers of acrylonitrile, butadiene, and styrene. A special fiber called Spandex is a block copolymer of a stiff polyurethane and a flexible polyester (see Sec. 10.4).

Copolymers may be alternating copolymers, in which there is a regular order of M_1 and M_2 in the chain, i.e., $(M_1M_2)_n$; random copolymers, in which the sequences of M_1 and M_2 are arranged in a random fashion, i.e., $M_1M_1M_2M_1M_2M_2 \ldots$; block copolymers, in which there are long sequences of the same repeating unit in the chain, i.e., $(M_1)_n(M_2)_n$; or graft copolymers, in which the chain extension of the second monomer is as branches, i.e.,



$$\begin{array}{l} | \\ M_1 \\ M_1{-}(M_2)_n{-} \\ M_1 \\ M_1 \\ |_m \end{array}$$

It is interesting to note that block copolymers may be produced from one monomer only if the arrangements around the chiral carbon atom change sequentially. The copolymers in which the tacticity of the monomers in each sequence differs are called stereoblock copolymers.

9.1 KINETICS OF COPOLYMERIZATION

Because of a difference in the reactivity of the monomers, expressed as reactivity ratios (r), the composition of the copolymer (n) may be different from that of the reactant mixture or feed (x). When x equals n, the product is said to be an azeotropic copolymer.

In the early 1930s, Nobel Laureate Staudinger analyzed the product obtained from the copolymerization of equimolar quantities of vinyl chloride (VC) and vinyl acetate (VAc). He found that the first product produced was high in VC, but as the composition of the reactant mixture changed because of a depletion of VC, the product was higher in VAc. This phenomenon is called the composition drift.

Wall showed that n was equal to rx when the reactivity ratio r was equal to the ratio of the propagation rate constants. Thus, r was the slope of the line obtained when the ratio of monomers in the copolymer (M_1/M_2) was plotted against the ratio of monomers in the feed (m_1/m_2). The Wall equation shown below is not a general equation.

$$n = \frac{M_1}{M_2} = r\frac{m_1}{m_2} = rx \tag{9.1}$$

The copolymer equation that is now generally accepted was developed in the late 1930s by a group of investigators including Wall, Dostal, Lewis, Alfrey, Simha, and Mayo. These workers considered the four possible chain extension reactions when M_1 and M_2 were present in the feed. As shown below, two of these equations are homopolymerizations, or self-propagating steps, and the other two are heteropolymerizations or cross-propagating steps. The ratio of the propagating rate constants are expressed as monomer reactivity ratios, where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. $M_1\cdot$ and $M_2\cdot$ are used as symbols for the macroradicals with M_1 and M_2 terminal groups, respectively.

Reactions	Rate expression	
$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1M_1\cdot$	$R_{11} = k_{11}[M_1\cdot][M_1]$	(9.2)
$M_1\cdot + M_2 \xrightarrow{k_{12}} M_1M_2\cdot$	$R_{12} = k_{12}[M_1\cdot][M_2]$	(9.3)
$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2M_2\cdot$	$R_{22} = k_{22}[M_2\cdot][M_2]$	(9.4)
$M_2\cdot + M_1 \xrightarrow{k_{21}} M_2M_1\cdot$	$R_{21} = k_{21}[M_2\cdot][M_1]$	(9.5)

Experimentally it is found that the specific rate constants for the reaction steps described above are essentially independent of chain length, with the rate of monomer addition primarily dependent only on the adding monomer unit and the growing end. Thus, the four copolymerizations between two comonomers can be described using only four equations.

The rate of consumption of M_1 and M_2 in the feed or reactant mixture during the early stages of the reaction can be then described by the following equations:

$$\text{Disappearance of } M_1\text{:}\ \frac{-d[M_1]}{dt} = k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1] \tag{9.6}$$

$$\text{Disappearance of } M_2\text{:}\ \frac{-d[M_2]}{dt} = k_{22}[M_2\cdot][M_2] + k_{12}[M_1\cdot][M_2] \tag{9.7}$$

Since it is experimentally observed that the number of growing chains remains approximately constant throughout the duration of most copolymerizations (that is there is a steady state in the number of growing chains), the concentrations of $M_1\cdot$ and $M_2\cdot$ are constant, and the rate of conversion of $M_1\cdot$ to $M_2\cdot$ is equal to the conversion of $M_2\cdot$ to $M_1\cdot$. Solving for $M_1\cdot$ gives

$$[M_1\cdot] = \frac{k_{21}\,[M_2\cdot]\,[M_1]}{k_{12}[M_2]} \tag{9.8}$$

The ratio of disappearance of monomers M_1/M_2 is described by Eq. (9.9a) from Eqs. (9.6) and (9.7).

$$\frac{d[M_1]}{d[M_2]} = \frac{[M]_1}{[[M_2]}\left(\frac{k_{11}[M_1\cdot] + k_{21}[M_2\cdot]}{k_{12}[M_1\cdot] + k_{22}[M_2\cdot]}\right) \tag{9.9a}$$

Substitution of $[M_1\cdot]$ into Eq. (10.9a) gives

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{\dfrac{k_{11}k_{21}[M_2\cdot][M_1]}{k_{21}[M_2]} + k_{21}[M_2\cdot]}{\dfrac{k_{12}k_{21}[M_2\cdot][M_1]}{k_{21}[M_2]} + k_{22}[M_2\cdot]}\right) \tag{9.9b}$$

Division by k_{21} and cancellation of the appropriate k's gives

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{\dfrac{k_{11}[M_2\cdot][M_1]}{k_{12}[M_2]} + [M_2\cdot]}{\dfrac{[M_2\cdot][M_2]}{[M_2]} + \dfrac{k_{22}[M_2\cdot]}{k_{21}}}\right) \tag{9.9c}$$

Substitution of $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ and cancellation of $[M_2\cdot]$ gives

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{\dfrac{r_1[M_1]}{[M_2]} + 1}{\dfrac{[M_1]}{[M_2]} + r_2}\right) \tag{9.9d}$$

Multiplication by $[M_2]$ yields what are generally referred to as the "copolymerization equations" [Eq. (9.10)], which gives the copolymer composition without the need to know any free radical concentration.

$$n = \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}\right) \tag{9.10a}$$

This equation, (9.10a) is also presented in another form that allows greater ease of seeing the relationship between the monomer feed, x, and copolymer composition. This is achieved by the following steps.

Multiplying through by $[M_1]$ and $[M_2]$ gives

$$n = \frac{d[M_1]}{d[M_2]} = \frac{[M_1]\, r_1\, [M_1] + [M_1][M_2]}{[M_2]\,[M_1] + [M_2]\, r_2\, [M_2]} \tag{9.10b}$$

Then, divide both the top and bottom by $[M_1]\,[M_2]$ to get the second form, 9.10c, of the copolymerization equation but in terms of the composition of the feed (x) on the composition of the copolymer (n) as shown below.

$$n = \frac{d[M_1]}{d[M_2]} = \frac{r_1([M_1]/[M_2]) + 1}{r_2([M_2]/[M_1]) + 1} = \frac{r_1 x + 1}{(r/x) + 1} \tag{9.10c}$$

The copolymer equations may be used to show the effect of the composition of the feed (x) on the composition of the copolymer (n). While the values of these two parameters are equal in azeotropic copolymerization, they are different in most copolymerizations. Hence, it is customary to make up for this difference in reactivity ratios by adding monomers continuously to the feed in order to produce copolymers of uniform composition.

For example, from Table 9.1, the reactivity ratios for butadiene and styrene are $r_1 = 1.39$ and $r_2 = 0.78$, respectively. Since the rate of consumption of butadiene (M_1) is faster than that of styrene (M_2), the compositions of the feed (x) would change rapidly if butadiene were not added to prevent a change in its composition, i.e., composition drift.

As shown by the following equation, an equimolar ratio of butadiene and styrene would produce a butadiene-rich copolymer in which there would be four molecules of butadiene to every three molecules of styrene in the polymer chain.

$$n = \frac{r_1 x + 1}{(r/x) + 1} = \frac{1.39(1) + 1}{(0.78/1) + 1} = \frac{2.39}{1.78} = 1.34 \tag{9.11}$$

The reactivity ratios may be determined by an analysis of the change in composition of the feed during the very early stages of polymerization. Typical free radical chain copolymerization reactivity ratios are listed in Table 9.1.

If the reactivity ratio for r_1, shown in Table 9.1, is greater than 1, then monomer M_1 tends to produce homopolymers, or block copolymers. Preference for reaction with the unlike monomer occurs when r_1 is less than 1. When both r_1 and r_2 are approximately equal to 1, the conditions are said to be ideal, and a random (not alternating) copolymer is produced, in accordance with the Wall equation. Thus, a perfectly random copolymer (ideal copolymer) would be produced when chlorotrifluoroethylene is copolymerized with tetrafluoroethylene.

When r_1 and r_2 are approximately equal to zero, as is the case with the copolymerization of maleic anhydride and styrene, an alternating copolymer is produced. In general, there will be a tendency toward alternation when the product of r_1r_2 approaches zero. In contrast, if the values of r_1 and r_2 are similar and the product r_1r_2 approaches 1, the tendency will be to produce random copolymers. The value of r_1r_2 for most copolymerizations is between 1 and 0, and thus this value may be used with discretion for estimating the extent of randomness in a copolymer.

In the absence of steric or polar restrictions, the assumptions used in the development of the copolymerization equation are valid. Temperature conditions below T_c and the polarity of solvents have little effect on free radical copolymerization. However, steric effects can be important. For example, as shown by the data in Table 9.1, styrene should tend to produce an alternating copolymer with fumaronitrile. However, since there is not enough space for the fumaronitrile mer (M_1) in alternating sequences, it is necessary

Table 9.1 Typical Free Radical Chain Copolymerization Reactivity Ratios at 60 °C[a]

M_1	M_2	r_1	r_2	r_1r_2
Acrylamide	Acrylic acid	1.38	0.36	0.5
	Methyl acrylate	1.30	0.05	0.07
	Vinylidene chloride	4.9	0.15	0.74
Acrylic acid	Acrylonitrile (50 °C)	1.15	0.35	0.40
	Styrene	0.25	0.15	0.04
	Vinyl acetate (70 °C)	2	0.1	0.2
Acrylonitrile	Butadiene	0.25	0.33	0.08
	Ethyl acrylate (50 °C)	1.17	0.67	0.78
	Maleic anhydride	6	0	0
	Methyl methacrylate	0.13	1.16	0.15
	Styrene	0.04	0.41	0.16
	Vinyl acetate	4.05	0.06	0.24
	Vinyl chloride	3.28	0.02	0.07
Butadiene	Methyl methacrylate	0.70	0.32	0.22
	Styrene	1.39	0.78	1.08
Chlorotrifluoroethylene	Tetrafluoroethylene	1.0	1.0	1.0
Isoprene	Styrene	1.98	0.44	0.87
Maleic anhydride	Methyl acrylate	0	2.5	0
	Methyl methacrylate	0.03	3.5	0.11
	Styrene	0	0.02	0
	Vinyl acetate (70 °C)	0.003	0.055	0.0002
Methyl acrylate	Acrylonitrile	0.67	1.26	0.84
	Styrene	0.18	0.75	0.14
	Vinyl acetate	9.0	0.1	0.90
	Vinyl chloride	5	0	0
Methyl isopropenyl ketone	Styrene (80 °C)	0.66	0.32	0.21
Methyl methacrylate	Styrene	0.50	0.50	0.25
	Vinyl acetate	20	0.015	0.30
	Vinyl chloride	12.5	0	0
α-Methylstyrene	Maleic anhydride	0.038	0.08	0.003
	Styrene	0.38	2.3	0.87
Styrene	p-Chlorostyrene	0.74	1.025	0.76
	Fumaronitrile	0.23	0.01	0.002
	p-Methoxystyrene	1.16	0.82	0.95
	Vinyl acetate	55	0.01	0.55
	Vinyl chloride	17	0.02	0.34
	2-Vinylpyridine	0.56	0.9	0.50
Vinyl acetate	Vinyl chloride	0.23	1.68	0.39
	Vinyl laurate	1.4	0.7	0.98
Vinyl chloride	Diethyl maleate	0.77	0.009	0.007
	Vinylidene chloride	0.3	3.2	0.96
N-Vinylpyrrolidone	Styrene (50 °C)	0.045	15.7	0.71

[a] Temperatures other than 60 °C are shown in parentheses.

Source: Data from Brandrup and Immergut, 1975.

that two styrene mers (M_2) be in the chain after each regular alternating sequence, i.e., —$M_1M_2M_2M_1M_2M_2M_1M_2$—.

While 1, 2-disubstituted vinyl monomers are not readily polymerized, they may form alternating copolymers. For example, stilbene and maleic anhydride produce an alternating copolymer but have little tendency to form homopolymers. It is now believed that a charge-transfer complex is the active species in alternating copolymerization.

The formation of these charge-transfer complexes is enhanced by the presence of salts such as zinc chloride. These complexes can be detected at low temperatures by ultraviolet or nuclear magnetic resonance spectrometry. Since the equilibrium constants for the formation of these charge complexes decrease as the temperature increases, random instead of alternating copolymers may be produced at elevated temperatures.

The resonance stability of the macroradical is an important factor in free radical propagation. Thus, a conjugated monomer such as styrene is at least 30 times as apt to form a resonance-stabilized macroradical as vinyl acetate, resulting in a copolymer rich in styrene. Providing there is not excessive steric hindrance, a 1,1-disubstituted ethylene monomer will polymerize more readily than the unsubstituted vinyl monomer.

Strongly electrophilic or nucleophilic monomers will polymerize exclusively by anionic or cationic mechanisms. However, monomers such as styrene or methyl methacrylate, which are neither strongly electrophilic nor nucleophilic, will polymerize by ionic and free radical chain polymerization mechanisms. As shown in Table 9.1, the values of r_1 and r_2 for these monomers are identical in free radical chain polymerization. Thus, the formation of a random copolymer would be anticipated when equimolar quantities of these two monomers are present in the feed.

In contrast, the reactivity ratios for styrene and methyl methacrylate are $r_1 = 0.12$ and $r_2 = 26.4$ in an anionic system. Thus, a copolymer rich in methyl methacrylate would be predicted. However, since $r_1 = 10.5$ and $r_2 = 0.1$ in cationic systems, the reverse would be true.

Butyl rubber is a random copolymer prepared by the cationic copolymerization of isobutylene ($r_1 = 2.5$) and isoprene ($r_2 = 0.4$) at -100°C. The elastomeric copolymer of ethylene and propylene is prepared with a homogeneous Ziegler-Natta catalyst in chlorobenzene using $VO(OR)_3$ as the catalyst and $(C_2H_5)_2AlCl$ as the cocatalyst. In this case, r_1r_2 is approximately 1, so the product tends to be a random copolymer. It is customary to add a diene monomer so that the product may be cured through crosslinking of the double bonds in the copolymer (EPDM).

The contrast between anionic, cationic, and free radical methods of addition polymerization is clearly illustrated by the results of copolymerization utilizing the three modes of initiation. The composition of initial copolymer formed from a feed of styrene and methyl methacrylate is shown in Fig. 9.1. Such results illustrate the variations of reactivities and copolymer composition that are possible from employing the different initiation modes. The free radical “tieline” resides near the middle since free radical polymerizations are less dependent on the electronic nature of the comonomers relative to the ionic modes of chain propagation.

9.2 THE Q-e SCHEME

A useful scheme for predicting r_1 and r_2 values for free radical copolymerizations was proposed by Alfrey and Price in 1947. The Alfrey-Price Q-e scheme is similar to the Hammett equation, except that it is not limited to substituted aromatic compounds. In the

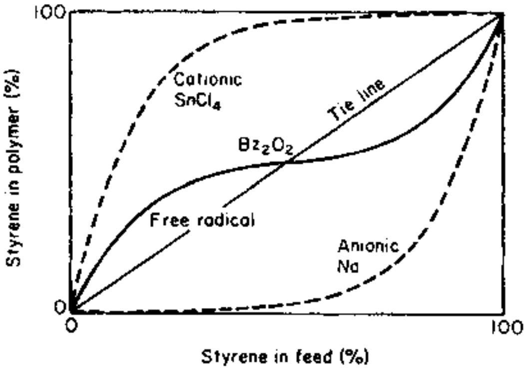


Figure 9.1 Instantaneous copolymer composition as a function of monomer composition and initiator employed for the comonomer system of styrene and methyl methacrylate utilizing different modes of initiation. From Y. Landler, Comptes Rendus, *230*:539 (1950). With permission of the Academie des Sciences, Paris, France; D. Pepper, Chem. Soc. Q. Rev., *8*:88 (1954). With permission of the Chemical Society (Great Britain).

semiempirical Q-e scheme, the reactivities or resonance effects of the monomers and macroradicals are evaluated empirically by Q and P values, respectively. The polar properties of both monomers and macroradicals are designated by arbitrary e values.

Thus, as shown in Table 9.2, Q_1 and Q_2 are related to the reactivity, and e_1 and e_2 are related to the polarity of monomers M_1 and M_2, respectively. Styrene, with Q and e values of 1.00 and -0.80, is used as the comparative standard. Higher Q values indicate greater resonance stability or reactivity, and higher e values (less negative) indicate greater electron-withdrawing power of the α substituents on the vinyl monomer.

Thus, as shown in Table 9.2, butadiene and isoprene with higher Q values are more reactive than styrene. Likewise, acrylonitrile and maleic anhydride with positive e values are more polar than styrene. While the Q-e scheme neglects steric factors, it is a useful guide when data for r_1 and r_2 are not available. The Alfrey-Price equation, in which P_1 relates to macroradical $M_1\cdot$, Q_2 relates to monomer M_2, and e_1 and e_2 relate to polarity, is shown below.

$$k_{11} = P_1Q_1e^{-e_1 2}$$
$$k_{12} = P_1Q_2e^{-e_1e_2}$$

therefore,

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2}e^{-e_1(e_1-e_2)}$$
$$k_{22} = P_2Q_2e^{-e_2 2} \tag{9.12}$$
$$k_{21} = P_2Q_1e^{-e_1e_2}$$
$$r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1}e^{-e_2(e_2-e_1)}$$
$$r_1r_2 = e^{-(e_2-e_2)^2} \text{ or } r_1r_2 = \text{exponential} - (e_1 - e_2)^2 \tag{9.13}$$

Table 9.2 Typical Q and e Values for Monomers

Monomers	Q	e
Benzyl methacrylate	3.64	0.36
Methacrylic acid	2.34	0.65
2-Fluoro-1,3-butadiene	2.08	−0.43
p-Cyanostyrene	1.86	−0.21
p-Nitrostyrene	1.63	0.39
2,5-Dichlorostyrene	1.60	0.09
Methacrylamide	1.46	2.24
p-Methoxystyrene	1.36	−1.11
2-Vinylpyridine	1.30	−0.50
p-Methylstyrene	1.27	−0.98
2-Vinylnaphthalene	1.25	−0.38
Isopropyl methacrylate	1.20	−0.15
Methacrylonitrile	1.12	0.81
p-Bromostyrene	1.04	−0.32
Styrene	1.00	−0.80
m-Methylstyrene	0.91	−0.72
n-Amyl methacrylate	0.82	−0.32
Methyl methacrylate	0.74	0.40
Acrylonitrile	0.60	1.20
Methyl acrylate	0.42	0.60
Vinylidene chloride	0.23	0.36
Vinyl chloride	0.044	0.20
Vinyl acetate	0.026	−0.22

Source: Data from Brandrup and Immergut, 1975.

It is important to note that while the reactivity is related to resonance stability of the macroradical $M_1\cdot$, the composition of the copolymer is related to the relative polarity of the two monomers M_1 and M_2.

9.3 COMMERCIAL COPOLYMERS

One of the first commercial copolymers was the copolymer of vinyl chloride (87%) and vinyl acetate (13%) (Vinylite, VYHH) that was introduced in 1928. As shown in Table 9.1, the r_1 value for vinyl acetate is 0.23 and r_2 for vinyl chloride is 1.68. Hence, a 4:1 molar ratio of VC to VAc in the feed produced VYHH as the initial copolymer, and it was necessary to continue to add the monomers in the correct proportions in order to obtain the same composition throughout the polymerization.

Because the presence of vinyl acetate mers disrupted the regular structure of PVC, the copolymer was more flexible and more soluble than the homopolymer. A copolymer of vinyl chloride and vinyl isobutyl ether (Vinoflex) has been produced in Germany and a copolymer of vinyl chloride and acrylonitrile (Vinyon, Dynel) has been used as a fiber in the United States. Copolymers of styrene and acrylonitrile are sometimes classified as high-performance or engineering plastics.

Copolymers of vinyl chloride and vinylidene chloride were introduced in the 1930s. The copolymer with a high vinyl chloride content was used as a plastic film (Pliovic), and the copolymer with a high vinylidene chloride content as been used as a film and filament (Saran). Three-component copolymers of vinyl chloride, vinyl acetate, and maleic anhydride have superior adhesive properties because of the polar anhydride groups present on the polymer chain.

Copolymers of ethylene and methacrylic acid (ionomers) also have good adhesive properties and transparency. When salts such as those of zinc, lithium, or sodium are added to these ionomers, they act like thermosetting plastics at room temperature but are readily molded since the ion pairs dissociate at processing temperatures.

Polybutadiene, produced in emulsion polymerization, is not useful as an elastomer. However, the copolymers with styrene (SBR) and acrylonitrile (Buna-N) are widely used as elastomers. Over 8 million tons of SBR were produced worldwide in 1995.

While most fibers are homopolymers, polycrylonitrile fibers cannot be readily dyed. However, this difficulty is overcome when acrylonitrile is copolymerized with a small amount of acrylic acid, acrylamide, vinylpyridine, or vinylpyrrolidone. The dyability of polypropylene fibers is improved by graft copolymerization with vinylpyrrolidone.

Ethylene-propylene copolymers show good resistance to ozone, heat, and oxygen. Two general types of ethylene-propylene elastomers are commercially available. Ethylene-propylene copolymers (EPMs) are saturated and require vulcanization employing free radical processes. They are used in a wide variety of automotive applications, including as body and chassis parts, bumpers, radiator and heater hoses, seals, mats, and weather-strips. EPMs are produced by solution polymerization employing Ziegler-Natta catalysts.

The second type of ethylene-propylene copolymer is the ethylene-propylene-diene terpolymers (EPDMs) EPDMs are made by polymerizing ethylene, propylene, and a small amount (3–9%) of nonconjugated diolefin employing Ziegler-Natta catalysts. The side chains permit vulcanization with sulfur. They are employed in the production of appliance parts, wire and cable insulation, coated fabrics, gaskets, hoses, seals, and high-impact polypropylene.

Driving Forces

The nature and importance of various driving forces contributing especially to tertiary and quaternary structures is becoming better understood. Often, the starting point for this understanding is coming from a better understanding of biomacromolecules. Major factors appear to be combinations of phillic and phobic forces and periodicity. Some of these factors can be discussed in terms of segmented block copolymers containing segments of varying structures. By varying the nature of the particular blocks, combinations of coils, chain-extended or chain-folded (beta-sheet), crystallites, and double-helices have been achieved. For instance, for a homologous series of segmented polyurethanes, holding the hard segment constant, chain folding is achieved by substitution of only minute amounts of the tetrametylene unit with hexamethylene or octamethylene.

An ABA triblock copolymer composed of a polyether center block and oligo(bipyridine) outer blocks becomes chain extended as copper I ions are introduced because of formation of oligo(bipyridine)-copper I tetra-coordinated supramolecular assemblies. These materials act like thermoplastic elastomers. Through the use of similar block copolymers with special bipyridine and bis(bipyridine) sequences, spontaneous self-assembly materials are formed when copper I is added. In the case of the bis(bipyridine), a double helical structure is formed.

Miscibility Mixing

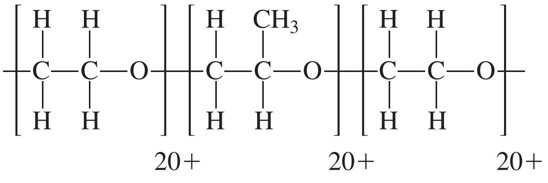
Miscibility is a mixing that is generally driven by entropy factors. For instance, the miscibility of multicomponent systems decreases as the rigidity of one of the components increases because of at least a decreased entropy effect and the formation of meso-structures that exclude molecular mixing with unlike chains. Thus, while the presence of rigid chain segments allow the formation of good meso-separated materials, it inhibits the formation of a molecular dispersion of the rod-like molecules in a coil-like matrix, which is the ideal polymer–polymer composite at the molecular level.

“Liking-liking-like best” (enthalpy effects) is generally only overcome when entropy factors are sufficient to overcome this tendency of a molecule to associate with itself. In some instances, energy terms can be used to drive the process. For instance, miscibility of otherwise immiscible rigid-rod, flexible, and random-coil polymers can be achieved through special complementary coupling of specially designed polymers and copolymers. Illustrative of this is the miscibility of ionomer blends. Thus, dispersions of rod-like molecules such as bipyridyl substituted polydiacetylenes, para or meta-linked poly(phenylene-pyridylacetylene) and sulfonic acid substituted poly(p-phenylene) can be achieved when coupled with polymers containing complementary ionic groups.

9.4 BLOCK COPOLYMERS

While block copolymers do not occur naturally, synthetic block copolymers have been prepared by all known polymerization techniques. Block copolymers consisting of long sequences of mers are produced inadvertently when hevea rubber is milled with other polymers or when mixtures of different polyesters or mixtures of polyesters and polyamides are melted.

The first commercial block copolymer was a surfactant (Pluronics) prepared by the addition of propylene oxide to polycarbanions of ethylene oxide. While neither water-soluble poly(ethylene oxide) nor water-insoluble poly(propylene oxide) exhibits surface activity, the ABA block copolymer consisting of hydrophilic and lyophilic segments, shown below, is an excellent surfactant.



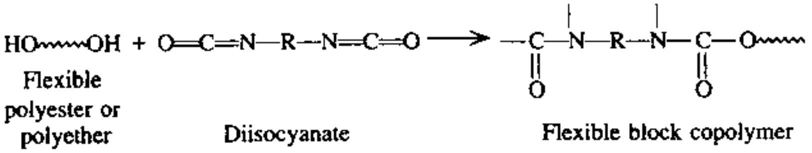
$$\left[-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{O}-\right]_{20+}\left[-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{O}-\right]_{20+}\left[-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{O}-\right]_{20+} \qquad (9.14a)$$

ABA copolymer of ethylene oxide and propylene oxide

The ethylene oxide block is hydrophilic, whereas the propylene oxide block is (relatively) hydrophobic. The copolymer forms micelles in aqueous solutions with the hydrophilic portions pointing outward, interacting with the water, while the hydrophobic portions forms the inner core, shielded from the water by the ethylene oxide–derived block. A micelle is also formed in organic liquids, but here the hydrophobic propylene oxide block “faces” outward while the ethylene oxide block acts as the inner core.

Joseph Shivers, a Dupont chemist, invented spandex in 1959 after about a ten-year search. It was first named Fiber K but Dupont chose the more appealing, smooth-like trade name of Lycra.

Elastomeric polyurethane fibers consisting of at least 85% segmented polyurethane are commercially available under the name Spandex. They are block copolymers and are among the first products specifically designed using the concept of soft and hard segments. The soft or flexible segment is composed of poly(ethylene oxide) chains that contain two hydroxyl end groups (one at each end of the poly(ethylene oxide) chain). The hard or stiff segment is derived from the reaction of the diisocyanate with the hydroxyl end groups forming polar urethane linkages that connect the poly(ethylene oxide)polymer segments through the urethane linkages. Such products are often referred to as “segmented polyurethane fibers.” They have found wide use in cloths including bras. Similar products have also been formed using hydroxyl-terminated polyethylene in place of the poly(ethylene oxide).



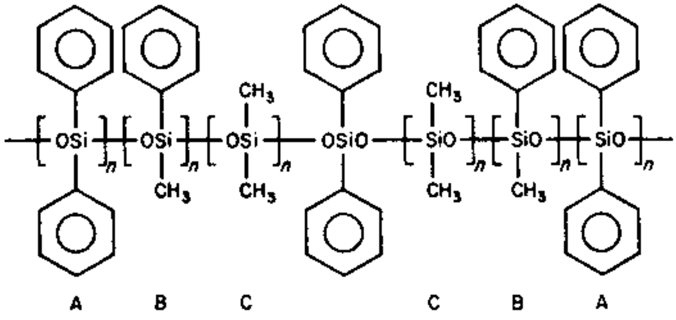
$$\mathrm{HO{\sim\sim}OH + O{=}C{=}N{-}R{-}N{=}C{=}O \longrightarrow -\underset{\|}{\overset{}{C}}\!{-}N{-}R{-}N{-}\underset{\|}{C}{-}O{\sim\sim}}$$

(9.14b)

A related product is formed from the analogous reaction using hydroxyl-terminated poly(ethylene oxide) with aromatic diacids to form a segmented aromatic polyester block copolymer that is sold under the trade name of Hytrel.

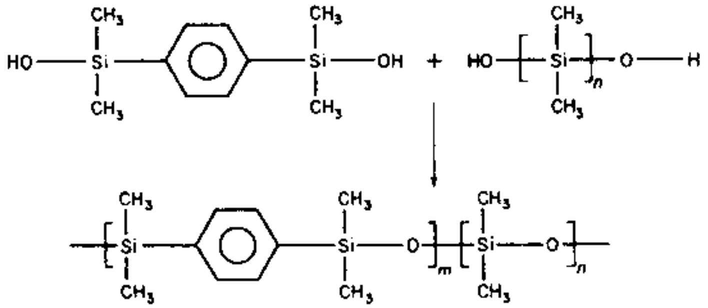
Polymers that contain two reactive end groups are referred to as “telechelic polymers.” Poly(ethylene oxide) itself is made from ethylene oxide through a base catalyzed ring-opening polymerization. While the major use of poly(ethylene oxide) is in the manufacture of polyurethane products, including foams, it can be synthesized giving viscous liquids to solids depending on the molecular weight. It is used as a surfactant, functional fluid, thickener, lubricant, and plasticizer. Further, the circuit boards that hold the electronic components of computers are made from poly(ethylene oxide).

ABA block copolymers of dimethylsiloxane(A)–diphenylsiloxane(B)–dimethylsiloxane(C) are synthesized by the sequential polymerization of reactants such as hexaethylcyclotrisiloxane and hexaphenylcyclotrisiloxane in the presence of an initiator such as dilithiodiphenlysilanolate and a promotor such as tetrahydrofuran. As shown in the following structure, ABCCBA siloxane block copolymers may be prepared in the same way.



(9.14c)

As shown in the following equation, linear polysilarylenesiloxanes are prepared by the condensation of silphenylenesiloxanes, such as p-bis(dimethylhydroxysilyl)benzene and polydimethylsiloxane in the presence of n-hexylamine-2-ethylhexoate.



(9.15)

Other siloxane block copolymers have been made from polysiloxanes and polyalkylene ethers, polysiloxanes and polyarylene ethers, and polysiloxanes and polyvinyl compounds. The latter are obtained by the coupling of polysiloxanes with polycarbanions of vinyl monomers such as styrene, α-methylstyrene, and isoprene. The chemistry of silicones is discussed in Chapter 12.

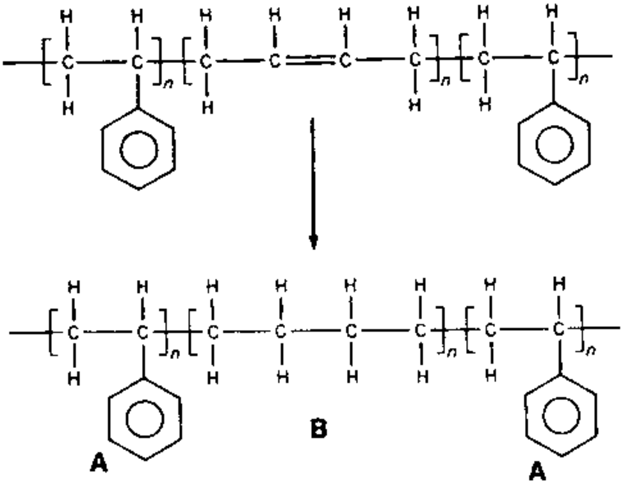
Block copolymers with segments or domains of random length have been produced by the mechanical or ultrasonic degradation of a mixture of two or more polymers such as hevea rubber and poly(methyl methacrylate) (Heveaplus). As shown by the following general equation, the products should have different properties than mixtures of the separate polymers, since segments of more than one polymer are present in the new chain.

$$\underset{\substack{n\\ \text{from}\\ \text{Macroradical}\\ \text{elastomer}\\ \text{molecule}}}{M_1M_1\cdot} \quad + \quad \underset{\substack{m\\ \text{Macroradical}\\ \text{from}\\ \text{plastic}\\ \text{molecule}}}{M_2M_2\cdot} \quad \rightarrow \underset{\substack{n+m\\ \text{Block}\\ \text{copolymer}}}{M_1 — M_2} \qquad (9.16a)$$

The impact resistance of polypropylene has been increased by the preparation of block copolymers (polyallomers) with small segments of polyethylene. These poly-allomers, and those with larger domains of polyethylene, are produced by Ziegler-Natta polymerization. Block copolymers have also been prepared from the same polymer with domains of different tacticity and with different configurations. For example, block copolymers with domains formed by the 1,2 and 1,3 polymerization of 4-methylpentene have been reported.

The most widely used chain reaction block copolymers are those prepared by the addition of a new monomer to a macroanion. The latter have been called “living polymers” by Szwarc. AB and ABA “block” copolymers called Soprene and Kraton, respectively, are produced by the addition of butadiene to styryl macroanions or macrocarbanions. As shown by the following equation, a more complex block copolymer is produced by the hydrogenation of poly(styrene-b-butadiene-b)styrene. The product is actually a saturated copolymer block of styrene (A), butene (B), and styrene (A).

Block copolymers have been prepared by free radical chain polymerization by introducing free radical ends, by the cleavage of weak links such as peroxy links, by using polyperoxides, such as phthaloyl polyperoxide as initiators, by introducing an active group by telomerization, or by using a complex compound such as azobiscyanopentanoic acid as the initiator. When only one of the isopropyl groups in diisopropylbenzene is oxidized to form the peroxide, this monofunctional initiator produces a polymer that may be oxidized to produce a new isopropyl peroxide, which can cause chain extension with a new monomer.



(9.16b)

The stable macroradicals produced in heterogeneous solution polymerization or those formed in viscous homogeneous solutions may be used to produce a wide variety of block copolymers. These systems must be oxygen-free and the new vinyl monomer must be able to diffuse into the macroradical. This diffusion is related to the difference in the solubility parameters between the new monomer and the macroradical. When this value is less than 3H diffusion takes place. The rate of diffusion is inversely related to the difference in solubility parameters ($\Delta\delta$) between the monomer and macroradical.

It is of interest to note that while acrylonitrile (δ) $=$ 10.8 H) will diffuse into acrylonitrile macroradicals ($\delta = 12.5 + \text{H}$), styrene ($\delta = 9.2$ H) will not diffuse into these macroradicals. However, acrylonitrile will diffuse into styryl macroradicals ($\delta = 9.2$ H) so that block copolymers of styrene and acrylonitrile are readily produced. Likewise, charge-transfer complexes of styrene and acrylonitrile and styrene and maleic anhydride will diffuse into acrylonitrile macroradicals.

When soluble organic initiators are used in emulsion polymerization in the absence of droplets, initiation takes place in the micelles and stable macroradicals are produced. Block copolymers may be formed by the addition of a second monomer after all of the primary radicals have been used up.

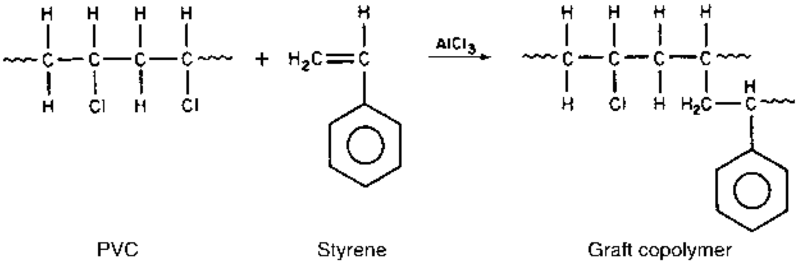
Today new copolymers are making use of the hard-soft block strategy where the hard segment is a block portion such as polyethylene that readily crystallizes forming a physical crosslink. The soft segment consists of blocks formed from alpha-olefins such as 1-butene, 1-hexane, and 1-octane where the substituted alkane arm discourages crystallization.

9.5 GRAFT COPOLYMERS

Since the major difference between block and graft copolymers is the position of chain extension, much of the information on block copolymerization may be applied to graft copolymers. The chain extensions in the latter are at branch points along the chain. Branch polymers are typically homograft polymers.

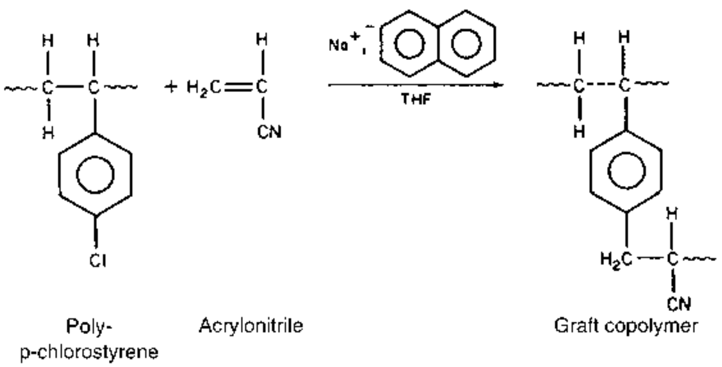
Graft copolymers of nylon, protein, cellulose, or starch or copolymers of vinyl alcohol may be prepared by the reaction of ethylene oxide with these polymers. Graft copolymers are also produced when styrene is polymerized by Lewis acids in the presence of poly-p-methoxystyrene. The Merrifield synthesis of polypeptides is also based on graft copolymers formed from chloromethylated polystyrene.

Isobutylene and butadiene will also form cationic graft copolymers with chloromethylated polystyrene. Styrene has been grafted onto chlorinated butyl rubber and PVC in the presence of Lewis acids. The latter reaction is as follows:



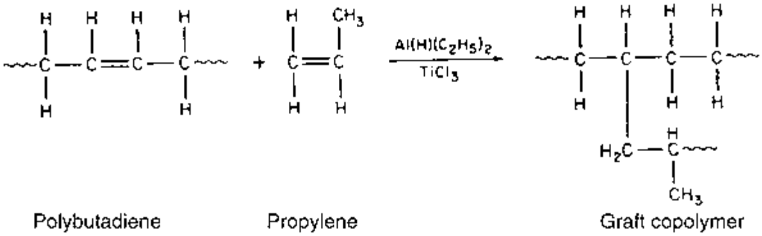
(9.17)

Acrylonitrile graft copolymers of poly-p-chlorostyrene may be produced by anionic polymerization techniques (Eq. 9.18).



(9.18)

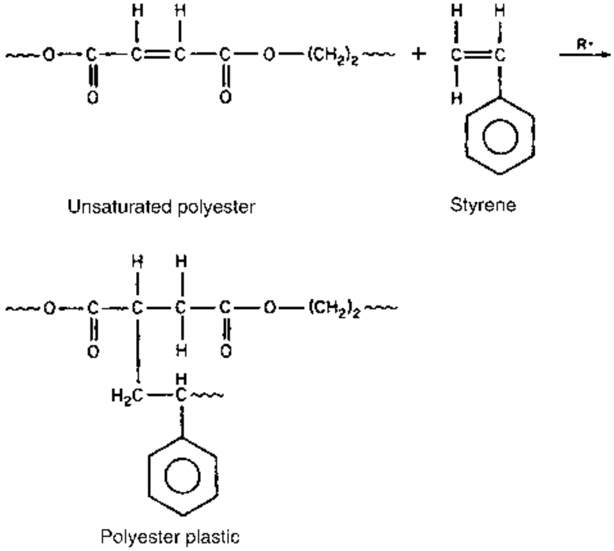
As shown in Eq. (9.19), graft copolymers are also produced from the reaction of vinyl compounds and unsaturated polymers in the presence of Ziegler-Natta catalysts.



(9.19)

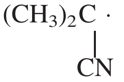
Graft copolymers of many polymers have been prepared by irradiation with visible light in the presence of a photosensitizer or ionization radiation and a vinyl monomer. While the normal procedure involves direct radiation of the mixture of polymer and monomer, better results are obtained when the polymer is preradiated. High-energy radiation often causes crosslinking.

The most widely used graft copolymer is the styrene-unsaturated polyester copolymer. This copolymer, which is usually reinforced by fibrous glass, is prepared by the free radical chain polymerization of a styrene solution of an unsaturated polyester. Since oxygen inhibits the polymerization, it is preferable to polymerize in an oxygen-free atmosphere. As is the case with many other graft copolymers, considerable homopolymer is also produced. The general reaction is as follows:



(9.20)

High-impact polystyrene (HIP) and some ABS copolymers may be produced by the free radical chain polymerization of styrene in the presence of an unsaturated elastomer. While azobisisobutyronitrile (AIBN) is a useful initiator for the polymerization of vinyl monomers, including styrene, it is not a satisfactory grafting initiator presumably because of the higher resonance stability of



$$(CH_3)_2\underset{\displaystyle CN}{\underset{|}{C}}\,\cdot$$

as compared to C_6H_5 COO · or C_6H_5 · from benzoyl peroxide. AIBN is not used as an initiator for styrene with unsaturated polyesters for the same reason.

The graft copolymers of acrylamide and cellulose or starch are of particular interest. These products, which are usually produced in the presence of cerium(IV) ions, have potential use as water absorbents and in enhanced oil recovery systems. The graft copolymers with acrylic acid or the hydrolyzed graft copolymers with acrylonitrile have exceptionally good water absorbency.

9.6 ELASTOMERS

As noted in Sec. 2.5, elastomers, or rubbers, are high polymers that typically contain chemical and/or physical crosslinks. While there are thermoplastic elastomers such as styrene-butadiene-styrene, (SBS) and block copolymers, most elastomers are thermosets. Elastomers are characterized by a disorganized (high-entropy) structure in the resting or nonstressed state. Application of stress is accompanied by a ready distortion requiring (relative to fibers and plastics) little stress to effect the distortion. This distortion brings about an aligning of the chains forming a structure with greater order. The driving force for the material to return to its original shape is largely a return to the original less organized state. While entropy is the primary driving force for elastomers to return to the original resting state, the crosslinks allow the material to return to its original shape giving the material what is often termed memory. Materials that allow easy distortion generally have minimal interactions between the same or different chains. This qualification is filled by materials that do not bond through the use of dipolar (or polar) or hydrogen bonding. Thus, the intermolecular and intramolecular forces of attraction are small relative to those required of fibers. Hydrocarbon polymers are examples of materials that have small inter- and intramolecular attractive forces.

As noted in Table 1.6, traditional synthetic rubbers were produced at the rate of about 5500 million pounds in 2000. Production of elastomeric materials typically requires the initial synthesis of the polymeric backbone, insertion of crosslinks through a process called vulcanization, addition of fillers and other additives such as carbon black, and, finally, the processing of the complex mixture.

The introduction of crosslinks to inhibit chain slippage is called vulcanizing (curing) in the rubber industry. Goodyear, in 1839, was the first to recognize the importance of introducing crosslinks. He accomplished this through the addition of sulfur to natural rubber (NR). Shortly thereafter, an accelerator [zinc(II) oxide] was added to the mixture to increase the rate of crosslinking. Other additives were discovered, often through observation of a problem and a somewhat trial-and-error approach to a solution.

Around 1915, Mote found that a superior abrasion-resistant elastomer was produced through the use of carbon black. Carbon black can be considered the result of the thermal decomposition of hydrocarbons. Today it is recognized that factors such as surface area, structure, and aggregate size are important factors in allowing the carbon black to impart particular properties to the rubber. For instance, high surface areas (small particle size) increase the reinforcement and consequently the tensile strength and improve the resistance to tearing and abrasion. Large aggregates give elastomers that have improved strength before curing, high modulus, and an improved extrusion behavior.

Rubbers typically have low hysteresis. Hysteresis is a measure of the energy absorbed when the elastomer is deformed. A rubber that absorbs a great amount of energy as it is deformed is said to have a high hysteresis. The absorbed energy is equivalent to the reciprocal of resilience such that a material with a low hysteresis has a high resilience and a material with a high hysteresis conversely has a low resilience. Rubbers with a particularly low hysteresis are used where heat buildup is not wanted, such as in tire walls. Rubbers with a high hysteresis are used where heat buildup is desirable, such as in tires to give the tread a better grip on the road and the tire a smoother ride.

Table 9.3 contains a listing of elastomers and sample applications.

Recycling

Typical thermosetting elastomers are difficult to recycle because their crosslinking prevents them from being easily solubilized when added to liquids and because the crosslinking prevents them from being easily reformed through application of heat or a combination of heat and pressure. Recycling can be accomplished through the particalizing (grinding into small particles) of the elastomeric material followed by a softening-up by application of a suitable liquid and/or heat and, finally, addition of a binder that physically or chemically allows the particles to be bound together in a desired shape.

Thermoplastic Elastomers

A number of thermoplastic elastomers have been developed since the mid-1960s. The initial thermoplastic elastomers were derived from plasticized PVC and are called *plasti-*

Table 9.3 Common Elastomers and Their Uses

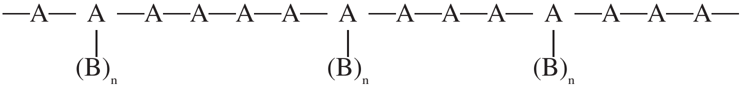
Common name (chemical composition)	Abbreviation	Uses and properties
Natural rubber (polyisoprene)	NR	General-purpose tires, bushings, and couplings, seals, footwear, belting. Good resilience
Styrene-butadiene-rubber (random co-polymer)	SBR	Tire tread, footwear, wire and cable covering, adhesives. High hysteresis
Butadiene rubber	BR	Tire tread, hose, belts. Very low hysteresis, high rebound
Butyl rubber (from isobutene) and 0.5–3% isoprene)	IIR	Inner tubes, cable sheathing, tank liners, roofing, seals, coated fabrics. Very low rebound, high hysteresis
Silicons (typically polydimethyl-siloxane)		Medical applications, flexible molds, gaskets, seals. Extreme use temperature range
Polyurethanes		Sealing and joining, printing rollers, fibers, industrial tires, footwear, wire and cable covering
Nitrile rubber (random copolymer of butadiene) and acrylonitrile	NBR	Seals automotive parts that are in contact with oils and gas, footwear, hose. Outstanding resistance to oils and gas, little swelling in organic liquids
Ethylene-propylene rubbers (random copolymers with 60–80% ethylene)	EP or EPM	Cable insulation, window strips. Outstanding insulative properties
Ethylene-propylene-diene (random terpolymer)	EPDM	Good resistance to weathering, resistant to ozone attack
Chloroprene rubber (polychloroprene)	CR	Wire and cable insulation, hose, footwear, mechanical automotive products. Good resistance to oil and fire, good weatherability
Acrylonitrile-butadiene-styrene (terpolymers)	ABS	Oil hoses fuel tanks, gaskets, pipe and fittings, appliance and automotive housings. Resistant to oils and gas
Ionomers (largely copolymers of ethyl-ene and acid-containing monomer reacted with metal ions)		Golf ball covers, shoe soles, weather stripping. Tough, flame-resistant, good clarity, good electrical properties, abrasion-resistant
Fluoroelastomers (fluorine-containing copolymers)		Wire and cable insulation, aerospace applications. Outstanding resistance to continuous exposure to high temperatures, chemicals, and fluids
Epichlorohydrin (epoxy copolymers)		Seals, gaskets, wire and cable insulation. Good resistance to chemicals
Polysulfide		Adhesive, sealants, hose binders. Outstanding resistance to oil and organic solvents

sols. Plastisols are formed from the fusing together of PVC with a compatible plasticizer through heating to about 200°C. A homogeneous matrix is formed. The plasticizer acts to lower the glass transition temperature of the PVC to below room temperature. Conceptually, this can be though of as the plasticizer acting to put additional distance between the PVC chains, thus lowering the inter- and intrachain attractive forces. The resulting rubbery materials are utilized in the construction of many products, including boot soles.

Thermoplastic elastomers contain two or more distinct phases and their properties depend on these phases being intimately mixed and small. These phases may be chemically or physically connected. In order that the material be a thermoplastic elastomer at least one phase must be soft or flexible under the operating conditions and at least one phase is hard with the hard phase(s) becoming soft (or fluid) at higher temperatures. Often the hard segments or phases are crystalline thermoplastics while the soft segments or phases are amorphous. In continuous chains containing blocks of hard and soft segments the molecular arrangement normally contains crystalline regions where there is sufficient length in the hard segment to form the crystalline regions and areas or phases where the soft segments form amorphous regions.

The hard/soft segment scenario is utilized in the formation of a number of industrially important thermoplastic elastomers. Representative examples of such thermoplastic elastomers based on block copolymers are given in Table 9.4.

Such hard/soft scenarios can also be achieved through employing grafts (Table 9.5) where the pendant group typically acts as the hard segment with the backbone acting as the soft segment. Below is a representation of a typical graft copolymer chain. In order for an effective network to be formed each “A” chain needs to have at least two “B” grafts to allow for formation of a continuous interlinked network. While there has been a lot of research done with such graft materials they have not yet become very important commercially.



$$-A-\underset{\substack{|\\(B)_n}}{A}-A-A-A-A-\underset{\substack{|\\(B)_n}}{A}-A-A-A-\underset{\substack{|\\(B)_n}}{A}-A-A-A- \tag{9.21}$$

Thermoplastic elastomers can also be achieved through physical mixing of hard and soft segments (Table 9.6). These are fine dispersions of a hard thermoplastic polymer and an elastomer. The two materials generally form interdispersed co-continuous phases. Often the physical combining is achieved through intense mechanical mixing but in some cases, such as with polyporpylene and ethylene-propylene copolymers the effect of blending is achieved through polymerizing the finely dispersed elastomer phase (ethylene-propylene copolymer) phase simultaneously with the hard polypropylene.

At times the phases are crosslinked during the mechanical mixing. This process is referred to as “dynamic vulcanization” and produces a finely dispersed discontinuous crosslinked elastomer phase. The products are referred to as thermoplastic vulcanizates or dynamic vulcanizates. The products of this process have an insoluble elastomer phase giving the material greater oil and solvent resistance. The crosslinking also reduces or eliminates the flow of this phase at high temperatures and/or under high stress. This allows the material better resistance to compression set.

Worldwide sales of thermoplastic elastomers are on the order of one and a half million tons with a value of about $5 billion.

Styrene-butadiene-styrene (SBS) block copolymers differ from the structurally related random copolymer of styrene and butadiene (SBR). Because the styrene and buta-

Table 9.4 Thermoplastic Elastomeric Block Copolymers

Hard segment	Soft or elastomeric segment	General type(s)
Polystyrene	Butadiene and polyisoprene[a]	Triblock, branched
Polystyrene	Poly(ethylene-co-butylene)[b]	Triblock
Polystyrene	Polyisobutylene	Triblock, branched
Poly(alpha-methylstyrene)	Polybutadiene	Triblock
Poly(alpha-methylstyrene)	Polyisoprene	Triblock
Poly(alpha-methylstyrene)	Poly(propylene sulfide)	Triblock
Polystyrene	Polydimethylsiloxane	Triblock, multiblock
iPolypropylene	Poly(alpha-olefins)	Mixed
iPropylene	aPolypropylene	Mixed
Polyethylene	Poly(alpha-olefins)[c]	Multiblock
Polyethylene	Poly(ethylene-co-butylene)	Triblock
Polyethylene	Poly(ethylene-co-propylene)	Triblock
Polyurethane	Polydiacetylenes	Multiblock
Polyurethane	Polyester or polyether[d]	Multiblock
Poly(methyl methacrylate)	Poly(alkyl acrylates)	Triblock, branched
Polysulfone	Polydimethylsiloxane	Multiblock
Polyetherimide	Polydimethylsiloxane	Multiblock
Polycarbonate	Polyether	Multiblock
Polycarbonate	Polydimethylsiloxane	Multiblock
Polyamide	Polyester or polyether[e]	Multiblock
Polyester	Polyether[f]	Multiblock

Sample trade names of block copolymers: [a]Kraton D, Cariflex TR, Taipol, Vector, Tufprene, Asaprene, Calprene, Europrene Sol T, Stearon, Flexprene, Quintac, Finaprene, Coperbo, Solprene, Stearon, and K-Resin. These products may be branched or linear with varying contents of the various components: [b]Elexar, C-Flex, Tekron, Hercuprene, Kraton G, Septon, Dynaflex, and Multi-Flex; [c]Flexomer, Exact, Affinity, and Engage; [d]Texin, Desmopan, Estane, Morthane, Elastollan, and Pellethane. [e]Montac, Pebax, Orevac, Vestamide, Grilamid, and Grilon; [f]Arnitel, Hytrel, Ecdel, Lomod, Riteflex, and Urafil.

Table 9.5 Thermoplastic Elastomers Based on Graft Copolymers

Hard pendant segment	Soft backbone
Polystyrene	Poly(butyl acrylate)
Polystyrene	Poly(ethyl-co-butyl acrylate)
Poly(4-chlorostyrene)	Polyisobutylene
Polystyrene and Poly(alpha-methylstyrene)	Polybutadiene
Polystyrene and Poly(alpha-methylstyrene)	Polyisobutylene
Polystyrene and Poly(alpha-methylstyrene)	Poly(ethylene-co-propylene)
Poly(methyl methacrylate)	Poly(butyl acrylate)
Polyindene	Polyisobutylene
Polyindene	Poly(ethylene-co-propylene)
Polyindene	Polybutadiene
Polyacenapthylene	Polyisobutylene

Table 9.6 Thermoplastic Elastomers Based on Hard-Soft Combinations

Hard polymer	Soft/elastomeric	Polymer structure
Polypropylene	Ethylene-propylene copolymer[a]	Blend
Polypropylene	Natural rubber[b]	Dynamic vulcanizate
Polypropylene	Ethylene-propylene-diene monomer[c]	Dynamic vulcanizate
Polypropylene	Butyl rubber[d]	Dynamic vulcanizate
Polypropylene	Nitrile rubber[e]	Dynamic vulcanizate
Polypropylene	Poly(propylene-co-1-hexene)	Blend
Polypropylene	Poly(ethylene-co-vinyl acetate)	Blend
Polypropylene	Styrene-ethylene-butylene-styrene + oil	Blend
Polystyrene	Styrene-butadiene-styrene + oil	Blend
Nylon	Nitrile rubber	Dynamic vulcanizate
Poly(vinyl chloride)	Nitrile rubber + diluent[f]	Blend, dynamic Vulcanizate
Chlorinated polyolefin	Ethylene interpolymer[g]	Blend

Sample tradenames [a]c-Flexothene, Ferroflex, Hifax, Polytrope, Ren-Flex, Telcar; [b]Geolast; [c]Hifax MXL, Santoprene, Sarlink 3000 and 4000, Uniprene; [d]Sarlink 2000, Trefsin; [e]Geolast, Vyram; [f]Apex N, Chemigum, Sarlink 1000; [g]Alcryn.

diene blocks are incompatible, they form separate phases joined at the junctures where the various blocks are connected. This gives an elastomeric material where the butadiene blocks form what are called soft segments and the styrene blocks form hard blocks. The junctures act as crosslinks between the phases, but these crosslinks can be mobilized through application of heat.

The block copolymer made from connecting blocks of polystyrene with blocks of polybutadiene illustrates the use of soft and rigid or hard domains in thermoplastic elastomers. The polystyrene blocks give rigidity to the polymer while the polybutadiene blocks act as the soft or flexible portion. The polystyrene portions also form semicrystalline domains that add to the strength of the copolymer and these domains also act as physical crosslinks allowing the soft portions to respond in an elastomeric manner, while the semicrystalline domains give the material the elastomeric memory. The polybutadiene blocks act as the continuous phase while the polystyrene blocks act as the discontinuous phase. Heating the material above the T_m of the polystyrene domains allows whole-chain mobility, which allows processability of the virgin material and subsequent reprocessability of used material. Upon cooling, the rigid domains reform. Block polystyrene-polybutadiene copolymers are used in the soles of many of the athletic shoes.

Thermoplastic elastomeric polyurethanes are made from the inclusion of polyether or polyester soft segments connected to hard segments through urethane linkages (Sec. 9.4), forming what is often called segmented polyurethanes. Again, these are block copolymers where the various blocks act to allow the material to have elastomeric properties as in the case of the SBS copolymers.

The copolymer of poly(butylene terephthalate) (PBT) and poly(tetramethylene ether glycol) (PTMEG) is marketed as a thermoplastic elastomer under trade names such as Hytrel (duPont) and Arnitel (Akzo) where the PBT acts as the hard segment and the PTMEG acts as the soft segment.

Ionomers are thermosets that can be processed as thermoplastics. They are another example of crosslinked materials that can be made to behave as thermoplastics (see Sec. 9.10).

9.7 NETWORKS—GENERAL

Polymer networks are generally of one of two types. Thermoset elastomers have chemical crosslinks where "unlinking" requires rupture of primary bonds. Thermoplastic elastomers have physical crosslinks that include chain entanglement and formation of crystalline or ordered domains that act as hard segments. Here, unlinking can be accomplished without rupture of primary bonds. For both types, stiffness and brittleness increase as the amount of crosslinking increases. Networks can also be divided according to flexibility. Highly crosslinked systems, such as phenol-formaldehyde resins are network systems, but they are very strong and brittle.

For elastomeric materials, high flexibility and mobility are required so that flexible nonpolar chain units are generally required. Such materials typically have low T_g values that allow ready segmental mobility to occur. Some materials can be "tricked" into being flexible below their T_g through introduction of appropriate flexibilizing agents including plasticizers (diluents). Others can be made to become elastomeric through heating above the T_g of the crystalline areas.

Many of the copolymers are designed to act as elastomeric materials containing complex networks. In general, most elastomers undergo ready extension up to a point where there is an abrupt increase in the modulus. The cause of this limited extensibility was for many years believed to be due to the molecular extent of uncoiling of the polymer segments composing the elastomeric material. Today we know that while such ultimate chain elongations may contribute to this rapid increase in modulus, the primary reason for many elastomeric materials involves strain-induced crystallization. As a general observation, when the large increase in modulus is mainly due to limiting chain extension the limit will not be primarily dependent on temperature and presence/absence of a diluent. Conversely, when the abrupt increase in modulus is dependent on temperature and diluent, the limiting factor is probably stress-induced crystallization.

Ultimate properties of toughness (energy to rupture), tensile strength, and maximum extensibility are all affected by strain-induced crystallization. In general, the higher the temperature the lower the extent of crystallization and consequently the lower these stress/strain related properties. There is also a parallel result brought about by the presence of increased amounts of diluent since this also discourages stress-related crystallization.

There are some so-called non-crystallizable networks where stress/strain behavior is fairly independent of diluent and temperature. One such system is formed from reaction of hydroxyl terminated polydimethylsiloxane, PDMS, through reaction with tetraethyl orthosilicate. While these materials are not particularly important commercially, they allow a testing of various effects in particular the so-called "weakest-link" theory where it is believed that rupture is initiated by the shortest chains because of their limiting extensibility. From such studies it was found that at long extensions that short chains, that should be the "weakest-link" or more aptly put, the "shortest-link," was not the limiting factor but rather the system "shared" the distortion throughout the network distributing the strain. This redistributing continues until no further distributing is possible at which case stress-induced rupture occurs. Introduction of short or limiting chains has a positive affect on the modulus related properties because shorter chains are better at distributing induced strain.

We are now able to construct so-called bimodal network systems composed of short and long (average length between crosslinks) chains and multimodel systems containing chains of predetermined differing lengths. It has been found that short chains are better at reapportioning applied stress/strain than longer chains so that greater elongation is required to bring about the “upturn” in modulus. In general, the stress strain curve for short chains is steeper than that for long chain networks as expected. Interestingly, a combination of short and long chained networks gives a stress strain curve that is between the one found for short chained networks and the one for long chained networks such that the area under the stress/strain curve, toughness, is much greater than for either of the monomodal systems. Products are being developed to take advantage of this finding.

Mismatching is important for some applications. Thus polar materials such as polyisoprene are ideal materials for hose construction where the liquid is nonpolar such as gasoline, flight fuel, lubricants, oils, etc., while nonpolar materials such as polyethylene intense copolymers would be suitable for use with transport and containment of polar liquids such as water.

Fillers are often added to polymeric networks. In particular, those elastomers that do not undergo strain-induced crystallization generally have some reenforcing filler added. The important cases involve carbon black that is added to many materials including natural rubber, and silica that is added to siloxane elastomers. These fillers generally give the materials increased modulus, tear and abrasion resistance, extensibility, tensile strength, and resilience. Counter, they often create other effects such as giving the materials generally a higher hysteresis (heat build up when the material is exposed to repeated cycles of stress/strain) and compression set (permanent deformation).

9.8 GENERAL INFORMATION ON BLOCK AND GRAFT COPOLYMERS

Unlike mixtures that may be separated, the copolymers that cannot be separated into components may consist of sequences of polymers with diverse properties. For example, block or graft copolymers of styrene and methacrylic acid are soluble in both polar and nonpolar solvents. The acrylic acid chains are extended in the former but are coiled in nonpolar solvents. Each segment of the chain or each long branch exhibits its own characteristic properties. Thus, the copolymer will not only exhibit different conformations in solvents but will have characteristic glass transition temperatures.

Elastomeric fibers and thermoplastic elastomers have been produced by controlling the size and flexibility of the domains in block and graft copolymers. These techniques have opened up new fields for the tailor-making of functional polymers.

ABS copolymers, based on a wide variety of formulations, are produced at an annual rate of over 500,000 tons. Some of these high-performance plastics are graft copolymers, but most are empirically developed blends of polystyrene and nitrile rubber [poly (butadiene-co-acrylonitrile)].

9.9 POLYMER MIXTURES—IPNs, COMPOSITES, BLENDS, AND ALLOYS

Copolymers are polymers composed of two or more different mer units. When such different mers occur in a random or alternating fashion, where the sequence of like mer units is small (generally less than six), the resulting physical properties are some average of the properties of each mer and the influence of surrounding like and unlike mers on each other. Such copolymers offer single physical responses such as having a single glass transition temperature. Examples of such copolymers include statistical, random, periodic, alternating, and block (for short blocks) copolymers.

There are also a number of polymer combinations where larger groupings of like mers or similar sequences of mers are chemically connected to one another. In these cases the various chain segments may act somewhat independent of one another such that the bulk material exhibits two glass transition temperatures or responds as a brittle material and as a tough material under different physical influences. While there is no common length of sequence that will "guarantee" this dualistic behavior, mer sequences of greater than about 10 are typically required. Terms such as star, block, graft, and starblock are common for such copolymers (Fig. 9.2). These copolymers may also exist as three-dimensional networks.

There also exist a number of polymer combinations that are linked together through secondary forces. This grouping includes interpenetrating polymer networks and polymer blends. These may be called "physical" copolymers.

On solidification, most small molecules crystallize with "their own," obeying the saying "like likes like" (see Sec. 17.2). Thus a solution containing benzoic acid and para-dichlorobenzene upon evaporation will produce mainly crystals of benzoic acid and crystals of para-dichlorobenzene and not crystals containing a mix of the two. Polymers, because of their large size and high viscosity, can be mixed and allowed to solidify such that solids consisting of combinations of different polymers can be achieved. This mixing or blending can give materials with properties similar to short sequenced copolymers or quite different, depending on the particular blend or property. Compatible blends exist as a single phase, whereas incompatible blends exist as two phases. Compatibilizing agents and other additives have been used to assist in the formation of blends.

Whether a particular polymer blend will be homogeneous (i.e., one phase) or phase-separated, or some combination, is dependent on many factors including the particular polymers, relative concentrations of the polymers, mixing process, processing conditions, and the presence of other additives including solvents. In theory, at equilibrium, mixing can be described in terms of the Gibbs free energy relationship for mixing at constant temperature as follows.

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{9.22}$$

When ΔG_m is positive over the entire composition range the two polymers separate into two phases so that each contains only one of the polymers (pure phase separation). For the polymers to form a homogeneous blend ΔG_m must be negative and the second derivative of ΔG_m with respect to volume fraction of the components must be greater than zero over the entire composition range. If ΔG_m is negative, but the second derivative of ΔG_m with respect to the volume fraction is not greater than zero, then the mixture separates into two phases, each containing some of both polymers. In real practice, equilibrium conditions are seldom achieved with polymer mixtures, but this thermodynamic approach predicts tendencies for two component polymer mixes.

In practice, most polymer pairs are immiscible because of the small entropy change that is associated with the mixing of two macromolecules. [By comparison, the entropy change associated with the mixing of two small molecules is much larger because of the much larger combinatorial arrangements associated with units that freely move without

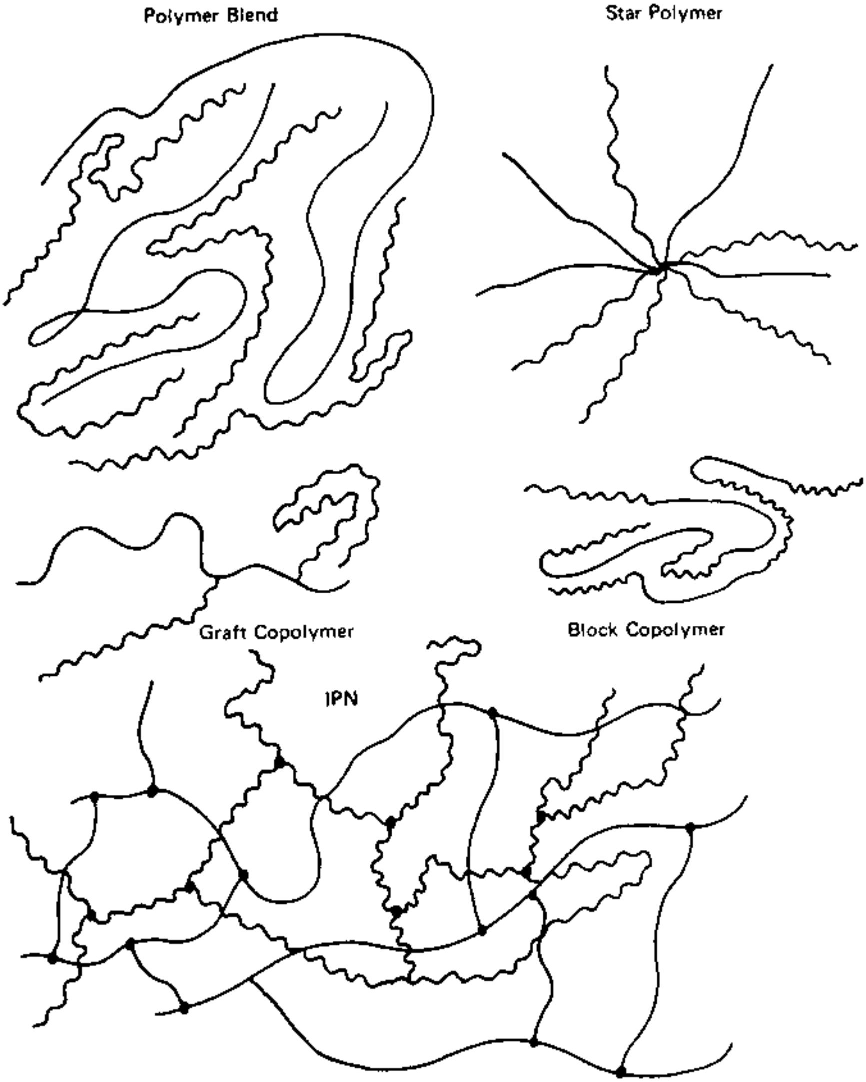


Figure 9.2 Polymer mixtures.

regards of nearest (connected) neighboring units. This small entropy change associated with polymer mixing is similar to the small entropy change associated with the dissolving of polymers where the result is that polymers are generally soluble in a smaller number of liquids than are smaller molecules with similar chemical and physical characteristics.]

Two-phase blends are often described in terms of a continuous phase and a dispersed phase. At times it is difficult to tell which is which. The impact strength of brittle materials can be improved by addition of a rubbery phase. Provided that the adhesion between the two phases is good, the rubber phase can provide an energy absorbing ability. Thus, a brittle polymer such as polystyrene (PS) can be given improved impact strength by addition of small dispersed particles of the rubber polybutadiene. Adhesion between the two phases is improved through graft polymerization of butadiene with the PS. This material is called high-impact polystyrene (HIPS). Its toughness is dependent on a dispersion of flexible elastomer molecules in a rigid polystyrene matrix. These blends may be made by mixing solutions or lattices of the components and by melt-mixing a mixture of the finely divided polymers. Thus HIP is a two-phase blend in which a graft copolymer is formed at the interface between the PS matrix and dispersed SBR or BR elastomer particles.

Nylon-phenolic blends are used as ablative heat shields on space vehicles during reentry when surface temperatures of several thousand degrees are attained.

ABS thermoplastics have a two-phase morphology consisting of elastomer particles dispersed in a styrene-acrylonitrile (SAN) copolymer matrix. Today the term *polymer alloy* is often applied to such rubber-toughened materials in which the matrix can be a mixture of polymer types.

ABS alloys with PVC, polyurethane (PU), and polycarbonate (PC) are widely used. The processing difficulties of poly(phenylene oxide) (PPO) are lessened by blending with PS. Elastomers and thermoplastic elastomers (TPEs) have been used to flexibilize polyolefins and nylons. Many useful blends have also been developed empirically because of material shortages or the need to meet unusual specifications. For example, the use of blends of natural, synthetic, and reclaimed elastomers and thermoplastics is standard practice in the rubber industry.

Interpenetrating polymer networks (IPNs) are described by Sperling to be an intimate combination of two polymers, both in network form, where at least one of the two polymers is synthesized and/or crosslinked in the immediate presence of the other. This is similar to taking a sponge cake, soaking in it warm ice cream, and refreezing the ice cream, resulting in a dessert (or mess) that has both spongy and stiff portions.

Such IPNs, grafts, blocks, and blends offer synergistic properties that are being widely exploited. Applications include impact-resistant plastics, specialty coating, adhesives, and thermoplastic elastomers. New combinations are being studied.

Composites consist of a continuous phase and a discontinuous phase. The difference between a blend and a composite is the size scale. Blends are mixtures of different polymer chains on a molecular level, whereas composites can be considered as mixtures on a macroscopic level. Fiber-reinforced materials are the major type of commercial composite. Examples include plywoods which are wood laminates bonded with a resin, usually PF and amino resins; particle boards made from waste-wood chips; and fiberglass. The topic of composites is discussed further in Chapter 13.

There continue to emerge new materials to meet new needs. Following is a brief description of some of these. Simultaneous interpenetrating networks (SINs) are products in which the connection of two differing materials occurs simultaneously.

A plastic or polymer alloy is a physical mixture of two or more polymers in a melt. While some crosslinking may occur, such materials are generally not viewed as copolymers, though they are presented in this chapter. Alloys using ABS are common.

Another new area of work involves fuzzy, cotton-ball-like polymers with sizes between those of small molecules and very large super macromolecules. These new materials have been given many names, including dendrites, superatoms, and mesoscopic materials. The size, shape, flexibility, and length of the "arms," hardness of the core, etc., can be varied depending on the need.

"Smart materials" (see Sec. 18.5) are materials whose response varies depending on a specific input. These include specifically compounded, blended, etc., materials such as HIPs, IPNs, and Silly Putty that react to external stress and strain dependent on the "interaction time." Today's smart material efforts are focused on piezoelectronic-embedded ceramics and organic polymers where electricity is generated as they are compressed and bent and where they will bend and twist as an electrical charge is passed through them.

9.10 DENDRITES

Along with the structures shown in Fig. 9.2, there exist other structurally complex molecules called dendrites. These molecules can act as spacers, ball-bearings, and building blocks for other structures. Usually they are wholly organic or contain metal atoms. They may or may not be copolymers depending on the particular synthetic route employed in their synthesis.

While some make a distinction between dendrimers and hyperbranched polymers, we will not do so here. In essence, hyperbranched polymers are formed under conditions that give a variety of related but different structures while dendrimers are formed one step at a time giving a fairly homogeneous product.

Dendrites are highly branched, usually curved, structures. The name comes from the Greek word for tree, *dendron*. Another term often associated with these structures is dendrimers, describing the oligomeric nature of many dendrites. Because of the structure, dendrites can contain many terminal functional groups for each molecule that can be further reacted. Also, most dendrites contain unoccupied space that can be used to carry drugs, fragrances, adhesives, diagnostic molecules, cosmetics, catalysts, herbicides, and other molecules.

The dendrite structure, is determined largely by the functionality of the reactants. The dendrite pictured in Fig. 9.3 can be considered as being derived from a tetrafunctional

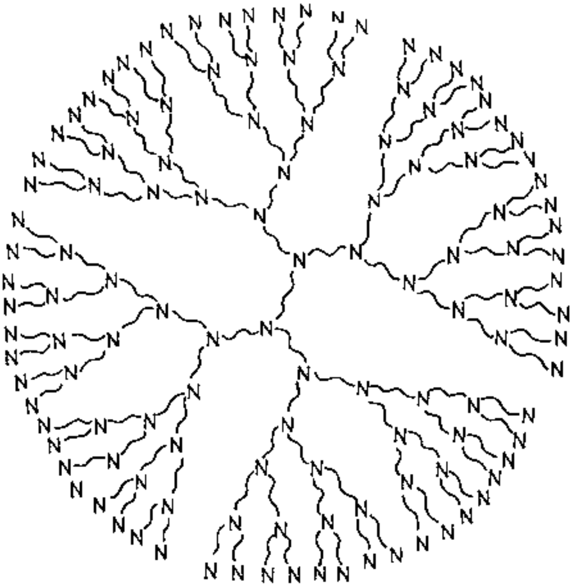


Figure 9.3 Dendrite structure derived from the reaction of 1,4-diaminobutane and acrylonitrile.

monomer formed from the reaction of 1,4-diaminobutane and acrylonitrile. The resulting polypropylenimine dendrimer has terminal nitrile groups that can be further reacted extending the dendrimer or terminating further dendrimer formation. The resulting molecule is circular with some three-dimensional structure. The dendrimer shown in Fig. 9.4 is derived from difunctional reactants that are bent so as to encourage fan-like expansion rather than the typical linear growth.

Numerous approaches have been taken in the synthesis of dendrites or dendrimers. These approaches can be divided into two groups. In divergent dendrimer growth, growth occurs outward from an inner core molecule (Fig. 9.3). In convergent dendrimer growth, developed by Frechet and others, various parts of the ultimate dendrimer are separately synthesized and then they are brought together to form the final dendrimer.

The somewhat spherical shape of dendimers gives them some different properties in comparison to more linear macromolecules. On a macroscopic level, dendimers act as ball-bearings rather than strings. In solution, viscosity increases as molecular weight increases for linear polymers. With dendimers, viscosity also increases with molecular weight up to a point after which viscosity decreases as molecular weight continues to increase.

Dendimers are being used as host molecules, catalysts, self-assembling nano-structures; analogues of proteins, enzymes, and viruses; and in analytical applications including ion exchange displacement chromatography and electrokinetic chromatography.

We are continuing to recognize that polymer shape is important in determining material property. Another group of structurally complex shapes is referred to as “stars.”

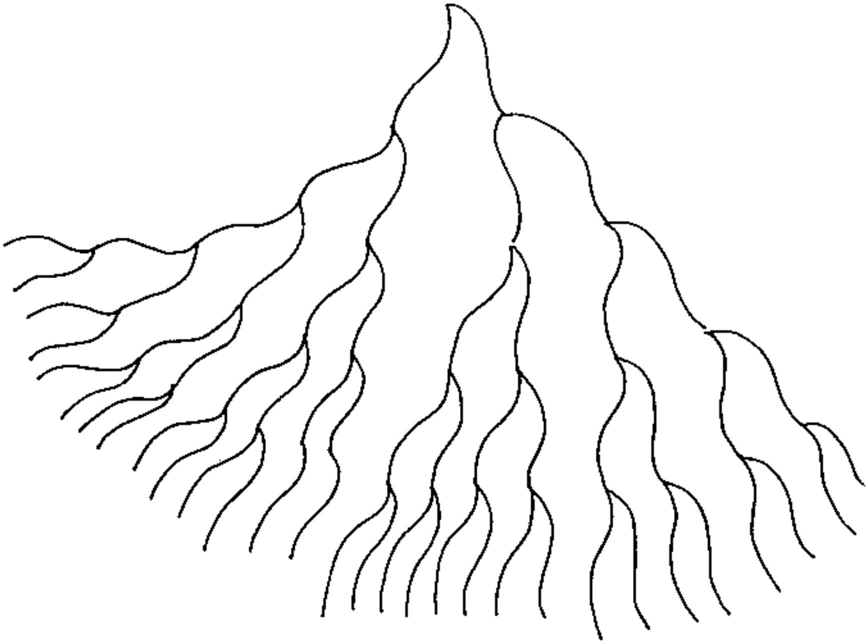
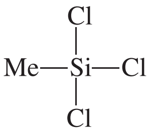


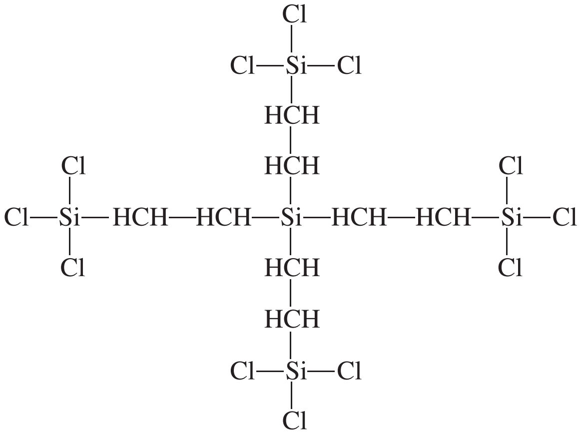
Figure 9.4 Dendrite structure derived from bent difunctional reactants.

There are a number of synthetic routes to star polymers. Fetters and co-workers developed a number of star polymers based on chlorosilanes. For instance, 3-, 12-, and 18-arm star polymers can be formed as shown below.



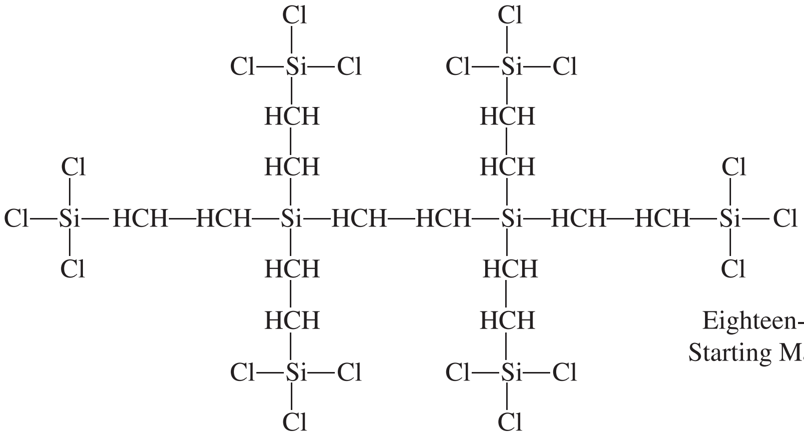
$$\begin{array}{ccc} & \mathrm{Cl} & \\ & | & \\ \mathrm{Me}- & \mathrm{Si} & -\mathrm{Cl} \\ & | & \\ & \mathrm{Cl} & \end{array}$$

Three-Arm Starting Material (9.23a)



$$\begin{array}{ccccccc}
 & & & \mathrm{Cl} & & & \\
 & & & | & & & \\
 & & & \mathrm{Cl{-}Si{-}Cl} & & & \\
 & & & | & & & \\
 & & & \mathrm{HCH} & & & \\
 & & & | & & & \\
\mathrm{Cl} & & & \mathrm{HCH} & & & \mathrm{Cl} \\
| & & & | & & & | \\
\mathrm{Cl{-}Si} & -\mathrm{HCH} & -\mathrm{HCH}- & \mathrm{Si} & -\mathrm{HCH} & -\mathrm{HCH}- & \mathrm{Si{-}Cl} \\
| & & & | & & & | \\
\mathrm{Cl} & & & \mathrm{HCH} & & & \mathrm{Cl} \\
 & & & | & & & \\
 & & & \mathrm{HCH} & & & \\
 & & & | & & & \\
 & & & \mathrm{Cl{-}Si{-}Cl} & & & \\
 & & & | & & & \\
 & & & \mathrm{Cl} & & &
\end{array}$$

Twelve-Arm
Starting Material (9.23b)



$$\begin{array}{cccccccccc}
 & & & \mathrm{Cl} & & & \mathrm{Cl} & & & \\
 & & & | & & & | & & & \\
 & & & \mathrm{Cl{-}Si{-}Cl} & & & \mathrm{Cl{-}Si{-}Cl} & & & \\
 & & & | & & & | & & & \\
 & & & \mathrm{HCH} & & & \mathrm{HCH} & & & \\
 & & & | & & & | & & & \\
\mathrm{Cl} & & & \mathrm{HCH} & & & \mathrm{HCH} & & & \mathrm{Cl} \\
| & & & | & & & | & & & | \\
\mathrm{Cl{-}Si} & -\mathrm{HCH} & -\mathrm{HCH}- & \mathrm{Si} & -\mathrm{HCH} & -\mathrm{HCH}- & \mathrm{Si} & -\mathrm{HCH} & -\mathrm{HCH}- & \mathrm{Si{-}Cl} \\
| & & & | & & & | & & & | \\
\mathrm{Cl} & & & \mathrm{HCH} & & & \mathrm{HCH} & & & \mathrm{Cl} \\
 & & & | & & & | & & & \\
 & & & \mathrm{HCH} & & & \mathrm{HCH} & & & \\
 & & & | & & & | & & & \\
 & & & \mathrm{Cl{-}Si{-}Cl} & & & \mathrm{Cl{-}Si{-}Cl} & & & \\
 & & & | & & & | & & & \\
 & & & \mathrm{Cl} & & & \mathrm{Cl} & & &
\end{array}$$

(9.23c)

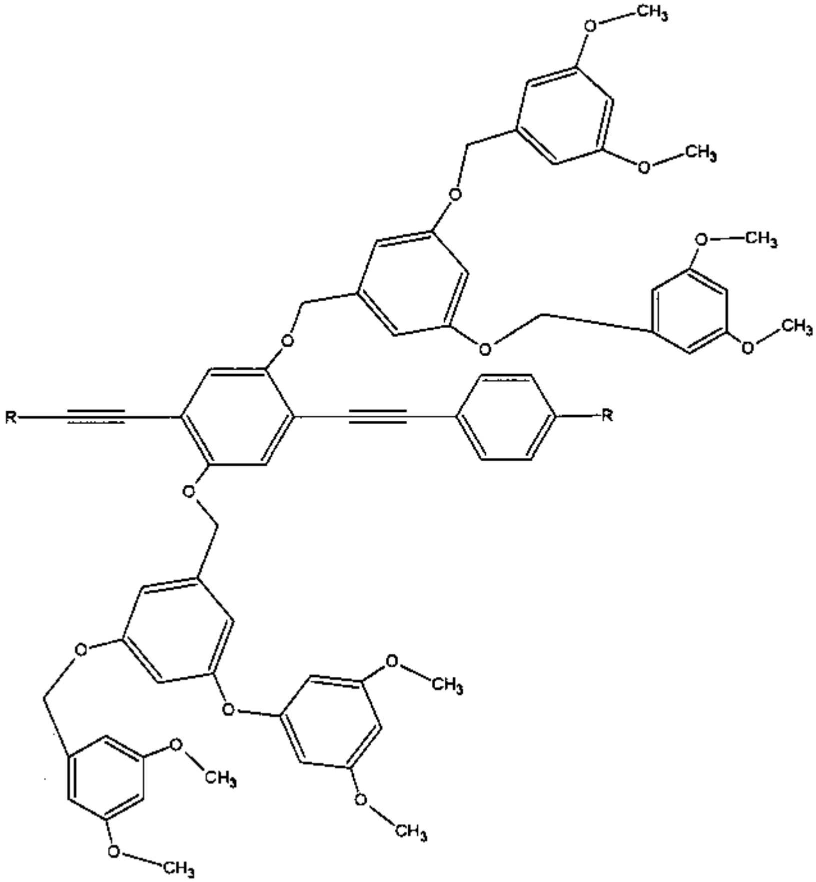
Eighteen-Arm
Starting Material

These arms are now reacted with other reactants such as living polystyrene or polybutadiene giving now the star polymers with the silicon-containing inner core and polymer outer core. Through control of the length of the grafted polystyrene or other reactant, the size of the "star" can be controlled.

For dendrimers made using flexible arms the core is mobile and depending upon the situation spends some time near the outer layer of the dendrimer sphere. Counter, stiff, rigid arms produce a dendrimer that "holds" its core within the interior of the dendrimer.

The term "generation" describes the number of times "arms" have been extended. The nature of each generation can be varied so that mixtures of steric requirements and hydrophobic/hydrophilic character can be introduced offering materials with varying structures and properties. By varying the hydrophobic and hydrophilic interactions and steric nature of the arms secondary and tertiary structural preferences can be imposed on the dendrimer.

The dendrite structure can be used as a synthetic tool to craft a particular property into an overall structure. For instance, the below structure is a combination of a conducting rigid rod backbone with dendritic structures radiating from the rigid rod. The backbone collects photons of visible light in the range of 300 to 450 nm. The dendritic envelope collects light in the ultraviolet region from 220 to 300 nm and transfers it to the backbone that then fluoresces blue light at 454 nm. Unprotected poly(phenyleneethynylene), the non-dendritic backbone alone, does emit light but suffers from both being brittle and from collisional quenching. The dendrimer product allows both flexibility and discourages collisional quenching by forcing a separation between the backbone rods. This shielding increases with each successive generation of the dendritic wedge. The structure shown is a first generation dendrimer wedge.



(9.24)

9.11 IONOMERS

Ionomers are ion-containing copolymers typically containing over 90% (by number) ethylene units, with the remaining being ion-containing units such as acrylic acid. These ionic sites are connected through metal atoms. Ionomers are often referred to as processable thermosets. They are thermosets because of the crosslinking introduced through the interaction of the ionic sites with metal ions. They are processable or exhibit thermoplastic behavior because they can be reformed through application of heat and pressure.

As with all polymers, the ultimate properties are dependent on the various processing and synthetic procedures to which the material is exposed. This is especially true for ionomers where the location, amount, nature, and distribution of the metal sites strongly determine the properties. Many industrial ionomers are made where a significant fraction of the ionomer is unionized and where the metal-containing reactants are simply added to the preionomer followed by heating and agitation of the mixture. These products often offer superior properties to ionomers produced from fully dissolved preionomers.

Bonding sites are believed to be of two different grouping densities. One of these groupings involves only a few or individual bondings between the acid groups and the metal atoms as pictured in Fig. 9.5. The second bonding type consists of large concentrations of acid groups with multiple metal atoms (clusters) as pictured in Fig. 9.6. This metal–acid group bonding (salt formation) constitutes sites of cross-linking. It is believed that the processability is a result of the combination of the movement of the ethylene units and the metal atoms acting as ball bearings. The sliding and rolling is believed to be a result of the metallic nature of the acid–metal atom bonding. (Remember that most metallic salts are believed to have a high degree of ionic, nondirectional bonding as compared with typical organic bonds where there is a high amount of covalent, directional bonding.) Carraher and co-workers have shown that the ethylene portions alone are sufficient to allow ionomers to be processed through application of heat and pressure.

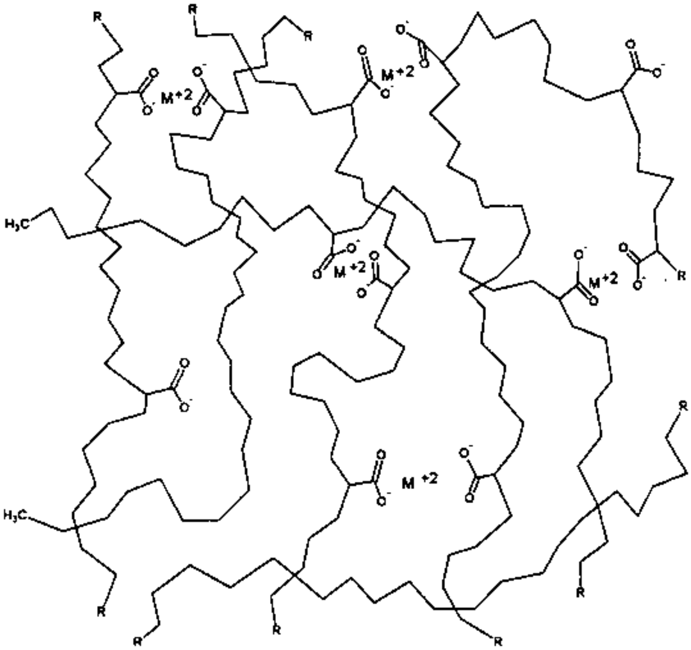


Figure 9.5 Ionomer bonding showing individualized bonding sites.

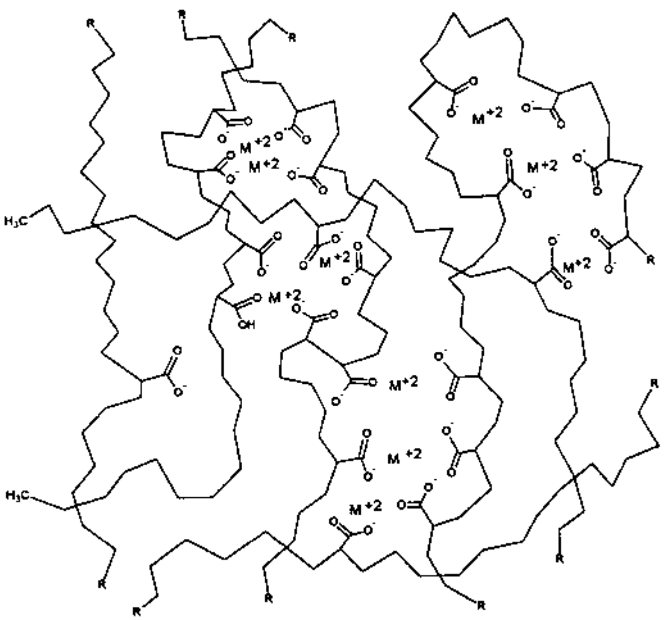


Figure 9.6 Ionomer bonding showing cluster bonding sites.

Ionomers are generally tough and offer good stiffness and abrasion resistance. They offer good visual clarity, high melt viscosities, superior tensile properties, good oil resistance, and are flame retarders. They are used in the automotive industry in the formation of exterior trim and bumper pads, in the sporting goods industry as bowling pin coatings and golf ball covers, and in the manufacture of roller skate wheels and ski boots. Surlyn [duPont; poly(ethylene-co-methacrylic acid)] is used in vacuum packaging for meats, in skin packaging for hardware and electronic items (e.g., seal layers and foil coatings of multiwall bags), and in shoe soles.

Sulfonated EPDM are formulated to form a number of rubbery products including adhesives for footwear and garden hoses. Perfluorinated ionomers marketed as Naflon (duPont) are used for membrane applications including chemical processing separations, spent acid regeneration, electrochemical fuel cells, ion-selective separations, electrodialysis, and in the production of chlorine. They are employed as solid state catalysts in chemical synthesis and processing, and are also used in blends with other polymers.

SUMMARY

1. Unlike homopolymers, which consist of chains with identical repeating units, copolymers are macromolecules with more than one repeating unit in the same molecule. These repeating units may be randomly arranged or they may alternate in the chain. Block copolymers are linear polymers that consist of long sequences of repeating units in the chain, and graft copolymers are branch polymers in which the branches consist of sequences of repeating units that differ from those in the backbone.

2. In the special case of azeotropic copolymerization, the composition of the copolymer is identical to that of the feed. However, copolymer compositions usually differ because of the difference in reactivity ratios or rates at which the different monomers add to macroradicals with similar end groups. The composition of the copolymer may be estimated from the copolymer equation:

   $$n = \frac{r_1 x + 1}{(r_2/x) + 1}$$

   where n and x are the molar ratios of the monomer in the copolymer and feed, respectively, and r_1 and r_2 are the reactivity ratios.
3. The product of the reactivity ratios r_1r_2 may be used to estimate the relative randomness of the copolymer. When $r_1r_2 \simeq 1$, the copolymer arrangement is random, and when $r_1r_2 \simeq 0$, the arrangement is alternating. The latter is the result of the homopolymerization of charge-transfer complexes which are unstable at elevated temperatures.
4. Strongly electrophilic or nucleophilic monomers will polymerize exclusively by anionic and cationic mechanisms. Those like styrene and methyl methacrylate, which are neither strong electrophiles nor nucleophiles, also polymerize by free radical mechanisms. Since these two monomers also polymerize by ionic mechanisms, the reactivity ratios for all three systems may be compared.
5. The Q-e scheme, in which Q is related to reactivity and e to polarity, may be used to predict reactivity ratios:

   $$r_1 = \frac{K_{11}}{k_{12}} = \frac{Q_1}{Q_2} e^{-e_1(e_1 - e_2)}$$

   Styrene, which is assigned a Q value of 1.00 and an e value of -0.80, is used as the comparative reference for determining Q-e values for other monomers.
6. The principal copolymers are SBR, butyl rubber, poly(vinyl chloride-co-vinyl acetate), Saran, ionomers, and Acrilan fibers.
7. Block and graft copolymers differ from mixtures but having the properties of each component. Thus, block copolymers may be used as thermoplastic elastomers and graft copolymers with a flexible backbone may be used for high-impact plastics.
8. Block and graft copolymers may be produced by step reaction polymerization and by chain reaction polymerization.
9. The principal block copolymers are thermoplastic elastomers and elastic fibers. The principal graft copolymers are ABS, HIP, polyester plastics, and grafted starch and cellulose.

GLOSSARY

AB: A block copolymer with two sequences of mers.
ABA: A block copolymer with three sequences of mers in the order shown.
ABS: A three-component copolymer of acrylonitrile, butadiene, and styrene.
AIBN: Azobisisobutyronitrile.
alloy: Rubber-toughened materials in which the matrix can be a mixture of polymer types.

alternating copolymer: An ordered copolymer in which every other building unit is different:

$(\text{—}M_1M_2\text{—})_n$

azeotropic copolymer: Copolymer in which the composition is the same as that of the feed.

blends: Mixtures of different polymers on a molecular level; may exist as one or two phases.

block copolymer: A copolymer of long sequences or runs of one mer followed by long sequences of another mer $(M_1)_m \times (M_2)_n$.

buna-N: An elastomeric copolymer of butadiene and acrylonitrile.

buna-S: An elastomeric copolymer of butadiene and styrene.

butyl rubber: An elastomeric copolymer of isobutylene and isoprene.

charge-transfer complex: A complex consisting of an electron donor (D) and an electron acceptor (A) in which an electron has been transferred from D to A, i.e., (D^+, A^-).

composites: Mixtures, on a macroscopic level, of different polymers, one forming a continuous phase and another a discontinuous phase.

composition drift: The change in composition of a copolymer that occurs as copolymerization takes place with monomers of different reactivities.

copolymer: A macromolecule consisting of more than one type of building unit or mer.

copolymer equation:

$$n = \frac{d[M_1]}{d[M_2]} = \frac{r_1x + 1}{(r_2/x) + 1}$$

$\Delta\delta$: Difference in solubility parameters.

dendrites: Complex molecules that are highly branched, usually with a curved structure.

domains: Sequences in block copolymers.

Dynel: Trade name for a copolymer of vinyl chloride and acrylonitrile.

e: Polarity of monomers

EMP: Copolymer of ethylene and propylene.

EPDM: Abbreviation for a curable (vulcanizable) terpolymer of ethylene, propylene, and diene.

graft copolymer: A branched copolymer in which the backbone and the branches consist of different mers.

GRS: A name used for SBR during World War II.

Heveaplus: Trade name for block copolymers of methyl methacrylate and hevea rubber.

HIP: High-impact polystyrene.

homopolymer: A macromolecule consisting of only one type of building unit or mer.

Hytrel: Trade name for a commercial TPE.

ideal copolymer: A random copolymer, $r_1 = r_2$ and $r_1r_2 = 1$.

interpenetrating polymer network (IPN): Intimate combination of two polymers, both in network form, where at least one of the two polymers is synthesized and/or crosslinked in the immediate presence of the other.

ionomers: Copolymers typically containing mostly ethylene units, with the remaining units being ion containing, such as acrylic acid neutralized through reaction with metals.

k_{11}: Rate constant for the addition of M_1 to M_1.

Kraton: Trade name for an ABA block copolymer of styrene and butadiene.

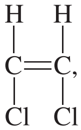
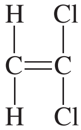
living polymers: A name used by Szwarc for macrocarbanions.

M_1: A macroradical with a chain end of M_1.
M_2: A macroradical with a chain end of M_2.
n: The molar ratio of mers M_1 and M_2 in a copolymer chain, i.e., M_1/M_2.
P: Reactivity or resonance effect of monomers.
Pliovic: Trade name for copolymers of vinyl chloride and vinylidene chloride.
Pluronics: Trade name for block copolymers of ethylene oxide and propylene oxide.
polyallomers: Block copolymers of ethylene and propylene.
polyester plastic: A name used to describe polymers produced by the polymerization of a solution of an unsaturated polyester in styrene.
Q: Reactivity or resonance effect of monomers.
Q-e scheme: A simiempirical method for predicting reactivity ratios.
r: Reactivity ratios.
r_1: k_{11}/k_{12}.
r_2: k_{22}/k_{21}.
r_1r_2: The product of the reactivity ratios which predict the extent of randomness in a copolymer chain. When r_1 and r_2 are similar and their product equals 1, the macromolecule is an ideal random copolymer.
random copolymer: A copolymer in which there is no definite order for the sequence of the different mers or building blocks ($—M_1M_2M_1M_1M_2M_1M_2M_2—$).
reactivity ratio (r): The relative reactivity of one monomer compared to another monomer.
Saran: Trade name for copolymers of vinylidene chloride and vinyl chloride.
SBR: The elastomeric copolymer of styrene and butadiene.
siloxane: $\left[\!-\mathrm{O{—}SiR_2{—}O}-\!\right]_n$
Solprene: Trade name for an AB block copolymer of styrene and butadiene.
Spandex: An elastic fiber consisting of a block copolymer of a polyurethane and a polyester.
TPE: Thermoplastic elastomer.
Vinoflex: Trade name for copolymers of vinyl chloride and vinyl isobutyl ether.
Vinylite: Trade name for copolymers of vinyl chloride and vinyl acetate.
Vinyon: Trade name for copolymers of vinyl chloride and acrylonitrile.
Wall equation: The predecessor to the copolymer equation.
x: Symbol for the molar of monomers in the feed, i.e., $[M_1]/[M_2]$.

EXERCISES

1. Draw representative structures for (a) homopolymers, (b) alternating copolymers, (c) random copolymers, (d) AB block copolymers, and (e) graft copolymers of styrene and acrylonitrile.
2. If equimolar quantities of M_1 and M_2 are used in an azeotropic copolymerization, what is the composition of the feed after 50% of the copolymer has formed?
3. Define r_1 and r_2 in terms of rate constants.
4. Do the r_2 and r_2 values increase or decrease during copolymerization?
5. What is the effect of temperature on r_1 and r_2?
6. What will be the composition of copolymers produced in the first part of the polymerization of equimolar quantities of vinylidene chloride and vinyl chloride?
7. What monomer may be polymerized by anionic, cationic, and free radical chain techniques?

8. Which chain polymerization technique would you select to polymerize (a) isobutylene, (b) acrylonitrile, and (c) propylene?
9. If $r_1r_2 \simeq 0$, what type of copolymer would be formed?
10. Show a structure for an AB block copolymer.
11. What is the value of r_1r_2 for an ideal random copolymer?
12. Which would polymerize more readily:

(a) 
$\mathrm{HClC{=}CHCl}$, or (b) 
$\mathrm{H_2C{=}CCl_2}$?

13. Explain why an equimolar mixture of styrene and maleic anhydride in decalin produces an alternating copolymer at 60°C and a random copolymer at 140°C.
14. What is the composition of the first copolymer chains produced by the copolymerization of equimolar quantities of styrene and methyl methacrylate in (a) free radical, (b) cationic, and (c) anionic copolymerization?
15. What is the composition of the first copolymer butyl rubber chains produced from equimolar quantities of the two monomers?
16. What is the composition of the first copolymer butyl rubber chains produced from a feed containing 9 mol of isobutylene and 1 mol of isoprene?
17. How would you ensure that production of butyl rubber of uniform composition in question 16?
18. Which would be more reactive in free radical polymerization: (a) p-methylstyrene or (b) m-methylstyrene?
19. What is the composition of the first polymer chains produced by the copolymerization of equimolar quantities of vinyl chloride and vinyl acetate?
20. What are the advantages, if any, of the vinyl chloride–vinyl acetate copolymer over PVC?
21. Why are ionomers superior to LDPE?
22. What is the difference between buna-S, GRS, and SBR?
23. What do the acrylonitrile comonomers, acrylic acid, acrylamide, vinylpyridine, and vinylpyrrolidone have in common?
24. Which sequence in the ABA block copolymer of ethylene oxide and propylene oxide is lyophilic?
25. What is the advantage of TPE, if any, over hevea rubber?
26. What is the advantage, if any, of the hydrogenated over the unhydrogenated ABA block copolymer of styrene-butadiene-styrene?
27. What product is obtained if 1.5 mol of styrene is copolymerized with 1 mol of maleic anhydride of benzene?
28. What precautions must be taken when making articles such as boats from fibrous glass-reinforced polyester plastics?
29. Are so-called polyester plastics crosslinked?
30. How could you use graft copolymerization techniques to reduce the water solubility of starch.
31. What is the end group when azobiscyanopentanoic acid is used as an initiator?

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10

Naturally Occurring Polymers

One of the strongest, most rapidly growing areas of polymer chemistry is that involving natural polymers. Our bodies are largely composed of polymers: DNA, RNA, proteins, and polycarbohydrates. These are related to aging, awareness, mobility, strength, and so on, i.e., all of the characteristics that contribute to our being alive and well. Many medical, health, and biological projects and advances are concerned with materials which are, at least in part, polymeric. There is an ever-increasing emphasis on molecular biology, i.e., chemistry applied to natural systems. Thus, an understanding of polymeric principles is advantageous to those desiring to pursue a career related to their natural environment.

Physically there is no difference in the behavior, study, or testing of natural and synthetic polymers, and information techniques suitable for application to synthetic polymers are equally applicable to natural polymers.

While the specific chemistry and physics dealing with synthetic polymers are complicated, the chemistry and physics of natural polymers are even more complex, complicated by a number of related factors, including (1) the fact that many natural polymers are composed of different, often similar, repeat units; (2) a greater dependency on the exact natural polymer environment; (3) the question of the real structure of the natural polymer in its natural environment; and (4) the fact that polymer shape and size are even more important to natural polymers than to synthetic polymers.

Industrially we are undergoing a reemergence of the use of natural polymers in many new and old areas. Since natural polymers are typically regenerable resources, nature can continue to synthesize as we harvest them. Many natural polymers are also present in large quantities. For instance, cellulose makes up about one-third of the bulk of the entire vegetable kingdom, being present in corn stocks, tree leaves, carrot tops, grass, and so on. With the realization that we must conserve and regulate our chemical resources comes from the awareness that we must find substitutes for resources that are not self-generating, such as oil, gas, and metals—thus, the underlying reason for the increased emphasis in polymer chemistry toward the use and modification of natural, regenerable polymers by industry.

The recognition that the supply of petroleum and coal is limited and relatively costly has led to an emphasis on natural, renewable materials as replacements or substitutes for product materials now derived from petroleum and coal. Also, renewable resources have valuable and sometimes different properties of their own.

Natural feedstocks must serve many human purposes. Carbohydrates as raw materials are valuable due to their actual or potential nutritional value. For example, protein plants are already utilizing rapidly reproducible bacteria that metabolize cellulose wastes. Thus, bacteria are added to a nutrient broth emphasizing cellulose; the bacteria feed on the mixture, converting it to more protein-rich bacteria; the bacteria are harvested and used as a protein feed meal. However, there is potentially available enough renewable carbohydrate to serve both food and polymer needs, and research into the modification of carbohydrates must continue at an increased rate.

When plant or animal tissues are extracted with nonpolar solvents, a portion of the material dissolves. The components of this soluble fraction are called lipids and include fatty acids, triacylglycerols, waxes, terpenes, prostaglandins, and steroids. The insoluble portion contains the more polar plant and animal components and crosslinked materials, including carbohydrates, lignin, proteins, and nucleic acids.

There are numerous natural materials and many ways to partition such materials. Table 10.1 contains one such listing along with suitable general subheadings. Table 10.2 lists a number of natural products as a function of general availability.

Finally, many potential renewable feedstocks are currently summarily destroyed or utilized in a noneconomical manner. Thus leaves and other plantstocks are “ritualistically” burned each fall. A number of these seemingly useless natural materials have already been utilized as feedstock sources for industrial products and more should be included.

Biological polymers represent successful strategies that are being studied by scientists as avenues to different and better polymers and polymer structure control. Sample “design rules” and approaches that are emerging include the following:

Identification of mer sequences that give materials with particular properties
Identification of mer sequences that key certain structural changes
Formation of a broad range of materials with a wide variety of general/specific properties and function (such as proteins/enzymes) through a controlled sequence assembly from a fixed number of feedstock molecules (proteins: about 20 different amino acids; five bases for nucleic acids; and two sugar units)
Integrated, in situ (in cells) polymer production with precise nanoscale control
Repetitive use of proven strategies with seemingly minor structural differences but resulting in quite divergent results (protein for skin, hair, and muscle)
Control of polymerizing conditions that allow steady state production far from equilibrium

There often occurs a difference in mind-set between the nucleic acid and protein biopolymers covered in this chapter and other biopolymers and synthetic polymers covered in other chapters. Nucleic acids and proteins are site specific with one conformation. Generally, if it differs from that specific macromolecule called for it is discarded. Nucleic acids and proteins are not a statistical average, but rather a specific material with a specific chain length and conformation. By comparison, synthetic and many other biopolymers

Table 10.1 Renewable Natural Material Groupings

- *Alkaloids*
  - Pyrrolidine, pyridine, pyrrolizidine, tropane
  - Quinolizidine, isoquinoline, piperidine, indole
  - Quinoline, quinazoline, acridone, steroidal, terpenoid
- *Amino acids*
- *Carbohydrates*
  - Simple (glucose, sucrose, fructose, lactose, galactose)
  - Complex (starch, cellulose, glycogen)
- *Drying oils and alkyd resins*
  - Linseed, cottonseed, castor, tung, soybean, oiticica, perilla, menhaden, sardine, corn, safflower, vernonia
  - Fossil resins—amber, kauri, congo
  - Oleoresins—damar, ester gum
- *Fungus, bacteria, and metabolites*
- *Heme, bile, and chlorophylls*
- *Lignins*
- *Lipids*
  - Simple (glycerol esters, cholesterol esters)
  - Phosphoglycerides
  - Sphingolipids (mucolipids, sulfatide, sphingomyelin, cerebroside)
  - Complex (lipoproteins, proteolipids, phosphatidopeptides)
- *Phenolic plant products*
  - Phenols, resorcinols, anthraquinones, naphthoquinones, hydrangenol, stilbenes, coumarins
- *Polyisoprenes*
- *Proteins*
  - Enzymes (lysozome, trypsin, chymotrypsin)
  - Transport and storage (hemoglobin, myoglobin)
  - Antibodies
  - Structural (elastin, actin, keratin, myosin, collagen, fibroin)
  - Hormones (insulin)
- *Purines, pyrimidines, nucleotides, nucleic acids*
- *Steroids*
  - Cholesterol, adrenocortical, bile acids
  - Ergosterol, agnosterol, desmosterol
- *Tannins*

Source: Carraher and Sperling, 1983. Used with permission.

are statistical averages of chain lengths and conformations. The distributions are often kinetically/thermodynamically driven.

This difference between the two divisions of biologically important polymers is also reflected in the likelihood that there are two molecules with the exact same structure. For molecules such as polysaccharides and those based on terpene-like structures the precise structures of individual molecules vary, but for proteins and nucleic acids the structures are identical from molecule to molecule. This can be considered a consequence of the general function of the macromolecule. For polysaccharides, the major, though not the sole functions, are energy and structural. For proteins and nucleic acids, main functions include memory and replication, in additional to proteins sometimes also serving a structural function.

Table 10.2 Relative Availability of Assorted Natural Products

- Small-scale (biomedical, catalysis)
  - Alkaloids
  - Heme, bile, and chlorophylls
  - Phenolic plant products
  - Steroids
  - Tannins
- Medium- (many with potential for large-) scale
  - Amino acids
  - Fungus, bacteria
  - Lipids
  - Proteins (specific)
  - Purines, pyrimidines, nucleotides, nucleic acids
- Large-scale
  - Carbohydrates
  - Drying oils, alkyd resins
  - Lignins
  - Polyisoprenes
  - Proteins (general)
  - Terpenes and terpenoids

Source: Carraher and Sperling, 1983. Used with permission.

Another difference between proteins and nucleic acids and other biopolymers and synthetic polymers involves the influence of stress–strain activities on the material's properties. Thus, application of stress on many synthetic polymers and some biopolymers encourages realignment of polymer chains and regions often resulting in a material with greater order and strength. Counter, application of stress to certain biopolymers, such as proteins and nucleic acids, causes a decrease in performance (through denaturation, etc.) and strength. For these biopolymers, this is a result of the biopolymer already existing in a compact and "energy favored" form and already existing in the "appropriate" form for the desired performance. The performance requirements for the two classifications of polymers is different. For one set, including most synthetic and some biopolymers, performance behavior involves response to stress–strain application with respect to certain responses such as chemical resistance, absorption enhancement, and other physical properties. By comparison, the most cited performances for nucleic acids and proteins involves selected biological responses requiring specific interactions occurring within a highly structured environment that demands specific shape and electronic requirements.

10.1 POLYSACCHARIDES

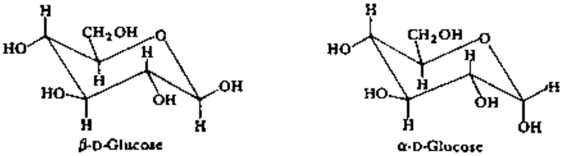
Carbohydrates are the most abundant organic compounds, constituting three-fourths of the dry weight of the plant world. They represent a great storehouse of energy as a food for humans and animals. About 400 billion tons of sugars is produced annually through natural photosynthesis, dwarfing the production of other natural products, with the exception of lignin. Much of this is produced in the oceans, pointing out the importance of harnessing his untapped source of food, energy, and renewable feedstocks.

The potential complexity of even the simple aldohexose monosaccharides is indicated by the presence of five different chiral centers, giving rise to 2^5 or 32 possible stereoisomeric forms of the basic structure, two of which are glucose and mannose. While these sugars differ in specific biological activity, their gross chemical reactivities are almost identical, permitting one to often employ mixtures within chemical reactions without regard to actual structure with respect to most physical properties of the resulting product.

Carbohydrates are diverse with respect to both occurrence and size. Familiar mono- and disaccharides include glucose, fructose, sucrose (table sugar), cellobiose, and mannose. Familiar polysaccharides are listed in Table 10.3 along with their natural sources, purity, molecular weight, amount, and location of source. For instance, cotton is a good source of cellulose, yet the amount of cellulose varies from 85% to 97% depending on the variety

Table 10.3 Naturally Occurring Polysaccharides

Polysaccharide	Source	Monomeric sugar unit(s)	Structure	Mol. wt.
Amylopectin	Corn, potatoes	D-Glucose	Branched	10^6–10^7
Amylose	Plants	D-Glucose	Linear	10^4–10^6
Chitin	Animals	2-Acetamidoglucose		
Glycogen	Animals (muscles)	D-Glucose	Branched	$>10^8$
Inulin	Artichokes	D-Fructose	Linear (largely)	10^3–10^6
Mannan	Yeast	D-Mannose	Linear	—
Cellulose	Plants	D-Glucose	Linear (2D)	10^6
Xylan	Plants	D-Xylose	Linear (largely)	—
Lichenan	Iceland moss	D-Glucose	Linear	10^5
Galactan	Plants	D-Galactose	Branched	10^4
Arabinoxylan	Cereal grains	L-Arabinofuranose linked to xylose chain	Branched	$>10^4$
Galactomannans	Seed mucilages	D-Mannopyranose chains with D-galactose side chains	Linear (largely)	10^5
Arabinogalactan	Lupin, soybean, coffee beans	D-Galactopyranose chain, side chain galactose and arabinose	Branched	10^5
Carrageenan	Seaweeds	Complex—contains β-galactopyranose linked to 3,6-anhydro-D-galactopyranose	Linear	10^5–10^6
Agar	Red seaweeds	Same as above except for L-galactopyranose	Linear	—
Alginic	Brown seaweeds	β-D-Mannuronic acid and α-L-guluronic acid	Linear	—



β-D-Glucose α-D-Glucose

Figure 10.1 Chair forms of α- and β-D-glucose present in an equilibrium of 36% α and 64% β in aqueous solutions.

of cotton plant, age of plant, and location of growth. Again, the gross chemical reactivity and resulting physical properties are largely independent of the source of cellulose.

The most important polysaccharides are cellulose and starch. These may be hydrolyzed by acids or enzymes to lower molecular weight carbohydrates (oligosaccharides) and finally to D-glucose. The latter is the building block, or mer, for carbohydrate polymers, and since it cannot be hydrolyzed further, it is called a monosaccharide. Cellobiose and maltose, which are the repeat units in cellulose and starch, are disaccharides, consisting of molecules of D-glucose joined together through carbon atoms 1 and 4.

The D-glucose units in cellobiose are joined by a β-acetal linkage while those in maltose are joined by an α-acetal linkage as shown in Fig. 10.2. The hydroxyl groups in the β form of D-glucose are present in the equatorial positions, and the hydroxyl on carbon 1 (the anomeric carbon atom) in the α form is in the axial position. While the chair forms shown for D-glucose, cellobiose, and maltose exist in all disaccharides and polysaccharides, simple Boeseken-Haworth perspective planar hexagonal rings will be used for simplicity in showing polymeric structures of most carbohydrates.

Accordingly, the molecular structures of cellobiose and maltose are shown in Fig. 10.2. The hydrogen atoms on the terminal carbon 1 and 4 atoms have been deleted to show the bonding present in cellulose and amylose starch. Amylodextrin is a highly branched polysaccharide with branches present on carbon 6.

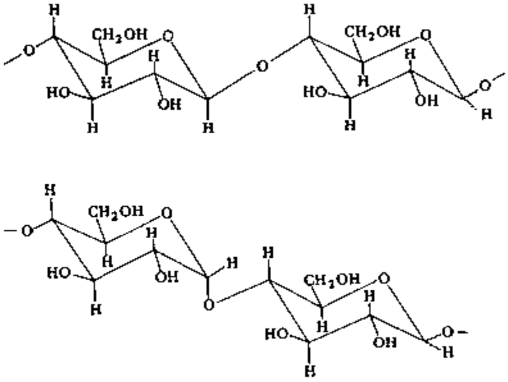


Figure 10.2 Chair form of cellobiose repeat unit in cellulose (top) and chair form of maltose repeat unit in amylose (bottom).

10.2 CELLULOSE

Cellulose was originally “discovered” by Payen in 1838. For thousands of years, impure cellulose formed the basis of much of our fuel and construction systems in the form of wood, lumber (cut wood), and dried plant material. It served as the vehicle for the retention and conveying of knowledge and information in the form of paper, and clothing in the form of cotton, ramie, and flax. Much of the earliest research was aimed at developing stronger materials with greater resistance to the natural elements (including cleaning) and to improve dyeability so that the color of choice by common people for their clothing material could be other than a drab white. In fact, the dyeing of textile materials (mainly cotton) was a major driving force in the expansion of the chemical industry in the latter part of the nineteenth century.

Cellulose is a polydisperse polymer with a degree of polymerization (DP) that ranges from 3500 to 36,000. Native cellulose is widely distributed in nature and is the principal constituent of cotton, kapok, flax, hemp, jute, ramie, and wood. Flax has a $\overline{\mathrm{DP}}$ of 36,000 or an average molecular weight of 5,900,000. Regenerated cellulose, such as rayon and cellophane, is produced by precipitating solutions of native cellulose in a nonsolvent.

Cellulose, which comprises more than one-third of all vegetable matter, is the world’s most abundant organic compound. Approximately 50 billion tons of this renewable resource are produced annually by land plants, which absorb 4×10^{20} cal of solar energy. Natural cotton fibers, which are the seed hairs from *Gossypium*, are about 1–2 cm in length and about 5–20 μm in diameter. The molecules in native cellulose are present in thread-like strands or bundles called fibrils.

Cellulose is not found in a pure form but rather is associated with other materials such as lignin and the so-called hemicelluloses. Cotton contains the purest form of cellulose. Wood, in its dry state, contains 40–55% cellulose, 15–35% lignin, and 25–40% hemicellulose. Plant pulp is the major source of commercial cellulose through the sulfite and the alkaline processes. The extraction of cellulose from plants is called pulping. Pulping is generally achieved using thermomechanical, chemical, or mechanical approaches. Pulp is dissolved when removal of the hemicelluloses and lignin are required. After pulping, the pulp is bleached to achieve the desired whiteness.

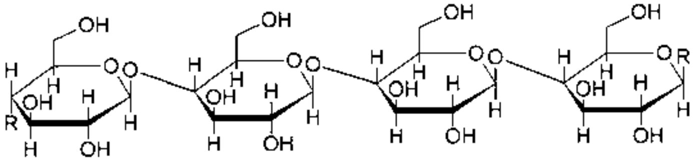
The major source for nontextile fibers is wood pulp. The major source for textile cellulose is cotton, which is pure enough to be directly used without purification.

Cellulose is used in the textile industry in cloths, cartons, carpets, blankets, and sheets. Paper is made from cellulose. Cellulosic fibers are also used as filter materials in artificial kidneys and reverse osmosis though today most kidney dialysis units use cuprammonium tubular films derived from cellulose rather than cellulose itself.

While the celluloses are often largely linear polymers, they are not soluble in water because of the presence of strong intermolecular hydrogen bonds and sometimes the presence of a small amount of crosslinking. Highly ordered crystalline cellulose has a density as high as 1.63 g cm^{-3}, while amorphous cellulose has a density as low as 1.47 g cm^{-3}. High molecular weight native cellulose, which is insoluble in 17.5% aqueous sodium hydroxide solution, is called α-cellulose. The fraction that is soluble in 17.5% sodium hydroxide solution but insoluble in 8% solution is called β-cellulose, and that which is soluble in 8% sodium hydroxide solution is called γ-cellulose.

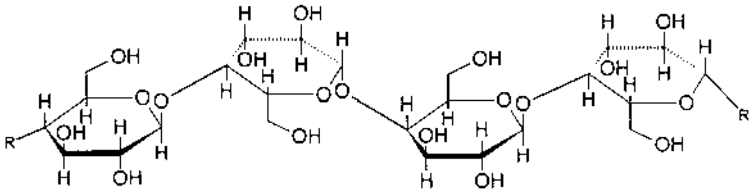
Strong caustic solutions penetrate the crystal lattice of α-cellulose and produce an alkoxide called alkali or soda cellulose. Mercerized cotton is produced by aqueous extraction of the sodium hydroxide. Cellulose ethers and cellulose xanthate are produced by reactions of alkyl halides or carbon disulfide, respectively, with the alkali cellulose.

Most linear celluloses may be dissolved in solvents capable of breaking the strong hydrogen bonds. These solvents include aqueous solutions of inorganic acids, calcium thiocyanate, zinc chloride, lithium chloride, dimethyl dibenzyl ammonium hydroxide, iron sodium tartrate, and cadmium or copper ammonia hydroxide (Schweitzer's reagent). Cellulose is also soluble in hydrazine, dimethyl sulfoxide in the presence of formaldehyde, and dimethyl formamide in the presence of lithium chloride. The average molecular weight of cellulose may be determined by measuring the viscosity of these solutions. The product precipitated by the addition of a nonsolvent to these solutions is highly amorphous regenerated cellulose.



(10.1)

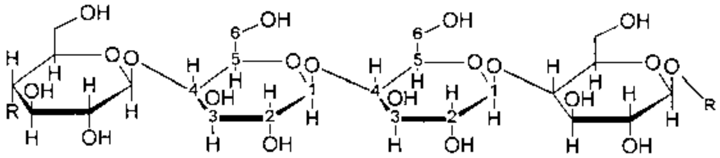
Cellulose



(10.2)

Cellulose 3d structure

The top structure is most commonly employed as a description of the repeat unit of cellulose but the lower structure more nearly represents the actual three-dimensional structure with each D-glucosyl unit rotated 180°. We will employ a combination of these two structural representations. Numbering is shown below and the type of linkage is written as 1→4, since the units are connected through oxygens contained on carbon 1 and 4 as below.



(10.3)

We also call the linkage, by agreement with the anometic nature of the particular carbons involved in linking together the glucosyl units, a *beta*; or *β linkage*. Thus, this linkage is a β 1→4 linkage. The other similar 1→4 linkage found in starch is called an alpha or α linkage. The geometric consequence of this difference is great. The linear arrangement of cellulose with the β linkage gives an arrangement where the OH groups reside somewhat uniformly on the outside of the chain allowing close contact and ready hydrogen bond formation between chains. This arrangement results in a tough, insoluble, rigid, and fibrous material that is well suited as cell wall material for plants. By comparison, the α linkage of starch (namely amylose) results in a helical structure where the hydrogen bonding is both interior and exterior to the chain allowing better wettability. This difference in bonding also results in one material being a "meal" for humans (the α linkage) whereas the other is a meal for termites. The reason for this is the difference in the composition of enzymes present in different species—humans with the enzyme capability to lyse or break α linkages and cows and termites and other species with symbiotic bacteria in their digestive systems that furnish the enzymes capable to digest or break the β glucoside linkages.

The various crystalline modifications have different physical properties and chemical reactivities. These variations are a consequence of the properties varying according to plant source, location in the plant, plant age, season, seasonal conditions, treatment, etc. Thus, in general, bulk properties of polysaccharides are generally measured with average values and tendencies given. These variations are sufficient for most applications but possibly not for specific biological applications where the polysaccharide is employed as a drug, within a drug delivery system, or as a biomaterial within the body.

Table 10.4 contains some average physical properties for cellulose.

Paper

It is believed that paper was invented by Ts'ai in China around the second century A.D. The original paper was a mixture of bark and hemp. Paper was first produced from rags in the United State by William Rittenhouse in Germantown, PA, in 1690. Paper was named after the papyrus plant, *Cyperus papyrus*.

Paper comes in many forms with many uses. The book you are reading is made from paper, we have paper plates, paper napkins, newspapers and magazines, cardboard boxes, in fact the amount of paper items is probably over twice that of all the synthetic polymers combined by weight. About 30% of paper is writing and printing paper. The rest is mainly used for tissues, toweling, and packaging. If you rip a piece of ordinary paper (not your book page please), you will see that it consists of small fibers. Most of these cellulosic fibers are randomly oriented, but a small percentage are oriented in one direction because the paper is made from a cellulose-derived watery slurry with the water largely removed through use of heated rollers.

Modern paper is made from wood pulp, largely cellulose, which is obtained by the removal of lignin (Section 10.9) from debarked wood chips by use of chemical treatments with sodium hydroxide, sodium sulfite, or sodium sulfate. Newsprint and paperboard, which is thicker than paper, often contains a greater amount of residual lignin.

Table 10.4 Average Specific Bulk Physical Properties for Cellulose

Density (specific gravity)	1.5–1.6
Average percentage crystallinity	
Native	70
Regenerated	40
Refractive index	1.5–1.6
Specific heat, J/g-degree	1.2
Ignition point, °C	>290
Heat of combustion, kJ/g	17
Resistance, Ω-cm	20,000
Insulating value, kV/cm	500

Wood is almost entirely composed of cellulose and lignin. In the simplest papermaking scheme, the wood is chopped (actually torn) into smaller fibrous particles as it is pressed against a rapidly moving pulp stone. A stream of water washes the fibers away dissolving much of the water-soluble lignin. The insoluble cellulosic fibers are concentrated into a paste called pulp. The pulp is layered into thin sheets and rollers are used to both squeeze out much of the water and to assist in achieving paper of uniform thickness. This paper is not very white. It is also not very strong because the remaining lignin is somewhat acidic (lignin contains acidic phenolic groups that hydrolyze to give a weakly acidic aqueous solution) that causes the hydrolytic breakdown of the cellulose. Most newsprint is of this type or it is regenerated, reused paper.

Pulping processes are designed to remove the nonsaccharide lignin portion of wood, which constitutes about 25% of the dry weight. The remaining is mostly cellulose with about 25% hemicellulose (noncellulose cell wall polysaccharides that are easily extracted by dilute aqueous base solutions). Pulping procedures can be generally classified as semichemical, chemical, and semimechanical. In semimechanical pulping, the wood is treated with water or sulfate, bisulfite, or bicarbonate solution that softens the lignin. The pulp is then ground or shredded to remove much of the lignin giving a purified or enriched cellulose content. The semichemical process is similar but digestion times are longer and digesting solutions more concentrated giving a product with less lignin, but the overall yield of cellulose-intense material is lowered by 70–80%. Further, some degradation of the cellulose occurs.

Most paper is produced by the chemical process where chemicals are employed to solubilize and remove most of the lignin. While overall yields are lower than the other two main processes, the product gives good quality writing and printing paper. Three main chemical processes are used. In the soda process, extracting solutions containing about 25% sodium hydroxide and 2.4% sodium carbonate are used. In the sulfite process the extracting solution contains a mixture of calcium dihydrogen sulfite and sulfur dioxide. The sulfate process utilizes sodium hydroxide, sodium monosulfide, and sodium carbonate in the extracting solution.

After the chemical treatment, the pulped wood is removed, washed, and screened. Unbleached, brown-colored paper is made directly from this material. Most whiten or bleached paper is made from treatment of the pulp with chlorine, chlorine dioxide, hypochlorite, and/or alkaline extraction. In general, sulfate pulped paper is darker and requires more bleaching and alkaline extraction to give a “white” pulp.

The sulfate process—also called the kraft process (the term “kraft” comes from the Swedish word for strong since stronger paper is produced)—is more commonly used. The kraft process is favored over the sulfite treatment of the paper because of environmental considerations. The sulfite process employs more chemicals that must be disposed of—particularly mercaptans (RSHs) that are quite odorous. Research continues on reclaiming and recycling pulping chemicals.

If pure cellulose was solely used to make paper, the fiber mat would be somewhat water-soluble with only particle surface polar groups and internal hydrogen bonding acting to hold the fibers together. White pigments such as clay and titanium dioxide are added to help “cement” the fibers together and to fill voids producing a firm, white writing surface. This often occurs as part of an overall coating process.

Most paper is coated to provide added strength and smoothness. The coating is basically an inexpensive paint that contains a pigment and a small amount of polymeric binder. Unlike most painted surfaces, most paper products are manufactured with a short lifetime in mind with moderate performance requirements. Typical pigments are inexpensive low-refractive index materials such as platelike clay and ground natural calcium carbonate. Titanium dioxide is used only when high opacity is required. The binder may be a starch or latex or a combination of these. The latexes are usually copolymers of styrene, butadiene, acrylic, and vinyl acetate. Other additives and coloring agents may also be added for special performance papers. Resins in the form of surface coating agents and other special surface treatments (such as coating with polypropylene and polyethylene) are used for paper products intended for special uses such as milk cartons, ice cream cartons, light building materials, and drinking cups. The cellulose supplies the majority of the weight (typically about 90%) and strength with the special additives and coatings providing special properties needed for the intended use.

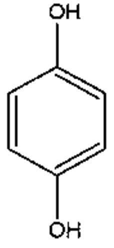
Recycling of paper continues to be advantageous. Today, up to about one half of our paper products are recycled, and this fraction is increasing as we do a better job of collecting and recycling paper products.

10.3 CELLULOSE-REGENERATING PROCESSES

Cellulose is sometimes used in its original form as fibers for textile and paper, but often it is modified through dissolving and reprecipitation or through chemical reaction. The xanthate viscose process which is used for the production of rayon and cellophane is the most widely used regeneration process. The cellulose obtained by the removal of lignin from wood pulp is converted to alkali cellulose. The addition of carbon disulfide to the latter produces cellulose xanthate.

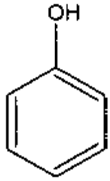
While terminal hydroxyl and aldehyde groups, such as are present in cellobiose, are also present in cellulose, they are not significant because they are present on very long chain polymeric molecules. For convenience, one may represent cellulose by the semiempirical formula $C_6H_7O_2(OH)_3$. This formula shows the three potentially reactive hydroxyl groups on each repeat unit in the chain.

The hydroxyl groups are not equivalent. For instance, the pKa values of the two ring hydroxyl groups are about 10 and 12—about the same as the hydroxyl groups on hydroquinone, and the first value about the same as the hydroxyl on phenol. The pKa value of the nonring or methylene hydroxyl group is about 14—about the same as found for typical aliphatic hydroxyl groups.



Hydroquinone

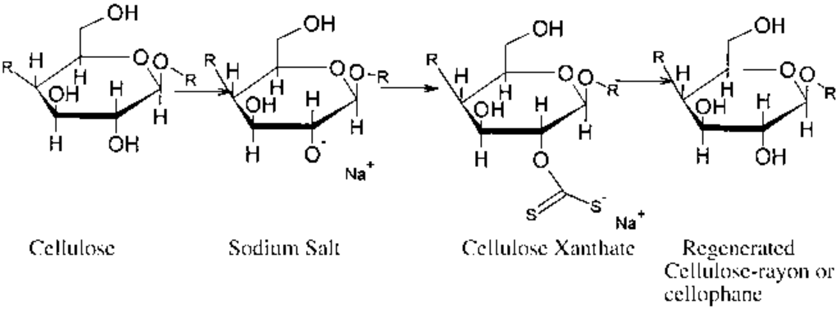
(10.4)



Phenol

(10.5)

In the cellulose regenerating process, sodium hydroxide is initially added such that approximately one hydrogen, believed to be predominately the hydroxyl group on carbons 2 or 3, is replaced by the sodium ion. This is followed by treatment with carbon disulfide forming cellulose xanthate, which is eventually changed back again and regenerated to cellulose. This sequence is depicted below.



(10.6)

The orange-colored xanthate solution, or viscose, is allowed to age and is then extruded as a filament through holes in a spinneret. The filament is converted to cellulose when it is immersed in a solution of sodium bisulfite, zinc sulfate, and dilute sulfuric acid. The tenacity, or tensile strength, of this regenerated cellulose is increased by a stretching process which reorients the molecules so that the amorphous polymer becomes more crystalline. Cellophane is produced by passing the viscose solution through a slit die into an acid bath.

Since an average of only one hydroxyl group in each repeating anhydroglucose unit in cellulose reacts with carbon disulfide, the xanthate product is said to have a degree of substitution (DS) of 1 out of a potential DS of 3. Alkyl halides, including chloroacetic acid, may react with soda cellulose to yield ethers with DS average values ranging from 0.1 to 2.9.

The DS of inorganic esters such as cellulose nitrate (CN) may be controlled by the concentration of the esterifying acids. However, in classic esterification with organic acids, an ester with a DS of approximately 3 is obtained. The more polar secondary and primary esters, with DS values of 2 and 1, respectively, are produced by partial saponification of the tertiary ester. The degree of esterification of cellulose solutions in dimethyl acetamide or dimethyl sulfoxide may be controlled by the time of reaction.

Partially degraded cellulose is called hydrocellulose or oxycellulose, depending on the agent used for degradation. The term holocellulose is used to describe the residue after lignin has been removed from wood pulp. Cellulose soluble in 17.5% aqueous sodium hydroxide is called hemicellulose. Tables 10.5 and 10.6 describe a number of important textile fibers, including cellulosic fibers.

The overall viscose process can be described as follows:

> Native cellulose → steeping/pressing → shredding → aging → xanthation → dissolving in sodium hydroxide → filtration → ripening/deaeration → regeneration in acid bath → stretching → cutting → finishing → drying

Ripening is an aging process. When cellulose xanthate is first dissolved it does not easily coagulate. More of the xanthate groups occupy the kinetically favored 2 and 3 hydroxyls acting to keep the cellulose units away from one another. After some time, the xanthate groups move from the kinetically favored positions, relocating to the thermodynamically favored 6 hydroxyl allowing the units to move closer to one another. Also, as ripening time increases, the xanthate concentration decreases also encouraging closer approach of the glucose units.

Table 10.5 Noncellulosic Textile Fibers

Fiber name	Definition	Properties	Typical uses	Patent names (assignees)
Acrylic	Acrylonitrile units, 85% or more by weight	Warm; lightweight; shape-retentive; resilient; quick-drying; resistant to sunlight	Carpeting, sweaters, skirts, baby clothes, socks, slacks, blankets draperies	Orion (Du Pont), Acrilan (Monsanto), Chemstrand (Monsanto)
Modacrylic	Acrylonitrile units, 35–85% by weight	Resilient; softenable at low temperatures; easy to dye; abrasion-resistant; quick-drying; shape-retentive; resistant to acids, bases	Simulated fur, scatter rugs, stuffed toys, paint rollers, carpets, hairpieces and wigs, fleece fabrics	Verel (Eastman), Dynel (Union Carbide)
Polyester	Dihydric acid–terephthalic acid ester, 85% or more by weight	Strong, resistant to stretching and shrinking; easy to dye; quick-drying; resistant to most chemicals; easily washed, wrinkle-resistant; abrasion-resistant; retains heat-set pleats and creases (permanent press)	Permanent press wear: skirts, shirts, slacks, underwear, blouses; rope, fish nets, tire cord, sails, thread	Vycron (Beaunit), Dacron (Du Pont), Kodel (Eastmant), Fortrel (Fiber Ind., Celanese), Chemstrand (polyester, Monsanto)
Spandex	Segmented polyurethane, 85% or more by weight	Light, soft, smooth, resistant to body oils; stronger and more durable than rubber; can be stretched repeatedly and to 500% without breaking; can retain original form; abrasion-resistant; no deterioration from perspirants, lotions, detergents	Girdles, bras, slacks, bathing suits, pillows	Lycra (Du Pont)
Nylon	Recurring amide groups	Exceptionally strong; elastic; lustrous; easy to wash; abrasion resistant; smooth, resilient, low moisture absorbency; recovers quickly from extensions	Carpeting, upholstery, blouses, tent, sails, hosiery, suits, stretch fabrics, tire cord, curtains, rope, nets, parachutes	Caprolan (Allied Chemical), Chemstrand (nylon, Monsanto), Astroturf (Monsanto), Celanese Polyester (Fiber Ind., Celanese), Cantrece (Du Pont)

Thorough control of the regeneration conditions, together with a wide variety of modifications, allows the production of a wide variety of products including high wet modulus fibers, hollow fibers, crimped fibers, and flame-resistant fibers.

While almost all rayon is produced using the viscose process, some fibers are still produced utilizing the cuprammonium process whereby the cellulose is dissolved in an ammonium-copper two-ion alkaline solution. Special films and hollow fibers for kidney

Table 10.6 Cellulosic Fibers

Fiber name	Definition	Properties	Typical uses	Patent names (assignees)
Rayon	Regenerated cellulose with substitutes no more than 15% of the hydroxyl groups' hydrogens	Highly absorbent; soft; comfortable; easy to dye; good drapability	Dresses, suits, slacks, blouses, coats, tire cord, ties, curtains, blankets	Avril (FMC Corp.), Cuprel (Beaunit), Zantrel (American Enka)
Acetate	Not less than 92% of the hydroxyl groups are acetylated, includes some triacetates	Fast-drying; supple; wide range of dyability; shrink-resistant	Dresses, shirts, slacks, draperies, upholstery, cigarette filters	Estron (Eastman), Celanese acetate (Celanese)
Triacetate	Derived from cellulose by combining cellulose with acetic acid and/or acetic anhydride	Resistant to shrinking, wrinkling, and fading; easily washed	Skirts, dresses, sportswear (pleat retention important)	Arnel (Celanese)

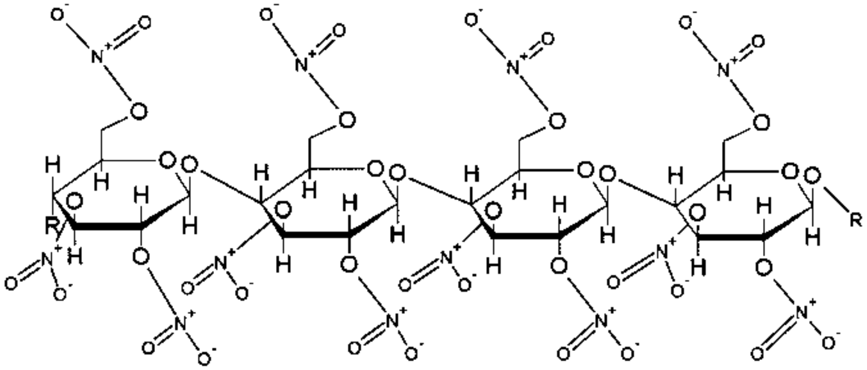
units use membranes prepared from fibers and films regenerated from the cuprammonium process.

10.4 ESTERS AND ETHERS OF CELLULOSE

It must be remembered that the three hydroxyl groups on the individual cellulose rings are not equivalent. The two ring hydroxyls are acidic with pKa values similar to hydroquinone while the third nonring hydroxyl is similar to an aliphatic hydroxyl in acidity. Thus, in an aqueous sodium hydroxide solution the two ring hydroxyls will be deprotonated at high pHs. In theory, all three hydroxyls can undergo reaction, but in actuality less than three undergo reaction because of reactivity restrictions and/or because of steric limitations. With many of the electrophilic/nucleophilic reactions it is the ring hydroxyls that are favored to react initially. The average number of hydroxyl groups that are reacted are often given as the degree of substitution, or DS.

Inorganic Esters

The most widely used so-called "inorganic ester" of cellulose is cellulose nitrate (CN), also called nitrocellulose and guncotton. Celluloid is produced from a mixture of CN and camphor. Cellulose nitrate was first made around in 1833, when cellulose-containing linen, paper, or sawdust was reacted with concentrated nitric acid. It was the first recognized "synthetic" cellulose product. Initially, CN was used as a military explosive, and improvements allowed the manufacture of smokeless powder. A representation of CN is given below.


(10.7)

Cellulose Nitrate

The development of solvents and plastizing agents for CN led to many new and useful nonexplosive uses. Celluloid was produced in 1870 from a mixture of CN and camphor. Films were cast from solution and served as the basis for the original still and motion pictures. After World War I, the development of stable CN solutions allowed the production of fast-drying lacquer coatings.

While CN played an important role in the development of technology, its importance today is greatly diminished. It is still used as a protective and decorative lacquer coating, in gravure inks, in water-based emulsions as coatings, and to a lesser extent in plastics and films.

Cellulose sulfate esters are also available from the reaction of cellulose with concentrated sulfuric acid.

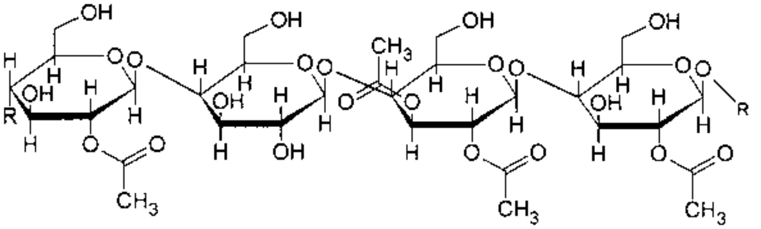
Cellulose phosphate esters are produced from reaction with phosphoric acid and urea. The products are used to treat hypercalciuria because of its ability to bind calcium. It has also been used for the treatment of kidney stones.

Organic Esters

The most important cellulose ester is cellulose acetate because of its use in fibers and plastics. It was first made in 1865 by heating cotton with acetic anhydride. During World War I, a cellulose acetate coating replaced the highly flammable CN coating on airplane wings and fuselage fabrics.

Varying properties of cellulose acetate are achieved by varying the amount of substitution. The melting point generally decreases with decreasing acetylation. Lower acetylations give products with greater solubility in polar liquids and corresponding decreased moisture resistance. Chain length and distribution of chain lengths are also important factors in determining the specific behavior and uses for cellulose acetates. Under the right conditions, cellulose esters form liquid crystals because of their rigid chain design.

Cellulose acetate is made using heterogeneous solutions containing cellulose, sulfuric acid as the catalyst, and acetic anhydride in acetic acid. Reaction occurs beginning with the surface or outermost layer and continues on layer by layer as new areas are exposed. When more homogeneous modification is desired, preswelling of the cellulose in water, aqueous acetic acid solutions, or glacial acetic acid is carried out.



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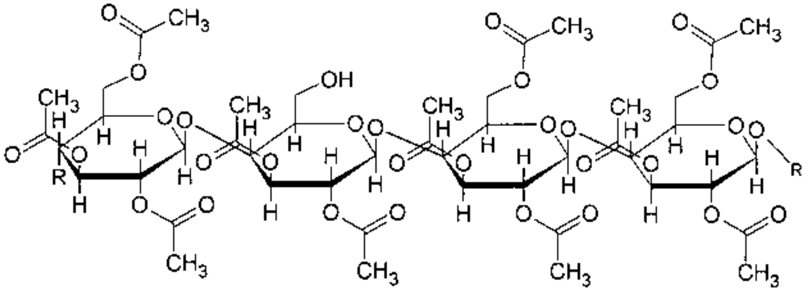


(10.9)

Reaction occurs differently since there are two “types” of hydroxyl groups (as noted before), the two ring hydroxyls and the methylene hydroxyl. In the typical formation of esters, such as cellulose acetate, the ring hydroxyl groups are acetylated initially (10.8) prior to the C-6 exocyclic hydroxyl. Under the appropriate reaction conditions reaction continues to almost completion with all three of the hydroxyl groups esterified (10.9). In triacetate products, only small amounts (on the order of 1%) of the hydroxyls remain free and of these generally about 80% are the C-6 hydroxyl.

The most common commercial products are the triacetate (DS approaching 3) and the secondary acetate (DS about 2.45).

While other organic esters are commercially available, namely, cellulose butyrate and cellulose propionate, by far the most widely used is cellulose acetate. Cellulose acetate is available as plastics, in films, sheets, fibers, and in lacquers. Cellulose acetate is used in the manufacture of display packaging and as extruded film for decorative signs, and to coat a variety of fibers. Injected molded products include toothbrush handles, combs, and brushes. It is also used in lacquers and protective coatings for metal, glass, and paper. Cellulose acetate films are used in reverse osmosis to purify blood, fruit juices, and brackish water. Some eyeglass frames are made of cellulose acetate. Biodegradable film, sponges, and microencapsulation of drugs for control release also utilize cellulose acetate. Cellulose triacetate is used for photographic film bases. Numerous continuous filament yarns, tows, staples, and fibers are made from cellulose acetate. The precise form of filament produced is controlled by a number of factors including the shape of the die.

As in all large-scale industrial processes, the formation of the cellulose esters involves the recovery of materials. Thus acetic anhydride is generally employed. After reaction, acetic acid and solvent is recovered. The recovered acetic acid is employed in the production of additional acetic anhydride. The recovered solvent is also reintroduced after treatment.

Cellulose esters are used as plastics for the formation by extrusion of films and sheets and by injection molding of parts. They are called thermoplastics and can be fabricated employing most of the usual techniques of (largely compression and injection) molding, extrusion and casting (Chapter 17). Cellulose esters plastics are noted for their toughness, smoothness, clarity, and surface gloss.

Acetate fiber is the generic name of a fiber that is partially acetylated cellulose. The fiber is also known as cellulose acetate and triacetate fiber. It is nontoxic and generally nonallergic, so is ideal from this aspect as clothing material.

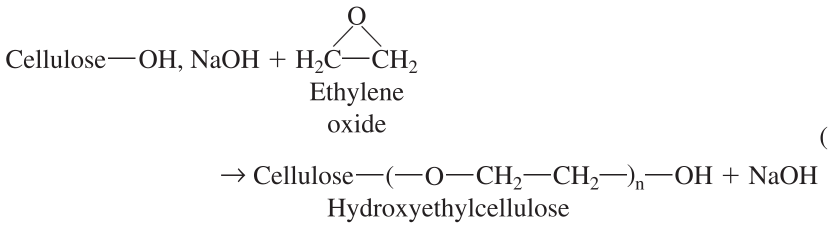
While acetate and triacetate differ only moderately in the degree of acetylation, this small difference accounts for differences in the physical and chemical behavior for these two fiber materials. Triacetate fiber is hydrophobic and application of heat can bring about a high degree of crystallinity that is employed to "lock-in" desired shapes (such as permanent press). Cellulose acetate fibers have a low degree of crystallinity and orientation even after heat treatment. Both readily develop static charge and thus antistatic surfaces are typically employed to clothing made from them.

For clothing application, there are a number of important performance properties that depend on the form of the textile. These properties include wrinkle resistance, drape, strength, and flexibility. These properties are determined using ASTM tests that often involve stress–strain behavior. Thus, the ability of a textile to resist deformation under an applied tensile stress is measured in terms of its modulus of elasticity or Young's modulus. As with any area of materials, specialty tests are developed to measure certain properties. Some of these are more standard tests like Young's modulus, while others are specific to the desired property measured for a specific application. For instance, resistance to slightly acidic and basic conditions is important for textiles that are to be laundered. Again, these are tested employing standard test procedures. In general, triacetate materials are more resistant than acetate textiles to basic conditions. Both are resistant to mild acid solutions but degrade when exposed to strong mineral acids. Further, behavior to various dry cleaning agents is important. As the nature of dry cleaning agents change, additional testing and modification in the fabric treatments are undertaken to offer a textile that stands up well to the currently employed cleaning procedures. Again, both are stable to perchloroethylene dry cleaning solvents but can soften when exposed to trichloroethylene for extended treatment. Their stability to light is dependent upon the wavelength, humidity present, and other factors. In general, they offer a comparable stability to light as that offered by cotton and rayon.

While cellulose acetates are the most important cellulose esters, they suffer by their relatively poor moisture sensitivity, limited compatibility with other synthetic resins, and a relatively high processing temperature.

Organic Ethers

Reaction with an epoxide such as ethylene oxide under alkaline conditions gives hydroxyethylcellulose (HEC).



$$\text{Cellulose—OH, NaOH} + \underset{\text{Ethylene oxide}}{H_2C\overset{O}{—}CH_2} \rightarrow \underset{\text{Hydroxyethylcellulose}}{\text{Cellulose—(—O—}CH_2\text{—}CH_2\text{—)}_n\text{—OH}} + \text{NaOH} \qquad (10.10)$$

This is an S_N2 reaction with the reaction proportional to the concentration of the epoxide and alkali cellulose, but since the base is regenerated, it is first order in epoxide.

$$\text{Rate} = k[\text{epoxide}] \tag{10.11}$$

Industrially, HECs with DS values below 2 are used. Low DS materials (to about 0.5) are soluble only in basic solutions while those with DS values of about 1.5 are water-soluble. Concentrated solutions of HEC are pseudoplastic with their apparent viscosities decreasing with increased rates of shear. Dilute solutions approach being Newtonian in their flow properties, even under a wide range of shear rates. Viscosity changes reversibly with temperature increasing when cooled and decreasing when heated.

HEC is used as a protective colloid in latex coatings and pharmaceutical emulsions; as a film former for fabric finishes, fiberous glass, and in aerosol starches; thickener for adhesives, latex coatings, toothpaste, shampoos and hair dressings, cosmetic creams and lotions, inks and joint cements; lubricant for wallpaper adhesives and in pharmaceutical gels; and as a water binding for cements, plastics, texture coatings, ceramic glazes, and in printing inks.

Sodium carboxymethylcellulose is formed by the reaction of sodium chloroacetate with basic cellulose solutions. The sodium form of carboxymethylcellulose is known as CMC or as a food grade product as cellulose gum. It is soluble in both hot and cold water.

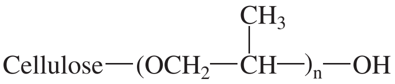
$$\begin{aligned} &\text{Cellulose—OH, NaOH} + \text{Cl—CH}_2\text{COONa} \\ &\quad \rightarrow \underset{\text{Sodium CMC}}{\text{Cellulose—O—CH}_2\text{—COONa}} \end{aligned} \tag{10.12}$$

The most widely used cellulose gums have DS values about 0.65–1.0. CMCs are used as thickening, binding, stabilizing, and film-forming agents.

Carboxymethylhydroxyethylcellulose (CMHEC) is synthesized from the reaction of hydroxethylcellulose with sodium chloroacetate. The product is a mixed ether. It has properties similar to both CMC and HEC. Like CMC it exhibits a high water binding ability and good flocculating action on suspended solids, but it is more compatible than CMC with salts. It forms ionic crosslinks in the presence of salt solutions containing multivalent cations allowing its viscosity to be greatly increased by the presence of such cations. Solutions can be gelled by addition of solutions of aluminum and iron salts.

It is a water-soluble material used in oil recovery and in hydraulic fracturing fluids.

Hydroxypropylcellulose (HPC) is a thermoplastic nonionic cellulose ether that is soluble in both water and a number of organic liquids. It is synthesized through reaction of the basic cellulose slurried with propylene oxide.



$$\text{Cellulose—(OCH}_2\text{—}\overset{\displaystyle \text{CH}_3}{\overset{|}{\text{CH}}}\text{—)}_n\text{—OH} \tag{10.13}$$

Hydroxypropylcellulose

Methyl and hydroxyalkylmethylcelluloses are nonionic polymers soluble in cool water. Methylcellulose (MC), hydroxyethylmethylcellulose (HEMC), and hydroxypropylmethylcellulose (HPMC) do not interact with cations forming insoluble salts, but electrolytes that compete with MC for water can cause precipitation.

MC is formed from basic cellulose and its reaction with chloromethane.

$$\text{Cellulose—OH, NaOH} + CH_3Cl \rightarrow \underset{\text{Methylcellulose}}{\text{Cellulose—O—}CH_3} \qquad (10.14)$$

Methylcellulose is used as an adhesive; in ceramics to provide water retention and lubricity; in cosmetics to control rheological properties and in the stabilization of foams; in foods as a binder, emulsifier, stabilizer, thickener, and suspending agent; in paints, paper products, and plywood as a rheology control for the adhesive; in inks and in textiles as a binder and for coatings.

Ethylhydroxyethylcellulose (EHEC) is a nonioinic mixed ether available in a wide variety of substitutions with corresponding variations in aqueous and organic liquid solubilities. It is compatible with many oils, resins, and plasticizers along with other polymers such as nitrocellulose. Water-soluble EHECs with DS values about 0.9 are non-Newtonian with viscosities decreasing with increasing shear rate with concentrated solutions exhibiting pseudoplastic rheological properties.

EHEC is synthesized through a two-step process beginning with the formation of the HEC-like product through reaction between the basic cellulose and ethylene oxide. The second step involves further reaction with ethyl chloride.

$$\underset{\text{Ethylhydroxyethylcellulose}}{\text{Cellulose—(—O—}CH_2CH_2\text{—)—}CH_2CH_3} \qquad (10.15)$$

Uses for the water-soluble EHEC include in water-borne paints, pastes, polymer dispersions, ceramics, and cosmetics and pharmaceuticals. Applications for organic soluble EHEC include inks, lacquers, and as coatings.

Cellulose undergoes reaction with activated ethylenic compounds such as acrylonitrile giving cyanoethylcellulose via a Michael addition.

$$\text{Cellulose—OH} + H_2C{=}CHCN \rightarrow \text{Cellulose—O—}CH_2\text{—}CH_2\text{—CN} \qquad (10.16)$$

10.5 STARCH

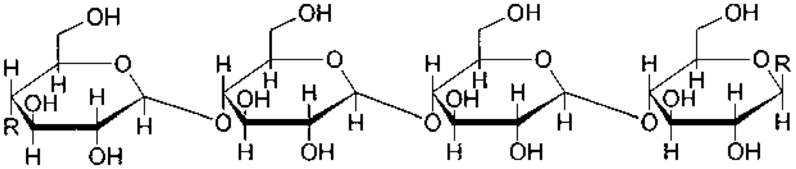
While cellulose is the major structural polysaccharide, plant energy storage and regulation utilizes a combination of similar polysaccharides that combined are referred to as starch. The two major components of starch are called amylopectin (the major constituent) and amylose (the minor constituent). Starches are usually present in the form of intramolecularly hydrogen-bonded polymer aggregates or granules.

Starch is the second most abundant polysaccharide weightwise. It is widely distributed in plants where it is stored as reserve carbohydrate in seeds, fruits, tubers, roots, and stems.

Commercially starch is prepared from corn, white potatoes, wheat, rice, barely, millet, cassava, tapioca, arrowroot, and sorghum. Amylopectin, which is sometimes called the B fraction, is usually the major type of starch present in grains. However, amylose, which is sometimes called the A fraction, is present exclusively in a recessive strain of wrinkled pea. Thus, the fraction of amylopectin and amylose varies with respect to the particular plant and the usual weather, age, and soil conditions. Amylose serves as a protective colloid. Mixtures of amylose and amylopectin, present in native starch, form suspensions when placed in cold water. An opalescent starch paste is produced when this suspension is poured into hot water.

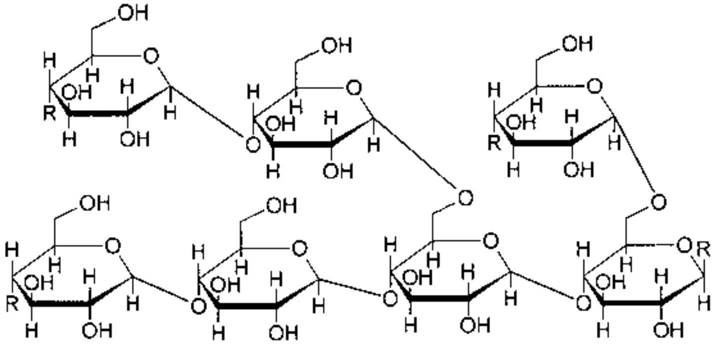
While cellulose can be considered a highly regular polymer of D-glucose with the units linked through a β-1,4 linkage, amylose is a linear polysaccharide with glucose units linked in an α-1,4 fashion while amylopectin contains glucose units with chains of α-1,4 glucopyranosyl units but with branching occurring on every 25–30 units, with the chain-branch occurring from the 6 position. While this difference in orientation in how the glucose units are connected appears small, it causes great differences in the physical and biological properties of cellulose and starch. For instance, humans contain enzymes that degrade the α-glucose units of starch allowing it to be metabolized as a major food source but we are not able to convert the β unit, found in cellulose, into glucose so that wood and other cellulose-intensive materials are not food sources for us. Also, the individual units of cellulose can exist in the chair conformation with all of the substituents equatorial, yet amylose must either have the glucosyl substituent at the 1 position in an axial orientation or exist in a nonchair conformation.

As noted before, starch can be divided into two general structures, branched amylopectin and largely linear amylose. Most starches contain about 10–20% amylose and 80–90% amylopectin, though the ratio can vary greatly.



(10.17)

Linear Amylose



(10.18)

Branched Amylopectin

Amylose typically consists of over 1000 D-glucopyranoside units. Amylopectin is a larger molecule containing about 6000 to 1,000,000 hexose rings essentially connected with branching occurring at intervals of 20–30 glucose units. Branches also occur on these branches giving amylopectin a fan or treelike structure similar to that of glycogen. Thus, amylopectin is a highly structurally complex material. Unlike nucleic acids and proteins where specificity and being identical are trademarks, most complex polysaccharides can boast of having the “mold broken” once a particular chain was made so that the chances of finding two exact molecules is very small.

An important characteristic of amylose is its ability to form a blue-colored solution in the presence of iodine. The formation of this complex has been widely employed for the detection of starch in general and amylose in particular. The iodine atoms are believed to lie along the hollow core of the amylose. While amylopectin also interacts with iodine, it does so much more weakly giving a reddish-purple complex.

Starch granules are insoluble in cold water but swell in hot water, first reversible until gelatinization occurs, at which point the swelling is irreversible. At this point the starch loses its birefringence, the granules burst, and some starch material is leached into solution. As the water temperature continues to increase to near 100°C, a starch dispersion is obtained. Oxygen must be avoided during heating or oxidative degradation occurs. Both amylose and amylopectin are then water-soluble at elevated temperatures. Amylose chains tend to assume a helical arrangement (Fig. 10.31) giving it a compact structure. Each turn contains six glucose units.

The flexibility of amylose and its ability to take on different conformations are responsible for the "retrogradation" and gelation of dispersions of starch. Slow cooling allows the chains to align to take advantage of inter- and intrachain hydrogen bonding, squeezing out the water molecules, leading to precipitation of the starch. This process gives retrograded starch, either in the presence of amylose alone or combined in native starch, which is generally difficult to redisperse. Rapid cooling of starch allows some inter- and intrachain hydrogen bonding, but also allows water molecules to be captured within the precipitating starch allowing it to be more easily redispersed (Fig. 10.3).

Most uses of starch make use of the high viscosity of its solutions and its gelling characteristics. Modification of starch through reaction with the hydroxyl groups lowers the gelation tendencies decreasing the tendency for retrogradation. Starch is the major

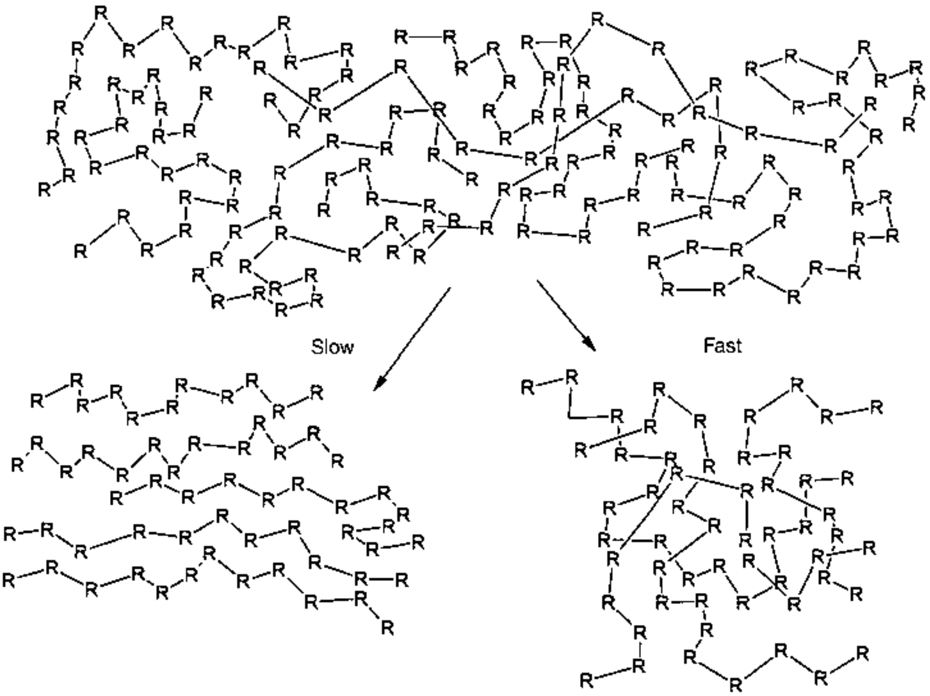


Figure 10.3 Behavior of amylose in a concentrated aqueous solution as a function of cooling rate.

source of corn syrup and corn sugar (dextrose or D-glucose). In addition to its use as a food, starch is used as an adhesive for paper and as a textile-sizing agent.

Oligomeric or small-chained materials called cyclodextrins are formed when starch is treated with a particular enzyme, the amylase of *Bacillus macerans*. These oligomeric derivatives generally consist of six, seven, eight, and greater numbers of D-glucose units joined through 1,4-α linkages to form rings. These rings are doughnut-like with the hydroxyl groups pointing upward and downward along the rim of the doughnut. Like crown ethers used in phase transfer reactions, the cyclodextrins can act as “host” to “guest” molecules. In contrast to most phase transfer agents, cyclodextrins have a polar exterior and nonpolar interior. The polar exterior allows the cyclodextrins, and often the associated guest, to be water-soluble. The nonpolar interior allows nonpolar molecules to be guest molecules. Cyclodextrins are being used as enzyme models since they can first bind a substrate and through substituent groups, act on the guest molecule—similar to the sequence carried out by enzymes (please see Secs. 15.14 and 15.15).

A major effort is the free-radical grafting of various styrenic, vinylic, and acrylic monomers onto cellulose, starch, dextran, and chitosan. The grafting has been achieved using a wide variety of approaches including ionizing and ultraviolet/visible radiation, charge-transfer agents, and various redox systems. Much of this effort is aimed at modifying the native properties such as tensile (abrasion resistance and strength) and care (crease resistance and increased soil and stain release) related properties, increased flame resistance, and modified water absorption. One area of emphasis has been the modification of cotton and starch in the production of super-absorbent material through grafting. These materials are competing with all synthetic crosslinked acrylate materials that are finding use in diapers, feminine hygiene products, wound dressings, and sanitary undergarments.

10.6 OTHER POLYSACCHARIDES

Polysaccharides can be divided by many means. Here we will look at the number of certain basic building units involved in the structure of the polysaccharide as a means of cataloging some important polysaccharides.

Homopolysaccharides

The best know homopolysaccharides are derived from D-glucose and known as glucans. Glucose has a number of reactive sites and a wide variety of polymers formed utilizing combinations of these reactive sites are found in nature. We have already visited the two most well-known members of this group—cellulose and starch containing amylose and amylopectin. Here we will visit some other important members.

Glycogen is a very highly branched glucan or polysaccharide formed from glucose. It is structurally similar to amylopectin though more highly branched. This greater branching gives glycogen a greater water solubility. Glycogens are the principle carbohydrate food reserve materials in animals. They are found in both invertebrates and vertebrates and likely found in all animal cells. The highest concentration of glycogen is found in muscle with the greatest amount found in our liver, the tissue from which it is most often isolated.

Glycogen is an amorphous polymer of high molecular weight, generally 10^6 to 10^9 Daltons. In spite of its high molecular weight, it has good water solubility because, as noted above, of its highly but loosely branched character. It is polydisperse with respect to molecular weight as are other polysaccharides. The particular molecular weight and molecular weight distribution varies within and between cells and metabolic need. It stores D-glucose units until needed as an energy source. It also serves as a buffering agent helping control the amount of glucose in the blood. It is stored in tissues as spherical particles called β particles.

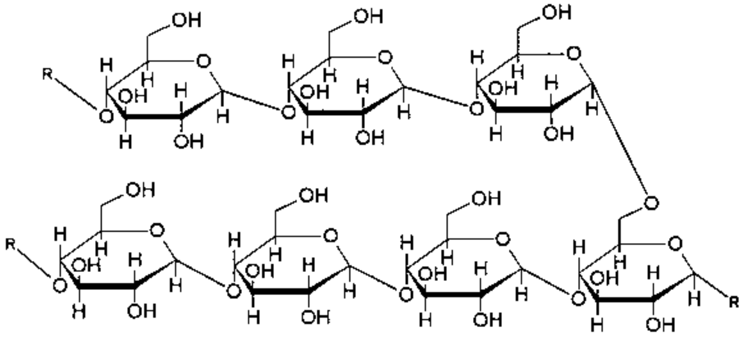
The average distance between branch points is only about 10–15 in comparison to amylopectin with about 20–30 units between branch points. Many glycogen particles contain small amounts of protein to which the polysaccharide chains are covalently bonded. Glycogen reacts weakly with iodine giving a yellow-orange color. It is believed that about 50 linear glucose units is required to form the blue complex found for amylose and because of the high degree of branching, few "runs" near 50 linear glucose units are found in glycogen.

Starch and glycogen are produced when the amount of glucose is high and are readily degraded back to glucose when energy is needed. In plants this degradation occurs mainly through the action of two enzymes known as α- and β-amylase. Interestingly, while the α-amylase can degrade starch and glycogen completely to glucose, β-amylase is not able to degrade the branch points.

In animals, glycogen degradation to give the glucose needed as an energy source or to increase the blood sugar concentration begins with the action of phosphorylase. Phosphorylase occurs in active (a) and inactive (b) forms. Phosphorylase b is converted into phosphorylase a by phosphorylation that occurs at the end of a series of events initiated by an increased intercellular concentration of cAMP and activation of the protein kinase (please see Fig. 10.12). This is reversed by a phosphoprotein phosphatase whose activity is hormonally regulated. Thus, phosphorylatin initiated by increased intracellular concentrations of cAMP inactivates glycogen synthetase and activates phosphorylase. This is an example of the complex steps that are moment-by-moment carried out in our bodies. Here, enzymes that are responsible for the glycogen metabolism do not act directly on glycogen but regulate the activity of other enzymes.

Skeletal muscle glycogen delivers glucose primarily as a response to contractile stress. Regulation occurs though both modification of the enzyme phosphorylase, primarily by the action of epinephrine adrenaline—and allosteric regulation of phosphorylase related to a demand for ATP.

Glycogen found in the liver seldom is utilized as a source of energy but rather is employed to regulate blood sugar levels. Some tissues, such as nerve and brain tissue, rely solely on glucose as their energy source so that a steady supply of sugar is essential to their well being. It is also found in some fungi and yeasts. Even some plants such as sweet corn synthesize a polysaccharide that is similar to glycogen.



(10.19)

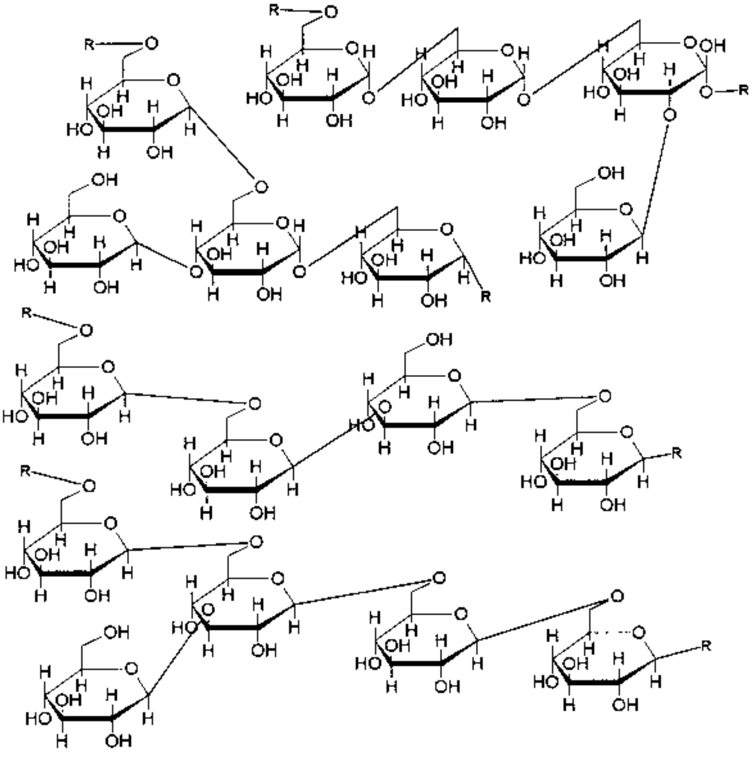
Glycogen

Dextrans are a high molecular weight branched extracellular polysaccharide synthesized by bacteria. These bacteria are found in many places including the human mouth where they flourish on sucrose-containing foods that become trapped between our teeth. The generated dextrans become part of the dental plaque and thus are involved in tooth decay. Dextran-causing bacteria can also infect sugar cane and sugar beet after harvest and act not only to decrease the yield of sucrose but also to interfere with sugar refining, clogging filters and pipelines. These bacteria can also contaminate fruit juices and wines, in fact any ready source of glucose or sucrose.

On the positive side, dextran itself has been refined and employed as a therapeutic agent in restoring blood volume for mass casualties. Natural dextrans are very high molecular weight (on the order of 10^8 to 10^9 Daltons) and are found to be unsuitable as a blood-plasma substitute. Lower molecular weight (about 10^6 Daltons) dextran is suitable and is often referred to as clinical dextran.

Dextran gels are commercially used. The gel formed from reaction with epichlorohydrin gives a crosslinked material used as a molecular sieve. Commercial crosslinked dextran is know as Sephadex™. Sephadex is formed in bead form from dissolving dextran in sodium hydroxide solution followed by dispersion in an immiscible organic liquid such as toluene containing poly(vinyl acetate) and finally added to epichlorohydrin. Different series of Sephadex are used industrially and in research. Ionic groups are often incorporated to give anionic and cationic dextrans and ion-exchange molecular sieves. Sulfate esters of dextran are also used in separations.

Below illustrates some typical units that compose dextrans.

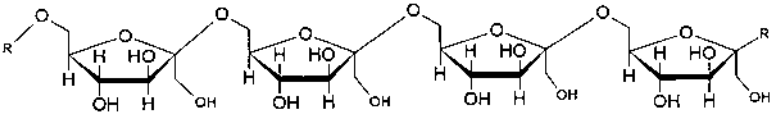


(10.20)

Representative Dextran structures. Top left: 1→6 linked glucose units with a 1→4 branch. Top right: linear 1→6 linked glucose units with a 1→2 branch. Middle: linear chain with both 1→6 and 1→3 linkages. Bottom: linear chain of 1→6 linked glucose units with a 1→3 branch. all links are α linkages.

Fructans

Fructans are polysaccharides composed of D-fructofuranose units. They are important in short-term energy reserves for grasses and some plants. Inulin, found in dahlias, and levans from grasses are examples of fructans. Levans are short linear polysaccharides composed of β, 2→1 linked fructose units as pictured below.

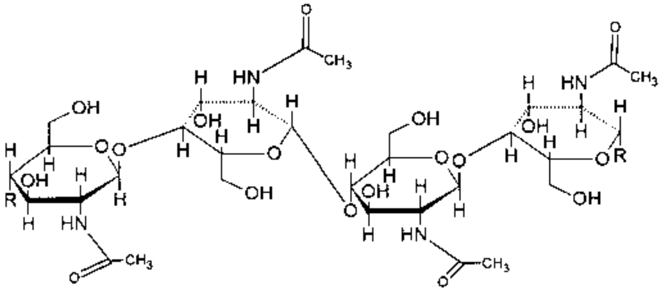


(10.21)

Levan

Chitin and Chitosan

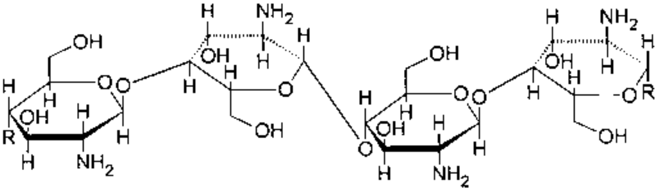
Chitin is generally a homopolymer of 2-acetamido-2-deoxy-D-glucose (*N*-acetylglucosamine) 1→4 linked in a β configuration; it is thus an amino sugar analog of cellulose. While it is widely distributed in bacteria and fungi, the major source is crustaceans. In fact, chitin is the most abundant organic skeletal component of invertebrates. It is believed to be the most widely distributed polysaccharide with the Copepoda alone synthesizing on the order of 10^9 tons each year. It is an important structural material often replacing cellulose in cell-walls of lower plants. It is generally found covalently bonded to protein. Invertebrate exoskeletons often contain chitin that provides strength with some flexibility along with inorganic salts such as calcium carbonate that provide strength. In a real sense this is a composite where the chitin holds together the calcium carbonate domains.



(10.22)

Chitin

Chitosan is produced from the deacetylation of chitin. Chitosan is employed in the food industry. It is a hemostatic from which blood anticoagulants and antithrombogenic have been formed. It is often sold as a body fat reducing agent or to be taken along with eating to encapsulate fat particles.



(10.23)

Chitosan

Both chitosan and chitin are greatly underused readily available abundant materials that deserve additional study as commercial materials and feedstocks. Chitin itself is not antigenic to human tissue and can be inserted under the skin or in contact with bodily fluids generally without harm. In the body chitin is slowly hydrolyzed by lysozyme and absorbed. Chitin and chitosan can be safely ingested by us and often we eat some since mushrooms, crabs, shrimp, many breads, and beer contain some chitin. Chitin and chitosan are believed to accelerate wound healing. Chitosan is also reported to exhibit bacteriacidal and fungicidal properties. Chitosan solutions are reported to be effective against topical fungal infections such as athlete's foot.

A continuing problem related to the introduction of bioengineering materials into our bodies is their incompatibility with blood. Many materials cause blood to clot (thrombosis) on the surfaces of the introduced material. Heparin (10.24) is an anticoagulant, nontoxic material that prevents clot formation when coated on vascular implants. While chitosan is a hemostatic material (stops bleeding by enhancing clotting), chitosan sulfate has the same anticoagulant behavior as heparin.

Cardiovascular disease is the leading cause of death in America. A contribution factor to cardiovascular disease is serum cholesterol. When ingested, chitosan exhibits hypocholesterolemic activity. Chitosan dissolves in the low pH found in the stomach and reprecipitates in the more alkaline intestinal fluid entrapping cholic acid as an ionic salt preventing its absorption by the liver. The cholic acid is then digested by bacteria in the large intestine. Chitosan may also act to increase the ratio of high density lipoprotein to total cholesterol. Chitosan has been studied in the formation of films including membrane-gels that immobilize enzymes and other materials because of the mild conditions under which they can be formed.

Chitosan has been used as a flocculate in wastewater treatment. The presence of the amine gives coacervation with negatively charged materials such as negatively charged proteins allowing removal of unwanted protein waste. The amine groups also capture metal ions, in particular polyvalent and heavy metal ions such as iron, lead, mercury, and uranium. Carraher, Francis, and Louda have also used chitosan to chelate with platinum salts to form materials with structures similar to the anticancer drug *cis*-dichlrodiamineplatinum II chlroide. The amine and hydroxyl groups can be modified through use of a wide range of reactions including formation of amides and esters.

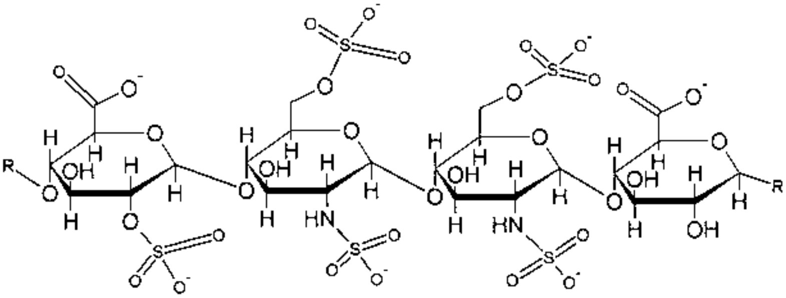
Thus, there exists sufficient reason to consider these abundant materials in dietary, biomedical, cosmetic, etc., applications.

Others

Mannans are found in plants, particularly some seeds, and in some microorganisms such as algae and yeasts. Xylans are an important component of "hemicellulose," the base soluble materials closely associated with cellulose that are present in the secondary cell walls of higher plants. They are generally composed of β, 1→4 linked D-xylopyranose units, thus the name. Arabinans are also plant material being present as a component of cell walls. Most arabinose-containing polysaccharides are actually combinations containing various saccharide units though there are some that contain largely only arabinose units.

Heteropolysaccharides

Heteropolysaccharides contain two or more different monosaccharides. Glycosaminoglycans are polysaccharides that contain aminosugar units. Most are of animal origin.

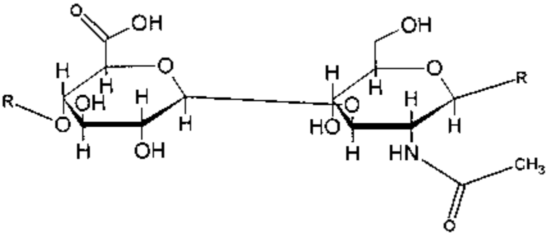


(10.24)

(Representative) Structure of heparin

Above is a representative structure of heparin that is complex containing D-glucuronic acid, L-iduronic acid, and D-glucosamine units. The glucosamine units may be *N*-acetylated or *N*-sulfonated. It is found in the lung, liver, and arterial walls of mammals. It is also found in intracellular granules of mast cells that line arterial walls and is released through injury. The glucuronic acid and iduronic acid units are not randomly present but occur in blocks. Heparin is found as the free polysaccharide and bonded to protein. Heparin acts as an anticoagulant, an inhibitor of blood clotting, and is widely used for this is medicine. In nature, its purpose appears to be to prevent uncontrolled clotting.

Hyaluronic acid is found in connective tissues, umbilical cord, skin, and it is the synovial fluid of joints. It can have very large molecular weights, to 10^7 Daltons making solutions of hyaluronic acid quite viscous. They can form gels. As a synovial fluid in joints it acts as a lubricant and in the cartilage it may also act, along with chondroitin sulfates, as a shock absorber. In some diseases such as osteoarthritis the hyaluronic acid of the joints is partially degraded resulting in a loss of elasticity of the area. The molecules can adopt a helical structure.

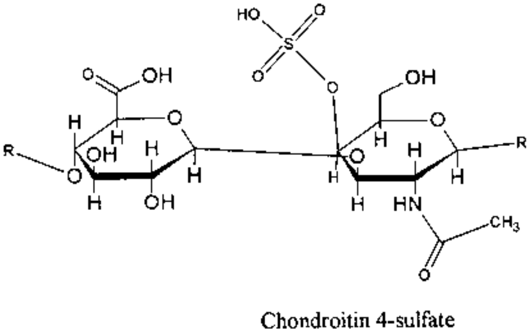


(10.25)

Hyaluronic Acid

Chondroitin sulfates are found in bone, skin, and cartilage but not as a free polysaccharide. Rather it exists as proteoglycan complexes where the polysaccharide is covalently bonded to a protein. The proteoglycan of cartilage contains about 10% protein, keratan sulfate (below), and chondroitin sulfate, mainly the 4-sulfate in humans. The chondroitin sulfate chains have a weight average molecular weight of about 50,000 Daltons, but the complex has a molecular weight of several million. Again, chondroitin sulfates can adopt a helical conformation. The function of proteoglycan in cartilage is similar to that of noncellulosic polysaccharides and protein in plant cell walls. In cartilage collagen fibers provide the necessary strength that is provided in plants by cellulose fibers. Thus, cartilage proteoglycan is an important part of the matrix that surrounds the collagen fibers giving it rigidity and incompressibility. This network can also act as a shock absorber since on compression the water is squeezed out to a near by uncompressed region acting to "share the load" by distributing a shock or stress/strain.

Chondroitin sulfate is sold as a health aid to "maintain healthy mobile joints and cartilage."



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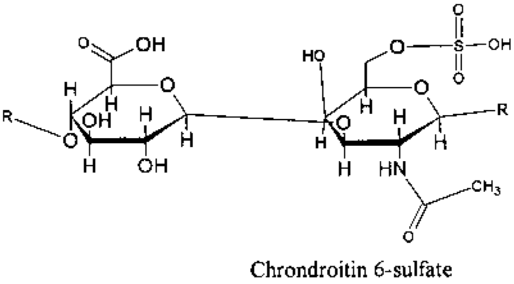
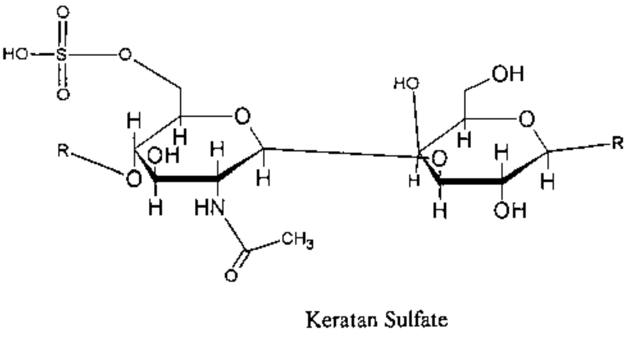


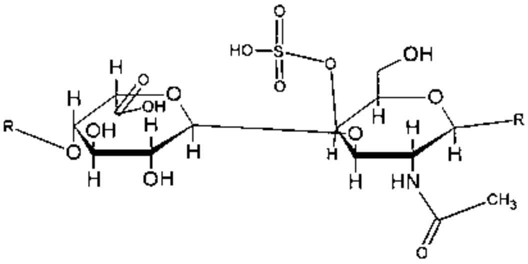
(10.27)

The second polysaccharide present in cartilage proteogylcan is keratan sulfate. It is generally found in shorter chains than chondroitin sulfate with a weight average molecular weight to about 20,000 Daltons. It is also found in the cornea of the eye.



(10.28)

Dermatan sulfate is found in the skin, arterial walls, and tendon where it is a part of another proteoglycan complex. It is about the same size as chondroitin sulfate and also able to form helical conformations.



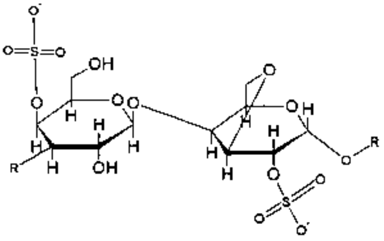
(10.29)

Dermatan Sulfate

There are two main divisions of polysaccharides that contain unmodified galactose groups: arabinogalactans that contain many plant gums and carrageenas and agar. Seaweeds represent a source of many polysaccharides including alginic acid, agar, and carrageenin. Alginic acid is a polymer of D-mannuronic acid and L-guluronic acid that may be arranged in a somewhat random fashion or in blocks. It is used as a stabilizer for ice cream, in paper coating, in the manufacture of expolosives, and in latex emulsions.

The carrageenans and agar are generally linear galactans where the monomeric units are joined by alternating 1→4 and 1→3 bonds consisting then of disaccharide units. Carrageenan is the name given to a number of sulfated polysaccharides found in many red seaweeds where they play a structural role. The approximate repeat units for two industrially important carrageenans are given below. Both are able to form double helices containing two parallel staggered chains creating a gel. There are three disaccharide units per helix turn. The sulfate units are located on the outside of the helix with the helical structure stabilized by internal hydrogen bonds. In nature, red seaweeds contain an enzyme that converts the galactose-6-sulfate of the k-carrageenan to 3,6-anhydrogalactose that causes a stiffening of the helix. It has been found that red seaweeds found where there is strong wave action contain a high proportion of anhydrogalactose. Thus, it appears that the seaweed is able to control its structure in response to external stimuli to minimize shredding by the increased wave action.

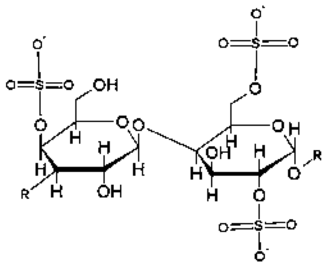
Because of its gelling ability, carrageenan is widely used as food thickeners and emulsion stabilizers in the food industry and is present in many dairy products including less expensive ice cream and other desert products providing a smooth, creamy texture. It is used as a stabilizer in foods such as chocolate milk.



(Main repeat unit)

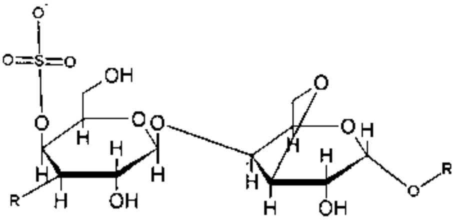
l-carrageenan

(10.30a)



(Less common repeat unit)

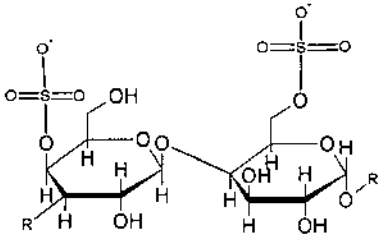
(10.30b)



(Main repeat unit)

K-carrageenan

(10.31a)

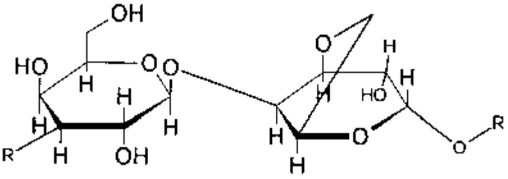


(Less common repeat unit)

(10.31b)

The name agar refers to a family of polysaccharides that contain alternating β-D-galactopyranose and 3,6-anhydro-α-L-galactopyranose units and is thus similar to a carrangeenan where the anhydro-L-galactose is substituted for the anhydro-D-galactose. It is employed as the basis of many microbiological media and in canned food because it can be sterilized. The latter is an advantage over gelatin that is not able to withstand sterilization.

Agarose is the agar polysaccharide with the greatest gelling tendency. It contains no glucuronic acid units. It can form a compact double helix with the two chains being parallel and staggered, as in the case of carrageenan, forming a gel. Agarose gels are employed in gel-permeation chromatography (GPC) and gel electrophoresis.



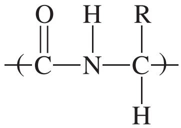
Agarose

(10.32)

Glycoproteins contain both saccharide and protein moieties with the protein being the major component, but both portions are involved in the overall biological activities.

10.7 PROTEINS

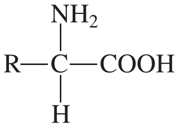
The many different monodisperse polymers of amino acids, which are essential components of plants and animals, are called *proteins*. This word is derived from the Greek *porteios*, "of chief importance." The 20 different α-amino acids are joined together by *peptide linkages*



$$\left(\overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle H}{|}}{N} - \underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle R}{|}}{C}} \right) \qquad (10.33)$$

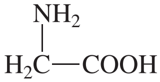
and are *polyamides* or *polypeptides*. The latter term is often used by biologists to denote oligomers or relatively low molecular weight proteins. (Note the structural similarities and differences between proteins and polyamides-nylons.)

All α-amino acids found in proteins



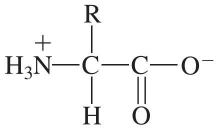
$$R-\overset{\overset{\displaystyle NH_2}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-COOH \qquad (10.34)$$

except glycine



$$H_2\overset{\overset{\displaystyle NH_2}{|}}{C}-COOH \qquad (10.35)$$

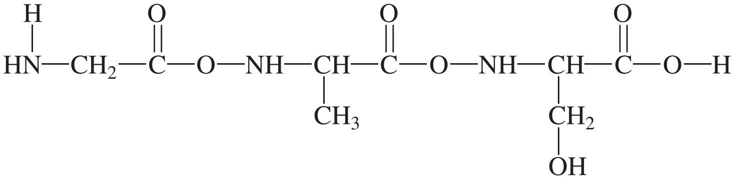
contain a chiral carbon atom and are L-amino acids. The net ionic charge of an amino acid varies with changes in the solution pH. The pH at which an amino acid is electrically neutral is called the *isoelectric point*. For simple amino acids (containing only one acid and one amine), this occurs at a pH of about 6 with the formation of a *dipolar* or *zwitterion* as shown below.



$$H_3\overset{+}{N}-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle O}{\|}}{C}-O^- \qquad (10.36)$$

Hence, α-amino acids, like other salts, are water-soluble, high-melting, polar compounds which migrate toward an electrode at pH values other than that of the isoelectric point in a process called *electrophoresis*.

In writing out sequences for polypeptides it is usual to use a three-letter abbreviation or a one-letter abbreviation starting with the N terminus to the left and going to the C-O terminus to the right. Thus the trimer

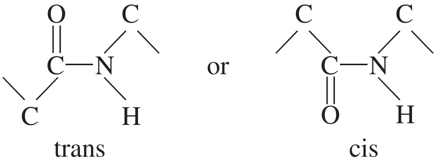


$$\overset{\overset{\displaystyle H}{|}}{HN}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-NH-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-O-NH-\underset{\underset{\underset{\underset{\displaystyle OH}{|}}{\displaystyle CH_2}}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-O-H \qquad (10.37)$$

becomes Gly-Ala-Ser or GlyAlaSer or EGAS where the E signals the N terminus. It is important to remember that all proteins are polypeptides.

The amino acids may be neutral, acidic, or basic, in accordance with the relative number of amino and carboxylic acid groups present. Cations can be formed with amino acids like tryptophan, lysine, histidine, and arginine, which have amine groups, whereas others that contain acid groups can be hydrolyzed to form anions like aspartic acid and glutamic acid. The presence of varying amounts of these amino acid moieties within a protein are primary driving forces for the separation of proteins using electrophoresis and result in polypeptides having different isoelectric points. If there are a number of acidic and/or basic groups on the polypeptide the molecule is said to be a polyampholyte if there are only positive or negative charges it is called a polyelectrolyte. The behavior of these charged polypeptides is similar to the behavior of other charged polymers. Thus, a fully hydrolyzed poly(acrylic acid) acts as a rod because the negative sites repeal one another while a polypeptide with a large number of negative sites will also be elongated. The spacing and number of these charged sites helps determine the tertiary structure of such polypeptides.

Even though the atoms within a peptide bond are coplanar, they can exist in two possible configurations; cis and trans.



(10.38)

The trans form is usually favored whenever there is a bulky group on the adjacent α carbon(s) because the groups will interfere more in the cis structure.

Proteins may be hydrolyzed by dilute acids, and the mixture of amino acids or residues produced may be separated and identified by paper chromatography. The reagent ninhydrin yields characteristic colored products with amino acids, and these may be determined colorimetrically. This chromatographic technique was developed by Nobel Laureates Martin and Synge.

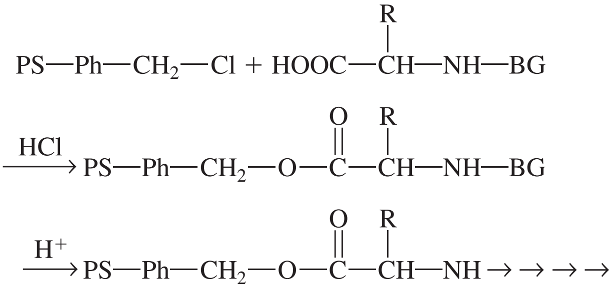
While humans synthesize about a dozen of the 20 amino acids needed for good health, the other 8 are obtained from outside our bodies, generally from eating foods that supply these *essential amino acids*. Different foods are good sources of different amino acids. Cereals are generally deficient in lysine. Thus, diets that emphasize cereals will also have other foods that can supply lysine. In the Orient the combination of soybean and rice supplies the essential amino acids while in Central America beans and corn are used.

Almost all of the sulfur needed for healthy bodies is found in amino acids as cysteine and methionine. Sulfur serves several important roles including as a crosslinking agent similar to that served by sulfur in the crosslinking vulcanization of rubber. This crosslinking allows the various chains, which are connected by these crosslinks, to “remember” where they are relative to one another. This crosslinking allows natural macromolecules to retain critical shapes to perform necessary roles.

While polypeptides can be synthesized by simply heating α-amino acids, the products obtained are random mixtures unless a single amino acid is used. Likewise, nylon-2, which is a homopolypeptide, may be prepared by the Leuch’s synthesis from N-carboxy-α-amino acid anhydrides. Polypeptides with specific sequences of amino acids can be prepared by protecting the N-terminal amino group by a reactant such as phthalic anhydride and removing the phthalimide group later by reacting with hydrazine.

The most widely used technique for producing polypeptides with specific sequences is the solid phase technique developed by Nobel Prize winner Bruce Merrifield in which all reactions take place on the surface of crosslinked polystyrene beads. The process begins with the attachment of the C-terminal amino acid to the chloromethylated polymer. Nucleophilic substitution by the carboxylate anion of an N-blocked protected C-terminal amino acid displaces chloride from the chloromethyl group forming an ester, protecting the C site while attaching it to the solid support. The blocking group is removed by addition of acid and the polymer containing the nonprotected N terminus is washed to remove unwanted byproducts. A peptide bond is formed by condensation to an N-blocked protected amino acid. Again, the solid phase system is washed to remove byproducts. The block group is removed by acid treatment and the site is ready for attachment by another amino acid. This cycle is repeated eventually producing the desired polypeptide without isolation of intermediate products.

These steps are outlined below:



$$
\begin{aligned}
&\mathrm{PS{-}Ph{-}CH_2{-}Cl} + \mathrm{HOOC{-}\overset{R}{\overset{|}{C}}H{-}NH{-}BG}\\
&\xrightarrow{\mathrm{HCl}} \mathrm{PS{-}Ph{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{R}{\overset{|}{C}}H{-}NH{-}BG}\\
&\xrightarrow{\mathrm{H^+}} \mathrm{PS{-}Ph{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{R}{\overset{|}{C}}H{-}NH} \rightarrow \rightarrow \rightarrow \rightarrow
\end{aligned}
\tag{10.39}
$$

where PS is polystyrene bead, Ph is phenyl group, and BG is the blocking group.

Some proteins transport and store smaller molecules. Thus, hemoglobin transports oxygen in erythrocytes and stores oxygen in muscles using myoglobin. Iron is transported in blood via transferrin and stored in the liver with another protein, ferritin. Antibodies give us immune protection through combination with foreign materials such as toxins, bacteria, and viruses. Other proteins are toxins such as those in venomous snakes and those that cause certain diseases such as cholera. Proteins are involved in movement brought about by a complex of chemical interaction activating sites along fibrous protein bundles. Proteins regulate growth and development at all levels—gene, cell, and organ. Proteins are used in various treatments such as the use of insulin in the treatment of diabetes. Some proteins are used as immunogens to vaccinate against other proteins. Thus, proteins play many essential roles allowing us to exist, to live, to grow, to think, and to act.

The shapes of macromolecules, both synthetic and natural, can be described in terms of primary, secondary, tertiary, and quaternary structure (Fig. 10.4). Protein structure will be used to illustrate these structures.

Primary Structure

The term *primary structure* is used to describe the sequence of amino acid units (configuration) in a polypeptide chain. The sequence for N-terminal amino acids in a chain may be determined by use of a technique developed by Nobel Laureate Sanger, who reacted the amino end group with 2,4-dinitrofluorobenzene and characterized the yellow aromatic amino acid produced by hydrolysis. This process is repeated after the end amino acid has been hydrolyzed off.

The C-terminal amino acids may be determined by using hydrazine to form hydrazides from the cleaved amino groups. Since the free carboxyl end group is not affected by hydrazine, the terminal amino acid is readily identified. The sequences of amino acids in several polypeptides, such as insulin and trypsin, have been identified by these techniques.

Secondary Structure

The term *secondary structure* is used to describe the molecular shape or conformation of a molecule. The most important factor in determining the secondary structure of materials

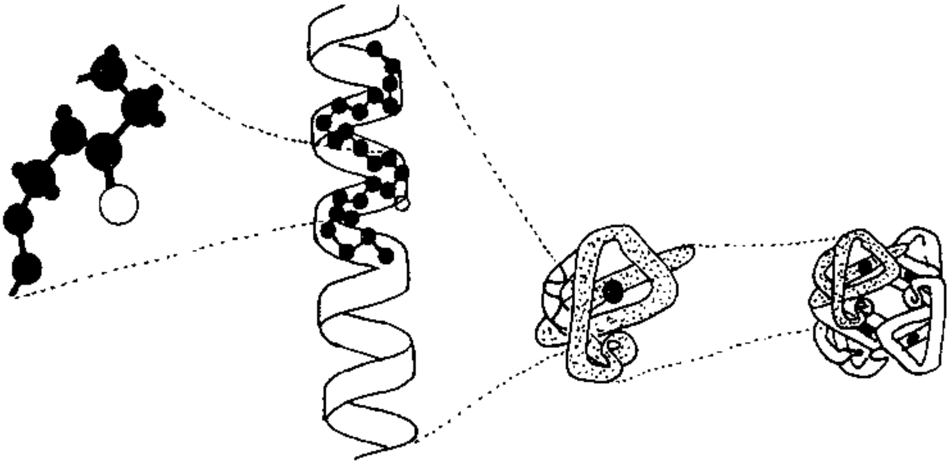


Figure 10.4 Four levels of structure elucidation. From left to right: primary, secondary, tertiary, and quaternary structures illustrated using a globular protein segment.

is its precise or primary structure. For proteins, it is then the amino acid sequence. Hydrogen bonding is also an important factor in determining the secondary structures of natural materials and those synthetic materials that can hydrogen-bond. In fact, for proteins, secondary structures are generally those that allow a maximum amount of hydrogen bonding. This hydrogen bonding also acts to stabilize the secondary structure while crosslinking acts to lock in a structure.

In nature, the two most common secondary structures are helical and sheets. In nature, extended helical conformations appear to be utilized in two major ways: to provide linear systems for the storage, duplication, and transmission of information (DNA, RNA), and to provide inelastic fibers for the generation and transmission of forces (F-actin, myosin, and collagen). Examples of the various helical forms found in nature are single helix (messenger and ribosomal DNA), double helix (DNA), triple helix (collagen fibrils), and complex multiple helices (myosin). Generally, these single and double helices are readily soluble in dilute aqueous solution. Often solubility is only achieved after the inter- and intrahydrogen bonding is broken.

The commonly occurring repetitive helical patterns for polypeptides are the α helix, the 2_7 ribbon, the 3_{10} helix, and the π helix. These structures are a consequence of repeated hydrogen bonding between peptide carboxyl and amino groups on the same polypeptide chain, along the direction of the chain, as shown in Fig. 10.5

There are a variety of examples in which linear or helical polypeptide chains are arranged in parallel rows. The two major forms that exist for proteins are illustrated in Figs. 10.6 and 10.7. The chains can have the N → C directions running parallel making a parallel β sheet, or they can have the N → C directions running antiparallel giving antiparallel β sheets.

As noted before, the structures of proteins generally fall into two groupings: fibrous and globular. The structural proteins such as the keratins, collagen, and elastin are largely fibrous. A recurring theme with respect to conformation is that the preferential secondary structures of fibrous synthetic and natural polymers approximates that of a pleated sheet

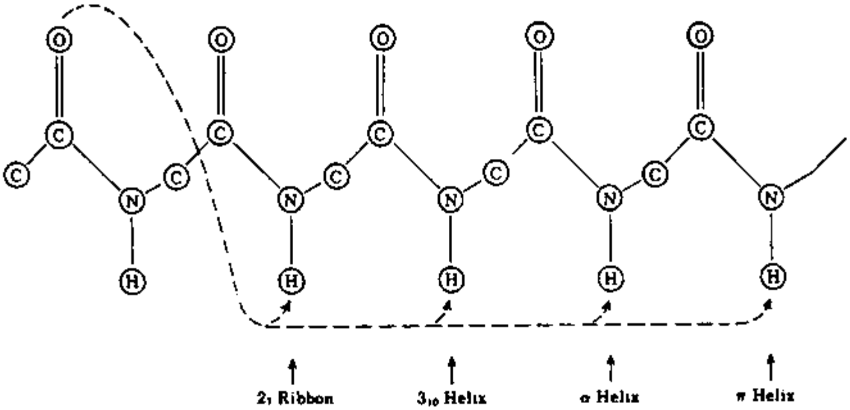


Figure 10.5 Commonly occurring repetitive helical patterns for polypeptides. (From J. Coates and C. Carraher, Polymer News, 9(3):77 (1983). Used with permission.)

or skirt or helix. The pleated sheet structures in proteins are referred to as β arrangements (Figs. 10.6–10.8). In general, proteins with bulky groups take on a helical secondary structure, whereas those with less bulky groups exist as β sheets.

Helices can be described by the number of amino acid residues in a complete "turn" (Figs. 10.5 and 10.9). In order to fit into a "good" helix, the amino acids must have the same configuration. For proteins, that configuration is described as an L configuration, with the helix being a "right-handed" helix. This right-handed helix is referred to as an α helix.

Keratins

As noted above, two basic "ordered" secondary structures predominate in synthetic and natural polymers. These are helices and the pleated sheet structures. These two structures

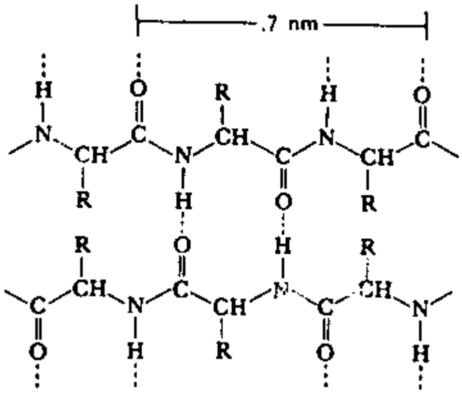


Figure 10.6 A β arrangement or pleated-sheet conformation of proteins. (From M. Stevens, *Polymer Chemistry—An Introduction*, Addison-Wesley, Reading, MA, 1975. With permission.)

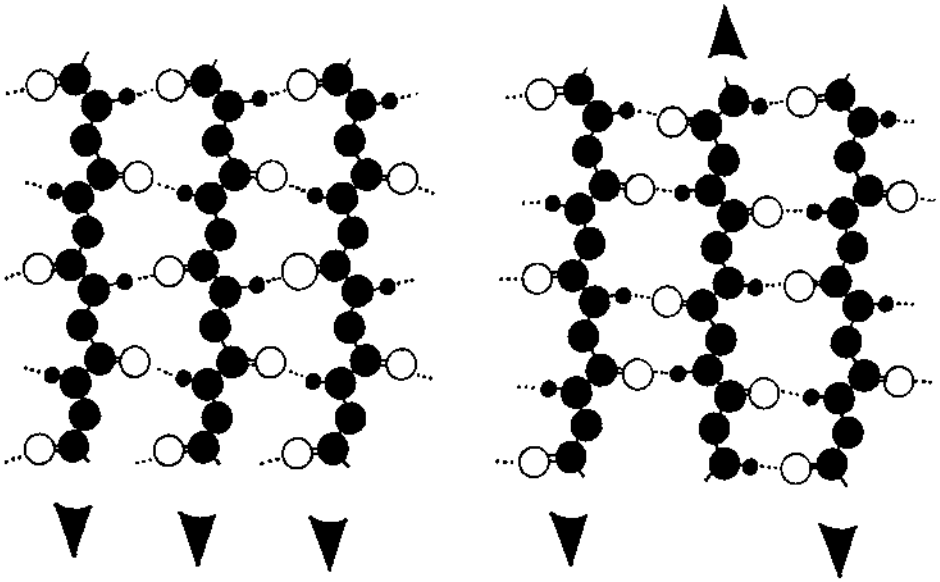


Figure 10.7 Outline of the two kinds of β sheets. The arrows point in the N → C direction for each chain. The sheet with the arrows going in the same direction is a parallel β sheet and the sheet with the arrows going in different directions is an antiparallel β sheet.

are illustrated by the group of proteins called the keratins. It is important to remember that hydrogen bonding is critical in both structures. For helices, hydrogen bonding occurs within a single strand, whereas in the sheets hydrogen bonding occurs between adjacent chains.

Helices are often described in terms of a repeat distance (the distance parallel to the axis in which the structure repeats itself), pitch (the distance parallel to the helix axis in

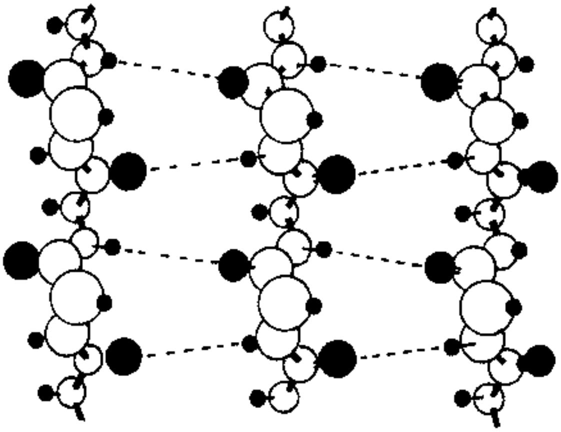


Figure 10.8 Parallel β-sheet structure for polyglycine.

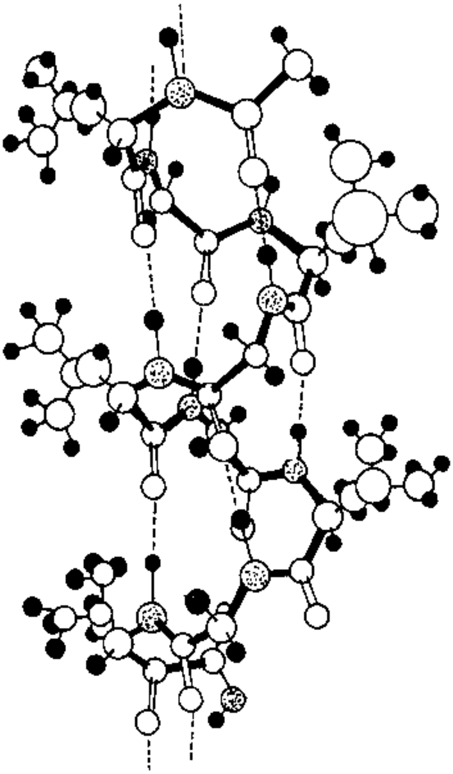


Figure 10.9 α-Keratin helix for the copolymer derived from glycine and leucine.

which the helix makes one turn), and rise (the distance parallel to the axis from the level of one repeat unit to the next).

Helices generally do not have an integral number of repeat units or residues per turn. The α helix repeats after 18 amino acid residues taking five turns to repeat. Thus, the number of residues per turn is $18/5 = 3.6$ residues/turn. For polypeptides, each carbonyl oxygen is hydrogen-bonded to the amindo proton on the fourth residue giving a "hydrogen-bonded loop" with 13 atoms. Helices are often described in terms of this number, n. Thus, the α helix is described as a 3.6_{13} helix. Because hydrogen bonds tend to be linear, the hydrogen bonding in proteins approximate this with the $\text{—N—H} \cdots \text{O=C}$ in a straight line. The "rise," h, of α-keratin (Fig. 6.9) is found by X-ray spectroscopy to be about 0.15 nm for each amino acid residue. The pitch, p, of a helix is given by $p = nh$. For α-keratin $p = 3.6$ amino acid residues/turn $\times$ 0.15 nm/amino acid residue $=$ 0.54 nm/turn.

Hair and wool are composed of α-keratin. A single hair on our head is composed of many strands of keratin. Coiled α-helices, chains of α-keratin, intertwine to form protofibrils that in turn are clustered with other protofibrils forming a microfibril. Hundreds of these microfibrils in turn are embedded in a protein matrix giving a macrofibril that in turn combines giving a human hair.

While combing will align the various hairs in a desired shape, after a while the hair will return to its "natural" shape through the action of the sulfur crosslinks pulling the hair back to its original shape.

Secondary bonding is involved in forming the helical structures allowing the various bundles of α-keratin to be connected by weak secondary interactions that in turn allow them to slide readily past one another. This sliding or slippage, along with the "unscrewing" of the helices, allows our hair to be flexible.

Some coloring agents and most permanent waving of our hair involves breakage of the sulfur crosslinks and a reforming of the sulfur crosslinks at new sites to "lock in" the desired hair shape.

Our fingernails are also composed of α-keratin, but keratin with a greater number of sulfur crosslinks giving a more rigid material. In general, for both synthetic and natural polymers, increased crosslinking leads to increased rigidity.

The other major structural feature is pleated sheets. Two kinds of pleated sheets are found. When the chains have their N → C directions running parallel they are called parallel β sheets. The N → C directions can run opposite to one another giving what is called an antiparallel β sheet (Figs 10.6 and 10.7). The β keratin (Fig. 10.10) that occurs in silk produced by insects and spiders is of the antiparallel variety. While α-keratin is especially rich in glycine and leucine, β-keratin is mostly composed of glycine and alanine with smaller amounts of other amino acids including serine and tyrosine. Sizewise, leucine offers a much larger grouping attached to the α carbon than does alanine. The larger size of the leucine causes the α-keratin to form a helical structure to minimize steric factors. By comparison, the smaller size of the alanine allows the β-keratin to form sheets. This sheet structure is partially responsible for the "softness" felt when we touch silk. While silk is not easily elongated because the protein chains are almost fully extended, β-keratin is flexible because of the low secondary bonding between sheets allowing the sheets to flow past one another.

In the silk fibroin structure almost every other residue is glycine with either alanine or serine between them, allowing the sheets to fit closely together. While most of the fibroin exists as β sheets, regions that contain more bulky amino acid residues interrupt

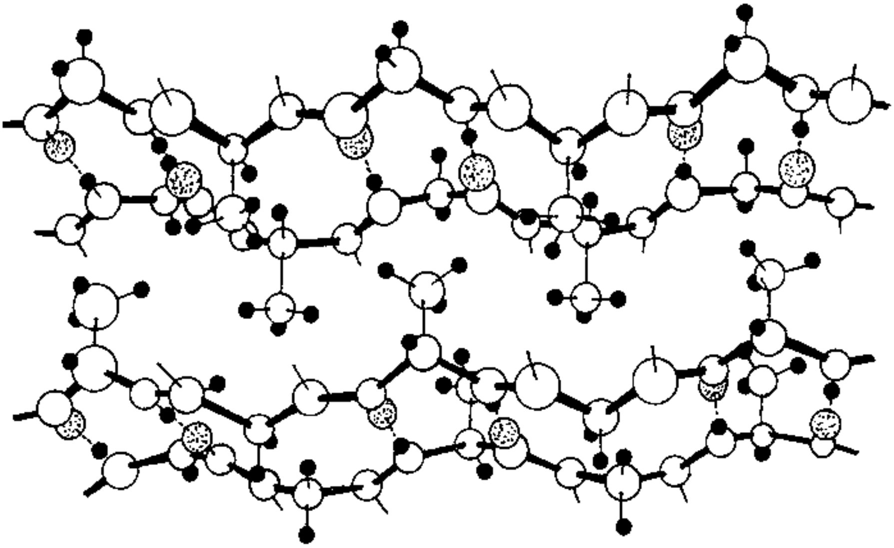


Figure 10.10 β-Keratin sheet for the copolymer derived from glycine and alanine.

the ordered β structure. Such disordered regions allow some elongation of the silk. Thus in the crystalline segments of silk fibroin there exists directional segregation using three types of bonding: covalent bonding in the first dimension, hydrogen bonding in the second dimension, and hydrophobic bonding in the third dimension. The physical properties of the crystalline regions are in accord with the bonding types. The polypeptide chains are virtually fully extended. There is a little puckering to allow for optimum hydrogen bonding. Thus the structure is inextensible in the direction of the polypeptide chains. On the other hand, the less specific hydrophobic (dispersive) forces between the sheets produces considerable flexibility. The crystalline regions in the polymers are interspersed with amorphous regions in which glycine and alanine are replaced by other amino acids with bulkier pendant groups which prevent the ordered arrangements described above. Furthermore, different silk worm species spin silks with differing amino acid composition and thus with differing degrees of crystallinity. The correlation between the extent of crystallinity and the extension at the break point is shown in Table 10.7.

The composition within a spider web is not all the same. We can look briefly at two of the general types of threads. One is known as the network or frame threads also called the dragline fabric. It is generally stiff and strong. The second variety is the catching or capture threads that are made of viscid silk that is strong, stretchy and covered with droplets of glue. The frame threads are about as stiff as nylon 66 thread and on a weight basis stronger than steel cable. Capture thread is not stiff but is more elastomeric like and on a weight basis about one third as strong as frame thread. While there are synthetic materials that can match the silks in both stiffness and strength there are few that come near the silk threads in toughness and their ability to withstand a sudden impact without breaking. Kevlar, which is used in bullet-resistant clothing, has less energy-absorbing capacity in comparison to either frame or capture threads. In fact, when weight is dropped onto frame silk, it adsorbs up to ten times more energy than Kevlar. On impact with frame thread, most of the kinetic energy dissipates as heat which, according to a hungry spider, is better than transforming it into elastic energy which might simply act to "bounce" the pray out of the web.

The frame threads are composed of two major components—highly organized microcrystals compose about one quarter of the mass and the other three quarters are composed of amorphous spaghettilike tangles. The amorphous chains connect the stronger crytalline portions. The amorphous tangles are dry, glassy-like acting as a material below its T_g. The amorphous chains are largely oriented along the thread length as are the microcrystals giving the material good longitudinal strength. As the frame threads are stretched the tangles straighten out allowing it to stretch without breaking. Because of the extent of the tangling there is a lessening in the tendency to form micro-ordered domaines

Table 10.7 Selected Properties as a Function of Silk Worm Species

Silk worm species	Approximate crystallinity (%)	% Extension at break point
Anaphe moloneyi	95	12.5
Bombyx mori	60	24
Antherea mylitta	30	Flow then extends to 35%

Source: Coates and Carraher, Polymer News, 9(3):77 (1983). Used with permission.

as the material is stretched though that also occurs. Frame thread can be reversibly stretched to about 5%. Greater stretching causes permanent creep. Thread rupture does not occur until greater extension, such as 30%. By comparison, Kevlar fibers break when extended only 3%.

The capture threads are also composed of the same kinds of components but here the microcrystals compose less than 5% of the thread with both the amorphous and microcrystalline portions arranged in a more random fashion within the thread. A hydrated glue that coats the thread acts as a plasticizer imparting to the chains greater mobility and flexibility. It stretches several times its length when pulled and is able to withstand numerous shocks and pulls appropriate to contain the prey as it attempts to escape. Further, most threads are spun as two lines so that the resulting thread has a kind of build in redundancy.

The spinning of each type of thread comes from a different emission site on the spider and the spider leaves little to waste, using unwanted and used web parts as another source of protein.

Cloning of certain spider genes have been included in goats to specify the production of proteins that call for the production of silklike fibroin threads that allow the production and subsequent capture of spiderlike threads as part of the goats milk.

The β-keratin structure is also found in the feathers and scales of birds and reptiles.

Wool, while naturally existing in the helical form, forms a pleated-skirt, sheetlike structure when stretched. If subjected to tension in the direction of the helix axes, the hydrogen bonds parallel to the axes are broken and the structure can be irreversibly elongated to an extent of about 100%.

Collagen

Collagen is the most abundant single protein in vertebrates, accounting for up to one-third of the total protein mass. Collagen fibers form the matrix or cement material in our bones where mineral materials precipitate. Collagen fibers constitute a major part of our tendons and act as a major part of our skin. Hence, it is collagen that is largely responsible for holding us together.

The basic building block of collagen is a triple helix of three polypeptide chains called the tropocollagen unit. Each chain is about 1000 residues long. The individual collagen chains form left-handed helices with about 3.3 residues per turn. In order to form this triple-stranded helix, every third residue must be glycine because glycine offers a minimum of bulk. Another interesting theme in collagen is the additional hydrogen bonding that occurs because of the presence of hydroxyproline derived from the conversion of proline to hydroxproline. The conversion of proline to hydroxproline involves vitamin C. Interestingly, scurvy, the consequence of a lack of vitamin C, is a weakening of collagen fibers giving way to lesions in the skin and gums and weakened blood vessels. Collagen fibers are strong. In tendons, the collagen fibers have a strength similar to that of hard-drawn copper wire.

Much of the toughness of collagen is the result of the crosslinking of the tropocollagen units to one another through a reaction involving lysine side chains. Lysine side chains are oxidized to aldehydes that react with either a lysine residue or with one another through an aldol condensation and dehydration resulting in a crosslink. This process continues throughout our life, resulting in our bones and tendons becoming less elastic and more brittle. Again, a little crosslinking is essential, but more crosslinking leads to increased fracture and brittleness.

Collagen is a major ingredient in some "gelation" materials. Here, collagen forms a triple helix for some of its structure while other parts are more randomly flowing single collagen chain segments. The bundled triple-helical structure acts as the rigid part of the polymer while the less ordered amorphous chains act as a soft part of the chain. The triple helix also acts as a noncovalently bonded crosslink.

Elastin

Collagen is found where strength is needed, but some tissues, such as arterial blood vessels and ligaments, need materials that are elastic. Elastin is the protein of choice for such applications. Elastin is rich in glycine, alanine, and valine, and it is easily extended and flexible. Its conformation approaches that of a random coil so that secondary forces are relatively weak allowing elastin to be readily extended as tension is applied. The structure also contains some lysine side chains that are involved in crosslinking. The crosslinking is accomplished when four lysine side chains are combined to form a desmosine crosslink (Fig. 10.11). This crosslink prevents the elastin chains from being fully extended and causes the extended fiber to return to its original dimensions when tension is removed. One of the areas of current research is the synthesis of polymers with desired properties based on natural analogues. Thus, elastinlike materials have been synthesized using glycine, alanine, and valine and some crosslinking. These materials approach elastin in its elasticity.

We are beginning to understand better how we can utilize the secondary structure of polymers as tools of synthesis. One area where this is being applied is in an area known as "folded oligomers." Here, the secondary structure of the oligomer can be controlled

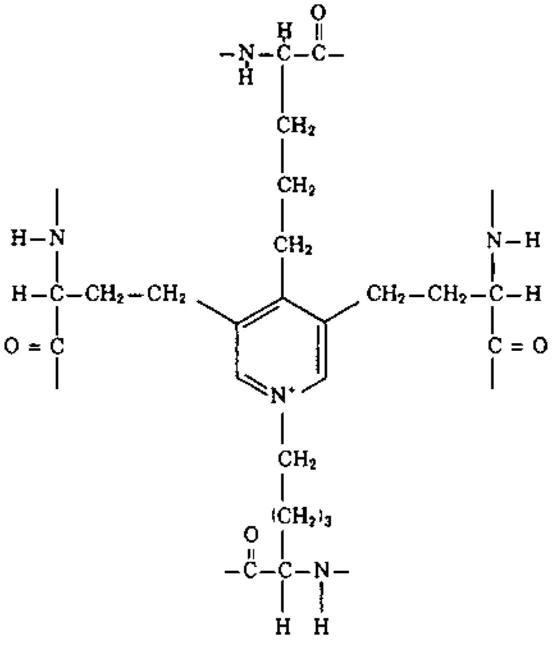


Figure 10.11 Central structure of desmosine.

through its primary structure and use of solvents. Once the preferred structure is achieved, the oligomers are incorporated into larger chains eventually forming structures with several precise structures "embedded" within them. The secondary structure of these larger polymers can also be influenced by the nature of the solvent allowing further structural variety. Addition of other species such as metal ions can assist in locking in certain structures and they can also act to drive further structural modification.

It has been found that for oligomeric peptides that the β structures are more stable requiring as few as 6 amino acid units, whereas those formed by α-oligomeric peptides are less stable and require at least 15 amino acid units to form stable helical structures.

Tertiary Structure

The term *tertiary structure* is used to describe the shaping or folding of macromolecules. These larger structures generally contain elements of the secondary structures. Often hydrogen bonding and crosslinking lock in such structures. As noted before, proteins can be divided into two broad groups—fiberous or fibrillar proteins, and globular proteins that are generally soluble in acidic, basic, or neutral aqueous solutions. Fibrous proteins are long macromolecules that are attached through either inter- or intrahydrogen bonding of the individual residues within the chain. Solubility, partial or total, occurs when these hydrogen bonds are broken.

Globular Proteins

There are a wide variety of so-called globular proteins. Many of these have various α and β structures embedded in the overall globular structure. The β sheets are often twisted or wrapped into a "barrel-like" structure. They contain portions that are β sheet structures and portions that are in an α conformation. Further, some portions of the globular protein may not be conveniently classified as either an α or a β structure.

These proteins are often globular in shape so as to offer a different "look" or polar nature to its outside than is present in its interior. Hydrophobic residues are generally found in the interior while hydrophilic residues are found on the surface interacting with the hydrophilic water-intense external environment. (This theme is often found for synthetic polymers that contain polar and nopolar portions. Thus, when polymers are formed or reformed in a regular water-filled atmosphere, many polymers will favor the presence of polar moieties on their surface.)

Folding depends on a number of interrelated factors. The chain folding process involves going from a system of random β and α conformations to a single folded structure. This change involves a decrease in the entropy or randomness. In order for folding to occur, this increase in order must be overcome by energy-related factors to allow the overall free energy to be favorable. These energy factors include charge–charge interactions, hydrogen bonding, van der Waals interactions, and hydrophilic/hydrophobic effects.

Within a particular globular polymer there may be one or more polypeptide chains folded backward and forward forming quite distinct structural domains. Each domain is characterized by a particular style of coiling or "sheeting," which may be nonrepetitive with respect to its peptide chain geometry or may be repetitive, conforming to one of several now well-recognized patterns. The specific chain conformations are determined by the side chain interactions of the amino acids superimposed on intrapeptide hydrogen bonding along the chain. The form of chain folding is thus ultimately determined by the amino acid sequence and the polymeric nature of the polypeptide chains, and is fundamental to the specific geometry of the given protein.

Protein units can be either negatively or positively charged. Attractions between unlike charges are important as are the repulsions between like changed units. As expected, these associations are pH-dependent with pH being one reason for conformation changes to occur. The ability to hydrogen-bond is also an important factor with respect to the internal folding scheme. Because the proteins are tightly packed, the weak van der Waals interactions can also play an important role in determining chain folding. The tendency for polarity-like segments to congregate can also be an important factor in chain folding. Thus, hydrophilic groupings generally are clustered to the outside of the globular protein allowing them to take advantage of hydrogen bonding and other polar bonding opportunities, while hydrophobic clusters of amino acid units occupy the internal regions of the protein taking advantage of hydrophobic interactions.

Globular proteins act in maintenance and regulatory roles i.e., functions that often require mobility and thus some solubility. Included in the globular grouping are enzymes, most hormones, hemoglobin, and fibrinogen that is changed into an insoluble fibrous protein fibrin that causes blood clotting.

Denaturation is the irreversible precipitation of proteins caused by heating, such as the coagulation of egg white as an egg is cooked, or by addition of strong acids, bases, or other chemicals. This denaturation causes permanent changes in the overall structure of the protein. The ease with which proteins are denatured makes it difficult to study protein structure. Nucleic acids also undergo denaturation.

Small changes in the primary structure of proteins can result in large changes in the secondary structure. For instance, researchers have interchanged the positions of two adjacent amino acid residues of a globular resulting in a β strand becoming a right-handed helix.

Molecular recognition is one of the keys to life. Scientists are discovering ways to both modify molecular recognition sites and "copy" such sites. One approach to modifying molecular recognition sites, namely enzymatic protein sites, is through what is referred to as *directed evolution*. Arnold and co-workers have employed the combinatorial approach (cf. Sec. 18.8) by taking an enzyme with a desired catalytic activity and encouraging it to undergo mutation; selecting out those mutations that perform in the desired manner; and repeating this cycle until the new enzymes perform as desired. Ratner and co-workers have taken another approach whereby templates containing the desired catalytic sites are made. First, the protein is mounted on a mica support. The target protein is coated with a sugar monolayer that allows for specific recognition. A fluoropolymer plasma film is deposited over the sugar monolayer. The fluoropolymer reverse image is attached to a support surface using an epoxy resin. Solvents are then added to etch away the mica, sugar, and original protein leaving behind a "nanopit" template that conforms to the shape of the original protein.

Quaternary Structure

The term *quaternary structure* is employed to describe the overall shape of groups of chains of proteins. For instance, hemoglobin is composed of four distinct but similar protein macromolecules, each with its own tertiary structure that comes together to give the quaternary hemoglobin structure (see Sec. 15.14).

Both synthetic and natural polymers have superstructures that influence/dictate properties of the material. Many of these primary, secondary, tertiary and quaternary structures are influenced in a similar manner. Thus, primary structure is a driving force for secondary structure. Allowed and preferred primary and secondary bonding influence structure. For most natural and synthetic polymers, hydrophilic and hydrophobic domains tend to cluster. Thus, most helical structures will have either a somewhat hydrophobic/hydrophilic inner core and the opposite outer core resulting from a balance between secondary and primary bonding factors and steric and bond angle constraints. Nature has used these differences in domain character to create the world about us. Thus, most cell membranes have a hydrophilic outer and inner layer (domain) that interacts with the largely polar, including hydrogen-bonding materials, "world" that exists on ether side of the membrane. The interior of the membrane is hydrocarbon-intensive acting as a barrier to intrusion of polar-intense materials including dissolved salts and selected nutrients.

As noted before, some proteins are linear with inner and intrachain associations largely occurring because of hydrogen bonding. Influences on globular protein structures are more complex but, again, the same features are at work. Globular proteins have irregular three-dimensional structures that are compact but which when brought together form quaternary structures that approach being spherical. While the overall structure is spherical the surface is irregular, with the irregularity allowing the proteins to perform a wide variety of specific biological functions.

The preferred folding conformation is again influenced by the same factors of bonding type (often hydrogen bond pairing), polarity, size, flexibility, and preferred bond angles. The folded conformations are possible because of the flexibility of the primary bonding present within proteins. Thus, the polar portions, namely the amine and carbonyl moieties, are fixed, but the carbon between the amine and carbonyl moieties is flexible. Again, the folding characteristics are driven by secondary bonding considerations, but the variety of possible folding conformations is allowed because of the flexibility of the carbon between the fixing points, the amine and carbonyl groups. Some folding is chemically "fixed" through insertion of crosslinks. In hair, these crosslinks are often disulfides, —S—S—.

When placed in water, the protein twists and folds achieving the optimum shape to "hide" its hydrophobic portions while "presenting" its hydrophilic portions to the water environment. The final shape is "predetermined" by the order of the particular amino acids present in the chain.

As noted earlier, the flexibility of proteins allows it to carry out a wide variety of tasks and the building sites of proteins generally produce a variety of different proteins. Our cells often build about 60,000 different kinds of proteins. A bacterial cell will synthesize over 1000 different types of proteins.

When a protein contains roughly more than about 200 amino acid groups, it often assumes two or more somewhat spherical tertiary structural units. These units are often referred to as *domains*. Thus, hemoglobin is a combination of four myoglobin-like units with each of the four units influenced by the other three, and where each unit contains a site to interact with oxygen (see Sec. 15.14). The interactions between each domain vary from high to low.

The specificity of enzymatic catalytic activity is dependent on tertiary structure. Phosphoglycerate kinase (Fig. 10.12) is a protein composed of 415 amino acids. The protein chain is folded back and forward forming a claw-like structure that has two rigid domains divided by a more flexible hinge region. Phosphoglycerate kinase binds to phosphoglycerate, a fragment of glucose, transferring the phosphate forming ATP. If the enzyme binds to the phosphoglycerate and water, the phosphate could react with the water rather than forming ATP. The protein is designed to circumvent this by having the essential parts present in both halves of the claw. As the enzyme binds the phosphoglycerate and

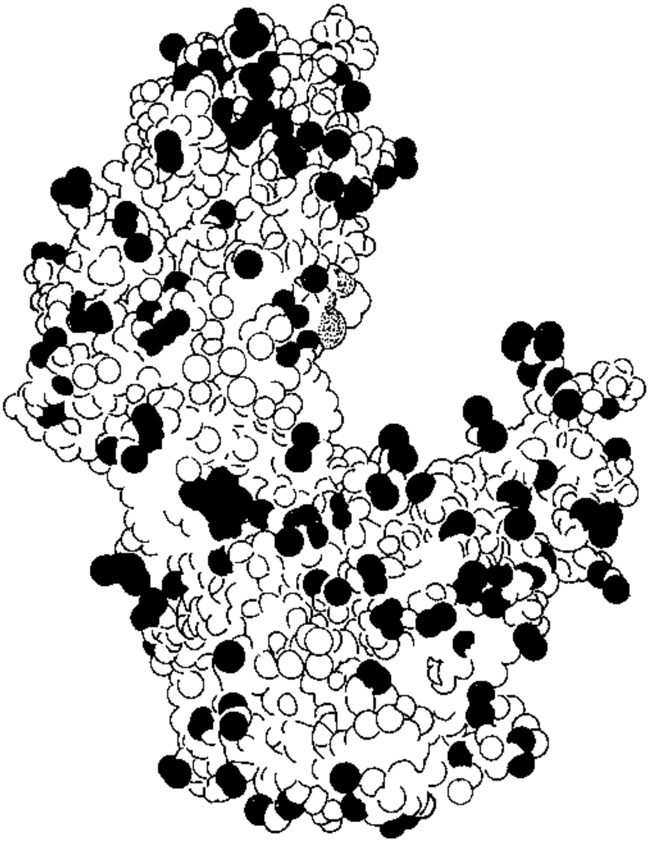


Figure 10.12 Protein enzyme phosphoglycerate kinase involved in the formation of adenosine-5′-triphosphate (ATP) from adenosine-5′-diphosphate (ADP).

the ADP, the claw closes bringing together the two necessary active parts, excluding water and other nonessential compounds. In Fig. 10.12 the phosphoglycerate is indicated by the “dotted” area about half-way up one of the two sections of the claw.

Figure 10.12 also illustrates the usual arrangement whereby hydrophilic areas, noted as darkened areas, radiate outward from the enzyme surface while less hydrophilic and hydrophobic areas tend to reside within the enzyme.

As an example of conformational change induced by the binding of a small molecule, we can consider the binding of oxygen to hemoglobin. Hemoglobin is composed of four very similar subunits, each containing a porphyrin ring enclosing a ferrous ion which is capable of binding, reversibly, a dioxygen molecule. Since the ferrous ions are relatively heavy atoms compared with the remainder of the atoms of the hemoglobin, the Fe^{II}–Fe^{II} distances are relatively easily determined by crystallographic techniques. Measurements of the Fe^{II}–Fe^{II} distances in fully oxygenated hemoglobin and in deoxyhemoglobin are given in Fig. 10.13.

As a consequence of the conformation change triggered by the high-spin to low-spin conversion of one Fe^{II} on binding dioxygen, the affinity for oxygen of the Fe^{II} in the

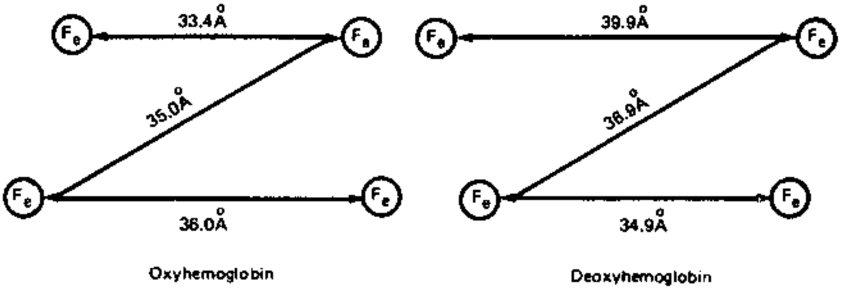


Figure 10.13 Fe^{II}–Fe^{II} distances in oxyhemoglobin and deoxyhemoglobin.

other subunits is changed, a so-called "cooperative effect." In addition, it is found that as O_2 is bound, a proton is more readily lost from the subunit—the Haldane effect. Finally, the small molecule 2,3-diphosphoglycerate can bind as an effector to a specific site on the subunit and in so doing distort the polymer toward the deoxy conformation, thus tending to cause O_2 to be released. The complex sets of interactions outlined here would be difficult to envisage in any structure less complex than a macromolecule. Table 10.8 contains a listing of shapes of selected proteins.

Because precipitated or crystalline materials have no substantial net charge, protein solubility in aqueous liquids is generally the least at the pH corresponding to the protein's isoelectric point and increases on either side of this as the net charge on the protein in increased. Most globular proteins unfold at some pH with major changes in its solubility since such unfolding typically exposes nonpolar portions. Many smaller proteins can unfold within seconds and larger proteins within several minutes. This is faster than is predicted if random unfolding were occurring. Thus, preferential unfolding and folding must occur.

Protein purification must be done under conditions where conformational and configurational changes are minimal. Such purification is carried out using size fractionation, chromatography of various types including affinity chromatography and electrophoresis, and reversible precipitation.

Many proteins contain side chains that may be amino acid–intensive, or contain saccharides, phosphates, esters, etc. Some proteins also contain prosthetic groups such as the heme or porphyrin group in hemoglobin. Many enzymes require cofactors to exert their catalytic action. The peptide portion of such an enzyme is often referred to as an apoenzyme. An organic cofactor can be referred to as a coenzyme and if the cofactor is covalently bonded to the enzyme is both a cofactor, coenzyme, and a prosthetic group. Some of the coenzymes are vitamins such as nicotinamide.

While enzymes are effective catalysts inside in the body, we have developed techniques for "capturing" some of this activity by immobilizing enzymes. The activity of many enzymes continues in this immobilized condition. In one approach, the enzyme is isolated and coupled to solvent-swellable gels using polyacrylamide copolymers that contain N-acryloxysuccinimide repeat units. The pendent groups react with the amino "ends" of the enzyme effectively coupling or immobilizing the enzyme. Modifications of this procedure have been used to immobilize a wide variety of enzymes. For instance, the particular reactive or anchoring group on the gel can be especially modified for a particular enzyme. Spacers and variations in the active coupling end are often employed. Amine groups on gels are easily modified to give other functional groups including alcohols,

Table 10.8 Shapes of Selected Biologically Important Proteins

Protein	Shape	Molecular weight (Das)	Comments
Myoglobin	3D, oblate spheroid	17,000	Temporary oxygen storage in muscles
Hemoglobin	3D, more spherical than myoglobin	64,000	Oxygen transport through body
Cytochrome c	3D, prolate spheroid	12,000–13,000	Heme-containing protein, transports electrons rather than oxygen
Enzymes	Somewhat common features a. α-Helix content not as high as myoglobin, but areas of β-sheeting not unusual. b. Water-soluble enzymes have a large number of charged groups on the surface and those not on the surface are involved in the active site. Large parts of the interior are hydrophobic. c. The active site is found either as a cleft in the macromolecule or shallow depression on its surface.		
Lysozyme	3D, short α-helical portions, region of antiparallel pleated sheet	14,600	Well studied, good illustration of shape–activity
Chymotrypsin and trypsin	3D, extensive β-structure		Hydrolysis of peptide bonds on the carboxyl side of certain amino acids
Insulin	3D, two α-helical sections in A chain, B chain has α-helix and the remainder is extended linear central core	6000	Regulation of fat, carbohydrate, and amino acid metabolism
Somatotropin (human)	3D, 50% α-helix	22,000	Pituitary hormone
Collagen	Tropocollagen, three left-handed helical chains would around each other giving a triple helix	3×10^5	Most abundant protein, major component of skin, teeth, bones, cartilage, and tendon
Keratin	Varies with source, 3D or 2D, most contain α-helix sections	$\sim 10^4$–10^5	Main structural material of skin, feathers, nail, horn, hair—protective coatings of animals
Fibroin	Varies with source, fibrous—linear with crosslinks—crystalline regions contain antiparallel, pleated sheets	365,000	A major constituent of silk
Elastin	Varies with source, crosslinked, mostly random coil with some α-helix	>70,000	Many properties similar to those of rubber; gives elasticity to arterial walls and ligaments

Source: Coates and Carraher, 1983. Used with permission.

acids, nitriles, and acids. Recently, other entities such as fungi, bacteria, and cells have been immobilized successfully. This technique allows the continuous synthesis of specific molecules.

10.8 NUCLEIC ACIDS

Nucleoproteins, which are conjugated proteins, may be separated into nucleic acids and proteins in aqueous sodium chloride. The name "nuclein," which was coined by Miescher

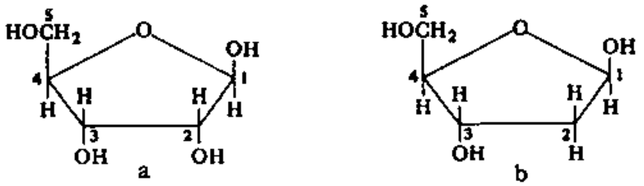
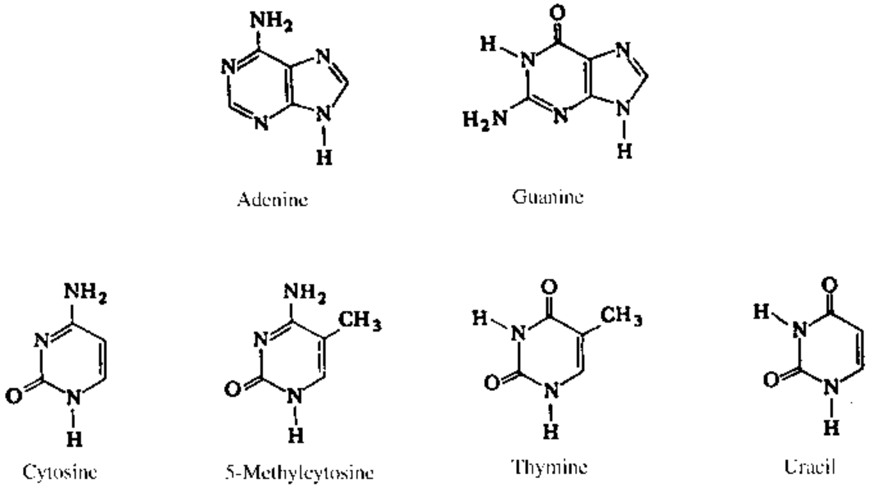


Figure 10.14 Boesekin-Haworth structure of (a) ribose and (b) deoxyribose.

in 1869 to describe products isolated from nuclei in pus, was later changed to *nucleic acid*. Pure nucleic acid was isolated by Levene in the early 1900s. He showed that either D-ribose or D-deoxyribose was present in what are now known as ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). These specific compounds were originally obtained from yeast and the thymus gland, respectively.

In 1944, Avery showed that DNA was capable of changing one strain of bacteria to another. It is now known that nucleic acids direct the synthesis of proteins. Thus, our modern knowledge of heredity and molecular biology is based on our knowledge of nucleic acids. There are two major types of nucleic acids: deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). The name nucleic acid is derived from the fact that they are acidic, containing a phosphoric acid moiety, and are found in the nuclei of cells.

Nucleic acids are high polymers consisting of a pentose sugar containing a heterocyclic base and a phosphate moiety. RNA contains the pentose ribose while DNA contains the pentose deoxyribose (Fig. 10.14). The two sugars are identical except that the deoxyribose contains a hydrogen on carbon 2 (thus the name deoxy or without one “oxy” or hydroxyl) while the ribose pentose contains a hydroxyl group on carbon 2. The sugars also contain a pyrimidine or purine base (Fig. 10.15) present on the 1-carbon replacing the hydroxyl group with a base. The combination of the pentose sugar and a purine or pyrimidine base is called a nucleoside.



Adenine

Guanine

Cytosine

5-Methylcytosine

Thymine

Uracil

Figure 10.15 Structural formulas of (top) purine and (bottom) pyrimidine bases in nucleic acids.

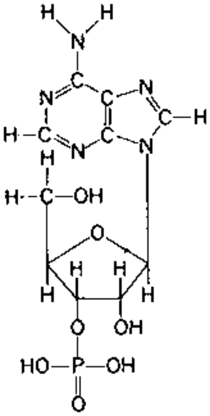


Figure 10.16 Adenylic acid, adenosine-3′-phosphate, nucleotide.

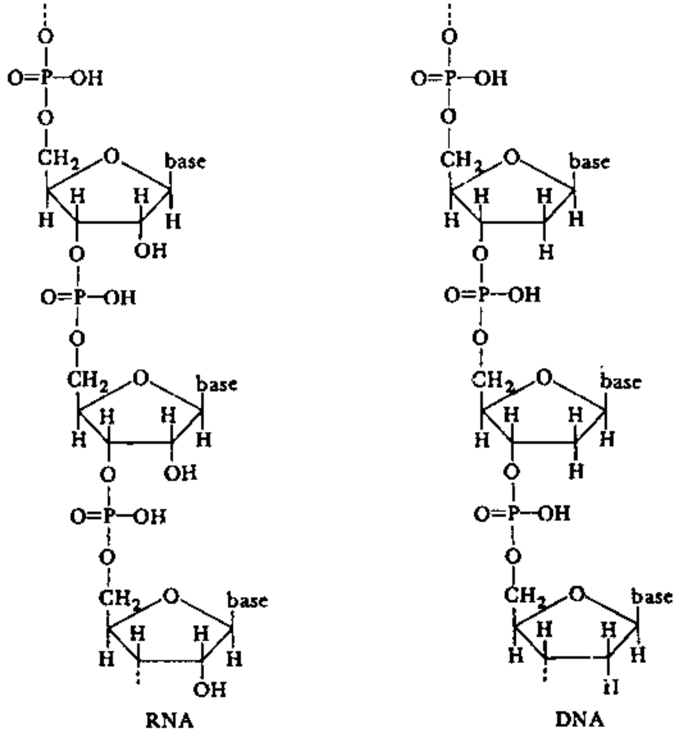
DNA and RNA contain one of five purine/pyrimidine bases (Fig. 10.15). Both DNA and RNA contain adenine and guanine. Uracil is found only in RNA, and thymine or methyluracil is found only in DNA. (It may be of help to remember that DNA was originally found in the thymus gland.) These bases can exist in a number of different ketoenol forms. Interestingly, they exist in the keto form in the nucleic acids.

The combination of a phosphate, a pentose sugar, and a purine or pyrimidine is called a nucleotide. Nucleotides are then phosphoric acid esters of nucleosides. Naturally occurring nucleotides can have the phosphate attached at the 3- or 5-carbon in the pentose sugar. The position of the phosphate on the pentose sugar is designated with a prime. The name for the ribose-containing adenine with the phosphate connected at the 3-carbon on the pentose is adenylic acid or, more precisely, adenosine-3′-phosphate (Fig. 10.16). When the ribose-containing adenine has a phosphate at the 5-carbon it is called adenosine-5′-phosphate (AMP). Two important 5′-nucleotides of adenine are adenosine-5′-diphosphate (ADP) and adenosine-5′-triphosphate (ATP). The hydrolysis of ATP to ADP is important in biological energy transfer with a net Gibbs free energy of about -8.4 kcal/mol (or about -35 kJ/mol). The energy to "drive" this reaction comes from carbohydrates by the process of glycolysis. ATP acts as a storage site for energy released during conversion of carbohydrates to carbon dioxide and water. ATP, ADP, and AMP are referred to as "high-energy" materials with the phosphate linkages being the sites of high energy.

Nucleic acids are polynucleotides attached by the phosphate moieties through the 3′ and 5′ sites on the pentose (Fig. 10.17 and 10.18).

Because the sugar moiety is not symmetrical each unit can be connected differently. Nucleic acids have order as shown in Fig. 10.17. This sense or directionality is such that the phosphodiester linkage between monomer units is between the 3′ carbon of one monomer and the 5′ carbon of the next unit. Thus, the two ends of a DNA are not alike-one containing an unreacted 5′ phosphate and the other an unreacted 3′ hydroxyl group. This is shown in short hand for a triphosphate derived from the base adenine, A, as

$$\text{p-5}'\text{-A-3}'\text{-p-5}'\text{-A-3}'\text{-p-5}'\text{-A-3}' \qquad \text{or} \qquad \text{pApApA} \qquad \text{or simply as} \qquad \text{AAA} \tag{10.40}$$



RNA DNA

Figure 10.17 Representative segments of nucleic acid polymeric chains.

The primary structure of nucleic acids also have individuality related to the base or nucleotide sequence. For a trimer containing C, A, T in that order, the description would be p-5′-C-3′-p-5′-A-3′-p-5′-T-3′ or simply CAT.

Nobel Laureates Watson and Crick correctly deduced that DNA existed as a double-stranded helix in which a pyrimidine base on one chain or strand was hydrogen-bonded to a purine base on the other chain. As illustrated in Fig. 10.18, the total distance for these pairs is 1.07 nm (10.7 Å). As shown, the base pairs are guanine-cytosine and adenine-thymine (which may be remembered from the mnemonic expression *G*ee-*C*AT). A sketch of the DNA double helix is shown in Fig. 10.19. The bases are said to be complementary because coupling in helical double strands only occurs between certain base pairs, such as G with C (Figs 10.17–10.19).

As seen in Fig. 10.18 the combination AT has two hydrogen bonds, while the combination GC has three double bonds contributing to making the GC a more compact structure. This results in a difference in the twisting resulting from the presence of the AT or GC units and combinations of these units result in structures that are unique to the particular combination. It is this twisting, and the particular base sequence, that eventually results in the varying chemical and subsequently biological activities of various combinations. The contributions to this twisting include other factors.

The stability of the DNA is due to both internal and external hydrogen bonding as well as ionic and other bonding. First, the internal hydrogen bonding is between the

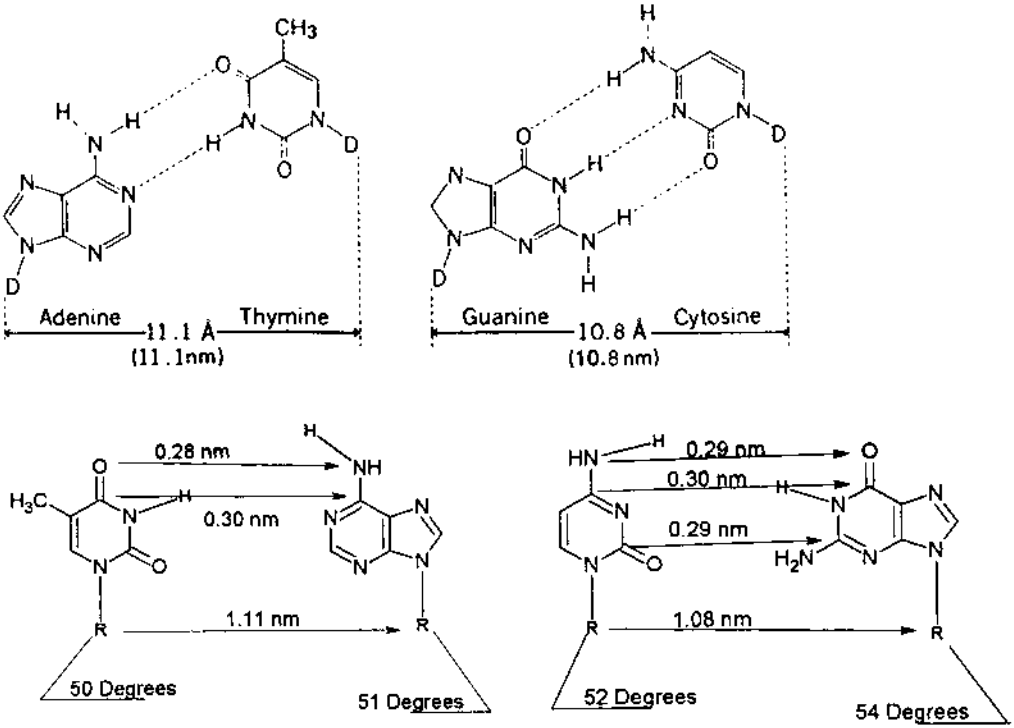


Figure 10.18 (Top) hydrogen bonding between preferred base pairs and (bottom) bond distances between preferred base pairs in DNA.

complementary purine–pyrimidine base pairs. Second, the external hydrogen bonding occurs between the polar sites along exterior sugar and phosphate moieties and water molecules. Third, ionic bonding occurs between the negatively charged phosphate groups situated on the exterior surface of the DNA and electrolyte cations such as Mg^{+2}. Fourth, the core consists of the base pairs, which, along with being hydrogen bonded, stack together through hydrophobic interactions and van der Waals forces. In order to take good advantage of pi-electron cloud interactions, the bases stack with the flat “sides” over one another so that they are approximately perpendicular to the long axis.

The AT and CG base pairs are oriented in such a manner so that the sugar-phosphate backbones of the two twined chains are in opposite or antiparallel directions with one end starting at the 5′ and ending at the 3′ and the starting end of the other across from the 5′

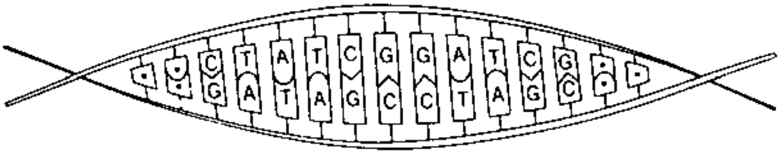


Figure 10.19 A schematic representation of the double helix of DNA.

end being a 3′ end and opposite the other 3′ end is a 5′ end. Thus, the two chains “run” in opposite directions.

The glucose bonds holding the bases onto the backbone are not directly across the helix from one another. Thus, the sugar-phosphate repeat units are not the same. This dislocation creates structures referred to as major and minor grooves as pictured in Fig. 10.26. It is known that at least some proteins that bind to DNA recognize the specific nucleotide sequences by “reading” the hydrogen bonding pattern presented by the edges of these grooves.

Double-stranded DNA takes on one of three secondary structures called A, B, and Z. The major form is the B structure existing almost exclusively in water-based solutions. Here, helical twisting results in a stacking where the average distance between the stacked bases is 0.34 nm with a sugar to sugar distance of 0.6 nm with the helix repeating about every 10 base pairs with a pitch of 0.34 nm. As noted above, the particular specifics vary with the base sequence. For the A form, the pitch or distance required to complete one helical turn is about 0.246 nm with one turn requiring about 11 base pairs. The base pairs are no longer nearly perpendicular to the helix axis as in the case for B DNA, but rather are tilted 19° with respect to the axis. Successive base pairs occur every 0.23 nm in comparison to 0.33 nm for the B form of DNA. The A form is thicker and not as long for the same number of base pairs. While dehydrated DNA can assume an A conformation under physiological conditions, it is unclear if “natural” DNA assumes this form. In fact, the A form is typical for short chained DNA chains in the crystalline form since here much of the DNA is dehydrated. The major groove is deepen while the minor groove is shallower for the A form. The A and B forms are called right handed forms or to have a right handed helical sense.

The Z form of DNA is a left-handed form. It is slimmer and elongated with a rise per base pair of 0.38 nm, about 12 base pairs per turn with a pitch of about 0.456 nm. Certain nucleotide sequences fold into left-handed Z helices more readily than do others; this includes alternating CG sequences. These is evidence that suggests that some natural DNA exists in the Z form.

In solution, DNA is a dynamic, flexible molecule. It undergoes elastic motions on a nanosecond time scale most closely related to changes in the rotational angles of the bonds within the DNA backbone. The net result of these bendings and twistings is that DNA assumes a roughly globular or spherical tertiary shape. The overall structure of the DNA surface is not that of a reoccurring “barber pole” but rather because of the particular base sequence composition each sequence will have its own characteristic features of hills, valleys, bumps, etc.

As the two strands in a double helix separate, they act as a template for the construction of a complementary chain. This process occurs enzymatically with each nucleotide being introduced into the growing chain through matching it with its complementary base on the existing chain. Thus, two identical strands are produced when one double-helix combination replicates.

DNA chains can contain 1 million subunits with an end-to-end contour length of about 1 mm. Even with the complexity of these large macromolecules, synthesis of new chains occurs generally without any change in the molecule. Even when changes occur, these giant molecules have built into them certain “correction” sequences that can recorrect when mistakes occur.

The transcription product of DNA is always single-stranded RNA. The single strand generally assumes a right-handed helical conformation mainly caused by base-stacking interactions also present in the DNA. The order of interaction is purine–purine >> purine–pyrimidine> pyrimidine–pyrimidine. The purine–purine interaction is so strong that a pyrimidine separating two purines is often displaced from the stacking order to allow the interaction between the two purines to occur. Base paring is similar to that of the DNA except that uracil generally replaces thymine. For coupled RNA the two strands are antiparallel as in DNA. Where complementary sequences are present, the predominant double-stranded structure is an A form right-handed double helix. Many RNAs are combinations of complementary two-stranded helices, single-stranded segments, as well as other complex structures. Hairpin curves are the most common type of more complex structure in RNA. Specific sequences, such as UUCG, are generally found at the ends of RNA hairpin curves. Such sequences can act as starting points for the folding of an RNA into its precise three-dimensional structure. The tertiary structures for RNAs is complex with combinations being present. For instance, the tertiary structure for the tRNA of yeast for phenylalanine consists of a cloverleaf including three loops formed by hairpin curves and double helix regions stabilized by hydrogen bonding. Hydrogen bonding sites that are not significant in the DNA structures are important. For instance the free hydroxyl on the ribose sugar moiety can hydrogen bond with other units.

There are four kinds of RNA. Messenger RNA (mRNA) varies greatly in size from about 75 units to over 3000 nucleotide units giving a molecular weight of 25,000 to one million. It is present at a percentage of about 2% of the total RNA in a cell. Transfer RNA (tRNA) has about 73–94 nucleotides with a corresponding molecular weight range of 23,000–30,000. It is present in the cell at a level of about 16%. The most abundant RNA, 82%, is the ribose RNA (rRNA), which has several groupings of molecular weight with the major ones being about 35,000 (about 120 nucleotide units), 550,000 (about 1550 units) and 1,100,000 (about 2900 units). Eukaryotic cells contain an additional type called small nuclear RNA (snRNA).

tRNA generally contains 73–94 nucleotides in a single chain, a majority of the bases are hydrogen-bonded to one another. Hairpin curves promote complementary stretches of base bonding giving regions where helical double stranding occurs. The usual overall structure can be represented as a cloverleaf with each cloverleaf containing four of these helical double stranded units. One of the loops acts as the acceptor stem that serves as the amino acid–donating moiety in protein synthesis.

rRNA is a part of the protein synthesizing machinery of cells, ribosomes. Ribosomes contain two subunits called “small” and “large” with ribosomal RNAs being part of both of these units. rRNAs contain a large amount of intrastrand complementary sequences and are generally highly folded. Interestingly, there is a similarity between the folded structures of rRNA from many different sources even though the primary structure, base sequence, is quite varied. Thus, there appears to be preferred folding patterns for rRNAs.

mRNA, is the carrier of messages that are encoded in genes to the sites of protein synthesis in the cell where this message is translated into a polypeptide sequence. Because mRNA is a transcribed copy of the genetic unit, it is sometimes referred to as being the “DNA-like RNA.” mRNA is made during transcription, an enzymatic sequence in which a specific RNA sequence is “copied” from a gene site. rRNA and tRNA are also made by transcription of DNA sequences but unlike mRNA, they are not subsequently translated to form proteins.

Actual reproduction steps involving DNA and RNA often occur in concert with protein where the protein can act as a clamp or vice holding the various important members involved with the particular reproduction step in place. Thus, the protein complex acts as an assembly line tunnel or doughnut with the reactants present within the interior.

Flow of Biological Information

Nucleic acids, proteins, some carbohydrates, and hormones are informational molecules. They carry directions for the control of biological processes. With the exception of hormones, these are macromolecules. In all of these interactions, secondary influences such as hydrogen bonding and van der Waals forces, and ionic bonds and hydrophobic/hydrophilic character play critical roles. Molecular recognition is the term used to describe the ability of molecules to recognize and interact bond-specifically with other molecules. This molecular recognition is based on a combination of these interactions just cited and on structure. Sections 15.14 and 15.15 illustrate some features of molecular recognition for proteins.

Molecular recognition interactions have several common characteristics. First, the forces that are involved in these interactions are relatively weak and are noncovalent. They are on the order of about 1–8 kcal/mol (1–30 kJ/mol) compared to covalent bonds of the order of about 80 kcal/mol (300 kJ/mol) for a C—C σ bond. A single noncovalent bond is generally not capable of holding molecules together for any length of time. But for macromolecules, there is a cumulative effect so that the forces are not singular but are multiplied by the number of such interactions that are occurring within the particular domain. Second, these interactions are reversible. Initial contact occurs as the molecules come into contact with one another often through simple diffusion or movement of the molecules or segments of the molecules. These initial contacts are often not sufficient to cause the needed binding though some transitory interactions occur. Even so, in some cases the cumulative bonding is sufficient to allow a transient but significant interaction to occur. This complex can then begin a specific biological process. Eventually thermal motions and geometrical changes cause the complex to dissociate. Ready reversibility is an important key that allows a relatively few "signaling" molecules to carry out their mission. Third, bonding between the particular molecular sites is specific. There must exist a combination of complementary bonding, hydrophobic–hydrophilic sites, ionic charge, and geometry that allows effective long-term (generally no more than several seconds) interactions to occur.

In general, the flow of biological information can be mapped as follows: DNA → RNA → protein → cell structure and function. The total genetic information for each cell, called the genome, exists in the coded two-stranded DNA. This genetic information is expressed or processed either through duplication of the DNA, so that it can be transferred during cell division to a daughter cell, or by transfer to manufactured RNA that in turn transfers the information to proteins that carry out the activities of the cell.

Duplication of double-stranded DNA is self-directed. The DNA, along with accessory proteins, directs the replication or construction of two complementary strands forming a new, exact replicate of the original DNA template. As each base site on the DNA becomes available through the unraveling of the double-stranded helix, a new nucleotide is brought into the process held in place by hydrogen bonding and van der Waals forces so that the bases are complementary. It is then covalently bonded through the action of an enzyme called DNA polymerase. After duplication, each DNA contains one DNA strand from the original double-stranded helix and one newly formed DNA strand. This is called semiconservative replication and increases the chance that if an error occurs, the original base sequence will be retained.

How is DNA suitable as a carrier of genetic information? First, because of the double-stranded nature and mode of replication, retention is enhanced. Second, DNA is particularly stable within both cellular and extracellular environments, including a good stability to hydrolysis in an aqueous environment. Plant and animal DNA have survived thousands of years. Using polymerase chain reactions we can reconstruct DNA segments allowing comparisons to modern DNA.

Transcription is the term used to describe the transfer of information from DNA to RNA. The genome is quite large, on the order of a millimeter in length if unraveled, but within it exists coding regions called genes. Transcription is similar to DNA replication except that ribonucleotides are the building units instead of deoxyribonucleotides; the base thymine is replaced by uracil; the DNA-RNA duplex unravels releasing the DNA to again form its double-stranded helix and the single-stranded RNA; and the enzyme linking the ribonucleotides together is called RNA polymerase.

Many viruses and retroviruses have genome that are single-stranded RNA instead of DNA. These include the AIDS virus and some retroviruses that cause cancer. Here, an enzyme called reverse transcriptase converts the RNA genome of the virus into the DNA of the host cell genome, thus infecting the host.

The transcription of the DNA gives three kinds of RNA: ribosomal (rR), messenger (mR), and transfer (tR). The most abundant RNA is rRNA. Most rRNA is large and is found in combination with proteins in the ribonucleoprotein complexes called ribosomes. Ribosomes are subcellular sites for protein synthesis.

tRNA is the smallest of the RNAs being less than 100 nucleotides long. It combines with an amino acid incorporating it into a growing protein. There is at least one tRNA for each of the 20 amino acids used in protein synthesis. mRNA is varied in size but each carries the message found in a single gene or group of genes. The sequence of bases in mRNA is complementary to the sequence of DNA bases. mRNA is unstable and short-lived so that its message for protein synthesis must be rapidly decoded. The message is decoded by the ribosomes that make several copies of the protein for each mRNA.

The ultimate purpose of DNA expression is protein synthesis. mRNA serves as the intermediate carrier of the DNA genetic information for protein synthesis. The DNA message is carried in the form of base sequences that are transferred to RNA also in terms of base sequences. Finally, these are transferred into amino acid sequences through a translation process based on the genetic code.

A set of coding rules are in force as in the translation process as follows: First, a set of three adjacent nucleotides compose the code for each amino acid. A single amino acid can have several triplet codes or codons. Since there are four different nucleotides (or four different bases) in DNA and RNA, there exist 4^3, or 64, trinucleotide combinations. Using U as a symbol for uracil, present in RNA, the triplet or code or codon UUU is specific for phenylalanine. Second, the code is nonoverlapping so that every three nucleotides code for an amino acid and the next three code for a second amino acid and the third set code for a third amino acid, etc. Third, the sets of nucleotides are read sequentially without punctuation. Fourth, the code is nearly universal. Fifth, there are codes for other than amino acids including stop or terminate, UAG, and start or initiate, AUG.

In essence, tRNA has two active sites one that is specific for a given amino acid and one that is specific for a given set of three bases. The tRNA “collects” an appropriate amino acid and brings it to the growing polypeptide chain inserting it as directed by the mRNA. These is then a collinear relationship between the nucleotide base sequence of a gene and the amino acid sequence in the protein.

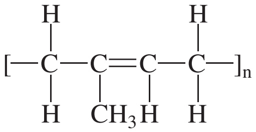
The amount, presence, or absence of a particular protein is generally controlled by the DNA in the cell. Protein synthesis can be signaled external to the cell or within the cell. Growth factors and hormones form part of this secondary messenger service.

The translation and transcription of DNA information in polymer synthesis and behavior, and the particular governing factors and features that control these reactions, are present in the synthesis and behavior of other macromolecules both synthetic and biological.

For the human genome there exist so-called coding or active regions (*exons*) and noncoding regions (*introns*). The average size of an exon is about 120–150 nucleotide units long or coding for about 40–50 amino acids. Introns vary widely in size from about 50 to over 20,000 units. About 5% of the genome is used for coding. It was thought that the other 95% was silent or junk DNA. We are finding that the introns regions play essential roles. Interestingly, introns are absent in the most basic prokaryotes, only occasionally found in eukaryotes, but common in animals.

A special section dealing with the exciting world of the human genome, chromosomes, genes and associated work on coupling the genome material with protein synthesis and activity is given in Section 18.10.

10.9 NATURALLY OCCURRING POLYISOPRENES



$$[-\underset{H}{\overset{H}{C}}-\underset{CH_3}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}-]_n \qquad (10.41)$$

Polyisoprenes (above) occur in nature as hard plastics called gutta percha and balata and as an elastomer or rubber known as *Hevea brasiliensis*, or natural rubber (NR). Approximately 50% of the 500 tons of gutta percha produced annually is obtained from trees grown on plantations in Java and Malaya. Balata and about 50% of the gutta percha used are obtained from trees in the jungles of South America and the East Indies. The first gutta-insulated submarine cable was installed between England and France in 1850. Gutta percha (*Palaquium oblongifolium*) continues to be used for wire insulation, and both this polyisoprene and balata (*Mimusops globosa*) are used as the covers for golf balls.

The hardness of these polydisperse naturally occurring crystalline polymers is the result of a trans configuration in 1,4-polyisoprene (see Figs 10.20 and 10.21). The chain extensions on opposite sides of the double bonds in the polymer chain facilitate good fit and cause inflexibility in these chains.

Gutta percha exists in the planar α form, which has an X-ray identity period of 0.87 nm (8.7 Å) and a melting point of 74°C. The α form is transformed to the β form when these trans isomers of polyisoprene are heated above the transition temperature of 68°C. The nonplanar β form has a melting point of 64°C and an identity period of 0.48 nm (4.8 Å). The latter corresponds to the length of the isoprene repeat unit in the polymer chain.

Both trans and cis isomers of polyisoprene are present in chicle, which is obtained from the *Achras sapota* tree in Central America. Since chicle is more flexible than gutta percha, it has been used as a base for chewing gum. Both trans and cis isomers of polyisoprene are also synthesized commercially.

Natural rubber, which is one of the most important biologically inactive, naturally occurring polymers, was used by the Mayan civilization in Central and South America

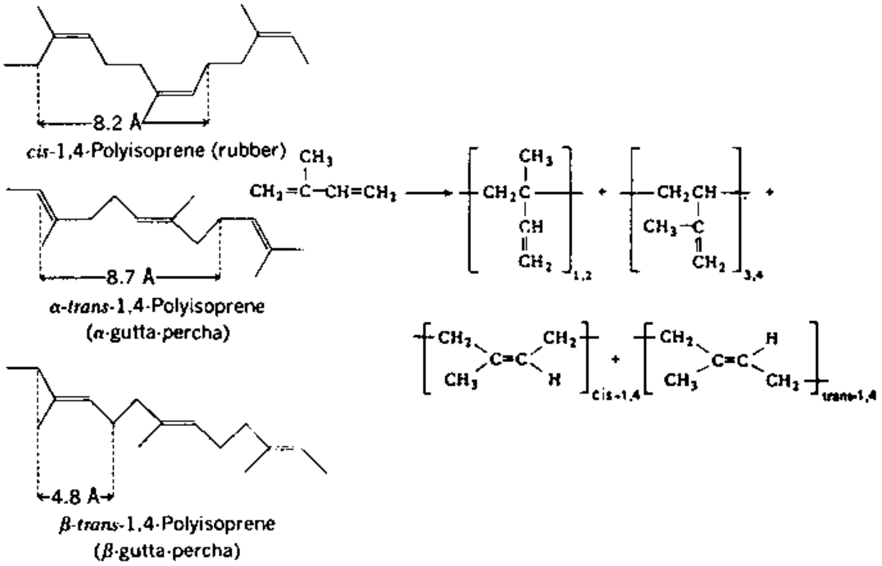


Figure 10.20 Abbreviated structural formulas for polyisoprenes. (From *Introduction to Polymer Chemistry* by R. Seymour, McGraw-Hill, New York, 1971. Used with permission.)

before the twelfth century. In addition to using the latex from the ule tree for the waterproofing of clothing, the Western Hemisphere natives played a game called "tlachtli" with large rubber balls. The object of this game was to insert the ball into a tight-fitting stone hole in a vertical wall using only the shoulder or thigh. The game ended once a goal was scored, and the members of the losing team could be sacrificed to the gods.

While natural rubber, or *caoutchouc*, was brought to Europe by Columbus, little use beyond erasing pencil marks was made of this important elastomer until the nineteenth century. Accordingly, Priestly coined the name *India rubber* to describe its major use at that time.

While less than 1% of the world's present supply of natural rubber is obtained from wild rubber trees, most of this elastomer was shipped from Central and South America prior to the twentieth century. The latex, which is an aqueous suspension of 30–35% cis-1,4-polyisoprene, occurs in microscopic tubules located between the bark and the cambian layer in the hevea plant. The latex is obtained by collecting the liquid which seeps out after tapping the hevea plants.

Hevea latex is also present in the household decorative rubber plant (*Ficus elastica*), milkweed (*Cryptostegia grandiflora*), goldenrod (*Solidago*), dandelions (*Taraxacum offinale* and *Koksagyhz*), creepers (*Landolphia*), and guayule (*Parthenium argentatum*).

In addition to the cultivation of *H. brasiliensis*, experimental plantations have been established for the cultivation of *F. elastica*, *Funtumia*, *Castilloa*, *Manihot*, *Koksagyhz*, and *P. argentatum*. While *F. elastica* continues to be used as a decorative plant, the cultivation of all nonhevea rubbers, except guayule, has been abandoned.

Much of the interest in the Russian dandelion and guayule resulted from successful growth in cooler temperature zones. As much as 200 kg of rubber per acre has been

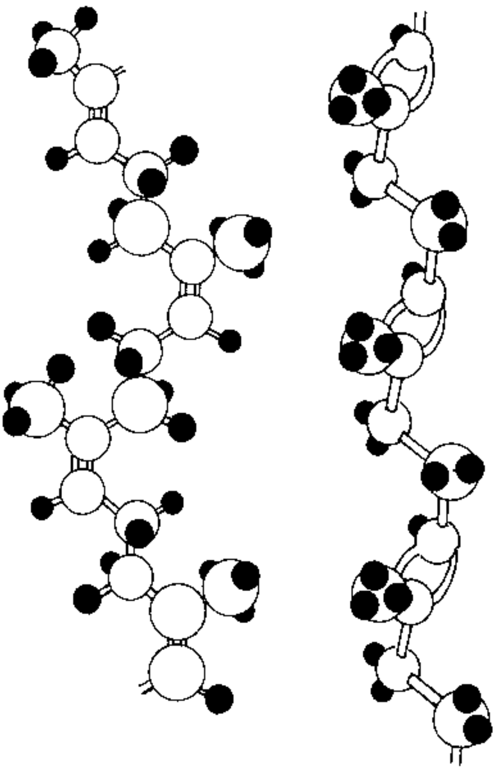


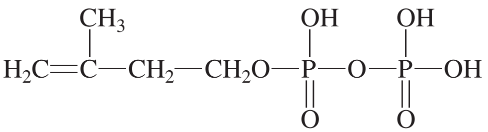
Figure 10.21 Ball-and-stick models of "soft" hevea rubber (cis-1,4-polyisoprene) (left) and "hard" gutta percha (trans-1,4-polyisoprene) (right).

obtained from the cultivation of dandelions in Turkestan (Uzbekistan), but this project was abandoned after the development of styrene-butadiene synthetic rubber (SBR).

Guayule, which grows in arid regions in southwestern United States and northern Mexico, can be mechanically harvested and is used as a replacement for hevea rubber in pneumatic tires. The guayule plant has a rubber content of about 10%. As much as 1500 kg of rubber per hectare (ha) may be obtained by crushing this plant (1 ha $\simeq$ 2.5 acres).

Approximately 99% of the present supply of natural rubber is obtained from the progenitors of a few thousand seedings smuggled out of Brazil by Wickham and Cross and cultivated in Ceylon in 1876. The first successful tappings of these trees were made in 1896. The plantations in Malaya and Indonesia now account for over 70% of the world's production of natural rubber.

This widely used elastomer (cis-1,4-polyisoprene) is not produced in nature by the polymerization of isoprene but by the enzymatic polymerization of isopentenylpyrophosphate:



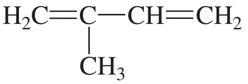
$$H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2{-}CH_2O{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle OH}{|}}{P}}{-}O{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle OH}{|}}{P}}{-}OH \qquad (10.42)$$

While the theoretical yield of hevea rubber is 9000 kg/ha, the best yields to date are 3300 kg/ha.

Charles Goodyear was born in 1800 in New Haven, Connecticut. He was driven to make rubber more temperature-stable. This passion affected his health and took what little money he had. On more than one occasion he lived in debtor’s prison. One of his jobs was to supply the U.S. government with waterproof mailbags, but the mailbags he prepared were sticky and malformed. After many unsuccessful attempts, one of which was to mix the rubber with sulfur, he accidently allowed a mixture of sulfur and rubber to touch a hot stove. The rubber did not melt but only charred a little. As are many of the so-called discoveries by chance or accident, his mind was ready for the result and by 1844 obtained a patent for a process he called “vulcanization” after the Roman god of fire, Vulcan. Vulcanization is the crosslinking reaction between the rubber chains and the sulfur.

Goodyear had trouble defending his patent, piling up huge debts before he died in 1860. Daniel Webster defended him in one of his patent infringement cases. By 1858 the value of rubber goods was about $5 million. The major rubber-producing plants clustered about Akron, Ohio with the Goodyear Company founded in 1870.

Chemists learned about the structure of rubber by degrading it through heating and analyzing the evolved products. One of the evolved products was isoprene, a five-carbon hydrocarbon containing a double bond. Isoprene is a basic building block in nature serving as the “repeat” unit in rubber and also the building block of steroids such as cholesterol.



$$\mathrm{H_2C{=}\underset{\substack{|\\ CH_3}}{C}{-}CH{=}CH_2} \qquad (10.43)$$

Isoprene

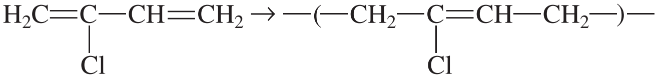
With knowledge that natural rubber had isoprene units, chemists worked to duplicate the synthesis of rubber except using synthetic monomers. These attempts failed until two factors were realized. First, after much effort it was discovered that the methyl groups were present in a cis arrangement. Second, it was not until the discovery of stereoregular catalysts that the chemists had the ability to form natural rubber-like material from butadiene.

The synthesis of a purely synthetic rubber, structurally similar to natural rubber, involved a number of scientists building on one anothers’ work along with a little creativity. Nieuwland, a Catholic priest, president of Notre Dame University, and a chemist, did extensive work on acetylene. He found that acetylene could be made to add to itself forming dimers and trimers.

$$\underset{\text{Acetylene}}{\mathrm{HC{\equiv}CH}} \rightarrow \underset{\text{Vinyl acetylene}}{\mathrm{H_2C{=}CH{-}C{\equiv}CH}} + \underset{\text{Divinyl acetylene}}{\mathrm{H_2C{=}CH{-}C{\equiv}C{-}CH{=}CH_2}} \qquad (10.44)$$

Calcott, a Dupont chemist, attempted to make polymers from acetylene, reasoning that if acetylene formed dimers and trimers, conditions could be found to produce polymers. He failed, but went to Carothers who had one of his chemists, Arnold Collins, work on the project. Collins ran the reaction described by Nieuwland, purifying the reaction mixture. He found a small amount of material that was not vinyl acetylene or divinyl acetylene. He set the liquid aside. When he came back, the liquid had solidified giving a material that seemed rubbery and even bounced. They analyzed the rubbery material and found that it was not a hydrocarbon but had chlorine in it. The chlorine had come from HCl that was used in Nieuwland's procedure to make the dimers and trimers, adding to the vinyl acetylene forming chloroprene.

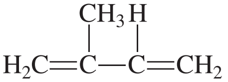
This new rubber was given the name Neoprene. Neoprene had outstanding resistance to gasoline, ozone, and oil in contrast to natural rubber. Today Neoprene is used in a variety of applications including as electrical cable jacketing, window gaskets, shoe soles, industrial hose, and heavy duty drive belts.



$$\mathrm{H_2C{=}\underset{\underset{\displaystyle Cl}{|}}{C}{-}CH{=}CH_2 \rightarrow -(-CH_2-\underset{\underset{\displaystyle Cl}{|}}{C}{=}CH-CH_2-)-} \qquad (10.45)$$

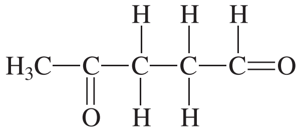
Chloroprene — Polychloroprene (Neoprene)

Prior to the discovery of the vulcanization or crosslinking of hevea rubber with sulfur by Charles Goodyear in 1838, Faraday had shown that the empirical formula of this elastomer is C_5H_8, and thus rubber is a member of the terpene group. The product obtained by pyrolysis of rubber was named isoprene by Williams in 1860 and converted to a solid (polymerized) by Bouchardat in 1879. Tilden suggested the formula that is now accepted for isoprene:



$$\mathrm{H_2C{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{C}{=}CH_2} \qquad (10.46)$$

Since levulinic aldehyde was produced by ozonolysis, Harries suggested the presently accepted structure for the polymer.



$$\mathrm{H_3C{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}\overset{\overset{\displaystyle H}{|}}{C}{=}O} \qquad (10.47)$$

The X-ray identity pattern of stretched natural rubber is 0.82 nm (8.2 Å), which represents two isoprene units in a cis configuration in the polymer chain. Rubber has a glass transition temperature of −85°C, but this is increased as the crosslinked density of vulcanized rubber increases. Unvulcanized rubber undergoes typical reactions of olefins, such as hydrogenation, chlorination, hydrohalogenation, epoxidation, and ozonolysis.

Natural rubber crystallizes when stretched in a reversible process. However, the sample remains in its stretched form (racked rubber) if it is cooled below its T_g. The racked rubber will snap back and approach its original form when it is heated above its T_g. Rubber that has been held in an extended form for long periods of time does not return to its original form immediately when the stress is relieved, since a relaxation process must occur before it decays completely to its original length. The delay in returning to the original form is called hysteresis.

These and other elastic properties of NR and other elastomers above the T_g are based on long-range elasticity. Stretching causes an uncoiling of the polymer chains, but these chains assume the most probable conformations if the stress is removed after a short period of time. Some slippage of chains occurs if the rubber is held in the stretched position for long periods of time.

The absence of strong intermolecular forces, the presence of pendant methyl groups, and the crankshaft action associated with the cis isomer all contribute to the flexibility of the natural rubber molecule. The introduction of a few crosslinks by vulcanization with sulfur reduces slippage of the chains but still permits flexibility in the relatively long chain sections between crosslinks (principal sections).

When a strip of natural rubber (NR) or synthetic rubber (SR) is stretched at a constant rate, the tensile strength required for stretching (stress, s) increases slowly until an elongation (strain, γ) of about 500% is observed. This initial process is associated with an uncoiling of the polymer chains in the principal sections.

Considerably more stress is required for greater elongation to about 800%. This rapid increase in modulus (G) is associated with better alignment of the polymer chains along the axis of elongation, crystallization, and decrease in entropy (ΔS). The work done in the stretching process (W_{el}) is equal to the product of the retractile force (f) and the change in length (dl). Therefore, the force is equal to the work per change in length.

$$W_{el} = f\,dl \qquad \text{or} \qquad f = \frac{W_{el}}{dl} \tag{10.48}$$

W_{el} is equal to the change in Gibbs free energy (dG), which under conditions of constant pressure is equal to the change in internal energy (dE) minus the product of the change in entropy and the Kelvin temperature.

$$f = \frac{W_{el}}{dl} = \frac{dG}{dl} = \frac{dE}{dl} - T\frac{dS}{dl} \tag{10.49}$$

The first term in Eq. (10.49) is important in the initial low-modulus stretching process, and the second term predominates in the second high-modulus stretching process. For an ideal rubber, only the second term is involved.

As observed by Gough in 1805 and confirmed by Joule in 1859, the temperature of rubber increases as it is stretched, and the stretched sample cools as it snaps back to its original condition. (This is easily confirmed by rapidly stretching a rubber band and placing it to your lips, noting that heating has occurred, and then rapidly releasing the tension and again placing the rubber band to your lips.) This effect was expressed mathematically by Kelvin and Clausius in the 1850s. The ratio of the rate of change of the retractive force (df) to the change in Kelvin temperature (dT) in an adiabatic process is equal to the specific heat of the elastomer (C_p) per degree temperature (T) times the change in temperature (dT) with the change in length (dl).

$$\frac{df}{dT} = -\frac{C_p}{T}\frac{dT}{dl} \tag{10.50}$$

Equation (10.50) may be transformed as shown in Eq. (10.51). Unlike most solids, natural rubber and other elastomers contract when heated.

$$\frac{dT}{df} = -\frac{T}{C_p}\frac{dl}{dT} \tag{10.51}$$

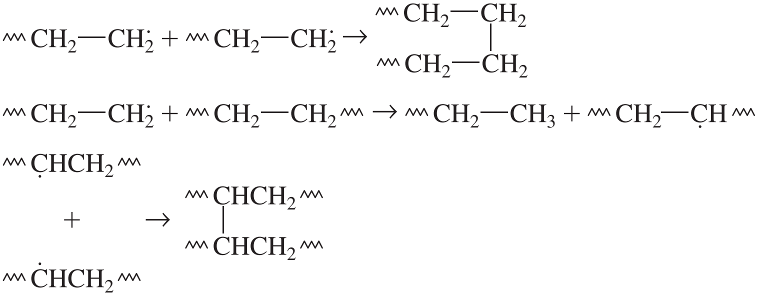
In the process of adding various essential ingredients or additives to crude rubber in a process called compounding, the rubber is masticated on a two-roll mill or in an intensive mixer at an elevated temperature in the presence of air. This mechanical action cleaves some of the carbon–carbon covalent bonds and produces macroradicals with lower $\overline{DP}$ values than the original macromolecule. The coupling of these macroradicals may be prevented if chain transfer agents, called peptizers, are present. As shown in the following equation, loosely bonded atoms or groups are abstracted from the chain transfer agent and dead polymers are produced.

$$\underset{\text{Rubber molecule}}{\sim CH_2{-}CH_2{-}CH_2{-}CH_2\sim} \xrightarrow{E} \underset{\text{Macroradicals}}{\sim CH_2{-}CH_2^{\cdot} + {}^{\cdot}CHCH_2{-}CH_2\sim}$$

$$\underset{\text{Macroradical}}{\sim CH_2{-}CH_2^{\cdot}} + \underset{\text{Chain transfer agent}}{HSR} \rightarrow \underset{\text{Dead polymer}}{\sim CH_2{-}CH_3} + \underset{\text{Free radical}}{{}^{\cdot}SR} \qquad (10.52)$$

$$\underset{\text{Macroradical}}{\sim CH_2{-}CH_2^{\cdot}} + \underset{\text{Free radical}}{{}^{\cdot}SR} \rightarrow \underset{\text{Dead polymer}}{\sim CH_2{-}CH_2{-}SR}$$

Vulcanization of both natural and synthetic rubber is a crosslinking reaction carried out on an industrial scale. The exact mechanism varies with the vulcanization technique employed. Physical crosslinking occurs through the mechanical cleaving of the carbon–carbon bond as noted above with subsequent rejoining of different chains.

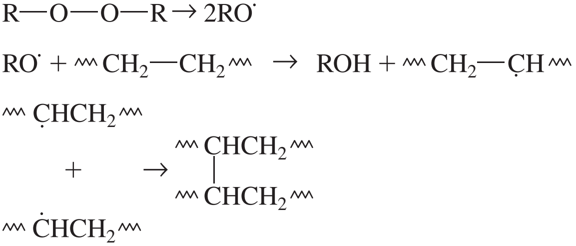


$$\sim CH_2{-}CH_2^{\cdot} + \sim CH_2{-}CH_2^{\cdot} \rightarrow \begin{array}{l}\sim CH_2{-}CH_2\\ \qquad\quad\;|\\ \sim CH_2{-}CH_2\end{array}$$

$$\sim CH_2{-}CH_2^{\cdot} + \sim CH_2{-}CH_2\sim \rightarrow \sim CH_2{-}CH_3 + \sim CH_2{-}\dot{C}H\sim$$

$$\begin{array}{l}\sim \dot{C}HCH_2\sim\\ \quad + \\ \sim \dot{C}HCH_2\sim\end{array} \rightarrow \begin{array}{l}\sim CHCH_2\sim\\ \quad\;|\\ \sim CHCH_2\sim\end{array} \qquad (10.53)$$

Peroxidase-initiated crosslinking proceeds by homolytic abstraction of a polymer chain hydrogen atom followed by radical recombination, i.e.,



$$R{-}O{-}O{-}R \rightarrow 2RO^{\cdot}$$

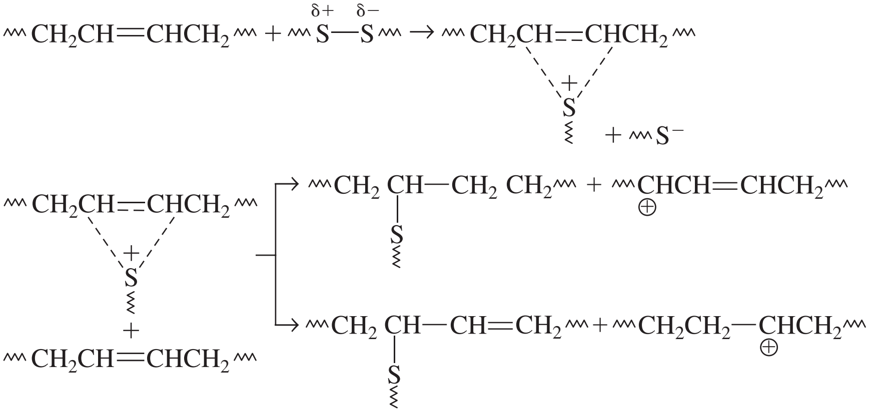
$$RO^{\cdot} + \sim CH_2{-}CH_2\sim \rightarrow ROH + \sim CH_2{-}\dot{C}H\sim$$

$$\begin{array}{l}\sim \dot{C}HCH_2\sim\\ \quad + \\ \sim \dot{C}HCH_2\sim\end{array} \rightarrow \begin{array}{l}\sim CHCH_2\sim\\ \quad\;|\\ \sim CHCH_2\sim\end{array} \qquad (10.54)$$

Unsaturated polymer hydrogen abstraction probably occurs largely at the allylic position.

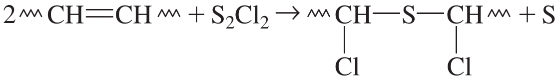
$$\sim CH_2CH{=}CHCH_2\sim + RO^{\cdot} \rightarrow \sim \dot{C}HCH{=}CHCH_2\sim + ROH \qquad (10.55)$$

The oldest method of vulcanization utilizing sulfur appears in part to occur through an ionic pathway involving addition to a double bond forming an intermediate sulfonium ion which subsequently abstracts a hydride ion or donates a proton, forming new cations for chain propagation. Other propagation steps may also occur.



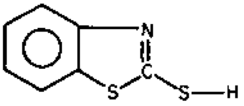
(10.56)

Cold vulcanization can occur by dipping thin portions of rubber into carbon disulfide solutions of S_2Cl_2.



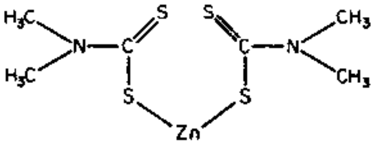
$$2 \sim\!CH{=}CH\!\sim + S_2Cl_2 \rightarrow \sim\!\underset{\displaystyle Cl}{\underset{|}{CH}}{-}S{-}\underset{\displaystyle Cl}{\underset{|}{CH}}\!\sim + S \qquad (10.57)$$

The long time required for vulcanization of rubber by heating with sulfur was shortened drastically by Oenslager, who used organic amines as catalysts, or accelerators, for the vulcanization of rubber in 1904. The most widely used accelerators are derivatives of 2-mercaptobenzothiazole (Captax). Other frequently used accelerators are zinc dimethyldithiocarbamate and tetramethylthiuram disulfide.



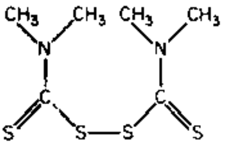
(10.58)

2-Mercaptobenzothiazole



(10.59)

Zinc dimethyldithiocarbamate



(10.60)

Tetramethylthiuram disulfide

Rubber compounding formulations also include antioxidants, such as phenyl-β-naphthylamine, which retards the degradation of rubber at elevated temperatures, and carbon black, which serves as a reinforcing agent. Amorphous silica is used in place of carbon black in compounding recipes for the white sidewalls of pneumatic tires. Since commercial β-naphthylamine is said to be carcinogenic, relatively pure phenyl-β-naphthylamine should be used. The key to prevention of rubber oxidation by an antioxidant depends on its ability to stop the propagation reaction and the chain reaction, or on its ability to destroy peroxides.

$$\begin{aligned}
&R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \text{ (propagation)} \\
&RO_2^{\cdot} + R'H \rightarrow R^{\cdot} + R'O_2H \text{ (chain reaction)} \qquad (10.61) \\
&R'O_2H + AH \text{ (antioxidant)} \rightarrow \text{stable products (peroxide destruction)}
\end{aligned}$$

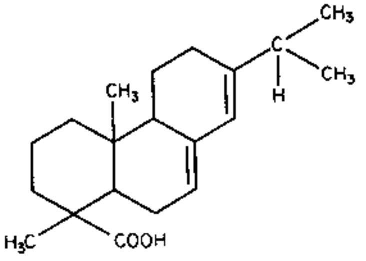
While natural rubber and cotton account for over 40% of total elastomer and fiber production, relatively small amounts of natural plastics and resins are used commercially. The principal products of this type are casein, shellac, asphalt or bitumen, rosin, and polymers obtained by the drying (polymerization) of unsaturated oils.

Shellac, which was used by Edison for molding his first phonograph records and is still used as an alcoholic solution (spirit varnish) for coating wood, is a crosslinked polymer consisting to a large extent of derivatives of aleuritic acid (9,10,16-trihydroxyhexadecanoic acid). Shellac is excreted by small coccid insects (*Coccus lacca*) which feed on the twigs of trees in Southeast Asia. Over 20 *lakshas* (Sanskrit for 100,000), or 2 million insects, must be dissolved in ethanol to produce 1 kg of shellac.

While naturally occurring bitumens were used by the ancients for caulking and waterproofing, they now account for less than 5% of this type of material. Large deposits of natural bitumens are located at Trinidad and Bermudez Lake in the West Indies and in Venezuela. Gilsonite, which was named after its discoverer, is found in Utah and Colorado. Most of today's asphaltic materials are obtained from petroleum-still residues.

Cold-molded filled asphaltic compositions have been used for battery cases and electrical components. Hot-melt asphaltic compositions may be converted to non-Newtonian fluids by passing air into the melt. Both blown and regular asphalt are used in highway construction, roofing, and flooring construction, and for waterproofing.

Rosin, the residue left in the manufacture of turpentine by distillation, is a mixture of the diterpene, abietic acid, and its anhydride. It is nonpolymeric but is used in the manufacture of synthetic resins and varnishes. Ester gum, a crosslinked ester, is obtained by the esterification of rosin with glycerol or pentaerythritol.



(10.62)

Abietic acid

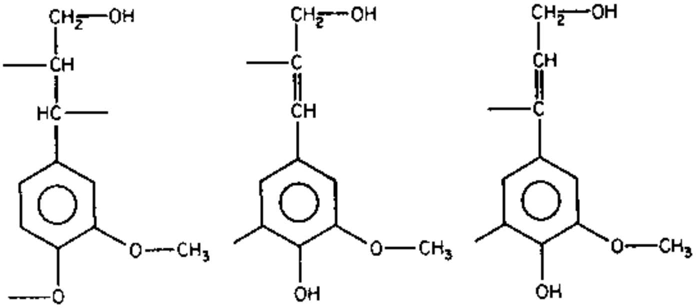


Figure 10.22 Possible units containing lignin.

Lignin is the major noncellulosic constituent of wood. Since its removal is the major step in the production of paper pulp, tremendous quantities of lignin are available as a byproduct of paper manufacture. Lignin is a complex polyphenolic, relatively low molecular weight polymer containing units similar to those described in Fig. 10.22. Its sulfonic acid derivative is used as an extender for phenolic resins, as a wetting agent for applications, such as oil drilling muds, and for the production of vanillin. This last use accounts for less than 0.01%, and all other uses account for less than 1% of this byproduct.

Many natural resins are fossil resins exuded from trees thousands of years ago. Recent exudates are called recent resins, and those obtained from dead trees are called semifossil resins. Humic acid is a fossil resin found with peat, brown coal, or lignite deposits throughout the world. It is a carboxylated phenolic-like polymer used as a soil conditioner, as a component of oil drilling muds, and as a scavenger for heavy metals.

Amber is a fossil resin found in the Baltic Sea regions, and sandarac and copals are found in Morocco and Oceania, respectively. Other copal resins, such as pontiac, kauri, manila, congo, and batu, are named after the geographic location of the deposit.

Casein, a protein from milk, under the name of Galalith has been used as a molding resin and as an adhesive. Unsaturated oils found in linseed, soybean, safflower, tung, oiticica, and menhaden are used as drying oils in surface coatings at an annual rate of over 300,000 tons. Regenerated proteins include soybeans (glycine max), maize (zein), and ground nuts (arachin).

Synthetic polymeric fibers, plastics, elastomers, and coatings have displaced the natural polymeric products to a large extent. However, the latter are renewable resources independent of the supply of petroleum. Thus, their use will continue to increase as long as there is sufficient land available for the economical cultivation of both food and polymeric crops.

10.10 POLYMER STRUCTURE

In 1954, Linus Pauling received the Nobel Prize for his insights into the structure of materials—in particular, proteins. While the protein chain may assume an infinite number of shapes or conformations, due to essentially free rotation about the various covalent bonds in the chain, Pauling showed that only certain conformations are preferred because of intramolecular and intermolecular hydrogen bonding.

Two major secondary structures are found in nature—the helix (Fig. 10.4) and the sheet (Fig. 10.7). The helix is also a major structure for many synthetic flexible polymers since it can take advantage of both intermolecular secondary bonding and relief of steric constraints. Some materials utilize a combination of helix and sheet structures. Thus, wool consists of helical protein chains connected to give a "pleated" sheet.

It is important to remember that while polymer scientists are making great progress in designing polymers with specific properties through manipulation of polymer structure, we have not approached nature in this, particularly with respect to tertiary and quaternary structures. Mimicking natural structures has become an important area of polymer research.

Most isotactic polymers and polymers with bulky substituents exist as short-range helices in solution and in the helical conformation in the crystalline phase if sufficient cooling time is allowed. For isotactic vinyl polymers, alternate bond chains take trans and gauche positions. The direction of the twist is such as to relieve steric hindrance generating a left- or right-handed helix.

The Watson and Crick model for the DNA double helix is only a generalized model to describe what we now know to be a wide variety of DNA structures. The DNA is actually a polyanion with the potential for a single negative charge per each repeat unit. Nature utilizes a combination of DNA structural elements to "code" messages. Much of the DNA structure acts as a "carrier" and "container." For instance, only about one in 10^4 sites are specific binding sites for six-base-pair restriction enzymes.

For double-stranded DNA, structural elements include major and minor grooves, supercoils, kinks, cruciforms, bends, loops, and triple strands (Fig. 10.23). Each of these structural elements can vary in length, shape, location, and frequency. Further, even the

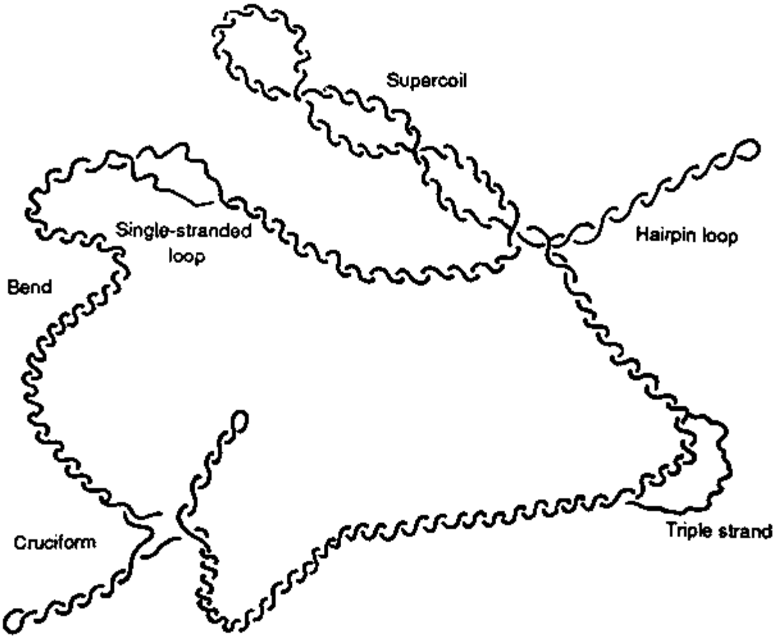


Figure 10.23 Representation illustrating unusual structural forms of nucleic acids.

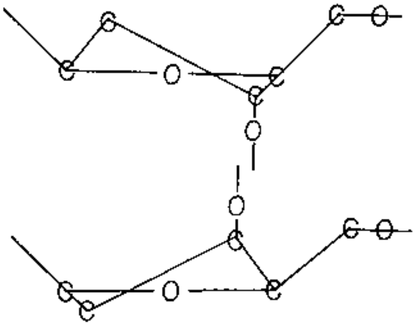


Figure 10.24 Two sugar "pucker" conformations found within DNA. The top form is commonly found in B-DNA, while the bottom form is often found in A-DNA.

"simple" DNA double helix can vary in pitch per turn of helix, number of units per helix turn, sugar pucker conformation, and helical sense.

Helical sense refers to whether the helix is left- or right-handed. The pentose sugar can be present in a wide variety of conformations. Two of these are shown in Fig. 10.24. Such variations can be responsible for variance in the orientation of the base pairs leading to varying pitch of the helix. The orientation of the base with respect to the sugar also varies. Usually the bases lie away from or anti to the sugar. Rotation of the base 180° about the glycosidic bond has the base "over" or syn to the sugar. Finally, while the bases pair typically in the mnemonic combination *Gee CAT*—i.e., guanine pairs with cytosine while adenine pairs with thymine—the planes of the paired bases vary to minimize steric requirements and bond angle constraints while maximizing hydrogen bonding (Fig. 10.25).

DNA's helical conformations thus far identified fall into three general groupings—A, B, and Z. Most DNAs are of the B form, which is a regular right-handed helix with the base pairs oriented approximately perpendicular to the helix axis giving well-defined major and minor grooves (Fig. 10.26). The B form has about a 33-Å pitch-per-helix turn with about 10 base pairs per turn and the base is situated anti to the sugar. The A form is found in fibers at low hydration and is mainly found in DNA-RNA hybrids and double-stranded RNA segments. Grooves of varying sizes are also present. There are about 10.7 base pairs per turn with about a 25-Å pitch-per-helix turn with the bases anti

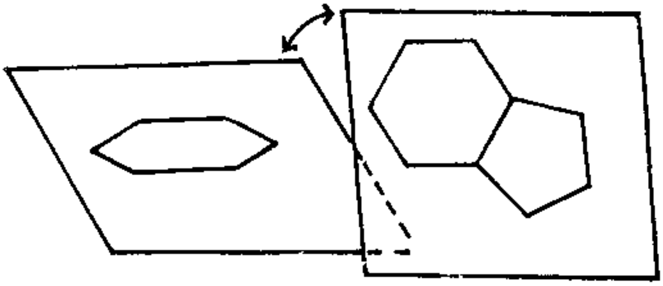


Figure 10.25 Illustration of twisting that occurs between paired bases in DNA.

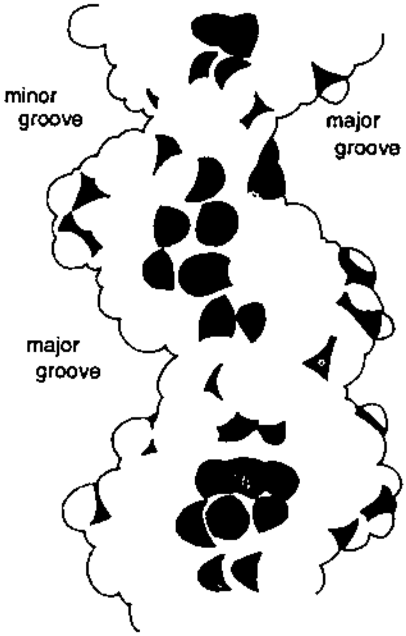


Figure 10.26 Silhouette emphasizing major and minor grooves that occur in B-DNA. Phosphorus atoms are darkened.

with respect to the sugar. It is also a right-handed helix. The Z-DNA is a left-handed helix with the cytosine base anti to the sugar, but the guanine base is syn to the sugar. The Z-DNA has about 12 base pairs and a pitch of about 46 Å per helix turn.

As noted before, other unusual conformations also exist, such as the loop, bend, and cruciform. It is now known that certain base sequences encourage each of these unusual conformations. Thus, a series of AT base pairs tends to “bend” the DNA. A sequence of six adjacent adenosine-containing units causes a bend of about 18°.

Electron microscopy shows that DNA consists of two general structures: linear and circular. The chromosomal DNA in bacteria is a closed circle, a result of covalent joining of the two ends of the double helix. Some circular double-stranded DNA structures are shown in Fig. 10.23. The chromosomal DNA in eukaryotic cells, like ours, is believed to be linear.

The most important of the secondary structures is supercooling. Supercoiling simply is the coiling of a coil or in this case a coiling of the already helical DNA. The typical DNA structure is the thermally stable form. Two divergent mechanisms are believed responsible for supercoiling. The first, and less prevalent, is illustrated by a telephone cord. The telephone cord is typically coiled and represents the “at rest” or “unstressed” coupled DNA. As I answer the telephone I have a tendency to twist it in one direction and after answering and hanging up the telephone for awhile it begins forming additional coils. Thus, additional coiling tends to result in supercoiling. The second, and more common form, involves the presence of less than normal coiling. This can be illustrated by taking a rubber band, breaking one end and then attaching it about a stationary object.

Begin bradding the two ends until just prior to a bunching or formation of supercoiling through over coiling. Then separate the two ends pulling them apart. The resulting strain produces supercoiling and illustrates supercoiling resulting in under coiling or under winding. Thus, under winding occurs when there are fewer helical turns than would be expected. Purified DNA is rarely relaxed.

Supercoiling with bacterial DNA gives a largely open, extended and narrow, rather than compacted, multibranched structure as depicted in Fig. 10.27.

By comparison, the DNA in eukaryotic cells is present in very compacted packages. Supercoiling forms the basis for the basic folding pattern in eukaryotic cells that eventually results in this very compacted structure. Subjection of chromosomes to treatments that partially unfold them show a structure where the DNA is tightly wound about "beads of proteins" forming a necklace-like arrangement where the protein beads represent precious stones embedded within the necklace fabric (Fig. 10.28). This combination forms the nucleosome, the fundamental unit of organization upon which higher-order packing occurs. The bead of each nucleosome contains eight histone proteins. Histone proteins are small basic proteins with molecular weights between 11,000 to 21,000 and specified by names such as H1, H2, and so on. H1 is especially important and its structure varies to a good degree from species to species whereas some of the other histones, such as H3 and H4, are very similar. Histones are rich in the amino acid residues from arginine and lysine.

While eukaryotic DNA is linear, because of its size, it acts as a closed loop allowing supercoil formation.

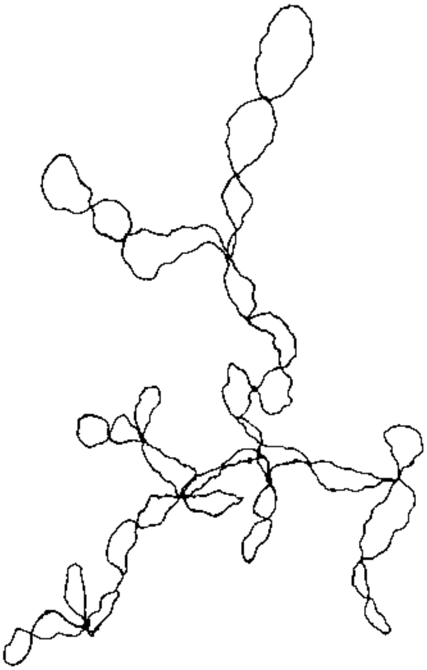


Figure 10.27 Depiction of a typical bacterial chromosome. Note the supercoils, branch points, intersections, and generally thin and open structure.

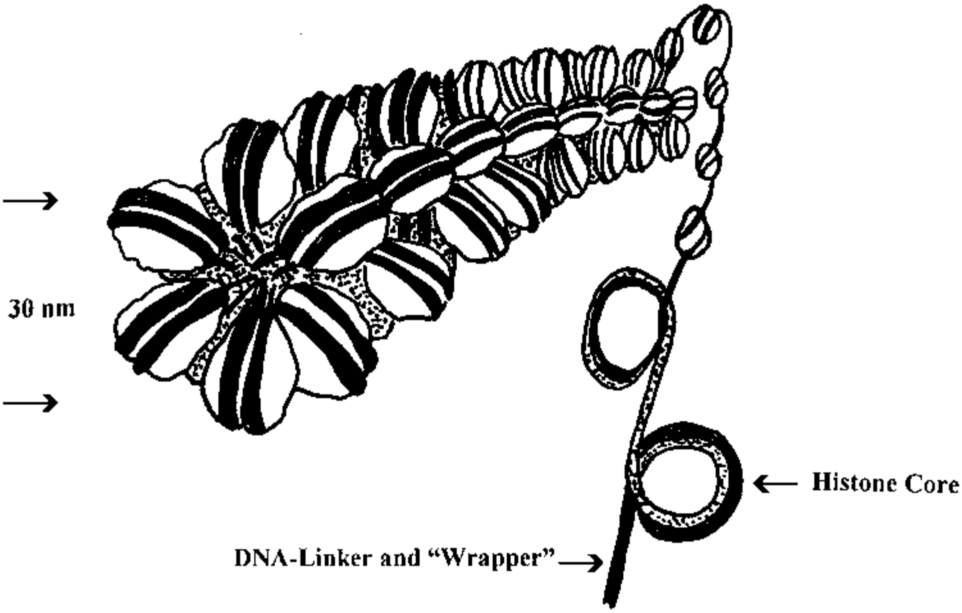


Figure 10.28 Illustration of regularly spaced nucleosomes consisting of histone protein bound to supercoiled DNA with DNA links between the histone bound units forming a 30 nm higher-order fiber.

Wrapping of DNA about a nucleosome core compacts the DNA length about sevenfold. The overall compacting though is about 10,000 fold. Additional compacting of about 100-fold is gained from formation of so called 30 nm fibers (Fig. 10.28). These fibers contain one H1 for nucleosome core. This organization does not occur over the entire chromosome but rather is punctuated by areas containing sequence-specific (non histone containing) DNA-binding proteins. The name "30 nm fibers" occurs because the overall shape is of a fiber with a 30 nm thickness. The additional modes of compaction are just beginning to be understood but may involve scaffold-assisting. Thus, certain DNA regions are separated by loops of DNA with about 20,000 to 100,000 base pairs with each loop possibly containing sets of related genes.

The scaffold contains several proteins, especially H1 in the core and topoisomerase II. Both appear important to the compaction of the chromosome. In fact, the relationship between topoisomerase II and chromosome folding is so vital that inhibitors of this enzyme can kill rapidly dividing cells and several drugs used in the treatment of cancer are topiosomerase II inhibitors.

This central theme concerning the major secondary structures found in nature is also illustrated with the two major polysaccharides derived from sucrose, i.e., cellulose and the major component of starch—amylose. Glucose exists in one of two forms (Fig. 10.29)—an alpha (α) and a beta (β) form, where the terms α and β refer to the geometry of the oxygen connecting the glucose ring to the fructose ring.

Cellulose is a largely linear homosaccharide of β-D-glucose. Because of the geometry of the β linkage, individual cellulose chains are typically found in nature to exist as sheets, the individual chains being connected through hydrogen bonding (Fig. 10.30). This sheet

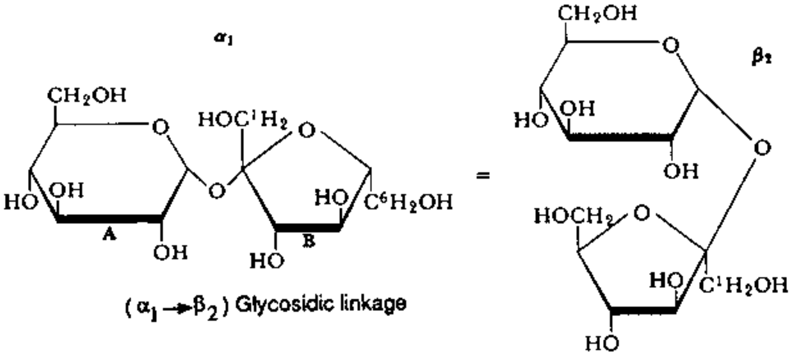


Figure 10.29 The α (left) and β (right) forms of D-glucose in sucrose.

structure permits the existence of materials with good mechanical strength, allowing them to act as the structural units of most plants.

Amylose, one of the two major components of starch, is a linear polymer of the α-D-glucose. Its usual conformation is as a helix with six residues per turn (Fig. 10.31). Starch is a major energy source occurring in plants, usually as granules.

10.11 GENETIC ENGINEERING

In its broadest sense, genetic engineering refers to any artificial process that alters the genetic composition of an organism. Such alterations can be effected indirectly through chemical methods, through radiation, or through selective breeding. Today the term usually refers to the processes whereby genes or portions of chromosomes are chemically altered.

The term clone comes from the Greek word *klon*, meaning a cutting used to propagate a plant. Cell cloning is the production of identical cells from a single cell. In like manner, gene cloning is the production of identical genes from a single gene, introduced into a

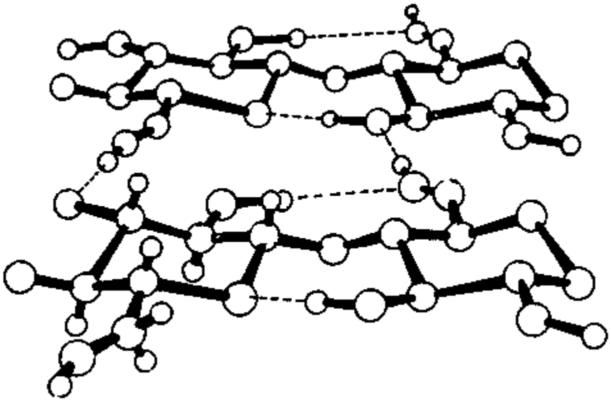


Figure 10.30 Sheet-like structural arrangement of cellulose derived from β-D-glucose units. Hydrogen bonding is noted by dotted line.

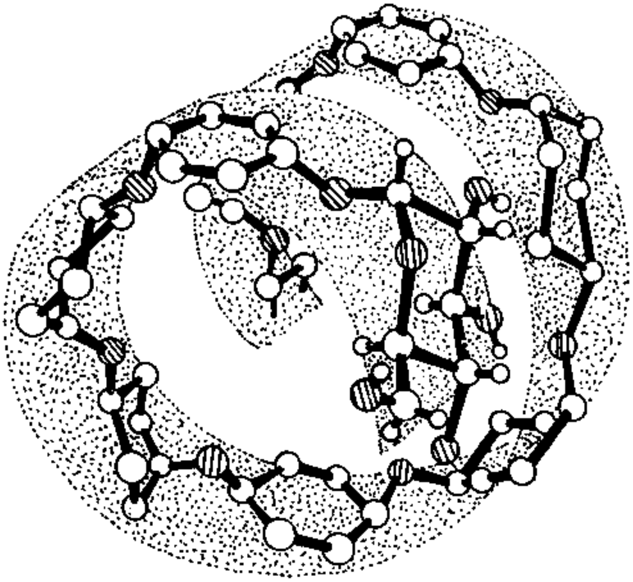


Figure 10.31 Helical structural arrangement of amylose derived from α-D-glucose units.

host cell. A gene is a chromosomal portion that codes for a single polypeptide or RNA. Gene splicing is currently practiced as the enzymatic attachment of one gene or gene segment to a gene or gene segment.

Enzymes (natural molecular catalysts, protein catalysts) have been found that act as designing tools for the genetic engineer. One of these enzyme groups consists of *restriction endonucleases*. These are highly specific enzymes that recognize specific series of base pairs up to six base pairs in length. They then can split the DNA at specific points within this region. Organisms produce restriction endonucleases that are specific for that organism. A second tool employed by the genetic engineer is the enzyme terminal transferase that adds deoxyribonuclease residues to the 3′ end of DNA strands generating 3′ tails of a single type of residue.

The genetic engineer employs special modified plasmid DNAs called vectors or carriers. These circularly shaped vectors can reproduce autonomously in a host cell. Plasmids have two other important properties. First, they can pass from one cell to another allowing a single "infected" bacterial cell to inject neighboring bacterial cells. Second, gene material from other cells can be easily formed into plasmids, allowing ready construction of modified carriers. *Escherichia coli*, better known simply as *E. coli*, is typically employed as the host cell.

Chemically, a gene is but a segment of the DNA chain coded to direct the synthesis of a specific protein. A single DNA molecule often contains many genes. Combinations of these genes along the DNA form chromosomes. The precise steps involved are not difficult to acquire or to understand. Genes are composed of long, linear DNA chains; actually they are composed of two such DNA chains existing in a helical conformation (see Fig. 10.19).

These DNA chains can be manipulated in a variety of ways, but of major interest here is the production of recombinant DNA. For instance, DNA that performs a desired role, such as the production of insulin, is appropriately isolated. The recovered DNA is then spliced using molecular scissors, i.e., specific enzymes. The molecular engineer has a wide variety of these molecular scissors that will “cut” at known sites.

One group of these enzymes the restriction endonucleases, was briefly described earlier. Certain restriction endonucleases cut double-stranded DNA asymmetrically in regions called palindromes, i.e., regions that read (have the identical sequence) the same left to right on one strand as right to left on the other. This produces what is referred to as “sticky ends” that form not only a “cleft” for attachment but also a single-stranded end that has the ability to pair with another similarly produced strand. Both strands of the twin strand have identical coding and a tendency to recombine with complementary strands from another organism.

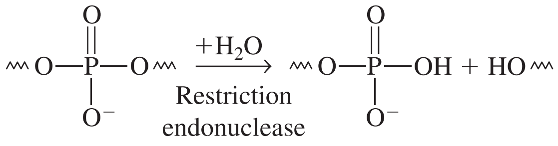
When mixed under the proper conditions in the presence of DNA-ligase, the lysed ends recombine and anneal rapidly in the correct sequence of base pairing. The hydrogen bonds that form reinforce the recombination reaction.

The resulting recombination products contain a wide variety of recombinant combinations as well as largely unrecombined fragments. This mixture is typically treated in one of two manners. The simplest case requires a chemical-resistant gene, i.e., resistant to an antibiotic such as tetracycline. The recombination product is plated onto a nutrient surface so that colonies can grow. These colonies are then treated with tetracycline. The survivors are transferred into the host organism so the new gene can express its protein.

In cases such as the synthesis of insulin, the recombination mixture is added to a host organism, such as a strain of *E. coli*. This infected mixture is then plated out. The individual colonies are then tested for insulin production. Those colonies that are potential producers are further plated out and grown for mass insulin production. Cells that take up or accept the recombinant DNA are called transformants. More specialized routines have been devised to increase the probability that the desired gene is incorporated into the host.

The steps involved in gene splicing, emphasizing the chemical nature of the individual steps, are as follows:

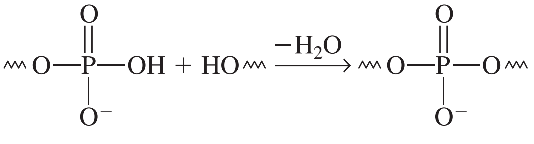
1. Lysing, which in reality is simply the hydrolysis of DNA units as follows:



$$\sim O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O\sim \xrightarrow[\text{Restriction endonuclease}]{+H_2O} \sim O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-OH + HO\sim$$

2. Construction of staggered (sticky) ends.
3. Recombination or lysation.
4. Chemical recombination of vector. (Insertion into host cell; recombining plasmid genes into the host genetic complement.)

   Steps 2, 3, and 4 can be considered chemically to be the reverse action to lysing. They are dehydration reactions that employ specific enzymes.



$$\sim O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-OH + HO\sim \xrightarrow{-H_2O} \sim O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O\sim$$

This reaction is analogous to esterification reactions including the sequence employed in the synthesis of polyesters.

5. Replication is identical to plating out of bacteria, fungi, and cell lines.
6. See step 2.
7. Annealing of base pairs. Here the major chemical driving force is simply the formation of secondary bonding (hydrogen bonding) between preferred base pairs.
8. Analysis and selection.

10.12 DNA PROFILING

DNA profiling, also called DNA typing or DNA fingerprinting, relies on technology developed within the past two decades. It is used in paternity identification, classification of plants, criminal cases, etc. We will concentrate on the use of DNA profiling in criminal cases. Here, questions of law become intertwined with statistical arguments and chemical behaviors.

DNA profiling is based on variations that exist in the DNA molecule between each individual's DNA (with the exception of identical siblings). Samples are generally derived from a person's blood, hair roots, semen, skin, and saliva.

Two major types of DNA profiling are the polymerase chain reaction (PCR) and the restriction fragment length polymorphism (RFLP) approaches. The PCR approach utilizes a sort of molecular copying process. Here, a specific DNA region is selected for investigation. The PCR sequence requires just a few nanograms of DNA.

The second approach focuses on sections of the DNA called restriction fragment length polymorphisms. Here DNA, isolated from the cell nucleus, is broken into pieces by restriction enzymes that cleave the DNA at specific sites. Thus, each time this base sequence appears in the DNA portion under study, the enzyme will sever the DNA chain. Because of the variability in DNA of individuals, the distance (number of individual phosphate units) between "slices" vary. These spliced fragments are separated largely according to length (size) by gel electrophoresis and transferred to a backing material, where radiolabeled probes that bind only specific DNA sequences are added. The location of the binding is determined using X-ray film that is sensitive to the nuclear breakdown of the radioactive probes. The X-ray film is then developed and analyzed.

Scientists have a number of different restriction enzymes that cut DNA at different specific sites. Thus, the previous sequence can be repeated using a different restriction enzyme giving a different DNA profile for the same DNA sample. Each additional "sequencing," using a different restriction enzyme, decreases the probability that another person will have the same cumulative DNA profile. For instance, for one restriction enzyme the computer data bank may say that the possibility that another person would have the same DNA profile is 1 in 100 (1%), for a second restriction enzyme the probability may be 1 in 1000 (0.1%), and for a third restriction enzyme the probability may be 1 in 500 (0.2%). The probability that the cumulative DNA profile would produce a matching pattern is $0.01 \times 0.001 \times 0.002 = 0.00000002$ or 0.000002% or 1 part in 50,000,000. There is a caution to using the "multiplication rule," in that DNA sequences are not *totally* random. In fact, DNA sequence agreements generally diverge as one's ancestors are less closely related.

The RFLP method requires a sample about 100 times larger than is required for the PCR approach, but with repeated sequences using different restriction enzymes, RFLP is more precise.

It must be noted that factors leading to DNA degradation, such as moisture, chemicals, bacteria, sunlight, and heat, will also impact negatively on DNA profiling since the precise sequences and lengths of the DNA may be changed.

10.13 MELANINS

Light is continuous ranging from wavelengths smaller than 10^{-12} cm (γ radiation) to greater than 10^8 cm. Radiation serves as the basis for the synthesis of many natural macromolecules via photosynthesis. Radiation is used commercially to increase the wood pulp yield through crosslinking and grafting of lignin and other wood components onto cellulosic chains. Radiation is also used in the synthesis and crosslinking of many synthetic polymers.

Radiation is also important in the synthesis and rearrangement of important "surface" macromolecules. Tanning of human skin involves the activation of the polypeptide melanin-stimulating hormone–β (MSH-β) that in turn eventually leads to the phenomena of tanning. Exposure to higher energy light from about 297 to 315 nm results in both tanning and burning, whereas exposure to light within the 315 to 330 nm region results mainly in tanning.

Ultraviolet (UV) radiation activates enzymes that modify the amino acid tyrosine in pigment-producing cells, the melanocytes. The enzyme tyrosinase, a copper-containing oxygenase, catalyzes the initial step, which is the hydroxylation of tyrosine to 3,4-dihydroxyphenylalanine that is oxidized to dopaquinone subsequently forming the melanins (Fig. 10.32). The concentration of tyrosine is relatively high in skin protein. These modified tyrosine molecules undergo condensation forming macromolecules known as melanins. Melanins have extended chain resonance where the π electrons are associated with the growing melanin structure. As the melanin structure grows, it becomes more colored

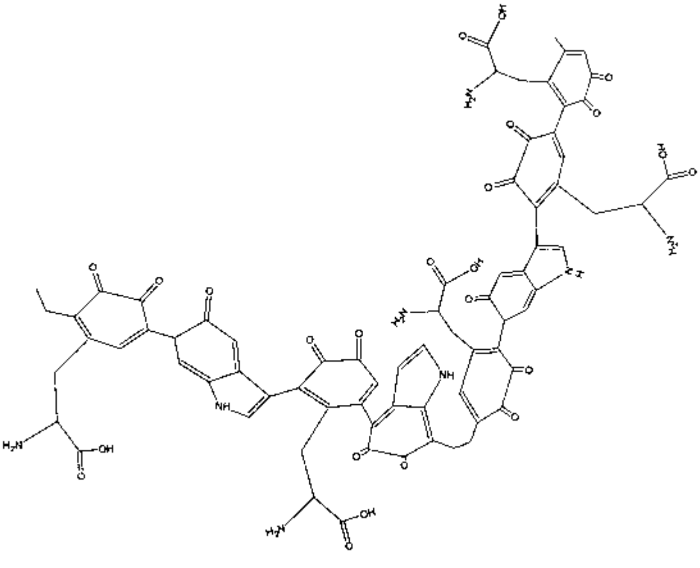


Figure 10.32 Representative structure of melanin.

giving various shades of brown color to our skin. This brown coloration acts to help protect deeper skin elements from being damaged by the UV radiation. The absence of the enzyme tyrosinase that converts tyrosine to melanin can lead to albinism.

At least two colored melanins are formed: a series of black melanins and a series of so-called "red melanins." Our skin pigmentation is determined by the relative amounts of these red and black melanins in our skin.

The concentration of melanin also contributes to the color of our hair (except for redheads where the iron-rich pigment trichosiderin dominates). The bleaching of hair, generally achieved through exposure to hydrogen peroxide, is a partial result of the oxidation of the melanin. A side reaction of bleaching is the formation of more sulfur crosslinks leading to bleached hair being more brittle because of the increased crosslinking causing to a decrease in hair flexability.

Melanin also provides a dark background in our eye's iris, is involved in animal color changes (such as the octopus and chameleon), is formed when fruit is bruised, and is partially responsible for the coloration of tea.

SUMMARY

1. Physically there are few differences in the behavior, study, or testing of natural and synthetic polymers. The fundamental principles that underpin the behavior of macromolecules apply equally to both synthetic and natural polymers. Both groupings contain members that exhibit characteristics that are unique to that grouping. Even so, differences within even these groupings are by degree rather than by kind with the fundamental laws continuing to be applicable.
2. Contributions from studying both natural and synthetic polymers are being used to forward the science of both sets of macromolecules.
3. Organic polymers are responsible for the life—both plant and animal—that exists. Their complexity allows for the variety that is necessary for life to occur, to reproduce, and to adapt. Structures of largely linear natural and synthetic polymers can be divided into primary structures used to describe the particular sequence of (approximate) repeat units, secondary structure used to describe the molecular shape or conformation of the polymer, tertiary structure that describes the shaping or folding of macromolecules, and quaternary structure that gives the overall shape of groups of tertiary-structured macromolecules. The two basic secondary structures are those of the helix and sheets.
4. Polysaccharides are the most abundant, on a weight basis, naturally occurring organic polymer. They are truly complex molecules with most structures representable only on an "average" basis. They are diverse with respect to both occurrence and size. The most important in terms of current knowledge, weight, and use are cellulose and starch. Cellulose is composed largely of D-glucose units that are associated with other materials such as lignin. Cotton is one of the purest forms of cellulose thought we get most of our cellulose from wood pulp. Cellulose becomes soluble in aqueous solutions only when the hydrogen bonds in the cellulose is broken.
5. While cellulose is used extensively itself in the form of paper and paper-based products, it also forms the basis of a number of synthetic including a variety of acetylated products such as rayon.

6. Starch is composed of two major components—amylopectin and amylose. It is the second most abundant polysaccharide and is found largely within plants.
7. Proteins are composed of 20 different α-amino acids and contain peptide linkages similar to those present in polyamides. With the exception of glycine, all amino acids contain a chiral carbon. The geometrical shape and behavior of the giant proteins is a product of the various preferred geometries that allow the molecules to balance factors such as preferred bond angle, secondary bonding forces (emphasizing hydrogen bonding), size, shape, hydrophobic–hydrophilic interactions, external/internal chemical environments, and crosslinking. Small chains of amino acids are referred to as peptides.
8. Secondary structures for proteins are generally fibrous and globular. Proteins such as keratins, collagen, and elastin are largely fibrous and have secondary structures of sheets and helices. Many of the globular proteins are composed of protein chains present in secondary structures approximating helixes and sheets.
9. Enzymes are one important group of proteins. They serve as natural catalysts immobilizing various components that will later be joined or degraded.
10. The two major types of nucleic acids are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Nucleic acids are polyphosphate esters containing the phosphate, sugar, and base moieties. Nucleic acids contain one of five purine/pyrimidine bases that are coupled within double-stranded helices. DNA, which is an essential part of the chromosome of the cell, contains the information for the synthesis of protein molecules. For double-stranded nucleic acids, as the two strands separate, they act as a template for the construction of a complementary chain. The reproduction or duplication of the DNA chains is called replication. The DNA undergoes semiconservative replication where each of the two new strands contains one of the original strands.
11. The flow of biological genome knowledge is from DNA to RNA via transcription and from RNA to direct protein synthesis via translation.
12. Polyisoprenes form the basis of many natural polymers including the two most widely known natural plastics, gutta percha and balata, and an elastomer known as *Hevea brasiliensis*, or natural rubber. The hard plastics balata and gutta percha are trans isomers while natural rubber is the cis isomer of 1,4-polyisoprene. The polymer chain of amorphous natural rubber and other elastomers uncoils during stretching and returns to its original low-entropy form when the material is above its T_g. Chain slippage is minimized through the presence of crosslinks. Unlike other solids, stretched rubber contracts when heated. The long-range elasticity is dependent on the absence of strong intermolecular forces. Eventually natural rubber formed the basis of the rubber industry after knowledge was obtained regarding such factors as crosslinking, which allowed the material to remain coherent but elastomeric even when exposed to moderate temperatures.
13. Genetic engineering is based on chemical manipulations that are exactly analogous to those carried out by chemists in basic chemistry laboratories, but it involves the use of biological agents.
14. Melanins are polymeric agents that play many roles in nature including, forming our skin pigmentation and with their growth through exposure to sunlight acting to protect us from the harmful effects of the sunlight.

GLOSSARY

A: an abbreviation for adenine.
accelerator: A catalyst for the vulcanization of rubber.
acetal linkage: The linkage between anhydroglucose units in polysaccharides.
adenine: A purine base present in nucleic acids.
adenosine: A nucleoside based on adenine.
adenosine phosphates: Phosphoric acid esters of adenosine.
adenylic acid: A nucleotide based on adenine.
ADP: adenosine diphosphate
alkali cellulose: Cellulose that has been treated with a strong caustic solution.
α-amino acid: A carboxylic acid with an amino group on the carbon next to the carboxyl group.
α arrangement: That present in an α helix.
α-cellulose: Cellulose that is insoluble in a 17.5% caustic solution.
α helix: A right-handed helical conformation.
amorphous silica: A filler used with polymers.
AMP: Adenosine monophosphate.
amylopectin: A highly branched starch polymer with branches or chain extensions on carbon 6 of the anhydroglucose repeating units.
amylose: a linear starch polymer.
antioxidant: A compound that retards the degradation of a polymer.
ATP: Adenosine triphosphate.
axial bonds: Bonds that are perpendicular and above or below the plane of the hexose ring, such as the hydroxyl group on carbon 1 in α-D-glucose.
balata: A naturally occurring plastic (trans-1,4-polyisoprene).
β arrangement: A pleated sheetlike conformation.
β-cellulose: Cellulose soluble in 17.5% but insoluble in 8% caustic solution.
Boeseken-Haworth projections: Planar hexagonal rings used for simplicity, instead of the staggered chain forms, to show the structure of saccharides such as D-glucose.
C: An abbreviation for cytosine.
carbohydrate: An organic compound with an empirical formula of CH_2O.
carbon black: Finely divided carbon used for the reinforcement of rubber.
carboxymethylhydroxyethylcellulose (CMHEC): Made from the reaction of sodium chloroacetate and hydroxethylcellulose.
carrageenin: Mixture of several polysaccharides containing D-galactose units; obtained from seaweed.
casein: Milk protein.
cellobiose: A disaccharide consisting of two D-glucose units joined by a β-acetal linkage. It is the repeating unit in the cellulose molecule.
cellophane: A sheet of cellulose regenerated by the acidification of an alkaline solution of cellulose xanthate.
celluloid: Product produced from a mixture of cellulose nitrate and camphor.
cellulose: A linear polysaccharide consisting of many anhydroglucose units joined by β-acetal linkages.
cellulose acetate: Product formed from the acetylation of cellulose; properties vary with degree of substitution.
cellulose nitrate: Also known as nitrocellulose and gun cotton; made from the reaction of cellulose and concentrated nitric acid.

codons: Sets of three adjacent nucleotides that “code” for a specific amino acid.

cellulose xanthate: The reaction product of soda cellulose and carbon disulfide.

chair form: The most stable conformation of a six-membered ring like D-glucose, named because of its slight resemblance to a chair in contrast to the less stable boat conformation.

chitin: A polymer of acetylated glucosamine present in the exoskeletons of shellfish.

chromatography: A separation technique based on the selective absorption of the components present.

codon: A trinucleotide with three different bases which provides the necessary information for protein synthesis.

collagen: A protein present in connective tissue.

compounding: The process of adding essential ingredients to a polymer such as rubber.

conjugated protein: The combination of a protein and a prosthetic group, such as a nucleic acid.

C-terminal amino acid: Amino acid with a carboxylic acid end group.

cyclodextrins: Oligomeric cyclic products formed form the reaction of starch treated with a certain enzyme.

cytosine: A pyrimidine base present in nucleic acids.

degree of substitution (DS): A number that designates the average number of reacted hydroxyl groups in each anhydroglucose unit in cellulose or starch.

denaturation: The change of conformation of a protein resulting from heat or chemical reactants.

deoxyribonucleic acid (DNA): A nucleic acid in which deoxyribose units are present.

dextran: A high molecular weight branched polysaccharide synthesized from sucrose by bacteria.

dextrin: Degraded starch.

D-glucose: A hexose obtained by the hydrolysis of starch or cellulose.

dipeptide: A dimer formed by the condensation of two amino acids.

disaccharide: A dinner of D-glucose or other monosaccharide, such as cellobiose.

DNA: Deoxyribonucleic acid.

DNA profiling: Identification method based on variations between individual’s DNA.

drying: Jargon used to describe the cross-linking of unsaturated polymers in the presence of air and a heavy metal catalyst (drier).

DS: Degree of substitution.

elastin: Protein that is the major material of arterial blood vessels and ligaments that is noted for its flexibility.

enzyme: A protein with specific catalytic activity.

equatorial bonds: Bonds that are essentially parallel to the plane of the hexose ring, such as those in β-D-glucose.

ester gum: The ester of rosin and glycerol.

ethylhydroxyethylcellulose (EHEC): Nonionic mixed ether formed from the reaction of HEC with ethyl chloride.

exons: Coding regions of human genome.

fibrillar protein: A hairlike, insoluble, intermolecularly hydrogen-bonded protein.

fibrils: Naturally occurring threadlike strands or bundles of fibers.

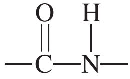
fossil resins: Resins obtained from the exudate of prehistoric trees.

G: An abbreviation for guanine.

Galalith: Commercial casein plastics.

γ-cellulose: Cellulose and derivatives soluble in 8% caustic solution.
genome: Total genetic information contained in a cell, organism, or virus.
globular proteins: Proteins with an overall globular structure formed form combinations of secondary structures including sheets and helices.
glycine: The simplest and only nonchiral α-amino acid.
glycogen: A highly branched polysaccharide which serves as the reserve carbohydrate in animals.
guanine: A purine base present in nucleic acids.
guayule: A shrub containing rubber (cis-1,4-polyisoprene).
gutta percha: A naturally occurring plastic (trans-1,4-polyisoprene).
Hevea brasiliensis: Natural rubber.
hexosans: Polysaccharides in which the repeating units are six-membered (pyranose) rings.
hormones: Organic compounds having specific biological effects.
humic acid: A polymeric aromatic carboxylic acid found in lignite.
hydrocellulose: Cellulose degraded (depolymerized) by hydrolysis.
hydroxyethylcellulose (HEC): Produced from the reaction of alkaline cellulose and ethylene oxide.
hydroxypropylcellulose: Thermoplastic nonionic cellulose ether formed from the reaction of alkaline cellulose and propylene oxide.
introns: Noncoding regions of human genome.
isoelectric point: The pH at which an amino acid does not migrate to either the positive or the negative pole in a cell.
keratin: A fibrillar protein.
latex: A stable dispersion of polymer particles in water.
lignin: The noncellulosic resinous component of wood.
long-range elasticity: The theory of rubber elasticity.
macroradical: A high molecular weight free radical.
maltose: A disaccharide consisting of two D-glucose units joined by an α-acetal linkage; the repeating unit in the starch molecule.
mer: The repeating unit in a polymeric chain.
mercerized cotton: Cotton fiber that has been immersed in caustic solution, usually under tension, and washed with water to remove the excess caustic.
methylcellulose (MC): Formed from the reaction of alkaline cellulose and chloromethane.
monosaccharide: A simple sugar, such as D-glucose, which cannot be hydrolyzed further.
myosin: A protein present in muscle.
native cellulose: Naturally occurring cellulose.
ninhydrin: A triketohydrindene hydrate which reacts with α-amino acids to produce characteristic blue to purple compounds.
NR: Symbol for natural rubber.
N-terminal amino acid: Amino acid with an amino end group.
nucleoside: The product obtained when phosphoric acid is hydrolyzed off a nucleotide combination of a pentose sugar and base.
nucleotide: Combination of a phosphate, a pentose sugar, and a base.
oligosaccharide: A relatively low molecular weight polysaccharide.
oxycellulose: Cellulose degraded (depolymerized) by oxidation.
paper chromatography: A technique used for separating amino acids in which paper serves as the stationary phase.

pentosans: Polysaccharides in which the repeating units are five-membered (furanose) rings.



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-$$

polyglycuronic acids: Also known as uronic or glycuronic acids, naturally occurring polysaccharides in which the hydroxyl on carbon 6 has been oxidized to form a carboxylic acid group.

polynucleotide: Nucleic acid.

polypeptide: A protein; often used for low molecular weight proteins.

polysaccharide: A polymer consisting of many hexose units, such as anhydroglucose.

primary structure: A term used to describe the primary configuration present in a protein chain.

prosthetic group: A nonproteinous group conjugated with a protein. Derived from the Greek *prosthesic*, in addition.

Protein: A polyamide in which the building blocks are α-amino acids joined by peptide linkages.

purine base: Compounds consisting of two fused heterocyclic rings, namely, a pyrimidine and an imidazole ring.

pyrimidine: A 1,3-diazine.

racked rubber: Stretched rubber cooled below its T_g.

rayon: Cellulose regenerated by acidification of a cellulose xanthate (viscose) solution.

recent resins: Resins obtained from the exudate of living trees.

regenerated cellulose: Cellulose obtained by precipitation from solution.

replication: Term used to describe duplications such as the duplication of DNA.

retrogradation: A process whereby irreversible gel is produced by the aging of aqueous solutions of amylose starch.

ribonucleic acid (RNA): A nucleic acid in which ribose units are present.

RNA: Ribonucleic acid: m-RNA, messenger RNA; r-RNA, ribosonal RNA; t-RNA, transfer RNA.

rosin: A naval stores product consisting primarily of abietic acid anhydride.

Schweitzer’s solution: An ammoniacal solution of copper hydroxide.

secondary structure: A term used to describe the conformation of a protein molecule.

semiconservative replication: Replication with retention of one of the original DNA strands.

semifossil resins: Resins obtained from the exudate of dead trees.

shellac: A natural polymer obtained from the excreta of insects in Southeast Asia.

soda cellulose: Cellulose that has been treated with a strong caustic solution.

Sodium carboxymethylcellulose: Formed from sodium chloroacetate with alkaline cellulose.

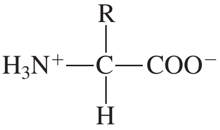
starch: A linear or branched polysaccharide consisting of many anhydroglucose units joined by α-acetal linkages. Amylose starch is a linear polymer, while amylodextrin is a branched polymer.

T: An abbreviation for thymine.

tenacity: A term for the tensile strength of fibers.

terpene: A class of hydrocarbons having the empirical formula C_5H_8.

tertiary structure: The shape or folding of a protein resulting from sulfur-sulfur crosslinks.
thymine: A pyrimidine base present in DNA.
transcription: Term used to describe the transfer of information from DNA to RNA.
translation: Term used to describe the transfer of information from RNA to protein synthesis.
U: An abbreviation for uracil.
uracil: A pyrimidine base present in RNA.
viscose: An alkaline solution of cellulose xanthate.
zwitterion: a dipolar ion of an amino acid:



$$H_3N^+—\underset{\displaystyle H}{\overset{\displaystyle R}{C}}—COO^-$$

EXERCISES

1. Why is starch digestible by humans? Why is cellulose not digestible by humans?
2. How does cellobiose differ from maltose?
3. Why is cellulose stronger than amylose?
4. How does the monosaccharide hydrolytic product of cellulose differ from that of starch?
5. Which has the higher molecular weight: (a) α-cellulose or (b) β-cellulose?
6. How many hydroxyl groups are present on each anhydroglucose unit in cellulose?
7. Which would be more polar—tertiary or secondary cellulose acetate?
8. Why would you expect chitin to be soluble in hydrochloric acid?
9. Which is more apt to form a helix: (a) amylose or (b) amylopectin?
10. Why is amylopectin soluble in water?
11. Define a protein in polymer science language.
12. Which α-amino acid does not belong to the L series?
13. To which pole will an amino acid migrate at a pH above its isoelectric point?
14. Why is collagen stronger than albumin?
15. What are the requirements of a strong fiber?
16. Which protein would be more apt to be present in a helical conformation: (a) a linear polyamide with small pendant groups or (b) a linear polyamide with bulky pendant groups?
17. What is the difference between the molecular weight of (a) ribose and (b) deoxyribose?
18. What is the repeating unit in the polymer chain of DNA?
19. Which is more acidic: (a) a nucleoside or (b) a nucleotide?
20. What base found in DNA is not present in RNA?
21. Why would you predict helical conformations for RNA and DNA?
22. If the sequence of one chain of a double helix is ATTACGTCAT, what is the sequence of the adjacent chain?
23. Why is it essential to have trinucleotides rather than dinucleotides as codons for directing protein synthesis?

24. How do the configurations differ for (a) gutta percha and (b) natural rubber?
25. What is the approximate Poisson ratio of rubber?
26. Will the tensile force required to stretch rubber increase or decrease as the temperature is increased?
27. Does a stretched rubber band expand or contract when heated?
28. List three requirements for an elastomer.
29. Why is there an interest in the cultivation of guayule?
30. Are the polymerization processes for synthetic and natural cis-polyisoprene (a) similar or (b) different?
31. What does the production of levulinic aldehyde as the product of the ozonolysis of natural rubber tell you about the structure of NR?
32. Why doesn't cold-racked rubber contract readily?
33. Why does a rubber band become opaque when stretched?
34. What is the most important contribution to retractile forces in highly elongated rubber?
35. What is present in so-called vulcanized rubber compounds?
36. What happens to a free radical, such as (·SR), during the mastication of rubber?
37. Why aren't natural plastics used more?
38. What type of solvent would you choose for shellac?
39. What type of solvent would you choose for asphalt?
40. Which is a polymer: (a) rosin or (b) ester gum?
41. If the annual production of paper is 100 million tons, how much lignin is discarded annually?
42. Is an article molded from Galalith valuable?

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11

Inorganic-Organic Polymers

11.1 INTRODUCTION

Classical polymer chemistry emphasizes materials derived from about a dozen elements (including C, H, O, N, S, P, Cl, and F). The following two chapters deal with polymers containing additional elements.

The present chapter will focus on inorganic polymers containing organic portions, which are called inorganic-organic polymers.

Elements such as silicon, sulfur, and phosphorus catenate similar to the way carbon does, but such catenation generally does not lead to (homo) chains with degrees of polymerization greater than 10. Further such products might be expected to offer lower thermal stabilities and possibly lower strengths than carbon-based polymers, since their bond energies are generally lower (Table 11.1). The alternative of utilizing heteroatomed backbones is attractive, since the resultant bond can exhibit greater bond energies.

One common misconception concerns the type of bonding that occurs between the inorganic and organic unit. With the exception of metals present in metallocene "sandwich" compounds, the organic to inorganic bonding is of the same general nature as that present in organic compounds. The percentage contribution of the organic-inorganic bonding due to covalent contributions is typically well within that found in organic acid, alcohol, and thio and nitro moieties (for instance, usual limits are about 5% ionic bonding character for the B-C bond to 55% for the Sn-O bond). Thus the same natural spatial, geometrical laws that apply to the bounding in organic compounds apply as well to the polymers covered in this chapter (except for some ionomer-like ionic bonding).

The number of potential inorganic-organic polymers is great. The inorganic portions can exist as oxides, salts, etc., in differing oxidation states and differing geometries.

The importance of inorganic polymers can be readily appreciated by considering the following. First, photosynthesis, the conversion of carbon dioxide and water by sunlight in the synthesis of saccharides, is based on a metal-containing polymer—chlorophyll.

Table 11.1 General Magnitudes of Bonds

Bond	General bond energy[a] (kcal/mol)	Ionic character[b] (%)
Al—O	140	60
B—C	90	5
B—N	110	20
B—O	115	45
Be—O	125	65
C—C	85	0
C—H	100	5
C—N	75	5
C—O	85	20
C—S	65	5
P—P	50	0
P—N	140	20
P—O	100	40
P—S	80	5
S—S	60	0
Si—Si	55	0
Si—C	75	10
Si—N	105	30
Si—O	110	50
Si—S	60	10
Sn—Sn	40	0
Sn—O	130	55
Ti—O	160	60

[a] Given to nearest 5 kcal/mol.

[b] Based on Pauling electronegativity values. The percentage of ionic bonding should be less where π-bonding occurs. Given to nearest 5%.

Also a number of critical enzymes, such as hemoglobin, contain a metal site as the key site for activity. Second, the inorganic-organic polymers produced thus far exhibit a wide range of properties not common to most organic polymers, including electrical conductivity, specific catalytic operations, wide operating temperatures, greater strengths, and greater thermal stabilities (Table 11.2). Third, inorganic polymers form the basis for many insula-

Table 11.2 Actual and Potential Smaller-Scale Applications for Inorganic-Organic Polymers

Biological	Anticancer, antiviral, treatment of arthritis, antibacterial, antifungal, antifouling, treatment of Cooley's anemia, algicides, molluscicides, treatment of vitamin deficiency
Electrical	Conductors, semiconductors, piezoelectronic, pyroelectronic, solar energy conversion, electrodes, computer chip circuitry
Analytical, catalytic, photo	UV absorption, laser, nonlinear optics
Building	Sealants, caulkants, lubricants, gaskets

Table 11.3 Relative Abundance of Selected Elements in Earth's Upper (10-Mile) Crust

Element	Weight (%)	Element	Weight (%)
Oxygen	50	Titanium	0.4
Silicon	26	Fluorine	0.3
Aluminum	7.3	Chlorine	0.2
Iron	4.2	Carbon	0.2
Calcium	3.2	Sulfur	0.1
Sodium	2.4	Phosphorus	0.1
Potassium	2.3	Barium	0.1
Magnesium	2.1	Manganese	0.1
Hydrogen	0.4		

tors and building materials. Fourth, inorganic elements are present in high abundance in the Earth's crust (Table 11.3).

The topic of metal-containing inorganic-organic polymers can be divided by many means. Here the topic will be divided according to the type of reaction employed to incorporate the inorganic and/or inorganic-containing moiety into the polymer chain—addition, condensation, and coordination. Emphasis is given to unifying factors and to metal-containing materials.

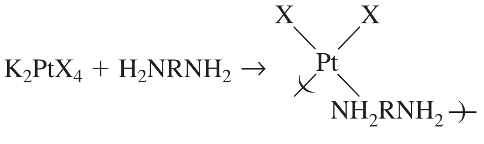
11.2 INORGANIC REACTION MECHANISMS

Many of the polymerizations and monomer syntheses are simple extensions of known inorganic, organometallic, and organic reactions. The types and language used to describe inorganic reaction mechanisms are more diversified than those employed by classical organic chemists.

The majority of inorganic reactions can be placed into one of two broad classes—oxidation–reduction reactions, including atom and electron transfer reactions, and substitution reactions.

Terms such as inner sphere, outer sphere, and photo-related reactions are employed to describe more reduction–oxidation (redox) reactions. Such reactions are important in the synthesis of polymers and monomers and in the use of metal-containing polymers as catalysts and in applications involving transfer of heat, electricity, and light. They will not be dealt with to any appreciable extent in this chapter.

Terms such as lability, inertness, ligand, associative, interchange, and dissociative are important when discussing substitution reactions. The ligand is simply (typically) the Lewis base that is substituted for and is also the agent of substitution. Thus in the reaction between tetrachloroplatinate and diamines to form the anticancer and antiviral platinum II polyamines [Eq. (11.1)], the chloride is the leaving group or departing legand, while the amine-functional group is the ligand that is the agent of substitution.



$$K_2PtX_4 + H_2NRNH_2 \rightarrow -\!\!\left(\, PtX_2 - NH_2RNH_2 \,\right)\!\!- \qquad (11.1)$$

where X = Cl, Br, or I.

There is a difference between the thermodynamic terms *stable* and *unstable* and the kinetic terms *labile* and *inert*. Furthermore, the difference between the terms stable and unstable and the terms labile and inert are relative. Thus $\mathrm{Ni(CN)}_4^{-2}$ and $\mathrm{Cr(CN)}_6^{-3}$ are both thermodynamically stable in aqueous solution, yet kinetically the rate of exchange of radiocarbon-labeled cyanide is quite different. The half-life for exchange is about 30 s for the nickel complex and 1 month for the chronmium complex. Taube has suggested that those complexes that react completely within about 60 s at 25°C should be considered labile while those taking longer should be called inert. This rule of thumb is often given in texts but is not in general use in the literature. Actual rates and conditions are superior tools for the evaluation of the kinetic/thermodynamic stability of complexes.

The term "D mechanism" (dissociation) is loosely comparable to S_N 1-type reaction mechanisms, but it does not imply the observed rate law. Here a transient intermediate is assumed to live long enough to be able to differentiate between various ligands, including the one just lost, and between solvent molecules. Thus the overall rate expression may be dependent on the nature of L,L′, solvents, or some combination.

$$\mathrm{ML_4} \leftrightarrows \mathrm{ML_3} + \mathrm{L} \tag{11.2}$$

$$\mathrm{ML_3} + \mathrm{L'} \rightarrow \mathrm{ML_3L'} \tag{11.3}$$

$$\mathrm{ML_3} + \mathrm{S} \rightleftarrows \mathrm{ML_3S} \tag{11.4}$$

In the I_d mechanism, dissociative interchange, the transition state involves extension of the M . . . L bond, but not rupture.

$$\mathrm{ML_4} + \mathrm{L'} \rightarrow \mathrm{ML_4L'} \rightarrow [\mathrm{L} \cdots \mathrm{ML_3} \cdots \mathrm{L'}] \rightarrow \mathrm{ML_3L'} + \mathrm{L} \tag{11.5}$$

The $\mathrm{ML_4L'}$ species is called an outer sphere complex, or, if $\mathrm{ML_4}$ is a cation and L an anion, the couple is called an ion pair.

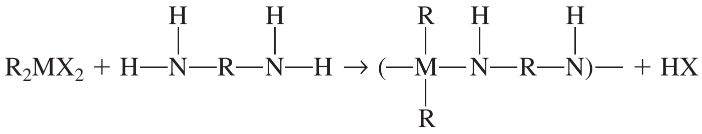
For the I_a mechanism, associative interchange, the interaction between M and L′ is more advanced in the transition state than in the case of the I_d. The $\mathrm{M} \cdots \mathrm{L'}$ bonding is important in defining the activated complex. Both of these interchange mechanisms are loosely connected to the S_N2-type reaction mechanism.

For the A mechanism, associative, there is a fully formed intermediate complex, $\mathrm{ML_4L'}$, which then dissociates, being roughly analogous to the E_1 type of reaction mechanism.

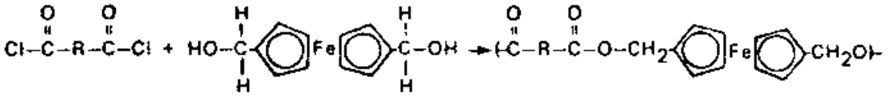
It is important to remember that the same factors that operate in regard to smaller molecules are in operation during a polymerization process. The same electronic, steric, mechanistic, kinetic, and thermodynamic directives present in the addition, condensation, etc., reactions occurring between small molecules are present as such molecule interactions lead to the formation of macromolecules.

11.3 CONDENSATION ORGANOMETALLIC POLYMERS

Condensation reactions exhibit several characteristics such as (typically) expulsion of a smaller molecule (often H_2O or HX) on reaction leading to a repeat unit containing fewer atoms than the sum of the two reactants, and most reactions can be considered in terms of polar (Lewis acid–base, nucleophilic–electrophilic) mechanisms. The reaction site can be at the metal atom adjacent to the metal atom [Eq. (11.6)] or somewhat removed from the metal atom [Eq. (11.7)].

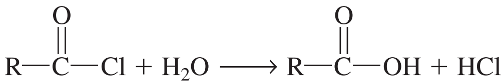


$$R_2MX_2 + H\overset{\displaystyle H}{\overset{|}{-N-}}R\overset{\displaystyle H}{\overset{|}{-N-}}H \rightarrow (\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R}{\overset{|}{-M-}}}}\overset{\displaystyle H}{\overset{|}{N}}-R-\overset{\displaystyle H}{\overset{|}{N}})- + HX \qquad (11.6)$$

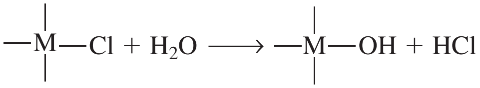


(11.7)

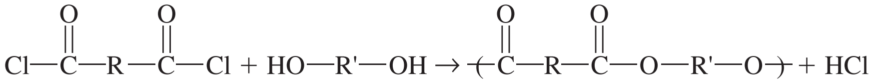
Research involving condensation organometallic polymers was catalyzed by the observation that many organometallic halides possess a high degree of covalent character within their composite structure and that they can behave as organic acids in many reactions, such as hydrolysis [Eqs. (11.8, 11.9)] and polyesterifications [Eqs. (11.10, 11.11)].



$$R-\overset{\displaystyle O}{\overset{\|}{C}}-Cl + H_2O \longrightarrow R-\overset{\displaystyle O}{\overset{\|}{C}}-OH + HCl \qquad (11.8)$$

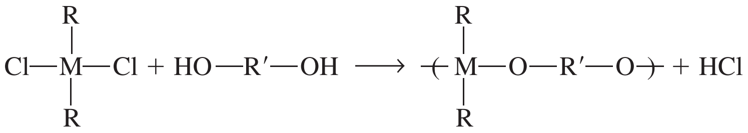


$$-\underset{|}{\overset{|}{M}}-Cl + H_2O \longrightarrow -\underset{|}{\overset{|}{M}}-OH + HCl \qquad (11.9)$$



$$Cl-\overset{\displaystyle O}{\overset{\|}{C}}-R-\overset{\displaystyle O}{\overset{\|}{C}}-Cl + HO-R'-OH \rightarrow (\overset{\displaystyle O}{\overset{\|}{C}}-R-\overset{\displaystyle O}{\overset{\|}{C}}-O-R'-O) + HCl$$

(11.10)

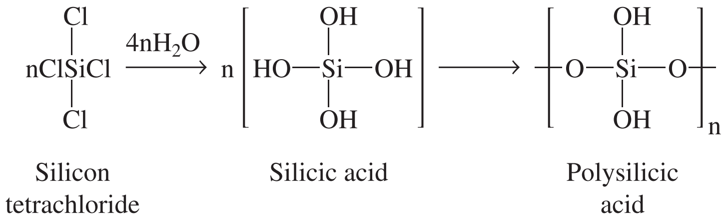


$$Cl-\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R}{\overset{|}{M}}}}-Cl + HO-R'-OH \longrightarrow (\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R}{\overset{|}{M}}}}-O-R'-O) + HCl \qquad (11.11)$$

Thus many of the affected organometallic polycondensations can be considered as extensions of organic polyesterification, polyamination, etc., reactions.

The most important organometallic polymers are the polysiloxanes based on the same Si-O linkage present in glass and quartz (Chapter 12). The polysiloxanes were incorrectly named silicones by Kipping in the 1920s, and this name continues to be widely used.

The production of silicate glass is believed to be a transcondensation of the siloxane linkages in silica in the presence of calcium and sodium oxides. Thus, some calcium and sodium silicates are produced in glass making, but the siloxane backbone remains intact. A comparable polysilicic acid is produced when silicon tetrachloride is hydrolyzed, as shown in the following equation:



$$n\,\mathrm{Cl}\underset{\substack{|\\ \mathrm{Cl}}}{\overset{\substack{\mathrm{Cl}\\ |}}{\mathrm{Si}}}\mathrm{Cl} \xrightarrow{4n\mathrm{H_2O}} n\left[\mathrm{HO{-}}\underset{\substack{|\\ \mathrm{OH}}}{\overset{\substack{\mathrm{OH}\\ |}}{\mathrm{Si}}}\mathrm{{-}OH}\right] \longrightarrow \left[-\mathrm{O{-}}\underset{\substack{|\\ \mathrm{OH}}}{\overset{\substack{\mathrm{OH}\\ |}}{\mathrm{Si}}}\mathrm{{-}O}-\right]_n \qquad (11.12)$$

The polysilicic acid condenses further to produce a crosslinked gel. This crosslinking may be prevented by replacing the hydroxyl groups in silicic acid by alkyl groups. Thus, Ladenburg prepared the first silicone polymer in the nineteenth century by the hydrolysis of diethyldiethoxysilane. Kipping recognized that these siloxanes were produced by the hydrolysis of dialkyldichlorosilanes in the early 1940s. In both cases, two of the hydroxyl groups shown in the formula for silicic acid in Eq. (11.12) were replaced by alkyl groups.

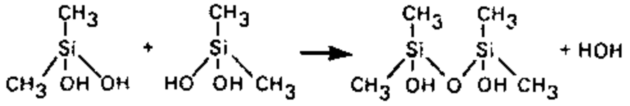
The instability of silicones is overcome by capping the hydroxyl end groups with a monofunctional trialkylchlorosilane or trialkylalkoxysilane. The monoalkyltrichlorosilane is used as a trifunctional crosslinking agent for silicones.

In 1945, Rochow discovered that a silicon-copper alloy reacted with organic chlorides forming a new class of compounds called organosilanes.

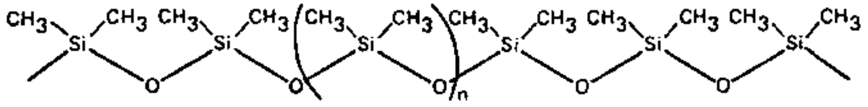
$$\mathrm{CH_3Cl} + \underset{\substack{\text{Silicon-}\\ \text{copper}\\ \text{alloy}}}{\mathrm{Si(Cu)}} \rightarrow \underset{\text{Dimethyldichlorosilane}}{\mathrm{(CH_3)_2SiCl_2}} + \mathrm{Cu} \qquad (11.13)$$

These compounds react with water forming dihydroxylsilanes [Eq. (11.14)] which in turn condense, splitting out water, eventually forming polysiloxanes [Eqs. (11.15 and 11.16)].

$$\mathrm{(CH_3)_2SiCl_2} + 2\mathrm{H_2O} \rightarrow \mathrm{(CH_3)_2Si(OH)_2} + 2\mathrm{HCl} \qquad (11.14)$$



(11.15)

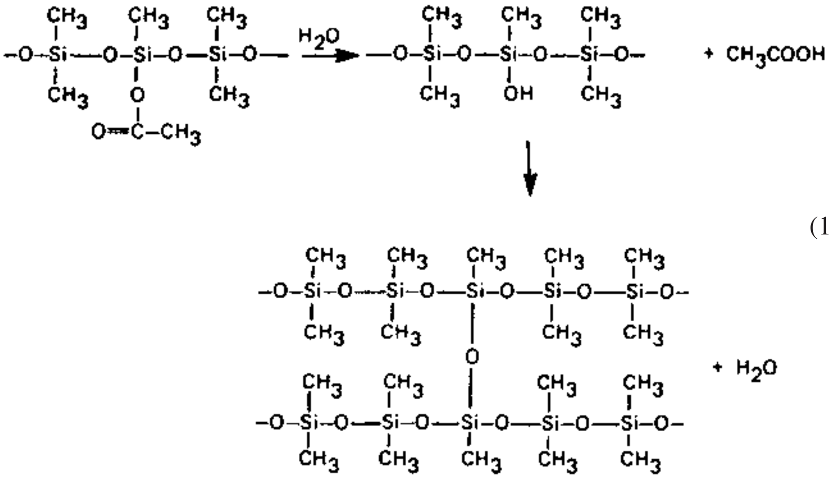


(11.16)

Organosiloxanes are characterized by combinations of chemical, mechanical, and electrical properties which taken together are not common to any other commercially available class of polymers. They exhibit relatively high thermal and oxidation stability, low power loss, high dielectric strength, and unique rheological properties, and are relatively inert to most ionic reagents.

As with alkanes, the oligomeric polysiloxanes are oils whereas high molecular weight polysiloxanes are solids. Silicone oils are prepared in the presence of hexamethyldisiloxane which produces trimethylsiloxyl-capped ends. The fluidity and viscosity of silicone oils is controlled by the ratio of hexamethyldisiloxane to dimethyldimethoxysilane (or other suitable silane) employed.

Room temperature–vulcanizing (RTV) silicone rubbers make use of the room temperature hydrolyzability of chloro, alkoxyl, and ester-silicone moieties. These high polymer silicones contain a specific amount of such easily hydrolyzable groups. These products are exposed to water-forming Si-OH products that subsequently form crosslinks resulting in a silicone rubber as follows:

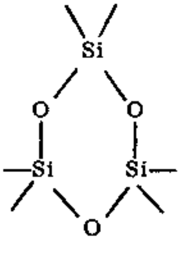


(11.17)

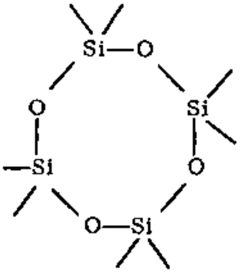
Silicones can also be cured (vulcanized, cross-linked) by free-radical reactions.

Currell and Parsonage recently reported the production of oligomeric silicones from mineral silicates. Products suitable for use as greases and cements and masonry waterproofing agents have already been produced.

The silicon reactants easily form six-and eight-membered cyclic compounds resulting in "wasted-loop" side reactions. Fortunately, the cyclic siloxanes can be removed by distillation and reintroduced in the feed.



Six-membered compound



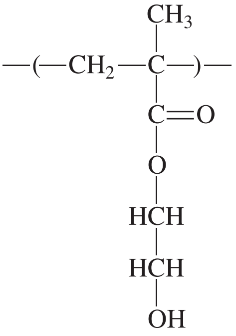
Eight-membered compound

Siloxanes find many uses. The initial footprints on the moon were made by silicone elastomer boots. Silicones are employed as high-performance caulks, lubricants, antifoaming agents, window gaskets, O rings, and sealants. Bouncing or Silly Putty is produced when polydimethylsiloxanes with capped ends are heated with boric acid.

The first Silly Putty™ was made over 50 years ago from mixing together silicone oil with boric acid. That original formula has changed little though colorants have been added giving the material brighter colors and some the ability to “glow-in-the-dark.” Silly Putty is a dilatant material (Sec. 5.1) meaning it has an inverse thioxtropy (a thioxotropic liquid is one whose viscosity decreases with time). In essence, the resistance of flow increases faster than the increases in the rate of low. Thus, under short interaction times (Sec. 5.1) it behaves as a solid where the various molecular components resist ready movement, acting as a solid and under sharp impact like hitting it with a hammer or rapidly “snapping” it, it will act as a brittle material. Under a relatively long interaction time the molecular chains are able to yield and the material acts as a liquid. Under moderate interaction times there is segmental movement and the material acts as a rubber.

James Wright, a researcher for General Electric, first discovered Silly Putty in 1943 during a search for synthetic rubber during WW II. Initially no practical use was found. By 1949 it found its way into a local toy store as a novelty item. Despite its good sales, the store dropped it after the first year. The next year Peter Hodson began packaging it in the now familiar plastic eggs, gave it the name “Silly Putty” and started the sales campaign. Today, it sells for about the same price—one dollar an egg—that it did in 1950. Today it sells at a rate of about 6 million eggs yearly equal to about 90 tons.

The first widely commercialized (till the late 1960s) contact lenses were based on poly(methyl methacrylate), which can be polished and is machinable. These contact lenses are rigid and do not permit gas exchange. They were followed by what we today call soft contact lenses. These lenses are based on crosslinked poly(2-hydroxyethyl methacrylate) (HEMA). Some of the contact lenses, particularly the so-called disposable lenses, contain small amounts of acrylic acid units that are about 50% ionized at a pH of about 7 corresponding to the approximate pH of the liquid in the eye. The ionized carboxylic acid groups help attract proteins, allowing them to have a greater compatibility with the eye. Acrylic acid units act as a wetting agent. These lenses are hydrogels with about 60% water. Efforts are underway to reduce the amount of water and to increase their oxygen permeability. It is important to note that the water associated with such polymers is of two kinds—one termed “bound water,” which remains in the system even after heating to over 100°C, and the second called “free water,” which evaporates under normal room conditions and is driven off with heating to about 100°C.

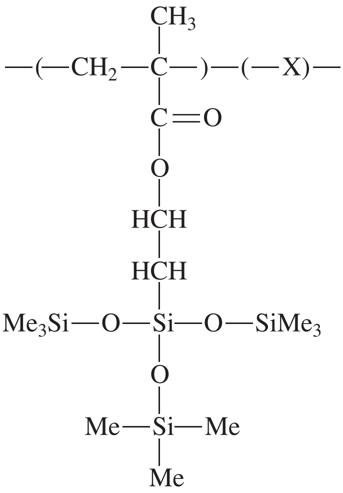


$$-(-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C(=O)-O-CH_2-CH_2-OH}{C}}-)-$$

Poly(hydroxyethyl methacrylate)

Gas permeability, particularly oxygen permeability, is critical if lenses are to be worn for hours and days at a time. While the HEMA lenses are soft, they do not have good oxygen permeability.

More recently, Joe Salamone and co-workers developed the next generation of contact lenses based on the presence of siloxane units. Siloxanes have good gas, including oxygen, permeability. These polymers are referred to as Tris materials and contain 2-hydroxyethyl groups modified through reaction with siloxanes producing gas-permeable voids. These polymers are generally copolymers where the X unit can vary. When wetting is needed, the X unit can be acrylic acid. These contact lens are generally hard and are machinable.



(Representative) Tris Structure

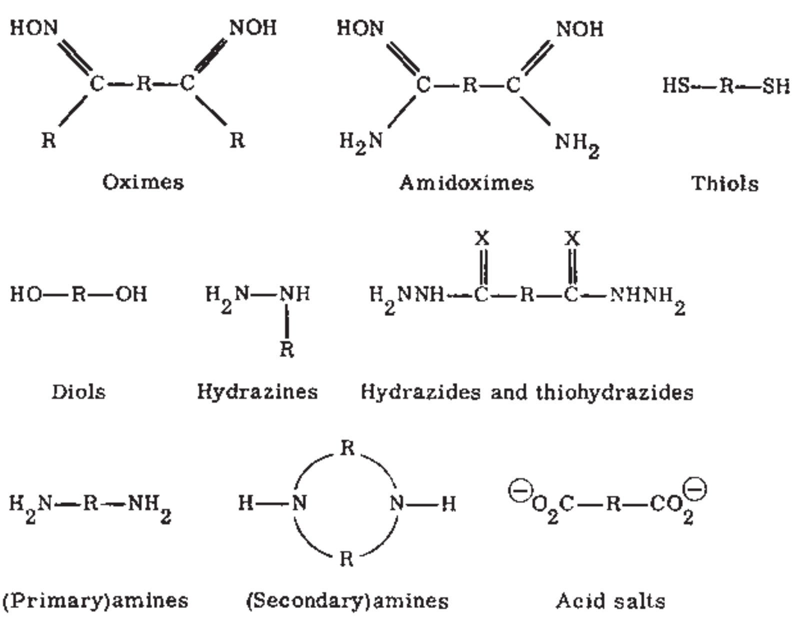
Soft lenses are generally cleaned using abrasives small enough that the abrasive marks do not affect visible light. Hard lenses are generally cleaned using solutions that contain enzymes that lyse (hydrolyze) proteins and other foreign matter that can accumulate on the lenses themselves.

Many of the new efforts involve the synthesis of flexible lenses that offer good gas permeability and lenses that fit the eye itself. One of these is based on poly(methyl methacrylate) as the lens material that is "slipped" into the lens area within the eye. These lenses contain flanges or feet that extend from the lens with the feet acting to anchor the lens.

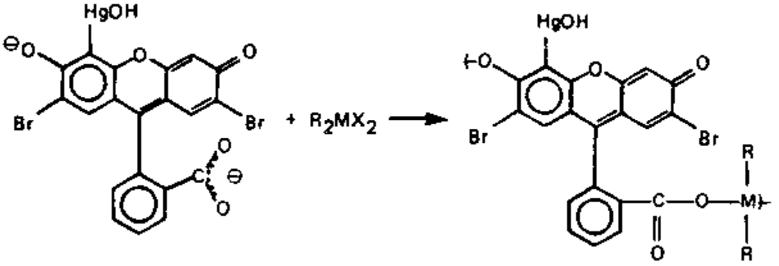
Carraher and co-workers have produced a wide variety of organometallic condensation polymers based on the Lewis acid–base concept. Polymers have been produced from the condensation of traditional Lewis bases such as diols (Table 11.4) with Lewis acids such as Cp_2TiCl_2 (Table 11.5, where Cp represents a cyclopentadienyl moiety). These polymers show promise in a wide variety of areas including electrical, catalytic, and biomedical applications.

One requirement for large-scale reclaiming will be ready identification of select materials. Organometallic polydyes offer one solution to the problem of content identification since such polydyes can be "permanently" incorporated into polymeric materials such as plastics, paper-based products, coatings, rubbers, and fibers. Furthermore, due to the variety of metals, organometallic materials, and dyes, a large array of combinations are readily available. Further, the presence of the metal allows for both optical and metal detection techniques to be employed. Organometallic polydyes is the name associated with products of metal-containing compounds and dyes. One such dye [Eq. (11.18)] is based on mercurochrome and dibutyltin dichloride. The resulting products are typically both colorful and antifungal. Such polydyes may also be useful in photosensitive media

Table 11.4 Lewis Bases Employed in the Synthesis of Condensation Organometallic Polymers



for photocopying; as permanent coloring agents in cloth, paper, sealants, coatings, and plastics; in biological applications such as specialty bandages and antifungal and antibacterial topical drugs; as specialty stains and toxins; and as radiation enhancers and targets for coating-curing applications.

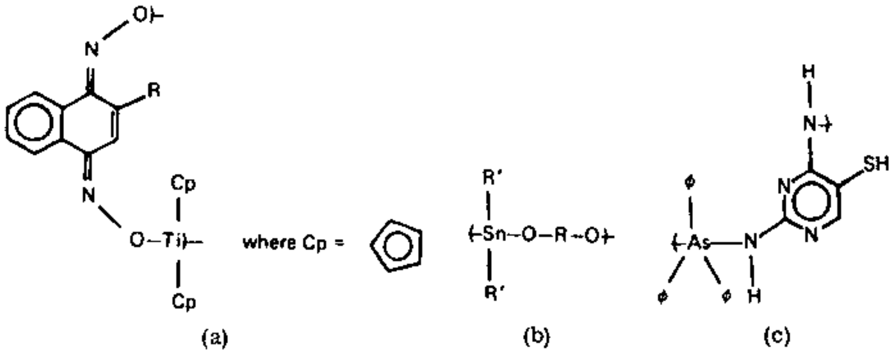


(11.18)

Condensation organometallic polymers have also been employed as biologically active agents, where the biological activity is derived from the polymer chain in total,

Table 11.5 Lewis Acids Employed in the Synthesis of Organometallic Polymers

R_2TiX_2	R_2SiX_2	R_3SbX_2	R_3Sb
R_2ZrX_2	R_2GeX_2	R_3As	R_3BiX_2
R_2HfX_2	R_2SnX_2	R_3AsX_2	R_2MnX_2
R_2PbX_2	R_2RuX_2		



Scheme 11.1

oligomeric portions of the chain or through control release of monomerlike fragments. The desired drug may be either or both comonomers. In the case of Scheme 11.1a, derived from reacting Cp_2 MCl_2 with the dioxime of vitamin K, the drug may be only the vitamin K moiety where M is Zr or both moieties where M is Ti since Cp_2 Ti-containing compounds are known to be antitumoral agents. The product in Scheme 11.1b is employed to deliver the dibutyltin moiety whereas in scheme 11.1c the pyrimidine moiety is included to encourage host acceptance and subsequent demise through release of the arsenic moiety. Thus, there exists a wide latitude within which to tailor-make products with desired biological activities.

A number of polymers (mostly containing the Cp_2Ti moiety) exhibit a phenomenon called “anomalous fiber formation,” reminiscent of “metallic whiskers.”

The Lewis acid–base condensations can also occur employing a polymer as one of the reactants. Thus, reactions analogous to those reported before have been carried out employing both synthetic and natural polymers. One illustration follows.

There exists a need to conserve our slowly renewable resources such as coal, oil, and gas. As the price of these natural resources increases and the supply dwindles, there is an increased awareness that alternative sources of inexpensive, large-quantity, readily available feedstocks must be pursued. The use of polyhydroxylic materials such as sugars and polysaccharides fulfills these requirements and is particularly desirable since they are continually replenished. The modification of carbohydrates such as sucrose, dextrose, dextran, and cellulose has been effected using a wide variety of reaction systems and metal-containing reactants. Potential uses range from specialty bandages to treated wood for improved hydrolytic and biological properties, to paint and plastic additives and for use in commercial insulation.

11.4 COORDINATION POLYMERS

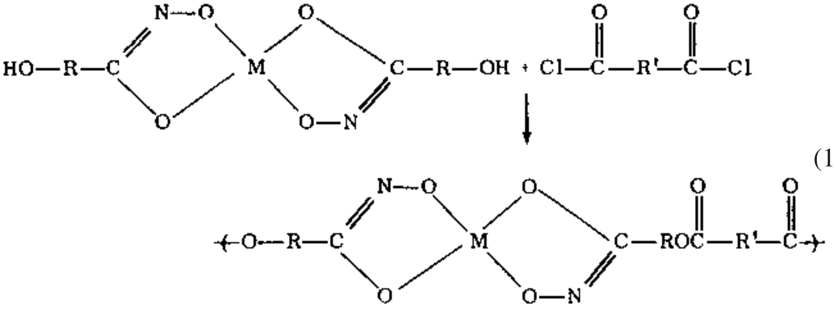
Coordination polymers have served humankind since before recorded history. The tanning of leather and generation of select colored pigments depend on the coordination of metal ions. A number of biological agents, including humans, owe their existence to coordinated polymers such as hemoglobin. Many of these coordination polymers have unknown and/or irregular structures.

The drive for the synthesis and characterization of synthetic coordination polymers was catalyzed by work supported and conducted by the United States Air Force in a search for materials which exhibited high thermal stabilities. Attempts to prepare stable, tractable coordination polymers which would simulate the exceptional thermal and/or chemical stability of model monomeric coordination compounds such as copper ethylenediaminobisacetylacetate(II) or copper phthalocyanine(I) have been disappointing at best. Typically only short chains were formed and the thermally stable “monomers” lost most of their stability when linked by the metals into polymeric units.

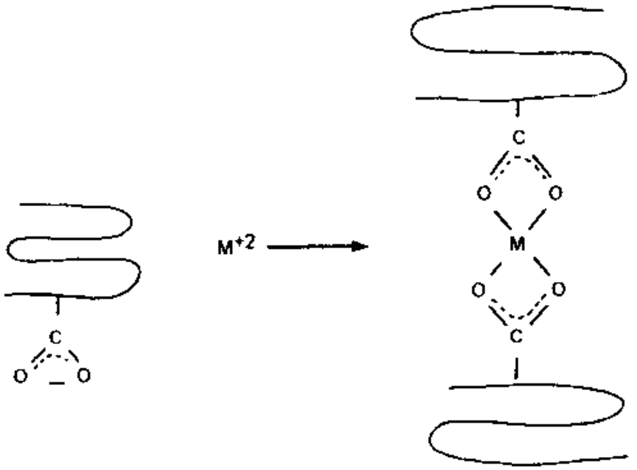
Bailar listed a number of principles that can be considered in designing coordination polymers. Briefly these are as follows. (1) Little flexibility is imparted by the metal ion or within its immediate environment; thus, flexibility must arise from the organic moiety. Flexibility increases as the covalent nature of metal–ligand bond increases. (2) Metal ions only stabilize ligands in their immediate vicinity; thus, the chelates should be strong and close to the metal atom. (3) Thermal, oxidative, and hydrolytic stability are not directly related; polymers must be designed specifically for the properties desired. (4) Metal–ligand bonds have enough ionic character to permit them to rearrange more readily than typical “organic bonds.” (5) Polymer structure (such as square planar, octahedral, planar, linear, network) is dictated by the coordination number and stereochemistry of the metal ion or chelating agent. Lastly, (6) employed solvents should not form strong complexes with the metal ion or chelating agent or they will be incorporated into the polymer structure and/or prevent reaction from occurring.

Coordination polymers can be prepared by a number of routes, with the three most common being (1) preformed coordination metal complexes polymerized through functional groups where the actual polymer-forming step may be a condensation or addition reaction [Eq. (11.19)]. (2) Metal chelation ligands [Eq. (11.20)]. (The ionomers produced by duPont consist of copolymers of ethylene with a small portion of methacrylic acid. The polymer chains are crosslinked by addition of metal ions [Eq. (11.20)]. These polymers exhibit good thermal stability and flame retardance. The ionomers are believed to contain domains of crystalline polyethylene bound together by the metal ion. This permits a favorable combination of high strength with some flexibility). (3) Polychelation through reaction of the metal-containing moiety with an appropriate Lewis base–containing reactant [Eq. (11.21)].

Carraher and co-workers employed the last process for the recovery of the uranyl ion. The uranyl ion is the natural water-soluble form of uranium oxides. It is also toxic, acting as a heavy metal toxin. Through the use of salts of dicarboxylic acids and polyacrylic acids, uranyl ion was removed to 10^{-5} molar with the resulting product being much less toxic.



(11.19)



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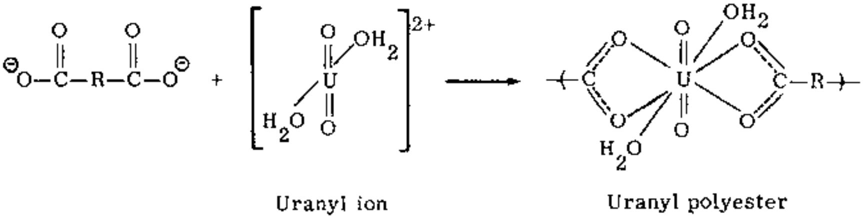


(11.21)

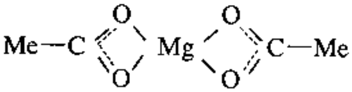
Many of the organometallic polymers are semiconductors with bulk specific resistivities for the range of 10^3 to 10^{12} ohm cm suitable for specific semiconductor activities. Furthermore, some exhibit interesting photoproperties. Some polymers degrade on heating to give metal oxides with the process suitable for the homogeneous doping of other polymers and matrices with metal sites.

In 1964, Rosenberg and co-workers found that bacteria failed to divide but continued to grow. The major cause of this inhibition to cell division is cis-dichlorodiamineplatinum II (c-DDP). It is now licensed under the name Platinol and employed extensively in combination with other drugs in the treatment of a wide variety of cancers. The use of c-DDP is complicated due to a number of negative side effects. Carraher and Allcock recognized that many of these side effects might be overcome if the platinum is present in a polymer that can act as a long-acting controlled-release agent.

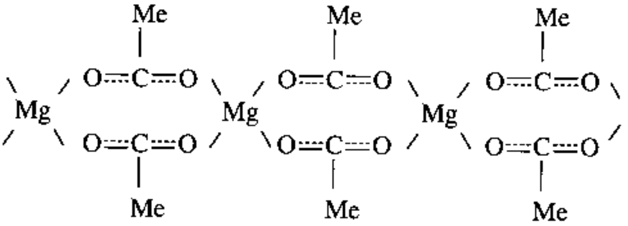
Carraher and co-workers synthesized many polymeric derivatives of c-DDP [Eq. (11.1)] employing nitrogen-containing Lewis bases. Some of the products show good inhibition to a wide variety of cancer cell lines, prolong the life expectancies of terminally ill test animals, are more toxic to cancer-like cells compared with analogous healthy cells, and are much less toxic. One of these polymers is also able to prevent the onset of virally related juvenile diabetes in test animals.

Simple chelation polymers are all around us, but they are not always recognized as such. During winter, the North experiences freezing temperatures and the associated ice. Sodium chloride and calcium chloride are the most used freezing point lowering agents. They are inexpensive and readily available. On the negative side, they adversely affect surrounding plant life and must be reapplied generally after each rain–ice cycle.

Recently, magnesium acetate has come into use for application in especially dangerous sites such as bridges. The acetate can be either internally bridged, where it is not polymeric:



or it can bridged forming a complex linear polymeric material:



Hellmuth believes that the polymeric material forms. If the magnesium acetate were simply the internally chelated material, then it should be quickly washed away. The combination of calcium and magnesium acetates is known as CMA. CMA is more expensive than sodium chloride or calcium chloride, but it does not damage plant life and has a much longer effective life. The polymer seeks the cracks and crevices in and around the pavement and remains until needed again to lower the freezing point of water. Often, one application of CMA is sufficient for a winter season.

11.5 ADDITION POLYMERS

A large number of vinyl organometallic monomers has been prepared, homopolymerized, and copolymerized with other classic vinyl monomers by Pittman and others. These include polymers containing Mo, W, Fe, Cr, Ir, Ru, and Co.

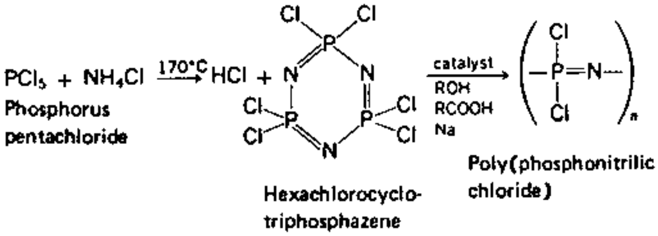
The effect that the presence of organometallic functions exerts in vinyl polymerizations is beginning to be understood in some instances. A transition metal may be expected, with its various readily available oxidation states and large steric bulk, to exert unusual electronic and steric effects during polymerization. The polymerization of vinylferrocene will be employed as an example. Its homopolymerization has been initiated by radical, cationic, coordination, and Ziegler-Natta initiators. Unlike the classic organic monomer styrene, vinylferrocene undergoes oxidation at the iron atom when peroxide initiators are employed. Thus, azo initiators (such as AIBN) are commonly used. Here we see one difference between an organic and an organometallic monomer in the presence of peroxide initiators. The stability of the ferricinium ion makes ferrocene readily oxidizable by peroxides, whereas styrene, for example, undergoes polymerization.

Unlike most vinyl monomers, the molecular weight of polyvinylferrocene does not increase with a decrease in initiator concentration. This is the result of vinylferrocene's anomalously high chain-transfer constant ($C_m = 2 \times 10^{-3}$ vs. 6×10^{-5} for styrene at 60°C). Finally, the rate law for vinylferrocene homopolymerization is first order in initiator in benzene. Thus, intramolecular termination occurs. Mossbauer studies support a mechanism involving electron transfer from iron to the growing chain radical to give a zwitterion that terminates and further results in a high-spin Fe(III) complex.

The great electron richness of vinylferrocene as a monomer is illustrated in its copolymerizations with maleic anhydride, where 1:1 alternating copolymers are obtained over a wide range of M_1/M_2 feed ratios and $r_1 \cdot r_2 = 0.003$. Subsequently, a large number of detailed copolymerization studies were carried out between vinylferrocene and classic organic monomers such as styrene, methacrylates, *N*-vinylcarbazole, and acrylonitrile. The relative reactivity ratios (r_1 and r_2) were obtained, and from them the values of the Alfrey-Price Q and e parameters were obtained. The value of e is a semiempirical measure of the electron richness of the vinyl group. The best value of e for vinylferrocene is about −2.1, which, when compared to the e values of maleic anhydride (+2.25), p-nitrostyrene (+0.39), styrene (−0.80), p-N,N-dimethylaminostyrene (−1.37), and 1,1′-dianisylethylene (−1.96), illustrates the exceptional electron richness of vinylferrocene's vinyl group.

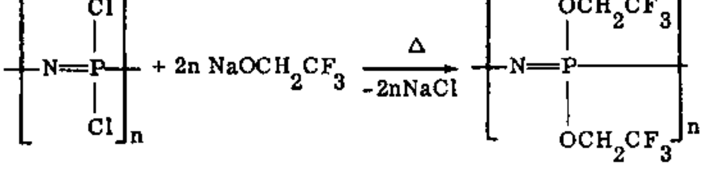
Remarkably, the presence of different metals or the presence of electron-withdrawing carbonyl groups on metal atoms attached to the N^5-vinylcyclopentadienyl group does not markedly diminish the electron richness of the vinyl group as measured by the Alfrey-Price e value.

Other inorganic polymers are formed from addition reactions. These include polyphosphazenes, polyphosphonitriles, and poly(sulfur nitride). Phosphonitrilic polymers have been known for centuries, but since they lacked resistance to water they were not of interest as commercial polymers. However, when the pendant chlorine groups are replaced by fluorine atoms, amino, alkoxy, or phenoxy groups, these polymers are much more resistant to moisture. Phosphonitrile fluoroelastomers (PNF-200) are useful throughout a temperature range of −56 to 180°C. Phosphazenes are produced by the thermal cleavage of a cyclic trimer obtained from the reaction of phosphorus pentachloride and ammonium chloride [Eq. (11.22)]. Similar reactions occur when the chloro group is replaced by fluoro, bromo, or isothiocyano groups.

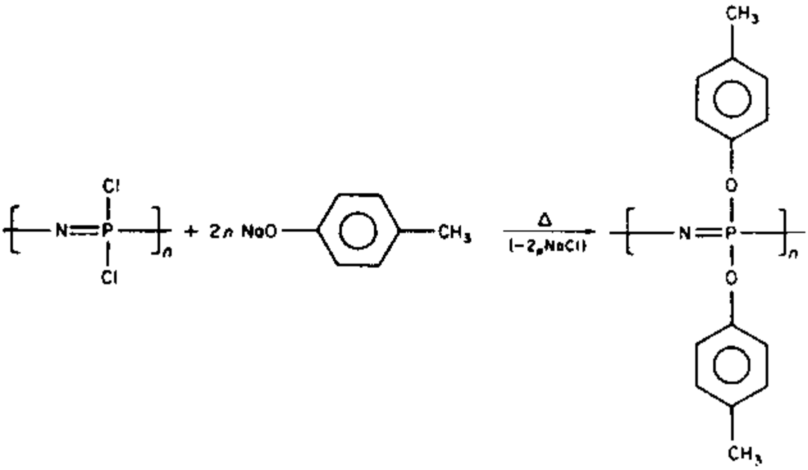


(11.22)

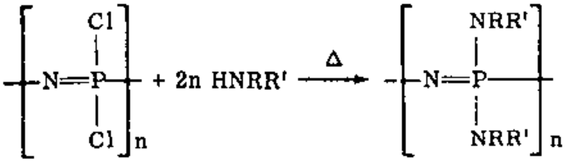
Amorphous elastomers are obtained when phosphazene is refluxed with nucleophiles, such as sodium trifluoroethoxide or sodium cresylate, and secondary amines (11.23–11.25). Copolymers are produced when mixtures of reactants are employed.



$$\left[-N=\underset{Cl}{\overset{Cl}{P}}-\right]_n + 2n\,NaOCH_2CF_3 \xrightarrow[-2nNaCl]{\Delta} \left[-N=\underset{OCH_2CF_3}{\overset{OCH_2CF_3}{P}}-\right]_n \qquad (11.23)$$



(11.24)



$$\left[\mathrm{N{=}P(Cl)_2}\right]_n + 2n\,\mathrm{HNRR'} \xrightarrow{\Delta} \left[\mathrm{N{=}P(NRR')_2}\right]_n \qquad (11.25)$$

Difunctional reactants such as dihydroxybenzenes (hydroquinone) produce cross-linked phosphazenes. Fibers may be made from polyphosphates and sheets may be pressed from polymeric black phosphorus. The latter is a semiconductor that reverts to white or red phosphorus when heated.

The observed low T_g values for most polyphosphazenes are consistent with the barriers to internal rotation being low and indicate the potential of these polymers for elastomer applications. In fact, theoretical calculations based on a rotational isomeric model assuming localized π bonding predict the lowest (100 cal/mol repeating unit) known polymer barrier to rotation for the skeletal bonds for polydifluorophosphazene.

Temperature intervals between T_g and T_m are unusually small and generally fall outside the frequently cited empirical relation $0.5 < T_g/T_m(A) < 0.67$. This behavior could be related to complications in the first-order transition generally found for organo-substituted phosphazenes and not common to other semicrystalline polymers. Two first-order transitions are usually observed for organo-substituted phosphazenes with a temperature interval from about 150°C to 200°C. The lower first-order transition can be detected using DSC, DTA, and TMA. Examination by optical microscopy reveals that the crystalline structure is not entirely lost but persists throughout the extended temperature range to a higher temperature transition, which appears to be T_m, the true melting temperature. The nature of this transition behavior resembles the transformation to a mesomorphic state similar to that observed in nematic liquid crystals. It appears from the relationship between the equilibrium melting temperature (heat and entropy of fusion; $T_m = H_m/S_m$) and the low value of H_m at T_m compared with the lower transition temperature that the upper transition, T_m, is characterized by a quite small entropy change. This may be due to an onset of chain motion between the two transitions leading to the small additional gain in conformational entropy at T_m.

The absence of an undetected endothermic transition at T_m for aryloxy polymers and polyarylaminophosphazenes indicates that the gain in conformational entropy at T_m for these products is indeed small.

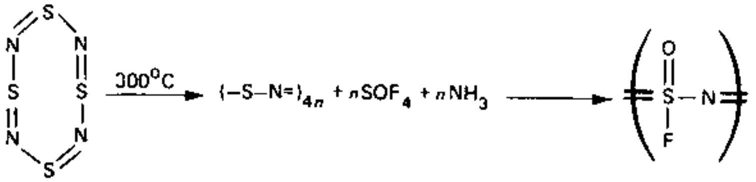
The lower transition is sensitive to structural changes and usually parallels T_g changes. Further, these are commonly noted as T_g values. This will be done here.

From a practical point of view, polyphosphazenes are usually soft just above the lower transition so that compression molding of films can be carried out. This suggests that the lower transition represents the upper temperature for most useful engineering applications of polyphosphazenes in an unmodified form. The results indicate that organization in the mesomorphic state, as influenced by thermal history, has a great effect on the transition from a crystalline state in an unmodified form.

Allcock and others have employed polyphosphazenes in a variety of uses including the broad areas of electrical and biomedical applications.

Sulfur nitride polymers $[(SN)_n]$, which have optical and electrical properties similar to those of metals, were synthesized in 1910. These crystalline polymers, which are superconductive at 0.25 K, may be produced by the room temperature solid-state polymerization of the dimer (S_2N_2). Amorphous polymers are also obtained from the tetramer.

A dark, blue-black, amorphous paramagnetic form of poly(sulfur nitride) may be produced by quenching the gaseous tetramer in liquid nitrogen. The tetramer is produced when the polymer is heated to 145°C. Golden metallic films of poly(sulfur nitride) are obtained when the gaseous tetramer is condensed on a glass surface at room temperature. Films of bromine-containing derivatives of poly(sulfur nitride) are superconductors at 0.31 K.



(11.26)

Much of the interest in the polysilanes, polygermanes, and polystannanes involves their σ-π delocalization and their σ-π delocalization when coupled with arenes or acetylenes. This is not unexpected since silicon exists as a covalent network similar to diamond. In exhibiting electrical conductivity germanium and tin show more typical “metallic” bonding. Some polystannanes have been referred to as “molecular metals.”

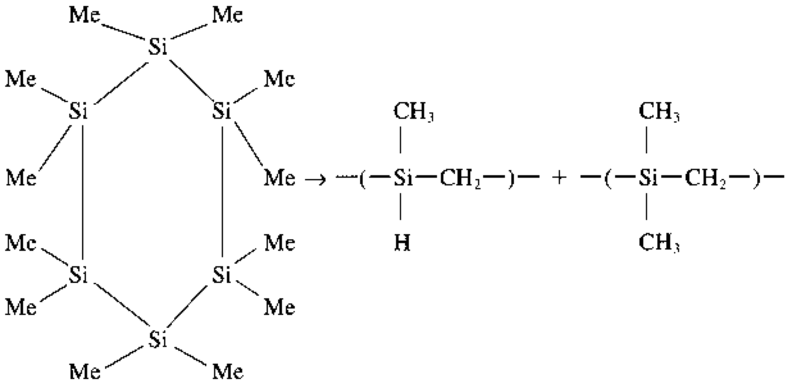
Because of the interesting electronic and physical properties of polysilanes, a number of potential uses have been suggested including precursors of β-SiC fibers, impregnation of ceramics, polymerization initiators, photoconductors for electrophotography, contrast enhancement layers in photolithography, deep-UV-sensitive photoresists, nonlinear optical materials, and self-developing by excimer laser or deep-UV exposure. The unusual absorption spectra of polysilanes have indicated potential use in a number of conducting areas.

One area of active interest in ceramics is the formation of ceramics that may contain some fiber structure. Currently, ceramics, while very strong, are very brittle. Introduction of thermally stable fiber-like materials might allow the ceramics some flexibility before cleavage. Such materials might be considered as ceramic composites where the matrix is the ceramic portion and the fibers are thermally stable. Introduction of the fibers during the ceramic formation step is a major obstacle that must be overcome. Carbon fibers have been investigated as have been other high-temperature materials such as the polysilanes.

Table 11.6 Nonoxide Ceramics Produced from the Pyrolysis of Polymeric Materials

Polymer(s)	Resultant ceramic
Poly(phosphonitric chlorides)	PN
Polysilanes, polycarbosilanes	SiC
Polyphenylborazole	BN
Polytitanocarbosilanes	Si-Ti-C
Polysilazanes	Si_3N_4, Si-C-N

Polysilanes are formed from the six-membered ring through extended heating at 400°C. Further heating gives silicon carbide.



(11.27)

Table 11.6 lists a number of nonoxide ceramics that have been produced from the pyrolysis of polymers.

11.6 SOL-GEL

In the sol-gel process, ceramic polymer precursors are formed in solution at ambient temperature; shaped by casting, film formation, or fiber drawing; and then consolidated to furnish dense glasses or polycrystalline ceramics. The most common sol-gel procedures involve alkoxides of silicon, boron, titanium, and aluminum. In alcohol-water solution, the alkoxide groups are removed stepwise by hydrolysis under acidic or basic catalysis and replaced by hydroxyl groups, which then form —M—O—M— linkages. Branched polymer chains grow and interconnect, forming a network that can span the entire solution volume. At this point, gel point, viscosity, and elastic modulus increase rapidly.

The gel is a viscoelastic material composed of interpenetrating liquid and solid phases. The network retards the escape of the liquid and prevents structural collapse. The shapes formed by casting, drawing of fibers, or film formation are locked in by the gel formation. Some gels are oriented by drawing or shearing. The gel is dried by evaporation forming a xerogel or by supercritical fluid extraction giving an aerogel. Consolidation to dense glasses or ceramics is carried out by thermal treatment and sintering.

Since both aerogels and xerogels have high surface areas and small pore diameters they are used as ultrafiltration media, antireflective coatings, and catalysts supports. Final densification is carried out by viscous sintering.

The rate of silicate sol and gel formation is pH- and water/alcohol-sensitive, as is the solubility of the amorphous silica that is formed. Silica networks are based on $(SiO_4)^{-4}$ tetrahedra modified by $(O_3Si\text{-}O^-, M^+)$ units. Addition of boron oxide, aluminium oxide, titanium (IV) oxide, or zirconium (IV) oxide often occurs.

The nature of the reactants can be varied giving various silicate-like products. Following is described the formation of borosilicate glasses using the sol-gel approach.

$$\mathrm{NaOR} + \mathrm{B(OR)_3} + \mathrm{Si(OR)_4} \xrightarrow[-\mathrm{HOR}]{\mathrm{H_2O}}$$

$$\mathrm{NaOH} + \mathrm{B(OH)_3} + \mathrm{Si(OH)_4} \xrightarrow[\text{via sol and gel}]{-\mathrm{H_2O}} \tag{11.28}$$

$$(\mathrm{Na_2O} \cdot \mathrm{B_2O_3} \cdot \mathrm{SiO_2}) \cdot \mathrm{H_2O} \xrightarrow[\Delta]{-\mathrm{H_2O}} \mathrm{Na_2O} \cdot \mathrm{B_2O_3} \cdot \mathrm{SiO_2}$$

The use of organically modified silicates (ceramers) gives a wide variety of products with a variety of structures and properties. Such ceramers have been used as adhesives for glass surfaces, protective coating for medieval stained glass, and scratch-resistant coatings for plastic eyeglass lenses. They have also been used in the reinforcement of plastics and elastomers, and their nanoscale pores allow their use as porous supports and as selective absorbents.

Sol-gel preparations of tetraethoxysilane can be spun into fibers once the appropriate viscosity has been achieved. These fibers are only slightly weaker than silica glass fibers.

Hybrid materials have been made by incorporating endcapped poly(tetramethylene oxide) blocks to tetramethoxysilane sol-gel glasses. These materials have high extensibility with interdispersed organic and inorganic regions.

SUMMARY

1. There is a wide variety of inorganic polymers. The potential uses are many and include the broad areas of biological, electrical, analytical, catalytic, building, and photo applications.
2. The bond strength for many combinations is higher than that of many carbon-intensive organic polymers leading to products with superior strength and thermal stabilities.
3. The majority of inorganic reactions are of two general groupings—redox (oxidation–reduction) and substitution.
4. The majority of the condensation polymerizations can be considered extensions of typical organic types of Lewis acid–base reactions.
5. Polysiloxanes (silicones) offer a good combination of properties not found in organic polymers. Silicones are employed in a number of applications, including antifoaming agents, lubricants, caulks, sealants, O rings, and gaskets.
6. Polyphosphazenes offer unique thermal properties and have shown a number of uses in the field of electronics.
7. Polymers of sulfur nitride decompose into tetramers when heated at 145°C, and interesting polymers with electrical conductivity are obtained when the gaseous tetramer is cooled.

8. The number and variety of organometallic polymers and potential applications for organometallic polymers are great. Because of the high cost of many of the metal-containing reactants, uses will probably be limited to applications employing minute quantities of the polymers.

GLOSSARY

amorphous: Noncrystalline.
borazoles: Molecules made up of boron and nitrogen atoms.
capping: Protecting the end groups.
carboranes: Molecules made up of carbon and boron atoms.
coordination polymers: Polymers based on coordination complexes.
Dexsil: Trade name for copolymers of carborane and siloxane.
ferrocene: A sandwichlike molecule of cyclopentadiene and iron.
inorganic polymers: Those containing elements other than typically carbon, nitrogen, and oxygen in their backbone or pendant groups.
M: Any metal.
metallocenes: Sandwichlike molecules of cyclopentadiene and metals.
PNF: Poly(phosphonitrilic fluoride).
polyphosphonitrile: Polymer with the repeat unit $\left[\overset{|}{\underset{|}{P}}{=}N \right]$.
RTV: Room temperature vulcanization.
silanes: A homologous series, like the alkanes, based on silicon instead of carbon.
SN: Sulfur nitride.

EXERCISES

1. What is meant by “lost loops” in the production of silicones?
2. How could you produce a silicone with a low DP?
3. What would you estimate the solubility parameters of silicones to be?
4. Sodium silicate is water soluble (forming water glass), but silicones are water repellents. Can you explain this difference?
5. How could you polymerize an aqueous solution of sodium silicate?
6. How could you explain the good temperature resistance of silicones?
7. Show the repeat unit for polydiethysiloxane.
8. What are the reactants used to make phosphazenes?
9. Why would you predict that the chloro groups in phosphonitrilic polymers would be attacked by water?
10. Which phosphazene would be more flexible—one made by a reaction of poly(phosphonitrilic chloride) with (a) sodium trifuloroethoxide, or (b) sodium trifluorobutoxide?
11. Show the structure of borazole.
12. Since tin-containing organometallic polymers are used in marine antifouling coatings, what would you predict about their water resistance?
13. In addition to high cost, name another disadvantage of coordination polymers.
14. What is the ceiling temperature of sulfur nitride polymers?

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12

Inorganic Polymers

12.1 INTRODUCTION

Just as polymers abound in the world of organics, so do they abound in the world of inorganics. Inorganic polymers are the major components of soil, mountains, and sand. Inorganic polymers are also extensively employed as abrasives and cutting materials [diamond, boron carbide, silicon carbide (carborundum), aluminum oxide], fibers (fibrous glass, asbestos, boron fibers), coatings, flame retardants, building and construction materials (window glass, stone, Portland cement, brick, tiles), and lubricants and catalysts (zinc oxide, nickel oxide, carbon black, graphite, silica gel, alumina, aluminum silicate, chromium oxide, clays, titanium chloride).

The first somewhat man-made, synthetic polymer was probably inorganic in nature. Alkaline silicate glass was used in the Badarian period in Egypt (about 12,000 B.C.) as a glaze, which was applied to steatite after it has been carved into various animal, etc., shapes. Faience, a composite containing a powdered quartz or steatite core covered with a layer of opaque glass, was employed from about 9000 B.C. to make decorative objects. The earliest known piece of regular (modern day type) glass, dated to 3000 B.C., is a lion's amulet found at Thebes and now housed in the British Museum. This is a blue opaque glass partially covered with a dark green glass. Transparent glass appeared about 1500 B.C. Several fine pieces of glass jewelry were found in Tutankhamen's tomb (ca. 1300 B.C.) including two bird heads of light blue glass incorporated into the gold pectoral worn by the Pharaoh.

As with the organic-containing inorganic polymers covered in the previous chapter, there are many methods of presenting the topic of inorganic polymers. Because of the

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Portions of this chapter are loosely based on columns appearing in *Polymer News*, Gordon and Breach, and used with permission of the editor, Gerald Kirschenbaum.

Table 12.1 Important Inorganic Polymers

Agate
Alumina
Aluminum oxide
Amosite
Amphiboles
Anorthite
Anthophyllite
Arsenic selenide
Arsenic sulfide
Asbestos
Berlinite
Beryllium oxide
Boehmite
Boron nitride
Boron oxides
Boron phosphate
Calcite
Carbon black
Cerium phosphate
Chabazite
Chalcedony
Chalcogens
Chert
Chrysotile
Coesite
Concrete
Cristobalite
Crocidolite
Diamond
Dickite
Edingtonite
Enstatite
Epistilbite
Faujasite
Feldspars
Flint
Fuller's earth
Garnet
Germanium selenide
Gibbsite
Glasses (many kinds)
Graphite
Halloysite
Heulandite
Hiddenite
Imogolite
Jasperite
Kaolinite
Keatite
Mesolite
Mica
Montasite
Montmorillonite
Mordenite
Muscovite
Nacrite
Natrolite
Phosphorus oxynitride
Polyphosphates (many)
Polyphosphazenes
Polysilicates (many)
Polysulfur (polymeric sulfur)
Pyrophyllite
Pyroxmangite
Quartz
Rhodonite
Scolecite
Serpentine
Silicon (many)
Silicon carbide
Spodumene
Stilbite
Stishorite
Sulfur nitride
Talc
Thomsonite
Titanium
Tremolite
Tridymite
Valentinite
Vermiculite
Wollastonite
Xonotlite
Ziolites
Zirconia

wide variety and great number of inorganic polymers, this chapter will focus on only a few of the more well-known inorganic polymers.

Table 12.1 contains a partial listing of common inorganic polymers.

12.2 PORTLAND CEMENT

Portland cement is the least expensive, most widely used synthetic inorganic polymer. It is employed as the basic nonmetallic, nonwoody material of construction. Concrete highways and streets span our countryside and concrete skyscrapers silhouette the urban skyline. Less spectacular uses are found in everyday life as sidewalks, fence posts, and parking bumpers.

The name "Portland" is derived from the cement having the same color as the natural stone quarried on the Isle of Portland, a peninsula on the south of Great Britain. The word cement comes from the Latin word *caementum*, which means "pieces of rough, uncut stone." Concrete comes from the Latin word *concretus*, meaning "to grow together."

Common cement consists of anhydrous crystalline calcium silicates (the major ones being tricalcium silicate, Ca_3SiO_5, and β-dicalcium silicate, Ca_2SiO_4), lime (CaO, 60%), and alumina (a complex aluminum-containing silicate, 5%). White cement is widely used and has been studied in good detail, its structure and the process whereby it is formed are not completely known. This is due to at least two factors. First, its three-dimensional arrangement of various atoms has a somewhat ordered array when any small (molecular level) portion is studied, but as larger portions are viewed, less order is observed. This arrangement is referred to as short-range order—long-range disorder and is a good description of many three-dimensional, somewhat amorphous inorganic and organic polymers. Thus, there exists only an average structure for the cement which varies with amount of water and other components, added, time after application (i.e., age of cement), and source of concrete mix and location (surface or internal). Second, three-dimensional materials are insoluble in all liquids; therefore, tools of characterization and identification that require materials to be in solution cannot be employed to assist in the structural identification of cement.

When anhydrous cement mix is added to water, the silicates react, forming hydrates and calcium hydroxide. Hardened Portland cement contains about 70% crosslinked calcium silicate hydrate and 20% crystalline calcium hydroxide.

$$2Ca_3SiO_5 + 6H_2O \rightarrow Ca_3SiO_2O_7 \cdot 3H_2O + 3Ca(OH)_2 \tag{12.1}$$

$$2Ca_2SiO_4 + 4H_2O \rightarrow Ca_3Si_2O_7 \cdot 3H_2O + Ca(OH)_2 \tag{12.2}$$

A typical cement paste contains about 60–75% water by volume and only about 40–25% solids. The hardening occurs through at least two major steps (Fig. 12.1). First a gelatinous layer is formed on the surface of the calcium silicate particles. The layer consists mainly of water with some calcium hydroxide. After about two hours the gel

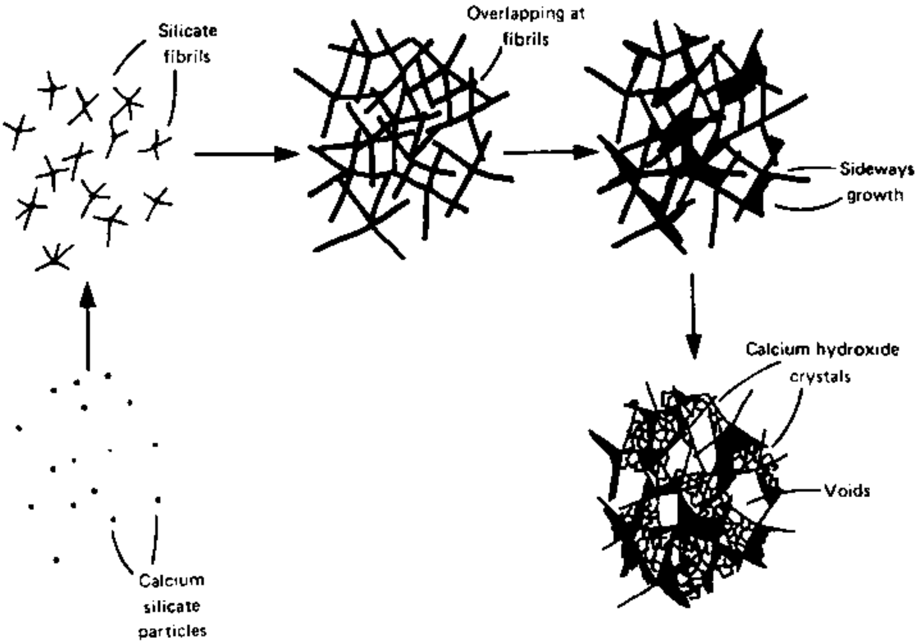


Figure 12.1 Steps in the hardening of Portland cement.

layer sprouts fibrillar outgrowths that radiate from each calcium silicate particle. The fibrillar tentacles increase in number and length, becoming enmeshed and integrated. The lengthwise growth slows, with the fibrils now joining up sideways, forming striated sheets that contain tunnels and holes. During this time, calcium ions are washed away from the solid silicate structure by water molecules and react further, forming additional calcium hydroxide. As particular local sites become saturated with calcium hydroxide, calcium hydroxide itself begins to crystallize, occupying once vacant sites and carrying on the process of interconnecting about and with the silicate "jungle."

In spite of the attempts by the silicate and calcium hydroxide to occupy all of the space, voids are formed, probably from the shrinkage of the calcium hydroxide as it forms a crystalline matrix. (Generally crystalline materials have higher densities than amorphous materials; thus a given amount will occupy less volume, leaving some unfilled sites.) Just as a chain is no stronger than its weakest link, so also is cement no stronger than its weakest sites, i.e., its voids. Much current research concerns attempts to generate stronger cement with a focus on filling these voids. Interestingly enough, two of the more successful cement void fillers are also polymers—dextran, a polysaccharide, and polymeric sulfur.

Table 12.2 shows a typical concrete mix. The exact amounts may vary by as much as 50% depending on the intended use and preference of the concrete maker.

The manufacture of Portland concrete consists of three basic steps—crushing, burning, and finish grinding. As noted before, Portland cement contains about 60% lime, 25% silicates, and 5% alumina with the remainder being iron oxide and gypsum. Most cement plants are located near limestone ($CaCO_3$) quarries since this is the major source of lime. Lime may also come from oyster shells, chalk, and a type of clay called marl. The silicates and alumina are derived from clay, silicon sand, shale, and blast-furnace slag.

The initial step in the manufacture of cement after the limestone rock is quarried is the powdering of the rock. The powdered rock is mixed together giving a material with a somewhat uniform composition. Two major systems are now employed to obtain the finished cement. In the dry process, the grinding and mixing are done on dry materials. As one would guess, this results in excessive particulate dust formation. In the wet process certain operations are carried out in a water slurry. In both processes, the material is further ground to a fine consistency through a pounding, shaking, and recombining process. Alumina, silicates, and iron oxide are added during this time.

In the dry process the mixture is fed directly into kilns for burning. In the wet process, preheating for removal of much of the water precedes introduction into the kiln. The material is typically placed into kilns (rotating at a rate of about one rotation per minute), which are heated to about 1500°C. Water and organics are burned away and the carbonates liberate carbon dioxide.

Table 12.2 Sample Concrete Mix

	Amount	
Material	By volume	By weight
Portland cement	90–100 lb (1 cubic foot)	90–100 lb (40–45 kg)
Water	5 $\frac{1}{2}$ gallons	45 lb (20 kg)
Sand	2 cubic feet	200 lb (90 kg)
Gravel (small rocks)	3 cubic feet	250 lb (120 kg)

$$Ca_3CO_3 \rightarrow CaO + CO_2 \quad (12.3)$$

These cement kilns are the largest pieces of moving machinery used in industry and can be 25 feet in diameter and 750 feet long. The heat changes the mixture into particles called clinkers, about the size of a marble. The clinkers are cooled and reground, with the final grinding producing Portland cement finer than flour. The United States produces over 60 million metric tons of Portland cement a year.

12.3 OTHER CEMENTS

There are a number of cements specially formulated for specific uses.

Air-entrained concrete contains small air bubbles formed by the addition of soaplike resinous materials to the cement or to the concrete when it is mixed. The bubbles permit the concrete to expand and contract (as temperature changes) without breaking (since the resistance of air to changes in volume is small).

Light-weight concrete may be made through use of light-weight fillers such as clays and pumice in place of sand and rocks or through the addition of chemical foaming agents that produce air pockets as the concrete hardens. These air pockets are usually much larger than those found in air-entrained concrete.

Reinforced concrete is made by casting concrete about steel bars or rods. Most large cement-intense structures such as bridges and skyscrapers employ reinforced concrete.

Prestressed concrete is typically made by casting concrete about steel cables stretched by jacks. After the concrete hardens, the tension is released, resulting in the entrapped cables compressing the concrete. Steel is stronger when tensed, and concrete is stronger when compressed. Thus prestressed concrete takes advantage of both of these factors. Archways and bridge connections are often made from prestressed concrete.

Concrete masonry is simply the name given to the cement building blocks employed in the construction of most houses, and it is simply a precast block of cement.

Precast concrete is concrete that is cast and hardened before it is taken to the site of construction. Concrete sewer pipes, wall panels, beams, girders, and spillways are all examples of precast concrete.

The aforementioned cements are all typically derived from Portland cement. Following are non-Portland cements.

Calcium-aluminate cement has a much higher percentage of alumina than does Portland cement. Furthermore, the active ingredients are lime, CaO, and alumina. In Europe it is called melted or fused cement. In the United States it is manufactured under the trade name Lumnite. Its major advantage is its rapidity of hardening, developing high strength within a day or two.

Magnesia cement is largely composed of magnesium oxide (MgO). In practice, the magnesium oxide is mixed with fillers and rocks and an aqueous solution of magnesium chloride. This cement sets up (hardens) within 2–8 h and is employed for flooring in special circumstances.

Gypsum, or hydrated calcium sulfate ($CaSO_4{\cdot}2H_2O$), serves as the basis of a number of products including plaster of Paris (also known as molding plaster, wall plaster, and finishing plaster), Keen's cement, Parisian cement, and Martin's cement.

The ease with which plaster of Paris and the other gypsum cements can be mixed and cast and the rapidity with which they harden contribute to their importance in the construction field as a major component for plaster wall boards. Plaster of Paris's lack of shrinkage in hardening accounts for its use in casts. Plaster of Paris is also employed as a dental plaster, pottery plaster, and as molds for decorative figures. Unlike Portland cement, plaster of Paris requires only about 20% water and dries to the touch in 30–60 min, giving maximum strength after 2 or 3 days. Portland cement requires several weeks to reach maximum strength.

12.4 SILICATES

Silicon is the most abundant metal-like element in the earth's crust. It is seldom present in pure elemental form, but rather is present in a large number of polymers largely based on the polycondensation of the orthosilicate anion, SiO^{4-} as illustrated by the following:

$$\begin{aligned}
\underset{1}{SO_4^{4-}} &\rightleftharpoons \underset{2}{Si_2O_7^{-6}} + O^{-2}\\
Si_2O_7^{6-} + SiO_4^{-4} &\rightleftharpoons \underset{3}{Si_3\,O_9^{6-}} + 2O^{2-}\\
2Si_2O_7^{6-} &\rightleftharpoons \underset{4}{Si_4O_{10}^{4-}} + 4O^{2-}\\
2Si_2\,O_7^{6-} &\rightleftharpoons \underset{5}{Si_4O_{11}^{6-}} + 3O^{2-}\\
2Si_2O_7^{6-} &\rightleftharpoons \underset{6}{Si_4O_{12}^{8-}} + 2O^{2-}\\
3Si_2O_7^{6-} &\rightleftharpoons \underset{7}{Si_6O_{18}^{12-}} + 3O2^{-}\\
SiO_4^{4-} &\rightarrow \rightarrow \text{etc. } \underset{8}{SiO_2}
\end{aligned} \tag{12.4}$$

The number listed with each product corresponds to the "geometrical ID number" given in Table 12.3, and the "structural geometry" given in Table 12.3 is depicted in Fig. 12.2.

Table 12.3 Inorganic Polymeric Silicates as a Function of Common Geometry

Geometric ID number (text)	Basic geometrical unit	Structural geometry (Fig. 12.2)	General silicate formula[a]	Examples[a]
1	Tetrahedran	A	SiO_4^{4-}	Granite olivine-$(Mg,Fe)_2SiO_4$ Fosterite-Mg_2SiO_4 Topez
2	Double tetrahedran	B	$Si_2O_7^{6-}$	Akermanite-$Ca_2MgSi_2O_7$
3	Triple ring	C	$Si_3O_9^{6-}$	Wollastonite
4	Tetra ring	D	$Si_4O_{12}^{6-}$	Neptunite
5	Six ring	E	$Si_6O_{18}^{12-}$	Beryl-$Al_2Be_3Si_6O_{18}$
6a	Linear chain	F	$Si_4O_{12}^{8-}$	Augite, enstatite-$MgSiO_3$ Diopside-$CaMg(SiO_3)_2$ Chrysotile-$Mg_6Si_4O_{11}(OH)_6$
6b	Double-stranded ladder	G	$Si_4O_{11}^{6-}$	Hornblende
7	Parquet (layered)	H	$Si_4O_{10}^{4-}$	Talc-$Mg_3Si_4O_{10}(OH)_2$ Mica-$KAl_3Si_3O_{10}(OH)_2$ Kaolinite-$Al_2Si_2O_5(OH)_4$ (Condensed) silicic acid-$H_2Si_2O_5$
8	Network	I	SiO_2	Quartz, feldspar (orthoclase)-$KAISi_3O_8$

[a] The formulas given are for the most part simplified.

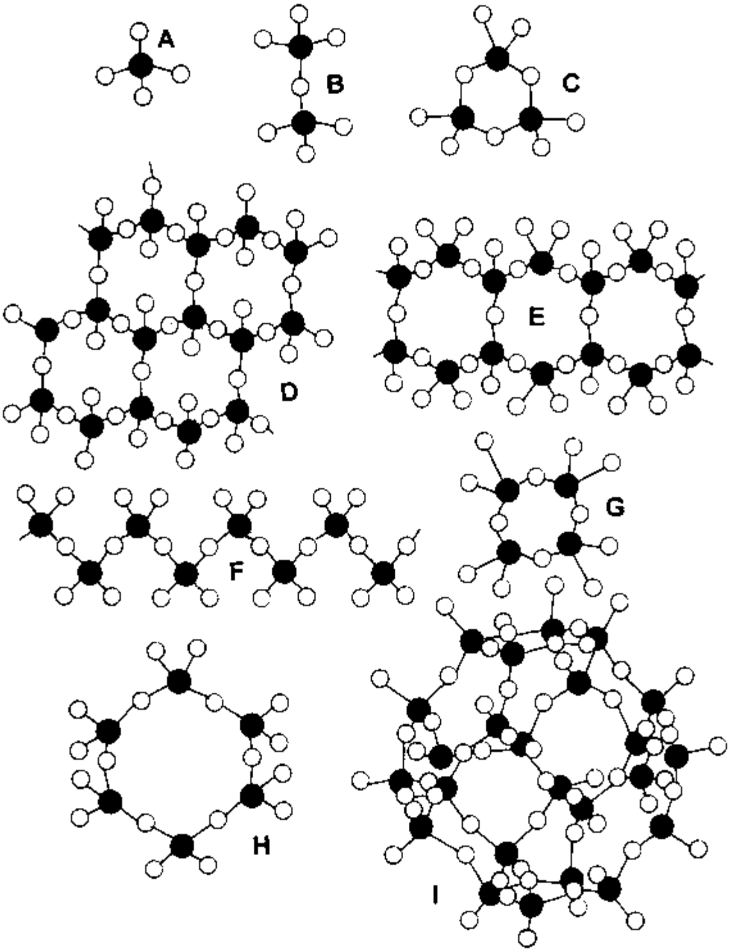


Figure 12.2 General silicate structures.

Each of these steps is based on a tetrahedral silicon atom attached to four oxygen atoms. The complexity and variety of natural occurring silicates is due to two major factors: (1), the ability of the tetrahedral SiO_4^{4-} unit to be linked together often giving polymeric structures; (2), the substitution of different metal atoms of the same approximate size as that of Si often occurs giving many different materials.

In the structures cited in Table 12.3, except for pure SiO_2, metal ions are required for overall electrical neutrality. These metal ions are positioned in tetrahedral, octahedral, etc., positions in the silicate-like lattice. Sometimes they replace the silicon atom. Kaolinite asbestos (Figure 12.3) has aluminum substituted for silicon in the gibbosite sheet.

Furthermore, sites for additional anions, such as the hydroxyl anion, are available. In ring, chain, and sheet structures neighboring rings, chains, and sheets are often bonded together by metal ions held between the rings. In vermiculite asbestos the silicate sheets are held together by nonsilicon cations (Figure 12.3).

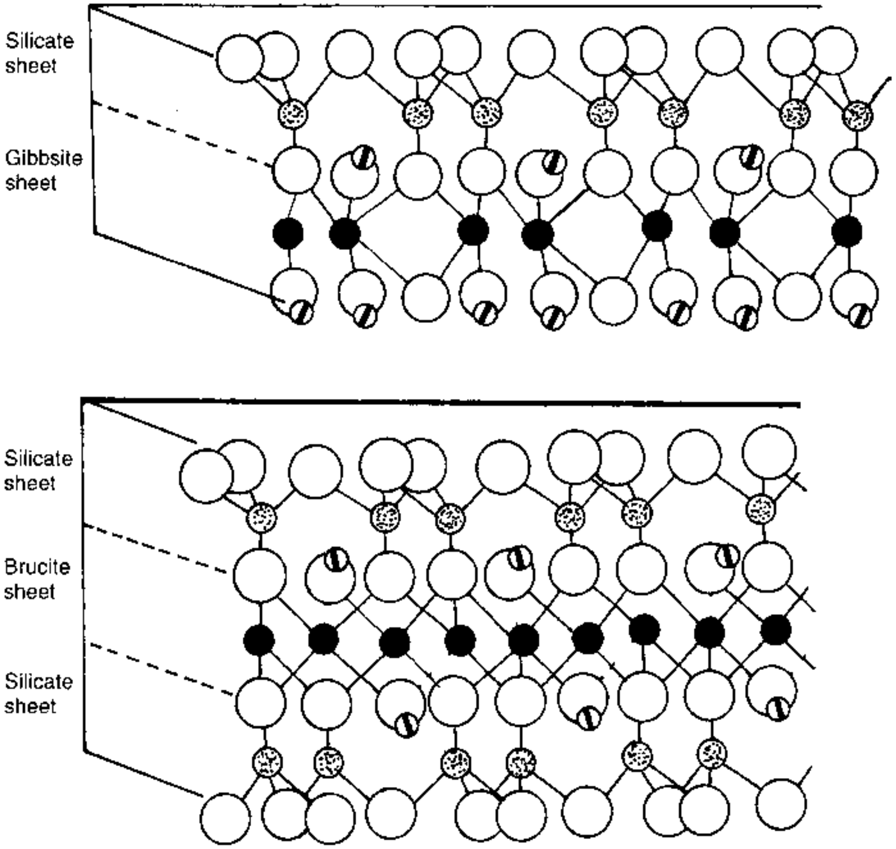


Figure 12.3 Structures of single-sided (top; kaolinite) and double-sided (bottom; vermiculite) layer asbestos where the single-striped atoms are hydrogen, open atoms are oxygen, speckled atoms are silicon, and solid atoms are aluminum (top structure) or magnesium (bottom structure).

For sheet-layered compounds, the forces holding together the various sheets can be substantially less than the forces within the individual sheets. Similar to graphite, such structures may be easily cleaved parallel to the sheets. Examples of such materials are mica, kaolinite, and talc.

Bonding occurs through a combination of ionic and covalent contributions just as are present in organic polymers except that the ionic character is a little higher. “Back bonding” from electrons associated with the oxygen to vacant orbitals in the silicon (or other tetrahedral metal atom) occurs giving the silicon-oxygen linkages some double- or π-bond character.

As noted before, cations other than silicon may occupy the tetrahedral centers. A major factor in predicting which cations will be found to substitute for silicon is ionic size. In general, cations whose size is about 0.03–0.1 nm are the best candidates. Si^{4+} has an ionic radius of about 0.041 nm. Cations such as Fe^{2+} (ionic radius 0.07 nm), Al^{3+} (0.05 nm), Ca^{2+} (0.1 nm), and Mg^{2+} (0.065 nm) are most often found in silicatelike structures and meet this requirement.

Most silicatelike polymers can be divided into three major classes—the network structures based on a three-dimensional tetrahedral geometry (such as quartz), layered geometries with stronger bonding occurring within the "two-dimensional" layer (such as talc), and linear structures.

Network

Quartz is an important network silicate (Sec. 12.6)

A number of tetrahedral silicatelike materials possess some AlO_4 tetrahedra substituted for the SiO_4 tetrahedra. Such structures offer a little larger "hole" in comparison to the entirely SiO_4 structures, allowing alkali and alkaline-earth cations to be introduced. Feldspar (orthoclase) is such a mineral. The aluminosilicate networks are almost as hard as quartz. For feldspar and other tetrahedral networks the number of oxygen atoms is twice the summation of silicon and other MO_4 cations.

The feldspars are widely distributed and compose almost two-thirds of all igneous rocks. Orthoclase and albite, $NaAlSi_3O_8$, are feldspars where one-fourth of the silicon atoms are replaced by aluminum, and anorthite, $CaAl_2Si_2O_8$, has one half of the silican atoms replaced by aluminum. Because the ionic radius of Na^+ (0.095 nm) and Ca^{2+} (0.1 nm) are about the same, solid solutions are often formed between albite and anorthite. Good stones of albite and orthoclase are known as moonstones.

Some of the network structures exhibit a framework sufficiently "open" to permit ions to move in and out. The zeolite minerals used for softening water are of this type.

Ultramarines are three-dimensional cagelike structures. They differ from feldspars and zeolites because of the large spaces within the structures that can contain cations and anions but no water, illustrating a natural "buckeyball-like" structure and cavity and a diversity of environment between the internal cage and external. Ultramarines can act as ion exchangers for both anions and cations. The blue color of ultramarines is due to the presence of the S_3^- ion although a yellow ion S_2^- also exists in the same structure.

Layer

Layered structures typically conform to the approximate composition $Si_4O_{10}^{4-}$ or $Si_2O_5^{2-}$. For most of these, three of the oxygen atoms of each tetrahedron are shared by other tetrahedra, and the fourth oxygen is present on one side of the sheet.

In talc and kaolinite the layers are neutral. Thus, the layers slide over one another easily imparting to these minerals a softness and ease in cleavage. In other minerals the layers are charged and held together by cations. In mica, the aluminosilicate layers are negatively charged and cations, generally K^+, are present between the layers giving the entire system of layers electronic neutrality. The ionic attractive forces between the layers result in mica being much harder than talc and kaolinite. Even so, these intersheet bonding forces are less than the "within-the-sheet" bonding forces, permitting relatively easy and clean cleavage of mica. Mica is used as an insulator for furnaces and electrical equipment. Montmorillonite is an important ingredient in soils and is employed industrially as a catalyst in the conversion of straight-chain hydrocarbons to more branched hydrocarbons.

Vermiculites are formed by the decomposition of mica. They contain layers of water and magnesium ions in place the potassium ions. When heated to 800–1100°C, vermiculite expands because of the conversion of the water to a gas. The expanded vermiculite has a low thermal conductivity and density and is used as a thermal and sound barrier and as an aggregate in light-weight concrete. It is also used as a moisture-retaining soil conditioner in planting.

A number of clays are layered, silicate-like materials. Most clays contain finely divided quartzs, micas, and feldspars. Iron oxide–rich clays are employed to make pottery and terra cotta articles. Clays containing iron oxide and sand are used to make bricks and tiles. Clays rich in calcium and magnesium carbonate are known as marls and are used in the cement industry (Sec. 12.2).

Kaolinite is the main constituent in China clay used to make porcelain. The layers are largely held together by van der Waals forces. Bentonite is used in cosmetics, as a filler for soaps, and as a plasticizer, and it is used in drilling muds as a suspension stabilizer. Bentonite and kaolinite clays are used, after treatment with sulfuric acid to create acidic surface sites, as petroleum cracking catalysts.

Asbestos also has a layered structure (Sec. 12.8).

Chain

Both single- and double-stranded chains are found. The most important members of single chains are the pyroxenes and includes diopside. The most important double-chained minerals are the amphiboles. Some of these contain hydroxyl and fluoride ions, bonded directly to the metal cation and not to the silicon atom.

Jade, which has been valued in carving by eastern Asians for centuries, is generally one of two minerals—pyroxene or jadeite, $NaAl(SiO_3)_2$, and the amphibole nephrite, $Ca_2(Fe^{2+}$ and/or $Mg^{2+})_5(SiO_4)_2(OH)_2$. X-Ray diffraction has shown the presence of triple chains in nephrite.

Because the interchain bonding is weaker than the Si-O backbone bonding, these chain structures can generally be easily cleaved between the chains.

Several amphiboles are fibrous and fibers from them can be processed to give heat-insulating materials. Among these are tremolite and crocidolite. These minerals are also used as fibers in composites.

12.5 SILICON DIOXIDE (AMORPHOUS)

Silicon dioxide (SiO_2) is the repeating general structural formula for the vast majority of rock, sand, and dirt about us and for the material we refer to as glass.

The term glass can refer to many materials, but here we will use the ASTM definition that glass is an inorganic product of fusion that has been cooled to a rigid condition without crystallization. In this section silicate glasses, the common glasses for electric light bulbs, window glass, drinking glasses, glass bottles, glass test tubes and beakers, and glass cookware, will be emphasized.

Glass has many useful properties, as listed in Table 12.4. It ages (changes chemical composition and/or physical property) slowly, typically retaining its fine optical and hardness-related properties for centuries. Glass is referred to as a supercooled liquid or a very viscous liquid. Indeed it is a slow-moving liquid, as attested to by sensitive measurements carried out in many laboratories. Concurrent with this is the observation that the old stained glass windows adorning European cathedrals are a little thicker at the bottom of each small, individual piece than at the top of the piece. For most purposes though, glass can be treated as a brittle solid that shatters on sharp impact.

Glass is mainly silica sand (SiO_2) and is made by heating silica sand and powdered additives together in a specified manner and proportion much as a cake is baked, following

Table 12.4 General Properties of Silicate Glasses

High transparency to light
Permanent (long-time) transparency
Hard
Scratch-resistant
Chemically inert
Low thermal expansion coefficients
Good electrical insulator
Wide range of colors possible
High sparkle
Good luster
Low porosity
Ease of reforming

a recipe that describes the items to be included, amounts, mixing procedure (including sequence), oven temperature, and heating time. The amounts, nature of additives, etc., all affect the physical properties of the final glass.

Typically cullet, recycled or waste glass (5–40%), is added along with the principal raw materials. The mixture is thoroughly mixed and then added to a furnace where the mixture is heated to near 1500°C to form a viscous, syrup-like liquid. The size and nature of the furnace corresponds to the glasses' intended uses. For small, individual items the mixture may be heated in small clay (refractory) pots.

Most glass is melted in large (continuous) tanks that can melt 400–600 metric tons a day for the production of other glass products. The process is continuous with raw materials fed into one end as molten glass is removed from the other. Once the process (called a campaign) is begun it is continued indefinitely, night and day, often for several years until the demand is met or the furnace breaks down.

A typical window glass will contain 95–99% silica sand with the remainder being soda ash (Na_2CO_3), limestone ($CaCO_3$), feldspar, and borax or boric acid along with the appropriate coloring and decolorizing agents, oxidizing agents, etc. As noted previously, 5–40% by weight of crushed cullet is also added. The soda ash, limestone, feldspar, and borax or boric acid all form oxides as they are heated, which become integrated into the silicon structure:

$$\underset{\substack{\text{Soda ash}\\ \text{(sodium carbonate)}}}{Na_2CO_3} \xrightarrow{\Delta} Na_2O + CO_2 \tag{12.5}$$

$$\underset{\substack{\text{Limestone}\\ \text{(calcium carbonate)}}}{CaCO_3} \xrightarrow{\Delta} CaO + CO_2 \tag{12.6}$$

$$\underset{\text{Feldspar}}{R_2OAl_2O_3{\cdot}6SiO_2} \xrightarrow{\Delta} R_2O + \underset{\substack{\text{Alumina}\\ \text{(aluminum oxide)}}}{Al_2O_3} + 6SiO_2 \tag{12.7}$$

$$\underset{\substack{\text{Boric}\\ \text{acid}}}{H_3BO_4} \xrightarrow{\Delta} \underset{\substack{\text{Boron}\\ \text{oxide}}}{B_2O_3} \tag{12.8}$$

The exact structure varies according to the ingredients and actual processing conditions (as how long heated at what temperature). As in the case of cement, glass is a three-dimensional array that offers short-range order and long-range disorder—it is amorphous offering little or no areas of crystallinity. The structure is based on the silicon atoms existing in a tetrahedral geometry with each silicon atom attached to four oxygen atoms, generating a three-dimensional array of inexact tetrahedrals. Thus structural defects occur, due in part to the presence of impurities such as Al, B, and Ca, intentionally introduced, and numerous other impurities not intentionally introduced. These impurities encourage the glass to cool to an amorphous structure since the different-sized impurity metal ions, etc., disrupt the rigorous space requirements necessary to exact crystal formation. Figure 12.4 is an illustration of this situation emphasizing the presence of the impurities.

Processing includes shaping and retreatments of glass. Since shaping may create undue sites of amorphous structure, most glass objects are again heated to near their melting point. This process is called *annealing*. Since many materials tend to form more ordered structures when heated and recooled slowly, the effect of annealing is to “heal” these sites of major dissymmetry. It is important to heal these sites since they represent preferential sites for chemical and physical attack such as fracture.

Four main methods are employed for shaping glass. They are drawing, pressing, casting, and blowing. Drawing is employed for shaping flat glass, glass tubing, and fiberglass. Most flat glass is shaped by drawing a sheet of molten (heated so it can be shaped but not so it freely flows) glass onto a tank of molten tin. Since the glass literally floats on the tin, it is called “float glass.” The temperature is carefully controlled. The glass

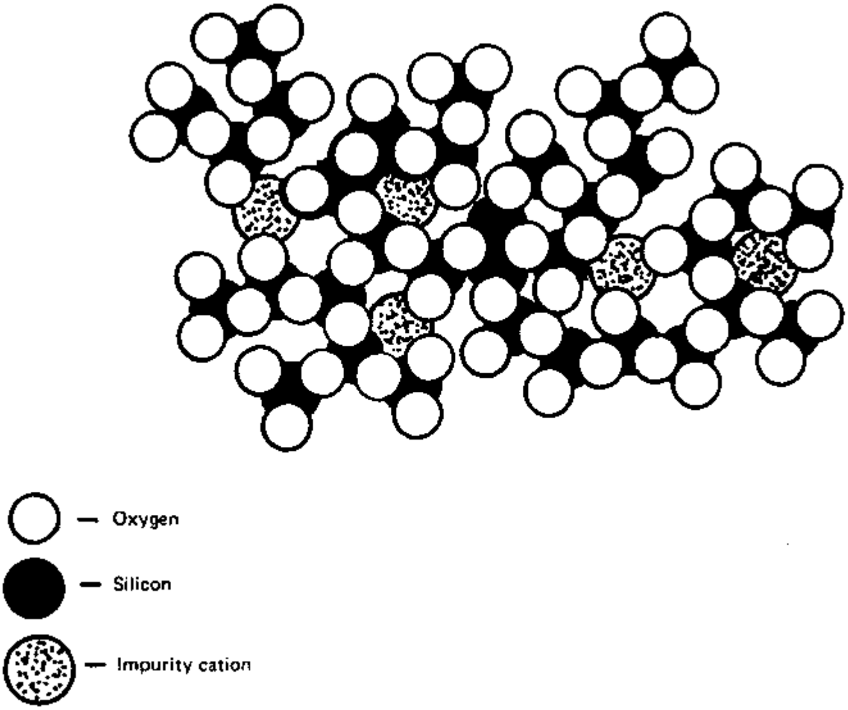


Figure 12.4 Two-dimensional representation of a multicomponent silicon dioxide–intensive glass.

from a “float bath” typically has both sides quite smooth with a brilliant finish that requires no polishing.

Glass tubing is made by drawing molten glass around a rotating cylinder of appropriate shape and size. Air can be blown through the cylinder or cone giving glass tubing used in the laboratory. Fiberglass is made by drawing molten glass through tiny holes, the drawing process helping to align the tetrahedral clusters.

Pressing is accomplished by simply dropping a portion of molten glass into a form and then applying pressure to ensure that the glass takes the form of the mold. Lenses, glass blocks, baking dishes, and ashtrays are examples of objects commonly press-processed.

The casting process involves filling molds with molten glass in much the same way that cement- and plaster of Paris–molded objects are produced. Art glass pieces are typical examples of articles produced by casting.

Glass blowing is one of the oldest arts known to man. For art or tailor-made blown objects, the working and blowing of the glass is done by a skilled worker who blows into a pipe intruded into the molten glass. The glass must be maintained at a temperature that permits working but not free flow, and the blowing must be at such a rate and controlled as to give the desired result. Mass-produced items are made using mechanical intense blowers, often having the glass blown to fit a mold much as the blow molding of plastics.

As noted above, annealing encourages the removal of stress and strain locations through raising the temperature to give nearly molten glass, which allows the glass to “heal” these stress and strain locations. Slow cooling will result in a glass containing larger areas of crystallinity resulting in stronger but more brittle glass. Tempering is the name given when the glass is rapidly cooled, resulting in a glass that is more amorphous as well as weaker but less brittle than more slowly cooled glass. The correlation between crystallinity, rate of cooling, and brittleness is readily demonstrated by noting that older window glass exposed to periods of full sun is quite brittle and easily shattered, since the sunlight raises the temperature sufficiently to permit small molecular movements (even in full sunlight the glass is not near the temperature to permit ready movement), and over a period of years this results in localized crystalline formation.

There is a wide variety of uses and kinds of glass. Silicon-based glasses account for almost all of the glasses manufactured. Silica is finely ground sand. Yet most sand is unsuitable for general glass making due to the presence of excessive impurities. Thus while sand is plentiful, sand that is useful in the production of glass is much less common. In fact, the scarcity of large deposits of glass sand is one major reason for the need to recycle glass items. The second major reason is associated with the lowered energy requirements for glass to be made molten again for reshaping compared with a virgin glass mixture, i.e., glass becomes molten at lower temperatures than are necessary to form molten glass from original feedstock.

Kinds of Glass

The types and properties of glass can be readily varied by changing the relative amounts and nature of ingredients. Soda-lime glass is the most common of all glasses, accounting for about 90% of glass made. Window glass, glass for bottles and other containers, glass for light bulbs, and many art glass objects are all soda-lime glass. Soda-lime glass typically contains 72% silica, 15% soda (sodium oxide, Na_2O), 9% lime (calcium oxide, CaO), and the remaining 4% minor ingredients. Its relatively low softening temperature and low thermal shock resistance limit its high-temperature applications.

Vycor, or 96% silicon glass, is made using silicon and boron oxide. Initially the alkali-borosilicate mixture is melted and shaped using conventional procedures. The article is then heat-treated, resulting in the formation of two separate phases—one high in alkalis and boron oxide, and the other containing 96% silica and 3% boron oxide. The alkali–boron oxide phase is soluble in strong acids and is leached away by immersion in hot acid. The remaining silica–boron oxide phase is quite porous. This porous glass is then again heated to about 1200°C, resulting in a 14% shrinkage due to the remaining portion filling the porous voids. The best variety is "crystal" clear and called fused quartz. The 96% silica glasses are more stable and exhibit higher melting points (1500°C) than soda-lime glass. Crucibles, ultraviolet filters, range burner plates, induction furnace linings, optically clear filters and cells, and super heat-resistant laboratoryware are often 96% silicon glass.

Borosilicate glass contains about 80% silica, 13% boric oxide, 4% alkali, and 2% alumina. It is more heat-shock-resistant than most glasses due to its unusually small coefficient of thermal expansion [typically between 2 and 5×10^{-6} cm/cm/°C (or simply 1/°C); for soda-lime glass 8 to 9×10^{-6} cm/cm/°C]. It is better known by such trade names as Kimax and Pyrex. Bakeware and glass pipelines are often borosilicate glass.

Lead glasses (often also called heavy glasses) are made by replacing some or all of the calcium oxide by lead oxide (PbO). Very high amounts of lead oxide can be incorporated—up to 80%. Lead glasses are more expensive than soda-lime glasses, and they are easier to melt and work with. They are more easily cut and engraved, giving a product with high sparkle and luster (due to higher refractive indexes). Fine glass and tableware are often lead glass.

Silicon glass is made by fusing pure quartz crystals or glass sand (impure crystals), and it is typically about 99.8% SiO_2. Silica glass has a high melting point (1750°C), making it hard to melt and difficult to fabricate.

Colored glass has been made for several thousands of years, first by Egyptians and later by Romans. Color is typically introduced by addition of transition metals and oxides. Table 12.5 contains a listing of selected inorganic colorants and the resulting colors. Because of the high clarity of glass, a small amount of coloring agent goes a long way. One part of cobalt oxide in 10,000 parts of glass gives an intense blue glass. The most well-known use for colored glass is in the construction of stained-glass windows. In truth, there are numerous other uses such as industrial color filters and lenses.

Table 12.5 Colorants for Stained Glass

Additive	Color(s)
Nickel oxide (NiO)	Yellow to purple
Calcium fluoride (CaF_2)	(Milky) white
Cobalt oxide (CoO)	Blue
Iron(II) compounds (salts and oxides)	Green
Iron(III) compounds (salts and oxides)	Yellow
Copper oxide (Cu_2O)	Red, blue, or green
Tin(IV) oxide (SnO_2)	Opaque
Manganese(IV) oxide (MnO_2)	Violet
Gold oxide (Au_2O_3)	Red

Coloring is usually one of three basic types:

1. Solution colors where the coloring agent such as oxides of transition metals (titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper) are dissolved in the glass.
2. Colloidal particle colors that are produced by the presence of certain small particles suspended in the glass. (Most ruby glass is made by introducing selenium, cadmium sulfide (CdS), and zinc oxide (ZnO) into the glass. This combination is believed to form small colloidal particles that result in the glass appearing to be ruby red-colored.)
3. Color caused by larger particles that can be seen under a regular microscope by the naked eye. Milky-colored opal and alabaster glasses are often of this variety.

Glazes are thin, transparent coatings (colored or colorless) fused on ceramic materials. Vitreous enamels are thin, normally opaque or semiopaque, colored coatings fused on metals, glasses, or ceramic materials. Both are special glasses but can contain little silica. They are typically low melting and often are not easily mixed in with more traditional glasses.

There also exist special glasses for special applications. Laminated automotive safety glass is a sandwich made by combining alternate layers of poly(vinyl butyral) (containing about 30% plasticizer) and soda-lime glass. This sticky organic polymer layer acts both to absorb sudden shocks (like hitting another car) and to hold broken pieces of the glass together. Bullet-proof (or, more correctly stated, bullet-resistant) glass is typically a thicker, multilayer form of safety glass.

Tempered safety glass is a single piece of specially heat-treated glass often used for industrial glass doors, laboratory glass, lenses, and side and rear automotive windows. Due to the tempering process, the material is much stronger than normal soda-lime glass. Optical fibers can be glass fibers that are coated with a highly reflective polymer coating such that light entering one end of the fiber is transmitted through the fiber (even around curves and corners as within a person's stomach), emerging from the other end with little loss of light energy. These optical fibers can also be made to transmit sound and serve as the basis for transmission of television and telephone signals over great distances.

Foam glass is simply soda-lime glass filled with tiny cells of gas. It is light weight and a good heat insulator. Optical glass for eyeglass lenses and camera lenses is again typically soda-lime glass, but it is highly purified so as to be highly transmissive of light. This special processing increases greatly the cost of this glass. There exist numerous other specialty glasses that are important in today's society—laser glasses, photosensitive glass, photochromic window and eyeglass glass, invisible glasses, and radiation absorbing glasses are only a few of these.

There are a number of silica-intensive fibers, many of them lumped together under the terms fibrous glass and fiberglass. A general-purpose soda-lime glass fiber may contain silica (72%), calcium oxide (9.5%), magnesium oxide (3.5%), aluminum oxide (2%), and sodium oxide (13%). Borosilicate fibers, synthesized for electrical applications where there is a danger of water, may contain silica (52%), calcium oxide (17%), magnesium oxide (5%), aluminum oxide (14%), sodium and potassium oxides (1%), and boric oxide (11%). Thus, through practice, various recipes have been developed for making fiberglass suitable for specific uses.

Table 12.6 Leading U.S. Glass Companies in Decreasing Order of Output

Owens-Illinois, Inc.
PPG Industries, Inc.
Corning Glass Works
Owens-Corning Fiberglass Corporation
Libbey-Owens-Ford Company

The fibers are produced by melting the “glass mixture” with the molten glass drawn through a number of orifices. The filaments are passed through a pan containing sizing solution onto a winding drum. The take-up rate of the filament is more rapid than the rate of flow from the orifices acting to align the molecules and draw the fibers into thinner filaments. Thus a fiber forced through a 0.1-cm orifice may result in filaments of 0.0005 cm diameter. This drawing increases the strength and flexibility of the fiberglass.

Applications of fiberglass include insulation (thermal and electrical) and the reinforcing of plastics.

Table 12.6 contains a listing of major glass-producing companies in the United States.

12.6 SILICON DIOXIDE (CRYSTALLINE FORMS)—QUARTZ FORMS

Just as silicon dioxide forms the basis of glass, so also does it form the basis of many of the rocks, grains of sand, and dirt particles that make up the Earth’s crust. Most rocks are inorganic polymers, but here we will deal with only a few of those containing significant amounts of silicon.

Silicon crystallizes in mainly three forms—quartz, tridymite, and cristobalite. After the feldspars, quartz is the most abundant mineral in the Earth’s crust, being a major component of igneous rocks and one of the most common sedimentary materials, in the form of sandstone and sand. Quartz can occur as large (several pounds) single crystals but is normally present as much smaller components of many of the common materials around us. The structure of quartz (Fig. 12.5) is a three-dimensional network of six-membered Si-O rings (three SiO_4 tetrahedra) connected such that every six rings enclose a 12-membered Si-O (six SiO_4 tetrahedra) ring.

Quartz is found in several forms in all three major kinds of rocks: -igneous, metamorphic, and sedimentary. Is is one of the hardest minerals known. Geologists often divide quartz into two major groupings—coarse crystalline and cryptocrystalline quartz.

Coarse crystalline quartz includes six-sided crystals and massive granular clumps. Some colored varieties of coarse crystalline quartz crystals, amethyst and citrine, are cut into gem stones. Others include pink (rose) and purple and milky quartz, but most coarse crystalline quartz is colorless and transparent. Sandstone is a ready example of granular quartz. Color is a result of the presence of small amounts of metal cations such as calcium, iron, magnesium, aluminum, and iron.

Cryptocrystalline forms contain microscopic quartz crystals and include the chalcedony grouping of rocks, including chert, agate, jasper, and flint.

Quartz exhibits an important property called the piezoelectric effect. When pressure is applied to a slice of quartz, it develops a net positive charge on one side of the quartz

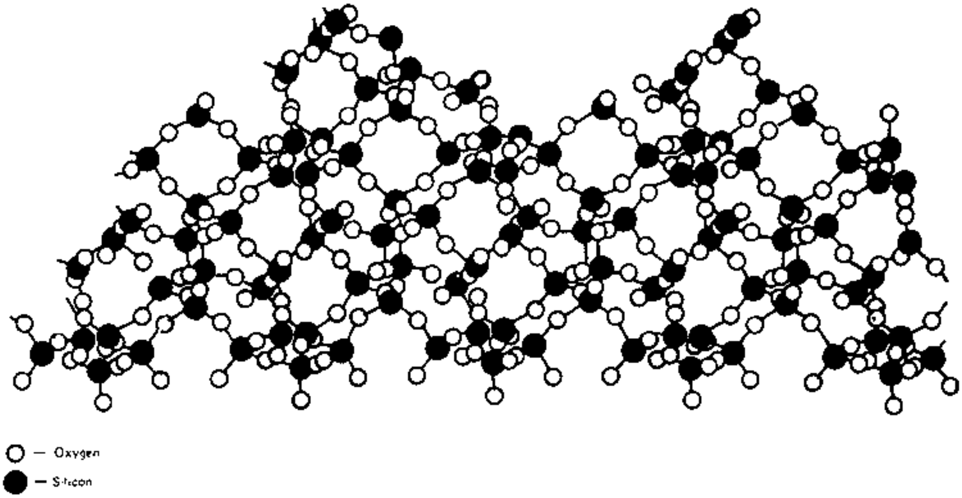


Figure 12.5 Structure of crystalline SiO_2 tetrahedra as found in quartz.

slice and a negative charge on the other. This phenomenon is piezoelectric generation of a voltage difference across the two sides of the quartz crystal. Furthermore, the same effect is found when pressure is applied not mechanically but through application of an alternating electrical field with only certain frequencies permitted to pass through the crystal. The frequencies allowed to pass very with the crystal shape and thickness. Such crystals are used in radios, televisions, and radar. This effect also forms the basis for quartz watches and clocks. Voltage applied to a quartz crystal causes the crystal to expand and contract at a set rate, producing vibrations. The vibrations are then translated into a uniform measure of time.

While quartz crystals are suitable for the production of optical lenses, most lenses are manufactured from synthetically produced quartz due to the scarcity of good-grade large quartz crystals.

The feldspars are the most abundant minerals in the Earth's crust, accounting for about 60% of all igneous rocks. They are derivatives of silica, where about one-half or one-quarter of the silicon atoms have been replaced by aluminum. The minerals can be divided into two groupings—alkali and plagioclase feldspars. All alkali feldspars contain potassium and most contain sodium. The most common alkaline feldspars are orthoclase, microcline, and sanidine. Most plagioclase feldspars contain calcium and sodium and include andesine and labradorite. Feldspar is used in the manufacture of certain types of glass and pottery. Some feldspar crystals; such as moonstone (white perthilte), Amazon stone (green microcline), and multicolored labradorite, are used as gem stones and in architectural decorations. Some feldspar is also used as a coating and filler in the production of paper.

The three-dimensional network in a typical feldspar is composed of eight-membered rings containing four tetrahedra (AlO_4 and/or SiO_4) linked through additional tetrahedra into chains.

Granite is a hard crystalline rock chiefly composed of quartz and feldspar. Many of the quartz and feldspar crystals are large enough to be seen by the naked eye. Quartz is transparent, much like glass. Feldspar is typically colored a dull white, gray, or pink. On a broken, cleaved rock surface, the feldspar crystals are smooth and reflect sunlight, being seen as “sparkling.” The dark-colored minerals in granite are mainly black mica and hornblende, also polymeric.

Granite is used in building bridges and buildings where great strength is needed. It is also employed in the construction of monuments and gravestones since it can be polished to give a lasting luster and because of its tendency to resist wear by the natural elements.

Granite was once melted rock like lava, but it remained deep underground where the Earth’s pressure acted to both encourage crystal formation and to encourage a slow cooling rate, which also encouraged crystal formation. Geological upheavals brought the granite from deep in the Earth’s mantle to the surface. At times, the melted pregranite rock was forced to the surface in its molten state where it cooled more rapidly and without benefit of high pressure, resulting in smaller crystals that can only be seen through a microscope. Such lava is called rhyolite.

Sand is loose grains of minerals or rocks, larger than silt but smaller than gravel. Sand can be divided by kind or size. Size differential is normally accomplished by simply placing the raw material on top of a series of wire screens of decreasing size. Most grains of sand are parts of rocks and have been weathered—thus they are usually smooth. The most common sand is largely quartz, although the sands of White Sands, New Mexico are largely gypsum grains. Most grains of sand are hues of brown and white with a few being clear quartz and others small red-colored rubies.

Soil contains mineral and organic particles, the majority by weight of the mineral particles being simply sand. The content of soil changes constantly. The organic particles bring organic nutrients to plants while the inorganic sand particles supply the mineral, trace element nutrients necessary to life. Plants demand a delicate balance of nutrients. Fortunately as one plant dies, it deposits both organic and inorganic nutrients for later generations. Soil erosion, flooding, and fires all result in drastic changes in the composition of soil and thus present local plants with new soil features that must be coped with if survival is to occur.

As noted in previous chapters, much organic decay material is polymeric. Thus soil is a complex, variable mixture of organic and inorganic polymers, small molecules, gases (nitrogen, oxygen, carbon monoxide, carbon dioxide, and methane), and water.

Micas are also composed of silicon-oxygen tetrahedra. The anionic charge on the silicate sheet is the result of the replacement of silicon by aluminum. Cations such as potassium are interspaced between these negatively charged sheets. Muscovite [$KAl_2(OH)_2Si_3AlO_{10}$] and phlogopite [$KMg_3(OH)_2Si_3AlO_{10}$] are naturally occurring micas employed in constructional and electrical engineering applications.

Synthetic mica is manufactured on a large scale for industrial consumption. The China clay or kaolin minerals are sheet polymers with a basic formula of $Al_2(OH)_4Si_2O_5$. Kaolinite, dickite, and nacrite all have this empirical composition, differing in the number of kaolin layers—keolinite with one layer per unit cell, dickite two, and nacrite six. Mica, clay-like silica, and fibrous glass are used as fillers and reinforcements in plastics and elastomers.

12.7 SILICON DIOXIDE IN ELECTRONIC CHIPS

Silicon dioxide plays a critical role in the electronics industry. The silicon used to produce silicon chips is derived from silicon dioxide. Semipure silicon dioxide (to about 99%) is prepared from the reaction of silicon dioxide with coke (a poor grade of graphite) using high temperature and an electronic arc.

$$SiO_2 + C \rightarrow Si + CO_2 \tag{12.9}$$

Even so, this level of purity falls far short of the purity need to produce the chips used in computers. The purity required is about 99.9999996% or a level of impurity of about 1 ppb. This is achieved through multistep processes. One of these requires the silicon to be heated with HCl at high temperatures forming the desirable volatile trichlorosilane. The vapor is condensed and then purified using distillation and absorption columns. The trichlorosilane is reacted with hydrogen gas at about 1200°C depositing polycrystalline chip-grade silicon. The other product of this reaction is HCl, which can be again used to create more trichlorosilane, thus eliminating the production of unwanted byproducts.

$$Si + HCl \rightarrow HSiCl_3 \tag{12.10}$$

$$HSiCl_3 + H_2 \rightarrow Si + HCl \tag{12.11}$$

Silicon dioxide is also used to insulate regions of the integrated circuit. Here silicon dioxide is grown on the silicon surface by heating the surface to about 1000°C in the presence of oxygen.

$$Si + O_2 \rightarrow SiO_2 \tag{12.12}$$

An alternate approach employs heating gaseous tetraethoxysilane to form layers of silicon dioxide.

$$Si(OC_2H_5)_4 \rightarrow SiO_2 + 2H_2O + 4C_2H_4 \tag{12.13}$$

12.8 ASBESTOS

Asbestos has been known and used for over 2000 years. Egyptians used asbestos cloth to prepare bodies for burial. The Romans called it *aminatus* and used it as a cremation cloth and for lamp wicks. Macro Polo described its use in the preparation of fire-resistant textiles in the thirteenth century. Asbestos is not a single mineral but rather a grouping of materials that give soft, threadlike fibers (Table 12.7). These materials are examples of two-dimensional sheet polymers containing two-dimensional silicate $(Si_4O_{10})^{4-}$ anions bound on either one or both sides by a layer of aluminum hydroxide [$Al(OH)_3$, gibbsite] or magnesium hydroxide [$Mg(OH)_2$, brucite]. The aluminum and magnesium are present as positively charged ions (cations). These cations can also contain a varying number of water molecules (waters of hydration) associated with them. The spacing between silicate layers varies with the nature of the cation and amount of its hydration.

Amphibole asbestos consists of a number of mineral types, including the cummingtonite-grunerite series, actinolite-tremolite series, anthophyllite, and crocidolite. Amphibole asbestos is generally coarser than serpentine asbestos. The amphibole asbestos contains silicate sheets with a wider number of cations, including iron, magnesium calcium, sodium, and aluminum. Amphibole asbestos is noted for its good resistance to both heat and acids. Kaolinite is the most important member of this group. It is actually a mixture of a number of asbestoses with the natural aggregates known as China clay or kaolin.

Due to its fibrous nature and ability to resist elevated temperature (compared with most organic-based fibers), chrysotile is used to make fabrics for the production of fire-resistant fabric, including laboratory glovewear and theater curtains. Shorter fibers are used

Table 12.7 Major Uses of Chrysotile Asbestos as a Function of Fiber Length

Description[a]	Uses
Crude (3/8 to 1 in. and unsorted)	Textiles, theater curtains, brake linings
2 M (medium; milled fibers)	Textiles, theater curtains, packings, brake linings
8 M (medium; milled fibers)	Shingles, cement pipe, insulating jackets, packings, gaskets, asbestos paper, mill-board, plastic fireproof cements, asbestos-asphalt roof coatings, electrical panels, insulation, plastic fillers
10 M (shortest; milled fibers)	Asbestos-cement sheets, asbestos-cement shingles, brake linings, asbestos paper, asphalt roof coatings, plastic fillers, welding, rods, floor tiles, boiler insulation

[a] Sized according to ability to pass through standardized screen meshes with the screen mesh sizes decreasing as screen number increases.

in electrical insulation and in automotive brake linings. The shortest fibers are employed in the production of cement pipe, floor tile, reinforced plastics, and reinforced caulking agents. A summary of uses is given in Table 12.7.

Though asbestos has been known and used for thousands of years, it is only in the last 60–80 years that the potential hazards of asbestos have been recognized. For instance, asbestos miners and manufacturing personnel who work with asbestos for 20 years or more are 10 times more likely than the general public to contract asbestosis. Families of asbestos workers and those living near the mines also have a greater than average incidence of asbestosis.

Asbestosis is a disease that blocks the lungs with thick fibrous tissue, causing shortness of breath, and swollen fingers and toes. Bronchogenic cancer (cancer of the bronchial tubes) is prevalent among asbestos workers who also smoke cigarettes. Asbestos also causes mesothelioma, a fatal cancer of the lining of the abdomen or chest. These diseases may lie dormant for many years after exposure.

The exact origin of these diseases is unknown, but they appear to be caused by particles (whether asbestos or other particulates) about 5–20 μm in length (2×10^{-4} in.), corresponding to the approximate sizes of the mucous openings in the lungs. Furthermore, the sharpness of asbestos fibers intensifies their toxicity, since these fibers actually cut the lung walls. When the walls heal, the deposited asbestos, if not flushed from the lungs, again cuts the lung walls as the individual coughs, with more scar tissue being formed. The cycle continues until the lungs can no longer function properly.

Because of its widespread use (see Table 12.7), small amounts of airborne asbestos are probably present throughout most of the United States. It is hoped that the amounts are small enough as to not be harmful.

12.9 POLYMERIC CARBON—DIAMOND

Just as carbon serves as the basic building element for organic materials, so also does it form a building block in the world of inorganic materials. Elemental carbon exists in two distinct crystalline forms—graphite and diamond. Graphite is the more stable allotrope of carbon, with graphite readily formed from heating diamonds.

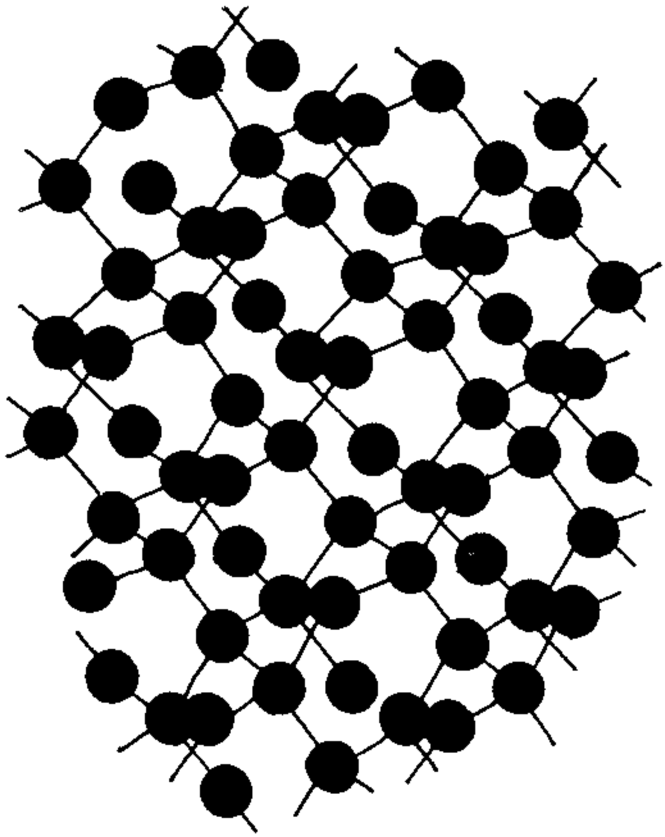


Figure 12.6 Representation of diamond, where each carbon is at the center of a tetrahedron composed of four other carbon atoms. Diamond is the hardest known natural material.

Natural diamonds (Fig. 12.6) were formed millions of years ago when concentrations of pure carbon were subjected by the Earth's mantle to great pressure and heat. The majority of diamonds (nongems) are now man-made. The majority of synthetic diamonds are no larger than a grain of common sand. By 1970, General Electric was manufacturing diamonds of gem quality and size through compressing pure carbon under extreme pressure and heat. These diamonds, available at a cost much higher than that of natural diamonds, are used for research. For instance, it was discovered that the addition of small amounts of boron to diamonds causes them to become semiconductors. Today such doped diamonds are used to make transistors.

Imitation diamonds are prevalent in the marketplace. These include spinel, strontium titanate glass, and yttrium aluminate. While they are less expensive than true diamonds, they can give good sparkle and be fashioned into diamond shapes. However, they are not as hard as real diamonds, and their luster is more easily marred through clouding and formation of surface scratches.

The major use of diamond is as an industrial shaping and cutting agent to cut, grind, and bore (drill) holes in metals and ceramics. Many record players employ a diamond needle to transmit differences in the record grooves into sound.

India was the earliest supplier of diamonds. In 1867 the first diamonds were discovered in South Africa, which has since become the largest supplier of diamonds. Diamonds have been discovered in many parts of Africa, including the Gold Coast, Angola, and Sierra Leone. While diamonds were discovered in Brazil in 1725, South America has only accounted for a small fraction of the diamonds found. Small deposits have also been found in Arkansas, Australia, the Ural Mountains (Russia), and Mexico. Diamonds are few in number even in the richest mines. For instance, it takes an average of about 15 metric tons of ore to find 1 g equivalent of diamond from the diamond fields of South Africa.

While diamonds can be cut, shaping has been done in the past by a trained gem cutter striking the rough diamond on one of its cleavage planes. These cleavage plates are called *faces* and represent sites of preferential cleavage and reflection of light. Thus, a gem cutter will seek out these cleavage planes in combinations that will result in a spectacular gem stone where the maximum amount of diamond is included in the gem stone. Unlike food or other commodities, the price of a diamond increases as the bulk increases.

12.10 POLYMERIC CARBON—GRAPHITE

While diamond is the hardest naturally occurring material, the most common form of crystalline carbon is the much softer graphite. Graphite occurs as sheets of hexagonally fused benzene rings (Fig. 12.7) or “hexachicken wire.” The bonds holding the fused hexagons together are traditionally primary, covalent bonds. The bonding between the sheets of fused hexagons consists of a weak overlapping of π electron orbitals and is considerably weaker than the bonding within the sheet. Thus, graphite exhibits many properties that are dependent on the angle at which they are measured. Furthermore, they show some strength when measured along the sheet but very little strength if the layers are allowed to slide over one another. Also, the fused hexagons are situated such that the atoms in each layer lie opposite to the centers of the six-membered rings in the next layer. This arrangement further weakens the overlapping of π electrons between layers such that the magnitude of layer-to-layer attraction is on the order of ordinary secondary van der Waals forces. The “slipperiness” of the layers accounts for graphite’s ability to be a good lubricant.

The variance of property with angle of applied force, light, magnetism, etc., is called anisotropic behavior. Calcite is anisotropic in its crystal structure, resulting in a dependency of its interaction with light with the angle of incidence of the light. This is employed in the construction of laboratory polariscopes. Certain organic polymers can also be made to be anisotropic in their reaction to light, electricity, magnetism, or other applied forces. This serves as the basis for many polarized sunglasses.

As with diamonds and most other natural materials, graphite’s discovery and initial usage is lost in antiquity. It was long confused with other minerals such as molybdenite (MoS_2). At one time it was known as plumbago (“like lead”), crayon noir, silver lead, black lead, and carbo mineralis. Werner, in 1789, first named it graphit, meaning (in Greek) “to write.”

While graphite has been extensively mined in China, Mexico, Austria, North and South Korea, and Russia, the majority of graphite used in the United States is manufactured from coke.

The Acheson process for graphite production begins by heating a mixture of charcoal, or coke, and sand. The silica is believed to be reduced to silicon that combines with carbon-forming silicon carbide, which subsequently dissociates into carbon and silicon.

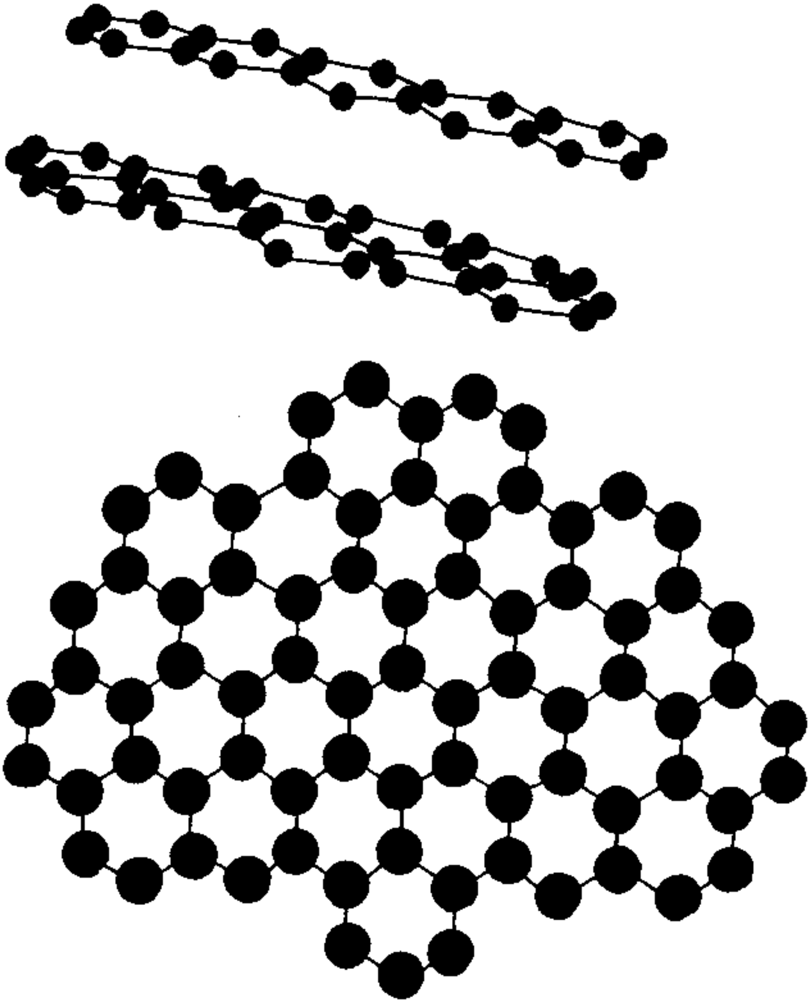


Figure 12.7 *Pictorial* representation of graphite emphasizing the layered (top) and sheet (bottom) nature of graphite.

The silicon vaporizes and the carbon condenses, forming graphite. Graphite may also be produced employing other processes. The precise properties of a graphite sample are dependent on the specific conditions employed in its production. For instance, certain processes will give graphite containing a large number of defects that allow a high permeability. Other processes, such as the high-temperature pyrolysis of hydrocarbon vapors, give a dense layer of graphite with few defects and a low gas permeability.

The properties of graphite led directly to its many uses in today's society. Because of its tendency to mark, hardened mixtures of clay and graphite are the "lead" in today's lead pencils. Graphite conducts electricity and is not easily burned. Thus, many industrial electrical contact points (electrodes) are made of graphite. Graphite is a good conductor of heat and is chemically quite inert, even at high temperatures. Thus many crucibles for melting metals are graphite-lined. Graphite has good stability even to strong acids; thus, it is employed to coat acid tanks. It is also effective at slowing down neutrons, and thus composite bricks and rods (often called carbon rods) are employed in some nuclear generators to regulate the progress of the nuclear reaction. As already noted, its “slipperiness” accounts for its use as a lubricant for clocks, door locks, and hand-held tools. Graphite is also the major starting material for the synthesis of synthetic diamonds. Graphite is sometimes used as a component of industrial coatings (paints). Dry cells and some types of alkali storage batteries also employ graphite. Graphite fibers are used for the reinforcement of thermosets and thermoplastics.

At ordinary pressures and temperatures, both graphite and diamond are stable. At high temperatures (1700–1900°C), diamond is readily transformed to graphite. The reverse transformation of graphite to diamond occurs only with application of great pressure and high temperatures. Thus, as noted before, the naturally more stable form of crystalline carbon is not diamond but rather graphite.

12.11 POLYSULFUR

Sulfur is present in the petrochemicals derived from once-living matter because of its presence in certain amino acids. Because of its removal from industrial waste, sulfur has been stockpiled and is available at a low price in large amounts. While the stable form of sulfur at room temperature is cyclooctasulfur, S_8, linear polysulfur is formed on heating. Unfortunately, the thermodynamically Stable form of sulfur is the cyclooctasulfur monomer and the polymer undergoes depolymerization after a while. Methods have been studied to inhibit this reversal process. Some have involved the addition of olefins such as limonene, myrcene, and cyclopentadiene to the ends to inhibit the depolymerization. Such stabilized polysulfur has been incorporated into concrete and asphalt mixes to strengthen them. Concrete blocks, posts, and parking tire restrainers containing polysulfur are now being produced.

12.12 CERAMICS

The term *ceramics* comes from the Greek word *keramos*, which means “potter’s clay” or “burnt stuff.” While traditional ceramics were often based on natural clays, today’s ceramics are largely synthetic materials. Depending on which ceramic and which definition is to be applied, ceramics have been described as inorganic ionic materials and as inorganic covalent (polymeric) materials. In truth, many ceramics contain both covalent and ionic bonds and thus can be considered as polymeric and nonpolymeric materials. Many of the new ceramics such as the boron nitriles and the silicon carbides are polymeric without containing any ionic bonds.

Ceramics are typically brittle; strong; resistant to chemicals such as acids, bases, salts, and reducing agents; and they are high melting. They were largely composed of carbon, oxygen, and nitrogen. They are now largely made from silicates such as clay, feldspar, bauxite, and silica but also contain other materials such as borides, carbides, silicides, nitrides.

They are generally made by two processes: sintering and fusing. In sintering, the starting material is reduced to a powder or granular form by a series of crushing, powdering, ball milling, etc. The ground preceramic material is then sized and separated according to particle size using different sized screens.

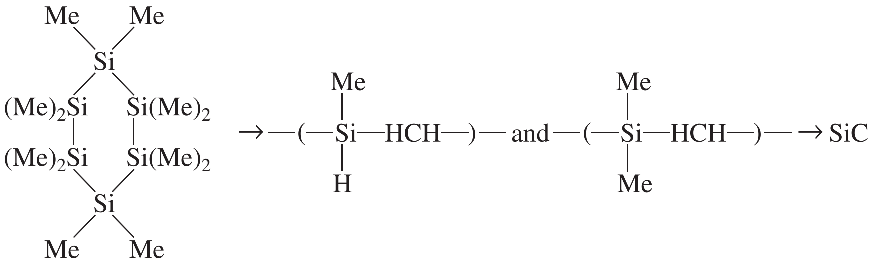
Ceramic material is generally shaped by pressing it into a form or through extruding, molding, jiggering, or slip-casting. Slip-casting uses a suspension of the preceramic material in water. The mixture must be dilute enough to allow it to be poured. Deflocculants are often added to assist in maintaining the suspension. The “slip” is poured into a plaster of Paris mold that absorbs water, leaving the finished shape. The preceramic material hardens next to the mold and surplus slip material poured off leaving a hollow item. At this point, the molded material is referred to as a “green body” which has little strength. Coffee pots and vases are formed using this technique.

In jiggering, machines press the preceramic material into a rotating mold of desired shape. Dinnerware products are often made using jiggering.

Abrasives and insulators are formed from simply pressing the preceramic material into a mold of desired shape. In extrusion, the preceramic material is forced through an opening in a “shaping” tool. Bricks and drain pipes are formed using extrusion.

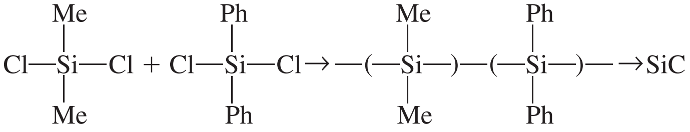
After the product has dried, it is heated or fired in a furnace or kiln. Modern ceramics generally require certain heating schedules that include the rate and duration of heating and under what conditions such as in the presence or absence of air. This is similar to procedures used to produce carbon fibers where the heating schedule is critical to the end product’s properties.

In one approach, six-membered silicon-containing rings are pyrolized giving mixed carbosilane preceramic polymers through heating to 400°C, and subsequently forming silicon carbides or poly carbosilanes at 800°C.



(12.14)

SiC fibers can be formed using dimethyldichlorosilicon and diphenyldichlorosilicon heated together.



$$\mathrm{Cl{-}\underset{Me}{\overset{Me}{Si}}{-}Cl + Cl{-}\underset{Ph}{\overset{Ph}{Si}}{-}Cl} \rightarrow -(-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-)-(-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-)- \rightarrow \mathrm{SiC} \tag{12.15}$$

Such “ceramic” fibers offer uniquely strong and resistant inexpensive materials including new ceramic composites that have great fracture toughness.

There are a number of other “nonoxygen” or nonoxide ceramics including phosphonitric chlorides (PN backbone), boron nitriles (BN), aluminum nitriles (AIN), titanocarbosilanes (Si-Ti-C backbone), and silazanes (Si-C-N backbones).

Many ceramic products have a glassy coating, called a *glaze*. The glaze increases the resistance of the material to gas. Solvent permeability makes the surface smoother. In art objects glaze is also used for decoration.

One group of advanced material ceramics are the zirconia ceramics. Most of these are based on zirconia [zirconium(IV) oxide] that contains small amounts of magnesia (magnesium oxide). They have bending strengths two to three times that of corundum and alumina; high fracture toughness (about five times that of corundum ceramics); high resistance to wear and corrosion; and they are high density (5.8 g/cm^3). They are used in the construction of shear blades in the textile industry, plungers in the food and drink industry, valves in the petroleum industry, and as milling balls in the materials industry.

Zirconia exists in three solid phases:

$$\text{Monoclinic} \leftarrow 1200^\circ\text{C} \rightarrow \text{tetragonal} \leftarrow 2400^\circ\text{C} \rightarrow \text{cubic} \leftarrow 2700^\circ\text{C} \rightarrow \text{liquid}$$

The transformation between the monoclinic and tetragonal phases involves large and abrupt volume changes introducing fractures in the material. This is minimized through the use of di- and trivalent oxides of cubic symmetry such as calcium oxide and magnesium oxide. This results in a lowering of the transition temperatures ($M \rightarrow T$ and $T \rightarrow C$) and also lowers the expansion coefficient of the zirconia and the subsequent volume changes associated with the phase changes thus reducing ceramic fracturing. The addition of calcium oxide or magnesium oxide is said to “stabilize” the ceramic.

Strength, brittleness, and solvent permeability properties are limited because of lack of control of the ceramic composition on a macro and micro level. Even small particle sizes are large compared with the molecular level. There have been a number of attempts to produce uniform ceramic powders including the sol-gel synthesis whereby processing involves a stable liquid medium, as well as coprecipitation where by two or more ions are precipitated simultaneously. More recently, Carraher and Xu have used the thermal degradation of metal-containing polymers to deposit metal atoms and oxides on a molecular level.

12.13 HIGH-TEMPERATURE SUPERCONDUCTORS

Discovery of the 123-Compound

In early 1986, George Bedorz and K. Alex Muller reported a startling discovery: a ceramic material, La-Ba-Cu-O, lost its resistance to electrical current at about 30 K. This was the first report of a so-called high-T_c superconductor. Intensive efforts were then concentrated on substituting the component ions with similar elements on both of the La and Ba sites. The first success was reported by Kishio et al. with an $(La_{1-x}Sr_x)_2CuO_4$ system that exhibited a T_c higher than the former by about 7 K. Then the substitution on the La sites led Wu et al. to find another superconductor, the Y-Ba-Cu-O system, with a T_c of 93 K, in February 1987. This finally broke the technological barrier of liquid nitrogen temperature. The superconducting phase was identified as $Y_1Ba_2Cu_3O_7$ (generally referred to as the *123-compound*).

The 123-compound, therefore, was the first of the 90 K–plus superconductors to be discovered, and it has been the most thoroughly studied.

Structure of the 123-Compound

The structure of the 123-compound is related to that of an important class of minerals called *perovskites*. These minerals contain three oxygen atoms for every two metal atoms. The new compound, with six metal atoms in its unit cell, would thus be expected to have nine oxygens if it were an ideal perovskite. In fact, it has, in most samples, between 6.5

and 7 oxygens. In other words, by comparison to an ideal perovskite, about one-quarter of the oxygens are missing. The unit cell of the 123-compound can be thought of as a pile of three cubes. Each cube has a metal atom at its center: barium in the bottom cube, yttrium in the middle one, and barium in the top one. At the corners of each cube a copper would be surrounded by six oxygens in an octahedral arrangement linked at each oxygen in an ideal perovskite. Each barium and yttrium would then be surrounded by 12 oxygens. But X-ray and neutron diffraction studies have shown that the unit cell doesn't conform to this simple picture because certain oxygen positions are vacant. All oxygen positions in the horizontal plane containing yttrium are vacant. The other vacancies are located in the top and bottom Cu-O planes. Several studies of the unit cell parameters indicate that the unit cell is orthorhombic with b slightly larger than a. The perpendicular square planar arrangements of copper and oxygen ions are linked together by sharing their corners, forming "linear chains" along the b axis of the structure. Linking of horizontal CuO_4 results in two-dimensional puckered sheets in the a-b plane of the structure.

As shown in Fig. 12.8, there are two nonequivalent Cu sites: Cu(1) in the chains, and Cu(2) in the planes. Above each Cu(2) there is an O(4) site (in a Ba plane); and in the Cu(2) planes there are O(2) and O(3) sites along the a and b axes, respectively. The oxygen atom site in the chains is labeled O(1). It was believed early on that the occurrence of Cu-O chains was crucial for obtaining high transition temperatures, but the recent discovery of the new Bi and T1 layered oxides, which do not have chains, have shown that this is not likely to be the key.

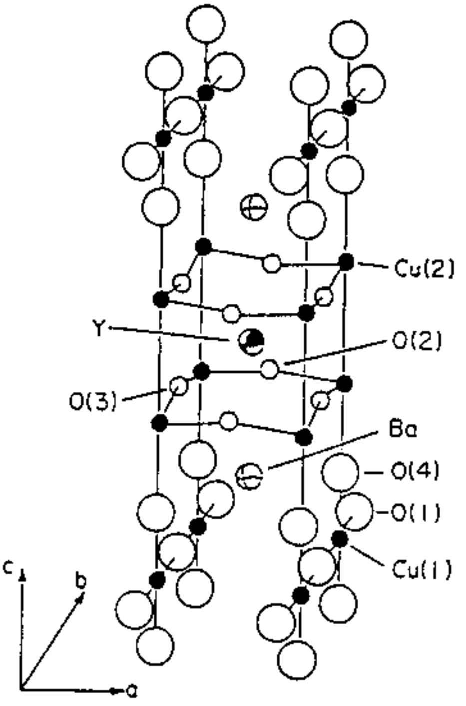


Figure 12.8 Structure of the 123-compound.

The two copper oxide layers can be considered as polymeric since the covalent character is in the same range as the carbon fluoride bond in Teflon. Thus, the 123-superconductive materials consist of two types of polymeric copper oxide layers held together by ionic bonding metals such as barium and yttrium. This theme of polymeric layers held together by ionic bonding to metals is often found in inorganic materials including many of the silicates including asbestos.

12.14 ZEOLITES

At least three major themes are helping drive polymer synthesis and use of polymers today. These involve synthesis and assembling on an individual scale (nanolevel), synthesis in confined spaces (selected inorganic zeolites and biological syntheses), and single-site catalysis (both selected biological and synthetic polymer synthesis). Superimposed on this are the applications aspects including the human genome/biomedical, electronic/communications, etc.

Zeolites include a whole group of aluminosilicates with an approximate formula of Si,AlO_4. With respect to type of bonding, zeolites can be divided into three groups. The natrolite group (mesolite, thomsonite, edingtonite, natrolite) consist of structures built up from rings of four $SiAlO_4$ tetrahedral linked together into chains with fewer linkages between the chains so that cleavage along the chain direction is preferred. These materials generally have a fibrous character. In the heulandite group (stilbite, epistilbite, and heulandite) the $SiAlO_4$ tetrahedra form sheets of six-membered rings with few linkages between the sheets. These materials are micalike in behavior. The third group, the so-called "framework zeolites," have the density of bonding similar in all three directions. This group includes most of the zeolites mentioned below.

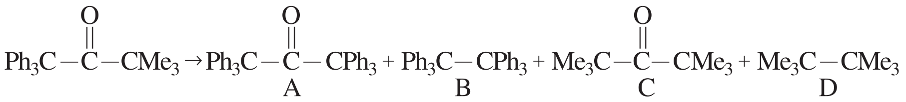
Framework zeolites can be described as aluminosilicates composed of tetrahedra linked by the sharing of oxygen atoms into rings and cages that can accommodate water molecules, metallic ions, as well as selected organic molecules. While there are a variety of structures, the framework zeolites can be briefly described as having an open arrangement of corner-sharing tetrahedra where the SiO_4 are partially replaced by AlO_4 units where there are enough cations present to be neutral. There are well over 100 different synthetic and natural framework zeolites know today with more being found. Magic-angle NMR indicates that there are five distinct zeolite groups where $n = 0–4$ for $Al(AlO)_n (SiO)_{4-n}$. The open structures give materials with lower densities (on the order of 2.0 to 2.2 g/ml), as expected, than similar materials with closed structures such as feldspar (density about 2.6–2.7 g/ml).

Molecular sieves was the name first given to framework zeolites dehydrated by heating in vacuum to about 350°C because of their ability to capture and remove water and certain other species. Today, other materials, such as microporous silicas and aluminum phosphate, are three-dimensional structures that are also employed as molecular sieves.

Syntheses that occur within confined spaces typically give products with a specificity that is not available in other modes. The specificity may be general such as in the case of the synthesis of lignins in plants where synthesis between plant layers produces a largely two-dimensional material with only an average structure. It may be highly to not totally selective as in the case of zeolites and hollow nanofibers. Or it may be essentially totally selective as in the case of many of the biologically important proteins and nucleic acids where both special and electronic interactions act to give a highly "preordained" structure.

Zeolites and related ordered clay-associated materials have been suggested to be involved in the initial primeval synthesis of basic elements of life. They are also being involved in the synthesis of an number of polymeric and nonpolymeric materials. Zeolites come in a variety of forms with differing shapes and sizes with researchers associating the particular size and shape with a particular desired synthesis. This is somewhat akin to the considerations that are made in effectively employing crown phase transfer agents and related materials.

Zeolites have been employed in the preferential synthesis of optically active sites and in determining the particular products formed from certain reactions. In looking at the products formed from the decomposition and reformations involving the unsymmetrical ketone the major products are a combination of products listed below.



$$\mathrm{Ph_3C{-}\overset{\overset{O}{\|}}{C}{-}CMe_3 \rightarrow \underset{A}{Ph_3C{-}\overset{\overset{O}{\|}}{C}{-}CPh_3} + \underset{B}{Ph_3C{-}CPh_3} + \underset{C}{Me_3C{-}\overset{\overset{O}{\|}}{C}{-}CMe_3} + \underset{D}{Me_3C{-}CMe_3}}$$

Employing a single zeolite that selectively accommodates the $\mathrm{Me_3C}$ radical results in a preferential formation of D and little C because of preferential diffusion of the $\mathrm{Me_3C}$ radical as it is formed with the other radicals being “washed” past. The use of two zeolites in conjunction, one preferentially accepting the $\mathrm{Me_3C}$ radical and the second accepting the $\mathrm{Ph_3C}$ radical results in the preferential formation of B and D.

An additional consideration involves matching the so-called “hardness” or flexibility of the confined space. Zeolites offer hard or inflexible confined spaces whereas liquid crystals and some other polymer media offer softer confined spaces. While the zeolites offer a “safe haven” for selected species enabling the hosted species a relatively long existence, they do not allow for ready movement and mixing. By comparison, a more flexible container such as especially designed polyethylenes allow a more flexible environment that allows for variations in the product sizes and shapes and some assembling to occur within the more flexible confines. Thus, photo-Fries reaction of 1-naphthyl esters was carried out in an appropriate zeolite and appropriate polyethylene. In solution, eight products are formed. In the zeolite only one product, the result of a specific geminate-pair recombination, is formed. In the polyethylene, several products are formed primarily the isomeric products of geminate-pair recombinations.

The catalytic, sorption, ion-exchange, shape, and size properties are dependent on the Al-Si ratio and placement. The Al content is decreased, for example, by treatment with silicon tetrachloride that removes aluminum as aluminum chloride. Counter, the aluminum content can be increased by exposure of the zeolite to aluminum chloride vapor.

SUMMARY

1. Inorganic polymers are widely employed in the construction and building businesses, as abrasives and cutting materials, as fibers, as coatings, as lubricants, and as catalysts. They also serve as the basis of rocks and soils.
2. Portland cement is the least expensive, most widely used synthetic polymer. It has a complex (short-range order with long-range disorder), three-dimensional structure. A typical cement paste contains Portland cement, sand, gravel, and about 75% water.

3. There are many specialty cements including reinforced concrete, light-weight concrete, prestressed concrete, calcium-aluminate cement, magnesia cement, and gypsum.
4. Silicon dioxide is present in nature in both amorphous and crystalline forms.
5. Amorphous silicon dioxide–intensive materials include a wide variety of glasses such as fiberglass, window glasses, Vycor glasses, borosilicate glasses, lead (or heavy) glasses, colored glasses, glasses, glazes, and tempered safety glass. Glass can be shaped by drawing, pressing, casting, and blowing.
6. Silicon dioxide also exists in crystalline forms that form the basis of many rocks, sands, and soils.
7. Asbestos is a widely employed, silicon oxide–intensive group of minerals. While these materials offer good thermal stabilities, great strength, and good flexibility, certain ones are responsible for selected illnesses.
8. Polymeric carbon exists in two common forms—as diamonds and as graphite, with the latter being thermodynamically more stable.
9. Diamonds are almost entirely pure carbon, where each carbon is at the center of a tetrahedron composed of four other carbon atoms. It is the hardest known natural material. Diamonds are commercially synthesized for industrial use as cutting and shaping agents.
10. Graphite occurs as sheets of hexagonally fused benzene rings. The bonds holding the fused benzene rings together are covalent bonds, while the bonding between the sheets results from the weak overlapping of π-electron orbitals. Thus, many of the properties of graphite are anisotropic. The weak forces holding the graphite sheets together are responsible for its “slipperiness.” Graphite is commercially made from charcoal or coke.
11. The 123-superconductive materials contain two polymeric copper oxide layers held together by ionic bonding to metal atoms. This theme of polymeric layers held together by ionic bonding to metal ions is often found in inorganic materials such as silicates and asbestos.

GLOSSARY

alumina: Complex aluminum-containing silicate.
anisotropic: Dependent on direction; directionally dependent.
annealing: Subjecting materials to heat near their melting point.
asbestos: Grouping of silica-intensive materials containing aluminum and magnesium that gives soft, threadlike fibers.
asbestosis: Disease that blocks lung sacks with thick fibrous tissue.
borosilicate glass: Relatively heat-shock-resistant glass with a small coefficient of thermal expansion (e.g., Kimax and Pyrex).
calcium-aluminate cement: Contains more alumina than Portland cement.
Chrysotile: Most abundant and widely used type of asbestos.
colored glass (stained glass): Glass containing coloring agents such as metal salts and oxides.
concrete: Combination of cement, water, and filler material such as rocks and sand.
diamond: Polymeric carbon where the carbon atoms are at centers of tetrahedra composed of four other carbon atoms; hardest known natural material.

feldspars: Derivatives of silica where one-half to one-quarter of the silicon atoms are replaced by aluminum atoms.

fibrous glass (fiberglass): Fibers of drawn glass.

float glass: Glass made by cooling sheets of molten glass in a tank of molten tin; most common window glass is of this type.

glass: Inorganic product of fusion which has been cooled to a rigid condition without crystallization; most glasses are based on amorphous SiO_2.

glass sand: Impure quartz crystals.

glaze: Thin, transparent coatings fused on ceramic materials.

granite: Hard crystalline rock containing mainly quartz and feldspar.

graphite: Polymeric carbon consisting of sheets of hexagonally fused rings where the sheets are held together by weak overlapping π-electron orbitals; anisotropic in behavior.

gypsum: $CaSO_2 \cdot 2H_2O$; serves as the basis of plaster of Paris, Martin's cement, Keen's cement, and Parisian cement; shrinks very little on hardening; rapid crying.

High-T_c superconductors: Polymeric copper oxide–containing materials that exhibit superconductivity above the boiling temperature of liquid nitrogen.

inorganic polymers: Polymers containing no organic portions.

kaolinite: Important type of asbestos.

lead glasses (heavy glass): Glass where some or all of the calcium oxide is replaced by lead oxide.

lime: $CaCO_3$ from oyster shells, chalk, and marl.

magnesia cement: Composed mainly of magnesium oxide; rapid hardening.

optical fibers: Glass fibers coated with highly reflective polymer coatings; allows light entering one end of the fiber to pass through to the other end with little loss of energy.

piezoelectric materials: Materials that develop net electronic charges when pressure is applied; sliced quartz is piezoelectric.

Portland cement: Major three-dimensional inorganic polymer construction material consisting of calcium silicates, lime, and alumina.

precast concrete: Portland concrete cast and hardened prior to it being taken to the site of use.

prestressed concrete: Portland concrete cast about steel cables stretched by jacks.

quartz: Crystalline forms of silicon dioxide; basic material of many sands, soils, and rocks.

recipe: Description of content, sequence, and amounts of materials that, when followed, produces a desired material.

reinforced concrete: Portland concrete cast about steel rods or bars.

safety glass: Laminated glass; sandwich containing alternate layers of poly(vinyl butyral) and soda-lime glass.

sand: Loose grains of minerals or rocks larger than silt but smaller than gravel.

sandstone: Granular quartz.

silica: Based on SiO_2; finely ground sand.

silicon glass: Made by fusing pure quartz crystals or glass sand; high melting.

soda: Na_2O.

soda ash: Na_2CO_3.

soda-lime glass: Most common glass; based on silica, soda, and lime.

soil: Contains mineral and organic particles; majority by weight is sand.

tempered safety glass: Single piece of specially heat-treated glass.

tempering: Process of rapidly cooling glass resulting in an amorphous glass that is weaker but less brittle.

vitreous enamels: Thin, normally somewhat opaque-colored inorganic coatings fused on materials.

Vycor: 96% silicon glass; made from silicon and boron oxide; best variety is called fused quartz.

EXERCISES

1. What properties of glass correspond to those of organic polymers?
2. Why is Portland cement an attractive large-bulk building material?
3. Name five important synthetic inorganic polymers. Name five important natural inorganic polymers.
4. Describe what is meant by three-dimensional polymers. Name five important three-dimensional inorganic polymers. Name two general properties typical of three-dimensional polymers.
5. Why are specialty cements and concretes necessary?
6. What is meant by the comment that “glass is a supercooled liquid?”
7. Briefly describe techniques employed to shape glass.
8. Why are specialty glasses important in today’s society?
9. Name two important inorganic fibers employed with resins to form useful materials. Describe briefly what fibers impart to the overall structure of these materials.
10. Which would you predict to be more brittle—quartz, fibrous glass, or window glass?
11. Briefly describe the piezoelectric effect.
12. We do not live a a risk-free society. Discuss this statement in terms of asbestos.
13. What does anisotropic behavior mean? Why does graphite exhibit anisotropic behavior?
14. Briefly compare the structures of diamond and graphite.

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13

Fillers and Reinforcements for Polymers

Some films, fibers, and plastics are used as unfilled polymers, but the strength and cost of most elastomers and plastic composites are dependent on the presence of appropriate fillers or reinforcements. Some rubber articles such as crepe rubber shoe soles, rubber bands, inner tubes, and balloons are unfilled. However, the tread stock in pneumatic tires would not be serviceable without the addition of carbon black or amorphous silica. For example, addition of these fillers increases the tensile strength of SBR from 100 to 4000 psi. Likewise, most high-performance plastics are composites of polymers reinforced by fibrous glass.

13.1 THEORY OF THE EFFECT OF FILLERS

Many naturally occurring functional materials, such as wood, bone, and feathers, are composites consisting of a continuous resinous phase and a discontinuous phase. The first synthetic plastics such as celluloid and Bakelite were also composites. Wood flour was used to reinforce the pioneer phenolic resins and is still used today for the same purpose.

According to the American Society for Testing and Materials standard ASTM D-883, a filler is a relatively inert material added to a plastic to modify its strength, permanence, working properties, or other qualities or to lower costs, while a reinforced plastic is one with some strength properties greatly superior to those of the base resin resulting from the presence of high-strength fillers embedded in the composition. According to ASTM, plastic laminates are the most common and the strongest type of reinforced plastic.

According to one widely accepted definition, fillers are comminuted spherical or spheroidal solids. Glass beads which meet the requirements of this definition are used to reduce mold wear and to improve the quality of molded parts. The word *extender*, sometimes used for fillers, is not always appropriate because some fillers are more expensive than the resin.

Current theories describing the action of spherical fillers in polymers are based on the Einstein equation shown below. Einstein showed that the viscosity of a viscous Newtonian fluid (η_0) was increased when small, rigid, noninteracting spheres were suspended in the liquid. According to the Einstein equation, the viscosity of the mixture (η) is related to the fractional volume (c) occupied by the spheres, and η is independent of the size of the spheres or the polarity of the liquid.

$$\eta = \eta_0(1 + 2.5c) \qquad \text{and} \qquad \eta_{sp}/c = 2.5 \tag{13.1}$$

Providing that c is less than 0.1, good agreement with the Einstein equation is noted when glass spheres are suspended in ethylene glycol. Maximum packing of spheres ($c = 90\%$) is attained when the composition equals 40% each of 20 and 325 mesh and 10% each of 35- and 100-mesh spheres.

The Einstein equation has been modified by including a hydrodynamics or crowding factor (β) which is equal to 1.35 and 1.91 for closely packed and loosely packed spheres, respectively. The modified Mooney equation shown below resembles the Einstein equation when $\beta = 0$.

$$\eta = \eta_0 \frac{2.5c}{1 - \beta c} \qquad \text{and} \qquad \eta_{rel}/c = 2.5 \tag{13.2}$$

Many other empirical modifications of the Einstein equation have been made to predict actual viscosities of resinous composites. Since the modulus (M) is related to viscosity, these empirical equations, such as the Einstein-Guth-Gold (EGG) equation [Eq. (13.3)], may be used to predict changes in modulus when spherical fillers are added.

$$M = M_0(1 + 2.5c - 14.1c^2) \tag{13.3}$$

Since carbon black and amorphous silica tend to form clusters of spheres (graping effect), an additional modification of the Einstein equation has been made to account for the nonspherical shape or aspect ratio (1/D). This factor (f) is equal to the ratio of the length (l) to the diameter (D) of nonspherical particles:

$$\eta = \eta_0(1 + 0.67fc + 1.62f^2c^2) \tag{13.4}$$

It is generally recognized that the segmental mobility of a polymer is reduced by the presence of a filler. Small particles with a diameter of less than 10 mm increase the crosslinked density, and active fillers increase the glass transition temperature (T_g) of the composite.

The high strength of composites is dependent on strong van der Waals interfacial forces. These forces are enhanced by the presence of polar functional groups on the polymer and by the treatment of filler surfaces with silanes, titanates, or other surface-active agents. Composites have been produced from almost every available polymer using almost every conceivable comminuted material as a filler.

13.2 FILLERS

Among the naturally occurring filler materials are cellulosics—such as wood flour, α-cellulose, shell flour, starch—and proteinaceous fillers such as soybean residues. Approximately 40,000 tons of cellulosic fillers is used annually by the American polymer industry. Wood flour, which is produced by the attrition grinding of wood wastes, is used as a filler for phenolic resins, dark-colored urea resins, polyolefins, and PVC. Shell flour, which lacks the fibrous structure of wood flour, has been made by grinding walnut and peanut shells. It is used as a replacement for wood flour.

α-Cellulose, which is more fibrous than wood flour, is used as a filler for urea and melamine plastics. Melamine dishware is a laminated structure consisting of molded resin-impregnated paper. Presumably, the formaldehyde in these thermosetting resins reacts with the hydroxyl groups in cellulose to produce a more compatible composite. Starch and soybean derivatives are biodegradable, and the rate of disintegration of resin composites may be controlled by the amount of these fillers present.

As was discussed in Chapter 9, many incompatible polymers are added to increase the impact resistance of other polymers such as polystyrene. Other comminuted resins such as silicones or polyfluorocarbons are added to increase the lubricity of other plastics. For example, a hot melt dispersion of polytetrafluoroethylene in poly(phenylene sulfide) is used as a coating for antistick cookware.

Since cellulose acetate butyrate is compatible with uncured polyester resins but incompatible with the cured resin, it is added to the premix to reduce shrinkage during curing. Finely divided polyethylene, which is also incompatible with polyester resins, is added to reduce surface roughness in the so-called low-profile resin technique.

Carbon black, which was produced by the smoke impingement process by the Chinese over 1000 years ago, is now the most widely used filler for polymers. Much of the 1.5 million tons produced annually in the United States is used for the reinforcement of elastomers. The most widely used carbon black is furnace carbon black. The particle size of this carbon black is about 0.08 mm. Its hardness on the Mohs scale is less than 1.

Carbon-filled polymers, especially those made from acetylene black, are fair conductors of heat and electricity. Polymers with fair conductivity have also been obtained by embedding carbon black in the surfaces of nylon or polyester filament reinforcements. The resistance of polyolefins to UV radiation is also improved by the incorporation of carbon black.

While glass spheres are classified as nonreinforcing fillers, the addition of 40 g of these spheres to 60 g of nylon-66 increases the flexural modulus, compressive strength, and melt index. The tensile strength, impact strength, creep resistance, and elongation of these composites are less than those of the unfilled nylon-66. A greater increase in flexural modulus is noted when the glass surface is altered by surface-active agents.

Milled glass fibers, multicellular glass nodules, and glass flakes have also been used as fillers. When added to resins, hollow glass and carbon spheres, called microballoons or microspheres, produce syntactic foams with varying specific gravities depending on the ratio of filler to resin. Superior high-performance composites are obtained when glass or graphite fibers are used as the additives.

Conductive composites are obtained when powdered metal fillers, metal flakes, or metal-plated fillers are added to resins. These composites have been used to produce forming tools for the aircraft industry and to overcome electromagnetic interference in office machines. Powdered lead-filled polyolefin composites have been used as shields for neutron and γ radiation. Zinc-filled plastics have been used as sacrificial composite electrodes, and magnetizable composites have been obtained by the incorporation of powdered aluminum-nickel alloys or barium ferrite.

Zinc oxide, which has a hardness of 2.5 on the Mohs scale, is used to a large extent as an active filler in rubber and as a weatherability improver in polyolefins and polyesters. Anatase and rutile titanium dioxide are used as white pigments and as weatherability improvers in many polymers. Ground barites ($BaSO_4$) yield X-ray-opaque plastics with controlled density.

The addition of finely divided calcined alumina, corundum, or silicon carbide produces abrasive composites. However, alumina trihydrate (ATH), which has a Mohs hardness of less than 3, serves as a flame-retardant filler in plastics. Zirconia, zirconium silicate, and iron oxide, which have specific gravities greater than 4.5, are used to produce plastics with controlled high densities.

Calcium carbonate, which has a Mohs hardness of 3, is available both as ground natural limestone and as synthetic chalk. This filler is widely used in paints, plastics, and elastomers. The volume relationship of calcium carbonate to resin or the pigment volume required to fill voids in the resin composite is called the pigment–volume concentration (PIVC). The critical PIVC (CPIVC) is the minimum required to satisfy the resin demand.

In contrast to the cubically shaped, naturally occurring calcium carbonate filler, the synthetic product produced by the addition of carbon dioxide to a slurry of calcium hydroxide is acicular, or needle-shaped. Calcium carbonate is used at an annual rate of 700 million tons as a filler in PVC, polyolefins, polyurethane foams, and in epoxy and phenolic resins (see Table 13.1).

Silica, which has a specific gravity of 2.6, is used as naturally occurring and synthetic amorphous silica, as well as in the form of large crystalline particulates such as sand and quartz.

Diatomaceous earth, also called infusorial earth and fossil flour, is a finely divided amorphous silica consisting of the skeletons of diatoms. This filler has a Mohs hardness of less than 1.5 in contrast to sharp silica sand, which has a value of 7. Diatomaceous earth is used to prevent a roll of film from sticking to itself (antiblocking) and to increase the compressive strength of polyurethane foams. Tripoli, or rotten stone, is porous silica formed by the decomposition of sandstone.

Pyrogenic, or fumed, silica is a finely divided filler obtained by reacting silicon tetrachloride in an atmosphere of hydrogen and oxygen. This filler is used as a thixotrope to increase the viscosity of liquid resins. Finely divided silicas are also produced by the acidification of sodium silicate solutions and by the evaporation of alcoholic solutions of silicic acid.

Sharp silica sand is used as a filler in resinous cement mortars. Reactive silica ash produced by burning rice hulls and a lamellar filler, novaculite, from the novaculite uplift in Arkansas, are also used as silica fillers in polymers.

Hydrated finely divided silicas which contain surface silanol groups are used for the reinforcement of elastomers. Extreme care must be taken in handling silica to prevent silicosis. Approximately 25 million tons of silica fillers is used annually by the polymer industry.

Both naturally occurring and synthetic silicates are also widely used as fillers. Hydrated aluminum silicate, or kaolin, has a specific gravity of 2.6 and a hardness value of 2.5 on the Mohs scale. Kaolin and other clays may be dissolved in sulfuric acid and regenerated by the addition of sodium silicate. Clays are used as fillers in synthetic paper, rubber, and bituminous products.

Mica, which has a specific gravity of 2.8 and a Mohs hardness value of 3, is a naturally occurring lamellar or plate-like filler with an aspect ratio below 30. However, much higher aspect ratios are obtained by ultrasonic delamination.

Talc is a naturally occurring fibrouslike hydrated magnesium silicate with a Mohs hardness of 1 and a specific gravity of 2.4. Since talc-filler polypropylene is much more

Table 13.1 Types of Fillers for Polymers

- I. Organic materials
  - A. Cellulosic products
    - 1. Wood products
      - a. Kraft paper
      - b. Chips
      - c. Coarse flour
      - d. Ground flour
        - (1) Softwood flour
        - (2) Hardwood flour
        - (3) Shell flour
    - 2. Comminuted cellulose products
      - a. Chopped paper
      - b. Diced resin board
      - c. Crepe paper
      - d. Pulp preforms
    - 3. Fibers
      - a. α-Cellulose
      - b. Pulp preforms
      - c. Cotton flock
      - d. Textile byproducts
      - e. Jute
      - f. Sisal
      - g. Rayon
  - B. Lignin-type products
    - 1. Ground bark
    - 2. Processed lignin
  - C. Synthetic fibers
    - 1. Polyamides (nylon)
    - 2. Polyesters (Dacron)
    - 3. Polyacrylonitrile (Orlon, Acrilan)
  - D. Carbon
    - 1. Carbon black
      - a. Channel black
      - b. Furnace black
    - 2. Ground petroleum coke
    - 3. Graphite filaments
    - 4. Graphite whiskers
- II. Inorganic materials
  - A. Silica products
    - 1. Minerals
      - a. Sand
      - b. Quartz
      - c. Tripoli
      - d. Diatomaceous earth
    - 2. Synthetic materials
      - a. Wet-processed silica
      - b. Pyrogenic silica
      - c. Silica aerogel
  - B. Silicates
    - 1. Minerals
      - a. Asbestos
        - (1) Chrysotile
        - (2) Amosite
        - (3) Anthophyllite
        - (4) Crocidolite
        - (5) Tremolite
        - (6) Actinolite
      - b. Kaolinite (China clay)
      - c. Mica
      - d. Nepheline syenite
      - e. Talc
      - f. Wollastonite
    - 2. Synthetic products
      - a. Calcium silicate
      - b. Aluminum silicate
  - C. Glass
    - 1. Glass flakes
    - 2. Solid glass spheres
    - 3. Hollow glass spheres
    - 4. Milled fibers
    - 5. Fibrous glass
      - a. Filament
      - b. Rovings
      - c. Woven roving
      - d. Yarn
      - e. Mat
      - f. Fabric
  - D. Metals
  - E. Boron filaments
  - F. Metallic oxides
    - 1. Ground material
      - a. Zinc oxide
      - b. Alumina
      - c. Magnesia
      - d. Titania
    - 2. Whiskers
      - a. Aluminium oxide (sapphire)
      - b. Beryllium oxide
      - c. Magnesium oxide
      - d. Thorium oxide
      - e. Zirconium oxide
  - G. Calcium carbonate
    - 1. Chalk
    - 2. Limestone
    - 3. Precipitated calcium carbonate
  - H. Polyfluorocarbons
  - I. Other fillers
    - 1. Whiskers (nonoxide)
      - a. Aluminum nitride
      - b. Beryllium carbide
      - c. Boron carbide
      - d. Silicon carbide
      - e. Silicon nitride
      - f. Tungsten carbide
    - 2. Barium ferrite
    - 3. Barium sulfate

resistant to heat than polypropylene, it is used in automotive accessories subject to high temperatures. Over 40 million tons of talc are used annually as fillers.

Nepheline syenite, a naturally occurring sodium potassium aluminum silicate filler, and wallastonite, an acicular calcium metasilicate filler, are used for the reinforcement of many plastics. Fibers from molten rock or slag (PMF) are also used for reinforcing polymers.

Asbestos is a naturally occurring magnesium silicate which, in spite of its toxicity, has been used for over 250 years as a flame-resistant fiber. Approximately 180 million tons of asbestos is used annually as an additive for polymers, but this use is decreasing (see also Sec. 12.8).

13.3 REINFORCEMENTS

According to the ASTM definition, fillers are relatively inert while reinforcements improve the properties of plastics. Actually, few fillers are used that do not improve properties, but reinforcing fibers produce dramatic improvements in the physical properties of the composites. Many fibrous reinforcements are available, but most theories have been developed as a result of investigations of fibrous glass, which is the most widely used reinforcement for polymers.

That filaments could be produced from molten glass was known for centuries, but fibrous glass was not produced commercially until the mid-1930s. Unlike the previously cited isotropic filler-resin composites, the stress in a fibrous glass-reinforced composite is concentrated at the fiber ends. Therefore, providing the strength of the fiber is greater than that of the resin, the properties of the composite are anisotropic and dependent on the direction of the stress.

The transverse modulus (M_T) and many other properties of a long fiber-resin composite may be estimated from the law of mixtures. The longitudinal modulus (M_L) may be estimated from the Kelly Tyson equation shown below; the longitudinal modulus is proportional to the sum of the fiber modulus (M_F) and the resin matrix modulus (M_M). Each modulus is based on the fractional volume (c). The constant k is equal to 1 for parallel continuous filaments and decreases for more randomly arranged shorter filaments.

$$M_L = kM_Fc_F + M_Mc_M \tag{13.5}$$

Since the contribution of the resin matrix is small in a strong composite, the second term in the Kelly Tyson equation may be disregarded. Thus, the longitudinal modulus is dependent on the reinforcement modulus, which is independent of the diameter of the reinforcing fiber. The full length of filament reinforcement is utilized in filament-wound and pultruded composites. In each case, the impregnated resin becomes part of the finished composite.

While unsuccessful attempts were made to use cotton threads as reinforcements, the first successful reinforcements were with fibrous glass. The latter may be spun from low-cost soda-lime, type E, or type C glass. In the spinning process, filaments are produced by passing the molten glass through orifices in the bushings.

In addition to the filament winding and pultrusion processes, chopped fibrous glass may be used as a reinforcement for spraying resin-impregnated chopped strand and for bulk molding compounds (BMC) and sheet molding compounds (SMC). The SMC is the most widely used form of molded fibrous glass resin composite.

In many processes, such as SMC, the fibers are not continuous. When they are longer than the critical length (l_c), it is necessary to modify the first term in the Kelly Tyson equation by multiplying by a factor $(l - l_c)/2$ in which l is equal to the actual fiber length. The constant k approaches 0.5 for two-directionally oriented fibers.

Fibrous glass–reinforced resinous composites were introduced in 1940, and their use has increased steadily since then. Their use was originally confined to thermosetting resins, but fibrous glass-reinforced thermoplastics such as nylon are now important composites. Over 500,000 tons of fibrous glass–reinforced composites are produced annually in the United States.

Short, randomly oriented glass fibers and those from nylon, aramids, poly(vinyl alcohol), polyacrylonitrile, and polyesters have been used successfully in the preparation of strong composites. Since these organic fibers crystallize, they serve as nucleating agents when used to reinforce crystallizable polymers such as polypropylene.

Polyester resin–impregnated fibrous glass roving or mat is used for SMC and BMC. The former is used like a molding powder and the latter is hot-pressed in the shape of the desired object, such as one-half of a suitcase. Chopped fibrous glass roving may be impregnated with resin and sprayed, and glass mats may be impregnated with resin just prior to curing.

The strongest composites are made from continuous filaments impregnated with resin before curing. These continuous filaments are wound around a mandrel in the filament-winding process and gathered together and forced through an orifice in the pultrusion molding process.

The first continuous filaments were rayon, and these as well as polyacrylonitrile fibers have been pyrolyzed to produce graphite fiber. High-modulus reinforcing filaments have also been produced by the deposition of boron atoms from boron trichloride vapors on tungsten or graphite filaments.

Small single crystals, such as potassium titanate, are being used at an annual rate of over 10,000 tons for the reinforcement of nylon and other thermoplastics. These PMRN composites are replacing die-cast metals in many applications. Another microfiber, sodium hydroxycarbonate (called Dawsonite), also improved the physical properties and flame resistance of many polymers. Many other single crystals, called whiskers, such as alumina, chromia, and boron carbide, have been used for making high-performance composites.

13.4 COUPLING AGENTS

The first commercial glass filaments were protected from breakage by a starch sizing which was removed before use in resin composites. Since poly(vinyl acetate) sizing, now in use, is more compatible with resins, it does not have to be removed from the glass surface. However, the interfacial attraction between fibrous glass and resins is poor, and strong composites require the use of coupling agents to increase the interfacial bond between the resin and reinforcing agent.

The original coupling agents, which were called promotors, were used to assure a good bond between rubber and the carbon black filler. The first commercial promotors were N-4-dinitroso-N-methylaniline and N-(2-methyl-2-nitropropyl)-4-nitrosoaniline. Presumably, coupling took place between carbon black and the N-nitroso group and between the elastomer and the p-nitroso group.

These promotors increased the tensile strength, modulus, and bound rubber content of rubber. While natural rubber is soluble in benzene, it becomes less soluble when carbon black or amorphous silica is added. The insoluble mixture of filler and rubber is called bound rubber.

Some of the original promotors or coupling agents for fibrous glass and polyester resins were silanes. It is assumed that the trimethoxy groups in a coupling agent such as γ-mercaptopropyltrimethoxysilane couple with the silanol groups on the surface of fibrous glass and that the mercapto groups couple with the polymer.

Many silane zirconate and titanate coupling agents have been developed for the treatment of different reinforcing agents and fillers used with specific polymers. While it is the custom to treat the surface of the filler, coupling may also occur when the silane or titanate derivative is added to the resin or the mixture of resin and filler.

It is believed that the continuous resin matrix in a composite transfers applied stress to the reinforcing discontinuous phase through the interface between the two components. This interfacial attraction is often weakened in the presence of moisture, but a strong interfacial bond is maintained when coupling agents are used.

The interfacial bond between calcium carbonate fillers and resins has been improved by surface treatment with stearic acid. The bond between silica and resins has been strengthened by the addition of O-hydroxybenzyl alcohol or ethylene glycol.

Titanate coupling agents such as triisostearylisopropyl titanate (TTS) are effective in reducing energy requirements for processing mixtures of fillers and resins. It has been proposed that monoalkyl titanates form titanium oxide monomolecular layers on the filler surface and modify the surface energy so that the viscosity of the resin-filler mixture is reduced.

Thus, ferric oxide loadings as high as 90% in nylon-66 and calcium carbonate loadings of 70% in PP are possible when appropriate titanates are added. The melt flow of the filled PP is similar to that of the unfilled polymer, but the impact strength of the composite is much higher than that of PP itself.

13.5 COMPOSITES

Composites (see also Sec. 17.5) are materials that contain strong fibers embedded in a continuous phase. The fibers are called “reinforcement” fibers and the continuous phase is called the matrix. While the continuous phase can be a metallic alloy or inorganic material, the continuous phase is typically an organic polymer that is termed a “resin.” Because of the use of new fibers and technology, most of the composites discussed in this section are referred to as “space age” and “advanced materials” composites. Composites can be fabricated into almost any shape, and after hardening, they can be machined, painted, etc., as desired.

Tables 13.2 and 13.3 contain a partial listing of the main materials employed in the fabrication of composites. It is important to note that many of the entries represent whole families of materials. Thus, there are many possible combinations, but not all combinations perform in a satisfactory manner. Generally good adhesion between the matrix and fiber is needed. Table 13.4 contains a listing of some of the more utilized combinations.

While there is a lot of science and space age technology involved in the construction of composites, many composites have been formulated through a combination of this science and trial-and-error, giving recipes that contain the nature and form of the fiber and matrix materials, amounts, additives, and processing conditions.

Composites have high tensile strengths (on the order of thousands of MPa), high Young’s modulus (on the order of hundreds of GPa), and good resistance to weathering

Table 13.2 Fibers Frequently Employed in Composites

Alumina (aluminum oxide)
Aromatic nylons
Boron
Carbon and graphite
Glass
Polyolefin
Silicon nitride (Si_3N_4)
Titanium carbide (TiC)
Tungsten carbide (WC)
Zirconia (ZrO_2)

Table 13.3 Polymer Resins Employed in the Fabrication of Composites

Thermosets	Thermoplastics
Epoxys	Nylons
Melamine-formaldehyde	Polycarbonates
Phenol-formaldehyde	Poly(ether ether ketone)
Polybenzimidazoles	Poly(ether ketone)
Polyimides	Poly(ether sulfones)
Polyesters	Poly(phenylene sulfide)
Silicones	

Table 13.4 Typically Employed Fiber/Resin Pairs

Alumina/epoxy
Alumina/polyimide
Boron/carbon/epoxy
Boron/epoxy
Boron/polyimide
Boron/carbon/epoxy
Carbon/acrylic
Carbon/epoxy
Carbon/nylon/epoxy
Carbon/polyimides
Glass/epoxy
Glass/carbon/polyester
Glass/polyester
Glass/polyimide
Glass/silicon
Nylon/epoxy

exceeding the bulk properties of most metals. The resinous matrix, by itself, is typically not particularly strong relative to the composite. Further, the overall strength of a single fiber is low. In combination, the matrix–fiber composite becomes strong. The resin acts as a transfer agent, transferring and distributing applied stresses to the fibers. Generally, the fibers should have aspect ratios (ratio of length to diameter) exceeding 100, often much larger. Most fibers are thin (less than 20 μm thick, about a tenth the thickness of a human hair). Fibers should have a high tensile strength and most have a high stiffness, i.e., low strain for high stress or little elongation as high forces are applied.

There exists a relationship between the ideal length of a fiber and the amount of adhesion between the matrix and the fiber. For instance, assume that only the tip, one end, of a fiber is placed in a resin (Fig. 13.1, top). The fiber is pulled. The adhesion is insufficient to hold the fiber, and it is pulled from the resin. The experiment is repeated until the fiber is broken (outside the matrix) rather than being pulled (without breaking) from the resin (Fig. 13.1, bottom). Somewhere between the two extremes, there is a length where there exists a balance between the strength of the fiber and the adhesion between the fiber and matrix. Most modern composites utilize fiber/matrix combinations that exploit this balance.

Fiber failure is usually of the catastrophic type, where the failure is sudden. This is typical in polymeric materials where the material is broken at the weak link.

Fibers

Most (up to 98%) of the fibers employed in composites today are of three general varieties—glass (Sec. 12.5), carbon (graphite; Sec. 12.10), and aromatic nylons (often referred to as aramids; Sec. 6.7). Asbestos, a major fiber of choice years ago, holds less than 1% of the fiber-composite market, with even this small amount on the decrease.

Glass

Fiberglass is manufactured from a number of materials that are largely composed of silicon dioxide that are cooled below their melting points (supercooled liquids) without crystallizing (Sec. 12.5). Other oxides are included giving glass fibers with differing characteristics. Table 13.5 contains a brief description of the most important glass fiber types.

The glass fibers are “pulled” from the melted glass, forming fibers that typically range from 2 to 25 μm in diameter. This pulling acts to orient the overall three-dimensional structure, producing a material with greater strength and stiffness along the axis of the pull.

As with other three-dimensional materials, the limits of the strength are due to the presence of voids. In the case of glass fibers, these voids largely occur on the surface of the fiber. Interestingly, adherence of water moisture, grease from handling, or other foreign materials can severely reduce the strength of the fibers. Thus, great care is taken to protect the surface by application of surface agents such as methacrylatochromic chloride, vinyl trichlorosilanes, and other silanes (Sec. 11.3). It is believed that these surface agents chemically react with the fiber surface, acting to repel and protect the surface from harmful agents such as water.

Carbon

Carbon can be made in many allotropic forms ranging from diamond (Sec. 12.9), graphite (Sec. 12.10), carbon black, and as high-strength fibers and whiskers known as carbon and

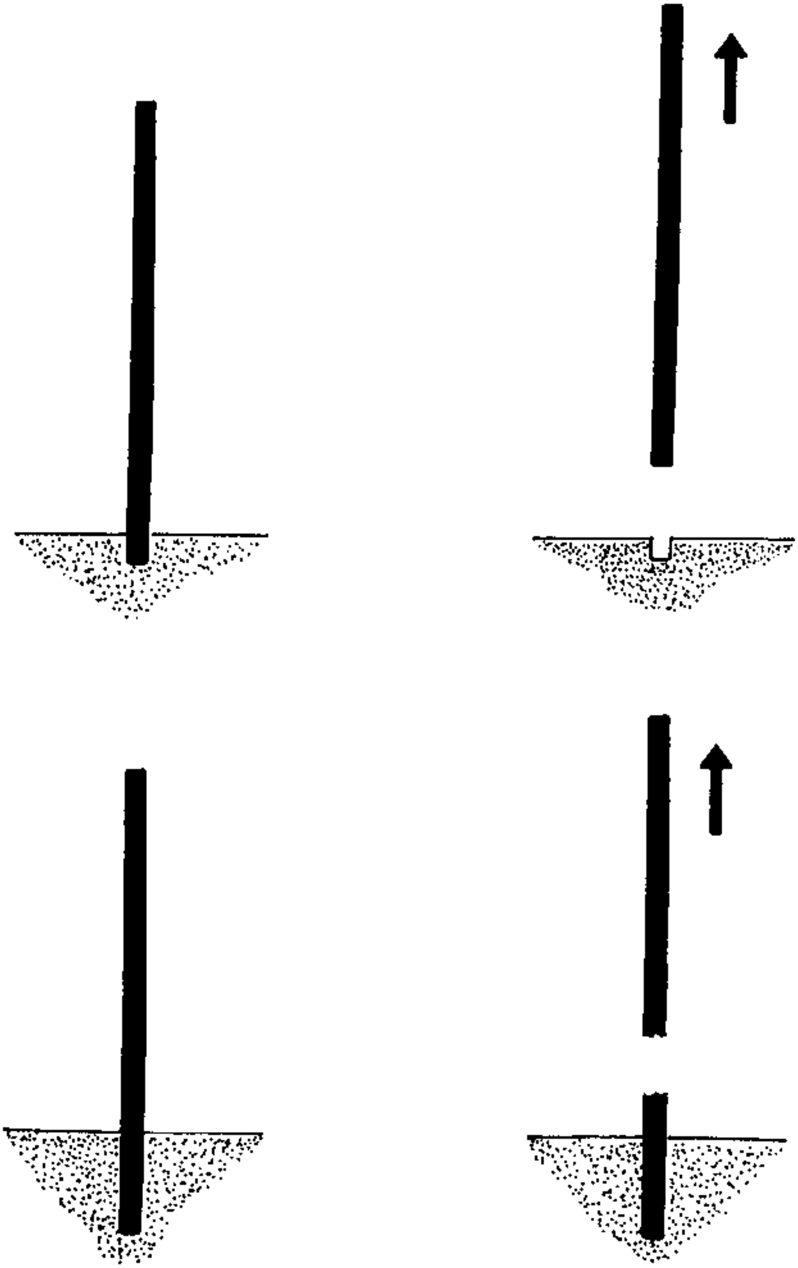

Figure 13.1 Tensile loading experiments performed on single fibers embedded in a matrix. The illustrations on the left are preapplication of the tensile loading, and those on the right are post application of the tensile loading.

Table 13.5 Types of Glass Fibers

Designation	General properties
C-glass	Chemical-resistant
E-glass	“Typical” glass fiber
R- and S-glass	Stiffer and stronger than E-glass

graphite fibers (Sec. 5.4, 15.11). Carbon whiskers are sheets of hexagonal carbon atoms layered like a laminate, one on top of the other in an ordered array. Leslie Phillips, one of the inventors of carbon fibers, describes them as bundles of oriented crystalline carbon held in a matrix of amorphous carbon (Fig. 13.2). Order is a key to the strength of these allotropic carbon forms.

As in glass fibers, carbon voids are present in the carbon fibers. The carbon fibers are treated by application of a surface treatment such as low molecular weight epoxy resin. Additionally, carbon fibers are also normally treated to improve adhesion to the resin.

Aromatic Nylons

Two general types of aromatic nylon fibers are produced. The less stiff variety is utilized in situations where flexibility is required. The second type is stiffer with a higher Young’s modulus and is employed for applications where greater strength is required and little flexibility is needed. Poor adhesion to the resin is desirable in some applications of aromatic nylon materials such as in body armor (bullet-resistant material), where the “delamination” is a useful mode for absorbing an impact.

Boron

Boron fibers (Sec. 17.5) are larger in diameter (often 50–150 μm) than many of the other fibers employed in composite manufacture. They are made from the high-temperature reduction of boron trichloride.

$$2BCl_3 + 3H_2 \rightarrow 2B + 6HCl$$

Polyolefins

The flow properties and consequences of flow in polymers are becoming better understood. It is known that elongational flow through orifices can result in the stretching of polymer

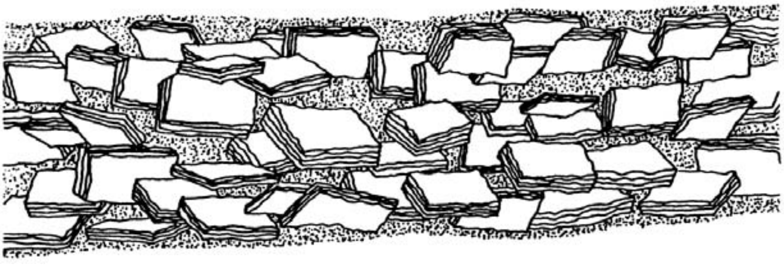

Figure 13.2 Idealized drawing of crystalline carbon bundles in a “sea of amorphous carbon.”

chains. Such polymer chains can become entangled, bringing about additional orientation as they flow. Finally, polymer solutions may be stable at rest, but under high rates of extrusion they may be removed from solution, forming a gel phase. These phenomena have allowed the production of a number of new polyolefin fibers, with an emphasis on the production of new polyethylene fibers (Sec. 7.6). Ultrahigh-modulus polyethylene (UHMPE) fibers have been produced which have a low density (about 0.96 g/cm^3) with a tensile strength of 1.5 GPa and a Young modulus of 70 GPa. They have a higher elongation at break, over two times greater than fiberglass and aromatic nylons.

Alumina

As in the case of carbon, aluminum oxide, or alumina, is allotropic, existing in different forms. Polycrystalline alumina produces fibers. Two commercially available forms have about 95% aluminum oxide and 5% silica. Both have a diameter of about 3 μm. One is referred to as low-density alumina fiber exhibiting a tensile strength of 2 GPa and a Young modulus of 200 GPa with a use temperature to about 900°C. The higher density material has a use temperature to 1600°C with a similar tensile strength and Young's modulus.

Single fibers can be spun from a single aluminum oxide crystal. Alumina whiskers (Sec. 5.4) are elongated crystals of α-alumina that are stable to temperatures of 1650°C for about 2 h, allowing their use in ceramic sintering and firing and in metal casting processes. Such whiskers have aspect ratios to only about 10.

Resins

Resin systems for composites can be divided into thermosetting and thermoplastic resins (Table 13.3). Most of the actual resin formations are complex, requiring many additives and supplemental treatments. Following is a brief discussion of the main resin components.

Thermosets

Polyimides. The formation of polyimide resins (Sec. 6.8) typically involves two reaction steps. First, a polyamic acid is formed through reaction of a diamine and dianhydride. Crosslinking then occurs, generally through application of heat, with the loss of water accompanying the cyclization of the polyamic acid forming the thermoset polyimide resin. Other reaction systems are similarly employed in the formation of polyimide resins. An important subgroup is the maleimide resins formed from bismaleimides. Polymerization occurs through reaction with the double bonds of the maleimides.

Like the polyimides themselves, the polyimide resins are known for their thermal stability.

Unsaturated polyesters. Typically, the precured (precrosslinked) polyesters are formed by reaction of an anhydride (usually maleic anhydride) or diacid with diols such as ethylene and propylene glycol (Sec. 6.6). These polyesters contain sites of unsaturation that are subsequently employed for the purposes of introducing crosslinks. Crosslinking can be accomplished through heating or through introduction of free radical initiators utilizing a comonomer such as a diallyl phthalate or styrene.

Epoxys. Most epoxy resins (Sec. 6.12) employed in composites are derived from the epichlorhydrin with aromatic amines and phenols. An intermediate chlorhydrin is formed that cyclizes forming an epoxy resin containing epoxy or glycidyl groups. These are then reacted with amines, anhydrides, carboxylic acids, and phenols resulting in an addition reaction that does not produce side products resulting in a three-dimensional network with few voids.

Phenol-formaldehyde and amino-formaldehyde. The phenol-formaldehyde resins (Sec. 6.15) and the amino-formaldehyde resins (Sec. 6.15) are among the oldest resin systems. Reaction of formaldehyde with more than equimolar amounts of phenol, in the presence of acid, gives preresins (called novolacs) that contain mainly aromatic phenol units connected by methylene bridges. These are subsequently crosslinked through reaction with reactants such as hexamethylenetetramine.

Resole prepolymers are made by reaction of formaldehyde with less than an equimolar amount of phenol, in the presence of base, forming hydroxymethylphenols. These prepolymers are less viscous in comparison with the novolac prepolymers, allowing their use in fiber situations where high flow is necessary for a good fiber–matrix mixing. Crosslinking occurs through heating with the elimination of water and formaldehyde from the reaction of hydroxymethyl groups forming “methylene” crosslinks.

Thermoplastics

Thermoplastic resins typically use simply the polymers (Table 13.3) involved in the fabrication of the composites. Some of these are only soluble in liquids that are difficult to remove because they are dipolar and high boiling. Further, many of the polymers have high melting ranges requiring high temperatures and pressures for processing. Finally, many of these polymers are rigid and adhere to the resin phase only with difficulty. In spite of these difficulties, these thermoplastic resins can offer good storage life and good damage tolerance.

Applications

Many of the applications for composite materials involve their (relative) light weight, resistance to weathering and chemicals, and ability to be easily fabricated and machined. Bulk applications employ composites that are relatively inexpensive. Combinations of rigorous specifications, low volume, specific machining and fabrication specifications, and price comparable to that of alternative materials and solutions allow more expensive specialized composites to be developed and utilized. Applications are increasing but can be roughly divided into seven areas.

Marine Craft

One of the largest and oldest applications of composites is in the construction of watergoing vessels from rowboats, sailboats, racing boats, and motor craft to large seagoing ships.

The use of fresh water—and salt water—resistant composites allowed the boating industry to grow from an almost “mom-and-pop” operation to the use of large boatyards producing craft in an assembly line—like fashion. Most boats are composed of fiberglass and fiberglass/carbon combination composites. Other fibers are also being utilized in the boating industry, including aromatic nylons and fiberglass/aromatic nylon combinations.

Outer Space

Because of the large amount of fuel required to propel spacecraft into outer space, weight reduction, offered by composites, is an essential ingredient in the construction of materials utilized in outer space.

Some of the solid propellant tanks are made from composites. The tanks are often composed of fiberglass and glass/carbon fiber–containing composites. In fact, the development of S-glass (Table 13.5) was a result of the space effort. Carbon fibers are employed in the construction of some of the nose fairings.

The reusable space shuttles contain various composites. The cargo bay doors are sandwich composites composed of carbon/epoxy/honeycomb materials. The "manipulator arm" used for loading the payload bay is composed of a number of composites including carbon/epoxy composite laminates and aromatic nylon laminates and sandwich materials. Composites are also used for the construction and mounting of mirrors, telescopes, solar panels, and antennae reflectors.

Biomaterials

Bones and skin are relatively light compared with metals. Composite structures can approach the densities of bone and skin and offer necessary inertness and strength to act as body part substitutes.

Power-assisted arms have been made by placing hot-form strips of closed-cell polyethylene (PE) foam over the cast of an arm. Grooves are cut into these strips prior to application and carbon/resin added to the grooves. The resulting product is strong and light, and the cushioned PE strips soften the attachment site of the arm to the living body. Artificial legs can be fashioned in glass/polyester and filled with polyurethane foam adding strength to the thin-shelled glass/polyester shell. Artificial legs are also made from carbon/epoxy composite materials. Some of these contain a strong interior core with a soft, flexible skin.

Carbon/epoxy plates are now used in bone surgery, replacing the titanium plates previously employed. Usually a layer of connective tissue forms about the composite plate.

Rejection of composite materials typically does not occur but, as is the case of all biomaterials, compatibility is a major factor. Often lack of biocompatibility has been found to result from impurities (often additives) found in the materials. Removal of these impurities allows these materials to be used.

Sports

Carbon and carbon/glass composites are being used to make advanced material fishing rods, bicycle frames, golf clubs, baseball bats, racquets, skis and ski poles, basketball backboards, etc. These come in one color—black—because the carbon fibers are black. Even so, they can be coated with any color desired.

Automobiles

Composites are being employed in a number of automotive applications. These include racing car bodies as well as "regular" automobiles. Most automobiles have the lower exterior panels composed of rubbery and/or composite materials. Other parts such as drive shafts and leaf springs, antennas, and bumpers in private cars and heavy trucks are being made from composite materials.

Industry

Industrial storage vessels, pipes, reaction vessels, and pumps are now made from composite materials. They offer the needed resistance to corrosion, acids and bases, oils and gases, and salt solutions, as well as the necessary strength and ease of fabrication to allow their continued adoption as a major industrial building material.

Aerospace

The Gulf War spotlighted the use of composite materials in new-age aircraft. The bodies of both the Stealth fighter and bomber are mainly carbon composites. The versatility is apparent when one realizes that the Gossamer Albatross, the first plane to cross the English Channel with human power, consisted largely of composite materials, including a carbon/epoxy and aromatic nylon composite body and propellers containing a carbon composite core.

The increase in use of composite materials by the aerospace industry is generally due to their outstanding strength and resistance to weathering and fraction and their light weight, allowing fuel reduction savings. Succeeding families of Boeing aircraft have used ever greater amounts of fiberglass composite material in their manufacture, from about 20 square yards for the 707, to 200 square yards for the 727, to 300 square yards for the 737 and over 1000 square yards for the 747. This amount is increased again in the Boeing 767 and includes other structural applications of other space-age composites. Thus, the Boeing 767 uses carbon/aromatic nylon/epoxy landing gear doors and wing-to-body fairings.

As noted above, most applications of composites in the aerospace industry involve decreased weight, resulting in increased (potential) payloads and decreased fuel consumption. Interestingly, the lack of even limited flexibility for many composites limits their use (currently) for large commercial aircraft where normal wing “flapping” amplitudes may be several feet during a flight. Even so, composite use is increasing in the construction of small aircraft such as the McDonnell Douglas F-18, where roughly 50% of the outer body surface is composite, with the remainder being largely a mixture of titanium, aluminum, and steel.

Other areas of increased composite use include helicopter blades (giving about a twofold increase in life expectancy compared to metal blades) and jet engines (e.g., turbo fans, cowling, container rings).

13.6 NANOCOMPOSITES

Nature has employed nanomaterials since the beginning of time. Much of the inorganic part of our soil is a nanomaterial with the ability to filter out particles often on a molecular or nano level. The driving force toward many of the nanomaterials is that they can offer new properties or enhanced properties unobtainable with so-called traditional bulk materials. Along with light weight and high strength-to-weight features and small size, new properties may emerge because of the very high surface area to mass, where surface atomic and molecular interactions become critical. The nano world is often defined for materials where some dimension is on the order of 1–100 nm. In a real way, single linear polymers are nanomaterials since the diameter of the single chain is within this range. The carbon–carbon bond length is on the order of 0.15 nm or the average zigzag bond length is about 0.13 nm. While some short to moderate-length vinyl polymers have contour lengths less than 100 nm, higher molecular weight polymers have contour lengths that far exceed this. Even so, individual polymer chains fall within the realm of nanomaterials when they act independently. Since the cumulative attractive forces between chains is large, polymer chains generally act in concert with other polymer chains leading to properties that are dependent on the bulk material. Chain folding, inexact coupling, and chain branching are some of the reasons that bulk properties fall short of theoretical properties, but with the ability to work with chains individually strength and related properties are approaching theoretical values. Much of the nano revolution with materials involves how to synthesize and treat materials on an individual basis as well as visualizing uses for these materials.

The ultimate strength and properties of many materials is dependent on the intimate contact between the various members. Thus, for ceramics, nano-sized particles allow a more homogeneous structure resulting in stronger ceramic materials.

Nanocomposites have also been with us since almost the beginning of time. Our bones are examples of nanocomposites. The reenforcement material is plate-like crystals of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, with a continuous phase of collagen fibers. The shell of a mollusk is microlaminated, containing as the reenforcement aragonite (a crystalline form of calcium carbonate), and the matrix is a rubbery material. Allowing nature to be a source of ideas is a continuing theme in synthetic polymer science, including modification of natural polymers. Much of the renewed interest in nanocomposite materials is the direct result of the availability of new nano building blocks.

Within a composite material, much of the ultimate strength comes from the intimate contact the fiber has with the matrix material. Nanofibers allow more contact between the fiber (on a weight basis) and the matrix resulting is a stronger composite because of an increased fiber surface–matrix interface.

A number of inorganic/organic nanocomposites have been made. These include nano inorganics including nanofibers from silicon nitride, titanium(IV) oxide, zirconia, alumina, titanium carbide, and tungsten carbide. This includes the use of special clays (layered silicates) mixed with nylons to form nanocomposites. The clay layers are separated, giving platelets about 1 nm thick. These nylon-clay microcomposites are used to make the air intake cover of some of the Toyota automobiles. These individual clay platelets have also been used to form nearly single-layer polymer chain sheets similar to lignin. The interaction with the silicate surface encourages the polymer chains to take different arrangements. To be effective the hydrophilic silicate surface is generally modified to accommodate the more hydrophobic common monomers and polymers.

While carbon fiber (thickness on the order of 1000 nm) composites offer very strong materials, carbon nanotubes make even stronger composites. These carbon nanotubes have aspect ratios of over 1000 (ratio of length to diameter). Furthermore, because some carbon nanotubes are electrically conductive, composites containing them can be made to be conductive. A number of carbon nanotube matrices have been made including using a number of engineering resins such as polyesters, nylons, polycarbonates, and poly(phenylene ether).

Individual polymer chains can be more flexible than groups of chains (bulk) even when the polymer is generally considered to be rigid. This is presumably because single chains have less torsional strain imparted by near-neighbors and various chain entanglements and associations are not present. Compared with carbon fibers, carbon nanotubes imbedded within a polymer matrix can withstand much greater deformations before they break. Further, nanomaterials are generally more efficient in transferring applied load from the nanomaterial to the matrix. These factors contribute to the greater strength of carbon nanotube composites.

As noted earlier (Sec. 13.5), adhesion between the reinforcing agent and matrix is important. Some matrix materials do not adhere well with certain fibers. This is partially overcome through introduction of defects or functional groups onto the nanomaterials that act as hooks to anchor them to the matrix material.

The presence of nanotubes has other effects on materials including optical properties. For instance, the addition of nanotubes dispersed in the luminescent polymer poly-(m-phenylenevinylene-co-2, 5-dioctoxy-p-phenylenevinylene) (PmPV) greatly increases its conductivity and luminescence. Some nanocomposites exhibit nonlinear optical behavior.

SUMMARY

1. According to Einstein's equation, spherical fillers of any size increase the viscosity of a fluid in accordance with the partial volume of the filler. The Einstein equation, which relates to moduli of composites, has been modified to account for filler aggregates and nonspherically shaped fillers.
2. Many comminuted materials, such as wood flour, shell flour, α-cellulose, starch, synthetic polymers, carbon black, glass spheres and flakes, powdered metals, metallic oxides, calcium carbonate, silica, mica, talc, clay, and asbestos, have been used as fillers in polymers.
3. When added to polymers, fibrous reinforcements are much more effective than spherical fillers in improving strength properties. The most widely used reinforcing fiber is fibrous glass. Its effect and that of other reinforcing fibers is dependent on fiber length and the interfacial bond between it and the continuous resin matrix.
4. Fibrous glass may be used in the form of resin-impregnated mat or roving in the SMC and BMC processes. Resin-impregnated glass filament may be wound on a mandrel or forced through an orifice and cured in the filament-winding and pultrusion processes, respectively.
5. Many sophisticated reinforcements based on graphite fibers, aramid fibers, boron-coated tungsten, and single crystals, such as those of potassium titanate and sapphire, have been used as the discontinuous phase in high-performance composites.
6. The interfacial bond between the resin and fibrous glass, as well as other fillers, may be improved by surface treatment with surface-active agents such as silances and titanates. These coupling agents not only improve physical properties of the composite but are effective in reducing the energy required in processing.

GLOSSARY

acicular: Needle-shaped.
α-Cellulose: Cellulose insoluble in 17.5% NaOH.
anisotopic: Properties vary with direction.
aramid: Nylon produced from aromatic reactants.
asbestos: Fibrous magnesium silicate.
aspect ratio: Ratio of length to diameter of particles.
ASTM: American Society for Testing and Materials.
ATH: Alumina trihydrate.
barites: Barium sulfate.
β: Hydrodynamic or crowding factor.
blocking: The sticking of sheets of film to each other.
BMC: Bulk molding compound; resin-impregnated bundles of fibers.
bound rubber: Rubber adsorbed on carbon black that is insoluble in benzene.

c: Fractional volume occupied by a filler.
carbon black: Finely divided carbon made by the incomplete combustion of hydrocarbons.
comminuted: Finely divided.
composites: Materials that contain strong fibers embedded in a continuous phase called a matrix or resin.
continuous phase: The resin in a composite.
coupling agents: Products such as silanes or organic titanates that improve the interfacial bond between filler and resin.
CPIVC: Critical pigment volume concentration.
D: Diameter.
diatomaceous earth: Siliceous skeletons of diatoms.
discontinuous phase: The discrete filler additive in a composite.
EGG: Einstein-Guth-Gold equation: $M = M_0(1 + 2.5c + 14.1c^2)$.
Einstein equation: $\eta = \eta_0(1 + 2.5c)$.
η: Coefficient of viscosity of a mixture of a solid and liquid.
η_0: Coefficient of viscosity of a liquid.
extender: A term sometimes applied to an inexpensive filler.
f: Aspect ratio (1/D).
Fiberglass: Trade name for fibrous glass.
fibrous filler: One in which the aspect ratio is at least 150:1.
fibrous glass: Filaments made from molten glass.
filament winding: A process in which resin-impregnated continuous filaments are wound on a mandrel and the composite is cured.
filler: Usually a relatively inert material used as the discontinuous phase of a resinous composite.
Fuller's earth: Diatomaceous earth.
graphite fibers: Fibers made by the pyrolysis of polyacrylonitrile fibers.
isotropic: Identical properties in all directions.
kaolin: Clay.
Kelly Tyson equation: $M_L = kM_FC_F + M_MC_M$.
l_c: Critical fiber length.
lamellar: Sheetlike.
laminate: A composite consisting of layers adhered by a resin.
low profile resins: Finely divided incompatible resins that make a rough surface smooth.
lubricity: Slipperiness.
M: Modulus of a composite.
M_0: Modulus of an unfilled resin.
M_F: Modulus of a fiber.
M_L: Longitudinal modulus.
M_M: Modulus of resin matrix.
M_T: Transverse modulus.
mesh size: Size of screens used to classify finely divided solids.
mica: Naturally occurring lamellar silicate.
microballoons: Hollow glass spheres.
microspheres: Hollow carbon spheres.
Mohs' scale: A scale of hardness from 1 for talc and 10 for diamonds.
Mooney equation: $\eta = \eta_0(2.5c/1 - \beta c)$.
novaculite: Finely ground quartzite rock.

PMRN: Composites reinforced by potassium titanate.
PP: Polypropylene.
promotor: Coupling agent.
pultrusion: A process in which bundles of resin-impregnated filaments are passed through an orifice and cured.
PIVC: Pigment–volume concentration.
reinforced plastic: A composite whose additional strength is dependent on a fibrous additive.
roving: A bundle of untwisted strands.
silanes: Silicon compounds corresponding to alkanes.
silanol group: SiOH.
SMC: Sheet molding compound; resin-impregnated mat.
strand: A bundle of filaments.
synenite: Igenous rock similar to feldspar.
syntactic foam: Composite of resin and hollow spheres.
talc: Naturally occurring hydrated magnesium silicate.
thixotrope: An additive which yields thixotropic liquids.
tripoli: Rotten stone; porous decomposed sandstone.
TTS: Triisostearylisopropyl titanate.
type C glass: Acid-resistant glass.
type E glass: Electrical grade glass.
van der Waals forces: Intermolecular attractions.
wallastonite: Acicular calcium metasilicate.
whiskers: Single crystals used as reinforcements.
wood flour: Attrition-ground, slightly fibrous wood particles.

EXERCISES

1. Name three unfilled polymers.
2. What is the continuous phase in wood?
3. What filler is used in Bakelite?
4. Name three laminated plastics.
5. How would you change a glass sphere from an extender to a reinforcing filler?
6. If one stirs a 5-mL volume of glass beads in 1 L of glycerol, which will have the higher viscosity, small or large beads?
7. When used in equal volume, which will have the higher viscosity: (a) a suspension of loosely packed spheres or (b) a suspension of tightly packed spheres?
8. Why is the segmental mobility of a polymer reduced by the presence of a filler?
9. What effect does a filler have on T_g?
10. Which would yield the stronger composite: (a) peanut shell flour or (b) wood flour?
11. What is the advantage and disadvantage, if any, of α-cellulose over wood flour?
12. What filler is used in decorative laminates such as Formica table tops?
13. Which is the filler (discontinuous phase) and which is the resin (continuous phase) in a cookware coating produced from (a) polytetrafluoroethylene (Teflon) and (b) poly(phenylene sulfide) (Ryton)?
14. Would finely divided polystyrene make a good low-profile resin for reinforced polyesters?
15. How would you make a conductive syntactic foam?

16. Which would be stronger: (a) a chair made from polypropylene or (b) one of equal weight made from cellular polypropylene?
17. What advantage would a barium ferrite–filled PVC strip have over an iron magnet?
18. How would you make X-ray-opaque PVC?
19. How would you make an abrasive foam from polyurethane?
20. How could you explain the flame-retardant qualities of ATH?
21. How would you explain the improvement in strength of composites with stearic acid–treated calcium carbonate?
22. How could you justify the high cost of pyrogenic silica?
23. In what elastomer would hydrated silica be most effective as a filler?
24. Why is a good interfacial bond between the filler surface and the resin essential?
25. Providing that the volumes of the fibers are similar, which will yield the stronger composite: fibers with (a) small or (b) large cross-sections?
26. How would you make a strong, corrosion-resistant pipe?
27. What is the advantage of BMC and SMC over hand lay-up techniques such as those used in boat building?
28. What technique would you use to incorporate large amounts of filler (e.g., 70% calcium carbonate) in a resin?

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14

Plasticizers, Stabilizers, Flame Retardants, and Other Additives

Additives are added to modify properties, assist in processing, and introduce new properties to a material. Additives can be added as solids, liquids, or gases. They are usually added mechanically (with or without subsequent chemical reaction), during formulation, or as the material is in the fluid state. Many additives have become parts of general formulations developed as much as an art as a science. Thus, a general paint formulation for a water-based paint has titanium dioxide as the white pigment, China clay as an extender, a fungicide, defoaming agent, a coalescing liquid, a surfactant-dispersing agent, and calcium carbonate as the extender. A typical tire tread recipe has a processing aid, accelerator activator, antioxidant, antiozonate, softener, finishing aid, retarder, vulcanizing agent, and accelerator as additives.

Typical additives include:

- Antiblocking agents
- Antifoaming agents
- Antifogging agents
- Antimicrobial agents
- Antioxidants
- Antistatic agents
- Blowing agents
- Coloring agents
- Coupling agents
- Curing agents
- Fillers
- Flame retardants
- Foaming agents
- Impact modifiers
- Low-profile materials
- Lubricants
- Mold release agents
- Odorants or fragrances
- Plasticizers
- Preservatives
- Reinforcements
- Slip agents
- Stabilizers, including
  - Radiation (UV/Vis)
  - Heat
- Viscosity modifiers
  - Flow enhancers
  - Thickening agents
  - Antisag materials

While the modulus of polymers is usually increased by the addition of fillers and reinforcements, it may be decreased by the addition of moderate amounts of plasticizers. Other essential additives such as antioxidants, heat stabilizers, ultraviolet (UV) stabilizers, and flame retardants may reduce the modulus and other physical properties. Thus, it may be necessary to add reinforcing agents to counteract the weakening effect of some other additives. Nevertheless, additives are essential functional ingredients of polymers, and whenever possible, each should be used in optimum amounts for the attainment of high-quality products.

14.1 PLASTICIZERS

Flexibilizing of polymers can be achieved through internal and external plasticization. Internal plastization can be produced through copolymerization giving a more flexible polymer backbone or by grafting another polymer onto a given polymer backbone. Thus, poly(vinylchloride-co-vinyl acetate) is internally plasticized because of the increased flexibility brought about by the change in structure of the polymer chain. The presence of bulky groups on the polymer chain increases segmental motion and placement of such groups through grafting acts as an internal plasticizer. However, linear groups with more than 10 carbon atoms reduce flexibility because of side-chain crystallization when the groups are regularly spaced. Internal plastization achieves its end goal at least in part through discouraging association between polymer chains.

External plasticization is achieved through incorporation of a plasticizing agent into a polymer through mixing and/or heating. The remainder of this section focuses on external plasticization.

Plasticizers should be relatively nonvolatile, nonmobile, inert, inexpensive, nontoxic, and compatible with the system to be plasticized. They can be divided based on their solvating power and compatibility. Primary plasticizers are used as either the sole plasticizer or the major plasticizer with the effect of being compatible with some solvating nature. Secondary plasticizers are materials that are generally blended with a primary plasticizer to improve some performance, such as flame resistance and mildew resistance, or to reduce cost. The division between primary and secondary plasticizers is at times arbitrary. Here we will deal with primary plasticizers.

According to the ASTM D-883 definition, a plasticizer is a material incorporated in a plastic to increase its workability and flexibility or distensibility. The addition of a plasticizer may lower the melt viscosity, elastic modulus, and glass transition temperature (T_g) of a plastic. Thus, the utility of cellulose nitrate (CN) produced by Schonbein in 1846 was limited until Parkes added castor oil to CN in 1865 and Hyatt added camphor to plasticize CN in 1870. Another plasticizer, tricresyl phosphate (TCP), was used to replace part of the camphor and reduce the flammability of celluloid in 1910.

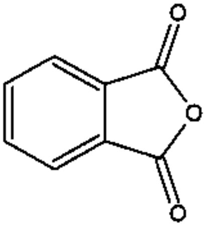
Waldo Semon patented the use of tricresyl phosphate as a plasticizer for poly(vinyl chloride) (PVC) in 1933. This was later replaced by the less toxic di-2-ethylhexyl phthalate (DOP), which is now the most widely used plasticizer. The annual worldwide production of plasticizers is 3.2 million tons, and the U.S. production is in excess of 1 million tons. In fact, plasticizers are major components of a number of polymer-containing products. For instance, the adhesive in automobile safety glass is typically composed mainly of poly(vinyl butyral) and about 30% plasticizer.

The effect of plasticizers may be explained by the lubricity, gel, and free volume theories. The first states that the plasticizer acts as an internal lubricant and permits the polymer chains to slip by each other. The gel theory, which is applicable to amorphous polymers, assumes that a polymer such as PVC has many intermolecular attractions that are weakened by the presence of a plasticizer such as DOP. It is assumed that the addition of a plasticizer increases the free volume of a polymer and that the free volume is identical for polymers at T_g.

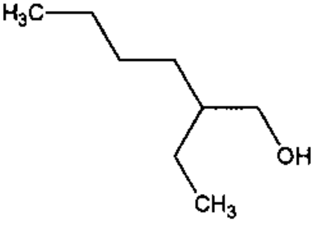
Most plasticizers are classified as to being general purpose, performance, or specialty plasticizers. General purpose plasticizers are those that offer good performance inexpensively. Most plasticizers are of this grouping. Performance plasticizers offer added performance over general purpose plasticizers generally with added cost. Performance plasticizers include fast solvating materials such as butyl benzyl phthalate and dihexyl phthalate; low-temperature plasticizers such as di-n-undecyl phthalate and di-2-ethylhexyl adipate; and so-called "permanent plasticizers" such as tri-2-ethylhexyl trimellitate, triisononyl trimellitate, and diisodecyl phthalate. Specialty plasticizers include materials that provide important properties such as reduced migration, improved stress–strain behavior, flame resistance, and increased stabilization.

The three main chemical groups of plasticizers are phthalate esters, trimellitate esters, and adipate esters. In all three cases, performance is varied through the introduction of different alcohols into the final plasticizer product. There is a balance between compatibility and migration. Generally the larger the ester grouping the less the migration up to a point where compatibility becomes a problem and where compatibility now becomes the limiting factor.

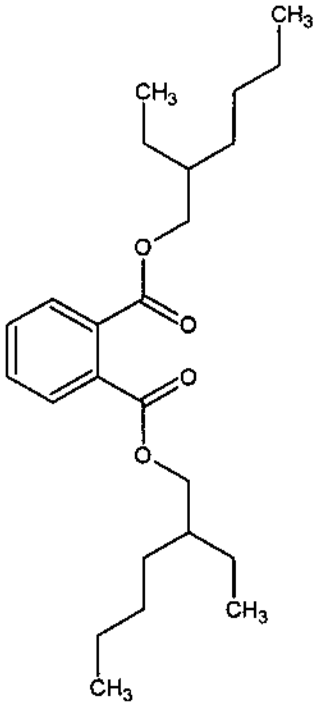
The most used phthalate ester is di-2-ethylhexyl phthalate, DOP, made from the reaction of 2-ethyl hexanol with phthalic anhydride.



(14.1)
Phthalic Anhydride

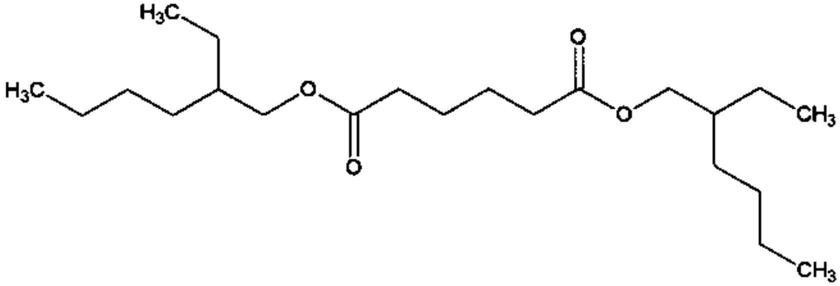


(14.2)
1-Ethyl Hexanol



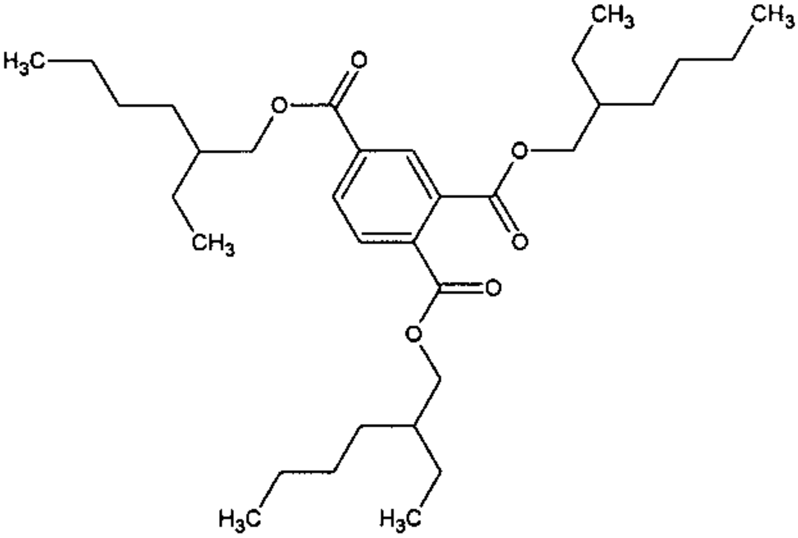
(14.3)
DOP

The most important adipate ester is also the di-2-ethylhexyl ester, di-2-ethylhexyl adipate, DOA.



(14.4)

There are several widely used trimellitate esters including tri-2-ethylhexyl trimellitate, TOTM.



(14.5)

TOTM

Compatibility is the ability to mix together without forming different phases. A good approach to measure likelihood of compatibility is solubility parameters (Sec. 3.2). Plasticizers with solubility parameters and type of bonding similar to those of the polymer are more apt to be compatible than when the solubility parameters are different. The solubility parameter for PVC (9.66) is near that of good plasticizers for PVC such as DOP (8.85). Table 14.1 contains solubility parameters for typical plasticizers.

The development of plasticizers has been plagued with toxicity problems. Thus, the use of highly toxic polychlorinated biphenyls (PCBs) has been discontinued. Phthalic acid esters, such as DOP, may be extracted from blood stored in plasticized PVC blood bags and tubing. These aromatic esters are also distilled from PVC upholstery in closed automobiles in hot weather. These problems have been solved by using oligomeric polyesters as nonmigrating plasticizers, instead of DOP.

Table 14.1 Solubility Parameters of Typical Plasticizers

Plasticizer	δ Solubility parameter (H)
Paraffinic oils	7.5
Dioctyl phthalate	7.9
Dibutoxyethyl phthalate	8.0
Tricresyl phosphate	8.4
Dioctyl sebacate	8.6
Triphenyl phosphate	8.6
Chlorinated biphenyl (Arochlor 1248)	8.8
Dihexyl phthalate	8.9
Hydrogenated terphenyl (HB-40)	9.0
Dibutyl sebacate	9.2
Dibutyl phthalate	9.3
Dipropyl phthalate	9.7
Diethyl phthalate	10.0
Dimethyl phthalate	10.7
Santicizer 8	11.9
Glycerol	16.5

Experimental investigations and assessments show that the average person takes in about 2 g a year of external plasticizers. Most of this is from traces of DOA migrating from food packaging. The so called No Observed Effect Level (NOEL) for DOA in rodents is about 40 mg per kg of body weight per day. Extrapolation for a person equates to 1000 g of plasticizer a year for a "safety factor" of about 500. Even so, increased efforts to evaluate the safety of plasticizers continues.

When present in small amounts plasticizers can act as antiplasticizers increasing the hardness and decreasing the elongation of the material partly due to their ability to fill voids. Inefficient plasticizers require larger amounts of plasticizer to overcome the initial antiplasticization. However, good plasticizers such as DOP change from antiplasticizers to plasticizers when less than 10% of the plasticizer is added to PVC.

Plasticizer efficiency is related to the ability of the plasticizer to soften the polymer and is defined as the ratio of the slope of the hardness (Sec. 5.4, Hardness) as a function of plasticizer concentration.

External plasticizers are not permanent. Plasticizer molecules associate with one another eventually creating "preferred" migration routes to the material's surface where the plasticizer is rubbed or washed away. The preferential association of plasticizer molecules also leaves certain sites less flexible and creates variations in material stress–strain and expansion/contraction behavior.

Plasticizers also extend the lower temperature range for use of materials since they both discourage polymer chain associative behavior and encourage segmental flexibility increasing the rotational freedom effectively decreasing the materials typical T_g.

Volume-wise, about 90% of plasticizers are used with PVC and PVC containing polymer systems.

Water is a widely utilized plasticizer in nature, permitting flexibility of much of the human body as well as the "bendability" of flowers, leaves, tree branches, and so on. Fats and many proteins also act as plasticizers in animals.

Plasticizer containment still remains a major problem, particularly for periods of extended use. For instance, most plastic floor tiles become brittle with extended use, mainly due to the leaching out of plasticizer. This is being overcome through many routes including surface treatment of polymer product surfaces affecting less porous surface features and use of branched polymers which can act as plasticizers to themselves. Being polymers themselves, the highly branched polymers are slow to leach because of physical entanglements within the total polymer matrix.

14.2 ANTIOXIDANTS

Antioxidants retard oxidative degradation. Heat, mechanical shear, ultraviolet (UV) radiation, and heat can be responsible for the formation of free radicals, which in turn can act to shorten polymer chains and increase crosslinking, both leading to a deterioration in material properties. Free radical production often begins a chain reaction. Primary antioxidants donate active hydrogen atoms to free radical sites, thereby quenching or stopping the chain reaction. Secondary antioxidants or synergists act to decompose free radicals to more stable products.

Polymers such as polypropylene (PP) are not usable outdoors without appropriate stabilizers because of the presence of readily removable hydrogen atoms on the tertiary carbon atoms. PP and many other polymers (RH) are attacked during processing or outdoor use in the absence of stabilizers because of a chain degradation reaction, as shown in the following equations.

By initiation:

$$\underset{\text{Polymer}}{\mathrm{R{-}H}} \rightarrow \underset{\substack{\text{Free}\\ \text{radicals}}}{\mathrm{R\cdot + H\cdot}} \tag{14.6}$$

By propagation:

$$\begin{aligned} &\underset{\substack{\text{Free}\\ \text{radicals}}}{\mathrm{R\cdot}} + \underset{\text{Oxygen}}{\mathrm{O_2}} \rightarrow \underset{\substack{\text{Peroxy}\\ \text{free}\\ \text{radical}}}{\mathrm{ROO\cdot}} \\ &\underset{\substack{\text{Peroxy}\\ \text{free}\\ \text{radical}}}{\mathrm{ROO\cdot}} + \underset{\text{Polymer}}{\mathrm{R{:}H}} \rightarrow \underset{\substack{\text{Dead}\\ \text{polymer}}}{\mathrm{ROOH}} + \underset{\substack{\text{Free}\\ \text{radical}}}{\mathrm{R\cdot}} \end{aligned} \tag{14.7}$$

By termination:

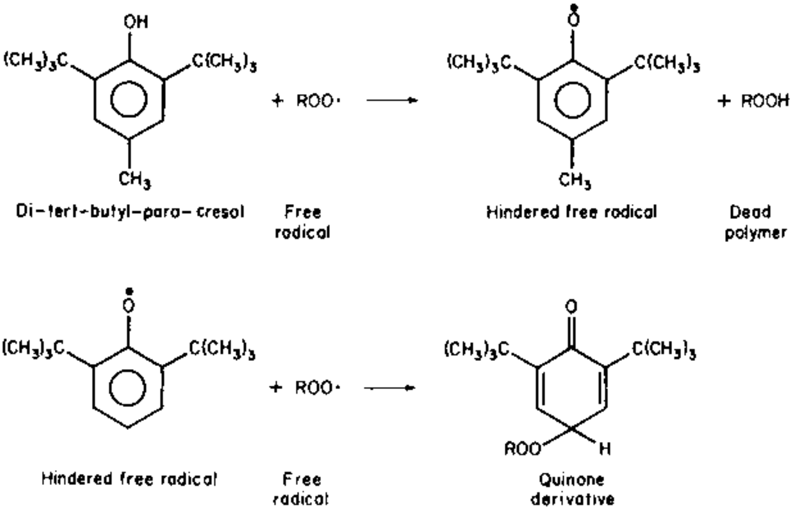
$$\begin{aligned} \mathrm{R\cdot + R\cdot} &\rightarrow \underset{\substack{\text{Dead}\\ \text{polymer}}}{\mathrm{R{:}R}} \\ \mathrm{R\cdot + ROO\cdot} &\rightarrow \underset{\substack{\text{Dead}\\ \text{polymer}}}{\mathrm{ROOR}} \\ \mathrm{ROO\cdot + ROO\cdot} &\rightarrow \underset{\substack{\text{Dead}\\ \text{polymer}}}{\mathrm{ROOR}} + \mathrm{O_2} \end{aligned} \tag{14.8}$$

The rate of the free radical chain reactions shown above is accelerated by the presence of heavy metals, such as cobalt(II) ions, as follows.

$$\begin{aligned} \mathrm{ROOH + Co^{2+}} &\rightarrow \mathrm{Co^{3+} + RO\cdot + OH^-} \\ \mathrm{ROOH + Co^{3+}} &\rightarrow \mathrm{ROO\cdot + H^+ + Co^{2+}} \end{aligned} \tag{14.9}$$

In contrast, the rate of chain reaction degradation is retarded by the presence of small amounts of antioxidants. Naturally occurring antioxidants are present in many plants, including hevea rubber trees. The first synthetic antioxidants were synthesized independently by Caldwell and by Winkelman and Gray by the condensation of aromatic amines with aliphatic aldehydes. While unpurified commercial products such as phenyl-β-naphthylamine are toxic, they are still used as antioxidants for rubber tires.

Many naturally occurring antioxidants are derivatives of phenol and hindered phenols, such as di-tert-butyl paracresol. As shown by the following equation, the antioxidant acts as a chain transfer agent to produce a dead polymer and a stable free radical that does not initiate chain radical degradation. However, the phenoxy free radical may react with other free radicals to produce a quinone derivative.



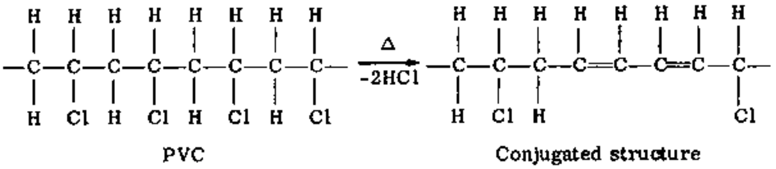
(14.10)

Since carbon black has many free electrons, it may be added to polymers such as polyolefins to retard free radical degradation of the polymer. It is customary to add small amounts of other antioxidants, such as aliphatic thiols or disulfides, to enhance the stabilization by a so-called "synergistic effect." The latter term is used to explain the more effective stabilization by a mixture of antioxidants. More than 3000 tons of antioxidants is used annually by the polymer industry in the United States.

14.3 HEAT STABILIZERS

Heat stabilizers are added to materials to impart protection against heat-induced decomposition. Such stabilizers are needed to protect a material when it is subjected to a thermal-intense process (such as melt extrusion) or when the material is employed under conditions where increased heat stability is needed.

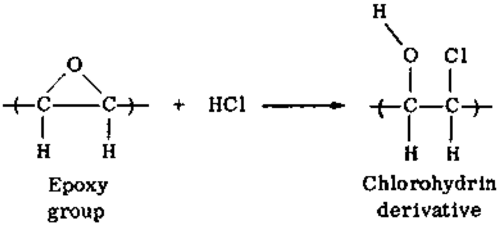
In addition to the free radical chain degradation described for polyolefins, another type of degradation (dehydrohalogenation) also occurs with chlorine-containing polymers such as PVC. As shown by the following equation, when heated PVC may lose hydrogen chloride and form a chromophoric conjugated polyene structure. Since the allylic chlorides produced are very unstable, the degradation continues as an unzipping type of chain reaction.



(14.11)

This type of degradation is accelerated in the presence of iron salts, oxygen, and hydrogen chloride. Toxic lead and barium and cadmium salts act as scavengers for hydrogen chloride and may be used as heat stabilizers in some applications, such as wire coating. Mixtures of magnesium and calcium stearates are less toxic. In spite of their toxicity, alkyltin mercaptides and alkyltin derivatives of thio acids have also been used. Dioctyltin salts are less toxic and produce clear PVC films.

Organic phosphites, such as mixed aryl and alkyl phosphites or triphenyl phosphite, form complexes with free metallic ions and prevent the formation of insoluble metal chlorides. Less toxic, epoxidized, unsaturated oils such as soy bean oil act as HCl scavengers as shown below.



(14.12)

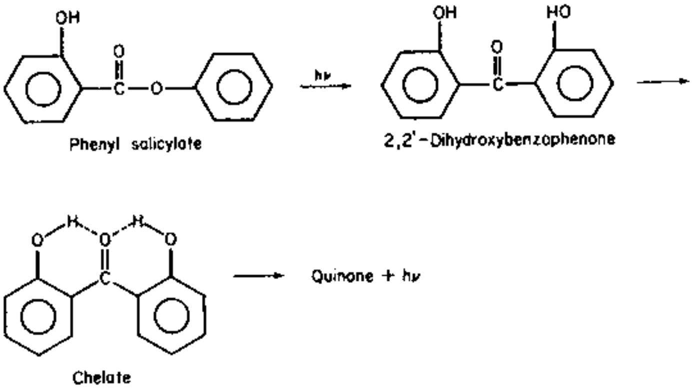
14.4 ULTRAVIOLET STABILIZERS

While much of the sun's high-energy radiation is absorbed by the atmosphere, some radiation in the 280- to 400-nm (UV) range reaches the Earth's surface. Since the energy of this radiation is 100 to 72 kcal, it is sufficiently strong to cleave covalent bonds and cause yellowing and embrittlement of organic polymers.

Polyethylene, PVC, polystyrene, polyesters, and polypropylene are degraded at wavelengths of 300, 310, 319, 325, and 370 nm, respectively. The bond energy required to cleave the tertiary carbon hydrogen bond in polypropylene is 90 kcal/mol, corresponding to a wavelength of 318 nm.

Since the effect of ultraviolet radiation on synthetic polymers is similar to its effect on the human skin, it is not surprising that UV stabilizers such as phenyl salicylate have been used for many years in suntanning lotions. As shown in Eq. (14.13), phenyl salicylate rearranges in the presence of high-energy radiation to form a 2,2′-dihydroxybenzophenone. The latter and other 2-hydroxybenozophenones act as energy transfer agents, i.e., they absorb energy to form chelates which release energy at longer wavelengths by the formation of quinone derivatives.

Many commercial UV stabilizers have alkoxyl groups on carbon-4 of the phenyl group. 2-Alkoxybenzophenones and those with bulky groups on carbon 6 are not useful as stabilizers. Other UV stabilizers are benzotriazoles, such as 2-(2′-hydroxyphenyl)benzotriazole; substituted acrylonitriles, such as ethyl-2-cyano-3,3′-diphenyl acrylate; metallic complexes, such as nickel dibutyldithiocarbamate; and pigments, such as carbon black.



(14.13)

The metal complexes function as energy transfer agents, free radical scavengers, and decomposers of hydroperoxides. The pigments absorb UV radiation and act as screening agents. More than 100,000 tons of UV stabilizers is used annually by the U.S. polymer industry.

14.5 FLAME RETARDANTS

While some polymers such as PVC are not readily ignited, most organic polymers, like other carbonaceous materials, will burn at elevated temperatures, such as those present in burning buildings. Polyolefins, SBR, EPDM, and wood, of course, will support combustion when ignited with a match or some other source of flame. In addition to burning, thermoplastics such as polyester fibers will melt, and other plastics such as PVC, polyurethanes, and proteins, when ignited, will produce smoke and toxic gases such as CO, HCl, and HCN.

Since some polymers are used as shelter and clothing and in household furnishing, it is essential that they have good flame resistance. Combustion is a chain reaction that may be initiated and propagated by free radicals like the hydroxyl free radical. As shown in Eq. (14.14), hydroxyl radicals may be produced by the reaction of oxygen with macroalkyl radicals. Halogen radicals produced by the reaction of hydroxyl radicals with halides, such as HX, may serve as terminators for the chain reaction.

$$\begin{array}{l}
\underset{\substack{\text{Macroalkyl}\\\text{radical}}}{\sim\!RCH_2\cdot} + \underset{\text{Oxygen}}{O_2} \rightarrow \underset{\substack{\text{Dead}\\\text{polymer}}}{\sim\!RCHO} + \underset{\substack{\text{Hydroxyl}\\\text{radical}}}{\cdot OH}\\[2ex]
\underset{\substack{\text{Hydroxyl}\\\text{radical}}}{\cdot OH} + \underset{\text{Polymer}}{\sim\!RCH_2H} \rightarrow \underset{\text{Macroradical}}{\sim\!RCH_2\cdot} + \underset{\text{Water}}{HOH}\\[2ex]
\underset{\substack{\text{Hydrogen}\\\text{halide}}}{HX} + \underset{\substack{\text{Hydroxyl}\\\text{radical}}}{\cdot OH} \rightarrow \underset{\text{Water}}{HOH} + \underset{\substack{\text{Halogen}\\\text{radical}}}{X\cdot}\\[2ex]
\underset{\substack{\text{Halogen}\\\text{radical}}}{X\cdot} + \underset{\text{Macroradical}}{\sim\!RCH_2\cdot} \rightarrow \underset{\substack{\text{Dead}\\\text{polymer}}}{RCH_2X}
\end{array} \qquad (14.14)$$

14.6 FLAME-RETARDANT MECHANISMS

Since halogen and phosphorus radicals couple with free radicals produced in the combustion process and terminate the reaction, many flame retardants are halogen or phosphorus compounds. These may be (1) additives, (2) external retardants, such as antimony oxide and organic bromides, or (3) internal retardants, such as tetrabromophthalic anhydride, which can become part of the polymer. More than 100,000 tons of flame retardants is used annually in the United States.

Fuel, oxygen, and high temperature are essential for the combustion process. Thus, polyfluorocarbons, phosphazenes, and some composites have flame-retardant properties since they are not good fuels. Fillers such as alumina trihydrate (ATH) release water when heated and hence reduce the temperature of the combustion reaction. Compounds such as sodium carbonate, which releases carbon dioxide, shield the reactants from oxygen.

Char, formed in some combustion processes, also shields the reactants from oxygen and retards the outward diffusion of volatile combustible products. Aromatic polymers tend to char, and some phosphorus and boron compounds catalyze char formation.

Synergistic flame retardants such as a mixture of antimony trioxide and an organic bromo compound are much more effective than single flame retardants. Thus, while a polyester containing 11.5% tetrabromophthalic anhydride burned without charring at high temperatures, charring but no burning was noted when 5% antimony oxide was added.

Since combustion is subject to many variables, tests for flame retardancy may not predict flame resistance under unusual conditions. Thus, a disclaimer stating that flame retardancy tests do not predict performance in an actual fire must accompany all flame-retardant polymers. Flame retardants, like many other organic compounds, may be toxic or may produce toxic gases when burned. Hence, extreme care must be exercised when using fabrics or other polymers treated with flame retardants.

14.7 COLORANTS

Color is a subjective phenomenon whose esthetic value has been recognized for centuries. Since it is dependent on the light source, the object, and the observer, color is not subject to direct measurement. Colorants that provide color in polymers may be soluble dyes or comminuted pigments.

Some polymeric objects, such as rubber tires, are black because of the presence of high proportions of carbon black filler. Many other products, including some paints, are white because of the presence of titanium dioxide, the most widely used inorganic pigment. Over 50,000 tons of colorants are used annually by the U.S. polymer industry.

Pigments are classified as organic or inorganic. The former are brighter, less dense, and smaller in particle size than the more widely used, more opaque inorganic colorants. Iron oxides or ochers, available as yellow, red, black, brown, and tan, are the second most widely used pigments.

Other pigments, such as yellow lead chromate, molybdate orange, yellow cadmium pigments, and green zinc chromate, are toxic. Green zinc chromate is a blend of yellow lead chromate and iron blue–iron(II) ferrocyanide, or Prussian blue. Ultramarine blue is also widely used as a pigment.

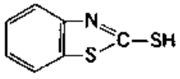
Carbon black is the most widely used organic pigment, but phthalocyanine blues and greens are available in many different shades and are also widely used. Other organic pigments are the azo dyestuffs such as the pyrazolone reds, diarylide yellows, dianisidine orange, and tolyl orange; quinacridone dyestuffs, such as quinacridone violet, magenta, and red; the red perylenes; acid and basic dyes, such as rhodamine red and Victoria blue;

anthraquinones, such as flavanthrone yellow; dioxazines, such as carbazole violet; and isindolines, available in the yellow and red range.

14.8 CURING AGENTS

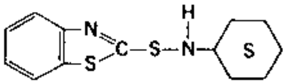
The use of curing agents began with the serendipitous discovery of vulcanization of hevea rubber with sulfur by Charles Goodyear in 1838. The conversion of an A- or B-stage phenolic novolac resin with hexamethylenetetramine in the early 1900s was another relatively early example of the use of a curing (crosslinking) agent. Organic accelerators, or catalysts, for the sulfur vulcanization of rubber were discovered by Oenslager in 1912. While these accelerators are not completely innocuous, they are less toxic than aniline, used prior to the discovery of accelerators. Sample accelerators are thiocarbanilide and 2-mercaptobenzothiazole (Captax).

Captax is used to the extent of 1% with hevea rubber and accounts for the major part of the 30,000 tons of accelerators used annually in the United States. Other accelerators, whose structural formulas are shown below, are 2-mercaptobenzothiazole sulfonamide (Santocure), used for the vulcanization of SBR, dithiocarbamates, and thiuram disulfides. The last, called ultraaccelerators, catalyze the curing of rubber at moderate temperatures and may be used in the absence of sulfur.



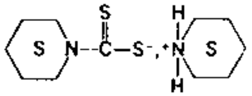
2-Mercaptobenzothiazole
(Captax)

(14.15)



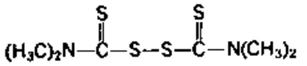
2-Mercaptobenzothiazole sulfenamide
(Santocure)

(14.16)



Piperidinium pentamethylene
dithiocarbamate (pip-pip)

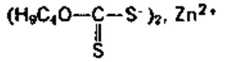
(14.17)



$(H_3C)_2N-\overset{S}{\overset{\|}{C}}-S-S-\overset{S}{\overset{\|}{C}}-N(CH_3)_2$

Tetramethyl thiuram disulfide
(Tuads)

(14.18)



$(H_9C_4O-\underset{S}{\underset{\|}{C}}-S^-)_2, Zn^{2+}$

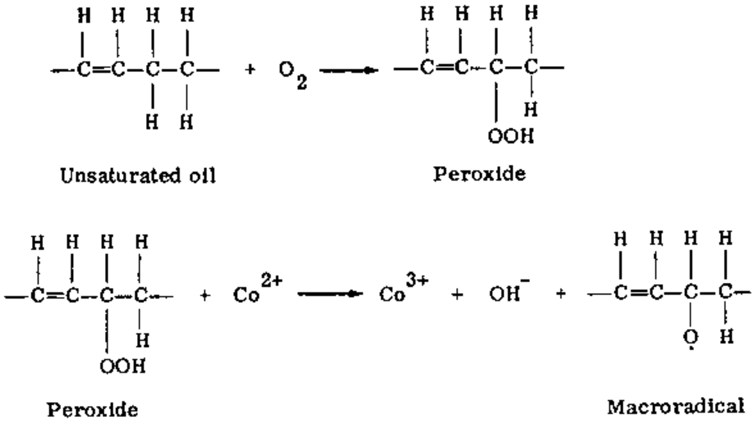
Zinc butyl xanthate

(14.19)

Initiators such as benzoyl peroxide are used not only for the initiation of chain reaction polymerization but also for the curing of polyesters and ethylene-propylene copolymers and for the grafting of styrene on elastomeric polymer chains. Peroxides such as 2,5-dimethyl-2,5-di(t-butylperoxy) hexyne-3 are used for crosslinking HDPE. Since these compounds contain weak covalent bonds, precautions must be taken in their storage and use to prevent explosions. Free radicals for crosslinking may also be produced by electrons, γ rays, or UV irradiation. The latter is more effective in the presence of additives such as the methyl ether of benzoin.

Unsaturated polymers such as alkyd resins may be cured or "dried" in the presence of oxygen, a salt of a heavy metal, and an organic acid called a drier. The commonly used metals are cobalt, lead, and manganese, and the most common organic acids are linoleic, abietic, naphthenic, octoic, and tall oil fatty acids.

As shown in Eq. (14.20), oxygen is now believed to form a peroxide in the presence of a drier, yielding a macroradical capable of crosslinking.



(14.20)

14.9 ANTISTATIC AGENTS (ANTISTATS)

Antistatic agents (antistats) dissipate static electrical charges. Insulating materials including most organic plastics, fibers, films, and elastomers can build up electrical charge. Because these largely organic materials are insulators, they are not able to dissipate the charge. Such charge buildup is particularly noticeable in cold, dry climates and leads to dust attraction and sparking. These charges, resulting from an excess or deficiency of electrons, may be counteracted by the use of air-ionizing bars during processing or by the addition of antistatic agents.

Antistatic agents may reduce the charge by acting as lubricants, or they may provide a conductive path for the dissipation of the charge. Most antistats are hygroscopic and attract a thin film of water to the polymer surface. Internal antistats are admixed with the polymer, while external antistats are usually sprayed on the polymer surface. Some examples of antistatic agents are quaternary ammonium compounds, hydroxyalkylamines, organic phosphates, derivatives of polyhydric alcohols such as sorbitol, and glycol esters of fatty acids.

14.10 CHEMICAL BLOWING AGENTS

Chemical blowing agents (CBAs) are employed to create lighter weight material through formation of a foam. Physical CBAs are volatile liquids and gases that expand and volatilize during processing through control of the pressure and temperature.

Cellular polymers not only provide insulation and resiliency but are usually stronger on a weight basis than solid polymers. Fluid polymers may be foamed by the addition of low-boiling liquids such as pentane or fluorocarbons, by blowing with compressed nitrogen gas, by mechanical heating, and by the addition of foaming agents. While some carbon dioxide is produced when polyurethanes are produced in the presence of moisture, auxiliary propellants are also added to the prepolymer mixture.

The most widely used foaming agents are nitrogen-producing compounds such as azobisformamide (ABFA). Other foaming agents, which decompose at various temperatures, are available. These may be used in extrusion, rotational molding, injection molding, and slush molding of plastisols. Plastisols consist of suspensions of polymer particles in a liquid plasticizer. These products, such as PVC plastisols, solidify when the temperature reaches a point at which the plasticizer penetrates the polymer particles.

14.11 COMPATIBILIZERS

Compatibilizers are compounds that provide miscibility or compatibility to materials that are otherwise immiscible or only partially miscible, yielding a homogeneous product that does not separate into its components. Typically compatibilizers act to reduce the interfacial tension and are concentrated at phase boundaries. Reactive compatibilizers react chemically with the materials they are to make compatible. Nonreactive compatibilizers perform their task by physically making the various component materials compatible.

14.12 IMPACT MODIFIERS

Impact modifiers improve the resistance of materials to stress. Most impact modifiers are elastomers such as ABS, BS, methacrylate–butadiene–styrene, acrylic, ethylene–vinyl acetate, and chlorinated polyethylene.

14.13 PROCESSING AIDS

Processing aids are added to improve the processing characteristics of a material. They may increase the rheological and mechanical properties of a melted material. Acrylate copolymers are often utilized as processing aids.

14.14 LUBRICANTS

Lubricants are added to improve the flow characteristics of a material during its processing. They operate by reducing the melt viscosity or by decreasing adhesion between the metallic surfaces of the processing equipment and the material being processed. Internal lubricants reduce molecular friction, consequently decreasing the material's melt viscosity and allowing it to flow more easily. External lubricants act by increasing the flow of the material by decreasing the friction of the melted material as it comes into contact with surrounding surfaces. In reality, lubricants such as waxes, amides, esters, acids, and metallic stearates act as both external and internal lubricants.

14.15 MICROORGANISM INHIBITORS

While most synthetic polymers are not directly attacked by microorganisms such as fungi, yeast, and bacteria, they often allow growth on their surfaces. Furthermore, naturally occurring polymeric materials such as cellulosics, starch, protein, and vegetable oil–based coatings are often subject to microbiological deterioration. Finally, some synthetics that contain linkages "recognized" by enzymes within the microorganism (such as amide and ester linkages) may also be susceptible to attack.

One major antimicrobial grouping is the organotin-containing compounds. These monomeric organotin-containing compounds are now outlawed because of the high "leaching" rates of these materials affecting surrounding areas. Even so, polymeric versions are acceptable and can be considered nonleaching or slowly leaching.

Organic fungistatic and bacteriostatic additives are currently employed, but in all cases formation of resistant strains and the toxicity of the bioactive additive must be considered.

PVC is also subject to pink staining as a result of the diffusion of byproducts of attack by microorganisms. Quaternary ammonium carboxylates and tributyltin compounds are effective preservatives against pink staining. Other effective preservatives or biocides are esters of p-hydroxybenzoic acid, N-(trichloromethylthio)-4-phthalimide, bis(tri-n-butyltin), and bis(8-quinolinato) copper.

SUMMARY

1. Stiff polymers such as PVC may be flexibilized by the addition of a nonvolatile compatible liquid or solid which permits slippage of polymer chains and thus reduces the T_g and modulus of the polymer. Comparable effects may be accomplished by introducing randomness into the polymer by copolymerization.
2. The rate of degradation of polymers may be retarded by the addition of chain transfer agents, called antioxidants, which produce inactive free radicals.
3. The rate of decomposition of polymers such as PVC at elevated temperatures may be decreased by the addition of heat stabilizers that react with the decomposition products, like HCl. Soluble organic metal compounds, phosphites, and epoxides act as thermal stabilizers or scavengers for HCl.
4. The degradative effects of high-energy photolytic decomposition of polymers by UV radiation may be lessened by the addition of compounds such as 2-hydroxybenzophenones which serve as energy transfer agents, i.e., they absorb radiation at low wavelengths and reradiate it at lower energy at longer wavelengths.
5. Since fuel, oxygen, and high temperature are essential for the combustion of polymers, the removal of any one of these prerequisites will retard combustion. Thus, additives which when heated produce water or carbon dioxide are effective flame retardants.
6. The rapid combustion of organic polymers at elevated temperatures is also retarded by the presence of flame retardants that terminate the free radical combustion reaction.
7. A wide variety of organic and inorganic pigments is used as additives to color polymers.
8. The rate of crosslinking of natural rubber by sulfur is accelerated by catalysts such as Captax, which are called accelerators. Initiators such as BPO, which produce free radicals and heavy metal salts (driers), will also promote crosslinking.
9. Antistats reduce the electrostatic charge on the surface of polymers.
10. Gas-producing additives are essential for the formation of cellular products.
11. Biocides are used as additives to prevent attack on polymers by microorganisms.
12. Lubricants serve as processing aids that prevent the sticking of polymers to metal surfaces during processing.

GLOSSARY

accelerator: A catalyst for the vulcanization of rubber.
antioxidant: An additive that retards the degradation of polymers.
antiplasticization: The hardening and stiffening effect observed when small amounts of a plasticizer are added to a polymer such as PVC.
antistat: An additive that reduces static charges on polymers.
biocide: An additive that retards attack by microorganisms.
Captax: 2-Mercaptobenzothiazole.
cellular polymers: Foams.
char: Carbonaceous residue produced by burning.
chelate: A cyclic complex resembling pincer-like claws.
chemical blowing agents: Volatile liquids and gases that expand and/or volatilize during processing of a polymeric material, creating pockets leading to lighter weight materials.
CN: Cellulose nitrate.
colorant: A dye or pigment.
compatibilizers: Chemicals that provide miscibility or compatibility to materials that are otherwise immiscible or only partially miscible, giving a homogeneous product.
curing agent: An additive that causes crosslinking.
$\Delta\delta$: Difference in solubility parameters.
dehydrohalogenation: Loss of HX.
DOP: di-2-Ethylhexyl phthalate.
drier: A catalyst that aids the reaction of polymers with oxygen.
drying: The crosslinking of an unsaturated polymer chain.
energy transfer agent: A molecule that absorbs high energy and reradiates it in the form of lower energy, i.e., longer wavelength.
flame retardant: An additive that increases the flame resistance of a polymer.
foaming agent: A gas producer.
free volume: Holes not occupied by polymer chains.
gel theory: The theory that assumes the presence of a pseudo-three-dimensional structure in PVC and that the intermolecular attractions are weakened by the presence of a plasticizer.
h: Planck's constant.
HDPE: High-density polyethylene.
heat stabilizers: Additives that retard the decomposition of polymers at elevated temperatures.
Hyatt, J. W.: The inventor of celluloid.
impact modifiers: Materials that improve the resistance of materials to stress.
internal plasticization: The flexibilization resulting from the introduction of bulky groups in a polymer by copolymerization.
lubricants: Materials that improve the flow characteristics of materials during processing.
lubricity theory: The theory that explains plasticization on the basis of an increase in polymer chain slippage.
microorganism inhibitors: Compounds that impart the ability to resist habitation and destruction by microorganisms.
mold release agent: A lubricant that prevents the polymer from sticking to the mold cavity.
nm: Nanometer (1×10^{-9}m); 1 nm = 10 Å.

v: Frequency.
ocher: An iron oxide pigment.
oligomeric polyesters: Low molecular weight polyesters.
PCB: Polychlorinated biphenyls.
pink staining: Discoloration of PVC resulting from attack by microorganisms.
plasticizer: A compatible nonvolatile liquid or solid which increases the flexibility of hard polymers.
plastisol: A suspension of finely divided polymer in a liquid plasticizer. The latter penetrates and plasticizes the polymer when heated.
PP: Polypropylene.
processing aid: A lubricant.
side-chain crystallization: A stiffening effect noted when long, regularly spaced bulky pendant groups are present on a polymer chain.
synergistic effect: The enhanced effect of a mixture of additives.
T_g: Glass transition temperature.
TCP: Tricresyl phosphate.
ultraaccelerator: A catalyst that cures rubber at low temperatures.
ultraviolet stabilizer: An additive that retards degradation caused by UV radiation.
UV: Ultraviolet.
vulcanization: Crosslinking with heat and sulfur.

EXERCISES

1. Cellulose nitrate explodes when softened by heat. What would you add to permit processing at lower temperatures?
2. PVC was produced in the 1830s but not used until the 1930s. Why?
3. What is the source of “fog” on the inside of the windshield on pre-1976 automobiles?
4. Can you propose a mechanism for antiplasticization?
5. Why is plasticized PVC said to be toxic?
6. The T_g decreases progressively as the size of the alkoxy group increases from methyl to decyl in polyalkyl methacrylates, but then increases. Explain.
7. Polypropylene (pp) is now used in indoor/outdoor carpets. However, the first PP produced deteriorated rapidly when subjected to sunlight because of tertiary hydrogen atoms present. Explain.
8. Tests showed that crude phenyl-β-naphthylamine was a carcinogen, but the mice used for testing lived longer than normal when injected with di-tert-butyl-paracresol. Explain.
9. Lead stearate is an effective thermal stabilizer for PVC, yet its use in PVC pipe is not permitted. Why?
10. When a PVC sheet fails in sunlight it goes through a series of colors before becoming black. Explain.
11. What would be the advantage of using epoxidized soybean oil as a stabilizer for PVC?
12. Why do PVC films deteriorate more rapidly when used outdoors?
13. Which of the following is more resistant to UV light: (a) polypropylene, (b) polyethylene, or (c) PVC?
14. Would 2-methoxybezophenone be useful as a UV stabilizer?
15. Would 3,3′-dihydroxybenzophenone be useful as a UV stabilizer?

16. Polytetrafluoroethylene is considered to be noncombustible. Yet two astronauts burned to death in a space capsule because of burning PTFE. Explain.
17. The disastrous effect of discarded burning cigarettes on polyurethane-"stuffed" upholstery has been lessened by the use of a protective film of neoprene. Yet disastrous fires have occurred, e.g., in jail cells. Explain.
18. The addition of Tris as a retardant was required for children's sleeping garments by a government order in the early 1970s. Nevertheless, the use of Tris was discontinued in 1977. Why?
19. Antimony oxide is a good flame retardant in the presence of organic halogen compounds. Would you recommend it for textile applications?
20. Is a phosphazene elastomer flame-resistant?
21. Cotton, wool, silk, flax, and wood, which are combustible, have been used for many centuries without flame retardants. Yet synthetic polymers that are not any more combustible are banned unless flame retardants are added. Why?
22. Was carbon black always used as a reinforcing filler for tires?
23. How would you explain the different colors of ocher ($Fe_2O_3 \cdot XH_2O$)?
24. What is the formula for Santocure?
25. How would you synthesize pip pip?
26. BPO is explosive. How would you store it?
27. Can you propose a better name for a drier?
28. What is the objection to the presence of static charges on polymer surfaces?
29. Explain how an internal antistat performs.
30. Why are foamed wire coatings preferred over solid coatings?
31. How would you design a foamed plastisol?
32. Why doesn't the liquid plasticizer penetrate a polymer particle such as PVC at ordinary temperatures?
33. Which would be more resistant to attack by microorganisms: (a) PVC or (b) plasticized PVC?
34. What naturally occurring fiber is more resistant to microbiological attack than nylon?
35. Sometimes molded plastics have opaque material called "bloom" on the surface. Explain.

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15

Reactions of Polymers

Synthesis and curing (crosslinking) of polymers and telomerization are chemical reactions which have been discussed in previous chapters. Other reactions of polymers, such as hydrogenation, halogenation, cyclization, and degradation, will be described in this chapter. Providing the reaction sites are accessible to the reactants, reactions take place that are similar to classic organic chemical reactions. The rates of reactions of polymers may be enhanced by the presence of neighboring groups. This effect is called anchimeric assistance.

15.1 REACTIONS WITH POLYOLEFINS

Deuterated polyethylene could be produced from high-density polyethylene (HDPE) but it is more readily produced by the polymerization of perdeuterated ethylene. The latter is prepared by the reduction of deuterated acetylene with chromium(II) sulfate in a dimethylformamide (DMF/H_2O) solution.

Polyethylene, like other alkane polymers, is resistant to chemical oxidation, but will burn in the presence of oxygen. The folds in crystalline polyethylene are less resistant to attack, and α, ω-dicarboxylic acids can be produced by the reaction of concentrated nitric acid on crystalline HDPE.

Polyolefins, like simple alkanes, may be chlorinated by chlorine at elevated temperatures or in the presence of ultraviolet light. This free radical reaction produces HCl and chlorinated polyolefins (Tyrin), which are used as plasticizers and flame retardants. The commercial product is available with various percentages of chlorine. Since a tertiary hydrogen atom is more readily replaced than a secondary hydrogen, polypropylene is more readily chlorinated than HDPE. HDPE is readily converted to polytetrafluoroethylene by direct fluorination using fluorine.

Sulfochlorinated polyethylene (Hypalon) is obtained when a suspension of polyethylene in carbon tetrachloride is chlorinated by a mixture of chlorine and sulfur dioxide in pyridine. The commercial product, which contains 27.5% chlorine and 1.5% sulfur, is soluble in tetralin. It may be used as a coating which may be cured with sulfur and diphenylguanidine.

A chlorinated product called poly(vinyl dichloride) (PVDC) is obtained when PVC is chlorinated. Since the heat resistance of PVDC is superior to that of PVC, it is used for hot water piping systems.

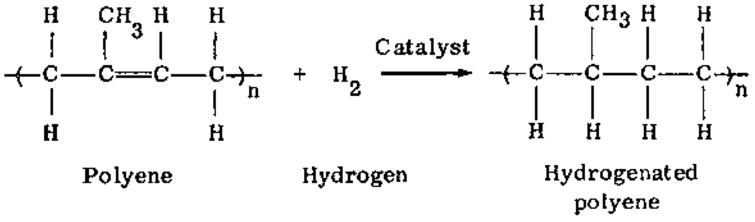
Polyolefins may be crosslinked by heating with peroxides such as di-tert-butyl peroxide or by irradiation. It is advantageous to crosslink these polymers after they have been fabricated, as in wire coatings. The crosslinked products are less soluble and more resistant to heat than are the linear polyolefins.

Reactions comparable to those described for HDPE take place with many organic polymers. The pendant groups may also react with appropriate reactants.

15.2 REACTIONS OF POLYENES

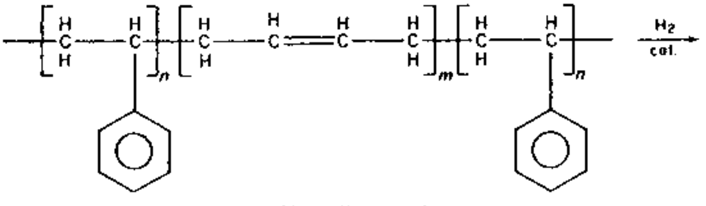
Providing the ethylenic groups are accessible, the reactions of polyenes are similar to the classic reactions of alkenes. Thus, as demonstrated by Nobel Laureate Hermann Staudinger, polyenes such as *Hevea brasiliensis* may be hydrogenated, halogenated, hydrohalogenated, and cyclized. In this classic experiment in the early 1900s, Harries produced ozonides of rubber. Epoxides were also obtained by peroxidation.

The hydrogenation of *H. brasiliensis* was investigated by Berthelot in 1869. The rate of this reaction with natural rubber, gutta percha, balata, or SBR may be followed by observing the changes in the glass transition temperature and the degree of crystallinity. The product obtained by the partial hydrogenation of polybutadiene (Hydropol) has been used as a wire coating.

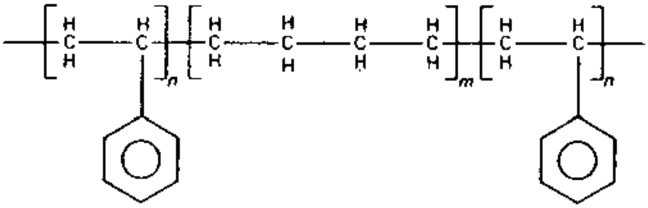


(15.1)

A saturated ABA block copolymer (Kraton) is produced by the hydrogenation of the ABA block copolymer of styrene and butadiene.



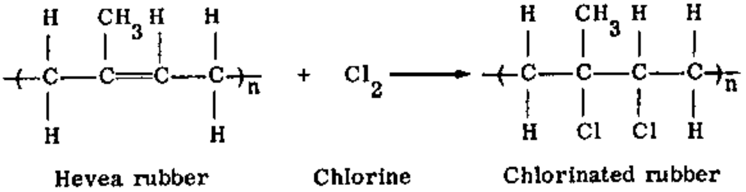
Block copolymer of butadiene and styrene



Block copolymer of styrene and butene

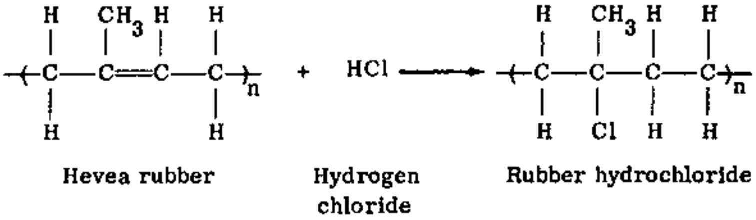
(15.2)

Chlorinated rubber (Tornesit or Parlon), which was produced by Traun in 1859, is available with varying amounts of chlorine and is used for the coating of concrete. While chlorinated NR is soluble in carbon tetrachloride, chlorinated SBR is insoluble, but both are soluble in benzene and chloroform.



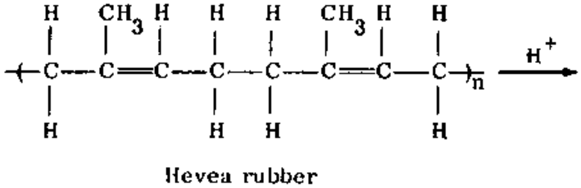
(15.3)

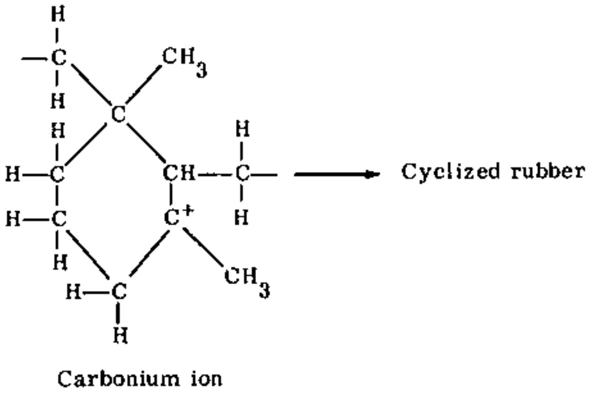
Hydrohalogenation of *H. brasiliensis* proceeds by an ionic mechanism to yield a Markownikoff addition product with the halogen on the tertiary carbon atom. The principal use of rubber hydrochloride (Pliofilm) is as a packaging film. Some cyclization of the polymer also takes place during hydrohalogenation.



(15.4)

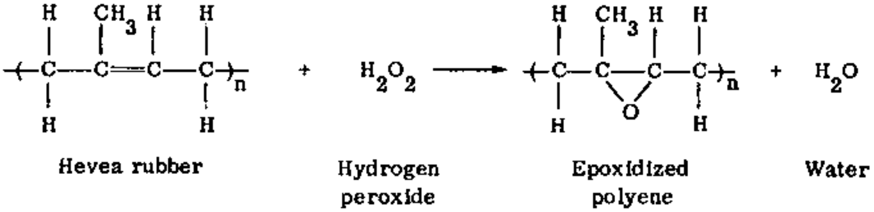
Staudinger prepared cyclized polydienes by heating rubber hydrochloride with zinc dust. Commercial cyclized rubber (Thermoprene and Pliolite) has been produced by heating rubber with sulfuric acid or Lewis acids, respectively. These cyclized products or isomerized polymers, which are soluble plastics, are used as adhesives and coatings.





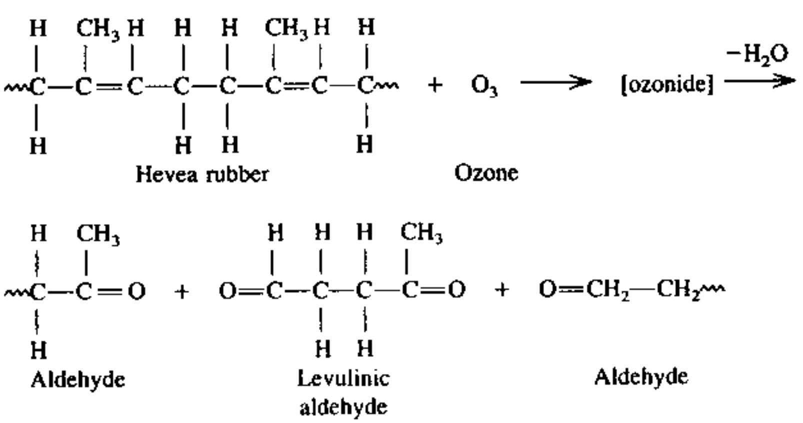
(15.5)

Hydrogen peroxide or peracetic acid is added to polyenes such as hevea rubber or unsaturated vegetable oils to produce epoxidized polybutadiene (Oxiron) or epoxidized vegetable oils, respectively. These products react readily with water, alcohols, anhydrides, and amines. The reaction product of hevea rubber and hydrogen peroxide is used as a specialty rubber. The reaction product of unsaturated vegetable oils is used as a PVC stabilizer.



(15.6)

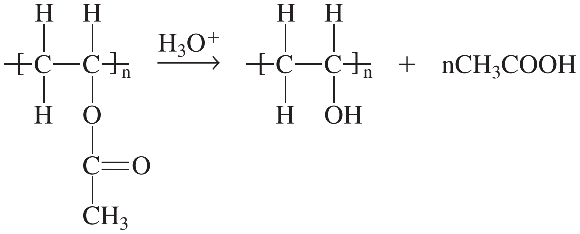
The reaction of ozone with polyenes yields ozonides which cleave to produce aldehydes in the presence of water and zinc dust. Since the ozonides are explosive, they are not usually isolated. As shown by the following equation, ozonolysis can be used as a diagnostic procedure to locate the position of the double bonds in polyenes.



(15.7)

15.3 REACTIONS OF ALIPHATIC PENDANT GROUPS

Esters such as poly(vinyl acetate) (PVAc) may be hydrolyzed to produce alcohols such as poly(vinyl alcohol) (PVA), which should have the same $\overline{DP}$ as the ester. In truth, PVAc contains some branching through the acetate portion that is eliminated upon hydrolysis. While the enol tautomer of acetaldehyde (vinyl alcohol) cannot be isolated, its water-soluble polymer can be obtained by the hydrolysis of any poly(vinyl carboxylic acid ester). The solubility of the product in water is dependent on the extent of hydrolysis.



$$\left[\mathrm{CH_2-CH(OCOCH_3)}\right]_n \xrightarrow{H_3O^+} \left[\mathrm{CH_2-CH(OH)}\right]_n + n\mathrm{CH_3COOH} \qquad (15.8)$$

Poly(vinyl acetate) Poly(vinyl alcohol) Acetic acid

The hydroxyl pendant groups in cellulose will form alkoxides with sodium hydroxide, and these alkoxides will produce ethers by the classic Williamson reaction. Thus, Suida produced methylcellulose in 1905 by the reaction of soda cellulose and methyl sulfate.

Alkylcellulose may also be produced by the reaction of soda cellulose and alkyl chlorides. Since these alkoxy pendant groups reduce the hydrogen-bonding forces, the partially reacted products are water soluble. This solubility in water will decrease as the degree of substitution (DS) increases.

$$\underset{\text{cellulose}}{\text{Cellulose—OH}} + \underset{\substack{\text{Sodium}\\\text{hydroxide}}}{\text{NaOH}} + \underset{\substack{\text{Alkyl}\\\text{chloride}}}{\text{RCl}} \rightarrow$$

$$\underset{\substack{\text{cellulose}\\\text{ether}}}{\text{Cellulose—OR}} + \underset{\substack{\text{Sodium}\\\text{chloride}}}{\text{NaCl}} + \underset{\text{Water}}{H_2O} \qquad (15.9)$$

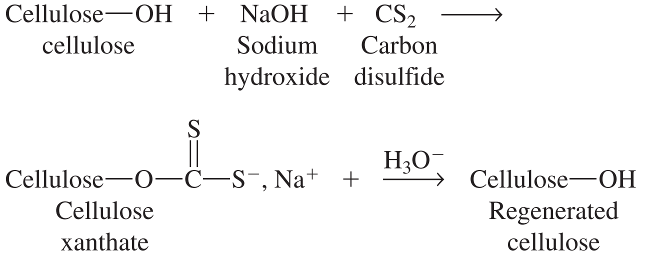
Methylcellulose is widely used as a viscosity improver and thickener. Ethylcellulose is used as a melt coating. One of the most widely used cellulosic ethers is carboxymethylcellulose (CMC). This water-soluble cellulosic derivative is produced by the reaction of soda cellulose and chloroacetic acid.

$$\underset{\text{cellulose}}{\text{Cellulose—OH}} + \underset{\substack{\text{Sodium}\\\text{hydroxide}}}{\text{NaOH}} + \underset{\substack{\text{Sodium salt}\\\text{of}\\\text{chloroacetic}\\\text{acid}}}{\mathrm{ClCH_2COONa}} \rightarrow \qquad (15.10)$$

$$\underset{\text{CMC}}{\text{Cellulose—}\mathrm{OCH_2COONa}} + \underset{\substack{\text{Sodium}\\\text{chloride}}}{\text{NaCl}} + \underset{\text{Water}}{H_2O}$$

CMC, with a DS of 0.5–0.8, is used in detergents and as a textile-sizing agent. Products with higher DS are used as thickeners and in drilling mud formulations. Aluminum or chromium ions will produce insoluble gels.

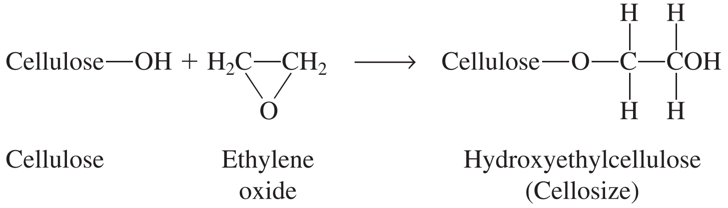
Water-soluble sodium cellulose xanthate, with a DS of about 0.5, is produced by the room temperature reaction of carbon disulfide and soda cellulose. Since xanthic acids are unstable, the cellulose is readily regenerated by passing extrudates into an acid bath. Rayon and cellophane are produced from cellulose xanthate in the viscose process.



$$\underset{\text{cellulose}}{\text{Cellulose—OH}} + \underset{\substack{\text{Sodium}\\\text{hydroxide}}}{\text{NaOH}} + \underset{\substack{\text{Carbon}\\\text{disulfide}}}{\text{CS}_2} \longrightarrow$$

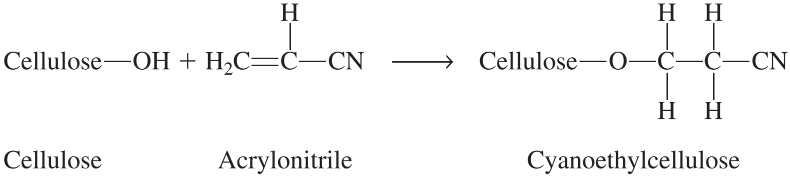
$$\underset{\substack{\text{Cellulose}\\\text{xanthate}}}{\text{Cellulose—O—}\overset{\overset{\text{S}}{\|}}{\text{C}}\text{—S}^-\text{, Na}^+} + \xrightarrow{H_3O^-} \underset{\substack{\text{Regenerated}\\\text{cellulose}}}{\text{Cellulose—OH}} \qquad (15.11)$$

Hydroxyethylcellulose and hydroxypropylcellulose are obtained from the reaction of soda cellulose and ethylene oxide or propylene oxide, respectively. The former (Cellosize) is used as a water-soluble sizing agent and descaling agent in boiler water.



$$\underset{\text{Cellulose}}{\text{Cellulose—OH}} + \underset{\substack{\text{Ethylene}\\\text{oxide}}}{\text{H}_2\text{C—CH}_2\text{(—O—)}} \longrightarrow \underset{\substack{\text{Hydroxyethylcellulose}\\\text{(Cellosize)}}}{\text{Cellulose—O—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{OH}} \qquad (15.12)$$

Cyanoethylcellulose is produced by the reaction of soda cellulose and acrylonitrile. This derivative is more resistant to abrasion and biological attack than is cellulose. Cyanoethylcellulose and graft copolymers of acrylonitrile and cellulose may be hydrolyzed to yield products with excellent water absorbency characteristics.

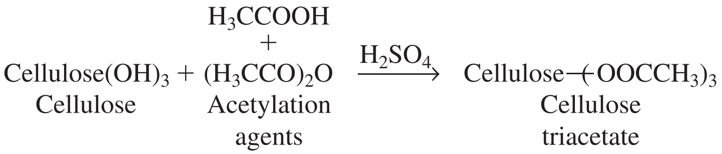


$$\underset{\text{Cellulose}}{\text{Cellulose—OH}} + \underset{\text{Acrylonitrile}}{\text{H}_2\text{C=}\overset{\text{H}}{\text{C}}\text{—CN}} \longrightarrow \underset{\text{Cyanoethylcellulose}}{\text{Cellulose—O—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—CN}} \qquad (15.13)$$

Cellulose nitrate (CN) (incorrectly called nitrocellulose) was one of the first synthetic plastics. The degree of substitution of CN is dependent on the concentration of the nitric acid used. The commercial product has a DS of about 2.0, corresponding to a nitrogen content of about 11%. Despite its flammability, CN plasticized by camphor is still used for personal accessories, toiletries, and industrial items. However, the principal use of CN is for coatings, in which the CN has a $\overline{\text{DP}}$ of 200 and a DS of about 2.0.

$$\underset{\text{Cellulose}}{\text{Cellulose}\text{—}(\text{OH})_2} + \underset{\substack{\text{Nitric}\\\text{acid}}}{2\text{HONO}_2} \xrightarrow{H_2SO_4} \underset{\substack{\text{Cellulose}\\\text{nitrate}}}{\text{Cellulose—(ONO}_2)_2} + \underset{\text{Water}}{2\text{H}_2\text{O}} \qquad (15.14)$$

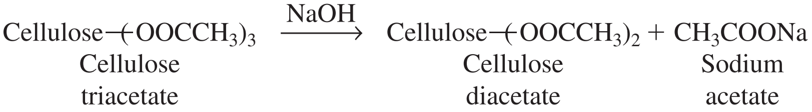
Cellulose triacetate (DS 2.8) was originally prepared by Schutzenberger and Naudine in 1865 by the reaction of cellulose with acetic acid and acetic anhydride in the presence of sulfuric acid. This ester, which has an acetyl content of 43%, is soluble in chloroform or in mixtures of methylene chloride and ethanol. When plasticized by ethyl phthaloyl ethyl glycolate, it is used as a film, a molding, and an extrusion. The unplasticized cellulose triacetate is used as a specialty fiber.



$$\underset{\text{Cellulose}}{\text{Cellulose(OH)}_3} + \underset{\substack{\text{Acetylation}\\\text{agents}}}{\overset{\substack{\text{H}_3\text{CCOOH}\\+}}{(\text{H}_3\text{CCO})_2\text{O}}} \xrightarrow{\text{H}_2\text{SO}_4} \underset{\substack{\text{Cellulose}\\\text{triacetate}}}{\text{Cellulose}\!-\!\!(\text{OOCCH}_3)_3} \qquad (15.15)$$

Cellulose diacetate may be produced directly by the acetylation of cellulose in a solution of dimethyl sulfoxide (DMSO) and formaldehyde, but this ester cannot be made directly from the acetylation of cellulose in a conventional process. The commercial product, which is also called secondary cellulose acetate ester, is produced by the partial saponification of cellulose triacetate.

Cellulose diacetate is widely used as extruded tape, in molded toys, electrical appliance housings, and sheet and blister packaging and fiber. Cellulose diacetate fiber, which is extruded from an acetone solution called "dope," is called acetate rayon.



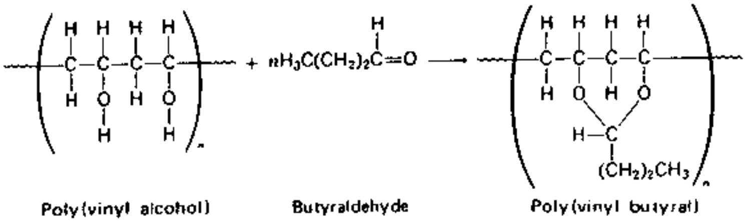
$$\underset{\substack{\text{Cellulose}\\\text{triacetate}}}{\text{Cellulose}\!-\!\!(\text{OOCCH}_3)_3} \xrightarrow{\text{NaOH}} \underset{\substack{\text{Cellulose}\\\text{diacetate}}}{\text{Cellulose}\!-\!\!(\text{OOCCH}_3)_2} + \underset{\substack{\text{Sodium}\\\text{acetate}}}{\text{CH}_3\text{COONa}} \qquad (15.16)$$

Cellulose propionate and cellulose acetate butyrate are also available commercially. These esters, which are more readily processed and more resistant to moisture than cellulose acetate, are used as sheets, tool handles, steering wheels, and for packaging.

In 1903 Edouard Benedictus, a French chemist, dropped a glass flask onto the floor. It broke, but the broken pieces retained the shape of the original flask instead of breaking into many pieces and scattering over the flood. He found that the inside of the flask had a thin film that was doing the "holding together." The film was the result of the evaporation of cellulose nitrate prepared from cotton and nitric acid. Shortly after the laboratory accident, he read about a girl who had been badly cut from flying glass resulting from an automobile accident. Latter he read about other persons being cut by flying glass in automobile accidents. He remembered the flask that did not break. He experimented with placing some of the cellulose nitrate between sheets of glass, using pressure to help adhere the glass with the cellulose nitrate. This was the first safety glass and it was called Triplex since it consisted of outer layers of glass and an inner layer of polymer. By 1909, Benedictus had patented the material and it came into use in automobiles.

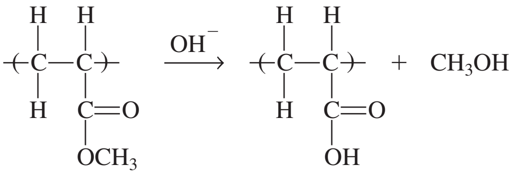
The first safety glass turned yellow after several years of exposure to light. The bonding layer was replaced in 1933 by cellulose acetate, made from the reaction of cotton with acetic acid. By 1939 this was replaced by poly(vinyl butyral).

Polyvinyl(vinyl formal) (PVF) and poly(vinyl butyral) (PVB) are produced by the reaction of poly(vinyl alcohol) (PVA) with formaldehyde or butyraldehyde, respectively. PVF has been used as a wire coating, and PVB forms the inner layer of safety-glass windshields. These products contain residual acetate and hydroxyl pendant groups.



(15.17)

Esters of polycarboxylic acids, nitrites, or amides may be hydrolyzed to produce polycarboxylic acids. Thus polyacrylonitrile, polyacrylamide, or poly(methyl acrylate) may be hydrolyzed to produce poly(acrylic acid).



$$\left(\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\underset{OCH_3}{C=O}}{C}}\right) \xrightarrow{OH^-} \left(\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\underset{OH}{C=O}}{C}}\right) + CH_3OH \qquad (15.18)$$

Poly(methyl acrylate)   Poly(acrylic acid)   Methanol

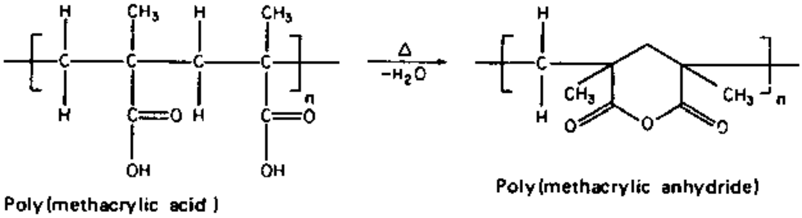
Poly(acrylic acid) and partially hydrolyzed polyacrylamide are used for the prevention of scale in water used for boilers and for flocculating agents in water purification. In the presence of aluminum ions, these polymeric acids produce flocs that remove impurities in water as they settle.

Neutralization of ionic polymers such as poly(acrylic acid) causes the now fully negatively charged carboxylate groups to repel one another, resulting in the chain changing conformation from that of a free-draining random shape to that approaching a rigid rod. This increase in length results in an increase in polymer viscosity. Polymer viscosity increases as the proportion of ionic groups increases. Addition of sodium chloride generally allows a return to a more random conformation and a subsequent decrease in viscosity.

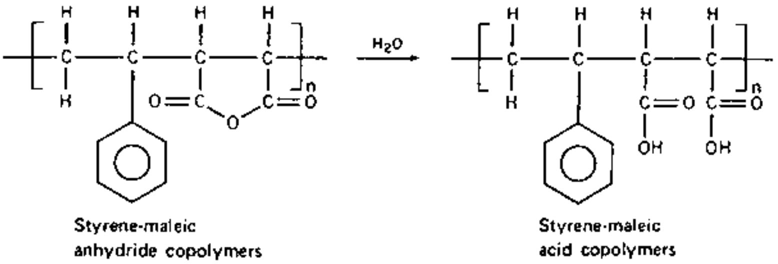
So-called supersluppers are generally starch with grafted acrylonitrile groups that in turn have been hydrolyzed giving sodium acrylate and acrylamide groups. Stirring can result in reduced viscosities when these materials are not crosslinked.

Some of the largest polymers, with molecular weights in of 10 million to 15 million daltons, contain sodium acrylate and acrylamide groups. Simple stirring can result in chain breakage for these materials. These copolymers are used in tertiary oil recovery and in water purification.

When heated, poly(methacrylic acid) loses water and forms a polymeric anhydride. The latter, as well as copolymers of maleic anhydride, such as styrene–maleic anhydride copolymers (SMAs), undergo characteristic anhydride reactions with water, alcohols, and amines to produce acids, esters, and amides.

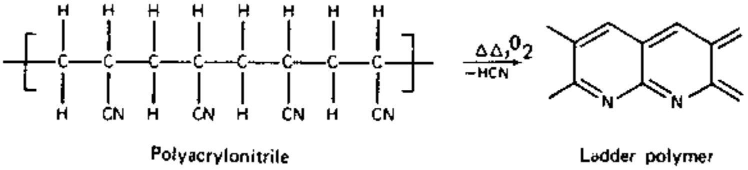


(15.19)



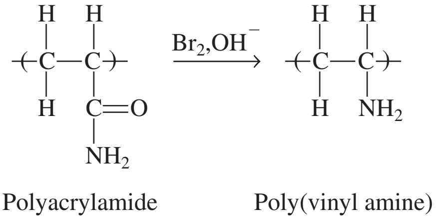
(15.20)

When heated, polyacrylonitrile forms a complex ladder polymer containing a quniazirine-like structure that approximates the structure shown below. This reaction is the first step in the formation of much of the carbon fibers (Sec. 15.11).



(15.21)

Poly(vinyl amine) is produced by the Hofmann degradation of polyacrylamide. Vinyl amine, like vinyl alcohol, is unstable. Thus its polymer is prepared by an indirect reaction. Poly(vinyl amine) is soluble in aqueous acids.

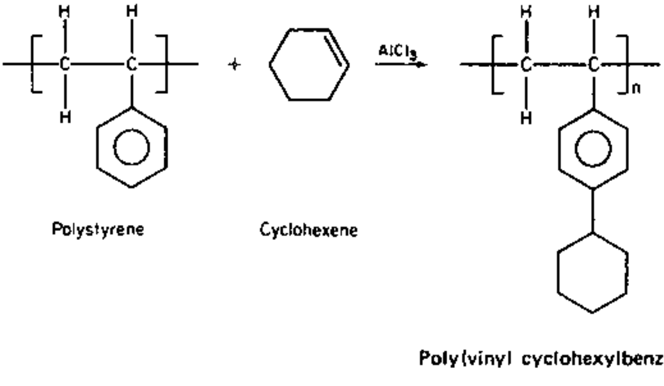


$$\left(\begin{array}{cc} \mathrm{H} & \mathrm{H} \\ | & | \\ \mathrm{C} & \mathrm{C} \\ | & | \\ \mathrm{H} & \mathrm{C{=}O} \\ & | \\ & \mathrm{NH_2} \end{array}\right) \xrightarrow{\mathrm{Br_2,OH^-}} \left(\begin{array}{cc} \mathrm{H} & \mathrm{H} \\ | & | \\ \mathrm{C} & \mathrm{C} \\ | & | \\ \mathrm{H} & \mathrm{NH_2} \end{array}\right) \qquad (15.22)$$

Polyacrylamide Poly(vinyl amine)

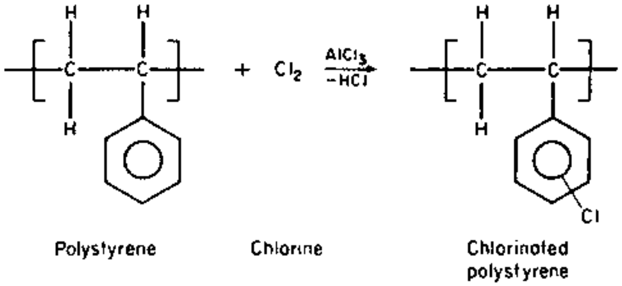
15.4 REACTIONS OF AROMATIC PENDANT GROUPS

Polymers with aromatic pendant groups, such as polystyrene, undergo all the characteristic reactions of benzene, such as alkylation, halogenation, nitration, and sulfonation. Thus, oil-soluble polymers used as viscosity improvers in lubricating oils are obtained by the Friedel-Crafts reaction of polystyrene and unsaturated hydrocarbons such as cyclohexene. Poly(vinyl cyclohexylbenzene) is produced in the latter reaction.



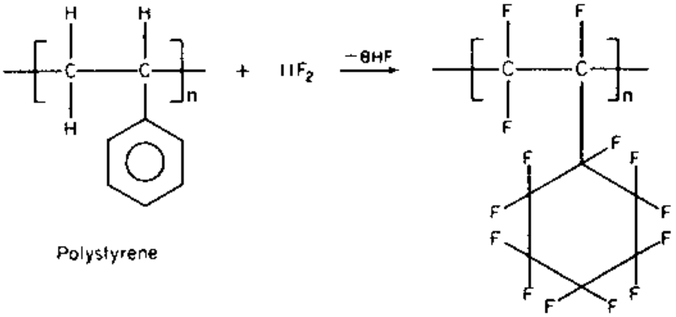
(15.23)

In the presence of a Lewis acid, halogens such as chlorine react with polystyrene to produce chlorinated polystyrene. The latter has a higher softening point than polystyrene.



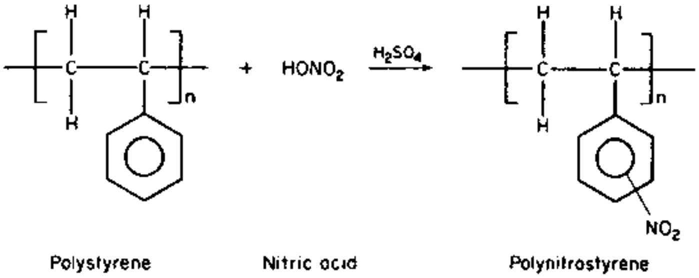
(15.24)

Perfluoropolystyrene is produced by the reaction of fluorine and polystyrene. This reaction may also be run on the surface (topochemical) of polystyrene articles.



(15.25)

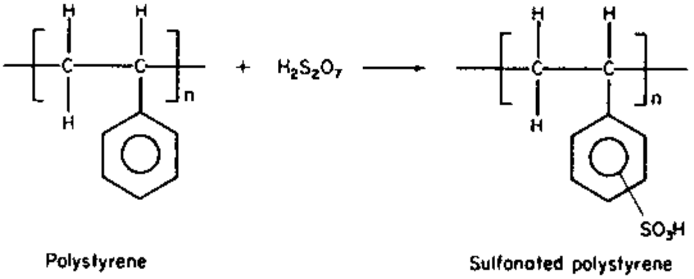
Polynitrostyrene is obtained by the nitration of polystyrene. The latter may be reduced to form polyaminostyrene. Polyaminostyrene may be diazotized to produce polymeric dyes.



(15.26)

Polystyrene and other aromatic polymers have been sulfonated by fuming sulfuric acid. Sulfonated crosslinked polystyrene has been used as an ion exchange resin.

So-called living polymers (cation propagation) can be used to form a variety of products through reaction with hydroxyl and dihydroxyl products (including hydroxyl-terminated polymers). 1,3-butadiene forming block copolymers, and reaction with ethylene oxide forming hydroxyl-terminated telechelic and macromers.



(15.27)

15.5 REACTIONS OF POLYAMIDES

Polyamides such as proteins or nylons may be reacted with ethylene oxide or formaldehyde. The latter serves as a crosslinking agent with proteins in embalming, leather production, and the stabilization of regenerated protein fibers.

15.6 POLYMERIZATION REACTIONS

The crosslinking of many thermosetting resins, such as novolac phenolic resins, takes place during the molding operation. Polymerization also occurs during the production of polyurethane (PU) foams and molded products. The latter are produced when liquid reactants are introduced in the injection molding press. One process is called liquid injection molding (LIM) and the other is called reaction injection molding (RIM). The latter has been used to mold automotive fascias, bumpers, and flexible fenders.

15.7 GENERAL DEGRADATION

Some reactions on polymers are intended and give a material with different desired properties. The (positive) modification of polymers is an area of vigorous activity. Other reactions on polymers are unintended and generally result in a material with unfavorable properties. Included in the latter are a whole host of polymer degradation reactions. Some of these degradation reactions are covered elsewhere (namely, 15.8, 15.16, and 17.12). Here we will focus on some general concepts. Degradation can be promoted by many means and any combination of means. The major means of polymer degradation are given in Table 15.1.

Table 15.1 Major Synthetic Polymer Degradative Agents

Degradation agent	Most susceptible polymer types	Examples
Acids and bases	Heterochain Polymers	Polyesters, polyurethanes
Moisture	Heterochain polymers	Polyesters, nylons, polyurethanes
High-energy radiation	Aliphatic polymers with quarternary carbons	Polypropylene, LDPE, PMMA, Poly(α-methylstyrene)
Ozone	Unsaturated polymers	Polybutadienes, polyisoprene
Organic liquids/vapors	Amorphous polymers	
Biodegradation	Heterochain polymers	Polyesters, nylons, polyurethanes
Heat	Vinyl polymers	PVC, poly(α-methylstyrene)
Mechanical (applied stresses)		

Backbone chain scission degradation can be divided as occurring via depolymerization, random chain breakage, weak-link or preferential site degradation, or some combination of these general routes. In depolymerization monomer is split off from an activated end group. This is the opposite of the addition polymerization and is often referred to as “unzipping.”

$$\mathrm{P{-}MMMMMMMM} \xrightarrow{-\mathrm{M}} \mathrm{P{-}MMMMMMM} \xrightarrow{-\mathrm{M}}$$

$$\mathrm{P{-}MMMMMMM} \xrightarrow{-\mathrm{M}} \mathrm{P{-}MMMMM} \xrightarrow{-\mathrm{M}} \text{etc.}$$

Chain scission is similar to the opposite of stepwise polycondensation where units are split apart in a random manner.

$$\mathrm{P_m{-}P_n} \rightarrow \mathrm{P_m} + \mathrm{P_n}$$

Depolymerization can result in backbone degradation and/or in the formation of cyclic (Sec. 15.11) or other products. The thermal degradation of PVA and PVC occurs with the splitting out of water or HCl followed by a combination of further chain degradation to give finally small products and formation of complex cyclic products. Elimination of HCl further accelerates additional HCl elimination and increased property loss. PVC degradation is decreased by addition of agents that impede degradation such as those that neutralize HCl, trap free radicals, and/or that react with the forming double bonds to impede further depolymerization. Commercial PVC often contains organotin or antimony mercaptide compounds that act as stabilizers (Sec. 14.3).

In general, for vinyl polymers thermal degradation in air (combustion) produces the expected products of water, carbon dioxide, and char along with numerous hydrocarbon products. Thermally, simple combustion of polymeric materials gives a complex of compounds that varies according to the particular reaction conditions. Application of heat under controlled conditions can result in true depolymerization generally occurring via an unzipping. Such depolymerization may be related to the ceiling temperature of the particular polymer. Polymers such as poly(methyl methacrylate) (PMMA) and poly (α-methylstyrene) depolymerize to give large amounts of monomer when heated under the appropriate conditions. Thermal depolymerization generally results in some char and formation of smaller molecules including water, methanol, and carbon dioxide.

Most polymers are susceptible to degradation under natural radiation, sunlight, and high temperatures even in the presence of antioxidants. Thus, LDPE sheets, impregnated with carbon black, become brittle after exposure to one year’s elements in South Florida. HDPE, while more costly, does stand up better to these elements, but again after several seasons, the elements win and the HDPE sheets become brittle and break. Long-term degradation is often signaled for clear polymers by a yellowing and a decrease in mechanical properties.

Most polymers are subject to oxidative degradation, particularly in the presence of other “enticers” such as heat, a good supply of air, various catalysts, high-energy radiation including UV and higher energy visible light, and mechanical stressing that not only exposes additional polymer to the “elements” but also brings about the actual breakage of bonds subsequently leading to additional breakdown (Sec. 15.16).

While polymers that contain sites of unsaturation, such as polyisoprene and the polybutadienes, are most susceptible to oxygen and ozone oxidation, most other polymers also show some susceptibility to such degradation including natural rubber, polystyrene, polypropylene, nylons, polyethylenes, and most natural and naturally derived polymers.

Because of the prevalence of degradation by oxidation, antioxidants (Sec. 14.3) are generally added. These antioxidants are generally compounds that readily react with free radicals or those that may act to lessen the effects of “enticers” such as UV radiation.

Mechanical degradation, while applied on a macro level, can result not only in chain rearrangement but in chain degradation. Such forces may be repetitive or abrupt, and may act on the polymer while it is in solution, melt, elastic, or below its T_g. Passage of polymer melts through a tiny orifice for fabrication purposes can result in both chain alignment and chain breakage. In the case of rubber, mastication of the elastomer, breaking polymer chains, is intentional, allowing easier deformation and processability. While shearing itself can result in chain breakage, chain breakage is often associated with localized heat buildup that is a consequence of chains “rubbing” together, etc. (molecular friction).

Most heterochained polymers, including condensation polymers, are susceptible to aqueous associated acid or base degradation. This susceptibility is due to a combination of the chemical reactivity of heteroatom sites and the materials being at least wetted by the aqueous solution, allowing contact between the proton or hydroxide ion to occur. Both of these factors are related to the difference in the electronegative of the two different atoms resulting in the formation of a dipole that acts as a site for nucleophilic/electrophilic chemical attack and that allows polar materials to come in contact with it. Such polymers can be partially protected by application of a thin film of hydrocarbon polymer that acts to repeal the aqueous solutions.

Enzymatic degradation is complex and not totally agreed on (Sec. 17.12). Microbes have enzymes, some of which are capable of breaking selected bonds such as those that appear naturally, including amide, ester, and ether linkages, and including both natural, naturally derived, and synthetic materials. While a purpose of these enzymes is to digest nutrients for the host, when polymers with susceptible linkages come in contact with a microbe that contains appropriate enzymes, polymer degradation can occur. While often similar to acid-and base-associated degradations, enzymatic degradations are more specific bringing about only specific reactions. Even so, it is often difficult to differentiate between the two and both may occur together.

Some polymer deterioration reactions occur without loss in molecular weight. These include a wide variety of reactions where free radicals (most typical) or ions are formed and crosslinking or other non–chain session reaction occurs. Crosslinking discourages chain and segmental chain movement. At times this crosslink is desired such as in permanent press fabric and in elastomeric materials. Often, though, the crosslinks bring about an increased brittleness beyond that desired. Some degradation reactions occur without an increase in crosslinking or a lessening in chain length. Thus, minute amounts of HCl, water, ester, etc., elimination can occur with vinyl polymers giving localized sites of double-bond formation. Because such sites are less flexible and because such sites are more susceptible to further degradation, these reactions are generally considered as unwanted.

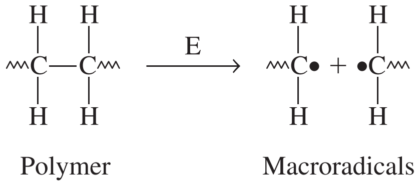
Crosslinking reactions can give products with desired increased strength, memory retention, etc. But accompanying such crosslinking may be unwanted increases in brittleness. Throughout the text, crosslinking is an important reaction that allows the introduction of desirable properties. For instance, crosslinking is the basis for many of the elastomeric materials.

15.8 DEGRADATION OF POLYMERS

In many chemical reactions with pendant groups, such as the hydrolysis of ester groups, the polymer is said to be degraded. However, since the degree of polymerization is unchanged, the integrity of the polymer chain is maintained. However, the DP is decreased when chain scission degradation occurs, and this type of degradation will be emphasized in this section.

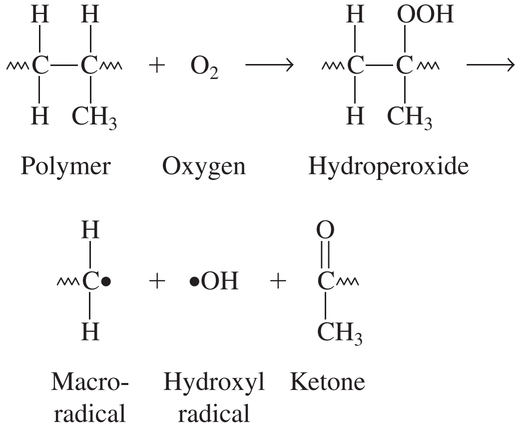
Saturated linear polymers such as HDPE are resistant to degradation, but slow degradation will occur in the presence of oxygen. UV light, heat, and impurities. Since tertiary carbon atoms are more readily attacked, polypropylene is less resistant to degradation than HDPE. Unsaturated polymers are even less resistant to degradation as evidenced by the ozonolysis of hevea rubber and the degradation of dehydrohalogenated PVC.

The kinetics of random chain scission are essentially the reverse of those in stepwise propagation. Much information on this type of degradation has been obtained from studies of the acid-catalyzed homogeneous degradation of cellulose in which $\overline{\mathrm{DP}}^{-1}$ increases with time. The initial degradation of polymeric hydrocarbons is usually the result of homolytic cleavage at weak points in the polymer chain. As shown in Eq. (15.28), the initial products are macroradicals.



$$\sim\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\sim \xrightarrow{\mathrm{E}} \sim\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\bullet + \bullet\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\sim \qquad (15.28)$$

As shown in Eq. (15.29), hydroperoxides are formed in the presence of oxygen. These readily cleaved hydroperoxides also yield macroradicals.



$$\sim\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{H}}{\mathrm{C}}}\sim + \mathrm{O_2} \longrightarrow \sim\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{OOH}}{\mathrm{C}}}\sim \longrightarrow \sim\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\bullet + \bullet\mathrm{OH} + \underset{\mathrm{CH_3}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}}\sim \qquad (15.29)$$

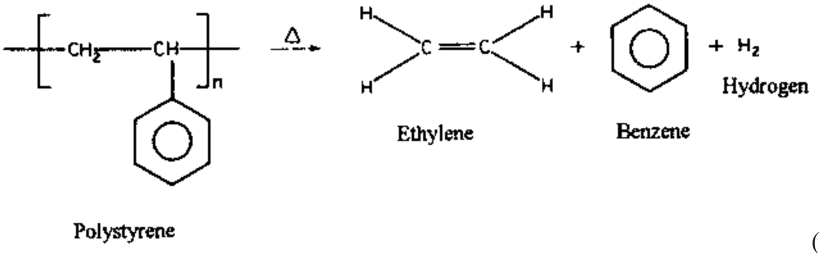
Oxidizing acids such as concentrated nitric acid will also cause scission at weak links. This hypothesis is verified by the attack by nitric acid on the folds of polyethylene crystals to produce α,ω-dicarboxylic acids. Acids and alkalies will also hydrolyze ester and amide linkages in the polymer chain.

While most polymers undergo random chain scission, polymers derived from 1,1-disubstituted vinyl monomers, such as poly(methyl methacrylate) (PMMA), depolymerize or unzip quantitatively when heated above the ceiling temperature (T_c). In contrast, polymers derived from monosubstituted vinyl monomers, such as polystyrene, degrade by both depolymerization and random chain scission reactions. Since higher temperatures favor the former, more than 85% styrene monomer is produced at 725°C.

Some degradation occurs when polymers are irradiated, but crosslinking is the predominant reaction. Thus, thermoplastic coatings may be applied and crosslinked by radiation after application.

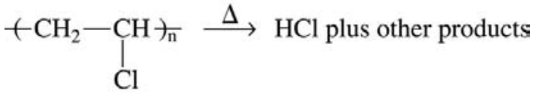
Today major items related to the topic of polymer degradation involve degradation of polymers for potential reuse of the degradation products and degradation of polymers as a "garbage" material.

Polystyrene gives different thermal degradation products dependent on the exact degradation conditions. Under one set of conditions the major products are benzene, hydrogen, and ethylene, all three of which are usable chemical molecules.



(15.30)

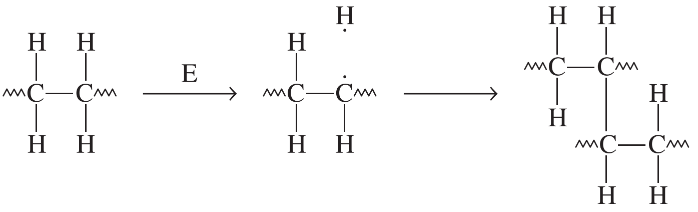
A major problem in the burning of polymers containing halogens, such as poly(vinyl chloride), is the emission of the hydrogen halide (e.g., hydrogen chloride), which is quite dangerous to human and plant life and is a major problem in the deterioration of commercial incinerators.



$$-\!\!\left(\mathrm{CH_2}-\underset{\displaystyle \mathrm{Cl}}{\underset{|}{\mathrm{CH}}}\right)_{\!n} \xrightarrow{\Delta} \text{HCl plus other products} \qquad (15.31)$$

Poly(vinyl chloride)

Radiation is also responsible for the deterioration of many polymeric materials. Radiation can form macroradicals as noted in Eqs. (15.28) and (15.32). Depending on the fate of the newly formed, energetic free radical, chain scission may occur, resulting in a decreased molecular weight, or crosslinking may occur which increases the stiffness of the material but may eventually lead to the formation of a hard, brittle material with little toughness.



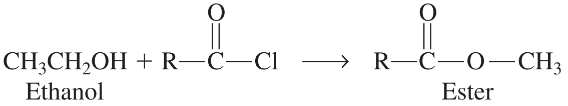
$$\sim\!\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{H}}{\overset{|}{\underset{|}{\mathrm{C}}}}}-\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{H}}{\overset{|}{\underset{|}{\mathrm{C}}}}}\!\sim \xrightarrow{E} \sim\!\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{H}}{\overset{|}{\underset{|}{\mathrm{C}}}}}-\overset{\displaystyle \mathrm{H}\cdot}{\underset{\displaystyle \mathrm{H}}{\underset{|}{\dot{\mathrm{C}}}}}\!\sim \longrightarrow \begin{array}{c} \sim\!\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{H}}{\overset{|}{\underset{|}{\mathrm{C}}}}}-\overset{\displaystyle \mathrm{H}}{\overset{|}{\mathrm{C}}}\!\sim \\ \quad | \\ \sim\!\underset{\displaystyle \mathrm{H}}{\underset{|}{\mathrm{C}}}-\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{H}}{\overset{|}{\underset{|}{\mathrm{C}}}}}\!\sim \end{array} \qquad (15.32)$$

Radiation-induced reactions occur on and within the body and are particularly important in materials exposed to the outdoors such as human skin and exterior house paints. Specific agents such as UV stabilizers are common additives to exterior paints. Such degradation typically occurs with UV and more energenic radiations but can occur with lower energy radiation (such as microwave) if the energy is quite intense.

For space exploration, high-energy radiation and the formation of ionic and free radical species are important causes of polymer degradation. Torre and Pippin recently noted the importance of atomic oxygen in materials degradation in long-term missions at low Earth orbitals. In general, increases in bond strength and bulk improve stability to atomic oxygen. For instance, the bond strength for C-F is about 20% greater than the C-H bond strength. Complete fluoridation of the ethylene structure (polytetrafluoroethylene) decreases the loss rate by a factor of 12 relative to polyethylene.

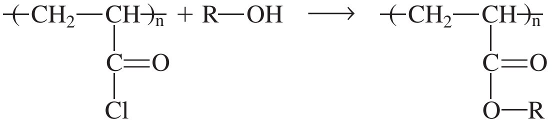
15.9 CONDENSATION AND CHELATION REACTIONS

In a broad sense, reactions that occur with smaller molecules also occur with macromolecules. Thus, reactions of acid chlorides with alcohols to give esters can occur whether the acid chloride is contained within a small molecule,



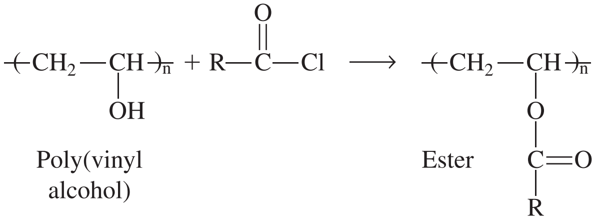
$$\underset{\text{Ethanol}}{CH_3CH_2OH} + R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \longrightarrow \underset{\text{Ester}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3} \tag{15.33}$$

within a polymer,



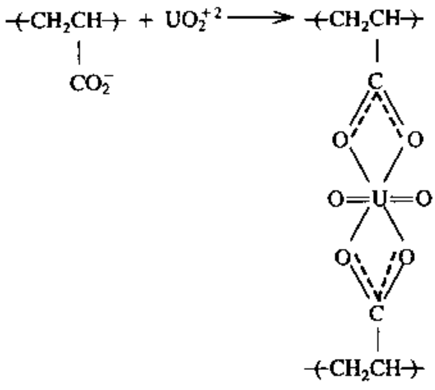
$$-\!\left(CH_2-\underset{\substack{|\\ C=O\\ |\\ Cl}}{CH}\right)_{\!n} + R-OH \longrightarrow -\!\left(CH_2-\underset{\substack{|\\ C=O\\ |\\ O-R}}{CH}\right)_{\!n} \tag{15.34}$$

or whether the alcohol is contained within a small molecule such as in Eq. (15.33) or within a polymer such as poly(vinyl alcohol).



$$\underset{\text{Poly(vinyl alcohol)}}{-\!\left(CH_2-\underset{\substack{|\\ OH}}{CH}\right)_{\!n}} + R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \longrightarrow \underset{\text{Ester}}{-\!\left(CH_2-\underset{\substack{|\\ O\\ |\\ C=O\\ |\\ R}}{CH}\right)_{\!n}} \tag{15.35}$$

This is true for both condensation reactions such as those noted above or for chelation reactions such as the following.



(15.36)

These reactions can occur with synthetic polymers and with natural macromolecules such as cellulose, proteins, and nucleic acids.

For most of these chemical modifications, special interactions may be important and can result in the reaction rate being greatly enhanced or decreased. Overberger and others have demonstrated many cases where polymers act as catalysts assisting the modification of the polymer, or specific polymers assisting "small molecule" reactions.

15.10 CROSSLINKED MATERIALS

Crosslinking reactions are commonplace for both natural and synthetic polymers. These crosslinks can act to lock in "memory" preventing free-chain movement. Some crosslinking can be desirable but can also give undesired properties. Crosslinking between chains does prevent free-chain movement often resulting in an increased strength, but also decreased flexibility and increased brittleness. (Such is often the world of polymers where there are apparent tradeoffs but where polymer scientists attempt to balance or circumvent the situation through structure and processing modifications.) Such crosslinking typically gives a product with poor or no solubility and can give an extended network product. Crosslinking discourages creep. Crosslinking within a polymer chain generally decreases chain mobility and crystallinity because the crosslinked moiety generally restricts at least local mobility and because it generally introduces unlike sites within the polymer chain.

Crosslinking can also be the result of the use of reactants that have a functionality greater than 2.

Physical crosslinking occurs when long chains entangle, effectively forming chemical "knots" between the various chains. Effects similar to those introduced through chemical crosslinking can also be accomplished through the use of sufficiently strong secondary bonding. Here we will consider only chemical crosslinking.

Crosslinking can occur without the addition of an external chemical agent or, as in the case of vulcanization, an external agent, a crosslinking agent, that is involved in the crosslinking is introduced.

Crosslinking can be effected through application of heat, mechanically, through exposure to ionizing and nonionizing (such as microwave) radiation, through exposure to active chemical agents, or through any combination of these.

While most crosslinking is not easily reversible, elastomeric ionomers can be considered as thermosets that can be processed as thermoplastics.

The progress of formation of a network polymer has been described using a variety of approaches. As the extent of crosslinking increases there is a steady increase in the viscosity of the melt. At some extent of crosslinking, there is a rapid increase in viscosity and the mixture becomes elastic and begins to feel like a rubber. At this point the mixture is said to be "gelled." Beyond this point the polymer is insoluble. Crosslinking can continue beyond this gel point.

Flory and others derived expressions describing the extent of reaction at the gel point using statistical methods. In general, the M_w at an extent of reaction p can be described by the expression

$$M_{w,p} = \frac{M_{w,0}\,(1 + p)}{(1 - p)(f - 1)} \tag{15.37}$$

where $M_{w,0}$ is the weight-average molecular weight at no reaction and $M_{w,p}$ is the weight average molecular weight at an extent of reaction p and f is the functionality. At the gel point, M becomes quite large approaching infinity, giving eventually

$$p_{gel} = 1/(f - 1) \tag{15.38}$$

For a system containing two types of functions

$$(p_{gel})^2 = \frac{1}{r(f' - 1)(f'' - 1)} \tag{15.39}$$

where r is the ratio of the two types of functionality f′ and f″.

This equation is valid when the ratio of the two types of reactant groups is about equal and where the reactivity of members within each of the two types is about the same, and finally when the reactivity of the two types of sites does not change during the process.

For the case where crosslinking occurs with the crosslinking sites contained in already formed polymer chains, average functionalities can be calculated based in terms of the weight average or number-average molecular weight. For the weight-average molecular weight the average degree of polymerization, DP_w, can be described where M_c is the weight-average molecular weight between crosslinkable sites and p is the fraction of repeat units reacted, i.e., the degree of conversion.

$$DP_w = \frac{M_w}{M_c} = \frac{f(1 + p)}{(1 - p)(1 - f)} \tag{15.40}$$

If $DP_{w,0}$ is the weight average degree polymerization of the initial mixture of long chains, then

$$DP_w = \frac{DP_{w,0}(1 - p)}{(1 - p)(DP_{w,0} - 1)} \tag{15.41}$$

and at the gel point the degree of polymerization approaches infinity giving

$$p_{gel} = 1/(DP_{w,0} - 1) \tag{15.42}$$

Equating the two equations for p_{gel} gives

$$DP_{w,0} - 1 = f - 1 \tag{15.43}$$

Similar expressions can be derived based on the number-average molecular weight so that at the gel point

$$p_{gel} = 1/DP_{n,0} \tag{15.44}$$

The degree of crosslinking can be expressed in terms of crosslinks per gram or per unit volume. If C is the moles of crosslinks per unit volume, n the number of network chains per unit volume, d the density of crosslinked polymer, and M_c the number-average molecular weight of the polymer segments between crosslinks, then

$$C = n/2 = d/2M_c \tag{15.45}$$

such that the number of moles of crosslinks per gram of network polymer is $1/2M_c$.

Swelling and mechanical measurements are generally employed to experimentally determine the degree of crosslinking.

Table 15.2 Industrially Important Crosslinked Polymers

Polymer type	Description
Phenol and amino resins	Sec.7.14
Alkyd resins (drying oils)	Sec. 7.5
Unsaturated polyesters	Sec. 7.5
Epoxy resins	Sec. 7.11
Concrete	Sec. 12.2
Silicon dioxide	Secs. 12.4–2.7, 15.9
Carbon	Secs. 12.9, 12.10
Siloxanes	Sec. 11.3
Isocyanates	Secs. 7.11, 10.4, 10.6
Acrylic copolymers	Secs. 10.3, 10.6
Unsaturated hydrocarbons	Secs. 10.6, 15.1, 15.2, 17.2
Saturated hydrocarbons	Secs. 10.4 to 10.6
Halogen-containing hydrocarbons	Secs. 10.6
Ionomers	Secs. 10.4, 10.6

Table 15.2 contains examples of crosslinked polymers that have industrial importance along with locations in the text where they are discussed in some detail.

15.11 INTERNAL CYCLIZATION

There are a number of important polymers that are formed through internal cyclization. In almost all cases these are five- and six-membered rings with the vast majority being six-membered. The tendency to form six-membered rings is related to a statistical feature. In studying the most probable distances from the beginning point using random statistics for units with a bond angle of about 109.5° (a tetrahedral), the most probable distance for a chain six units long is back at the starting point. The number of units required before the most probable distance is the starting point is dependent on the bond angle and is called the Kuhn element. As note before, the Kuhn element for connected methylenes is six. The Kuhn element for sp^2 geometry is not six, but in this case, the driving force is the formation of six-membered rings with three alternating π bonds, i.e., the formation of the aromatic structure.

Often these internal cyclizations are incomplete giving products with mixed moieties. Even so, such internal cyclization is the source of a number of interesting and important polymers.

A number of ladder-like structures have been synthesized from the internal cyclization of polymers. Following are several examples that illustrate this. The most important commercial products are those utilized to form the so-called “carbon fibers.”

Carbon fibers and associated composite materials are the result of internal cyclization. Polyacrylonitrile, when heated, undergoes internal addition forming a condensed polycyclic material called “black orlon” (Sec. 9.4). Further heating to about 1000°C removes the hydrogen atoms and most of the nitrogens giving a polyaromatic structure containing about 95% carbon (Fig. 15.1). Further heating to about 2800°C gives a product with almost 99% carbon. These products can be forced through tiny holes to form tiny fiber-like materials (fibrals) that are combined to give fibrous-like materials that can finally

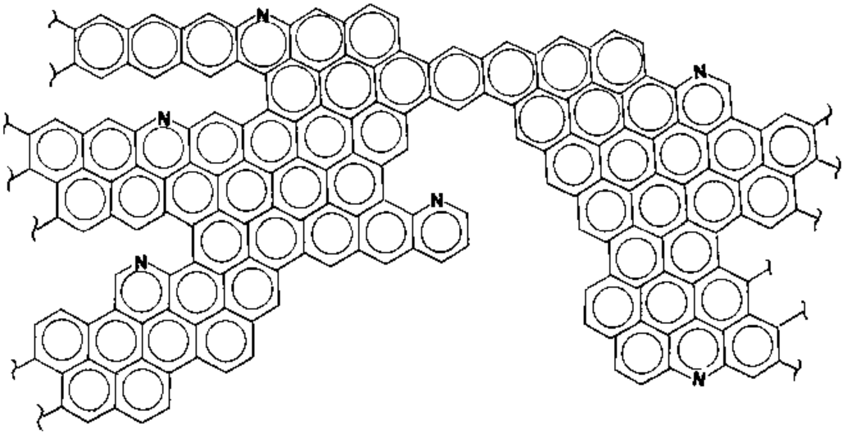


Figure 15.1 Idealized structure of “black orlon.”

be woven together to give fabrics. The fibrals, fibers, and fabrics act as the fibrous portion of many high-strength composite materials (Sec. 13.5). These fibers are light-weight, very strong, chemically inert, and can form semiconductors and conductor materials.

Carbon forms a number of important allotropic materials. Along with the carbon fibers noted before, pyrolysis of carbon-containing materials can give carbon black and graphite (Sec. 12.10). Diamonds can be formed (Sec. 12.9) under high temperature and pressure. Carbon black is a mixture of moieties generally obtained from the incomplete combustion of hydrocarbons, but carbon black can be obtained from the burning of most carbon-intense materials. Carbon black exists as chains of carbon atoms. Commercial grade carbon black is used in tires, inks, water purification, paints, and batteries. All three of these are formed naturally, although they are also produced commercially.

A new class of carbon-based materials were first characterized in 1985. They are often called “buckeyballs” named after the geodesic domes of Buckminster Fuller. These molecules are now called fullerenes. Fullerenes are polygon-like structures whereby each connective point contains a carbon. Thus, C_{60} has the geometry of a truncated icosahedron with 12 pentagonal faces and 20 hexagonal faces. The seams of a soccer ball have this shape. Dependent on the particular structure, treatment, and surrounding environment, fullerenes can be made that are conductors, insulators, or semiconductors.

There are a number of so-called nanotubes. Many of these are formed through self-assembly of peptides (Sec. 15.13). The nanotube structure is varied dependent on the particular amino acids in the peptide.

Carbon nanotubes are formed from exposing graphite, heated to about 1200°C, to a high-energy laser beam. Parts of the graphite are vaporized with some forming nanotubes upon cooling. These nanotubes can be considered as elongated fullerenes, cylindrical graphite, or hollow carbon fibers (above). Their synthesis is an example of internal polymer cyclization reactions. They are composed of a hollow tube with fused hexagonals forming the outer skin. These nanotubes are about 1/50,000 the width of a strand of human hair.

Carbon nanotubes come in different diameters and lengths. Below (Fig. 15.2) is an illustration of one nanotube in terms of a skeletal and a space-filling model. Different sized nanotubes have differing properties and capabilities.

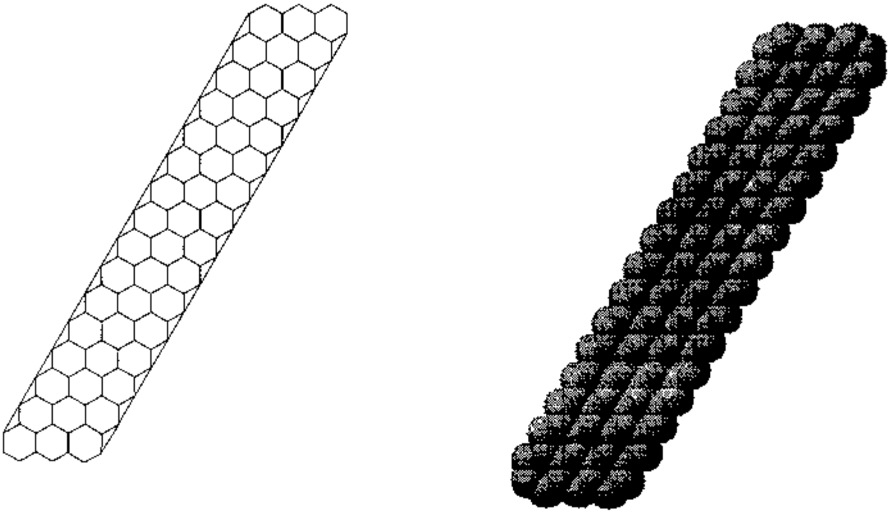


Figure 15.2 Skeletal (left) and space-filling (right) models of a representative carbon-based nanotube.

As with fullerenes, the nanotubes can be conductors, insulators, or semiconductors. When the carbon rings are lined up with the main axis of the nanotube, the nanotube conducts electrical charge. When the hexagonal rings are twisted, the nanotube acts as a semiconductor or nonconductor. When two nanotubes are joined, one nanotube a conductor and the second a semiconductor, the junction acts as a diode, permitting current to flow in only one direction.

Small diameter, such as 4 Å, non-doped carbon nanotubes are also "one-dimensional" superconductors at relatively high temperatures (about 20 K). The smaller diameter tubes offer greater curvature of the tube that increases the interaction between the electrons and the lattice vibrations known as phonons that are necessary for superconductivity. For comparison, alkali metal doped fullerenes superconduct at temperatures to 40 K and electron hole-doped fullerene crystals superconduct at 52 K.

Along with the useful electrical properties, carbon nanotubes are also very strong, offering a material that is hundreds of times stronger than steel on a weight basis. They also exhibit interesting catalytic properties.

Many of the applications of carbon nanotubes utilize groups or bundles of nanotubes. We often think that the behavior of a material is independent of the amount of material present. We know that this is not the case when there are large surface-area-to-bulk ratios and that there is a tradeoff between so-called bulk properties and properties based on surface area when the surface-area-to-bulk ratios are large. Many of the nanomaterials have large enough surface-area-to-bulk ratios so that these surface properties become important. Bundles of carbon nanotubes have been made into electrodes that expand and contract in response to applied voltage. These are electromechanical actuators (Smart Materials, Sec. 18.5), i.e., materials that convert electrical energy to mechanical energy. Mechanical actuation occurs because the nanotubes are "injected" with an electrical change. An electrode is made using two-sided Scotch tape and arranging the nanotubes on both sides of the tape. As with a supercapacitor, the charge is balanced at the opposite electrode giving an electrochemical double-layer charge, possible because of the high surface area of the nanotubes. When voltage is applied, the electrodes bend because of the unequal expansion of the nanotube-constructed electrodes. While both sides of the tape elongate, one side experiences greater elongation acting to coil over its partner.

Diene polymers undergo cyclization in the presence of cationic initiators such as sulfuric acid; 1,2- and 3,4-diene polymers undergo this cyclization forming extensive fused ring groupings.

The polymerization of butadiene using certain catalytic systems such as butyllithium and tetramethylenethylene diamine gives poly(1,2-polybutadiene). The polybutadiene, in turn, can undergo internal cyclization reactions via cationic reactions forming a sort of linear saturated polycyclohexane. Further heating, resulting in dehydrogenation, with chloranil gives a fused ring product similar to that of carbon fibers when heated to about 1500°C. This material is sold under the trade name of Pluton by 3M. This sequence is depicted below (Fig. 15.3). While the final product is insoluble and infusible, prespinning is done on the soluble saturated intermediate. Other materials have been successfully heated to give high-strength carbon fiber–like products including rayon, PVC, and PPO.

Related to these are the formation of a conjugated but not fully aromatic ladder polymer containing fused cyclohexane rings from the thermal reaction of poly(methylvinyl ketone) with the elimination of water at about 300°C. This reaction illustrates the partial

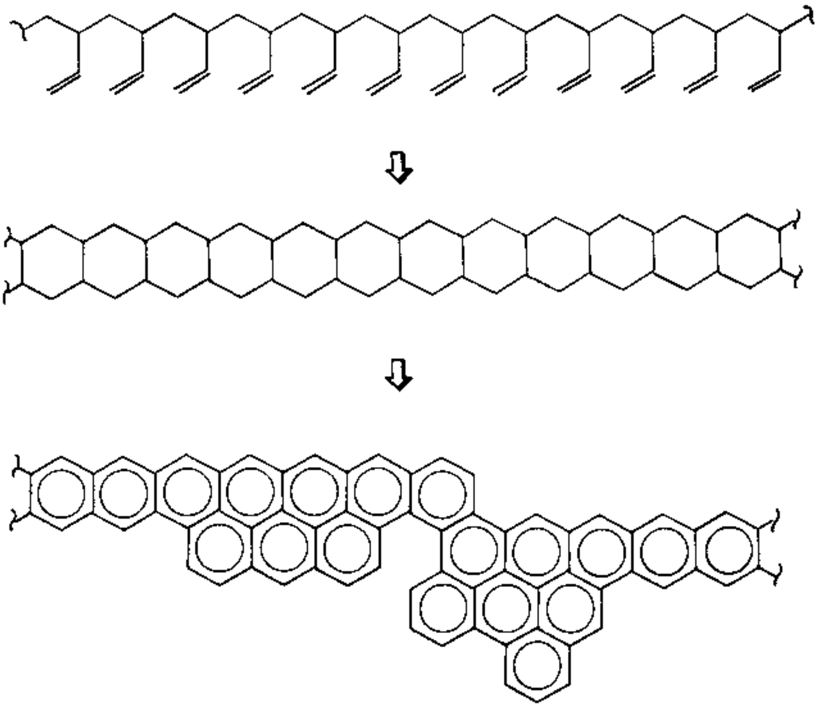
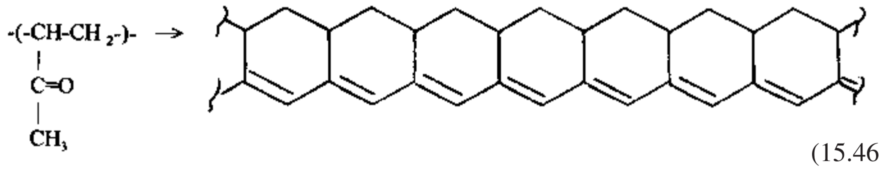


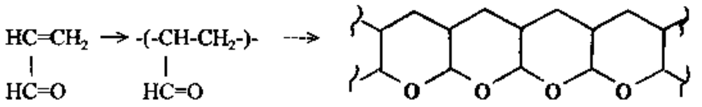
Figure 15.3 Idealized structures for the synthesis of carbon-like materials from poly(1,2-butadiene).

conversion that generally occurs with most synthetic procedures utilizing polymers such as poly(methyl vinyl ketone) giving only about 90% conversion.



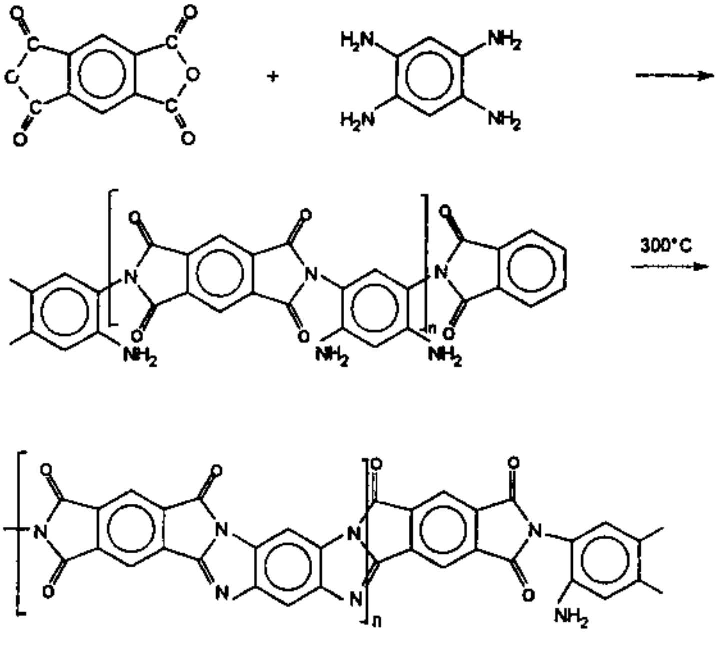
(15.46)

Poly(vinyl aldehyde), synthesized from the free radical polymerization of acrolein, is converted to fused tetrahydropyran rings in the presence of acid catalysts.



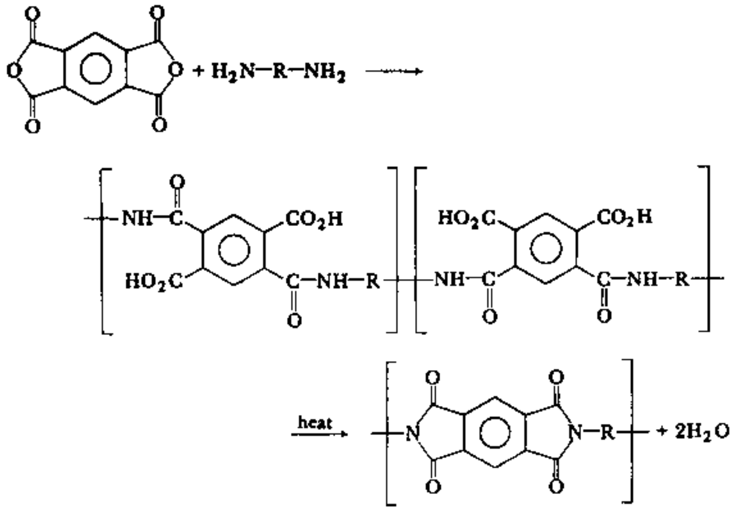
(15.47)

A number of other complex structures are formed from the internal cyclization of polymers. For instance, polypyrones, derived from the reaction of aromatic tetraamines with tetracarboxylic acids or dianhydrides, when heated to about 300°C form the polypyrone.

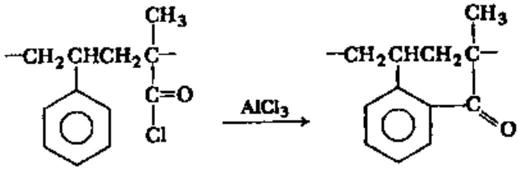


(15.48)

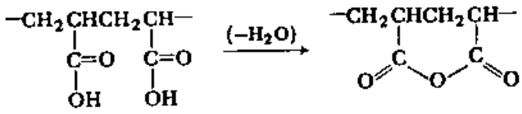
A number of polyimides have been synthesized. Polyimides are prepared from the reaction of dianhydrides and diamines. For many products the initial step is the formation of the polyamide followed by the internal cyclization forming the polyimide. The formation of the stable five-membered imide appears to be the driving force for the internal cyclization rather than the crosslinking reaction.


(15.49)

A wide variety of other internal cyclization reactions have been reported including the Friedel-Crafts reaction of the copolymer containing adjacent units of methacrylyl chloride and styrene,


(15.50)

and the dehydration reaction of poly(acrylic acid) to give the corresponding anhydride.


(15.51)

15.12 REACTIVITIES OF END GROUPS

Polymers containing one reactive end group are often referred to as macromolecular monomers or macromers. They can be represented as

M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—reactive group

They are used in the formation of a number of products, including star polymers and certain graft polymers.

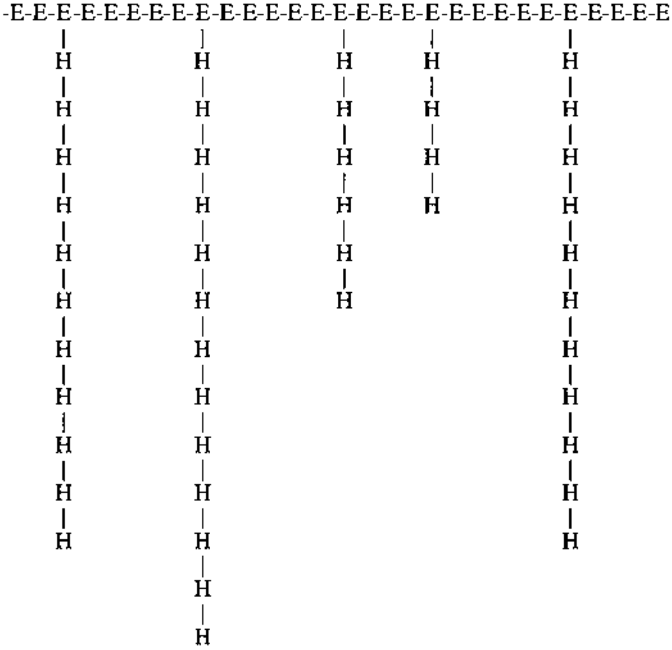
Polymers that contain two active end groups are referred to as telechelic polymers. These are then of the form:

Reactive group—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—reactive group

Telechelic polymers are also used in the synthesis of many products, including segmented polyurethane and polyester products.

Macromers are “short” polymers that contain an active end group. This end group can be a site of unsaturation, heterocycle, or other group that can further react. Macromers are usually designed as intermediates in the complete synthesis of a polymeric material. These macromers can be introduced as side chains (grafts) or they may serve as the backbones (comonomer) of polymers. The macromers can also act as separate phases.

Macromers have been used to produce thermoplastic elastomers. Generally, the backbone serves as the elastomeric phase while the branches serve as the hard phases. These structures are often referred to as comb-shaped because of the similarity between the rigid part of the comb and its teeth and the structure of these graft polymers.

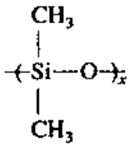


Block copolymers are also produced using such macromers. Again, the various units of the polymer can be designed to act as needed with hard/soft or hydrophilic/hydrophobic or other combinations. Also, these macromers generally have two active functional groups that allow polymerization to occur.

Telechelics can be used as crosslinkers between already formed polymers when both ends are active. These functional groups could be either two vinyl ends or two Lewis acids or bases such as two hydroxyl or amine groups. Interpenetrating polymer networks (IPNs) and related structures such as dendrites and stars can also be formed using macromers and telechelics.

The use of placing specific end groups onto polymers and oligomers is widespread and will be illustrated here for dimethylsiloxanes. These end groups are given various names, often dependent on their intended use. Some of these names are capping agent, blocking agent, chain length modifier, and coupling agent. For instance, siloxanes containing unreactive trimethylsiloxyl groups are formed from addition of hexamethyldisiloxane to the reaction system. These products can be used as fluids for a variety of applications according to the viscosity of the siloxane, which is dependent on the chain length of the material. Fluid siloxanes are employed as antifoaming agents, for flow control in coating applications, as heat exchangers in baths and thermostats, as dielectric material in rectifiers and other electronics, and for electronic cooling applications in magnetrons and klystrons. Intermediate molecular weight trimethylsiloxyl-terminated liquids are used as mold release agents, in timing devices, as dielectric fluids, as hydraulic fluids, in inertial guidance systems, in polish formulations, and in grease and oil formulations. High molecular weight materials are employed as internal lubricants and process aids for thermoplastics. They are also used as liquid springs in shock absorbers, as impact modifiers for thermoplastic resins, and as band-ply lubricants in the rubber industry.

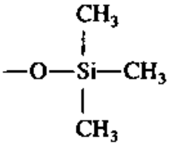
Polydimethylsiloxane



$$\left(\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right)_x$$

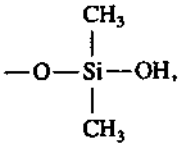
(15.52)

trimethylsiloxy group



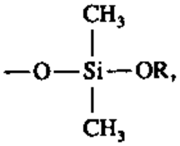
$$-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3}$$

Reactive end groups such as silanol, alkoxy, vinyl, and hydrogen can be formed from reaction of water, alcohol, divinyltetramethyldisiloxane, or tetramethyldisiloxane, respectively, with chlorosilane end groups.



$$-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{OH},$$

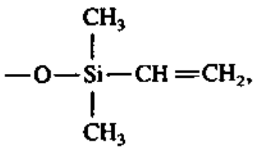
silanol



$$-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{OR},$$

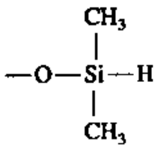
alkoxy

(15.53)



$$-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH}=\mathrm{CH_2},$$

vinyl



$$-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{H}$$

hydrogen

These reactive end groups can be further reacted to form a wide variety of useful materials. The formation of room temperature vulcanizing liquid rubbers (RTVs) illustrates this point. Most silicone RTV adhesives, sealants, and caulks are moisture curing, i.e., they contain a hydroxyl-capped silane that is reacted with acyloxy, amine, oxime, or alkoxyl moisture-sensitive compounds. Reaction with acyloxyl-capped siloxanes results in the formation of acetic acid, producing a vinegar-like odor (also see Sec. 11.3).

$$\begin{aligned}
&\text{Acyloxy}\\
&\equiv\text{Si-OH} + \text{AcOSi}\equiv \;\longrightarrow\; \equiv\text{Si-O-Si}\equiv + \text{AcOh}\\
&\text{Amine}\\
&\equiv\text{Si-OH} + \text{Me}_2\text{NSi}\equiv \;\longrightarrow\; \equiv\text{Si-O-Si}\equiv + \text{Me}_2\text{NH}\\
&\text{Oxime}\\
&\equiv\text{Si-OH} + \text{R}_2\text{C}\equiv\text{NOSi} \;\longrightarrow\; \equiv\text{Si-O-Si}\equiv + \text{R}_2\text{C}\equiv\text{NOH}\\
&\text{Alkoxy}\\
&\equiv\text{Si-OH} + \text{MeOSi}\equiv \;\longrightarrow\; \equiv\text{Si-O-Si}\equiv + \text{MeOH}
\end{aligned}\tag{15.54}$$

15.13 SUPRAMOLECULES AND SELF-ASSEMBLY

The terms self-assembly, self-organization, and self-synthesis are closely related and sometimes used interchangeably. Self-assembly involves the aggregation of molecules, including macromolecules, into thermodynamically stable structures that are held together often using secondary bonding including hydrogen bonding, van der Waals and electrostatic forces, π–π interactions, and hydrophobic and hydrophilic interactions. The term self-organization is used for situations where the secondary bonding interactions are more specific and directional, giving a higher degree of order to the self-assembled molecules. Finally, the term self-synthesis includes self-assembly and self-organization, but also includes situations where self-replication and template-type synthesis occur.

Self-assembly is the spontaneous organization of molecules into stable, well-defined structures with the driving forces being noncovalent associations. The final structure is normally near or at the thermodynamic equilibrium arrangement allowing it to readily spontaneously form. Such formations can be done under conditions where defects are either minimized or eliminated. In nature, self-assembly is common—such as the folding of proteins, formation of the DNA double helix, etc.

Self-assembled monolayers, SAMs, are the most widely studied nonnatural self-assembly systems. They are generally spontaneously formed from chemisorption and self-organization of organic molecules onto appropriate surfaces.

Natural polymers utilize a combination of primary and secondary forces and bond angles and distances to form polymers with both long-range (multimacromolecular) and short-range structures with both structures essential for the proper functioning of the macromolecular structure. While most synthetic polymer chemists have focused on what is referred to as primary and secondary structures (short-order structure control; Sec. 10.7), work is just beginning on the development of appropriate structure control to allow tertiary and quaternary structural control (long-range control). While the backbones of these structures are held together with primary bonds, the secondary, tertiary, and quaternary structures are generally driven by secondary forces with the resulting tertiary and quaternary structures fixed in place through a combination of these secondary forces and small amounts of covalent crosslinking.

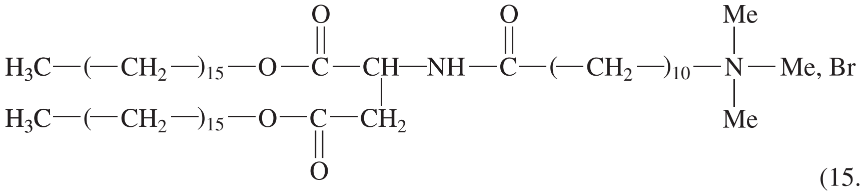
Several strategies are being developed that allow this long-range control including the use of secondary forces to hold in place monomers that subsequently will be polymerized in place. In another approach, already molecular "architectured" templates are employed to hold the polymer, prepolymer, or monomers in the desired shape with subsequent reactions and interactions enacted producing a material with a somewhat robust tertiary and quaternary structure. Some of these "molecular molds" are being produced using so-called nanotechnology.

Self-assembly tendencies are apparent in the simple crystallization of inorganics and organics. Structure, size, and chemical tendencies (such as "like-liking-like" and "unlikes" repelling, secondary and primary bonding tendencies) are all involved, except that proteins do so in a much more diverse manner than so-called simple crystallization of common organics and inorganics. As noted above, we are beginning to understand the nuances involved with the self-assembling formation of giant macromolecules including organizations such as those present in the cells of our bodies. We are beginning to understand the major factors involved in making the cell membranes and are starting to mimic these features to form synthetic biological-like membranes. We are using self-assembling concepts and approaches to develop a large number of interesting and potentially useful macromolecular materials.

One of the applications of molecular self-assembling is the formation of ultrathin films using both synthetic and natural surfaces as two-dimensional templates. As noted above, the same chemical and physical factors that we recognize in other areas are at work here. We will begin considering the formation of a simple bilayer membrane such as that present in natural cell membranes. Using the concept of like-liking-like and unlikes rejecting one another, we see that the orientation of molecules with two different polar environments will vary depending on the particular environment in which they are placed. For a common soap molecule with hydrophilic and hydrophobic ends, the like ends will congregate together and will reside either internally together or externally together. This is exactly the same concept as given in most general chemistry texts when considering the formation of micelles in commercial detergents. In the presence of water the hydrophilic ends face outward and in a nonpolar organic solvent the polar ends face inward. Researchers have extended these simple concepts to include specially designed molecules that contain not only the heads and tails, but also spacers and conductors, and to vary the flexibility of the various parts of the molecule, spacing and number of heads and tails, etc. Furthermore, particular structures can be created through control of the nature of the liquid.

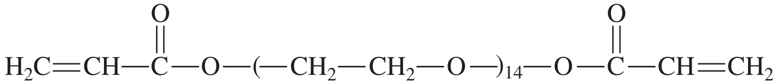
An important concept in the creation of some of these structures is that a primary driving force is the solute–solvent immiscibilities (energy; enthalphic). Thus, the magnitude of the cohesive energy of the solute may be a secondary factor in determining these supermolecular or supramolecular structures for such systems.

The self-assembling character of bilayer membranes is demonstrated by the formation of freestanding cast films from aqueous dispersions of synthetic bilayer membranes. The tendencies for association are strong enough to allow the addition of "guest" molecules (nanoparticles, proteins, and various small molecules) to these films where the connective forces are secondary in nature and not primary. Synthetic polymer chemists have made use of these self-assembling tendencies to synthesize monolayer films. Essentially a monomer that contains both reactive groups and hydrophobic and hydrophilic areas are "cast" onto an appropriate template that "self-assembles" the monomer, holding it for subsequent polymerization. Thus, a bilayer structure is formed by



$$\begin{array}{l} H_3C-(-CH_2-)_{15}-O-\overset{O}{\overset{\|}{C}}-\underset{|}{CH}-NH-\overset{O}{\overset{\|}{C}}-(-CH_2-)_{10}-\overset{Me}{\overset{|}{\underset{\underset{Me}{|}}{N}}}-Me,\ Br \\ H_3C-(-CH_2-)_{15}-O-\underset{\underset{O}{\|}}{C}-CH_2 \end{array} \qquad (15.55)$$

The bisacrylate monomer



$$H_2C{=}CH-\overset{O}{\overset{\|}{C}}-O-(-CH_2-CH_2-O-)_{14}-O-\overset{O}{\overset{\|}{C}}-CH{=}CH_2 \qquad (15.56)$$

is accommodated by this bilayer. The bisacrylate is photopolymerized. While there is some change in the particular bond lengths, the bilayer still holds on and a coherent film is formed. The bilayer template is subsequently washed away by addition of methanol leaving a flexible, self-supporting film. Polymerization can also result in the creation of different bond lengths that can act to "release" the newly formed monolayer. Multilayered structures can be made by simply allowing the outer surface of one monolayer to act as the template for the next.

Inorganics can also be synthesized and used as templates. Thus, controlled siloxane networks were formed when dispersions of alkoxysilanes [such as $(MeO)_3SiMe$] are mixed with the suitable template matrices. Ultrafine particles of metal oxides can be used as starting materials for the formation of metal oxide films. For instance, a mixture of a double-chained ammonium amphiphile and an aqueous solution of aluminum oxide particles (diameter about 10–100 nm) gives a multilayered aluminum oxide film when calcinated at over 300°C.

Metal-ligand structures, such as porphyrin-based structures, are able to "control" the geometry of forming superstructures. The interactions between the various internally chelated porphyrin metal and a combination of the planarity and $\pi-\pi$ interactions between the porphyrin rings drive the resulting structures. Connecting groups can act as spacers or act as additional geometry-determining features. Smaller metal-based groups have been used to self-assemble structures such as nanocages that can have within them molecules that give the combination cage and captive molecule unique chemical and electrical environments. A nanocage has been formed using six cis-protected palladinum(II) nitrate molecules and four tridendate tripyridyl molecules. These structures, unlike other self-assembly molecules considered here, have primary bonds as major contributors to the self-assembly process. Many of these excursions are the exercise of combining organometallic chemistry with structural knowledge and purpose.

Graphite and carbon fibers have been used at templates. Thus, nylon-6 has been polymerized on a graphite matrix. Such syntheses of polymers in the presence of a solid template where the solid acts as a template have been described as polymerized-induced epitaxy (PIE). The monomer and resulting film is adsorbed on the template surface through only van der Waals forces. After polymerization, the polymer is washed from the template. The recovered polymer retains "special" structural features introduced by the template.

Block copolymers with amphphilic groups have been used to give molecules with several "levels" of molecular architecture. Thus, a block copolymer of styrene and 4-vinylpyridine and long-tailed alkylphenols contains polar groups in the backbone that associate with the alkylphenol chains forming hydrogen bonds resulting in a bottle-brush-like structure. If the alkyl tails on the polymer are so strongly repulsed by the amphiphilic portions, microphase separation between the tails and the rest of the copolymer results. Here the alkylphenol portion, which is hydrogen-bonded to the vinylpyridine blocks, separates as a microphase inside the poly(4-vinylpyridine) block domains. If the copolymer is heated, the bottle-brush structure undergoes an order–disorder transition around 100°C and a second-order–order transition about 150°C as the amphiphilic alkylphenol chains diffuse into the polystyrene-rich domains and cylindrical structures are formed.

While much of the emphasis on inter- and intramolecular interactions, secondary bonding, and forces associated with association and dissociation involve attractive forces, we are finding that phobic effects are also important and for some systems are actually the major factors. Briefly, this can be described by such sayings as "The enemy of my enemy is my friend," or "Given the choice between bad and worse, bad wins out." Formation of many of the self-assemblies are due in large measure to such phobic factors.

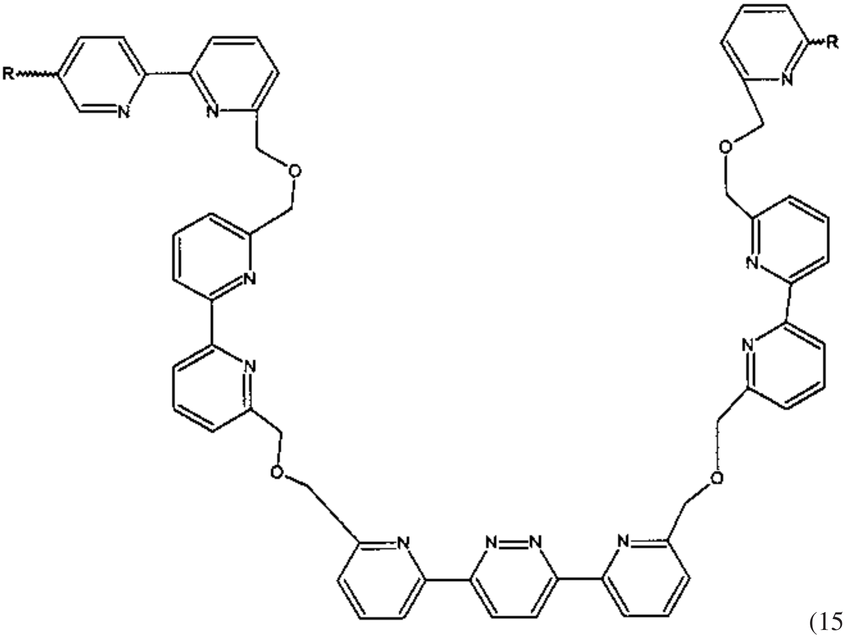
As we learn more about what drives molecular shapes, we are finding more applications using this information to design, on a molecular level, oligomeric and polymeric chains. It is also becoming more apparent to us that we have been forming organized structures without knowing it.

Considering only Lewis acid-base or donor-acceptor interactions, we can envision a hydrogen bond donor site such as an alcohol, acid, thiol, or amine, and an acceptor site such as a carbonyl oxygen on another molecule or part of the molecule. These components will bind with one another, acting to bind either the molecules containing the two differing bonding sites, or if the two sites are on the same molecule attempt to contort, twist the molecule allowing the preferred bonding to occur.

Synthetic shapes are generally limited to sheets and polyhedral structures. Yet nature produces a much wider variety of shapes including curves, spirals, ripples, bowls, pores, tunnels, spheres, and circles. We are beginning to master such shapes. We are beginning to make these shapes based on specially "grown" shapes that act as templates for further growth. For instance, Geofreey Ozin and co-workers mixed together alumina, phosphoric, and decylamine in an aqueous solution of tetraethylene glocol. After days, millimeter-sized aluminophosphate solid spheres and hollow shells were formed with the surfaces sculpted into patterns of pores, meshes, ripples, bowls, etc. A decylammonium dihydrogen-phosphate liquid-crystal phase was forming, and this surfactant, along with the glycol, was forming bilayer vesicles. The vesicles acted in different ways with some fusing to one another, others splitting apart or collapsing, giving a variety of structures. Thus, appropriate conditions can be selected that favor certain template structures to produce an array of geometric structures. Further, the templates themselves can be used to make selective separations. In a related study, the group employed a silica precursor tetraethyl orthosilicate. Here, the orthosilicate units assembled together forming micelles, which in turn, acted as liquid-seed crystals growing other assemblies with varying shapes. Rapid growth in the axial direction produces rope-like structures that can be made to form circles and loops through application of external forces. Other structures include egg shapes, disks, spirals, knots, and spheres.

Metal coordination is another important bonding opportunity with respect to self-assembly. This is important in many natural molecules such as hemoglobin and chlorophyll, where the metal atom acts as both the site of activity and as a "centralizing" agent with respect to shape, and thus acts as a nucleating agent for self-assembly.

Numerous metal chelating designs can be envisioned. Below is one made by Daniel Funeriu and co-workers. The end structure is dependent upon the nature of the metal. For instance, a wreath-shaped double-helical complex is formed when $FeCl_2$ is added with each wreath containing five iron ions with each iron having three bonding sites. Further, the wreath size is such that it will selectively bind the chloride or other similarly sized ions because the source of the iron is the iron chloride. The ratio of reactants is also important, and by varying the ratio different structures can be formed including wire and tape-like structures. Again, it is up to the researcher to utilize information at hand to construct these self-assemblies.



(15.57)

There are many potential and real applications of self-assembly.

Pharmaceutical chiral drug sales top $100 billion yearly worldwide. More than half of the drugs on the market are asymmetric molecules with about 90% administered as racemates. Generally, one optical center of a drug will have the desired activity, while the other often produces negative side effects. Because of this, the FDA issued a statement in 1992 saying that for every new racemic drug, the two enantiomers must be treated as separate substances that are required to undergo pharmacokinetic and topological studies.

One direct approach to the separation of chiral compounds is called molecular imprint polymers (MIPs), which involve the formation of a three-dimensional cavity with the shape and electronic features that are complementary to the imprinted or target molecule.

While MIPs are part of the current nano revolution, its roots are found in the antibody formation theory of Pauling's. While the particulars were wrong, the general concept is good.

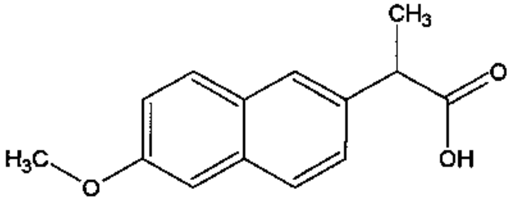
In the formation of MIPs, the target drug is added to a solvent along with selected polymers. It is important that the liquid, self-assembling polymer(s), and template molecule complement one another. The specific bonding can be a combination of covalent and noncovalent bonding. Here, we will look at an instance involving only noncovalent bonding. The main secondary bonding interactions include metal-ligand complexations, hydrogen bonding, and ionic, dipolar, hydrophobic, and $\pi-\pi$ interactions.

Because most drugs have both polar and nonpolar regions, solvents and vinyl monomers that contain both polar and nonpolar regions are often employed. Where aromatic rings are present, polymers such as 4-vinyl pyridine and styrene are often utilized because of their ability to "fit" such structures, their ability to bond through overlap of π systems, and their ability to be readily polymerized via a variety of methods (such as UV, heat, and use of free radical initiators). Hydrogen bonding solvents are generally discouraged because of their tendency to form strong bonds with the template molecule and after evacuation of the template site, with polar portions of the template site. Often dipolar aprotic solvents are employed that offer both polar and nonpolar sites.

In general the sequence is

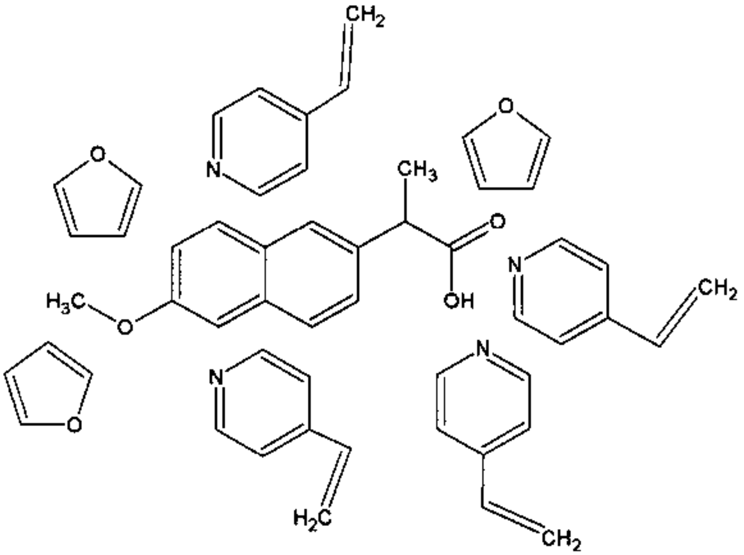
> mixing together of the template, polymer, and solvent → self-assembly about the template → polymerization → extraction of template molecule → grinding, sieving, and column packing

A number of drugs have been successfully separated using MIPs. Naproxen™, (S)-6-methosy-α-methyl-2-naphthaleneacetic acid, is a nonsteroidal anti-inflammatory drug (NSAID) that is administered as the "S" enantiomer. Naproxen will be used to illustrate the MIP sequence. Naproxen has both polar and nonpolar domains. It also has a fused-ring aromatic site.



(15.58)

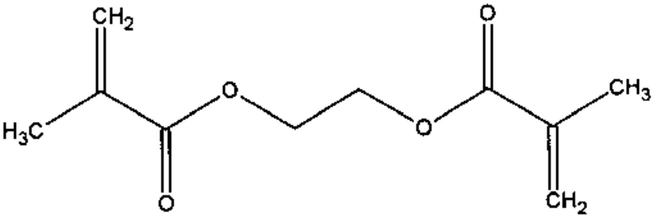
Solvents and self-assembling polymer(s) that have both polar and nonpolar portions are chosen. The polymers and solvents then self-assemble about the target molecule. This arrangement is then exposed to UV radiation, heat, and or catalysts that effectively form a polymeric "cocoon" about the target molecule. After polymerization and the formation of the "cocoon" around the target molecule, the solvent molecules and target molecule are removed exposing a partially completed cavity with both structural (both shape and spatial configuration) and electronic characteristics complementing the target molecule. For Naproxen, the solvent is tetrahydrofurane (THF), and the monomer is 4-vinyl pyridine. Below is an illustration of a possible self-assembly arrangement involving only the vinyl pyridine and THF. Around the acid group there are two vinyl pyridines, both with the nitrogens pointed toward the Naproxen template molecule, one making use of hydrogen bonding and one bonded through dipolar interactions to the electron deficient "acid" carbon. This gives an electron-rich region. Around the naphthalene-ring portion are also located vinyl pyridine molecules, except they have the nitrogens "pointed" away, creating a nonpolar region. These self-assemblies vary from template site to template site and this variation in specific site structure is at least partially responsibile for the broadening of the chromatography peak associated with the template molecule. Assembly also occurs above and below the Naproxen, again with appropriate secondary bonding occurring, including pi-bonding interactions between the aromatic sites on the Naproxen and the furane and vinyl pyridine.



(15.59)

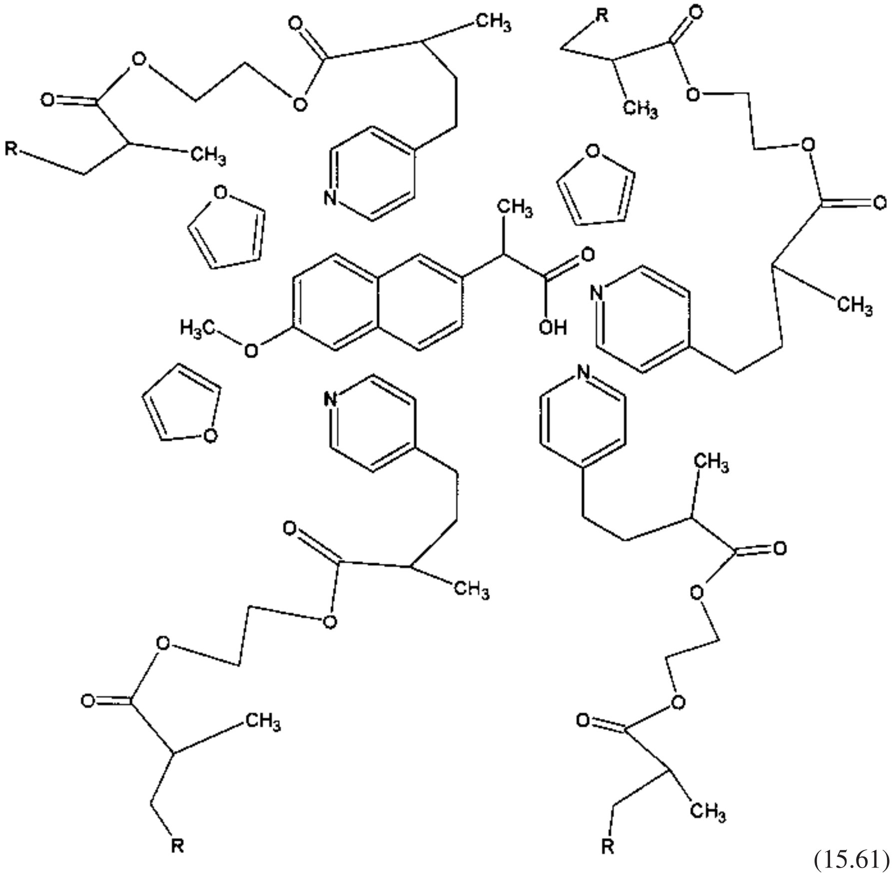
The ratio of THF and 4-vinylpyridine is important since both assemble around the Naproxen. If there are too many solvent molecules present, the “cocoon” cavity will not be sufficient to retain the template molecule imprint. If the concentration of vinyl pyridine is too high, the “cocoon” structure will be too complete and prevent both the exit of the target molecule and entrance of other Naproxen molecules during the separation procedure.

Added along with the “imprinting” vinyl pyridine are crosslinkers, spacers or “porogens.” These crosslinkers or spacers should be miscible with the other ingredients but have shapes that are dissimilar so that they do not also become an integral part of the assembly around the template molecule. For Naproxen, the crosslinker is ethylene glycol dimethylacrylate (EDMA), below (15.60).



(15.60)

Again, the conditions, amounts, and identity of reactants are carefully selected to allow ready entrance and acceptance of the target molecules. Eventually, a matrix is formed containing the molecularly imprinted sites locked into a matrix such as illustrated below (15.61).



(15.61)

After polymerization, the MIP or functionalized polymer matrix is dried, ground, sieved, and packed.

On the column, the eluding liquid is important. The liquid must dissolve the desired compound, but it should not be too good of a solvent or it will inhibit the release of the desired molecule allowing it to interact with the template cavity. In the case of Naproxen, there is a further consideration. Naproxen has an acid function that was "templated" in the protonated form. Thus, acetic acid, along with THF and heptane, was added to insure that the Naproxen was present in the needed correct geometry.

As with most processes, MIPs have both positive and negative aspects. On the positive side, with the correct choice of original polymer and solvent almost any molecule can be employed as a template, including much larger molecules. (This approach is not realistic for synthetic polymers where the short-range geometry is varied and where the long range geometry is not fixed. It might be feasible for natural polymers where the structures are fixed.) Further, since the desired compound is the one that is preferentially being attracted by the template site, it is the last to be eluded from the column so that additional work is not needed to identify where the target molecules are. Increased temperatures can also be employed, presumably to the range of 180–200°C so that high temperature isolations can be effected. In general, with the possible exception of the target compound, the reagents are inexpensive so that such selective molecular sieves are relatively inexpensive.

On the negative side, there is excessive broadening of the elution band caused by a number of features including the heterogeneity of the imprint as noted before.

One problem with nanomolecules is ready alignment. On a molecular level, AFM and related tools can be used to align such individual or nanomolecules, but this is impractical on a large scale. Thus, strategics are being developed to accomplish this. One approach for single-walled carbon nanotubes (SWNTs) is to physically or chemically anchor molecules onto tubes and to have these anchors direct the nanomolecules into desired arrays or organizations.

While simple layered and linear structures are generally employed to describe the concept, the self-assembling approach holds for any two- and three-dimensional structure under the appropriate conditions. As in many areas of research, the potential is limited only by our imagination.

15.14 TRANSFER AND RETENTION OF OXYGEN

Today the polymer chemist should be aware of both synthetic, inorganic, and biological macromolecules. The field of biological macromolecules is large and is one of the most expanding areas of knowledge today. It involves gene splicing and other related biological engineering aspects, neurobiology, many areas of medicine, biological reactions and drugs, neuroreceptors—the very elements of life and death, of though and action, pain and health, of biological transference, of energy and biological matter. The polymer scientist can learn from these advances but must also contribute to their understanding on a molecular and chain aggregate level.

The scientist who investigates biological macromolecules works typically with quite complex systems; yet, through persistence, the use of state-of-the-art instrumentation and techniques, and the use of scientific intuition (at times, simply educated guesses), the world of some of these natural macromolecules is yielding information allowing an understanding on a molecular level. A striking example of this involves oxygen transfer and retention of mammals.

Oxygen retention and transfer involves the iron-containing organometallic planer porphyrin-containing structure called *heme* (Fig. 15.4). The iron is bonded through what can be considered classical coordination. The ferrous or iron (II) ion has six coordination sites. Four of these coordination sites are occupied by the nitrogen atoms of the four pyrrole-related rings of the porphyrin shown in Fig. 15.4. A fifth site is occupied by one of the nitrogens of an imidazole side chain found as part of the protein structure and located just opposite the planer porphyrin moiety. The sixth site acts to bind oxygen. The iron remains in the $+2$ oxidation state, whether oxygen is being bound or the site is vacant. An additional histidine is present, residing in the protein chain opposite the sixth site of the iron atom. This second histidine does not bind iron but serves to stabilize the binding site for oxygen. Experimentally, isolated heme does not bind oxygen. Instead a complex protein wrapping is necessary to both assist binding and protect the binding site from foreign competitor molecules that could render the heme site inactive, either through structural change, change in iron oxidation state, or through occupation of the site, thus preventing oxygen access to the active binding site.

The precise electronic environment of iron deserves special comment. In deoxyhemoglobin, the iron atom has four unpaired electrons, but in oxyhemoglobin iron has no unpaired electrons. The iron in the oxygen-free deoxyhemoglobin is referred to as “high-spin” iron, whereas the iron in oxyhemoglobin is called “low-spin” iron. Hund’s rule of

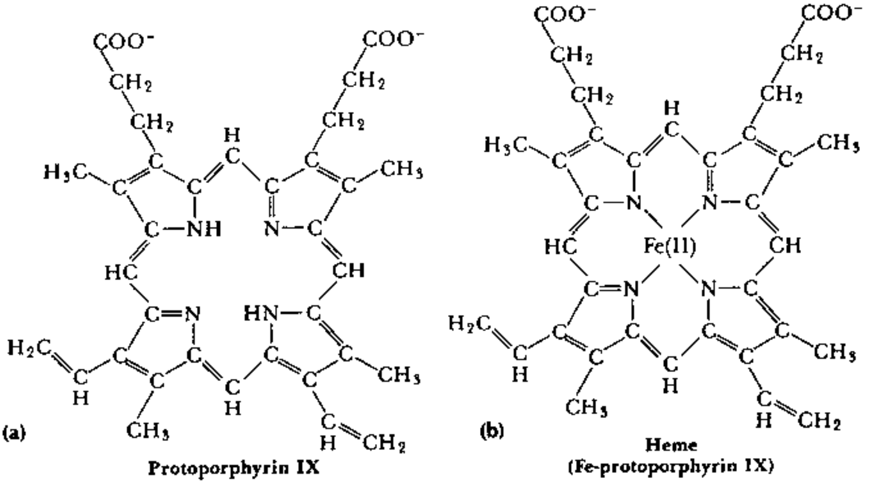


Figure 15.4 (a) Porphyrin structure that serves as the basis of heme. Upon addition of iron, this porphyrin, which is called protoporphyrin IX, forms (b) the heme group.

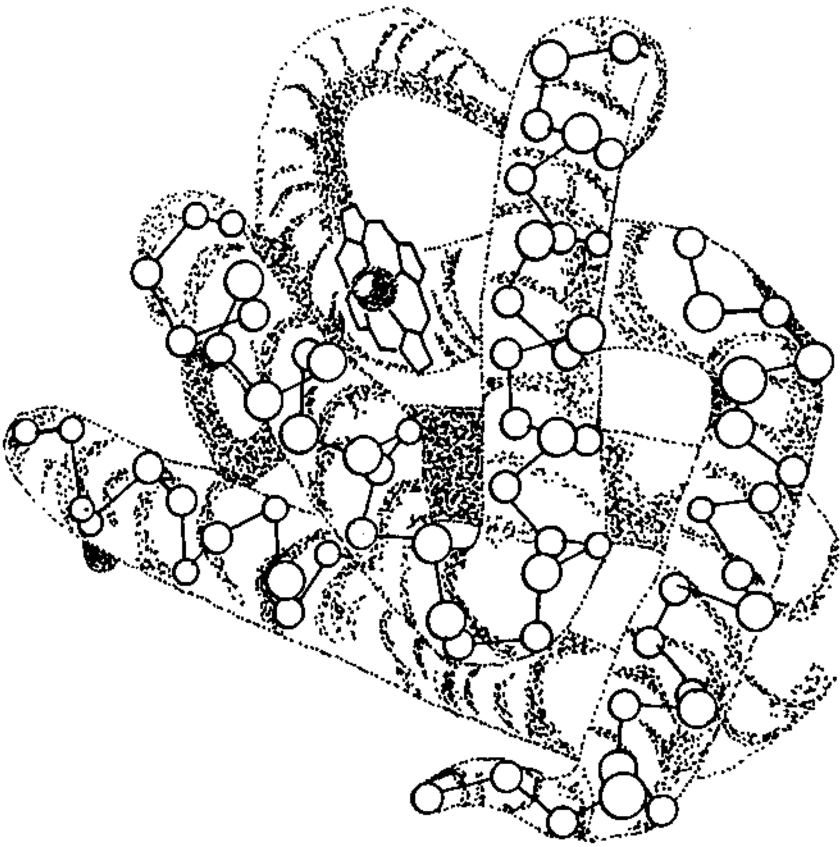


Figure 15.5 Generalized myoglobin structure showing some amino acid units as open circles illustrating the "folded" tertiary structure.

maximum multiplicity calls for the most energy-favored, lowest energy form to be the structure containing the highest number of unpaired electrons. The binding of oxygen, itself with two unpaired electrons, is probably the result of a favored energy of binding brought about through the coupling of the two sets of unpaired electrons—the favorable energy allowing the violation of Hund's rule.

There are two major protein-/heme-binding macromolecules. These are myoglobin (Fig. 15.5), which is used as an oxygen *storage* molecule in mammalian muscle, and hemoglobin, which is active in the *transport* of oxygen. Myoglobin is single-stranded with one heme site per chain, whereas hemoglobin is composed of four protein chains, each one containing a single heme site. There are two sets of equivalent chains composing the quaternary structure of hemoglobin. These two types of chains are referred to as α and β chains. The α chains contain 141 units and the β chains contain 146 units. The myoglobin contains 153 units. Each of these three chains is similar and each forms the necessary environment to allow the heme site to bind oxygen in a reversible manner. The protein segments can be described to be loosely helical with about 60–80% of the structure helical. The various segments of these chains are given specific designations for identification

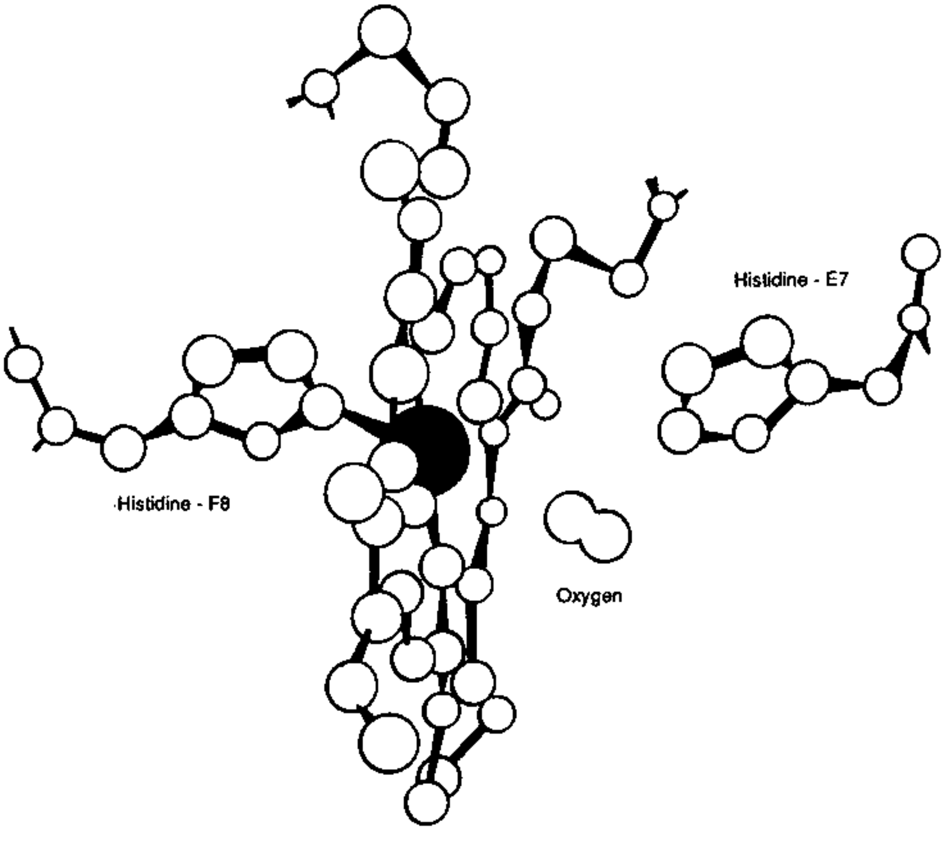


Figure 15.6 Oxygen binding site illustrating the positions of the surrounding nitrogen-containing groups of the porphyrin, the binding and nonbinding positions of the histidine groups, and the entrance of oxygen.

purposes. For instance, the histidine that binds iron at the fifth site on the heme moiety resides as a side chain at the F8 location, i.e., the eighth amino acid unit in the F segment. The nonbinding histidine is located at the seventh amino acid unit in the E segment, i.e., E7 (Fig. 15.6).

While the three chains are similar in overall structure, there exist somewhat subtle differences. For instance, the quaternary structure of hemoglobin permits interaction between the four chains. Thus, structural movement brought about through binding of oxygen at one of the four heme sites on hemoglobin acts to make it easier for subsequent addition of oxygen at other heme sites. Such cooperative binding of oxygen is not possible in the single-chained myoglobin. The result of this cooperative binding is clearly seen in a comparison of oxygen binding by both myoglobin and hemoglobin as a function of oxygen pressure (Fig. 15.7). As seen, the oxygen binding by myoglobin occurs, to a large extent, even at low oxygen pressure, and this behavior is referred to as hyperbolic. By comparison, the binding by hemoglobin increases more slowly as the pressure of oxygen increases, occurring in what is referred to as sigmoidal fashion. Thus, the initial binding of oxygen by a heme site on hemoglobin is relatively difficult, becoming increasingly easier as the number of heme sites binding oxygen increases.

On a molecular level, the binding of oxygen is accompanied with the F subunit moving towards the H subunit, forcing the tyrosine amino acid–derived unit located at HC2 to move so that a hydrogen bond is formed with the peptide subunit at FG5. This movement causes a disruption of the ionic bonds that hold the precise structure of the

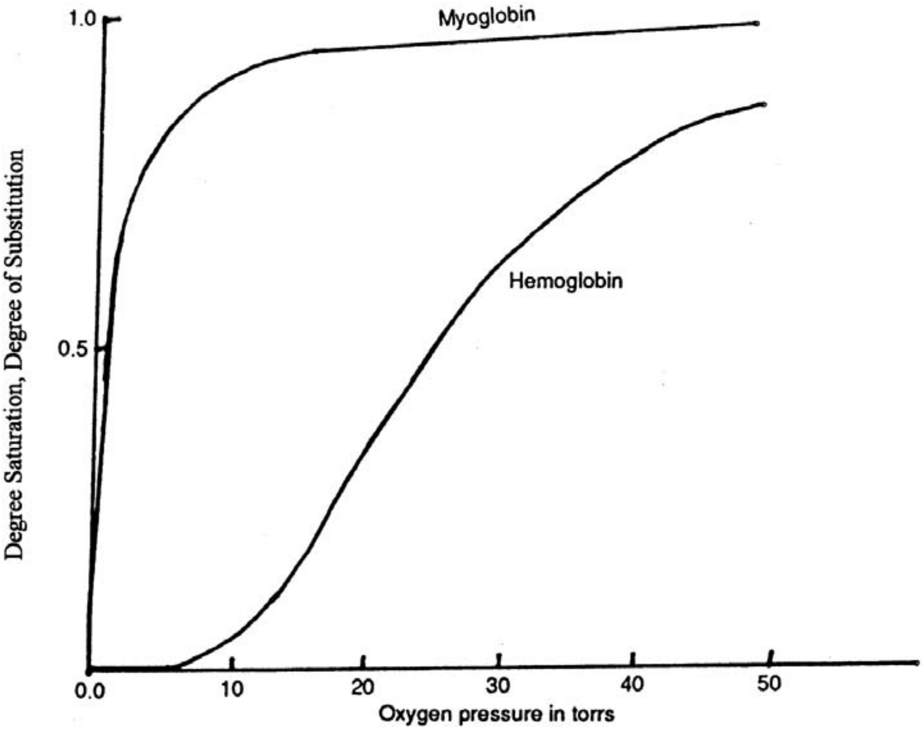


Figure 15.7 Degree of saturation as a function of oxygen pressure.

deoxyhemoglobin, i.e., the ionic crosslinks. This structural reorganization is transmitted to the other chains through cooperative interactions, making the remaining heme sites more vulnerable to oxygen binding.

The differences in oxygen binding characteristics are related to the differing roles of hemoglobin and myoglobin. Thus, myoglobin is employed for the storage of oxygen in muscle. Binding must occur even at low oxygen contents. Hemoglobin is active in the transport of oxygen and becomes saturated only at higher oxygen concentrations. The oxygen content in the alveoli portion of our lungs is on the order of 100 torr (1 atm of pressure is 760 torr). Here almost total saturation of the heme binding sites in hemoglobin occurs. By comparison, the oxygen level in the capillaries of active muscles is on the order of 20 torr, allowing for the hemoglobin to deliver about 75% of its oxygen and for myoglobin to almost reach saturation with respect to oxygen binding sites.

Conformational changes accompany the binding and release of oxygen. These changes are clearly seen by superimposing the oxygen-containing form of hemoglobin-oxyhemoglobin over the non-oxygen-containing structure of hemoglobin-deoxyhemoglobin (Figs. 15.8 and 15.9).

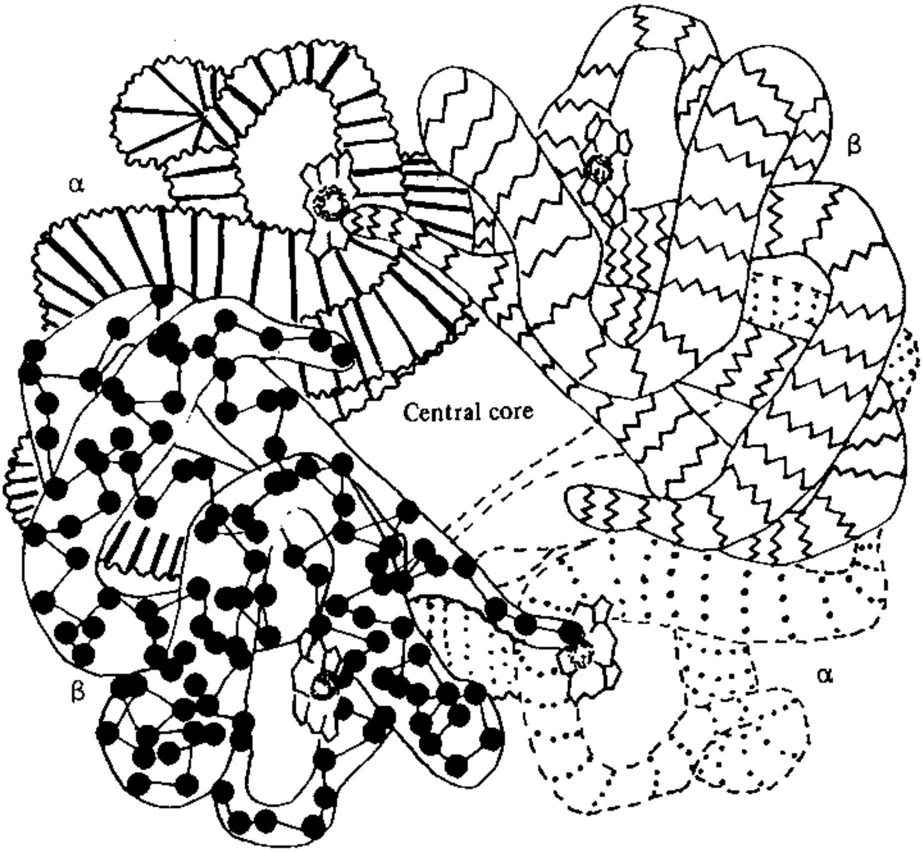


Figure 15.8 Space-filling model of deoxyhemoglobin. Note the four intertwined protein subunits and the four heme sites.

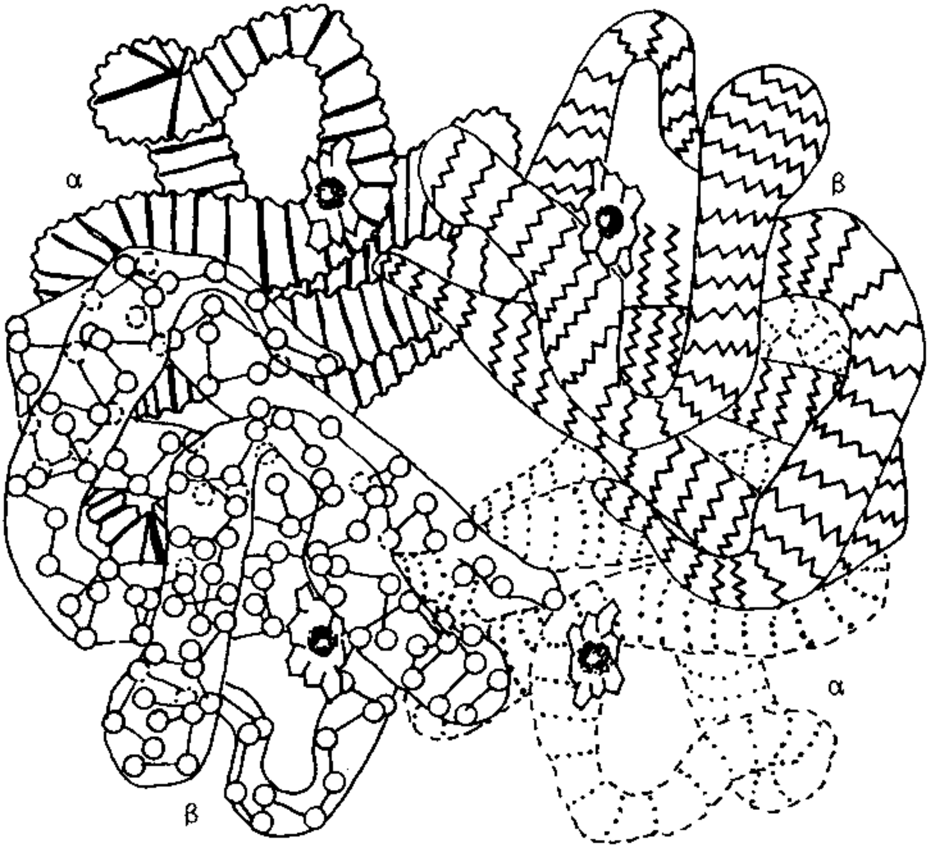


Figure 15.9 Space-filling model of oxyhemoglobin. Note the small shifts in the overall geometry of the various protein chains and the decreased size of the inner core. The top left segment and the lower right segment are known as α chains, while the upper right and lower left chains are referred to as β chains.

Bonding changes involving iron also occur as oxygen is bound. For deoxyhemoglobin, the iron is bonded to the four porphyrin nitrogens through electrostatic, ionic bonding, whereas in oxyhemoglobin the iron is bonded to the nitrogen through covalent bonds.

As noted before, the behavior of hemoglobin involves the interaction between the α and β chains. While these chains are similar, there exist sufficient differences that the presence of four β chains joined similarly to hemoglobin behaves as myoglobin, not hemoglobin.

While typically present in natural deoxyhemoglobin, 2,3-bisphosphoglycerate (BPG) is bound electrostatically to the central core intersecting the four main protein chains of hemoglobin (Fig. 15.10). Figures cited for deoxyhemoglobin behavior are typically for BPG-bound hemoglobin. The presence of BPG has a major affect on the oxygen binding characteristics of hemoglobin. For instance, for non-BPG-containing hemoglobin, almost all of the heme sites are occupied at a pressure of 10 torr, whereas the bound hemoglobin contains less than 10% of its sites bound by oxygen at 10 torr pressure. As noted before,

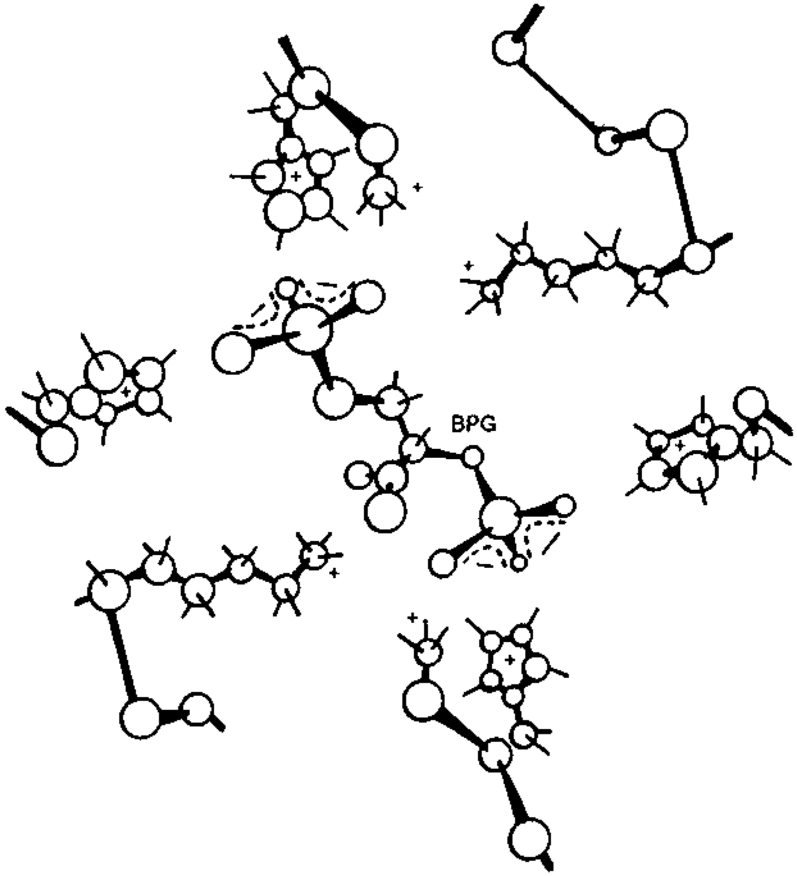
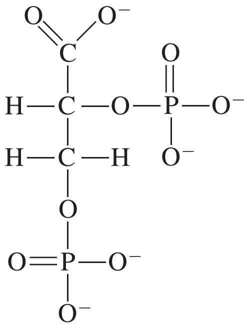


Figure 15.10 Central core binding of 2,3-bisphosphoglycerate (BPG) to deoxyhemoglobin.

natural BPG-bound hemoglobin contains less than half its heme sites bound at about 20 torr pressure, allowing it to deliver oxygen to the active muscles.



(15.62)

2,3-bisphosphoglycerate (BPG)

DPG binds to the non-oxygen-binding deoxyhemoglobin, influencing favorably its tendency to bind to oxygen. As oxygen is bound, structural changes occur, as noted previously. One pronounced change occurs in the inner core where the BPG resides. The cavity becomes smaller, forcing the exit of DPG. In fact, DPG does not bind fully to oxygenated hemoglobin because the inner core area is too small to accommodate DPG.

Additional factors affect the behavior of hemoglobin. Two major factors are pH and the amount and form of carbon dioxide. We recall that dissolved carbon dioxide resides as a hydrated species that acts as an acid we call carbonic acid, H_2CO_3 or, in reality, H_2OCO_2. In the presence of base, carbon dioxide forms salts, with the combination of carbon dioxide and its salts acting as a buffer preventing or minimizing drastic pH changes. Both carbon dioxide and H^+ bind directly and reversibly to iron at the sixth binding site. At high pH, i.e., in highly acidic solutions, the tendency to bind oxygen by hemoglobin is decreased. Increased concentrations of carbon dioxide also act to decrease the oxygen binding capacity of hemoglobin. Further, the non-oxygen-bound form of hemoglobin has a greater affinity for H^+ than does the bound form. Thus, at high concentrations of H^+ and carbon dioxide, oxygen binding is discouraged and carbon dioxide binding is favored. High carbon dioxide concentrations are found in active metabolizing muscles where the oxygen concentration is also low. Thus, hemoglobin takes on oxygen in the lungs and transports it to the actively metabolizing sites, exchanging the bound oxygen for carbon dioxide, which is then transferred to the lungs where the carbon dioxide is released and oxygen bound. Of interest is the insensitivity of myoglobin's ability to bind oxygen with respect to pH and the concentration of carbon dioxide.

Changes in overall structure and reactivity are also common for many synthetic polymers. Thus, the neutralization of poly(acrylic acid) causes the polymer chain to become elongated. Associative and electrophilic changes are well known in polymers undergoing modification.

15.15 NATURE'S MACROMOLECULAR CATALYSTS

Probably the most important reaction occurring on polymers involves the catalytic activity of a class of proteins called enzymes. The catalytic action is a result of a lowering of the activation energy for the rate-determining step in the reaction. In general terms, the catalytic action results from the formation of a complex between the enzyme and the molecule undergoing reaction. The decreased activation energy is a result of the reacting molecules(s) being held by the enzyme in such a manner as to favor the appropriate reaction to occur. The two primary models currently employed to describe the formation of the complex between the reacting molecule(s) and the enzyme are the classical lock-and-key model and the induced-fit model. Briefly, the lock-and-key model calls for an exact or highly similar complementary fit between the enzyme and the reacting molecule(s) (Fig. 15.11). Geometry plays an essential part in permitting the electronic (polar and electrostatic) attractions to form the necessary complex. Release is encouraged by the new geometry and electronic distribution of the resulting products of the reaction being dissimilar in comparison to the original reactant molecule(s). The induced-fit model is similar except that the enzyme originally does not fit the required shape. The required shape is achieved upon binding—the binding causing needed "assisting factors" or proximity and orientation to effect a decrease in the energy of the transition state.

Enzyme reactions generally follow one of two kinetic behaviors (see Sec. 15.12). Briefly, the oxygen binding curve for myoglobin is hyperbolic, whereas that for hemoglo-

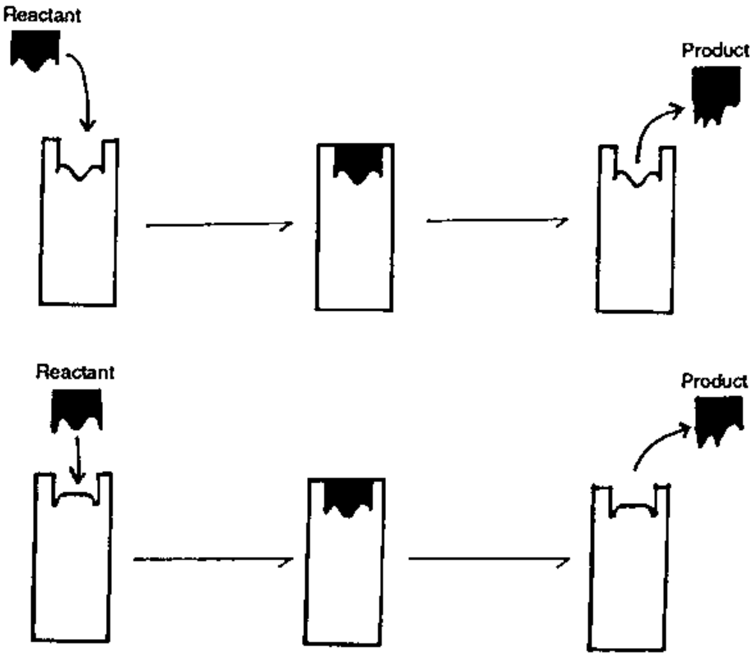


Figure 15.11 The two major models for the binding of reactant molecules to the active sites of nonallosteric enzymes. The top sequence describes the essential steps in the lock-and-key model, where the reactant(s) is attracted to the active site on the enzyme where the active site is a cavity of the same general size, shape, and (complementary) electronic features. Binding occurs and the appropriate reaction(s) occurs resulting in a change in the geometry and electronic configuration of the product, causing its release. The second model (below) describes the induced-fit model where the individual steps are similar to the lock-and-key except the reactants "induce" a change in the conformation of the active site on the enzyme, allowing it to accept the reactant(s).

bin is sigmoidal (Fig. 15.12). In general, it is found that similar enzymes such as myoglobin follow a similar hyperbolic relationship between reaction extent and reaction time. More complex enzymes such as hemoglobin follow a sigmoidal relationship between reaction extent and reaction time. The primary difference involves the ability of different portions of the overall hemoglobin structure to affect other, removed reaction sites. Molecules in which various removed sites affect the reactivity of other removed sites are called allosteric enzymes.

The Michaelis-Menten model is commonly employed in describing nonallosteric enzyme reactions. The overall model can be pictured as follows, where E represents the enzyme and M the reacting molecule(s).

$$\mathrm{E} + \mathrm{M} \underset{k_{-1}}{\overset{\mathrm{k}_1}{\rightleftarrows}} \mathrm{EM} \overset{\mathrm{k}_2}{\rightleftarrows} \mathrm{E} + \mathrm{P} \tag{15.63}$$

Here EM represents the enzyme complex and P the product(s). The rate of complex formation is described as

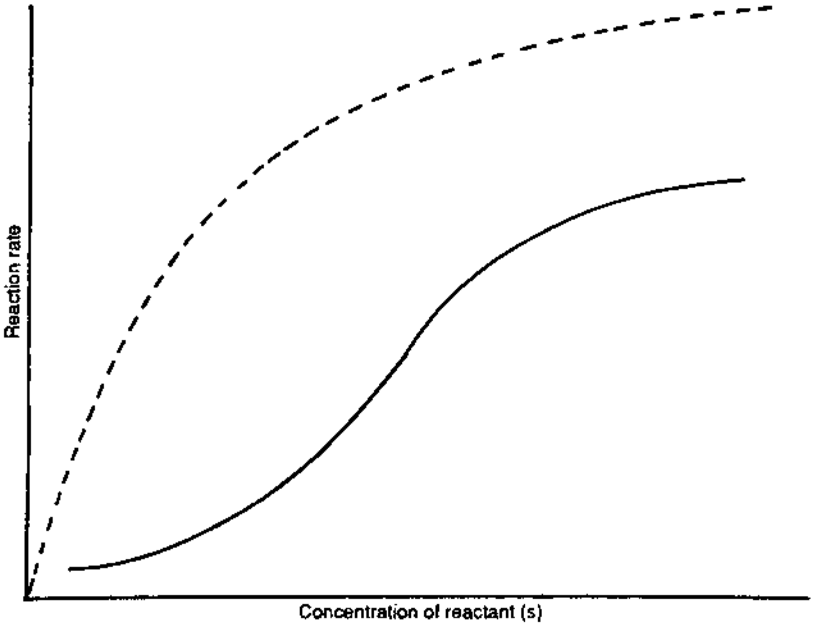


Figure 15.12 Dependence of reaction rate showing sigmoidal (solid line) and hyperbolic (dashed line) behaviors.

$$\text{Rate of complex formation} = \frac{\Delta[\mathrm{EM}]}{\Delta \mathrm{t}} = \mathrm{k}_1[\mathrm{E}][\mathrm{M}] \tag{15.64}$$

The complex then either returns to form the initial reactants or forms the product(s) and the free enzyme. In kinetic terms, the change, or rate of breakdown of the complex is described as

$$\text{Rate of complex change} = -\frac{\Delta[\mathrm{EM}]}{\Delta \mathrm{t}} = k_1[\mathrm{EM}] + \mathrm{k}_2[\mathrm{EM}] \tag{15.65}$$

The negative sign associated with the equation means that the terms are describing the rate of decrease in complex concentration. The rate of complex formation is rapid, and fairly soon the rate at which the complex is formed is equal to the rate at which it breaks down. Such a situation is called a steady state. Mathematically, this is described by

$$\frac{\Delta[\mathrm{EM}]}{\Delta \mathrm{t}} = -\frac{\Delta[\mathrm{EM}]}{\Delta \mathrm{t}} \tag{15.66}$$

and

$$\mathrm{k}_1[\mathrm{E}][\mathrm{M}] = k_{-1}[\mathrm{EM}] + \mathrm{k}_2[\mathrm{EM}] \tag{15.67}$$

Often it is difficult to directly measure the concentration of E as the reaction progresses. Thus, the concentration of E is generally substituted for using the relationship

$$[E] = [E]_0 - [EM] \tag{15.68}$$

where $[E]_0$ is the initial enzyme concentration.
Substitution of this description for [E], that is Eq. (15.68), into Eq. (15.67) gives

$$k_1 ([E]_0[M] - [EM][M]) = k_{-1}[EM] + k_2 [EM] \tag{15.69}$$

Separating out of [EM] on the right-hand side gives

$$k_1([E]_0[M] - [EM][M]) = (k_{-1} + k_2) [EM] \tag{15.70}$$

Combining specific rate constants from both sides of the equation gives

$$[E]_0[M] - [EM][M] = K [EM] \tag{15.71}$$

Now moving the [EM] containing terms to the right side of the equation gives

$$[E]_0[M] = K[EM] + [EM][M] \tag{15.72}$$

Separating out of [EM] on the right gives

$$[E]_0[M] = [EM] (K + [M]) \tag{15.73}$$

Now division of both sides by K + [M] gives (15.74).

Equation (15.64) can now be solved for [EM], giving

$$[EM] = \frac{[E]_0[M]}{K + [M]} \tag{15.74}$$

where K is a collection of rate constants.

The initial rate of product formation, R_i for the Michaelis-Menten model depends only on the rate of complex breakdown, i.e.:

$$R_i = k_2[EM] \tag{15.75}$$

Substitution of Eq. (15.74) into Eq. (15.75) gives

$$\text{Rate}_i = \frac{k_2[E]_0[M]}{K + [M]} \tag{15.76}$$

This expression is dependent on the concentration of M and describes the initial part of the plot given in Fig. 15.13.

Generally, the concentration of M far exceeds that of the enzyme sites such that essentially all of the enzyme sites are complexed, i.e., $[EM] = [E]_0$ (This is similar to a situation that occurs regularly in south Florida, where four- and six-lane roads are funneled into a two-lane section of road. The "rate-determining step" is how many cars can get through the bottleneck, not the number of cars attempting to drive through the two-lane portion. The bottleneck or two-lane portion represents the enzyme active sites, and the automobiles represent the molecules undergoing reaction.) Thus, the rate of product formation is maximized under these conditions. This maximum rate, R_m, allows us to substitute $[E]_0$ for [EM] in Eq. (15.76) to give

$$R_m = k_2[E]_0 \tag{15.77}$$

Since the enzyme concentration is constant, the rate of product formation under these conditions is independent of [M] and is said to be zero order (Fig. 15.13).

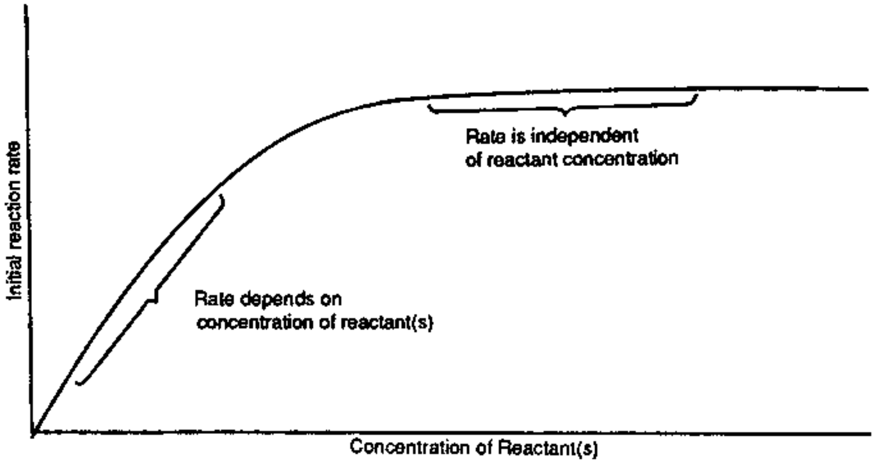


Figure 15.13 Plot of the initial rate of reaction as a function of reactant concentration when the concentration of the enzyme remains constant. The initial reaction rate varies initially until the number of reactants clearly outnumbers the number of reaction sites on the enzyme, at which time the rate becomes zero order, independent of the reactant concentration.

The maximum rate is directly related to the rate at which the enzyme "processes" or permits conversion of the reactant molecule(s). The number of moles of reactants processed per mole of enzyme per second is called the turnover number. Turnover numbers vary widely. Some are high, such as for the scavenging of harmful free radicals by catalase, with a turnover number of about 40 million. Other turnover numbers are small, such as for the hydrolysis of bacterial cell walls by the enzyme lysozyme, with a turnover number of about one-half.

The Michaelis-Menten approach does not describe the behavior of allosteric enzymes, such as hemoglobin, where rate curves are sigmoidal rather than hyperbolic. A more complex model is called for to account for the biofeedback that occurs with allosteroid enzymes. Such affects may be positive, such as those associated with hemoglobin, where binding by one site changes the geometry and electronic environments of the other remaining sites, allowing these additional sites to bind oxygen under more favorable conditions. The affects may also be negative, such as that of cytidine triphosphate, which inhibits ATCase and catalyzes the condensation of aspartate and carbamoyl phosphate–forming carbamoyl aspartate.

Two major models are typically used: the concerted model and the sequential model. In the concerted model, the enzyme has two major conformations—a relaxed form that can bind the appropriate reactant molecule(s) and a tight form that is unable to tightly bind the reactant molecule(s). In this new model, all subunits containing reactive sites change at the same time (Fig. 15.14). An equilibrium exists between the active and inactive structures. Binding at one of the sites shifts the equilibrium to favor the active relaxed form.

The major feature in the sequential model is the induction of a conformational change from the inactive tight form to the active relaxed form as the reacting molecule(s) is bound at one of the sites. This change from an unfavorable to a favorable structure is signaled

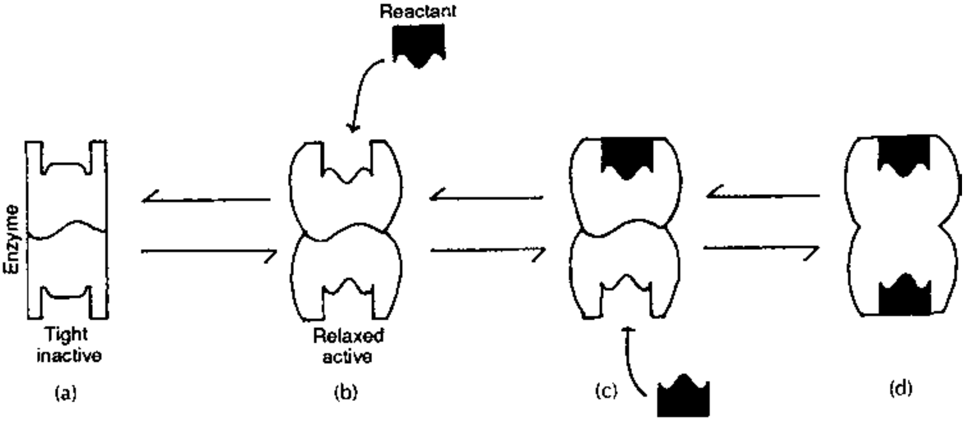


Figure 15.14 Concerted model for allosteric enzymes. The major steps are (a) and (b). An equilibrium exists between the tight and relaxed forms of the allosteric enzyme. (b) The reactant molecule(s) approaches the reactive site of one of the enzyme portions present in the relaxed form. (c) Binding occurs, shifting the equilibrium to the relaxed form(s). (d) The second site is bound.

to other potentially reactive sites bringing about a change to the more favored structural arrangement in these other sites (Fig. 15.15).

Structural changes can be brought about through simple electrostatic and steric events caused by the presence of the reacting molecule(s). Structure changes also result as cross-linking and other primary bonding changes occur. Chymotrypsinogen is formed in the pancreas. It is inactive, fortunately, as it resides in the pancreas. When needed, it is secreted into the small intestine where it is activated by trypsin through cleavage of the peptide

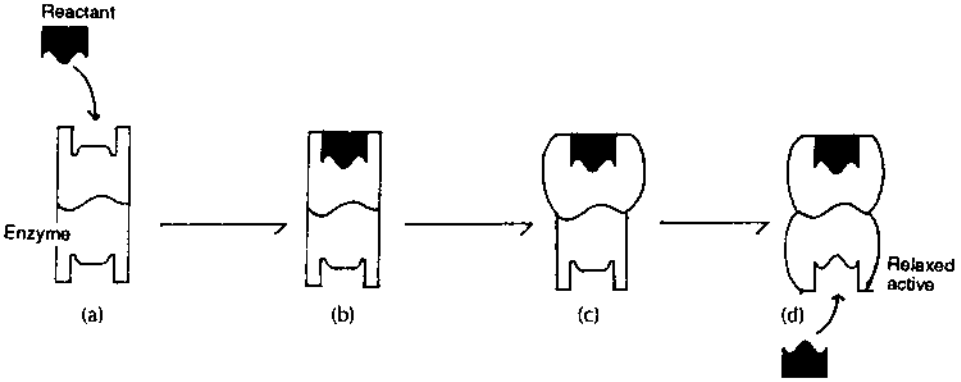


Figure 15.15 Sequential model for allosteric enzymes. The individual steps are as follows: (a) the reactive molecule(s) approach the reactive site, which typically has a cavity similar to, but not the same as, the reactant molecule(s); (b) a conformational change is effected so that the reactive molecule(s) can be bound; (c) the bound portion of the enzyme changes shape; this shape change is transmitted to the other unit(s) containing active sites; (d) the remaining enzyme portion containing active sites undergoes a conformational change that makes binding easier.

bond that resides between the 15 and 16 amino acid units counting from the N end of the chymotrypsinogen. The rearranged conformation is active and is called π-chymotrypsin, which folds back on itself to remove two dipeptide fragments—Ser 14–Arg 15 and Thr 147–Asn 148—finally yielding the active form called α-chymotrypsin. In this form, the α-chymotrypsin catalyzes peptide bonds adjacent to aromatic amino acid–containing sites. While the most important activities of chymotrypsin are those that occur in our bodies, it has also been employed, as have a number of other biologically active agents, to perform selective functions with synthetic molecules. Of interest is the fact that α-chymotrypsin is held together by a set of disulfide crosslinks (Fig. 15.16).

Several generalities exist with respect to the nature of the active site. First, the active site typically occupies only a small portion of the enzyme. Some of the remainder of the enzyme acts to create the needed chemical and geometrical environment necessary for the active site to create the needed chemical and geometrical environmental necessary for the active site to function appropriately. Yet, it is still unknown what other functions are

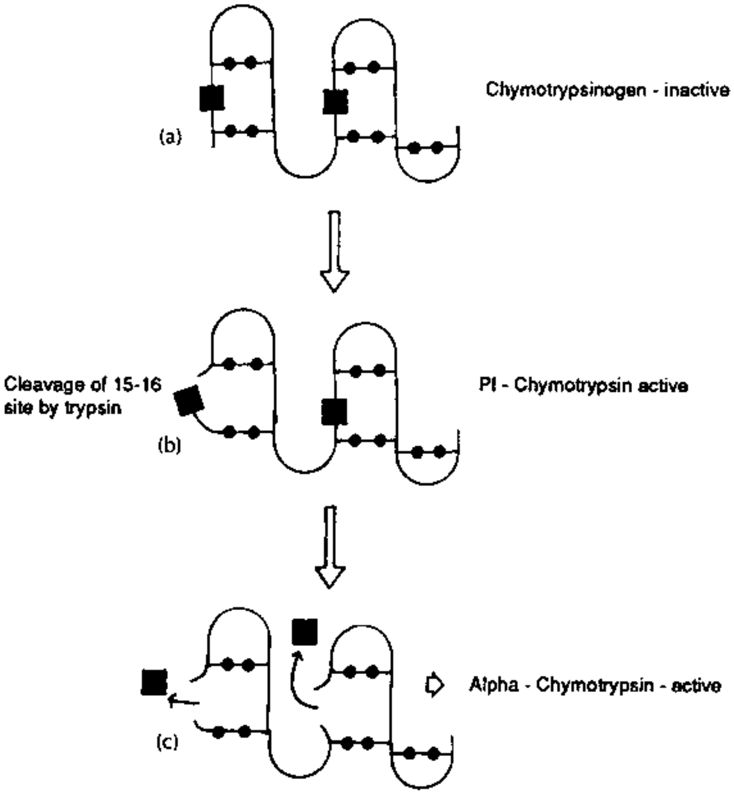


Figure 15.16 Description of the activation of chymotrypsinogen: (a) The inactive chymotrypsinogen with five disulfide crosslinks (solid circles). (b) Cleavage of the peptide bond between the arginine in the 15-position from the N-terminal end and the isoleucine at the position. (c) The active π-form of chymotrypsin is now free to move and it carries out three additional cleavages, resulting in the splitting "out" of two dipeptide units and finally the formation of the active α-chymotrypsin.

carried out by this “extra” bulk. Second, the active site typically exists as a hole, cleft, or crevice. It has a three-dimensionality that allows it to be specific both with respect to the molecules allowed to “approach” it and with respect to providing the needed geometry and electronic arrangement to perform the necessary “catalytic activity.” Water is usually not present in the reactive site. Third, the reactive molecule(s) is generally held by numerous secondary forces, including van der Waals forces, hydrogen bonding, and hydrophobic interactions. Fourth, the catalytic site is often mediated by the presence of functional groups such as the side chains of histidine in the case of hemoglobin. Fifth, the activity of enzymes is sensitive to pH and can be sensitive to the presence of other reactive sites. Finally, reactive sites can undergo conformational changes prior to, during, and subsequent to binding.

15.16 MECHANISMS OF ENERGY ABSORPTION

Let us consider a force, stress, acting on a material producing a deformation. The action of this force can be described in terms of two models—a Hookean spring and a Newtonian dashpot (see Secs. 5.1 through 5.3). In the Hookean spring, the energy of deformation is stored in the spring and may be recovered by allowing the spring to act on another load or through release of the stress; in either case, the site is returned to zero strain. A Newtonian dashpot is pictorially a frictionless piston and is used to describe chains flowing past one another. The energy of deformation is converted to heat. In actuality, the deformation of most plastics results in some combination of Hookean and Newtonian behavior. The Newtonian behavior results in net energy absorption by stressed material, some of this energy producing the work of moving chains past one another in an irreversible manner while some of the energy is converted to heat.

There are three major mechanisms of energy absorption: shear yielding, crazing, and cracking. The latter two are often dealt with together and called normal stress yielding.

We can distinguish between a crack and a craze. When stresses are applied to polymeric materials, the initial deformation involves shear flow of the macromolecules past one another if it is above T_g, or bond bending, stretching, or breaking for glassy polymers. Eventually a crack will begin to form, presumably at a microscopic flaw, then propagate at high speed, often causing catastrophic failure.

The applied stress results in a realigning of the polymer chains, resulting in greater order but decreased volume taken up by the polymer chains, i.e., an increase in free volume. This unoccupied volume often acts as the site for opportunistic smaller molecules to attack, leading to cracking and crazing and eventual property failure.

A crack is an open fissure, whereas a craze is spanned top to bottom by fibrils that act to resist entrance of opportunistic molecules such as water. Even here some smaller molecular interaction can occur with the void space, and eventually the specimen is weakened.

Crazing and cracking can be induced by stress or combined stress and solvent action. For general polymers they show similar features. To the naked eye, crazing and cracking appear to be a fine, microscopic network of cracks generally advancing in a direction at right angles to the maximum principal stress. Such stress yielding can occur at low stress levels under long-term loading. Suppression of stress yielding has been observed for some polymers by imposition of high pressure.

In shear yielding, oriented regions are formed at 45° angles to the stress. No void space is produced in shear yielding.

Crazing often occurs prior to and in front of a crack tip. As noted before, the craze portion contains both fibrils and small voids that can be exploited after the stress is released or if the stress is maintained, since, while many materials are somewhat elastic, most plastics are not ideal elastomers and additional microscopic voids occur each time a material is stressed.

Aqueous solutions of surface-active materials, such as detergents, can produce brittle cracking, particularly in stressed materials. The term environmental stress cracking (ESC) was introduced to describe such situations. ESC is now more widely applied to describe the promotion of slow, brittle failure in stressed materials by organic substances.

Subjection of polymeric materials to organic liquids and gases can also promote formation of networks of small voids—crazes—particularly in amorphous polymers where voids can be either unfilled or occupied by smaller, somewhat readily removed molecules. These voids are sites of opportunity for organic materials to exploit further.

In both ESC and environmental crazing, direct chemical attack on the polymer chain is minor or not involved. It appears that the organic liquid or other promoting substance is absorbed or locally dissolved at the defects so as to assist further failure, possibly by plasticization of the stressed material or modification of the surface energy.

All three mechanisms result in a difference in the optical properties of the polymeric materials because of the preferential reorientation, with realignment of the polymer chains resulting in a change in optical properties such as refractive index, allowing detection through various optical methods including visual examination, microscopy, and infrared spectroscopy of films. Thus crazed and cracked sites of optically clear materials appear opaque, whereas shear-yielded sites may appear to be "wavy" when properly viewed by the naked eye employing even partially refracted light. Thus the three major types of energy absorption can be differentiated though they may appear in combination.

It is important to emphasize that the surface layers of a polymeric material are frequently different from that of the bulk material and are typically more susceptible to environmental attack. Thus special surface treatments are often employed in an attempt to protect the surface molecules.

Directly related to energy absorption is energy dissipation. Generally, the better a material can dissipate or share applied energy the more apt it is to retain its needed properties subsequent to the applied energy. Polymers dissipate applied energies through a variety of mechanisms including rotational, vibrational, electronic, and translational modes.

One area that illustrates aspects important to energy dissipation is the fabrication of protective armor. Such armor includes helmets, vests, vehicle exteriors and interiors, riot shields, bomb blankets, explosive containment boxes (aircraft cargo), and bus and taxi shields. In each case energy dissipation is a critical element in the desired behavior of the device. To illustrate this let us look at body armor.

Most of the so-called bullet-proof vests were made of polycarbonates. More recently, layers of polyethylene were found to have similar "stopping power" for a lesser weight of material. Today, most body armor is a complex of polymeric materials. Rapid dissipation of energy is critical, allowing the impact energy to be spread into a wide area. Materials should be strong enough so as not to immediately break when impacted and have enough contact with other parts of the body armor to allow ready transfer of some of the impact energy. If the material can adsorb some of the energy through bond breakage or heating, then additional energy can be absorbed at the site of impact. Along with high strength, the material should have some ability to stretch, i.e., allowing the material to transfer some of the energy to surrounding material. If the connective forces between the components are too strong, total energy dissipation is reduced because a strong bond discourages another way of reducing the impact energy, i.e., allowing the various materials to slide past one another. Thus, a balance is needed between material strength, strength of bond holding the components together, and the ability to readily dissipate the impact energy.

Recently, it was found that some sequences of layered materials are more effective at energy dissipation than others. One of the better combinations is obtained when aramid layers are adjacent to ultrahigh molecular weight polyethylene.

Another factor is breaking up the projectile. This is again done using polymeric materials, here composites such as boron carbide ceramics in combination with aramids, ultrahigh molecular weight polyethylene, or fibrous glass.

In many fictional space adventures, spaceships and space shelters on distance planets are able to "heal" themselves. Such healing is here today, at least in a small way. Plastic resins have been incorporated within structures as microcapsules that polymerize and solidify when disrupted through stress/strain and corrosion. Thus, microcapsules containing the resin are mixed into items where prolonged functioning is important, such as implanted body parts, electronic circuit boards, aircraft, and satellite components. As defects become sensed by the microcapsule due to predesigned factors such as stress/strain, the microcapsules rupture releasing the resin that either solidifies or polymerizes forming the needed bonding to bridge the defect. One such microcapsule contains dicyclopendadiene and a liquid tricyclic diolefin with the combination showing rapid polymerization, good stability to heat, light, and moisture, and good adhesion to a number of materials.

15.17 RECENT TRENDS

Today modifications can be roughly grouped into two categories: (1) physical modifications, including entanglement and entrapment and radiation-induced changes, and (2) chemical modifications where chemical reactions on the polymer are emphasized. This distinction is often unclear at best.

Modification through exposure to radiation (thermal, light, and particle) continues to be at the forefront of many areas of polymer modification. A major problem involves use of industrial radiation curing of coatings surfaces because of the present practical limitation in depth of cure penetration.

The problem is common to the application of all industrial coatings. Potential solutions are numerous, including (1) repeatable coating application (negative features include time, adhesion of the separate coats, and increased energy of radiation (currently largely ruled out due to energy, safety, and cost considerations); (2) formulation of polymer mixtures that can be "set" with radiation but that continue to cure on standing by a slower mechanism; and (3) addition of species that can transfer "captured" radiation to a greater depths.

The advent of computer chips and laser signal and controlling devices will permit more complex modifications to be carried out on an industrial scale.

A remaining problem and one where no real widespread solution has even been (experimentally) proposed is the adequate description of molecular weight of crosslinked materials and the interrelationship(s) of amount and type of crosslinking, polymer molecular weight, and physical and chemical characteristics. Related to this is the need to better control the extent and location (i.e., random, homogeneous, etc.) of modifications on polymers. Some of the good nuclear magnetic resonance work concerning identification of sequence with copolymers can be utilized in the description of many graph and block copolymers. Mass spectrophotometry utilizing laser excitation of modified polymers may make possible a better description of the actual framework of many crosslinked modified materials since laser excitation allows the examination of both small and large (to greater than 1000 amu) fragments.

The construction of a powerful, continuously variable wavelength laser is approaching reality. Such a laser could be of great use in tailoring polymer modifications through activation of only selected sites for reaction. A number of groups are currently conducting selected reactions utilizing laser energy, so the needed technology is becoming available.

While much of the current and recent research has emphasized modification of synthetic polymers, increasing efforts will undoubtedly focus on the modification of regenerable polymers and on the blending of natural polymers with natural polymers and with synthetic polymers through block, graft, etc., approaches.

The need for replacement of objects currently derived from nonregenerable materials (most plastics, rubbers, elastomers, metals) with objects derived from regenerable materials is critical and must be continually emphasized in our research efforts.

The use of polymers as catalysts may involve the chemical modification of the polymer, with adjacent or neighboring side groups assisting in the catalysis event, or may involve no real modification at all, such as in the case of anchored metal catalysts where the polymer can act as a site for reaction without undergoing permanent chemical modification.

Another area in need of work is on-site grafting—attachment of polymeric materials on biological sites such as particularly badly broken bones. Here the leg is surgically opened and a polymeric material chemically attached after suitable bone activation. The polymeric material degrades after its use period is up. This area is mentioned only to reinforce the notion that interdisciplinary team efforts and polymer chemists with broad training are needed to make the best use of applications of polymer modifications.

The area of delivery of biologically active materials will also involve, in great part, polymer modifications. For instance, Gebelein describes the ideal polymer for good drug delivery as being composed of three parts—one to give the overall polymer the desired solubility, the second containing the drug to be delivered, and the third containing chemical units to direct the overall material only to the site where the drug is to be delivered. It may be possible to combine several of these aspects by a judicious choice of polymeric units, but presently more fruitful approaches include grafting the desired components together forming the needed overall polymeric properties. As a side comment, relatively little work has been done with the generation of “directing groups,” and this is an area where much work is needed if the advantages of polymeric drugs are to be realized.

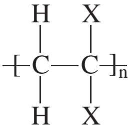
SUMMARY

1. In addition to the reactions occurring during synthesis, telomerization, and crosslinking, polymers, like small molecules, may also react with selected reactants if the reaction sites are accessible.

2. Saturated polymeric hydrocarbons such as HDPE may be chlorinated, sulfochlorinated, or oxidized.
3. Polyenes such as hevea rubber may be hydrogenated, halogenated, hydrohalogenated, cyclized, epoxidized, and ozonized. While many of these plastics are used commercially, ozonide formation is also used to determine the position of double bonds in the polyene.
4. Pendant groups such as the ester groups in poly(vinyl acetate) may be hydrolyzed to yield poly(vinyl alcohol). The latter and other polymeric alcohols, such as cellulose, undergo typical reactions of alcohols, such as the formation of ethers, xanthates, inorganic and organic esters, and acetals.
5. Esters, amides, or nitriles of polycarboxylic acids may be hydrolyzed to produce polycarboxylic acids. When heated, the latter form polymeric anhydrides, which undergo typical reactions of anhydrides, such as hydrolysis, alcoholysis, and amidation. When heated, polyacrylonitrile forms a dark ladder polymer. Polyamines are produced by the Hofmann degradation of polyamides.
6. Phenyl pendant groups such as those present in polystyrene undergo all of the characteristic reactions of benzene, such as alkylation, halogenation, nitration, and sulfonation.
7. Degradation, in which the degree of polymerization is reduced, may occur by random chain scission, by depolymerization, or both. In the former reaction, which may occur in the presence of oxygen, UV light, heat, and impurities, tertiary carbon atoms are preferentially attacked. The latter is the preferred reaction for 1,1-disubstituted polymers such as PMMA.
8. Biomacromolecular scientists are rapidly understanding more fully biomacromolecules. Much of the work involves investigating reactions involving enzymes where shape, size, and electronic configuration are essential to the catalytic nature of these biomacromolecules. The activity of myoglobin can be described mathematically using the Michaelis-Menten approach. The two major models describing the activity of nonallosteric enzymes such as myoglobin are the lock-and-key model and the induced fit model. Hemoglobin is an example of an allosteric enzyme where the two popular models are the concerted model and the sequential model.

GLOSSARY

acetate rayon: Cellulose diacetate.
anchimeric reactions: Those enhanced by the presence of neighboring groups.
cellophane: Regenerated cellulose sheet.
Cellosize: Trade name for hydroxyethylcellulose.
cellulose diacetate: Cellulose acetate with a DS of about 2.0.
cellolose triacetate: Cellulose acetate with a DS of about 3.0.
chain scission: Breaking of a polymer chain.
CMC: Carboxymethylcellulose.
CN: Cellulose nitrate.
curing: Crosslinking to produce a network polymer.
cyclized rubber: Isomerized rubber containing cyclohexane rings.
deuterated polyethylene: Polyethylene in which ^1H is replaced by ^2H.
1,1-disubstituted polymers:



$\left[-CH_2-CX_2- \right]_n$

DMF: Dimethylformamide.

DMSO: Dimethyl sulfoxide.

dope: Jargon for a solution of cellulose diacetate in acetone.

DP: Average degree of polymerization.

DS: Degree of substitution.

fascias: Panels in the front and rear of an automobile.

halogenation: Reaction of a halogen such as chlorine with a molecule.

heme: Iron containing active site for hemoglobin and myoglobin.

hemoglobin: Allosteric enzymes responsible for the transport of oxygen in our bodies. It contains four "myoglobin-like" protein chains, each containing a single heme active site. The four units are interdependent, working together to give hemoglobin the necessary selectivity and oxygen binding characteristics.

homolytic cleavage: Breaking of a covalent bond to produce two radicals.

hydrogenation: The addition of hydrogen to an unsaturated molecule.

Hydropol: Trade name for hydrogenated polybutadiene.

Hypalon: Trade name for sulfochlorinated polyethylene.

induced-fit model: One of two basic models employed to describe the enzymatic behavior of nonallosteric molecules. Here the steps are similar to the lock-and-key model except the reactants "induce" a change in the conformation of the active site allowing the active site to bind with the reactant.

isomerization: Term often applied to cyclization reactions of polymers.

Kraton: Trade name for ABA block copolymer of styrene (A) and butadiene (B).

Kuhn element: The number of repeat units needed so that the most probably distance between the first unit and the growing end is back at the first unit again.

ladder polymer: Polymer having a double-stranded backbone.

LIM: Liquid injection molding.

lock-and-key model: One of two basic models used to describe the selectivity and catalytic nature of nonallosteric enzymes. In the model the reactant(s) is attracted to the active site on the enzyme, which is of the same general size, shape, and complementary electronic nature as the reactant(s).

macromolecular monomers (macromers): Polymers containing one reactive end group.

myoglobin: Nonallosteric enzyme responsible for the storage of oxygen in our bodies. It contains an iron-porphyrin catalytic site responsible of its enzyme activity. The activity follows the kinetic scheme described by Michaelis-Menten.

nitrocellulose: Incorrect name used for cellulose nitrate.

NR: *Hevea brasiliensis*, for natural rubber.

Oxiron: Trade name for epoxidized polybutadiene.

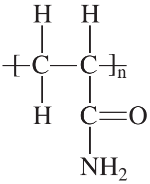
ozonolysis: Reaction of an unsaturated organic compound with ozone followed by cleavage with zinc and water.

Parlon: Trade name for chlorinated rubber.

perfluoropolystyrene: Polystyrene in which all hydrogenatoms have been replaced by fluorine.

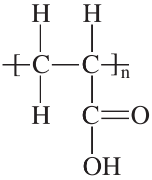
Pliofilm: Trade name for rubber hydrochloride.

PMMA: Poly(methyl methacrylate).
polyacrylamide:



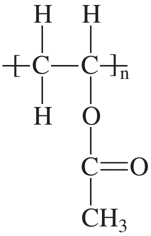
$$\left[\mathrm{CH_2{-}CH(C({=}O)NH_2)}\right]_n$$

poly(acrylic acid):



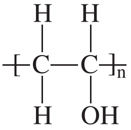
$$\left[\mathrm{CH_2{-}CH(C({=}O)OH)}\right]_n$$

Poly(vinyl acetate):



$$\left[\mathrm{CH_2{-}CH(O{-}C({=}O)CH_3)}\right]_n$$

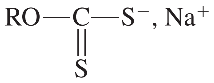
Poly(vinyl alcohol):



$$\left[\mathrm{CH_2{-}CH(OH)}\right]_n$$

PU: Polyurethane.
PVA: Poly(vinyl alcohol).
PVAc: Poly(vinyl acetate).
PVB: Poly(vinyl butyral).
PVDC: Poly(vinyl dichloride), or chlorinated PVC.
PVF: Poly(vinyl formal).
rayon: Regenerated cellulose filaments.
RIM: Reaction injection molding.
SMA: Copolymer of styrene and maleic anhydride.
soda cellulose: Reaction product of cellulose and sodium hydroxide.
Telechelic polymers: Polymers containing two reactive end groups.
telomerization: Abstraction of an atom by a macroradical.
topochemical reactions: Reactions on the surface of a polymer.

Tornesit: Trade name for chlorinated rubber.
Tyrin: Trade name for chlorinated polyethylene.
viscose process: Production of regenerated cellulose from cellulose xanthate.
Williamson reaction: Reaction of an alkoxide and an alkyl chloride.
xanthate:



$$RO{-}\underset{\underset{S}{\|}}{C}{-}S^{-}, Na^{+}$$

EXERCISES

1. What is the general mechanism for the curing of step-reaction polymers?
2. What is the general mechanism for the curing of unsaturated polymers?
3. Write the formula for perdeuterated polyethylene.
4. Explain why good yields of α,ω-dicarboxylic acids can be obtained by the reaction of concentrated nitric acid on crystalline HDPE.
5. Write the formula for diphenylguanidine.
6. How would you crosslink a polyethylene coating after it is applied to a wire?
7. How would you prepare a block copolymer of styrene and an alternating copolymer of ethylene and propylene?
8. What is the difference between completely hydrogenated *Hevea brasiliensis* and completely hydrogenated gutta percha?
9. Explain why the use of rubber hydrochloride film is limited.
10. Which would be more resistant to ozone: (a) *H. brasiliensis or* (b) cyclized rubber?
11. Name a use for epoxidized vegetable oil.
12. What product would be produced by the ozonolysis of polybutadiene?
13. Write the structural formula for the polymeric hydrolytic products from (a) poly (vinyl acetate) and (b) poly(methyl methacrylate).
14. Why is commercial methylcellulose more soluble in water than cellulose?
15. Why is CMC used in detergent formulations?
16. Propose a mechanism for the use of hydroxyethylcellulose or poly(acrylic acid) as a descaling agent.
17. What is the DS of cellulose nitrate when it is used as an explosive?
18. Why is the DS of cellulose triacetate only 2.8?
19. Which is more polar: (a) cellulose triacetate or (b) cellulose diacetate?
20. Why is it not possible to prepare pure poly(vinyl butyral)?
21. Why is poly(acrylic acid) an effective flocculating agent?
22. Propose a use for pyrolyzed filaments of polyacrylonitrile.
23. What monomer would be obtained by the decomposition of PVA?
24. Which would be more resistant to nitric acid: (a) polystyrene or (b) perfluoropolystyrene?
25. What ions would be removed from water by sulfonated polystyrene: (a) cations or (b) anions?
26. What reaction occurs when tannic acid is added to proteins such as those present in cowhide?
27. What chain-reaction polymerization reactions take place in the molding operation?

28. Propose a procedure for recovering monomeric methyl methacrylate from scrap PMMA.
29. Which will produce the larger yield of monomer when heated at moderate temperatures: (a) polystyrene or (b) poly-α-methylstyrene?

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16

Synthesis of Reactants and Intermediates for Polymers

Many of the difunctional reactants used for the production of step-reaction polymers are standard organic chemicals. However, because the degree of polymerization ($\overline{\mathrm{DP}}$) is dependent on high purity, these reactants must be adequately purified.

Impurities in the vinyl monomer may reduce the degree of polymerization through telomerization reactions. Less active impurities may not affect the rate or degree of polymerization, but may be present as contaminants in the polymer. Impurities in any polymerization may produce undesirable properties.

This chapter is divided into several sections with the first section describing the use of common starting materials, also known as feedstocks. As with most synthetic organic materials, the original feedstocks, or starting materials, are found in nature as hydrocarbons, petrochemicals, and carbon (coal).

16.1 MONOMER SYNTHESIS FROM BASIC FEEDSTOCKS

Most of the monomers widely employed for both vinyl and condensation polymers are derived indirectly from simple feedstock molecules. The synthesis of monomers is a lesson in inventiveness. The application of the saying that necessity is the mother of invention has led to the sequence of chemical reactions where little is wasted and byproducts from one reaction are employed in another reaction as an integral starting material. Following is a brief look at some of these pathways traced from basic feedstock materials. It must be remembered that often many years of effort were involved in discovering the conditions of pressure, temperature, catalysts, etc., that must be present as one goes from the starting materials on the left-hand side to the right-hand side of the arrow. The specific conditions and alternative routes are given in Secs. 16.2 and 16.3 and are indicated in Figs. 16.1–16.5.

Fossil fuels refer to materials formed from the decomposition of once living matter. Because these once living materials contain sulfur and heavy metals such as iron and cobalt, they must be removed either prior or subsequent to use.

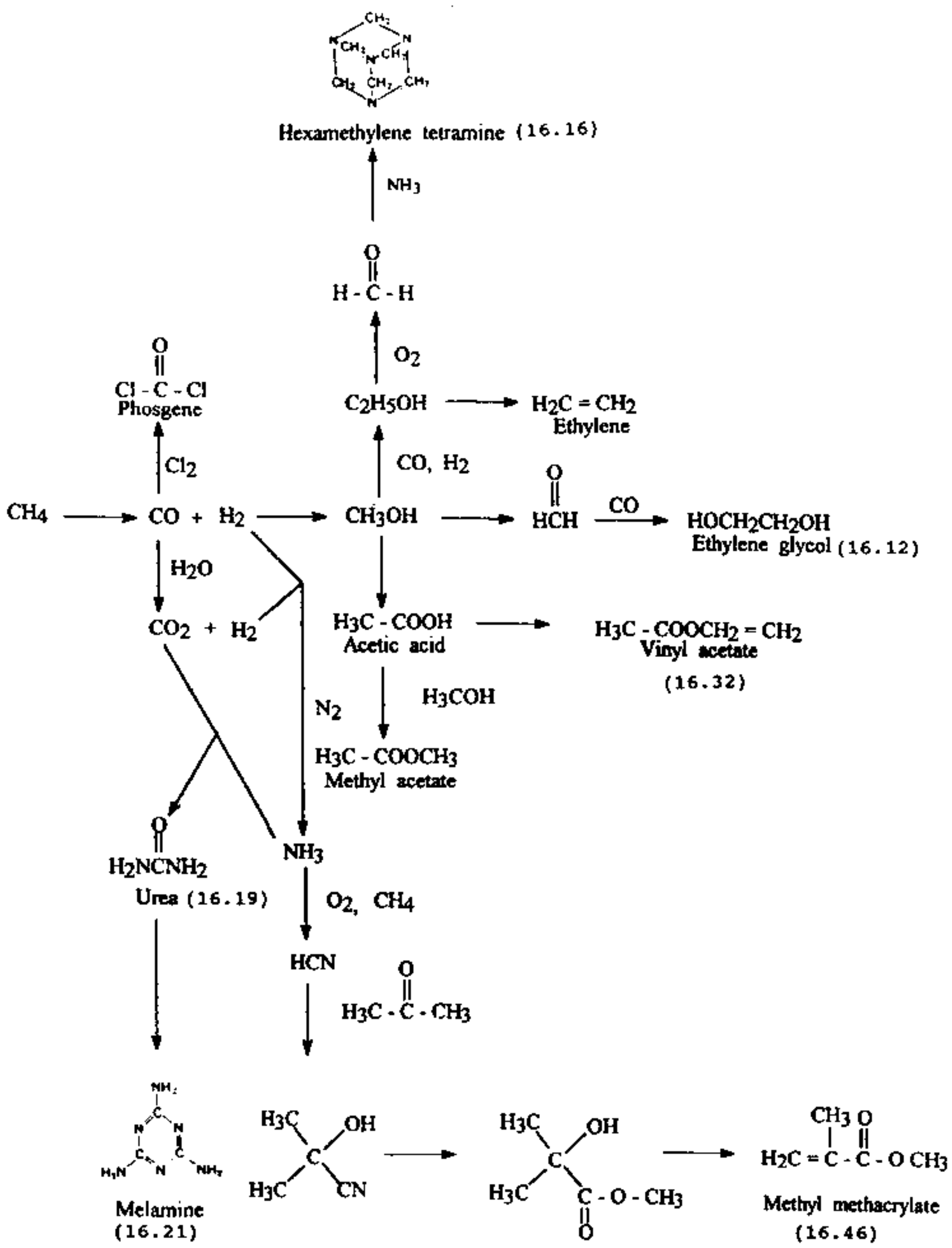


Figure 16.1 Monomer synthesis chemical flow diagram based on methane feedstock.

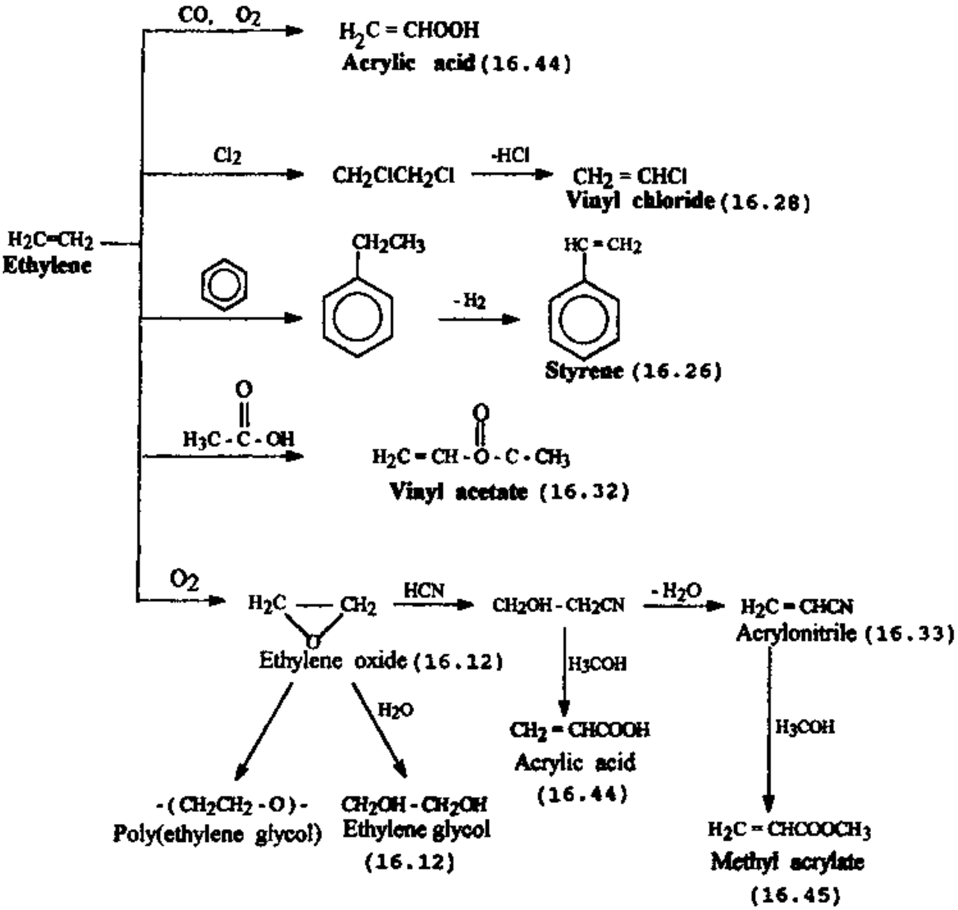


Figure 16.2 Monomer synthesis chemical flow diagram based on ethylene feedstock.

The major fossil fuels are coal and petroleum. Marine organisms were typically deposited in muds and under water, where anaerobic decay occurred. The major decomposition products are hydrocarbons, carbon dioxide, water, and ammonium. These deposits form much of the basis for petroleum resources. Many of these deposits are situated so that the evaporation of the more volatile products such as ammonia and water occurred, giving petroleum resources with little nitrogen- or oxygen-containing products. By comparison, coal is formed from plant material that has decayed to graphite carbon and methane.

Only about 5% of the fossil fuels consumed today are used as feedstocks for the production of today's synthetic carbon–based products. This includes the products produced by the chemical and drug industry with a major portion acting as the feedstocks for plastics, elastomers, coatings, fibers, etc.

The major petroleum resources contain linear, saturated hydrocarbons (alkanes), cyclic alkanes, and aromatics. For the most part, this material is considered to have a low free energy content.

Raw or crude petroleum materials are separated into groups of compounds with similar boiling points by a process called fractionation. Table 16.1 contains a brief listing

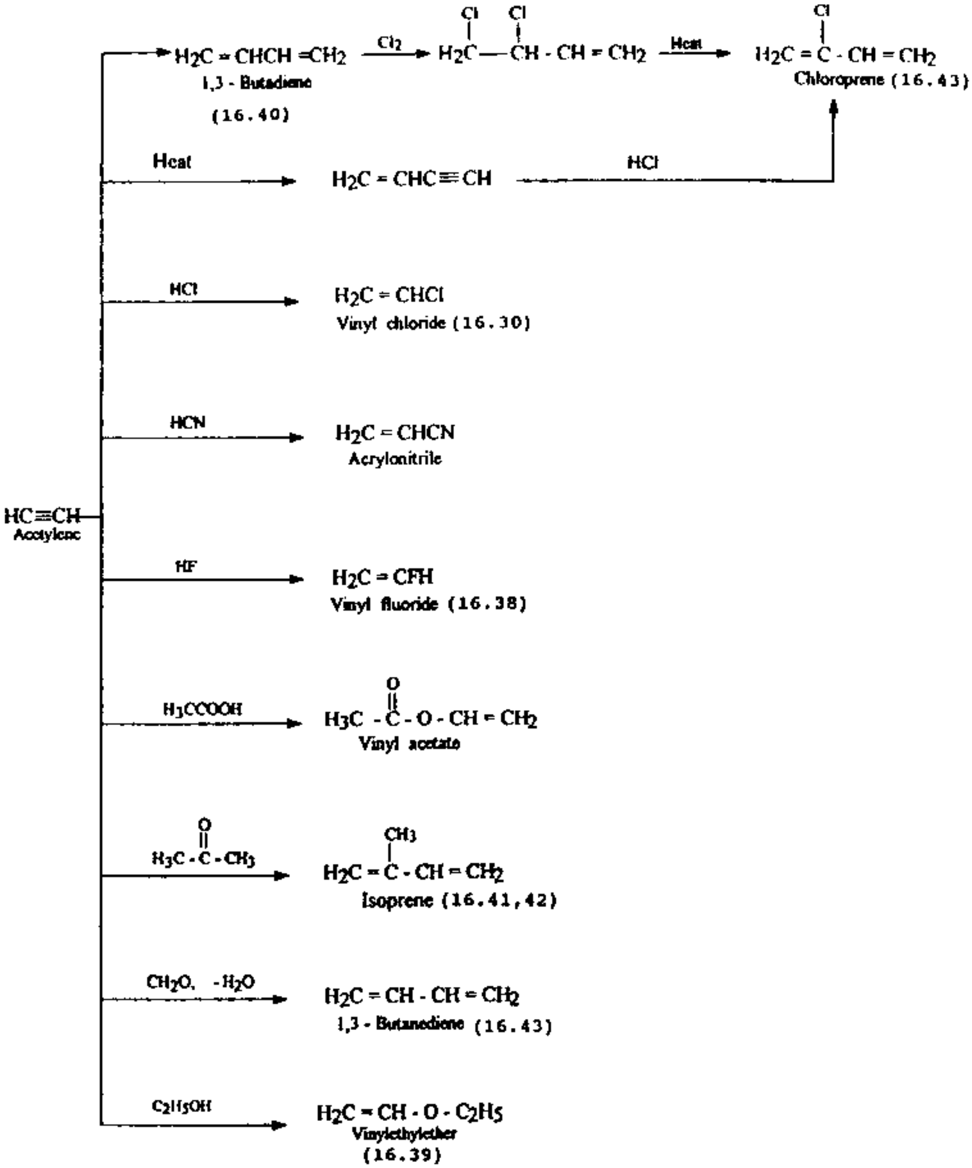


Figure 16.3 Monomer synthesis chemical flow diagram based on acetylene feedstock.

of typical fraction-separated materials. Accompanying or subsequent to this fractionation occurs a process called "cracking" whereby the hydrocarbon molecules are heated over catalysts that allow the hydrocarbon molecules to break up and then reform into structures that contain more "branching" and consequently are more energetic (e.g., upon combustion they will burn with a larger amount of energy given off per weight or volume of hydrocarbon fuel). Most of our gasolines are produced by this cracking process. Petroleum process-

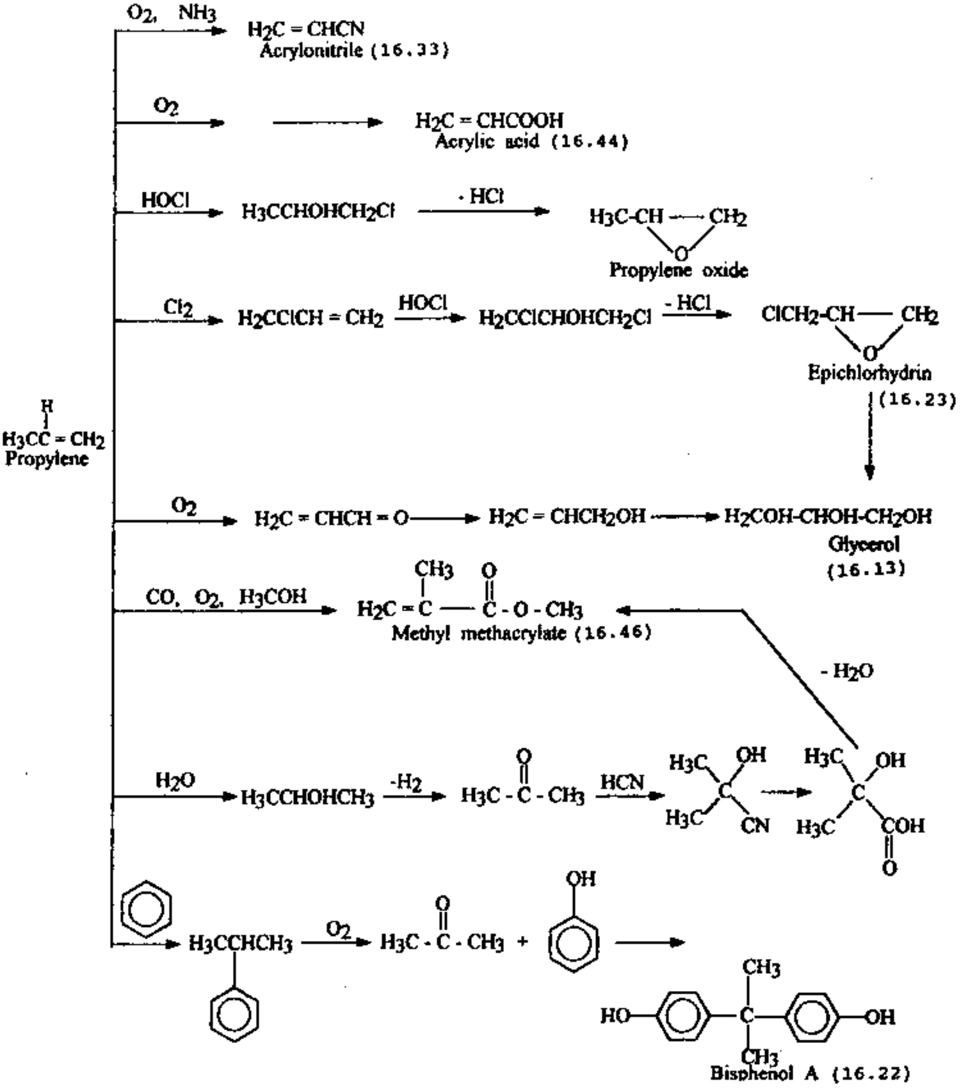


Figure 16.4 Monomer synthesis chemical flow diagram based on propylene feedstock.

ing also provides the basic feedstocks for materials that eventually end up as today's synthetic polymers.

In 1925, Phillips Petroleum Company was only one of dozens of small oil companies in Oklahoma. The only distinction was the large amount of natural gasoline (or naphtha), the lightest liquid fraction (Table 16.1), found in its crude oil. As was customary, Phillips, and most of the other oil companies of the time, employed a distillation process to isolate the butane and propane. Even so, they were sued for the use of this distillation process probably because they were small, had no real research capacity of their own, and no real

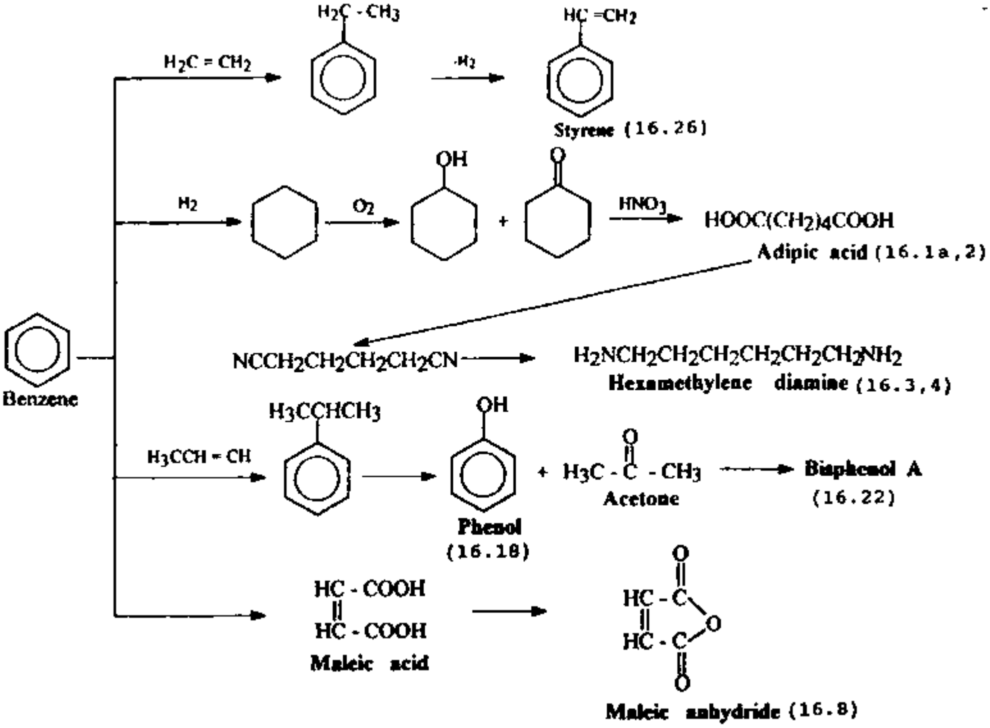


Figure 16.5 Monomer synthesis chemical flow diagram based on benzene feedstock.

legal defense team. Frank Phillips elected to fight, supposedly including an argument that the ancient Egyptians had used a similar process to create an alcoholic equivalent to an Egyptian alcoholic drink. Phillips won the suit but became convinced that if the company was to remain successful, it would need to have a research effort. During the early dust bowl years, 1935, they established the oil industry's first research team in Bartlesville, OK. George Oberfell, hired by Phillips to fight the lawsuit, planned the initial research efforts that involved three main initiatives. First, to develop technology to use light hydrocarbons in new ways as motor fuels. Second, to develop markets for butane and propane.

Table 16.1 Typical Straight Chain Hydrocarbon Fractions Obtained from Distillation of Petroleum Resources

Boiling range (°C)	Average number of carbon atoms	Name	Possible uses
<30	1–4	Gas	Heating
30–180	5–10	Gasoline	Automobile fuel
180–230	11–12	Kerosene	Jet fuel, heating
230–300	13–17	Light gas oil	Diesel fuel, heating
305–400	18–25	Heavy gas oil	Heating

And finally, to find new uses for the light hydrocarbons outside the fuel market. All three objectives were achieved.

Frederick Frey and Walter Shultze were instrumental as early researchers. Frey was among the first to dehydrogenate paraffins catalytically to olefins and then the olefins to diolefins that serve as feedstocks to the production of many of today's polymers. In competition with Bakelite, he discovered the preparation of polysulfone polymers made from the reaction of sulfur dioxide and olefins creating a hard Bakelite-like material. Frey and Schultz also developed a process that allowed the production of 1,3-butadiene from butane that allowed the synthesis of synthetic rubber.

Probably Frey's most important invention involved the use of hydrogen fluoride to convert light olefins produced as by products of a catalytic cracker into high-octane motor and aviation fuels. This process is still widely used. It came at a critical time for the United States' World War II efforts allowing fuel production for the Allied forces. This fuel allowed aircraft faster liftoffs, more power, and higher efficiency.

Here we will divide the synthesis of monomers according to the number of carbons involved in the initial steps from the original fractionation and cracking process. Often important products can be obtained from several chemical sequence scenarios. The following will emphasize some of these alternate routes. As noted above, the precise reaction conditions needed for each step are the consequence of a great deal of hard work and may vary from company to company. The following focuses on tracing the chemical "stream" from selected petroleum feedstock molecules to the synthesis of important monomers.

Methane forms the basis for the single-carbon fraction. The major products derived from methane with respect to polymer formation are given in Fig. 16.1. The interconnectiveness and available alternative routes for the synthesis of the materials are illustrated in Fig. 16.1. Thus, both hydrogen cyanide and methanol are produced from the methane stream, and both are involved in the synthesis of methyl methacrylate (MMA). As will be seen later, hydrogen cyanide is also involved in the synthesis of acrylic acid and methyl acrylate (Fig. 16.2) and acrylonitrile (Fig. 16.3). Methanol is also used in the synthesis of methyl acrylate and acrylic acid (Fig. 16.2) and MMA from propylene (Fig. 16.4). Methanol in turn serves as a basis for the production of ethanol, which in turn is utilized in the synthesis of formaldehyde and vinyl ethyl ether (Fig. 16.3).

Formaldehyde, produced in the methane stream, serves as the basis of the formaldehyde-intensive resins, namely, phenyl-formaldehyde ("Bakelite"-like) resins, urea-formaldehyde resins, and melamine-formaldehyde resins. Formaldehyde is also involved in the synthesis of ethylene glycol, one of two comonomers in the production of poly(ethylene terephthalate). Formaldehyde also serves as the basic feedstock for the synthesis of polyacetals.

Another important use for methane is its conversion to synthesis gas (or syn-gas), a mixture of hydrogen gas and carbon monoxide as shown in Fig. 16.1. Synthesis gas can also be derived from coal. When this occurs, it is called water gas. Interestingly, the reaction of methane to give carbon monoxide and hydrogen can be reversed so that methane can be produced from coal through this route.

Ethylene represents the two-carbon precursor (Fig. 16.2). Here, depending on the reaction conditions, a wide variety of intermediates and products can be formed. Of course, polyethylene itself is part of the ethylene stream. Its copolymerization yields a large number of industrially important copolymers, terpolymers, graft polymers, and block polymers.

Propylene is the basic three-carbon building block considered here (Fig. 16.4). Again, its polymerization gives polypropylene and its copolymerization gives a wide variety of co- and terpolymers. Here the ingeniousness of some of the synthetic routes is illustrated in the conversion of benzene, through reaction with propylene, to cumene and the consequent oxidation forming phenol and acetone that subsequently act to form bisphenol A, a basic building block for a number of esters, as well as furnishing the native compounds themselves, both of which are involved in numerous other important reactions. Phenol is involved in the synthesis of phenol-formaldehyde resins, adipic acid, and 1,6-hexanediamine (hexamethylenediamine; Fig. 16.5). Acetone, in turn, is also involved in numerous important synthetic steps and is employed as a commercial solvent. Acetone is involved in the synthesis of methyl methacrylate (Fig. 16.4) and isoprene (Fig. 16.3).

The synthesis of various acrylic esters can occur from the subsequent reaction of alcohols with acrylic acid (Fig. 16.4).

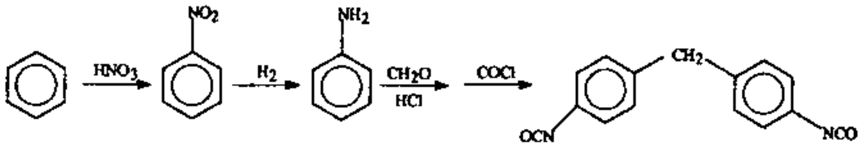
The major members of the four-carbon feedstock molecules are 1,3-butadiene and isobutylene, both involved in the synthesis of a number of polymers, copolymers, and terpolymers. Butadiene is copolymerized with styrene to form SBR rubber, with acrylonitrile to form nitrile rubbers, and with both styrene and acrylonitrile to form ABS rubbers. Isobutylene is copolymerized with isoprene to form butyl rubbers.

Benzene forms the basis for a number of monomers (Fig. 16.5), including those that retain their aromatic character and those that become fully or partially saturated, such as adipic acid, which forms the basis for both many aliphatic polyesters and nylon-66.

Styrene is produced from benzene and ethylene, as shown in Fig. 16.5, and from the reaction of ethylbenzene through an alternative route, also producing both the styrene monomer and propylene oxide as shown in Eq. (16.27).

Other aromatics are also part of the aromatic stream. Toluene is used to produce benzene through dehydroalkylation and is used in the production of isocyanides for the production of polyurethanes. The three xylene isomers can be oxidized, forming three important reactants. Oxidation of meta-xylene gives isophthalic acid, and oxidation of para-xylene gives terephthalic acid used in the production of poly(butylene terephthalate), as well as polyethylene terephthalate (PET). Oxidation of ortho-xylene can give phthalic anhydride used in the production of unsaturated polyesters.

Diisocyanates serve as the basis for the polyurethane industry (along with dialcohols). These can be produced from benzene or toluene. The formation of methylenediphenylisocyanate (MDI) is briefly described as follows.



MDI

(16.1)

Cyclohexanone (Fig. 16.5) also acts as a precursor to the formation of caprolactam, as shown in Eq. (16.11). It is employed in the synthesis of nylon-6.

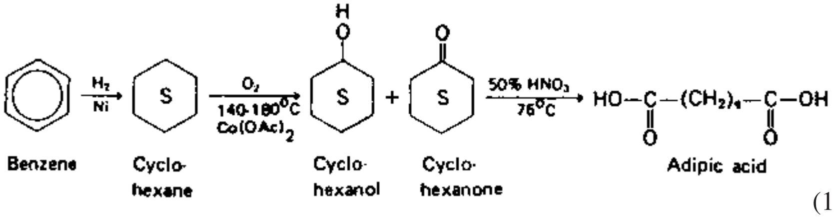
Another two-carbon feedstock is acetylene. Acetylene is typically obtained from coal by converting coke calcium carbide and then treating the calcium carbide with water. As shown in Fig. 16.3, a number of important monomers can be made from acetylene. Even so, because of the abundance of other starting materials from petroleum reserves, only some of the routes shown in Fig. 16.3 are widely used.

Isoprene (2-methyl-1,3-butadiene), shown as derived from acetylene feedstock (Fig. 16.3), is commercially formed from a number of additional routes. It is also produced from isoamylene recovered from one of the gasoline streams with subsequent dehydrogenation [Eq. (16.41)]. Dimerization of propylene to 2-methyl-l-pentene, isomerization to 2-methyl-2-pentene, and finally pyrolysis to isoprene and methane is also a route to isoprene. One industrially important route starts with acetylene and acetone, while another begins with isobutylene and formaldehyde [Eq. (16.42)].

In summary, monomer synthesis from basic, readily available inexpensive feedstocks based on fossil fuels is both an art and a science developed over the past half century or so. It represents a delicate balance and interrelationship of feedstocks and so-called byproducts from one reaction that are critical reactants in another reaction. Monomer and polymer synthesis continues to undergo change and improvement.

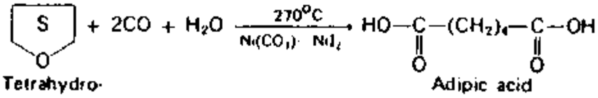
16.2 REACTANTS FOR STEP-REACTION POLYMERIZATION

Adipic acid (1,4-butanedicarboxylic acid) is used for the production of nylon-66 and may be produced by the oxidation of cyclohexane using air or nitric acid, from furfural or from 1,3-butadiene. Cyclohexane is obtained by the Raney nickel-catalytic hydrogenation of benzene. Both the cyclohexanol and cyclohexanone produced by the cobalt(II) acetate–catalyzed air oxidation of cyclohexane are oxidized to adipic acid by heating with 50% nitric acid; 1.8 billion lb of adipic acid is produced annually in the United States.



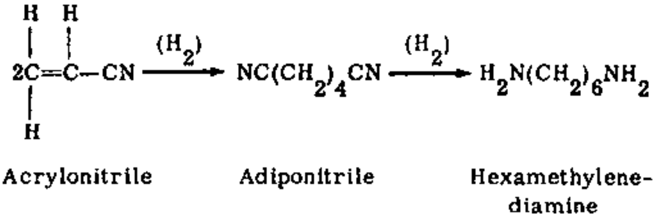
(16.1a)

Tetrahydrofuran (THF), which is obtained from furfural, may be carbonylated in the presence of nickel carbonyl–nickel iodide catalyst [Eq. (16.2)]. Furfural is a chemurgic product obtained by the steam-acid digestion of corn cobs, oat hulls, bagasse, or rice hulls.



(16.2)

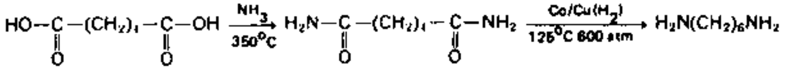
Adiponitrile may be produced by the hydrodimerization of acrylonitrile or from 1,3-butadiene via 1,4-dicyanobutene-2 [Eq. (16.3)]. Adiponitrile can be hydrogenated to form hexamethylenediamine.



$$2\overset{\substack{H\\|}}{\underset{\substack{|\\H}}{C}}{=}\overset{\substack{H\\|}}{C}{-}CN \xrightarrow{(H_2)} NC(CH_2)_4CN \xrightarrow{(H_2)} H_2N(CH_2)_6NH_2$$

(16.3)

Hexamethylenediamine (1,6-diaminohexane), which is used for the production of nylon-66, is also obtained by the liquid phase catalytic hydrogenation of adiponitrile or adipamide. The latter is obtained by the ammonation of adipic acid [Eq. (16.4)].

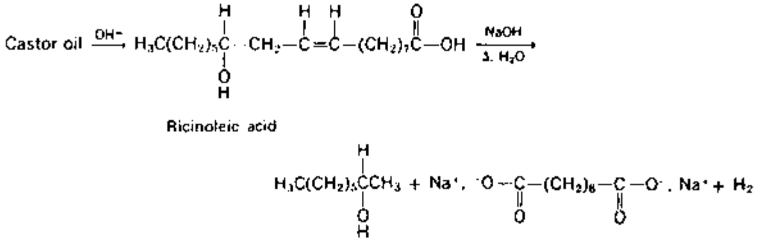


$$\mathrm{HO{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_4{-}\underset{\underset{O}{\|}}{C}{-}OH \xrightarrow[350^\circ C]{NH_3} H_2N{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_4{-}\underset{\underset{O}{\|}}{C}{-}NH_2 \xrightarrow[125^\circ C\ 600\ atm]{Co/Cu(H_2)} H_2N(CH_2)_6NH_2}$$

Adipic acid Adipamide Hexamethylene-diamine

(16.4)

Sebacic acid (decanedioic acid, or 1,8-octane dicarboxylic acid), which has been used for the production of nylon-610, has been produced from 1,3-butadiene and by the dry distillation of castor oil (ricinolein) with sodium hydroxide at 250°C. The cleavage of the ricinoleic acid produces 2-octanol (isocapryl alcohol) and the sodium salt of sebacic acid.



$$\mathrm{Castor\ oil \xrightarrow{OH^-} H_3C(CH_2)_5\overset{\overset{H}{|}}{\underset{\underset{\underset{H}{O}}{|}}{C}}{-}CH_2{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-}(CH_2)_7\overset{\overset{O}{\|}}{C}{-}OH \xrightarrow[\Delta,\ H_2O]{NaOH}}$$

Ricinoleic acid

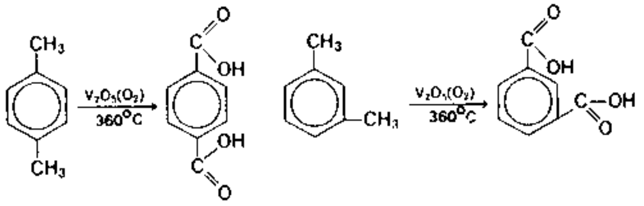
$$\mathrm{H_3C(CH_2)_5\overset{\overset{H}{|}}{\underset{\underset{\underset{H}{O}}{|}}{C}}CH_3 + Na^+,\ {}^-O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_8{-}\underset{\underset{O}{\|}}{C}{-}O^-.\ Na^+ + H_2}$$

2-Octanol Sodium sebacate Hydrogen

(16.5)

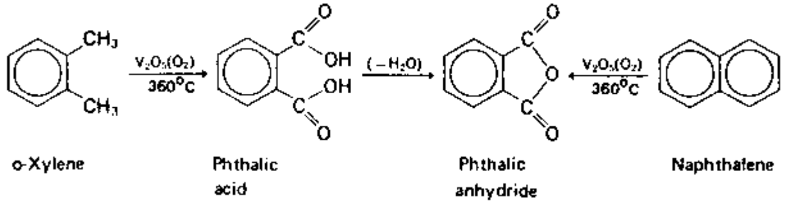
Phthalic acid (1,2-benzene dicarboxylic acid), isophthalic acid (1,3-benzene dicarboxylic acid), and terephthalic acid (1,4-benzene dicarboxylic acid) are made by the selective catalytic oxidation of the corresponding xylenes. Terephthalic acid may also be produced by the isomerization of its isomers by heating the potassium salts in the presence of cadmium iodide.

About 8 billion lb of terephthalic acid is produced annually in the United States. Phthalic acid is converted to phthalic anhydride when heated. This acid may also be produced by the classic oxidation of naphthalene and by the hydrolysis of terephthalonitrile.



p-Xylene Terephthalic acid m-Xylene Isophthalic acid

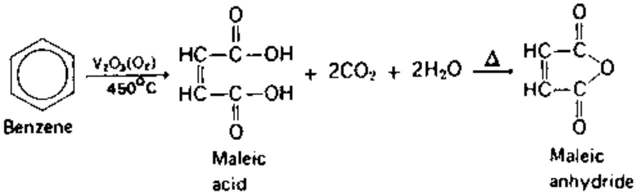
(16.6)



o-Xylene Phthalic acid Phthalic anhydride Naphthalene

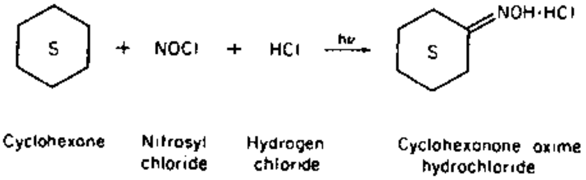
(16.7)

Maleic anhydride (2,5-furandione, toxilic anhydride) is obtained as a byproduct (about 6%) in the production of phthalic anhydride, and by the vapor phase oxidation of butylene or crotonaldehyde. It is also obtained by the dehydration of maleic acid and by the oxidation of benzene. Maleic anhydride is used for the production of unsaturated polyester resins. This reactant, like most reactants, including benzene, is fairly toxic.

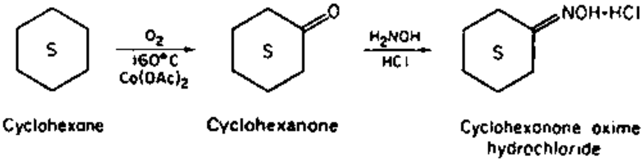


(16.8)

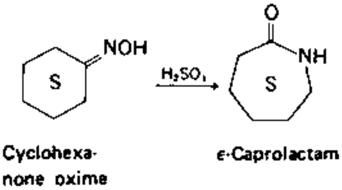
2-Pyrrolidone is a lactone used for the production of nylon-4. This reactant may be produced by reductive ammonation of maleic anhydride. ε-Caprolactam, which is used for the production of nylon-6, may be produced by the Beckman rearrangement of cyclohexanone oxime [Eq. (16.11)]. The oxime may be produced by the catalytic hydrogenation of nitrobenzene, the photolytic nitrosylation of cyclohexane [Eq. (16.9)], or the classic reaction of cyclohexanone and hydroxylamine [Eq. (16.10)]. ε-Caprolactam is also produced by the nitrosylation of cyclohexane carboxylic acid. The latter is obtained by the hydrogenation of benzoic acid, which is obtained by the oxidation of toluene. Nearly one-half of the production of caprolactam is derived from phenol.



(16.9)

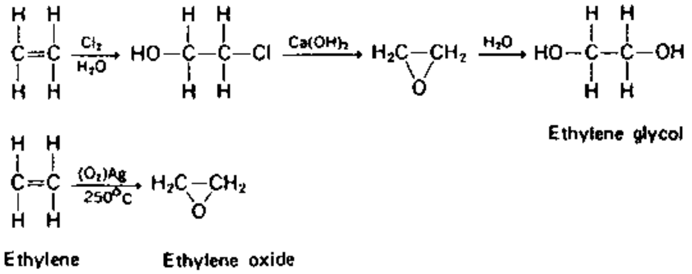


(16.10)



(16.11)

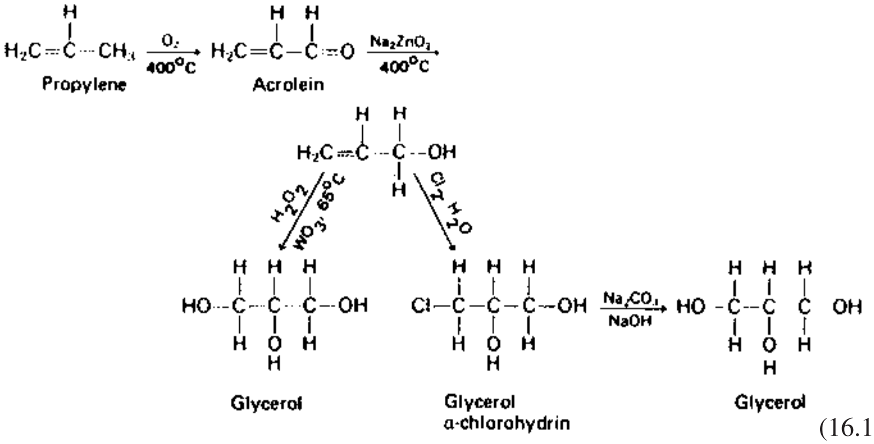
Ethylene oxide (oxirane), used for the production of ethylene glycol and poly (ethylene oxide), is obtained by the catalytic oxidation of ethylene [Eq. (16.12)]. Ethylene glycol, used for the production of polyesters, is produced by the hydrolysis of ethylene oxide [Eq. (16.12)]. Ethylene oxide and ethylene glycol are produced at an annual rate of 8 billion lb. and 5.2 billion lb., respectively, in the United States.



(16.12)

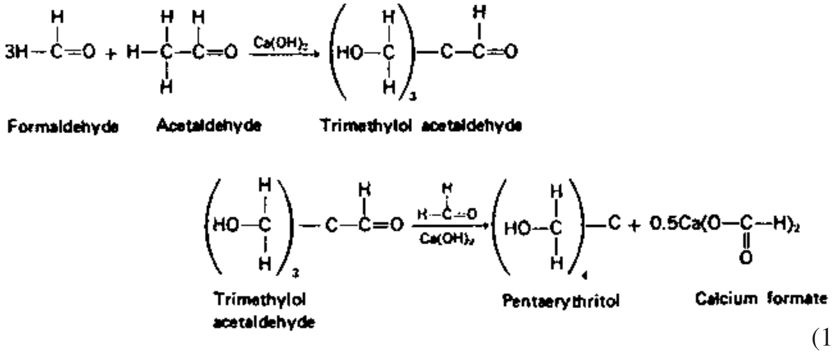
Propylene oxide is obtained by the oxidation of propylene in a similar manner.

Glycerol (glycerin), used for the production of alkyds, is produced by the catalytic hydroxylation or the hypochlorination of allyl alcohol. The latter is produced by the reduction of acrolein, which is obtained by the oxidation of propylene [Eq. (16.13)].



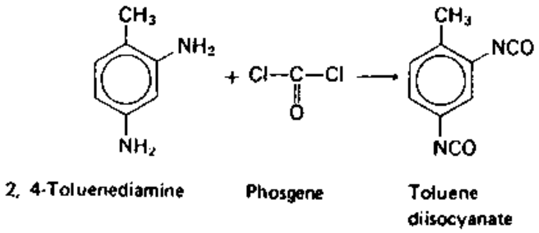
(16.13)

Pentaerythritol, used in the production of alkyds, is produced by a crossed Cannizzaro reaction of the aldol condensation product of formaldehyde and acetaldehyde. The byproduct, calcium formate, serves as the major source of formic acid.



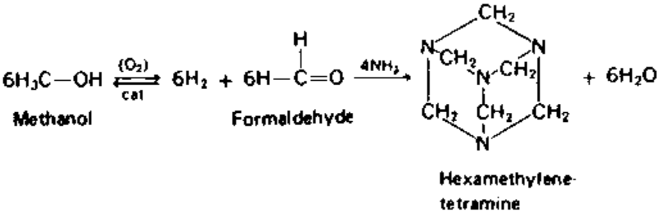
(16.14)

2,4-Toluene diisocyanate (TDI), used for the production of polyurethanes and polyureas, is obtained by the phosgenation of 2,4-toluenediamine. Phosgene is obtained by the reaction of chlorine and carbon monoxide. TDI may also be produced by the catalytic liquid phase reductive carbonylation of dinitrotoluene.



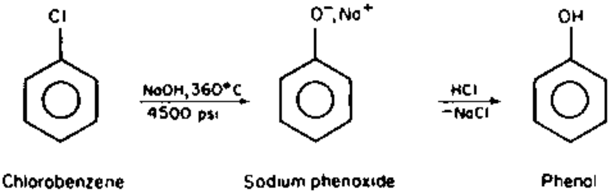
(16.15)

Formaldehyde, which is used for the production of phenolic and amino resins, is produced at an annual rate of over 7 billion lb. by the catalytic hot-air oxidation of methanol. Hexamethylenetetramine (hexa) is produced by the condensation of ammonia and 30% aqueous formaldehyde (formalin).

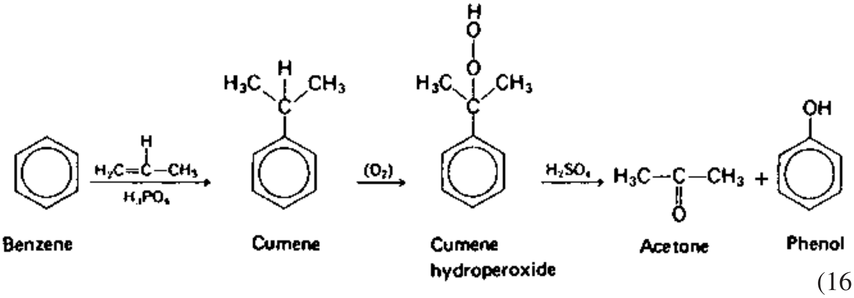


(16.16)

While some phenol is produced by the nucleophilic substitution of chlorine in chlorobenzene by the hydroxyl group [Eq. (16.17)], most synthetic phenol (carbolic acid, phenylic acid) is produced by the acidic decomposition of cumene hydroperoxide [Eq. (16.18)]. The cumene is obtained by the oxidation of cumene hydroperoxide.



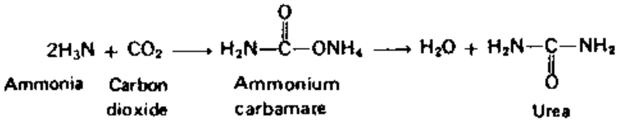
(16.17)



(16.18)

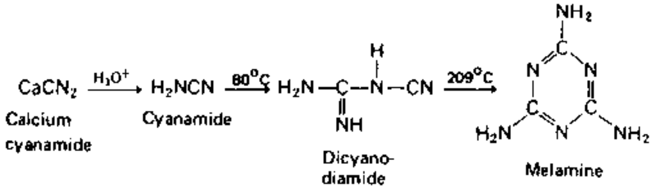
Some of the newer processes for synthesizing phenol are the dehydrogenation of cyclohexanol, the decarboxylation of benzoic acid, and the hydrogen peroxide hydroxylation of benzene. Phenol, which is used for production of phenol-formaldehyde resins as well as a starting material for the synthesis of many important materials, is produced at an annual rate of over 4 billion lb.

Urea (carbamide), used for the production of urea-formaldehyde resins, is produced at an annual rate of about 18 billion lb. by the in situ decomposition of ammonium carbamate at 5 atm pressure. The latter is obtained by the condensation of liquid ammonia and liquid carbon dioxide at a temperature of 200°C and at a pressure of 200 atm.

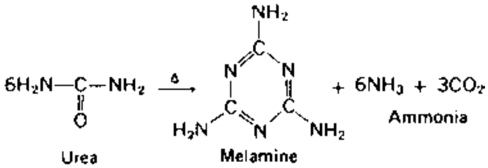


$$2H_3N + CO_2 \longrightarrow H_2N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}ONH_4 \longrightarrow H_2O + H_2N{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}NH_2 \tag{16.19}$$

Melamine (cyanuramide) is obtained by heating dicyanodiamide (dicy) [Eq. (16.20)]. The latter is obtained by heating cyanamide. Melamine, which is used for the production of melamine-formaldehyde resins, is also obtained by the heating of urea [Eq. (16.21)].

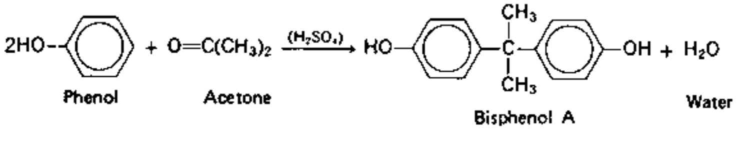


(16.20)



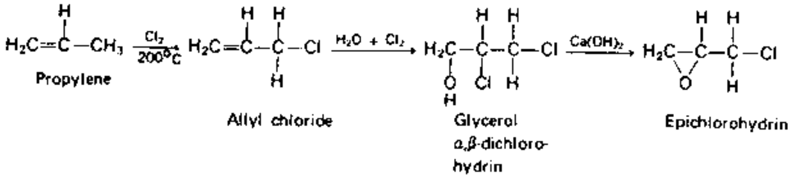
(16.21)

Bisphenol A [(bis-4-hydroxyphenyl)dimethylmethane], used for the production of epoxy resins and polycarbonates, is obtained by the acidic condensation of phenol and acetone. In this reaction, the carbonium ion produced by the protonation of acetone attacks the phenol molecule at the para position to produce a quinoidal oxonium ion which loses water and rearranges to a p-isopropylphenol carbonium ion. The water attacks another phenol molecule in the para position to produce a quinoidal structure which rearranges to bisphenol A. Recently, it has been found that bisphenol A is an endocrine system disrupter. The consequences of this are still being determined.



(16.22)

Epichlorohydrin (chloropropylene oxide), used for the production of epoxy resins, is obtained by the dehydrochlorination of glycerol α,β-dichlorohydrin (2,3-dichloro-1-propanol). The hydrin is produced by chlorohydrination of allyl chloride.



(16.23)

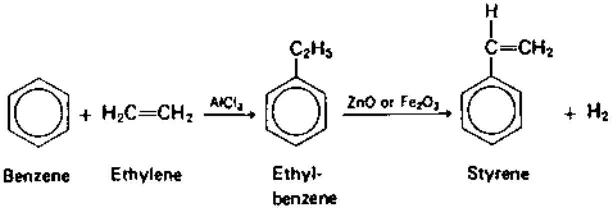
Methyltrichlorosilane is readily produced by the Grignard reaction of silicon tetrachloride and methylmagnesium chloride [Eq. (16.28)]. Dimethyldichlorosilane is obtained by the reaction of methylmagnesium chloride and methyltrichlorosilane [Eq. (16.25)]. Since the silicon atom is less electronegative than carbon, chlorine is much more electronegative than silicon and is a good leaving group in nucleophilic substitution reactions.

H_3CMgCl	$+$	$SiCl_4$	$\rightarrow$	H_2CSiCl_3	$+$	$MgCl_2$	
Methylmagnesium chloride		Silicon tetrachloride		Methyltrichlorosilane		Magnesium chloride	(16.24)

H_3CMgCl	$+$	H_3CSiCl_3	$\rightarrow$	$(H_3C_2)SiCl_2$	$+$	$MgCl_2$	
Methylmagnesium chloride		Methylchlorosilane		Dimethyldichlorosilane		Magnesium chloride	(16.25)

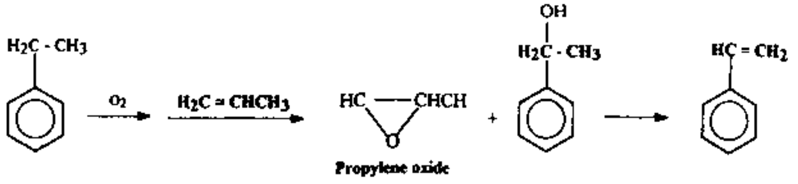
16.3 SYNTHESIS OF VINYL MONOMERS

Styrene, which is one of the most important aromatic compounds, is produced at an annual rate of about 11 billion lb by the catalytic vapor phase dehydrogenation of ethylbenzene. The latter is obtained by the Friedel-Crafts condensation of ethylene and benzene. Styrene can also be produced by the palladium acetate–catalyzed condensation of ethylene and benzene and by the dehydration of methylphenylcarbinol obtained by the propylation of ethylbenzene hydroperoxide. Because of its toxicity, the concentration of styrene in the atmosphere must be limited to a few parts per million.



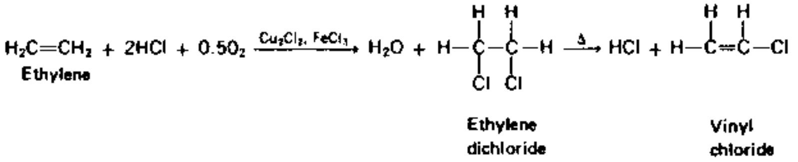
(16.26)

A process to produce styrene monomer and propylene oxide simultaneously was introduced in 1969.



(16.27)

Vinyl chloride (chloroethene, VCM), which was formerly obtained from acetylene, is now produced at an annual rate of about 15 billion lb. by the transcatalytic process in which chlorination of ethylene, oxychlorination of byproduct hydrogen chloride, and dehydrochlorination of ethylene dichloride take place in a single reactor.



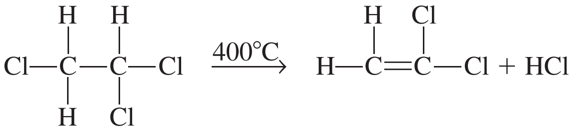
(16.28)

VCM is also produced by the direct chlorination of ethylene and the reaction of acetylene and HCl [Eq. (16.29)]. The HCl generated in the chlorination of ethylene can be employed in the reaction with acetylene allowing a useful coupling of these two reactions [Eq. (16.30)].

$$\mathrm{CH_2{=}CH_2 + Cl_2 \longrightarrow ClCH_2CH_2Cl \xrightarrow[-\,HCl]{\Delta} CH_2{=}CHCl} \tag{16.29}$$

$$\mathrm{HC{\equiv}CH \xrightarrow[HgCl_2]{HCl} CH_2{=}CHCl} \tag{16.30}$$

Vinylidene chloride is produced by the pyrolysis of 1,1,2-trichloroethane at 400°C in the presence of lime or caustic. Since both vinyl chloride and vinylidene chloride are carcinogenic, their concentrations in air must be kept to a few parts per million or less.

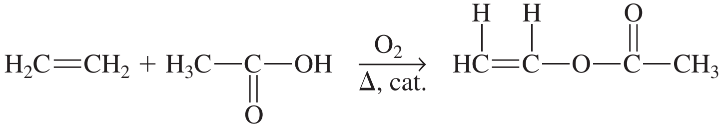


$$\mathrm{Cl{-}\underset{H}{\overset{H}{C}}{-}\underset{Cl}{\overset{H}{C}}{-}Cl \xrightarrow{400^\circ C} H{-}\overset{H}{C}{=}\overset{Cl}{C}{-}Cl + HCl} \tag{16.31}$$

1,1,2-Trichloroethane

Vinylidene chloride

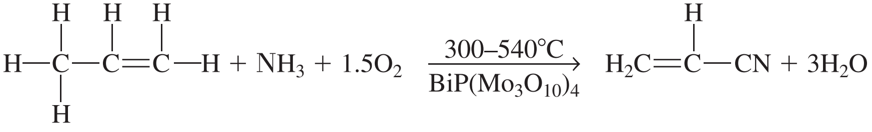
Vinyl acetate, which is produced annually at a rate of 2.9 billion lb., was formerly obtained by the catalytic acetylation of acetylene. However, this monomer is now produced by the catalytic oxidative condensation of acetic acid and ethylene [Eq. (16.32)]. Other vinyl esters may be obtained by the transesterification of vinyl acetate with higher boiling carboxylic acids.



$$\mathrm{H_2C{=}CH_2 + H_3C{-}\underset{\underset{O}{\|}}{C}{-}OH \xrightarrow[\Delta,\ cat.]{O_2} H\overset{H}{C}{=}\overset{H}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3} \tag{16.32}$$

Ethylene Acetic acid Vinyl acetate

Acrylonitrile (vinyl cyanide) is produced at an annual rate of 3 billion lb. by the ammoxidation of propylene. Since this monomer is carcinogenic, considerable care must be taken to minimize exposure to acrylonitrile.



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{C}{-}H + NH_3 + 1.5O_2 \xrightarrow[BiP(Mo_3O_{10})_4]{300\text{–}540^\circ C} H_2C{=}\overset{H}{C}{-}CN + 3H_2O} \tag{16.33}$$

Propylene Ammonia Acrylonitrile

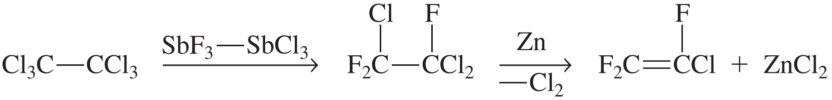
Ethylene, propylene, and butylene are produced at annual rates of 52 billion, 29 billion, and 0.4 billion lb., respectively, by the vapor phase cracking of light oil fractions of petroleum feedstocks or petroleum gases. The acetylenes, produced as byproducts, are selectively absorbed, and the monomers are obtained by fractional distillation.

Tetrafluoroethylene is obtained by the thermal dehydrochlorination of chlorodifluoromethane [Eq. (16.35)]. The latter is produced by the reaction of chloroform and hydrogen fluoride [Eq. (16.34)].

$$\underset{\substack{\text{Hydrogen}\\\text{fluoride}}}{HF} + \underset{\text{Chloroform}}{HCCl_3} \longrightarrow \underset{\substack{\text{Hydrogen}\\\text{chloride}}}{HCl} + \underset{\substack{\text{Chlorodi-}\\\text{fluoromethane}}}{HCClF_2} \qquad (16.34)$$

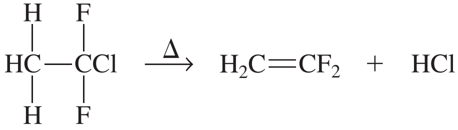
$$\underset{\substack{\text{Chlorodi-}\\\text{fluoromethane}}}{2\overset{\displaystyle H}{\overset{|}{C}}ClF_2} \xrightarrow[600^\circ]{\Delta} \underset{\substack{\text{Hydrogen}\\\text{chloride}}}{2HCl} + \underset{\substack{\text{Tetrafluoro-}\\\text{ethylene}}}{F_2C{=}CF_2} \qquad (16.35)$$

Trifluoromonochloroethylene is obtained by the zinc metal dechlorination of trichlorotrifluoroethane. The latter is produced by the fluorination of hexachloroethane.



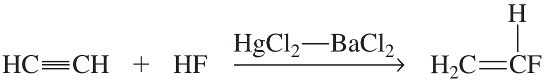
$$\underset{\substack{\text{Hexachloro-}\\\text{ethane}}}{Cl_3C{-}CCl_3} \xrightarrow{SbF_3{-}SbCl_3} \underset{\substack{\text{Trichlorotri-}\\\text{fluoroethane}}}{F_2\overset{\displaystyle Cl}{\overset{|}{C}}{-}\overset{\displaystyle F}{\overset{|}{C}}Cl_2} \xrightarrow[-Cl_2]{Zn} \underset{\substack{\text{Trifluoro-}\\\text{monochloro-}\\\text{ethylene}}}{F_2C{=}\overset{\displaystyle F}{\overset{|}{C}}Cl} + \underset{\substack{\text{Zinc}\\\text{chloride}}}{ZnCl_2} \qquad (16.36)$$

Vinylidene fluoride is produced by the thermal dehydrochlorination of 1,1,1-monochlorodifluoroethane.



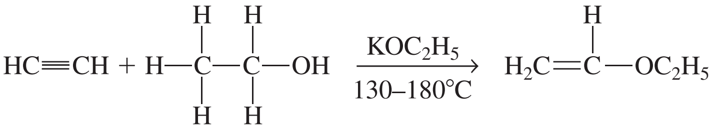
$$\underset{\substack{\text{1,1,1-Monochlorodi-}\\\text{fluoroethane}}}{H\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}\overset{\displaystyle F}{\underset{\displaystyle F}{\overset{|}{\underset{|}{C}}}}Cl} \xrightarrow{\Delta} \underset{\substack{\text{Vinylidene}\\\text{fluoride}}}{H_2C{=}CF_2} + \underset{\substack{\text{Hydrogen}\\\text{chloride}}}{HCl} \qquad (16.37)$$

Vinyl fluoride may be obtained by the catalytic hydrofluorination of acetylene.



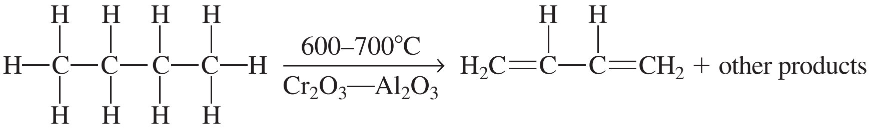
$$\underset{\text{Acetylene}}{HC{\equiv}CH} + \underset{\substack{\text{Hydrogen}\\\text{fluoride}}}{HF} \xrightarrow{HgCl_2{-}BaCl_2} \underset{\substack{\text{Vinyl}\\\text{fluoride}}}{H_2C{=}\overset{\displaystyle H}{\overset{|}{C}}F} \qquad (16.38)$$

Vinyl ethyl ether is obtained by the ethanolysis of acetylene in the presence of potassium ethoxide.



$$\underset{\text{Acetylene}}{HC{\equiv}CH} + \underset{\text{Ethanol}}{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}OH} \xrightarrow[130\text{–}180^\circ C]{KOC_2H_5} \underset{\text{Vinyl ethyl ether}}{H_2C{=}\overset{\displaystyle H}{\overset{|}{C}}{-}OC_2H_5} \qquad (16.39)$$

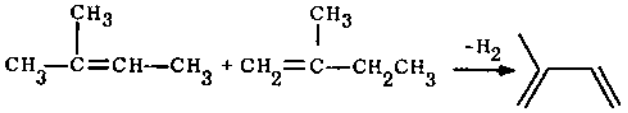
1,3-Butadiene, which is used for the production of elastomers, is produced at an annual rate of 4 billion lb. by the catalytic thermal cracking of butane and as a byproduct of other cracking reactions.



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H} \xrightarrow[Cr_2O_3{-}Al_2O_3]{600\text{–}700^\circ C} \mathrm{H_2C{=}\overset{H}{C}{-}\overset{H}{C}{=}CH_2} + \text{other products}$$

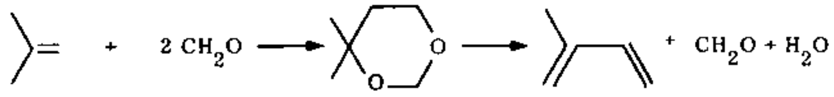
Butane 1,3-Butadiene (16.40)

The isoprene monomer is not readily available from direct cracking processes. Several routes are employed for its synthesis. One route begins with the extraction of isoamylene fractions from catalytically cracked gasoline streams. Isoprene is produced by subsequent catalytic dehydrogenation.



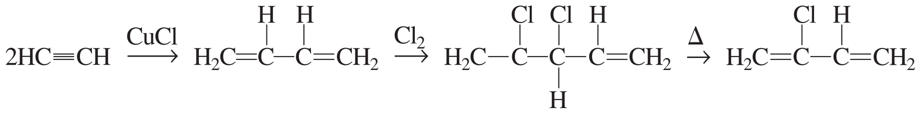
Isoprene (16.41)

Dimerization of propylene is also used to produce isoprene. Several steps are involved [Eq. (16.42)]. First, dimerization of propylene to 2-methyl-1-pentene occurs. Then isomerization to 2-methyl-2-pentene is effected. Finally, the 2-methyl-2-pentene is pyrolized to isoprene and methane. Another multistep synthesis starts with acetylene and acetone. Perhaps the most attractive route involves formaldehyde and isobutylene.



Isobutylene Formaldehyde Isoprene (16.42)

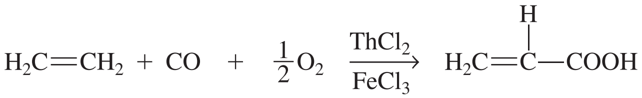
Chloroprene, used for the production of neoprene rubber, is obtained by the dehydrochlorination of dichlorobutene. The latter is produced by the chlorination of 1,3-butadiene, which in turn is synthesized from acetylene.



$$2HC{\equiv}CH \xrightarrow{CuCl} \mathrm{H_2C{=}\overset{H}{C}{-}\overset{H}{C}{=}CH_2} \xrightarrow{Cl_2} \mathrm{H_2C{-}\overset{Cl}{C}{-}\underset{H}{\overset{Cl}{C}}{-}\overset{H}{C}{=}CH_2} \xrightarrow{\Delta} \mathrm{H_2C{=}\overset{Cl}{C}{-}\overset{H}{C}{=}CH_2}$$

Acetylene 1,3-Butadiene Dichlorobutene Chloroprene (16.43)

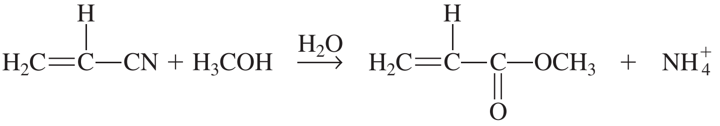
Acrylic acid may be prepared by the catalytic oxidative carbonylation of ethylene or by heating formaldehyde and acetic acid in the presence of potassium hydroxide.



$$H_2C{=}CH_2 + CO + \frac{1}{2}O_2 \xrightarrow[FeCl_3]{ThCl_2} H_2C{=}\overset{\displaystyle H}{\overset{|}{C}}{-}COOH \qquad (16.44)$$

Ethylene Carbon monoxide Oxygen Acrylic acid

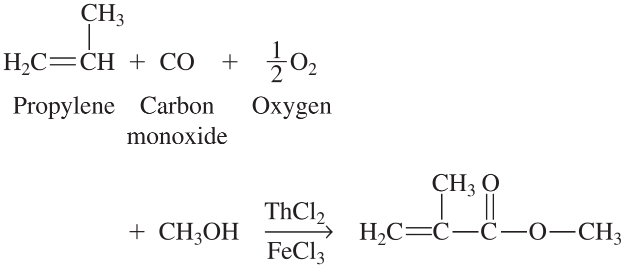
Methyl acrylate may be obtained by the addition of methanol to the reactants in the previous synthesis for acrylic acid or by the methanolysis of acrylonitrile.



$$H_2C{=}\overset{\displaystyle H}{\overset{|}{C}}{-}CN + H_3COH \xrightarrow{H_2O} H_2C{=}\overset{\displaystyle H}{\overset{|}{C}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}OCH_3 + NH_4^+ \qquad (16.45)$$

Acrylonitrile Methanol Methyl acrylate Ammonium ion

Methyl methacrylate may be prepared by the catalytic oxidative carbonylation of propylene in the presence of methanol.



$$H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}H + CO + \frac{1}{2}O_2 + CH_3OH \xrightarrow[FeCl_3]{ThCl_2} H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}CH_3 \qquad (16.46)$$

Propylene Carbon monoxide Oxygen

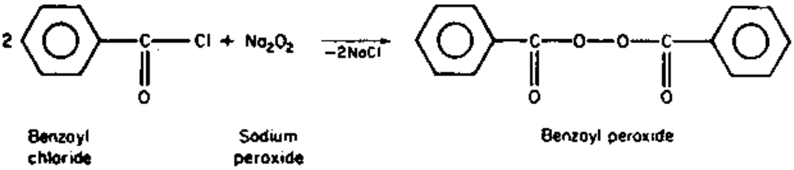
Methanol Methyl methacrylate

Other esters of acrylic and methacrylic acid may be prepared by transesterification with higher boiling alcohols.

16.4 SYNTHESIS OF FREE RADICAL INITIATORS

Free radical initiators are compounds containing covalent bonds that readily undergo homolytic cleavage to produce free radicals. The most widely used organic free-radical initiators are peroxides and azo compounds.

Benzoyl peroxide is produced when benzoyl chloride and sodium peroxide are stirred in water.



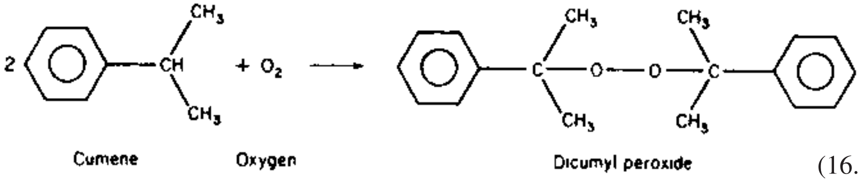
(16.47)

tert-Butyl hydroperoxide is produced by the acid-catalyzed addition of hydrogen peroxide to isobutylene [Eq. (16.48)]. tert-Butyl peroxide is produced when tert-butyl hydroperoxide is added to isobutylene [Eq. (16.49)].

$$\underset{\text{Isobutylene}}{(CH_3)_2C{=}CH_2} + \underset{\substack{\text{Hydrogen}\\\text{peroxide}}}{H_2O_2} \xrightarrow{H_2SO_4} \underset{\substack{\text{tert-Butyl}\\\text{hydroperoxide}}}{(CH_3)_3COOH} \qquad (16.48)$$

$$\underset{\text{Isobutylene}}{(CH_3)_2C{=}CH_2} + \underset{\substack{\text{tert-Butyl}\\\text{hydroperoxide}}}{(CH_3)_2COOH} \xrightarrow{H_2SO_4} \underset{\substack{\text{tert-Butyl}\\\text{peroxide}}}{(CH_3)_3COOC(CH_3)_3} \qquad (16.49)$$

Dicumyl peroxide is produced by the air oxidation of cumene.



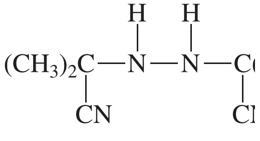
(16.50)

All initiators are potentially explosive compounds and must be stored and handled with care. 2,2′-Azobisisobutyronitrile (AIBN, 2,2-dicyano2,2-azopropane) is obtained from the reaction of acetone with potassium cyanide and hydrozine hydrochloride. As shown in Eq. (16.51), the reaction of potassium cyanide with hydrazine hydrochloride produces hydrogen cyanide and hydrazine. The latter reacts with acetone to form acetone dihydrazone, which reacts with the former (HCN) to produce a substituted hydrazone, which is then oxidized to AIBN by sodium hypochlorite. When methyl ethyl ketone is used in place of acetone, 2,2′-azobis-2-methylbutyronitrile is produced.

$$\underset{\substack{\text{Potassium}\\\text{cyanide}}}{2KCN} + \underset{\substack{\text{Hydrazine}\\\text{hydrochloride}}}{Cl^-,{}^+H_3N{-}NH_3^+, Cl^-} \xrightarrow[\text{—KCl}]{} \underset{\substack{\text{Hydrogen}\\\text{cyanide}}}{2HCN} + \underset{\text{Hydrazine}}{H_2N{-}NH_2}$$

$$\underset{\text{Acetone}}{(CH_3)_2C{=}O} + \underset{\text{Hydrazine}}{H_2N{-}NH_2} \longrightarrow \underset{\text{Acetone dihydrazone}}{(CH_3)_2C{=}N{-}N{=}C(CH_3)_2}$$

$$\underset{\text{Acetone dihydrazone}}{(CH_3)_2C{=}N{-}N{=}C(CH_3)_2} + \underset{\substack{\text{Hydrogen}\\\text{cyanide}}}{2HCN} \longrightarrow \qquad (16.51)$$

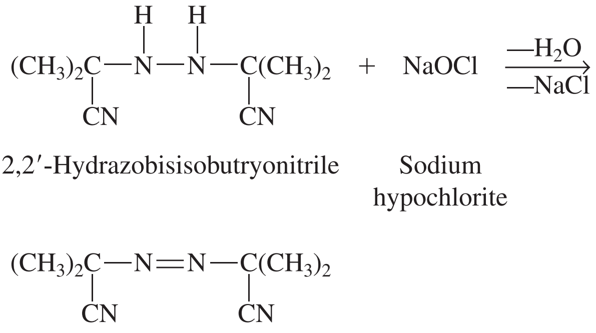


$$(CH_3)_2\underset{\displaystyle CN}{\underset{|}{C}}{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\underset{\displaystyle C}{\underset{|}{C}}$$

2,2′-Hydrazobisisobutry

Table 16.2 Physical Properties of Polymer Condensation Reactants

Compound	Melting point (ºC)	Boiling point (ºC)	Specific gravity	Index of refraction
Adipic acid	152	265^{10}	$1.360^{25/4}$	
Epichlorohydrin	−57	117^{156}	$1.183^{25/25}$	1.4397^{18}
Ethylene glycol	−15.6	198	$1.113^{19/4}$	1.4318^{20}
Ethylene oxide	−111.7	10.7	$0.887^{7/4}$	$1.3599^{8.4}$
Formaldehyde	−92	−21	0.815^{20}	
Furfural	−39	162	$1.159^{20/4}$	1.5261^{20}
Furfuryl alcohol	—	169.5^{752}	$1.129^{25/4}$	1.4852^{20}
Glycerol	18.2	290	$1.261^{20/4}$	1.4729^{20}
Hexamethylenediamine	42	204.5		
Maleic anhydride	60	202	1.5	
Melamine	354	—	1.5373^{25}	
Pentaerythritol	262	276^{30}		
Phenol	43	181.8^{8}	$1.071^{25/4}$	1.54^{45}
Phthalic acid (o)	231	—	$1.593^{20/4}$	
Isophthalic acid (m)	347			
Terephthalic acid (p)	300(s)			
Phthalic anhydride	132	284.5	1.527^{4}	
Pyromellitic dianhydride	287	397–400	1.68	
Sebacic acid	135.5	294.5^{100}	$1.207^{25/4}$	1.42^{133}
Urea	132.7	—	$1.335^{20/4}$	



$$(CH_3)_2\underset{CN}{C}-\overset{H}{N}-\overset{H}{N}-\underset{CN}{C}(CH_3)_2 + NaOCl \xrightarrow[-NaCl]{-H_2O} (CH_3)_2\underset{CN}{C}-N{=}N-\underset{CN}{C}(CH_3)_2$$

2,2′-Hydrazobisisobutryonitrile

Sodium hypochlorite

AIBN

The physical constants of polymer reactants and monomers are listed in Tables 16.2 and 16.3. Data on initiators are listed in Chapter 8.

SUMMARY

1. Feedstocks for the synthesis of monomers of basic polymeric materials must be readily available and inexpensive because they are utilized in polymer synthesis in large quantities, allowing the polymeric materials to be inexpensive. Basic feedstocks are petrochemical and coal-based.

Table 16.3 Physical Properties of Vinyl Monomers

Compound	Melting point (°C)	Boiling point (°C)	Density	Index of refraction
Acrylamide	85	125^{25}	1.122^{30}	
Acrylic acid	12	141	1.0511^{20}	1.4224^{20}
Methyl acrylate	−75	80	0.953^{20}	1.3984^{20}
Acrylonitrile	−83.6	79	0.8060^{20}	1.393^{20}
1,3-Butadiene	−109	−4.4	0.6211^{20}	1.4292^{-25}
Chloroprene	—	59.4	0.9583^{20}	1.4583^{20}
Chlorotrifluoroethylene	−158	−28		
1-Butene	−185	−6.3	0.5951^{20}	1.3962^{20}
Isobutylene (2-methylpropene)	−141	−6.6	$0.6266^{-6.6}$	1.3814^{-25}
Ethylene	−169	−104	0.566^{-102}	1.363^{-100}
Tetrafluoroethylene	−142.5	−76.3	1.519^{20}	
Isoprene	−146	34	0.6806^{20}	1.4194^{20}
Methacrylic acid	15.5	161	1.0153^{20}	1.43143^{20}
Methyl methacrylate	−48	101	0.936^{20}	1.413^{20}
Methacrylonitrile	−36	90.3	0.7998^{20}	1.4007^{20}
Methyl isopropenyl ketone	−54	98	0.8550^{20}	1.4220^{20}
Propylene	−185	−48	0.5139^{-20}	
Styrene	−30.6	145.2	0.9090^{20}	1.54682^{20}
α-Methylstyrene	−23.2	163.4	0.9165^{10}	1.5386^{20}
Vinyl acetate	—	72.5	0.9338^{20}	1.3953^{20}
Vinyl chloride	−154	−14	0.99176^{15}	1.398^{15}
Vinyl ethyl ether	−115	35	0.7589^{20}	1.3767^{20}
Vinyl fluoride	−161	−72		
Vinylidene chloride	−122	31.7	1.2129^{20}	1.4249^{20}
2-Vinylpyridine	—	80^{29}	0.9985^{0}	1.5494^{20}

2. Monomer synthesis is both an art and science developed by great and ongoing research efforts allowing the inexpensive and safe availability of the starting materials which the polymer industry is based. Commercial monomer synthesis is based on both the availability of inexpensive materials derived from basic feedstocks and on an "interconnectiveness" between products and synthetic by-products that are essential to the synthesis of other essential materials.
3. The precise conditions of synthesis have been developed through a combination of trial-and-error and "high" science. These conditions are continually being refined thorough research. Reactions and reaction conditions employed for monomer synthesis are similar to those employed for other commercial organic synthesis.

GLOSSARY

AIBN: 2,2′-Azobisisobutyronitrile.

Cannizzaro reaction: An internal oxidation-reduction reaction of aldehydes.

carbamide: Urea.
carcinogenic: Cancer producing.
chemurgic compound: Compound made from a plant source.
chloroprene: 2-Chloro-1,3-butadiene.
Friedel-Crafts condensation: Condensation that takes place in the presence of a Lewis acid, such as aluminum chloride.
Grignard reagent: RMgX.
isophthalic acid: The meta isomer.
Raney nickel: A porous nickel catalyst produced from a nickel-aluminum alloy.
TDI: 2,4-Toluene diisocyanate.
terephthalic acid: The para isomer of the dicarboxylic acid of benzene.
THF: Tetrahydrofuran.
VCM: Vinyl chloride.

EXERCISES

1. Why are there so many methods for the preparation of adipic acid?
2. Write the equations for the industrial synthesis of the following:
    a. Adipic acid
    b. Hexamethylenediamine
    c. Sebacic acid
    d. Terephthalic acid
    e. Maleic anhydride
    f. ε-Caprolactam
    g. Ethylene oxide
    h. Glycerol
    i. Pentaerythritol
    j. TDI
    k. Hexamethylenetetramine
    l. Phenol
    m. Urea
    n. Melamine
    o. Bisphenol A
    p. Epichlorohydrin
    q. Methyltrichlorosilane
    r. Styrene
    s. Vinyl chloride
    t. Vinyl acetate
    u. Acrylonitrile
    v. Vinyl ethyl ether
    w. Methyl methacrylate
    x. Benzoyl peroxide
    y. tert-Butyl peroxide
    z. AIBN
3. Name a reactant or monomer produced by the following:
    a. Grignard reaction
    b. Friedel-Crafts reaction
    c. Beckman rearrangement

d. A chemurgic process
e. A crossed Cannizzaro reaction

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17

Polymer Technology

Today nearly 10,000 American companies are active in the general area of synthetic polymers. Following is a brief description of these companies divided according to their function.

Manufacturers: There are over 200 major manufacturers of general purpose polymers and numerous other manufacturers of specialty polymers.

Processors: Some companies manufacture their own polymeric materials for subsequent processing, but the majority purchase the necessary polymeric materials from other companies. Processors may specialize in the use of selected polymers, such as nylons and polycarbonates, or focus on particular techniques of processing, such as coatings, films, sheets, laminates, and bulk molded and reinforced plastics.

Fabricators and finishers: The majority of companies are involved in the fabrication and finishing of polymers, i.e., production of the end products for industrial and general public consumption. Fabrication can be divided into three broad areas: machining, forming, and fashioning. Machining includes grinding, sawing, drilling, turning on a lathe, cutting, tapping, reaming, and milling. Forming includes molding and other methods of shaping and joining by welding, gluing, screwing, or other techniques. Fashioning includes cutting, sewing, sheeting, and sealing. Fabrication sequences vary with the polymeric material and desired end product.

While much classic polymer technology was developed without the benefit of science, modern polymer technology and polymer science are closely associated. The technology of fibers, elastomers, coatings, and plastics is discussed in this chapter.

Polymer Processing

Polymer processing can be defined as the process whereby raw materials are converted into products of desired shape and properties. Thermoplastic resins are generally supplied as pellets, marbles, or chips of varying sizes, and they may contain some or all of the desired additives. When heated above their T_g, thermoplastic materials soften and flow as viscous liquids that can be shaped using a variety of techniques and then cooled to "lock" in the micro- and gross structure

Thermosetting feedstocks are normally supplied as meltable and/or flowable prepolymer, oligomers, or lightly or noncrosslinked polymers that are subsequently crosslinked forming the thermoset article.

The processing operation can be divided into three general steps: preshaping, shaping, and postshaping. In preshaping, the intent is to produce a material that can be shaped by application of heat and/or pressure. Important considerations include

Handling of solids and liquids including mixing, low, compaction, and packing
Softening through application of heat and/or pressure
Addition and mixing/dispersion of added materials
Movement of the resin to the shaping apparatus through application of heat and/or pressure and other flow aiding processes, and
Removal and (desired recycling) of unwanted solvent, unreacted monomer(s), byproducts, and waste (flash)

The shaping step may include any single or combination of the following:

Die forming (including sheet and film formation, tube and pipe formation, fiber formation, coating, and extrusion)
Molding and casting
Secondary shaping (such as film and blow molding, thermoforming), and
Surface treatments (coating and calendering)

Postshaping processes include welding, bonding, fastening, decorating, cutting, milling, drilling, dying, and gluing.

Polymer processing operations can be divided into five broad categories:

Spinning (generally for fibers)
Calendering
Coating
Molding
Injection

Essentially all of the various processing types utilize computer-assisted design (CAD) and computer-assisted manufacture (CAM). CAD allows the design of a part and incorporates operating conditions to predict behavior of the pieces prior to real operation. CAD also transfers particular designs and design specifications to other computer-operated systems (CAMs), which allow the actual construction of the part or total apparatus. CAM systems operate most modern processing systems, many allowing feedback to influence machine operation. Table 17.1 lists some of the major forms of each of these processing groups. Processing and performance are interrelated to one another and to additional factors. Jaffe relates these major groups of factors in an interactive diamond given below (Figure 17.1). Understanding these factors and their interrelationships becomes increasingly important as the specific performance requirements become more specific. Performance is related to the chemical and physical structure and to the particular processing performed on the material during its lifetime. The physical structure is a reflection of both the chemical structure and the total history of the synthesis and subsequent exposure of the material to

Table 17.1 Major Forms of Polymer Processing Groupings

Process	Typical form of product
Calendering	Films, sheets
Coating	Film
Injection	Solid
Reaction injected	
Reciprocating screw	
Two-stage	
Molding	
Blow	Hollow
Displacement	
Extrusion	
Injection/transfer	
Stretch	
Cold solid	
Compression	Solid, hollow
Rotational	Solid, hollow
Thermoforming	Hollow
Transfer	Solid
Spinning	Fibers
Dry	
Gel	
Melt	
Reaction	
Wet	

additional forces. These “additional” forces are included under the broad idea of processing and include any influence that contributes to the secondary (and greater) structure—stress/strain, light, chemical, etc. The portion of the diamond relating processing to physical structure encompasses the study of structure—property relationships. A single material may be processed using only a single process somewhat unique to that material (such as liquid crystals) or by a variety of processes (such as polyethylene), where the particular technique is dictated by such factors as end use and cost.

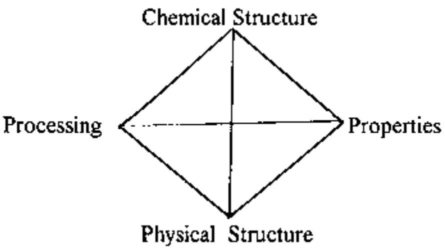

Figure 17.1 Relationships that influence the important interrelationships that exist for polymeric materials with respect to processing and end-product properties.

Secondary Structure—Mesophases

Primary and secondary structures greatly influence possible processing scenarios. Here, the secondary structure is generally the same as the physical structure and the primary structure is generally the same as the chemical structure. The end properties and uses are governed by intrinsic properties that, in turn, are related to the primary and secondary structure—the chemical and physical structures.

The term "meso" will be used to describe local chain organizations that occur within the nano- and microscale regions (Fig. 17.2). While the terms *mesophase* and *mesoregions* have been employed in describing order within liquid crystals, the definition will be broadened to include other ordered regions within a material's physical or secondary structure. We generally describe a polymer's secondary structure, in simple terms of ordered and disordered or crystalline and amorphous. The ordered regions can be further described in terms of mesoregions or mesophases according to their permanency and ability to influence changes within and around these regions.

Jaffe describes four mesophase classifications. Permanent mesogens are materials whose microstructures are highly fixed such as in liquid crystalline polymers (LCs). LCs are characterized by highly ordered structures in the quiescent state. They exhibit relatively low viscosities in uniaxiel flows and can be easily realigned through application of processing forces such as extrusion. To be processed, such polymers must be in the mesogenic state below their decomposition temperature. This can be achieved through the use of a specific solvent or the introduction of special comonomer units that allow them to melt (or soften), but that are introduced in such a manner as to preserve their LC character. As solids, such materials exhibit high molecular orientation, tensile moduli (near to theoretical), poor compression (that is little unoccupied volume), poor shear behavior, and high tensile strengths (on the order of 4 GPa). Such materials are anisotropic conductors and generally offer good liquid and gas barrier properties. Properties are controlled by the inherent chemical structure, molecular orientation, defect occurrences, and stress transfer mechanisms. Defects often act as the "weaklinks" in a chain, limiting mechanical properties so that defect detection, and elimination/curtailment are important and can be dependent on the processing conditions. Only certain processing techniques are suitable.

Accessible mesogens are formed from polymers that are thermotropic (that is, polymers that have a phase organization that is temperature dependent) but have an accessible isotrophic phase below their decomposition temperature. Such polymers can be processed either when the material is in its mesogen or ordered state using LC-type processing forming strong well-ordered products, or at temperatures where the ordered mesogen structure is absent. In temperature assisted systems, the material is rapidly cooled, quenched, preventing the mesogen structure formation producing a metastable isotropic

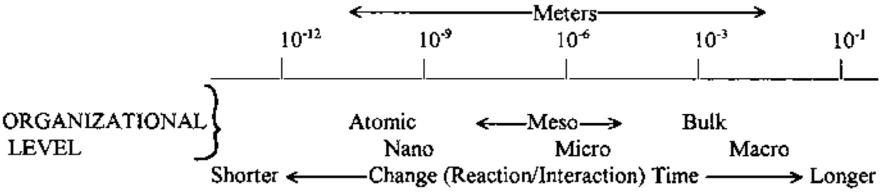

Figure 17.2 Relationship between organizational level and size.

glass or rubber. The metastable material can be processed employing less energy and force followed by a simple annealing and slower cooling that allows the formation of the ordered mesogenic structures along with the appearance of associated properties.

Examples of assembled mesogens include groups of polymer coils and polymers with side-chains that can form such mesogens. In the former case, tertiary-mesophase structures can be formed when the bundles of coiled chains come together.

Transient mesogens are regions present in flexible, random coil polymers often caused by application of external forces including simple flowing/shearing. These fixed regions occur through local segmental chain movements that happen within the chain network at points of minimum chain entropy such as sites of entanglements. They are fibrillar-like and appear to be the nucleating phase key to the row and shish-kabob-like structures in oriented polymer crystals.

These latter groups include many of the so-called “crystalites” and “crystalline” regions of common polymers.

Understanding the factors that govern the formation of mesogens will assist in determining the processing conditions for the production of materials with specified amounts, sizes, and distribution of such crystalline microstructures. Mesophases can be local or permeate the entire structure. They can be large or small, and present in a random or more ordered arrangement.

17.1 FIBERS

Polymer Processing—Spinning and Fiber Production

Introduction

Most polymeric materials are controlled by the Federal Trade Commission (FTC) with respect to the relationship between the name and content. This includes fibers. While the FTC controls industry in the United States, the international standards are generally determined by the International Organization for Standardization, ISO (Appendix J). Table 17.2 contains a brief listing of some of the ISO and FTC names for some of the most utilized fibers.

Table 17.2 Generic Names for Synthetic Fibers According to the ISO and FTC

ISO	FTC
Acetate	Acetate
Acrylic	Acrylic
Aramid	Aramid
Chlorofiber	Vinyon/saran
Cupro/viscose/modal/ deacetylated acetate	Cupra/rayon
Elastane	Spandex
Glass	Glass
Modacrylic	Modacrylic
Nylon/polyamide	Nylon/polyamide
Polyester	Polyester
Polyethylene/polypropylene-polyolefin olefin	Vinylal vinal

Table 17.3 U.S. Production of Synthetic Fibers for 1998

Fiber production	(In millions of lb.)
Acrylics	350
Cellulosic (acetate, rayon)	370
Nylons	2900
Olefins	2800
Fiberous glass	ca 1800
Polyesters	3900

Fiber production continues to increase for most general groupings. Table 17.3 contains approximate U.S. production of the major fibers.

The dimensions of a filament or yarn are expressed in terms of a unit called the "tex" which is a measure of the fineness or linear density. One tex is 1 g per 1000 m or 10^{-6} kg/m. The tex has replaced denier as a measure of the density of the fiber. One denier is 1 g per 9000 m, so 1 denier $=$ 0.1111 tex.

While some natural materials produced "natural" fibers, fibers from synthetic and regenerated natural polymers are generally produced using one of the spinning processing techniques. Three spinning processes are generally employed in the large-scale commercial production of fibers. The first produces fiber from the melted polymer—melt spinning. The other two techniques form fibers from concentrated polymer solutions—dry and wet spinning. Figure 17.3 illustrates the essentials of these three spinning techniques. Table 17.4 is a listing of the most common polymers made into fibers by these three processes.

Melt Spinning

Melt spinning was developed in the 1930s. In melt spinning, the polymer is melted or extruded, clarified by filtration, and pumped through a die having one or more small holes. The die is called a spinneret. For melt and dry spinning, the spinneret is made of stainless steel or nickel alloy. For wet spinning, if the bath is corrosive, it is made of glass or a precious metal such as a platinum alloy. The number, shape, and size of the hole can vary considerably. The number of holes ranges from several to several thousand. For continuous filament formation, the number of holes is on the order of 10 to 100. The exit hole is usually circular giving round fibers. Other shaped holes are also employed to produce fibers with varying shapes.

The extruded fiber is then often uniaxially stretched by take-up rollers rotating at different speeds. The fiber stretching encourages the polymer chains to aline on a molecular level producing increased strength in the direction of the pull.

To produce the melted polymer, the polymer chips, rods, marbles, or sheets are heated forming a melted pool of material. In order to minimize oxidation, the melted polymer is blanketed by an inert gas, such as nitrogen. The fluidicity (inverse of viscosity) of the melt increases with increased temperature as does the cost to provide the necessary energy and tendency for unwanted reactions to occur. Thus, the polymer melt is generally aided to and through the spinneret by means of an extruder that may also be used to supply some or all of the heating. Typical melt spinning temperatures are given in Table 17.5.

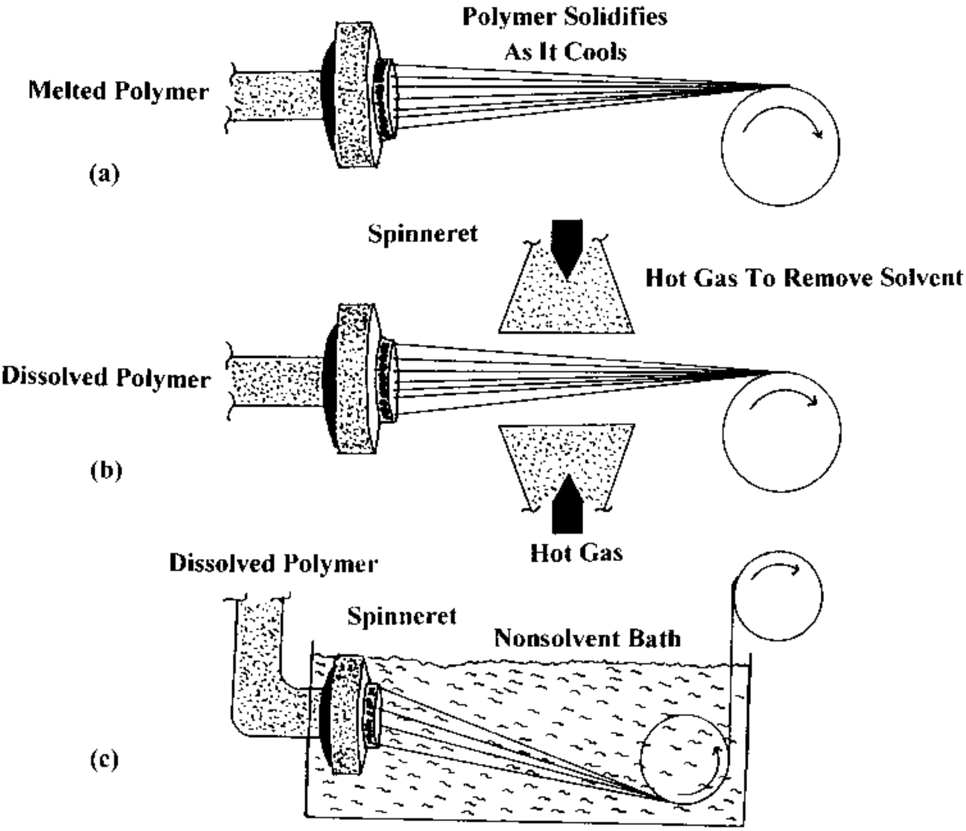

Figure 17.3 Fiber production using the three major spinning techniques.

Table 17.4 (Preferred) Spinning Processes

		Wet spinning	
Melt spinning	Dry spinning	Coagulation	Regeneration
Nylon	Acetate	Acrylic	Viscose
Polyester	Triacetate	Aramid	Cupro
Polyethylene	Acrylic	Elastane/Spandex	
Polypropylene	Elastine/Spandex	Poly(vinyl chloride)	
Poly(vinylene chloride)	Poly(vinyl chloride)		
	Aramid		
	Modacrylic		
	Vinyal		

Table 17.5 Typical Spinning Temperatures for Selected Polymers

Polymer	Melting point, °C	Spinning temperature, °C
Nylon-6	220	280
Nylon-6,6	260	290
Poly(ethylene terephthalate)	260	290
Poly(vinylidene chloride), copolymers	120–140	180
Poly(tetramethylene-N,N′-hexamethylene dicarbamate)	180	220
Poly(p-phenylene sulfide)	290	300
Polyethylene	ca 130	220–300
Polypropylene	170	250–300

Many nylon and polyester assemblies are configured so that there is a continuous progression from the melt formation of the polymer, and without hardening, the melted polymer is melt spun into fibers.

Monofilament is produced at a lower spinning speed in comparison with chopped filament because of the problem of heat buildup within the monofilament. The monofilament is generally cooled by passing it through cold water or by winding it on to a cold quench roll.

Dry Spinning

Polymer concentrations on the order of 20 to 40% are employed in dry and wet spinning. In the dry spinning process, the solution is filtered and then forced through a spinneret into a spinning cabinet through which heated air is passed to dry the filament. For economical reasons, the gas is usually air, but inert gasses such as nitrogen and superheated water are sometimes used.

Volatile solvents are used to assist in the drying. Water has been used for some systems, such as poly(vinyl alcohol), where the polymer is water-soluble. Solvent removal and recycling is important. Spinning is usually carried out using either low (about 1–2%) or high (10–50%) solvent in the filament. The amount of solvent influences the drawing process. In high solvent cases the filaments are plasticized allowing greater extension of the filament and greater alignment of the polymer chains to occur at lower temperatures and lower stresses. The extra solvent is removed just prior to, during, or subsequent to stretching. Just prior to extrusion, the polymer solution is heated to just above its boiling point, increasing the likelihood for ready removal of the solvent.

Dry spinning produced fibers have lower void concentrations in comparison to melt spun fibers because the presence of solvent molecules cause voids that are often “remembered” by the polymer. This is reflected by greater densities and lower dyeability for the dry spun fibers.

Fiberous glass is the most important inorganic fiber. It is produced by melt spinning in both a continuous filament and staple form. The molten glass is fed directly from the furnace, or melted from rods or marbles, to the spinneret. As the fiberous glass emerges it is attenuated, quenched, lubricated, and wound forming a yarn or continuous filament. The temperature for spinning is on the order of 1200 to 1500°C. This temperature is important since it controls the output, and in conjunction with the removal speed, helps control the properties of the resultant fiber including thickness and density.

Refractory fibers are produced from molten alumina-silica through centrifugal spinning and air and steam-cooling. Typically about equal amounts of silica and alumina are heated together to give a material with a melting point of about 1800°C. A higher alumina content or addition of a small amount of boric or chromic acid give a fiber with a higher use temperature. In centrifugal spinning, the melt or solution is placed on the outer edge of a disk that is rapidly rotated. As the material is cooled and/or solvent removed fibers are formed.

Boron nitride, silicon carbide, boron, and silicon fibers are also made into high strength fibers. For instance, boron fibers are made by depositing boron on heated tungsten filament followed by heating at high temperatures in the presence of ammonia.

Wet Spinning

Wet spinning is similar to dry spinning except that fiber formation results from the coagulation of the polymer solution as it is introduced into a nonsolvent bath. Since the coagulation process is relatively long, the linear velocity of wet spinning is less than for either melt or dry spinning. Wet spinning allows the placement of holes in the spinneret face to be closer together allowing productivity to be increased. Even so, it remains the slowest of the traditional spinning processes. The equipment used for wet spinning is similar to that used in dry spinning, though it is not necessary to heat the polymer solution to a high temperature. The spinnerets are immersed in tanks containing the nonsolvent. Wet spinning is the most complex of the three spinning processes typically including washing, stretching, drying, crimping, finish application, and controlled relaxation to form tow material. Spinning of natural-derived materials generally include additional steps including ageing or ripening to achieve the desired viscosity and chain length.

Fibers made from wet spinning generally have high void contents in comparison to all of the other processes giving them increased dyeability. The surface is rougher with longitudinal serrations and from a round die hole, it has an approximately circular to bean-shaped diameter.

Hollow fibers for gas and liquid separation are prepared through passing the air through the material just prior to entrance into the nonsolvent bath.

Other Spinning Processes

There are a number of lesser used, but still important, spinning processes. Following is a summary of some of these. In *reaction spinning*, a prepolymer is generally used that is further reacted upon by a material that is may be in solution in a bath. Further treatments may included crosslinking of the fiber. The most important example is the production of selected segmented polyurethane elastomeric fibers. Here, the prepolymer is the soft segment generally a low-molecular-weight polyether or polyester. Reaction with an aromatic diisocyanate converts the end groups, generally hydroxyls, into isocyanate groups. The bath contains a diamine such as 1,2-diaminoethane. The reaction between the amine and isocyanate forms the hard urea linkages. Some segmented polyurethanes, such as Lycra, are formed using conventional dry spinning.

Fibers can be formed from intractable materials such as ceramics and polytetrafluoroethylene through extrusion of a suspension of fine particles in a solution of a matrix polymer. The matrix polymer-intractable material is coagulated embedding and aligning the intractable material in the matrix polymer. The filament is then heated decomposing the matrix polymer. During this process, the material is sintered and drawn giving small, often with little flexibility, fibrils.

Gel spinning is used to produce high strength and modulus fibers. High-molecular-weight (such as 10^6 Daltons for polyethylene) polymer is dissolved in a high-temperature solvent at low concentration (ca 1%). The hot solution is extruded into a cooling zone such as a liquid nonsolvent. The resulting gel-like filament contains polymer with lots of entrapped liquid. This gel-like filament can be easily highly drawn. The drawing can be carried out even though liquid is removed prior to drawing. What occurs is that the low density of polymer chains in the gel allows a decreased chain entanglement allowing greater linear chain conformations to occur as the fiber is drawn.

Some low-orientation polymers exhibit what is referred to as necking. In necking, a filament extends preferentially at only selected sites known as necks or necking sites. This behavior occurs with many thermoplastic materials near their T_g. At lower temperatures, brittle fracture may occur at high tensions instead of necking. At higher temperatures, filament extension occurs uniformly without preferred necking sites. Commercially, filament extension is carried out at sufficient temperatures to avoid necking. For multifilament yarns, filament elongation is generally carried out by first heating the filament with subsequent application of the stress necessary to stretch the filament. For monofilaments and tows, the heating and application of the stress occur together.

Along with centrifugal spinning, there are several additional fiber forming techniques that are employed in fiber formation that do not employ a spinneret. In *electrostatic spinning* a high voltage, generally >5000 volts, is applied to a viscous solution of the polymer dissolved in a volatile solvent with a high dielectric constant but low conductivity contained in a fine capillary tube. A stream of filaments emerge from the capillary. These filaments are collected on a suitable surface.

Nonspinning Fiber Production

Fibers can also be made using specific conditions employing blow-molding of a melt. They can also be mechanically made by machining. Thus, polytetrafluoroethylene fibers are made by machining a thin film from a block of the polymer and then drawing the film at 300°C.

Fibers can be made from directly pulling some of the polymer from the melt. Similarly, fibers can be made using the interfacial process with fibers being formed as reaction of the two coreactants occur at or near the interface. Neither instance has been used in industrial-scale fiber formation.

Fibers are commercially made from uniaxially drawn film. The film is extruded, slit into tapelike strips, drawn, fibrillated, and wound. As in the case of spinning, the drawing produces preferred alignment of the polymer chains along the axis of pull. If the drawing precedes slitting, the fiber gives some cross orientation and is less apt to split.

Fibrillation can be achieved mechanically by drawing and pulling thin sheets of polymer. This is compounded if twisting is also involved. A rough idea of this process can be demonstrated by cutting several ribbons of film from a trashbag. Take one and pull. It will elongate and eventually form a somewhat thick filament-like material. Do the same to another strip except also twist it.

Film can be heated and/or stretched and cut eventually giving filament-like materials. Unfibrillated slit-film materials are used in weaving sacks and other packaging. Randomly fibrillated slit-film material is used to make twins and ropes, while controlled fibrillated material is used to make yarns for use in carpet backings and furnishing fabrics.

Whiskers can be made of some metals from simple scraping of the metal to from filament-like whiskers of high strength. Carraher and co-workers have produced a number of metal-containing polymers, generally rigid-rod like, that spontaneously form fiber-like structures from the reaction solution or when mechanically agitated, fiber-like organizations form.

General

Since there are many natural fibers, much fiber technology was developed before the twentieth century. Long, thread-like cells of animal and vegetable origin have been used for centuries for textiles, paper, brushes, and cordage. The animal protein fibers, namely, wool and silk, are no longer competitive with other fibers unless their production is subsidized. The vegetable cellulosic fibers—cotton, kapok, abaca, agave, flax, hemp, jute, kenaf, and ramie—are still in use, but cotton is no longer the "king of fibers" (Table 17.2).

Regenerated proteins from casein (lanital), peanuts (ardil), soybeans (aralac), and zein (vicara) are used as specialty fibers, but cellulose acetate and regenerated cellulose (rayon) are used in relatively large quantities. Cellulose triacetate fibers (Tricel) are produced by the acetylation of α-cellulose, and cellulose diacetate fiber (acetate rayon) is produced by the partial deacetylation of the triacetate. Further deacetylation (saponification) yields regenerated cellulose. Table 17.6 shows the physical properties of typical fibers.

Most regenerated cellulose (rayon) is produced by the viscose process in which an aqueous solution of the sodium salt of cellulose xanthate is precipitated in an acid solution. The relatively weak fibers produced by this wet spinning process are stretched in order

Table 17.6 Physical Properties of Typical Fibers[a]

Polymer	Tenacity (g/denier)	Tensile strength (kg/cm^2)	Elongation (%)
Cellulose			
Cotton	2.1–6.3	3–9000	3–10
Rayon	1.5–2.4	2–3000	15–30
High-tenacity rayon	3.0–5.0	5–6000	9–20
Cellulose diacetate	1.1–1.4	1–1500	25–45
Cellulose triacetate	1.2–1.4	1–1500	25–40
Proteins			
Silk	2.8–5.2	3–6000	13–31
Wool	1.0–1.7	1–2000	20–50
Vicara	1.1–1.2	1–1000	30–35
Nylon-66	4.5–6.0	4–6000	26
Polyester	4.4–5.0	5–6000	19–23
Polyacrylonitrile (acrylic)	2.3–2.6	2–3000	20–28
Saran	1.1–2.9	1.5–4000	20–35
Polyurethane (Spandex)	0.7	630	575
Polypropylene	7.0	5600	25
Asbestos	1.3	2100	25
Glass	7.7	2100	3.0

[a] The fineness of a fiber can be expressed by a unit called the denier, which is the mass (in grams) of 9000 m of fiber.

to produce strong (high-tenacity) rayon. The annual production of acetate rayon and rayon in the United States is 208 million lb. and 290 million lb. respectively.

While no truly synthetic fibers were produced before 1936 about 60 billion lb. of these important products is now produced annually (Table 17.3). The leading fiber is poly(ethylene terephthalate) (polyester, Dacron, Terylene, Kodel, Vycron), which is produced at an annual rate of 40 billion lb. by melt spinning.

Nylon-66 and nylon-6 fibers are also produced by melt-spinning molten polymers at an annual rate of over 10 billion lb. Acrylic fibers (Acrilan, Orlon) are produced at an annual rate of over 7 billion lb. by dry spinning.

Polyurethane (Perlon, Spandex), polypropylene, and polyethylene fibers are produced by the melt spinning of molten polymers. The total annual polyolefin fiber production in the United States is about 2.8 billion lb. Polyurethane (PU) fibers are produced in large quantities in Germany, but these are used as specialty fibers in the United States. Over 600 million lb. of these fibers is produced by the melt spinning process.

Filaments of thermoplastics such as polypropylene may also be produced by a fibrilation process in which strips of film are twisted, and these fibrils are heated and stretched. In addition to the traditional spinning and weaving processes, textiles may be produced in the form of nonwoven textiles by the fiber bonding process. Bonding results from the addition of thermoplastics or by admixing thermoplastic fibers with cotton or rayon fibers before bonding by heat.

17.2 ELASTOMERS

Prior to World War II, hevea rubber accounted for over 99% of all elastomers used, but synthetic elastomers account for more than 70% of all rubber used today. Natural rubber and many synthetic elastomers are available in latex form. The latex may be used, as such, for adhering carpet fibers or for dipped articles, such as gloves, but most of the latex is coagulated and the dried coagulant used for the production of tires and mechanical goods.

Over 5.5 billion lb. of synthetic rubber is produced annually in the United States. The principal elastomer is the copolymer of butadiene (75%) and styrene (25%) (SBR), produced at an annual rate of over 1 million tons by the emulsion polymerization of butadiene and styrene. The copolymer of butadiene and acrylonitrile (Buna-H, NBR, Hycar) is also produced by the emulsion process at an annual rate of about 200 million lb.

Likewise, neoprene is produced by the emulsion polymerization of chloroprene at an annual rate of 126,000 tons. Butyl rubber is produced by the low-temperature cationic copolymerization of isobutylene (90%) and isoprene (10%) at an annual rate of 146,000 tons.

Polybutadiene, polyisoprene, and ethylene-propylene copolymer rubber (EPDM) are produced by anionic polymerization processes at annual rates of 550,000, 100,000, and 330,000 tons, respectively. One of the original synthetic elastomers (Thiokol), as well as polyfluorocarbon elastomers (Viton), silicone (Silastic), polyurethane (Adiprene), and phosphazenes, are specialty elastomers. The physical properties of typical elastomers are shown in Table 17.7.

Polymer–Polymer Immiscible Systems

The most common result of mixing two polymers is phase separation. This is a result of a combination of "like–liking–like" (like molecules gathering, excluding unlike polymer

Table 17.7 Physical Properties of Typical Elastomers

	Pure gum vulcanizates		Carbon-black reinforced vulcanizates	
	Tensile strength (kg cm^{-2})	Elongation (%)	Tensile strength (kg cm^{-2})	Elongation (%)
Natural rubber (NR)	210	700	315	600
Styrene-butadiene rubber (SBR)	28	800	265	550
Acrylonitrile-butadiene rubber (NBR)	42	600	210	550
Polyacrylates (ABR)			175	400
Thiokol (ET)	21	300	85	400
Neoprene (CR)	245	800	245	700
Butyl rubber (IIR)	210	1000	210	400
Polyisoprene (IR)	210	700	315	600
Ethylene-propylene rubber (EPM)		300		
Polyepichlorophydrin (CO)				
Polyfluorinated hydrocarbons (FPM)	50	600		
Silicone elastomers (SI)	70	600		
Polyurethane elastomers (AU)	350	600	420	500

chains) and a less favorable, lower entropy change for polymers compared with smaller molecules. In other words, the major factor for solution of large and small molecules is an increased randomness, which works to offset the (energy-related) tendency for like–linking–like. This entropy factor is generally relatively small for polymer–polymer combinations.

The tendency of polymer combinations to phase-separate has been greatly exploited recently. New major groupings of polymers have been developed, including polymer blends, graft and block copolymers, and interpenetrating polymer networks (IPNs).

The emphasis on finding polymers that are complementary has led to a number of new polymer blends. The complementary nature can result from attraction due to polar–polar (dipole–dipole) interactions or hydrogen bonding between the two polymers.

The behavior of graft copolymers and IPNs is illustrated by the polymer mixture called high-impact polystyrene (HIPS). The addition of SBR [poly(butadiene-co-styrene], which is elastic, to polystyrene allows the more brittle polystyrene to confer toughness, with the SBR domains acting to absorb sudden shocks. This gives an overall material with some flexibility while the PS regions contribute to the material's overall strength. The varying percentage of PS and SBR and the size of PS-SBR domains can lead to materials with a wide variety of physical properties.

Elastomer Processing

The processing of elastomeric (rubbery) material is quite varied depending on its end use, form of the material (that is dry or in solution), and the material processed. Latex forms of rubber can be properly mixed with additives using simple (or more complex) stirring and agitation. The mixing/agitation should be such as to not cause a separation or breakdown of the latex or foam formation. Straight, coagulant, and heat-assisted dipping processes are commonly used to produce a variety of tubes, gloves, etc. Latexes are also used to make thread for the garment industry, and adhesives for shoes, carpets, and tape formation.

Following we will look at the processing involving bulk rubber. The manufacture of rubber products from this material can be divided into four steps:

1. Mastication
2. Incorporation or compounding
3. Shaping
4. Vulcanization

The shaping and vulcanization steps are combined in a number of processes such as transfer or injection molding or may be separated as in the extrusion and subsequent vulcanization sequence. An outline of these steps is given in Figure 17.4.

We will look at the processing of natural dry rubber first since its processing is similar to other elastomers and because of its historical importance. Natural rubber is a dispersion of rubber particles in water. Unvulcanized raw rubber obtained by coagulation and drying has large chains with chain lengths on the order of 10^5 carbons.

Mastication is intended to bring the material to the necessary consistency to accept the compounding ingredients. Mastication results in a lowering of chain size to an average chain length on the order of 10^4 carbons. Two basic types of internal mixers are in use. The Banbury has rotors rotating at different speeds creating a "kneading" action such as that employed in handling bread dough. A shearing action between the rotors and the walls of the mixer is also achieved. The Shaw Intermix employs rotors that turn at the same speed and closely intermesh causing an intracompound friction for mixing, thus closely resembling a mill's mixing action.

The next step is the incorporation of various additives: *compounding*. Typical additives include filler, processing aids, activators, processing aids, age resistors, sulfur, antiox-

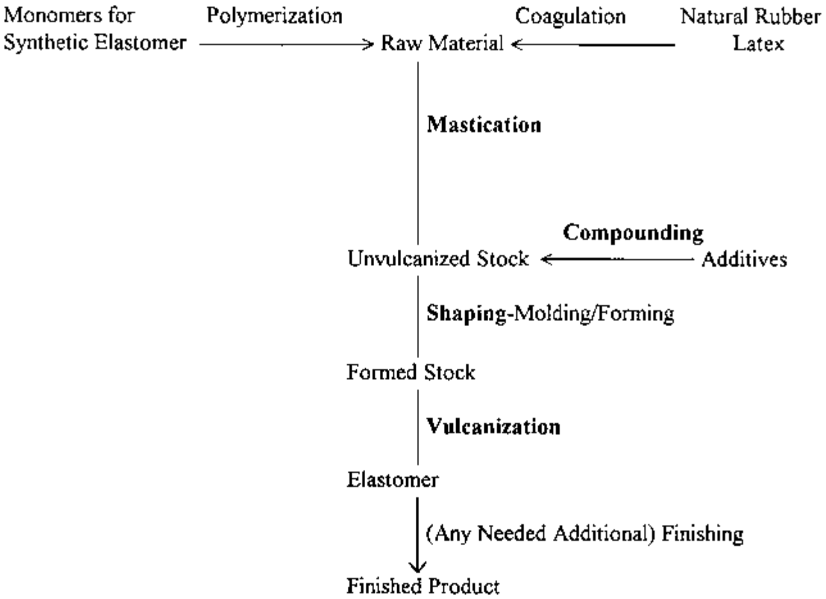

Figure 17.4 Outline of steps involved in the processing to form elastomeric materials.

idants and antiozone compounds, extenders, plasticizers, blowing agents, pigments, and accelerators.

An important aspect in the compounding is the amount of crystallization of the rubber. If the rubber is in a highly crystalline state it will mix poorly if at all. Thus, partially crystallized rubber must be heated before it will yield to mixing.

Stabilizers are materials that help the rubber withstand oxidative ageing and ozone attack. They act by intercepting the active free radicals breaking the free-radical–associated degradation process. Amines and phenols are generally employed. Reinforcing fillers, of which carbon black is the most important, are added to improve the mechanical properties such as hardness, abrasion resistance, modulus, and tear resistance. It is believed that the rubber adheres to the carbon surface. Carbon black also helps in retarding UV degradation and increases the electrical conductivity, reducing triboelectric charging and acting as an antistatic material.

Natural rubber can be compounded without fillers to give a vulcanized material with high elongation (to about 800%) and high tensile strength (about 28 M Pa)

Internal mixers fragment the large rubber molecules by high shear forces. Depending on the particular assembly and ingredients, the created free radicals can combine to give larger molecules or may form smaller chains. Breakdown is often assisted by the use of chemical peptizers such as thiophenols, mixtures of salts of saturated fatty acids, and aromatic disulfides. The fatty acids generally act as dispersing agents and processing aids.

The viscous prerubber is now *shaped* by addition to a mold of the desired shape. Addition can be achieved by simply pouring the material into the mold, but usually the material is added to the mold employing the usual molding addition (extrusion, compression, and transfer) techniques. The material can also be treated using most of the other "thermoplastic" processing techniques such as calendering, coating, and extrusion.

The material is now heated to cure, set, or *vulcanize* (all terms are appropriate) the material into the (typically) finished shape. Between 1–5% of sulfur (by weight) is added in typical black rubber mixes giving a vulcanized material with an average of about 500 carbon atoms between crosslinks. Larger amounts of sulfur will give a tougher material eventually giving a somewhat brittle, but quite strong, ebonite as the amount of sulfur is increased to about 40%. Sometimes, additional finishing may be desirable including painting, machining, grinding, and cutting.

These steps are typical for most of the synthetic elastomers. The use of sulfur for vulcanization is common for the production of most elastomers. Magnesium and zinc oxides are often used for the crosslinking of polychloroprene (CR). Saturated materials such as ethylene-propylene (EPM) and fluoroelastomers are crosslinked using typical organic crosslinking agents, such as peroxides.

Carbon black is widely used as a reinforcing agent for most synthetic elastomers. Carbon black is especially important for synthetic elastomers such as styrene-butadiene rubber (SBR), nitrile rubber (NBR), and polybutadiene (BR) that do not crystallize at high strains. Thus, noncarbon-filled SBR has a tensile strength of about 2 MPa, and with addition of carbon black this increases to about 20 MPa.

The above processing applies to the processing of typical bulk carbon backbone—intensive elastomers. Other important classes of elastomers are also available. Polyurethanes represent a broad range of elastomeric materials. Most polyurethanes are either hydroxyl or isocyanate terminated. Three groups of urethane elastomers are commercially produced. Millable elastomers are produced from the curing of the isocyanate group using trifunctional glycols. These elastomers are made from high polymers made by the chain extension of the polyurethane through reaction of the terminal isocyanate groups with a polyether or polyester. Low-molecular-weight isocyanate terminated polyurethanes are cured through a combination of chain extension by reaction with a hydroxyl-terminated polyether or polyester and trifunctional glycols giving cast elastomers. Thermoplastic elastomers are block copolymers formed from the reaction of isocyanate-terminated polyurethanes with hydroxyl-terminated polyethers or polyesters. These are generally processed as thermoplastic materials as are the thermoplastic elastomers. Many of these materials have little or no chemical crosslinking. The elastomeric behavior is due to the presence of physical hard domains that act as crosslinks. Thus, SBR consists of soft butadiene blocks sandwiched between polystyrene hard blocks. These hard blocks also act as a well dispersed fine-particle reinforcing material increasing the tensile strength and modulus. The effectiveness of these hard blocks greatly decreases above the T_g (about 100°C) of polystyrene.

Silicons form another group of important elastomers. Again, processing typically does not involve either carbon black or sulfur.

17.3 FILMS AND SHEETS

Films such as regenerated cellulose (cellophane) are produced by precipitating a polymeric solution after it has passed through a slit die. Other films, such as cellulose acetate, are cast from a solution of the polymer, but most films are produced by the extrusion process. Some relatively thick films and coextruded films are extruded through a flat slit die, but most thermoplastic films, such as polyethylene film, are produced by the air blowing of a warm extruded tube as it emerges from the circular die as shown in Fig. 17.5

Films and sheeting are also produced employing calendering (Fig. 17.6). The technique is also employed to apply coatings to textiles or other supporting material. In calendering, the polymeric material is passed between a series of counterrotating rolls. The surface may be smooth or textured depending on the roller surfacing. In applying a coating to a second material, the coating compound is passed through one set of rollers while the material to be coated is passed through a second set of rollers along with the coating compound.

The most widely used films are low-density polyethylene (LDPE), cellophane, poly(ethylene terephthalate) (PET), poly(vinyl chloride) (PVC), cellulose acetate, polyfluorocarbons, nylons, polypropylene, polystyrene, and Saran. Films of ultrahigh molecular weight polyethylene (UHMWPE), polyamides, and polytetrafluoroethylene are produced by skiving molded billets. The strength of many films, such as PET, is improved by biaxial orientation.

Most of the thermoplastics used as films may also be extruded as relatively thick sheets. These sheets may also be produced by pressing a stack of film at elevated temperature (laminating) or by the calendering process.

Wire is coated by being passed through a plastic extruder, but most substances are coated by polymers from solutions, emulsions, or hot powders. The classic brushing process has been replaced to a large extent by roll coating, spraying, and hot powder coating. The application of polymers from water dispersions to large objects, such as automobile frames, has been improved by electrodeposition of the polymer on the metal surface.

Printing inks are highly filled solutions of resins. The classic printing inks were drying oil–based systems, but the trend in this $800 million business is toward solvent-free inks.

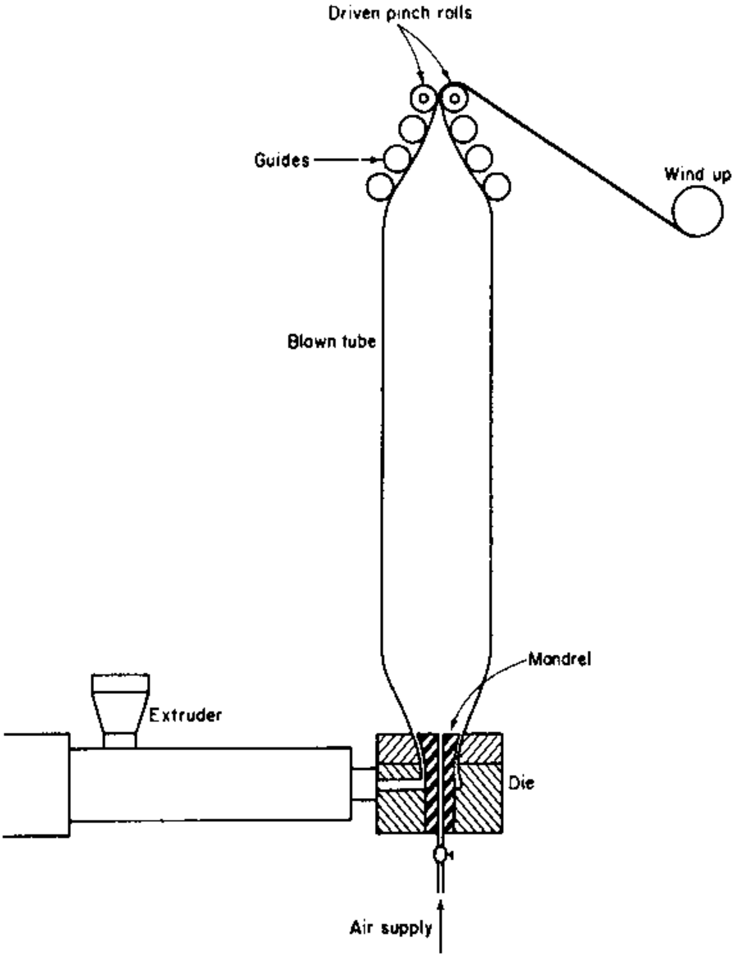

Figure 17.5 Film formation through extrusion. (From N. Bikalis, *USP Extrusion and Other Plastics Operations*, Wiley-Interscience, 1971; with permission.)

The permeability to gases and the tearing strength of selected films are shown in Table 17.8

Calendering

Calendering is simply the squeezing or extruding of a material between pairs of corotating, parallel rollers to form films and sheets. It can also be used to mix and impregnate, such as in the case of embedding fiber, into slightly melted matrix material to form impregnated composite tapes. It can also be used to combine sheets of material such as sheets of impregnated paper and fiber-woven and nonwoven mats to form laminar composite materials. It is also used in processing certain rubber material and textiles. Calendering is also employed in conjunction with other processing techniques such as extrusion in the formation of films from extruded material. It is also used to coat, seal, laminate, sandwich, finish, and emboss.

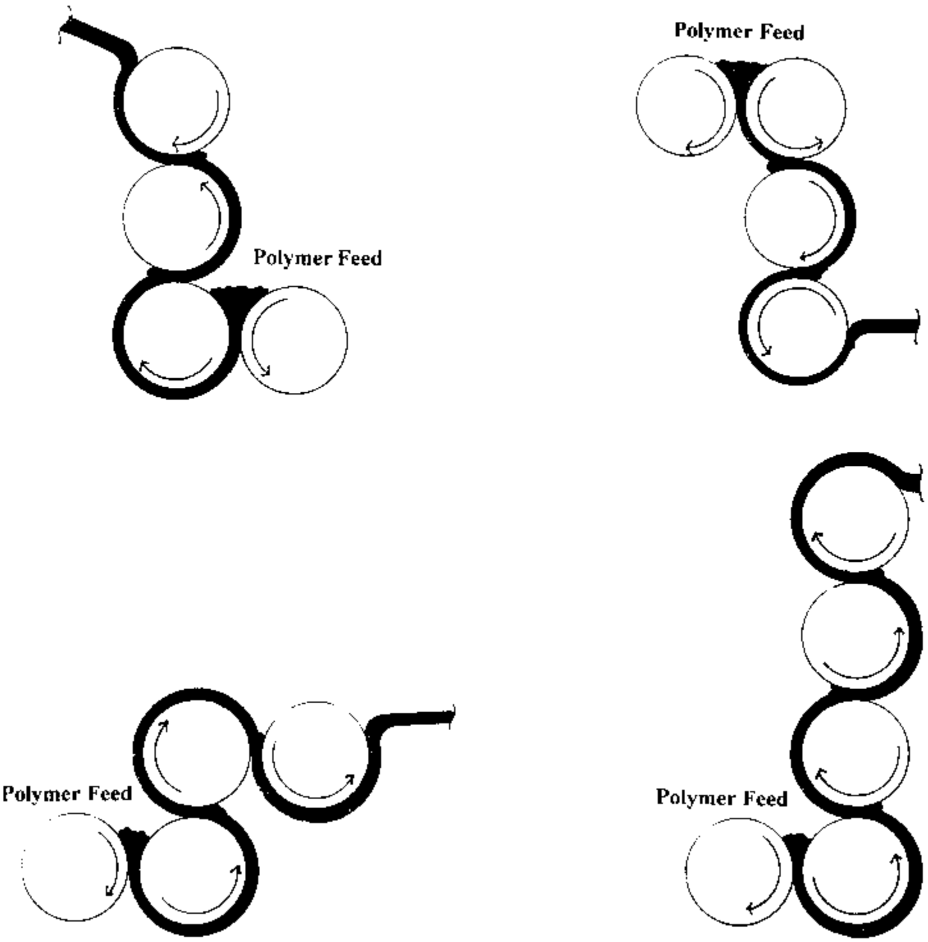

Figure 17.6 Calendering assemblies: top left, four-roll “L” calender; top right, four-roll inverted “L” calender; bottom left, four-roll “Z” calender; and bottom right, five-roll “L” calender (shown in a reversed position).

The particular processing has usually been developed using the classical mix of experimentation and science. Because of the wide variation in desired end product and range of processing properties of the elastomers and thermoplastics processed using calendering, a wide variety of assemblies and conditions are employed. The number and positioning of rollers is important in the design of the procedure. Some common designs are given in Figure 17.6. At each step, additional ingredients and addition of additional layers can be accomplished.

The major bulk-processed thermoplastic using calendering is poly(vinyl chloride) sheets and films including blends and copolymers. A sample recipe to produce PVC sheets might include a plasticizer such as a dialkyl phthalate, pigment, filler, lubricant, and stabilizer. A partial flow chart illustrates the particular features of the production of a PVC sheet as follows.

Table 17.8 Permeability to Gases (cm/day/100 in.^{2}/mil at 25 °C)

Polymer	MVT	Co_2	H_2	N_2	O_2	Initial tearing strength (g/mil)
Cellophane	0.4–134	0.4–0.6	1.2–2.2	0.5–1.6	0.2–5.0	2–20
Polyethylene (I)	1.0–1.5	2700	—	180	500	100–500
Polyethylene (III)	0.3	580	—	42	185	16–300
Rubber hydrochloride	—	288–13,500	—	—	38–2250	60–1600
Cellulose acetate	30–40	860–1000	835	30–40	117–150	1–2
Cellulose acetate butyrate	30–40	6000	—	250	950	5–10
Ethylcellulose	4.8–14.2	5000	—	600	2000	215–395
Plasticized poly(vinyl chloride)	4	100–3000	—	—	30–2000	60–1400
Saran	—	12	—	—	2.4	10–100
Poly(vinyl alcohol)	—	200	—	—	120	785–890
Poly(ethylene terephthalate)	1.7–1.8	15–25	100	0.017–1.0	6.0–8.0	12–27
Polystyrene (oriented)	7.0–10.0	900	—	—	350	5.0
Polycarbonate	11.0	1075	1600	50	300	20–25
Polyurethane	45–75	465–1650	—	41–119	75–327	220–710
Nylon-66	3–6	9.1	—	0.35	5.0	—
Nylon-6	5.4–20	10–12	110	0.9	2.6	50–90
Poly(vinyl fluoride)	3.24	11.1	58	0.25	3	12–100

> Raw materials → mixing of raw materials specified amounts (with heating) → cooling → milling powdering/chipping of mixed material → feeding of stock into first calender nip → calendering → stripping and drawdown (if needed) → embossing (if needed) → relaxing and tempering → cooling → trimming (if needed) → stacking (or continued processing) → quality control → sales → fabrication into final product

Because of the variation in flexibility, the terms film and sheet vary with materials. For PVC, films have a thickness of 6 mils (0.15 mm) and less while sheets are thicker than this. While PVC is relatively rigid with a tensile modulus greater than about 690 M Pa (105 psi) thin films are easily folded. Films are generally shipped as rolls with the PVC rolled about a central rigid core. Sheets are generally shipped as flat layered sheets.

In addition to controlling the recipe materials and PVC properties including molecular weight and molecular weight distribution, the major processing considerations are

Calender speed
Temperature
Thickness/gauge
Orientation
Finish
Embossing

Films and thin sheets are typically drawn to impart additional unidimensional strength. For films, both unidirectional and bidirectional drawing is used. The effectiveness of the drawing is temperature related. For PVC above 190°C little orientation results from drawing; from 160 to 180°C orientation is achieved that can be locked in by rapid cooling;

and below 150°C strains are introduced that attempt to be recover as the film is stored at room conditions. Shrink-wrapping PVC film is uniaxially or biaxially stretched from 160 to 180°C and rapidly cooled. After packaging, a heat tunnel causes the desired shrinking to occur.

Embossing is also quite temperature dependant. The temperature must be high enough to accept the embossing from a colder embossing roll that allows rapid cooling to lock in the figure. If it is too low the embossing depth will diminish, and if it is too high then movement will occur before the embossing can be captured giving an embossing that lacks sharpness and clarity.

Paper and nonwoven fabrics can also be processed involving calendering. A coherent mat or web is preformed. The (typically) wet web is dried and calendered to develop the desired material. Paper calendering typically uses wider rollers with more nip is that are run at lower pressures and higher speeds in comparison with the processing of thermoplastics and elastomers.

Supercalendering polishes the material by passing it through filler and polished metal rollers that act to polish the surface.

17.4 POLYMERIC FOAMS

Prior to 1920, the only flexible foam available was the natural sponge, but chemically foamed rubber and mechanically foamed rubber latex were introduced prior to World War II. These foams may consist of discrete unit cells (unicellular, closed cell), or they may be made up of interconnecting cells (multicellular, open cells), depending on the viscosity of the system at the time the blowing agent is introduced.

Unicellular foams are used for insulation, buoyancy, and flotation applications, while multicellular foams are used for upholstery, carpet backing, and laminated textiles. Expanded polystyrene (Styrofoam), which is produced by the extrusion of polystyrene beads containing a volatile liquid, is used to produce low-density moldings such as foamed drinking cups and insulation board. The K value for these products is on the order of 0.24 Btu.

Foamed products are also produced from PVC, LDPE, urea resins, ABS, and PU. The last are versatile products which range from hard (rigid) to soft (flexible). These are produced by the reaction of a polyol and a diisocyanate. Polyurethane planks are available in a wide variety of specific gravities.

The residual gases in many polymeric foams and their flammability are causes for concern. However, over 1.5 million tons of foamed plastic is produced annually, and this volume is increasing at an annual rate of about 10%.

17.5 REINFORCED PLASTICS (COMPOSITES) AND LAMINATES

Composites

Theoretical and material considerations for composites are dealt with in Sections 13.3–13.6. Here we will focus more on processing considerations.

Composites are generally composed of two phases, one called the continuous or matrix phase that surrounds the discontinuous or dispersed phase. There are a variety of

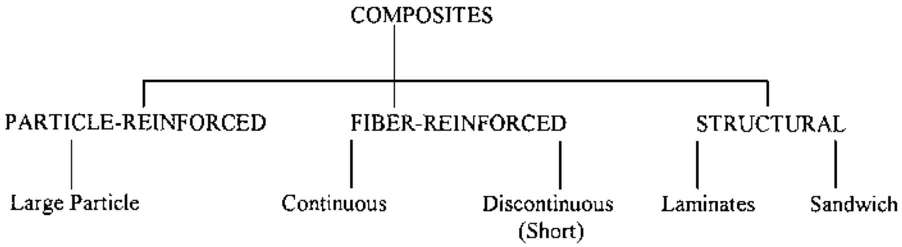

Figure 17.7 Classification of polymer-intense composites.

polymer-intense composites that can be classified as shown in Figure 17.7. Many of these composite groups are used in combination with other materials including different types of composites and like types of composites except differing in orientation.

Many naturally occurring materials such as wood are reinforced composites consisting of a resinous continuous phase and a discontinuous fiberous reinforcing phase.

The modern ski is a good example of the use of composites to make a product with unique properties (Fig. 17.8). The top and sides are composed of ABS polymer that has a low T_g allowing it to remain flexible even at low temperatures. It is employed for cosmetic and containment purposes. Polyurethane forms the core and a damping layer that acts as a filler and improves chatter resistance. The base is a carbon-impregnated matrix composite that is hard, strong, and with good abrasion resistance. There are numerous layers of fiberous glass that are a mixture of bidirectional layers to provide torsional stiffness, unidirectional layers that provide longitudinal stiffness, with bidirectional layers

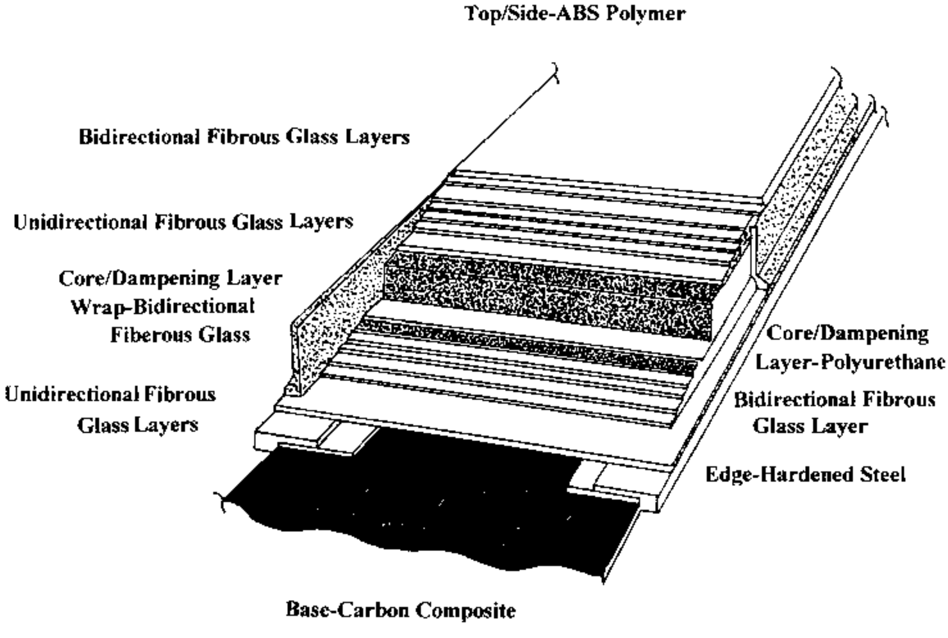

Figure 17.8 Cut-away illustration of a modern ski.

of fiberglass acting as outer layers to the polyurethane layers composing a torsional box. The only major noncomposite material is the hardened steel edge that assists in turning by cutting into the ice. They all work together to give a light, flexible, shock absorbing, tough ski.

Composites are also used extensively where light but very strong materials are needed, such as in the construction of the new Boeing 767, where composites play a critical role in the construction of the exterior (Fig. 17.9). They are also used where excessive high heat stability is needed, such as in the reusable space vehicle (Fig. 17.10).

Here we will briefly look at each of the main groupings of composites.

Particle-Reinforced Composites: Large-Particle Composites

Some materials to which fillers have been added can be considered composites. These include a number of the so-called cements including concrete (Sec. 12.2). As long as the added particles are relatively small, of roughly the same size, and evenly distributed throughout the mixture, there can be a reinforcing effect. The major materials in Portland cement concrete are the Portland cement, a fine aggregate (sand), coarse aggregate (gravel and small rocks), and water. The aggregate particles act as inexpensive fillers. The water is also inexpensive. The relatively expensive material is the Portland cement. Good strength is gained by having a mixture of these such that there is a dense packing of the aggregates and good interfacial contact, both achieved by having a mixture of aggregate sizes—thus the use of large gravel and small sand. The sand helps fill the voids between the various

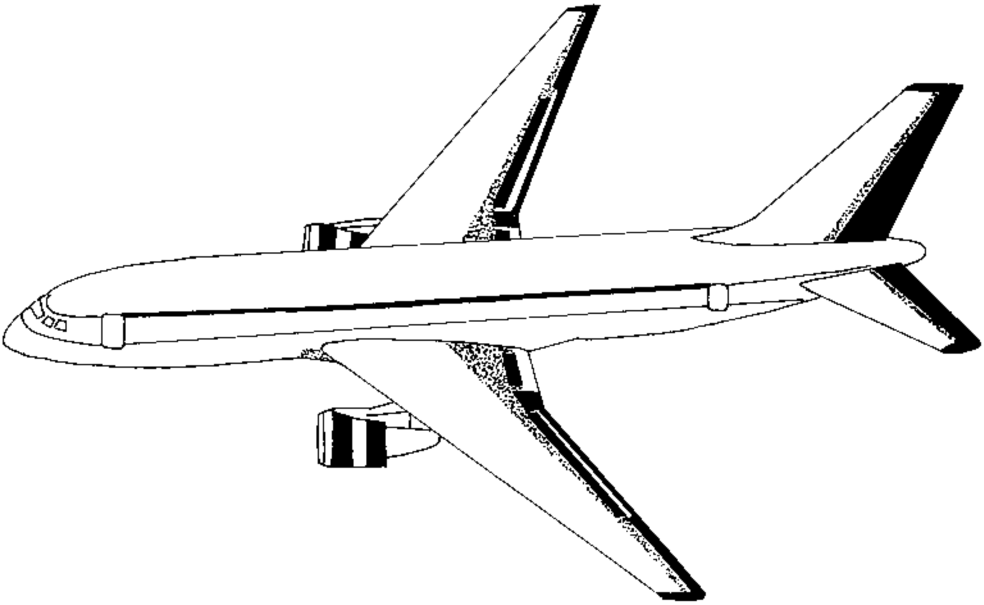

Figure 17.9 Use of graphite (solid) and graphite/Kevlar (dotted) composites in the exterior of the Boeing 767 passenger jet. Sites include wing tips, fixed trailing edge panels, inboard and outboard spoilers, inboard and outboard ailerons for the large wings, and the fin tip, rudder, elevators, stabilizer tips, and fin fixed trailing edge panels for the tail wings.

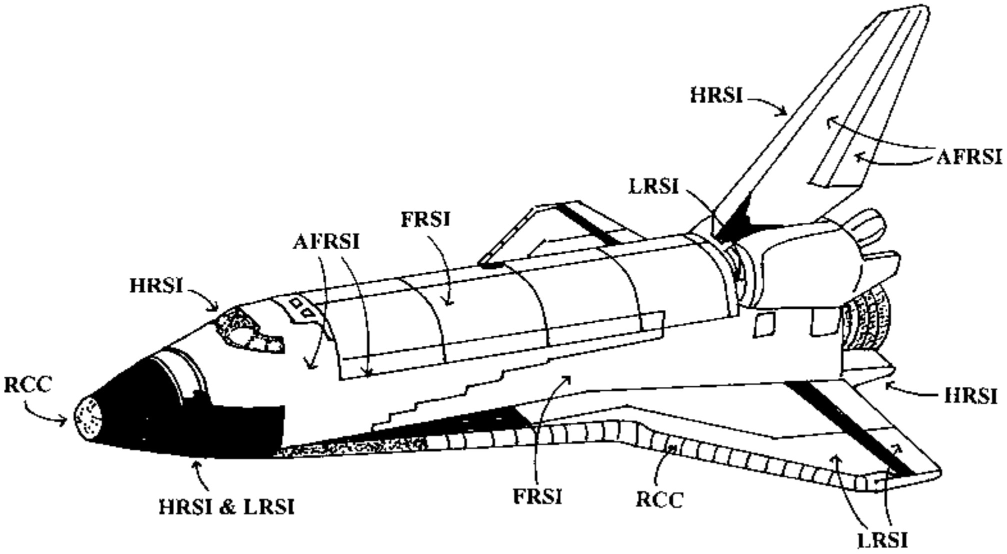

Figure 17.10 Locations of various advanced materials, including composites, employed for heat protection in the Space Shuttle Orbiter. The descriptions of the materials are given in Table 17.9.

larger gravel particles. Mixing and contact is achieved with the correct amount of water. Enough water must be present to allow a wetting of the surfaces to occur along with providing some of the reactants for the setting up of the cement. Too much water creates large voids and weakens the concrete.

Fiber-Reinforced Composites

Mathematically, the critical fiber length necessary for effective strengthening and stiffening can be described as follows.

Table 17.9 Materials Used for Heat Protection in the Space Shuttle Orbiter[a]

Identifier	Maximum operating temperature, °C	Description of Material
Advanced flexible reusable surface insulation	810	Quartz batting sandwiched between AFRSI quartz and fiberous glass fabric
Felt reusable surface insulation	400	Nylon felt with a silicone rubber FRSI coating
High-temperature reusable surface	1250	Silica tiles, borosilicate glass coating insulation-HRSI with silicon boride, SiB_4, added
Low-temperature reusable surface	650	Silica tiles with a borosilicate coating insulation-LRSI
Reinforced carbon-carbon-RCC	1650	Pyrolized carbon–carbon coated with silicon carbide, SiC

[a] These locations are given in Fig. 17.10.

Critical fiber length = ultimate or tensile strength × fiber diameter/2 ×
fiber-matrix bond strength of the shear yield strength of the matrix,
whichever is smaller

Fibers where the fiber length is greater than this critical fiber length are called continuous fibers, while those that are less than this critical length are called discontinuous or short fibers. Little transference of stress and thus little reinforcement is achieved for short fibers. Thus, fibers whose lengths exceed the critical fiber length are used.

Fibers can be divided according to their diameters. Whiskers are very thin single crystals that have large length to diameter ratios. They have a high degree of crystalline perfection and are essentially flaw free. They are some of the strongest materials know. Whisker materials include graphite, silicon carbide, aluminum oxide, and silicon nitride. Fine wires of tungsten, steel, and molybdenum are also used, but here, even though they are fine relatively to other metal wires, they have large diameters. The most used fibers are "fibers" which are either crystalline or amorphous, or semicrystalline with small diameters.

Processing of Fiber-Reinforced Composites

There exists a wide variety of particular processing operations, but briefly they can be described in terms of filament winding, preimpregnation of the fiber with the partially cured resin, and pultrusion. Pultrusion is used to produce rods, tubes, beams, etc., with continuous fibers that have a constant cross-sectional shape. The fiber (as a continuous fiber bundle, weave, or tow) is impregnated with a thermosetting resin and pulled through a die that shapes and establishes the fiber to resin ratio. This stock is then pulled though a curing die that can machine or cut producing the final shape such as filled and hollow tubes and sheets.

The term used for continuous fiber reinforcement preimpregnation with a polymer resin that is only partially cured is "prepreg." Prepreg material is generally delivered to the customer in the form of a tape. The customer than molds and forms the tape material into the desired shape finally curing the material without having to add any additional resin. Preparation of the prepreg can be carried out using a calendering process. Briefly, fiber from many spools are sandwiched and pressed between sheets of heated resin with the resin heated to allow impregnation but not so high as to be very fluid.

Thus, the fiber is impregnated in the partially cured resin. Depending upon the assembly the fiber is usually unidirectonal, but can be made so that the fibers are bidirectional or some other combination. The process of fitting the pregpreg into, generally onto, the mold is called "lay-up." Generally a number of layers of prepreg are used. The lay-up can be done by hand, called "hand lay-up," automatically, or some combination of automatic and hand lay-up. As expected, hand lay-up is more costly but is needed where one-of-a-kind products are produced and by the occasional customer.

In filament winding, the fiber is wound to form a desired pattern, usually but not necessarily hollow and cylindrical. The fiber is passed through the resin and then spun onto a mandrel. After the desired number of layers of fiber are added, it is cured. Prepregs can be filament wound. With the advent of new machinery, complex shapes and designs of the filament can be readily wound.

Structural Composites

Structural composites can be combinations of homogeneous and composite materials. Laminar composites are composed of two-dimensional sheets that generally have a preferred high-strength direction. The layers are stacked so that the preferred high-strength directions are different, generally at right angles to one another. The composition is held together by a resin. This resin can be applied as simply an adhesive to the various surfaces of the individual sheets or the sheet can be soaked in the resin prior to laying the sheets together. In either case, the bonding is usually of a physical type. Plywood is an example of a laminar composite. Laminar fiberous glass sheets are included as part of the modern ski construction. These fiberous glass sheets are fiber-reinforced composites used together as laminar composites.

Laminar materials are produced by a variety of techniques. Coextrusion blow molding produces a number of common food containers that consist of multilayers, such as layers consisting of polypropylene/adhesive/poly(vinyl alcohol)/adhesive/adhesive/polypropylene.

Sandwich composites are combinations where a central core(s) is surrounded generally by stronger outer layers. Sandwich composites are present in the modern ski and as high temperature stable materials used in the space program. Some cores are very light acting something like a filler with respect to high strength, with the strength provided by the outer panels. Simple corrugated cardboard is an example of a honeycomb core sandwich structure, except that the outer paper-intense layers are not particularly strong. Even in the case of similar polyethylene and polypropylene corrugated structures, the outer layers are not appreciatively stronger than the inner layer. In these cases, the combination acts to give a lightweight somewhat strong combination, but they are not truly composites but simply exploit a common construction.

Laminating

Laminating is a simple binding together of different layers of materials. The binding materials are often thermosetting plastics and resins. The materials to be bound together can be paper, cloth, wood, or fibrous glass. These are often referred to as the reinforcing materials. Typically, sheets, impregnated by a binding material, are stacked between highly polished metal plates, subjected to high pressure and heat in a hydraulic press producing a bonded product which may be subsequently treated, depending on its final use (Fig. 17.11). The end product may be flat, rod-shaped, tubular, rounded, or some other formed shape.

Reinforced plastics differ from high-pressure laminates in that little or no pressure is employed. For instance, in making formed shapes, impregnated reinforcing material is cut to a desired shape, the various layers are added to a mold, and the molding is completed by heating of the mold. This process is favored over the high-pressure process because of the use of a simpler, lower cost mold and production of strain-free products. A simple assembly for the production of reinforced materials is shown in Fig. 17.12.

17.6 MOLDING

Molding is a general technique that can be used with plastics and thermosetting materials when employing mobile prepolymer. Molding can be used to produce sheetlike, foamed, hollow, or solid materials and from very small to very large objects. Here we will look at various molding processes.

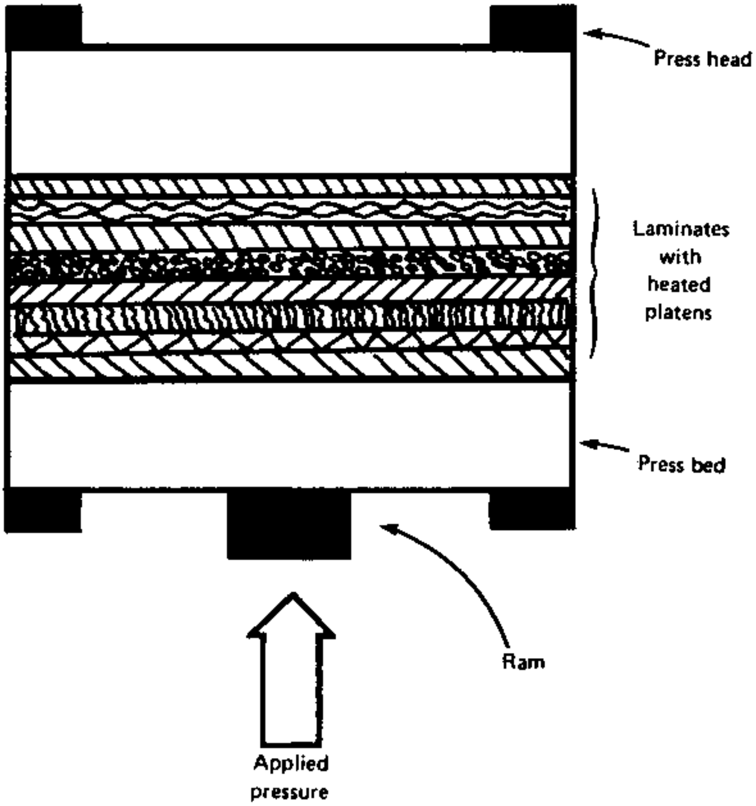

Figure 17.11 Assembly employed for the fabrication of laminates.

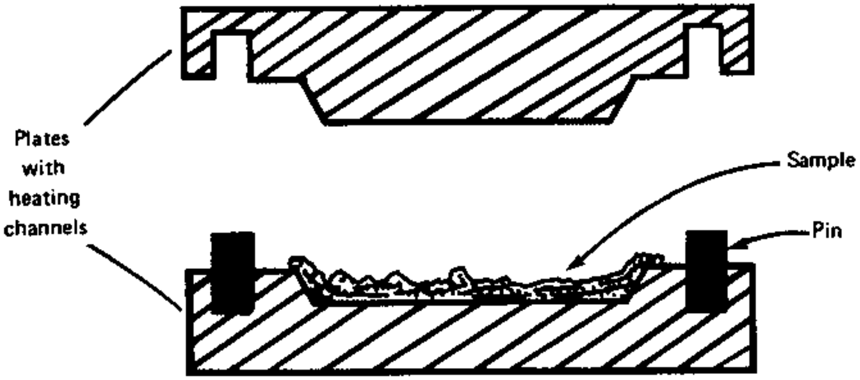

Figure 17.12 Assembly employed for production of reinforced plastics.

Injection Molding

The most widely employed processing techniques for thermoplastics are extrusion and injection molding. Injection molding is also used to produce some thermoset products utilizing fluid prepolymer. Injection molding involves forcing (injecting) a molten polymer into a mold where it cools, becoming solid; the mold separates, allowing the molded material to be released. The mold parts are joined and the process begins again.

Injection molding allows the rapid, economical production of small to large parts. It provides close tolerances, and the same machine can be used to mold many different articles. Parts can be molded combining the polymer with other polymers and with any number of additives. Further, it can be run so that various parts can be easily married as part of an entire or combined-parts production assembly of an article. The ability to easily modify the operating conditions of the injection molding machine is important because of the variety of articles that may be needed, variety of material employed to produce the same (general) article, variety of materials to produce different injection-molded articles, and the variability of supposedly the same polymer material from batch to batch.

Injection molding is not new. A patent was issued in 1872 for an injection molding machine for camphor-plasticized cellulose nitrate, celluloid. Almost all of the machines used today are reciprocating or two-stage screw types. Both types employ a reciprocating Archimedean-like screw similar to that of a screw extruder. A few are of the plunger type.

A traditional injection apparatus consists of a hopper that feeds the molding powder to a heated cylinder, where the polymer is melted and forced forward by a reciprocating plunger or screw. The cooled part is ejected when the mold opens and then the cycle is repeated. The molten material passes from the nozzle through a tapered sprue, a channel or runner, and a small gate into the cooled mold cavity. The polymer in the mold is easily broken off at the gate site and the materials in the sprue, runner, and gate are ground and remolded. An illustration of such an injection molding press is given in Figure 17.13. The hopper (a) feeds the molding powder to a heated cylinder (b) where the polymer is melted and forced forward by a reciprocating plunger (c) (or screw). The molten material advances toward a spreader or torpedo into a cool, closed, (here) two-piece mold (d). The cooled part is ejected when the mold opens and then the cycle is repeated. The molten plastic is

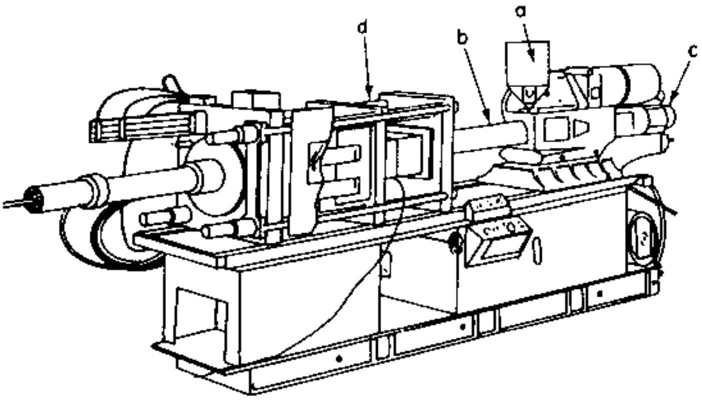

Figure 17.13 Cross section of an injection-molding press. (From *Modern Plastics Technology* by R. Seymour, 1975, Reston Publishing Co., Reston, Virginia. Used with permission.)

passed from the nozzle through a tapered sprue, runner, and a small gate into the cooled mold cavity (Fig. 17.14). The plastic in the narrow gate section is easily broken off and excess material remaining within the sprue, runner, and gate ground and remolded.

In a reciprocating screw machine, the material is collected in front of the screw that continues to move backward as additional material is melted. The area where the melted material is collected corresponds to the heating chamber or pot in a two-stage system. The material is melted by the internally generated heat caused by the friction of the polymer segments and chains rubbing against one another. The screw is also good at mixing so that additive introduction and mixing of different polymers can be achieved in the same step as overall polymer melting.

In the reciprocating screw system, the polymer material is fed from the hopper, melted (or plasticized) in the screw, and forced past a one-way valve at the injection end of the screw. The material accumulates at the front of the screw, forcing the screw, its drive and motor, and the pistons of hydraulic injection cylinders back. When the screw reaches a certain point, rotation stops and the injection part of the cycle begins. The hydraulic cylinders push the screw, and the material caught in front of it, through the injection port. A one-way valve prevents material from passing back over the screw turns. In this system, the screw also acts as the injection ram.

Thermoset materials can be produced using modified reciprocating screw systems. The screw is designed differently and heating is often done with hot water. The material cannot be allowed to cure in the cylinder or the whole assembly must be cleaned out with the thermoset removed by chipping. In the two-stage screw or screw plunger system, a fixed screw is used for heating. It differs from the reciprocating system in the location of the material. In the reciprocating system, the material or pot is located in front of the screw, while in the two-stage system it resides in a separate compartment. Both systems are reciprocating machines.

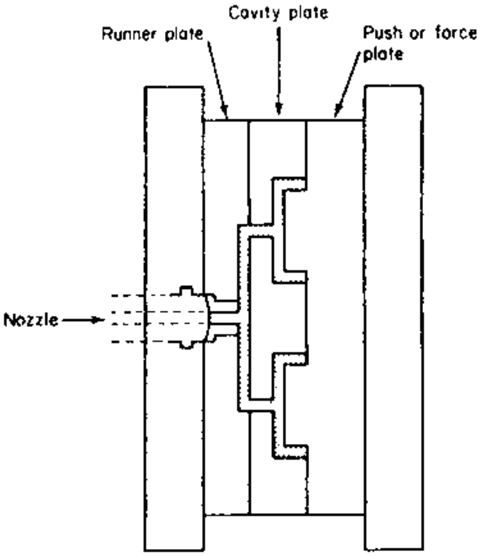

Figure 17.14 Injection mold in closed position (part d in Fig. 17.13). (Adapted from *Modern Plastics Technology* by R. Seymour, 1975, Reston Publishing Company, Reston, Virginia.)

The two-stage system offers several advantages in comparison to the reciprocating screw system. The two-stage system has lighter bearings and does not need a heavy thrust assemble because the screw does not act as a ram. The extruder barrel does not need to be as strong because of this and the screw end does not wear out so often. Thus, maintenance and wear are less. The screw pumps act only against the injection ram whereas in the reciprocating system the screw must push again both the material and the carriage. Further, the load is limited to the length of the feed channel in the reciprocating system, whereas the load can be easily varied by varying the size of the pot in the two-stage system.

On the other hand, the two-stage system requires two cylinders, two sets of heat controls, occupies more space, is more difficult to clean and assemble, and it cannot easily process materials particularly sensitive to heat.

As the size of the molded product becomes larger, it is more difficult to control uniformity and to maintain a sufficient clamping force to keep the mold closed during filling. Reaction injection molding (RIM) overcomes these problems by carrying out the polymerization reaction largely in the mold. The most widely used RIM materials are polyurethane and polyurethane-reinforced elastomeric materials. Most of the automotive interior panels (such as dashboards) are produced using RIM.

The design and construction of the mold is very important. The parts, usually steel, that enclose the cavity and cores are the mold base, mold frame, die base, die set or shoe, and mold frame. Generally there are two-plate and three-plate molds. The two mold types are similar in design and operation. In the three-plate system, an additional plate is inserted between the clamping plate and the so-called “A” plate.

On a molecular level, partially crystalline to amorphous polymers are normally used. As the material is heated, Brownian motion occurs resulting in a more random chain arrangement. When a unidirectional force is applied to a resting polymer melt, the chains tend to move away from the applied force. If the applied force is slow enough to allow the Brownian movement to continue to keep the polymers in a somewhat random conformation, then the movement of the polymer melt is proportional to the applied stress, that flow is Newtonian.

As the rate of movement increases, chain alignment occurs along the direction of the flow with movement too fast for Brownian factors to return the system to a somewhat random state; flow is then non-Newtonian. Most systems are operated, at least at the injection stage, under non-Newtonian conditions so that some polymer alignment occurs. If the polymer melt flow rate continues to increase, polymer chains align parallel to the flow plane and eventually reach a point where it again becomes Newtonian. Even so, the polymer chains have been aligned as the flow processes moved through the non-Newtonian flow range.

As the molten polymer is injected into the cold mold, it rapidly solidifies locking in at least some of the “orientated” chain conformations. As the material enters the cold mold, the flow turbulence occurring with the outer-most layers is generally sufficient to result in a more randomized, more amorphous outer structure. As the outermost chains cool, they “drag” the next chains effectively aligning them, giving a more ordered structure. Finally, the cooling of the inner material is slowed because of the heat uptake of the outer layers allowing Brownian movement to again somewhat randomize these chains. Thus, the structure of the molded part is varied and can be further varied by controlling the flow rate, cooling rate, and flow and cooling temperatures for a specific injected-produced

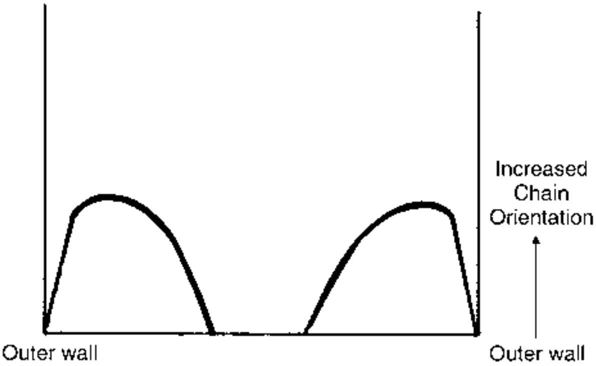

Figure 17.15 Idealized relationship between the distance from the outer wall and chain alignment.

material. Figure 17.15 contains an idealized relationship between the distance from the outer wall of a tube and the amount of chain aligning.

This complex combination of different orientations can be visually observed using birefringence measurements. Briefly, if a clear injected-molded or other produced material is placed between two polarizing light filters, one of which is rotated, a series of colored bands appear that are related to the orientation of the stress that is directly related to polymer chain orientation. Birefringence increases as one moves from the outer wall inward, increasing to a point after which it decreases toward the center of the article. As expected, the amount of orientation influences a number of important properties so that the conditions under which injection molding, or any other processing, occur are important to the end-use performance of the material.

Machine-milling, drilling, cutting, etc., also influences the structure that can either increase or decrease the order within the machined area depending upon the conditions of machining.

Blow Molding

Most molded material, as well as most processed material, will have a different surface or skin composition compared with the bulk or core material. Take a look at a common disposable polystyrene foam plate. The surface or skin is smooth. Break it and look at the core, and it is different being more cellular. This difference is greater than having simply a difference in appearance. There also exists different fine, molecular-level differences. These molecular structures and associated bulk properties are controlled in part by the particular processing and processing particulars.

Blow molding has been used for many years in the creation of glass bottles. In about 1872, the blow molding of thermoplastic objects began by the clamping of two sheets of cellulose nitrate between two mold cavities. Steam was injected between the two sheets, softening the sheets and pushing the material against the mold cavities. But, it was not until the late 1950s that large-scale use of blow molding began with the introduction of blow-molded high-density polyethylene (HDPE) articles.

Figure 17.16 contains a sketch of an extrusion blow-molding scheme. Here, a heat-softened hollow plastic tube, or parison, is forced again the walls of the mold by air pressure. The sequence of material introduction into the mold and subsequent rejection

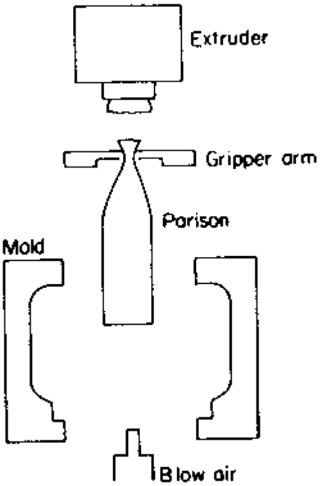

Figure 17.16 Sketch of extrusion blow-molding scheme. (From *Modern Plastics Technology* by R. Seymour, 1975, Reston Publishing Co., Reston, Virginia. Used with permission.)

of the material from the mold is generally rapid and automated. Approximately one million tons of thermoplastics are produced by this technique annually.

While there is a wide variety of blow-molding techniques, there are three main blow-molding procedures:

Injection blow-molding that employs injection-molded "test-tube" shaped preforms or parisons
Extrusion blow molding that uses an extruded tube preform or parison, and
Stretch blow molding that employs an injection-molded, extrusion blow-molded preform, or extruded tube preform

The major difference between injection and extrusion blow molding is the way the soft hollow tube (called a preform or parison) is made. In injection blow molding, two different molds are used. One mold molds the preform and the other is used in the actual blow-molding operation to give the final, shaped article. In the molding process, the softened material preform, from the preform mold, is introduced into the blowing mold and blow molded to fit the cavity of the second "finished" blow mold. This process is sometimes also called transfer blow molding because the injected preform is transferred from the preform mold to the final blow mold. This allows better control of the product wall thickness and the thickness of the various curved locations. The sequence is illustrated in Fig. 17.17.

Injection blow molding is typically used to produce smaller articles, generally with a total volume of 500 mL or less. Because two molds are used, there is little waste material that must be recycled and there is no bottom weld joint. It allows the production of small articles that at times are very difficult to manufacture in any other way.

Related to injection blow molding is displacement blow molding, where a predetermined amount of softened thermoplastic is deposited into a cupel, a hollow mold that is in the shape of a preform. A core rod is inserted into the cupel, displacing some of the resin and packing it into the neck-finished area. The preform is heat managed and held

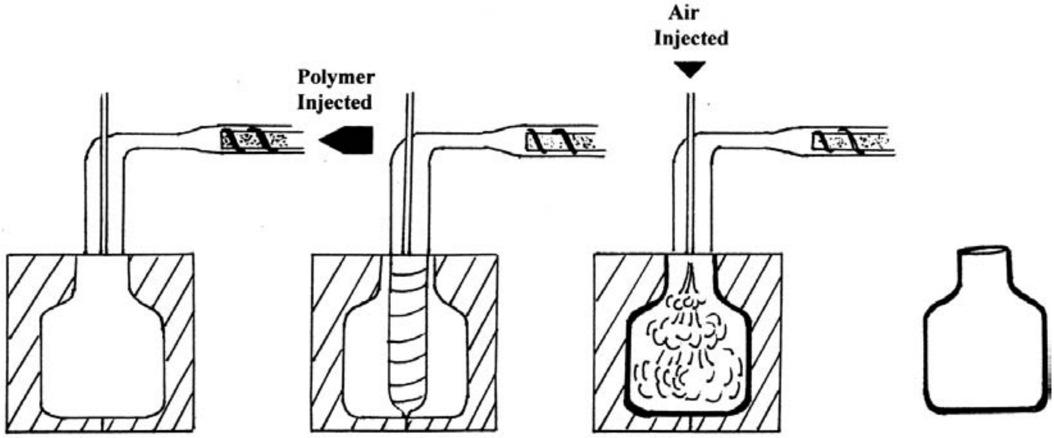

Figure 17.17 Injection blow-molding sequence. From left to right: vacant premold, premold closed with premold material added and preform formed, preform removed, preform transferred to the final blow mold, and injection of air or other gas into the softened thermoplastic forcing it against the blow mold walls (next drawing), and finally after cooling and form setting opening of the mold to release the structure.

on the core rod as the cupel is moved away. The finished blow mold then closes on the preform and air is injected, forcing the molten resin against the mold walls. This allows a reduction in the mold stress for the produced article since some of the "stretching" is already accomplished by the cupel-related step.

Extrusion blow molding is the most common process used to produce hollow articles larger than 250 mL up to about 10,000 L. In extrusion blow molding, the softened material is extruded continuously or intermittently. The preform is introduced, the mold halves close, and air or other gas is introduced forcing the preform material against the mold surfaces. After cooling, the mold is opened and the formed article rejected. Articles with handles and offset necks can be manufactured using extrusion blow molding. Figure 17.18 illustrates the steps used in extrusion blow molding.

Unlike injection blow molding, extrusion blow molding produces waste that must be cut away and recycled. The excess is produced as the two halves of the mold are pressed together.

In continuous extrusion blow molding, the preform is continuously produced at the same rate as the article is molded, cooled, and released. To avoid interference with the preform formation, the mold-clamping step must be rapid to capture the preform and move it to the blow-mold station. There are various modifications of this that allow essentially continuous operation.

In the rising-mold approach, the preform is continuously extruded directly above the mold. The cycle is extrusion of the preform, mold closing, air injection, cooling of the article and mold, mold opening and release of the article, open mold raising to the preform and the cycle beginning anew. It is similar to the piston action on an automobile as the rocker arm moves up and down, except here it is the mold that is moving up and down and the extrusion point forming the preform is stationary.

The rotary wheel modification employs a number of molds that rotate in and out of line with the extruder. As each mold is moved in line with the extruder it is injected with

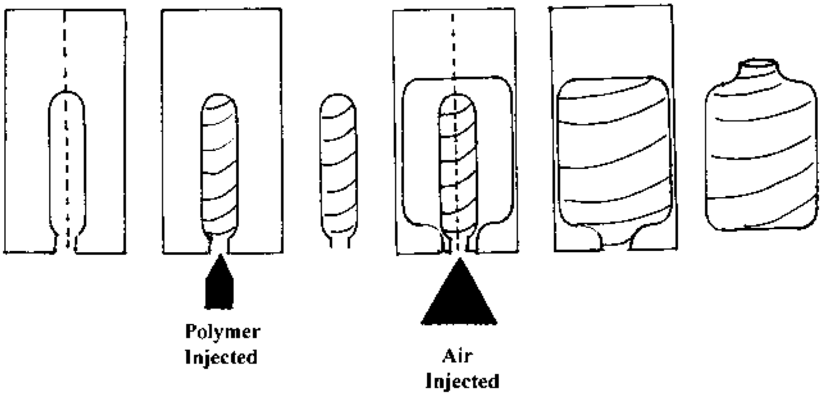

Figure 17.18 Steps employed in simple extrusion blow molding. From left to right: mold closed, soften material introduced, air or other gas injected forcing the softened thermoplastic against the walls of the mold, and after suitable cooling the mold is opened giving the article.

the premold material. As it cycles through the sequence to form and release the article it again advances toward being in line with the extruder and again beginning the cycle. Heat sensitive poly(vinyl chloride) and high-density polyethylene are/most often used in continuous extrusion blow-molding processes.

In intermittent extrusion processes, a single extruder is married to several molds that operate in sync. Because of this intermittent operation, non–heat-sensitive materials, such as most of the polyolefins, are often processed using this technique.

Wall and curved surface thickness is a major problem with extrusion blow molding, with thicker walls being common at the bottom. This is partially overcome by injection of the air using a programmed orifice. Extrusion blow molding can be used to form simple thermoplastics and all types of composites.

Stretch blow molding is employed for making larger bottles from 500 mL to 25 L. Here, uni- and biaxial stretching is used to gain additional strength because of the gain in molecular orientation of some materials. This allows the production of a product of equal or lesser weight to be produced that has an increase in transparency, strength, impact, stiffness, and a better liquid and gas barrier.

Stretching is best done just above the material's T_g, allowing a balance between good alignment because of ease in chain movement, and a decreased tendency to form crystalline areas in the melt allowing ready flow of material. A diagram illustrating this for a typical polymer in found in Fig. 17.19.

In the one-step process, preform production, stretching, and blowing all occur in the same machine. In the two-step sequence, the preform is produced in a separate step. The preform can be stretched prior to blowing in either the one-step or two-step process. In the one-step process, the preform is simply stretched just prior to, during, or just after the air is blown into the preform forcing it against the cavity walls.

Multilayered articles can be made by co-injection blow-molding or co-extrusion methods. A three-layer system generally contains a barrier layer sandwiched between two "exterior" layers. These are actually laminar products. In the co-extrusion sequence, several extruders can be used to place the material into the mold. The multilayer container is then produced from blowing air into the preform.

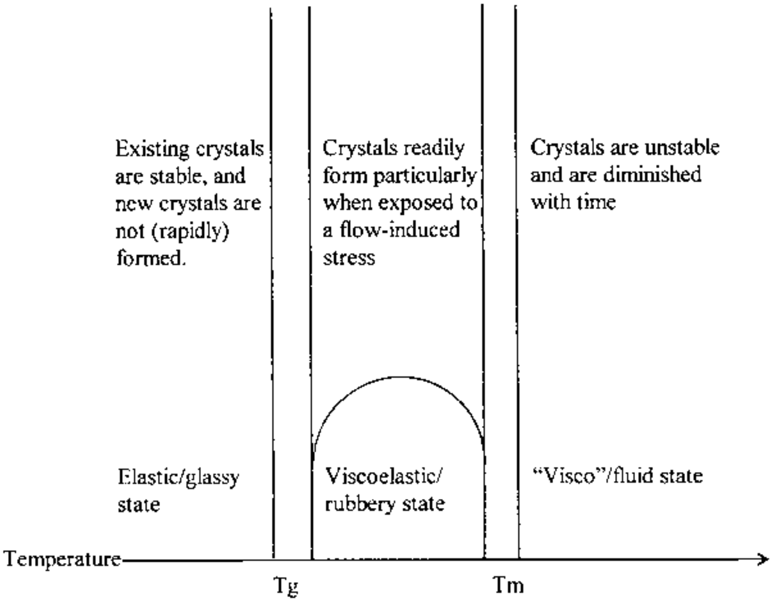

Figure 17.19 Idealized formation of order, crystals, as a function of temperature. The raised curve between the T_g and T_m ranges illustrate an idealized rate of crystal formation. This figure is sometimes referred to as the "Molder's Diagram of Crystallization."

Rotational Molding

In rotational molding, also known as rotomolding, the mold (or cavity) is filled with material, either as a solid, powder, or liquid. The mold is closed, placed in a heated oven, and then rotated biaxially. The mold is then cooled, opened, and the article recovered. Powders of about 35 mesh (500 μm) are typical, though different sizes are also employed. The distribution of particles and additives is determined by mixing and rotation ratio.

The most common assembly is the so-called "carousel" type that consists of an oven, cooling station, and a loading/unloading station. The mold is placed on a spindle or arm that is rotated 360°. Most modern assemblies are computer controlled so that rate and duration of rotation, heating, and rotation cycles are controlled. For large articles, a shuttle-type of apparatus can be employed. Here, the mold is fitted onto a movable bed that is loaded and then moved into the oven area. The mold assembly is such that the mold can be moved biaxially. In the clamshell design, all of the operations—loading, heating, rotating, cooling, and unloading—are carried out in one chamber.

While vinyl plastisols were initially the most widely rotational molded materials, today the most employed material is polyethylene. Other materials, including nylons, polycarbonates, poly(vinyl chloride), polyesters, acetals, acrylics, ABS, cellulosic-derived, epoxies, fluoro-containing polymers, phenolics, polystyrene, silicons, polypropylene, and polybutylenes have been molded using this process. Of the varieties of polyethylene, crosslinkable and linear low-density polyethylenes are the most often used. A number of copolymers, such as the copolymer of ethylene vinyl acetate and ethylene, gives articles with good impact properties when created using rotational molding.

Almost any mold design can be incorporated into rotational molding. Tanks used for agricultural, chemical, and recreational vehicle industries are made using rotational molding, as are containers used for packaging and material handling, battery cases, portable toilets, vacuum cleaner housings, light globes, and garbage containers. Rotational molding produces little waste and produces a material with uniform wall thickness as well as strong corner sections.

Compression and Transfer Molding

While there are a number of molding processes, compression and transfer molding are the main techniques for molding articles from thermosetting materials. In compression or transfer molding, the material, thermoplastic or thermoset material, is heated sufficiently to soften or plasticize the material to allow it to enter the mold cavity. The softened material is held against the mold by pressure. For thermoplastics, it is then cooled below the T_g, thus locking in its shape. For thermosets, it is held until crosslinking occurs, thereby locking in its shape.

The most widely employed molding process is compression molding, where the material is placed in the bottom half of an open, heated mold. The second half of the mold is closed and brings heat and pressure against the material, softening the material further and eventually allowing it to crosslink, if it is a thermoset. When completed, the pressure is released, and the article is removed from the mold. Generally excess material, or flash, is produced. Figure 17.20 contains a representation of a compression molding assembly.

Compression molding is one of the oldest materials handling processes. Ancient Chines employed compression molding to form articles from paper mache. Rubber articles were made in the early nineteenth century from composites of woody fibers and gum shellac. Baekeland used compression molding to make many of his early phenol-formaldehyde products.

Transfer (or plunger) molding introduces the to-be-molded material after the mold is closed through a small opening or gate. This process can be used when additional materials, such as a glass globe or other designed object, are placed in the mold prior to closing the mold.

In true transfer or pot-type molding, the mold is closed and placed in a press. The softened material is introduced into an open port at the top of the mold. The plunger is placed into the pot, and the press is closed. As the press closes, it pushes against the plunger forcing the molding material into the mold cavity. Excess molding compound is used to ensure that there is sufficient material to fill the mold. After the material is cured and/or cooled, the plunger and the part are removed from the mold. In plunger molding, the plunger is part of the press rather than part of the mold. Because of this, it can be smaller than the pot-type plunger. The clamping action of the press keeps the mold closed. Here, there is less material waste compared with the pot-type molding.

In cold molding, the compound is compacted in a mold at around room temperature. The compressing operation is similar to that employed in the production of KBr pellets from powdered KBr. The compound generally contains a lot of filler and binder. The compacted material is removed from the mold and placed in an oven where it becomes crosslinked. Ceramic materials are often produced using cold molding.

While most molding involves thermosetting materials such as phenol, urea, and melamine-formaldehyde prepolymers, many elastomeric and thermoplastic materials are molded. These include unsaturated polyesters, alkyd resins, epoxys, poly(vinyl chloride),

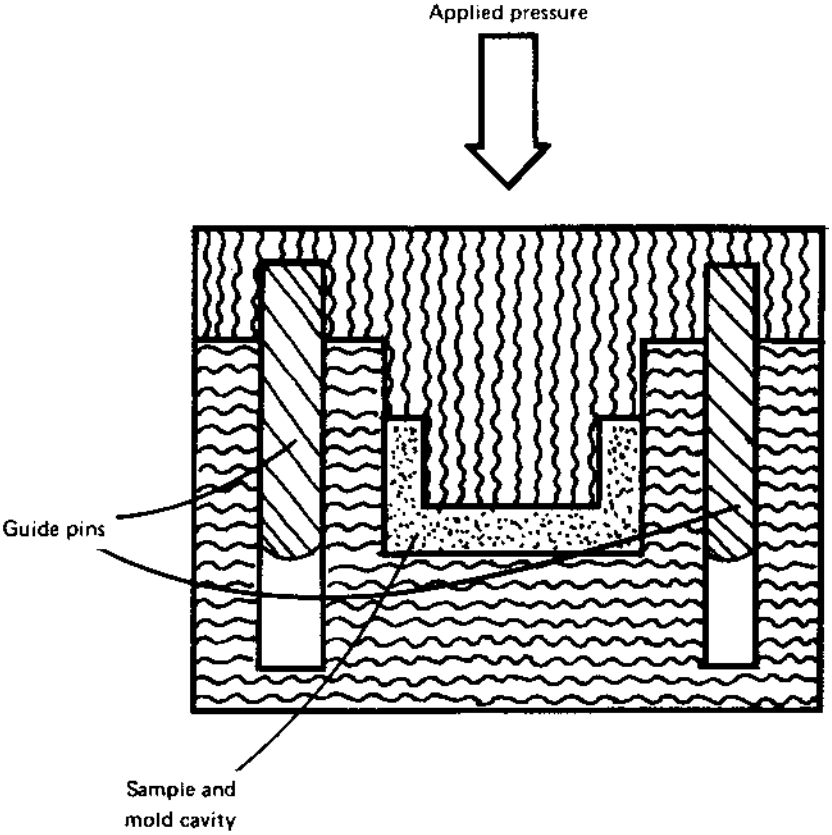

Figure 17.20 Representation of a compression molding assembly.

silicones, synthetic and natural elastomers, and diallyl phthalate polymers where the molded end products are also generally thermosets. Because all of these materials are good heat-insulating materials, the charge is generally preheated before it is introduced into the mold. With thermosets, slow heating may give crosslinking prior to the desired time, so that rapid heating is preferred followed by fast introduction into the mold. In compression molding, the rapid closing of the mold causes some frictional heating, and in transfer molding, frictional heating is produced from the rapid and forced flow of the material through small gates into the mold cavity.

Some thermosets are postheated to finish curing, allowing better control of the final amount of crosslinking and thus properties. Without postcuring, the product may continue to undergo crosslinking over the next months giving a material with varying properties over this period of time. Some of the thermosets, particularly the formaldehyde resins, give off some gas during polymerization. These gasses can be retained within the mold increasing the pressure, or released during the process. If the gasses are retained during the process, the part can be recovered without noticeable effects, but if it is removed too soon, blisters and ruptures may occur as a result of these gasses. However, often the gas is released periodically during the molding process. The time of opening is called the dwell, and the step is referred to as “breathe and dwell.” Timing and duration of the breath and dwell steps are important.

While curing reactions occur at room pressures, it is important for good mold contact to employ high pressures, generally on the order of 20–70 M Pa, though some molding processes can get by with low pressure (0.7–7 M Pa). Under pressure, the molecules behave as non-Newtonian fluids and some ordering occurs. Further, forced flow of polymers and prepolymers into the mold causes some aligning of the molecules. Thus, the fine structure, and associated properties, can be somewhat controlled by flow rates, heating/cooling, curing rate and extent, and pressure with speed associated with many of these factors. For instance, if a homogeneous, isotropic behaving material is wanted, the flow rate into the mold should be slow and the flow pathway short. Further, for thermosetting materials, the time that the material is preheated should be low and the rate rapid. Thus, there exists many balances where the end result is reached, not surprisingly, through a mix of science and practice (trial and error). Each machine, mold, and material will present a new opportunity for determining the optimum set of conditions.

In solvent molding, a mold is immersed in a solution and withdrawn, or a mold is filled with a polymer and evaporation or cooling occurs, producing an article such as a bathing cap. Solvent molding and casting are closely related.

Thermoforming

Thermoforming involves heating a sheet or thick film just above its T_g or T_m, stretching it against a rigid mold, cooling, and trimming the formed part. Inexpensive aluminum, wood, epoxy, and steel molds are often employed. This allows the construction of inexpensive molds that allow the production of low-volume articles. All thermoplastic materials that can be formed into sheets can be thermoformed provided that the heating does not exceed the ability of the sheet to support itself. A simple plug-assisted vacuum thermoforming sequence is given in Fig. 17.21.

Thermoforming is employed to convert extruded sheets into smaller items such as packaging containers, plates, trays, bathtubs, pickup truck liners, freezer liners, cabinery, and cups. The skin packaging that involves a flexible plastic skin drawn tightly over an article on a card backing is made by thermoforming. Thermoforming permits the production of small to large articles, including those with thin walls, such as drinking cups. Thus, thermoforming is employed to produce articles with a relatively high surface to thickness ratio.

Multilayered materials can be readily formed using thermoforming, including food packaging that may involve inclusion of layers of ethylene-vinyl alcohol copolymers, polystyrene, polyolefins, and/or copolymers of vinylene dichloride and vinyl chloride. Microwavable food trays from (crystallized) poly(ethylene terephthate) are manufactured using thermoforming.

Polystyrene is the most widely used resin material for thermoforming. High-impact polystyrene (HIPS) is the most widely used, being employed largely in the packaging areas including disposables (foam drinking cups, lids, lunch trays, and food-service containers), packaging for medical devices, and food packaging (meat and poultry trays, egg cartons, dairy and delicatessen containers, and barrier packages). ABS is thermoformed to produce more durable articles, such as refrigerator inner door liners, recreational vehicle and boat parts, automotive panels, picnic coolers, and luggage exteriors. High-density polyethylene is used in the manufacture of pickup truck liners, golf cart tops, and sleds. Crystallized

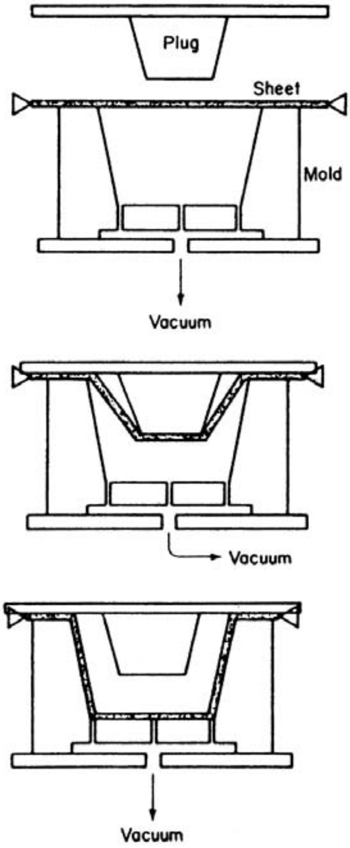

Figure 17.21 Steps in plug-assisted vacuum thermoforming. (From *Modern Plastics Encyclopedia*, McGraw-Hill, New York, 1976–77; with permission.)

poly(ethylene terephthalate) (PET) is used in the thermoforming of food trays that can be heated in a microwave or regular oven. Also used to make frozen-food oven-friendly trays is coextruded polycarbonate-polyetherimide. Polycarbonates and poly(methyl methacrylate) are thermoformed to produce skylights, windows, tub and shower stalls, and outdoor display signs. Poly(vinyl chloride) is used in the production of blister packaging of pharmaceuticals, foods, cosmetics, and hardware.

Thermoforming is easily carried out for materials where the "sag" temperature is broad. Amorphous resins such as foamed, oriented, and high-impact polystyrene (HIPS) acrylics, and poly(vinyl chloride) are primary resins employed in thermoforming. Semicrystalline thermoformable resins include both high-density and low-density polyethylene. Control of conditions is more important where the "sag" temperature range is narrower, such as for semicrystalline resins like polypropylene, some polyesters, and fluoropolymers. The range for effective sag can be increased through the introduction of appropriate branching, copolymerization, and addition of selected additives including crystallization modifiers. While these molding techniques are generally adaptable to the production of thermoset materials, thermoforming is carried out using thermoplastic materials. There are a wide variety of thermoforming techniques in use today.

Vacuum can be used in a process called basic vacuum forming (Fig. 17.22, far left). The sheet is fixed to a frame, heated, and vacuum applied that implodes the sheet to conform to the mold contour. The vacuum site is generally at the base of the male mold. It cools as it comes into contact with the cold mold. For thick sheets, extra cooling is supplied by means of forced air or mist-sprayed water. Articles formed using vacuum forming typically have thinner walls the further the sheet must travel to the mold location. The excess plastic material is trimmed and reused. At times vacuum forming is run in-line with a sheeting extruder.

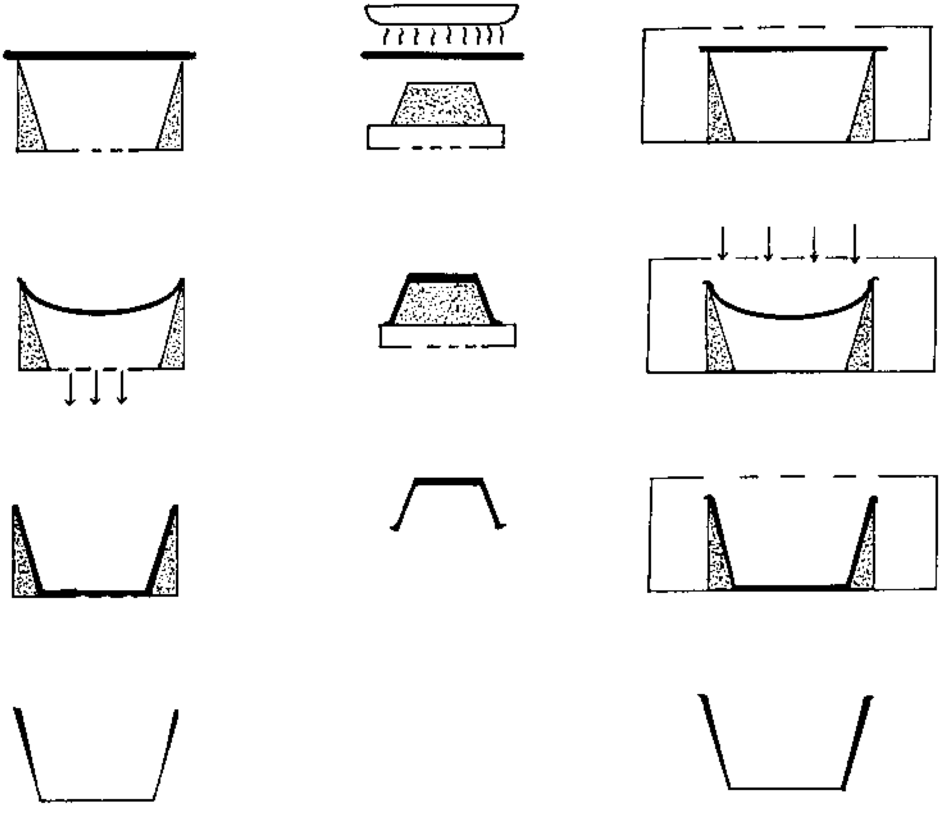

Figure 17.22 Basic vacuum forming, far left from top to bottom: thermoplastic sheet is clamped and heated; vacuum beneath the heated sheet causes the atmospheric pressure to push the thermoplastic against the mold; the thermoplastic fits against the mold; and after cooling the article is removed. Typically, the bottom and lower sides are thinner than the upper sides. Many of the alternative thermoforming techniques have been developed to overcome this variation in thickness. In drape forming (center), the thermoplastic sheet is heated, then either pulled over the mold or the mold is pushed into the sheet with vacuum assisting the sheet process; after cooling the article is obtained. In pressure forming (far right), the sheet is clamped and heated, excess pressure from above the mold is applied pushing the softened thermoplastic against the mold, and after cooling the article is released.

In drape forming (Fig. 17.22, middle), the thermoplastic sheet is clamped and heated and the assembly then sealed over a male mold. The mold may be forced into the sheet or the sheet may be pulled into the mold by introduction of a vacuum between the sealed sheet and mold. By draping the sheet over the mold, the part of the sheet touching the mold remains close to the original thickness, Foamed polystyrene and polyolefins are generally used in this procedure.

In pressure forming (Fig. 17.22, far right), positive pressure is employed to assist the sheet contents into the mold. The major advantage of pressure forming is a decreased cooling time. Crystalline polystyrene, high-density polyethylene, and oriented polypropylene are used in this procedure.

After the heated sheet is sealed across the mold, a shaped plug is pushed into the sheet, stretching it as it enters into the mold cavity in plug-assisted forming (Fig. 17.23, far left). The plug is generally of such a size and shape as to assist in the formation of the final mold shape and generally occupies about 90% of the mold volume. As it gets near the bottom of the mold, full vacuum is applied.

A variety of the plug-assisted process is the prestretching-bubble techniques. In pressure-bubble plug-assisted forming (Fig. 17.23, middle), a heated sheet is sealed across a female cavity and pressure is blown through the cavity, forcing the sheet from the mold. An “assist-plug” is then forced against the blown bubble with the heated sheet beginning to form about the plug as it forces the sheet against the female mold. As it nears contact with the female mold bottom, vacuum is applied through the mold causing the material to collapse onto to mold. Alternatively, positive pressure can be applied on the “plug” side forcing the sheet against the mold walls. In the reverse of the pressure-bubble technique, called vacuum snapback forming (Fig. 17.23, far right), the heated sheet is sealed against a vacuum female cavity and controlled vacuum draws the concave shaped sheet away from the entering male mold. The male mold is then pressed against the sheet and vacuum applied through the male mold and/or pressure applied from the female cavity side, forcing the material against the male mold. Luggage and automotive parts are made using this technique.

In pressure-bubble vacuum snapback (Fig. 17.23, far left), the heated sheet is clamped and sealed against a pressure box. Air is forced through the female pressure box forcing the sheet to push outward from the pressure box. A male mold is then pressed against the bubble and as it pushes into the pressure box, excess air is forced from the pressure box forcing the heated sheet to take the shape of the male mold. The major difference between the vacuum snapback and pressure-bubble vacuum snapback is that in the vacuum snapback process, vacuum from a female pressure box distorts the sheet away from the male mold and into the female pressure box, while in the pressure-bubble vacuum snapback, excess pressure from the female pressure box forces the heated sheet toward the male mold and away from the female pressure box.

Similar to pressure-bubble vacuum snapback forming, air slip forming (Fig. 17.24, middle) seals a heated sheet to the surface of a pressure chamber employing a male mold. It differs in the way the bubble is produced. Here, the heated sheet is clamped above a male mold. Pressure against the mold is created by the upward motion of the male mold toward the sheet, causing it to bubble away from the oncoming mold. At the right time, a vacuum is applied through the male mold that causes the sheet material bubble to collapse and form about the male mold.

Trapped-sheet contact heat-pressure forming utilizes a heating plate that contains many small vacuum and air-pressure holes. A sheet is placed between the heating plate

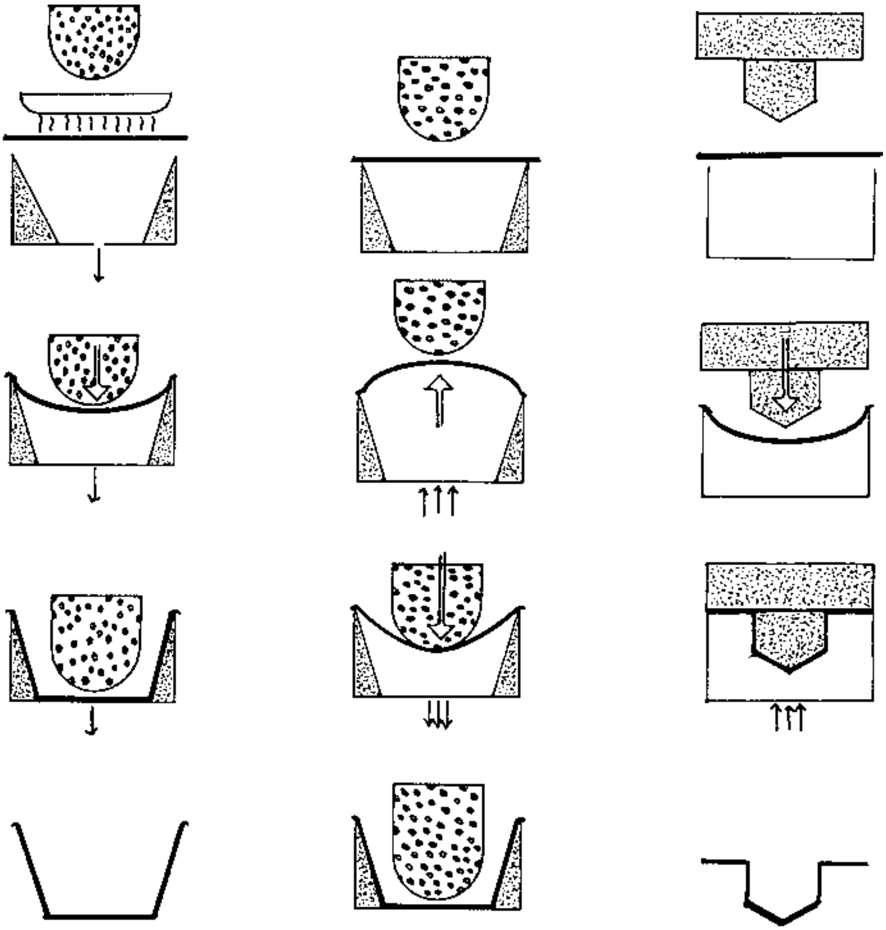

Figure 17.23 In plug assist forming (far left), the thermoplastic sheet is heated, a plug with a shape somewhat similar to the mold cavity pushes the sheet against the mold cavity forming a seal, vacuum is applied on the mold side to assist the sheet material to conform to the mold, the material is cooled, and the article is removed. For pressure bubble-plug assist vacuum forming (middle), the thermoplastic sheet is clamped over the mold, excess air is introduced through the mold cavity pushing the softened sheet outward away from the mold cavity, and the plug is pushed against the thermoplastic sheet "prestretching" it, driving it toward the mold cavity. Vacuum is then applied within the mold assisting the collapse of the softened material against the mold walls. In vacuum snapback forming (far right), the thermoplastic sheet is heated and then clamped and sealed over a female vacuum box. Vacuum is applied within the female vacuum box causing the thermoplastic sheet to sag inward; the mold is then pushed against the soften material and excess pressure is then applied from within the female vacuum box assisting in the placement of the thermoplastic material about the mold.

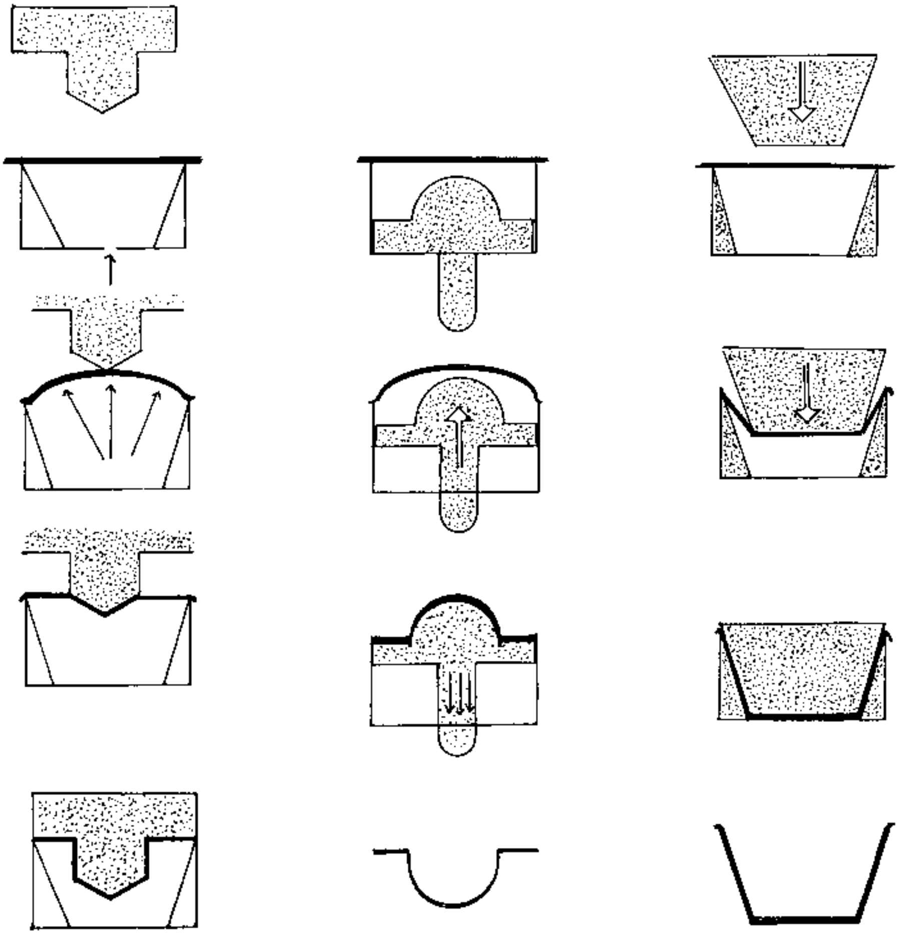

Figure 17.24 Selected basic vacuum-assisted thermoforming techniques. For pressure bubble vacuum snapback (far left), the thermoplastic sheet is clamped and sealed against a pressure box, excessive air is supplied from the female pressure box causing the sheet to "bubble" away from the pressure box toward the mold, and the mold is pushed toward the softened sheet material into the female mold. The air pressure within the mold is maintained at a constant value and vacuum is applied to the mold side, assisting in the formation of the material about the "plunger" mold. In air-slip forming (middle), the heated thermoplastic sheet is clamped over the mold, the movable mold is pushed toward the softened sheet, causing excess pressure building that causes the formation of a "bubble" pushing away from the mold and mold cavity. Vacuum is applied, assisting the collapse of the bubble against the movable mold, and the article is cooled and recovered. In matched mold forming (far right), the heated sheet may be clamped or simply laid (draped) over the female mold part; as the mold closes trapped air is removed, the article is molded, and removed after cooling.

and female mold. Initially, excess air pressure from the mold pushes the sheet into contact with the heating plate. The heating plate then heats the sheet, and after desired heating, vacuum is applied from the female and/or pressure applied through the heating plate pulls/pushes the heated sheet material into the female mold. Additional pressure can be used for trimming the article. Candy and cookie box liners and some medical packaging is made using this process.

These bubble-associated processes are aimed at prestretching the heated sheet to allow more even walls and bottoms to be formed.

In matched-mold forming (Fig. 17.24, far right), a heated sheet is placed between matched female and male mold parts. As the two mold halves close, they distort the sheet to their shape. The air between the mold halves is removed. The article walls are more uniform than for many of the thermoforming techniques. This technique is used for the production of foamed polystyrene and foamed polyolefin food containers. A number of other techniques have been developed either to handle special materials or to create specific articles.

17.7 CASTING

Casting is employed in making special shapes, sheets, films, tubes, and rods from both thermoplastic and thermosetting materials. The essential difference between most molding processes and casting is that no added pressure is employed in casting. In this technology, the polymer or prepolymer is heated to a fluid, poured into a mold, cured at a specified temperature, and removed from the molds. Casting of films and sheets can be done on a wheel or belt or by precipitation. In the case of a wheel or belt, the polymer is spread to the desired thickness onto a moving belt as the temperature is increased. The film is dried and then stripped off. “Drying” may occur through solvent evaporation, polymerization, and crosslinking.

17.8 EXTRUSION

Extrusion is involved in a number of processing operations and is widely used. Here, we will look at extrusion as it is involved in several of these processes. These processing operations can be used together or separately. A representative extruder is shown in Figure 17.25. The extruder accepts granulated thermoplastic in a hopper (c), plasticizes the polymer, and forces it from the feed throat (d) through a die (f). The die may be circular for the production of a rod or pipe, or flat for the production of a sheet, or it may have any desired profile for the continuous production of almost any uniformly shaped product. The screw (a) advances the polymer through a heated cylinder (barrel) (b) to a breaker plate and protective screen pack (e) before it enters the die (f). The extrusion process may be divided into a feed or transport zone, a compression or transition zone, and a metering zone. Over one million tons of extruded pipe are produced annually in the United States. Properties of some molded or extruded plastics are given in Table 17.10.

In extrusion, a fluid material, generally rendered a fluid material through heating, is forced through a shaping device. Since there is a need for quickness and because the preshaped material is quite viscous, extrusion requires high pressure to drive or force the melt through a die. The melts can be extruded as pipers, sheets, films, or into molds.

Extruders can be described in terms of their length, *l*, and screw diameter, *d*, by the ratio *l*/*d*.

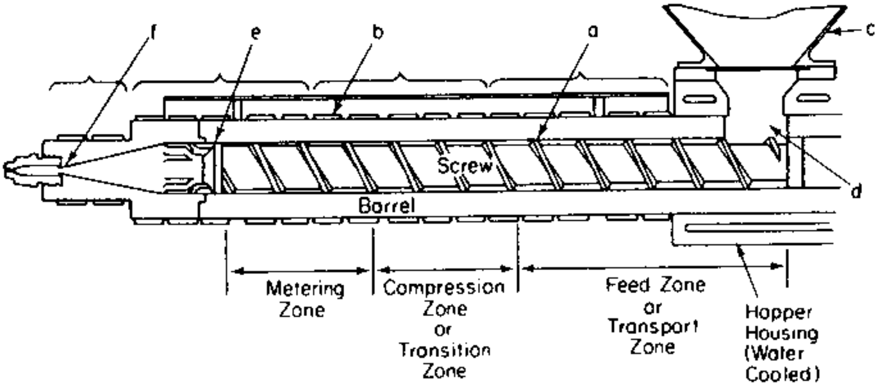

Figure 17.25 Sketch details of screw and extruder zones. (From *Modern Plastics Technology* by R. Seymour, 1975, Reston Publishing Co., Reston, Virginia. Used with permission.)

Melt-fed extruders have *a* l/*d* ratio of about 8; solid-fed extruders often have *l*/*d*'s in the range of 20–40. Large extruders can produce 20 tons per h of extruded material.

Along with moving and shaping the molten material, extruders also act to disperse additives and are often the agent for creating heat, thus enabling the material to become molten.

Twin-screw extruders are gaining in use, especially where additive and ingredient mixing is required. Such extruders are able to produce blends and alloys with unique and desired properties. Twin-screw extruders are often classified as being tangential or intermeshing with the intermeshing being further divided into counter-rotating or corotating.

Reactive extrusion is the term used to describe the use of an extruder as a continuous reactor such as polymerization or polymer modification. Twin-extruders allow multiple steps to be carried out in a somewhat continuous manner with a single machine mixing, melting, metering, reacting, and allowing the mixing and addition of additives including additives (such as copolymers).

There are a number of dies, each when coupled as part of the entire extruder produces a variety of materials with a variety of properties. Films and sheets can be produced using slit or sheet dies that have adjustable gap openings. Flat or circular dies are employed in extrusion coating operations. Tubular dies are employed in the formation of pipe and tubing. The pipe/tube can be linear or curved as desired and produced with a large variety of sizes and lengths. Generally the pipe/tube is produced in a continuous fashion and cut to the desired length.

In foam extrusion physical blowing agents, gas or low boiling liquid, is dissolved and retained in the solution by the extruder. As the molten material exits the die, the pressure release causes spontaneous foaming.

17.9 COATINGS

The fundamental purpose for painting is decorating, whereas the purpose for coating is for protection. While technically these two terms may have different meanings, the terms can be considered interchangeable, and we will follow this practice here.

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Table 17.10 Properties of Molded Plastics

Polymer	Tensile strength (kg cm^{-2})	Flexural strength (kg cm^{-2})	Heat deflection point (@18.6 kg cm^{-2})	Dielectric constant (at 60 cycles)	Power factor (at 60 cycles)
Phenol, formaldehyde resin	280	945	57		
Wood, flour-filled	535	700	121	6.0	0.08
Glass, fiber-filled	840	2100	232	7.1	0.05
Urea-formaldehyde, α-Cellulose-filled	630	980	135	8.0	0.04
Melamine-formaldehyde, α-cellulose-filled	700	910		8.7	0.05
Alkyd resin, glass-filled	490	1050	130	5.7	0.010
Allyl resin, glass-filled	595	1050	232	4.4	0.03
Epoxy resin, glass-filled	1400	2450	224	4.2	0.025
Polyethylene (type I) (LDPE)	112		38	2.3	0.0005
Polyethylene (type II) (IIDPE)	315	70	49	2.3	0.0005
Polypropylene	343	490	57	2.4	0.0005
Ionomers	315		38	2.4	0.002
			a, 4, 6 kg cm^{-2}		
Polystyrene	595	770	85	2.5	0.0002
Poly(methyl methacrylate)	770	1680	99	3.0	0.007
ABS copolymer	490	770	93	3.5	0.005
Polytetrafluoroethylene	245		60	2.1	0.0002
Cellulose acetate	385	630	66	5.5	0.05
Acetal resins	700	980	124	3.7	
Phenoxy resin	595	875	82	4.1	0.0012
Polycarbonate	630	945	135	3.0	0.0007
Polysulfone	700	1050	174	3.1	0.008
Poly(phenylene oxide)	770	1050	190	2.6	0.0003
Nylon-66, mineral-filled	980	1000	166		
Poly(butylene terephthalate)	560	1000	66	3.29	
Polyimide	1190	1100	132	3.43	
Polymethylpentene	2800			2.12	0.00007
Poly(phenylene sulfide)	7000	14000	137		
Polyurethane	2800				0.03

Governmental edicts concerning air, water, solid particulates, and worker conditions are having real effects on the coatings industry with the generation of new coating techniques. Paint solvents in particular are being looked at in view of increased environmental standards. The volatile organic compound (VOC) regulations under Titles I and VI of the Clean Air Act specify the phasing out of ozone-depleting chemicals—namely, chlorinated solvents—by the year 2000. Baseline solvent emissions are to be decreased. These and related regualtions affect the emission of *all* organic volatiles, whether in coatings or in other volatile-containing materials.

A major driving force in coatings continues to be a move toward water-based coatings. Another is to eliminate the “door” of the coating. Most waterborne coatings actually have about 8–10% nonaqueous solvent. The odor we get as the coating is drying is mainly due to the solvent evaporating. Work continues to develop the right balance of properties and materials that allow the latex particles to flow together and coalesce into suitable films without the need of nonaqueous liquids.

Another area of active research is the development of paints that dry under extreme or unusual conditions including under water and on cool substrates. The latter allows the painting season for exterior coating to be extended, particularly in the northern states.

Work continues on making more durable exterior paints. Remember that there is a difference in requirements of exterior and interior paints. For instance interior paints are generally required to be faster drying and more durable against scrapes and punctures since it is the inside of the house that generally experiences such traumatic events. By comparison, exterior paints need to remain flexible and adhered under different humidities and temperatures. A more durable exterior coating should allow it a longer lifetime because it can better withstand stress caused by the pounding of the rain, sticks, and human-afflicted dings and dents. Binders or coating resins are critical to the performance of coatings. They bind the components together. Since the primary cost of most commercial application of coatings is labor, the market will allow price increases for products that give added positive properties.

Paint manufacturers in the United States sell about 1,300 million gallons of coating material annually, or about 4 gallons for every man, woman, and child. This paint is used commercially to coat display cases, aluminum cans, washing machines, and automobiles; we use it to protect both the interior and exterior of our homes, as well as to paint baby beds, chairs, and picture frames.

Paint is typically a mixture of a liquid and one or more colorants (pigments). The liquid is called a vehicle or binder (adhesive) and may include a solvent or thinner along with the coating agent. The colored powders are called pigments.

Pigments may be prime or inert. Prime pigments give paint its color. These may be inorganic, such as titanium dioxide (TiO_2O_2) for white (also contained in many paints of other colors) or oxides (Fe_2O_3, Fe_3O_4, FeO) for browns, yellows, and reds, or organic, such as phthalocyanine for greens and blues. Inert pigments such as clay, talc, calcium carbonate ($CaCO_3$), and magnesium silicate make the paint last longer (acting as fillers and extenders) and may contribute to the protective coating as do mica chips in some latex paints. The paint may also contain special agents or additives that perform specific roles.

Vehicles include liquids such as oils (both natural, modified natural) and resins and water. A latex vehicle is made by suspending synthetic resins, such as poly(methyl methacrylate), in water. This suspension is called an emulsion, and paints using such vehicles are called latex, waterborne, or emulsion paints. When the vehicle comes in contact with air, it dries or evaporates, leaving behind a solid coating. For latexes, the water evaporates, leaving behind a film of the resin.

Paints are specially formulated for specific purposes and locations. The following list includes brief descriptions of the more popular paint types.

Oil paints: Oil paints consist of a suspension of pigment in a drying oil, such as linseed oil. The film is formed by a reaction involving atmospheric oxygen which polymerizes and crosslinks the drying oil. Catalysts may be added to promote the crosslinking reaction. Oil paints, once dried (cured, crosslinked), are no longer soluble, although they can be removed through polymer degradation using the appropriate paint stripper.

Oil varnishes: Varnish coatings consist of a polymer, either natural or synthetic, dissolved in a drying oil together with appropriate additives as catalysts to promote the crosslinking with oxygen. When dried, they produce a clear, tough film. The drying oil is generally incorporated, along with the dissolved polymer, into the coating.

Enamels: Enamel is an oil varnish with a pigment added. The added polymer is typically selected to provide a harder, glossier coating than the oil varnish mixture.

Lacquers: Lacquers consist of polymer solutions to which pigments have been added. The film is formed through simple evaporation of the solvent leaving the polymer film as the coating. These coatings are formed without subsequent crosslinking; thus, the surface exhibits poor resistance to some organic solvents.

Latex paints: Latex paints today account for more than one-half of the commercial paint sold. They are characterized by quick drying (generally several minutes to several hours), little odor, and easy cleanup (with water). Latex paints are polymer latexes to which pigments have been added. The film is formed by coalescence of the polymer particles on evaporation of the water. The polymer itself is not water-soluble, though these paints are called waterborne coatings.

Because of the need to reduce environmental pollution, the trend is toward highsolids coatings with a solvent–volume concentration of less than 20%. Plastisols, which are solvent-free, consist of polymers, such as PVC, dispersed in liquid plasticizers, such as DOP. These plastisols may be coated on substrates and fused at 160°C.

Coatings are used for a wide variety of applications. About one-third are used as architectural coatings (exterior and interior house, undercoatings, stains, varnishes, primers, sealers); one-third as the original coatings of manufactured goods (appliances, automotive, electrical, factory-finished wood products, metal furniture, paper, film, foil, coil coating, machine and equipment coatings); and the last major classification of special-purpose coatings accounts for a little less than one-third of the total amount (aerosols, bridge maintenance, arts, crafts, marine, roofs, swimming pool, traffic paints, auto refinishing).

Processing

Many different process are used to apply a thin layer of liquid-melted polymer or polymer solution (or dispersion) including rollers, spraying, calendering, and brushing. Here, we will look at the industrial application of coatings onto film and sheet-like materials. Figure 17.26 contains examples of general coating processes employed to achieve this. The moving sheet is called a web. In roll coating (Fig. 17.26, left side), the lower roller picks up the coating material and then transfers it to the second roller, and finally to one surface of the mat. Spacing of the rollers, viscosity of the polymer solution in the dip tank, and roller speed and size control the thickness of the applied coating.

In blade coating (Fig. 17.26, upper right-hand side), a flexible blade helps control the coating thickness. The blade may be located after the bath or within the bath as part of the roller system. The blade is flexible and adjustable so that the amount of coating material can be controlled by application of force on the blade and/or distance the blade is from the web or roller. Both of these processes are forms of calendaring. The third main coating process involves direct application of the coating material forming a so-called fluid curtain (Fig. 17.26, lower right-hand side). This process, curtain coating, is usually used in conjunction with a curing process. The coating thickness is controlled by web speed, polymer concentration, and rate of application from the extruder. Coatings can be divided according to formulation, drying mechanism, or other system of categorizing. Table 17.11 contains a summary of coatings according to drying mechanism.

A coating is normally a mixture of various components. For instance, the label on a latex emulsion-type paint might have as major components poly(methyl methacrylate), titanium dioxide as the white pigment, and water. It could also have china clay and calcium carbonate as extenders, carboxymethylcellulose as a colloid thickener, a defoaming agent, a plasticizer, a surfactant dispersing aid, additional coloring agents, and an added fungicide.

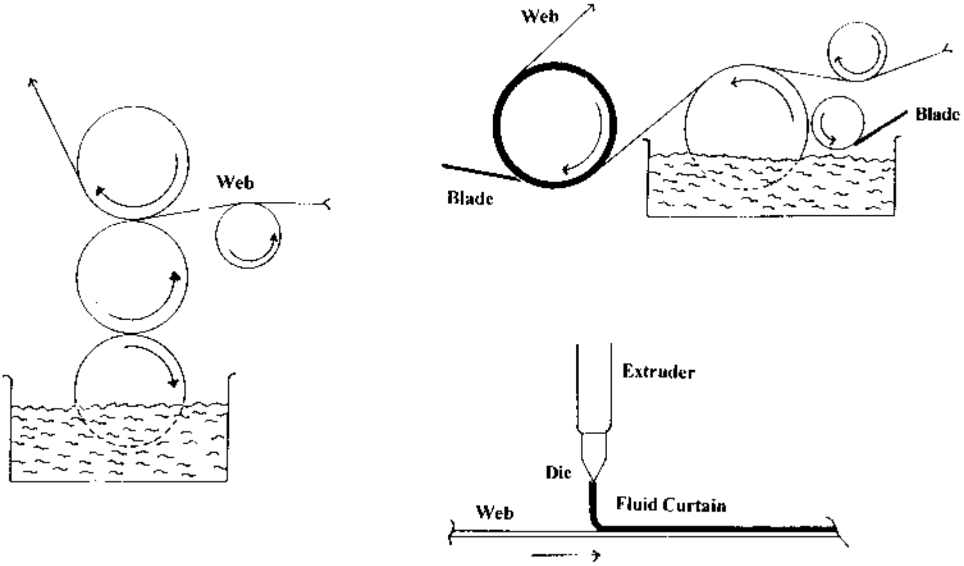


Figure 17.26 Three principal industrial coatings processes for films and thin sheets: (left) roll coating, (upper right) blade coating, (lower right) curtain coating.

Table 17.11 Major Coatings Systems as a Function of Drying Mechanism

- A. Film formation through chemical reaction
  - a. Through reaction of unsaturated double-bond sites with oxygen
    - Alkyds
    - Drying oils-fatty acid and related
  - b. Cold curing and thermosetting by reaction with vehicle components
    - Epoxies
    - Polyurethanes
    - Unsaturated polyesters
    - Urea and melamine-formaldehyde
- B. Film formation through evaporation
  - a. Solution types
    - Bituminous coatings
    - Cellulose derived-acetate, acetate butyrate, ethyl, nitrate
    - Chlorinated rubbers
    - Poly(acrylic esters) such as poly(methyl methacrylate)
    - Poly(vinyl chloride) copolymers
  - b. Dispersion types
    - Poly(acrylic esters) such as poly(methyl methacrylate)
    - Poly(vinyl acetate) and copolymers
    - Poly(vinyl chloride) organosols
    - Poly(styrene-co-butadiene)

The hiding power is a measure of the ability of the coating to achieve a specified degree of "hiding" or obliteration. Industrially, it is often tested by comparing the reflectance of the coated surface overpainting a black surface (that is, the tested paint applied over a black surface) with white panels. The ability to cover or hide is related to the scattering of incident light hitting the surface and returning to the observer or light meter. As the film surface increases, the ability of light to penetrate the surface coating and be scattered from the under coating (black for tests) lessens. For a simple white latex paint, no absorption occurs, and we can consider the scattering occurring at the interfaces of the transparent polymer matrix and the dispersed pigment particles. The scattering coefficient of polymers can be obtained from reflectance measurements. While the refractive indices for most polymers do not widely vary (generally about 1.5), the scattering coefficients can vary widely. For good scattering, the refractive index of the polymer should differ from that of the pigment. For instance, while calcium carbonate, with a refractive index of about 1.6, is often used as a pigment in paints, it has a much lower hiding power than titanium dioxide (rutile titanium IV oxide), with a refractive index of about 2.8.

Scattering efficiency increases as the pigment surface area becomes larger, thus smaller particles aid in increasing the scattering to a lower limit determined by the wavelength of light, thereafter reduced size produces a rapid loss in scattering efficiency. For good scattering, and good hiding power, the particles should be dispersed in a homogeneous manner so that dispersing agents are commonly used.

Surface Treatments

To promote good adhesion, the adhered surface generally undergoes surface treatment. Following is a brief summary of some of the most common surface treatments.

Simple cleaning: This may include simple washing away of grease and grime that has accumulated through handling and processing. Generally volatile liquids that dissolve away the unwanted surface agent are applied and subsequently washed or wiped away.

Plasma or CAUSING treatment: Crosslinking by activated species of inert gas. CAUSING, or plasma treatments, involve bombardment of the surface with ions of an inert gas at low pressure. Here the surface itself or surface with a thin layer of adhesive is treated.

Surface grafting: Specific units are grafted onto the surface that subsequently provide a more favorable surface for bonding with the adhesive or coating agent. Grafting can occur through introduction of the grafting agent and subsequent treatment with an appropriate chemical or radiation source.

Coupling agent: Coupling agents are often added that act to lock-in, normally through chemical bonding, to both the surface and adhesive or coating agent. Thus, for glass, silanes are often added so that one portion of the silane reacts with SiOH groups in the glass with the other portion selected so that it will react with the adhesive/coating.

Corona discharge: The surface is exposed to a corona discharge in air generally under atmospheric pressure. Depending upon the surface, functional groups are created that can subsequently react with the adhesive/coating. Thus, for polyethylene, carbonyl and sites of unsaturation are created that can subsequent react with polar adhesives/coatings.

Transcrystalline growth: For instance, polyolefins molded against a high energy metallic surface have transcrystalline growth promoted at the polyolefin surface. Nucleation of crystallites radiating into the interior of the polymer occurs acting to drive lower molecular weight and more amorphous portions away from the surface resulting in a stronger surface.

Acid etching: Many surfaces are treated with acids such as chromic acid that result in an etched surface with additional polar functional groups enhancing adhesion through a possible combination of polar effects, chemical bonding, and simple interlocking effects.

17.10 ADHESIVES

In contrast to coatings, which must adhere to one surface only, adhesives are used to join two surfaces together. Resinous adhesives were used by the Egyptians at least 6000 years ago for bonding ceramic vessels. Other adhesives, such as case in from milk, starch, sugar, and glues from animals and fish, were first used about 3500 years ago.

Adhesion occurs generally through one or more of the following mechanisms. Mechanical adhesion with interlocking occurs when the adhesive mixture flows about and into two rough substrate faces. This can be likened to a hook and eye, where the stiff plastic-like hooks get caught in the fuzz-like maze of more flexible fibers. Chemical adhesion is the bonding of primary chemical groups. Specific or secondary adhesion occurs when hydrogen bonding or polar (dipolar) bonding occurs. Viscosity adhesion occurs when movement is restricted simply due to the viscous nature of the adhesive material.

Adhesives can be divided according to the type of delivery of the adhesive or by type of polymer employed in the adhesive. Following are short summaries of adhesives divided according to these two factors.

Solvent-based adhesives: Adhesion occurs through action of the adhesive on the substrate. Solidification occurs on evaporation of the solvent. Bonding is assisted if the solvent partially interacts, or, in the case of model airplane glues, actually dissolves some of the plastic (the adherent). Thus, model airplane glues often contain volatile solvents, such as toluene, which can dissolve the plastic, forming what is called a solvent weld.

Latex adhesives: These adhesives are based on polymer latexes and require that the polymers be near the T_g so that they can flow and provide good surface contact when the water evaporates. It is not surprising that the same polymers that are useful as latex paints are also useful as latex adhesives. Latex adhesives are widely employed for bonding pile to carpet backings.

Pressure-sensitive adhesives: These are actually viscous polymer melts at room temperature. The polymers must be applied at temperatures above their T_g to permit rapid flow. The adhesive is caused to flow by application of pressure. When the pressure is removed, the viscosity of the polymer is high enough to hold and adhere to the surface. Many tapes are of this type where the back is smooth and coated with a nonpolar coating so as not to bond with the “sticky” surface. The two adhering surfaces can be separated, but only with difficulty.

Hot-melt adhesives: Thermoplastics often form good adhesives simply by melting, followed by subsequent cooling after the plastic has filled surface voids. Nylons are frequently employed in this manner. Electric glue guns typically operate on this principle.

Reactive adhesives: These additives are either low molecular weight polymers or monomers that solidify by polymerization and/or crosslinking reactions after application. Cyanoacrylates, phenolics, silicone rubbers, and epoxies are examples of this type of adhesive. Plywood is formed from impregnation of thin sheets of wood with resin, with the impregnation occurring after the resin is placed between the wooden sheets.

Thermosets: Phenolic resins produced by the reaction of phenol and formaldehyde were used as adhesives by Leo Baekeland in the early 1900s. This inexpensive resin is still used for binding thin sheets to wood to produce plywood. Urea resins produced by the reactions of urea and formaldehyde have been used since 1930 as binders for wood chips in particle board.

Unsaturated polyester resins have replaced lead for auto body repair, and polyurethanes are being used to bond polyester cord to rubber in tires, to bond vinyl film to particle board, and to function as industrial sealants. Epoxy resins are used in automotive and aircraft construction and as a component of plastic cement.

Elastomers: Solutions of natural rubber (NR) have been used for laminating textiles for over a century. The Macintosh raincoat, invented in 1825, consisted of two sheets of cotton adhered by an inner layer of natural rubber.

Pressure-sensitive tape, such as Scotch Tape, consisting of a coating of a solution of a blend of natural rubber and an ester of glycerol and abietic acid (rosin) on cellophane, was developed over a half century ago. More recently, natural rubber latex and synthetic rubber (SR) have been used in place of the natural rubber solution. The requirement for pressure-sensitive adhesives is that the elastomers have a glass-transition temperature below room temperature.

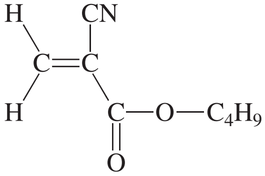
Styrene-butadiene rubber (SBR) is now used as an adhesive in carpet backing and packaging. Neoprene (polychloroprene) may be blended with a terpene or phenolic resin and used as a contact adhesive for shoes and furniture.

Contact adhesives are usually applied to both surfaces, which are then pressed together. Liquid copolymers of butadiene and acrylonitrile with carboxyl end groups are used as contact adhesives in the automotive industry.

Thermoplastics, which melt without decomposition when heated, may also be used as adhesives. Polyamides and copolymers of ethylene and vinyl acetate (EVA) are used as melt adhesives. Over 200 million pounds of EVA are used annually as hot-melt adhesives. Copolymers of methyl methacrylate and other monomers are used as adhesives in the textile industry.

Anaerobic adhesives consist of mixtures of dimethacrylates and hydroperoxides (initiators) which polymerize in the absence of oxygen. They are used for anchoring bolts.

One of the most interesting and strongly bonded adhesives are cyanoacrylates (Super Glue, Krazy Glue). These monomers, such as butyl-α-cyanoacrylate, polymerize spontaneously in the presence of moist air, producing excellent adhesives. These adhesives, which have both cyano and ester polar groups in the repeating units of the polymer chain, are used in surgery and for mechanical assemblies.



(17.1)

Butyl-α-cyanoacrylate

Table 17.12 Major Adhesives

Adhesive material	Amount used (billions of lb.)
Synthetic	
Polyurethanes	0.25
Acrylics	0.34
Epoxies, polyesters, and others	0.34
Elastomers	1.27
Vinyls	1.52
Melamines and ureas	1.61
Phenolics	3.13
Natural-based	
Starch and dextrin	2.81
Sodium silicates	0.39
Others	1.65

While naturally occurring resins formerly dominated the adhesive field, they now account for only about one-third of this more than $8 billion market (Table 17.12). As noted before, there are a wide variety of applications ranging from fast-drying glues such as the cyanoacrylates, to basic "school glues" often based on aqueous solutions of poly(vinyl alcohol), to the phenolics to produce plywood, to solvent-based styrene-butadiene rubber (SBR), emulsions to bind carpets, etc. Table 17.13 gives major usage areas for these adhesives. Most are used in construction and packaging.

Many seemingly simple applications are actually complex. The labels on commercial dry cell batteries can contain over a dozen layers each present for a specific purpose. While price is one major consideration, ease of application is another. Thus, while naturally derived adhesives are less expensive, synthetic materials may be chosen because of ready application and consistency of the end product.

Important factors involved with pressure-sensitive adhesion are a balance between allowing molecular interaction between the adhesive and the adherent (often referred to as "wetting") and the dynamic modulus of the adhesive mixture. This also involves a balance between "pull-off-rate" and "wetting rate." Mechanical adhesion with interlocking and diffusion factors are less important than for permanent adhesion.

Pressure-sensitive adhesives such as present in "pull-off" tabs such as Post-it Notes, contain components similar to those present in more permanent Scotch Tape, except that

Table 17.13 Areas of Adhesive Use

Area	Amount used (billions of lb.)
Industrial products	0.25
Household and other	0.25
Durable goods	0.74
Nondurable goods	1.35
Packaging	4.80
Construction	4.92

particles of emulsified glassy polymer are added to reduce the contact area between the adhesive and the substrate.

Some polymers, such as polyethylene, might appear to be a decent adhesive material, but even in its melt, it is not exceptionally tacky. This is believed to be because of the high degree of chain entanglement. Since the dynamic modulus increases with increasing chain entanglement, PE is not "tacky" (does not easily contact and wet a substrate), and it is not useful as a pressure-sensitive adhesive.

SUMMARY

1. Synthetic fibers are produced by forcing a solution of polymer or a molten polymer through small holes in a spinneret. The extrudate from the solution may be precipitated in the wet spinning process, or the solvent may be evaporated in the dry spinning process. The molten extrudate is cooled in the melt spinning process. Graphite filaments are produced by the pyrolysis of polyacrylonitrile filaments, pitch, or other suitable material followed by forcing the molten mass through small holes.
2. The most widely used elastomer, SBR, is obtained by coagulation of an emulsion of a copolymer of butadiene and styrene. In addition to being produced by the free radical emulsion polymerization technique, elastomers are also produced by cationic copolymerization (butyl rubber) and by anionic polymerization (polybutadiene).
3. Films may be cast from melt or solution or extruded from a slit die, but most film is produced by air-blowing a warm tubular extrudate and slitting the expanded tube.
4. Wire and paper may be coated by use of an extruder, but most coatings consist of solutions or aqueous dispersions of polymers. The trend in the coatings industry is toward lower concentrations of volatile organic solvents.
5. Polymeric foams may be produced by the mechanical frothing of a latex or by the use of gaseous propellants. The latter may be produced in situ in polyurethane or added during processing.
6. Composites consisting of a reinforcing fiber and a resin have excellent strength properties. Graphite–epoxy resin composites are superior to many classic construction materials.
7. Thermosets may be compression molded by heating a prepolymer under pressure in a mold cavity. Thermoplastics are usually injection molded in a fast, automated process in which a granulated polymer is heat softened or plasticated in a barrel and forced into a closed cooled mold by a reciprocating ram or screw. The molded part is ejected when the mold opens and the process is repeated.
8. Hollow articles such as bottles are produced by air-blowing a heat-softened tube or parison into a two-component mold.
9. Articles like containers or boats may be produced by the thermoforming of plastic sheets.
10. Pipe and various profiles may be produced continuously by forcing heat-softened polymer through a die and cooling the extrudate.
11. Chemical companies can perform several functions such as manufacturing, processing, fabrication, and finishing of polymer-containing materials.

12. Laminating conceptually is simply the binding together of different layers of materials. Examples include safety glass, formica, and plywood.
13. While the term “painting” emphasizes a decorative aspect and the term “coating” a protective aspect, the terms are generally used interchangeably. Paint is typically a mixture of a liquid (called a binder or vehicle) and one or more colorants (pigments) and may contain a solvent or thinner. Oil paints consist of a suspension of pigment in a drying oil. Oil varnish contains a polymer dissolved in a drying oil with appropriate additives. Enamels are oil varnishes that contain a pigment. Latexes are polymer emulsions to which pigments have been added.
14. Adhesion can occur through mechanisms that include mechanical, specific or secondary bonding, viscosity, and chemical routes. There are many types of adhesives—solvent-based, latex, pressure-sensitive, hot-melt, and reactive; thermosets, elastomers, and thermoplastic.

GLOSSARY

abaca: A hemp-like fiber from the Philippines.
acetate rayon: Cellulose diacetate fibers.
Acrilan: Polyacrylonitrile-based fibers.
acrylic fibers: Fibers based on polyacrylonitrile.
adhesive: Material that binds, holding together two surfaces.
Adiprene: Polyurethane elastomer.
agave: Fibers from the leaves of the desert century plant.
Aralac: Soybean fiber.
Ardil: Peanut fiber.
biaxial orientation: The process is which a film is stretched in two directions at right angles to each other.
BMC: Bulk-molding compound.
Btu: British thermal unit.
buna-N: Acrylonitrile-butadiene copolymer.
calender: A machine for making polymeric sheet, containing counterrotating rolls.
casting: Production of film by evaporation of a polymeric solution.
cellophane: Regenerated cellulosic film.
charge: The amount of polymer used in each molding cycle.
coextruded film: One produced by the simultaneous extrusion of two or more polymers.
combinatorial chemistry: approach whereby materials are developed and tested in an almost assembly line fashion; allows the ready determination of specific properties for a number of similar but unlike materials.
Dacron: Poly(ethylene terephthalate) fiber.
DMF: Dimethylformamide.
draw: Depth of mold cavity.
drying oils: Liquids employed in coatings that will be cured, crosslinked.
dry spinning: Process for obtaining fiber by forcing a solution of a polymer through holes in a spinneret and evaporating the solvent from the extrudate.
elastomer: Rubber.
electrodeposition: The use of an electric charge to deposit polymer film or aqueous dispersion onto a metal substrate.
enamel: Oil varnish that contains a pigment.

engineering material: Material that can be machined, cut, drilled, sawed, etc.; must have enough dimensional stability to allow these actions to be carried out on them

EPDM: Curable ethylene-propylene copolymer elastomer.

extrusion: A fabrication process in which a heat-softened polymer is forced continually by a screw through a die.

fibrillation: Process for producing fiber by heating and pulling twisted film strips.

filament: A continuous thread.

filament winding: Process in which filaments are dipped in a prepolymer, wound on a mandrel, and cured.

flax: The thread-like fiber from the flax plant.

gate: Thin sections of runner at the entrance of a mold cavity.

geotextiles: Polymeric mats, sheets, and textiles employed in the control of soil, water, etc., in geological applications.

hemp: Fiber from plants of the nettle family.

hevea rubber: *Hevea brasiliensis*, natural rubber.

high-density polyethylene: Polyethylene that contains a relatively high degree of crystallinity with a low degree of branching, typically made using solid state catalysts.

Hycar: Buna-N elastomer.

jute: Plant fiber used for making burlap.

kapok: Seed fibers from the tropical silk tree.

kenaf: Cellulose fiber from the kenaf plant.

Kodel: Poly(ethylene terephthalate) fiber.

K value: A measure of thermal conductivity in Btu.

lacquers: Polymer solutions to which pigments have been added.

lamination: The plying up of sheets.

Lanital: Casein fiber.

latex: Stable dispersion of a polymer in a water.

linear low-density polyethylene: A copolymer of ethylene and about 10% of an α-olefin; it has densities and properties between LDPE and HDPE.

liquid crystals: Materials that undergo physical reorganization where at least one of the arrangement structures involves molecular alignment along a preferred direction, causing the material to exhibit nonisotropic behavior.

mechanical goods: Industrial rubber products such as belts.

melt spinning: Process of obtaining fibers by forcing molten polymer through holes in a spinneret and cooling the filaments produced.

molding powder or compound: A premix of resin and other additives used as a molding resin.

multicellular: Open cells.

Neoprene: Polychloroprene.

nonwoven textiles: Sheet produced by binding fibers with a heated thermoplastic.

nylon-4,6: Engineering material formed from 1,4-butanediamine and adipic acid.

oil paints: Suspension of pigments in a drying oil.

oil varnish: A polymer dissolved in a drying oil.

parison: A short plastic tube which is heated and expanded by air in the blow-molding process.

Perlon: Polyurethane fibers.

PET: Poly(ethylene terephthalate).

phosphazene: Polyphosphonitrile elastomer.

photoconductive: Material that is conductive when exposed to light.

photoresponsive: Material whereby some property changes when it is exposed to light.

pigment: Coloring material (colorant).

polyacetylene: polymer whose conductivity increases when doped.

poly(butylene terephthalate) (PBT): Engineering polyester that quickly crystalizes formed from 1,4-butanediol and terephthalic acid.

polyoxymethylene (POM): Engineering material formed from the polymerization of formaldehyde.

printing ink: Highly pigmented coatings used in the printing of sheets.

PTFE: Polytetrafluoroethylene

PU: Polyurethane.

pultrusion: Process in which filaments are dipped in a prepolymer, passed through a die, and cured.

rayon: Regenerated cellulosic fiber.

recycling codes: Designations that allow easy, quick identification of a number of plastics used in the container manufacture.

rotational molding: Polymer added to a warm, rotating mold; centrifugal force distributes the polymer evenly.

rovings: Multiple untwisted strands of filaments.

runner: Channel between the sprue and the mold cavity.

saponification: Alkaline hydrolysis of an ester.

SBR: Styrene-butadiene copolymer elastomer.

screen pack: A metal screen which prevents foreign material from reaching the die in an extruder.

silk: Natural protein fiber.

smart materials: Materials that react to an externally applied action such as the application of light, magnet, heat, electricity, and pressure in a “smart” manner.

SMC: Sheet-molding compound.

solvent molding: Immersion of a mold into a polymer solution resulting in the mold being coated with a polymeric film.

Spandex: Elastic Polyurethane fiber.

specific strength: Strength based on mass rather than area.

spinneret: A metal plate with many uniformly sized, minute holes.

sprue: Tapered orifice between nozzle and runner. This term is also applied to plastic material in the sprue.

structural foams: Polymeric foamed articles with a dense surface.

Styrofoam: Foamed polystyrene.

technology: Applied science.

tenacity: Fiber strength.

Terylene: Poly(ethylene terephthalate).

thermoforming: The shaping of a hot thermoplastic sheet.

Thiokol: Polyolefin sulfide elastomer.

transfer molding: A process in which a preheated briquette or preform is forced through an orifice into a heated mold cavity.

Tricel: Cellulose triacetate.

UHMWPE: Ultrahigh molecular weight polyethylene polymer.

ultrahigh molecular weight polyethylene: High-density PE with over 100,000 ethylene units; the size allows the chains to intertangle, increasing its strength.

ultralinear polythylene: Polyethlene produced with soluble stereoregulating catalysts; has a narrow molecular weight distribution, high crystallinity, low branching.

unicellular: Closed coatings.
vehicle: Liquid in a coating.
Vicara: Zein fiber.
viscose process: Regeneration of cellulose fibers by precipitation of the sodium salt of cellulose xanthate in acid.
Viton: Polyfluorocarbon elastomer.
Vycron: Poly(ethylene terephthalate).
wet spinning: Obtaining fibers by precipitation of polymeric solutions.
wool: Nature protein fiber.
zein: Protein from maize (corn).

EXERCISES

1. Which is more important: (a) polymer science or (b) polymer technology?
2. Name three important natural fibers.
3. Name an important regenerated fiber.
4. Why is secondary cellulose acetate more widely used than the tertiary cellulose acetate?
5. What is the difference between rayon and cellophane?
6. Name three important synthetic fibers.
7. Name an elastomer produced by (a) cationic, (b) anionic, (c) free-radical, and (d) step-reaction polymerization techniques.
8. How is LDPE film produced?
9. Why is there a trend toward the use of less solvent in polymeric coatings?
10. What is meant by trade sales?
11. Why is a plastisol stable at room temperature?
12. How would you produce a unicellular foam?
13. Which foam is preferable for upholstery: (a) unicellular, or (b) multicellular?
14. Why do non-flame-retardant foams burn readily?
15. What reinforced plastic has been used as an automobile body?
16. Why is graphite-reinforced epoxy resin a good candidate for parts in future automobiles?
17. Why are molded thermoplastics used more than molded thermosets?
18. How could you increase the output of an injection molding press?
19. Why are structural foams used for complex furniture?
20. What are some of the advantages of a blow-molded PET bottle?
21. Why would an article be thermoformed instead of molded?
22. What is the limit to the length of an extrudate such as PVC pipe?
23. Name three popular laminates.
24. Why are the terms painting and coating often used interchangeably?
25. Why have latex waterborne coatings been popular with the general public?
26. Differentiate between oil paints, oil varnishes, latexes, enamels, and lacquers.
27. Briefly discuss the popular mechanisms related to adhesion and the general types of adhesives.

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18

Special Topics

18.1 CONDUCTIVE POLYMERIC MATERIALS

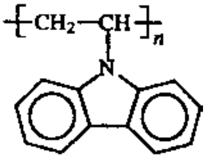
Chemistry is moving to center stage in many areas of medicine, biology, engineering, and physics. While solid-state physics is traditionally based on silicon, polymers offer a much wider vista of opportunities for application and fine-tuning those applications. Some areas are based on single crystals that may be small in our sight, but are large when compared to individual molecules. Even single silicon wafers with a minimum pattern dimension of 200 nm is on the order of ten times the size of individual molecules. Eventually, electronic, photonic, and stress-strain behavior individuality can be placed into single giant chains, creating chains that behave as entire assemblies behave today.

Conductance behavior is dependent on the material and what is conducted. For instance, polymeric materials are considered poor conductors of sound, heat, electricity, and applied forces in comparison to metals. Typical polymers have the ability to transfer and “mute” these factors. For instance, as a force is applied, a polymer network transfers the forces between neighboring parts of the polymer chain and between neighboring chains. Because the polymer matrix is seldom as closely packed as a metal, the various polymer units are able to absorb (mute; absorption through simple translation or movement of polymer atoms; vibrational and rotational changes) as well as transfer (share) this energy. Similar explanations can be given for the relatively poor conductance of other factors.

Even so, polymers can be designed that compete with metals and other nonpolymer materials in the area of conductance. Following are described some of these. Covered elsewhere are other materials that act similar to metals in the conductance of specific factors. For instance, force transference of ceramics is similar in some ways to that of metals because of a number of factors including the inability of the tightly packed ceramics to mute applied forces and their ability to directly pass along the results of such applied forces or stresses.

Photoconductive and Photonic Polymers

Some polymeric materials become conductive when illuminated with light. For instance, poly(N-vinylcarbazole) is an insulator in the dark, but when exposed to UV radiation it becomes conductive. Addition of electron acceptors and sensitizing dyes allows the photoconductive response to be extended into the visible and near-IR regions. In general, such photoconductivity is dependent on the materials ability to create free-charge carriers, electron holes, through absorption of light, and to "move" these carriers when a current is applied.



(18.1)

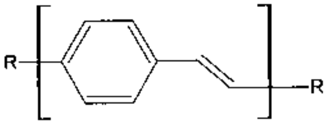
Related to this are materials whose response to applied light varies according to the intensity of the applied light. This kind of behavior is referred to as nonlinear behavior. In general, polymers with whole-chain delocalization or large-area delocalization where electrons are optically excited may exhibit such nonlinear optical behavior.

Photoresponsive sunglasses whose color or tint varies with the intensity of the sunlight is an example of nonlinear optical material. Some of the so-called smart windows are also composed of polymeric materials whose tint varies according to the incident light. Currently, much material is stored using electronic means but optical storage is becoming commonplace with the use of CD-ROM and WORM devices. Such storage has the advantages of rapid retrieval and increased knowledge density (more information stored in a smaller space).

Since the discovery of doped polyacetylene, a range of polymer-intense semiconductor devices has been studied. Included are normal transistors and FETs (field-effect transistors) and photodiodes and LEDs (light-emitting diodes). Like conductive polymers, these materials obtain their properties because of their electronic nature, specifically the presence of conjugated π bonding systems.

In electrochemical light emitting cells, the semiconductive polymer can be surrounded asymmetrically with a hole-injecting material on one side and a low work function electron injecting metal (such as magnesium, calcium, or aluminum) on the other side. The emission of light results from a radiative charge carrier recombining in the polymer as electrons from one side and holes from the other recombine.

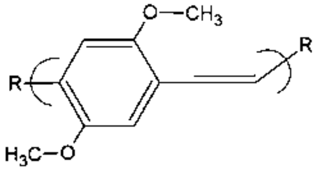
Poly(p-phenylene vinylene), PPV, poly(p-phenylene vinylene) was the first reported (1990) polymer to exhibit electroluminescence. PPV was employed as a semiconductor layer. As noted above, the layer was sandwiched between a hole-injecting electrode and electron-injecting metal on the other. PPV has an energy gap of about 2.5 eV and thus produces a yellow-green luminescence. Today, other materials are available that give a variety of colors.



(18.2a)

Poly(p-phenylene vinylene)

A number of poly(arylene vinylene), PPV, derivatives have been prepared. Attachment of electron-donating substituents, such as dimethoxy groups (Str. 18.2b), act to stabilize the doped cationic form and thus lower the ionization potential. These polymers exhibit both solvatochromism (color change as solvent is changed) and thermochromism (color is temperature dependent).



(18.2b)

Poly(2,5-dimethoxy-p-phenylene vinylene)

Electrically Conductive Polymers

The search for flexible, noncorrosive inexpensive conductive materials has recently focused on polymeric materials. This search has increased to include, for some applications, nano-sized fibrils and tubes. The conductivity for general materials is noted in Fig. 18.1. As seen, most polymers are nonconductive and in fact, are employed in the electronics industry as insulators.

The Nobel Prize in Chemistry for 2000 was given to Alan MacDiarmid, Alan Heeger, and Hideki Shirakawa for the discovery and development of electrically conductive polymers.

In 1975 MacDiarmid and Heeger began studying the metallic properties of inorganic poly(sulfur nitride) (Sec. 11.5) but shifted their efforts to polyacetylene after visiting with Shirakawa. While the synthesis of polyacetylene was known for years, Shirakawa and coworkers, using a Ziegler-Natta catalyst, prepared it as a silvery film in 1974. In spite of its metallic appearance, it was not a conductor. In 1977, using techniques MacDiarmid and Heeger developed for poly(sulfur nitride), Shirakawa, MacDiarmid, and Heeger were able to increase the conductivity of trans-polyacetylene samples, after doping, to a conductivity of about 10^3 S/meter, or 1 S/cm. They found that oxidation with chlorine, bromine, or iodine vapor made polyacetylene film 10^9 times more conductive than the nontreated film. This treatment with a halogen was called "doping" by analogy with the doping

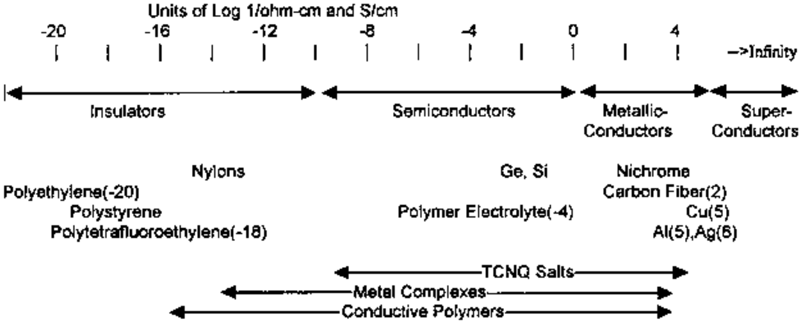


Figure 18.1 Electrical conductivity for various materials. S = Sieman = 1/ohm.

employed with semiconductors. Other oxidizing "doping" agents have been used, including arsenic pentafluoride. Reducing agents such as metallic sodium have also been successfully used. This chemical doping transforms the polyacetylene from an insulator or semiconductor to a conductor.

A critical structural feature for conductive polymers is the presence of conjugated double bonds. For polyacetylene, every backbone carbon is connected by a stronger localized σ bond. They are also connected by a network of alternating less localized and weaker π bonds. While conjugation is present, it is localized enough to prevent ready delocalization of the π-bond electrons. The dopants cause the introduction of sites of increased or deficiency of electrons. When there is a deficiency of electrons, or a hole, created, electrons flow to fill this hole with the newly created hole causing other electrons to flow to fill the new hole, etc., allowing a charge to migrate within and between the polyacetylene chains.

In general, the Huckel theory predicts that π electrons can be delocalized over an entire chain containing adjacient π bonds with the activation energy for delocalization decreasing as the chain length increases. Doping provides a ready mechanism for delocalization to occur.

Ordinary polyacetylene is composed of small fibers (fibrils) that are randomly oriented. Conductivity (Sec. 4.2) is decreased because of the contacts between the various random fibrils. Two approaches have been taken to align the polyacetylene fibrils. The first approach is to employ a liquid crystal solvent for the acetylene polymerization and to form the polymer under external perturbation. The second approach is to mechanically stretch the polyacetylene material causing the fibrils to align. The conductivity of polyacetylene is about 100 times greater in the direction of the "stretch" in comparison to that perpendicular to the stretch direction. Thus, the conductivity is isotropic. By comparison, the conductivity of metals such as copper and silver is anisotropic. Of interest is the nonconductivity of diamond, which has only ordered σ bonds and thus no "movable" electrons and the isotropic behavior of graphite. Graphite, similar to polyacetylene, has a series of alternative π bonds (see Sec. 12.9 and 12.10) where the conductivity in the plane of the graphite rings is about 10^6 times that at right angles to this plane.

Polyacetylene has been produced by several methods, many utilizing the Zeigler-Natta polymerization systems. Both cis- and trans-isomers exist (Fig. 18.2). The cis-polyacetylene is copper-colored with films having a conductivity of about 10^{-8} S/meter. By comparison, the transpolyacetylene is silver-colored with films having a much greater conductivity on the order of 10^{-3} S/meter. The cis isomer is changed into the thermodynamically more stable trans isomer by heating. As noted above, conductivity is greatly increased when the trans-polyacetylene is doped (to about 10^2–10^4 S/cm). Conductivity is dependent on the micro- or fine structure of the fibrils, doping agent, extent, and technique, and aging of the sample.

Polyacetylene was initially produced using Ziegler-Natta systems producing what have become known as Shirakawa polyacetylene. These materials are not easily processable and are mainly fibrillar. Recently other approaches have been taken. In the Durham route, the metathesis polymerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0]deca-3,7,9-triene gives a high molecular weight soluble precursor polymer that is thermally converted to polyacetylene (Scheme 18.1). The precursor polymer is soluble in common organic liquids and is easily purified by reprecipitation. The end product can be aligned giving a more compact material with bulk densities on the order of 1.05 to 1.1 g/cc.

Grubbs and others have used the ring-opening metathesis polymerization to produce thick films of polyacetylene and polyacetylene derivatives (Scheme 18.2).

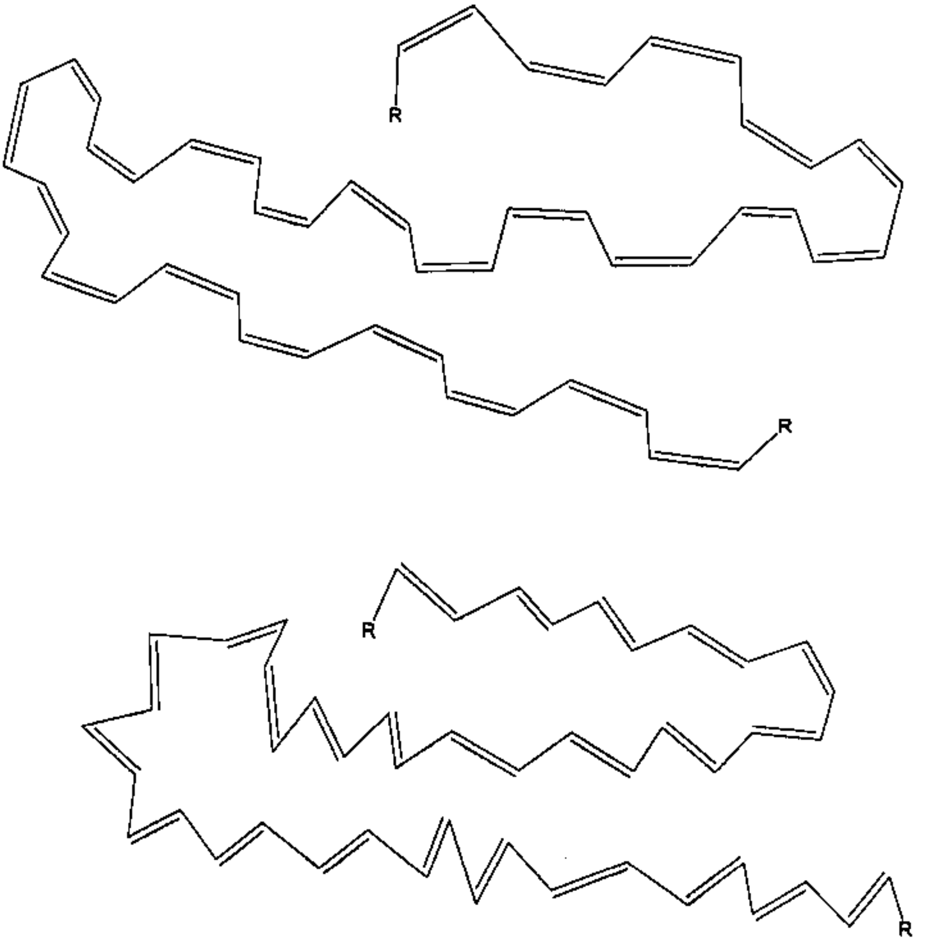
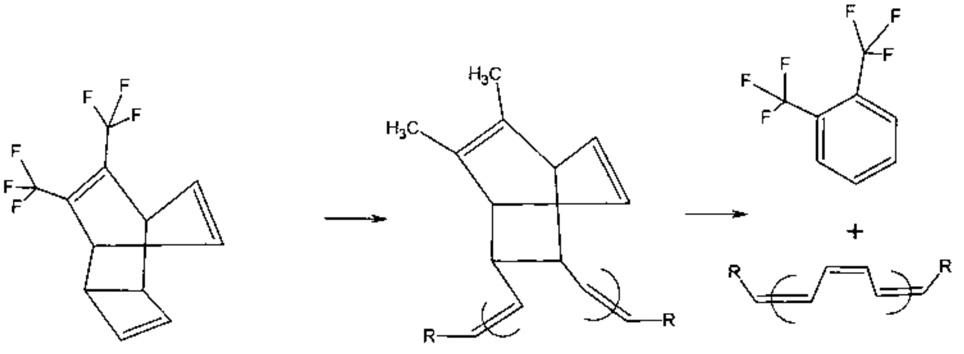
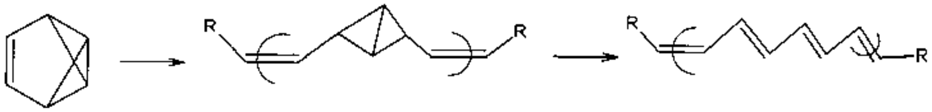


Figure 18.2 cis- (top) and trans- (bottom) polyacetylene.



Scheme 18.1



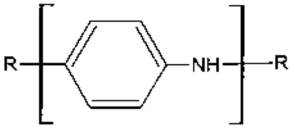
Scheme 18.2

Polyacetylene has good inert atmospheric thermal stability but oxidizes easily in the presence of air. The doped samples are even more susceptible to air. Polyacetylene films have a lustrous, silvery appearance and some flexibility. Other polymers have been found to be conductive. These include poly(p-phenylene) prepared by the Freidel-Crafts polymerization of benzene, polythiophene and derivatives, poly(phenylene vinylene), polypyrrole, and polyaniline. The first polymers commercialized as conductive polymers were polypyrrole and polythiophene because of their greater stability to air and the ability to directly produce these polymers in a doped form. While their conductivities (often on the order of 10^4 S/meter) are lower than that of polyacetylene, this is sufficient for many applications.

Doped polyaniline is employed as a conductor and as an electromagnetic shielding for electronic circuits. Poly(ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonic acid is used as an antistatic coating material to prevent electrical discharge exposure on photographic emulsions and is also used as a hole injecting electrode material in polymer light-emitting devices. Organic soluble substituted polythiophenes with good conductivities have been prepared. Poly(3-hexylthiophene) has a room temperature conductivity of about 100 S/cm; poly(3-metnylthiophene) has a conductivity of 500 S/cm; and a poly(3-alkylether)thiphene) with a conductivity of about 1000 S/cm has been reported. The unsubstituted polythiophene has a conductivity in the range of 50 to 100 S/cm. The fact that all of these substituted polythiophenes have similar conductivities indicates that there is little twisting of the backbone conjugation as alkyl substituents are added.

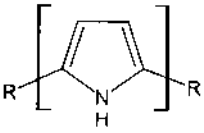
Polythiophene derivatives are being used in field-effect transistors. Polypyrrole is being used as microwave-absorbing “stealth” screen coatings and in sensing devices. Poly(phenylene vinylidene) derivatives are being used in the production of electroluminescent displays.

Following are the structures of some of the more common conjugated polymers, along with poly(acetylene), that can be made conductive through doping. As noted before, doping causes and electrical imbalance that allows electrons to flow when an electrical potential is applied. The band gap is the energy needed to promote an election from the valence band to the empty energy or conductive band. Metals have zero band gaps while insulators such as polyethylene have large band gaps, meaning that a lot of energy is needed to promote an electron to an empty band. Semiconductors have small band gaps where valence electrons can be moved into the conductance band through application of relatively small potential energies.



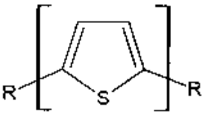
Polyalanine

(18.3)



Polypyrrole

(18.4)



Polythiophene

(18.5)

The optical behavior can be used to help in the understanding of these conductive materials. π-conjugation often occurs in the visible region so that most, if not all, of these conductive polymers are colored. Color changes are an important probe in assisting the characterizing the effects of various doping agents. Changes in the spectra allow various mechanisms to be studied. Because many of the polythiophene derivatives are organic soluble, spectral changes can be more easily studied. The electronic absorption spectra of a variety of polythiophene derivatives indicate that the band edge for conductivity begins about 2 eV.

Water-soluble derivatives of polythiophene have been made allowing counterions bound to the polymer backbone to "self-dope" with the protons (such as lithium and sodium ions) injecting electrons into the π-system. Thus, combinations of sodium salts and so-called "proton salts" (such as prepared from poly-3-(2-ethanesulfonate)thiophene) have been prepared that are both water-soluble and conducting.

Another area of activity involves the synthesis of material with small band gaps that would allow activation to occur at room temperature without doping. Polyisothianaphthene has been produced with a band gap of about 1 eV. Lateron polymers with alternating donor and acceptor units give band gaps of about 0.5 eV.

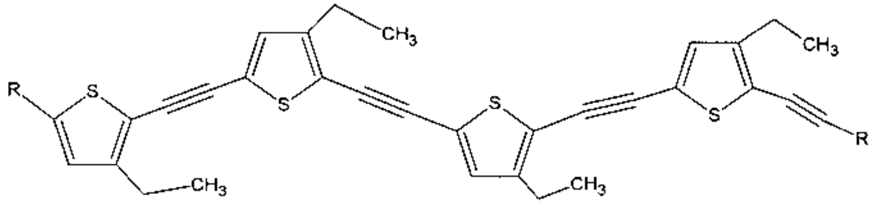
While the amount of electricity that can be conducted by polymer films and "wires" is limited, on a weight basis the conductivity is comparable to that of copper. These polymeric conductors are lighter, some more flexible, and they can be laid down in wires that approach one atom thickness. They are being used as cathodes and solid electrolytes in batteries, and potential uses include in fuel cells, smart windows, nonlinear optical materials, light-emitting diodes, conductive coatings, sensors, electronic displays, and electromagnetic shielding.

There is a large potential for conducting polymers as corrosion inhibiting coatings. For instance, the corrosion protection ability of polyaniline is pH dependent. At lower pH's, polyaniline-coated steel corrodes about 100 times more slowly than noncoated steel. By comparison, at a pH of about 7 the corrosion protection time is only twice for polyaniline-coated steel. Another area of application involves creation of solid-state rechargeable batteries and electrochromic cells. Polyheterocycles have been cycled thousands of times with retention of over 50% of the electrochromic activity for some materials after 10,000 cycles. Infrared polarizers based on polyaniline have been shown to be as good as metal wire polarizers.

They also find use in nonlinear optical devices such as in optoelectronics, that is for signal processing and optical communications. Some of the new conducting polymers offer such benefits as flexibility, high damage threshold, ultrafast response in the subpicosecond range, and good mechanical strength. Polyheterocyclic conducting polymers have shown a wide variation in color as they are electronically converted between oxidized and reduced forms. The instability of some of the polymers is being used to monitor moisture, radiation, mechanical, and chemical destruction.

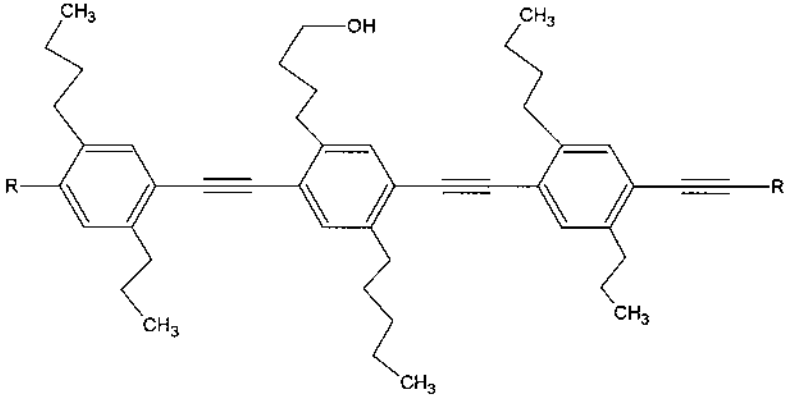
Nano-wires

Part of the nano revolution involves the electronics industry and the synthesis of so-called "nano" or molecular wires for electronic applications. Basically, molecular wires contain a series of double or double and triple bonds that have what can be referred to as "whole-chain" resonance. Polyacetylene is an example of a molecule that exhibits whole-chain resonance or delocalization of electrons where the activation energy for delocalization is relatively low. The search is on for nano-wires that are more flexible. Often this flexibility is achieved through a balance of the conductive inner core backbone that is characteristically rigid with a flexible outer core composed of covalently bonded groups that act to decrease the tendency to form highly crystalline structure and which encourage flexibility as illustrated below. As in many of the new areas creativity is important. Often, the molecular wires are created one step at a time with the eventual joining of chains or simply the use of the single chain.



Poly(thiophene ethynylene)

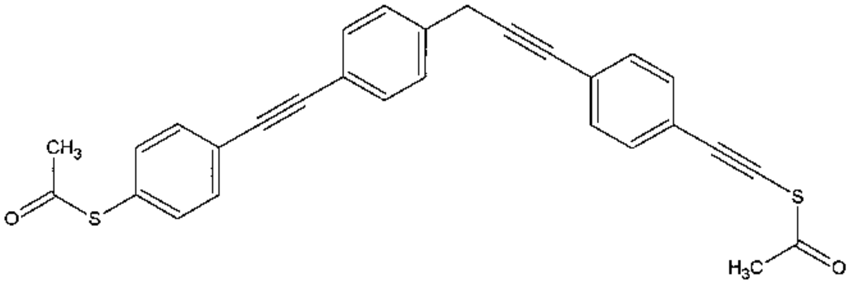
(18.6)



Phenylene-acetylene backbone copolymer

(18.7)

While we call these materials polymeric, in truth they are oligomeric, often intentionally made to be oligomers with specific lengths intended to connect other molecules or molecular devices. Thus, we can design molecules with particular lengths, conductivity, and the ability to molecularly connect to other molecules. Thus, nonconductive molecules, such as methylene units, can be added to decrease electronic conductance. These nonconductive moieties are referred to as barriers. Below is a phenylene-acetylene grouping containing a barrier methylene.



(18.8)

Chain ends are often functionalized with groups that can react with specific sites on another molecule. These functionalized sites are referred to as molecular alligator clips. The chain shown above has two such functionalized groups or alligator clips, one on each end. These molecular alligator clips are normally designed to attach or anchor to a metal surface. Thus, this molecular is a candidate to connect two electrodes, acting as a molecular wire.

Of importance to their use in electronics, these chains are able to conduct in the microamp region, the same region that most computing instruments operate and individual chains can conduct in the tenth of a microamp range.

18.2 GEOTEXTILES*

Geotextiles play a major role in geotechnical engineering. Fifty years ago the area of geotextiles did not exist, although forms of geotextiles have existed for thousands of years. Reinforced soil was employed by the Babylonians 3000 years ago in the construction of pyramid-like towers, or ziggurats. One famous ziggurat, the Tower of Bable, collapsed.

For thousands of years the Chinese used wood, straw, and bamboo for soil reinforcement, including construction of the Great Wall. In fact, the Chinese symbol for civil engineering can be translated as “earth and wood.” The Dutch have made extensive use of natural fibrous materials in their age-old battle with the sea. The Romans used wood and reed for foundation reinforcement.

By the 1920s, cotton fabrics were tested as a mode of strengthening road pavements in the United States. These field trials were not followed by application. The British army during World War II used armored vehicles designed to lay rolls of canvas on the ground.

The modern materials for geotextiles have been produced by the polymer (textile) industry since the early 1900s. These include PVC, polyester, nylon, and polypropylene fibers. In the 1950s, the original technology for manufacturing plastic nets was developed by the packaging industry. In the 1960s, manufacturing processes for nonwoven fabrics made from continuous synthetic filaments were developed. The stage was set for the birth of geotextiles. In 1957, nylon-woven fabric sandbags were employed at the closing of the Pluimpot, Netherlands. (As a part of this overall project, called the Delta Project, more than 10 million m^2 of geotextiles has been used.) In 1958, a woven fabric of poly(vinylidene chloride) monofilaments was produced by Carthage Mills and utilized for coastal erosion control in Florida. In 1958 and 1959, synthetic sandbags were used in West Germany and Japan for the control of soil erosion. By 1966, a nonwoven fabric composed of staple fibers was initially employed as a geotextile in an asphalt overlay. Synthetic nets were initially employed in 1967 for reinforcement of soft soil in Japan. Since the early 1970s, many products have been developed, including mats (Enka, Netherlands, 1972), grids (Nethon, UK, 1981), and composites for drainage.

A geotextile can perform several functions. These include:

1. Fluid transmission—collecting a liquid or gas and conveying it within the geotextile’s own plane toward an outlet.
2. Separation—acting to divide geological materials for containment and prevention of mixing.
3. Protection—alleviation or distribution of stresses and strains. For instance, a geotextile may be placed on a surface to prevent its damage by light, rain, traffic, etc., or may be placed between two materials, acting to dissipate the load applied to one with respect to the second.

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* This section is based on an article appearing in *Polymer News*, Vol. 13, No. 4, and is used with permission.

4. Filtration—allowing liquid or small particulant material to pass through while retaining larger materials.
5. Tension member—providing tensile modulus and strength to a soil.
6. Tensioned membrane—allows for a balance in pressure difference between materials.

While geotextiles are typically employed as two-dimensional sheets, three-dimensional action is easily achieved through folding, sandwiching, and engulfing procedures. The field of geotextiles will gather in importance as we attempt to build structures and grow crops on less friendly terrain. It will also be a major factor in the containment of bulk and specialty chemicals and in the protection of our water sources.

In 1985, over 300 million m^2 of geotextiles was used in more than 100,000 projects. About one-half of the sales are in the United States and Canada, two-fifths in Europe, and the remainder in Japan and other countries. In North America, about two-thirds of the geotextiles are nonwovens and one-third wovens. In Europe about four-fifths are nonwovens and one-fifth wovens, and in Japan about three-fifths are wovens, one-fifth nets and grids, and one-fifth nonwovens.

18.3 SOLID WASTE

Polymers are giant molecules and macromolecules. They include natural organic (proteins, nucleic acids, polysaccharides such as starch and cellulose, wool, hair, skin, teeth, lignin), inorganic (sand, granite, quartz), and synthetic [plastics, elastomers (rubbers), fibers, concrete (cement), glass, paper] polymers. They compose the large bulk by weight and by volume of what is termed solid waste.

Fortunately, the synthetic materials offer few immediate health problems but, in the more distant future, they offer both a resource problem (i.e., they are made utilizing non-rapidly renewable resources and their synthesis is typically energy-demanding) and a disposal problem. In today’s marketplace, the United States consumes about 75 billion lb. of synthetic polymers (plastics and synthetic fibers and rubbers) annually, or 300 lb. per person. Paper products are produced at a rate almost double this yearly.

The following remarks will concentrate on the general area of solid waste, emphasizing synthetic polymeric materials, i.e., elastomers, fibers, plastics, and glass.

Biodegradable and Recyclable Products

Many states propose to deal with the problem of solid waste through legislation dealing with biodegradation and recycling. Recycling means many things. For instance, PVC can burn to give hydrogen chloride, ethylene, etc., which in turn can, after several energy-intensive steps, be returned to vinyl chloride and finally again to PVC. While this has been accomplished on a small scale, it has not been accomplished on anything larger than a small pilot plant scale. Further, it is both economically and energetically unfavorable. Next, PVC is not just PVC; rather, it is composed, as are *most* commercially processed polymers of coloring agents, antioxidants, stabilizers, plasticizers, etc.; in fact, 20–40% of the PVC is not PVC but, rather, additives. Finally, collecting PVC or any homogeneous grouping of solid material is a difficult, untested task at best.

Glass is composed of the same material as most sand, i.e., silicon dioxide. Material capable of producing commercial glass is not abundant. Fortunately, glass is readily recognizable to the public, and commercial and public collection of glass products is underway.

Waste glass (also called recycled or cullet) has found many uses, ranging from filler in asphalt road material to composing 5–40% of “glass-making recipes.”

Numerous uses for recycled rubber tires have been shown to be industrially feasible. These include use of tire hides as automotive bumper guards, capped tires, and filler. Rubber by its very nature of being a three-dimensional, highly crosslinked material makes true chemical recycling difficult. Commercially, the major option is to grind the rubber into small “chunks” and to apply “adhesives” to “recombine” the rubber pieces. The resulting rubber is acceptable for nondemanding applications such as rubber toys and place mats but is not acceptable for demanding applications such as rubber gaskets, tire hides, hoses, and belts.

“Paper” is not “paper” is not “paper.” Recycled paper probably cannot be recycled again. Most paper today contains a wide variety of additives. The amount and type of additive determines which paper can be recycled.

The previous examples are intended to describe some of the real problems associated with the term “recyclable.”

“Biodegradable” may also mean many things. For instance, two types of common drinking cups were placed on the shores of Lake Ontario. The polystyrene cup had photoactive agents placed within it. After 3 months the cup appeared largely degraded, and by 6 months it was declared degraded. If “out of sight, out of mind” applies, then the styrofoam cup was degraded. However, the photoactive agents simply allowed the cup to disappear into microscopic particles that were blown away—not truly becoming part of the “natural seascape.” The typically acclaimed biodegradable paper cup was largely unchanged after 2 years on the beach. The polyethylene outer cover was erased after one-half year—yet the paper cup persisted.

It is clear that the enemy has been sighted, and the enemy is us (after Pogo).

Biodegradable Polymers

Traditional applications of synthetic polymers are based largely on their biological inertness compared with natural polymers. Now the “worm has turned,” and there is interest in producing polymers that are biodegradable. As is the case with the whole solid waste question, the literature is extensive, sometimes confusing and contradictory and often of little scientific value.

Biodegradation of general nonmedical materials can be divided into microbial and chemical degradation. Chemical degradation includes wind and rain erosion, oxidation, photodegradation, acid/base water, and thermal degradation. Microbial testing includes real-site testing and laboratory testing. Fungi are used more frequently than bacteria. The degree of degradation of a polymer is typically determined by observing the evidence of colony growth, oxygen consumption, increase in cell count mass or count, or production of carbon dioxide. Most of these can give results that are open to interpretation, since polymers contain additives that may well mask what is really occurring. More reliable, yet much more time consuming, is to actually measure changes in the polymer. Changes in molecular weight distribution, solution viscosity, tensile strength, and morphological changes have all been employed. Procedures have been worked out for this and may be adaptable for some cases. Purified buffered enzymes are also employed for analysis, but it is unknown if there exist today bacteria or fungi that contain or can be made to contain such enzymes.

General Structure–Property Relationships

Polymers can be divided according to general susceptibility to either chemical or microbial degradation. A typical division would include polymers with hydrolyzable backbones. Most natural polymers are of this variety including polysaccharides, proteins, and nucleic acids, but not terpene-based materials such as the natural rubbers.

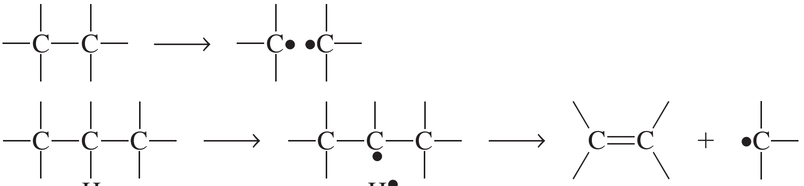
Synthetic polymers with hydrolyzable backbones include the polyurethanes, polyethers, polyesters, and nylons (polyamides). These materials are typically susceptible to acid- and/or base-induced (either chemically or microbially produced) degradation. Polymers with wholly carbon backbones or with large amounts of hydrocarbon crosslinks are much less susceptible to acid- and/or base-induced degradation. Many of these polymers resist microbial and “natural” chemical-induced degradation. Poly(vinyl alcohol) is among the most readily biodegradable of these materials, being readily degraded in waste water-activated sludges. Conversely, poly(methyl methacrylate) and polycyanoacrylates generally resist biodegradation.

Chemical Degradations

Nonagriculture commercial methods of solid waste disposal have largely involved burning, landfill, composting, or microbial disintegration and scraping or recycling. Landfill and burning has accounted for the large bulk of commercial solid-waste disposal. Landfills are no longer an alternative, and in much of the United States it has really never been a choice. Burning was largely done with little control of oxygen; thus, the adage that effluents of burning are carbon dioxide and water is approximate at best. Airborne particulants often result and, even with scrubbers, etc., undesired elements can reach our air, water, and food supply. Finally, within compacted areas free from readily available sources of oxygen, degradation is often quite slow. Thus, newspapers, raw organic matter, yard waste, etc., have been found in landfills little changed from when they were first introduced many years before.

Common backbone bond-scission reactions in polymers include the following:

1. *Homolytic bond cleavage*, to generate a pair of free radicals. This results in chain degradation or free radical formation on a backbone that may be followed by a proton shift and subsequent chain scission.

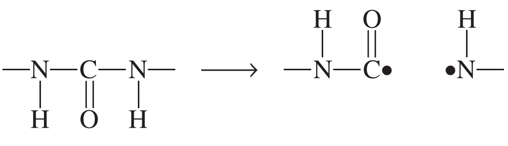


$$-\mathrm{C}-\mathrm{C}- \longrightarrow -\mathrm{C}\bullet\ \bullet\mathrm{C}-$$

$$-\mathrm{C}-\underset{\mathrm{H}}{\mathrm{C}}-\mathrm{C}- \longrightarrow -\mathrm{C}-\underset{\bullet}{\mathrm{C}}-\mathrm{C}- \ \ \mathrm{H}\bullet \longrightarrow \mathrm{C}{=}\mathrm{C} + \bullet\mathrm{C}-$$

(18.9)

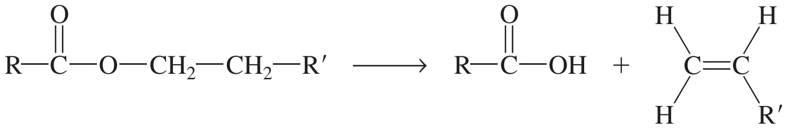
These two reactions are initiated by high-energy radiation and heat. Exposure to UV radiation can also lead to bind scission in carbonyl-containing polymers (i.e., nylons, polyurethanes, polyesters, and polyketones).



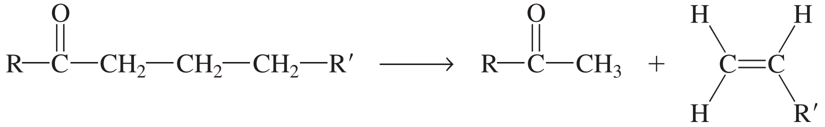
$$-\underset{\mathrm{H}}{\mathrm{N}}-\underset{\mathrm{O}}{\mathrm{C}}-\underset{\mathrm{H}}{\mathrm{N}}- \longrightarrow -\overset{\mathrm{H}}{\mathrm{N}}-\overset{\mathrm{O}}{\mathrm{C}}\bullet \quad \bullet\overset{\mathrm{H}}{\mathrm{N}}-$$

(18.10)

2. *Bond rearrangement*. Certain polyketones and polyesters when exposed to UV radiation undergo bond rearrangement leading to backbone breakage.

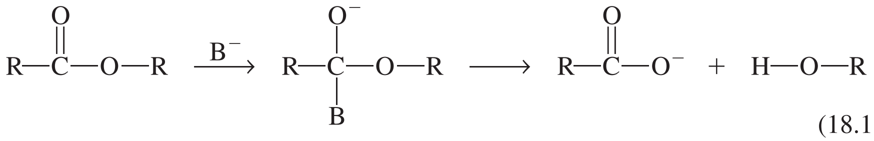


(18.11)



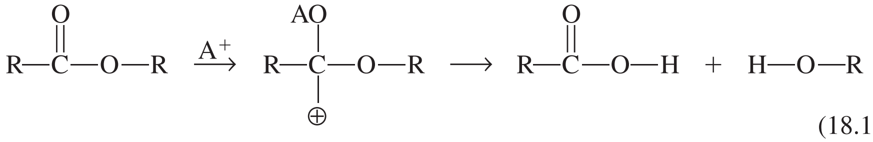
(18.12)

3. *Ionic bond scission*. Most polymers containing noncarbon atoms within their backbone undergo acid- and/or base-catalyzed bond scission. Where B^- represents a base and A^+ represents an acid, we have the following illustration of ionic bond scission.



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R} \xrightarrow{B^-} \mathrm{R{-}\underset{\underset{\displaystyle B}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}{-}O{-}R} \longrightarrow \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-} + \mathrm{H{-}O{-}R}$$

(18.13)



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R} \xrightarrow{A^+} \mathrm{R{-}\underset{\underset{\displaystyle \oplus}{|}}{\overset{\overset{\displaystyle AO}{|}}{C}}{-}O{-}R} \longrightarrow \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H} + \mathrm{H{-}O{-}R}$$

(18.14)

Polymers susceptible to ionic degradation include polycarbonates, siloxanes, polyesters, nylons, polyurethanes, polysaccharides, and polyethers.

4. *Oxidation*. Almost all organic polymers are subject to either extremely long-term oxidation or thermally induced oxidation. The typical final products for compounds containing carbon, nitrogen, sulfur, oxygen, and hydrogen with an excess of oxygen are carbon dioxide, nitrogen oxides (of various forms), water, and sulfur oxides. Halide-containing polymers typically generate the corresponding hydrogen halide gases but may also generate quite toxic intermediates such as ClCOCl. The sulfur oxides, nitrogen oxides, and hydrogen halides are toxic and must be "scrubbed" before gases containing them are sent into the atmosphere.

5. *Metal-catalyzed degradations*. Many commercial polymers contain metallic impurities derived from additives, metal catalysis, or introduction during workup or processing. Metal-containing pigments can be added to protect against or to sensitize materials to photodegradation. Trace amounts of transition metals may accelerate thermal degradation of polymers.

Fortunately, industrial, academic, and governmental groups are focusing attention on the problem with short-range solutions often available. Longer term solutions await further breakthroughs, but the technology and science exists that should allow these breakthroughs to occur. Of greater concern than the scientific and technological aspects is the ability to educate ourselves sufficiently to take part in recycling efforts and the ability to perform decent solid waste conservation on a meaningful scale.

18.4 RECYCLING CODES

Most of us have seen the triangle symbol with three arrows and realize that it has something to do with recycling. This symbol was initially developed by the Society of Plastics Industry as a resin/plastic identification code. It was devised largely for use on containers, but today the "chasing-arrows" triangle is being utilized as a universal symbol for recycling.

The SPI Resin Identification Code utilizes the numbers 1–7 and bold, capital letters as shown below.

Poly(ethylene terephthalate)—**PET** or **PETE**

PET is the plastic used to package the majority of soft drinks. It is also used for some liquor bottles, peanut butter jars, and edible-oil bottles. About one-quarter of plastic bottles are **PET.PET** bottles can be clear: they are tough and hold carbon dioxide well.

High-density polyethylene—**HDPE**

Polyethylene is available in a wide variety of molecular weights with varying branching. **HDPE** accounts for over 50% of the plastic bottle market. It is used to contain milk, juices, margarine, and some grocery snacks. **HDPE** is easily formed through application of heat and pressure; it is relatively rigid and low cost.

Poly(vinyl chloride)—**PVC** or **V**

Poly(vinyl chloride) can be used "pure" or as a blend to make a wide variety of products including **PVC** pipes, food packaging film, and containers for window cleaners, edible oils, and solid detergents. **PVC** accounts for only about 5% of the container market.

Low-density polyethylene—**LDPE**

Low-density polyethylene is similar in gross structure to **HDPE** except that it contains a variety of branching, resulting in a material that has a lower softening temperature, and it is amorphous, making products derived from it more porous and less tough. **LDPE** is a major material for films from which trash bags and bread bags are made. While it is more porous than **HDPE**, it does offer a good inert barrier to moisture.

Polypropylene—**PP**

Polypropylene has good chemical resistance to chemicals and fatigue. Films and fibers are made from it. **PP** is the least used, of the major plastics, for household items. Some screw-on caps, lids, yogurt tubs, margarine cups, straws, and syrup bottles are made of **PP**.

Polystyrene—**PS**

Polystyrene is used in a wide variety of containers, including those known as "styrofoam" plates, dishes, cups, etc. Cups, yogurt containers, egg cartons, meat trays, and plates are made from **PS**.

"Other plastics

A wide variety of other plastics are coming to the marketplace, including a number of copolymers, alloys, blends, and multilayered combinations."

18.5 SMART MATERIALS

Smart materials have been with us for some time, though the term is relatively new. Some of the first smart materials were piezoelectric materials, including poly(vinylene fluoride), that emit an electric current when pressure is applied and change volume when a current is passed through them. Most smart materials are polymeric in nature or have polymers forming integral parts of the "smart material" system.

Today's research concentrates not only on the synthesis of new smart materials, but also on the application of already existing smart materials. Much of the applications involve assemblage of smart material portions and envisioning uses for these smart materials. Thus, it is possible that since application of pressure to a piezoelectric material causes a discharge of current, a portion of a wing could be constructed such that appropriate "warping" of a wing would result from an "electronic feedback" mechanism employing a computer coupled with a complex system of electronic sensing devices. Almost instantaneous, self-correcting changes in the overall wing shape would act to allow safer and more fuel-efficient air flights. Similar applications involving adjustable automotive wind foils are possible. Such pressure-sensing devices could also be used to measure application of "loads" through reaction of the piezoelectric sensors to stress/strain. Again, application of these computer-linked sensors would allow redistribution of loads and/or reconfiguration of the load-bearing structure(s) to compensate for stress/strain imbalances.

Smart materials are materials that react to an externally applied force—electrical, stress/strain (including pressure), thermal, light, and magnetic. A smart material is not smart simply because it responds to external stimuli, but it becomes smart when the interaction is used to achieve a defined engineering or scientific goal. Thus, most materials, including ceramics, alloys, and polymers, undergo volume changes as they undergo phase changes. While the best known phase changes are associated with the total changes in matter state such as melting/freezing, many more subtle phase changes occur. For polymers the best known secondary transitional phase change is the glass transition, T_g, where local segmental mobility occurs. Volume changes associated with T_g are well known and used as a measure of the crystallinity of a polymer. Along with T_g, polymers can undergo a number of other volume-changing transitions. These polymers then become smart only when the volume-changing ability is applied, such as in sensing devices. Multiple switching devices can be constructed to detect and redirect electrical signals as a function of temperature from such materials.

The use of smart materials as sensing devices and shape-changing devices has been enhanced due to the increased emphasis on composite materials that allow the introduction of smart materials as components. A typical smart material assembly might contain:

Sensor components containing smart materials that monitor changes in pressure, temperature, light, current, and/or magnetic field

Communications network that relays changes detected by the sensor components via fiberoptics or conductive "wire" (including conductive polymer channels)

Actuator part that reacts to the action command.

The actuator part may also be a smart material such as a piezoelectric bar placed in a wind foil that changes orientation according to a current "ordered" by the computer center to allow better handling and more fuel-efficient operation of a machine such as an automobile.

Thus, the smart material may act as a sensor component, as an actuator part, or by itself as described earlier. The smart material may act on a molecular level, as in sensors, or as bulk material, such as in wind foils.

We are aware that muscles contract and expand in response to electrical, thermal, and chemical stimuli. Certain polymeric materials, including synthetic polypeptides, are known to change shape on application of electrical current, temperature, and chemical environment. For instance, selected bioelastic smart materials expand in salt solutions and may be used in desalination efforts. They are also being investigated in tissue reconstruction, as adhesive barriers to prevent adhesion growth between surgically operated body parts, and in controlled drug release where the material is designed to behave in a predetermined manner according to a specified chemical environment. The molecular design can be tailored, giving materials with varying biodegradabilities.

Most current efforts include three general types of smart materials: piezoelectric, magnetostrictive (materials that change their dimension when exposed to a magnetic field), and shape memory alloys (materials that change shape and/or volume as they undergo phase changes). Conductive polymers and liquid crystalline polymers can also be used as smart materials, since many of them undergo relatively large dimensional changes when exposed to the appropriate stimulus such as an electric field.

New technology is being combined with smart materials called micromachines, i.e., machines smaller than the width of a human hair, of the order of micrometers. Pressure and flow meter sensors are being investigated and commercially made.

18.6 CONSTRUCTION AND BUILDING

The use of polymeric materials as basic structural materials is widespread and of ancient origin. Today the use of synthetic polymers in building and construction is increasing at a rapid rate. The use of plastics alone is approaching 10% of the total cost of building and construction in the United States (Table 18.1). Uses of plastics are given in Table 18.2. By weight, plastics accounts for only about 2%, but the total use of polymeric materials by weight is about 80% (concrete, lumber, ceramic, wood panels, plastics; Table 18.3).

As lighter and stronger polymeric materials become available, their impact on the building and construction industry and on other industries will increase. Furthermore, as materials that perform specific tasks become available, they too will be integrated into the building and construction industry. This includes devices for gathering and storage of solar energy and smart materials including smart windows.

Table 18.1 Values of Plastics in Construction in the United States

Plastic	$ (billion)
Poly(vinyl chloride)	2.1
Phenolics	1.2
Polyurethanes	1.1
Polyethylene	0.5
Polystyrene	0.4
Urea and melamine	0.3
Acrylates	0.3
Other	0.7

Table 18.2 Major Plastic Applications in Building and Construction

Plastic	Use(s)
ASA	Window frames
Acrylics	Lighting fixtures and glazing
PVC and chlorinated PVC	Hot and cold water pipe; moldings, siding, window frames
Melamine and urea formaldehyde	Laminating for countertops, adhesives for wood, plywood, and particle board
Phenol formaldehyde	Electrical devices and plywood adhesive
Poly(ethylene terephthalate)	Countertops and sinks
Polycarbonates	Window and skylight glazing
Polyethylene	Pipe, wire, and cable covering
Poly(ethylene oxide)	Roofing panels
Polystyrene	Insulation and sheathing
Polyurethane	Insulation and roofing systems

18.7 HIGH-PERFORMANCE THERMOPLASTICS

The terms *high-performance, engineering*, and *advanced thermoplastics* are often used interchangeably. High-performance thermoplastics generally contain little or no light crosslinking.

The term *engineering materials* refers to materials that have enough dimensional stability sufficient to allow them to be cut, machined, drilled, etc. The most common engineering thermosets are materials such as the phenol and amino plastics (Sec. 6.14) that are crosslinked three-dimensional networks.

There are a number of engineering materials that can be molded through application of heat and pressure. These materials, when used in bulk, are known as engineering thermoplastics. They retain their mechanical functionality even when subjected to mechanical stress/strain, vibration, friction, flexure, etc.

These materials are rapidly replacing metals because they offer advantages such as lightness per strength, corrosion resistance, self-lubrication, economy and breath in fabrication, and in some cases transparency and ease in decoration. The need for engineering plastics is increasing as the need for electrical devices that are small and light-weight continues. In 1999 more than 15 million pounds of engineering thermoplastics was used in the United States.

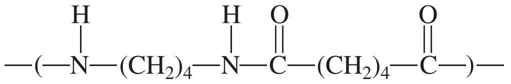
Table 18.3 Use of Materials in Building and Construction

Material	Weight (billion lb.)	%
Concrete	250	50
Lumber	60	12
Ceramic	50	10
Wood panels	20	4
Iron and steel	15	3
Plastics	10	2
Other	95	19

Nylon-66 was the first engineering thermoplastic and to 1953 represented the entire annual engineering thermoplastic sales. Nylon-66 is tough, rigid, and does not need to be lubricated. It has a relatively high use temperature (to about 270°C) and is used in the manufacture of automotive gears to hair brush handles.

Most polymers progress from a glass solid to a softer solid and then to a viscous "taffy-like" stage, allowing easy heat-associated fabrication. Nylon-66 has an unusually sharp transition from the solid to the soft stage, requiring that fabrication be closely watched.

Nylon-46 was developed by DSM Engineering Plastics in 1990 and sold under the trade name Stanyl giving a nylon that has a higher heat and chemical resistance for use in the automotive industry and in electrical applications. It has a T_m of 295°C and can be made more crystalline than nylon-66.

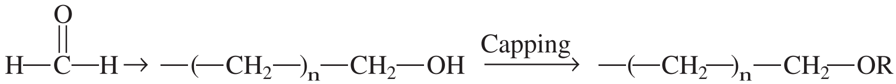


$$\text{—(—}\overset{\overset{\displaystyle H}{|}}{N}\text{—}(CH_2)_4\text{—}\overset{\overset{\displaystyle H}{|}}{N}\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}(CH_2)_4\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—)—} \qquad (18.15)$$

Nylon 6

A number of aromatic polyamides, aramids (Sec. 6.7) have been produced that are strong, can operate under high temperatures, and have good flame-retardant properties.

The next engineering thermoplastics to enter the market were the polyacetals derived from formaldehyde and known as polyoxymethylenes (POMs) (Sec. 6.12). While formaldehyde can be easily polymerized, it also depolymerizes easily while undergoing depolymerization through an unzipping process. Blocking or capping of the terminal hydroxyl group allows the production of stable polyacetals.



$$H\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}H \rightarrow \text{—(—}CH_2\text{—)}_n\text{—}CH_2\text{—}OH \xrightarrow{\text{Capping}} \text{—(—}CH_2\text{—)}_n\text{—}CH_2\text{—}OR$$

(Capped) Polyoxymethylene

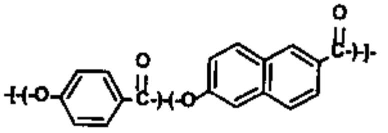
(18.16)

POMs are highly crystalline, creep-resistant, rigid, fatigue-resistant, mechanically strong and tough, solvent-resistant, and self-lubricating. Even when capped, they retain the tendency to unzip when heated to high temperatures. They are used in the manufacture of rollers, conveyor chains, housings, bearings, and gears.

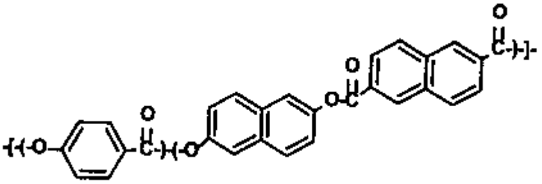
While a number of polyesters have been considered as engineering thermoplastics, only several have become widely used. While PET is the most widely used polyester, it does not crystallize very rapidly, thus discouraging its use in rapid molding processes since a highly crystallized material is needed to meet the demands of an engineering plastic. Thus, PET is used as a fiber, etc., but is not widely used as an engineering plastic.

By comparison, poly(butylene terephthalate) (PBT) is used as an engineering thermoplastic since it can be crystalized quickly allowing rapid fabrication. It has low moisture absorption, good self-lubrication, good retention of mechanical properties at elevated temperatures, and offers good solvent resistance and fatigue resistance. It is used in numerous "under-the-hood" automotive applications including ignition systems. It is also used in athletic goods, small- and large-appliance components, power tools, and electrical applications.

The most commercially important polyester liquid crystalline polymers (Sec. 18.17) are based on p-hydroxybenzoic acid. Because of the rapid changes that have occurred in liquid crystals, (LCs), a wide variety of materials have been made. In 1985, Celanese (now Ticona) commercialized Vectra based on copolymers of p-hydroxybenzoic acid with 6-hydroxy-2-naphthoic acid or with 2,6-dihydroxynaphthalene and 2,6-naphthylene dicarboxylic acid (below).



(18.17)



(18.18)

These polymers are rigid and exist in ordered domains. When shear is applied, such as forcing solutions of LCs to flow, little resistance is encountered because the chains readily align themselves.

Polyester LCs are used in surgical devices and electronic connectors.

Polycarbonates have been made using various bisphenols though the most widely produced material is derived from bisphenol A (Sec. 6.6). Polycarbonates exhibit good impact strength, are heat-resistant, have good electrical properties and high dimensional stability. They also offer good transparency that allows their use in replacing glass or cases where good transparency is needed such as in safety glazing, automotive headlamp lenses, light covers, CDs, and in ophthalmic applications.

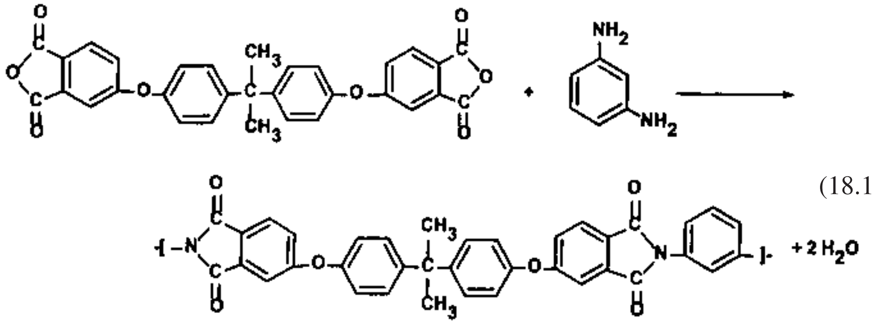
They also offer inherent flame retardancy probably due to two features. First, some of the polymer, the carbonate moiety, is already fully oxidized. Second, the aromatic portions degrade to give polycyclic and fused ring aromatic cyclic products that give char that acts to "cover" the fire.

Poly(phenylene ether) (PPE) or poly(phenylene oxide) (PPO) (Sec. 6.12) shows total compatibility with polystyrene, allowing a number of different combinations to be formed giving rise to the Noryl family of blends and alloys. These two combine each offering the product needed properties. PPO brings fire retardancy to the material and contributes a high heat distortion temperature of greater than 100°C, allowing the products to be cleaned and used in boiling water. PS contributes ease of fabrication to the couple. Both exhibit outstanding electrical properties and good water resistance. Furthermore, the blend gives a material with a lower density than most engineering materials.

Polyarylsulfones offer materials with good thermaloxidative stability, solvent resistance, creep resistance, and good hydrolytic stability (Sec. 6.13). Low flammability and low smoke evolution encourages its use in aircraft and transportation applications. It holds up to repeated steam sterilization cycles and thus is used in a wide variety of medical applications such as life support parts, autoclavable tray systems, and surgical and laboratory equipment. Blown molded products include suction bottles, surgical hollow shapes, and tissue culture bottles.

The aromatic polyketones offer good thermal stability, good environmental resistance, good mechanical properties, resistance to chemicals at high temperatures, inherent flame retardancy, good friction and wear resistance, and good impact resistance. Poly(etherether ketone) (PEEK) became commercialized in 1980 under the trade name Victrex (Sec. 6.14). It is used in the chemical process industry as compressor plates, pump impellers, bearing cages, valve seats, and thrust washers; in the aerospace industry as aircraft fairings, fuel valves, and radomes, and in the electrical industry as semiconductor wafer carriers and in wire coatings.

Polyetherimide (PEI), was first announced by General Electric scientists in 1982. It offers good stiffness, impact strength, transparency, low smoke generation, broad chemical resistance, good heat resistance, good electrical properties, and good flame resistance. It also offers good processability and a good resin can be made from it allowing for easy molding. Uses may include in internal components of microwave ovens, electrical applications, and in transportation.



(18.19)

With the advent of the soluble stereoregulating catalysts (Sec. 7.5), so-called older polymers have been synthesized with additional control over the structure giving products with enhanced strength and dimensional stability. Amorphous polystyrene (PS), is relatively brittle, requiring a plasticizer to allow it to become flexible. Use of soluble stereoregulating catalysts has allowed the synthesis of syndiotactic polystyrene (SPS). The SPS is a semicrystalline polymer with a T_m of about 270°C and a T_g of about 100°C with good solvent and chemical resistance. Dow commercialized SPS under the trade name Questra in 1997. It is believed to be used in specialty electrical and under-the-hood automotive applications.

Many applications require materials to be stable above 200°C. These thermoplastic materials are referred to high-temperature thermoplastics. Table 18.4 contains some of the new advanced thermoplastic materials.

18.8 COMBINATORIAL CHEMISTRY

Combinatorial chemistry is an approach whereby compounds are synthesized and/or treated *en masse*. Combinatorial chemistry is a result of a number of factors including computerization of testing so that a single or small batch of tests can be carried out rapidly and the development of good separation tools (e.g., chromatographic methods) that allow the ready separation of materials. Its aim is to discover materials more quickly and inexpensively by creating and evaluating materials on a large (numberwise) scale. It is being used in chemistry, pharmaceutical research, medicine, and molecular biology. In this approach,

Table 18.4 Advanced High-Temperature Thermoplastics and Their Applications

Material	Heat deflection temp. (°C)	Properties
Poly(alkylene carbonate)	—	Leaves no degradation residue
Polyamide imide	280	Good wear, friction and solvent resistance
Polyaniline	70	Conducts electricity
Polyarylate (aromatic polyesters)	175	Good toughness, UV stability, flame retarder
Polybenzimidazoles	440	Good hydrolytic, dimensional, and compressive stability
Polyether imide	220	Good chemical and dimensional stability and good creep resistance
Polyethersulfone	200	Good chemical resistance and stability to hydrolysis
Polyimide	360	Good toughness
Polyketones	330	Good chemical resistance, strength, and stiffness
Poly(phenylene ether)	170	Often alloyed with PS
Poly(phenylene sulfide)	260	Good dimensional stability and chemical resistance
Polyphenylsulfone	260	Good chemical resistance
Polyphthalamide	290	Good mechanical properties
Polysulfone	175	Good rigidity

additional analysis, such as structure and composition, is carried out only on materials that show the desired property (or that might exhibit unusual results).

The target or specific property desired is selected and the materials synthesized or treated are tested against the desired property. Problems can arise because the wrong target or test may be chosen, so that selecting desired properties and tests that allow this property to be appropriately evaluated is important. Further, such selective targeting for a specific narrow property may result in the elimination of materials that may have outstanding properties in related or unrelated areas.

Such an approach may appear “shotgun” but should be designed with some structure–property relationships in mind. Property differences, as a part of the overall result analysis, are also important. Libraries of tested results are being developed.

In many property areas, both chemical and physical structures are critical. Thus, toughness may be dependent not only on bulk and internal structures, but surface contour, pore size, precise chemical nature of the surface, etc., might also be important.

A simple example involves the search for better adhesives. Cyanoacrylate polymers show good adhesion to a wide variety of surfaces. These polymers are not water-soluble (but are water sensitive). Thus a search for either a water-soluble or water-compatible material might involve the synthesis of copolymers with vinyl acetate because poly(vinyl acetate) has some water compatibility and because vinyl acetate units can be hydrolyzed giving vinyl alcohol units poly(vinyl alcohol) itself is water-soluble. Thus, prior knowledge of the properties of the reactants was considered in designing the study. Next, a rapid test that can be used to give a “first approximation” of the adhesive strength of the material is chosen. Additionally, a ready test for the water compatibility and/or solubility of the materials is chosen. Finally, products are synthesized varying the ratios of the cyanoacrylate monomer, such as butyl-α-cyanoacrylate, and vinyl acetate. Some of each product is subjected to varying amounts of hydrolysis. The products are now divided by molecular weight and composition, and tested. The results will hopefully give both the composition of materials that exhibit both good adhesion and water compatibility/solubility.

Langer and co-workers synthesized a series of copolymers containing various amounts of diacrylate and amine monomers investigating copolymer composition with the ability to act as transport DNA into cells. They screened 140 copolymers as synthetic gene-delivery vectors. Of these 56 were able to bind DNA. These polymers were then screened for their ability to facilitate the transfer of plasmid DNA into a common monkey cancer cell line. Two of the copolymers with quite varied compositions showed good activity—one expected and the other unexpected. The expected copolymer composition would have been a selected composition in a typical search and the other would have been omitted. Thus, combinatorial-like approaches can offer unexpected results to problems.

18.9 SYNTHETIC BIOMEDICAL POLYMERS

Synthetic polymers have been studied for some time for their use in the general field of medicine. Initial results were average. More recently, because of a better understanding of the importance of surface, avoidance of contaminants, control of molecular weight and molecular weight distribution the use of synthetic polymers in the biomedical sciences is increasing. Polymers are viewed as important biomedical materials for a number of reasons, some of which appear contradictory-but only because different uses require different properties. Some of the important properties are the ability to tailor make structures, surface control, strength, flexibility, rigidity, inertness/reactivity, light weight, ease of fabrication, ability to achieve a high degree of purity, lack of and because of their water solubility/compatability, bioerodability, and the ability of some of them to stand long-term exposure to the human body—a truly hostile environment. Fighting against some of the biomaterials is their limited (by volume) use. Thus, researchers are often limited to using commercial materials made for other applications. However, as the use of these important materials increases, manufacturers will become more interested in tailor-making materials if for no other reason than the high cost per unit volume.

Long-term inertness without loss of strength, flexibility, or other necessary physical property is needed for use in artificial organs, prostheses, skeletal joints, etc. Bioerodability is needed when the polymer is used as a carrier such as in controlled release of drugs, removal of unwanted materials, or where the material's purpose is short-lived such as in stutures and frames for natural growth.

Material surface is critical. While the nature of the material is important, the surface of the material is critical. The human body wants to wrap around or connect to bodies its domain. In some cases the desired situation is little or no buildup on the polymer. Here, surface slickness is needed. Siloxanes and fluorinated materials such as PTFE are generally slick, but other materials can be made slick through surface treatments that presents to the body few voids and irregularities at the atomic level. In other cases, bodily buildup is desired, and surfaces and materials that assist this growth are desired. Surface hydrophobicity/hydrophilicity, presence/absence of ionic groups, chemical and physical (solid or gel) surface are all important considerations as one designs a material for a specific application.

Ability to function in the long term is an ongoing problem. In general, polyurethanes degrade after about 1.5 years, nylons lose much of their mechanical strength after about

3 years, and polyacrylonitrile loses about 25% strength after 2 years. On the long side, PTFE loses less than 10% strength after about a year and siloxanes retain most of their properties after 1.5 years.

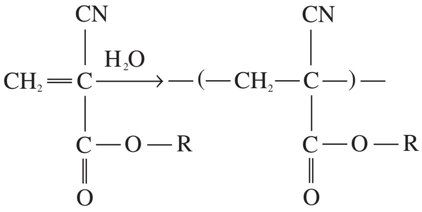
Following is a brief look at some of the varied uses, real and future, for synthetic polymers. These are intended to be illustrative only. The field of biomedical materials is rapidly growing and it is extensive.

There has been a lot of effort to construct artificial hearts for human use. These hearts are largely composed of polymeric materials. Even with the problems associated with organ transplant, the use of artificial hearts may never be widespread. This is because of several trends. First, many biological solutions to biological problems reside with the use of biological materials to solve biological problems. With the advent of increased, effectiveness of cloning and related advances, suitable biological replacements may be grown from a person's cells thus ensuring compatibility. Second, related to the first, regeneration of essential parts of vital organs is becoming more practical. Third, because of nanotechnology and related electrical and optical advances, surgery to locate and repair imperfections is improving. Fourth, our autoimmune system is divided into two main systems—one guards against "small" invading organisms such as viruses, bacteria, and pollen. The second group acts to reject whole organisms such as the heart through rejection of foreign body tissue. Purine nucleoside phosphorylase (PNP) is a human enzyme that serves at least two major functions. First, PNP acts to degrade unleased molecules including foreign nucleic acids. It is necessary to our immune system as it fights disease. Some anticancer drugs are synthetic nucleosides and nucleotides such as poly(I)-poly(C), which are employed to directly attack selected cancerous tumors. PNP degrades such nucleic acid-related materials before they reach the tumor. Neutralization of PNP just prior to administration of the synthetic nucleic acid–related material would allow lower dosages to be used. Second, PNP is an integral part of the body's T-cell immunity system, which rejects foreign tissue. Effort is currently underway to effectively inhibit only the PNP action, allowing the first autoimmune system to work while also allowing organ transplantation without rejection. Recently, through the use of zero gravity conditions, crystals of PNP have been growth of sufficient size to allow structural determination. With this structure efforts are underway to detect sites of activity and drugs that would allow these sited to be neutralized when needed.

Even so, synthetic polymers have been important in replacing parts of our essential organs. Thus, silicon balls are used in the construction of mechanical heart valves. Many of these fail after some time and they are being replaced by a flap valve made from pyrolytic carbon or polyoxymethylene. Aneurisms can be repaired through reinforcement of the artery wall with a tube of woven PTFE or polyester. Replacement of sections of the artery can be done using a tube of porous PTFE. One remaining problem is the difference in elasticity between the woven and porous materials and the arteries themselves.

Carbon fiber composites are replacing screws for bone fracture repair and joint replacements. These fiber composites are equally strong and chemically inert. By comparison, the metals they replace are often alloys that may contain metals to which the patient may be allergic.

Polymers are also used as sutures. Fighters and other athletes have used poly(α-cyanoacrylates) (superglues) to quickly stop blood flow in surface cuts. Today superglue is also used in place of or along with more traditional polymeric suture threads for selected surface wounds, internal surgery, and retinal and corneal surgery. The α-cyanoacrylate polymers undergo anionic polymerization in the presence of water.



$$\mathrm{CH_2{=}C(CN)(C({=}O){-}O{-}R)} \xrightarrow{H_2O} \mathrm{{-}({-}CH_2{-}C(CN)(C({=}O){-}O{-}R){-}){-}} \tag{18.20}$$

Poly (α-cyanoacrylate)

Siloxanes are the most extensively used biomaterials. They are used for a number of reasons including flexibility, chemical and biological inertness, low capacity to bring about blood clotting, overall low degree of biological toxicity, and good stability within biological environments.

Artificial skin had been made from a bilayer fabricated from a crosslinked mixture of bovine hide, collagen, and chondroitin-b sulfate derived from shark cartilage with a thin top layer of siloxane. The siloxane layer acts as a moisture and oxygen permeable support and to protect the lower layer from the “outer world” allowing skin formation to occur in conjunction with the lower layer. Poly(amino acid) films have also been used as an artificial skin. Research continues for a skin that can be effectively used to cover extensive wounds and burns.

Controlled release of drugs using polymer-intensive materials is becoming commonplace. The release pack can be attached externally such as many of the nicotine patches that deliver controlled amounts of nicotine transdermally. The release pack can also be introduced beneath the skin or within the body as is the case with many diabetes treatment assemblies.

Controlled release of drugs can be envisioned as occurring via three major routes. One approach utilizes diffusion-controlled release through membranes or matrices. Here the rate of release is controlled by the permeability of the membrane or matrix. In the second approach, the drug is captured within a matrix that undergoes degradation, usually through aqueous-assisted solubilization or degradation (including hydrolysis). Here the rate of drug release is dependent on the break-up of the typically polymeric matrix. For the second approach, a number of polymers have been used including poly(glycolic acid) and polyanhydrides. The third approach involves simple degradation of a drug-containing polymer where the drug moiety is present as part of the polymer backbone or as side chains. Degradation of the polymer results in the release of the drug in some fashion.

Implant materials can be divided into two general categories dependent on the time requirement. Those that are present for release of a drug or to hold a broken bond in place until sufficient healing occurs are termed “short-term use.” The second group includes materials that are to function over a longer time such as for the life of the patient. In the first case, degradation is generally required, while for the longer term material inertness and long-term stability are typically needed. There are times when this is not true. For instance, some of the newer biomaterials act as scaffolds that promote tissue growth by providing a three-dimensional framework with properties that encourage favorable cell growth. This material may be designed to be either short or long term.

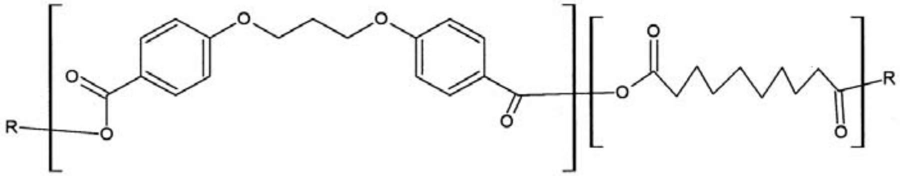
One approach to designing scaffolding material involves the intended use of certain amino acid-containing units on the polymeric scaffold placing amino acids or amino acid sequences that will encourage cell growth. Thus a series of amino acid containing copolymers were synthesized including ethyl, butyl, hexyl, and octyl esters and while all four had similar structure, poly(PCPPSA anhydride had the most favorable response. Others have coupled amino acids with the poly(lactic acid-co-glycolic acid) polymers.

Another aspect related to control release of drugs concerns the type of structures that currently appear to be working. Not unexpectedly, because of compatibility and degradation purposes, most of the effort on the control release formulations include polymers that have both a hydrophobic and hydrophilic portion with the material necessarily containing atoms in addition to carbon. Another concern is that the products of degradation are not toxic or do not go on to form toxic materials. It has also been found that amorphous materials appear to be better since they are more flexible and permit more ready entrance of potential degradative compounds. These structural concerns are also true for most diagnostic techniques where the particular diagnostic site is embedded within the mixed polarity material.

Another area of activity involves the synthesis of supermolecular layers that are connected through crosslinking giving essentially one-molecule thick micelles. Depending on the particular template and solvents employed these monolayers can be designed to have almost any combination of hydrophilic and hydrophobic sites. Again, specific control of release rates, degradation times and routes, biocompatibility or incompatibility are possible. Many of these micelle-based delivery systems are based on a poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) triblock or on a polypeptide and poly(ethylene oxide) combination. Drug delivery has also been achieved using conducting electroactive polymers formed through controlled ionic transport of counterions (dopants) in and out of membranes.

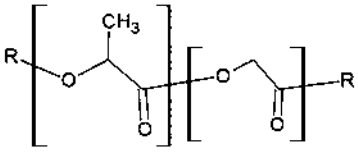
Another approach is the use of hydrogels that shepherd drugs though the stomach and into the more alkaline intestine. Hydrogels are crosslinked, hydrophillic polymer networks that allow the smaller drugs access to their interior and that can be designed to inflate, swell at the desired site to deliver the drug. These hydrogels have largely been formed form materials with a poly(acrylic acid) backbone.

Following are structures for some of the most widely employed temporary implant materials and as coatings/encapsulating materials.



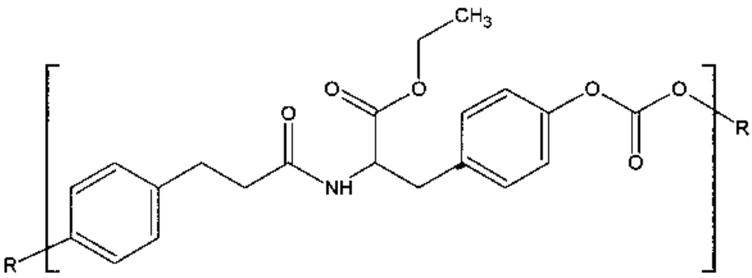
Poly(bis(p-carboxyphenoxylpropane-co-sebacic acid anhydride), Poly(PCPP-SA anhydride)

(18.21)



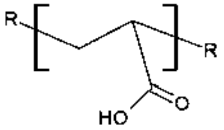
(18.22)

Poly(lactic acid-co-glycolic acid)



(18.23)

Poly(desaminotyrosyltyrosine ethyl ester carbonate), poly(DTE carbonate)

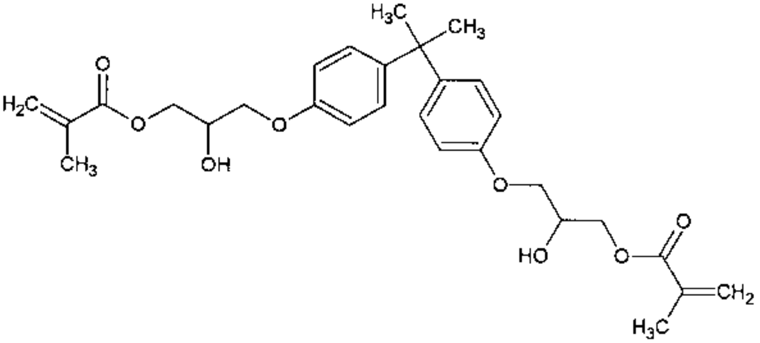


(18.24)

Poly(acrylic acid)

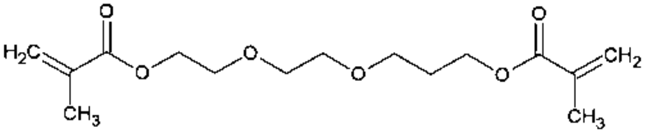
Along with the organic materials a number of inorganic materials are also being considered as degradable implant material. A porous form of β-tricalcium phosphate had been used for the repair of bone voids and related defects in the spine, pelvis, arms, and legs.

Polymers are used extensively in dentistry. Dental restorative composites generally consist of di- and trifunctional monomer systems, which provide the crosslinking necessary to form a strong matrix once polymerized. Reinformcing fillers such as silanized quarts, ceramics, hybrid filler such as prepolymerized resins on fumed or pyrogenic silica, and ceramics act as the dispersed phase of the composite. The diluent or continuous phase is the mono- and difunctional monomer that decreases the viscosity of di- and trifunctional monomers that finally act to form the stable composite matrix. Dental sealants are similar except the filler material is either not present or in lesser concentration. Many of the restorative composites are based on modified dimethacrylates the most common being 2,2-bis[p-(2′-2-hydroxy-3′-methacryloxypropoxy)phenyl]-propane, bis-GMA, and triethyleneglycol dimethacrylate (TEGDMA).



(18.25)

Bis-GMA



(18.26)

TEGDMA

These two are used either separately or as a mixture. Because of the presence of the somewhat flexible ethylene oxide and related units and use of appropriate fillers, these materials give composite fillings with lower polymerization shrinkage, enchanced mechanical properties, lower solubility and water adsorption, better thermal expansion characteristics, good biocompatibility, with aesthetic properties closely matching those of the tooth itself.

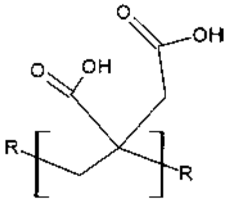
Some other fillings employ urethanedimethacrylate (1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane), UDMA in place of bis-GMA. This is an active area of research with new monomer systems being introduced in an ongoing manner.

Cavity varnishes are used to seal the exposed dentinal tubules and protect the pulp from the irritation of chemicals in the filling materials. They are generally largely natural rubber or a synthetic polymeric resin such as 2-hydroxyethyl methacrylate (HEMA).

Almost all denture bases are made of methacrylic (acrylic) resins that give good fit and a natural appearance. A compression molding process is used where the monomer-polymer dough or slurry containing poly(methyl methacrylate) or poly(methyl acrylate). Often there is a change in the contour of the soft tissue and a liner is fitted onto the denture base. Silicon reliners are often used for this purpose.

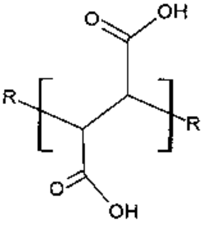
Plastic acrylic denture teeth are made by injection or transfer molding. Acrylic teeth have a higher strength than porcelain teeth and break less readily. However, they cold flow, have a greater water absorption, and they have a higher wear rate than porcelain teeth.

Many of the dental polymer cements are glass-ionomer combinations made from ionomer-forming polymers that contain acid groups such as poly(acrylic acid), poly(itaconic acid), poly(maleic acid), and poly(2-butene-1,2,3-tricarboxylic acid). These polyalkenoate cements are set-up through reaction with an alumino-silicate-fluoride glass with the polyacids hydrolyzing the glass network releasing the aluminum and calcium ions and forming a silaceous hydrogel. The acid groups chelate with the released metal cations forming a crosslinked matrix.



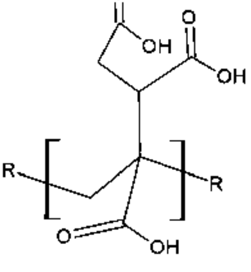
Poly(itaconic acid)

(18.27)



Poly(maleic acid)

(18.28)



Poly(2-butene-1,2,3-tricarboxylic acid)

(18.29)

Also included in the general grouping of biomaterials are the new electronics that are being developed including nanotechnology. These electronic biomaterials will need to be encapsulated sufficiently to protect them from the body and to protect the body from hostile actions against the presence of the foreign object; or they will need to be made with a coatings material that will act as an encapsulating material to the electronics device. Special care will need to be taken with respect to adhesive materials that connect the electrical device to the particular site for activity and/or interactions between the electromagnetic messages and surrounding tissue. Again, adhesive, encapsulating, and shielding materials will be largely polymeric.

A number of siloxane-containing controlled release packs have been devised and are in use. Glaucoma, motion sickness, and diabetes have been treated using drugs dispersed in a silicon matrix. This kind of pack must be placed near the site of intended activity for greatest effectiveness.

Elastomeric siloxanes have also been used in encapsulating drugs, implant devices, and in maxillofacial applications to replace facial portions lost through surgery or trauma. Transcutaneous nerve stimulators are made from “conductive” siloxanes. These are employed in the treatment of chronic severe pain through application of low-level voltage to the nerves, disrupting transmission of pain impulses to the brain. Siloxanes are also used in extracorporeal blood oxygenation employed in the heart–lung assist machine that is routinely used in open heart surgery. The “heart” of the apparatus is the membrane that must allow ready transport of oxygen and carbon dioxide yet retain moisture and blood cells. The siloxane membranes can be made using polyester or PTFE screen in an organic dispersion of silicon rubber. When dried, thin films are obtained that are used in the heart–lung assist device.

Silioxane-containing devices have been also used as contact lenses (Sec. 11.3), tracheostomy vents, tracheal stents, antireflux cuffs, extracorporeal dialysis, ureteral stents, tibial cups, synovial fluids, toe joints, testes penile prostheses, gluteal pads, hip implants, pacemakers, intra-aortic balloon pumps, heart valves, eustachian tubes, wrist joints, ear frams, finger joints, and brain membranes. Almost all of the siloxane polymers are based on various polydimethylsiloxanes.

The kidney removes waste from our blood. Because of partial or total kidney failure, many persons are on hemodialysis. The first hemodialysis units were large and by today’s standards not very effective. The semipermeable tubes, made mainly of cellophane, had very limited lifetimes. Initially dialysis treatment was expected to be for terminal patients only. But as the life expectancy of dialysis patients has increased along with the demand for dialysis, smaller and more efficient dialysis machines have emerged. At the core of these advances is the filtering material. Today bundles of microscopic hollow fibers are used in the construction of hemodialysis cells. The fibers are “heparinized” to discourage blood clotting. The fibers are mainly composed of polyacrylonitrile. Polycarbonate, cellulose acetate, and rayon fibers are also being used.

18.10 THE HUMAN GENOME AND PROTEOMICS

The Human Genome—General

The unraveling of much of the human genome is one of the most important advances made since our dawning. An online tour of the human **genome** (defined terms appear as bold) is found at a number of Web sites allowing access to some of this valuable information. Some of these sites are http://genome.ucsc.edu,www.nature.com/genomics/human/papers, www.sciencemag.org/contents/vol291/issue5507, www.ncbi.nlm.nih.gov/sitemap/index.html#humangenome, www.nhgri.nih.gov/data/, www.celera.com, www.ensembl.org/genome/central/, http://genome.ucsc.edu, http://genome.cse.ucsc.edu, and http://genome.wustl.edu/gsc/human/mapping.

There are two general kinds of cells, those having a membrane-bounded nucleus called eukaryotic cells, and those without a nuclear envelope called prokaryotic cells. Humans have eukaryotic cells. All eukaryotic cells contain a nucleus that contains the genome, the complete set of genes. Unless noted otherwise, our discussion will be restricted to eukaryotic cells.

The human genome and other mammalian cells contain about 600 times as much DNA as *Escherichia coli*. Many plants and amphibians contain an even greater amount. While eukaryotic cells contains more DNA than do bacterial cells (prokaryotic cells), the gene density of bacterial cells is greater. For instance, human DNA contains about 50 genes per ml, while *E. coli* contains in excess of 2500 genes per ml. As will be noted, the human genome, while it contains a lot of nongene material, this nongene material appears to be active in the organization of the chromosome structure playing a number of roles including supplying hyperfine contours to assist in the replication, protection, and selectivity of the sites. The contour length, the stretched out helical length, of the human genome material in one cell is about 2 m in comparison with about 1.7 m for *E. coli*. An average human body has about 10^{14} cells giving a total length that is equivalent in length to traveling to and from the earth and sun about 500 times or 1000 one way trips.

Replication occurs with a remarkably high degree of fidelity such that errors occurs only once per about 1000 to 10,000 replications or an average single missed base for every 10^9 to 10^{10} bases added. This highly accurate reproduction occurs because of a number of reasons including probably some that are as yet unknown. As noted before, the GC group has three hydrogen bonds while the AT has two. In vitro studies have found that DNA polymerases inserts one incorrect base for every 10^4 to 10^5 correct ones. Thus, other features are in place that assist in this process. Some mistakes are identified and then corrected. One mechanism intrinsic to virtually all DNA polymerases is a separate $3'$–$5'$ exonuclease activity that double-checks each nucleotide after it has been added. This process is very precise. If a wrong base has been added this enzyme prevents addition of the next nucleotide removing the mispaired nucleotide and then allowing the polymerization to continue. This activity is called proofreading and it is believed to increase the accuracy another 10^2–10^3-fold. Combining the accuracy factors results in one net error for every 10^6 to 10^8 base pairs, still short of what is found. Thus, other factors are at work.

In general, replication occurs simultaneously as both strands are unwound. Replication is bidirectional with both ends of the loop having preferentially active starting points or sites. A new strand is synthesized in the $5'$ to $3'$ direction with the free $3'$ hydroxyl being the point at which the DNA is elongated. Because the two DNA strands are antiparallel, the strand serving as the template is read from its $3'$ end toward its $5'$ end. If DNA replication always occurs in the $5'$ to $3'$ direction, then how can it occur simultaneously? The answer is that one of the strands is synthesized in relatively short segments. The leading strand, or the strand that is going “naturally” in the correct direction, replicates somewhat faster than the so called “lagging” strand that is synthesized in a discontinuous matter with the required direction and occurs at the opposite end of the particular segment. This is consistent with the observation that all new strands, and here strand segments, are synthesized in a $5'$ to $3'$ manner.

As a scientist, along with knowledge comes questions that in turn point to gathering more information. We have already noted that the precise folding and compaction for chromosomal DNA is not yet fully know (Sec. 10.10). Further, as noted above, we are not fully aware of how replication occurs in such a precise manner.

A third major area of evolving knowledge involves how so much information is packed into the relatively small number of genes we believe we now have. Not long ago we believed that the number of human genes was on the order of 100,000, a number that appeared appropriate even after the first two animal genomes were deciphered. The roundworm, sequenced in 1998 has 19,098 genes, and in 2000 the fruit fly was found to have 13,601 genes. Currently the number of human genes is believed by many, but not all, to be on the order of 30,000–40,000, less than half of the original number. This means that the genes are probably more complex than originally believed. It is now believed that the reason why we are able to function with so few genes is that our genes carry out a variety of activities. This ability is a consequence of several features. One involves the coordinated interactions between genes, proteins, and groups of proteins with variations of the interactions changing with time and on different levels. There is then a complex network with its own dynamics. It is a network that is probably largely absent in lower species such as the roundworm. The roundworm is a little tubed animal with a body composed of only 959 cells, of which 302 are neurons in what passes for a brain. Humans, by comparison, have 100 trillion cells including 100 billion brain cells. While protein domains exist in primitive animals such as the roundworm, they are not as “creative” as those found in more advanced animals. These domains that we have allow the “creation” of more complex proteins.

It appears that another way to gain complexity is the division of genes into different segments and by using them in different combinations increasing the possible complexity. These protein coding sequences are known as *exons* and the DNA in between them as *introns*. The initial transcript of a gene is processed by a splicesome that strips out the introns and joins the exons together into different groupings governed by other active agents in the overall process. This ability to make different proteins from the same gene is called *alternative splicing*. Alternative splicing is more common with the higher species. Related to this is the ability of our immune system to cut and paste together varying genetic segments that allow the immune system to be effective against unwanted invaders.

In *eukaryotic* cells, transcription and translation occur in two distinct temporal and spacial events, whereas in *prokaryotic* cells it occurs in one step. Humans have eukaryotic cells, so we will look at this process. Transcription occurs on DNA in the nucleus, and translation occurs on *ribosomes* in the cytoplasm.

Our genes are split into coding, or exon, and noncoding, or intron, regions. The introns are removed from the primary transcript when it is made into a so-called “mature” or completed RNA—namely mRNA, tRNA, rRNA, etc.

Such split genes occur in a wide variety of sizes and interruptions. Even so, the transcription must be precise. Several features are worth noting about this process. First, the order of the exons is fixed as is the size and order of the introns; also, the order of the exons on the mature RNA is the same as in the original DNA. Second, each gene has the same pattern and size of exons and introns in all tissues and cells of the organism and, with the exception of the immune response and the major histocompatibility complex, no cell-specific arrangements exist. Third, many introns have nonsense codons in all three reading frames so nuclear introns are nontranslatable. Introns are found in the genes of mitochondria and chromoplasts as well as in nuclear genes.

We must remember that each of these steps consist of simple (though complex when considered as a whole) chemical reactions.

Another source of increased complexity involves the fact that human proteins often have sugars and other chemical groups attached to them allowing subtle, and possibly not so subtle, changes in behavior to occur.

Also, it has been found that at least some of the DNA sequences in our genome, about 75%, is apparently nonactive material. The coding regions may occupy only about 1 to 1.5% of the genome. (It must be remembered that while only a small amount contain coding regions, the structure about these regions is also important and that these structures are also important to the overall activity of the gene.) These so-called “active regions” are not evenly distributed across the cell’s 23 pairs of *chromosomes* but are arranged in patches or regions, some being gene-rich and others gene-poor or deprived. They appear to be sticky, liking to associate with one another. They can be compared to the United States, where most of the people occupy a small fraction of the land area with large areas having only a low population. There are even preferred base sequences for these different regions. The populated regions tend to be high in C and G sequences whereas nonpopulated areas, regions were there are few active areas, have higher amounts of A and T sequences. These differences in preferential sequencing actually help account for the banding found in chromosome patterns. The light bands are rich in C and G and the dark ones in A and T.

Gene expression simply refers to its transcription resulting subsequently, in most cases, the synthesis of a protein or protein part. The flow of information typically is DNA → RNA → protein → cell structure and function. Transcription is the term used to describe the transfer of information form the DNA to RNA; the flow of information from the RNA to the protein is called translation. Genes whose product is needed essentially all the time are present at a constant amount in virtually every cell. Genes for enzymes of the central metabolic pathways are of this type and are often called *housekeeping genes*. Unvarying expression of a gene is called *constitutive gene expression*.

The cellular levels of some gene products vary with time in response to molecular signals. This is called *regulated gene expression*. Gene products that increase in concentration are called *inducible* and the process of increasing their expression is called *induction*. Conversely, gene products that decrease in concentration in response to a molecular signal are said to be repressible and the precess called *repression*. Transcription is mediated and regulated by protein-DNA interactions. Thus, while we will focus on the DNA, protein interactions are critical to the operation and expression of genes.

We are beginning to understand some of the language of genes. We are already aware of the sequences that code for particular amino acids. We are also becoming more aware of the meaning of other sequences. Many of these sequences are involved with transcription regulation. Promoters are DNA sites where the RNA polymerase can bind leading to initiation of transcription. They are generally located nearby the gene. There are a number of these sequences. The CAAT box has a consensus sequence of GGCCAATCT, and its presence indicates a strong promoter site. One or more copies of the sequence GGGCGG, called the GC box, are often found upstream from transcription start sites of housekeeping genes. The TATA box has a sequence of TATAAAA.

Enhances are DNA sequences that assist the expression of a given gene and may be located several hundred or thousand base pairs from the gene. They are also called upstream activation sequences because they exist somewhat removed from transcription start site. Their location varies between genes. Such sequences are bidirectional occurring the same in both directions.

Response elements are promoter modules in genes responsive to common regulation. Examples include the heat shock element (HSE), with a sequence CNNGAANNTCCNNG (where "N" is unspecified); the glucocorticoid response element (GRE), with a sequence of TGGTACAAATGTTCT, and the metal response element (MRE), with a sequence of CGNCCCGGNCNC. HSEs are located about 15 base pairs upstream from a transcription start site of a variety of genes whose expression is dramatically changes in response to elevated temperatures. The response to steroid hormones depends on the presence in certain genes of a GRE positioned about 250 base pairs upstream from the transcription start point.

The complexity of these response elements can be seen in considering the metallothionein gene. Metalothionein is a metal binding protein produced by the metallothionein gene. It protects against heavy metal toxicity by removing excess amounts from the cell. Its concentration increases in response to the presence of heavy metals such as cadmium or in response to glucocorticoid hormones. The metallothionein gene promotion package consists of two general promoter elements, namely a TATA box and GC box; two basal level enhancers; four MREs; and one GRE. These elements function independently of one another with any one able to activate transcription of the gene to produce an increase in the metallothionein protein.

As expected, it is both the composition and the shape that is driven by the composition that are important. This shape is maintained through a combination of hydrophilic and hydrophobic interactions, crosslinks, preferred bond angles, and inter- and intrachain interactions. It is a complex combination, but one where we are beginning to understand some of the basics.

The age distribution for various genome sequences is done by comparing changes in similar sequences found in "older" species. This dating has several important assumptions. First, that the rate of sequence divergence is constant over time and between lineages. Second, that the "standard" older sequence is in fact a source of the sequence and that the date for this source is appropriate. These assumptions are at best appropriate so that results derived from such studies need to be considered in this light.

Our genome contains a history of its development, including incorporation and infection by *viruses* and bacteria. Some of these "additions" form part of the so-called "dead regions," while others may allow desired activities to occur. Thus, it is possible that a foreign incorporated bacterial sequence allows the encoding of monoamine oxidase, which is an important degradative enzyme for the central nervous system. The presence of such apparently foreign information in our genome may mean that there is a dynamic nature to our genome that allows for the inclusion of new information into present genomes, and probably, the converse, the removal of segments of information from our genome.

Even so, the large majority of our genome is not borrowed, but rather developed on its own possibly through what are called jumping genes or *transposons* that caused themselves to be reproduced and inserted into the genomes. The *euchromatic* portion of the human genome has a higher density of transposables than found for other species. Further, the human genome has more ancient transposables, whereas other species have more recent transposables.

Most of these transposons move so that the new location is almost selected at random. Insertion of a transposon into an essential gene could kill the cell so that transposition is somewhat regulated and not frequent. Transposons are one of the simplest molecular parasites. In some cases, they carry gene information that is of use to the host.

The most important group of transposons is believed to be the Long Interspersed Element, or LINE groupings (there are three LINE families with only the LINE1 family active), which encode instructions for whatever they need, including copying its DNA into RNA, copying the RNA back into DNA, and moving out of and into the chromosome. LINEs are only about 6000 base pairs in length (6 kb). Interestingly, most of these LINEs are found in the C and G rich or gene poor regions of the genome. The LINEs have other "parasites" accompanying them called *Alu* elements that are only about 300 base pairs long, and these sequences are the most abundant sequences in our genome. (They are given the name Alu because their sequence generally includes one copy of the recognition sequence for the restriction endonuclease AluI.) While Alu elements cannot replicate on their own, they "borrow" the needed hardware from the LINE segments to reproduce. Because of their active nature, they can cause trouble. For instance, in the development of an egg or sperm cell, a replicating Alu segment can be inserted, resulting in a child with a genetic disease. But Alu segments do perform positive functions. They become activated when the body is exposed to stresses, helping modulate the body's response, such as sudden changes in temperature and light and exposure to alcohol. Alu segments are found only in the higher primates and are responsive to a large family of receptor proteins that allow cells to recognize potent hormones, such as estrogen, retionic acid, and thyroid hormone. Their presence appears to allow the surrounding site to be more flexible and to slightly change in shape when exposed to these hormone and hormone-like chemical agents.

In humans, the LINE and Alu families account for about 60% of all interspersed repeat sequences, but there are not dominant families in the other species thus far studied. Alu segments compose about 1–3% of the total DNA and Alu, and similar dispersed repeating sequences comprise about 5–10% of human DNA.

In humans, while less than 5% of the genome contains *coding* sequences, about 50% contain so-called *repeating sequences*. Such sequences are often included in the category of junk DNA, yet they provide a lot of information and some function. Such segments act, as noted above, as a kind of palaeontological record of past interactions with various bacteria and viruses; they can act as passive markers for studying mutation and selection; and they can be active providing shape and function allowing the same sequence to behave in a different fashion because of the presence of these junk sequences.

Repeating sequences can be divided into five classes: first, *transposon*-derived repeats, some of which have been briefly dealt with before. About 45% of our genome is derived from transposable elements. It is possible that some of the other "unique" DNA may also be derived from ancient transposable element copies that we have not yet recognized. The second class is partially or inactive retransposed copies of cellular genes called *processed pseudogenes*. Short, simple repeating sequences such as AAAAAA, CACACACACA, etc., make up the third class. Fourth are short, segmental duplications that have been copied from one region of the genome into another region. These sequences are typically 10,000–300,000 base pairs long (10–300 kb). Fifth are blocks of tandemly repeated sequences.

There are four types of so-called "transposon-derived repeating sequences" of which three transpose through RNA intermediates and one transposes directly as DNA (the latter considered below). We have already identified the long interspersed elements, LINES.

The second set are called short interspersed elements, SINEs, of which the Alu's are the only active members that exist in the human genome.

The third group are the LTR retrotransposons that are flanked by long terminal direct repeats that contain all the transcriptional regulatory elements. LTR genes can encode a protease, reverse transcriptase, RNAse H, and integrase. Transposition occurs through a retroviral mechanism with reverse transcription occurring in a cytoplasmic virus-like particle. While a wide variety of LTRs exist, it is believed that only the endogenous retroviruses (ERVs) are active in humans.

The last group of transposable elements is the DNA transposons that resemble bacterial transposons. They tend to have short life spans within a species. Humans have at least seven families of DNA transposons. Their replication is lessened by the presence of inactive copies so as the number of inactive copies accumulate, transposition becomes less efficient.

As part of the overall human genome, the LINEs, SINEs, LTR, and DNA retroposons make up 20%, 13%, 8%, and 3% (total of 44%) of the repeat sequences.

Such repeats are often included as "junk." Again, the so-called "junk" in our genome may not be junk but rather part of a complex of shape and electrical nature that forms the basis for the chemistries of the various polymeric molecules.

This massive amount of information should not be considered as insurmountable or only material to be marveled at but not understood. Much of the chemistry is already available to "mine" this information successfully. Much of it is understandable in somewhat simple terms, generally only after we have discovered the key to this simplicity. For instance, there is a marked decrease in the frequency of the dinucleotide CpG in some areas of the genome. The deficiency is believed to be due to the fact that most CpG nucleotides are methylated on the cytosine base and spontaneous deamination of the methyl-cytosine residue creates T residues. Thus, CpG dinucleotide sequences mutate to TpG dinucleotides. But there still remains some questions. There are certain regions or islands where the CpG sequences exist in a nonmethylated form and where the frequency of CpG occurs within the expected or normal rate. Why? These CpG islands are of particular interest because they are associated with the 5′ ends of genes.

Another broad finding in examining the human genome regards the rate of *recombination*. Recombination involves the cleavage, rejoining, and insertion of sequences of nucleic acids by enzymes. In fact, recombinant DNA is the result of such recombination. In general, the average recombination rate increases as the length of the chromosome arm decreases. Long chromosome arms have a recombination rate that is about half that of shorter arms. Second, the recombination rate is less near the *centromere* and greater in the more distance portions of the chromosomes. This effect is most pronounced for males. The centromere is an essential site for the equal and orderly distribution of chromosomal units during cell formation, meiosis.

Why these differences? A higher rate of recombination increases the likelihood of at least one crossover during meiosis of each chromosome arm. Such crossovers are necessary for normal meiotic disjunction of homologous chromosome pairs in eukaryote cells. Recombination occurs with the greatest frequency during meiosis, the process where diploid cells with two sets of chromosomes divide producing haploid gametes—sperm cells or ova—with each gamete having only one member of each chromosome pair.

The "crossing over" is not entirely random. Even so, in general, the frequency of homologous recombination in any region separating two points on a chromosome is proportional to the distance between the points. A homologous genetic recombination is simply the recombination between two DNAs of similar (not necessarily the same) sequence. Homologous recombination serves several functions. First, it contributes to the repair of certain types of DNA damage. Second, it provides a transient physical link between chromatids that encourages orderly segregation of chromosomes during the first meiotic cell division. Third, it enhances genetic diversity.

Since such crossover sequences are important, it is possible that they are present to an extent in each arm to insure that crossover occurs, but the full answer is not currently known and since shorter arms are shorter, the density or frequency of them is greater.

We need to remember that our present knowledge of the human genome is a rough map without complete knowledge of the stop lights, detours, alternative routes, pot holes, etc., to use metamorphic language relating a paper map to the actual physical terrain. Scaffolds are being built to fill these knowledge gaps, with time, allowing the scaffolding to become part of a solid building.

The Human Genome—Chromosomes

The preliminary investigation of chromosomes has resulted in several reoccurring themes being evident. One theme is that nature magnifies small differences; often the difference in only a single base pair can lead to marked differences in our overall predicted health, etc. The second theme involves the interrelativeness of the genes with one another and with various proteins that are created by them. A third theme will not be dealt with to much extent. That theme concerns the fact that even though we talk about a common human genome, there are within this human genome sufficient differences to make each of us individuals with our own aspirations and dreams, tendencies toward particular foods and diseases, etc. Even so, most of the human genome is the same with small variances, influenced by our outward environment, resulting in a divergent population of human beings.

We often think of chromosomes as being flat with little or no geographical topology because the sheet of paper or screen we view them on is flat. They are not flat, and it is that three-dimensional structure that assists the various genes in performing their function in designing needed proteins. The secondary structure of chromosomes is more or less helical with as varying clefts, as shown in Fig. 10.26, causing DNA to have varying structures. The transfer of information from the DNA template to protein synthesis, and less so to RNA, is described in the section "Flow of Biological Information" (Sec. 10.8).

Our bodies have about 100 trillion cells and inside each cell is a nucleus; with the exception of egg and sperm cells, inside each nucleus is two copies of the human genome made from DNA with protein building genes contained within chromosomes that make up the human genome. There are a few exceptions to this including the following: Not all genes are DNA, but some contain RNA. Not all genes code for proteins. Some are transcribed into RNA that become part of a ribosome or transfer RNA. While most gene-associated reactions are catalyzed by proteins, a few are catalyzed by RNA. Again, while many proteins are designed by a single gene, some are designed by several genes.

The human genome comes in 23 packages, with each package being a chromosome. This number 23 is important. If we have more or less than 23 then we may well be in great trouble. Only chromosome 21 can be present with more than one copy to have a healthy body, but unfortunately those with an extra chromosome 21 are not normal, but rather have Down's syndrome. The chromosomes are named in general order of size starting from the largest as chromosome 1 through 22, though it has recently been found that chromosome 21 is smaller than chromosome 22. We also have as the remaining chromosome the twined sex chromosomes with women having two large X chromosomes and men having one large X and a small Y. The X chromosome, in size, falls between chromosomes 7 and 8 while the Y chromosome is indeed the smallest. Note that even through the XY chromosome combinations are together one chromosome, researchers often refer to each part in terms of a chromosome though in truth they are only a part of the total twined sex chromosome. The variation from the smallest to the largest of the chromosomes is about 25-fold.

While 23 chromosomes is a relatively large number, it is by no means the largest number of chromosomes within a species. Normal chromosome numbers for selected organisms appear below.

Organism	Chromosome number[a]
Bacteria	1
Fruit fly	4
Pea	7
Frog	13
Fox	17
Cat	19
Mouse	20
Rat	21
Rabbit	22
Human	23
Ape	24
Chicken	39

[a] The diploid chromosome number is double this number except for bacteria.

All eukaryotic cells in our bodies contain the same 23 chromosomes with the same DNA base sequences. The lone differences are the mitochondria. The mitochondria in typical somatic cells contains less than 0.1% of the cell's DNA, but in fertilized and dividing egg cells this number is greater. Mitochondrial DNA, mtDNA, is much smaller, often containing less than 20,000 base pairs. The value for humans is 16,569 base pairs. The mtDNA is a circular duplex. mDNA codes for the mitochondrial tRNAs and rRNAs but only a fraction of the mitochondrial proteins. Over 95% of the mitochondrial proteins are encoded by nuclear DNA. The mitochondria divides when the cell divides.

The association of a particular disease with a particular gene or group of genes is rapidly increasing. A spot check of *www.ncbi.nlm.nih.gov/omim,* the online version of Mendelian Inheritance in Man (OMIN), gives an ongoing updated progress report of this activity. Currently, about 1500 disease mutations have been entered. With the advent of the mapping comes a number of shifts in thinking and activity. Thus, we will move from so-called "map-based" gene discovery to looking at the particular activity of gene sequences; from association of particular gene-associated diseases to looking at tendency and susceptibility for given conditions and the variation with tendency/susceptibility between individuals; from looking at the activity of a single gene or gene location to investigating combined activities of several genes from varying locations; from so-called "genomics" or studying of genes themselves to protenomics and studying of the interaction between the genes and proteins; from gene action to gene regulation; and from specific mutations to the mechanisms and causes of such mutations. Much of this is a guessing game—we hope an educated and educating guessing game. It is currently very costly. As new techniques and strategiees are developed, the cost should decrease.

As noted above, one of the important themes is that small, or seemingly small, changes in the genetic code can have profound effects. Many of the better known diseases contain the names of the discoverers or unfortunate victim(s). The Wolf-Hirschhorn disease and Huntington's chorea are such diseases. They are wholly genetically based or in their case, the result of a missing (Wolf-Hirschhorn) or mutated (Huntington's) gene. It is believed that the genetic origin of the disease is contained in chromosome 4. The coding that is responsible for Huntington's disease is the sequence CAG. This replication occurs varying times. If this sequence occurs 35 times or less then you will not develop the disease. Counter, if you have this sequence 39 times or more, then you will develop this disease with the onset noticeably beginning in mid-life with a slight lose in balance. There begins a decline in metal capacity, and an onset in the jerking of limbs. This continues until death. It generally takes 15 to 30 years to run its course, but there is currently no cure. In general, the greater number of repeat sequences, the earlier the onset of the disease. If you have 40 repeat units, you will exhibit the disease at about 60; if 42 repeat units, you will exhibit the disease by 40; and at 50 repeat units you will be well along in the progress of the disease, and most likely dead, by 30. Thus, the frequency of this sequence in this particular chromosome determines one's outcome with respect to this disease. While both diseases are rare, it is the Huntington's disease that killed noted folk balladeer Woody Guthrie in 1967.

In Huntington's disease, long repeat sequences of CAG appear. The CAG codon codes for glutamine, so that areas that emphasize the buildup of this amino acid appear to offer a greater incidence of certain neurological diseases possibly wherever they are found. This may be due to a buildup of glutamine over a time with the glutamine-rich proteins being "sticky" and more apt to remain at the particular site rather than "moving on" to do what they were supposed to do. After some time, this buildup becomes great enough to block the healthy activity of the gene causing problems and possibly leading to death or noticeable loss of function of the cell. This buildup and death of a significant number of cells takes time, so that is probably why these diseases take time to make themselves known. As an aside, it is interesting that some health potions emphasize the presence of glutamine, but it must be remembered that while the presence of some glutamine is essential to living, it is not the presence of glutamine that may cause these diseases, but rather the coding on the DNA.

Other repeat sequences appear to also offer problems. Many begin in C and end in G. Thus we have large numbers of repeats of CCG and CGG (that code for proline and arginine) that are believed to give a disposition to certain nerve degeneration related diseases.

Another phenomenon is worth mentioning here. There appears to be a tendency for such repeats to become longer through each replication cycle. This is called anticipation and is believed to be related to a very slight tendency for the replication cycle to "lose count" of the number of repeats as the number of exact repeats becomes large, say 30 or more. Again, this is a reason why some diseases take time to manifest themselves, since it takes time for the number of replications to increase to a "dangerous" length.

The Huntington scenario paints a sad picture for our ability to "cure" those with the disease. Are we to modify each chromosome 4 in the billions of cells in our brain? And if so, how? It is not the sequence itself, but rather the length of the sequence that is the problem. All of us have some of these repeat sequences and they are necessary for other essential activities.

While certain behavioral and nonbehavioral diseases are believed to be monogenic, diseases such as Huntington's, cyctic fibrosis, Marfan's, and Hirschsprung result in the specified disease, the outward appearance or result (phenotype) of the disease varies between individuals. For instance, for Marfan's syndrome, there is a level below which the mutant protein does not exhibit itself in an outward manner. Most of these diseases have modifier genes that cause modifications in the outward demonstration of the disease and play a key role in the clinical symptoms. Further, the particular metabolic pathways are often varied with several of the steps being important and the importance of each mechanistic pathway may vary with individual.

We are learning external ways to identify activities and actions that may be related to our genome makeup. One of these observations involves changes in the capacity of individuals to "learn" with age. It appears that the ability to learn language, grammar precisely, decreases as we grow older and is most apparent in children. Thus, ability to learn a language appears to be gene-related. There are genetic conditions that are related to our linguistic ability. One is Williams' syndrome, where affected children have very low general intelligence, but have a vivid and loquacious ability to use language, chattering on in long and elaborate sentences. Thus, they have a heightened ability to learn language. Williams' syndrome is caused by a change in a gene found on chromosome 11.

Another gene-related disease is known as specific language impairment (SLI), where individuals with general intelligence have lowered linguistic ability. SLI is believed to be related to a gene found on chromosome 7.

Genes are related with all aspects of our lives. Someone has said we are what we eat. We can extend this to say that we become what our genes do with what we eat. There is a group of genes called apolipoprotein or APO genes. There are four basis types of APO genes, interestingly known as A, B, C, and E (no explanation for what happened to D; known as APOA, APOB, etc.). Here, we will focus on a specific gene that appears on chromosome 19 know as APOE. As we eat, the various food parts are digested and broken down. Both fats and cholesterol are brought through our bloodstream by lipoproteins, some called very-low-density lipoproteins (VLDLs). These fats and cholesterol are brought to various parts of the body to act as fuel and building blocks. As the triglycerides are delivered, the proteins are then called low-density lipoproteins (LDL), known to many of us as "bad cholesterol." After delivering the cholesterol, it becomes high-density lipoproteins (HDL), also known to us as "good cholesterol" which then returns to the liver to be replenished with cholesterol and fats. The APOE protein acts to effect the transfer between VLDL proteins and a receptor on a cell that needs some triglycerides. APOB serves a similar role except in delivering cholesterol. Thus, the presence and effectiveness of genes that code for the APO genes helps control our weight and health, affecting such items as buildup on our arteries.

APOE is unusual in that it is polymorphic having several versions. The three most common are know as E2, E3, and E4. E3, deemed the best variety of APOE, is the most common in Europeans with about 80% having at least one copy and about 40% with two copies. But about 7% have two copies of the E4 gene, the worst variety, and they are at high risk of early heart disease. These trends of APOE are geographical and correlate with the frequency of heart disease. Thus, the frequency of E4 is about three times as high in Sweden and Finland as in Italy, and the frequency of coronary heart disease is also about three times as high in Sweden and Finland in comparison to Italy. On a race basis, orientals have the lowest frequency of E4 (ca 15%), with American blacks, Africans, and Polynesians all having higher values of E4, about 40%. Diet also contributes so that while New Guineans have a high frequency of E4, their diet is low in fats, and they have a low incidence of heart disease. But when they change their diet so that it is similar to many American diets, they become more susceptible to heart disease.

Our blood type is determined by a gene that is present on chromosome 9, near the end of the long arm. There are four general blood types, A, AB, B, and O. Some of these are "intermixable," while others are not. For instance, A blood from a person is compatible with A and AB; B with B and AB; AB only with AB; and O blood is compatible with all of the blood types—a person with type O is then a universal donor. These compatibility scenarios are not race-related. For all but the Native Americans who have almost universally type O, the rest of us have about 40% type O; 40% type A; 15% type B; and 5% with type AB. (Some of the Inuits are type AB or B and some Native Canadians are type A.) A and B are codominant versions of the same gene, and O is the "recessive" form of this gene.

The active codons of the blood-type gene are about 1000 base pairs long and are divided into six short and one longer sequence of exons. The difference between the type A and type B gene is seven letters of which three do not make any difference in the amino acid coded for. The four truly different bases are positioned at sites 523, 700, 793, and 800 and are C, G, C, G for type A, and G, A, A, C for type B blood. Type O people have just a single change from the type A people with a deletion in the type A base at base pair 258, omitting the G base. While this appears to be very minor, it is significant in that it causes a reading or frame-shift mutation. These seemingly minor changes are sufficient to cause the body to have an immune response to different types of blood. Even so, while this causes a different type of blood, it appears to have little or nothing to do with other parts of the overall human genome, so that tendencies toward cancer, ageing, etc., are not influenced by this change but it appears to have something to do with some general tendencies toward some diseases. For instance, those with AB blood are the most resistant toward cholera, while those with type O blood are most susceptible. Those with two copies for the sickle-cell mutation generally contract sickle-cell anemia, while those with one copy of the mutation are more susceptible to contracting sickle-cell anemia than the general public, but they are more resistant to malaria. Some of these connections can be found in tracing the ancestry of individuals with the particular connections between blood type and susceptibility.

Recently we have been working on Parkinson's disease. Parkinson's disease, and other similar diseases, are due to a depletion of dopamine in the corpus striatum. Direct addition of dopamine is not effective in its treatment, presumably because dopamine does not cross the blood–brain barrier. However, levodopa, the metabolic precursor of dopamine, does cross the blood–brain barrier and then is believed to be converted to dopamine in the basal ganglia.

On the short arm of chromosome 11 is a gene known as D4DR that manufactures the protein dopamine receptor. It is active in some parts of the brain and not active in other parts. Dopamine is a neurotransmitter released from the end of neutrons by an electrical signal. When the dopamine receptor is exposed to dopamine, it also releases an electrical signal. In general, much of the brain activity is related to such stimulation of chemical reactions by electrical changes, and counter, electrical current calling for chemical reactions. Many of these exchanges occur essentially at the same time.

Our brain is often compared to the operation of a computer. In some sense it is similar, but in other senses it is not. In our brain "switches" are activated and closed, opened and shut, not simply by electrical charge, but rather by an electrical switch associated to a very sensitive, selective chemical site.

Brain sites that have an active D4DR are then part of the brain's dopamine-mediated system. A lower amount of dopamine causes this part of the brain's system to either shut down or be less than fully active and in extreme cases resulting in Parkinson's and related diseases. Excess of dopamine may lead to schizophrenia. Some hallucinogenic drugs act to increase the amount of dopamine. Thus, there is a narrow margin between good health and illness.

D4DR has a variable repeat sequence in it about 48 base pairs in length. Most of us have between 4 to 7 such sequences. The larger the number of repeat units, the more ineffective the dopamine receptor is at capturing dopamine, while a low number of such repeat sequences means the D4DR gene is highly responsive to dopamine. In some preliminary personality studies focusing on the number of these repeat sequence, it was found, in general, that those with only a few (one or two) sequences appeared to be more adventuresome than those with a larger number of repeat sequences. Again, here we are looking at tendencies that are greatly shaped by our individual circumstances. Behavior tendencies are also implicated by other monoamines such as norepinephrine and serotonin.

Such wholly-caused gene diseases are at one end of the spectrum. More likely, gene composition declares tendencies, some of these are somewhat random tendencies and others are related to our lifestyles—both voluntary and involuntary. Thus, single genes that dictate aggression, being good natured, intelligence, criminal impulse, etc. are not present. Most of our tendencies are just that—tendencies—and such tendencies are complex and involve the interaction of many genes and the associated proteins, as well as external forces and opportunities. Genes in such multiple-gene systems are called quantitative trait loci (QTIs), because they are apt to produce similar behaviors within different people.

Behavioral related illnesses and patterns, both so-called "healthy" and "non healthy," are complex and involve many factors including external factors, both learned and simply exposed-to factors. As these studies continue, two features are emerging. First is a tendency (not certainty) for this trait to be inherited. This tendency is generally greater than is the tendency with respect to physical disease. Second, environment plays a role. Similar environments produce similar people and different environments for related people produce different people.

As noted before, there are probably few single-gene-associated (monogenic) diseases; most involve a number of genes. These diseases are called complex or multifactorial diseases, or as noted before, called quantitative trait locus (QTL) disorders or diseases.

Similar animal studies are useful in studying such diseases where a so-called "similar animal" is available. The term similar animal simply means an animal that contracts the same disease because of a similarity in the disease-causing gene complex. Because of the similarity found between the genes of varying species, such similar animals should be available for many diseases.

Attention deficit hyperactivity disorder is believed to be related to genes associated with the dopamine system, namely DAT1, DRD4, and DRD5. Schizophrenia has been reported linked to genes on chromosomes 1, 5, 6, 10, 13, 15, and 22. As the human genome map is better understood, such combinations will become more evident. Finding such QTLs is the initial step. Next comes identifying the particular interactions between the

QTLs and the various proteins produced by them, and finally what, if anything, can or should be done to correct or modify the situation.

The Huntington-related problems, while deadly, are visually simple in relation to some other gene-related problems. Asthma is a disease that has multiple causes and symptoms and appears to be the consequence of groups of genes acting in multiple ways, some of which may be positive and others that cause asthma. Asthma, allergy, anaphylaxis, and eczema are all caused by mast cells altered and triggered by immunoglobulin-E molecules. I am allergic to certain foods and used to be allergic to certain plants like ragweed. I outgrew much of the ragweed-like allergies, but retain the food allergies. This is typical: Allergies can come and go, are of varying severities, and can vary with age, sex, and race. While there is evidence to tie asthma to genes, the precise group of genes remains unknown and surely will be more complex than that of the Huntington-related diseases.

A brief review of the meiosis process is in order. In the first step, the chromosomes of a cell containing six chromosomes, three homologous pairs, are replicated and held together at their *centromeres*. Each replicated double-stranded DNA is called a *chromatid* or *sister chromatid*. In the next step, the three homologous sets of chromatids align forming *tetrads*, which are held together by covalent bonding at homologous junctions called *chiasmata*. Crossovers (recombinations) occur such that the two tethered chromosomes segregate properly to opposite poles in the next step. This is followed by the homologous pairs separating and migrating toward opposite poles of the dividing cells. This first meiotic division gives two daughter cells, each with three pairs of chromatids. The homologous pairs again line up across the center or equator of the cell in preparation for separation of the chromatids, chromosomes. The second meiotic division produces four haploid daughter cells that can act as gametes. Each cell has three chromosomes, half the number of the diploid cell. The chromosomes have resorted and recombined.

We have just considered mitosis in general. We can take a simplistic look at the determination of whether a given embryo is a male or female. Females have two X chromosomes, while males have one X and one Y, so that the ability of the X chromosome to overwhelm the Y chromosomes and give only female embryos is favored on a statistical basis. On a size basis, the Y chromosome is the smallest of all the chromosomes while the X is among the largest. Further, the Y chromosome is largely composed of noncoding DNA, giving few targets for the X chromosome to interact with. The gene on the Y chromosome that makes men men is called the SRY gene. The SRY gene interacts with the DAX gene on the X chromosome. In some sense, these two genes are antagonistic to one another, where two DAX genes overcome the single SRY gene but one SRY gene overcomes one DAX gene. Depending upon the particular course of events, the outcome is a male or female. The SRY gene, when activated, ignites a whole cascade of events that leads to the maculation of the embryo. The SRY gene is peculiar in that it is remarkably consistent between men, with essentially no variations in the coding regardless of race. Further, the human SRY gene is very different from those of other primates.

For many species, this XY battle greatly favors one sex, generally the female, over the other. For instance in the butterfly *Acrea encedon*, 97% of the butterflies are female. But in humans, the competition is such that the ratio of males to females is about but not exactly, one to one.

We will look at another example where the “equal” splitting of chromosome information is not entirely true. Some families have members that exhibit two related diseases. Those with the Prader-Willi syndrome are characterized with small hands and feet, have underdeveloped sex organs, are generally obese, and are also often mildly mentally retarded. Those with the Angelman's syndrome are taut, thin, insomnic, small-headed, move jerkily, have a happy disposition, are always smiling, are generally unable to speak, and are mentally retarded. In both cases, a section of chromosome 15 is missing. In the Prader-Willi syndrome, the missing part is from the father's chromosome, but in the Angelman's syndrome, the missing part is from the mother's chromosome. Thus, the two diseases differ depending whether it is transmitted through the male or female.

Related to this are recent attempts to produce unisex children—that is, embryos that are from male–male and female–female sources of chromosomal material. In both cases, the attempts failed. The "two-mother-derived" chromosomes could not make a placenta, and the "two-father-derived" chromosomes could not make a discernible head. Chromosomes from both sexes are required to give a healthy, successful embryo.

We now move to what makes a single egg–sperm combination grow into a child. It is a combination of special events of which we will look at only one aspect. The machinery to construct a person is found in our chromosomes. One cluster of these developmental genes is found in the middle of chromosome 12. Within these genes is a grouping of homeotic genes that reside in the same general area. These genes are called the Hox genes and affect the parts of the body in the exact sequence that they appear in the fruit fly: mouth, face, top of head, neck, thorax, front half of abdomen, rear half of abdomen, and finally the other parts of the abdomen. Also found in each of these homeotic genes is the same sequence of about 180 base-pairs long that is believed to act as a switch to turn on or off each gene referred to as the homeobox. Mice were examined and also found to have such homeotic genes and homeoboxes. Mice have 39 Hox genes in four clusters with some differences, but many similarities, with the fruit fly. We have the same Hox clusters as mice with one such cluster, Cluster C, on chromosome 12. A practical implication is that all the work done with other species, such as the fruit fly, may be useful as we look at our own genome with at least such developmental genes.

The similarity of the embryo genes between us and other species allows developmental scientists a filled table of data to sort over. It does not eliminate nor confirm a so-called "master designer" since one can argue about the simplicity and interrelatedness of the design as to origin and the ability through ordinary evolution to design such complex items as our human eye.

The imprinted region of chromosome 15 contains about 8 genes, one of which is responsible, when broken, for Angelman syndrome—a gene called UBE_3A. Beside this gene are the two top candidates for the Prader-Willi syndrome when broken, one called the SNRPN gene and the other called IPW.

While these diseases normally occur because of mutation of these genes, it may also occur from a pair of parental chromosomes failing to separate, with the egg ending up with two copies of the parental chromosome. After fertilization with a sperm, the embryo has three copies of that chromosome, two from the mother and one from the father. While the embryo generally dies, in some cases it persists. If it persists and it is chromosome 21, then the result is a Down, syndrome child. But normally the body detects the mistake and "kills" one of them. It does so nearly randomly, so that there is about a one-third chance of eliminating the paternal-derived chromosome. Generally, there is no problem, but if the tripled chromosome is number 15 then there are two copies of UBE_3A, the maternally imprinted gene, and no copies of SNRPN (or IPW) exist resulting in a Prader-Willi syndrome child. Recently it has been found that UBE_3A is switched on in the brain. This leads us to another unfolding saga, that of imprinted genes being controlled "directly" by the brain. In mice, it is believed that much of the hypothalamus, found at the base of the brain, is built by imprinted genes derived from the father, while much of the forebrain is built by imprinted genes derived from the mother.

What is intelligence? There are different "kinds" of intelligence. The so-called "IQ Intelligence" appears to be related to the ability to gain, understand, remember, and relate information, and it is believed that about one-half is in some way related to our genes. So, unlike the Huntington diseases, while there is a genetic link, it is not an absolute link. Several chromosomes and genes within these chromosomes are beginning to be identified as "smart" genes. One of these genes, called IGF_2R, is found on the long arm of chromosome 6. This gene was first linked to liver cancer, so it shows the variety of capability that may be present within a single gene. IGF_2R is a large gene with the typical exons and introns. Among its varied activities is its involvement in the metabolism of sugar. One form of this gene is found in greater frequency in supposedly super-smart people than in so-called "average intelligence" people. Thus, there appears to be a relationship between the occurrence of one form of this gene and intelligence. This is circumstantial evidence at best, but it is a start. An interesting side note is the observation that people with high IQs are, on the average, more effective at metabolizing sugar, and that this gene is sometimes connected with insulin related proteins and the ability to metabolize sugar.

We again must not believe that IQ-related intelligence irrevocably binds us or propels us. Harvard did a study some time ago where they tried to relate intelligence to success (whatever success is) and came up with a relationship that success was related to intelligence times the square of effort.

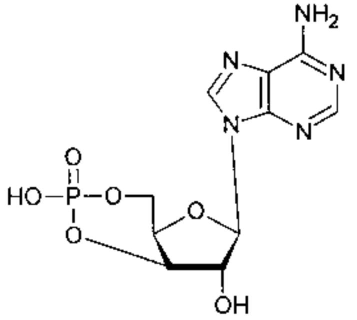
Learning is related to intelligence. In general, the more apt we are to learn, retain, integrate, and use information the more intelligent we are. Since our brains are really limited in storage of information and for other reasons, intelligence requires an interesting mix of remembering and forgetting, a short term memory and a long-term memory. Our input is also mixed. We have a kind of filtering system that filters out supposedly unwanted input, such as a constant ticking of a clock or constant hum of the fluorescent light.

One of the active agents is cyclic AMP. A protein called CREB (for CRE binding protein; CRE is simply a specific DNA unit, part of a gene, that is called the cyclic AMP response element or site) is activated altering the shape and functioning of the synapse in our brains when exposed to cyclic AMP or some related compound in our brains. Genes that are activated are called *CRE genes*. CREB, when phosphorylated, binds to the CREs near certain genes acting as a transcription factor and turning on or activating the genes. Animals without the CREB-producing gene are able to learn, but do not possess long-term memory. It is believed by some that the CREB-related genes are in fact essential to our learning and memory and act as master switches in activating other genes necessary in our learning/memory process. The CREB gene is on chromosome 2. A related and essential gene that helps CREB perform is found on chromosome 16 and is given the name CREBBP.

Another essential "learning gene," related to alpha-integrin, is also found on chromosome 16: (Integrins are proteins with two unlike units called alpha and beta that are anchored to the plasma membrane. They act as molecular adhesives and also as receptors and signal transducers.) This gene, called the *volado* (in Chilean means "forgetful") gene, appears to be a player in memory and it is not involved in the cyclic AMP sequence. The volado gene codes for one of the subunits of alpha-intergin. The volado's gene appears to act to tighten connections between neurons as we learn.

We are aware of certain drugs that interfere with the activity of integrins by interfering with a process called long-term potentiation (LTP), which is an essential part of creating a memory. In the base of our brain is a part called the hippocampus (Greek for seahorse). A part of the hippocampus is called the Ammon's horn (named for the Egyptian god associated with the ram). The Ammon's horn has a large number of pyramidal-shaped neurons that assemble the inputs of secondary neurons. Single inputs appear not to "fire" these neurons, but when two or more inputs arrive at the same time the neuron fires. Once fired, it is easier to again fire when one of the two original inputs arrive. Thus, in a real sense memories are made in the hippocampus. In relation to the human genome, the brain is much more complex, and it is controlled by a matrix of activities including our genome. It operates on a three-dimensional network rather than a one- or two-dimensional somewhat flat chromosome face—so artificial intelligence has a long way to go to mimic the human brain.

It is a group of genes found on several chromosomes that give us the ability to learn and retain information. We are just beginning to discover the genome elements responsible for this wonderful ability.



(18.30)

Cyclic AMP

Only vertebrates show an immune response. If foreign objects, called *antigens*, gain entry into our bloodstream, a molecular-level protection system, called the *immune response*, goes into action. This response involves production of proteins capable of recognizing and destroying the antigen. It is normally mounted by certain white blood cells called the "*B*" and "*T*" *cell lymphocytes* and *macrophages*. B cells are called that because they mature in the bone marrow, and T cells mature in the thymus gland. Antibodies that "recognize" and bind antigens are immunoglobulin proteins secreted from B cells. Because the antigens can be quite varied from the protein inserted from an insect bite, to pollen, etc., the number of proteins that can "recognize" and bind this variety of invaders must be quite large. Nature's answer to creating such a great host of antibodies is found in the organization of the immunoglobulin genes that are scattered among multiple-gene segments in germline cells (sperm and eggs). During our development and the formation of B lymphocytes, these segments are brought together and assembled by DNA rearrangement (genetic recombination) into complete genes. DNA rearrangement, or gene reorganization, provides a mechanism for creating a variety of protein isoforms from a limited number of genes. DNA rearrangement occurs in only a few genes, those encoding the antigen-binding proteins of the immune response—the T cell receptors and the immunoglobulins. The gene segments encoding the amino-terminated part of the immunoglobulin proteins are also quite susceptible to mutation. The result is a collective population of B cells within most of us with the ability of producing the needed vast number of antibodies. Thus, gene variety is produced near to conception.

As noted before, a single gene may play several roles, or at least the proteins derived from them may. Several genes have been associated with the early onset of Alzheimer's disease, two found on chromosome 14, one on chromosome 21, and interestingly one on chromosome 19, none other than APOE. It is not unexpected (many results are not unexpected after the fact) that a blood–lipid related gene is associated with a brain disease. It has been found for some time that those with Alzheimer's disease had high cholesterol levels. Again, the bad actor is the E4 variety. For those families that are prone to Alzheimer's disease, those with no E4 gene have about a 20% chance of contracting the disease; those with one E4 almost 50% with a mean age of 75 for onset; and for those with two E4 genes, the probability is over 90% with the mean age of onset about 68 years of age. Other genes also affect the incidence of Alzheimer's disease. For instance, the incidence of contracting the disease is much higher for whites with the same E4 amounts in comparison to blacks and Hispanics.

The difference between E4 and E3 is a signal base pair, the 334th base pair with the E4 having a G instead of an A.

The body is a marvelous "machine", growing, learning, and performing its own maintenance. Much of this maintenance is a sort of self-preservation or self-protection to maintain its own original molecular design. Involved with much of this are DNA repair enzymes that continuously monitor the genome to correct damaged nucleotides and nucleotide sequences that are damaged through self-inflected mutations or through environmentally related damage, such as exposure to various chemical agents and radiation. There are currently about 150 known human DNA repair genes where the function (or at least one function) is known along with its location within the genome. The particular sequence is also known for most of these; the sequences for many of these genes have been known for several years, but the specific location and proximity to other genes has only become known with the recent human genome project. These repair genes perform a number of functions. MSH2 and MSH3 found on chromosomes 2 and 5 are involved with mismatch and loop recognition repair. A group of genes known as fanconi anemia (FAN genes) are found on chromosomes 3, 6, 9, 11, 16, etc., and are involved with repair of DNA crosslinks. The overall shape of these DNA repair proteins is rapidly being uncovered and active sites being identified.

Now let us look briefly at an aspect of aging. We are given, or so we are told in literature, our fourscore or 80 years. We are not able to describe why eighty, but can comment on why this number is not much larger. The human genome is much longer lived and its copying has occurred many times. Yet the cells in our body have only replicated a few times in comparison. Even the more active cells have replicated only several hundred times. Part of the answer resides on chromosome 14 in a gene called TEP_1. This gene forms a protein that is part of the telomerase system. Lack of telomerase causes senescence. Addition of telomerase allows some cells a much longer lifetime. Telomers, produced by telomerase, occur at the end of chromosomes. These telomers are included in the so-called "junk" with a seemingly uncoded sequence, TTAGGG. This sequence is repeated many times. This sequence is the same for all mammals and is the same for most living species. Typically, each time the chromosome is reproduced, the number of "telomer sequences" decreases, at the average rate of about 30 base pairs a year, and may be partially responsible for the various cells "wearing out." By the time we reach our fourscore years, we have lost about 40% of the telomer sequences.

The telomerase contains RNA, which is used as the template for making telomeres, and a protein part that resembles reverse transcriptase, the enzyme responsible for the production of transposons and retroviruses. Telomerase acts to repair the ends of chromosomes, relengthening the telomere ends. Thus, the lack of telomerase appears to cause the aging and eventual death of at least some of our cells. The relation to aging is much less certain, and surely more complicated. Thus, those with Werner's syndrome where rapid aging occurs, start out with the same average length of telomers, but the telomers shorten more rapidly so that at least cell aging involves not only the length of telomers, but also the rate at which they become shorter. Recently, it was found that certain genes on chromosome 6 appear with differing versions for long-lived males, and other versions for long-lived females.

In the laboratory, the immortal cell lines are those derived from cancer. The most famous is the HeLa cancer cells that many researchers use as one of the cell lines tested against various anticancer agents. The HeLa cells are derived from Henrietta Lacks, a black woman, who died from cervical cancer. They are so strong that they are known to invade other cell lines, both healthy and other cancer cell lines, giving contaminated or mutated cell lines. HeLa cells have good telomerase levels. If antisense RNA is added to HeLa cells so that the RNA contains the opposite message to the ordinary RNA in the telomerase, the effect is to block the telomerase and the HeLa cells are no longer immortal and die after about 25 replications.

It is estimated that about 700 genes are probably involved in the overall aging process, and TEP_1 is only one of these.

It can be argued as to whether all cancers occur as a direct result of our genes, but the relationship between cancer and genes is present. We are aware that many chemical agents and high-energy radiation that result in cancer do so through damaging DNA. Oncoviruses are also known to cause cancer, and these oncoviruses are not viruses but are really genes. In general, cancer genes are genes that cause growth. Fortunately, we have other genes that detect excessive growth and whose job it is to stop the growth. These genes are called tumor-suppressor genes as opposed to the oncogenes. The misfunctioning of either can result in cancer. If the oncogenes are not switched off then cancer occurs, and if the tumor-suppressor genes are not permitted to work, cancer occurs.

On the short arm of chromosome 17 is a gene called TP_{53}. This gene is a tumor-suppressor gene and it codes for the production of a protein called p53 that is being tested as an anticancer drug. TP_{53} is found to be broken in over 50% of tested human cancers and is found broken in 95% of those with lung cancer. The most resistant cancers such as melanoma, lung, colorectal, and bladder are ones where mutated TP_{53} are found. Further, where a patent initially responds to treatment, but then develops resistant cells, again it is often found that the TP_{53} genes have mutated. (Thus, it should be possible to look at this gene to see if it has been mutated to see if additional chemo may be useful in the treatment of a particular cancer.) Those born with one of the two TP_{53} genes broken have a 95% chance of developing cancer, and generally early in their lives. We can look at the progress of colorectal cancer. Here, cancer begins with a mutation of the tumor-suppressor gene APC. If the developing polyp then undergoes a second mutation causing an oncogen to operate without restraint, the polyp becomes an adenoma. If the adenoma then undergoes a third mutation of a tumor-suppressor gene, then it continues to grow. If a fourth mutation occurs, now in the TP_{53} gene, it becomes a full-blown carcinoma. Many other cancers follow a similar scenario often with TP_{53} as the final mutated tumor-suppressor gene. Thus, this gene appears to be important in the production of cancer and in the fight against it.

TP_{53} is about 1179 base-pairs long and it encodes for the production of the protein p53. This protein is normally rapidly degraded by other enzymes with a half-life of only about 20 min. When a certain signal occurs, protein production greatly increases, and its degradation becomes less rapid. The signal appears to be caused by selective damage to DNA with the damaged parts calling for production of excess p53. The p53 protein then "takes over" the cell, activating—essentially causing the cell to either stop making DNA until repair is made—or signals to the cell to commit suicide. Another indicator for p53 is a shortage of cellular oxygen. Cancerous cells often outgrow their oxygen availability so that they send out new arteries to capture more oxygen for themselves. Some of the drugs being developed are aimed at preventing such adventurous artery formation.

Opposing forces operate in our bodies, often guided by our genes. These opposing forces or activities are both important but become dangerous when not held in check. Thus, oncogenes cause cell growth necessary for injury repair and cell replacement. They are held in check by tumor-suppressor genes. Interestingly, some oncogenes, such as the MYC gene, also hold in their code cell death. The death code is held in check by chemical signals know as survival signals. Thus, if the MYC cell begins to operate in a cancer mode, the cell is signaled to kill itself. There are in fact three different oncogenes, MYC, RAS, and BCL-2 that appear to hold one another in balance. Normal cells can exist only if all three of these oncogenes are operating "correctly."

When we take the sum total of humanity, it is not our human genomes, but rather a complex group of events that include our genome that actually make us what we are. In some cases, the genome casts boundaries; but more likely, it tells us probabilities, though some outcomes are so sure as to be nearly certainties. We are humans with moral, ethical, and gene-driven tendencies and freedoms. We have just begun another trip where moral, ethical, and gene-driven aspects all play a role—good fortune and wisdom to us in this new adventure.

The secrets of the human genome are just beginning to be uncovered, discovered, understood, and finally utilized. It is an eventful, important trip to which we are both witness to and have an essential stake in, and some of us may take an active part in.

I refer you to this timely, lively, interesting, and easy-to-read book: M. Ridley, *Genome*, HarperCollins, NY, 1999, for an "easy read" about the human genome.

18.11 PROTEOMICS

We have looked especially at the human genome (Sec. 18.10), but the same techniques that have been used to decode the human genome have also been used, and are being used, to decode other important genomes. The aim of many of these "decodings" is to select sites of opportunity with respect to future drugs and treatments.

British scientists have deciphered the genetic blueprint of *Yersinia pestis*, the bubonic plague, a.k.a. Black Death, the microbe that killed one-third of medieval Europe [Nature 413, 523–527 (2001)]. While bubonic plague is no longer so feared, it nevertheless represents one of a host of similar potential biological weapons, and so understanding its blueprint might assist us in understanding other similar bacteria. It will also assist in developing antibiotics and vaccines to treat this and similar diseases. Unfortunately, bubonic plague still kills about 2000 people yearly and the incidence is increasing. The plague is the original biological weapon used in 1347 by the Tartars laying siege to the Genoese-controlled Black Sea port of Caffa. They hurled the bodies of plague victims over the city walls and when the infected Genoese sailors returned to Italy, it signaled the beginning of the Black Death.

It is interesting to note that most infectious diseases mutate readily, with many mutating toward destruction, but during its infectious stage this ability to mutate makes it difficult to control. This may include tuberculosis, anthrax, and typhoid, that appear to be of relatively recent origin. Thus, several thousand years ago, *Yersinia pseudotuberculosis* was a somewhat benign gut-dwelling bacteria. *Y. pestis* is a descendent of *Y. pseudotuberculosis. Y. Pestis* mutated to live in blood instead of the intestine to cause swelling, coughing, and hemorrhaging. It infected human beings through fleas, often found on rats. The mutations resulted in *Y. Pestis* having about 150 pseudogenes, redundant stretches of DNA that were no longer active in the organism. The key to its success, and hopefully eventual demise, is the high ability to shuffle parts of its chromosome. Of the almost 150 pseudogenes, 51 are a consequence of disruption by insertion sequence elements comprising about 3.7% of the complete genome.

Among acquired DNA are several genes that appear to come from other insect pathogens. These acquired genes may have allowed the jump from the gut of animals to the flea, rats and other animals, and to us. The genome sequence of *Y. Pestis* also has a range of genes that appear to encode previously unknown surface antigens that may play a role in its virulence.

Malaria is caused by four closely related parasites. The most dangerous is *Plasmodium falciparum*. The Malaria Genome Sequencing Consortium in 1999 announced the mapping of its genome (Nature, August 5, 1999). It contains 215 protein-encoding genes. To sequence the genome, the "whole-sequence shotgun" approach was used. Essentially, this approach shreds the chromosome into small segments that are then sequenced and finally pieced together. This was particularly difficult in this case because of the large numbers of repeated sequences. As in the case of the human genome, a centromere was identified along with telomers appearing near the ends of genes. Also near the ends are genes that are needed by the organism to cause malaria in human beings.

Cholera is one of the most rapidly "common" fatal illnesses, often killing within hours. During the nineteenth century, it was know as King Cholera, being responsible for millions of deaths. While somewhat under control, recent outbreaks have affected many nations. Most antibiotics and medicines have little effect on cholera; it can be treated through replacing fluids and minerals lost by vomiting and diarrhea. It is caused by the bacteria *Vibrio cholerae* whose genome was recently decoded [Nature, 406, 477–483 (2000)]. Its particular genome should allow researchers to uncover the answer to several puzzles. First, determining how cholera can exist in two such different surroundings. Between epidemics, it lives in saltwater estuaries. The second involves the splitting of its DNA between two circular chromosomes. Essential functions appear to be divided between the two chromosomes. The larger loop is involved in DNA replication, cell division, and protein translation, while the smaller loop is involved with sugar transport, DNA repair, and metabolism. Genes calling for diarrhea symptoms are found in the larger loop.

Another of apocalyptic diseases has also been undressed and decoded. Louse-borne typhus has been responsible for millions of deaths. There are several strains of typhus. The so-called "Madrid E" strain of *Rickettsia prowazekii* has a relatively small genome with only 1,111,523 base pairs. That is only about one quarter of its distant relative *Escherichia coli*. This is not surprising. *Rickettsias* do not live among human and animal cells but rather they live within them. Like viruses, these bacteria are obligate intracellular parasites and cannot propagate outside a host cell. It does not need genes for enzymes needed to make amino acids and that are needed to make proteins, or nucleotides to repair or make their own DNA, but rather “borrow” the hosts machinery. As noted above, many infectious bacteria are undergoing a sort of devolution into oblivion. The genome of *R. prowazekii* has about 25% of its DNA as junk, whereas many bacteria have only about 10% junk. *R. prowazekii* is unable to respire by digesting glucose in the absence of oxygen, a process know as anaerobic glycolysis, a biochemical pathway known to almost all living organisms. Instead it has genes that allow aerobic respiration to occur where energy from carbohydrates is turned into ATP with the help of oxygen.

The major reason for carrying out each of these genome decodings is to relate particular genes and gene segments to possible drugs and related treatments. Critically involved in most of this next effort is “proteomics.” Probably for defensive reasons, because of the overwhelming amount of information, possibilities, and techniques required, subdivisions are present so that some research groups focus on protein structures, others on DNA structures, others on the interaction between the two, others on target molecules/sites and still others deal with specific diseases or biological responses. One such subdivision has been given the name “proteomics,” which deals with the interfacing or bridging between genomics or gene information and drug or target molecule activity. While we have uncovered over 75,000 sequences of the human genome, we have just begun to look at this “raw” information for actual active or target sites. We need to remember that we are looking at the master template, the DNA genome, its interactions with various proteins at each of the real and potential sites of action, and finally target sites and molecules to effect specific biological responses. Let us remember that this is polymer science in its truest form.

Almost three quarters of the known proteins have no known cellular function, but as we have learned in the past, nature seldom has true “junk” in its biological pile of macromolecules. In addition to identifying specific target and target molecules, other discoveries are important such as new enzymes, signaling molecules, pathways, and finally mechanistic behaviors and factors. Identification of such factors will allow better drug discovery and activity downstream. Factors that will be needed in this hunt include the following.

1. There is needed a more complete understanding of the behavior of particular proteins. This includes such seemingly pedestrian, but critical, activities as providing pure and structurally and chemically unaltered proteins. This “unaltered” form includes confirmational as well as configurational aspects. It is known that proteins and protein fragments may be misfolded when reproduced employing a variety of reproductive techniques. These wrong structures can cause incorrect test results and when present as part of a large data bank, point the scientist in the wrong direction, or alternately, not point them in the right direction.

2. While we have over 100,000 proteins in each of us, only a fraction are expressed in any given cell type. Thus, it is a complex and puzzling problem to accurately match protein activity to some biological response. One emerging tool is to measure the relative abundance of mRNA in a cell because there is a not unexpected relationship between protein concentration and mRNA concentration. However, these correlations do not always follow, sometimes because the regulatory processes occur after transcription, so that caution must be exercised. Thus, the direct measure of the concentration of the particular protein is a better measure. Such protein determination is often achieved by traditional analytical tools such as coupling some chromatography technique such as electrophoresis

with MALDI (mass spectrometry). Other biological techniques are employed, and sometimes these are coupled with traditional analytical techniques.

3. Screens are being developed that look at the many potentially active sites on each of the genome fragments. These screens often evaluate selected catalytic activity of the particular sites. As we look at the large proteins and DNA fragments, we need to be aware that the presence or absence of small possibly important molecules is critical to the site activity. Again, knowing the precise identity of the site in question is critical. We also need to be aware that the particular site testing may be the wrong test and may not unlock the true site function or capabilities.

4. Simple language. Because of the need for the involvement of diverse groups, common language problems will develop. This is true even between seemingly like medically related specialities. Thus, it is important that we define our terms as we work with other colleagues in related fields.

5. We need to recognize important driving or overriding factors. Structure is one of these. It is being found that structural similarities may be employed as one (notice only one) factor in determining site activity. Thus, it is important that precise three-dimensional site geometry is known including surrounding geometries. This is time and instrument intensive and short cuts are being developed, but as always caution must be exercised. Creation of shared structural data banks is occurring. Computer modeling efforts are particularly useful in helping solve such structural problems.

6. If the vast array of sites and site-important molecules is not enough, protein–protein interactions are part of most cellular processes including carbohydrate, lipid, protein, and nucleic acid metabolism, signal transduction, cellular architecture, and cell-cycle regulation. In fact, many of the major diseases are believed to involve a breakdown in such protein–protein interactions. These include some cancer, viral infections, and autoimmune disorders.

Techniques to discover the identity of such protein–protein interactions are evolving. One approach involves protein affinity chromatography. Here, the purified protein of interest is immobilized on a solid polymer support and proteins that associate with them are identified by electrophoresis and MALDI. There exists a wide number of modifications to the affinity chromatography approach. For instance, a number of proteins can be fixed to the support in such a manner to look at target molecule interactions as well as nucleic acid protein interactions, etc. You can also run through a variety of possible binders and select the ones that bind most strongly for further study. Thus, affinity chromatography is a powerful and versatile tool in this search.

A large sea of information is becoming available to us. How do we handle it? What sense does it make? Again, we will turn to two powerful tools, the computer and ourselves.

18.12 OPTICAL FIBERS

Today, almost all telecommunication occurs via optical fibers rather than metallic wires. Signal transmission with metallic wires was via electrons, while transmission through optical fibers is via photons. For a rough comparison, two small optical fibers can transmit the equivalent of over 25,000 telephone calls simultaneously or in one second the information equivalent to about 2 hours of TV shows. On a weight basis, 1 g of optical fiber has the transmission capability of about 300,000 g of copper wire. The signal loss must be small. For a typical system the loss over a ten mile distance is about that found for the transmission of light through an ordinary pane of window glass.

Optical fibers connect the two longest links of a typical optical fiber communications system. Briefly, an input signal enters an encoder generally in electrical form with the encoder transforming it into digitized bits of 1's and 0's. This electrical signal is then converted into an optical message in an electrical-optical converter. This converter is often a semiconductor laser that emits monochromatic coherent light. The message then travels through optical fibers to its target destination. Where that distance is large, such as between countries, repeater devices are employed that amplify the signal. Finally, at its destination, the message, in photonic form, is reconverted to an electric signal and then decoded.

The optical fiber is formed from a combination of polymeric materials. It typically consists of a core, cladding, and coating. The core does the actual transmission of the photons; the cladding constrains the light so it will travel within the core with little signal power loss and little pulse distortion; and the coating helps protect the inner material from damage and external pressures. There is a variety of materials that can be used in the construction of the optical fiber. Based on the core-cladding combination, there are three types of optical systems: the step-index, the graded index, and single-mode fibers.

Most of the "long-distance" systems use high-purity silica glass as the core material. These fibers are thin with a thickness of the order of 5–100 μm. Containment and retention of the signal is made possible because of the use of laser light and its total reflectance as it travels through the fiber. This containment is accomplished by using cladding and coating materials of differing refractive indexes from the core material. In the step-index approach, the index of refraction of the cladding is slightly less than that of the core. Here, the output pulse is a little broader than the input because the light travels slightly different paths as they travel through the fiber. This is overcome through the use of graded index materials where impurities such as boron oxide or germanium dioxide are added to the silica glass so that the index of refraction varies parabolically across the cross section of the optical fiber core. Thus, the velocity of light varies according to where it is within the core, being greater at the periphery and less at the center. Thus, light that must travel a longer pathway through the outer periphery travel faster than those close to the center somewhat balancing themselves to minimize distortion.

Organic core optical materials are also in use. Such materials, in comparison to the silica cored materials, are lighter in weight, offer better ductility, have larger core diameters, and are less sensitive to vibrational stresses. They are often considered for shorter distances. For the step index approach, where the refractive index of the cladding material should be a little less than that of the core material, a number of materials are possible. Two often used combinations are polystyrene core with poly(methyl methacrylate) cladding and a poly(methyl methacrylate) core with fluorinated polymers as the cladding. Since the fiber core is to be optically clear, amorphous organic polymers are used. Also, to avoid unwanted scattering, the polymer must be of high purity since impurities will cause sites of differing refractive indexes and the associated difference in the speed of propagation of the signal. The organic fibers are generally made by melt spinning with the core-cladding structure formed by extrusion.

The types of optical loss for both silica-glass-cored fibers and organic-cored fibers are similar, but do differ in relative importance. In the visible wavelength region there are both absorption and scattering losses. Absorption losses include higher harmonic molecular vibration modes in the infrared region and electronic transitional absorption in the ultraviolet region. Scattering losses include Rayleigh scattering and loss due to imperfections in the waveguide structure, mismatching of the core-cladding boundary interface, and birefringence due to fiber drawing as the fiber was formed.

18.13 POLYMERIZATION REACTORS

Polymerization can occur within glass ampules, large-scale batch reactors, within laboratory beakers—flow-through systems, etc. The processes used for small preparation in the research laboratory can be similar or dissimilar to that employed for the industrial-scale preparation of pound and larger quantities. While the kind of polymerization influences molecular weight and molecular-weight distribution, polymer structure and composition, as well as some of the physical characteristics, the kind of reactor also influences these factors. The reactor must allow adequate temperature control, mix of reactants and, if needed, catalysts (and at time a number of additives), reactant homogeneity, blending/mixing, etc. It must also allow for the economical "mass production" of the material. While there exists a wide variety of commercial reactors we will look at only three of the most used styles—batch, plug flow, and continuous stirred-tank reactors.

Batch. In batch reactions, the reactants are added (charged) to the reactor, mixed for a specific time and temperature, and then removed (discharged). Batch reactors are generally simple and can vary from being relatively small (such as gallon size) to large (several hundred gallon size) with the reaction occurring under varying conditions throughout the reaction vessel with time giving products that vary with time and secondarily, location within the vessel. This second condition is referred to as the polymerization occurring under non-steady-state or unsteady-state conditions.

The general material balance can be described as follows.

$$\begin{matrix}\text{Rate of}\\ \text{monomer flow}\\ \text{into reactor}\end{matrix} = \begin{matrix}\text{Rate of}\\ \text{monomer flow}\\ \text{from reactor}\end{matrix} + \begin{matrix}\text{Rate of}\\ \text{monomer loss}\\ \text{through reaction}\end{matrix} + \begin{matrix}\text{Rate of polymer}\\ \text{accumulation in}\\ \text{reactor}\end{matrix} \tag{18.31}$$

In a batch system the first two terms are zero since monomer is only added once and leaves only once, after the reaction is completed.
Thus,

$$\begin{aligned} 0 = {} & \text{Rate of monomer loss through reaction} \\ & + \text{Rate of polymer accumulation} \end{aligned} \tag{18.32}$$

$$0 = d[M]/dt + R_p \tag{18.33}$$

or

$$-d[M]/dt = R_p \tag{18.34}$$

For free radical polymerization, we have from Eq. (9.24)

$$R_p = k'[M][I]^{1/2} = k''[M] \tag{18.35}$$

or

$$dt = d[M]/k''[M] \tag{18.36}$$

Integration gives

$$\log([M]/[M_0]) = -k''t \tag{18.37}$$

and

$$[M] = [Mo]e^{-k''t}$$

and

$$\% \text{ Conversion} = 100\ ([M_0] - [M]/[M_0]) = 100(1 - e^{-k''t}) \tag{18.38}$$

This was derived assuming uniform concentration so that good mixing is important for this relationship to hold. It also assumes a constant temperature. Both these assumptions are only approached in most batch systems. Further, stirring becomes more difficult as conversion increases so that both control of localized temperature and concentration becomes more difficult. In reality, this relationship holds for only a few percentage points of conversion. Overall, temperature is a major concern for vinyl polymerizations because they are relatively quite exothermic. This is particularly important for bulk polymerizations. This, coupled with the general rapid increase in viscosity leads to the Trommsdorff-like effects.

Plug flow (tubular). A plug flow or tubular flow reactor is tubular in shape with a high length to diameter, 1/d, ratio. In an ideal case (as in most ideal cases such as an ideal gas, this only approached reality), flow is orderly with no axial diffusion and no difference in velocity of any members in the tube. Thus, the time a particular material remains within the tube is the same as that of any other material. We can derive relationships for such an ideal situation for a first-order reaction. One that relates extent of conversion with mean residence time t, for free radical polymerizations is

$$[M] = [M_0]\, e^{-k''t} \tag{18.39}$$

and

$$k'' = -(1/\tau)\ \text{In}\ ([M]/[M_0]) \tag{18.40}$$

Again, while such relationships are important, they are approximate at best. For vinyl polymerizations, temperature control is again difficult with temperature increasing from the cooling reactor wall to the center of the tube, and along with high and different viscosities lead to broad molecular weight distributions. Further, these factors contribute to differences in initiator and monomer concentrations again leading to even greater molecular weight distributions.

Continuous stirred tank reactor. In the continuous stirred-tank reactor (CSTR), instant mixing to achieve a homogeneous reaction mixture is assumed so that the composition throughout the reactor is uniform. During the reaction, monomer is fed into the system at the same rate as polymer is withdrawn. The “heat” problem is somewhat diminished because of the constant removal of heated products and the addition of nonheated reactants.

In a CSTR, each reaction mixture component has an equal chance of being removed at any time regardless of the time it has been in the reactor. Thus, in a CSTR, unlike the tubular and bach systems, the residence time is variable. The residential times can take the exponential form

$$R(t) = e^{-t/\tau} \tag{18.41}$$

where R(t) is the residence time distribution, $t =$ time, and τ is the mean residence time which is a ratio of the reactor volume to the volumetric flow rate. The residence time distribution influences the mixing effectiveness, which in turn determines the uniformity of the composition and temperature of the reactants in the reactor and ultimately the primary and secondary polymer structure.

Table 18.5 Listing of Selected Polymerization Processes and the Most Industrially Employed Reactor Types

Polymerization reaction	Polymerization process	Batch	Plug flow	CSTR
Step-wise	Solution	X	X	
Chain—free radical	Bulk	X		X
	Solution	X	X	X
	Suspension	X		
	Emulsion	X		X
	Precipitation	X		X
Chain—ionic	Solution	X		
	Precipitation	X	X	X

Table 18.5 contains a listing of selected polymerization processes and most employed industrial reactor types.

18.14 MATERIAL SELECTION CHARTS

In the selection of a material for a specific application many considerations are involved. Let us consider making a shaft for a blade that mixes saltwater with non-saltwater for controlled saline irrigation. The shaft material must be strong and lightweight and able to absorb twisting shear. While strength and weight are only two important considerations we will focus on only these two. A mathematical relationship between weight or mass and strength for a cylindrical shaft can be made such that

$$\text{Mass is proportional to [density/(shear stress)}^{2/3}] \times \text{some safety factors} \qquad (18.42)$$

This tells us that the best lightweight material to make our shaft out of a material with a low density/(shear stress)$^{2/3}$ ratio.

Often, the inverse of this ratio is employed and given the name performance index, P. (There are performance indexes for many different relationships between various physical behaviors.) Here then

$$\text{P} = (\text{shear stress})^{2/3}/\text{density} \qquad (18.43)$$

Taking the log of both sides gives

$$\log \text{P} = 2/3 \log \text{shear stress} - \text{density} \qquad (18.44)$$

Rearrangement gives

$$\log \text{shear strength} = 3/2 \log + 3/2 \log \text{P} \qquad (18.45)$$

This expression tells us that a plot of the log of the shear strength versus log density will give a family of straight and parallel lines each with a slop of 3/2 with each straight light corresponding to a different performance index, P. These lines are called design guidelines. Figure 18.3 contains a general plot of log shear strength versus density for a number of materials grouped together under common headings. It also contains design guideline lines for P = 10 (bottom line) and 100 (top line) (M Pa)$^{2/3}$ g/cc. Within each circle are particular materials with appropriate strength and density values. For instance, polytetrafluoroethylene exists in the midrange, extreme right on the "polymers" circle and so has a relatively

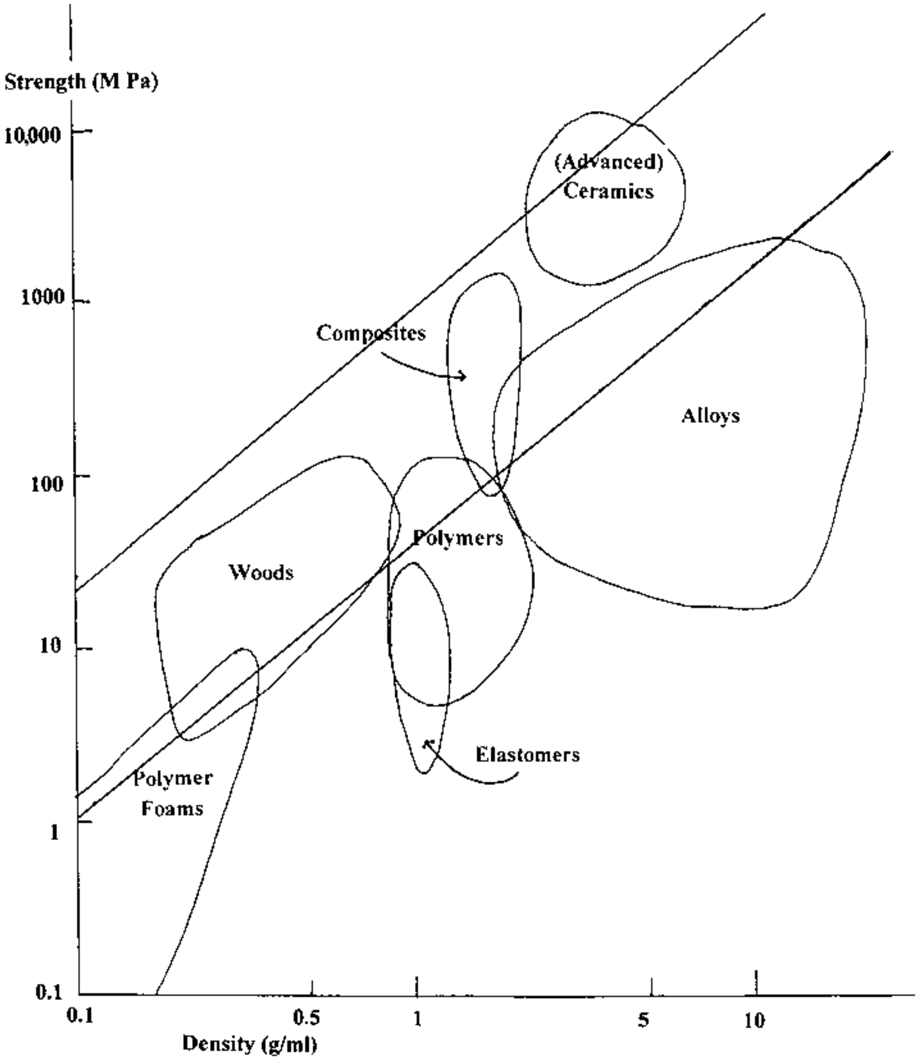


Figure 18.3 Materials selection chart for a material's strength as a function of density.

high density and strength, while polypropylene exists in the upper left corner of the "polymers" circle and has a relatively low density and relatively good strength. Such charts allow the quick focusing in on the general type of material that exhibits needed characteristics.

In general, those materials found along a single line will all perform similarly as a material for our shaft. The greater the P value, the greater the performance indices. For sake of argument, let us select the P = 10 line (the linear solid line running from about 1 M Pa through the lower regions of "woods" and the lower tip of "composites"). Here we have most of the woods, some polymers, most composites, many alloys and some advanced ceramics that fulfill the strength requirement, and woods and some polymers that are more apt to fill the low-density requirement. We can then say that the shaft must be lightweight and have a shear strength in excess of 50 M Pa. This eliminates the woods and some of the polymers but does include some of the engineering polymers and some of the metallic alloys. We might also specify that the material should not be brittle and have a good tolerance to saltwater. This means we might look at the upper end of the engineering polymers for our material.

Such plots of one material property versus another material property are called materials selection charts and are important in eliminating or including materials for specific application. Today, with the modern modeling systems and ability to do multivariant analyses, many different requirements can be examined simultaneously with such studies aiding in the determination of specific materials property needs, and which materials can meet these specifications.

18.15 BITUMENS

The petroleum industry, including the commercial bitumen industry, was born in the United States on August 27, 1859, when Colonel Drake drilled about 70 feet near Titusville, Pennsylvania, to “bring in” the first producing well. By 1908, Henry Ford began to mass-produce his Model “T” Ford creating an additional need for this petroleum in the form of gasoline. The distillation residue became more plentiful and a need for large-scale usage of bitumens was increased.

Even so, bitumens are a very old material. They were used in the waterproofing of the cradle that baby Moses was floated in. It was used by the ancient Egyptians in their mummification process. Bitumens were used in sand stabilization and for lighting the naval base by the Second Muslim Caliph, Omar ben Khattab, at Basra on Shattul-Arab on the West Coast of what is now Saudi Arabia around 640 A.D.

Bitumens occur naturally or are formed as the residue in the distillation of coal tar, petroleum, etc. Industrially, the two most important bitumens are asphalt and coal tar. Gilsonite is the third important derivative and occurs naturally. Asphalt is a brown to black tar-like variety of bitumen that again occurs naturally or is the residue of distillation. Coal tar is the black, thick-liquid obtained as the residue from the distillation of bituminous coal.

Bitumens are examples of materials that have only an approximate structure. Bitumens are carbon-intense small polymers with molecular weights from about 200–1000 Daltons for coal tar with a calculated average number of carbons in a chain of about 15–70. Asphalt has a molecular weight averaging about 400–5000 Daltons with a calculated average number of carbons in a chain of about 30 to about 400. Thus, they are generally oligomeric to short polymers. Asphalt has a C/H ratio of about 0.7 while coal tar has a C/H ratio of about 1.5 approaching that of a typical hydrocarbon where the C/H ratio is about 2.

As with most nonpolar hydrocarbon-intense polymers, bitumens exhibit good resistance to attack by inorganic salts and weak acids. They are dark, generally brown to black, with their color difficult to mask with pigments. They are thermoplastic materials with a narrow service temperature range unless modified with fiberous fillers and/or synthetic resins. They are abundant materials that are relatively inexpensive, thus their use in many bulk applications.

At temperatures above the T_g, bitumens generally show Newtonian behavior. Below the T_g, bitumens have rheological properties similar to elastomers.

Bitumens are consumed at an annual rate in excess of 75 billion lb. in the United States. Bitumens are generally used in bulk such as pavements (about 75%), and in coatings for roofs (15%), driveways, adhesive applications, construction, metal protection, etc., where the bitumen acts as a weather barrier. Bituminous coatings are generally applied either hot or cold. Hot-applied coatings are generally either filled or nonfilled. Cold-applied coatings are generally either nonwater or water-containing. In the hot-applied coatings, the solid is obtained through a combination of cooling and liquid evaporation which in the cold-applied coatings the solid material is arrived at through liquid evaporation. One often used coating employs aluminum pigments compounded along with solvents. These coatings are heat reflective and decrease the energy needs of building using them. The aluminum-metallic appearance is generally more desirable than black, and the reflective nature of the aluminum reflects light that may damage the bitumen coating allowing the coating a longer useful life.

Today, many of the bitumen coatings contain epoxy resins, various rubbers, and urethane polymers.

18.16 CARBON NANOTUBES

General

There are several materials that form so-called “nanotubes” including boron-nitrogen compounds. Here we will focus on nanotubes derived from carbon. Carbon nanotubes (CNTs) have probably been made in small amounts since the first fires reduced trees and organic material to ashes. It was not until recently, as part of the so-called “nano revolution,” that we first recognized the existence of these nanotubes. Sumio Iijima, NEC Fundamental Research Laboratory in Japan, first observed carbon nanotubes as byproducts of the arc-discharge synthesis of fullerenes.

Carbon nanotubes are carbon allotropes that have attracted much attention. Some have suggested that carbon nanotubes will be one of the most important twenty-first century materials because of the exceptional properties and ready abundance of the feedstock, carbon.

CNTs are generally classified into two groups. Multiwalled carbon nanotubes (MWCNTs) are comprised of 2–30 or more concentric graphitic layers with diameters ranging from 10–50 nm with lengths that can exceed 10 μm. Single-walled carbon nanotubes (SWCNTs) have diameters ranging from 1.0–1.4 nm with lengths that can reach several μm.

An ideal CNT can be envisioned as a single sheet of fused hexagonal rings, that is graphite, that has been rolled up forming a seamless cylinder with each end “capped” with half of a fullerne molecule. Single-walled CNT can be thought of as the fundamental cylindrical structure, with multiwalled CNTs simply being concentric tubes. They can also be conceived of as being the fundamental building block of ordered arrays of single-walled nanotubes called *ropes*.

Structure

Geometrically, carbon nanotubes can be described in terms of a two-dimensional graphene (graphite) sheet (Fig. 18.4). A chiral vector is defined on the hexagonal lattice as

$$C_h = n\mathbf{a}_1 + m\mathbf{a}_2 \tag{18.46}$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are unit vectors, and n and m are intergers, also tube indices. The chiral angle is measured relative to the direction defined by $n\mathbf{a}_1$.

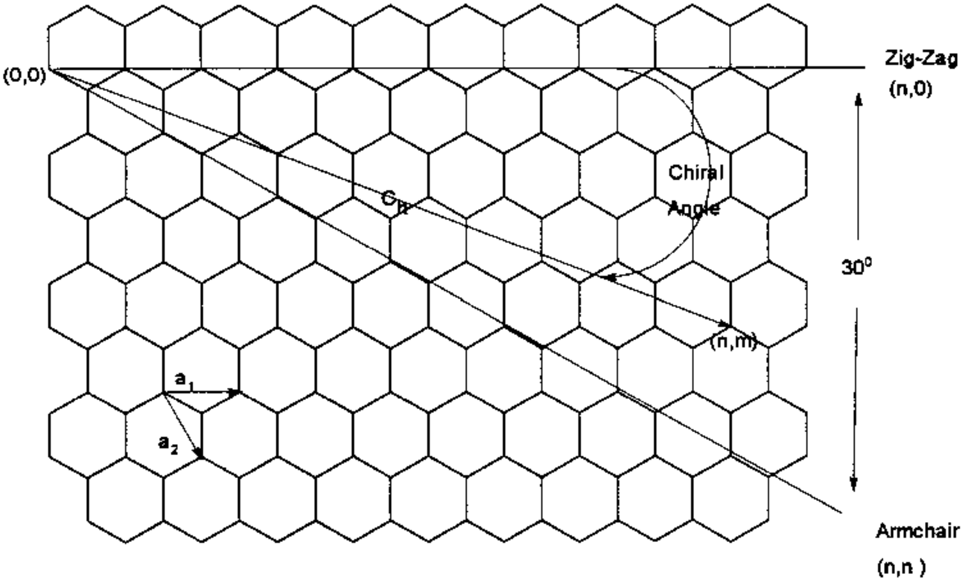


Figure 18.4 Graphite sheet representation showing the θ or chiral angle. For a chiral angle of 0°, the structure is a zigzag, for 30° it is an armchair, and in between it is helical. The figure is drawn with a 30° angle between the zigzag and armchair.

When the graphene sheet is rolled up forming a nanotube, the two ends of the chiral vector meet one another. The chiral vector thus forms the circumference of the CNTs circular cross section. Different values of n and m give different nanotube structures with different diameters.

There are three general types of CNT structures. The *zigzag* nanotubes correspond to (n,0) or (0,m) and have a chiral angle of 0°. The carbon–carbon bond position is parallel to the tube axis. *Armchair* nanotubes have $(m = n)$ with a chiral angle of 30°. The carbon–carbon positions are perpendicular to the tube axis. *Chiral* or helical nanotubes have general (n,m) values and a chiral angle of between 0° and 30° and as the name implies, they are chiral. These three general types of CNTs are pictured in Fig. 18.5.

Geometrically, the three general structures can be conceptually described in terms of rolling a flat sheet (a.k.a. graphite sheet). Take a sheet of paper and drawn a straight line down the middle from top to bottom. This will act as the axis line for a linear set of fused hexagonals. If the sheet is made into a cylinder so the line goes from the top to bottom of the open ends, it represents the armchair form. By comparison, formation of a cylinder so that the line runs through the middle of the cylinder gives a zigzag representation (Fig. 18.6). Finally, formation of a cylinder so that the cylinder line is other than perpendicular or parallel gives a helical representation.

In real life, nothing is perfect—such is the case with CNTs. The defects are mainly inclusion of wrong-membered rings. Pentagonal defects, that is the replacement of a hexagonal with a five-membered ring, results in a positive curvature causing the tube to curve inward like a horseshoe. The closure of an open cylindrical surface necessarily involves topological defects—often formation of pentagons. Heptagonal defects result in a negative curvature with the lattice looking expanded around the defect.

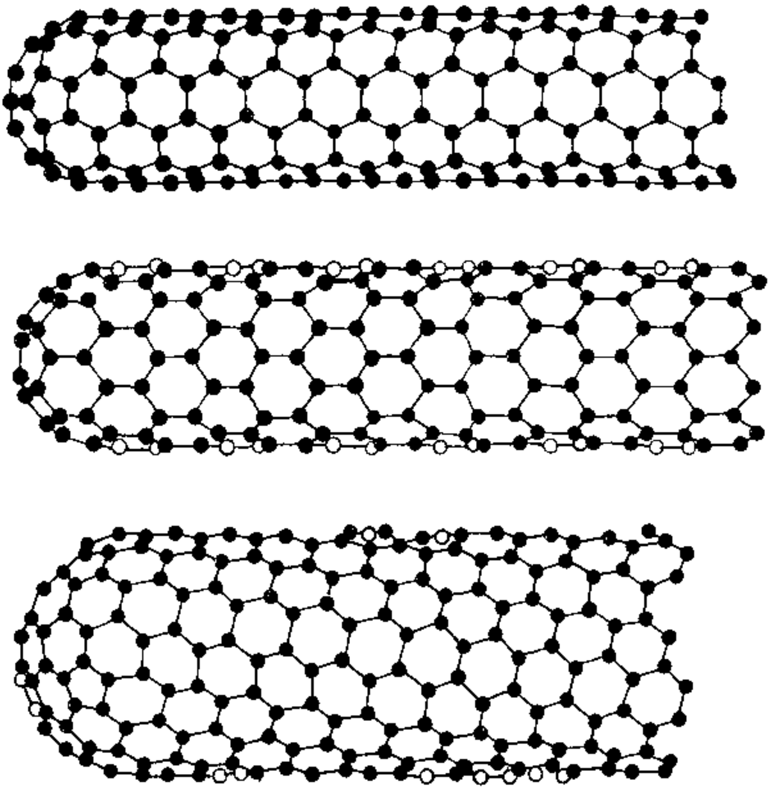


Figure 18.5 Representations of the three major structural forms of carbon nanotubes: (top) armchair, (middle) zigzag, and (bottom) helical.

The tendency to include pentagonal units can be seen by comparing the presence of pentagonal units in fullerene structures. The C_{60} structure contains twelve pentagons and twenty hexagons. The larger the fullerene the smaller the ratio of pentagons to hexagons consistent with the use of pentagons to “cause” sharper bends and greater curvature in comparison to hexagons. Interestingly, fullerene C_{60} is one of the most strained molecules known but it exhibits good kinetic stability. It begins to decompose at about 750°C. There are a number of higher numbered (carbon number) fullerenes including C_{70}, C_{76}, C_{78} (two geometric isomers), C_{80}, . . . Fullerenes can act as a source of the carbon nanotubes with the different-sized fullerenes producing different nanotubes. The three general structures of nanotubes can be produced using different fullerenes with C_{60} giving armchair nanotubes, C_{70} giving zigzag structures and C_{80} giving helical forms of nanotubes. Figure 18.7 contains representations of these three fullerenes.

This difference in structure also influences the electrical conductivity with the armchair form being conductive or metal-like in its conductivity and most of the other forms act as semiconductors.

The ends of the nanotubes can be opened by oxidation. During oxidation the sites corresponding to the defects are selectively attacked. The caps where the defects, often simply the presence of pentagons constitutes a defect, are concentrated are destroyed by

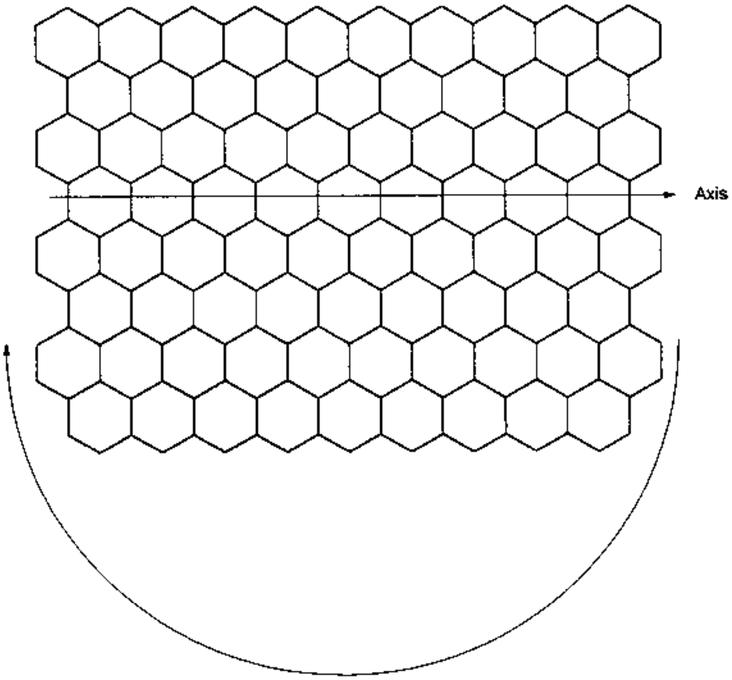


Figure 18.6 Representation of graphite sheet showing the hexagonal axis and folding to give a zigzag tube.

such a reaction. The reason the defect sites are preferentially attacked is not completely clear; one possibility involves the higher chemical potential associated with the defect sites and another possibility is the higher energies associated with changes in curvature which has been introduced into the network by defects. Two approaches are largely employed in the oxidation process. The first one is gas phase oxidation where the CTNs are placed in an oven and the temperature slowly raised to about 750°C. Air and oxygen are gently blown through the oven. This process requires the material remain about 20 min at the maximum temperature. The second technique is the liquid-phase oxidation. Exposure

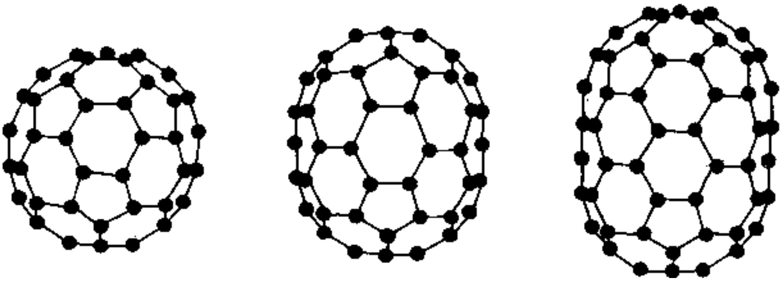


Figure 18.7 Representations of C_{60} (left), C_{70} (middle), and C_{80} (right) fullerene structures.

of the CNTs to common oxidants such as nitric and sulfuric acid and their mixtures open the nanotubes. The best results are obtained with acidic solutions of potassium permanganate.

Synthesis

While predetermined structural control can be achieved through the use of bucky-balls of specific size, general synthesis of CNTs on a somewhat larger scale occurs through one of three techniques.

A. Electric Arc Discharge

Multiwalled carbon nanotubes are generally formed using a chamber filled with an inert gas, often helium, using a pressure of about 500 torr. The two electrodes are moved together until arcing occurs. The electrodes become red hot and a plasma forms. Once the arc stabilizes the rods are kept apart while a deposit forms. Deposited on the surface of the cathode are two carbon-containing portions. The inner core has the fabric structure growing along the length of the cathode forming nanotubes and polyhedrol graphite nanoparticles. The outer shell consists of crystalline graphite.

Single-walled carbon nanotubes (SWCNTs) were first formed by Donald Bethume of IBM while trying to place a cobalt atom inside of a buckyball to form so-called “cobalt endohedral metallofullerenes.” Cobalt powder was placed in a little hole drilled axially in the graphite anode of the carbon arc. They carried out the experiment but instead of obtaining the expected flocculate powder-like, they obtained a rubbery textured product. When they looked at the rubbery soot in a transmission electron microscope they found that this special soot contained single-walled nanotubes. Today, mixtures of cobalt-iron, cobalt-nickel, nickel-iron, and cobalt-platinum are used to make SWCNTs using electric arc discharge. It is believed that the catalysts sit inside the growing tube assisting in its formation.

Typical yields are about 30%. The disadvantage of the electric arc discharge method is that the tubes tend to be short (50 μm or less) and deposited in random sizes and directions.

B. Laser Ablation

Laser ablation was used when C_{60} was first discovered. A pulsed laser is employed. The laser beam hits graphite mounted in a quartz tube that has been heated to 1200°C. The laser blast is rapid, only 5–10 billionths of a second resulting in temperatures greater than 3000°C, often closer to 10,000°C in the laser-induced plasma plume. Rapid cooling, within a μsec or so, occurs as the plume expands into the surrounding inert gas atmosphere (generally argon at about 500 torr). Because this occurs within an oven-heated quartz at 1200°C, the expanding carbon vapor plume does not cool to below 1200°C. The laster beam scans across the target surface under computer control maintaining a smooth, uniform face for vaporization. The carrier gas flow sweeps most of the carbon species produced by the laser vaporization, and that has undergone high-temperature condensation processes, from the furnace zone depositing it as soot on a conical water-cooled copper rod. The products are normally mixtures of multiwalled carbon nanotubes and fullerenes.

When the graphite target rod is replaced with a composite graphite/catalyst rod, the product yield give about 70% SWCNTs with only 1% fullerenes. A typical graphite/catalyst rod can be made by mixing finely divided graphite powder with about 1 atom % of a 50/50 mixture of nickel and cobalt powders. The diameter range can be controlled by varying reaction temperature. This method is the most costly of the three because it requires expensive lasers.

Chemical Vapor Deposition

Morinubo Endo of Shinshu University in Japan was the first to make nanotubes using chemical vapor deposition. The substrate is placed in an electric furnace. The oven is heated to 1000°C with hydrogen as the carrier gas. Ultrafine particles of iron (ca 10 nm diameter) or iron-containing compounds such as iron (III) nitrate or ferrocene, are used as a catalyst. The carbon-bearing compound such as methane or benzene is added. The carbon-bearing compounds decompose under the oxygen-free conditions giving up carbon atoms. The carbon atoms recombine in the form of nanotubes. Better nanotubes are formed when the products are further heated to about 3000°C. Chemical vapor deposition can be scaled up for industrial production but the products are usually multiwalled nanotubes riddled with defects so that the products will have tensile strengths less than one tenth that found for tubes made by arc discharge.

Mechanism

There are several main theories concerning the formation of carbon nanotubes. One theory explains the tube growth in the arc-discharge method of synthesis. This is called the electric field theory, and has the electric fields present at the nanotube tips as the driving force tube formation. The space distribution of a potential has a steep drop near the cathode in a region of positive space charge called the *cathode layer*. Essentially all the potential drop occurs in this region. The space charge is calculated to be 12 μm for typical discharge conditions. This is also the distance of the main potential drop in the interelectrode region and thus the distance for the positive ion acceleration moving toward the cathode. The average electric field in this region is about 2×10^4 V/cm.

The interelectrode gas is a mixture of neutral helium atoms, singly ionized carbon ions, and neutral carbon species. The temperature of the interelectrode gas is about 4000 K which is close to the melting point, 4100 K, and the boiling point, 4470 K of graphite. The carbon surface begins to evaporate, producing a thin layer of saturated carbon vapors near the surface (about 2–3 μm thick) covering the cathode surface. The velocity distribution of carbon atoms in the vapor layer is Maxwellian (isotropic). The collision frequency of carbons in this layer is much higher (due to the higher density of carbon atoms) than in the plasma in the interelectrode space. Thus, the vapor layer is the most appropriate location for reactions involving carbon to carbon or carbon with carbon clusters to occur.

Within the vapor layer there are two groups of carbon particles having different velocity distributions. The first group, the carbons that are evaporated from the cathode surface, have a Maxwellian velocity distribution corresponding to a temperature of about 4000 K. The second group is composed of ions arriving with the ion current (the ions being accelerated in the gap between the positive space charge and the cathode). This group is more monoenergetic and monodirectional in velocity (along the current direction with a velocity about 10 times higher than the thermal velocity of the carbons of the first group) and direction.

As discharge begins, during the time for the increase of the ion current to a stable value, the velocity distribution of carbons in the vapor layer is predominantly Maxwellian. There is no axis of symmetry in the reaction region. This condition favors the formation of three-dimensional structures without any axis of symmetry, such as buckyballs and nanoparticles. As the directed current increases, formation of open structures—concave and convex—begins.

During the stable stage of the discharge, the current of carbon ions flows to the vapor layer in the direction perpendicular to the cathode surface. The mean free path for a carbon–carbon collision in this layer is about 15 μm, which is larger than the thickness of the layer (2–3 μm). Because of this randomization (or isotropization) of the directed ion, motion by collisions in the vapor layer is very small. The main deceleration of the carbon ions occurs as a result of collisions with carbons on the cathode surface. Thus, prior to these collisions, the ions of the current maintain their direction. Therefore, the carbons arriving with the ion current are involved in the formation of elongated structures and are mainly responsible for the construction of tubs that are aligned along the direction of motion. Counter, the presence in the layer of carbons having a Maxwellian distribution leads to the attachment of these carbons to the elongated structure previously formed. This process favors the thickening of the tube, that is, formation of multiwalled CNTs. Nucleation on the sides of the tubes can be simply due to condensation and annealing of carbon on the inner tube being structurally, at least partially, driven by the existing CNTs. The processes of deceleration, recombination of carbon ions, and attachment occurs almost simultaneously.

Current instabilities, which do not significantly change external conditions of the discharge (voltage, current, etc.) interrupt tube growth. Cathode spot instability leads to termination of the ion current in one place and the dominance in the interaction zone of the Maxwellian carbons. This leads to the closure of tube ends and termination of tube growth. At the same time, new structures and nanoparticles begin forming. The return of the current spot to the same place assists in restarting the ion current and formation of CNT during the next cycle.

Another theory emphasizes the self-assembly process and was initially suggested by Smalley of Rice University. Here, it is argued that carbon has a great drive to spontaneously assemble forming various nano objects. When carbon is vaporized in an inert atmosphere, the carbon atoms do not have anything other than carbon-containing atoms/groupings to react with. As they begin to condense they begin to aggregate. It has long been known that carbon has a special ability to cluster in the gas phase at high temperatures. When carbon vapor equilibrates with its solid at 3000–4000 K, carbon is able to form clusters. These clusters are so stable that they are the dominant species—substantially more abundant than the single carbon atom in the gas phase. When the clusters contain fewer than 25 carbon atoms, they consist of linear chains and monocyclic rings. This is called a one-dimensional structure. As clusters grow larger reaching 20–35 atoms, they begin to favor two-dimensional sheet-like structures composed of polycyclic networks. However, these open graphene-like sheets have many gangling bonds along their periphery. Due to the high energy of dangling bonds, these species are unstable. While the major structural unit is hexagonal, pentagons are also incorporated into the clusters. These pentagons encourage curvature of the growing graphene-like clusters, allowing the dangling bonds to join together forming curved structures. The reduction of energetically costly dangling bonds offsets the additional strain energy incurred by the formation of these three-dimensional structures. Continued growth and incorporation of pentagons with simultaneous curving induced by the pentagons produces closed, cage-like structures, the buckyballs. If closure is prevented, then tubular structures are possible.

If the carbon density is high, the open shell will sometimes nucleate a second layer before closing. These additional layers are more rapid growing because they "self-assemble" about the existing structure. If the outer layer reaches the edge of the inner shell before either closes, an adatom "spot-weld" (bridging between adjacent layers) that stabilizes the open conformation slows the rate of closure. During this period, carbon feedstock from the high-density vapor plume adds to the open edges, forming the body of the nanotube. Additional outer layers may then grow by island nucleation and anneal on the underlying nanotube template. It is possible that more than one mechanism may be in control during the growth of single and multiwalled nanotubes.

Properties

One of the major reasons for the intense interest in CNT is their extreme and varied properties. Table 18.6 contains a comparison between single-walled CNTs and competitive materials/techniques.

Applications

Electrical

Nanotubes can be metallic or semiconducting, depending on their diameters and helical arrangement. Armchair (n = m) tubes are metallic. For all other tubes (chiral and zigzag) when tube indices (n + m)/3 are integers the tubes are metallic—otherwise they are semiconducting. Carbon nanotubes can in principle play the same role as silicon does in electronic circuits, but on a molecular scale where silicon and other standard semiconductors cease to work. Single carbon nanotube bundles have been used to construct elementary computing circuits known as *logic gates*.

Table 18.6 Comparison of Selected Properties of SWCNTs with a Typical Competitive Material

Property	Single-walled carbon nanotubes	Comparison
Size	0.6 to 1.8 nm in diameter	Electron beam lithography can create lines 50 nm wide and a few nm thick
Density	1.33 to 1.40 g/cc	Aluminum has a density of 2.7 g/cc and titanium has a density of 4.5 g/cc
Tensile strength	ca 45 billion Pascals	High-strength steel alloys break at about 2 billion Pascals
Resilience	Can be bent at large angles and restraightened without damage	Metals and carbon fibers fracture at grain boundaries
Current carrying capacity	Estimated at 1 billion A/cc	Copper wires burn out at about 1 million A/cc
Heat transmission	Predicted to be as high as 6000 W/mK	Diamond transmits 3320 W/mK
Field emission	Can activate phosphors at 1 to 3 Volts if electrodes are spaced 1 μm apart	Molybdenum tips require fields of 50 to 100 V/μm and have limited lifetimes
Temperature stability	Stable up to 2800°C in vacuum, 750°C in air	Metal wires in microchips melt at 600–1000°C

Mechanical

CNTs have superior resilience and tensile strength. They can be bent and pressed over a large angle before they begin to ripple or buckle, finally developing kinks. Until the elastic limit is exceeded, the deformations are elastic with the deformation disappearing when the stress is removed. It is envisioned that buildings and bridges built from them may sway during an earthquake rather than fracture and crumblie.

Field emission

When stood on end and electrified, carbon nanotubes act as lightning rods, concentrating the electrical field at their tips. While a lightning rod conducts an are of electricity to a ground, a nanotube emits electrons from its tip at a rapid rate. Because the ends are so sharp, the nanotube emits electrons at lower voltages than do electrodes made from other materials and their strength allow nanotubes to operate for longer periods without damage. Field emission is important in several industrial areas, including lighting and displays. Commercial use of CNTs as field emitters has begun. Vacuum-tube lamps in six colors that are twice as bright, longer-lived, and at least 10 times more energy-efficient as conventional lightbulbs are being tested.

Hydrogen and ion storage

While we can picture CNTs as being composed of hexagonal carbon atoms with lots of empty space between the carbons, atoms “thrown” against them generally just bounce off. Even helium atoms at an energy up to 5 eV do not readily penetrate the nanotube. Thus the graphene sheet and CNTs are really membranes or fabrics that are one atom thick made of the strongest material that is also impenetrable (to a limit). Thus, CNTs can be used for hydrogen storage in their hollow centers with release being controlled, allowing them to act as inexpensive and effective fuel cells.

Chemical and genetic probes

Nanotube-tipped atomic force microscopes can trace a strand of DNA and identify chemical markers that reveal DNA fine structure. A miniaturized sensor based on coupling the electronic properties of nanotubes with the specific recognition properties of immobilized biomolecules through attaching organic molecules—handles—to these tubular nanostructures has been constructed. In one study, the π-electron network on the CNT is used to anchor a molecule containing a planar pyrenyl group that irreversibly adsorbs to the surface of the SWNT. The anchored molecules have a “tail” to which proteins, or a variety of other molecules, can be covalently attached. The result is that these molecules are immobilized on the sidewall of the nanotube with high specificity and efficiency. The molecule’s tail is tipped with a succinimidyl ester group, which is readily displaced when an amine group attacks the ester function, forming an amide bond. Thus, the CNTs are used as both highly sensitive probes and highly selective immobilizing sites that allow specific reactions to occur.

Analytical tools

Single-walled CNTs are being used as tips of scanning probe microscopes. Because of their strength, stability, and controllable and reproducible size, the tub probes allow better image fidelity and longer tip lifetimes.

Superconductors

Carbon nanotubes offer unique electronic properties due to quantum confinement. According to quantum confinement, electrons can only move along the nanotube axis. Metallic CNTs are found to be high-temperature superconductors.

18.17 LIQUID CRYSTALS

Every day of our lives we run across liquid crystals (LCs). They are commonly found in computer monitors, digital clocks, and other read-out devices, for example.

Reintzer, in 1888, first reported liquid crystal behavior. In working with cholesteryl esters, he observed that the esters formed opaque liquids, which on heating turned clear. We now know that, as a general rule, many materials are clear if they are anisotropic, random, or if the materials are composed of ordered molecules or segments of molecules, whereas they are opaque if they contain a mixture of ordered and disordered regions. Lehmann interpreted this behavior as evidence of a third phase that exists between the solid and isotropic liquid states. This new phase was named by Lehmann the *liquid crystal* phase. Friedel called this phase the *mesophase*, after the Greek word *mesos*, meaning intermediate. The initial molecules investigated as liquid crystals were large monomeric molecules.

Flory, in 1956, predicted that solutions of rod-like polymers could also exhibit liquid crystal behavior. The initial synthetic polymers found to exhibit liquid crystal behavior were concentrated solutions of poly(γ-benzylglutamate) and poly(γ-methylglutamate). These polymers exist in a helical form that can be oriented in one direction into ordered groupings, giving materials with anisotropic properties.

Liquid crystals are materials that undergo physical reorganization whereby at least one of the rearranged structures involve molecular alignment along a preferred direction causing the material to exhibit nonisotropic behavior and associated birefringent properties, i.e., molecular asymmetry. Stirring of LCs can cause alignment of polymer segments, resulting in an elongation of the polymer chain and a subsequent increase in viscosity with the formation of the LC. As the concentration of the polymer LC increases, solution viscosity increases until LC formation occurs, at which point viscosity generally decreases as the concentration of LC continues to increase. Prior to LC formation, the solution is isotropic. After LC formation, the polymer solution is anisotropic.

Liquid crystalline materials can be divided into two large groups: thermotropic and lyotropic. Thermotropic LCs are formed when “pure” molecules such as cholesteryl form ordered structures upon heating. When LCs occur through mixing with solvent, they are called lyotropic LCs.

Thermotropic LC can be further divided into (1) enantiotropic materials, where the LC phases are formed on both heating and cooling cycles, and (2) mesotropic materials, where the LCs are stable only on supercooling from the isotropic melt. The mesotropic LCs have been further divided into three groups:

Smectic, meaning “soap”
Nematic, meaning “thread”
Cholesteric, derived from molecules with a chiral center

Liquid crystal polymers are typically composed of materials that are rigid and rod-like with a high length-to-breadth ratio or materials that have a disk shape. The smaller groups that give the material LC behavior are called *mesogens*. These mesogens are simply portions of the overall polymer that are responsible for forming the anisotropic liquid crystal and that in fact form the LC segments. Such mesogens can be composed of segments from the backbone of the polymer, segments from the side chain, or segments from both the backbone and side chain.

The mesogens form the ordered structures necessary to give the overall material anisotropic behavior. A number of different mesogen groupings have been identified. Chains arranged so that the mesogen portions are aligned in one preferred direction with the ordering occurring in a three-dimensional layered fashion compose one group of arrangements called smectic arrangements (Fig. 18.8). Here the lateral forces between the mesogen portions are relatively higher than the lateral forces between the nonmesogen portions, allowing a combination of segments that permit "flowing" (the passage of nonmesogen portions) and segments that retain contact (mesogen portions) as the material flows imparting a "memory"-type behavior of the material. A number of different "packings" of the mesogens have been identified (Fig. 18.8). The most ordered of the mesogenic groupings is called smectic B, which is a hexagonally, close-packed structure present in a three-dimensional arrangement. A much less ordered grouping is called the smectic A phase, in which there is a somewhat random distribution of the mesogens between the layers.

Nematic LCs offer much less order in comparison to smectic arrangements. Here, the directional ordering of the mesogen portions along one axis is retained but the centers of gravity of the mesogen portions are no longer coupled (Fig. 18.8). Thus, the forces between the chains are less, resulting in a generally greater fluidity for nematic LCs in comparison with smectic structures. Nematic LCs still offer nonlinear behavior.

The chiral nematic assembly is formed by materials with chiral centers and that form a nematic phase. Here, a "chiral-imposed twist" is imparted to the linear chains composing each layer, resulting in a three-dimensional helical arrangement.

The molecular asymmetry typically occurs not because of intermolecular interaction but because two molecules cannot occupy the same space at the same time. Molecular chains can exist in a random arrangement until a given concentration is exceeded, causing the molecules to rearrange in a more ordered fashion to accommodate the larger number of molecules within the same volume. Often, this occurs such that there is an ordered phase and a more random phase. As the concentration of polymer increases, the ordered phase becomes larger at the expense of the disordered phase. This increase in polymer concentration can occur via several routes, such as addition of polymer, addition of a solution containing a higher concentration of polymer, and evaporation of the solvent.

For crystalline polymer systems, transition from the crystalline structure to a mesosphere occurs, whereas in amorphous polymer systems, the mesophase occurs after the T_g has occurred. Some polymer liquid crystal systems form several mesophases, which can be detected using differential scanning colorimetry, X-ray diffraction, and polarizing microscopy.

LC polymers include aromatic nylons (aramids), aromatic polyesters, poly(alkyl isonitriles), and polyorganophosphazines. Sample LCs are shown in Fig. 18.9.

Introduction of flexible "spacer" units such as methylene, methylene oxide, and dimethylsiloxane groups lowers the melting point and increases the temperature range within which the mesophase is stable. Often these spacer units are introduced by copolymerization. Thus, preformed *p*-acetoxybenzoic acid is reacted with poly(ethylene tereph-

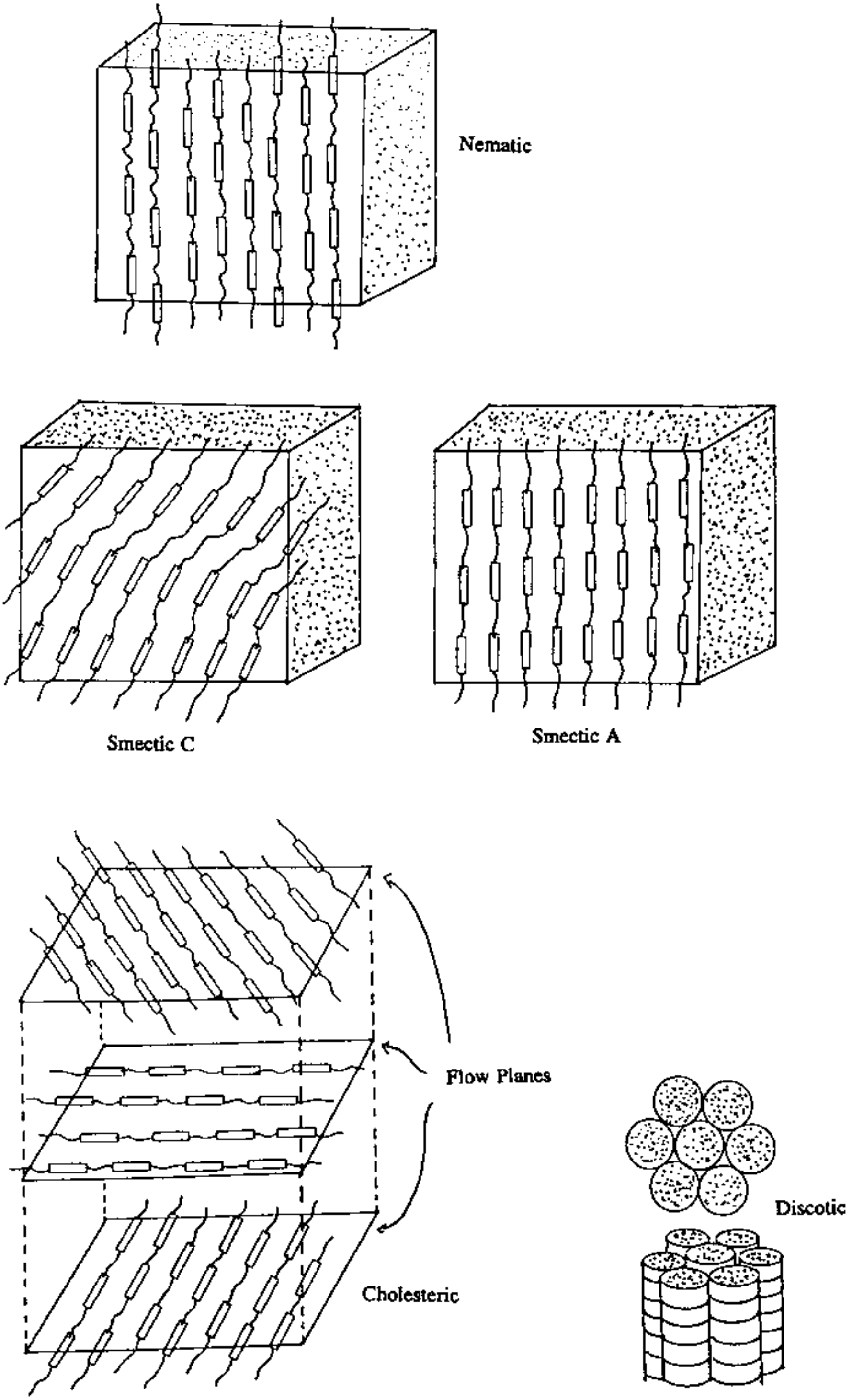


Figure 18.8 Different mesophasic structures where the mesogenic unit is designated as ▭.

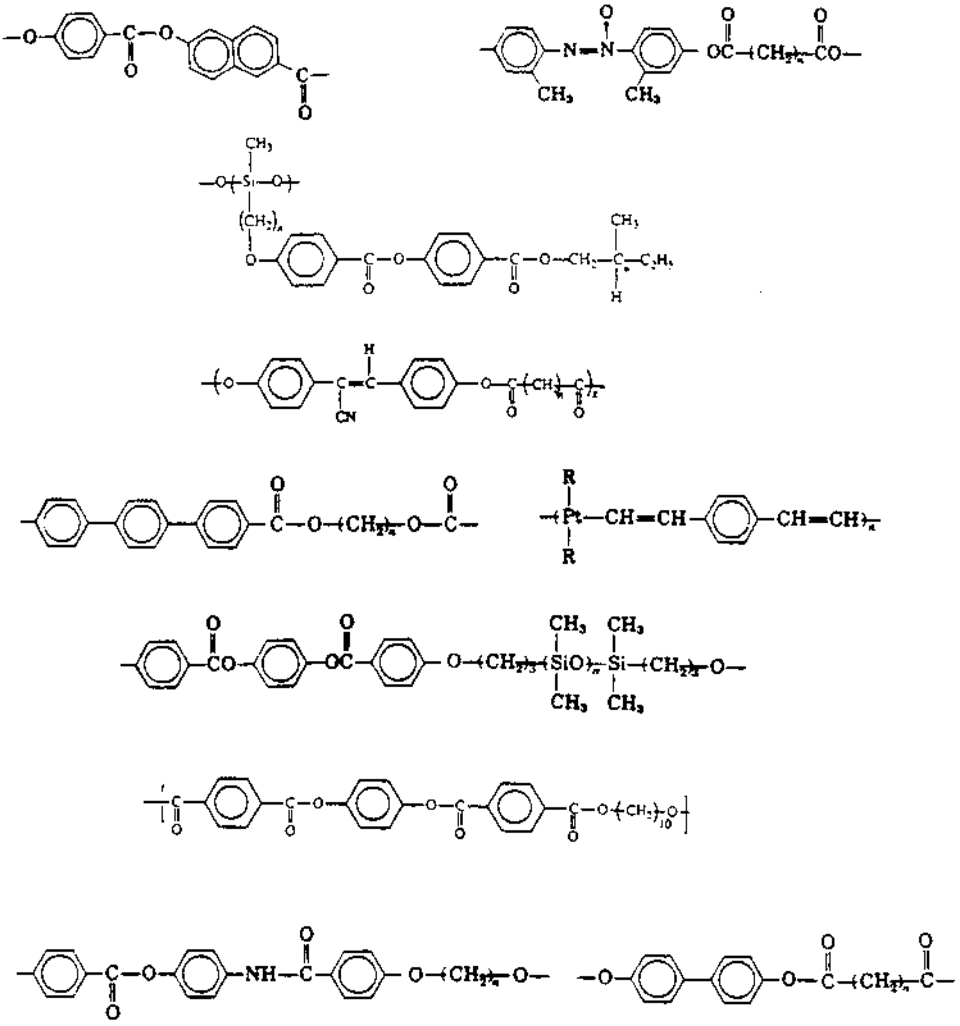
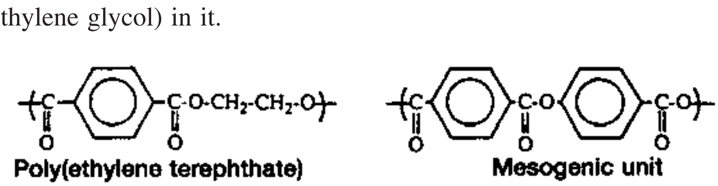


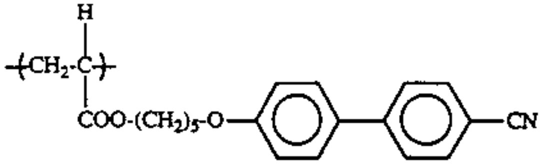
Figure 18.9 Representative structures of polymeric liquid crystals.

thalate), introducing a mesogenic unit in a polymer that has flexible spacer units (from the ethylene glycol) in it.



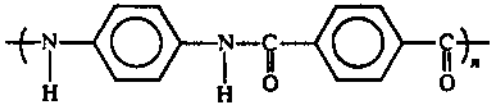
(18.47)

Along with the mesogen units contained within the mesogenic unit polymer backbone the mesogen units can occur as side chains. These mesogen units can be introduced either through reaction with monomers that contain the mesogen unit or through introduction with already formed polymers.



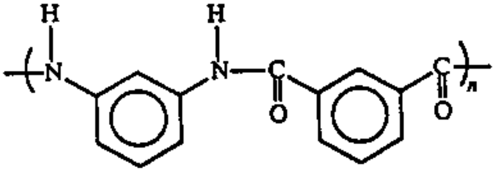
(18.48)

While most of us connect LCs with watches and PC screens, LC polymers can include all polymers, such as aramids, that take on a rigid rod configuration somewhere within the polymer where the "popular" LC behavior is not involved. Aramid fibers are quite strong, with twice the tenacity and almost 10 times the modulus of aliphatic nylons, such as nylon-66. Many of these aramid fibers are stronger than steel wire on a weight basis. Three of the best known aramid fibers are pictured below.



(18.49)

Poly(p-phenylene terephthalamide), Kevlar



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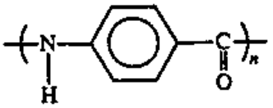
Poly(m-phenylene isophthalamide), Nomex



(18.51)

Poly(p-benzamide), Fiber B

These aramid fibers are often employed alone or with carbon or glass fibers for doors, aircraft panels, sporting goods, bulletproof vests, tires, flooring, and car bodies.

LC materials have also been employed as films, plastics, and resins. Poly(1,4-benzoate) has been marketed under the name Ekonol. It decomposes before it melts, hence it does not form LC melts. Copolymerization with 4,4′-biphenol and terephthalic acid gives Ekkeel, which does melt before it decomposes. Certain forms can be compression-molded and others injection-molded. Reaction of poly(1,4-benzoate) with PET gives a material that can be injection-molded. These LCs are chemical-resistant, with high tensile strength.

In general, because of the high order present in LCs, especially within their ordered state, they have low void densities and as such exhibit good stability to most chemicals including acids, bleaches, common liquids, etc.; low gas permeability; relatively high densities; strength and stiffness with tensile moduli of the order of 10–25 GP s and tensile strengths in the range of 120–260 M Pa.

Today, there exists a number of routes for processing that have been modified for LC materials. In general, they offer low shrinkage and warpage during molding, good repeatability from part to part, and low heats of fusion allowing rapid melting and cooling during processing.

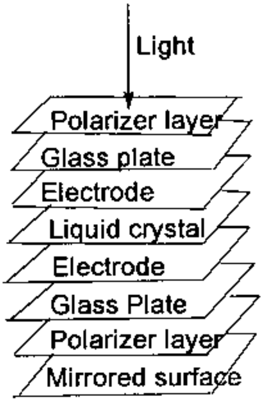


Figure 18.10 LCD illustration.

Their low melt viscosity permits molding of thin sections and complex shapes. Counter, their tendency to form ordered structures causes LC materials to be particularly susceptible to molecular orientation effects during processing.

We can look at one illustration of the use of LC materials (Fig. 18.10). A typical LC display (LCD) may contain thin layers of LC molecules sandwiched between glass sheets. The glass sheets have been rubbed in different directions and then layered with transparent electrode strips. The outside of each glass sheet is coated with a polarizer material oriented parallel to the rubbing direction. One of the sheets is further coated with a material to make it a reflecting mirror. The LC molecules preferentially align along the direction that the two glass surfaces have been rubbed. Because the two glass surfaces are put at 90° to one another, the liquid crystal orientation changes as one goes from one glass surface to the other creating a gradual twist of 90°.

Ordinary light consists of electromagnetic waves vibrating in various planes perpendicular to the direction of travel. As light hits the first polarizer material only light that vibrates in a single plane is allowed to pass through. This plane-polarized light then passes through the layers of LCs that effectively twists the plane of the light 90°, allowing the "twisted" light to pass through the second polarized surface, striking the mirrored surface, and "bouncing back" being seen as a white background.

The LCD image is formed as a voltage is applied to an appropriate pattern of tiny electrodes that causes reorientation in the liquid crystals. Orientated liquid crystals no longer are at 90° to one another and thus are unable to transmit light through to the mirrored surface and thus appear as dark areas. This combination of dark and light surfaces then creates the LCD image.

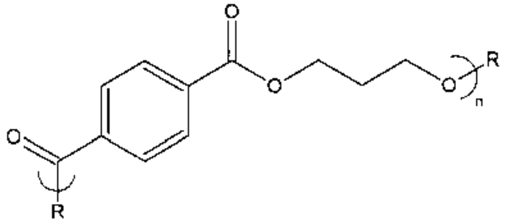
Assemblies similar to the above have been employed to create images in clocks and watches and other similar LCD image-containing products. LC films with mesogenic side chains have been used in information storage devices.

18.18 EMERGING POLYMERS

A number of smaller scale polymeric materials will continue to enter the marketplace on a regular basis. These include biomaterials and electronics materials where the cost per pound is high and the poundage is low, generally well less than a hundred tons a year. These are materials that fulfill specific needs.

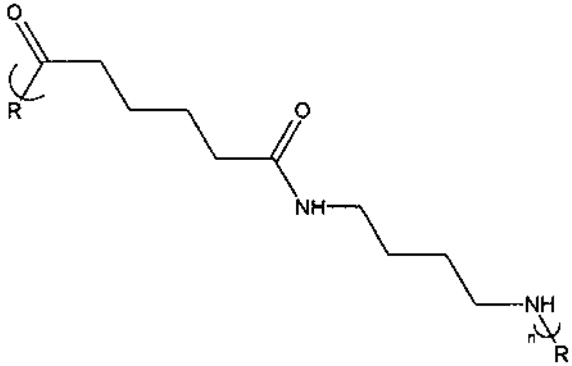
The number of new larger scale giant molecules that enter the marketplace will be small. It has been estimated that it takes about $1 billion to introduce and establish a new material. It is a daunting task with no guarantee of success. In the past, new giant molecules cold be introduced that offered improvements in a number of areas and thus would attract a market share in a number of application areas. Today, there are already a wide range of materials for most application areas that compete for that particular market share, so that it is difficult for any material to significantly break in to any market area. A new material needs a "flagship" property that a particular market needs.

Dupont and Shell have developed a new polyester, poly(trimethylene terephthalate) (PTT) that is structurally similar to poly(ethylene terephthalate) (PET), except that 1,3-propanediol, (PDO) is used in place of ethylene glycol (Sec. 6.6). The extra carbon in Sorona allows the fiber to be more easily colored giving a material that is softer to the touch with greater stretch for textile use. Further, it offers good wear and stain resistance for carpet use. The ready availability of the monomer PDO is a major consideration with efforts underway to create PDO from the fermentation of sugar through the use of biocatalysts for this conversion. Sorona and Lycra blends have already been successfully marketed. Sorona is also targeted for use as a resin and film.



Poly(trimethylene terephthalate), PTT

In 1990, DMS introduced nylon 4,6 called Stanyl, based on the reaction between adipic acid and 1,4-diaminobutane (Sec. 6.7). Stanyl can withstand temperature to about 300°C allowing it to create a niche between conventional nylons and high-performance materials. It has not been able to break into the film market and only now has begun to be accepted for tire cord applications. About 10,000 tons of Stanyl were produced in 2001.



Nylon 4,6

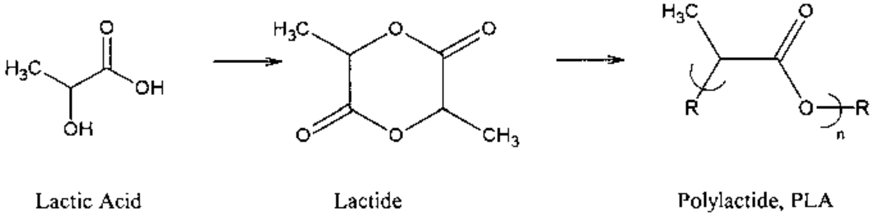
In 1997, Dow introduced syndiotactic polystyrene (Sec. 8.6) under the tradename Questra. The technology for the production of Questra is based on relatively new technology and science involving soluble stereoregulating catalysts (Sec. 7.5) that produce polystyrene that has a fixed and repeating geometry as each new styrene monomer unit is added to the growing polystyrene chain. Targeted areas include medical, automotive, and electronic applications.

Several other products have been developed based on the relatively new soluble stereoregulating catalysis systems (Sec. 7.5). Index was introduced in 1998 and is intended to compete with block copolymers such as styrene-butadiene-styrene, flexible PVC, polyurethanes, and polyolefins. It is an ethylene-styrene interpolymer. Dow is also developing soundproofing and packaging foam applications for Index. Hoechst (now Ticona) developed Topas in the 1980s and in 2000 began commercial production of it. Topas is a cycloolefin copolymer and has high moisture-barrier properties and is being considered for use in blister packaging for pharmaceuticals. It is also being used in resealable packages where it provides stiffness to the sealing strip and in toner resin applications, and it is being blended with linear low-density and low-density polyethylene to provide stiffness and to improve sealing properties.

A number of new materials are looking toward being involved in the upcoming move toward blue-light CDs. For any of these to become important materials in this area, they will need to improve on the present polycarbonate-based materials.

In 2000, GE introduced a new polyester carbonate (Sec. 6.6) based on resorcinol arylates it called W-4, now marketed as Sollx. Sollx does not need to be painted, it offers good weather, chip, scratch, and chemical resistance, and is being used as the fenders for the new Segway Human Transporter. It is also aimed at automotive uses, including body panels. Sollx is coextruded into two layers, one clear and one colored, to simulate automotive paint. It is then thermoformed and molded into the finished product.

Several new ventures are based on using natural, renewable materials as the starting materials instead of petrochemicals. These products are know as “green” products since they are made from renewable resources and they can be composted. Along with the production of 1,3-propanediol by Shell and Dupont to produce nylon 4,6, Cargill Dow is making polylactide (PLA) beginning with corn-derived dextrose, which is fermented making lactic acid. The lactic acid is converted into lactide, a ring compound, that is polymerized through a ring opening.



PLA looks and processes like polystyrene. It has the stiffness and tensile strength of PET, and offers good odor barrier and resists fats, oils, and greases. PLA is being considered for use in fibers and in packaging. As a film, PLA has good deadfold properties, that is, the ability to be folded and to stay folded. It is being used as a fiber for apparel and carpeting applications. It is being sold as a bridge between synthetic and natural fibers in that it processes like synthetic fibers but has the touch, comfort, and moisture-management of natural fibers.

GLOSSARY

active site: Region of an enzyme or chromosome that binds the substrate molecule and catalytically transforms it.

alpha helix: Helical conformation of a chain, usually with maximal interchain hydrogen bonding; one of the most common “natural” structures.

AluI: One of a family of restriction endonucleases that are site specific endodeoxyribonucleases that cause cleavage of both strands of DNA within or near a specific site recognized by the enzyme; it’s recognition sequence is AG/CT.

antibody: Defense protein synthesized by the immune system of vertebrates.

anticodon: Specific sequence of three nucleotides in t-RNA, complementary to a condon for an amino acid in mRNA.

antigen: Molecules capable of eliciting the synthesis of a specific antibody.

attenuator: RNA sequence involved in regulating the expression of certain genes; also functions as a transcription terminator.

base pair: Two nucleotides in nucleic acid chains that are paired by hydrogen bonding of their bases; like Gee CAT representing the preferred pairing of G with C and A with T.

chromosome: Single large DNA molecule and its associated proteins that contains many genes. It stores and transmits genetic information.

centromere: Specialized site within a chromosome that serves as the attachment point for the mitotic or meiotic spindle during cell division that allows proteins to link to the chromosome. This attachment is essential for the equal and orderly distribution of chromosomes sets to daughter cells. It is about 130 base pairs in length and is rich in A=T pairs.

clones: Descendants of a single cell.

cloning: Production of large numbers of identical DNA molecules, cells, or organisms from a single ancestral DNA molecule, cell, or organism.

codon: Sequence of three adjacent nucleotides in a nucleic acid that codes for a specific amino acid.

cofactor: A coenzyme or other cofactor required for enzyme activity.

combinatorial chemistry: Approach whereby materials are developed and tested in an almost assembly line fashion, allows the ready determination of specific properties for a number of similar but unlike materials.

complementary: Molecular surfaces with chemical groups arranges to interact specifically with the chemical groupings on another molecular surface or molecule.

denatured: Partial or complete unfolding of the specific native conformation of a polypeptide, protein, or nucleic acid.

degenerate code: Code where a single element in one language is specified by more than one element in a second language.

diploid: Having two sets of genetic information, such as a cell having two chromosomes of each type.

domain: Distinct structural unit of a polypeptide.

engineering material: Material that can be machined, cut, drilled, sawed, etc., must have enough dimensional stability to allow these actions to be carried out on them.

enhancers: DNA sequences that help the expression of a specific gene; may be located close to or far from the particular gene.

enzyme: Molecule, protein or RNA, that catalyzes a particular chemical reaction.

eukaryote: Unicellular or multicellular organism with cells having a membrane-bounded nucleus, several chromosomes, and internal organelles.

exon: Segment of an eukaryotic gene that encodes a portion of the final product of the gene; part that remains after post-transcriptional processing and is transcribed into a protein or incorporated into the structure of an RNA. See also intron.

gene: Chromosomal segment that codes for a single functional polypeptide or RNA chain.

gene expression: Transcription, and for proteins, translation, giving the product of a gene; a gene is expressed within its biological product is present and active.

gene splicing: Enzymatic attachment of one gene or part of a gene to another.

genetic code: Set of triplet code words in DNA or mRNA coding for the specific amino acids of proteins.

genetic information: Information contained in a sequence of nucleotide bases in chromosomal DNA or RNA.

genetic map: Diagram showing the relative sequence and position of specific genes within a chromosome.

genome: All of the genetic information encoded in a cell or virus.

genotype: Genetic makeup of an organism as distinct from its physical characteristics.

geotextile: Polymeric mats, sheets, and textiles employed in the control of soil, water, etc., in geological applications.

immune response: Ability of a vertebrate to create antibodies to an antigen, a molecule typically a macromolecule, foreign to the host.

inducer: signal molecule which, when attached to a regulatory protein, produces an increase expression of a specific gene.

intron: Most genes are divided into two coding regins—one called exons or coding regions and the second called introns or noncoding regions.

in vitro: Literally means “in glass,” but today means outside the normal biological environment.

in vivo: Means “in life” and within the normal biological environment.

phenotype: The observable, physical characteristics of an organism.

photoconductive: Material that is conductive when exposed to light.

photoresponsive: Material whereby some property changes when it is exposed to light.

plasmid: Extrachromosomal, independently replicating, small circular DNA molecule often used in genetic engineering.

primer: Oligomeric molecule to which an enzyme adds additional monomeric subunits.

probe: Labeled fragment of a nucleic acid containing a nucleotide sequence complementary to a gene or genomic sequence that one wants to detect.

prokaryotic cell: Single-celled Bacteria with a single chromosome, no nuclear envelope and no membrane-bounded organelles.

recombination: Enzymatic process whereby the linear arrangement of nucleic acid sequences in a chromosome is altered by cleavage and rejoining.

recycling codes: Designations that allow easy, quick identification of a number of plastics used in the manufacture of containers.

repressor: Protein molecule, that binds to the regulatory sequence or operator for a gene blocking its transcription.

ribosomal RNA, rRNA: Class of RNA that serve as components of ribosomes.

ribosome: Very large complex of rRNAs and proteins; site of protein synthesis.

silent mutation: Mutation in a gene that causes no detectable change in the biological functioning of the gene.

smart material: Materials that react to an externally applied action such as the application of light, magnet, heat, electricity, and pressure.

sticky ends: Two DNA ends in the same or different DNA with short overhanging single-stranded segments that are complementary to one another, helping the joining of the two sites.

structural gene: Gene coding for a protein or RNA as distinct from regulatory genes.

technology: Applied science.

template: Pattern or surface upon which mirror-image replication can occur.

transcription: Enzymatic process where genetic information contained in one strand of DNA is employed to make a complementary sequence of bases in an mRNA.

transfer RNA, tRNA: Class of RNAs, each of which combine covalently with a specific amino acid as the initial step in protein synthesis.

translation: Process where the genetic information present in mRNA specifies the sequence of amino acids within a protein synthesis.

transposition: Movement of one gene or set of genes form one site in the genome to another site.

transposons: Segments of DNA, found in almost all cells, that move or "hop" from one place on a chromosome to another on the same or different chromosome.

virus: Self-replicating nucleic acid–protein complex that requires an intact host cell for replication; its genome can be either DNA or RNA.

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Appendix A: Symbols

A_0	Original concentration
A	Concentration at time T
Å	Angstrom unit (10^{-8} cm)
A	Arbitrary constant
A	Area
A	Arrhenius constant
A	Lewis acid
A	Antioxidant free radical
Ac	Acetyl group
Ar	Aryl group
AA	Reactant (step reactions)
ABS	Copolymer from acrylonitrile, butadiene, and styrene
AIBN	2,2′-Azobisisobutyronitrile
ANSI	American National Standards Institute (formerly American Standards Association)
AR	Acrylate
ASTM	American Society for Testing Materials
ATR	Attenuated total reflectance spectroscopy
AU	Polyurethane
AXF	Polydiphenylethane
a	Constant in the WLF equation
a	Exponent
a_r	Shift factor

B	Virial constant
BPO	Benzoyl peroxide

BSI	British Standards Institute
BTU	British thermal unit
b	Arbitrary constant
bp	Boiling point
C	Arbitrary constant
C	Catalyst–cocatalyst complex
C	Celsius (centrigrade)
C	Concentration
C	Degree of crystallinity
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CED	Cohesive energy density
CMC	Carboxymethylcellulose
CN	Cellulose nitrate
CO	Polyepichlorohydrin
CPVC	Critical pigment volume concentration
CR	Neoprene
C_p	Specific heat
C_s	Chain transfer constant
c	Velocity of light (3 × 10 cm/s)
cal	Calorie
cm	Centimeter
cm^{-1}	Reciprocal centimeter
cm^3	Cubic centimeter
co	Copolymer
cp	Chemically pure
D	Debye units (dipole)
D	Density
D	Dextro
D	Diameter
D	Diffusion constant
$\overline{\mathrm{DN}}\mathrm{A}$	Deoxyribonucleic acid
$\overline{\mathrm{DP}}$	Average degree of polymerization
DRS	Dynamic reflectance spectroscopy
DS	Degree of substitution
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DWV	Drain, waste, and vent pipe
d	Density
d	Dextro
d	Diameter
d	Total derivative (infinitesimal change)
E_a	Energy of activation
E	Energy content
E	Energy of vaporization

E	Young's modulus of elasticity
ECO	Epichlorohydrin elastomer
EEK	Accelerated test with sunlight at constant right angle
EGG	Einstein-Guth-Gold equation
EMMA	Equatorial mounting with mirrors (accelerated sunlight test)
EP	Epoxy resin
EPM	Poly(ethylene-co-propylene)
EPDM	Poly(ethylene-co-propylne) crosslinked
EPR	Electron paramagnetic resonance spectroscopy
ESR	Electron spin resonance spectroscopy
ET	Thiokol
ETA	Electrothermal analysis
e	Base of natural logarithms (2.718)
e	Exponential
e	Polarity factor (Alfrey-Price equation)

F	Fahrenheit
F	Mole fraction of monomers in copolymer
F	Stress (filled elastomers)
F_g	Fractional free volume (plasticizers)
FEP	Copolymer of tetrafluoroethylene and hexafluoropropylene
FPM	Polyfluorinated hydrocarbon
f	Aspect ratio
f	Efficiency factor (chain reactions)
f	Force
f	Functionality factor (step reactions)
f	Segmental friction factor
ft	Foot

G	Gauche conformation
G	Gibbs free energy
G	Modulus
G	Molar attraction constant (small)
GC	Gas chromatography
GPC	Gel permeation chromatography
GRS	Poly(butadiene-co-styrene)
g	Gauche conformation
g	Gram
g	Gravity
gr	Graft (copolymer)

H	Arbitrary constant
H	Enthalpy (heat content)
H	Hydrogen atom
H	Latent heat of transition
H	Magnetic field strength
H	Proportionality constant in light scattering
HIPS	High-impact polystyrene

h	Height
h	Planck's constant (6.625×10^{-27} erg-s) = 6.6×10^{-34} J-S
hp	Horsepower
h	Hour
I	Initiator (chain reactions)
I	Intensity
I	Spin of nucleus
IIR	Butyl rubber
IR	Infrared
ISO	International Standards Organization
IUPAC	International Union of Pure and Applied Chemistry
i	Incident ray
in.	Inch
it	Isotactic
K	Arbitrary constant
K	Constant in Mark-Houwink equation
K	Kelvin
K	Kinetic constant in Avrami equation
K	Rate constant
K	Thermal conductivity factor
k	Specific rate constant
kcal	Kilocalorie
kg	Kilogram
L	Length
L	Levo
LIM	Liquid injection molding
l	Length
l	Levo
l_c	Critical fiber length
LLDPE	Linear, low-density polyethylene
ln	Natural logarithm
log	Logarithm (base 10)
M	Chain stiffener constant
M	Molecular weight
M	Monomer (chain reaction)
[M]	Monomer concentration
M	Quantum number
M—	Free radical chain (macroradical)
Me	Methyl radical
MF	Melamine-formaldehyde resin
MR	Molar refraction
MVT	Moisture vapor transmission
MWD	Molecular weight distribution
M	Modulus

M_F	Modulus of a fiber
M_L	Longitudinal fiber
M_M	Modulus of resin matrix
M_O	Modulus of an unfilled resin
M_T	Transverse modulus
$\overline{M}$	Average molecular weight
$\overline{M}_n$	Number-average molecular weight
$\overline{M}_v$	Viscosity average molecular weight
$\overline{M}_w$	Weight-average molecular weight
m	Consistency factor (power law)
m	Meta isomer
m	Meter
m	Mole fraction of reactants (copolymers)
m	Number of mers in polymer chain
mL	Milliliter
mp	Melting point
N	Nitrogen atom
n	Number of units or items
NBR	Poly(butadiene-co-acrylonitrile)
NBS	National Bureau of Standards
NMR	Nuclear magnetic resonance spectroscopy
NR	Natural rubber
$\overline{N}_n$	Number-average molecular weight
n	Index of flow (power law)
n	Index of refraction
n	Mole (step reactions) fraction
n	Normal (continuous chain, linear)
n	Number of mers in polymer chain
n	Numbers of theoretical plates
n	Ratio of mers in copolymer
nm	Nanometers
NMR	Nuclear magnetic resonance spectroscopy
O	Oxygen atom
OI	Oxygen index
OMP	Organometallic polymer
o	Ortho isomer
oz	Ounce
P	Phosphorus atom
P	Polymer chain
P	Polymer radical
P	Pressure
P	Resonance-stability (Alfrey-Price equation)
PA	Polyamide (nylon)
PBI	Polybenzimidazole
PBT	Poly(butylene terephthalate)

PC	Polycarbonate
PCB	Polychlorinated biphenyls
PE	Polyethylene
PEEK	Poly(ether ether ketone)
PET	Poly(ethylene terephthalate)
PF	Phenol-formaldehyde resin
PGC	Pyrolysis gas chromatography
PMMA	Poly(methyl methacrylate)
PMR	Proton magnetic resonance spectroscopy
PNF	Polyphosphonitrilic fluorides
POM	Polyoxymethylene, polyformaldehyde, acetals
PP	Polypropylene
PPO	Poly(phenylene oxide)
PPS	Poly(phenylene sulfide)
PS	Polystyrene
PTFE	Polytetrafluoroehylene
PU	Polyurethane
PVA	Poly(vinyl alcohol)
PVAc	Poly(vinyl acetate)
PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)
PVDC	Poly(vinylidene chloride)
p	Para isomer
p	Pressure
p	Probability, fractional yield (Carothers)
p	Propagation
psi	Pounds per square inch

Q	Quantity of heat, rate of heat flow
Q	Resonance-stability factor (Alfrey-Price equation)
q	Electronic charge

R	Alkyl radical
R	Gas constant (1.986 cal/mole °K)
R	Rate (chain reactions)
R	Run number (copolymers)
R•	Free radical
RF	Radiofrequency
RIM	Reaction injection molding
RNA	Ribonucleic acid
r	Distance between centers of charge of dipoles
r	Radius
r	Ratio of reactants (step reaction)
r	Reactivity ratio (copolymers)
r	Refracted ray
$\bar{r}$	Average end-to-end distance
S	Entropy
S	Radius of gyration

S	Sedimentation constant
S	Solvent
S	Sulfur atom
SAM	Poly(styrene-co-acrylonitrile)
SBR	Poly(butadiene-co-styrene) elastomer
SEM	Scanning electron microscopy
SI	Silicone
SMA	Copolymer of styrene and maleic anhydride
SMC	Sheet molding compound
SN	Sulfur nitride
SPE	Society of Plastics Engineers
SPI	The Society of the Plastics Industry
SR	Synthetic rubber
S_N	Nucleophilic substitution
s	Stress
st	Syndiotactic

T	Absolute temperature (°A or K)
T	Tentative (ASTM)
T	Trans
TAPPI	Technical Association of the Pulp and Paper Industry
TDI	Toluenediisocyanate
TGA	Thermal gravimetric analysis
TMMV	Threshold molecular weight value
TPE	Thermoplastic elastomer
TPX	Poly-4-methylpentene
T_c	Ceiling temperature
T_c	Cloud point temperature
T_g	Glass transition temperature
T_m	Melting point
t	Termination (chain reaction)
t	Trans isomer
tit	Threodiisotactic
tst	Threosyndiotactic
tr	Transfer

UF	Urea-formaldehyde resin
UHMWPE	Ultrahigh molecular weight polyethylene polymer
UV	Ultraviolet

V	Volume
V_e	Elution volume
V_F	Fraction volume

WLF	Williams-Landel-Ferry equation
WS	Polyurethane
$\overline{W}_n$	Weight-average molecular weight
w	Width
w	Work

X	Ratio of reactants (copolymer)
X	Substutent (vinyl monomer)
yd	Yard
z	Critical chain length
α	Carbon atom adjacent to a functional group
α	One configuration of an isomer
α	Branching coefficient
α	First in a series
α_F	Expansion coefficient
α_c	Critical value for incipient gelation
β	One configuration of an isomer
β	Second carbon atom away from a functional group
β	Second in a series
γ	Magnetogyric ratio (nmr)
γ	Hydrogen bonding index (Lieberman)
γ	Strain
γ	Third carbon atom away from a functional group
Δ	Change
Δ	Heat
δ	Chemical shift (nmr)
δ	Expansion factor (solution process)
δ	Fourth carbon atom away from a functional group
δ	Solubility parameter (Hildebrand)
ε	Fifth carbon atom away from a functional group
η	Molar absorption coefficient
η	Viscosity
η_r	Reduced viscosity
η_{rel}	Relative viscosity
η_{sp}	Specific viscosity
$[\eta]$	Intrinsic viscosity (viscosity number)
Θ	Flory critical miscibility temperature, at which polymer-solvent interaction is zero
θ	Angle of scattering
λ	Wavelength
λ	Distance from origin to vertices of tetrahedra in filler
μ	Dipole moment
μ	Measure of polymer-solvent interaction (Flory-Huggins)
μ	Micron (10^{-4} cm, 10^4 Å)
μ	Nuclear magnetic moment
ν	Average kinetic chain length of chain-reaction polymers
ν	Frequency (vibrations/sec)
ν	Kinetic chain length
π	Bond formed by the side-to-side overlap of two p_z orbitals, which accounts for the high activity of vinyl monomers
π	Osmotic pressure

ρ	Density
Σ	Summation
σ	Sigma bonds
τ	Orientation relaxaton or retardation time
τ	Relaxation time
τ	Turbidity or scattered flux
τ	Universal viscosity constant (Flory)
ϕ	Jump frequency in hole filling (solution)
ϕ	Related to viscosity in Herschel-Bulkley equation
ω	Last in a series (e.g., carbon farthest away from functional group)
χ	Thickness
[ ]	Concentration

Appendix B: Trade Names

Trade or brand name	Product	Manufacturer
Abafil	Reinforced ABS	Rexall Chemical Co
Abalyn	Abietic acid derivative	Hercules, Inc
Abcite	Plastic sheet	E. I du Pont de Nemours & Co., Inc.
Absafil	ABS polymers	Fiberfil
Absinol	ABS	Dart Industries
Abson	ABS polymers	B. F Goodrich Chemical Co.
Acelon	Cellulose acetate	May & Baker Plastics Ltd
Acetophane	Cellulose acetate film	UCB-Sidac
Aclar	Polyfluorocarbon film	Allied Chemical Corp
Acralen	Styrene-butadiene latex	Farbenfabriken Bayer AG
Acronal	Polyalkyl vinyl ether	General Aniline Film Corp.
Acrylacon	Fibrous glass-reinforced polymers	Rexall Chemical Co
Acrylafil	Reinforced polymers	Rexall Chemical Co
Acrylaglas	Fiberglass-reinforced styrene-acrylonitrile	Dart Industries
Acrylicomb	Acrylic honeycomb	Dimensional Plastics, Corp.
Acrylux	Acrylic	Westlake Plastics
Acrilan	Polyacrylonitrile	Chemstrand Co
Acrylan-Rubber	Butyl acrylate-acrylonitrile copolymer	Monomer Corp.
Acrylite	Poly(methyl methacrylate)	American Cyanamid Co
Acryloid	Resin solutions	Rohm & Haas Co.
Acrysol	Thickeners	Rohm & Haas Co
Actol	Polyethers	Allied Chemical Corp.
Adipol	Plasticizer	FMC Corp

Trade or brand name	Product	Manufacturer
Adiprene	Urethane elastomers and prepolymer	E I du Pont de Nemours & Co , Inc
Admex	Plasticizers	Ashland Chemical Co
Advastab	Antistatic agents	Cincinnati Milacron Chemicals, Inc
Aerodux	Resorcinol formaldehyde resin	Ciba (A R L) Ltd
Aeroflex	Polyethylene extrusions	Anchor Plastics
Aeron	Plastic coated nylon	Flexfilm Products
Afcolene	Polystyrene and SAV copolymers	Pechiney-Saint Gobain
Afcoryl	ABS polymers	Pechiney-Saint-Gobain
Affinity	Polyethylene copolymer with poly(alpha olefins)	Dow Chemical Co
Agerite series	Antioxidants	R T Vanderbilt Co , Inc
Agro	Rayon fibers	Beaunit Mills Corp
Akulon	Nylon 6	AKU/Neth
Alathon	Polyethylene	E I du Pont de Nemours & Co , Inc
Albacar	Calcium carbonate filler	Pfizer Corp
Albertols	Phenolic resins	Chemische Werke, Albert
Alcryn	Chlorinated polyolefin blend with ethylene interpolymer	Advanced Polymer Alloys
Aldocryl	Acetal resin	Shell Chemical Co
Alfane	Epoxy resin cement	The Atlas Mineral Products Co
Algil	Styrene copolymer monofilament	Shawinigan Chemicals, Ltd , also Polymer Corp
Algoflon	Polytetrafluoroethylene	Montecatini
Alkathene	Polyethylene resins	Imperial Chemical Industries Ltd
Alkon	Acetal copolymer	Imperial Chemical Industries Ltd Celanese Corp of America
Alkor	Furan resin cement	Atlas Minerals Products Co
Alloprene	Chlorinated natural rubber	Imperial Chemical Industries Ltd
Alphalux	Poly(phenylene oxide)	Marbon Chemical Co
Alsibronz	Wet ground muscovite mica	Franklin Mineral Products Co
Alsilate	Clays	Freeport Kaolin Co
Alsynite	Reinforced plastic panels	Reichhold Chemicals, Inc
Amberlac	Modified alkyd resins	Rohm & Haas Co
Amberol	Phenolic resins	Rohm & Haas Co
Amberlite	Ion exchange resins	Rohm & Haas Co
Ameripol	Polyisoprene	Firestone Tire and Rubber Co
Amer Plate	PVC sheets	Ameron Corrosion Control
Amerith	Cellulose nitrate	Celanese Corp of America
Amilan	Nylon	Tojo Rayon Co
Ampcoflex	Rigid poly(vinyl chloride)	Atlas Mineral Products Co
Ancorex	ABS extrusions	Anchor Plastics
Antarox	Low foaming wetting agent	GAF Corp
Antiblaze	Organic phosphorus flame retardants	Mobil Chemical Co
Antron	Nylon fiber	E I du Pont de Nemours & Co , Inc

Trade or brand name	Product	Manufacturer
Anvyl	Vinyl extrusions	Anchor Plastics
Apex N	PVC blend with nitrile rubber	Teknor Apex
Apogen	Epoxy resins	Apogee Chemical
Araclor	Polychlorinated polyphenyls	Monsanto
Aralac	Protein fiber	Imperial Chemical Industries Ltd
Araldite	Epoxy resins	Ciba (A. R. L.) Ltd
Ardil	Protein fiber	Imperial Chemical Industries Ltd.
Armite	Vulcanized fiber	Spaulding Fibre Co.
Armorite	Vinyl coating	John L. Armitage & Co.
Arnel	Cellulose triacetate	Celanese Corp of America
Arnite	Poly(ethylene terephthalate)	Algemene Kuntstzijde Unie N V
Arnitel	Polyester block copolymer with polyether	DSM
Arochem	Modified phenolic resins	Ashland Chemical
Aroclor	Chlorinated polyphenyls	Monsanto Chemical Co.
Arodure	Urea resins	Ashland Chemical Co
Arofene	Phenolic resins	Ashland Chemical Co
Aroplaz	Alkyd resins	Ashland Chemical Co
Aropol	Polyester resins	Ashland Chemical Co
Aroset	Acrylic resins	Ashland Chemical Co.
Arothane	Polyester resins	Ashland Chemical Co.
Artfoam	Rigid urethane foam	Strux Corp
Arylon	Polyaryl ethers	Uniroyal
Arylon T	Polyaryl ethers	Uniroyal
Asaparene	Linear block styrene copolymer with butadiene	Asahi
Astrel	Polyarylsulfone	3M Co
Ascot	Polyolefin sheet–coated spunbounded	Appleton Coated Paper Co.
Astralit	Vinyl copolymer sheets	Dynamit Nobel/America
Astroturf	Synthetic turf–nylon and polyethylene	Monsanto
Astyr	Butyl rubber	Montecatini
Atlac	Polyester cast resin	ICI America Inc
Atomite	Calcium carbonate	Thompson, Weinman & Co.
Avisco	PVC film	FMC Corp
Avistar	Polyester film	FMC Corp.
Avisun	Polypropylene	Avisum Corp.
Avron	Rayon fiber	American Viscose Corp
Azdel	Fibrous glass–reinforced ABS copolymer sheet	Generic name
Azocel	Azodicarbonamide blowing agent	Fairmont Chemical Co.
Aztran	Poromeric sheet	B F Goodrich Chemical Co.
Bakelite	Phenol-formaldehyde	Union Carbide Chemicals Co
Barden	Kaolin clay	Huber, J. M , Corp.
Barex	Barrier resin	Vistron Corp.
Baygal	Polyester for casting resins	Farbenfabriken Bayer AG
Baylon	Polycarbonate	Farbenfabriken Bayer AG
Baypren	Polychloroprene	Farbenfabriken Bayer AG
Beckacite	Modified phenolic	Reichhold Chemicals, Inc.: Beck, Koller & Co , Ltd

Trade or brand name	Product	Manufacturer
Beckamine	Urea formaldehyde	Reichhold Chemicals Inc Beck, Koller & Co Ltd
Beckopox	Epoxy resins	Reichhold Chemicals Inc
Beckosol	Alkyd resins	Reichhold Chemicals Inc Beck Koller & Co Ltd
Beetle	Urea formaldehyde resins	American Cyanamid Co
Bemberg	Rayon fiber	Beaunit Mills Corp
Bentone	Gelling agent	Kronos Titan GmbH
Bexone F	Poly(vinyl formal)	British Xylonite
Benvic	Poly(vinyl chloride)	Solvay & Cie S A
Betalux	TFE filled acetal	Westlake Plastics
Bexphane	Polypropylene	Bakelite Xylonite Ltd
Blanex	Polyethylene cross linked	Richhold Chemicals
Blapol	Polyethylene compounds	Richhold Chemicals
Blendex	ABS resin	Borg-Warner Corp
Bolta Flex	Vinyl sheeting and film	General Tire & Rubber Co
Bolta Thene	Rigid olefin sheets	General Tire & Rubber Co
Boltaron	Plastic sheets	General Tire & Rubber Co
Bonadur	Organic pigments	American Cyanamid Co
Bondstrand	Filament wound fiberglass reinforced plastics	Ameron Corrosion Control Div
Borofil	Boron filaments	Texaco Corp
Boronol	Polyolefins with boron	Allied Resinous Products Inc
Bostik	Epoxy and polyurethane adhesives	Bostik Finch
Bronco	Supported vinyl or pyroxylin	General Tire & Rubber Co
Budene	cis 1 4 Polybutadiene	Goodyear
Busan	Flame retardant microbiocide	Buckman Laboratories
Butacite	Poly(vinyl acetal) resins	E I du Pont de Nemours Co Inc
Bukaton	Butadiene copolymers	Imperial Chemical Industries Ltd
Butaprene	Styrene butadiene elastomers	Firestone Tire & Rubber Co
Butarez CTL	Telechelic butadiene polymer	Phillips Petroleum Co
Buton	Butadiene styrene resin	Enjay Chemical Co
Bu Tuf	Polybutene	Petrotex Chemical Corp
Butvar	Poly(vinyl butyral) resin	Shawinigan Resins Corp
BXL	Polysulfone	Union Carbide
Cab O Sil	Colloidal silica	Cabot Corp
Cadco	Plastic rod etc	Cadillac Plastics
Cadon	Nylon filament	Chemstrand Corp
Cadox	Organic peroxides	Cadet Chemical Corp
Calprene	Linear and branched styrene copolymers with butadiene	Repsol
Calwhite	Calcium carbonate	Georgia Marble Co
Camel Carb	Calcium carbonate	Harry T Campbell Sons' Corp
Capran	Nylon 6	Allied Chemical Corp
Captax	Accelerator (2 mercaptor benzothiazole)	Goodyear Tire & Rubber Co

Trade or brand name	Product	Manufacturer
Carbaglas	Fiberglass-reinforced polycarbonate	Dart Inds
Carbitol	Solvents	Union Carbide Corp
Carboloy	Cemented carbides	General Electric Co
Carbomastic	Epoxy coal tar coating	Carboline Co.
Carbopol	Water-soluble resins	B F. Goodrich Chemical Co
Carboset	Acrylic resins	B. F. Goodrich Chemical Co
Carbospheres	Hollow carbon spheres	Versar, Inc.
Carbowax	Poly(ethylene glycols)	Union Carbide Chemical Co
Cariflex I	cis-1, 4-Polyisoprene	Shell Chemical Co
Cariflex TR	Linear and branched styrene block copolymers	Shell Chemical Co.
Carina	Poly(vinyl chloride)	Shell Chemical Co Ltd
Carinex	Polystyrene	Shell Chemical Co. Ltd
Carolux	Flexible filled urethane foam	North Carolina Foam
Carstab	Urethane foam catalysts	Cincinnati Milacron Chemicals, Inc
Castcar	Cast polyolefin films	Mobil Chemical
Castethane	Castable polyurethanes	Upjohn Co
Castomer	Urethane elastomer and coatings	Baxenden Chemical & Witco Chemical Corp.
Catalac	Phenol-formaldehyde resin	Catalin Ltd
Celanar	Polyester film and sheeting	Celanese Plastics Co
Celanex	Thermoplastic polyester	Celanese Plastics Co
Celatron	Polystyrene	Celanese Plastics Co
Celcon	Acetal copolymers	Celanese Plastics Co.
Celgard	Microporous polypropylene film	Celanese Plastics Co
Celite	Diatomite filler	Johns-Manville Corp
Cellasto	Microcellular urethane elastomer	North American Urethanes
Cellofoam	Polystyrene foam board	United States Mineral Products Co.
Cellonex	Cellulose acetate	Dynamit Nobel/America
Cellon	Cellulose acetate	Dynamit Nobel
Cellosize	Hydroxyethyl cellulose	Union Carbide Corp.
Celluliner	Expanded polystyrene foam	Gilman Brothers
Cellulite	Expanded polystyrene foam	Gilman Brothers
Celluloid	Plasticized cellulose nitrate	Celanese Plastics Co.
Celogan	Blowing agents	Uniroyal, Inc
Celpak	Rigid polyurethane foam	Dacar Chemical
Celramic	Glass nodules	Pittsburgh Corning Corp.
Cerex	Styrene copolymer	Monsanto Chemical Co.
C-Flex	Linear block styrene copolymer with ethylene-butylene	Consolidated Polymer Technologies
Chemigum	Urethane elastomer	Goodyear Tire & Rubber Co.
Chem-o-sol	PVC plastisol	Chemical Products Co
Chempro	Ion-exchange resin	Freeman Chem Corp
Celthane	Rigid polyurethane foam	Dacar Chemical
Chemfluor	Fluorocarbon plastics	Chemplast, Inc
Chemglaze	Polyurethane-based coating	Lord Corp.
Chemgrip	Epoxy adhesives for TFE	Chemplast, Inc.

Trade or brand name	Product	Manufacturer
Chlorowax	Chlorinated paraffins	Diamond Alkali Co
Cibanite	Aniline-formaldehyde resin	Ciba Products Co
Cimglas	Fiberglass-reinforced polyester	Cincinnati Milacron
Cis-4	cis-1,4-Polybutadiene	Phillips Petroleum Co
Clarite	PVC stabilizers	National Lead Co
Clocel	Rigid urehtane foam	Baxenden Chemical
Clopane	PVC tubing and film	Clopay Corp
Cloudfoam	Polyurethane foam	International Foam
Co Rexyn	Polyester resins, coatings, pastes	Interplastic Corp
Cobex	Poly(vinyl chloride)	Bakelite Xylonite Ltd
Cobocell	Cellulose acetate butyrate tubing	Cobon Plastics
Coboflon	Teflon tubing	Cobon Plastics
Cobothane	Ethylene–vinyl acetate tubing	Cobon Plastics
Collodion	Solution of cellulose nitrate	Generic name
Colovin	Calendered vinyl sheeting	Columbus Coated Fabrics
Conathane	Polyuethane compounds	Conap, Inc
Conolite	Polyester laminate	Woodall Industries
Coperba	Linear styrene block copolymers with butadiene	Petroflex
Coral rubber	cis Polyisoprene	Firestone Tire & Rubber Co
Cordo	PVC foam and films	Ferro Corp
Cordoflex	Polyvinylidene fluoride solutions	Ferro Corp
Cordura	Regenerated cellulose	E I du Pont de Nemours & Co , Inc
Corfam	Poromeric film	E I du Pont de Nemours & Co , Inc
Corlite	Reinforced foam	Snark Products
Coro-Foam	Urethane foam	Cook Paint & Varnish
Corval	Rayon fiber	Courtaulds
Corvel	Plastic coating powders	The Polymer Corp
Corvic	Vinyl polymers	Imperial Chemical Industries Otd
Courlene	Polyethylene (fiber)	Courtaulds
Coverlight HTV	Vinyl-coated nylon fabric	Reeves Brothers
Covol	Poly(vinyl alcohol)	Corn Products Co
Crastin	Poly(ethylene terephthalate)	Ciba Geigy
Creslan	Acrylonitrile–acrylic ester copolymers	American Cyanamid Co
Cronar	Polyethylene	E I du Pont de Nemours & Co , Inc
Cryowrap	Thermoplastic sheets and films	W R Grace & Co
Cryovac	Polypropylene film	W R Grace & Co
Crystalex	Acrylic resin	Rohm & Haas Co
Crystalon	Rayon fiber	American Enka Corp
Crystic	Polyester resins	Scott Bader Co
Cumar	Coumarone indene resins	Allied Chemical Corp
Curithane	Polyaniline polyamines	Upjohn
Curon	Polyurethane foam	Reeves Brothers
Cyanaprene	Polyurethane	American Cyanamid Co
Cyanolit	Cyanoacrylate adhesive	Leader, Denis Ltd
Cyasorb	Ultraviolet absorbers	American Cyanamid Co

Trade or brand name	Product	Manufacturer
Cycloset	Cellulose acetate fiber	E. I du Pont de Nemours & Co , Inc.
Cycolac	Acrylonitrile-butadiene-styrene copolymer	Borg-Warner Corp.
Cycolon	Resinous compositions	Borg-Warner Corp
Cycoloy	Polymers with ABS alloy resins	Borg-Warner Corp
Cycopoac	ABS and nitrile barrier	Borg-Warner Corp.
Cymac	Thermoplastic molding materials	American Cyanamid Co.
Cymel	Melamine molding compound	American Cyanamid Co.
Cyovin	Self-extinguishing ABS graft-polymer blends	Borg-Warner Corp.
Cyglas	Glass-filled polyester	American Cyanamid
Dabco	Triethylenediamine	Air Products Co
Dacovin	Rigid poly(vinyl chloride)	Diamond Alkali Co.
Dacron	Polyester fiber	E I. du Pont de Nemours & Co., Inc
DAP	Diallyl phthalate monomer	FMC Corp
Dapon	Diallyl phthalate prepolymer	FMC Corp.
Daponite	Dapon-fabric laminates	FMC Corp.
Daran	Poly(vinylidene chloride) emulsion coatings	W R Grace & Co.
Daratak	PVA emulsions	W C. Grace
Darex	Styrene copolymer resin	W. R. Grace & Co.
Darvan	Poly(vinylidene cyanide)	Celanese Corp. of America
Darvic	Poly(vinyl chloride)	Imperial Chemical Industries, Ltd
Davon	TFE	Davies Nitrate
Daxad	Dispersing agents	W. R. Grace & Co
Decanox	Organic peroxides	Wallace & Tiernan, Inc
Deenax	Antioxidants	Enjay Chemical Co.
Degalan	Poly(methyl methacrylate)	Degussa
Delrin	Acetal polymer	E I du Pont de Nemours & Co., Inc
Densite	Urethane foam	Tenneco Chemical
Derakane	Polyester resin	Dow Chemical Co
Derolite	Ion-exchange resin	Diamond Alkali Co.
Desmodur	Isocyanates for polyurethane foam	Farbenfabriken Bayer AG
Desmopan	Polyurethanes	Farbenfabriken Bayer AG
Desmophen	Polyesters and polyethers for polyurethanes	Farbenfabriken Bayer AG
Devran	Epoxy resins	Devoe & Reynolds Co.
Dexel	Cellulose acetate	British Celanese Ltd.
Dexon	Polypropylene-acrylic	Exxon Chemical
Dexsil	Polycarboranesiloxane	Olin Mathieson Corp
Diakon	Poly(methyl methacrylate)	Imperial Chemical Industries Ltd.
Diall	Diallyl phthalate	Allied Chemical Corp
Diaron	Melamine resins	Reichhold Chemicals
Dicalite	Diatomaceous earth	Dicalite/Grefco, Inc.
Dielux	Acetals	Westlake Plastics

Trade or brand name	Product	Manufacturer
Diene	Polybutadiene	Firestone Tire & Rubber Co
Dimetcote	Protective coating	Americoat Corp
Diolen	Poly(ethylene terephthalate)	ENKA Glazstoft
Dion	Polyester resin	Diamond Alkali Co
Dolphon	Epoxy and polyester resins	John C Dolph
Dorvon	Polystyrene foam	Dow Chemical
Doryl	Poly(diphenyl oxide)	Westinghouse Electric Corp
Dow Corning	Silicons	Dow Corning
Dowex	Ion exchange resins	Dow Chemical Co
Dralon	Polyacrylonitrile fiber	Farbenfabriken Bayer AG
Dri Lite	Expanded polystyrene	Poly Foam
Duco	Cellulose nitrate lacquers	E I du Pont de Nemours & Co Inc
Dulac	Lacquers	Sun Chemical Corp
Dulux	Polymeric enamels	E I du Pont de Nemours & Co Inc
Duolite	Ion exchange resin	Diamond Alkali Co
Duracel	Lacquers	Maas & Waldstein
Duracon	Acetal copolymers	Polyplastics
Dural	Acrylic modified PVC	Alpha Chemical & Plastics
Duralon	Furan molding resins	U S Stoneware Co
Durane	Polyurethanes	Raffi & Swanson
Duramac	Alkyd resins	Commercial Solvents Corp
Duraplex	Alkyd resins	Rohm & Haas Co
Duraspan	Spandex fibers	Carr Fulflex Corp
Durelene	PVC tubing	Plastic Warehousing
Durethan	Nylon 6	Farbenfabriken Bayer AG
Durethan U	Polyurethanes	Farbenfabriken Bayer AG
Durethene	Polyethylene film	Sinclair-Koppers Co Inc
Durez	Phenolic resins	Hooker Chemical & Plastics
Durathon	Polybutylene resins	Witco Chemical Corp
Durite	Phenolic resins	The Borden Co
Duron	Phenolics	Firestone Foam
Dutral	Ethylene propylene copolymer	Montecatini
Dyal	Alkyd resins	Sherwin Williams Co
Dyalon	Urethane elastomers	Thombert
Dyfoam	Expanded polystyrene	W C Grace
Dylan	Polyethylene resins	Sinclair Koppers Co Inc
Dynaflexl	Linear block styrene copolymers	GLS
Dynel	Vinyl chloride–acrylonitrile copolymers	Union Carbide Corp
Dylel	ABS copolymer	Sinclair Koppers Co Inc
Dylene	Polystyrene resins	ARCO Polymer Inc
Dylite	Expandable polystyrene	Sinclair Koppers Co Inc
Dynafilm	Polypropylene film	U S Industrial Chemicals Co , Div National Distillers & Chemical Corp
Dynel	Modacrylic fiber	Union Carbide Corp
Dyphene	Phenol formaldehyde resins	Sherwin-Williams Co
Dyphos	Stabilizer for poly(vinyl chloride)	National Lead Co

Trade or brand name	Product	Manufacturer
E-Foam	Epoxies	Allied Products
Easypoxy	Epoxy adhesive kits	Conap, Inc
Ebolan	TFE materials	Chicago Gasket Co
Ecavyl	Poly(vinyl chloride)	Kuhlmann
Eccosil	Silicon resins	Emerson & Cuming
Eccospheres	Hollow glass spheres	Emerson & Cummings Inc
Ecdel	Polyester block copolymer with polyether	Eastman Kodak Co
Elastolit	Urethane engineering thermoplastics	North American Urethanes
Elastollan	Polyurethane block copolymer with polyehter/polyester	BASF Corp
Elastollyx	Urethane Engineering thermoplastics	North American Urethanes
Elastolur	Urethane coatings	BASF Corp
Elastonate	Urethane isocyanate prepolymers	BASF Corp
Elastonol	Urethane polyester polyols	North American Urethanes
Elastopel	Urethane engineering thermoplastics	North American Urethanes
Elastothane	Polyurethane elastomer	Thiokol Corp
Electroglas	Cast acrylic	Glasflex Corp
Elexar	Linear styrene block copolymer with ethylene-butylene	Teknor Apex
Elf	Carbon black	Cabot Corporation
El Rexene	Polyolefin resins	Rexall Chemical Co
El Rey	Low density polyethylene	Rexall Chemical Co
Elvace	Acetate ethylene copolymers	E I du Pont de Nemours & Co , Inc
Elvacet	Poly(vinyl acetate) emulsion	E I du Pont de Nemours & Co , Inc
Elvacite	Acrylic resins	E I du Pont de Nemours & Co , Inc
Elvamide	Nylon resins	E I du Pont de Nemours & Co , Inc
Elvanol	Poly(vinyl alcohol) resins	E I du Pont de Nemours & Co , Inc
Elvax	Poly(ethylene-co vinyl acetate)	E I du Pont de Nemours & Co , Inc
Elvic	Poly(vinyl chloride)	Solvay
Engage	Polyethylene copolymer with poly(alpha-olefins)	Dow Chemical Co
Enkalure	Nylon fiber	American Enka Corp
Enrad	Preirradiated polyethylene	Enflo Corp
Enrup	Thermosetting resin	United States Rubber Co
Ensocote	PVC lacquer coatings	Uniroyal
Ensolex	Cellular plastic sheets	Uniroyal
Ensolite	Cellular plastic sheets	Uniroyal
Epibond	Epoxy adhesive resin	Furane Plastics, Inc
Epicure	Curing agents for epoxy resins	Celanese Corp
Epikote	Epoxy resins	Shell Chemical Co

Trade or brand name	Product	Manufacturer
Epilox	Epoxy resins	Leuna
Epi Rez	Epoxy cast resin	Celanese Corp
Epi Tex	Epoxy ester resins	Hoechst Celanese
Epikote	Epoxy resins	Shell Chemical
Epocap	Two part epoxy compounds	Hardman
Epocast	Epoxy resins	Furane Plastics Inc
Epocrete	Two part epoxy compounds	Hardman
Epocryl	Epoxy acrylate resin	Shell Chemical Co
Epodite	Epoxy resins	Showa Highpolymer Co
Epolast	Two part epoxy compounds	Hardman
Epolene	Low melt polyethylene	Eastman Chemical Products, Inc
Epolite	Epoxy compounds	Hexcel Corp
Epomarine	Two part epoxy compounds	Hardman
Epon	Epoxy resins	Shell Chemical Co
Eponol	Linear polyether resins	Shell Chemical Co
Eposet	Two part epoxy compounds	Hardman
Epotuf	Epoxy resins	Reichhold Chemical Co
Epoxylite	Epoxy resins	Epoxylite Corp
Escon	Polypropylene	Enjay Chemical Co
Estane	Polyurethane resins	B F Goodrich Chemical Co
Estron	Cellulose acetate filament	Eastman Chemical Products Inc
Ethafoam	Polyethylene foam	Dow Chemical Co
Ethocel	Ethyl cellulose	Dow Chemical Co
Ethofil	Fiberglass reinforced polyethylene	Dart Industries
Ethoglas	Fiberglass reinforced polyethylene	Dart Industries
Ethosar	Fiberglass reinforced polyethylene	Dart Industries
Ethron	Polyethylene	Dow Chemical Co
Ethylux	Polyethylene	Westlake Plastics
Europrene Sol T	Linear and branched styrene copolymers	Enichem
Evenglo	Polystyrene	Sinclair Koppers Co Inc
Everflex	PVA copolymer emulsion	W C Grace
Everlon	Polyurethane foam	Stauffer Chemical
Exact	Polyethylene copolymer with poly(alpha olefins)	Exxon
Excelite	Polyethylene tubing	Thermoplastic Processes
Exon	Poly(vinyl chloride)	Firestone Plastics
Extane	Polyurethane tubing	Pipeline Service Co
Extrel	Plastic films	Exxon Chemical Co U S A
Extren	Fiberglass reinforced polyester	Morrison Molded Fiber Glass Co
Fabrifil	Chopped rag fillers	Microfibers Inc
Fabrikoid	Pyroxylin coated fabrics	E I du Pont de Nemours & Co Inc
Facilon	Reinforced PVC fabric	Sun Chemical
Fassgard	Vinyl coated nylon	M S Fassler & Co
Fasslon	Vinyl coating	M S Fassler & Co
Felor	Nylon filaments	E I du Pont de Nemours & Co Inc

Trade or brand name	Product	Manufacturer
Ferroflex	Polypropylene blend with EPDM or EPR	Ferro
Fertene	Polyethylene	Montecatini
Fibercast	Reinforced plastic pipe	Fibercast Co
Fiberglas	Fibrous glass	Owens Corning Fiberglas Corp
Fiberite	Phenolic molding compounds	Fiberite Corp
Fibro	Rayon	Courtaulds NA, Inc
Filabond	Unsaturated polyester	Reichhold
Filfrac	Cut cotton fiber	Rayon Processing Co of Rhode Island
Finaprene	Linear styrene block copolymers with butadiene	Fina
Firemaster	Fire retardants	Michigan Chemical Corp
Firmex	Carbon black	Columbian Carbon Co
Flakeglas	Glass flakes for reinforcements	Owens-Corning Fiberglas Corp
Flectol	Amine type antioxidants	Monsanto Co
Flexane	Polyurethanes	Devcon Corp
Flexocel	Polyurethane foam	Baxenden Chemical
Flexol	Plasticizers	Union Carbide Chemical Co
Flexomer	Polyethylene copolymer with poly(alpha olefins)	Union Carbide
Flexothene	Propylene blend with EPDM or EPR	Equistar
Flexprene	Linear block styrene copolymer with butadiene	Teknor Apex
Floranier	Cellulose	Rayonier, Inc
Flovic	Poly(vinyl acetate)	Imperial Chemical Industries, Ltd
Fluokem	Teflon spray	Bel-Art Products
Fluon	Polytetrafluoroethylene	Imperial Chemical Industries, Ltd
Fluon	PTFE powders and dispersions	Imperial Chemical Industries, Ltd
Fluorel	Poly(vinylidene fluoride)	Minnesota Mining and Mfg Co
Fluorglas	PTEF impregnated materials	Dodge Industries
Fluorobestos	Asbestos-Teflon composite	Raybestos Manhattan, Inc
Fluorocord	Fluorocarbon material	Raybestos Manhattan Inc
Fluorofilm	Cast Teflon films	Dilectrix Corp
Fluoron	Polychlorotrifluoroethylene	Stokes Molded Products
Fluoroplast	Polytetrafluoroethylene	U S Gasket Co
Fluororay	Filled fluorocarbon	Raybestos Manhattan, Inc
Fluorored	TFE compounds	John L Dore Co
Fluorosint	TFE—fluorocarbon composition	Polymer Corp
Foamex	Poly(vinyl formal)	General Electric Co
Foamthane	Polyurethane foam	Pittsburgh Corning Corp
Formadall	Polyester premix	Woodall Industries
Formaldafil	Fiberglass-reinforced acetals	Dart Industries
Formaldaglass	Fiberglass-reinforced acetals	Dart Industries
Formaldasar	Fiberglass-reinforced acetals	Dart Industries
Formex	Poly(vinyl acetal)	General Electric Co

Trade or brand name	Product	Manufacturer
Formica	Thermosetting laminates	Formica Corp
Formrez el	Liquid resins for urethane elastomers	Witco Chemical Co
Formvar	Poly(vinyl formal)	Shawinigan Resins Corp
Forticel	Cellulose propionate	Celanese Corp of America
Fortiflex	Polyethylene	Celanese Plastics Co
Fortisan	Saponified cellulose acetate	Celanese Corp of America
Fortrel	Polyester fiber	Fiber Industries Inc
Fostacryl	Poly(styrene coacrylonitrile)	Foster Grant Co
Fostalene	Plastic	Foster Grant Co
Fosta Net	Polystyrene foam mesh	Foster Grant Co
Fosta Tuf Flex	High impact polystyrene	Foster Grant Co
Fostafoam	Expandable polystyrene beads	Foster Grant Co
Fostalite	Light stabilized polystyrene	Foster Grant Co
Fostarene	Polystyrene	Foster Grant Co
FPC	PVC resins compound	Firestone Tire & Rubber Co
Freon	Blowing agents	E I du Pont de Nemours & Co , Inc
Furname	Epoxy and furan resins	Atlas Mineral Products Co
Futron	Polyester	Fusion Rubbermaid
Fyberoid	Fishpaper	Wilmington Fibre Specialty Co
Fyrol	Flame retardants	Stauffer Chemical Co
Galalith	Casein plastics	Generic name
Gama-Sperse	Calcium carbonate	Georgia Marble Co
Gantrez	Poly(vinyl ether comaleic anhydride)	Dyestuff Chemical Div , General Aniline & Film Corp
Garan	Fibrous glass roving	Johns Manville Corp
Garan Finish	Sizing for glass fibers	Johns Manville Corp
Garox	Organic peroxides	Ram Chemicals Inc
Gedamine	Unsaturated polyester	Charbonnages
Gelva	Poly(vinyl acetate)	Shawinigan Resins Corp
Gelvatex	Poly(vinyl acetate) emulsions	Shawinigan Resins Corp
Gelvatol	Poly(vinyl alcohol)	Shawinigan Resins Corp
Gemon	Malefamide	General Electric Co
Genaire	Poromeric film	General Tire & Rubber Co
Genal	Thermosets	General Electric Co
Genthane	Polyurethane elastomer	General Tire & Rubber Co
Genetron	Fluorinated hydrocarbon monomers and polymers	Allied Chemical Co
Gentro	Butadiene copolymer	General Tire & Rubber Co
Geolast	Polypropylene dynamic vulcanizate with nitrile rubber	AES
Geon	Poly(vinyl chloride)	B F Goodrich Chemical Co
Gil Fold	Polyethylene sheets	Gilman Brothers
Glaskyd	Glass reinforced alkyd resin	American Cyanamid Co
Glufil	Shell flour	Agrashell Inc
Glyptal	Alkyd coating	General Electric Co
Gracon	PVC	W C Grace
GravoFLEX	ABS sheets	Hermes Plastics
GravoPLY	Acrylic sheets	Hermes Plastics

Trade or brand name	Product	Manufacturer
Grex	Polyethylene	W R. Grace & Co.
Grilamid	Polyamide copolymer with polyether/polyester	EMS America
Grilon	Polyamide copolymer with polyether/polyester	EMS America
Halar	Polyfluorocarbons	Allied Chemical Co
Halex	Polyfluorocarbon	Allied Chemical Co.
Halon	Fluorochlorocarbon	Allied Chemical Co
Halowax	Chlorinated naphthalene	Union Carbide Corp
Harflex	Plasticizers	Wallace & Tiernan, Inc
Haylar	CTFE	Allied Chemical
Haysite	Polyester laminates	Synthane-Taylor
HB-40	Hydrogenated terphenyl	Monsanto Co.
Hercocel	Cellulose acetate	Hercules Powder Co
Hercoflex	Phthalate plasticizers	Hercules Powder Co.
Hercolyn	Hydrogenated methyl abietate	Hercules Powder Co
Hercose	Cellulose acetate-propionate	Hercules Powder Co.
Herculoid	Cellulose nitrate	Hercules Powder Co.
Herculon	Polypropylene	Hercules Powder Co
Herox	Nylon	E I du Pont de Nemours & Co , Inc.
Het anhydride	Chlorendic anhydride	Hooker Chemical Corp.
Hetrofoam	Fire-retardant urethane foam	Hooker Chemical Corp
Hetron	Fire-retardant polyester resins	Hooker Chemical Corp
Heaveaplus	Copolymer of methyl methacrylate and rubber	Generic name
Hexcel	Structural honeycomb	Hexcel Products, Inc
Hex-One	HDPE	Gulf Oil
H-film	Polyamide film from pyromellitic anhydride and 4,4-diaminodiphenyl ether	E. I. du Pont de Nemours & Co , Inc
Hi-Blen	ABS polymers	Japanese Geon Co
Hi-fax	High-density polyethylene	FMC Corp ; Hercules Powder Co
Hifax	Polyporpylene blend with EPDM or EPR	Himont
Hipack	Polyethylene	Showa Highpolymer Co
Hi-Sil	Amorphous silica	PPG Corp.
Hi-Styrolux	High-impact polystyrene	Westlake Plastics
Hitalex	Polyethylene	Hitachi Chemical Co
Hitanol	Phenol-formaldehyde resins	Hitachi Chemical Co.
Horse Head	Zinc oxide pigments	New Jersey Zinc Co
Hostadur	Poly(ethylene terephthalate)	Farbwerke Hoechst AG
Hostaflon C2	Polychlorotrifluorethylene	Farbwerke Hoechst AG
Hostaflon TF	Polytetrafluoroethylene	Farbwerke Hoechst AG
Hostalen	Polyethylene	Farbwerke Hoechst AG
Hostalen GC	HDPE/LDPE	Hoechst
Hostyren	Polystyrene	Hoechst
Hurcuprene	Linear block styrene copolymer with butadiene or ethylene-butylene	J-Von

Trade or brand name	Product	Manufacturer
Hyamine	Cationic surfactants	Rohm & Haas Co
Hycar	Butadiene acrylonitrile copolymer	B F Goodrich Chemical Co
Hydraflex	Printing ink	Sun Chemical Corp
Hydrepoxy	Water based epoxies	Allied Products
Hydrin	Epichlorohydrin rubber	Goodrich Hercules
Hydrocal	Gypsum	U S Gypsum Co
Hydro Foam	Expanded phenol formaldehyde	Smithers Co
Hydropol	Hydrogenated polybutadiene	Phillips Petroleum Co
Hylar	Poly(ethylene terephthalate)	E I du Pont de Nemours & Co Inc
Hylene	Organic isocyanates	E I du Pont de Nemours & Co Inc
Hypalon	Chlorosulfonated polyethylene	E I du Pont de Nemours & Co, Inc
Hytrel	Polyester block copolymer with polyether/polyester	Du Pont
Igepal	Wetting agents	General Aniline & Film Corp
Igepon	Surfactants wetting agents	General Aniline & Film Corp
Implex	Acrylic resins	Rohm & Haas Co
Insurok	Phenol formaldehyde molding compounds	The Richardson Co
Intamix	Rigid PVC	Diamond Shamrock Corp
Ionac	Ion exchange resins	Permutit Co
Ionol	Antioxidant	Shell Chemical Co
Irganox	Antioxidants	Geigy Chemical Corp
Irrathene	Irradiated polyethylene	General Electric Co
Irvinil	PVC resins	Great American Chemical
Isoderm	Urethane integral skinning foam	Upjohn
Isofoam	Polyurethane foam resins	Isocyanate Products Inc
Isomid	Polyester polyamide film magnet wire	Schenectady Chemicals Inc
Isonate	Diisocyanates	Upjohn Co
Isonol	Propoxylated amines	Upjohn Co
Isoteraglas	Isocyanate elastomer–coated Dacron glass fabric	Natvar Corp
Isothane	Polyurethane foam	Bernel Foam Products
Iupilon	Polycarbonate	Mitsubishi Edogawa Chemical Co
Jay Flex	Plasticizers	Enjay Chemical Co
Jetfoam	Polyurethane foam	International foam
Jet Kote	Furane resin coatings	Furane Plastics Inc
Kadox	Zinc oxide	New Jersey Zinc Co
Kalex	Urethane resin	Di Acro Kaufman
Kalite	Precipitated calcium carbonate	Diamond Alkali Co
Kalmac	Calcium carbonate	Georgia Marble Co
Kalspray	Rigid urethane foam	Baxenden Chemical
Kaofil	Coating and filler clay	Thiele Kaolin Co
Kapsol	Plasticizers	Ohio Apex Div FMC Corp
Kapton	Polyimide	E I du Pont de Nemours & Co, Inc

Trade or brand name	Product	Manufacturer
Kardel	Polystyrene film	Union Carbide Corp.
Kaurit	Urea-formaldehyde resins	Badische Anilin & Coda-Fabrik AG
Kelburon	Polypropylene/EP	DSM N V
Kel-F	Trifluorochloroethylene resins	Minnesota Mining & Mfg. Co
Keltrol	Copolymers	Textron, Inc.
Kematal	Acetal copolymers	Imperial Chemical Industries, Ltd
Kenflex	Hydrocarbon resins	Kenrich Petrochemicals, Inc
Ken-U-Thane	Polyurethane	Kenrich Petrochemicals, Inc
Kessco	Plasticizers	Kessler Chemical Co , Inc.
Ketac	Ketone-aldehyde resin	American Cyanamid Co.
Kinel	Maleimide	Rhone-Poulenc
Kodacel	Cellulose acetate film	Eastman Chemical Products, Inc
Kodaflex	Plasticizers	Eastman Chemical Products, Inc.
Kodar	Copolyesters	Eastman Chemical
Kodel	Polyester fibers	Eastman Kodak Co.
Kohinor	Vinyl resins	Pantasote Co
Kollidon	Poly(vinyl pyrrolidone)	General Aniline & Film Corp.
Kolorbon	Rayon fiber	American Enka Corp.
Kopox	Epoxy resin	Koppers Co.
Korad	Acrylic film	Rohm & Haas Co
Korez	Phenolic resin cement	Atlas Mineral Products Company
Koroseal	Poly(vinyl chloride)	B F Goodrich Chemical Co
Kosmos	Carbon black	United Carbon Co.
Kotol	Resin solutions	Uniroyal, Inc.
Kralac	ABS resins	Uniroyal, Inc
Kralastic	ABS	Uniroyal, Inc
Kralon	High-impact styrene and ABS resins	Uniroyal, Inc
Kraton	Butadiene block copolymers	Shell Chemical Co.
Kraton	Linear and branched styrene block copolymers	Shell Chemical Co
Kraton D	SBS or SIS terpolymers	Shell Chemical Co
Kraton IPN	SEBS-Polyester	Shell Chemical Co
Krene	Plasticized vinyl film	Union Carbide Corp.
K-Resin	Butadiene-styrene copolymer	Phillips Petroleum Co.
K-Resin	Branched styrene block copolymers with butadiene	Phillips
Kriston	Allyl ester casting resins	B F Goodrich Chemical Co
Kroniflex	Phosphate ester plasticizer	FMC Corp.
Kronisol	Dibutoxyethyl phthalate	FMC Corp
Kronitex	Tricresyl phosphate	FMC Corp.
Kronox	Titanium dioxide	Kronis Titan
Kronox	Plasticizer	FMC Corp
Krystal	PVC sheet	Allied Chemical
Krystaltite	PVC shrink film	Allied Chemical
Kurlon	Poly(vinyl alcohol) fibers	
Kydene	Acrylic-PVC powder	Rohm & Haas Co
Kydex	Acrylic-poly(vinyl chloride) sheet	Rohm & Haas Co

Trade or brand name	Product	Manufacturer
Kylan	Chitin	
Kynar	Poly(vinylidene fluoride)	Pennwalt Chemicals Corp
Lamabond	Reinforced polyethylene	Columbian Carbon Co
Lamar	Mylar vinyl laminates	Morgan Adhesives
Laminac	Polyester resins	American Cyanamid Co
Lanital	Fiber from milk protein	Shia Viscosa
Laurox	Polymerization catalysts	Akzo Chemie Nederland BV
Laguval	Polyester resins	Farbenfabriken Bayer AG
Last-A-Foam	Plastic foam	General Plastics Mfg
Lekutherm	Epoxy resins	Farbenfabriken Bayer AG
Lemac	Poly(vinyl acetate)	Borden Chemical Co
Lemol	Poly(vinyl alcohol)	Borden Chemical Co
Levapren	Ethylene vinylacetate copolymers	Farbenfabriken Bayer AG
Lexan	Polycarbonate resin	General Electric Co
Lindol	Phosphate plasticizers	Stauffer Chemical Co
Lock Foam	Polyurethane foam	Nopco Chemical Co
Lomod	Polyester block copolymer with polyether	General Electric
Lucidol	Benzoyl peroxide	Wallace and Tiernan, Inc
Lucite	Poly(methyl methacrylate) and copolymers	E I du Pont de Nemours & Co Inc
Ludox	Colloidal silica	E I du Pont de Nemours & Co Inc
Lumarith	Cellulose acetate	Celanese Corp of America
Lumasite	Acrylic sheet	American Acrylic Corp
Lumite	Saran filaments	Chicopee Manufacturing Co
Luperco	Organic peroxides	Pennwalt Corp
Luperox	Organic peroxides	Pennwalt Corp
Lupoy	Polycarbonate/ABS	LG Chemical
Lustran	Molding and extrusion resins	Monsanto Chemical Co
Lustrex	Polystyrene	Monsanto Chemical Co
Lutonal	Poly(vinyl ethers)	Badische Anilin & Soda Fabrik AG
Lutrex	Poly(vinyl acetate)	Foster Grant Co
Luvican	Poly(vinyl carbazole)	Badische Anilin & Soda-Fabrik AG
Lycra	Spandex fibers	E I du Pont de Nemours & Co Inc
Macal	Cast vinyl film	Morgan Adhesives Co
Madurik	Melamine formaldehyde resins	Casella Farbwerke Mainkur AG
Makrolol	Polycarbonate film	Naftone Inc
Makrolon	Polycarbonate	Farbenfabriken Bayer AG
Marafoam	Polyurethane foam	Marblette Co
Maraglas	Epoxy resin	Marblette Co
Maranyl	Nylons	Imperial Chemical Industries Ltd
Maraset	Epoxy resin	The Marblette Corp
Marathane	Urethane materials	Allied Products
Maraweld	Epoxy resin	Marblette Co
Marbon	Polystyrene and copolymers	Borg Warner Corp
Marlex	Polyolefin resins	Phillips Chemical Co

Trade or brand name	Product	Manufacturer
Marvibond	Metal-plastics laminates	Uniroyal, Inc
Marvinol	Poly(vinyl chloride)	Uniroyal, Inc
Melan	Melamine resins	Hitachi Chemical Co , Ltd
Meldin	Polyimides	Dixon Corp
Melinex	Poly(ethylene terephthalate)	Imperial Chemical Industries Ltd
Melit	Melamine formaldehyde resins	Societa Italiana Pesine
Melmac	Melamine molding materials	American Cyanamid Co
Melolam	Melamine resin	Ciba Geigy
Melurac	Melamine urea resins	American Cyanamid Co
Meraklon	Polypropylene	Montecatini
Merlon	Polycarbonate	Mobay Chemical Co
Metallex	Cast acrylic sheets	Hermes Plastics
Methocel	Methylcellulose	Dow Chemical Co
Meticone	Silicon rubber	Hermes Plastics
Metre-Set	Epoxy adhesives	Metachem Resins Corp
Micarta	Thermosetting laminates	Westinghouse Electric Corp
Micro-Matte	Extruded acrylic sheet with matte finish	Extrudaline Inc
Micronex	Carbon black	Columbian Carbon Co
Micropel	Powdered nylon	Nypel Inc
Microsol	Vinyl plastisol	Michigan Chrome & Chemical
Microthene	Powdered polyethylene	U S Industrial Chemicals Co
Milmar	Polyester	Morgan Adhesives
Minex	Aluminum silicate filler	American Nepheline Corp
Mini Vaps	Expanded PE	Malge Co
Minit Grip	Epoxy adhesives	High Strength Plastics Corp
Minit Man	Epoxy adhesives	Kristal Draft Inc
Minlon	Reinforced nylon	E I du Pont de Nemours & Co , Inc
Mipolam	Poly(vinyl chloride)	Dynamit Nobel
Mipoplast	PVC sheets	Dynamit Nobel/America
Mirasol	Alkyd resins	C S Osborn Chemicals
Mirbane	Amino resin	Showa Highpolymer Co
Mirrex	Calendered PVC	Tenneco Chemicals
Mista Foam	Urethane foam	M R Plastics & Coatings
Modulene	Polyethylene resin	Muehlstein & Co
Mogul	Carbon black	Cabot Corp
Molplen	Polypropylene	Novamont Corp
Moltopren	Polyurethane foam	Farbenfabriken Bayer AG
Molycor	Fiberglass reinforced epoxy tubing	A O Smith, Inland, Inc
Mondur	Organic isocyanates	Mobay Chemical Co
Monocast	Nylon	Polymer Corp
Montac	Polyamide copolymer with polyether/polyester	Monsanto
Montrek	Polyethyleneimine	Dow Chemical Co
Moplen	Polypropylene	Montecatini
Morthane	Polyurethane block copolymer with polyether/polyester	Morton Int
Mowlith	Poly(vinyl acetate)	Farbwerke Hoechst AG

Trade or brand name	Product	Manufacturer
Mowiol	Poly(vinyl alcohol)	Farbwerke Hoechst AG
Mowital	Poly(vinyl butyral)	Farbwerke Hoechst AG
Multi flex	Linear block styrene copolymers with ethylene propylene	Multibase
Multrathane	Urethane elastomer	Mobay Chemical
Multron	Polyesters	Mobay Chemical Co
Mycalex	Inorganic molded plastic	Mycalex Corp of America
Mylar	Polyester film	E I du Pont de Nemours & Co Inc
Nacconate	Organic diisocyanate	Allied Chemical Corp
Nadic	Maleic anhydride	Allied Chemical Corp
Nalgon	Plasticized poly(vinyl chloride)	Nalge Co
Napryl	Polypropylene	Pechiney Saint Gobain
Natene	Polyethylene	Pechiney Saint Gobain
Natsyn	cis 1 4 Polyisoprene	Goodyear Tire & Rubber Co
Naugahyde	Vinyl-coated fabric	U S Rubber Co
Neboy	Petroleum hydrocarbon resin	Neville Chemical Co
NeoCryl	Acrylic resins and emulsions	Polyvinyl Chemicals
Neoprene	Polychloroprene	E I du Pont de Nemours & Co Inc
NeoRez	Styrene emulsions and urethane solusions	Polyvinyl Chemicals
NeoVac	PVA emulsions	Polyvinyl Chemicals
Neozone	Antioxidants	E I du Pont de Nemours & Co Inc
Nepoxide	Epoxy resin coating	Atlas Minerals & Chemicals Div ESB
Nestrite	Phenolic and urea-formaldehyde	James Ferguson & Sons
Nevidene	Coumarone indene resin	Neville Chemical Co
Nevillac	Modified coumarone indene resin	Neville Chemical Co
Niax	Polyol polyesters	Union Carbide Corp
Nimbus	Polyurethane foam	General Tire & Rubber Co
Nipeon	Poly(vinyl chloride)	Japanese Geon Co
Nipoflex	Ethylene–vinyl acetate copolymer	Toyo Soda Mfg Co
Nipolon	Polyethylene	Toyo Soda Mfg Co
Nitrocol	Nitrocellulose based pigment dispersions	J C Osburn Chemicals
Noan	Styrene–methyl methacrylate copolymer	Richardson Corp
Nob Lock	PVC sheets	Ameron Corrosion Control
Nomex	Nylon	E I du Pont de Nemours & Co Inc
Nopcofoam	Polyurethane foams	Nopco Chemical Co
Norchem	LDPE resin	Northern Petrochemical Co
Nordel	Ethylene propylene	E I du Pont de Nemours & Co Inc
Noryl	Poly(phenylene oxide)	General Electric Co
Novacite	Altered novaculite	Malvern Minerals Co
Novodur	ABS polymers	Farbenfabriken Bayer AG
Nuba	Modified coumarone	Neville Chemical Co

Trade or brand name	Product	Manufacturer
Nuclon	Polycarbonate	Pittsburgh Plate Glass Co
Nukem	Acid-resistant resin cements	Amercoat Corp
Numa	Spandex fibers	American Cyanamid Corp
Nupol	Thermosetting acrylic resin	Freeman Chemical
Nyglathane	Glass-filled polyurethane	Nypel, Inc
Nylafil	Reinforced nylon	Rexall Chemical Co
Nylaglas	Fiberglass-reinforced nylon	Dart Industries
Nylasar	Fiberglass-reinforced nylon	Dart Industries
Nylasint	Sintered nylon parts	The Polymer Corp
Nylatron	Filled nylons	The Polymer Corp
Nylon	Polyamides	E I du Pont de Nemours & Co , Inc
Nylo-Seal	Nylon-11 tubing	Imperial-Eastman Corp
Nylux	Nylons	Westlake Plastics
Nyplube	TFE-filled nylons	Nypel, Inc
Nyreg	Glass-reinforced nylon	Nypel, Inc
Oasis	Expanded phenol-formaldehyde	Smithers Co
Olefane	Polypropylene film	Avisun Corp
Olefil	Filled PP resin	Amoco Chemicals
Oleflo	PP resin	Amoco Chemicals
Olemer	Propylene copolymer	Avisun Corp
Oletac	Amorphous PP	Amoco Chemicals
Opalon	Poly(vinyl chloride)	Monsanto Chemical Co
Oppanol B	Polyisobutylene	Badische Anilin & Soda-Fabrik AG
Oppanol C	Poly(vinyl isobutylether)	Badische Anilin & Soda-Fabrik AG
Orevac	Polyamide copolymer with polyether/polyester	Atochem
Orgalacqe	Epoxy and PVC powders	Aquitaine-Organico
Orgamide R	Nylon-6	Aquitaine-Organico
Orlon	Acrylic fiber	E I du Pont de Nemours & Co , Inc
Ortix	Poromeric film	Celanese Corp
Oxiron	Epoxidized polybutadiene	
Panarez	Hydrocarbon resins	Amoco Chemical Corp
Panda	Vinyl and urethane-coated fabric	Pandel-Bradford
Panelyte	Laminates	Thiokol Chemical Co
Papi	Polymethylene, polyphenyl isocyanate	Upjohn Co
Paracon	Polyester rubber	Bell Telephone Laboratories
Paracryl	Butadiene-acrylonitrile copolymer	U S Rubber Co
Paradene	Coumarone-indene resins	Neville Chemical Co
Paralac	Polyester resin	ICI
Paraplex	Plasticizers	Rohm & Haas Co
Parfe	Rayon fiber	Beaunit Mills Corp
Parlon	Chlorinated rubber	Hercules Corp
Parylen C	Polymonochloro-p-xylene	Union Carbide Corp
Parylen N	Polyxylene	Union Carbide Corp
Pearlon	Polyethylene film	Visking Corp

Trade or brand name	Product	Manufacturer
Pebax	Polyamide block copolymer with polyether/polyester	Elf Atochem
Pee Vee Cee	Rigid poly(vinyl chloride)	ESB Corp
Pelaspan	Expandable polystyrene	Dow Chemical Co
Pellethene	Thermoplastic urethane	Upjohn
Pellon Aire	Nonwoven textile	Pellon Corp
Pentalyn	Abietic acid derivative	Hercules Co Inc
Penton	Chlorinated polyether resins	Hercules Co Inc
Perbunan N	Butadiene acrylonitrile copolymers	Farbenfabriken Bayer AG
Percadox	Organic peroxides	Cadet Chemical Corp
Peregal	Antistatic agents	General Aniline & Film Corp
Perlon	Polyurethane filament	Farbenfabriken Bayer AG
PermaRex	Cast epoxy	Permali Inc
Permelite	Melamine resin	Melamine Plastics
Permutit	Ion exchange resin	Permutit Co
Perspex	Acrylic resins	Imperial Chemical Industries Ltd
Petra	Polyester sheets	Allied Chemical
Petrothene	Polyethylene	National Distillers & Chemical Corp
Pevalon	Poly(vinyl alcohol)	May and Baker Ltd
Phenoxy	Polyhydroxy ether of bisphenol A	Union Carbide Corp
Phenoweld	Phenolic adhesive	Hardman Inc
Philjo	Polyolefin film	Phillips Joana Co
Philprene	Styrene butadiene rubber	Phillips Petroleum Co
Phosgard	Phosphorus compounds	Monsanto Co
Picco	Hydrocarbon resins	Hercules Inc
Piccocumaron	Hydrocarbon resins	Hercules Inc
Piccoflex	Acrylonitrile styrene resins	Pennsylvania Industrial Chemical
Piccolastic	Polystyrene resin	Pennsylvania Industrial Chemical
Piccolyte	Terpene polymer resins	Hercules Inc
Piccotex	Vinyl toluene copolymers	Pennsylvania Industrial Chemical
Piccoumaron	Coumarone indene resins	Pennsylvania Industrial Chemical
Piccovar	Alkyl aromatic resins	Pennsylvania Industrial Chemical
Pienco	Polyester resins	American Petrochemical
Pip Pip	Rubber accelerator	Generic name
Plaskon	Amino resins	Allied Chemical Corp
Plastacel	Cellulose acetate flake	E I du Pont de Nemours & Co Inc
Plastanox	Antioxidant	American Cyanamid Corp
Plastigel	Liquid thickeners	Plasticolors Inc
Plastylene	Polyethylene	Pechiney Saint Gobain
Plenco	Phenolic resins	Plastics Engineering Co
Pleogen	Polyester resins and gels	Whittaker Corp
Plexiglas	Acrylic sheets	Rohm & Haas Co
Plexigum	Acrylate and methacrylate resins	Rohm & Haas Co
Plicose	Polyethylene	Diamond Shamrock Corp
Pliobond	Adhesive	Goodyear Tire & Rubber Co
Pliofilm	Rubber hydrochloride	Goodyear Tire & Rubber Co
Plioflex	Poly(vinyl chloride)	Goodyear Tire & Rubber Co

Trade or brand name	Product	Manufacturer
Pliolite	Cyclized rubber	Goodyear Tire & Rubber Co
Pliothene	Polyethylene rubber blends	Ametek/Westchester
Pliovic	Poly(vinyl chloride)	Goodyear Tire & Rubber Co
Pluracol	Polyethers	Wyandotte Chemicals Corp
Pluragard	Urethane foams	BASF Wyandotte Corp
Pluronic	Polyethers	BASF Wyandotte Corp
Plyfoam	PVC foam	
Plyocite	Phenol-impregnated materials	Reichhold Chemicals, Inc.
Plyophen	Phenolic resins	Reichhold Chemicals, Inc
Pluronics	Block polyether diols	Wyandotte Corp.
Polex	Oriented acrylic	Southwestern Plastics
Pollopas	Urethane-formaldehyde materials	Dynamit Nobel/America
Polvonite	Cellular plastic material	Voplex Corp
Polyallomer	Ethylene block copolymers	Eastman Chemical Products
Poly-Dap	Diallyl phthalate resins	U S Polymeric
Polycarbafil	Fiberglass-reinforced polycarbonates	Dart Industries
Polycure	Cross-linked polyethylene	Crooke Color & Chemical
Poly-eth	Polyethylene	Gulf Oil Corp.
Poly-eze	Ethylene copolymers	Gulf Oil Corp
Polyfoam	Polyurethane foam	General Tire & Rubber
Polygard	Stabilizer	Goodyear Tire & Rubber Co
Poly-Gard	Solventless epoxies	Richhold Chemicals
Polyimidal	Polyimide thermoplastics	Raychem Corp
Polylite	Polyester resins	Reichhold Chemicals, Inc
Polylumy	Polypropylene	Kohjin Co
Polymet	Plastic-filled sintered metal	Polymer Corp
Polymin	Polyethyleneimine	Badische Anilin & Soda-Fabrik AG
Polymul	Polyethylene emulsions	Diamond Shamrock Chemical
Poly-pro	Polypropylene	Gulf Oil Corp
Polyox	Water-soluble resins	Union Carbide Corp.
Polysizer	Poly(vinyl alcohol)	Showa Highpolymer Co.
Polyteraglas	Polyester-coated Dacron glass fabric	Natvar corp
Polytrope	Polyporpylene blend with EPDM or EPR	Schulmam
Polyviol	Poly(vinyl alcohol)	Wacker Chemie GmbH
Powminco	Asbestos fibers	Powhatan Mining Co.
PPO	Poly(phenylene oxide)	Hercules, Inc
Pro-fax	Polypropylene resins	Hercules Powder Co
Profil	Fiberglass-reinforced polypropylene	Dart Industries
Proglas	Fiberglass-reinforced polypropylene	Dart Industries
Prohi	HDPE	Protective Lining Corp.
Propathene	Polypropylene	Imperial Chemical Industries Ltd
Propiofan	Poly(vinyl propionate)	BASF
Propylsar	Fiberglass-reinforced polypropylene	Dart Industries

Trade or brand name	Product	Manufacturer
Propylux	Polypropylene	Westlake Plastics
Protectolite	Polyethylene film	Protective Lining Corp
Protron	Ultrahigh strength PE	Protective Lining Corp
Purilon	Rayon	FMC Corp
PYR ML	Polyimide	E I du Pont de Nemours & Co Inc
Q Cel	Inorganic hollow microspheres	Philadelphia Quartz Co
Quadrol	Poly(hydroxy amine)	Wyandotte Chemicals Inc
Quelflam	Polyurethanes	Baxenden Chemical
Quintac	Linear styrene block copolymer with isoprene	Nippon Zeon
Ravinil	Poly(vinyl chloride)	ANIC S P A
Raybrite	Alpha cellulose filler	Rayonier Inc
Rayflex	Rayon	FMC Corp
Regalite	Press polished PVC	Tenneco Advanced Materials
Ren Flex	Polypropylene blend with EPDM or EPR	D & S
REN Shape	Epoxy	Ren Plastics
Ren Thane	Urethane elastomers	Ren Plastics
Resiglas	Polyester resins	Kristal Draft Inc
Resimene	Urea and melamine resins	Monsanto Co
Resinol	Polyolefins	Allied Resinous Products Inc
Resinox	Phenolic resins	Monsanto Co
Resistoflex	Poly(vinyl alcohol)	Resistoflex Corp
Resloom	Melamine resins	Monsanto Co
Resolite	Urea formaldehyde resins	Ciba Geigy
Resorasabond	Resorcinol and phenol resorcinol	Pacific Resins & Chemicals
Restfoam	Urethane foam	Stauffer Chemical
Restirolo	Polystyrene	Societa Italiana Resine
Rexolene	Cross linked polyolefin	Brand Rex Co
Rexolite	Polystyrene	Brand Rex Co
Reynolon	Plastic films	Reynolds Metals Co
Reynosol	Urethane PVC	Hoover Ball & Bearing Co
Rezimac	Alkyds	Commercial Solvents Corp
Rezyl	Alkyd varnish	Sinclair Koppers Co Inc
Rhodiod	Cellulose acetate	M & B Plastics Ltd
Rhonite	Resins for textile finishes	Rohm & Haas Co
Rhoplex	Acrylic emulsions	Rohm & Haas Co
Riblene	Polyethylene	ANIC S P A
Richfoam	Polyurethane foam	E R Carpenter Co
Rigidex	Polyethylene	BP Chemicals (U K) Ltd
Rigidite	Acrylic and polyester resins	American Cyanamid
Rigidsol	Rigid plastisol	Watson Standard Co
Rigolac	Polyester resins	Showa Highpolymer Co
Rilsan	Nylon 11	Aquitaine Organico
Rimplast	Blends of TPEs with silicone rubbers	Petrarch Systems
Riteflex	Polyester block copolymer with polyether	Hoechst
Rolox	Two part epoxies	Hardman Inc

Trade or brand name	Product	Manufacturer
Roskydal	Urea formaldehyde resins	Farbenfabriken Bayer AG
Royalex	Cellular thermoplastic sheets	Uniroyal
Royalite	Thermoplastic sheet material	Uniroyal, Inc
Roylar	Polyurethanes	Uniroyal, Inc
Rucoam	Vinyl materials	Hooker Chemical
Rucon	Poly(vinyl chloride)	Hooker Chemical Corp
Rucothane	Polyurethanes	Hooker Chemical Corp
Rulan	Flame-retardant plastic	E I du Pont de Nemours & Co , Inc
Rulon	Flame retardant	E I du Pont de Nemours & Co , Inc
Ryton	Poly(phenylene sulfide)	Phillips Petroleum Co
Saflex	Poly(vinyl butyral)	Monsanto Co
Safom	Polyurethane foam	Monsanto Co
Santicizer	Plasticizers	Monsanto Co
Santocel	Silica aerogel fillers	Monsanto Co
Santocure	Accelerator	Monsanto Co
Santoflex	Antioxidants	Monsanto Co
Santolite	Sulfonamide resin	Monsanto Co
Santonox	Antioxidant	Monsanto Co
Santoprene	Polypropylene dynamic vulcanizate with EPDM	AES
Saran	Poly(vinylidene chloride)	Dow Chemical Co
Sarlink 1000	PVC dynamic vulcanizate with nitrile rubber	DSM
Sarlink 3000 & 4000	Polypropylene dynamic vulcanizate with EPDM	DSM
Satin Foam	Extruded polystyrene foam	Dow Chemical
Scotch	Adhesives	Minnesota Mining & Mfg Co
Scotchcast	Epoxy resins	Minnesota Mining & Mfg Co
Scotchpak	Polyester film	Minnesota Mining & Mfg Co
Scotchpar	Polyester film	3M Co
Scotchweld	Adhesives	Minnesota Mining & Mfg Co
Seilon	Thermoplastic sheets	Seiberling Rubber Co
Selectron	Polyester resins	PPG Corp
Selecttrofoam	Polyurethane foam	PPG Industries
Shareen	Nylon	Courtaulds North America
Shuvin	Vinyl molding material	Reichhold Chemicals
Silastic	Silicone materials	Dow Corning Corp
Silon TSR	PDMS/PTFE	BioMed Sciences
Sipon	Alkyl and aryl resin	Alcolac, Inc
Silastomer	Silicones	Midland Silicones Ltd
Silbon	Rayon paper	Kohjin Co
Silene	Calcium silicate	PPG Corp
Silocet	Silicon rubber	ICI
Silvacon	Lignin extenders	Weyerhauser Co
Siponate	Alkyl and aryl sulfonates	Alcolac Inc
Sirfen	Phenol formaldehyde resins	Societa Italiana Resine
Sir-pel	Poromeric film	Georgia Bonded Fibers
Sirtene	Polyethylene	Societa Italiana Resine

Trade or brand name	Product	Manufacturer
Skinwich	Polyurethane integral skinning foam	Upjohn
Softlite	Ionomer foam	Gilman Brothers
Solarflex	Chlorinated polyethylene	Pantasote Co
Solithane	Urethane prepolymers	Thiokol Corp
Solprene	Branched block copolymer of styrene with butadiene	Phillips
Sonite	Epoxy resin	Smooth On, Inc
Solvar	Poly(vinyl acetate)	Shawinigan Resins Corp
Solvic	Poly(vinyl chloride)	Solvay & Cie
Soreflon	Polytetrafluoroethylene	Rhone Poulenc
Spandal	Polyurethane laminates	Baxenden Chemical
Spandex	Polyurethane filaments	E I du Pont de Nemours & Co Inc
Spandofoam	Polyurethane foam	Baxenden Chemical
Spandoplast	Expanded polystyrene	Baxenden Chemical
Spectran	Polyester	Monsanto Textiles
Spenkel	Polyurethane resin	Textron Inc
S polymers	Butadiene styrene copolymer	Esso Labs
Spraythane	Urethane resin	Thiokol Chemical Corp
Staflex	Vinyl plasticizers	Reichhold Chemical Inc
Standlite	Phenol formaldehyde resins	Hitachi Chemical Co
Starex	Poly(vinyl acetate)	International Latex & Chemical Corp
Statex	Carbon black	Columbian Carbon Co
Stearon	Linear block styrene copolymers with butadiene	Firestone Tire & Rubber Co
Stepton	Linear styrene block copolymers	Kuraray
Structo Foam	Foamed polystyrene slab	Stauffer Chemical Co
Strux	Cellular cellulose	Aircraft Specialties
Sty Grade	Degradable additive for polymers	Bio Degradable Plastics Inc
Stylafoam	Coated polystyrene sheets	Gilman Brothers
Stymer	Styrene copolymer	Monsanto Co
Stypol	Urea-formaldehyde resins	Freeman
Styrafil	Fiberglass reinforced polystyrene	Dart Industries, Inc
Styraglas	Fiberglass reinforced polystyrene	Dart Industries Inc
Styrex	Resin	Dow Chemical Co
Styrocel	Polystyrene (expandable)	Styrene Products Ltd
Styroflex	Biaxially oriented polystyrene film	Natvar Corp
Styrofoam	Extruded expanded polystyrene foam	Dow Chemical Co
Styrolus	Polystyrene	Westlake Plastics
Styron	Polystyrene	Dow Chemical Co
Styronol	Polystyrene	Allied Resinous Prods
Sulfasar	Fiberglass reinforced polysulfone	Dart Industries
Sulfil	Fiberglass-reinforced polysulfone	Dart Industries
Sullvac	Acrylonitrile-butadiene styrene copolymer	O Sullivan Rubber Corp
Sunlon	Nylon resins	Sun Chemical Corp

Trade or brand name	Product	Manufacturer
Super Aeroflex	Linear PE	Anchor Plastic Co
Super Coilife	Epoxy potting resin	Westinghouse Electric
Super Dylan	High-density polyethylene	Arco Polymer Co
Superflex	Grafted high-impact polystyrene	Gordon Chemical
Superflow	Polystyrene	Gordon Chemical
Surflex	Ionomer film	Flex-O-Glass, Inc.
Surlyn	Ionomer resins	E I du Pont de Nemours & Co , Inc.
Syn-U-Tex	Urethane-formaldehyde and melamine-formaldehyde	Celanese Coatings Co.
Swedcast	Acrylic sheet	Swedlow, Inc
Sylgard	Silicone casting resins	Dow Corning Corp
Sylplast	Urea-formaldehyde resins	Sylvan Plastics, Inc
Synpro	Metallic stearates	Dart Industries, Inc.
Syntex	Alkyd resins	Celanese Corp
Synthane	Laminated plastic products	Synthane Corp
Syretex	Styrenated alkyd resins	Celanese Coatings Co.
Taipol	Linear and branched styrene block copolymers	Taiwan Synthetic Rubber Co
TanClad	Spray or dip plastisol	Tamite Inds
TDI	Tolylene diisocyanate	E I du Pont de Nemours & Co , Inc
Tedlar	Polyvinyl fluorocarbon resins	E. I du Pont de Nemours & Co , Inc
Teflon	Fluorocarbon resins	E. I. du Pont de Nemours & Co , Inc
Teflon FEP	TFE copolymer	E. I du Pont de Nemours & Co , Inc.
Teflon TFE	Polytetrafluoroethylene	E I du Pont de Nemours & Co , Inc
Teglac	Alkyd coatings	American Cyanamid Co.
Tego	Phenolic resins	Rohm & Haas Co
Tekron	Linear block styrene copolymer with ethylene-butylene	Teknor Apex
Telcar	Polypropylene blend with EPDM or EPR	Teknor Apex
Tempra	Rayon fiber	American Enka Corp.
Tempreg	Low-pressure laminate	U.S Plywood Corp
Tenamene	Antioxidants	Eastman Kodak Co.
Tenite	Cellulose derivatives	Eastman Kodak Co.
Tenn Foam	Polyurethane foam	Morristown Foam Corp.
Tenox	Antioxidant	Eastman Chemical Products, Inc
Teracol	Poly(oxytetramethylene glycol)	E I du Pont de Nemours & Co , Inc
Tere-Cast	Polyester casting resins	Reichhold Chemicals
Terluran	ABS polymers	Badische Anilin & Soda-Fabrik AG
Terucello	Carboxymethyl cellulose	Showa Highpolymer Co
Terylem	Poly(ethylene terephthalate)	ICI
Terylene	Polyester fiber	ICI

Trade or brand name	Product	Manufacturer
Tetran	Tetrafluoroethylene	Pennsalt Chemical Corp
Tetra Phen	Phenolic resins	Georgia Pacific
Tetra Ria	Amino resins	Georgia Pacific
Tetralov	Filled TFE molding resins	Whitford Chemical
Tetronic	Polyethers	Wyandotte Chemical Corp
Texicote	Poly(vinyl acetate)	Scott Bader Co
Texileather	Pyroxylin leather cloth	General Tire & Rubber Co
Texin	Urethane elastomer	Mobay Chemical Co
Textolite	Laminated plastic	General Electric Co
Thermaflow	Reinforced polyesters	Atlas Powder Co
Thermalux	Polysulfones	Westlake Plastics
Thermasol	Vinyl plastisols and organosols	Lakeside Plastics
Thermax	Carbon black	Commercial Solvents Corp
Thermco	Expanded polystyrene	Holland Plastics
Thiokol	Poly(ethylene sulfide)	Thiokol Corp
Thornel	Graphite filaments	Union Carbide Corp
Thurane	Polyurethane foam	Dow Chemical Co
Tinuvin	Ultraviolet stabilizers	Geigy Industrial Chemicals Div Geigy Chemical Corp
Ti Pure	Titanium dioxide pigments	E I du Pont de Nemours & Co Inc
Titanox	Titanium dioxide pigments	Titanium Pigment Corp
T Lock	PVC sheets	Amercoat Corp
Topel	Rayon fiber	Courtaulds
TPX	Poly 4 methylpentene 1	Imperial Chemical Industries, Ltd
Trans 4	trans 1 4 Polybutadiene	Phillips Petroleum Co
Tran Stay	Polyester film	Transiwrap Co
Trem	Viscosity depressant	Nopco Chemical Div Diamond Shamrock Chemical Co
Trevarno	Resin impregnated cloth	Coast Mfg & Supply Corp
Tri Foil	TFE coated aluminum foil	Tri Point Inds
Trilon	TFE	Dynamit Nobel/America
Triocel	Rayon acetate	Celanese Fibers
Trithene	Trifluorochloroethylene	Union Carbide Corp
Trolen	Polyethylene	Dynamit Nobel AG
Trolitan	Phenol formaldehyde resins	Dynamite Nobel/America
Trosifol	Poly(vinyl butyral) film	Dynamite Nobel/America
Trosiplast	Poly(vinyl chloride)	Dynamit Nobel AG
Trubyte	Acrylic based multicomponent dental systems	Dentsply
Trulon	Poly(vinyl chloride) resin	Olin Corp
Tuads	Accelerator	R T Vanderbilt Co
Tuffak	Polycarbonates	Rohm & Haas
Tufprene	Linear block styrene copolymer with butadiene	Asahi
Tuftane	Polyurethane	B F Goodrich Chemical
Tusson	Rayon fiber	Beaunit Mills Corp
Tybrene	ABS polymers	Dow Chemical Co
Tygon	Vinyl copolymer	U S Stoneware Co

Trade or brand name	Product	Manufacturer
Tylose	Cellulose ethers	Farbwerke Hoechst AG
Tynex	Nylon bristles and filaments	E I du Pont de Nemours & Co , Inc
Tyril	Styrene-acrylonitrile copolymer	Dow Chemical Co
Tyrilfoam	Styrene/Acrylonitrile foam	Dow Chemical Co
Tyrin	Chlorinated polyethylene	Dow Chemical Co
Ucon	Lubricants	Union Carbide Corp
Udel	Plastic film	Union Carbide Corp
Uformite	Urea resins	Rohm & Haas Co
Ultramid	Nylons	Badische Anilin & Soda-Fabrik AG
Ultrathene	Finely divided polyolefins	National Distillers & Chemical Corp
Ultrapas	Melamine-formaldehyde resins	Dynamit Nobel AG
Ultron	Vinyl film	Monsanto Co
Ultryl	Poly(vinyl chloride)	Phillips Petroleum Co
Unifoam	Polyurethane foam	William T Burnett & Co
Unipoxy	Epoxy resins and adhesives	Kristal Kraft Co
Unitane	Titanium dioxide	American Cyanamid Co
Unox	Epoxides	Union Carbide Corp
Updown	Polychloroprene foam	
Urac	Urea-formaldehyde resins	American Cyanamid Co
Urafil	Fiberglass-reinforced polyurethane	Dart Industries
Uraglas	Fiberglass-reinforced polyurethane	Dart Industries
Uralite	Polyurethanes	Hexcel Corp
Urapol	Polyurethane elastomeric coatings	Gordon Chemicals
Urapac	Rigid polyurethane	North American Urethanes
Urapol	Polyurethane elastomeric coatings	Poly Resins
Urecoll	Urea-formaldehyde resins	BASF Corp
Uscolite	ABS copolymer	U S Rubber Co
U-Thane	Rigid insulation polyurethane	Upjohn
Uvex	Cellulose acetate butyrate	Eastman Kodak Co
Uvinul series	Ultraviolet light absorbers	General Aniline & Film Corp
Valox	Poly(butylene terephthalate)	General Electric Co
Valsof	PE emulsions	United Merchants & Manfs
Vanstay	Stabilizers	R T Vanderbilt Co
Varcum	Phenolic resins	Reichhold Chemicals, Inc
Varex	Polyester resins	McClosky Varnish Co
Varkyd	Alkyd and modified alkyd resins	McCloskey Varnish Co
Varsil	Silicon-coated fiberglass	New Jersey Wood Finishing Co
Vazo	Azobisisobutyronitrile	E I du Pont de Nemours & Co , Inc
V del	Polysulfone resins	Union Carbide Corp
Vector	Linear styrene block copolymers with butadiene/isoprene	Dexco
Vectra	PP fibers	Exxon Chemical
Velene	Polystyrene-foam laminates	Scott Paper Co
Velon	Poly(vinyl chloride)	Firestone Tire & Rubber Co

Trade or brand name	Product	Manufacturer
Verel	Modacrylic staple fibers	Eastman Chemical Products Inc
Versamid	Polyamide resins	General Mills Inc
Versel	Polyester thermoplastic	Allied Chemical Corp
Versi Ply	Co extruded film	Pearson Inds
Vespel	Polymellitimide	E I du Pont de Nemours & Co., Inc
Vestamid	Nylon 12	Chemische Werke Huls AG
Vestolit	Poly(vinyl chloride)	Chemische Werke Huls AG
Vestyron	Polystyrene	Chemische Werke Huls AG
VGB	Acetaldehyde aniline accelerator	Uniroyal Corp
Vibrathane	Polyurethane intermediates	Uniroyal Corp
Vibrin	Polyester resins	Uniroyal Corp
Vibrin Mat	Polyester glass molding material	W R Grace
Vibro Flo	Epoxy and polyester coating powders	Armstrong Products
Vicara	Protein fiber	Virginia Caroline Chem Corp
Viclan	Poly(vinylidene chloride)	Imperial Chemical Industries Ltd
Vicron	Fine calcium carbonate	Pfizer Minerals Pigments & Metals
Videne	Polyester film	Goodyear Tire & Rubber Co
Vinac	Poly(vinyl acetate) emulsions	Air Reduction Co
Vinapas	Poly(vinyl acetate)	Wacker Chemie GmbH
Vinidur	Poly(vinyl chloride)	BASF Corp
Vinoflex	Poly(vinyl chloride)	BASF Corp
Vinol	Poly(vinyl alcohol)	Air Reduction Co
Vinsil	Rosin derivative	Hercules Inc
Vinylite	Poly(vinyl chloride covinyl acetate)	Union Carbide Corp
Vinyon	Poly(vinyl chloride coacrylonitrile)	Union Carbide Corp
Vipla	Poly(vinyl chloride)	Montecatini Edison S p A
Viscalon	Rayon fiber	American Enka Corp
Viskon	Nonwoven fabrics	Union Carbide Corp
Vistanex	Polyisobutylene	Enjay Chemical Co
Vitel	Polyester resins	Goodyear Tire & Rubber Co
Vithane	Polyurethanes	Goodyear Tire & Rubber Co
Viton	Copolymer of vinylidene fluoride and hexafluoropropylene	E I du Pont de Nemours & Co Inc
Vituf	Polyester resins	Goodyear Tire & Rubber
Volara	Closed cell LDPE foam	Voltek Inc
Volaron	Closed cell LDPE foam	Voltek Inc
Volasta	Closed cell medium density PE foam	Voltek Inc
Voranol	Polyurethane resins	Dow Chemical
Vulcaprene	Polyurethane	Imperial Chemical Industries Ltd
Vulkollan	Urethane elastomer	Mobay Chemical Co
Vult Acet	PVA latexes	General Latex & Chemical
Vultafoam	Polyurethane foam	General Latex & Chemical

Trade or brand name	Product	Manufacturer
Vultathane	Polyurethane coatings	General Latex & Chemical
Vybak	Poly(vinyl chloride)	Bakelite Xylonite Ltd
Vycron	Polyester fiber	Beaunit Mills Corp
Vydax	Release agent	E I du Pont de Nemours & Co , Inc
Vydyne	Nylon resins	Monsanto Co
Vygen	Poly(vinyl chloride)	General Tire & Rubber Co
Vynaclor	PVC emulsions	B F Goodrich Chemical
Vynaloy	Vinyl sheets	B F Goodrich Chemical
Vynex	Rigid vinyl sheeting	Nixon-Baldwin Chemicals, Inc
Vyram	Rigid poly(vinyl chloride)	Monsanto Co
Vyram	Polypropylene dynamic vulcanizate with natural rubber	AES
Vyrene	Spandex fiber	U S Rubber Co
Webril	Nonwoven fabric	The Kendall Co
Weldfast	Epoxy and polyester adhesives	Fibercast Co
Wellamid	Nylon-66 and -6 molding resins	Wellman, Inc
Welvic	Poly(vinyl chloride)	Imperial Chemical Industries, Ltd
Whirlclad	Plastic coatings	The Polymer Corp
Whirlsint	Powdered polymers	The Polymer Group
Whitcon	Fluoroplastic lubricants	Whitford Chemical Corp
Wicaloid	Styrene/Butadiene emulsions	Ott Chemical Co
Wicaset	PVC emulsions	Ott Chemical Co
Wilfex	Vinyl plastisols	Flexible Products Co
Wing-stay	Alkylated phenol antioxidants	Goodyear Tire & Rubber Co
Wintrol	Retarders	Stepan Chemical Co
XT Polymer	Acrylics	American Cynamid Co
Xylon	Nylon-66 and Nylon-6	Dart Industries
Xylonite	Cellulose nitrate	B X Plastics, Inc
Zantrel	Rayon fiber	American Enka Corp
Zee	Polyethylene wrap	Crown Zellerbach Corp
Zefran	Acrylic fiber	Dow Chemical Co
Zelan	Water repellent	E I du Pont de Nemours & Co , Inc
Zelec	Lubricant and release agent	E I du Pont de Nemours & Co , Inc
Zelux	PE films	Union Carbide Corp
Zendel	Polyethylene	Union Carbide Corp
Zerlon	Acrylic/Styrene copolymer	Dow Chemical
Zerok	Protective coatings	Atlas Minerals & Chemicals Div
Zetafax	Poly(ethylene-co-acrylic acid)	Dow Chemical Co
Zetafin	Poly(ethylene-co-ethyl acrylate)	Dow Chemical Co
Zytel series	Nylons	E I du Pont de Nemours & Co , Inc

Appendix C: Sources of Laboratory Exercises

The Education Committees of the Divisions of Polymer Chemistry and Polymeric Materials: Science and Engineering strongly advise that laboratory experiences illustrating principles presented in the lecture material be included in introductory courses of polymer chemistry. The extent and type of these laboratory experiences will vary from teacher to teacher and from course to course, and may include lecture demonstrations, group experiments, and individual laboratory exercises.

There is no single, dominating, polymer laboratory textbook. A listing of recent books written specifically as laboratory manuals follows. This is followed by a list, divided into several categories, of *Journal of Chemical Education* articles related to polymers. To minimize problems, all exercises should emphasize safety-related aspects and should be performed by the instructor before asking the students to perform them.

Teachers just beginning to master polymer lecture and laboratory are encouraged initially to emphasize the lecture portion by utilizing simple exercises demonstrating solution of polymers, increase in viscosity of dilute polymer solutions, and synthesis of a condensation and a vinyl polymer. Help should be available from surrounding chemical industry personnel involved with polymers or from a nearby school employing a person experienced with polymers. Such associations can become mutually beneficial.

Again, the *safety* and *toxicological* aspects associated with each exercise must be stressed. Some of the monomers may be quite toxic, but it should be emphasized to students that the resulting polymers are not typically toxic.

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Appendix D: Syllabus

Three interrelated questions can be addressed when considering the construction of course syllabi. These questions are (1) topics to be covered, (2) order in which these topics should be covered, and (3) proportion of time spent on each topic. Just as with other areas of chemistry, such as general and organic chemistry, there exists a healthy variety of topics, extent of coverage of each topic, and a certain order to follow.

The problem with respect to polymer science is compounded in that there exists a wide variety of introductory polymer courses with respect to duration. Typically the duration of such courses fall within the range of 30–90 hours of lecture (1 quarter to 2 semesters—3 hours credit), with 45 hours being the most common.

One major assumption agreed upon by most academic and industrial polymer scientists and associated education committees is that there should be both a core of material common to introductory courses and a portion of optional material reflecting individual interests of teachers, student bodies, and local preferences and circumstances. (For instance, if a student population within an introductory course is largely premedicine, then topics related to natural polymers might be emphasized, while student populations high in material sciences and engineering might benefit from greater emphasis on polymer rheology and dynamics.) This assumption was utilized in the generation of the first ACS Standardized Examination in Polymer Chemistry (1978) and is continuing to be utilized in deliberations made by the Joint Committee on Polymer Education.

The Polymer Syllabus Committee developed a proposal listing broad topic areas and suggested times to be devoted to each topic area. This listing is given below, along with associated chapters in the present text for ready identification.

Basically, the Syllabus Committee has proposed that all lecture courses include portions of the first seven topics with the level and extent of coverage guided by such factors as available class time, additional topics covered, interest of instructor, student interests, class composition, etc. It must be emphasized that the “optional topics” listed are not to be considered limiting and that additional topics can be introduced, again dependent on factors such as available time.

Topics	Amount of course time (%)	Chapter
Major Topics		
Introduction	5	1
Morphology	10	2
Stereochemistry		
Molecular interactions		
Crystallinity		
Molecular weights	10	3
Average molecular weight		
Fractionation of polydisperse systems		
Characterization techniques		
Testing and characterization of polymers	10	4, 5
Structure-property relationships		
Physical tests		
Instrumental characterizations		
Step-reaction polymerizations	10	6
Kinetics		
Polymers produced by step polymerizations		
Chain-reaction polymerization	10	7, 8
Kinetics of ionic chain-reaction polymerization		
Kinetics of free-radical chain-reaction polymerization		
Polymers produced by chain-reaction polymerization		
Copolymerization	10	9
Kinetics		
Types of copolymers		
Polymer blends		
Principal copolymers		
Optional Topics	35	
Rheology (flow properties—viscoelasticity)		5
Solubility		3
Natural and biomedical polymers		10
Additives		13, 14
Fillers		
Plasticizers		
Stabilizers		
Flame retardants		
Colorants		
Reactions of polymers		15
Synthesis of polymer reactants		16
Polymer technology		17
Plastics		
Elastomers		
Fibers		
Coatings and adhesives		

The Syllabus Committee and other committees derived from the Joint Polymer Education Committee have considered the question of order of topics, concluding that almost any order of topics is possible and practical in given situations, i.e., the decision was made not to agree on a given order of topic introduction. The present text is written to permit the various chapters to be considered in almost any order without significant loss of teaching and learning effectiveness. Thus there exists both a freedom in choice of topics, depth of coverage, and order for presentation of topics, as well as some guidelines regarding the important subjects every polymer science teacher should consider.

Appendix E: Polymer Core Course Committees

The ACS Committee on Professional Training in its 1979–1980 publication "Undergraduate Professional Education in Chemistry: Criteria and Evaluation Procedures" notes

> In view of the current importance of inorganic chemistry, biochemistry, and polymer chemistry, advanced courses in these areas are especially recommended and students should be strongly encouraged to take one or more of them. Furthermore, the basic aspects of these three important areas should be included at some place in the core material.

It is with respect to the directive given in the final sentence quoted above that a series of committees was developed under the Joint Polymer Education Committee. Topics related to polymer chemistry (principles, illustrations, and application) should be included in all of the core courses within the training of an undergraduate chemistry major at an appropriate level.

Six committees, hereafter called the Core Course Committees, were formed in 1980. An overall philosophy was developed of trying, wherever possible, to use polymers to enhance topics essential to the core courses consistent with the general CPT philosophy of a constant volume (time) curricula for chemistry majors. Realistic expectations were sought. Polymer topics, principles, and illustrations were to be introduced to help, complement, and complete a student's formal training, but *not* at the exclusion of other essential core course concepts.

Eight objectives were generated as guidelines for the Core Course Reports. These are:

1. Determine general topics to be included in each core course.
2. Determine depth of coverage of each topic.
3. List short, specific polymer illustrations that can be used in teaching key concepts to students.

4. Find timely illustrations of polymer science and include enough specific information so that the examples can be used directly by teachers.
5. Determine a general estimate of time that should be spent on polymer-related topics in each course.
6. Evaluate available texts.
7. Assess overall state of affairs in each course.
8. Develop examples of questions and answers—multiple choice, short answers, essays.

Core Course Reports have been published and are available in the *Journal of Chemical Education*. Those published are: Introduction—J. Chem. Ed. *60*(11):971 (1983); General—*60*(11):973 (1983); Samples—*61*:161 (1984); Inorganic—*61*:230 (1984); Physical—Part I—*62*:780 (1985); and Part II—*2*:1030 (1985); Chemical Engineering—*62*: 1079 (1985).

Appendix F: Polymer Models

Unfortunately, we cannot readily observe molecules, even macromolecules, at the molecular level. Thus, we resort to models to convey molecular shapes and sizes. Following is a brief discussion of simple models employed to illustrate giant molecules.

Many of the most often employed models are quite simple and are used to illustrate the one-dimensionality of linear polymers. Items such as rope, wire, string, thread, and yarn are typically used. Extensions include calculations based on the diameter of a string, etc., and the corresponding lengths of string involved.

Physical crosslinking and general amorphous random chain shapes are readily illustrated by folding together several strings, strands of long spaghetti, etc. Removal of one piece of string involves movement and possible entanglement (physical crosslinking) with accompanying portions of string. Chemical crosslinks can be demonstrated by physically attaching several chains together using paper clips, strips of tape, wire, additional small pieces of string, etc. The concepts of number of repeat units (degree of polymerization) for both vinyl (using similarly colored beads) and condensation (using alternately beads of two different colors), and types of copolymers (alternating, branched, graft, random, or block) can be readily illustrated through the use of pop beads. Thus random copolymers are represented through the use of pop beads of two colors, popped together in a random sequence, alternating copolymers through arrangement of the beads by alternating color and block copolymers through attachment of sequences of same-colored beads. Representation of graft copolymers and chemical crosslinking requires a second hole to be appropriately drilled into some of the beads. The concept of the preferential head-to-tail orientation can also be presented through use of pop beads with the hole end representing the head or tail portion, etc. Ball-and-stick models can be employed to illustrate most of the previously mentioned concepts but are often reserved for difficult-to-demonstrate concepts such as conformation, configuration, and tacticity (atactic, isotactic, and syndiotactic).

Concepts of polymer drag in viscous fluids, physical crosslinking, etc., can be illustrated through use of numbers of wires bent at predetermined lengths at an almost tetrahedral angle. Styrofoam balls, marbles, etc., can be added to assist in illustrating free volume and viscous drag. The wire represents the atoms present in the polymer backbone. A randomization of the bonding direction will give wire polymers that can also be used to describe average end-to-end distances and other random flight aspects.

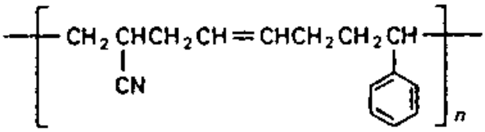
Most synthetic polymers, when allowed, will form shapes dependent primarily on size and electronic nature such as to minimize steric and electronic constraints and to maximize electronic associations. The major space-saving or sterically minimizing shape for linear macromolecules is that of a helix. A simple rope or string drawn in two and twisted readily illustrates the double helix associated with double-helical DNAs, whereas a simple twisting of the rope illustrates the helical nature of many synthetic isotactic vinyl polymers. The second major shape employed by nature in space-limiting situations is that of a puckered or pleated sheet. (A good illustration of this is a pleated skirt). This geometry allows ready, rapid low extensions, but inhibits more radical mobility (stretching). The helical, space-saving shape can be further illustrated by additions onto the chains by way of toothpicks, pieces of paper, etc., to represent side chains of vinylic substitutions.

Paper models have been effectively employed to illustrate tacticity, chain folding, and a number of other geometrical concepts. These often require special folding skills.

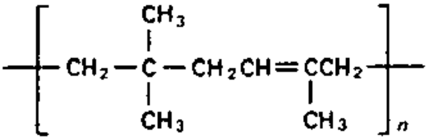
Appendix G: Structures of Common Polymers

SYNTHETIC

Acrylonitrile-butadiene-styrene terpolymer (ABS)

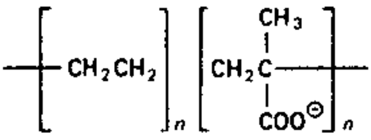


Butyl rubber



$$\left[\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2CH}{=}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{CH_2} \right]_n$$

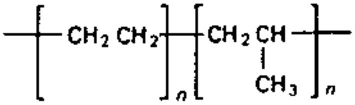
Ethylene-methacrylic acid copolymers (Ionomers)



$$\left[\mathrm{CH_2CH_2}\right]_n\left[\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{COO^{\ominus}}}{\mathrm{C}}}\right]_n$$

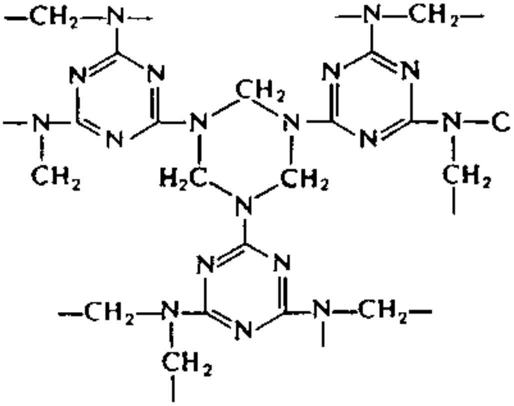
The diagrams represent idealized structures in the form of regularly repeating units. This is especially true for the natural polymers and copolymers.

Ethylene-propylene elastomers

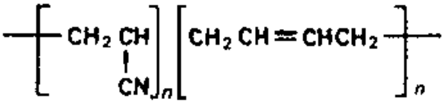


$$-\!\left[CH_2CH_2\right]_n\!\left[CH_2\underset{\substack{|\\CH_3}}{CH}\right]_n\!-$$

Melamine-formaldehyde resins (MF)

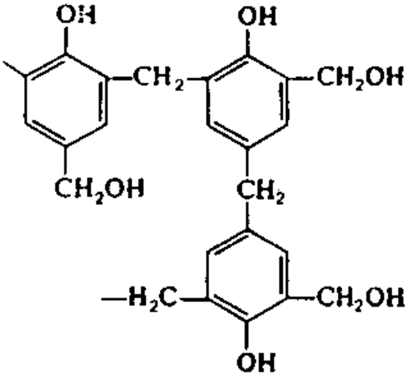


Nitrile Rubber (NBR)

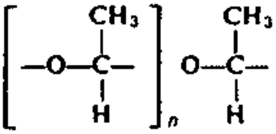


$$-\!\left[CH_2\underset{\substack{|\\CN}}{CH}\right]_n\!\left[CH_2CH{=}CHCH_2\right]_n\!-$$

Phenol-formaldehyde resins (PF)

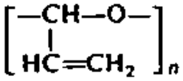


Polyacetaldehyde



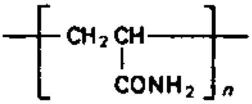
$$\left[-O-\overset{CH_3}{\underset{H}{C}}-\right]_n O-\overset{CH_3}{\underset{H}{C}}-$$

Polyacrolein



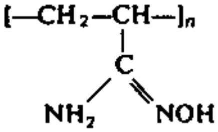
$$\left[-\underset{HC=CH_2}{CH}-O-\right]_n$$

Polyacrylamide



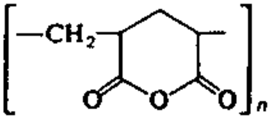
$$-\left[CH_2\underset{CONH_2}{CH}-\right]_n-$$

Poly(acrylamide oxime)

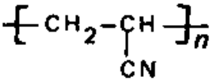


$$[-CH_2-\underset{\underset{NH_2\quad NOH}{C}}{CH}-]_n$$

Poly(acrylic anhydride)

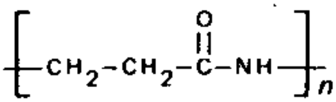


Polyacrylonitrile



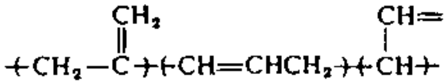
$$-\left[CH_2-\underset{CN}{CH}-\right]_n$$

Poly(β-alanine) (3-Nylon)



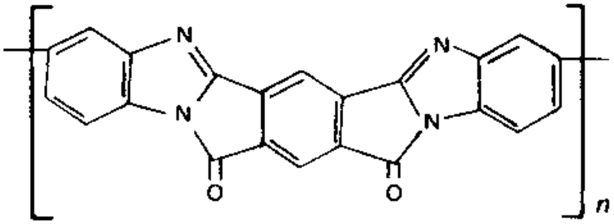
$$-\left[CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH-\right]_n$$

Polyallene

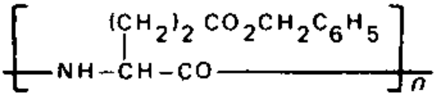


$$-\!\!\left(CH_2-\overset{\overset{CH_2}{\|}}{C}\right)\!\!-\!\!\left(CH=CHCH_2\right)\!\!-\!\!\left(\overset{\overset{CH=CH_2}{|}}{CH}\right)\!\!-$$

Polybenzobenzimidazole from pyromellitic dianhydride and tetraminobiphenyl

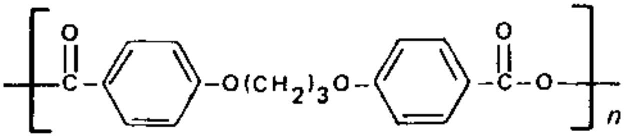


Poly(γ-benzyl-L-glutamate)



$$\left[NH-\overset{\overset{(CH_2)_2CO_2CH_2C_6H_5}{|}}{CH}-CO\right]_n$$

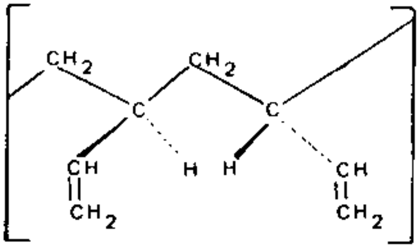
Poly(1,3-bis(p-carboxyphenoxy)propane anhydride)



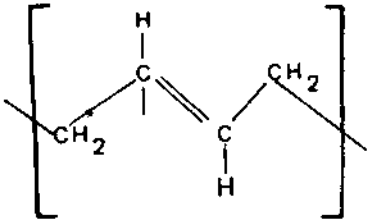
Polybutadiene (Butadiene rubber, BR)

$$-\!\!\left[CH_2CH=CHCH_2\right]_n\!\!-$$

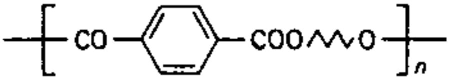
1,2-Polybutadiene



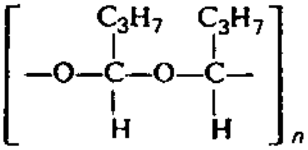
trans-1,4-Polybutadiene



Poly(butylene terephthalate) (PBT)

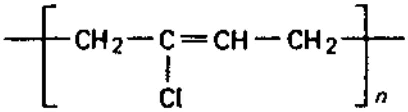


Poly-n-butyraldehyde



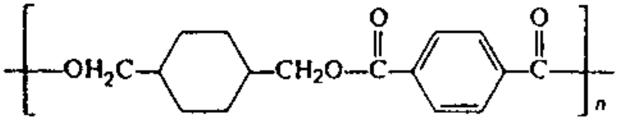
$$\left[-O-\underset{H}{\overset{C_3H_7}{C}}-O-\underset{H}{\overset{C_3H_7}{C}}- \right]_n$$

Polychloroprene

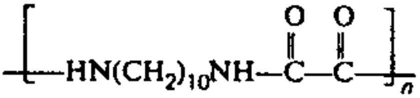


$$-\left[CH_2-\underset{Cl}{C}=CH-CH_2 \right]_n-$$

Poly(1,4-cyclohexanedicarbinyl terephthalate)
or Poly(oxyterephthaloyloxymethylene-1,4-cyclohexylenemethylene)

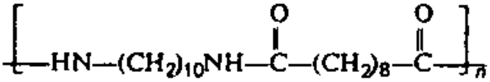


Poly(decamethyleneoxamide)



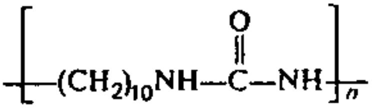
$$\left[HN(CH_2)_{10}NH-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}- \right]_n$$

Polydecamethylenesebacamide (10-10 Polyamide)



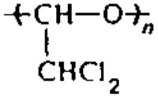
$$\left[HN-(CH_2)_{10}NH-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}- \right]_n$$

Polydecamethyleneurea



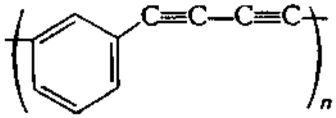
$$\left[(CH_2)_{10}NH-\overset{O}{\overset{\|}{C}}-NH \right]_n$$

Polydichloroacetaldehyde

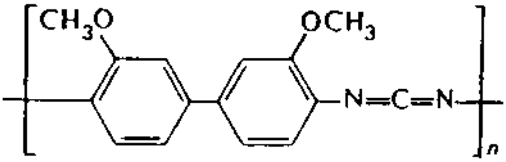


$$\left(\underset{CHCl_2}{\underset{|}{CH}}-O \right)_n$$

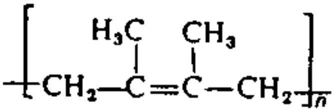
Polydiethynylbenzene
or Poly(1,3-phenylene-1,3-butadiyne-1,4-diyl)



Poly(3,3'-dimethoxy-4-4'-biphenylene carbodiimide)

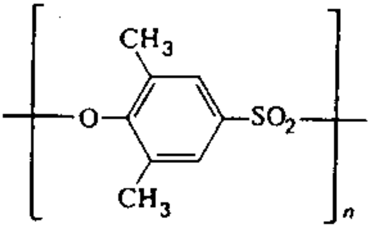


Poly(2,3-dimethylbutadiene)

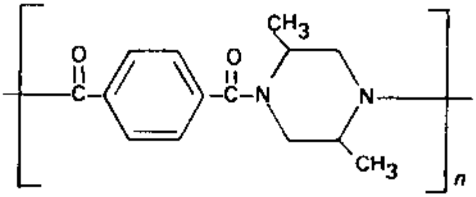


$$\left[CH_2-\overset{\overset{H_3C}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_2 \right]_n$$

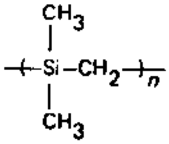
Poly(3,5-dimethyl-1,4-phenylene sulfonate)



Poly(2,5-dimethylpiperazine terephthalamide)



Polydimethylsilmethylene

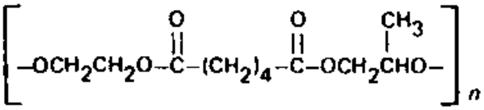


$$\left(-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_2- \right)_n$$

Polyethylene (PE)

$$-\!\!\left[\mathrm{CH_2CH_2}\right]_n\!\!-$$

Poly(ethylene-co-propylene adipate)

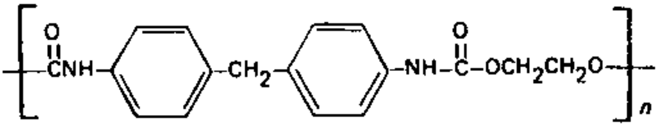


$$\left[-\mathrm{OCH_2CH_2O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-(\mathrm{CH_2})_4-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OCH_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HO}-\right]_n$$

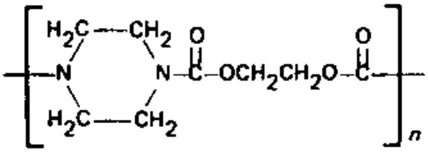
Poly(ethylene glycol) (PEG)

$$\mathrm{HOCH_2CH_2}-\!\!\left[\mathrm{OCH_2CH_2}\right]_n\!\!-\mathrm{OH}$$

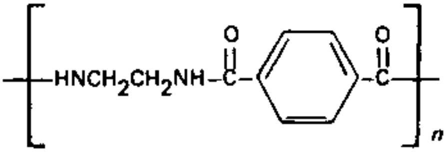
Poly(ethylene methylene bis(4-phenylcarbamate))



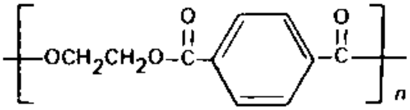
Poly(ethylene N, N'-piperazinedicarboxylate)



Poly(ethylene terephthalamide)



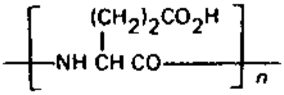
Poly(ethylene terephthalate) (PET)



Poly(ethylene tetrasulfide)

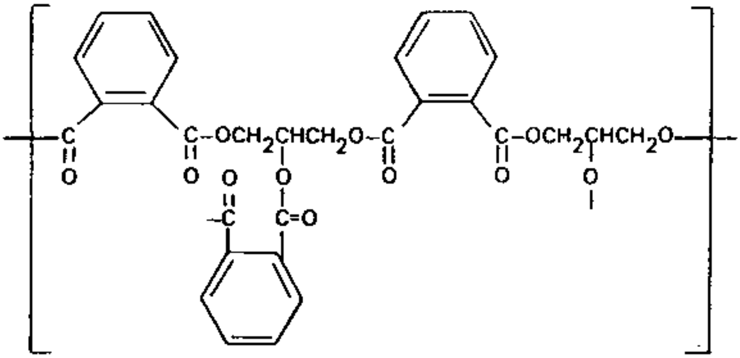
$$\left[-CH_2CH_2-SSSS-\right]_n$$

Poly-α-L-glutamic acid

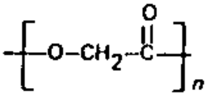


$$\left[-NH\,\underset{}{\overset{(CH_2)_2CO_2H}{\overset{|}{CH}}}\,CO-\right]_n$$

Poly(glyceryl phthalate)

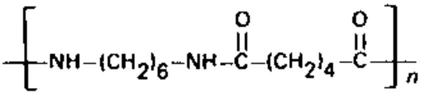


Poly(glycolic ester)



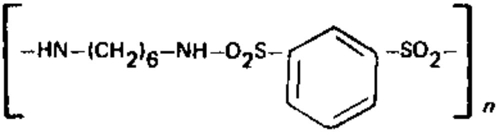
$$\left[-O-CH_2-\overset{O}{\overset{\|}{C}}-\right]_n$$

Poly(hexamethyleneadipamide) (6–6 Nylon)

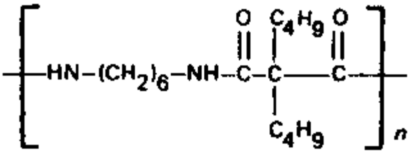


$$\left[-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

Poly(hexamethylene m-benzenedisulfonamide)

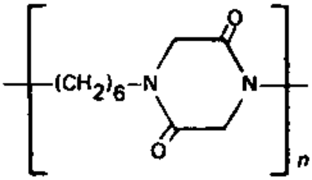


Poly(hexamethylenedi-n-butylmalonamide)

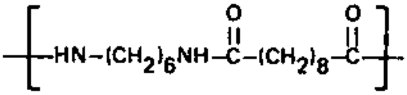


$$\left[-HN-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-\underset{C_4H_9}{\overset{C_4H_9}{C}}-\overset{O}{\overset{\|}{C}}- \right]_n$$

Poly(N, N'-hexamethylene-2, 5-diketopiperazine)



Polyhexamethylenesebacamide (6–10 Nylon)

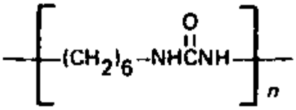


$$\left[-HN-(CH_2)_6NH-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}- \right]$$

Poly(hexamethylene thioether)

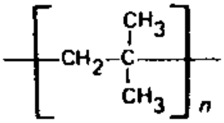
$\left[-(CH_2)_6-S- \right]_n$

Polyhexamethyleneurea



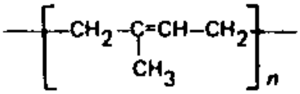
$$\left[-(CH_2)_6-NH\overset{O}{\overset{\|}{C}}NH- \right]_n$$

Polyisobutylene (PIB)



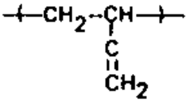
$$\left[-CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}- \right]_n$$

Polyisoprene



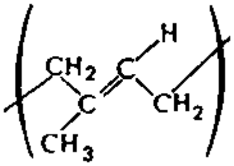
$$\left[-CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH_2- \right]_n$$

3,4-Polyisoprene

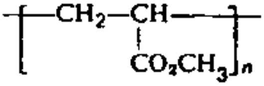


$$\left(-CH_2-\underset{\substack{|\\ C\\ \|\\ CH_2}}{CH}- \right)$$

trans-1,4-Polyisoprene

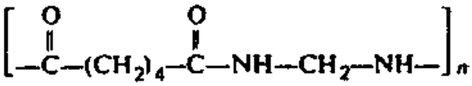


Poly(methyl acrylate)



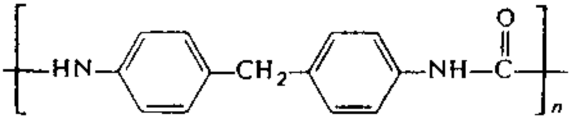
$$\left[-CH_2-\underset{CO_2CH_3}{\underset{|}{CH}}- \right]_n$$

Polymethyleneadipamide (1-6 Nylon)

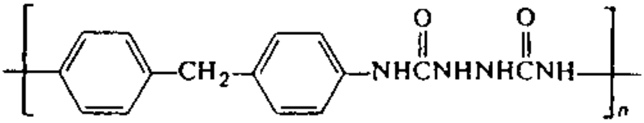


$$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-CH_2-NH- \right]_n$$

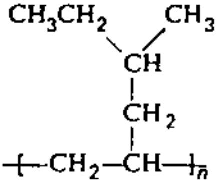
Poly[methylene bis(4-phenylurea)]



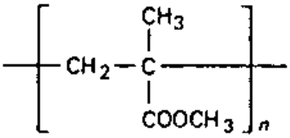
Poly[methylene bis(4-phenylurethylene)]



Poly(4-methyl-1-hexene)

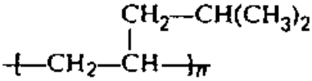


Poly(methyl methacrylates) (PMMA)



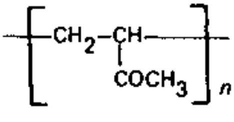
$$\left[\mathrm{CH_2}-\underset{\mathrm{COOCH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}- \right]_n$$

Poly(4-methyl-1-pentene)



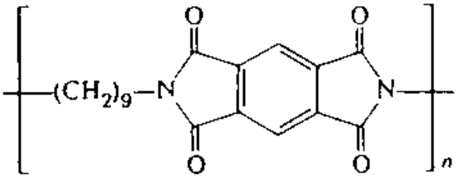
$$\left(\mathrm{CH_2}-\overset{\mathrm{CH_2-CH(CH_3)_2}}{\mathrm{CH}}- \right)_n$$

Poly(methyl vinyl ketone)

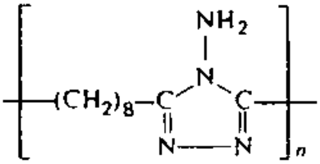


$$\left[\mathrm{CH_2}-\underset{\mathrm{COCH_3}}{\mathrm{CH}}- \right]_n$$

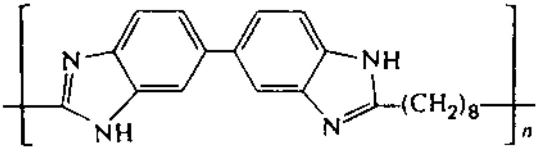
Polynonamethylenepyromellitimide



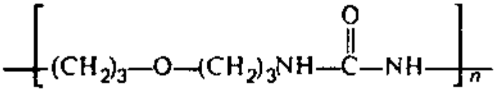
Poly(3,5-octamethylene-4-amino-1,2,4-triazole)



Poly(2,2'-octamethylene-5,5'-dibenzimidazole)

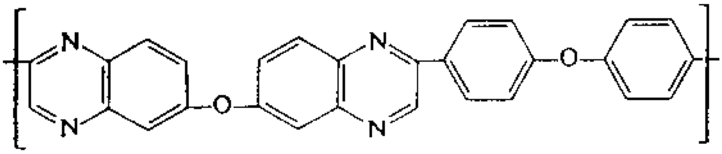


Poly(4-oxaheptamethyleneurea)



$$\left[(CH_2)_3-O-(CH_2)_3NH-\overset{\overset{\displaystyle O}{\|}}{C}-NH \right]_n$$

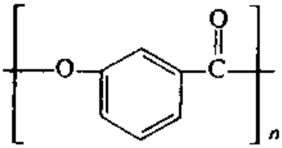
Poly[2,2'-(4,4'-oxydiphenylene)-6,6'-oxydiquinoxaline]



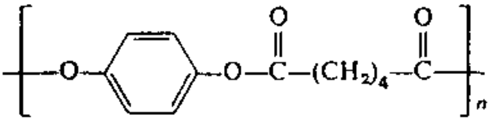
Polyoxymethylene
Polyacetal

$$-\!\left[\text{OCH}_2\right]_n\!-$$

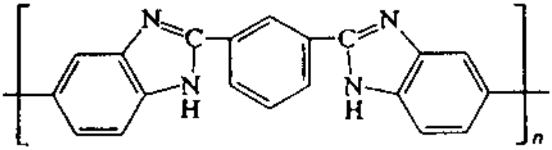
Poly(m-phenyl carboxylate)



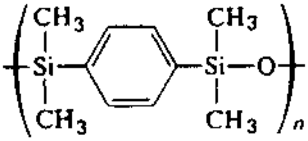
Poly(1,4-phenylene adipate)



Poly[2,2'(m-phenylene)-5,5'(6,6'-benzimidazole)]

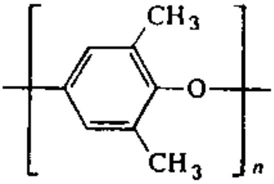


Poly[p-phenylene bis(dimethylsiloxane)]
[Poly(tetramethyl-p-silylphenylenesiloxane]

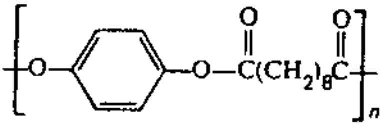


Poly(phenylene oxide) (PPO)

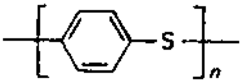
Poly(2, 6-dimethyl-p-phenylene ether)



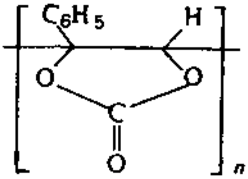
Poly(1, 4-phenylene sebacate)



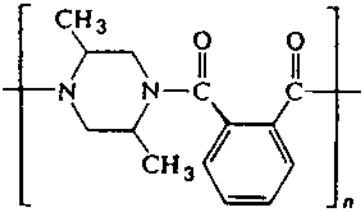
Poly(phenylene sulfide) (PPS)



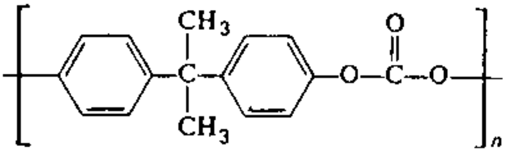
Poly(phenyl vinylene carbonate)



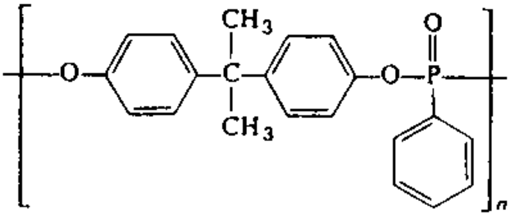
Poly(N, N'-phthaloyl-trans-2, 5-dimethylpiperazine)



Poly[2, 2-propanebis(4-phenyl carbonate)]



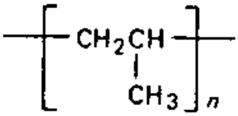
Poly[2, 2-propanebis(4-phenyl phenylphosphonate)]



Polypropanesultam

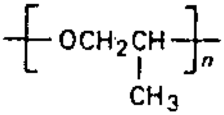
$\left[(CH_2)_3SO_2NH \right]_n$

Polypropylene (PP)



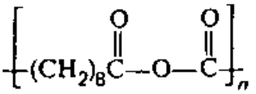
$\left[CH_2CH(CH_3) \right]_n$

Poly(propylene glycol) (PPG)



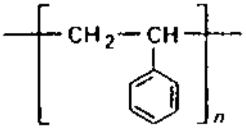
$\left[OCH_2CH(CH_3) \right]_n$

Poly(sebacic anhydride)



$$\left[(CH_2)_8\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}} \right]_n$$

Polystyrene (PS)



Polytetrafluoroethylene (PTFE)

$$\left[CF_2CF_2 \right]_n$$

Poly(tetrafluoro-1,2,3,4-tetrathiane)

$$\left[-CF_2CF_2SSSS- \right]_n$$

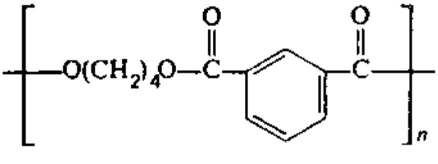
Poly(tetrafluoro-1,2,3-trithiolane)

$$\left[-CF_2CF_2SSS- \right]_n$$

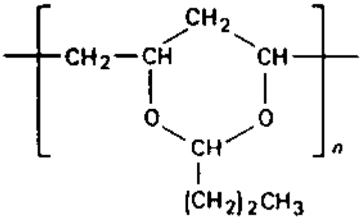
Poly(tetramethylene hexamethylenedicarbamate)

$$\left[-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-NH(CH_2)_6NH-\overset{O}{\overset{\|}{C}}-O- \right]_n$$

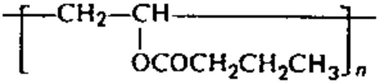
Poly(tetramethylene isophthalate)



Poly(vinyl butyral) (PVB)

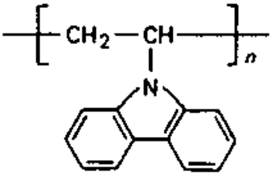


Poly(vinyl butyrate)

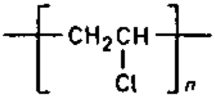


$$\left[\mathrm{CH_2-\underset{\displaystyle OCOCH_2CH_2CH_3}{CH}}\right]_n$$

Poly(vinyl carbazole)

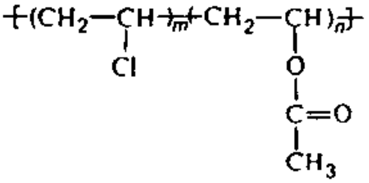


Poly(vinyl chloride) (PVC)



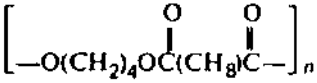
$$\left[\mathrm{CH_2\underset{\displaystyle Cl}{CH}}\right]_n$$

Poly(vinyl chloride-co-vinyl acetate)



$$\left[(\mathrm{CH_2-\underset{\displaystyle Cl}{CH}})_m(\mathrm{CH_2-\underset{\displaystyle O-\overset{\displaystyle }{C}(=O)-CH_3}{CH}})_n\right]$$

Poly(tetramethylene sebacate)

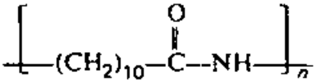


$$\left[-O(CH_2)_4O\overset{O}{\overset{\|}{C}}(CH_8)\overset{O}{\overset{\|}{C}}-\right]_n$$

Polythiazyl

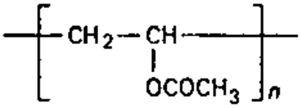
$$-\!\!\left[S=N\right]_n\!\!-$$

Poly(11-undecanoamide)



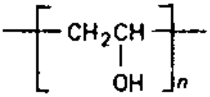
$$-\left[(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-NH-\right]_n$$

Poly(vinyl acetate) (PVAc)



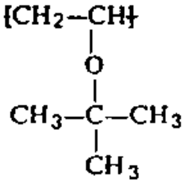
$$-\!\!\left[CH_2-\underset{OCOCH_3}{\underset{|}{CH}}-\right]_n\!\!-$$

Poly(vinyl alcohol) (PVA)



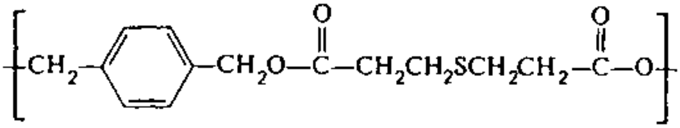
$$-\!\!\left[CH_2\underset{OH}{\underset{|}{CH}}\right]_n\!\!-$$

Poly(vinyl t-butyl ether)

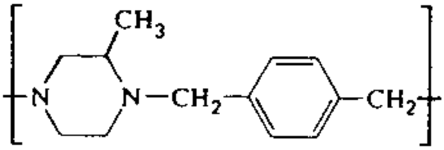


$$[CH_2-\underset{\underset{\underset{CH_3-\underset{\underset{CH_3}{|}}{C}-CH_3}{|}}{O}}{\underset{|}{CH}}]$$

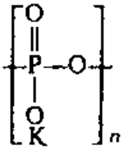
Poly(p-xylylene thiodipropionate)



Poly(1,4-xylylenyl)-2-methylpiperazine

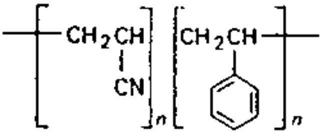


Potassium polymetaphosphate

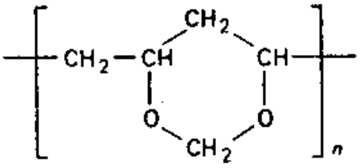


$$\left[-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle \overset{\displaystyle O}{}\atop \displaystyle K}{|}}{P}}-O- \right]_n$$

Styrene-acrylonitrile copolymer (SAN)



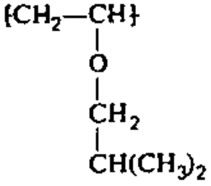
Poly(vinyl formal) (PVF)



Poly(vinylidene chloride)

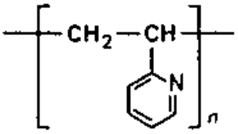
$$-\!\!\left[CH_2CCl_2\right]_n\!\!-$$

Poly(vinyl isobutyl ether)

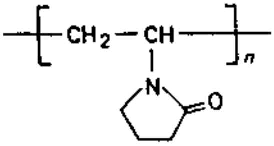


$$\{CH_2-CH(OCH_2CH(CH_3)_2)\}$$

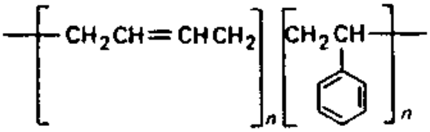
Poly(vinyl pyridine)



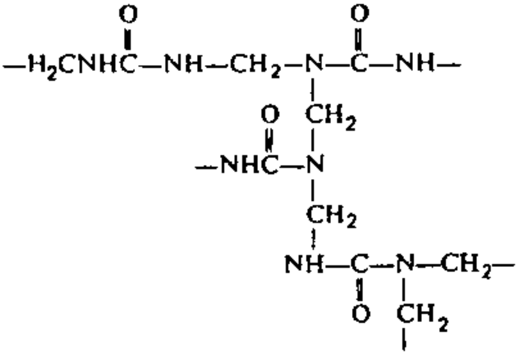
Poly(vinyl pyrrolidone)



Styrene-butadiene rubber (SBR)

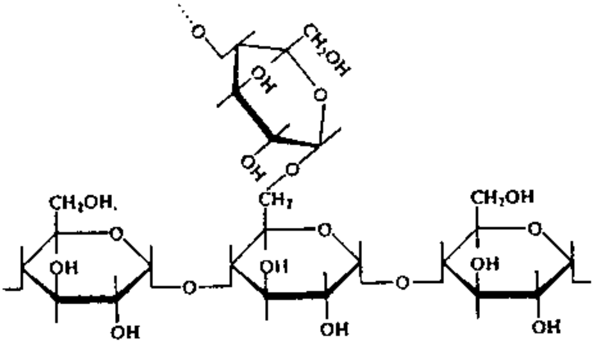


Urea-formaldehyde resins (UF)

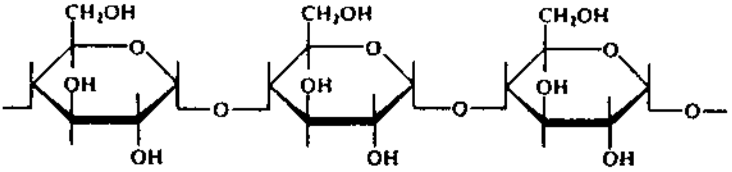


POLYSACCHARIDES: PARTIAL STRUCTURES

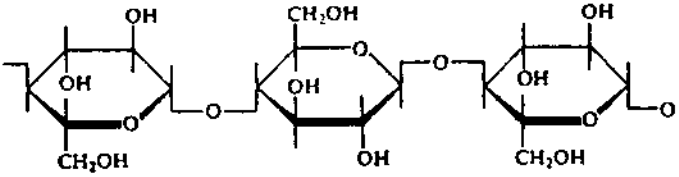
Amylopectin—details of branch-point



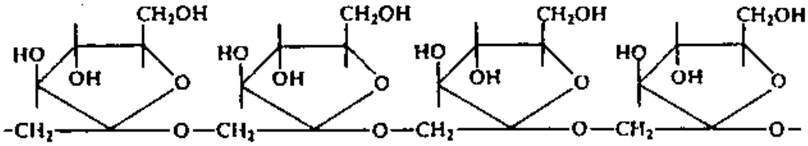
Linear amylose



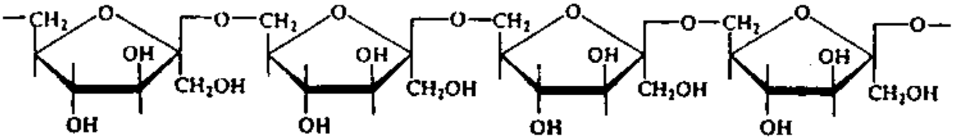
Cellulose



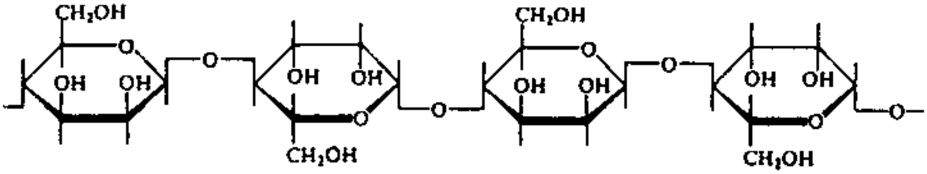
Inulin



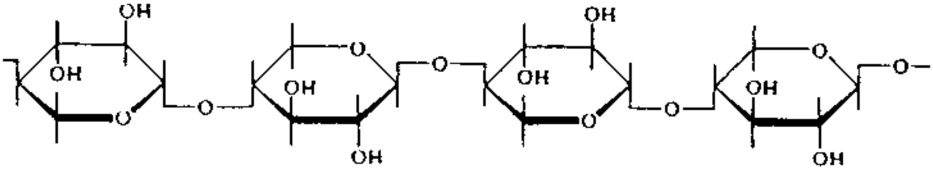
Levan



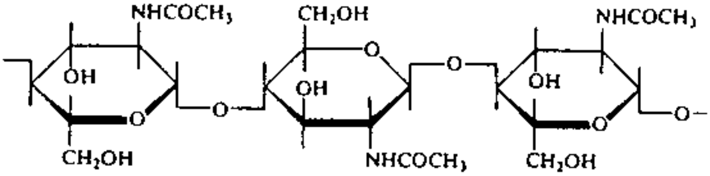
Mannan



Xylan



Chitin



Appendix H: Mathematical Values and Units

Prefixes for Multiples and Submultiples

Multiple or submultiple		Prefix	SI symbol
10^{12}	100 000 000 000	tera	T
10^{9}	1000 000 000	giga	G
10^{6}	1000 000	mega	M
10^{3}	1000	kilo	k
10^{2}	100	hecto	h
10^{1}	10	deka	da
10^{0}	1		
10^{-1}	0.1	deci	d
10^{-2}	0.01	centi	c
10^{-3}	0.001	milli	m
10^{-6}	0.000 001	micro	μ
10^{-9}	0.000 000 001	nano	n
10^{-12}	0.000 000 000 001		
10^{-15}		femto	f
10^{-18}		atto	a

Conversion Factors

Unit	Value
1 Angstrom (Å)	$= 10^{-10}$ m $= 10^{-8}$ cm $= 10^{-7}$ mm $= 10^{-4}$ μm $= 10^{-1}$ nm
1 atmosphere (atm)	$= 1.013 \times 10^{5}$ Pa $= 1.01325$ bar
1 bar	$= 10^{5}$ Pa $= 0.9869$ atm $= 14.5038$ psi
1 calorie (NBS)	$= 4.184$j $= 3.9657 \times 10^{-3}$ BTU
1.24 electron volts (eV)	$= 28.59$ kcal mol^{-1} (= 1000 mm)
1 gigapascal (GPa)	$= 10^{9}$ Pa $= 10^{4}$ bar $= 10$ kbar
1 g/cm^{3}	$= 10^{3}$ kg m^{-3} $= 1$ Mg/m^{3}
1 kilobar (kbar)	$= 10^{8}$ Pa $= 986.9$ atm
1 kilopascal (kPa)	$= 1000$ Pa $= 10^{-2}$ bar
1 kilocalorie (NBS)	$= 4.184 \times 10^{10}$ erg $= 4.84$ J $= 3.966$ Btu
1 liter (L)	$= 1.0567$ quart (US)
1 megagram m^{-3} (Mg/m^{3})	$= 10^{3}$ kg/m^{3} $= 1$ g/cm^{3}
1 meter (m)	$= 3.28084$ feet
1 millimeter (mm)	$= 0.0394$ in.
1 micrometer (μm)	$= 10^{4}$ Å $= 10^{-3}$ mm $= 10^{-6}$ m $= 1$ μm
1 nanometer (nm)	$= 10$ Å $= 10^{-9}$ m
1 ounce (avoir)	$= 28.35$ g
1 point (gem)	$= 10^{-2}$ carat $= 0.04$ pearl grain
1 poise	$= 10^{-1}$ N s m^{-2}
1 pound (avoir) (lb)	$= 453.59$ g
1 stoke	$= 10^{-4}$ m^{2} s^{-1}

Units of Measurement

Quantity	Unit	SI symbol	Formula
Acceleration			m/s^{2}
Amunt of substance	mole	mol	
Area			m^{2}
Bulk modulus			N/m^{2}
Chemical potential	joule	J	Nm
Compressibility			1/Pa
Density			kg/m^{3}
Electrical charge	coulomb	C	A s
Electrical capacitance	farad	F	A s/V
Electrical conductivity	siemens	S	A/V
Electrical current	ampere	A	
Electrical field strength			V/m
Electrical inductance	henry	H	V s/A
Electrical resistance	ohm	Ω	V/A
Electromotive force	volt	V	W/A
Energy	joule	J	N m
Enthalpy	joule	J	N m
Entropy			J/K
Force	newton	n	kg m/s^{2}
Frequency	hertz	Hz	(cycle)/s^{2}

Units of Measurement (continued)

Quantity	Unit	SI symbol	Formula
Gibbs free energy	joule	J	N m
Heat capacity			J/K
Heat flow			J/s m^2
Helmholtz free energy	joule	J	N m
Illuminance	lux	lx	1m/m^2
Length	meter	m	
Luminance			cd/m^2
Luminous flux	lumen	lm	cd sr
Luminous intensity	candela	cd	
Magnetic field strength			A/m
Magnetic flux	weber	Wb	V s
Magnetic flux density	tesla	T	Wb/m^2
Magnetic permeability			H/m
Magnetic permittivity			F/m
Mass	kilogram	kg	
Power	watt	W	J/s
Pressure	pascal	Pa	N/m^2
Resistivity			Ω m
Shear modulus			N/m^2
Surface tension			N/m
Temperature	kelvin	K	
Thermal conductivity			W/mk
Thermal expansion			1/K
Time	second	s	
Velocity			m/s
Viscosity (dynamic)			Ns/m^2
Viscosity (kinematic)			m^2/s
Voltage	volt	V	W/A
Volume			m^3
Wavelength			m
Wavenumber			1/m
Work	joule	J	N/m
Young's modulus			N/m^2

Physical Constants

Quantity		Numerical value (SI)	Numerical value (cgs)
Acceleration due to gravity at earth's surface	g		
Equator	g	9.7805 m s^{-2}	9.7805 × 10^2 cm s^{-2}
Avogadro's constant	N_A	6.02252 × 10^{23} mol^{-1}	6.02252 × 10^{23} mol^{-1}
Boltzmann's constant	k	1.380622 × 10^{-23} J K^{-1}	1.380622 × 10^{-16} erg K^{-1}
Electron charge		1.6021917 × 10^{-19}C	1.6021917 × 10^{-20} emu
Faraday's constant	F	9.64870 × 10^4 mol^{-1}	9.64870 × 10^3 emu mol^{-1}
Gas constant	R	8.31432 J mol^{-1} K^{-1}	1.9872 cal mol^{-1} K^{-1}
Gravitational constant	G	6.6732 × 10^{-11} N m^2 kg^{-2}	6.6732 × 10^{-8} dyne cm^2 g^{-2}
Permittivity of a vacuum	ε_0	8.8419413 × 10^{-12} F m^{-1}	1.0 dyne cm^2 $statcoul^{-2}$
Permeability of a vacuum	μ_0	1.2566371 × 10^{-6} H m^{-1}	
Planck's constant	h	6.626196 × 10^{-34} J s	6.626196 × 10^{-27} erg s
Velocity of light in a vacuum	c	2.99792458 × 10^8 m s^{-1}	2.99792458 × 10^{10} cm s^{-1}

Appendix I: Comments on Health

Synthetic polymers, like most biological polymers, are nontoxic under normal and intended use Most of the additives employed in today s polymer industry are also relatively non toxic Even so, care should be exercised when dealing with many of the monomers of synthetic polymers and when dealing with polymeric materials under extreme conditions such as the high temperatures that may be employed in the processing of some polymeric materials or when polymers are involved in commercial or domestic fires

FIRE

Fire hazards involve not only burning—most deaths occur from the ingestion of volatiles produced by the fire Carbon monoxide the major cause of death, causes unconsciousness in less than 3 minutes due to its preferential attack on hemoglobin (see Sec 15 14)

Interestingly, one important observation concerning burning in general is whether colored smoke is produced Some materials burn producing lots of darkly colored smoke Some of this colored smoke may be due to the production of aromatic systems including fused ring systems which may or may not contain harmful chemical species, including respiratory toxins and cancer-causing agents For instance, PVC often emits hydrogen chloride as a major degradation product As the hydrogen chloride is eliminated "conjugation" of the backbone occurs accompanied by the formation of fused ring compounds Emission of hydrogen chloride can occur at temperatures employed for the processing of some polymers Because of the elimination of hydrogen chloride by PVC, care is exercised in the processing of PVC products by manufacturers who do not want to put their workers at risk In contrast, polyacrylonitrile does not typically emit hydrogen cyanide upon burning Instead, internal cyclization occurs, resulting in the formation of major amounts of char In fact the pyrolysis of polyacrylonitrile forms the basis for the production of carbon fibers

Table I.1 Descriptions of Toxic Measures

TDLo/Toxic Dose Low—The lowest dose introduced by any route other than inhalation over any period of time that produces any toxic effect in humans or to produce carcinogenic, teratogenic, mutagenic, or neoplastic effects in humans or animals.

TCLo/Toxic Concentration Low—Any concentration in air that causes any toxic effect in humans or produces a carcinogenic, teratogenic, mutagenic, or neoplastigenic toxic effect in humans or animals

LDLo/Lethal Dose Low—The lowest dose introduced by any route other than by inhalation over any time to have caused death in humans or the lowest single dose to have caused death in animals.

LD_{50}/Lethal Dose Fifty—A calculated dose expected to cause the death of 50% of a tested population from exposure by any route other than inhalation.

LCLo/Lethal Concentration Low—The lowest concentration in air to have caused death in a human or death in animals when exposed for 24 hours or less

LC_{50}/Lethal Concentration Fifty—A calculated concentration of a substance in air that would cause death in 50% of a test population from exposure for 24 hours or less

MEASURES OF TOXICITY

Toxicity involves the affect of various materials on living objects such as bacteria, fungi, yeast, plants, mice, fish, and humans. Tests to determine the toxicity of various substances are typically done either in situ or in vitro. In situ tests are carried out at the location where the toxicity is in question. For example, in situ tests of the ability of cancer drugs to inhibit human ovarian cancer are carried out within the living beings In vitro tests are examinations made away from the location where the toxicity is in question. Thus, testing various agents on human cancer cell lines in a petri dish constitutes an in vitro examination.

While we are mainly concerned with the affects of various agents on humans, we often employ test animals, such as specially genetically developed mice and rats, as measures of an agent's toxicity. While it is assumed that there is a relationship between the type and level of toxicity to these mice and rats and the toxicity to humans, this relationship is not always apparent. Even so, such animal tests are generally foundational in the assignment of allowed exposure levels to specific agents. It is known that the toxicity varies between species, amount administered, type of administration, and duration of exposure. This difference is a consequence of a number of factors, including the tendencies of certain agents to affect certain parts of the body including varying tendencies for the agents to become concentrated within specific organs and tissues and their mechanism(s) of action. Table I.1 lists some toxicity definitions utilized in toxicology today.

As noted before, while commercially available synthetic polymers are relatively nontoxic, the monomers themselves vary greatly in toxicity. (For instance, ethyleneimine, an acknowledged cancer-causing agent, has an LD_{50} (oral/rat) of 15 mg/kg while polyethyleneimine has an LD_{50} (oral/rat) of 3300 mg/kg. This points out the need for monomers and other potentially toxic agents to be removed from polymers.) Table I.2 contains the time-weighted average (TWA) for some monomers as cited by the United States Occupational Standards. For comparison, entries for some well-known toxic compounds have been added.

CUMULATIVE AFFECTS

While exposure of the general public to toxins is dangerous and to be avoided, exposure of people that deal with commercial chemicals on a daily basis is even more important.

Table I.2 TWA Values for Selected Monomers and Additional Recognized Toxins

Chemical	TWA (ppm)
Acetic anhydride	5
Acrylonitrile	20
Benzene	10
1,3-Butadiene	1000
Carbon monoxide	50
Chloroprene	25
1,2-Ethylenediamine	10
Ethylene oxide	50
Formaldehyde	3
Hydrazine	1
Hydrogen cyanide	10
Phenol	5
Styrene	100
Vinyl chloride	500

Such people must take special care to avoid exposure to dangerous chemicals, since many of these accumulate in our bodies over a long time. slowly building to levels that may be unhealthy.

Most of the toxic and undesirable chemicals of a decade ago have been eliminated from the common workplace. This includes halogenated hydrocarbons such as carbon tetrachloride and aromatic hydrocarbons such as benzene. Further, chemicals that are known to be potentially toxic, such as some monomers, are being eliminated from polymeric materials to within the limits of detection

We are also becoming more aware of the effects of nonchemical hazards in the workplace. These hazards are being dealt with as they become known. Some of these possible hazards include exposure to certain radiations employed in materials processing, machine and other noise. machine operation, and exposure to other potential safety situations.

Industrial recognition of customer and employee safety is a major factor behind the international programs known as ISO 9000 and ISO 14000 (Appendix J) Further, a number of national agencies and associations deal with aspects of the environmental and personal safety issues, including the Environmental Protection Agency, National Fire Protection Association. Occupational Safety and Health Administration, Department of Transportation, Food and Drug Administration. and the National Institute for Occupational Safety and Health.

ENVIRONMENT

Today industry and business recognize that part of doing business is taking care of the environment. Along with various government agencies and associated laws, business and industry are finding that good environmental practices are good business. Advances continue with respect to lowering potentially harmful emissions as solid waste or into the water and air shared by all of us. Chemical industries are taking the lead in this clean-up process (see also ISO 9000 and 14000; Appendix J). A combination of watchful vigilance and trust is needed to continue this effort.

Further readings are found in an ongoing series that appears in Polymer News.

Endocrines-I. Mimics and disruptors, *23*(5):167–169 (1998)
Endocrines-II. Fundamentals, *21*(11):382–385 (1998)
Endocrines-III Structural considerations, *24*(4):131–132 (1999).
Fundamentals for human risk assessments, *23*(6):198–200 (1998)
Epidemiological contributions to risk assessments, *23*(9).311–312 (1998)
Toxicity indicator values—ERPGs and WEELs, *24*(1):23–25 (1999)
Toxicity indicator values—RfD, RfC, NOAEL, LOAEL, and other measures, *24*(2).58–59 (1999).
Fundamentals of toxicology—Basics, *24*(5):159–161 (1999)
Basics of toxicology testing, *24*(7):233–234 (1999)
Human responses to toxicological testing, *24*(8).275–276 (1999)
Biotransformations, *24*(9) 311–312 (1999)
Influence of route of exposure, *24*(8) 250–253 (1999).
Developmental toxicology, *25*(1).20–22 (2000).
Fundamentals of cancer—Risk assessments, *25*(3) 90–91 (2000)
Cancer bioassays, *25*(5) 162–164 (2000).
Short and long-term bioassays, *25*(8).270–272 (2000).
Cancer risk assessment, *25*(12) 414–415 (2000).
Biomedical neurotoxicity, *26*(8) 276–278 (2001).
Immunotoxicity, *26*(10):349–351 (2001).
Fundamentals of neurotoxicity, *26*(3).95–96 (2001).

Appendix J: Comments on ISO 9000 and 14000

The International Organization for Standardization (ISO) has members in about 100 countries working to develop common global standards. The ISO 9000 series encompasses the product development sequence from strategic planning to customer service. Currently, it is a series of five quality system standards, with two of the standards focusing on guidance and three contractual standards.

ISO 9000 certification is often obtained to promote a company's perceived quality level, for supplier control, and to promote certain management practices—often Total Quality Management (TQM) management practices. It is used as a global standardizing "tool" with respect to business and industry in its broadest sense, including banking, volunteer organizations, and most aspects of the chemical (including the polymer) industry.

ISO 9000 requires what is called a third-party assessment but involves developing first and second-party strategies. First party refers to the supplier company that requests ISO 9000 certification. Second party refers to the customer whose needs have been met by the first party through the use of quality management procedures achieved through ISO 9000 compliance. Third party refers to an outside reviewer that certifies that the first party has satisfied ISO 9000 procedures.

While ISO 9000 is a management tool, it affects the way industry does business and deals with quality control issues, such as how machinery and parts manufactured by a company are monitored for quality. It focuses on satisfying the customer—the purchaser of the raw materials, manufactured parts, or assembled items—and includes the eventual end-customer—the general public. It is an attempt to assure quality goods.

ISO 14000 is a series of standards intended to assist in managing the impact of manufactured materials including finished products and original feedstocks. It addresses the need to have one internationally accepted environmental management system that involves cradle-to-grave responsibility for manufactured materials, emphasizing the impact of products, operations, and services on the environment.

Further readings related to the ISO series are found in a series of *Polymer News* articles as follows:

Theories of Management, *19*(12):373–376 (1994).
Managerial Tools and Opportunities, *20*(5):147–151 (1995).
Total Quality Management, *20*(9):278–281 (1995).
ISO 9000, *21*(1):21–24 (1996).
Environmental Management Standards: ISO 14,000–21(5):167–169 (1996).

Additional readings include: Total Quality Management Applied to Industry—ISO 9000, Journal of Polymer Materials, 12(1), 1–9 (1996) and ISO 9000 (An Industrial Management Tool), Polymeric Materials Encyclopedia, CRC Press, Boca Raton, FL, J. Salamone, Editor, 3481–3484 (1996) all by Shawn M. Carraher and Charles Carraher.

Appendix K: Electronic Education—Web Sites

The amount of polymer-related information that appears on the World Wide Web is rapidly increasing. In general, polymer-related material can be obtained from "surfing" the "POLY.COM" and looking for specific topics. Following is one site developed with the cooperation of PolyEd for polymer education use.

www.psrc.usm.edu/macrog/index.html

Following are other sites that may be of use. The author welcomes additions; please send the site address and a short description to carraher@fau.edu. Due to ever-changing conditions, some of the following sites may have been renamed, moved, recreated, etc.

POLYED AND IPEC

www.polyed.org General site for PolyEd, the joint polymer education for the ACS Divisions of Polymer Chemistry and Polymeric Materials: Science and Engineering

www.ipeconline.org General site for IPEC, a joint society group that focuses on K–12 science education utilizing polymers as the connective material

BIOMACROMOLECULES

http://biotech.icmb.utexas.edu Contains a glossary of over 6700 terms related to biochemistry and biotechnology.

http://www/gdb.org/Dan/DOE/prim1.html Contains a primer on molecular genetics

http://web.indstate.edu/them/mwking/biomols.html Chemistry of nucleic acids http://moby.ucdavis.edu/HRM/Biochemistry/molecules.htm Molecular models of nucleic acids

http://moby.ucdavis.edu/HRM/Biochemistry/molecules.htm Models of secondary and tertiary protein structures

http://expasy.hcuge.ch/pub/Graphics/IMAGES/GIF Images of many proteins

http://www.rcsb.org/pdb Protein data bank

http://www.ncbi.nlmnih.gov/Entrez Protein data bank

http://www.ilstu.edu/depts/chemistry/che242/struct.html Structures of many saccharides

NANO MATERIALS

www.nano.gov NSF site for the National Nanotechnology Initiative

www.nano.org.uk/index.html Institute of Nanotechnology in Stirling, Scotland

http://cnst.rice.edu Center for Nanoscale Science and Technology at Rice University

http://ipt.arc.nasa.gov:80/index.html NASA Integrated Product Team on Devices and Nanotechnology

COATINGS

http://cage.rti.org/altern.htm Coating Alternative Guide, CAGE, information about different coatings

http://www.execpc.com/~rustoleu/coatings.htm Corrosion and protective coatings and paint resources

http://www.coatingsstech.org/ Federation of Societies for Coatings Technology, FSCT, home site

http://www.iscc.org/ Inter-Society Color Council-organization that promotes application of coatings and color

http://www.nace.org/ National Association of Corrosion Engineers, NACE, home Web site

http://www.paint.org/ National Paint and Coatings Association, NPCA, home Web site

http://www.paintcoatings, net/pcnmain.htm Paint coatings network giving directories, trade shows, product news, and related articles

http://www.pra.org.uk/index.htm Paint Research Association

http://www.jvhltd.com/paintwebs/default1.html Paint Web sites for suppliers

http://protectivecoatings.com Protective coatings worldwide information resource site

OTHERS

Most producers have individual sites that may contain useful, general, and specific product information.

www.pct.edu/prep Plastics Resources for Educators Plastics—emphasizes polymer processing http://russo.chem.1 su.edu/howto/HowTo.html Experimentation with polymer solutions

http://www.msi.com Computer modeling of polymers—synthetic and natural—go to “WebLab Viewer Lite”

www.teachingplastics.org General interest articles about specific polymer applications

http://www.asm-intl.org/index.htm ASM—materials engineering society

http://www.astm.org/ ASTM home site for technical standards

Appendix L: Introduction to the Stereogeometry of Polymers

The precise stereogeometry of molecules is important in determining the physical properties of a material, and it is critical in determining the biological properties of materials. Most synthetic and nonspecific natural polymers are a mix of stereoshapes with numerous stereocenters along the polymer chain. For polypropylene, every other backbone carbon is most likely a stereocenter. Even polyethylene has stereochemical sites wherever there is branching. The imprecise structures of most natural nonspecific polymers, such as the polyisoprenes and polysaccharides, have stereocenters at each branch. For stereospecific natural polymers, the entire geometry is critical to the proper behavior and activity of the material. Thus, stereogeometry is important and a brief review is in order.

We have two general types of isomers: constitutional isomers that have the same number and kind of atoms but connected in a different order, such as cis and tran arrangements, and stereoiosomers. We have two types of steroisomers: **diastereomers** that are not mirrior images of one another and **enantioimers** that are mirror image stereoisomers. Just as our hands cannot be superimposed on its mirror image, enantiomers are nonsuperimposible on one another. **Chiral** objects or sites are enantiomeric. In fact, the term "chiral" comes from the Greek word for hand, *kheir*. By comparison, an **achiral** object, like a simple nail, ball, basket, and white pocketless T-shirt, are all superimposible on their mirror image.

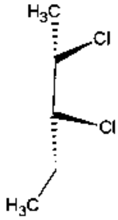
A collection containing only one enantiomeric form of a chiral molecule is referred to by several names including enantiopure, enantiomerically pure, or **optically pure**. A sample containing predominantly one enantiomer is called enantiomerically enriched or **enantioenriched**. A collection containing equal amounts of two enantiomeric forms of a chiral molecule is called a racemic mixture or **racemate**.

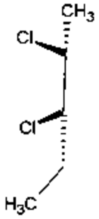
Unlike other stereoisomers, enantiomers have identical physical properties and consequently are difficult to separate. A process where enantiomers are separated is called **resolution**.

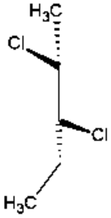
Diastereomers are non-enantiomeric isomers that result when more than one stereocenter is present in a molecule. The distinction between diasteromers and enantiomers is not always clear, but in general enantiomers have mirror images whereas diasteromers are not mirror images of one another. As such diastereomers have different physical properties, different boiling and melting points, solubilities, etc.

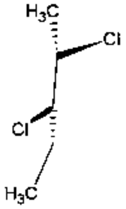
The total number of stereoisomers due to tetrahedral stereocenters does not exceed 2^n where n is the number of tetrahedral sterocenters. For a compound with two stereocenters $n = 2$ giving a total of 4 (maximum) steroisomers.

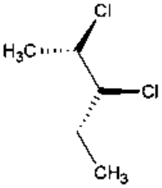
Following are four formula isomers drawn for a compound, 2,3-dichlorohexane, with two stereocenters, first drawn in the more conventional straight-chain manner and below in more conformationally-correct forms.

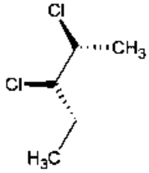

1

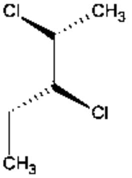

2

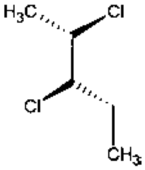

3


4


1


2


3

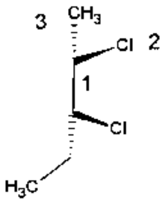

4

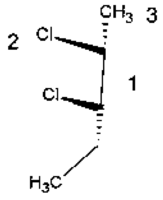
Structures (top and bottom) 1 and 3, as well as 2 and 4 and structures 1 and 4, are steroisomers, but they are not mirror images of one another—thus they are diastereomers. Structures (top and bottom) 1 and 2, as well as 3 and 4, are mirror images of one another, so they are a pair of compounds that are not superposable and are enantiomers to one another; that is, 1 and 2 are enantiomers and 3 and 4 are enantiomers.

Enantiomers can rotate the plane of polarized light. If the rotation is positive then the enantiomer is given the symbol "+" or "d" and is referred to as a *dextrorotary enantiomer*. Counter, if the compound causes the light to be rotated in the negative direction, the compound is given the symbol "−" or "l" and referred to as a *levorotatory enantiomer*. An equal mixture of two enantiomers, racemates, do not rotate plane-polarized light because the rotation due to one enantiomer is canceled by that of the other. There is no relationship between the absolute configuration, S or R, and the direction of rotation of plane-polarized light (+ or −).

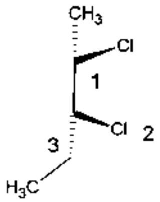
The absolute configuration about each stereogeometrical site is most often determined using the Cahn-Ingold-Prelog sequence rules. (These rules are found in most organic texts.) For tetrahedral carbons containing four different groups, we determine the group with the highest priority and assign it the number 1 and the group with the lowest priority the number 4. We then view the molecule having at its center the particular stereocarbon in question and arrange at the top the number 1 group. In doing so we can see if the direction of going from 1 → 2 → 3 is clockwise, R, or counterclockwise, S.

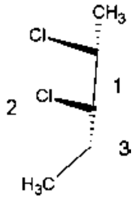
For structure 1 given above, looking only at the top stereocarbon, the arrangement is counterclockwise and so this particular site is designated as S. For structure 2 above, again looking only at the top stereocarbon, the arrangement is clockwise and so that carbon is designated as R.





Now looking at only the second carbon we have for the first compound a clockwise arrangement meaning it is R, and for the second compound the arrangement is clockwise so it is designated as S.

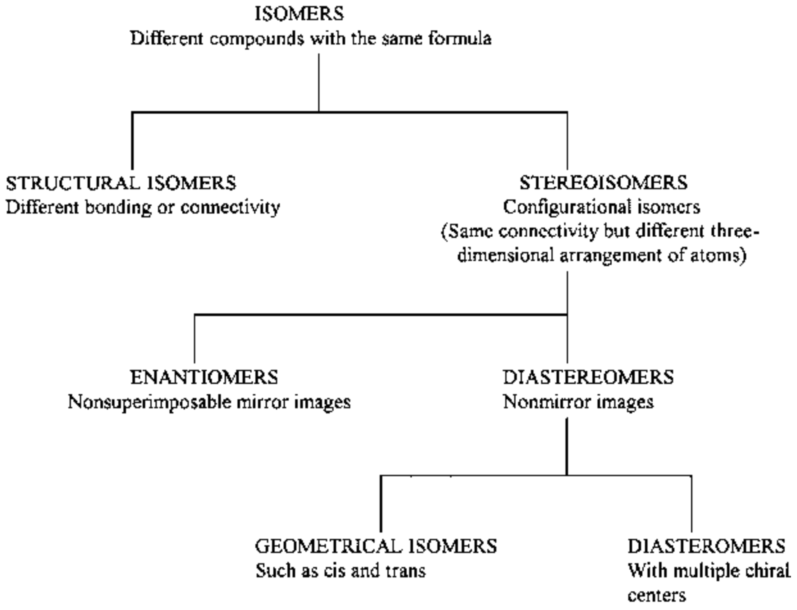




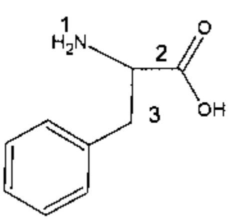
Thus the two stereocarbons in the first compound would be designated as S, R or 2S, 3R and compound two as R, S or 2R, 3S with the numbers indicating the position of the carbon atoms.

Often you will find that both the stereogeometry and rotation of light are given.

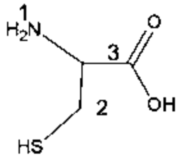
We can develop a concept map that describes the possible geometrical isomers as follows.



With the exception of alanine, all of the naturally occurring amino acids contain a chiral carbon adjacent to the amino acid grouping. All of these amino acids are of the l or L form meaning they rotate light in a negative direction. The rules governing specifying the absolute configuration are such that you can get both S and R forms of the amino acids. Thus L-phenylalanine is an S enantomer while L-cysteine is a R enantomer.



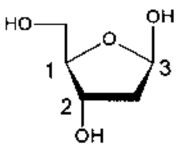
L-Phenylalanine or
S-Phenylalanine

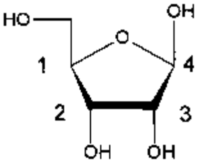


L-Cysteine or
R-Cysteine

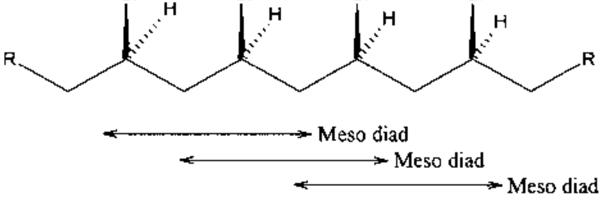
As noted above, with the exception of alanine, the addition of amino acids to form polypeptides allows for a large number of sterochemical isomers to be formed, even considering that all are of the L form. But nature does not allow for this diversity but rather selects only one configuration for a sequence to occur in its synthesis of structural-specific proteins such as those employed as enzymes. Even those employed for other activities such as muscle have a specific geochemistry. In fact, the cell produces only geometry-specific polypeptides.

Nature is also selective in the geometry involved in nucleic acid synthesis. This specificity involves both the base order and the particular sugar employed. For DNA the employed sugar is β-2-deoxy-D-ribose, deoxyribose (below left). Deoxyribose has three chiral centers but only one of them is employed in the synthesis of nucleic acids. Ribose, the sugar employed in the synthesis of RNA, has four geometric sites (below right).



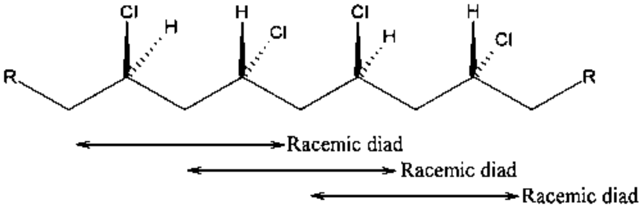


Now let us examine simple, only one site of substitution per repeat unit, vinyl polymers. When we look at a polymer chain we will focus only on combinations of diads or couples. For our discussion we will use segments of poly(vinyl chloride). The geometries can be divided into three general groups. One where the substitutes, or here chloride atoms, are all identical with adjoining neighbors compose meso diads. Polymers or sections of polymers that contain meso diads are referred to as isotactic.



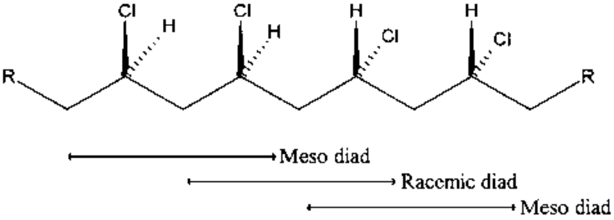
Isotactic Poly(vinyl chloride) Segment

The second grouping is where the geometry of the substitutes alternate on the chiral carbons that contain the chloride atoms. Here each diad is racemic. Such segments are referred to as syndiotactic segments.



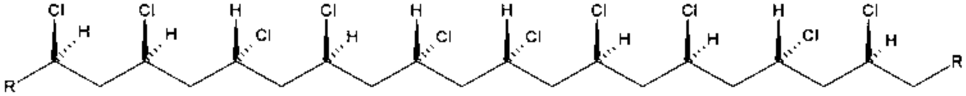
Syndiotactic Poly(vinyl chloride) Segment

The third group consists of mixtures of racemic and meso diads. These sequences are given the name atactic or "having nothing to do with tacticity or orderly arrangement."



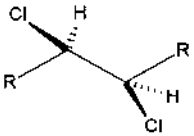
Atactic Poly(vinyl chloride) Segment

Stereoregular polymers are those that contain large segments of ordered segments. In truth, even stereoregular polymers contain some atactic regions. Even so, polymers that contain large fractions of ordered segments exhibit a greater tendency to form crystalline regions and to exhibit, relative to those containing large amounts of atactic regions, greater stress–strain values, greater resistance to gas flow, greater resistance to chemical degradation, lower solubilities, etc.

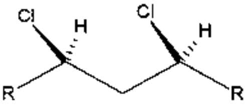


Atactic Poly(vinyl chloride) Segment

While the situation with respect to simple vinyl polymers is straight forward, the tacticity and geometrical arguments are more complicated for more complex polymers. Here we will only briefly consider this situation. Before we move to an illustration of this let us view two related chloride-containing materials, pictured below. We notice that by inserting a methylene between the two chlorine-containing carbons the description of the structure changes from being racemic to meso. Thus, there exists difficulty between the historical connection of meso with isotactic and racemic with syndiotactic.

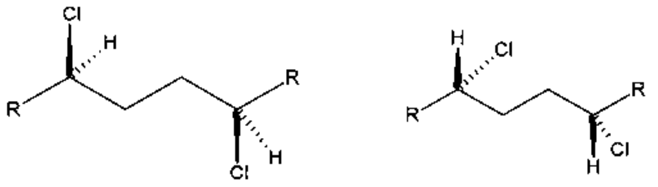


2R,3R-dichloro diad
Racemic



2R,4S-dichloro diad plus inserted methylene
Meso

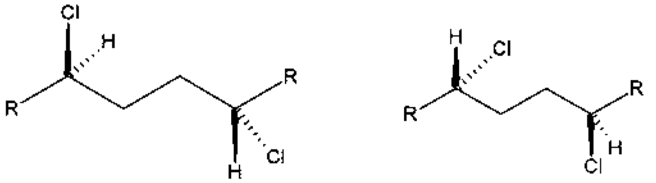
Let now move to the insertion of another methylene forming the following segments. The first set contains racemic pairs.



2R,5R dichloro segment 2S,5S-dichloro segment

Racemic Pairs

The second pair contains a meso pairing.

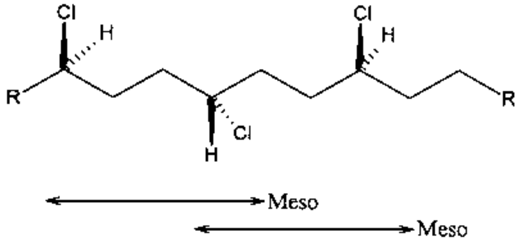


2R,5S-dichloro segment 2S,5R-dichloro segment

Meso Pair

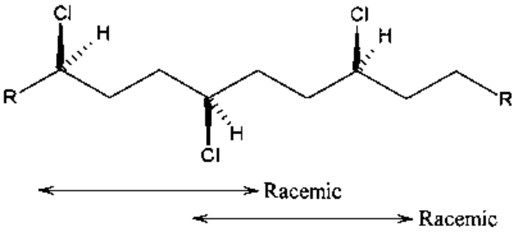
Now let us look at triad segments of our poly(vinyl chloride). The first one had meso adjacent units and is isotactic by definition of the meso, racemic argument but the adjacent chlorides are not on one side of the plane.

Isotactic



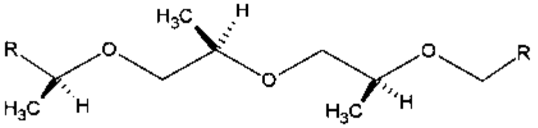
The second pair contains racemic diads and is syndiotactic by the meso, racemic argument but with the chloride atoms on the same side.

Syndiotactic

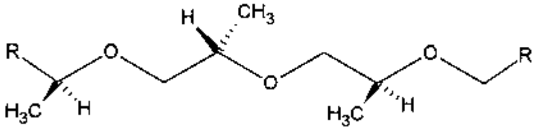


We will now consider segments of a polymer derived form the polymerization of propylene oxide. Here the simplest approach is to simply consider this an extension of the case immediately above except where the chloride atoms are substituted by methyl radicals and the next methylene is now an oxygen atom. Thus, we can make the same assignments based on the meso, racemic considerations.

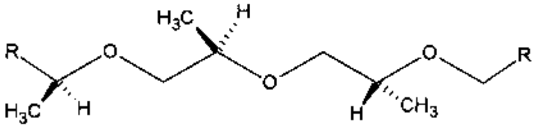
Syndiotactic



Isotactic

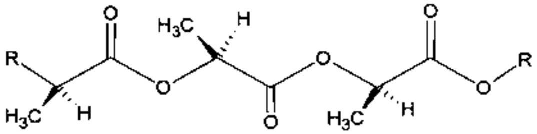


Atactic

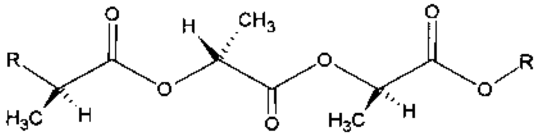


Similarity, we can make assignments for poly(lactic acid) except considering that the carbon next to the chloride-containing carbon has a methyl group, the next following methylene is now a carbonyl, and the next following methylene is an oxygen.

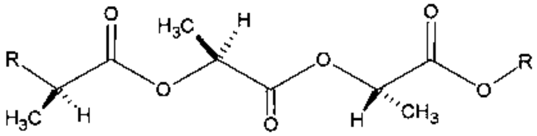
Syndiotactic



Isotactic



Atactic



Appendix M: Variability of Measurements

In research and product development and control there exists a variability in the particular value measured, such as percentage yield, melting point, tensile strength, and electrical conductivity as you repeat the measurement. Accuracy concerns how close to the true value your measured value is. Unless there is an established value for a particular material, the values you obtain may well contribute to the "true" value. Precision deals with the closeness of a group of measurement to one another.

Today, with spectral measurements where many measurements are made in a short time and those measurements undergo some type of statistical treatment, such as FT-IR, the statistical treatment of results has already been done. By comparison, many measurements are done more or less singularly. This is true for most physical testing measurements. Thus, to evaluate the tensile strength of a polycarbonate plastic sheeting sample, "dog-bones" of the shape given in Fig. 5.7 are cut from several sheets picked at random and tested under an appropriate set of conditions. These results are then statistically treated and the reported value given along with the variability. Following is a brief summary of one of the more statistically common treatments for such measurements.

The first step involves calculation of the average value, A, which is simply the summation of the individual values, A_i, divided by the number of measurements or observations, n. This is described mathematically as

$$A = (\Sigma\ A_i)/n)$$

where the summation is for all of the "n" values. The most common statistical measure of the variability, dispersion or scatter, is the standard deviation, s, defined as

$$s = [(\Sigma\ (A_i - A)^2)/n - 1]^{1/2}$$

The smaller the value of "s," the greater the precision of the measurements. Some testing calls for the precision to be within some "s" value, such as one "s," two "s," or three "s" values etc.