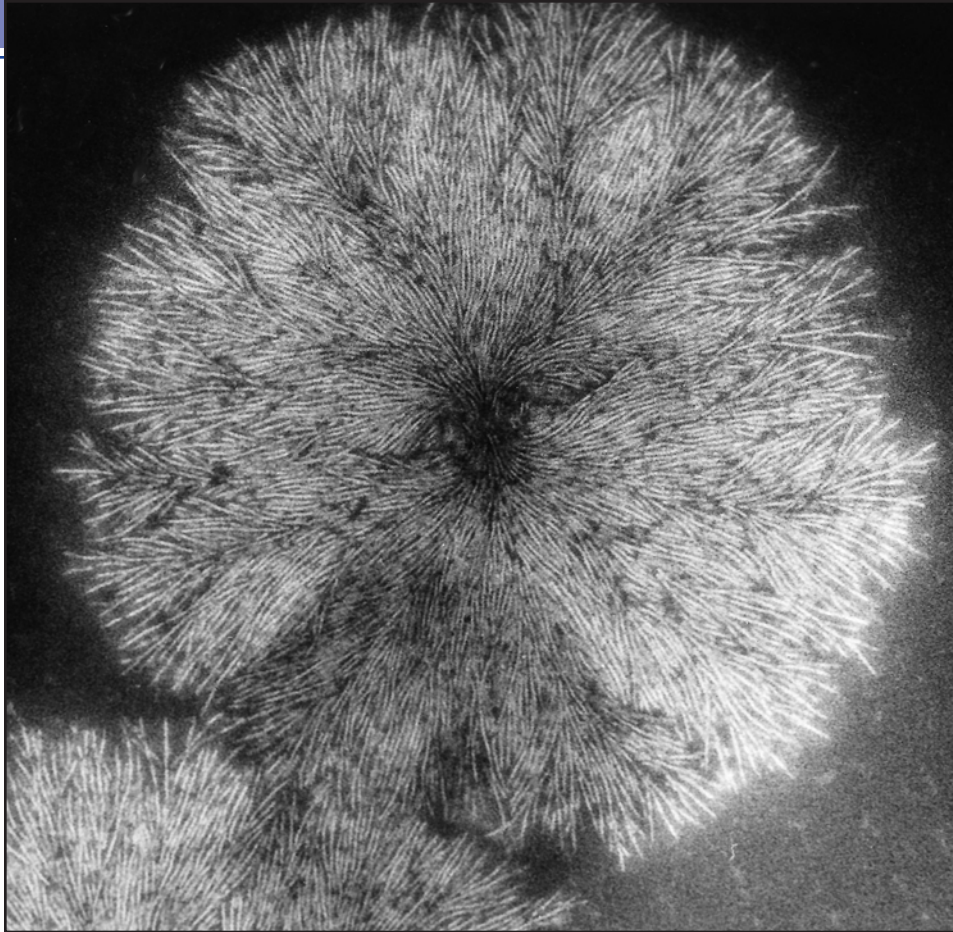


Chapter 14 Polymer Structures



Transmission electron micrograph showing the spherulite structure in a natural rubber specimen. Chain-folded lamellar crystallites approximately 10 nm thick extend in radial directions from the center; they appear as white lines in the micrograph. 30,000 \times . (Photograph supplied by P. J. Phillips. First published in R. Bartnikas and R. M. Eichhorn, *Engineering Dielectrics*, Vol. IIA, *Electrical Properties of Solid Insulating Materials: Molecular Structure and Electrical Behavior*, 1983. Copyright ASTM, 1916 Race Street, Philadelphia, PA 19103. Reprinted with permission.)

WHY STUDY *Polymer Structures*?

A relatively large number of chemical and structural characteristics affect the properties and behaviors of polymeric materials. Some of these influences are as follows:

1. Degree of crystallinity of semicrystalline polymers—on density, stiffness, strength, and ductility (Sections 14.11 and 15.8).
2. Degree of crosslinking—on the stiffness of rubber-like materials (Section 15.9).
3. Polymer chemistry—on melting and glass-transition temperatures (Section 15.14).

Learning Objectives

After careful study of this chapter you should be able to do the following:

1. Describe a typical polymer molecule in terms of its chain structure and, in addition, how the molecule may be generated from repeat units.
2. Draw repeat units for polyethylene, poly(vinyl chloride), polytetrafluoroethylene, polypropylene, and polystyrene.
3. Calculate number-average and weight-average molecular weights, and degree of polymerization for a specified polymer.
4. Name and briefly describe:
 - (a) the four general types of polymer molecular structures,
 - (b) the three types of stereoisomers,
 - (c) the two kinds of geometrical isomers,
 - (d) the four types of copolymers.
5. Cite the differences in behavior and molecular structure for thermoplastic and thermosetting polymers.
6. Briefly describe the crystalline state in polymeric materials.
7. Briefly describe/diagram the spherulitic structure for a semicrystalline polymer.

14.1 INTRODUCTION

Naturally occurring polymers—those derived from plants and animals—have been used for many centuries; these materials include wood, rubber, cotton, wool, leather, and silk. Other natural polymers such as proteins, enzymes, starches, and cellulose are important in biological and physiological processes in plants and animals. Modern scientific research tools have made possible the determination of the molecular structures of this group of materials, and the development of numerous polymers, which are synthesized from small organic molecules. Many of our useful plastics, rubbers, and fiber materials are synthetic polymers. In fact, since the conclusion of World War II, the field of materials has been virtually revolutionized by the advent of synthetic polymers. The synthetics can be produced inexpensively, and their properties may be managed to the degree that many are superior to their natural counterparts. In some applications metal and wood parts have been replaced by plastics, which have satisfactory properties and may be produced at a lower cost.

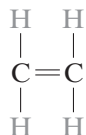
As with metals and ceramics, the properties of polymers are intricately related to the structural elements of the material. This chapter explores molecular and crystal structures of polymers; Chapter 15 discusses the relationships between structure and some of the physical and chemical properties, along with typical applications and forming methods.

14.2 HYDROCARBON MOLECULES

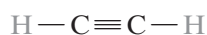
Since most polymers are organic in origin, we briefly review some of the basic concepts relating to the structure of their molecules. First, many organic materials are *hydrocarbons*; that is, they are composed of hydrogen and carbon. Furthermore, the intramolecular bonds are covalent. Each carbon atom has four electrons that may participate in covalent bonding, whereas every hydrogen atom has only one bonding electron. A single covalent bond exists when each of the two bonding atoms contributes one electron, as represented schematically in Figure 2.10 for a molecule of methane (CH_4). Double and triple bonds between two carbon atoms involve the sharing of two and three pairs of electrons, respectively. For example, in ethylene,

14.2 Hydrocarbon Molecules • 491

which has the chemical formula C_2H_4 , the two carbon atoms are doubly bonded together, and each is also singly bonded to two hydrogen atoms, as represented by the structural formula



where — and = denote single and double covalent bonds, respectively. An example of a triple bond is found in acetylene, C_2H_2 :



unsaturated

Molecules that have double and triple covalent bonds are termed **unsaturated**. That is, each carbon atom is not bonded to the maximum (four) other atoms; as such, it is possible for another atom or group of atoms to become attached to the original molecule. Furthermore, for a **saturated** hydrocarbon, all bonds are single ones, and no new atoms may be joined without the removal of others that are already bonded.

saturated

Some of the simple hydrocarbons belong to the paraffin family; the chainlike paraffin molecules include methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). Compositions and molecular structures for paraffin molecules are contained in Table 14.1. The covalent bonds in each molecule are strong, but only weak hydrogen and van der Waals bonds exist between molecules, and thus these hydrocarbons have relatively low melting and boiling points. However, boiling temperatures rise with increasing molecular weight (Table 14.1).

Hydrocarbon compounds with the same composition may have different atomic arrangements, a phenomenon termed **isomerism**. For example, there are two isomers

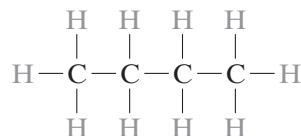
isomerism

Table 14.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

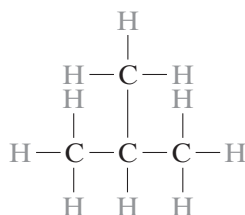
Name	Composition	Structure	Boiling Point ($^{\circ}C$)
Methane	CH_4	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array}$	-164
Ethane	C_2H_6	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	-88.6
Propane	C_3H_8	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	-42.1
Butane	C_4H_{10}		-0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

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for butane; normal butane has the structure



whereas a molecule of isobutane is represented as follows:



Some of the physical properties of hydrocarbons will depend on the isomeric state; for example, the boiling temperatures for normal butane and isobutane are -0.5 and -12.3°C (31.1 and 9.9°F), respectively.

There are numerous other organic groups, many of which are involved in polymer structures. Several of the more common groups are presented in Table 14.2, where R and R' represent organic groups such as CH_3 , C_2H_5 , and C_6H_5 (methyl, ethyl, and phenyl).



Concept Check 14.1

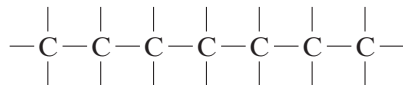
Differentiate between polymorphism (see Chapter 3) and isomerism.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

14.3 POLYMER MOLECULES

macromolecule

The molecules in polymers are gigantic in comparison to the hydrocarbon molecules already discussed; because of their size they are often referred to as **macromolecules**. Within each molecule, the atoms are bound together by covalent interatomic bonds. For carbon chain polymers, the backbone of each chain is a string of carbon atoms. Many times each carbon atom singly bonds to two adjacent carbon atoms on either side, represented schematically in two dimensions as follows:



Each of the two remaining valence electrons for every carbon atom may be involved in side-bonding with atoms or radicals that are positioned adjacent to the chain. Of course, both chain and side double bonds are also possible.

repeat unit

monomer

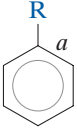
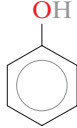
These long molecules are composed of structural entities called **repeat units**, which are successively repeated along the chain.¹ The term **monomer** refers to the small molecule from which a polymer is synthesized. Hence, monomer and repeat unit mean different things, but sometimes the term monomer or monomer unit is used instead of the more proper term repeat unit.

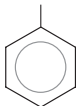
polymer

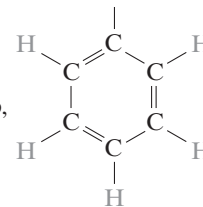
¹ A repeat unit is also sometimes called a mer. “Mer” originates from the Greek word *meros*, which means part; the term **polymer** was coined to mean “many mers.”

14.4 The Chemistry of Polymer Molecules • 493

Table 14.2 Some Common Hydrocarbon Groups

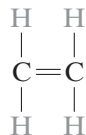
Family	Characteristic Unit		Representative Compound
Alcohols	$R-OH$	$\begin{array}{c} H \\ \\ H-C-OH \\ \\ H \end{array}$	Methyl alcohol
Ethers	$R-O-R'$	$\begin{array}{c} H & H \\ & \\ H-C-O-C-H \\ & \\ H & H \end{array}$	Dimethyl ether
Acids	$\begin{array}{c} OH \\ \\ R-C \\ \\ O \end{array}$	$\begin{array}{c} H & OH \\ & \\ H-C-C \\ & \\ H & O \end{array}$	Acetic acid
Aldehydes	$\begin{array}{c} R \\ \\ C=O \\ \\ H \end{array}$	$\begin{array}{c} H \\ \\ C=O \\ \\ H \end{array}$	Formaldehyde
Aromatic hydrocarbons			Phenol

^aThe simplified structure  denotes a phenyl group,

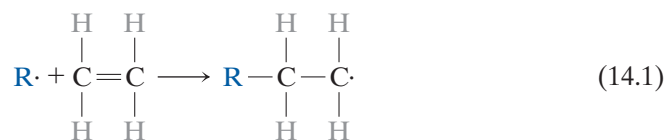


14.4 THE CHEMISTRY OF POLYMER MOLECULES

Consider again the hydrocarbon ethylene (C_2H_4), which is a gas at ambient temperature and pressure, and has the following molecular structure:

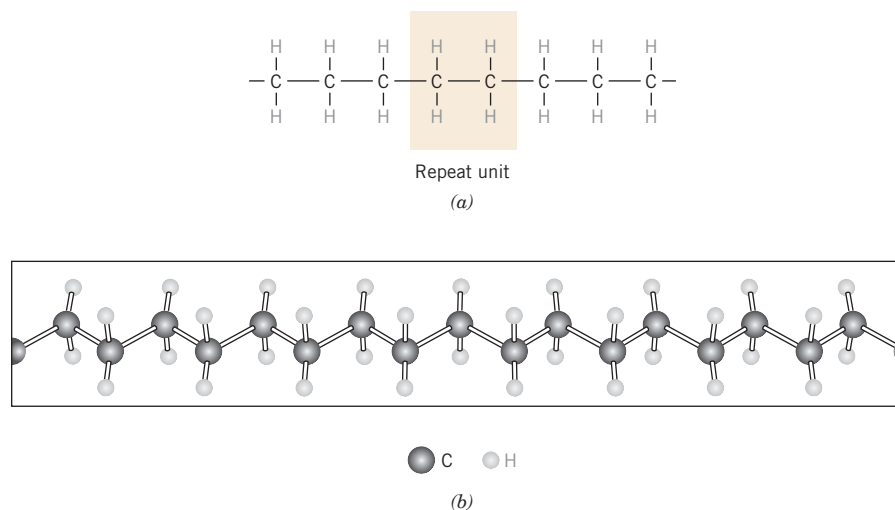


If the ethylene gas is reacted under appropriate conditions, it will transform to polyethylene (PE), which is a solid polymeric material. This process begins when an active center is formed by the reaction between an initiator or catalyst species ($R\cdot$) and the ethylene monomer, as follows:

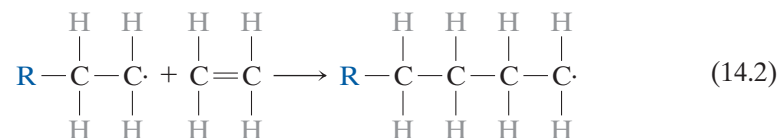


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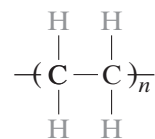
Figure 14.1 For polyethylene, (a) a schematic representation of repeat unit and chain structures, and (b) a perspective of the molecule, indicating the zigzag backbone structure.



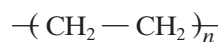
The polymer chain then forms by the sequential addition of monomer units to this active growing chain molecule. The active site, or unpaired electron (denoted by \cdot), is transferred to each successive end monomer as it is linked to the chain. This may be represented schematically as follows:



The final result, after the addition of many ethylene monomer units, is the polyethylene molecule;² a portion of one such molecule and the polyethylene repeat unit are shown in Figure 14.1a. This polyethylene chain structure can also be represented as



or alternatively as



Here the repeat units are enclosed in parentheses, and the subscript n indicates the number of times it repeats.³

The representation in Figure 14.1a is not strictly correct in that the angle between the singly bonded carbon atoms is not 180° as shown, but rather close to 109° . A more accurate three-dimensional model is one in which the carbon atoms form a zigzag pattern (Figure 14.1b), the C—C bond length being 0.154 nm. In this discussion, depiction of polymer molecules is frequently simplified using the linear chain model shown in Figure 14.1a.

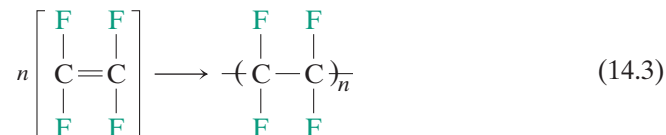
² A more detailed discussion of polymerization reactions including both addition and condensation mechanisms is given in Section 15.20.

³ Chain ends/end-groups (i.e., the Rs in Equation 14.2) are not normally represented in chain structures.

14.4 The Chemistry of Polymer Molecules • 495



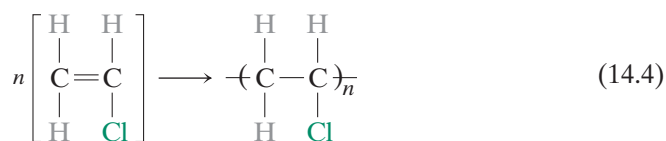
Of course polymer structures having other chemistries are possible. For example, the tetrafluoroethylene monomer, $\text{CF}_2=\text{CF}_2$, can polymerize to form *polytetrafluoroethylene* (PTFE) as follows:



Polytetrafluoroethylene (having the trade name TeflonTM) belongs to a family of polymers called the fluorocarbons.

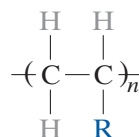


The vinyl chloride monomer ($\text{CH}_2=\text{CHCl}$) is a slight variant of that for ethylene, in which one of the four H atoms is replaced with a Cl atom. Its polymerization is represented as



and leads to *poly(vinyl chloride)* (PVC), another common polymer.

Some polymers may be represented using the following generalized form:



where the “R” depicts either an atom [i.e., H or Cl, for polyethylene or poly(vinyl chloride), respectively], or an organic group such as CH_3 , C_2H_5 , and C_6H_5 (methyl, ethyl, and phenyl). For example, when R represents a CH_3 group, the polymer is *polypropylene* (PP). Poly(vinyl chloride) and polypropylene chain structures are also represented in Figure 14.2. Table 14.3 lists repeat units for some of the more common polymers; as may be noted, some of them—for example, nylon, polyester, and polycarbonate—are relatively complex. Repeat units for a large number of relatively common polymers are given in Appendix D.

When all the repeating units along a chain are of the same type, the resulting polymer is called a **homopolymer**. Chains may be composed of two or more different repeat units, in what are termed **copolymers** (see Section 14.10).

The monomers discussed thus far have an active bond that may react to form two covalent bonds with other monomers forming a two-dimensional chain-like molecular structure, as indicated above for ethylene. Such a monomer is termed **bifunctional**. In general, the **functionality** is the number of bonds that a given monomer can form. For example, monomers such as phenol–formaldehyde (Table 14.3), are **trifunctional**; they have three active bonds, from which a three-dimensional molecular network structure results.

homopolymer

copolymer

bifunctional

functionality

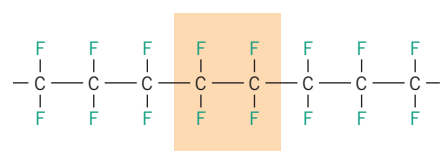
trifunctional

Concept Check 14.2

On the basis of the structures presented in the previous section, sketch the repeat unit structure for poly(vinyl fluoride).

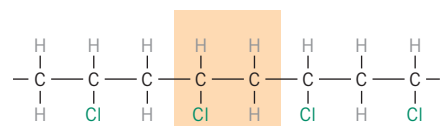
[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

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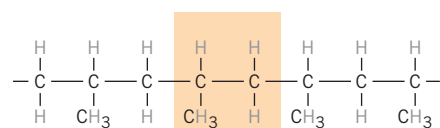
Repeat unit

(a)



Repeat unit

(b)








Repeat unit

(c)

Figure 14.2 Repeat unit and chain structures for (a) polytetrafluoroethylene, (b) poly(vinyl chloride), and (c) polypropylene.


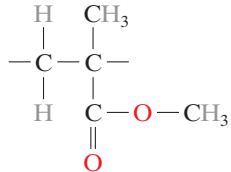

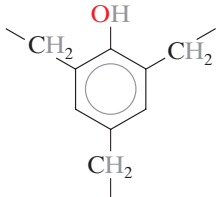

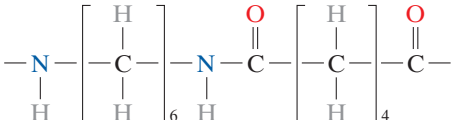

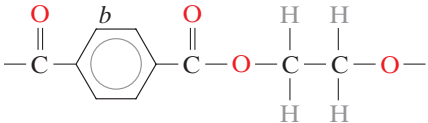

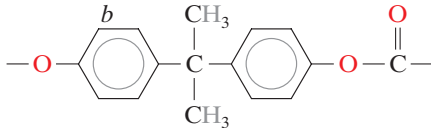
Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials


Polymer	Repeat Unit
 Polyethylene (PE)	$\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array}$
 Poly(vinyl chloride) (PVC)	$\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{Cl} \end{array}$
 Polytetrafluoroethylene (PTFE)	$\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{F} & \text{F} \end{array}$
 Polypropylene (PP)	$\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{CH}_3 \end{array}$
 Polystyrene (PS)	$\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{C}_6\text{H}_5 \end{array}$

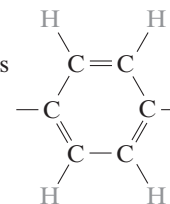
(Continued)

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Table 14.3 (Continued)

Polymer	Repeat Unit
 Poly(methyl methacrylate) (PMMA)	
 Phenol-formaldehyde (Bakelite)	
 Poly(hexamethylene adipamide) (nylon 6,6)	
 Poly(ethylene terephthalate) (PET, a polyester)	
 Polycarbonate (PC)	

^b The  symbol in the backbone chain denotes an aromatic ring as



14.5 MOLECULAR WEIGHT

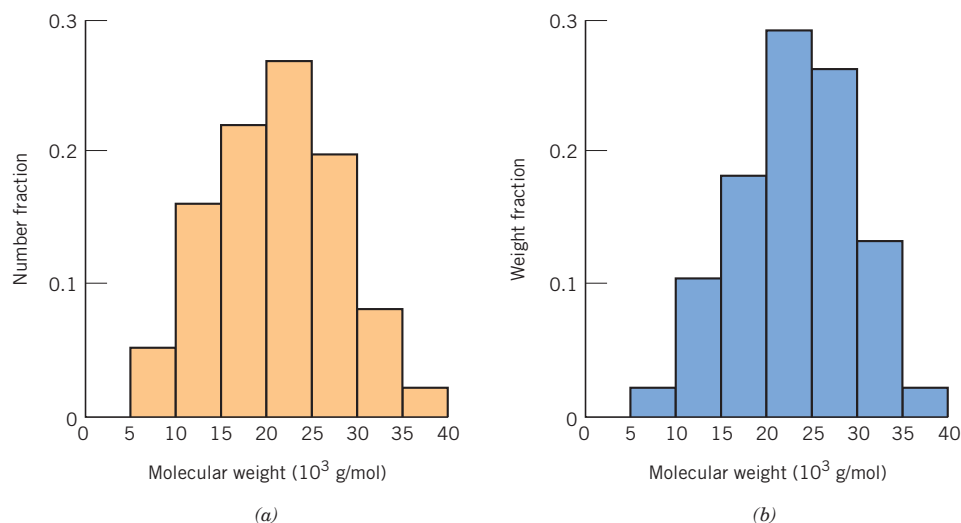
Extremely large molecular weights⁴ are observed in polymers with very long chains. During the polymerization process not all polymer chains will grow to the same length; this results in a distribution of chain lengths or molecular weights. Ordinarily, an average molecular weight is specified, which may be determined by the measurement of various physical properties such as viscosity and osmotic pressure.

There are several ways of defining average molecular weight. The number-average molecular weight \bar{M}_n is obtained by dividing the chains into a series of size

⁴ “Molecular mass,” “molar mass,” and “relative molecular mass” are sometimes used and are really more appropriate terms than “molecular weight” in the context of the present discussion—in actual fact, we are dealing with masses and not weights. However, molecular weight is most commonly found in the polymer literature, and thus will be used throughout this book.

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Figure 14.3
Hypothetical
polymer molecule
size distributions
on the basis of
(a) number and
(b) weight fractions
of molecules.



ranges and then determining the number fraction of chains within each size range (Figure 14.3a). The number-average molecular weight is expressed as

Number-average
molecular weight

$$\bar{M}_n = \sum x_i M_i \quad (14.5a)$$

where M_i represents the mean (middle) molecular weight of size range i , and x_i is the fraction of the total number of chains within the corresponding size range.

A weight-average molecular weight \bar{M}_w is based on the weight fraction of molecules within the various size ranges (Figure 14.3b). It is calculated according to

Weight-average
molecular weight

$$\bar{M}_w = \sum w_i M_i \quad (14.5b)$$

where, again, M_i is the mean molecular weight within a size range, whereas w_i denotes the weight fraction of molecules within the same size interval. Computations for both number-average and weight-average molecular weights are carried out in Example Problem 14.1. A typical molecular weight distribution along with these molecular weight averages is shown in Figure 14.4.

degree of
polymerization

An alternate way of expressing average chain size of a polymer is as the **degree of polymerization**, DP , which represents the average number of repeat

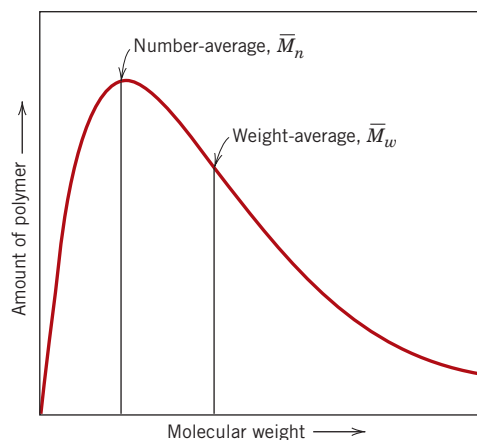


Figure 14.4 Distribution of molecular weights for a typical polymer.

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units in a chain. DP is related to the number-average molecular weight \bar{M}_n by the equation

$$DP = \frac{\bar{M}_n}{m} \quad (14.6)$$

where m is the repeat unit molecular weight.

Degree of polymerization—dependence on number-average and repeat unit molecular weights

EXAMPLE PROBLEM 14.1**Computations of Average Molecular Weights and Degree of Polymerization**

Assume that the molecular weight distributions shown in Figure 14.3 are for poly(vinyl chloride). For this material, compute (a) the number-average molecular weight, (b) the degree of polymerization, and (c) the weight-average molecular weight.

Solution

(a) The data necessary for this computation, as taken from Figure 14.3a, are presented in Table 14.4a. According to Equation 14.5a, summation of all the $x_i M_i$ products (from the right-hand column) yields the number-average molecular weight, which in this case is 21,150 g/mol.

(b) To determine the degree of polymerization (Equation 14.6), it is first necessary to compute the repeat unit molecular weight. For PVC, each repeat unit consists of two carbon atoms, three hydrogen atoms, and a single chlorine atom (Table 14.3). Furthermore, the atomic weights of C, H, and Cl are, respectively, 12.01, 1.01, and 35.45 g/mol. Thus, for PVC

$$\begin{aligned} m &= 2(12.01 \text{ g/mol}) + 3(1.01 \text{ g/mol}) + 35.45 \text{ g/mol} \\ &= 62.50 \text{ g/mol} \end{aligned}$$

and

$$DP = \frac{\bar{M}_n}{m} = \frac{21,150 \text{ g/mol}}{62.50 \text{ g/mol}} = 338$$

(c) Table 14.4b shows the data for the weight-average molecular weight, as taken from Figure 14.3b. The $w_i M_i$ products for the size intervals are tabulated in the right-hand column. The sum of these products (Equation 14.5b) yields a value of 23,200 g/mol for \bar{M}_w .

Table 14.4a Data Used for Number-Average Molecular Weight Computations in Example Problem 14.1

Molecular Weight Range (g/mol)	Mean M_i (g/mol)	x_i	$x_i M_i$
5,000–10,000	7,500	0.05	375
10,000–15,000	12,500	0.16	2000
15,000–20,000	17,500	0.22	3850
20,000–25,000	22,500	0.27	6075
25,000–30,000	27,500	0.20	5500
30,000–35,000	32,500	0.08	2600
35,000–40,000	37,500	0.02	750
			$\bar{M}_n = 21,150$

Table 14.4b Data Used for Weight-Average Molecular Weight Computations in Example Problem 14.1

Molecular Weight Range (g/mol)	Mean M_i (g/mol)	w_i	$w_i M_i$
5,000–10,000	7,500	0.02	150
10,000–15,000	12,500	0.10	1250
15,000–20,000	17,500	0.18	3150
20,000–25,000	22,500	0.29	6525
25,000–30,000	27,500	0.26	7150
30,000–35,000	32,500	0.13	4225
35,000–40,000	37,500	0.02	750
			$\overline{M}_w = 23,200$

Many polymer properties are affected by the length of the polymer chains. For example, the melting or softening temperature increases with increasing molecular weight (for \overline{M} up to about 100,000 g/mol). At room temperature, polymers with very short chains (having molecular weights on the order of 100 g/mol) exist as liquids or gases. Those with molecular weights of approximately 1000 g/mol are waxy solids (such as paraffin wax) and soft resins. Solid polymers (sometimes termed *high polymers*), which are of prime interest here, commonly have molecular weights ranging between 10,000 and several million g/mol. Thus, the same polymer material can have quite different properties if it is produced with a different molecular weight. Other properties that depend on molecular weight include elastic modulus and strength (see Chapter 15).

14.6 MOLECULAR SHAPE

Previously, polymer molecules have been shown as linear chains, neglecting the zigzag arrangement of the backbone atoms (Figure 14.1*b*). Single chain bonds are capable of rotating and bending in three dimensions. Consider the chain atoms in Figure 14.5*a*; a third carbon atom may lie at any point on the cone of revolution and still subtend about a 109° angle with the bond between the other two atoms. A straight chain segment results when successive chain atoms are positioned as in Figure 14.5*b*. On the other hand, chain bending and twisting are possible when there is a rotation of the chain atoms into other positions, as illustrated in Figure 14.5*c*.⁵ Thus, a single chain molecule composed of many chain atoms might assume a shape similar to that represented schematically in Figure 14.6, having a multitude of bends, twists, and kinks.⁶ Also indicated in this figure is the end-to-end distance of the polymer chain r ; this distance is much smaller than the total chain length.

Polymers consist of large numbers of molecular chains, each of which may bend, coil, and kink in the manner of Figure 14.6. This leads to extensive intertwining and entanglement of neighboring chain molecules, a situation similar to a heavily tangled fishing line. These random coils and molecular entanglements are responsible

⁵ For some polymers, rotation of carbon backbone atoms within the cone may be hindered by bulky side group elements on neighboring chains.

⁶ The term *conformation* is often used in reference to the physical outline of a molecule, or molecular shape, that can only be altered by rotation of chain atoms about single bonds.

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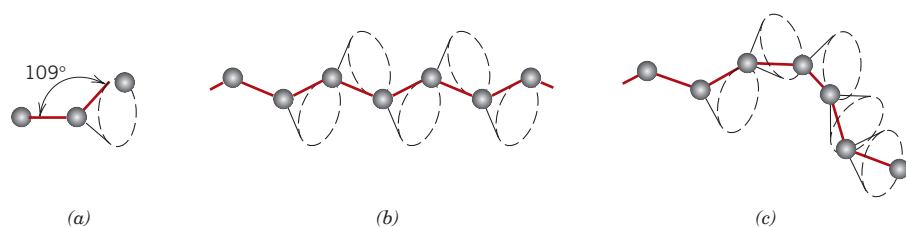


Figure 14.5 Schematic representations of how polymer chain shape is influenced by the positioning of backbone carbon atoms (gray circles). For (a), the rightmost atom may lie anywhere on the dashed circle and still subtend a 109° angle with the bond between the other two atoms. Straight and twisted chain segments are generated when the backbone atoms are situated as in (b) and (c), respectively. (From *Science and Engineering of Materials*, 3rd edition by Askeland. © 1994. Reprinted with permission of Nelson, a division of Thomson Learning: www.thomsonrights.com. Fax 800 730-2215.)

for a number of important characteristics of polymers, to include the large elastic extensions displayed by the rubber materials.

Some of the mechanical and thermal characteristics of polymers are a function of the ability of chain segments to experience rotation in response to applied stresses or thermal vibrations. Rotational flexibility is dependent on repeat unit structure and chemistry. For example, the region of a chain segment that has a double bond ($C=C$) is rotationally rigid. Also, introduction of a bulky or large side group of atoms restricts rotational movement. For example, polystyrene molecules, which have a phenyl side group (Table 14.3), are more resistant to rotational motion than are polyethylene chains.

14.7 MOLECULAR STRUCTURE

The physical characteristics of a polymer depend not only on its molecular weight and shape but also on differences in the structure of the molecular chains. Modern polymer synthesis techniques permit considerable control over various structural possibilities. This section discusses several molecular structures including linear, branched, crosslinked, and network, in addition to various isomeric configurations.

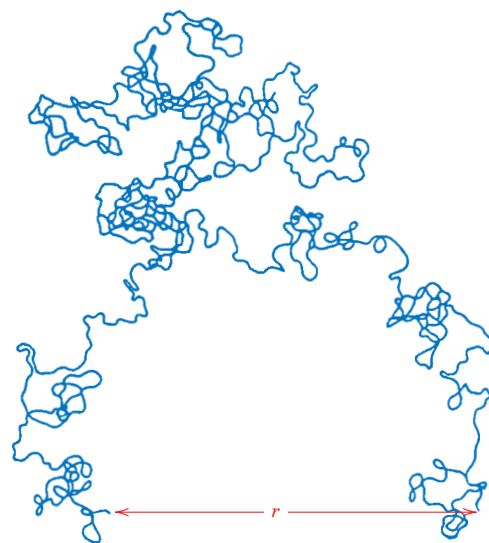


Figure 14.6 Schematic representation of a single polymer chain molecule that has numerous random kinks and coils produced by chain bond rotations. (From L. R. G. Treloar, *The Physics of Rubber Elasticity*, 2nd edition, Oxford University Press, Oxford, 1958, p. 47.)

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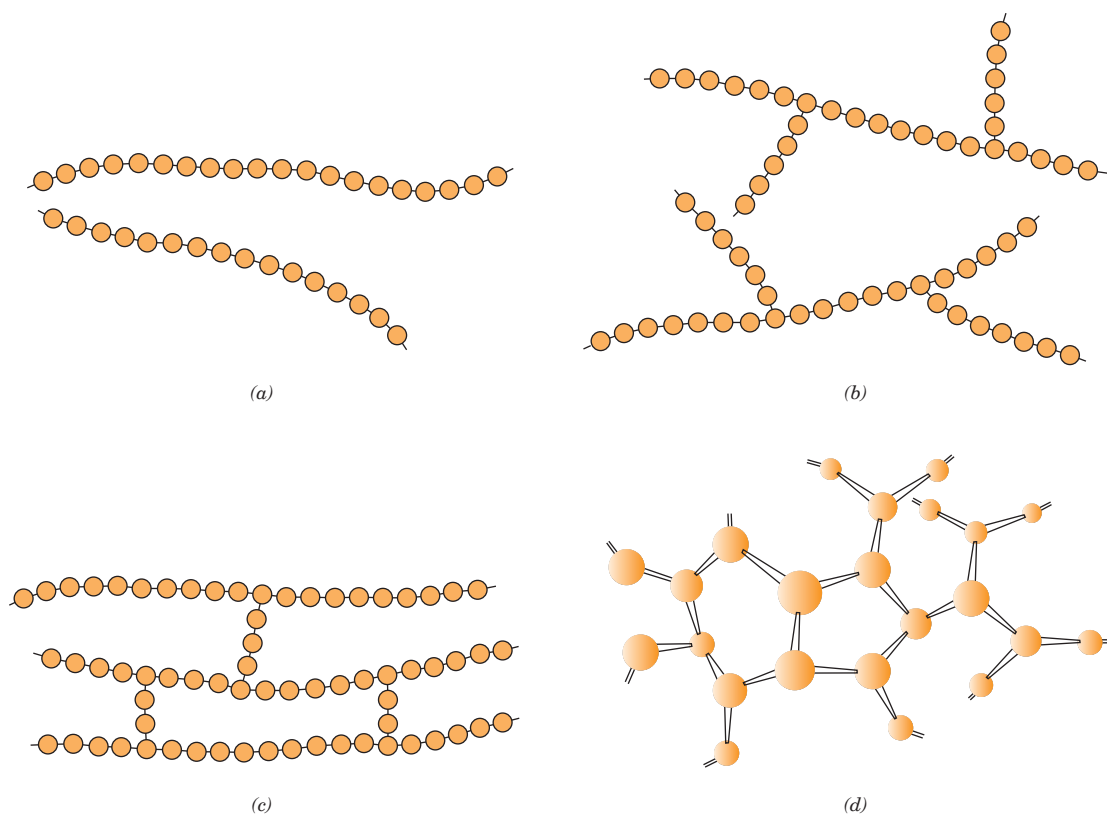


Figure 14.7 Schematic representations of (a) linear, (b) branched, (c) crosslinked, and (d) network (three-dimensional) molecular structures. Circles designate individual repeat units.

Linear Polymers

linear polymer

Linear polymers are those in which the repeat units are joined together end to end in single chains. These long chains are flexible and may be thought of as a mass of spaghetti, as represented schematically in Figure 14.7a, where each circle represents a repeat unit. For linear polymers, there may be extensive van der Waals and hydrogen bonding between the chains. Some of the common polymers that form with linear structures are polyethylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), nylon, and the fluorocarbons.

Branched Polymers

branched polymer

Polymers may be synthesized in which side-branch chains are connected to the main ones, as indicated schematically in Figure 14.7b; these are fittingly called **branched polymers**. The branches, considered to be part of the main-chain molecule, may result from side reactions that occur during the synthesis of the polymer. The chain packing efficiency is reduced with the formation of side branches, which results in a lowering of the polymer density. Those polymers that form linear structures may also be branched. For example, high density polyethylene (HDPE) is primarily a linear polymer, while low density polyethylene (LDPE) contains short chain branches.

Crosslinked Polymers

crosslinked polymer

In **crosslinked polymers**, adjacent linear chains are joined one to another at various positions by covalent bonds, as represented in Figure 14.7c. The process of

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crosslinking is achieved either during synthesis or by a nonreversible chemical reaction. Often, this crosslinking is accomplished by additive atoms or molecules that are covalently bonded to the chains. Many of the rubber elastic materials are crosslinked; in rubbers, this is called vulcanization, a process described in Section 15.9.

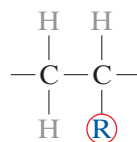
Network Polymers**network polymer**

Multifunctional monomers forming three or more active covalent bonds, make three-dimensional networks (Figure 14.7d) and are termed **network polymers**. Actually, a polymer that is highly crosslinked may also be classified as a network polymer. These materials have distinctive mechanical and thermal properties; the epoxies, polyurethanes, and phenol-formaldehyde belong to this group.

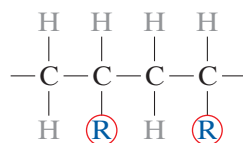
Polymers are not usually of only one distinctive structural type. For example, a predominantly linear polymer might have limited branching and crosslinking.

14.8 MOLECULAR CONFIGURATIONS

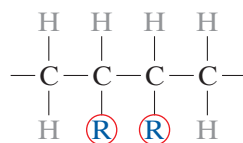
For polymers having more than one side atom or group of atoms bonded to the main chain, the regularity and symmetry of the side group arrangement can significantly influence the properties. Consider the repeat unit



in which R represents an atom or side group other than hydrogen (e.g., Cl, CH₃). One arrangement is possible when the R side groups of successive repeat units are bound to alternate carbon atoms as follows:



This is designated as a head-to-tail configuration.⁷ Its complement, the head-to-head configuration, occurs when R groups are bound to adjacent chain atoms:



In most polymers, the head-to-tail configuration predominates; often a polar repulsion occurs between R groups for the head-to-head configuration.

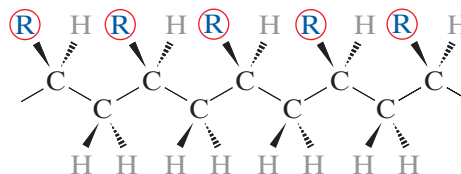
Isomerism (Section 14.2) is also found in polymer molecules, wherein different atomic configurations are possible for the same composition. Two isomeric subclasses, stereoisomerism and geometrical isomerism, are topics of discussion in the succeeding sections.

⁷ The term *configuration* is used in reference to arrangements of units along the axis of the chain, or atom positions that are not alterable except by the breaking and then reforming of primary bonds.

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Stereoisomerism**stereoisomerism**

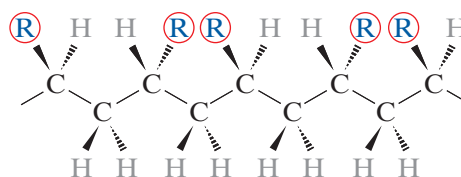
Stereoisomerism denotes the situation in which atoms are linked together in the same order (head-to-tail) but differ in their spatial arrangement. For one stereoisomer, all the R groups are situated on the same side of the chain as follows:

**isotactic configuration**

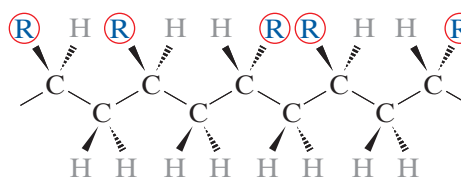
This is called an **isotactic configuration**. This diagram shows the zigzag pattern of the carbon chain atoms. Furthermore, representation of the structural geometry in three dimensions is important, as indicated by the wedge-shaped bonds; solid wedges represent bonds that project out of the plane of the page, dashed ones represent bonds that project into the page.⁸

syndiotactic configuration

In a **syndiotactic configuration**, the R groups alternate sides of the chain:⁹

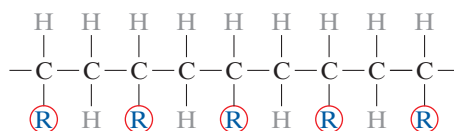


and for random positioning.

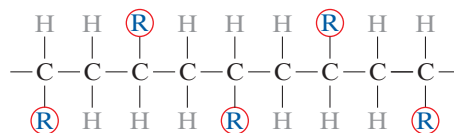
**atactic configuration**

the term **atactic configuration** is used.¹⁰

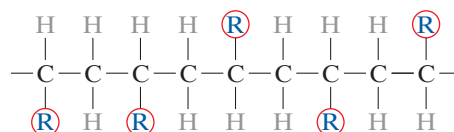
⁸ The isotactic configuration is sometimes represented using the following linear (i.e., nonzigzag) and two-dimensional schematic:



⁹ The linear and two-dimensional schematic for syndiotactic is represented as



¹⁰ For atactic the linear and two-dimensional schematic is



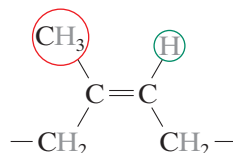
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Conversion from one stereoisomer to another (e.g., isotactic to syndiotactic) is not possible by a simple rotation about single chain bonds; these bonds must first be severed, and then, after the appropriate rotation, they are reformed.

In reality, a specific polymer does not exhibit just one of these configurations; the predominant form depends on the method of synthesis.

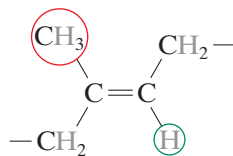
Geometrical Isomerism

Other important chain configurations, or geometrical isomers, are possible within repeat units having a double bond between chain carbon atoms. Bonded to each of the carbon atoms participating in the double bond is a side group, which may be situated on one side of the chain or its opposite. Consider the isoprene repeat unit having the structure



cis (structure)

in which the CH_3 group and the H atom are positioned on the same side of the double bond. This is termed a **cis** structure, and the resulting polymer, *cis*-polyisoprene, is natural rubber. For the alternative isomer

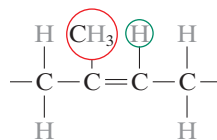


trans (structure)

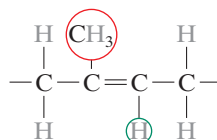
the **trans** structure, the CH_3 and H reside on opposite sides of the double bond.¹¹ *Trans*-polyisoprene, sometimes called gutta percha, has properties that are distinctly different from natural rubber as a result of this configurational alteration. Conversion of trans to cis, or vice versa, is not possible by a simple chain bond rotation because the chain double bond is extremely rigid.

Summarizing the preceding sections, polymer molecules may be characterized in terms of their size, shape, and structure. Molecular size is specified in terms of molecular weight (or degree of polymerization). Molecular shape relates to the degree of chain twisting, coiling, and bending. Molecular structure depends on the manner in which structural units are joined together. Linear, branched, crosslinked,

¹¹ For *cis*-isoprene the linear chain representation is as follows:

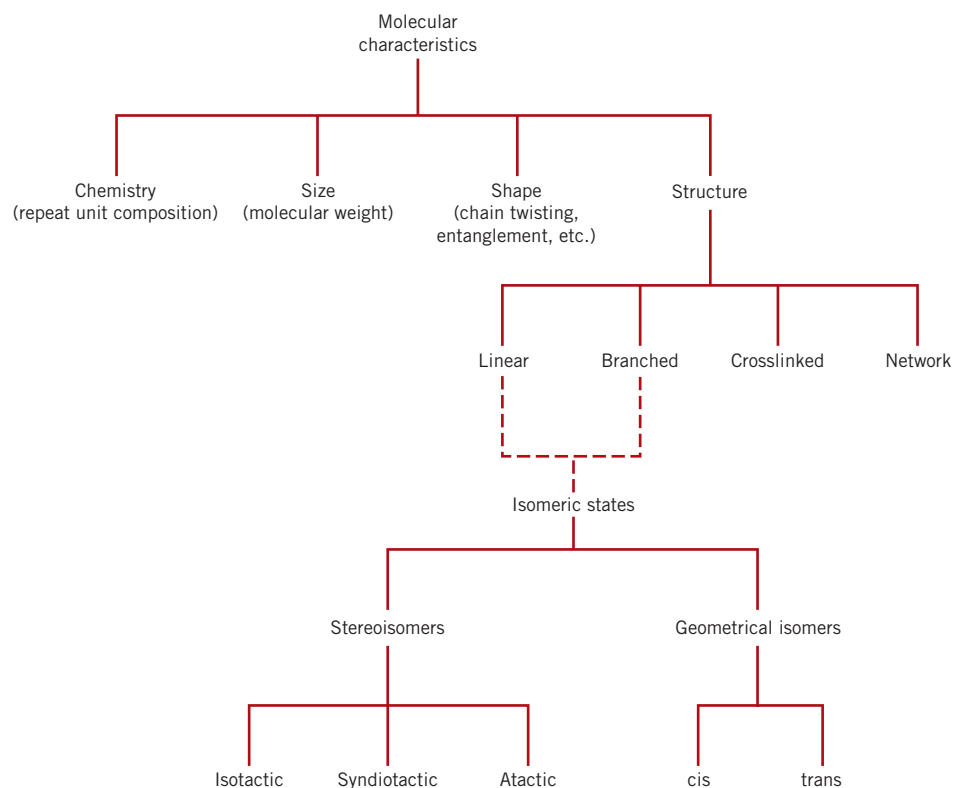


whereas the linear schematic for the *trans* structure is



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Figure 14.8
Classification
scheme for the
characteristics of
polymer molecules.



and network structures are all possible, in addition to several isomeric configurations (isotactic, syndiotactic, atactic, cis, and trans). These molecular characteristics are presented in the taxonomic chart, Figure 14.8. Note that some of the structural elements are not mutually exclusive of one another, and, in fact, it may be necessary to specify molecular structure in terms of more than one. For example, a linear polymer may also be isotactic.

 **Concept Check 14.3**

What is the difference between *configuration* and *conformation* in relation to polymer chains?

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

14.9 THERMOPLASTIC AND THERMOSETTING POLYMERS

**thermoplastic
polymer**

**thermosetting
polymer**

The response of a polymer to mechanical forces at elevated temperatures is related to its dominant molecular structure. In fact, one classification scheme for these materials is according to behavior with rising temperature. *Thermoplastics* (or **thermoplastic polymers**) and *thermosets* (or **thermosetting polymers**) are the two subdivisions. Thermoplastics soften when heated (and eventually liquefy) and harden when cooled—processes that are totally reversible and may be repeated. On a molecular level, as the temperature is raised, secondary bonding forces are

14.10 Copolymers • 507

diminished (by increased molecular motion) so that the relative movement of adjacent chains is facilitated when a stress is applied. Irreversible degradation results when a molten thermoplastic polymer is raised to too high of a temperature. In addition, thermoplastics are relatively soft. Most linear polymers and those having some branched structures with flexible chains are thermoplastic. These materials are normally fabricated by the simultaneous application of heat and pressure (see Section 15.22). Most linear polymers are thermoplastics. Examples of common thermoplastic polymers include polyethylene, polystyrene, poly(ethylene terephthalate), and poly(vinyl chloride).

Thermosetting polymers are network polymers. They become permanently hard during their formation, and do not soften upon heating. Network polymers have covalent crosslinks between adjacent molecular chains. During heat treatments, these bonds anchor the chains together to resist the vibrational and rotational chain motions at high temperatures. Thus, the materials do not soften when heated. Crosslinking is usually extensive, in that 10 to 50% of the chain repeat units are crosslinked. Only heating to excessive temperatures will cause severance of these crosslink bonds and polymer degradation. Thermoset polymers are generally harder and stronger than thermoplastics and have better dimensional stability. Most of the crosslinked and network polymers, which include vulcanized rubbers, epoxies, and phenolics and some polyester resins, are thermosetting.

**Concept Check 14.4**

Some polymers (such as the polyesters) may be either thermoplastic or thermosetting. Suggest one reason for this.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

14.10 COPOLYMERS

Polymer chemists and scientists are continually searching for new materials that can be easily and economically synthesized and fabricated, with improved properties or better property combinations than are offered by the homopolymers previously discussed. One group of these materials are the copolymers.

Consider a copolymer that is composed of two repeat units as represented by ● and ● in Figure 14.9. Depending on the polymerization process and the relative fractions of these repeat unit types, different sequencing arrangements along the polymer chains are possible. For one, as depicted in Figure 14.9a, the two different units are randomly dispersed along the chain in what is termed a **random copolymer**. For an **alternating copolymer**, as the name suggests, the two repeat units alternate chain positions, as illustrated in Figure 14.9b. A **block copolymer** is one in which identical repeat units are clustered in blocks along the chain (Figure 14.9c). Finally, homopolymer side branches of one type may be grafted to homopolymer main chains that are composed of a different repeat unit; such a material is termed a **graft copolymer** (Figure 14.9d).

When calculating the degree of polymerization for a copolymer, the value m in Equation 14.7 is replaced with the average value \bar{m} that is determined from

$$\bar{m} = \sum f_j m_j \quad (14.7)$$

In this expression, f_j and m_j are, respectively, the mole fraction and molecular weight of repeat unit j in the polymer chain.

random copolymer

alternating
copolymer

block copolymer

graft copolymer

Average repeat unit
molecular weight for
a copolymer

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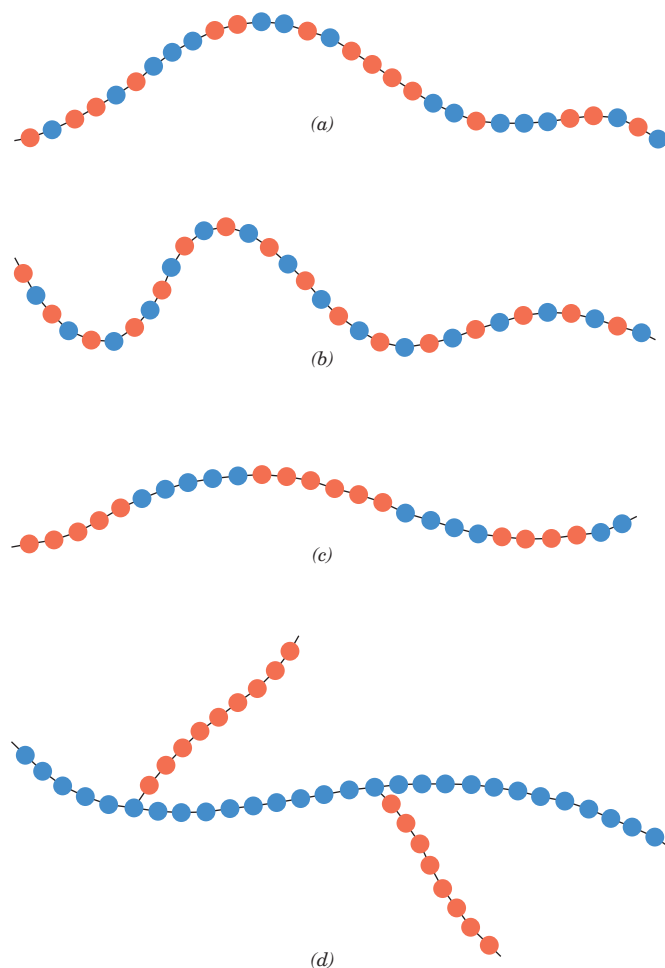


Figure 14.9 Schematic representations of (a) random, (b) alternating, (c) block, and (d) graft copolymers. The two different repeat unit types are designated by blue and red circles.

Synthetic rubbers, discussed in Section 15.16, are often copolymers; chemical repeat units that are employed in some of these rubbers are contained in Table 14.5. Styrene–butadiene rubber (SBR) is a common random copolymer from which automobile tires are made. Nitrile rubber (NBR) is another random copolymer composed of acrylonitrile and butadiene. It is also highly elastic and, in addition, resistant to swelling in organic solvents; gasoline hoses are made of NBR. Impact modified polystyrene is a block copolymer that consists of alternating blocks of styrene and butadiene. The rubbery isoprene blocks act to slow cracks propagating through the material.








14.11 POLYMER CRYSTALLINITY

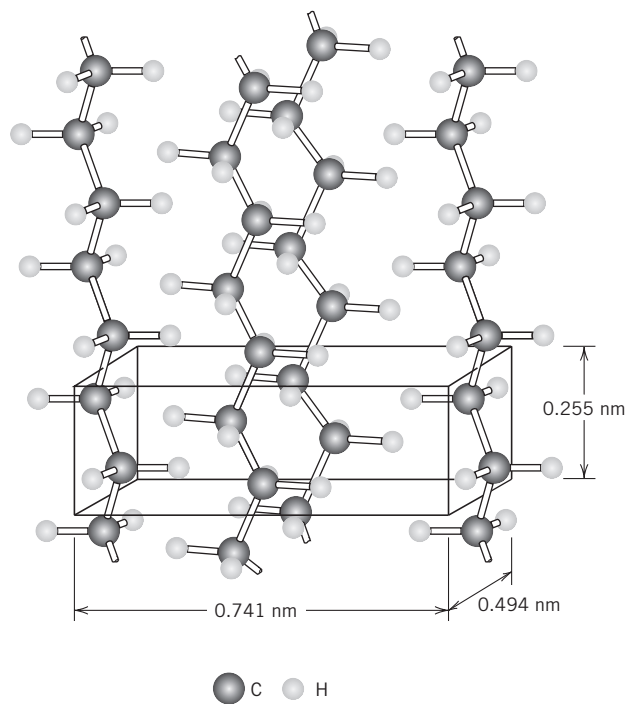
polymer crystallinity

The crystalline state may exist in polymeric materials. However, since it involves molecules instead of just atoms or ions, as with metals and ceramics, the atomic arrangements will be more complex for polymers. We think of **polymer crystallinity** as the packing of molecular chains to produce an ordered atomic array. Crystal structures may be specified in terms of unit cells, which are often quite complex. For example, Figure 14.10 shows the unit cell for polyethylene and its relationship to the molecular chain structure; this unit cell has orthorhombic geometry (Table 3.2). Of course, the chain molecules also extend beyond the unit cell shown in the figure.

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Table 14.5 Chemical Repeat Units That Are Employed in Copolymer Rubbers

Repeat Unit Name	Repeat Unit Structure	Repeat Unit Name	Repeat Unit Structure
 Acrylonitrile	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{C}\equiv\text{N} \end{array}$	 Isoprene	$\begin{array}{c} \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\ \quad \quad \quad \\ \text{H} \quad \quad \quad \text{H} \end{array}$
 Styrene	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array}$	 Isobutylene	$\begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array}$
 Butadiene	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\ \quad \quad \quad \\ \text{H} \quad \quad \quad \text{H} \end{array}$	 Dimethylsiloxane	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}-\text{O}- \\ \\ \text{CH}_3 \end{array}$
 Chloroprene	$\begin{array}{c} \text{H} \quad \text{Cl} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\ \quad \quad \quad \\ \text{H} \quad \quad \quad \text{H} \end{array}$		

**Figure 14.10** Arrangement of molecular chains in a unit cell for polyethylene. (Adapted from C. W. Bunn, *Chemical Crystallography*, Oxford University Press, Oxford, 1945, p. 233.)

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Molecular substances having small molecules (e.g., water and methane) are normally either totally crystalline (as solids) or totally amorphous (as liquids). As a consequence of their size and often complexity, polymer molecules are often only partially crystalline (or semicrystalline), having crystalline regions dispersed within the remaining amorphous material. Any chain disorder or misalignment will result in an amorphous region, a condition that is fairly common, since twisting, kinking, and coiling of the chains prevent the strict ordering of every segment of every chain. Other structural effects are also influential in determining the extent of crystallinity, as discussed below.

The degree of crystallinity may range from completely amorphous to almost entirely (up to about 95%) crystalline; in contrast, metal specimens are almost always entirely crystalline, whereas many ceramics are either totally crystalline or totally noncrystalline. Semicrystalline polymers are, in a sense, analogous to two-phase metal alloys, discussed previously.

The density of a crystalline polymer will be greater than an amorphous one of the same material and molecular weight, since the chains are more closely packed together for the crystalline structure. The degree of crystallinity by weight may be determined from accurate density measurements, according to

$$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100 \quad (14.8)$$

where ρ_s is the density of a specimen for which the percent crystallinity is to be determined, ρ_a is the density of the totally amorphous polymer, and ρ_c is the density of the perfectly crystalline polymer. The values of ρ_a and ρ_c must be measured by other experimental means.

The degree of crystallinity of a polymer depends on the rate of cooling during solidification as well as on the chain configuration. During crystallization upon cooling through the melting temperature, the chains, which are highly random and entangled in the viscous liquid, must assume an ordered configuration. For this to occur, sufficient time must be allowed for the chains to move and align themselves.

The molecular chemistry as well as chain configuration also influence the ability of a polymer to crystallize. Crystallization is not favored in polymers that are composed of chemically complex repeat units (e.g., polyisoprene). On the other hand, crystallization is not easily prevented in chemically simple polymers such as polyethylene and polytetrafluoroethylene, even for very rapid cooling rates.

For linear polymers, crystallization is easily accomplished because there are few restrictions to prevent chain alignment. Any side branches interfere with crystallization, such that branched polymers never are highly crystalline; in fact, excessive branching may prevent any crystallization whatsoever. Most network and crosslinked polymers are almost totally amorphous because the crosslinks prevent the polymer chains from rearranging and aligning into a crystalline structure. A few crosslinked polymers are partially crystalline. With regard to the stereoisomers, atactic polymers are difficult to crystallize; however, isotactic and syndiotactic polymers crystallize much more easily because the regularity of the geometry of the side groups facilitates the process of fitting together adjacent chains. Also, the bulkier or larger the side-bonded groups of atoms, the less tendency there is for crystallization.

Percent crystallinity (semicrystalline polymer)—dependence on specimen density, and densities of totally crystalline and totally amorphous materials

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For copolymers, as a general rule, the more irregular and random the repeat unit arrangements, the greater is the tendency for the development of noncrystallinity. For alternating and block copolymers there is some likelihood of crystallization. On the other hand, random and graft copolymers are normally amorphous.

To some extent, the physical properties of polymeric materials are influenced by the degree of crystallinity. Crystalline polymers are usually stronger and more resistant to dissolution and softening by heat. Some of these properties are discussed in subsequent chapters.

**Concept Check 14.5**

(a) Compare the crystalline state in metals and polymers. **(b)** Compare the non-crystalline state as it applies to polymers and ceramic glasses.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

EXAMPLE PROBLEM 14.2**Computations of the Density and Percent Crystallinity of Polyethylene**

(a) Compute the density of totally crystalline polyethylene. The orthorhombic unit cell for polyethylene is shown in Figure 14.10; also, the equivalent of two ethylene repeat units is contained within each unit cell.

(b) Using the answer to part (a), calculate the percent crystallinity of a branched polyethylene that has a density of 0.925 g/cm^3 . The density for the totally amorphous material is 0.870 g/cm^3 .

Solution

(a) Equation 3.5, utilized in Chapter 3 to determine densities for metals, also applies to polymeric materials and is used to solve this problem. It takes the same form—viz.

$$\rho = \frac{nA}{V_C N_A}$$

where n represents the number of repeat units within the unit cell (for polyethylene $n = 2$), and A is the repeat unit molecular weight, which for polyethylene is

$$\begin{aligned} A &= 2(A_C) + 4(A_H) \\ &= (2)(12.01 \text{ g/mol}) + (4)(1.008 \text{ g/mol}) = 28.05 \text{ g/mol} \end{aligned}$$

Also, V_C is the unit cell volume, which is just the product of the three unit cell edge lengths in Figure 14.10; or

$$\begin{aligned} V_C &= (0.741 \text{ nm})(0.494 \text{ nm})(0.255 \text{ nm}) \\ &= (7.41 \times 10^{-8} \text{ cm})(4.94 \times 10^{-8} \text{ cm})(2.55 \times 10^{-8} \text{ cm}) \\ &= 9.33 \times 10^{-23} \text{ cm}^3/\text{unit cell} \end{aligned}$$

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Now, substitution into Equation 3.5, of this value, values for n and A cited above, as well as N_A , leads to

$$\begin{aligned}\rho &= \frac{nA}{V_c N_A} \\ &= \frac{(2 \text{ repeat units/unit cell})(28.05 \text{ g/mol})}{(9.33 \times 10^{-23} \text{ cm}^{-3}/\text{unit cell})(6.023 \times 10^{23} \text{ repeat units/mol})} \\ &= 0.998 \text{ g/cm}^3\end{aligned}$$

(b) We now utilize Equation 14.8 to calculate the percent crystallinity of the branched polyethylene with $\rho_c = 0.998 \text{ g/cm}^3$, $\rho_a = 0.870 \text{ g/cm}^3$, and $\rho_s = 0.925 \text{ g/cm}^3$. Thus,

$$\begin{aligned}\% \text{ crystallinity} &= \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100 \\ &= \frac{0.998 \text{ g/cm}^3 (0.925 \text{ g/cm}^3 - 0.870 \text{ g/cm}^3)}{0.925 \text{ g/cm}^3 (0.998 \text{ g/cm}^3 - 0.870 \text{ g/cm}^3)} \times 100 \\ &= 46.4\%\end{aligned}$$

14.12 POLYMER CRYSTALS

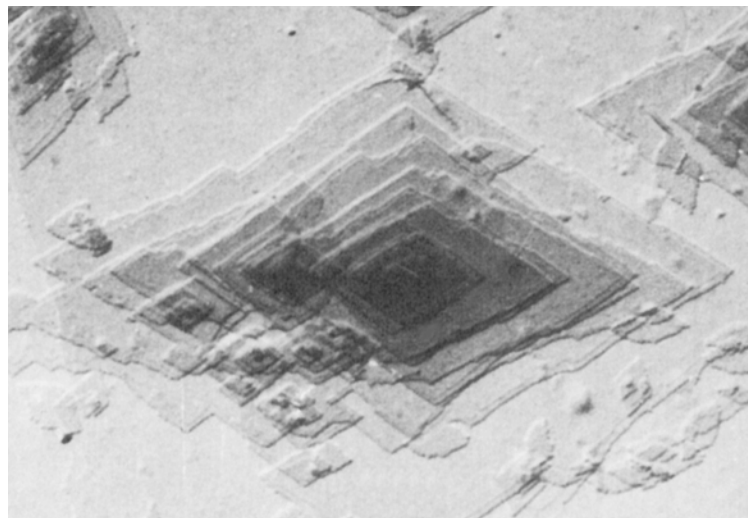
crystallite

It has been proposed that a semicrystalline polymer consists of small crystalline regions (**crystallites**), each having a precise alignment, which are interspersed with amorphous regions composed of randomly oriented molecules. The structure of the crystalline regions may be deduced by examination of polymer single crystals, which may be grown from dilute solutions. These crystals are regularly shaped, thin platelets (or lamellae), approximately 10 to 20 nm thick, and on the order of 10 μm long. Frequently, these platelets will form a multilayered structure, like that shown in the electron micrograph of a single crystal of polyethylene, Figure 14.11.

chain-folded model

The molecular chains within each platelet fold back and forth on themselves, with folds occurring at the faces; this structure, aptly termed the **chain-folded model**, is

Figure 14.11
Electron micrograph of a polyethylene single crystal. 20,000 \times . [From A. Keller, R. H. Doremus, B. W. Roberts, and D. Turnbull (Editors), *Growth and Perfection of Crystals*. General Electric Company and John Wiley & Sons, Inc., 1958, p. 498.]



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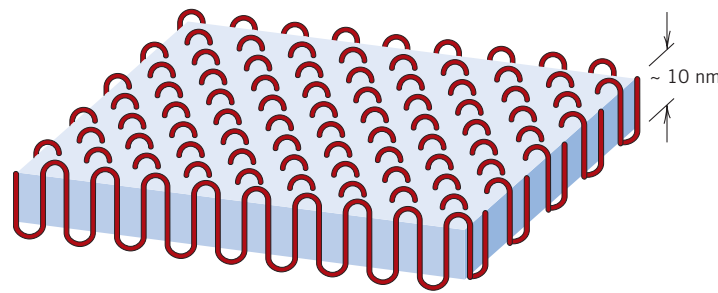


Figure 14.12 The chain-folded structure for a plate-shaped polymer crystallite.

illustrated schematically in Figure 14.12. Each platelet will consist of a number of molecules; however, the average chain length will be much greater than the thickness of the platelet.

spherulite

Many bulk polymers that are crystallized from a melt are semicrystalline and form a **spherulite** structure. As implied by the name, each spherulite may grow to be roughly spherical in shape; one of them, as found in natural rubber, is shown in the transmission electron micrograph, the chapter-opening photograph for this chapter. The spherulite consists of an aggregate of ribbon-like chain-folded crystallites (lamellae) approximately 10 nm thick that radiate outward from a single nucleation site in the center. In this electron micrograph, these lamellae appear as thin white lines. The detailed structure of a spherulite is illustrated schematically in Figure 14.13. Shown here are the individual chain-folded lamellar crystals that are separated by

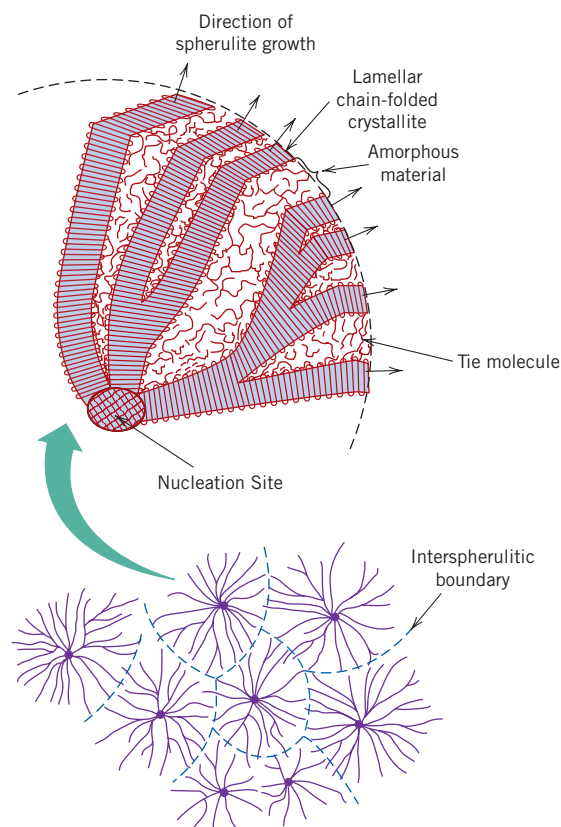
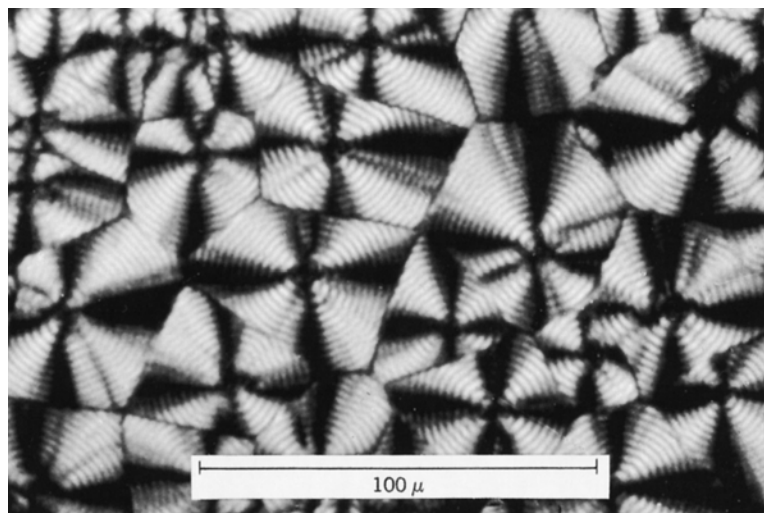


Figure 14.13 Schematic representation of the detailed structure of a spherulite.

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Figure 14.14 A transmission photomicrograph (using cross-polarized light) showing the spherulite structure of polyethylene. Linear boundaries form between adjacent spherulites, and within each spherulite appears a Maltese cross. 525 \times . (Courtesy F. P. Price, General Electric Company.)



amorphous material. Tie-chain molecules that act as connecting links between adjacent lamellae pass through these amorphous regions.

As the crystallization of a spherulitic structure nears completion, the extremities of adjacent spherulites begin to impinge on one another, forming more or less planar boundaries; prior to this time, they maintain their spherical shape. These boundaries are evident in Figure 14.14, which is a photomicrograph of polyethylene using cross-polarized light. A characteristic Maltese cross pattern appears within each spherulite. The bands or rings in the spherulite image result from twisting of the lamellar crystals as they extend like ribbons from the center.

Spherulites are considered to be the polymer analogue of grains in polycrystalline metals and ceramics. However, as discussed above, each spherulite is really composed of many different lamellar crystals and, in addition, some amorphous material. Polyethylene, polypropylene, poly(vinyl chloride), polytetrafluoroethylene, and nylon form a spherulitic structure when they crystallize from a melt.

14.13 DEFECTS IN POLYMERS

The point defect concept is different in polymers than in metals (Section 4.2) and ceramics (Section 12.5) as a consequence of the chain-like macromolecules and the nature of the crystalline state for polymers. Point defects similar to those found in metals have been observed in crystalline regions of polymeric materials; these include vacancies and interstitial atoms and ions. Chain ends are considered to be defects because they are chemically dissimilar to normal chain units. Vacancies are also associated with the chain ends (Figure 14.15). However, additional defects can result from branches in the polymer chain or chain segments that emerge from the crystal. A chain section can leave a polymer crystal and reenter it at another point creating a loop, or can enter a second crystal to act as a tie molecule (see Figure 14.13). Screw dislocations also occur in polymer crystals (Figure 14.15). Impurity atoms/ions or groups of atoms/ions may be incorporated in the molecular structure as interstitials; they may also be associated with main chains or as short side branches.

Furthermore, the surfaces of chain-folded layers (Figure 14.13) are considered to be interfacial defects, as are also boundaries between two adjacent crystalline regions.

Table 14.6 Permeability Coefficients P_M at 25°C for Oxygen, Nitrogen, Carbon Dioxide, and Water Vapor in a Variety of Polymers

Polymer	Acronym	P_M [$\times 10^{-13}$ (cm ³ STP)(cm)/(cm ² -s-Pa)]			
		O ₂	N ₂	CO ₂	H ₂ O
Polyethylene (low density)	LDPE	2.2	0.73	9.5	68
Polyethylene (high density)	HDPE	0.30	0.11	0.27	9.0
Polypropylene	PP	1.2	0.22	5.4	38
Poly(vinyl chloride)	PVC	0.034	0.0089	0.012	206
Polystyrene	PS	2.0	0.59	7.9	840
poly(vinylidene chloride)	PVDC	0.0025	0.00044	0.015	7.0
Poly(ethylene terephthalate)	PET	0.044	0.011	0.23	—
Poly(ethyl methacrylate)	PEMA	0.89	0.17	3.8	2380

Source: Adapted from J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe, and D. R. Bloch (Editors), *Polymer Handbook*, 4th edition. Copyright © 1999 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

the product of the diffusion coefficient (D) and solubility of the diffusing species in the polymer (S)—i.e.,

$$P_M = DS \quad (14.10)$$

Table 14.6 presents the permeability coefficients of oxygen, nitrogen, carbon dioxide, and water vapor in several common polymers.¹²

For some applications, low permeability rates through polymeric materials are desirable, as with food and beverage packaging and automobile tires and inner tubes. Polymer membranes are often used as filters, to selectively separate one chemical species from another (or others) (i.e., the desalinization of water). In such instances it is normally the case that the permeation rate of the substance to be filtered is significantly greater than for the other substance(s).

EXAMPLE PROBLEM 14.3

Computations of Diffusion Flux of Carbon Dioxide Through a Plastic Beverage Container and Beverage Shelf Life

The clear plastic bottles used for carbonated beverages (sometimes also called “soda,” “pop,” or “soda pop”) are made from poly(ethylene terephthalate)(PET). The “fizz” in pop results from dissolved carbon dioxide (CO₂);

¹² The units for permeability coefficients in Table 14.6 are unusual, which are explained as follows: When the diffusing molecular species is in the gas phase, solubility is equal to

$$S = \frac{C}{P}$$

where C is the concentration of the diffusing species in the polymer [in units of (cm³ STP)/cm³ gas] and P is the partial pressure (in units of Pa). STP indicates that this is the volume of gas at standard temperature and pressure [273 K (0°C) and 101.3 kPa (1 atm)]. Thus, the units for S are (cm³ STP)/Pa-cm³. Since D is expressed in terms of cm²/s, the units for the permeability coefficient are (cm³ STP)(cm)/(cm²-s-Pa).

Case Study:
“Chemical Protective Clothing,”
Chapter 22, which
may be found at
www.wiley.com/college/callister
(Student Companion Site)

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and, because PET is permeable to CO₂, pop stored in PET bottles will eventually go “flat” (i.e., lose its fizz). A 20 oz. bottle of pop has a CO₂ pressure of about 400 kPa inside the bottle and the CO₂ pressure outside the bottle is 0.4 kPa.

(a) Assuming conditions of steady state, calculate the diffusion flux of CO₂ through the wall of the bottle.

(b) If the bottle must lose 750 (cm³ STP) of CO₂ before the pop tastes flat, what is the shelf-life for a bottle of pop?

Note: Assume that each bottle has a surface area of 500 cm² and a wall thickness of 0.05 cm.

Solution

(a) This is a permeability problem in which Equation 14.9 is employed. The permeability coefficient of CO₂ through PET (Table 14.6) is 0.23×10^{-13} (cm³ STP)(cm)/(cm²-s-Pa). Thus, the diffusion flux is equal to

$$\begin{aligned} J &= -P_M \frac{\Delta P}{\Delta x} = -P_M \frac{P_2 - P_1}{\Delta x} \\ &= -0.23 \times 10^{-13} \frac{(\text{cm}^3 \text{ STP})(\text{cm})}{(\text{cm}^2)(\text{s})(\text{Pa})} \frac{(400 \text{ Pa} - 400,000 \text{ Pa})}{0.05 \text{ cm}} \\ &= 1.8 \times 10^{-7} (\text{cm}^3 \text{ STP})/(\text{cm}^2\text{-s}) \end{aligned}$$

(b) The flow rate of CO₂ through the wall of the bottle \dot{V}_{CO_2} is equal to

$$\dot{V}_{\text{CO}_2} = JA$$

where A is the surface area of the bottle (i.e., 500 cm²); therefore,

$$\dot{V}_{\text{CO}_2} = [1.8 \times 10^{-7} (\text{cm}^3 \text{ STP})/(\text{cm}^2\text{-s})](500 \text{ cm}^2) = 9.0 \times 10^{-5} (\text{cm}^3 \text{ STP})/\text{s}$$

The time it will take for a volume (V) of 750 (cm³ STP) to escape is calculated as

$$\begin{aligned} \text{time} &= \frac{V}{\dot{V}_{\text{CO}_2}} = \frac{750 (\text{cm}^3 \text{ STP})}{9.0 \times 10^{-5} (\text{cm}^3 \text{ STP})/\text{s}} = 8.3 \times 10^6 \text{ s} \\ &= 97 \text{ days (or about 3 months)} \end{aligned}$$

SUMMARY**Hydrocarbon Molecules****Polymer Molecules****The Chemistry of Polymer Molecules**

Most polymeric materials are composed of very large molecular chains with side-groups of various atoms (O, Cl, etc.) or organic groups such as methyl, ethyl, or phenyl groups. These macromolecules are composed of repeat units, smaller structural entities, which are repeated along the chain. Repeat units for some of the chemically simple polymers [i.e., polyethylene, polytetrafluoroethylene, poly(vinyl chloride), and polypropylene] were presented.

518 • Chapter 14 / Polymer Structures**Molecular Weight**

Molecular weights for high polymers may be in excess of a million. Since all molecules are not of the same size, there is a distribution of molecular weights. Molecular weight is often expressed in terms of number and weight averages. Chain length may also be specified by degree of polymerization, the number of repeat units per average molecule.

Molecular Shape**Molecular Structure****Molecular Configurations****Copolymers**

Several molecular characteristics that have an influence on the properties of polymers were discussed. Molecular entanglements occur when the chains assume twisted, coiled, and kinked shapes or contours. With regard to molecular structure, linear, branched, crosslinked, and network structures are possible, in addition to isotactic, syndiotactic, and atactic stereoisomers, and the cis and trans geometrical isomers. The copolymers include random, alternating, block, and graft types.

Thermoplastic and Thermosetting Polymers

With regard to behavior at elevated temperatures, polymers are classified as either thermoplastic or thermosetting. The former have linear and branched structures; they soften when heated and harden when cooled. In contrast, thermosets, once having hardened, will not soften upon heating; their structures are crosslinked and network.

Polymer Crystallinity**Polymer Crystals**

When the molecular chains are packed in an ordered atomic arrangement, the condition of crystallinity is said to exist. In addition to being entirely amorphous, polymers may also exhibit varying degrees of crystallinity; that is, crystalline regions are interdispersed within amorphous areas. Crystallinity is facilitated for polymers that are chemically simple and that have regular and symmetrical chain structures. Many semicrystalline polymers form spherulites; each spherulite consists of a collection of ribbon-like chain-folded lamellar crystallites that radiate outward from its center.

Defects in Polymers

Although the point defect state concept in polymers is different than metals and ceramics, vacancies, interstitial atoms, and impurity atoms/ions and groups of atoms/ions as interstitials have been found to exist in crystalline regions. Other defects include chains ends, dangling and loose chains, as well as dislocations.

Diffusion in Polymeric Materials

With regard to diffusion in polymers, small molecules of foreign substances diffuse between molecular chains, by an interstitial-type mechanism from one amorphous region to an adjacent one. Diffusion (or permeation) of gaseous species is often characterized in terms of the permeability coefficient, which is the product of the diffusion coefficient and solubility in the polymer. Permeation flow rates are expressed in terms of a modified form of Fick's first law.

IMPORTANT TERMS AND CONCEPTS

Alternating copolymer	Graft copolymer	Polymer crystallinity
Atactic configuration	Homopolymer	Random copolymer
Bifunctional	Isomerism	Repeat unit
Block copolymer	Isotactic configuration	Saturated
Branched polymer	Linear polymer	Spherulite
Chain-folded model	Macromolecule	Stereoisomerism
Cis (structure)	Molecular chemistry	Syndiotactic configuration
Copolymer	Molecular structure	Thermoplastic polymer
Crosslinked polymer	Molecular weight	Thermosetting polymer
Crystallite	Monomer	Trans (structure)
Degree of polymerization	Network polymer	Trifunctional
Functionality	Polymer	Unsaturated

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QUESTIONS AND PROBLEMS

Hydrocarbon Molecules

Polymer Molecules

The Chemistry of Polymer Molecules

- 14.1** On the basis of the structures presented in this chapter, sketch repeat unit structures for the following polymers: **(a)** polychlorotrifluoroethylene, and **(b)** poly(vinyl alcohol).

Molecular Weight

- 14.2** Compute repeat unit molecular weights for the following: **(a)** polytetrafluoroethylene, **(b)** poly(methyl methacrylate), **(c)** nylon 6,6, and **(d)** poly(ethylene terephthalate).
- 14.3** The number-average molecular weight of a polystyrene is 500,000 g/mol. Compute the degree of polymerization.
- 14.4 (a)** Compute the repeat unit molecular weight of polypropylene.
(b) Compute the number-average molecular weight for a polypropylene for which the degree of polymerization is 15,000.
- 14.5** Below, molecular weight data for a polytetrafluoroethylene material are tabulated. Compute **(a)** the number-average molecular weight, **(b)** the weight-average molecular weight, and **(c)** the degree of polymerization.

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Molecular Weight Range (g/mol)	x_i	w_i
10,000–20,000	0.03	0.01
20,000–30,000	0.09	0.04
30,000–40,000	0.15	0.11
40,000–50,000	0.25	0.23
50,000–60,000	0.22	0.24
60,000–70,000	0.14	0.18
70,000–80,000	0.08	0.12
80,000–90,000	0.04	0.07

- 14.6** Molecular weight data for some polymer are tabulated here. Compute **(a)** the number-average molecular weight, and **(b)** the weight-average molecular weight. **(c)** If it is known that this material's degree of polymerization is 477, which one of the polymers listed in Table 14.3 is this polymer? Why?

Molecular Weight Range (g/mol)	x_i	w_i
8,000–20,000	0.05	0.02
20,000–32,000	0.15	0.08
32,000–44,000	0.21	0.17
44,000–56,000	0.28	0.29
56,000–68,000	0.18	0.23
68,000–80,000	0.10	0.16
80,000–92,000	0.03	0.05

- 14.7** Is it possible to have a poly(vinyl chloride) homopolymer with the following molecular weight data, and a degree of polymerization of 1120? Why or why not?

Molecular Weight Range (g/mol)	w_i	x_i
8,000–20,000	0.02	0.05
20,000–32,000	0.08	0.15
32,000–44,000	0.17	0.21
44,000–56,000	0.29	0.28
56,000–68,000	0.23	0.18
68,000–80,000	0.16	0.10
80,000–92,000	0.05	0.03

- 14.8** High-density polyethylene may be chlorinated by inducing the random substitution of chlorine atoms for hydrogen.
- (a)** Determine the concentration of Cl (in wt%) that must be added if this substitution occurs for 8% of all the original hydrogen atoms.

- (b)** In what ways does this chlorinated polyethylene differ from poly(vinyl chloride)?

Molecular Shape

- 14.9** For a linear polymer molecule, the total chain length L depends on the bond length between chain atoms d , the total number of bonds in the molecule N , and the angle between adjacent backbone chain atoms θ , as follows:

$$L = Nd \sin\left(\frac{\theta}{2}\right) \quad (14.11)$$

Furthermore, the average end-to-end distance for a series of polymer molecules r in Figure 14.6 is equal to

$$r = d\sqrt{N} \quad (14.12)$$

A linear polyethylene has a number-average molecular weight of 300,000 g/mol; compute average values of L and r for this material.

- 14.10** Using the definitions for total chain molecule length, L (Equation 14.11) and average chain end-to-end distance r (Equation 14.12), for a linear polytetrafluoroethylene determine:

- (a)** the number-average molecular weight for $L = 2000$ nm;
(b) the number-average molecular weight for $r = 15$ nm.

Molecular Configurations

- 14.11** Sketch portions of a linear polypropylene molecule that are **(a)** syndiotactic, **(b)** atactic, and **(c)** isotactic.
- 14.12** Sketch cis and trans structures for **(a)** butadiene, and **(b)** chloroprene.

Thermoplastic and Thermosetting Polymers

- 14.13** Make comparisons of thermoplastic and thermosetting polymers **(a)** on the basis of mechanical characteristics upon heating, and **(b)** according to possible molecular structures.
- 14.14** **(a)** Is it possible to grind up and reuse phenol-formaldehyde? Why or why not?
(b) Is it possible to grind up and reuse polypropylene? Why or why not?

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Copolymers

- 14.15** Sketch the repeat structure for each of the following alternating copolymers: **(a)** poly(ethylene-propylene), **(b)** poly(butadiene-styrene), and **(c)** poly(isobutylene-isoprene).
- 14.16** The number-average molecular weight of a poly(acrylonitrile-butadiene) alternating copolymer is 1,000,000 g/mol; determine the average number of acrylonitrile and butadiene repeat units per molecule.
- 14.17** Calculate the number-average molecular weight of a random poly(isobutylene-isoprene) copolymer in which the fraction of isobutylene repeat units is 0.25; assume that this concentration corresponds to a degree of polymerization of 1500.
- 14.18** An alternating copolymer is known to have a number-average molecular weight of 100,000 g/mol and a degree of polymerization of 2210. If one of the repeat units is ethylene, which of styrene, propylene, tetrafluoroethylene, and vinyl chloride is the other repeat unit? Why?
- 14.19 (a)** Determine the ratio of butadiene to acrylonitrile repeat units in a copolymer having a number-average molecular weight of 250,000 g/mol and a degree of polymerization of 4640.
- (b)** Which type(s) of copolymer(s) will this copolymer be, considering the following possibilities: random, alternating, graft, and block? Why?
- 14.20** Crosslinked copolymers consisting of 35 wt% ethylene and 65 wt% propylene may have elastic properties similar to those for natural rubber. For a copolymer of this composition, determine the fraction of both repeat unit types.
- 14.21** A random poly(styrene-butadiene) copolymer has a number-average molecular weight of 350,000 g/mol and a degree of polymerization of 5000. Compute the fraction of styrene and butadiene repeat units in this copolymer.

Polymer Crystallinity
(Molecular Structure)

- 14.22** Explain briefly why the tendency of a polymer to crystallize decreases with increasing molecular weight.

- 14.23** For each of the following pairs of polymers, do the following: (1) state whether or not it is possible to determine whether one polymer is more likely to crystallize than the other; (2) if it is possible, note which is the more likely and then cite reason(s) for your choice; and (3) if it is not possible to decide, then state why.

- (a)** Linear and atactic poly(vinyl chloride); linear and isotactic polypropylene.
- (b)** Linear and syndiotactic polypropylene; crosslinked *cis*-isoprene.
- (c)** Network phenol-formaldehyde; linear and isotactic polystyrene.
- (d)** Block poly(acrylonitrile-isoprene) copolymer; graft poly(chloroprene-isobutylene) copolymer.

- 14.24** The density of totally crystalline nylon 6,6 at room temperature is 1.213 g/cm³. Also, at room temperature the unit cell for this material is triclinic with lattice parameters

$$\begin{aligned} a &= 0.497 \text{ nm} & \alpha &= 48.4^\circ \\ b &= 0.547 \text{ nm} & \beta &= 76.6^\circ \\ c &= 1.729 \text{ nm} & \gamma &= 62.5^\circ \end{aligned}$$

If the volume of a triclinic unit cell, V_{tri} , is a function of these lattice parameters as

$$V_{\text{tri}} = \frac{abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}}{2\cos\alpha\cos\beta\cos\gamma}$$

determine the number of repeat units per unit cell.

- 14.25** The density and associated percent crystallinity for two poly(ethylene terephthalate) materials are as follows:

ρ (g/cm ³)	Crystallinity (%)
1.408	74.3
1.343	31.2

- (a)** Compute the densities of totally crystalline and totally amorphous poly(ethylene terephthalate).
- (b)** Determine the percent crystallinity of a specimen having a density of 1.382 g/cm³.

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14.26 The density and associated percent crystallinity for two polypropylene materials are as follows:

ρ (g/cm ³)	Crystallinity (%)
0.904	62.8
0.895	54.4

- (a) Compute the densities of totally crystalline and totally amorphous polypropylene.
 (b) Determine the density of a specimen having 74.6% crystallinity.

Diffusion in Polymeric Materials

14.27 Consider the diffusion of oxygen through a low density polyethylene (LDPE) sheet 15 mm thick. The pressures of oxygen at the two faces are 2000 kPa and 150 kPa, which are maintained constant. Assuming conditions of steady state, what is the diffusion flux [in (cm³ STP)/cm²-s] at 298 K?

14.28 Carbon dioxide diffuses through a high density polyethylene (HDPE) sheet 50 mm thick at a rate of 2.2×10^{-8} (cm³ STP)/cm²-s at 325 K. The pressures of carbon dioxide at the

two faces are 4000 kPa and 2500 kPa, which are maintained constant. Assuming conditions of steady state, what is the permeability coefficient at 325 K?

14.29 The permeability coefficient of a type of small gas molecule in a polymer is dependent on absolute temperature according to the following equation:

$$P_M = P_{M_0} \exp\left(-\frac{Q_p}{RT}\right)$$

where P_{M_0} and Q_p are constants for a given gas-polymer pair. Consider the diffusion of water through a polystyrene sheet 30 mm thick. The water vapor pressures at the two faces are 20 kPa and 1 kPa, which are maintained constant. Compute the diffusion flux [in (cm³ STP)/cm²-s] at 350 K? For this diffusion system

$$P_{M_0} = 9.0 \times 10^{-5} \text{ (cm}^3 \text{ STP)/cm}^2\text{-s-Pa}$$

$$Q_p = 42.3 \text{ kJ/mol}$$

Also, assume a condition of steady state diffusion.