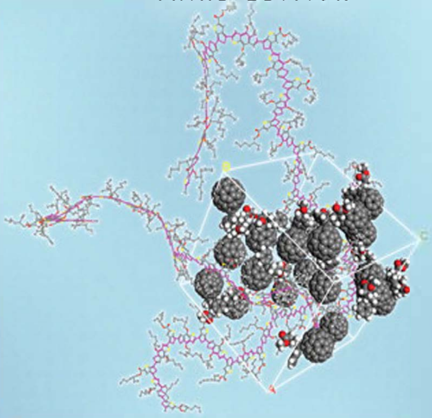
POLYMER SCIENCE & TECHNOLOGY

THIRD EDITION



JOEL R. FRIED

POLYMER SCIENCE AND TECHNOLOGY

Third Edition

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Joel R. Fried

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To my parents, who provided the opportunities, support, and guidance, and to my wife, Ava, and sons, Marc and Aaron, for their love, patience, and understanding.

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CONTENTS

PREFACE

Polymer Science and Technology, *Third Edition*, provides new and expanded coverage in a number of areas of contemporary interest in polymer science and technology. In particular, Chapter 2 on polymer synthesis provides new coverage of controlled radical polymerization, polymerization in ionic liquids, and the use of click chemistry and green chemistry. Chapter 4, on solid-state properties, includes added coverage on the use of microscopy and scattering methods in solid-state characterization. Chapter 7, on additives, blends, and composites, includes a new section on block copolymers as well as expanded coverage of nanocomposites including the use of buckyballs, carbon nanotubes, graphene, and POSS as nanofillers. Electrospinning has been added to the discussion of fiber-spinning operations in Chapter 8. Coverage of biomedical engineering and drug delivery, solar cells, and sensors has been included in Chapter 12, on polymers for advanced technologies. In addition, an entirely new chapter on correlations and simulation methods in polymer science has been added. This new chapter includes expanded treatment of group-correlation methods to predict polymer properties that has previously appeared in a number of earlier chapters in the second edition. Totally new is the inclusion of topological indices and artificial neural networks to predict properties. For the first time in an introductory polymer textbook, the fundamentals and applications of computational polymer science including the use of molecular dynamics and Monte Carlo methods are presented with a number of examples and exercise problems.

Joel R. Fried
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About the Cover Illustration

The cover illustration shows a molecular simulation of a blend of 37 wt% of functionalized C_{60} fullerene, PCBM, (space-filling representation) in an amorphous cell containing a thiophene copolymer. This system has been reported to provide attractive photovoltaic properties for polymeric photovoltaic cells. Simulations of polymeric systems are described in Chapter 13 of this third edition.

PREFACE TO THE SECOND EDITION

The second edition provides new and expanded coverage of important topics in polymer science and engineering and includes additional example calculations, homework problems, and bibliographic references. Additional topics in the treatment of polymer synthesis (Chapter 2) include metallocene catalysis, atom transfer radical and plasma polymerization, the genetic engineering of polymers, and the use of supercritical fluids as a polymerization medium. The new field of dynamic calorimetry (temperature-modulated DSC) has been added to the coverage of polymer viscoelasticity in Chapter 5. Chapter 6 provides expanded coverage of biodegradable polymers while Chapter 7 introduces the important new area of nanocomposites. Chapter 8 has been totally revised to include coverage of biopolymers and naturally occurring polymers including chitin and chitosan, while material on commodity thermoplastics has been moved to Chapter 9. In Chapter 10, new engineering and specialty thermoplastics including dendrimers, hyperbranched polymers, and amorphous Teflon are discussed. Examples of polymer-processing modeling have been expanded to include wire-coating operations in Chapter 11. The topic of drag reduction has been moved from Chapter 12 to the coverage of polymer rheology in Chapter 11, which now also includes an introduction to melt instabilities. The discussion of the electrical and optical applications of engineering polymers has been enhanced and new coverage of barrier polymers has been provided in Chapter 12.

Although the intended audience for this text is advanced undergraduates and graduate students in chemical engineering, the coverage of polymer science fundamentals (Chapters 1 through 5) is suitable for a semester course in a materials science or chemistry curriculum. Chapters 6 and 7 discuss more specialized topics such as polymer degradation, recycling, biopolymers, natural polymers, and fibers. Sections from this coverage can be included to supplement the basic coverage provided by the earlier chapters. Chapters 9 and 10 survey the principal categories of polymers—commodity thermoplastics, elastomers, thermosets, and engineering and specialty polymers. Material from these chapters may be included to supplement and reinforce the material presented in the chapters on fundamentals and provides a useful reference source for practicing scientists and engineers in the plastics industry. Polymer engineering principles including rheology and processing operations, introduced in Chapter 11, can be used as the basis of a short course on polymer engineering at the senior undergraduate and graduate level. Chapter 12 describes polymers used in areas of advanced technology including membrane separations, electrolytes for batteries and fuel cells, controlled drug release, nonlinear optical applications, and light-emitting diodes and displays. This coverage may be used as reference material for scientists and engineers and provides a basis for short courses in such areas as membrane science and technology and polymer physics.

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PREFACE TO THE FIRST EDITION

At least dozens of good introductory textbooks on polymer science and engineering are now available. Why then has yet another book been written? The decision was based on my belief that none of the available texts fully address the needs of students in chemical engineering. It is not that chemical engineers are a rare breed, but rather that they have special training in areas of thermodynamics and transport phenomena that is seldom challenged by texts designed primarily for students of chemistry or materials science. This has been a frustration of mine and of many of my students for the past 15 years during which I have taught an introductory course, *Polymer Technology*, to some 350 chemical engineering seniors. In response to this perceived need, I had written nine review articles that appeared in the SPE publication *Plastics Engineering* from 1982 to 1984. These served as a hard copy for my students to supplement their classroom notes but fell short of a complete solution.

In writing this text, it was my objective to first provide the basic building blocks of polymer science and engineering by coverage of fundamental polymer chemistry and materials topics given in Chapters 1 and 7. As a supplement to the traditional coverage of polymer thermodynamics, extensive discussion of phase equilibria, equation-of-state theories, and UNIFAC has been included in Chapter 3. Coverage of rheology, including the use of constitutive equations and the modeling of simple flow geometries, and the fundamentals of polymer processing operations are given in Chapter 11. Finally, I wanted to provide information on the exciting new materials now available and the emerging areas of technological growth that could motivate a new generation of scientists and engineers. For this reason, engineering and specialty polymers are surveyed in Chapter 10 and important new applications for polymers in separations (membrane separations), electronics (conducting polymer), biotechnology (controlled drug release), and other specialized areas of engineering are given in Chapter 12. In all, this has been an ambitious undertaking and I hope that I have succeeded in at least some of these goals.

Although the intended audience for this text is advanced undergraduates and graduate students in chemical engineering, the coverage of polymer science fundamentals (Chapters 1 through 7) should be suitable for a semester course in a materials science or chemistry curriculum. Chapters 8 through 10, intended as survey chapters of the principal categories of polymers—commodity thermoplastics and fibers, network polymers (elastomers and thermoplastics), and engineering and specialty polymers—may be included to supplement and reinforce the material presented in the chapters on fundamentals and should serve as a useful reference source for the practicing scientist or engineer in the plastics industry.

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ACKNOWLEDGMENTS

This text in its three editions could not have been completed without the help of many colleagues who provided figures and photographs and offered important advice during its preparation. I am particularly indebted to those colleagues who read all or sections of the first edition and offered very helpful advice. These included Professor James E. Mark of the University of Cincinnati, Professor Otto Vogl of the Polytechnic University, Professor Erdogan Kiran of Virginia Polytechnic Institute, Professor Paul Han of the University of Akron, Professor Donald R. Paul of the University of Texas at Austin, and Professor R. P. Danner of Penn State. Appreciation is also extended to many students and colleagues at the University of Cincinnati who have provided important comments over the past few years following the publication of the first edition. These include Professor Michael Greenfield of the University of Rhode Island, Professor Zvi Rigbi of the Technion, Professors U. Sundararaj and Philip Choi of the University of Alberta, Professor Jin Chuk Zjung of Pohang University of Science and Technology, and Professor Carlos Co of the University of Cincinnati. Appreciation is also extended to those who kindly assisted in reviewing portions of the third edition. These include Professors George Odian and Alan Lyons of the College of Staten Island (City University of New York), Dr. Donald Klosterman of the University of Dayton Research Institute, Professor Pengyu Ren of the University of Texas at Austin, and Professors Rufina Alamo, Daniel Hallinan, and Biwu Ma of Florida State University.

I also wish to thank those colleagues who kindly provided some key illustrations and photos. These include Dr. Roger Kambour of General Electric, Professor Bill Koros of the Georgia Institute of Technology, Professor Paul Philips of the University of Tennessee, Dr. Marty Matsuo of Nippon Zeon (Japan), Dr. Robert

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Dr. Joel R. Fried is professor and chair of the department of chemical and biomedical engineering at Florida State University. Previously, he was professor and the Wright Brothers Endowed Chair in Nanomaterials at the University of Dayton. He is also professor emeritus of chemical engineering and a fellow of the graduate school at the University of Cincinnati, where he directed the Polymer Research Center and served as head of the Department of Chemical Engineering over a career of 32 years. During this time he has advised more than sixty graduate and postdoctoral students, many of whom are currently in academic positions or have prominent positions in industry. Dr. Fried holds B.S. degrees in biology and chemical engineering, and an M.E. degree in chemical engineering from Rensselaer Polytechnic Institute. He also holds M.S. and Ph.D. degrees in polymer science and engineering from the University of Massachusetts, Amherst. Prior to his academic career, Dr. Fried was a senior engineer at the Monsanto Corporate R&D Center in St. Louis and an associate staff member of the GE Corporate R&D Center near Schenectady, New York. At Monsanto, he was a member of a fundamental research group developing hollow fiber membranes for industrial gas separations.

Dr. Fried is an instructor for the short course on Polymer Science and Technology at the National Meetings of the American Chemical Society and has been a course instructor on extrusion for the Plastics Institute of America. He is the author of more than one hundred and fifty publications, including many book chapters and monographs. Dr. Fried has served as editor of *Polymer Contents* and associate editor of *Computational and Theoretical Polymer Science*, has served on the editorial boards of *Polymer* and *Polymer Engineering*, and is a frequent consultant to industry. Current research interests focus on experimental studies and simulations of ion and small molecule transport through polymeric, biological, and biomimetic membranes for separations, energy, and sensor applications.

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CHAPTER 1

Introduction to Polymer Science

The word *polymer* is derived from the classical Greek words *poly* meaning "many" and *meres* meaning "parts." Simply stated, a polymer is a long-chain molecule that is composed of a large number of *repeating units* of identical structure. Certain polymers, such as proteins, cellulose, and silk, are found in nature, while many others, including polystyrene, polyethylene, and nylon, are produced only by synthetic routes. In some cases, naturally occurring polymers can also be produced synthetically. An important example is natural (Hevea) rubber, known as polyisoprene in its synthetic form.

Polymers that are capable of high extension under ambient conditions find important applications as elastomers. In addition to natural rubber, there are several important synthetic elastomers including nitrile and butyl rubber. Other polymers may have characteristics that enable their fabrication into long fibers suitable for textile applications. The synthetic fibers, principally nylon and polyester, are good substitutes for naturally occurring fibers such as cotton, wool, and silk.

In contrast to the usage of the word *polymer*, those commercial materials other than elastomers and fibers that are derived from synthetic polymers are called *plastics*. A typical commercial plastic resin may contain two or more polymers in addition to various additives and fillers. These are added to improve a particular property such as processability, thermal or environmental stability, or mechanical properties.

The birth of polymer science may be traced back to the mid-nineteenth century. In the 1830s, Charles Goodyear developed the vulcanization process that transformed the sticky latex of natural rubber into a useful elastomer for tire use. In 1847, Christian F. Schönbein reacted cellulose with nitric acid to produce cellulose nitrate. This was used in the 1860s as the first man-made thermoplastic, celluloid. In 1907, Leo Hendrik Baekeland [1] produced Bakelite (phenol−formaldehyde resin). Glyptal (unsaturated-polyester resin) was developed as a protective coating resin by General Electric in 1912.

By the 1930s, researchers at DuPont in the United States had produced a variety of new polymers including synthetic rubber and more “exotic” materials such as nylon and Teflon. By 1938, Dow had produced polystyrene in commercial scale for the first time and, in 1939, polyethylene (low-density) was made by scientists at ICI in England. Efforts to develop new polymeric materials, particularly synthetic rubber, were intensified during World War II when many naturally occurring materials such as Hevea rubber were in short supply. In the 1950s, Karl Ziegler and Giulio Natta independently developed a family of stereospecific transition-metal catalysts that made possible the commercialization of polypropylene as a major commodity plastic. The 1960s and 1970s witnessed the development of a number of high-performance engineering plastics polymers that could compete favorably with more traditional materials, such as metals, for automotive and aerospace applications. These included polycarbonate, poly(phenylene oxide), polysulfones, polyimides, aromatic polyamides such as Kevlar, and other high-temperature rigid-chain polymers. More recently, specialty polymers with electrically conducting, photoconducting, and liquid-crystalline properties have appeared for a variety of applications.

Today, polymeric materials are used in nearly all areas of daily life and their production and fabrication are major worldwide industries. The annual U.S. production of plastics and synthetic fibers in 2012 and the average annual change in production over the decade from 2002 to 2012 are given in Table 1-1. In 2012, the total U.S. production of synthetic fibers (principally non-cellulosic) and plastics was 2.81 and 34.1 million metric tons, respectively. Among plastics, the largest shares of the total production in 2012 were the polyethylenes, followed by polypropylene, poly(vinyl chloride) (PVC), and polystyrene. Although not specifically listed by the data given in Table 1-1, thermosetting resins (principally phenolic, urea, and melamine resins) typically represent around 10% of the total plastics production while synthetic rubbers, such as styrene–butadiene rubber (SBR) and polybutadiene, represent only about 6% of the total production in recent years.

Table 1-1 U.S. Production of Major Plastics and Synthetic Fibers in 2012[a]

	Thousands of Metric Tons[b]	Annual Change (%), 2002−12
PLASTICS		
Polyethylene		
Low-density	3123	-1.5
Linear low-density	8098	1.7
High-density	8046	1.1
Polypropylene	7405	-0.4
Polystyrene	2473	-2.0
PVC & copolymers	6944	0.0
SYNTHETIC FIBERS		
Non-cellulosic		
Nylon	562	-6.6
Olefin	1021	-3.1
Polyester	1203	-2.2
Cellulosic		
Acetate & rayon	27	-10.3

[a] Data reported in *Chemical and Engineering News*, July 1, 2013, p. 44.
[b] Conversion: 2,206.6 lbs per metric ton.

1.1 Classification of Polymers

Thousands of different polymers have been synthesized and more will be produced in the future. Conveniently, all polymers can be assigned to one of two groups based upon their processing characteristics or the type of polymerization mechanism. A more specific classification can be made on the basis of polymer structure. Such groupings are useful because they facilitate the discussion of properties.

1.1.1 Thermoplastics and Thermosets

All polymers can be divided into two major groups based on their thermal processing behavior. Those polymers that can be heat-softened in order to process into a desired form are called *thermoplastics*. Waste thermoplastics can be recovered and refabricated by application of heat and pressure. Polystyrene is an important example of a commercial thermoplastic. Other major examples are the polyolefins (e.g., polyethylene and polypropylene) and poly(vinyl chloride). In comparison, *thermosets* are polymers whose individual chains have been chemically linked by covalent bonds during polymerization or by subsequent chemical or thermal treatment during fabrication. Once formed, these crosslinked networks resist heat softening, mechanical deformation, and solvent attack, but cannot be thermally processed. Such properties make thermosets suitable materials for composites, coatings, and adhesive applications. Principal examples of thermosets include epoxy, phenol–formaldehyde resins, and unsaturated polyesters that are used in the manufacture of glass-reinforced composites such as Fiberglas (see Section 7.4).

1.1.2 Classification Based upon the Mechanism of Polymerization

In addition to classifying polymers on the basis of their processing characteristics, polymers may also be classified according to their mechanism of polymerization. An early scheme classifies polymers as either *addition* or *condensation*—a scheme attributed to Wallace Carothers [2], a pioneer of the polymer industry working at DuPont from 1928 until his untimely death in 1937. Polystyrene, which is polymerized by a sequential addition of styrene monomers (see Figure 1-1), is an example of an addition polymer. Most important addition polymers are polymerized from olefins and vinyl-based monomers. A few other polymers that are traditionally recognized as belonging to the addition class are polymerized not by addition to an ethylene double bond but through a ring-opening polymerization of a sterically strained cyclic monomer. An example is the ring-opening polymerization of trioxane to form polyoxymethylene (an engineering thermoplastic), which is illustrated in Figure 1-2. Table 1-2 lists the chemical structure of the repeating units and the commonly used nomenclature of some of the most important addition-type polymers derived from substituted ethylene.

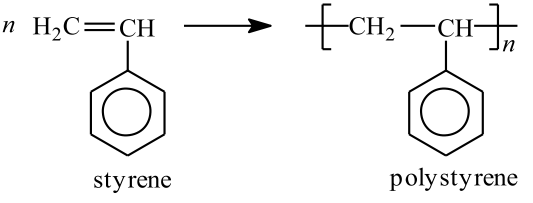


Figure 1-1 Polymerization of styrene.

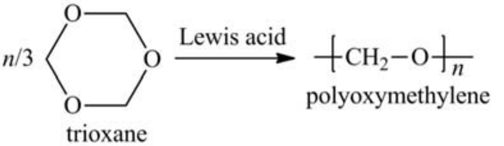
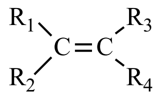
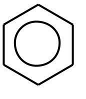
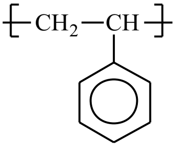


Figure 1-2 Ring-opening polymerization of trioxane.

Table 1-2 Examples of Some Important Addition Polymers Derived from Ethylene



Polymer	R_1	R_2	R_3	R_4	Repeating Unit
Polyethylene	H	H	H	H	$-[CH_2-CH_2]-$
Polypropylene	H	H	H	CH_3	$-[CH_2-CH(CH_3)]-$
Poly(vinyl chloride)	H	H	H	Cl	$-[CH_2-CH(Cl)]-$
Polyacrylonitrile	H	H	H	$C\equiv N$	$-[CH_2-CH(C\equiv N)]-$
Poly(vinyl acetate)	H	H	H	$-O-C(=O)-CH_3$	$-[CH_2-CH(O-C(=O)-CH_3)]-$
Polystyrene	H	H	H		
Poly(methyl methacrylate)	H	H	CH_3	$-C(=O)-O-CH_3$	$-[CH_2-C(CH_3)(C(=O)-O-CH_3)]-$
Poly(vinylidene chloride)	H	H	Cl	Cl	$-[CH_2-C(Cl)(Cl)]-$

Condensation polymers are obtained by the random reaction of two molecules. A molecule participating in a polycondensation reaction may be a monomer, oligomer, or higher-molecular-weight intermediate each having complementary functional end units, such as carboxylic acid or hydroxyl groups. Typically, condensation polymerizations occur by the liberation of a small molecule in the form of a gas, water, or salt. Any high-yield condensation reaction such as esterification or amidation can be used to obtain a high-molecular-weight polymer. An example of a condensation polymerization is the synthesis of nylon-6,6 by the polycondensation of adipic acid and hexamethylenediamine as illustrated in Figure 1-3A. This polymerization is accompanied by the liberation of two molecules of water for each repeating unit. Another important example of a polycondensation, illustrated in Figure 1-3B, is the preparation of polycarbonate from bisphenol-A and phosgene. In this case, two molecules of hydrogen chloride are formed for each repeating unit. Alternatively, if the *sodium salt* of bisphenol-A was used in the polymerization, the by-product of the condensation would be sodium chloride rather than hydrogen chloride. The salt will precipitate out of the organic solvent used for the polymerization and, therefore, can be easily and safely removed. Some other examples of condensation polymers are given in Table 1-3.

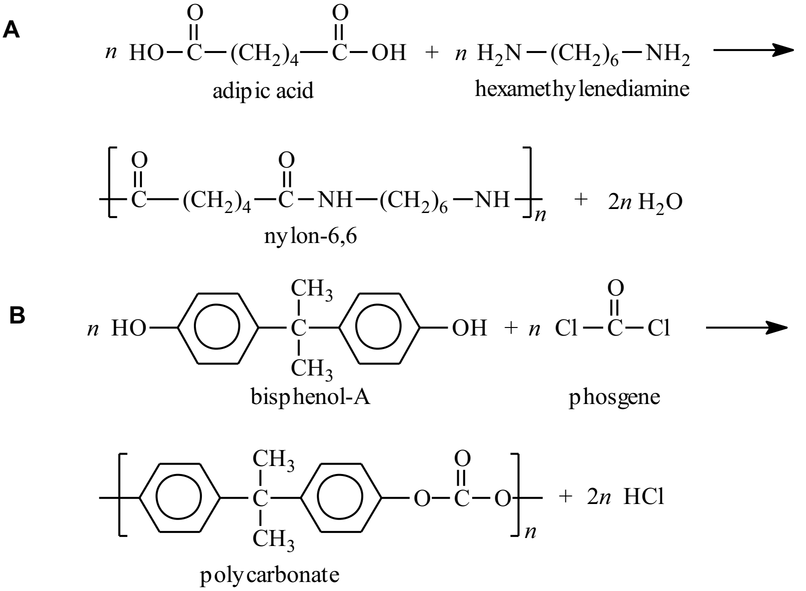
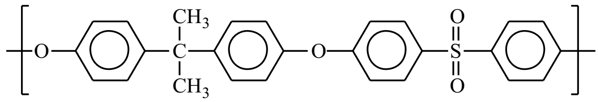
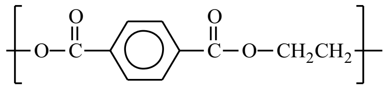
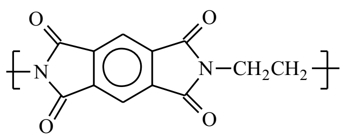


Figure 1-3 Two examples of a condensation polymerization. **A**. Polyamidation of nylon-6,6. **B**. Polymerization of bisphenol-A polycarbonate.

Table 1-3 Examples of Some Condensation Thermoplastics

Polymer	Repeating Unit
Polysulfone	
Poly(ethylene terephthalate)	
Poly(hexamethylene sebacamide) (nylon-6,10)	$\left[NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}} \right]$
Poly(ethylene pyromellitimide)	

More recently, another classification scheme based on polymerization kinetics has been adopted over the more traditional addition and condensation categories. According to this scheme, all polymerization mechanisms are classified as either *step* growth or *chain* growth. Most condensation polymers are step growth, while most addition polymers are chain growth; however, a number of important exceptions exist, as will be discussed in Chapter 2. During chain-growth polymerization, high-molecular-weight polymer is formed early during the polymerization, and the polymerization yield, or the percent of monomer converted to polymer, gradually increases with time. In step-growth polymerization, high-molecular-weight polymer is formed only near the end of the polymerization (i.e., at high monomer conversion, typically >98%). Details of the mechanisms for chain-growth and step-growth polymerizations are discussed in Chapter 2.

1.1.3 Classification Based upon Polymer Structure

In addition to classification based upon processing and polymerization characteristics, polymers may also be grouped based upon the chemical structure of their backbones. For example, polymers having all carbon atoms along their backbone are important examples of *homochain* polymers. They may be further classified depending upon whether there are single or double bonds along their backbone. Carbon-chain polymers with only single bonds along the backbone are called *polyalkylenes* (or polyalkylidenes). Examples of polyalkylenes include polystyrene, the polyolefins (e.g., polyethylene and polypropylene), and poly(vinyl chloride). Carbon-chain polymers with double bonds along the chain such as the diene elastomers—polyisoprene and polybutadiene—are called *polyalkenylenes*. Another example of a polyalkenylene is polyacetylene, an electrically conducting polymer (see Section 10.2.7).

Heterochain polymers that contain more than one atom type in their backbone are grouped according to the types of atoms and chemical groups (e.g., carbonyl, amide, or ester) located along the backbone. The most important classes of organic heterochain polymers are listed in Table 1-4. Another important class of heterochain polymers includes polysiloxanes. These have a –Si–O– backbone with methyl or other substituent groups attached to silicon.

Table 1-4 Backbone Structures of Some Important Organic Heterochain Polymers

Polymer Classification	Backbone Group
Carbon–Oxygen Polymers	
Polyethers	$-\text{C}-\text{O}-$
Polyesters of carboxylic acids	$-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{O}-$
Polyanhydrides of carboxylic acids	$-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-$
Polycarbonates	$-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{O}-$
Carbon–Sulfur Polymers	
Polythioethers	$-\text{S}-\text{C}-$
Polysulfones	$-\underset{\underset{\text{O}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}-\text{C}-$
Carbon–Nitrogen Polymers	
Polyamines	$-\text{C}-\text{N}-$
Polyimines	$-\text{C}=\text{N}-$
Polyamides	$-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{N}-$
Polyureas	$-\text{N}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{N}-$

1.2 Polymer Structure

The properties of polymers are strongly influenced by details of the chain structure. These details include the overall chemical composition and the sequence of monomer units in the case of copolymers, the stereochemistry or tacticity of the chain, and the geometric isomerization in the case of diene-type polymers for which several synthesis routes may be possible.

1.2.1 Copolymers

Often, it is possible to obtain polymers with new and desirable properties by linking two or three different monomers or repeating units during the polymerization. Polymers with two different repeating units in their chains are called *copolymers*. When there are three chemically different repeating units, the resulting polymer is termed a *terpolymer*. Commercially, the most important copolymers are derived from vinyl monomers such as styrene, ethylene, acrylonitrile, and vinyl chloride.

The exact sequence of monomer units along the chain can vary widely depending upon the relative reactivities of each monomer during the copolymerization process. At the extremes, monomer placement may be totally random or may be perfectly alternating, as illustrated in Figure 1-4. The actual sequence of monomer units is determined by the relative reactivities of the monomers as will be described for free-radical copolymerization in Section 2.2.1. Under special circumstances, it is possible to prepare copolymers that contain a long block of one monomer (A) followed by a block of the other monomer (B). These are called AB-block copolymers. ABA-triblock copolymers have a central B block joined by A blocks at both ends. A commercially important ABA-triblock copolymer is polystyrene-*block*-polybutadiene-*block*-polystyrene or SBS, a thermoplastic elastomer (see Section 9.2.3). In addition to these copolymer structures, *graft* copolymers can be prepared by polymerizing a monomer in the presence of a fully formed polymer of another monomer. Graft copolymers are important as elastomers (e.g., SBR) and high-impact polymers (e.g., high-impact polystyrene and acrylontrile−butadiene−styrene or ABS resin).

1.2.2 Tacticity

In addition to the type, number, and sequential arrangement of monomers along the chain, the *spatial* arrangement of substituent groups is also important in determining properties. The possible steric configurations of an asymmetric vinyl-polymer chain can be best represented by drawing the chain in its extended-chain or planar zigzag conformation, as illustrated in Figure 1-5. A *conformation* describes the *geometrical* arrangement of atoms in the polymer chain while *configuration* denotes the *stereochemical* arrangement of atoms. Unlike the conformation, the configuration of a polymer chain cannot be altered without breaking chemical bonds. For long, flexible polymer chains, the total number of conformations is nearly infinite. The extended-chain conformation for vinyl polymers is often the lowest-energy conformation.

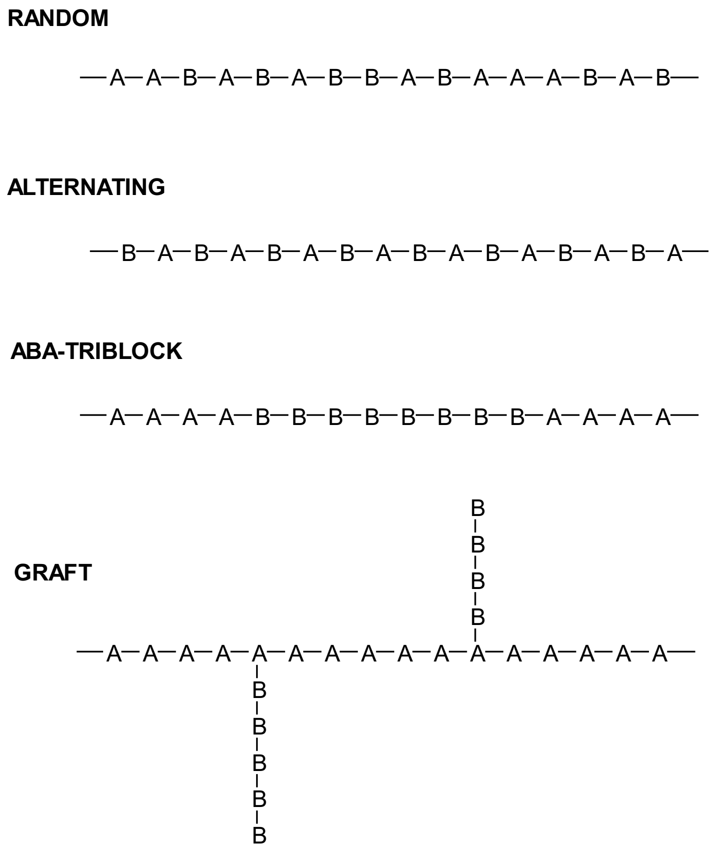


Figure 1-4 Possible structures of copolymers containing A and B repeating units.

As illustrated in Figure 1-5, several different placements of the asymmetric substituent group, R, are possible. As examples, a substituent group may be a methyl group as in polypropylene, a chlorine atom as in poly(vinyl chloride), or a phenyl ring as in polystyrene. In one configuration, all the R groups may lie on the same side of the plane formed by the extended-chain backbone. Such polymers are termed *isotactic*. If the substituent groups regularly alternate from one side of the plane to the other, the polymer is termed *syndiotactic*. Polymers with no preferred placement are *atactic*. More complicated arrangements of substituent groups are possible in the case of 1,2-disubstituted polymers; however, these are commercially less important and will not be discussed here.

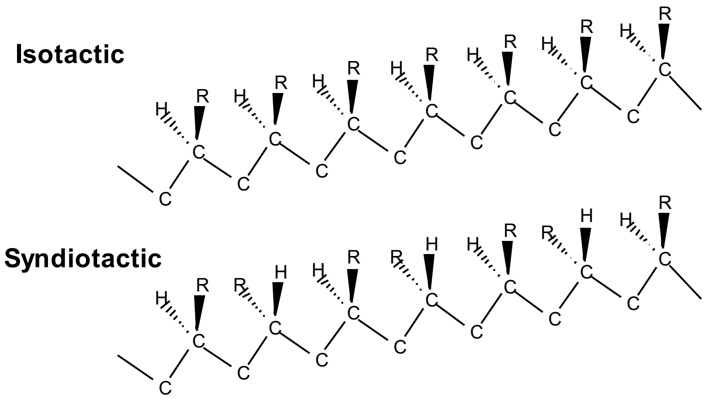


Figure 1-5 Two forms of stereochemical configuration of an extended-chain vinyl polymer having a substituent group R other than hydrogen.

In general, tactic polymers (i.e., isotactic or syndiotactic) are partially crystalline, while atactic polymers are *amorphous* indicating the absence of all crystalline order. In addition to crystallinity, other polymer properties, such as thermal and mechanical behavior, can be significantly affected by the tacticity of the polymer as later examples will show. Whether a specific polymer will be atactic, isotactic, or syndiotactic depends upon the specific conditions of the polymerization, such as the temperature and choice of solvent, as will be discussed in Chapter 2. Commercial polypropylene is an important example of an isotactic polymer. Atactic and syndiotactic forms of this polymer can also be prepared by controlling the polymerization conditions. Atactic polypropylene is an amorphous, tacky polymer with no commercial importance. Commercial poly(vinyl chloride) (PVC) is an example of a polymer with imperfect tactic structure. Although the overall structure of commercial-grade PVC can be reasonably characterized as atactic, there are populations of repeating units whose sequences are highly syndiotactic and that impart a small degree of crystallinity to the commercial resin. Space-filling (CPK) models of a short PVC chain having eight repeating units with all isotactic and all syndiotactic placements of the chlorine atoms are shown in Figure 1-6. Using special polymerization methods, PVC with very high syndiotactic or isotactic content can be made (see Section 9.1.2); however, these crystalline stereoisomers of PVC offer no important advantage compared to the commercial plastic. In the case of polystyrene, syndiotactic polystyrene has been obtained by metallocene polymerization (see Section 2.2.3) and is being studied as an alternative to the atactic "crystal grade" plastic for some applications (see Section 9.1.2).

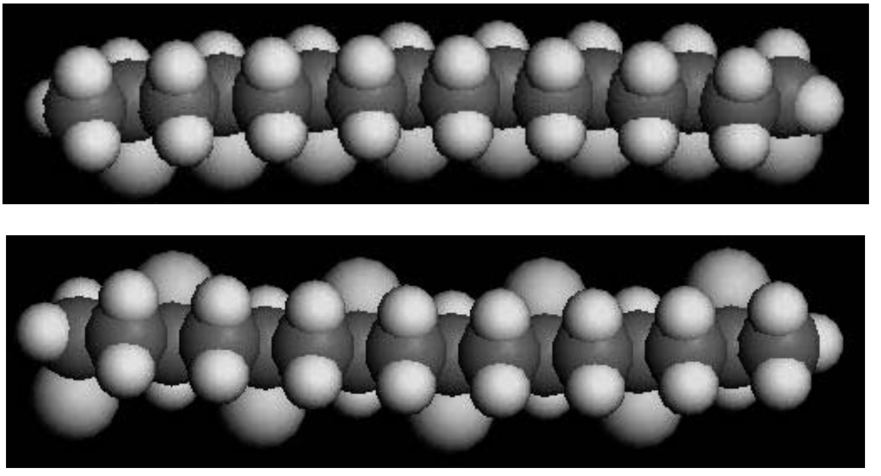


Figure 1-6 Views of computer-generated chains of eight repeating units (octamer) of vinyl chloride with *isotactic* (top) and *syndiotactic* (bottom) structures are shown. These views are looking down on the chain with the chlorine atoms (large spheres) sitting at the base of each chain. Small light gray spheres represent hydrogen atoms while larger dark gray spheres identify the carbon atoms.

1.2.3 Geometric Isomerism

When there are unsaturated sites along a polymer chain, several different isomeric forms are possible. As illustrated by Figure 1-7, 1,3-butadiene (structure A) can be polymerized to give 1,2-poly(1,3-butadiene) (B) or either of two *geometric isomers* of 1,4-poly(1,3-butadiene) (C and D). The numbers preceding the *poly* prefix designate the first and last carbon atoms of the backbone repeating unit. 1,2-poly(1,3-butadiene) has a vinyl-type structure, where the substituent group (ethene) contains an unsaturated site; therefore, this geometric isomer can be atactic, syndiotactic, or isotactic. In the case of the commercially more important 1,4-poly(1,3-butadiene), all four carbons in the repeating unit lie along the chain. Carbons 1 and 4 can lie either on the same side of the central double bond (i.e., *cis*-configuration, C) or on the opposite side (i.e., *trans*-configuration, D). The structure of polybutadiene used in SBR rubber (i.e., a copolymer of styrene and butadiene) is principally the *trans*-1,4 isomer with some *cis*-1,4- and 1,2-poly(1,3-butadiene) content.

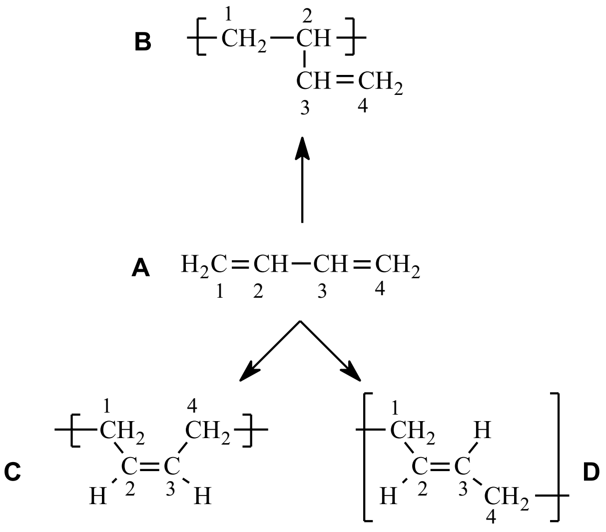


Figure 1-7 Alternative pathways for the polymerization of 1,3-butadiene (**A**) to give 1,2-poly(1,3-butadiene) (**B**), *cis*-1,4-poly(1,3-butadiene) (**C**), or *trans*-1,4-poly(1,3-butadiene) (**D**).

1.2.4 Nomenclature

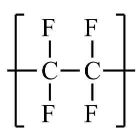
As the preceding examples illustrate, a very large number of different polymer structures are possible. In order to identify these as unambiguously as possible, it is important to have a robust nomenclature system. As is already evident, simple vinyl polymers are designated by attaching the prefix *poly* to the monomer name (e.g., polystyrene, polyethylene, and polypropylene); however, when the monomer name consists of more than one word or is preceded by a letter or number, the monomer is enclosed by parentheses preceded by the prefix *poly*. For example, the polymer obtained from the polymerization of 4-chlorostyrene is poly(4-chlorostyrene) and that from vinyl acetate is poly(vinyl acetate). Tacticity may be noted by prefixing the letter *i* (isotactic) or *s* (syndiotactic) before *poly* as in *i*-polystyrene. Geometric and structural isomers may be indicated by using the appropriate prefixes, *cis* or *trans* and 1,2- or 1,4-, before *poly*, as in *trans*-1,4-poly(1,3-butadiene).

Nomenclature rules for non-vinyl polymers such as condensation polymers are generally more complicated than for vinyl monomers. These polymers are usually named according to the initial monomer or the functional group of the repeating unit. For example, the most important commercial nylon, commonly called nylon-6,6 (66 or 6/6), is more descriptively called poly(hexamethylene adipamide) denoting the polyamidation of hexamethylenediamine (alternatively called 1,6-hexane diamine) with adipic acid (see Figure 1-3A). Similarly, the aliphatic nylon obtained by the polyamidation of hexamethylenediamine with a 10-carbon dicarboxylic acid, sebacic acid, is nylon-6,10 or poly(hexamethylene sebacamide) (see structure shown in Table 1-3).

In some cases, "common" names are used almost exclusively in place of the more chemically correct nomenclature. For example, the polycondensation of phosgene and bisphenol-A—the common name for 2,2-bis(4-hydroxyphenyl)propane—produces the engineering thermoplastic, polycarbonate (Figure 1-3B). Often, the prefix bisphenol-A is placed before polycarbonate to distinguish it from other polycarbonates that can be polymerized by using bisphenol monomers other than bisphenol-A, such as tetramethylbisphenol-A.

For many years, the International Union of Pure and Applied Chemistry (IUPAC) and the American Chemical Society (ACS) have developed a detailed, structure-based nomenclature for polymers. In addition, an industrial standard (ASTM D-4000) for specifying specific commercial grades of reinforced and nonreinforced plastics has been offered by the American Society for Testing and Materials (ASTM).

The IUPAC structure-based rules for naming organic, inorganic, and coordination polymers have been compiled in several publications [3–8]. Although such nomenclature provides an unambiguous method for identifying the large number of known polymers (more than 60,000 polymers are listed in the Chemical Abstracts Service (CAS) Chemical Registry System, semi-systematic or trivial names and sometimes even principal trade names (much to the displeasure of the manufacturer) continue to be used in place of the sometimes unwieldy IUPAC names. As examples, the IUPAC name for polystyrene is poly(1-phenylethylene) and that for polytetrafluoroethylene



is poly(difluoromethylene)—a polymer more typically recognized by its trademark, Teflon. The IUPAC name for the polycarbonate of bisphenol-A mentioned earlier is poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene).

For convenience, several societies have developed a very useful set of two-, three-, and four-letter abbreviations for the names of many common thermoplastics, thermosets, fibers, elastomers, and additives. Sometimes, abbreviations adopted by different societies for the same polymer may vary, but there is widespread agreement on the abbreviations for a large number of important polymers. These abbreviations are convenient and widely used. As examples, PS is generally recognized as the abbreviation for polystyrene, PVC for poly(vinyl chloride), PMMA for poly(methyl methacrylate), PTFE for polytetrafluoroethylene, and PC for bisphenol-A polycarbonate. A listing of commonly accepted abbreviations is given in Appendix A at the end of this book.

Following IUPAC recommendations, copolymers are named by incorporating an italicized connective term between the names of monomers contained within parentheses or brackets or between two or more polymer names. The connective term designates the type of copolymer as indicated for six important classes of copolymers in Table 1-5.

Table 1-5 Scheme for Naming Copolymers

Type	Connective	Example
Unspecified	-*co*-	Poly[styrene-*co*-(methyl methacrylate)]
Statistical[a]	-*stat*-	Poly(styrene-*stat*-butadiene)
Random	-*ran*-	Poly[ethylene-*ran*-(vinyl acetate)]
Alternating	-*alt*-	Poly[styrene-*alt*-(maleic anhydride)]
Block	-*block*-	Polystyrene-*block*-polybutadiene
Graft	-*graft*-	Polybutadiene-*graft*-polystyrene

[a] A statistical polymer is one in which the sequential distribution of the monomeric units obeys statistical laws. In the case of a random copolymer, the probability of finding a given monomeric unit at any site in the chain is independent of the neighboring units in that position.

1.3 Molecular Weight

1.3.1 Molecular-Weight Distribution

A typical synthetic polymer sample contains chains with a wide distribution of chain lengths. This distribution is seldom symmetric and contains some molecules of very high molecular weight. A representative distribution is illustrated in Figure 1-8. The exact breadth of the molecular-weight distribution depends upon the specific conditions of polymerization, as will be described in Chapter 2. For example, the polymerization of some olefins can result in molecular-weight distributions that are extremely broad. In other polymerizations, polymers with very narrow molecular-weight distributions can be obtained. As will be shown in subsequent chapters, many polymer properties, such as melt viscosity, are dependent on molecular weight and molecular-weight distribution. Therefore, it is useful to define molecular-weight averages associated with a given molecular-weight distribution as detailed in this section.

Figure 1-8 A representation of a continuous distribution of molecular weights shown as a plot of the number of moles of chains, *N*, having molecular weight *M*, against *M*.

1.3.2 Molecular-Weight Averages

For a discrete distribution of molecular weights, an average molecular weight, $\bar{M}$, may be defined as

$$\boxed{\bar{M} = \frac{\sum_i N_i M_i^{\alpha}}{\sum_i N_i M_i^{\alpha-1}}} \tag{1.1}$$

where N_i indicates the number of moles of molecules having a molecular weight of M_i and the parameter α is a weighting factor that defines a particular average of the molecular-weight distribution. The weight, W_i, of molecules with molecular weight M_i is then

$$W_i = N_i M_i \,. \tag{1.2}$$

Molecular weights that are important in determining polymer properties are the number-average, $\bar{M}_{\mathrm{n}}$ ($\alpha = 1$), the weight-average, $\bar{M}_{\mathrm{w}}$ ($\alpha = 2$), and the *z*-average, $\bar{M}_{\mathrm{z}}$ ($\alpha = 3$), molecular weights.

Since the molecular-weight distribution of commercial polymers is normally a continuous function, molecular-weight averages can be determined by integration if the appropriate mathematical form of the molecular-weight distribution (i.e., *N* as a function of *M* as illustrated in Figure 1-8) is known or can be approximated. Such mathematical forms include theoretical distribution functions derived on the basis of a statistical consideration of an idealized polymerization, such as the Flory, Schultz, Tung, and Pearson distributions [9] (see Example 1.1 and Problem 1.3) and standard probability functions, such as the Poisson and logarithmic-normal distributions.

It follows from eq. (1.1) that the *number-average molecular weight* for a discrete distribution of molecular weights is given as

$$\bar{M}_{\mathrm{n}} = \frac{\sum_{i=1}^{N} N_i M_i}{\sum_{i=1}^{N} N_i} = \frac{\sum_{i=1}^{N} W_i}{\sum_{i=1}^{N} \left(W_i / M_i\right)} \tag{1.3}$$

where N is the total number of molecular-weight species in the distribution. The expression for the number-average molecular weight of a continuous distribution function is

$$\bar{M}_{\mathrm{n}} = \frac{\int_0^{\infty} NM\,dM}{\int_0^{\infty} N\,dM}. \tag{1.4}$$

The respective relationships for the *weight-average molecular weight* of a discrete and a continuous distribution are given by

$$\bar{M}_{\mathrm{w}} = \frac{\sum_{i=1}^{N} N_i M_i^2}{\sum_{i=1}^{N} N_i M_i} = \frac{\sum_{i=1}^{N} W_i M_i}{\sum_{i=1}^{N} W_i} \tag{1.5}$$

and

$$\bar{M}_{\mathrm{w}} = \frac{\int_0^{\infty} NM^2 dM}{\int_0^{\infty} NMdM}. \tag{1.6}$$

In the case of high-molecular-weight polymers, the number-average molecular weight is directly determined by membrane osmometry, while the weight-average molecular weight is determined by light-scattering and other scattering techniques as described in Chapter 3. As mentioned earlier, a higher moment of the molecular-weight distribution is the *z*-average molecular weight $\left(\bar{M}_z\right)$ where $\alpha = 3$. As discussed later in Chapter 3 (Section 3.3.3), a viscosity-average molecular weight, $\bar{M}_{\mathrm{v}}$, can be obtained from dilute-solution viscometry. The viscosity-average molecular weight falls between $\bar{M}_{\mathrm{n}}$ and $\bar{M}_{\mathrm{w}}$ depending upon whether the solvent is a good or poor solvent for the polymer. In the case of a good solvent, $\bar{M}_{\mathrm{v}} = \bar{M}_{\mathrm{w}}$.

A measure of the breadth of the molecular-weight distribution is given by the ratios of molecular-weight averages. For this purpose, the most commonly used ratio is $\bar{M}_{\mathrm{w}} / \bar{M}_{\mathrm{n}}$, called the *polydispersity index* or PDI [9]. Recent IUPAC recommendations suggest the use of the term *molar-mass dispersity*, D_{M}, for this ratio

[10]. The PDIs of commercial polymers vary widely. For example, commercial grades of polystyrene with a $\bar{M}_n$ of over 100,000 have polydispersity indices between 2 and 5, while polyethylene synthesized in the presence of a stereospecific catalyst may have a PDI as high as 30.* In contrast, the PDI of some vinyl polymers prepared by "living" polymerization (see Chapter 2) can be as low as 1.06. Such polymers with nearly *monodisperse* molecular-weight distributions are useful as molecular-weight standards for the determination of molecular weights and molecular-weight distributions of commercial polymers (see Section 3.3.4).

Example 1.1

A polydisperse sample of polystyrene is prepared by mixing three *monodisperse* samples in the following proportions:

1 g	10,000 molecular weight
2 g	50,000 molecular weight
2 g	100,000 molecular weight

Using this information, calculate the number-average molecular weight, weight-average molecular weight, and PDI of the mixture.

Solution

Using eqs. (1.3) and (1.5), we obtain the following:

$$\bar{M}_n = \frac{\sum_{i=1}^{3} N_i M_i}{\sum_{i=1}^{3} N_i} = \frac{\sum_{i=1}^{3} W_i}{\sum_{i=1}^{3} \left(W_i / M_i\right)} = \frac{1+2+2}{\frac{1}{10,000}+\frac{2}{50,000}+\frac{2}{100,000}} = 31,250$$

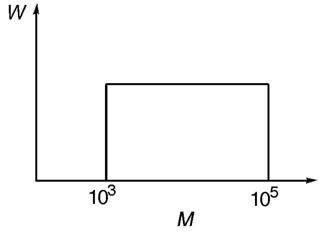
$$\bar{M}_w = \frac{\sum_{i=1}^{3} N_i M_i^2}{\sum_{i=1}^{3} N_i M_i} = \frac{\sum_{i=1}^{3} W_i M_i}{\sum_{i=1}^{3} W_i} = \frac{10,000+2\left(50,000\right)+2\left(100,000\right)}{5} = 62,000$$

$$\text{PDI} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{62,000}{31,250} = 1.98$$

* New metallocene-catalyzed polymerizations can produce polyolefins and other polymers with very controlled structures and narrow-molecular-weight distributions (see Section 2.2.3).

Example 1.2

A polymer is fractionated and is found to have the continuous molecular-weight distribution shown below as a plot of the weight, W, of molecules having molecular weight, M, versus M. Given this molecular-weight distribution, calculate $\bar{M}_n$ and $\bar{M}_w$.



Solution

Using eqs. (1.4) and (1.6), we obtain the following:

$$\bar{M}_n = \frac{\int_{10^3}^{10^5} dM}{\int_{10^3}^{10^5} (1/M)\, dM} = \frac{10^5 - 10^3}{\ln\left(10^5/10^3\right)} = 21{,}498$$

$$\bar{M}_w = \frac{\int_{10^3}^{10^5} M\,dM}{\int_{10^3}^{10^5} dM} = \frac{\left(M^2/2\right)_{10^3}^{10^5}}{9.9\times 10^4} = 50{,}500$$

Example 1.3

The single-parameter Flory distribution is given as

$$W(X) = X(\ln p)^2\, p^X$$

where X is the degree of polymerization and p is the fractional monomer conversion in a step-growth polymerization. Using this equation, obtain expressions for the number-average and weight-average *degrees of polymerization** in terms of X and p.†

Solution

Using the following geometric series:

* Note that $\bar{M}_n = M_o \bar{X}_n$ and $\bar{M}_w = M_o \bar{X}_w$ where M_o is the molecular weight of one repeat unit.

† For a comprehensive treatment of molecular-weight distributions, see Chapter VIII in Paul J. Flory's *Principles of Polymer Chemistry*.

$$\sum_{X=1}^{\infty} p^{X-1} = 1 + p + p^2 + p^3 + \cdots = \frac{1}{1-p} \qquad (-1 < p < 1)$$

$$A = \sum_{X=1}^{\infty} X p^{X-1} = 1 + 2p + 3p^2 + \cdots = \frac{1}{1-p}$$

$$B = \sum_{X=1}^{\infty} X^2 p^{X-1} = 1 + 2^2 p + 3^2 p^2 + \cdots$$

Since it can be shown that $B(1-p) = A(1+p)$, it follows that

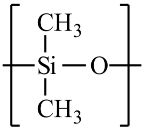
$B = \dfrac{1+p}{1-p}$, and then

$$\bar{X}_n = \frac{\sum_{X=1}^{\infty} W(X)}{\sum_{X=1}^{\infty} W(X)/X} = \frac{(\ln p)^2 p \sum_{X=1}^{\infty} X p^{X-1}}{(\ln p)^2 p \sum_{X=1}^{\infty} p^{X-1}} = \frac{\sum_{X=1}^{\infty} X p^{X-1}}{\sum_{X=1}^{\infty} p^{X-1}} = \frac{1/(1-p)^2}{1/(1-p)} = \frac{1}{1-p}$$

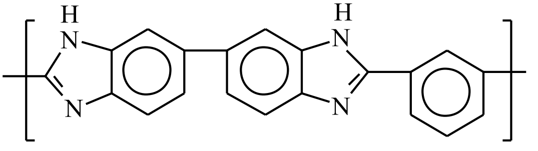
$$\bar{X}_w = \frac{\sum_{0}^{\infty} X W(X)}{\sum_{0}^{\infty} W(X)} = \frac{(\ln p)^2 p \sum_{X=1}^{\infty} X^2 p^{X-1}}{(\ln p)^2 p \sum_{X=1}^{\infty} X p^{X-1}} = \frac{\sum_{X=1}^{\infty} X^2 p^{X-1}}{\sum_{X=1}^{\infty} X p^{X-1}} = \frac{(1+p)/(1-p)^3}{1/(1-p)^2} = \frac{1+p}{1-p}$$

1.4 Chemical Structure and Thermal Transitions

As the previous discussion has shown, many important synthetic polymers such as polystyrene and poly(methyl methacrylate) consist of long, flexible chains of very high molecular weight. In many cases, individual chains are randomly coiled and intertwined with no molecular order or structure. Such a physical state is termed *amorphous*. Commercial-grade (atactic) polystyrene and poly(methyl methacrylate) are examples of polymers that are amorphous in the solid state. Below a certain temperature called the glass-transition temperature (T_g), long-range, cooperative motions of individual chains cannot occur; however, short-range motions involving several contiguous groups along the chain backbone or substituent group are possible. Such motions are called *secondary-relaxation* processes and can occur at temperatures as low as 70 K. By comparison, glass-transition temperatures vary from 150 K for polymers with very flexible chains such as polydimethylsiloxane

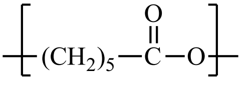


to well over 600 K for those with highly rigid aromatic backbones such as the high-modulus fiber poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) (see Section 10.2.1)

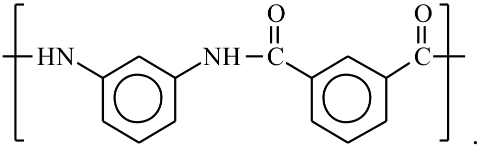


with a T_g reported in the range from 700 to 773 K.

Polymer chains with very regular structures, such as linear polyethylene and isotactic polypropylene, can be arranged in highly regular structures called crystallites. Each crystallite consists of rows of folded chains. Since sufficient thermal energy is needed to provide the necessary molecular mobility for the chain-folding process, crystallization can occur only at temperatures above T_g. If the temperature is too high, chain folds become unstable and high thermal energy disorders the crystallites—a crystalline–amorphous transition then occurs. The temperature that marks this transition is called the *crystalline-melting temperature* or T_m. Crystalline melting temperatures can vary from 334 K for simple, flexible-chain polyesters such as polycaprolactone



to over 675 K for aromatic polyamides such as poly(*m*-phenylene isophthalamide) (Nomex)



As an approximate rule of thumb, T_g is one-half to two-thirds of T_m expressed in absolute temperature (Kelvins). The glass-transition and crystalline-melting temperatures can be determined by a wide range of techniques including measurement of volume (dilatometry), specific heat (calorimetry), and mechanical properties, particularly modulus (e.g., dynamic mechanical analysis), as discussed in Chapter 4.

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PROBLEMS

1.1 A polymer sample combines five different molecular-weight fractions of equal weight. The molecular weights of these fractions increase from 20,000 to 100,000 in increments of

20,000. Calculate $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$. Based upon these results, comment on whether this sample has a broad or narrow molecular-weight distribution compared to typical commercial polymer samples.

1.2 A 50-g polymer sample was fractionated into six samples of different weights given in the table below. The viscosity-average molecular weight, $\bar{M}_v$, of each was determined and is included in the table. Estimate the number-average and weight-average molecular weights of the original sample. For these calculations, assume that the molecular-weight distribution of each fraction is extremely narrow and can be considered to be *monodisperse*. Would you classify the molecular-weight distribution of the original sample as narrow or broad?

Fraction	Weight (g)	$\bar{M}_v$
1	1.0	1500
2	5.0	35,000
3	21.0	75,000
4	15.0	150,000
5	6.5	400,000
6	1.5	850,000

1.3 The Schultz–Zimm [11] molecular-weight-distribution function can be written as

$$W(M) = \frac{a^{b+1}}{\Gamma(b+1)} M^b \exp(-aM)$$

where a and b are adjustable parameters (b is a positive real number) and Γ is the gamma function (see Appendix E) that is used to normalize the weight fraction.

(a) Using this relationship, obtain expressions for $\bar{M}_n$ and $\bar{M}_w$ in terms of a and b and an expression for M_{max}, the molecular weight at the peak of the $W(M)$ curve, in terms of $\bar{M}_n$.

(b) Derive an expression for M_{max}, the molecular weight at the peak of the $W(M)$ curve, in terms of $\bar{M}_n$.

(c) Show how the value of b affects the molecular-weight distribution by graphing $W(M)$ versus M on the same plot for b = 0.1, 1, and 10 given that $\bar{M}_n = 10{,}000$ for the three distributions.

Hint: $\int_0^\infty x^n \exp(-ax)\,dx = \Gamma(n+1)/a^{n+1} = n!/a^{n+1}$ (if n is a positive integer).

1.4 The following requested calculations refer to Examples 1.1, 1.2, and 1.3 in the text:

(a) Calculate the z-average molecular weight, $\bar{M}_z$, of the discrete molecular weight distribution described in Example 1.1.

(b) Calculate the z-average molecular weight, $\bar{M}_z$, of the continuous molecular-weight distribution shown in Example 1.2.

(c) Obtain an expression for the z-average degree of polymerization, $\bar{X}_z$, for the Flory distribution described in Example 1.3.

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Index

A

B

G

H

N

O

P

Q

R

S

T

U

V

W

X

Y

Z