

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.

13.1 INTRODUCTION

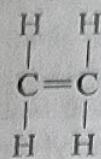
Naturally occurring polymers—those derived from plants and animals—have been used for many centuries; these materials include wood, rubber, cotton, wool, leather, and silk. Other natural polymers such as proteins, enzymes, starches, and cellulose are important in biological and physiological processes 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 In some applications metal and wood parts have been replaced by plastics, which have satisfactory properties and may be produced at a lower cost.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 14 discusses the relationships between structure and some of the physical and chemical properties, along with typical applications and forming methods.

13.2 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, 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 :



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.

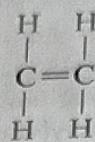
Some of the simple hydrocarbons belong to the paraffin family; the chainlike paraffin molecules include methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). Compositions and molecular structures for paraffin molecules are contained in Table 13.1. The covalent bonds in each molecule 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 13.1).

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

Table 13.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: $\text{C}_n\text{H}_{2n+2}$

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

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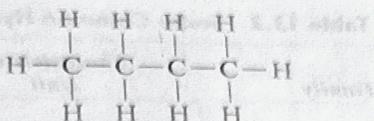
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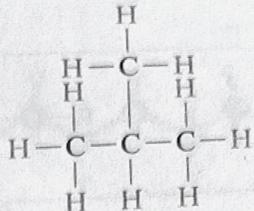
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Ethane	C_2H_6	$\begin{array}{ccccc} \text{H} & & \text{H} & & \\ & & & & \\ \text{H} - & \text{C} & - & \text{C} & - \text{H} \\ & & & & \\ \text{H} & & \text{H} & & \end{array}$	-88.6
Propane	C_3H_8	$\begin{array}{ccccc} \text{H} & & \text{H} & & \text{H} \\ & & & & \\ \text{H} - & \text{C} & - & \text{C} & - & \text{C} & - \text{H} \\ & & & & & & \\ \text{H} & & \text{H} & & \text{H} & & \end{array}$	-42.1
Butane	C_4H_{10}		-0.5
Pentane	C_5H_{12}		36.1
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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°C 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 13.2, where R and R' represent organic groups such as CH_3 , C_2H_5 , and C_6H_5 (methyl, ethyl, and phenyl).

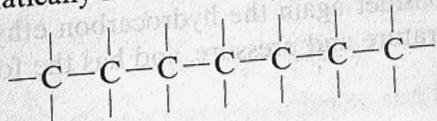
Concept Check 13.1

Differentiate between polymorphism (see Chapter 4) and isomerism.

[The answer may be found in enclosed CD.]

3.3 POLYMER MOLECULES

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 carbons 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.

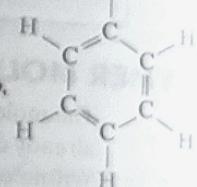
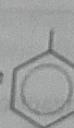
These long molecules are composed of structural entities called **repeat units**, which are successively repeated along the chain.¹ The term **monomer** refers to the small molecule from which a polymer is synthesized. Hence, monomer and repeat unit mean different things, but sometimes the term monomer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

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."

Table 13.2 Some Common Hydrocarbon Groups

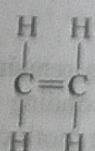
Family	Characteristic Unit	Representative Compound
Alcohols	$R-OH$	Methyl alcohol
Ethers	$R-O-R'$	Dimethyl ether
Acids	$R-C(OH)=O$	Acetic acid
Aldehydes	$R-C(=O)H$	Formaldehyde
Aromatic hydrocarbons	C_6H_5R	Phenol

* The simplified structure  denotes a phenyl group,



13.4 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:

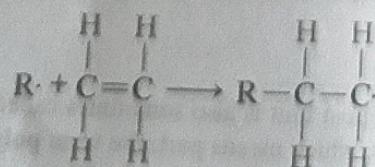
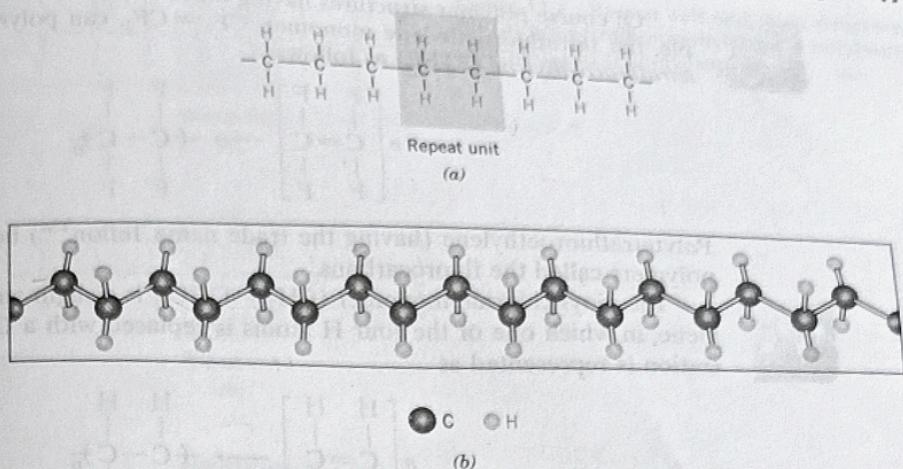
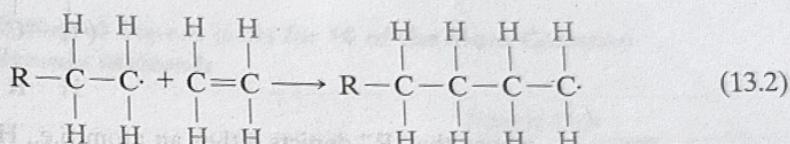


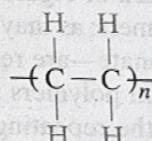
Figure 13.1 For polyethylene, (a) a schematic representation of repeat unit and chain structures, and (b) a perspective of the molecule, indicating the zigzag backbone structure.



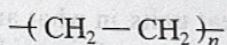
The polymer chain then forms by the sequential addition of monomer units to this active growing chain molecule. The active site, or unpaired electron (denoted by \cdot), is transferred to each successive end monomer as it is linked to the chain. This may be represented schematically as follows:



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 13.1a. 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

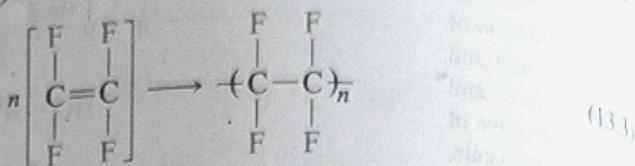
The representation in Figure 13.1a is not strictly correct in that the angle between the singly bonded carbon atoms is not 180° as shown, but rather close to 109° . A more accurate three-dimensional model is one in which the carbon atoms form a zigzag pattern (Figure 13.1b), the C—C bond length being 0.154 nm. In this discussion, depiction of polymer molecules is frequently simplified using the linear chain model shown in Figure 13.1a.

² A more detailed discussion of polymerization reactions including both addition and condensation mechanisms is given in Section 14.20.

³ Chain ends/end-groups (i.e., the R_s in Equation 13.2) are not normally represented in chain structures.

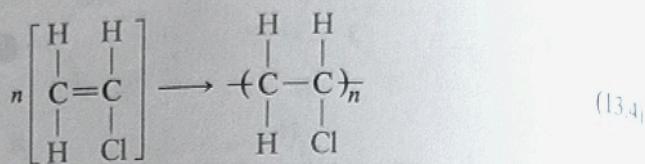


Of course polymer structures having other chemistries are possible. For example, the tetrafluoroethylene monomer, $\text{CF}_2=\text{CF}_2$, can polymerize to form *Polytetrafluoroethylene* (PTFE) as follows:



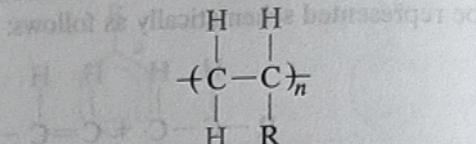
Polytetrafluoroethylene (having the trade name **Teflon™**) belongs to a family of polymers called the fluorocarbons.

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:



(CD)



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 13.2. Table 13.3 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 13.10).

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 13.3), are **trifunctional**; they have three active bonds, from which a three-dimensional molecular network structure results.

Concept Check 13.2

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 in enclosed CD.]

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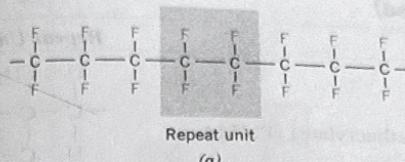


Figure 13.2 Repeat unit and chain structures for (a) polytetrafluoroethylene, (b) poly(vinyl chloride), and (c) polypropylene.

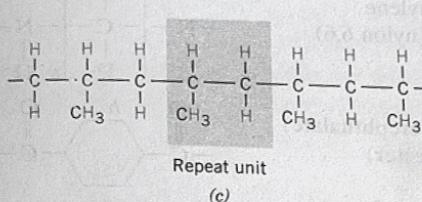
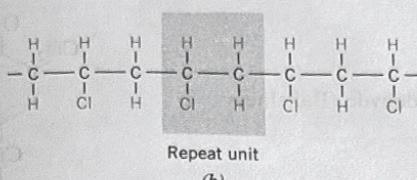
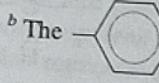
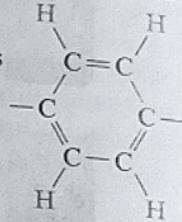


Table 13.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

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

(Continued)

Table 13.3 (Continued)

Polymer	Repeat Unit
 Poly(methyl methacrylate) (PMMA)	$\begin{array}{c} \text{H} & \text{CH}_3 \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{C}-\text{O}-\text{CH}_3 \\ \\ \text{O} \end{array}$
 Phenol-formaldehyde (Bakelite)	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2-\text{C}_6\text{H}_3(\text{CH}_2)_2-\text{CH}_2 \end{array}$
 Poly(hexamethylene adipamide) (nylon 6,6)	$\begin{array}{c} \text{H} \\ \\ -\text{N}-\left[\begin{array}{c} \text{H} \\ \\ -\text{C}- \\ \\ \text{H} \end{array}\right]_6\text{H}-\text{N}-\text{C}(=\text{O})-\left[\begin{array}{c} \text{H} \\ \\ -\text{C}- \\ \\ \text{H} \end{array}\right]_4\text{C}(=\text{O})- \end{array}$
 Poly(ethylene terephthalate) (PET, a polyester)	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}-\text{C}(=\text{O})-\text{O}- \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
 Polycarbonate (PC)	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{O}-\text{C}(=\text{O})- \end{array}$
^b The  symbol in the backbone chain denotes an aromatic ring as	
	

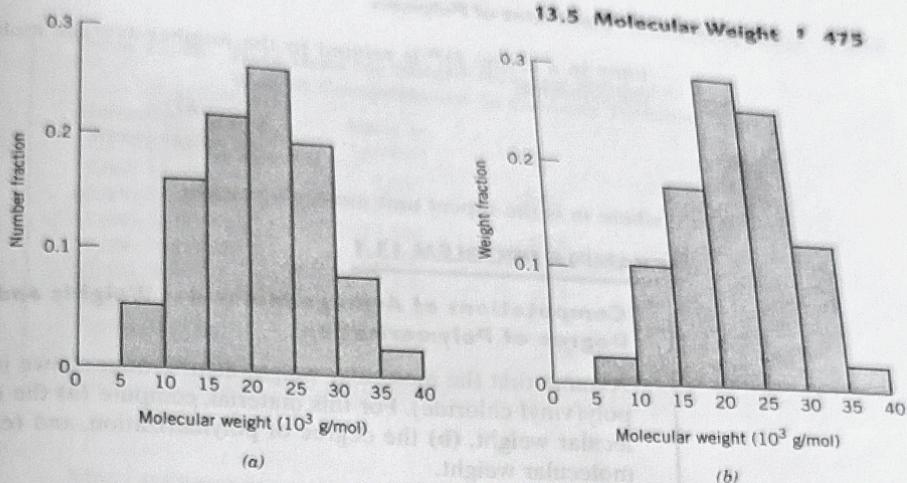
13.5 MOLECULAR WEIGHT

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.

Figure 13.3
Hypothetical
polymer molecule
size distributions
(a) number and
(b) weight fractions
of molecules.



ranges and then determining the number fraction of chains within each size range (Figure 13.3a). The number-average molecular weight is expressed as

$$\bar{M}_n = \sum x_i M_i \quad (13.5a)$$

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 13.3b). It is calculated according to

$$\bar{M}_w = \sum w_i M_i \quad (13.5b)$$

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 13.1. A typical molecular weight distribution along with these molecular weight averages is shown in Figure 13.4.

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 13.4 Distribution of molecular weights for a typical polymer.

