

CHAPTER 1

INTRODUCTION

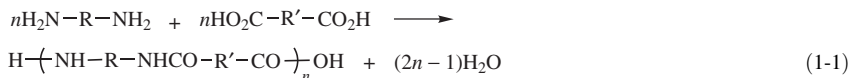
Polymers are macromolecules built up by the linking together of large numbers of much smaller molecules. The small molecules that combine with each other to form polymer molecules are termed *monomers*, and the reactions by which they combine are termed *polymerizations*. There may be hundreds, thousands, tens of thousands, or more monomer molecules linked together in a polymer molecule. When one speaks of polymers, one is concerned with materials whose molecular weights may reach into the hundreds of thousands or millions.

1-1 TYPES OF POLYMERS AND POLYMERIZATIONS

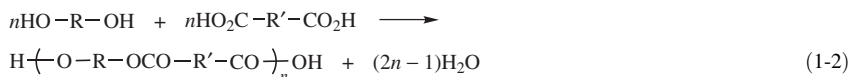
There has been and still is considerable confusion concerning the classification of polymers. This is especially the case for the beginning student who must appreciate that there is no single generally accepted classification that is unambiguous. During the development of polymer science, two types of classifications have come into use. One classification is based on polymer structure and divides polymers into *condensation* and *addition* polymers. The other classification is based on polymerization mechanism and divides polymerizations into *step* and *chain* polymerizations. Confusion arises because the two classifications are often used interchangeably without careful thought. The terms *condensation* and *step* are often used synonymously, as are the terms *addition* and *chain*. Although these terms may often be used synonymously because most condensation polymers are produced by step polymerizations and most addition polymers are produced by chain polymerizations, this is not always the case. The condensation–addition classification is based on the composition or structure of polymers. The step–chain classification is based on the mechanisms of the polymerization processes.

1-1a Polymer Composition and Structure

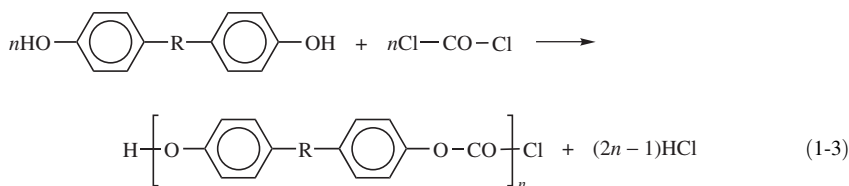
Polymers were originally classified by Carothers [1929] into condensation and addition polymers on the basis of the compositional difference between the polymer and the monomer(s) from which it was synthesized. Condensation polymers were those polymers that were formed from polyfunctional monomers by the various condensation reactions of organic chemistry with the elimination of some small molecule such as water. An example of such a condensation polymer is the polyamides formed from diamines and diacids with the elimination of water according to



where R and R' are aliphatic or aromatic groupings. The unit in parentheses in the polyamide formula repeats itself many times in the polymer chain and is termed the *repeating unit*. The elemental composition of the repeating unit differs from that of the two monomers by the elements of water. The polyamide synthesized from hexamethylene diamine, $\text{R} = (\text{CH}_2)_6$, and adipic acid, $\text{R}' = (\text{CH}_2)_4$, is the extensively used fiber and plastic known commonly as nylon 6/6 or poly(hexamethylene adipamide). Other examples of condensation polymers are the polyesters formed from diacids and diols with the elimination of water and the



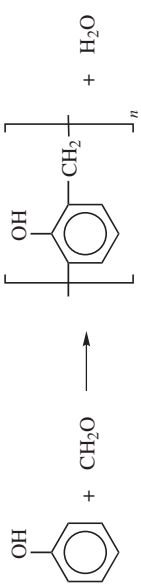
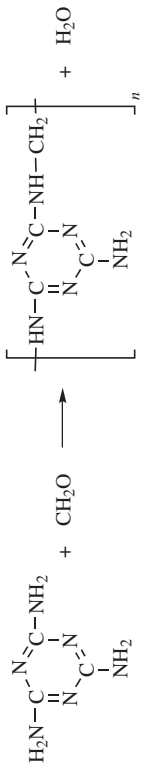
polycarbonates from the reaction of an aromatic dihydroxy reactant and phosgene with the elimination of hydrogen chloride:



The common condensation polymers and the reactions by which they are formed are shown in Table 1-1. It should be noted from Table 1-1 that for many of the condensation polymers there are different combinations of reactants that can be employed for their synthesis. Thus polyamides can be synthesized by the reactions of diamines with diacids or diacyl chlorides and by the self-condensation of amino acids. Similarly, polyesters can be synthesized from diols by esterification with diacids or ester interchange with diesters.

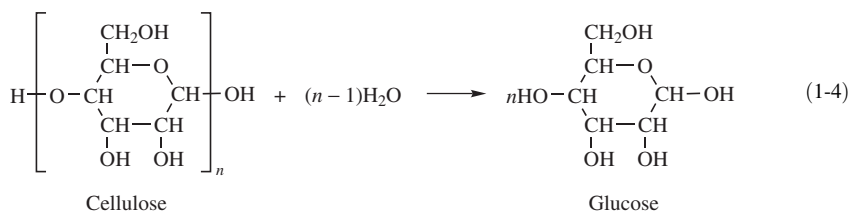
Some naturally occurring polymers such as cellulose, starch, wool, and silk are classified as condensation polymers, since one can postulate their synthesis from certain hypothetical reactants by the elimination of water. Thus cellulose can be thought of as the polyether formed by the dehydration of glucose. Carothers included such polymers by defining condensation polymers as those in which the formula of the repeating unit lacks certain atoms that are present in the monomer(s) from which it is formed or to which it may be degraded. In this

TABLE 1-1 Typical Condensation Polymers

Type	Characteristic Linkage	Polymerization Reaction
Polyamide	$-\text{NH}-\text{CO}-$	$\text{H}_2\text{N}-\text{R}-\text{NH}_2 + \text{HO}_2\text{C}-\text{R}'-\text{CO}_2\text{H} \longrightarrow \text{H}(\text{NH}-\text{R}-\text{NHCO}-\text{R}'-\text{CO})_n\text{OH} + \text{H}_2\text{O}$ $\text{H}_2\text{N}-\text{R}-\text{NH}_2 + \text{ClCO}-\text{R}'-\text{COCl} \longrightarrow \text{H}(\text{NH}-\text{R}-\text{NHCO}-\text{R}'-\text{CO})_n\text{Cl} + \text{HCl}$ $\text{H}_2\text{N}-\text{R}-\text{CO}_2\text{H} \longrightarrow \text{H}(\text{NH}-\text{R}-\text{CO})_n\text{OH} + \text{H}_2\text{O}$ Naturally occurring polypeptide polymers; degradable to mixtures of different amino acids.
Protein, wool, silk	$-\text{NH}-\text{CO}-$	$\text{H}(\text{NH}-\text{R}-\text{CONH}-\text{R}'-\text{CO})_n\text{OH} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{N}-\text{R}-\text{CO}_2\text{H} + \text{H}_2\text{N}-\text{R}'-\text{CO}_2\text{H}$
Polyester	$-\text{CO}-\text{O}-$	$\text{HO}-\text{R}-\text{OH} + \text{HO}_2\text{C}-\text{R}'-\text{CO}_2\text{H} \longrightarrow \text{H}(\text{O}-\text{R}-\text{OCO}-\text{R}'-\text{CO})_n\text{OH} + \text{H}_2\text{O}$ $\text{HO}-\text{R}-\text{OH} + \text{R}'\text{O}_2\text{C}-\text{R}'-\text{CO}_2\text{R}'' \longrightarrow \text{H}(\text{O}-\text{R}-\text{OCO}-\text{R}'-\text{CO})_n\text{OH} + \text{R}''\text{OH}$ $\text{HO}-\text{R}-\text{CO}_2\text{H} \longrightarrow \text{H}(\text{O}-\text{R}-\text{CO})_n\text{OH} + \text{H}_2\text{O}$
Polyurethane	$-\text{O}-\text{CO}-\text{NH}-$	$\text{HO}-\text{R}-\text{OH} + \text{OCN}-\text{R}'-\text{NCO} \longrightarrow (\text{O}-\text{R}-\text{OCO}-\text{NH}-\text{R}'-\text{NH}-\text{CO})_n$
Polysiloxane	$-\text{Si}-\text{O}-$	$\text{Cl}-\text{SiR}_2-\text{Cl} \xrightarrow[\text{-HCl}]{\text{H}_2\text{O}} \text{HO}-\text{SiR}_2-\text{OH} \longrightarrow \text{H}(\text{O}-\text{SiR}_2)_n\text{OH} + \text{H}_2\text{O}$
Phenol-formaldehyde	$-\text{Ar}-\text{CH}_2-$	
Urea-formaldehyde	$-\text{NH}-\text{CH}_2-$	$\text{H}_2\text{N}-\text{CO}-\text{NH}_2 + \text{CH}_2\text{O} \longrightarrow (\text{HN}-\text{CO}-\text{NH}-\text{CH}_2)_n + \text{H}_2\text{O}$
Melamine-formaldehyde	$-\text{NH}-\text{CH}_2-$	
Polysulfide	$-\text{S}_m-$	$\text{Cl}-\text{R}-\text{Cl} + \text{Na}_2\text{S}_m \longrightarrow (\text{S}_m-\text{R})_n + \text{NaCl}$
Polyacetal	$-\text{O}-\underset{\text{R}}{\text{CH}}-\text{O}-$	$\text{R}-\text{CHO} + \text{HO}-\text{R}'-\text{OH} \longrightarrow (\text{O}-\text{R}'-\text{OCHR})_n + \text{H}_2\text{O}$

4 INTRODUCTION

sense cellulose is considered a condensation polymer, since its hydrolysis yields glucose, which contains the repeating unit of cellulose plus the elements of water

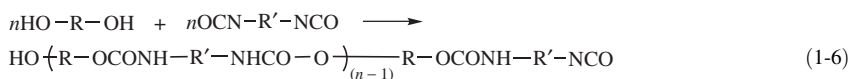


Addition polymers were classified by Carothers as those formed from monomers without the loss of a small molecule. Unlike condensation polymers, the repeating unit of an addition polymer has the same composition as the monomer. The major addition polymers are those formed by polymerization of monomers containing the carbon-carbon double bond. Such monomers will be referred to as *vinyl monomers* throughout this text. (The term *vinyl*, strictly speaking, refers to a $\text{CH}_2=\text{CH}-$ group attached to some substituent. Our use of the term *vinyl monomer* is broader—it applies to all monomers containing a carbon-carbon double bond, including monomers such as methyl methacrylate, vinylidene chloride, and 2-butene as well as vinyl chloride and styrene. The term *substituted ethylenes* will also be used interchangeably with the term vinyl monomers.) Vinyl monomers can be made to react with themselves to form polymers by conversion of their double bonds into saturated linkages, for example



where Y can be any substituent group such as hydrogen, alkyl, aryl, nitrile, ester, acid, ketone, ether, and halogen. Table 1-2 shows many of the common addition polymers and the monomers from which they are produced.

The development of polymer science with the study of new polymerization processes and polymers showed that the original classification by Carothers was not entirely adequate and left much to be desired. Thus, for example, consider the polyurethanes, which are formed by the reaction of diols with diisocyanates without the elimination of any small molecule:



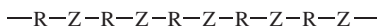
Using Carothers' original classification, one would classify the polyurethanes as addition polymers, since the polymer has the same elemental composition as the sum of the monomers. However, the polyurethanes are structurally much more similar to the condensation polymers than to the addition polymers. The urethane linkage ($-\text{NH}-\text{CO}-\text{O}-$) has much in common with the ester ($-\text{CO}-\text{O}-$) and amide ($-\text{NH}-\text{CO}-$) linkages.

To avoid the obviously incorrect classification of polyurethanes as well as of some other polymers as addition polymers, polymers have also been classified from a consideration of the chemical structure of the groups present in the polymer chains. Condensation polymers have been defined as those polymers whose repeating units are joined together by functional

TABLE 1-2 Typical Addition Polymers

Polymer	Monomer	Repeating Unit
Polyethylene	$\text{CH}_2=\text{CH}_2$	$-\text{CH}_2-\text{CH}_2-$
Polyisobutylene	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{CH}_3 \end{array}$
Polyacrylonitrile	$\text{CH}_2=\text{CH}-\text{CN}$	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CN} \end{array}$
Poly(vinyl chloride)	$\text{CH}_2=\text{CH}-\text{Cl}$	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{Cl} \end{array}$
Polystyrene	$\text{CH}_2=\text{CH}-\phi$	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \phi \end{array}$
Poly(methyl methacrylate)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{CO}_2\text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{CO}_2\text{CH}_3 \end{array}$
Poly(vinyl acetate)	$\text{CH}_2=\text{CH}-\text{OCOCH}_3$	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{OCOCH}_3 \end{array}$
Poly(vinylidene chloride)	$\begin{array}{c} \text{Cl} \\ \\ \text{CH}_2=\text{C} \\ \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{Cl} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{Cl} \end{array}$
Polytetrafluoroethylene	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \text{C}=\text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array}$	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{F} \quad \text{F} \end{array}$
Polyisoprene (natural rubber)	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$

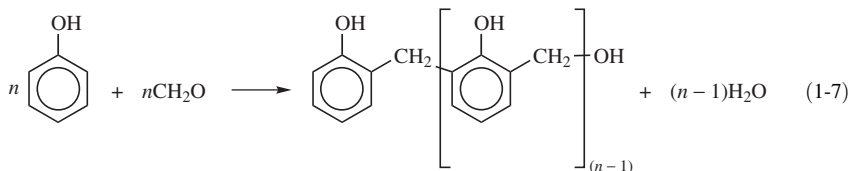
units of one kind or another such as the ester, amide, urethane, sulfide, and ether linkages. Thus the structure of condensation polymers has been defined by



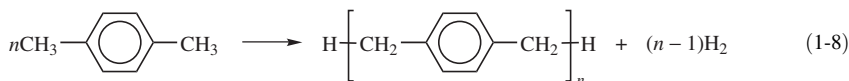
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where R is an aliphatic or aromatic grouping and Z is a functional unit such as $-\text{OCO}-$, $-\text{NHCO}-$, $-\text{S}-$, $-\text{OCONH}-$, $-\text{O}-$, $-\text{OCOO}-$, and $-\text{SO}_2-$. Addition polymers, on the other hand, do not contain such functional groups as part of the polymer chain. Such groups may, however, be present in addition polymers as pendant substituents hanging off the polymer chain. According to this classification, the polyurethanes are readily and more correctly classified as condensation polymers.

It should not be taken for granted that all polymers that are defined as condensation polymers by Carothers' classification will also be so defined by a consideration of the polymer chain structure. Some condensation polymers do not contain functional groups such as ester or amide in the polymer chain. An example is the phenol-formaldehyde polymers produced by the reaction of phenol (or substituted phenols) with formaldehyde



These polymers do not contain a functional group within the polymer chain but are classified as condensation polymers, since water is split out during the polymerization process. Another example is poly(*p*-xylene), which is produced by the oxidative coupling (dehydrogenation) of *p*-xylene:



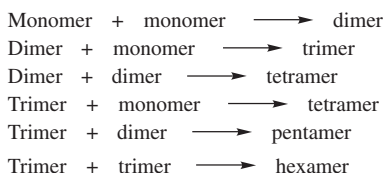
In summary, a polymer is classified as a condensation polymer if its synthesis involves the elimination of small molecules, or it contains functional groups as part of the polymer chain, or its repeating unit lacks certain atoms that are present in the (hypothetical) monomer to which it can be degraded. If a polymer does not fulfill any of these requirements, it is classified as an addition polymer.

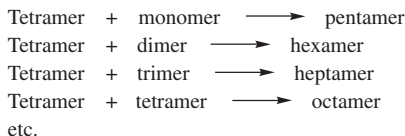
1-1b Polymerization Mechanism

In addition to the structural and compositional differences between polymers, Flory [1953] stressed the very significant difference in the mechanism by which polymer molecules are built up. Although Flory continued to use the terms condensation and addition in his discussions of polymerization mechanism, the more recent terminology classifies polymerizations into step and chain polymerizations.

Chain and step polymerizations differ in several features, but the most important difference is in the identities of the species that can react with each other. Another difference is the manner in which polymer molecular size depends on the extent of conversion.

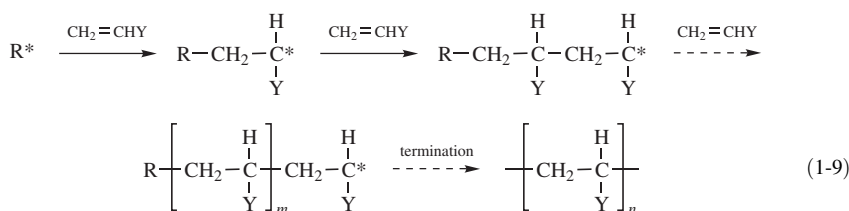
Step polymerizations proceed by the stepwise reaction between the functional groups of reactants as in reactions such as those described by Eqs. 1-1 through 1-3 and Eqs. 1-6 through 1-8. The size of the polymer molecules increases at a relatively slow pace in such polymerizations. One proceeds from monomer to dimer, trimer, tetramer, pentamer, and so on





until eventually large-sized polymer molecules have been formed. The characteristic of step polymerization that distinguishes it from chain polymerization is that reaction occurs between any of the different-sized species present in the reaction system.

The situation is quite different in chain polymerization where an initiator is used to produce an initiator species R^* with a reactive center. The reactive center may be either a free radical, cation, or anion. Polymerization occurs by the propagation of the reactive center by the successive additions of large numbers of monomer molecules in a chain reaction. The distinguishing characteristic of chain polymerization is that polymer growth takes place by monomer reacting only with the reactive center. Monomer does not react with monomer and the different-sized species such as dimer, trimer, tetramer, and n -mer do not react with each other. By far the most common example of chain polymerization is that of vinyl monomers. The process can be depicted as



Each monomer molecule that adds to a reactive center regenerates the reactive center. Polymer growth proceeds by the successive additions of hundreds or thousands or more monomer molecules. The growth of the polymer chain ceases when the reactive center is destroyed by one or more of a number of possible termination reactions.

The typical step and chain polymerizations differ significantly in the relationship between polymer molecular weight and the percent conversion of monomer. Thus if we start out step and chain polymerizations side by side, we may observe a variety of situations with regard to their relative rates of polymerization. However, the molecular weights of the polymers produced at any time after the start of the reactions will always be very characteristically different for the two polymerizations. If the two polymerizations are stopped at 0.1% conversion, 1% conversion, 10% conversion, 40% conversion, 90% conversion, and so on, one will always observe the same behavior. The chain polymerization will show the presence of high-molecular-weight polymer molecules at all percents of conversion. There are no intermediate-sized molecules in the reaction mixture—only monomer, high-polymer, and initiator species. The only change that occurs with conversion (i.e., reaction time) is the continuous increase in the number of polymer molecules (Fig. 1-1a). On the other hand, high-molecular-weight polymer is obtained in step polymerizations only near the very end of the reaction (>98% conversion) (Fig. 1-1b). Thus both polymer size and the amount of polymer are dependent on conversion in step polymerization.

The classification of polymers according to polymerization mechanism, like that by structure and composition, is not without its ambiguities. Certain polymerizations show a linear increase of molecular weight with conversion (Fig. 1-1c) when the polymerization

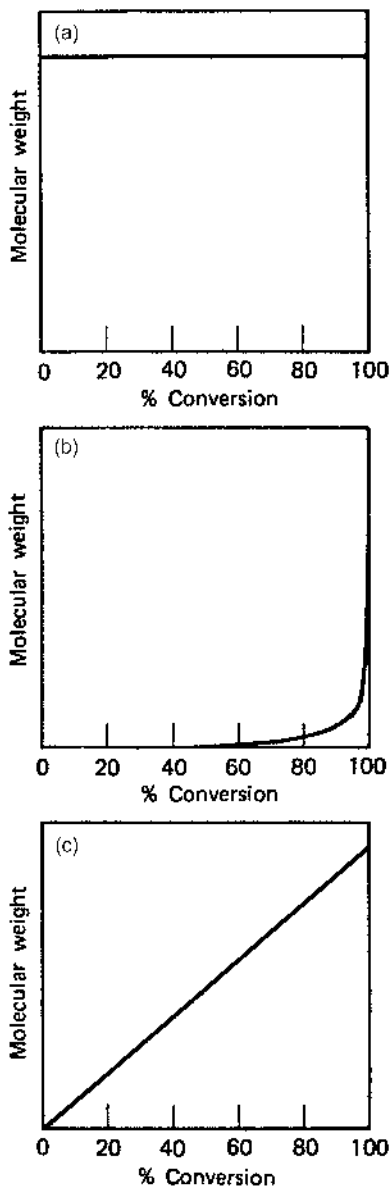
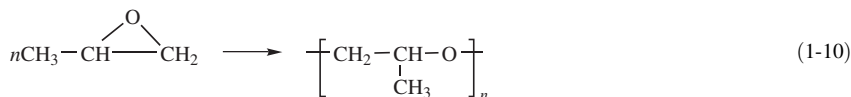


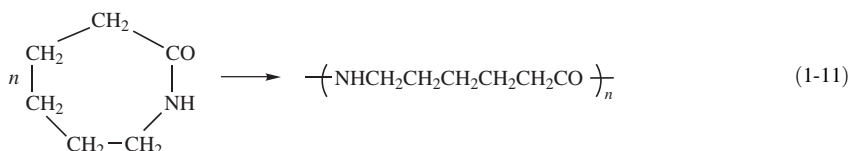
Fig. 1-1 Variation of molecular weight with conversion; (a) chain polymerization; (b) step polymerization; (c) nonterminating chain polymerization and protein synthesis.

mechanism departs from the normal chain pathway. This is observed in certain chain polymerizations, which involve a fast initiation process coupled with the absence of reactions that terminate the propagating reactive centers. Biological syntheses of proteins also show the behavior described by Fig. 1-1c because the various monomer molecules are directed to react in a very specific manner by an enzymatically controlled process.

The ring-opening polymerizations of cyclic monomers such as propylene oxide



or ϵ -caprolactam



usually proceed by the chain polymerization mechanism, but the dependence of polymer molecular weight on conversion almost never follows the behavior in Fig. 1-1a. Ring-opening polymerizations often follow the behavior in Fig. 1-1c.

The International Union of Pure and Applied Chemistry [IUPAC, 1994] suggested the term *polycondensation* instead of step polymerization, but polycondensation is a narrower term than step polymerization since it implies that the reactions are limited to condensations—reactions in which small molecules such as water are expelled during polymerization. The term step polymerization encompasses not only condensations but also polymerizations in which no small molecules are expelled. An example of the latter is the reaction of diols and diisocyanates to yield polyurethanes (Eq. 1-6). The formation of polyurethanes follows the same reaction characteristics as the formation of polyesters, polyamides, and other polymerizations in which small molecules are expelled.

Ring-opening polymerizations point out very clearly that one must distinguish between the classification of the polymerization mechanism and that of the polymer structure. The two classifications cannot always be used interchangeably. Polymers such as the polyethers and polyamides produced in Eqs. 1-10 and 1-11, as well as those from other cyclic monomers, must be separately classified as to polymerization mechanism and polymer structure. These polymers are structurally classified as condensation polymers, since they contain functional groups (e.g., ether, amide) in the polymer chain. They, like the polyurethanes, are not classified as addition polymers by the use of Carothers' original classification. The situation is even more complicated for a polymer such as that obtained from ϵ -caprolactam. The exact same polymer can be obtained by the step polymerization of the linear monomer ϵ -amino-caproic acid. It should suffice at this point to stress that the terms condensation and step polymer or polymerization are not synonymous nor are the terms addition and chain polymer or polymerization, even though these terms are often used interchangeably. The classification of polymers based only on polymer structure or only on polymerization mechanism is often an oversimplification that leads to ambiguity and error. Both structure and mechanism are usually needed in order to clearly classify a polymer.

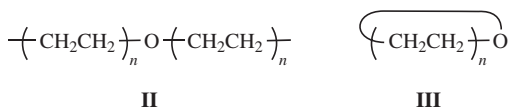
1-2 NOMENCLATURE OF POLYMERS

Polymer nomenclature leaves much to be desired. A standard nomenclature system based on chemical structure as is used for small inorganic and organic compounds is most desired.

Unfortunately, the naming of polymers has not proceeded in a systematic manner until relatively late in the development of polymer science. It is not at all unusual of a polymer to have several names because of the use of different nomenclature systems. The nomenclature systems that have been used are based on either the structure of the polymer or the source of the polymer [i.e., the monomer(s) used in its synthesis] or trade names. Not only have there been several different nomenclature systems, but their application has not always been rigorous. An important step toward standardization was initiated in the 1970s by the International Union of Pure and Applied Chemistry.

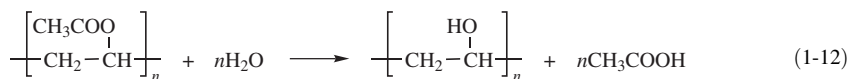
1-2a Nomenclature Based on Source

The most simple and commonly used nomenclature system is probably that based on the source of the polymer. This system is applicable primarily to polymers synthesized from a single monomer as in addition and ring-opening polymerizations. Such polymers are named by adding the name of the monomer onto the prefix "poly" without a space or hyphen. Thus the polymers from ethylene and acetaldehyde are named *polyethylene* and *polyacetaldehyde*, respectively. When the monomer has a substituted parent name or a multiworded name or an abnormally long name, parentheses are placed around its name following the prefix "poly." The polymers from 3-methyl-1-pentene, vinyl chloride, propylene oxide, chlorotrifluoroethylene, and ϵ -caprolactam are named poly(3-methyl-1-pentene), poly(vinyl chloride), poly(propylene oxide), poly(chlorotrifluoroethylene), and poly(ϵ -caprolactam), respectively. Other examples are listed in Table 1-2. The parentheses are frequently omitted in common usage when naming polymers. Although this will often not present a problem, it is incorrect and in some cases the omission can lead to uncertainty as to the structure of the polymer named. Thus the use of polyethylene oxide instead of poly(ethylene oxide) can be ambiguous in denoting one of the following possible structures:



instead of the polymer, $\left(\text{CH}_2\text{CH}_2\text{—O} \right)_n$, from ethylene oxide.

Some polymers are named as being derived from hypothetical monomers. Thus poly(vinyl alcohol) is actually produced by the hydrolysis of poly(vinyl acetate)



It is, however, named as a product of the hypothetical monomer vinyl alcohol (which in reality exists exclusively as the tautomer—acetaldehyde).

Condensation polymers synthesized from single reactants are named in a similar manner. Examples are the polyamides and polyesters produced from amino acids and hydroxy acids, respectively. Thus, the polymer from 6-aminocaproic acid is named poly(6-aminocaproic acid)



6-Aminocaproic acid



Poly(6-aminocaproic acid)

It should be noted that there is an ambiguity here in that poly(6-aminocaproic acid) and poly(ϵ -caprolactam) are one and the same polymer. The same polymer is produced from two different monomers—a not uncommonly encountered situation.

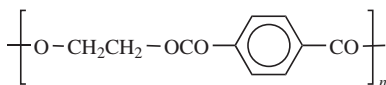
1-2b Nomenclature Based on Structure (Non-IUPAC)

A number of the more common condensation polymers synthesized from two different monomers have been named by a semisystematic, structure-based nomenclature system other than the more recent IUPAC system. The name of the polymer is obtained by following the prefix *poly* without a space or hyphen with parentheses enclosing the name of the structural grouping attached to the parent compound. The parent compound is the particular member of the class of the polymer—the particular ester, amide, urethane, and so on. Thus the polymer from hexamethylene diamine and sebacic acid is considered as the substituted amide derivative of the compound sebacic acid, $\text{HO}_2\text{C}(\text{CH}_2)_8\text{CO}_2\text{H}$, and is named poly(hexamethylene sebacamide). Poly(ethylene terephthalate) is the polymer from ethylene glycol and terephthalic acid, $p\text{-HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$. The polymer from trimethylene glycol and ethylene diisocyanate is poly(trimethylene ethyleneurethane)



Poly(hexamethylene sebacamide)

IV



Poly(ethylene terephthalate)

V



Poly(trimethylene ethyleneurethane)

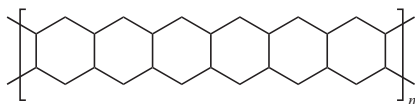
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A suggestion was made to name condensation polymers synthesized from two different monomers by following the prefix *poly* with parentheses enclosing the names of the two reactants, with the names of the reactants separated by the term *-co-*. Thus, the polymer in Eq. 1-7 would be named poly(phenol-*co*-formaldehyde). This suggestion did not gain acceptance.

1-2c IUPAC Structure-Based Nomenclature System

The inadequacy of the preceding nomenclature systems was apparent as the polymer structures being synthesized became increasingly complex. The IUPAC rules allow one to name

single-strand organic polymers in a systematic manner based on polymer structure (IUPAC, 1991, 1994, 2002, in press; Panico et al., 1993; Wilks, 2000). Single-strand organic polymers have any pair of adjacent repeat units interconnected through only one atom. All the polymers discussed to this point and the large majority of polymers to be considered in this text are single-strand polymers. *Double-strand* polymers have uninterrupted sequences of rings. A ladder polymer is a double-strand polymer in which adjacent rings have two or more atoms in common, for example, structure **VII**. Some aspects of double-strand polymers are considered in Secs. 2-14a and 2-17d.



VII

The basis of IUPAC polymer nomenclature system is the selection of a preferred *constitutional repeating unit* (abbreviated as CRU). The CRU is also referred to as the *structural repeating unit*. The CRU is the smallest possible repeating unit of the polymer. It is a bivalent unit for a single-strand polymer. The name of the polymer is the name of the CRU in parentheses or brackets prefixed by *poly*. The CRU is synonymous with the repeating unit defined in Sec. 1-1a except when the repeating unit consists of two symmetric halves, as in the polymers $\text{-(CH}_2\text{CH}_2\text{)}_n\text{-}$ and $\text{-(CF}_2\text{CF}_2\text{)}_n\text{-}$. The CRU is CH_2 and CF_2 , respectively, for polyethylene and polytetrafluoroethylene, while the repeating unit is CH_2CH_2 and CF_2CF_2 , respectively.

The constitutional repeating unit is named as much as possible according to the IUPAC nomenclature rules for small organic compounds. The IUPAC rules for naming single-strand polymers dictate the choice of a single CRU so as to yield a unique name, by specifying both the *seniority* among the atoms or subunits making up the CRU and the direction to proceed along the polymer chain to the end of the CRU. A CRU is composed of two or more *subunits* when it cannot be named as a single unit. The following is a summary of the most important of the IUPAC rules for naming single-strand organic polymers:

1. The name of a polymer is the prefix *poly* followed in parentheses or brackets by the name of the CRU. The CRU is named by naming its subunits. Subunits are defined as the largest subunits that can be named by the IUPAC rules for small organic compounds.
2. The CRU is written from left to right beginning with the subunit of highest seniority and proceeding in the direction involving the shortest route to the subunit next in seniority.
3. The seniority of different types of subunits is heterocyclic rings > heteroatoms or acyclic subunits containing heteroatoms > carbocyclic rings > acyclic subunits containing only carbon. The presence of various types of atoms, groups of atoms, or rings that are not part of the main polymer chain but are substituents on the CRU do not affect this order of seniority.
4. For heterocyclic rings the seniority is a ring system having nitrogen in the ring > a ring system having a heteroatom other than nitrogen in the order of seniority defined by rule 5 below > a ring system having the greatest number of heteroatoms > a ring system having the largest individual ring > a ring system having the greatest variety of heteroatoms > a ring system having the greatest number of heteroatoms highest in the order given in rule 5.
5. For heteroatom(s) or acyclic subunits containing heteroatom(s), the order of decreasing priority is O, S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, Hg. (Any heteroatom

has higher seniority than carbon—rule 3.) The seniority of other heteroatoms within this order is determined from their positions in the periodic table.

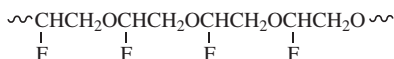
6. For carbocyclic rings the seniority is a ring system having the greatest number of rings > the ring system having the largest individual ring > the ring system having the greatest number of atoms common to its rings.

7. For a given carbocyclic or heterocyclic ring system: (a) when rings differ only in degree of unsaturation, seniority increases with degree of unsaturation; (b) for the same ring system, seniority is higher for the ring system having the lowest location number (referred to as *locant*), which designates the first point of difference for ring junctions.

8. These orders of seniority are superseded by the requirement of minimizing the number of free valences in the CRU, that is, the CRU should be a bivalent unit wherever possible.

9. Where there is a choice subunits should be oriented so that the lowest locant results for substituents.

Let us illustrate some of these rules by naming a few polymers. For the polymer

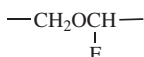


VIII

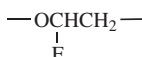
the possible CRUs are



IX



X



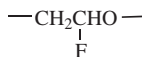
XI



XII



XIII

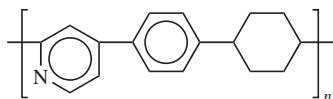


XIV

Note that CRUs **XII–XIV** are simply the reverse of CRUs **IX–XI**. Application of the nomenclature rules dictates the choice of only one of these as the CRU. That oxygen has higher seniority than carbon (rule 5) eliminates all except **XI** and **XII** as the CRU. Application of rule 8 results in **XI** as the CRU and the name poly[oxy(1-fluoroethylene)]. Choosing **XII** as the CRU would result in the name poly[oxy(2-fluoroethylene)], which gives the higher locant for the fluorine substituent. The name poly[oxy(fluoromethylenemethylene)] is incorrect because it does not define the largest possible subunit (which is CHFCH₂ vs. CHF plus CH₂).

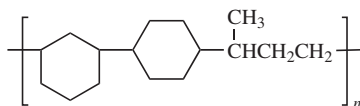
Rule 7 specifies —CH=CH— as the correct CRU in preference to =CH—CH=, since the former is bivalent, while the latter is tetravalent. The polymer —(CH=CH)—_n is poly(ethene-1,2-diyl).

The higher seniority of heterocyclic rings over carbocyclic rings (rule 3) and the higher seniority with higher unsaturation for cyclic subunits (rule 7a) yield the CRU **XV** with the name poly(pyridine-2,4-diyl-1,4-phenylenecyclohexane-1,4-diyl).



XV

The higher seniority of cyclic subunits over acyclic subunits (rule 3) and the higher seniority of a subunit with lower locant(s) relative to the same subunit with higher locant(s) (rule 7b) yield the CRU **XVI** with the name poly(cyclohexane-1,3-diylcyclohexane-1,4-diyl-1-methylpropane-1,3-diyl). Note that all acyclic subunits except CH_2 and CH_2CH_2 are named as alkane- α , ω -diyl. CH_2 and CH_2CH_2 subunits are named *methylene* and *ethylene*, respectively.

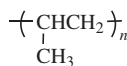
**XVI**

In the IUPAC system locants are placed immediately before the part of the name to which they apply; for instance subunits such as pyridine-2,4-diyl and 1-methylpropane-1,3-diyl. One of the few exceptions is the phenylene subunit, for example, 1,4-phenylene in **XV**. The IUPAC nomenclature system is always evolving and some of the details (e.g., the names of some subunits) have changed in recent years. One should use caution when using less recent nomenclature references than those listed in this text.

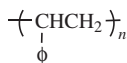
The IUPAC nomenclature system recognizes that most of the common (commercial) polymers have source-based or semisystematic names that are well established by usage. IUPAC does not intend that such names be supplanted by the IUPAC names but anticipates that such names will be kept to a minimum. The IUPAC system is generally used for all except the common polymers. The IUPAC names for various of the common polymers are indicated below the more established source or semisystematic name in the following:

**XVII**

Polyethylene or polyethene
Polymethylene

**XVIII**

Polypropylene or polypropene
Poly(1-methylethylene)

**XIX**

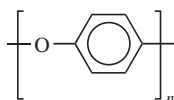
Polystyrene
Poly(1-phenylethylene)

**XX**

Poly(methyl acrylate)
Poly[1-(methoxycarbonyl)ethylene]

**XXI**

Polyformaldehyde
Poly(oxymethylene)

**XXII**

Poly(phenylene oxide)
Poly(oxy-1,4-phenylene)



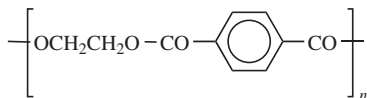
XXIII

Poly(hexamethylene adipamide)
Poly(iminohexanedioyliminohexane-1,6-diyl)



XXIV

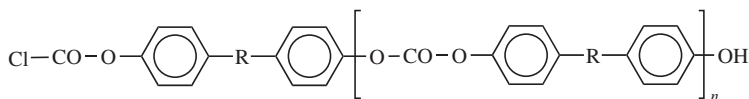
Poly(ϵ -caprolactam) or poly(ϵ -aminocaproic acid)
depending on the source of polymer
Poly[imino(1-oxohexane-1,6-diyl)]



XXV

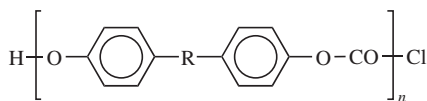
Poly(ethylene terephthalate)
Poly(oxyethyleneoxyterephthaloyl)

The IUPAC nomenclature will be used in this book with some exceptions. One exception is the use of well-established, non-IUPAC names for most of the commonly encountered polymers of commercial importance. Another exception will be in not following rule 2 for writing the constitutional repeating unit (although the correct IUPAC name will be employed). Using the IUPAC choice of the CRU leads in some cases to structures that are longer and appear more complicated. Thus the IUPAC structure for the polymer in Eq. 1-3 is



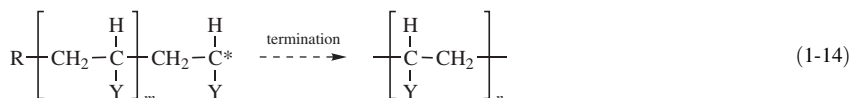
XXVI

which is clearly not as simple as

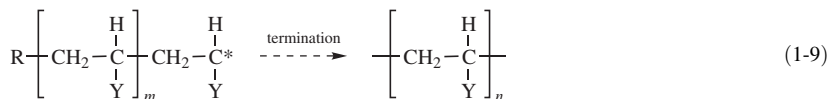


XXVII

although both **XXVI** and **XXVII** denote the exact same structure. This type of problem arises only with certain polymers and then only when the drawn structure is to include the ends of the polymer chain instead of simply the repeating unit or the CRU. The CRU will also generally not be used in equations such as Eq. 1-9. The polymerization mechanism in such reactions involves the propagating center on the substituted carbon atom of the monomer. Using



the CRU would yield Eq. 1-14 in place of Eq. 1-9, which appears unbalanced and confusing, at least to the beginning student, compared to



Equation 1-9 has the repeating unit written the same way on both sides, while Eq. 1-14 has the repeating unit reversed on the right side relative to what it is on the left side.

Before proceeding one needs to mention *Chemical Abstracts* (CA), a journal published by the American Chemical Society, that abstracts the world's chemical literature and has developed its own nomenclature rules. The CA rules are generally very close to the IUPAC rules, but there are some differences. Most of the differences are not important at the level of the discussions in this book. One difference that needs to be mentioned is the placement of locants. CA does not place locants immediately before the part of the name to which they apply. Thus, the CA name for the first subunit in **XV** is 2,4-pyridinediyl instead of pyridine-2,4-diyl. The difference between IUPAC and CA is also seen in the placement of locants in naming vinyl monomers such as $\text{CH}_2=\text{CHCH}_2\text{CH}_3$. The IUPAC name is but-1-ene; the CA name is 1-butene. Most chemists tend to follow the CA placement of locants for small molecules. This text will generally follow the IUPAC rule for locants for CRU subunits, but the CA rule for monomers.

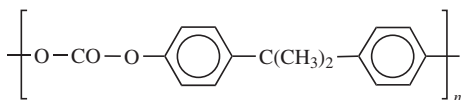
1-2d Trade Names and Nonnames

Special terminology based on trade names has been employed for some polymers. Although trade names should be avoided, one must be familiar with those that are firmly established and commonly used. An example of trade-name nomenclature is the use of the name nylon for the polyamides from unsubstituted, nonbranched aliphatic monomers. Two numbers are added onto the word "nylon" with the first number indicating the number of methylene groups in the diamine portion of the polyamide and the second number the number of carbon atoms in the diacyl portion. Thus poly(hexamethylene adipamide) and poly(hexamethylene sebacamide) are nylon 6,6 and nylon 6,10, respectively. Variants of these names are frequently employed. The literature contains such variations of nylon 6,6 as nylon 66, 66 nylon, nylon 6/6, 6,6 nylon, and 6-6 nylon. Polyamides from single monomers are denoted by a single number to denote the number of carbon atoms in the repeating unit. Poly(ϵ -caprolactam) or poly(6-aminocaproic acid) is nylon 6.

In far too many instances trade-name polymer nomenclature conveys very little meaning regarding the structure of a polymer. Many condensation polymers, in fact, seem not to have names. Thus the polymer obtained by the step polymerization of formaldehyde and phenol is variously referred to a *phenol-formaldehyde polymer*, phenol-formaldehyde resin, phenolic, phenolic resin, and phenoplast. Polymers of formaldehyde or other aldehydes with urea or melamine are generally referred to as *amino resins* or *aminoplasts* without any more specific names. It is often extremely difficult to determine which aldehyde and which amino monomers have been used to synthesize a particular polymer being referred to as an *amino resin*. More specific nomenclature, if it can be called that, is afforded by indicating the two reactants as in names such as urea-formaldehyde resin or melamine-formaldehyde resin.

A similar situation exists with the naming of many other polymers. Thus the polymer **XXVII** is usually referred to as "the polycarbonate from bisphenol A" or *polycarbonate*. The

IUPAC name for this polymer is poly(oxycarbonyloxy-1,4-phenylenedimethylmethylene-1,4-phenylene).



XXVII

1-3 LINEAR, BRANCHED, AND CROSSLINKED POLYMERS

Polymers can be classified as *linear*, *branched*, or *crosslinked* polymers depending on their structure. In the previous discussion on the different types of polymers and polymerizations we have considered only those polymers in which the monomer molecules have been linked together in one continuous length to form the polymer molecule. Such polymers are termed

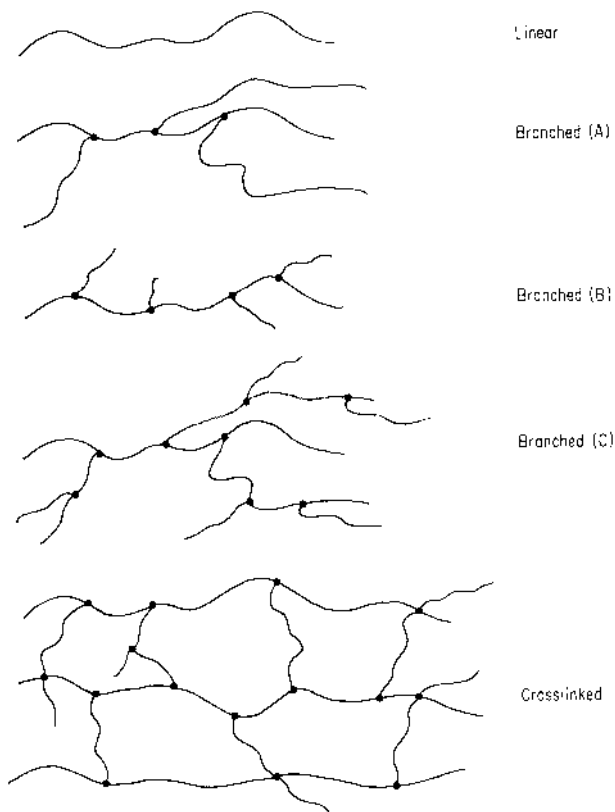
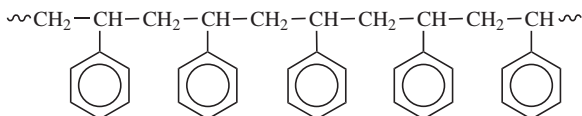


Fig. 1-2 Structure of linear, branched, and crosslinked polymers.

linear polymers. Under certain reaction conditions or with certain kinds of monomers the polymers can be quite different.

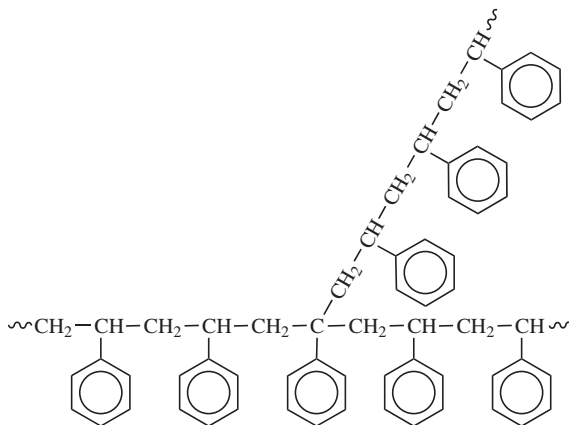
Branched polymers, polymers with more than two chain ends per molecule, can form in both step and chain polymerizations. Branched polymer molecules are those in which there are side branches of linked monomer molecules protruding from various central branch points along the main polymer chain. The difference between the shapes of linear and branched polymer molecules can be seen from the structural representations in Fig. 1-2. The branch points are indicated by heavy dots. The illustrations show that there are several different kinds of branched polymers. The branched polymer can be comblike in structure with either long (A) or short (B) branches. When there is extensive branching, the polymer can have a dendritic structure in which there are branches protruding from other branches, that is, branched branches (C). The presence of branching in a polymer usually has a large effect on many important polymer properties. The most significant property change brought about by branching is the decrease in crystallinity. Branched polymers do not pack as easily into a crystal lattice as do linear polymers.

It is important to point out that the term *branched polymer* does not refer to linear polymers containing side groups that are part of the monomer structure. Only those polymers that contain side branches composed of complete monomer units are termed *branched polymers*. Thus polystyrene **XXVIII** is classified as a linear polymer, and not as a branched polymer,



XXVIII

because the phenyl groups are part of the monomer unit and are not considered as branches. Branched polystyrene would be the polymer **XXIX** in which one has one or more polystyrene branches protruding from the main linear polystyrene chain.



XXIX

When polymers are produced in which the polymer molecules are linked to each other at points other than their ends, the polymers are said to be *crosslinked* (Fig. 1-2). Crosslinking can be made to occur during the polymerization process by the use of appropriate monomers. It can also be brought about after the polymerization by various chemical reactions. The crosslinks between polymer chains can be of different lengths depending on the crosslinking method and the specific conditions employed. One can also vary the number of crosslinks so as to obtain lightly or highly crosslinked polymers. When the number of crosslinks is sufficiently high, a *three-dimensional* or *space network* polymer is produced in which all the polymer chains in a sample have been linked together to form one giant molecule. Light crosslinking is used to impart good recovery (elastic) properties to polymers to be used as rubbers. High degrees of crosslinking are used to impart high rigidity and dimensional stability (under conditions of heat and stress) to polymers such as the phenol-formaldehyde and urea-formaldehyde polymers.

1-4 MOLECULAR WEIGHT

The molecular weight of a polymer is of prime importance in the polymer's synthesis and application. Chemists usually use the term *molecular weight* to describe the size of a molecule. The more accurate term is molar mass, usually in units of g mol^{-1} . The term molecular weight is the ratio of the average mass per formula unit of a substance to $\frac{1}{12}$ th of the mass of an atom of ^{12}C and is dimensionless (IUPAC, 1991, in press). This text will use *molecular weight* throughout irrespective of the units, because molecular weight is the more familiar term for most chemists.

The interesting and useful mechanical properties that are uniquely associated with polymeric materials are a consequence of their high molecular weight. Most important mechanical properties depend on and vary considerably with molecular weight as seen in Fig. 1-3. There is a minimum polymer molecular weight (A), usually a thousand or so, to produce any significant mechanical strength at all. Above A, strength increases rapidly with molecular weight until a critical point (B) is reached. Mechanical strength increases more slowly above B and eventually reaches a limiting value (C). The critical point B generally corresponds to the minimum molecular weight for a polymer to begin to exhibit sufficient strength to be useful. Most practical applications of polymers require higher molecular weights to obtain higher strengths. The minimum useful molecular weight (B), usually in the range 5000–10,000, differs for different polymers. The plot in Fig. 1-3 generally shifts to the right as the magnitude of the intermolecular forces decreases. Polymer chains with stronger

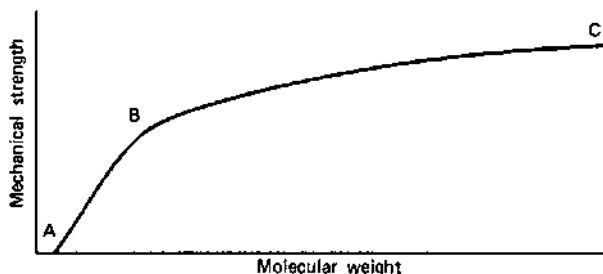


Fig. 1-3 Dependence of mechanical strength on polymer molecular weight.

intermolecular forces, for example, polyamides and polyesters, develop sufficient strength to be useful at lower molecular weights than polymers having weaker intermolecular forces, for example, polyethylene.

Properties other than strength also show a significant dependence on molecular weight. However, most properties show different quantitative dependencies on molecular weight. Different polymer properties usually reach their optimum values at different molecular weights. Further, a few properties may increase with molecular weight to a maximum value and then decrease with further increase in molecular weight. An example is the ability to process polymers into useful articles and forms (e.g., film, sheet, pipe, fiber). Processability begins to decrease past some molecular weight as the viscosity becomes too high and melt flow too difficult. Thus the practical aspect of a polymerization requires one to carry out the process to obtain a compromise molecular weight—a molecular weight sufficiently high to obtain the required strength for a particular application without overly sacrificing other properties. Synthesizing the highest possible molecular weight is not necessarily the objective of a typical polymerization. Instead, one often aims to obtain a high but specified, compromise molecular weight. The utility of a polymerization is greatly reduced unless the process can be carried out to yield the specified molecular weight. The control of molecular weight is essential for the practical application of a polymerization process.

When one speaks of the molecular weight of a polymer, one means something quite different from that which applies to small-sized compounds. Polymers differ from the small-sized compounds in that they are polydisperse or heterogeneous in molecular weight. Even if a polymer is synthesized free from contaminants and impurities, it is still not a pure substance in the usually accepted sense. Polymers, in their purest form, are mixtures of molecules of different molecular weight. The reason for the polydispersity of polymers lies in the statistical variations present in the polymerization processes. When one discusses the molecular weight of a polymer, one is actually involved with its average molecular weight. Both the average molecular weight and the exact distribution of different molecular weights within a polymer are required in order to fully characterize it. The control of molecular weight and molecular weight distribution (MWD) is often used to obtain and improve certain desired physical properties in a polymer product.

Various methods based on solution properties are used to determine the average molecular weight of a polymer sample. These include methods based on colligative properties, light scattering, and viscosity [Heimenz, 1984; Morawetz, 1975; Slade, 1998; Sperling, 2001]. The various methods do not yield the same average molecular weight. Different average molecular weights are obtained because the properties being measured are biased differently toward the different-sized polymer molecules in a polymer sample. Some methods are biased toward the larger-sized polymer molecules, while other methods are biased toward the smaller-sized molecules. The result is that the average molecular weights obtained are correspondingly biased toward the larger- or smaller-sized molecules. The following average molecular weights are determined:

1. The *number-average molecular weight* $\overline{M}_n$ is determined by experimental methods that count the number of polymer molecules in a sample of the polymer. The methods for measuring $\overline{M}_n$ are those that measure the colligative properties of solutions—vapor pressure lowering (vapor pressure osmometry), freezing point depression (cryoscopy), boiling point elevation (ebulliometry), and osmotic pressure (membrane osmometry). The colligative properties are the same for small and large molecules when comparing solutions at the same molal (or mole fraction) concentration. For example, a 1-molal solution of a polymer of molecular weight 10^5 has the same vapor pressure, freezing point, boiling point, and osmotic

pressure as a 1-molal solution of a polymer of molecular weight 10^3 or a 1-molal solution of a small molecule such as hexane. $\overline{M}_n$ is defined as the total weight w of all the molecules in a polymer sample divided by the total number of moles present. Thus the number-average molecular weight is

$$\overline{M}_n = \frac{w}{\sum N_x} = \frac{\sum N_x M_x}{\sum N_x} \quad (1-15)$$

where the summations are over all the different sizes of polymer molecules from $x = 1$ to $x = \infty$ and N_x is the number of moles whose weight is M_x . Equation 1-15 can also be written as

$$\overline{M}_n = \sum \underline{N}_x M_x \quad (1-16)$$

where $\underline{N}_x$ is the mole fraction (or the number-fraction) of molecules of size M_x . The most common methods for measuring $\overline{M}_n$ are membrane osmometry and vapor pressure osmometry since reasonably reliable commercial instruments are available for those methods. Vapor pressure osmometry, which measures vapor pressure indirectly by measuring the change in temperature of a polymer solution on dilution by solvent vapor, is generally useful for polymers with $\overline{M}_n$ below 10,000–15,000. Above that molecular weight limit, the quantity being measured becomes too small to detect by the available instruments. Membrane osmometry is limited to polymers with $\overline{M}_n$ above about 20,000–30,000 and below 500,000. The lower limit is a consequence of the partial permeability of available membranes to smaller-sized polymer molecules. Above molecular weights of 500,000, the osmotic pressure of a polymer solution becomes too small to measure accurately. End-group analysis is also useful for measurements of $\overline{M}_n$ for certain polymers. For example, the carboxyl end groups of a polyester can be analyzed by titration with base and carbon–carbon double bond end groups can be analyzed by ^1H NMR. Accurate end-group analysis becomes difficult for polymers with $\overline{M}_n$ values above 20,000–30,000.

2. Light scattering by polymer solutions, unlike colligative properties, is greater for larger-sized molecules than for smaller-sized molecules. The average molecular weight obtained from light-scattering measurements is the *weight-average molecular weight* $\overline{M}_w$ defined as

$$\overline{M}_w = \sum w_x M_x \quad (1-17)$$

where w_x is the weight fraction of molecules whose weight is M_x . $\overline{M}_w$ can also be defined as

$$\overline{M}_w = \frac{\sum c_x M_x}{\sum c_x} = \frac{\sum c_x M_x}{c} = \frac{\sum N_x M_x^2}{\sum N_x M_x} \quad (1-18)$$

where c_x is the weight concentration of M_x molecules, c is the total weight concentration of all the polymer molecules, and the following relationships hold:

$$w_x = \frac{c_x}{c} \quad (1-19)$$

$$c_x = N_x M_x \quad (1-20)$$

$$c = \sum c_x = \sum N_x M_x \quad (1-21)$$

Since the amount of light scattered by a polymer solution increases with molecular weight, this method becomes more accurate for higher polymer molecular weights. There is no upper limit to the molecular weight that can be accurately measured except the limit imposed by insolubility of the polymer. The lower limit of $\overline{M}_w$ by the light scattering method is close to 5000–10,000. Below this molecular weight, the amount of scattered light is too small to measure accurately.

3. Solution viscosity is also useful for molecular-weight measurements. Viscosity, like light scattering, is greater for the larger-sized polymer molecules than for smaller ones. However, solution viscosity does not measure $\overline{M}_w$ since the exact dependence of solution viscosity on molecular weight is not exactly the same as light scattering. Solution viscosity measures the *viscosity-average molecular weight* $\overline{M}_v$ defined by

$$\overline{M}_v = \left[\sum w_x M_x^a \right]^{1/a} = \left[\frac{\sum N_x M_x^{a+1}}{\sum N_x M_x} \right]^{1/a} \quad (1-22)$$

where a is a constant. The viscosity- and weight-average molecular weights are equal when a is unity. $\overline{M}_v$ is less than $\overline{M}_w$ for most polymers, since a is usually in the range 0.5–0.9. However, $\overline{M}_v$ is much closer to $\overline{M}_w$ than $\overline{M}_n$, usually within 20% of $\overline{M}_w$. The value of a is dependent on the hydrodynamic volume of the polymer, the effective volume of the solvated polymer molecule in solution, and varies with polymer, solvent, and temperature.

More than one average molecular weight is required to reasonably characterize a polymer sample. There is no such need for a monodisperse product (i.e., one composed of molecules whose molecular weights are all the same) for which all three average molecular weights are the same. The situation is quite different for a polydisperse polymer where all three molecular weights are different if the constant a in Eq. 1-22 is less than unity, as is the usual case. A careful consideration of Eqs. 1-15 through 1-22 shows that the number-, viscosity-, and weight-average molecular weights, in that order, are increasingly biased toward the higher-molecular-weight fractions in a polymer sample. For a polydisperse polymer

$$\overline{M}_w > \overline{M}_v > \overline{M}_n$$

with the differences between the various average molecular weights increasing as the molecular-weight distribution broadens. A typical polymer sample will have the molecular-weight distribution shown in Fig. 1-4. the approximate positions of the different average molecular weights are indicated on this distribution curve.

For most practical purposes, one usually characterizes the molecular weight of a polymer sample by measuring $\overline{M}_n$ and either $\overline{M}_w$ or $\overline{M}_v$. $\overline{M}_v$ is commonly used as a close approximation of $\overline{M}_w$, since the two are usually quite close (within 10–20%). Thus in most instances, one is concerned with the $\overline{M}_n$ and $\overline{M}_w$ of a polymer sample. The former is biased toward the lower-molecular-weight fractions, while the latter is biased toward the higher-molecular-weight fractions. The ratio of the two average molecular weights $\overline{M}_w/\overline{M}_n$ depends on the breadth of the distribution curve (Fig. 1-4) and is often useful as a measure of the polydispersity in a polymer. The value of $\overline{M}_w/\overline{M}_n$ would be unity for a perfectly monodisperse polymer. The ratio is greater than unity for all actual polymers and increases with increasing polydispersity.

The characterization of a polymer by $\overline{M}_n$ alone, without regard to the polydispersity, can be extremely misleading, since most polymer properties such as strength and melt viscosity are determined primarily by the size of the molecules that make up the bulk of the sample by weight. Polymer properties are much more dependent on the larger-sized molecules in a

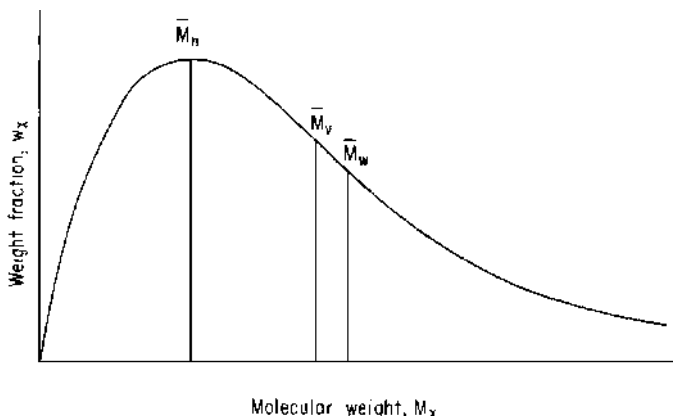


Fig. 1-4 Distribution of molecular weights in a typical polymer sample.

sample than on the smaller ones. Thus, for example, consider a hypothetical mixture containing 95% by weight of molecules of molecular weight 10,000, and 5% of molecules of molecular weight 100. (The low-molecular-weight fraction might be monomer, a low-molecular-weight polymer, or simply some impurity.) The $\bar{M}_n$ and $\bar{M}_w$ are calculated from Eqs. 1-15 and 1-17 as 1680 and 9505, respectively. The use of the $\bar{M}_n$ value of 1680 gives an inaccurate indication of the properties of this polymer. The properties of the polymer are determined primarily by the 10,000-molecular-weight molecules that make up 95% of the weight of the mixture. The weight-average molecular weight is a much better indicator of the properties to be expected in a polymer. The utility of $\bar{M}_n$ resides primarily in its use to obtain an indication of polydispersity in a sample by measuring the ratio $\bar{M}_w/\bar{M}_n$.

In addition to the different average molecular weights of a polymer sample, it is frequently desirable and necessary to know the exact distribution of molecular weights. As indicated previously, there is usually a molecular weight range for which any given polymer property will be optimum for a particular application. The polymer sample containing the greatest percentage of polymer molecules of that size is the one that will have the optimum value of the desired property. Since samples with the same average molecular weight may possess different molecular weight distributions, information regarding the distribution allows the proper choice of a polymer for optimum performance. Various methods have been used in the past to determine the molecular weight distribution of a polymer sample, including fractional extraction and fractional precipitation. These methods are laborious and determinations of molecular weight distributions were not routinely performed. However, the development of *size exclusion chromatography* (SEC), also referred to as *gel permeation chromatography* (GPC) and the availability of automated commercial instruments have changed the situation. Molecular-weight distributions are now routinely performed in most laboratories using SEC.

Size exclusion chromatography involves the permeation of a polymer solution through a column packed with microporous beads of crosslinked polystyrene [Potschka and Dublin, 1996; Yau et al., 1979]. The packing contains beads of different-sized pore diameters. Molecules pass through the column by a combination of transport into and through the beads and through the interstitial volume (the volume between beads). Molecules that penetrate the beads are slowed down more in moving through the column than molecules that do not penetrate the beads; in other words, transport through the interstitial volume is faster than through

the pores. The smaller-sized polymer molecules penetrate all the beads in the column since their molecular size (actually their hydrodynamic volume) is smaller than the pore size of the beads with the smallest-sized pores. A larger-sized polymer molecule does not penetrate all the beads since its molecular size is larger than the pore size of some of the beads. The larger the polymer molecular weight, the fewer beads that are penetrated and the greater is the extent of transport through the interstitial volume. The time for passage of polymer molecules through the column decreases with increasing molecular weight. The use of an appropriate detector (refractive index, viscosity, light scattering) measures the amount of polymer passing through the column as a function of time. This information and a calibration of the column with standard polymer samples of known molecular weight allow one to obtain the molecular weight distribution in the form of a plot such as that in Fig. 1-4. Not only does SEC yield the molecular weight distribution, but $\overline{M}_n$ and $\overline{M}_w$ (and also $\overline{M}_v$ if a is known) are also calculated automatically. SEC is now the method of choice for measurement of $\overline{M}_n$ and $\overline{M}_w$ since the SEC instrument is far easier to use compared to methods such as osmometry and light scattering.

1-5 PHYSICAL STATE

1-5a Crystalline and Amorphous Behavior

Solid polymers differ from ordinary, low-molecular-weight compounds in the nature of their physical state or *morphology*. Most polymers show simultaneously the characteristics of both crystalline and amorphous solids [Keller et al., 1995; Mark et al., 1993; Porter and Wang, 1995; Sperling, 2001; Woodward, 1989; Wunderlich, 1973]. X-Ray and electron diffraction patterns often show the sharp features typical of three-dimensionally ordered crystalline solids as well as the diffuse, unordered features characteristic of amorphous solids. (Amorphous solids have sometimes been referred to as highly viscous liquids.) The terms *crystalline* and *amorphous* are used to indicate the ordered and unordered polymer regions, respectively. Different polymers show different degrees of crystalline behavior. The known polymers constitute a spectrum of materials from those that are completely amorphous to others that possess low to moderate to high crystallinity. The term *semicrystalline* is used to refer to polymers that are partially crystalline. Completely crystalline polymers are rarely encountered.

The exact nature of polymer crystallinity has been the subject of considerable controversy. The *fringed-micelle* theory, developed in the 1930s, considers polymers to consist of small-sized, ordered crystalline regions—termed *crystallites*—imbedded in an unordered, amorphous polymer matrix. Polymer molecules are considered to pass through several different crystalline regions with crystallites being formed when extended-chain segments from different polymer chains are precisely aligned together and undergo crystallization. Each polymer chain can contribute ordered segments to several crystallites. The segments of the chain in between the crystallites make up the unordered amorphous matrix. This concept of polymer crystallinity is shown in Fig. 1-5.

The *folded-chain lamella* theory arose in the last 1950s when polymer single crystals in the form of thin platelets termed *lamella*, measuring about $10,000 \text{ \AA} \times 100 \text{ \AA}$, were grown from polymer solutions. Contrary to previous expectations, X-ray diffraction patterns showed the polymer chain axes to be parallel to the smaller dimension of the platelet. Since polymer molecules are much longer than $100 \text{ \AA}$, the polymer molecules are presumed to fold back and forth on themselves in an accordionlike manner in the process of crystallization. Chain

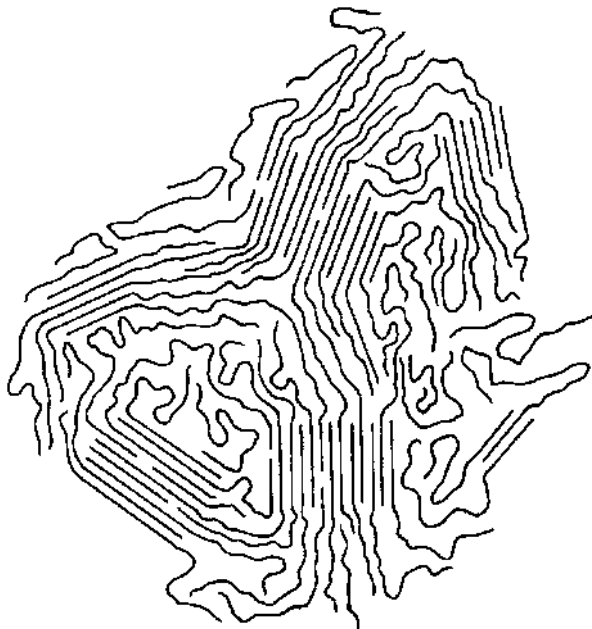


Fig. 1-5 Fringed-micelle model of polymer crystallinity.

folding was unexpected, since the most thermodynamically stable crystal is the one involving completely extended chains. The latter is kinetically difficult to achieve and chain folding is apparently the system's compromise for achieving a highly stable crystal structure under normal crystallization conditions. Two models of chain folding can be visualized. Chain folding is regular and sharp with a uniform fold period in the *adjacent-reentry* model (Fig. 1-6). In the *nonadjacent-reentry* or *switchboard* model (Fig. 1-7) molecules wander through the non-regular surface of a lamella before reentering the lamella or a neighboring lamella. In the chain-folded lamella picture of polymer crystallinity less than 100% crystallinity is attributed to defects in the chain-folding process. The defects may be imperfect folds, irregularities in packing, chain entanglements, loose chain ends, dislocations, occluded impurities, or numerous other imperfections. The adjacent reentry and switchboard models differ in the details of

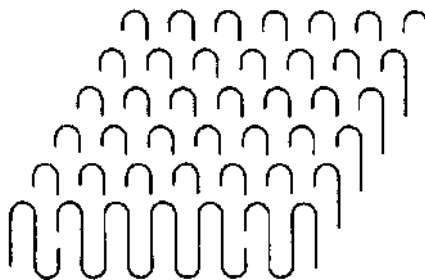


Fig. 1-6 Adjacent reentry model of single crystal.

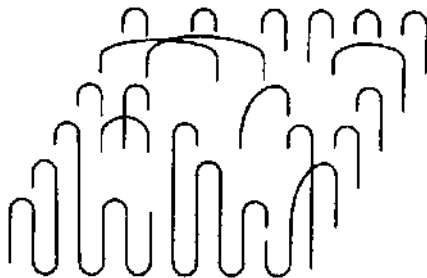


Fig. 1-7 Switchboard model of single crystal.

what constitutes the chain-folding defects. The switchboard model indicates that most defects are at the crystal surfaces, while the adjacent-reentry model indicates that defects are located as much within the crystal as at the crystal surfaces.

Folded-chain lamella represent the morphology not only for single crystals grown from solution but also polymers crystallized from the melt—which is how almost all commercial and other synthetic polymers are obtained. Melt-crystallized polymers have the most prominent structural feature of polymer crystals—the chains are oriented perpendicular to the lamella face so that chain folding must occur. Chain folding is maximum for polymers crystallized slowly near the crystalline melting temperature. Fast cooling (quenching) gives a more chaotic crystallization with less chain folding. Melt crystallization often develops as a spherical or spherulitic growth as seen under the microscope. Nucleation of crystal growth occurs at various nuclei and crystal growth proceeds in a radial fashion from each nucleus until the growth fronts from neighboring structures impinge on each other. These spherical structures, termed *spherulites*, completely fill the volume of a crystallized polymer sample. Spherulites have different sizes and degrees of perfection depending on the specific polymer and crystallization conditions.

A spherulite is a complex, polycrystalline structure (Fig. 1-8). The *nucleus* for spherulitic growth is the single crystal in which a multilayered stack is formed, and each lamella extends to form a *lamellar fibril*. The flat ribbonlike lamellar fibrils diverge, twist, and branch as they grow outward from the nucleus. Growth occurs by chain folding with the polymer chain axes being perpendicular to the length of the lamellar fibril. The strength of polymers indicates that more than van der Waals forces hold lamellae together. There are *interlamellar* or *intercrystalline fibrils* (also termed *tie molecules*) between the lamellar fibrils within a spherulite and between fibrils of different spherulites. Some polymer molecules simultaneously participate in the growth of two or more adjacent lamellae and provide molecular links that reinforce the crystalline structure. The chain axes of tie molecules lie parallel to the long axes of the link—each link between lamellae is an extended-chain type of single crystal. The tie molecules are the main component of the modern picture of polymer crystallinity, which is a carryover from the fringed-micelle theory. The amorphous content of a semicrystalline, melt-crystallized polymer sample consists of the defects in the chain-folding structure, tie molecules, and the material that is either, because of entanglements, not included in the growing lamellar fibril or is rejected from it owing to its unacceptable nature; low-molecular-weight chains and nonregular polymer chain segments, for example, are excluded.

Some natural polymers such as cotton, silk, and cellulose have the extended-chain morphology, but their morphologies are determined by enzymatically controlled synthesis and crystallization processes. Extended-chain morphology is obtained in some synthetic

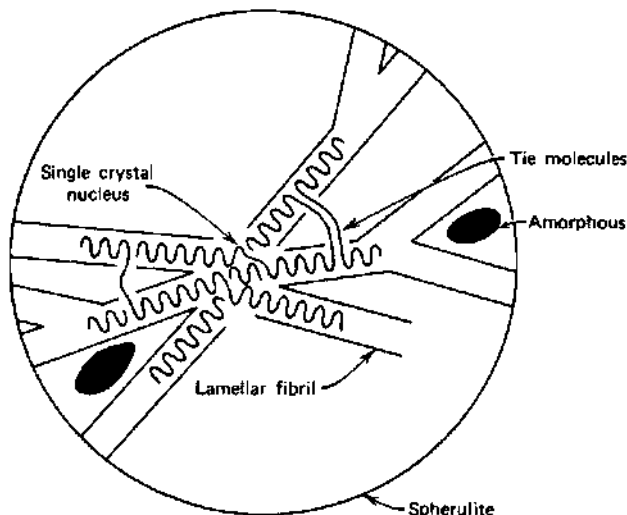


Fig. 1-8 Structural organization within a spherulite in melt-crystallized polymer.

polymers under certain circumstances. These include crystallization from the melt (or annealing for long time periods) under pressure or other applied stress and crystallization of polymers from the liquid crystalline state. The former has been observed with several polymers, including polyethylene and polytetrafluoroethylene. The latter is observed with polymers containing stiff or rigid-rod chains, such as poly(*p*-phenyleneterephthalamide) (Sec. 2-8f). Extended-chain morphology is also obtained in certain polymerizations involving conversion of crystalline monomer to crystalline polymer, for example, polymerization of diacetylenes (Sec. 3-16c).

A variety of techniques have been used to determine the extent of crystallinity in a polymer, including X-ray diffraction, density, IR, NMR, and heat of fusion [Sperling, 2001; Wunderlich, 1973]. X-ray diffraction is the most direct method but requires the somewhat difficult separation of the crystalline and amorphous scattering envelopes. The other methods are indirect methods but are easier to use since one need not be an expert in the field as with X-ray diffraction. Heat of fusion is probably the most often used method since reliable thermal analysis instruments are commercially available and easy to use [Bershtein and Egorov, 1994; Wendlandt, 1986]. The difficulty in using thermal analysis (differential scanning calorimetry and differential thermal analysis) or any of the indirect methods is the uncertainty in the values of the quantity measured (e.g., the heat of fusion per gram of sample or density) for 0 and 100% crystalline samples since such samples seldom exist. The best technique is to calibrate the method with samples whose crystallinities have been determined by X-ray diffraction.

1-5b Determinants of Polymer Crystallinity

Regardless of the precise picture of order and disorder in polymers, the prime consideration that should be emphasized is that polymers have a tendency to crystallize. The extent of this crystallization tendency plays a most significant role in the practical ways in which polymers are used. This is a consequence of the large effect of crystallinity on the thermal, mechanical,

and other important properties of polymers. Different polymers have different properties and are synthesized and used differently because of varying degrees of crystallinity. The extent of crystallinity developed in a polymer sample is a consequence of both thermodynamic and kinetic factors. In this discussion we will note the general tendency to crystallize under moderate crystallization conditions (that is, conditions that exclude extremes of time, temperature, and pressure). Thermodynamically crystallizable polymers generally must crystallize at reasonable rates if crystallinity is to be employed from a practical viewpoint. The extent to which a polymer crystallizes depends on whether its structure is conducive to packing into the crystalline state and on the magnitude of the secondary attractive forces of the polymer chains. Packing is facilitated for polymer chains that have structural regularity, compactness, streamlining, and some degree of flexibility. The stronger the secondary attractive forces, the greater will be the driving force for the ordering and crystallization of polymer chains.

Some polymers are highly crystalline primarily because their structure is conducive to packing, while others are crystalline primarily because of strong secondary attractive forces. For still other polymers both factors may be favorable for crystallization. Polyethylene, for example, has essentially the best structure in terms of its ability to pack into the crystalline state. Its very simple and perfectly regular structure allows chains to pack tightly and without any restrictions as to which segment of one chain need line up next to which other segment of the same chain or of another chain. The flexibility of the polyethylene chains is also conducive to crystallization in that the conformations required for packing can be easily achieved. Even though its secondary attractive forces are small, polyethylene crystallizes easily and to a high degree because of its simple and regular structure.

Polymers other than polyethylene have less simple and regular chains. Poly(ϵ -caprolactom) can be considered as a modified polyethylene chain containing the amide group in between every five methylenes. Poly(ϵ -caprolactom) and other polyamides are highly crystalline polymers. The amide group is a polar one and leads to much larger secondary attractive forces in polyamides (due to hydrogen bonding) compared to polyethylene; this is most favorable for crystallization. However, the polyamide chains are not as simple as those of polyethylene and packing requires that chain segments be brought together so that the amide groups are aligned. This restriction leads to a somewhat lessened degree of crystallization in polyamides than expected, based only on a consideration of the high secondary attractive forces. Crystallinity in a polymer such as a polyamide can be significantly increased by mechanically stretching it to facilitate the ordering and alignment of polymer chains.

Polymers such as polystyrene, poly(vinyl chloride), and poly(methyl methacrylate) show very poor crystallization tendencies. Loss of structural simplicity (compared to polyethylene) results in a marked decrease in the tendency toward crystallization. Fluorocarbon polymers such as poly(vinyl fluoride), poly(vinylidene fluoride), and polytetrafluoroethylene are exceptions. These polymers show considerable crystallinity since the small size of fluorine does not preclude packing into a crystal lattice. Crystallization is also aided by the high secondary attractive forces. High secondary attractive forces coupled with symmetry account for the presence of significant crystallinity in poly(vinylidene chloride). Symmetry alone without significant polarity, as in polyisobutylene, is insufficient for the development of crystallinity. (The effect of stereoregularity of polymer structure on crystallinity is postponed to Sec. 8-2a.)

Polymers with rigid, cyclic structures in the polymer chain, as in cellulose and poly(ethyleneterephthalate), are difficult to crystallize. Moderate crystallization does occur in these cases, as a result of the polar polymer chains. Additional crystallization can be induced by mechanical stretching. Cellulose is interesting in that native cellulose in the form of cotton is much more crystalline than cellulose that is obtained by precipitation of cellulose from

solution (Sec. 9-3a). The biosynthesis of cotton proceeds with an enzymatic ordering of the polymer chains in spite of the rigid polymer chains. Excess chain rigidity in polymers due to extensive crosslinking, as in phenol-formaldehyde and urea-formaldehyde polymers, completely prevents crystallization.

Chain flexibility also effects the ability of a polymer to crystallize. Excessive flexibility in a polymer chain as in polysiloxanes and natural rubber leads to an inability of the chains to pack. The chain conformations required for packing cannot be maintained because of the high flexibility of the chains. The flexibility in the cases of the polysiloxanes and natural rubber is due to the bulky Si—O and *cis*-olefin groups, respectively. Such polymers remain as almost completely amorphous materials, which, however, show the important property of elastic behavior.

1-5c Thermal Transitions

Polymeric materials are characterized by two major types of transition temperatures—the *crystalline melting temperature* T_m and the *glass transition temperature* T_g . The crystalline melting temperature is the melting temperature of the crystalline domains of a polymer sample. The glass transition temperature is the temperature at which the amorphous domains of a polymer take on the characteristic properties of the glassy state—brittleness, stiffness, and rigidity. The difference between the two thermal transitions can be understood more clearly by considering the changes that occur in a liquid polymer as it is cooled. The translational, rotational, and vibrational energies of the polymer molecules decrease on cooling. When the total energies of the molecules have fallen to the point where the translational and rotational energies are essentially zero, crystallization is possible. If certain symmetry requirements are met, the molecules are able to pack into an ordered, lattice arrangement and crystallization occurs. The temperature at which this occurs is T_m . However, not all polymers meet the necessary symmetry requirements for crystallization. If the symmetry requirements are not met, crystallization does not take place, but the energies of the molecules continue to decrease as the temperature decreases. A temperature is finally reached—the T_g —at which long-range motions of the polymer chains stop. Long-range motion, also referred to as *segmental motion*, refers to the motion of a segment of a polymer chain by the concerted rotation of bonds at the ends of the segment. [Bond rotations about side chains, e.g., the C—CH₃ and C—COOCH₃ bonds in poly(methyl methacrylate), do not cease at T_g .]

Whether a polymer sample exhibits both thermal transitions or only one depends on its morphology. Completely amorphous polymers show only a T_g . A completely crystalline polymer shows only a T_m . Semicrystalline polymers exhibit both the crystalline melting and glass transition temperatures. Changes in properties such as specific volume and heat capacity occur as a polymer undergoes each of the thermal transitions. Figure 1-9 shows the changes in specific volume with temperature for completely amorphous and completely crystalline polymers (the solid lined plots). T_m is a first-order transition with a discontinuous change in the specific volume at the transition temperature. T_g is a second-order transition involving only a change in the temperature coefficient of the specific volume. (A plot of the temperature coefficient of the specific volume versus temperature shows a discontinuity.) The corresponding plot for a semicrystalline polymer consists of the plot for the crystalline polymer plus the dotted portion corresponding to the glass transition. A variety of methods have been used to determine T_g and T_m , including dilatometry (specific volume), thermal analysis, dynamic mechanical behavior, dielectric loss, and broad-line NMR. The most commonly used method is differential scanning calorimetry (DSC). DSC reflects the change in heat capacity of a sample as a function of temperature by measuring the heat flow required to

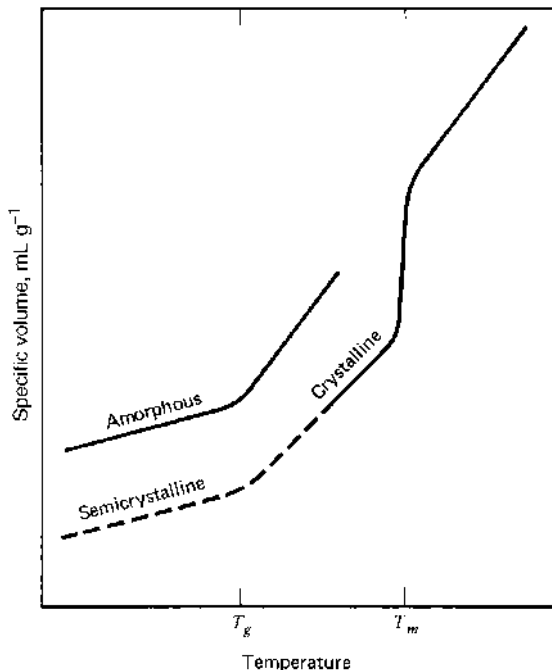


Fig. 1-9 Determination of glass transition and crystalline melting temperatures by changes in specific volume.

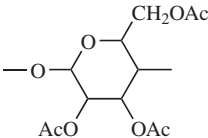
maintain a zero temperature differential between an inert reference material and the polymer sample.

The melting of a polymer takes place over a wider temperature range than that observed for small organic molecules such as benzoic acid, due to the presence of different-sized crystalline regions and the more complicated process for melting of large molecules. T_m , generally reported as the temperature for the onset of melting, is determined as the intersection from extrapolation of the two linear regions of Fig. 1-9 (before and after the onset). T_g also occurs over a wide temperature range and is determined by extrapolation of the two linear regions, before and after T_g . The glass transition is a less well understood process than melting. There are indications that it is at least partially a kinetic phenomenon. The experimentally determined value of T_g varies significantly with the timescale of the measurement. Faster cooling rates result in higher T_g values. Further, significant densification still takes place below T_g with the amount dependent on the cooling rate. Perhaps the best visualization of T_g involves the existence of a modest range of temperatures at which there is cessation of segmental motion for polymer chain segments of different lengths (~ 5 – 20 chain atoms).

Some polymers undergo other thermal transitions in addition to T_g and T_m . These include crystal–crystal transitions (i.e., transition from one crystalline form to another and crystalline–liquid crystal transitions).

The values of T_g and T_m for a polymer affect its mechanical properties at any particular temperature and determine the temperature range in which that polymer can be employed. The T_g and T_m values for some of the common polymers are shown in Table 1–3 [Brandrup et al., 1999; Mark, 1999]. (These are the values at 1 atm pressure.) Consider the manner in

TABLE 1-3 Thermal Transitions of Polymers^a

Polymer	Repeating Unit	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$
Polydimethylsiloxane	$-\text{OSi}(\text{CH}_3)_2-$	-127	-40
Polyethylene	$-\text{CH}_2\text{CH}_2-$	-125	137
Polyoxymethylene	$-\text{CH}_2\text{O}-$	-83	181
Natural rubber (polyisoprene)	$-\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2-$	-73	28
Polyisobutylene	$-\text{CH}_2\text{C}(\text{CH}_3)_2-$	-73	44
Poly(ethylene oxide)	$-\text{CH}_2\text{CH}_2\text{O}-$	-53	66
Poly(vinylidene fluoride)	$-\text{CH}_2\text{CF}_2-$	-40	185
Polypropene	$-\text{CH}_2\text{CH}(\text{CH}_3)-$	-1	176
Poly(vinyl fluoride)	$-\text{CH}_2\text{CHF}-$	41	200
Poly(vinylidene chloride)	$-\text{CH}_2\text{CCl}_2-$	-18	200
Poly(vinyl acetate)	$-\text{CH}_2\text{CH}(\text{OCOCH}_3)-$	32	
Poly(chlorotrifluoroethylene)	$-\text{CF}_2\text{CFCl}-$		220
Poly(ϵ -caprolactam)	$-(\text{CH}_2)_5\text{CONH}-$	40	223
Poly(hexamethylene adipamide)	$-\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO}-$	50	265
Poly(ethylene terephthalate)	$-\text{OCH}_2\text{CH}_2\text{OCO}-\text{C}_6\text{H}_4-\text{CO}-$	61	270
Poly(vinyl chloride)	$-\text{CH}_2\text{CHCl}-$	81	273
Polystyrene	$-\text{CH}_2\text{CH}\phi-$	100	250
Poly(methyl methacrylate)	$-\text{CH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{CH}_3)-$	105	220
Cellulose triacetate			306
Polytetrafluoroethylene	$-\text{CF}_2\text{CF}_2-$	117	327

^aData from Brandrup et al. [1999].

which T_g and T_m vary from one polymer to another. One can discuss the two transitions simultaneously since both are affected similarly by considerations of polymer structure. Polymers with low T_g values usually have low T_m values; high T_g and high T_m values are usually found together. Polymer chains that do not easily undergo bond rotation so as to pass through the glass transition would also be expected to melt with difficulty. This is reasonable, since similar considerations of polymer structure are operating in both instances. The two thermal transitions are generally affected in the same manner by the molecular symmetry, structural rigidity, and secondary attractive forces of polymer chains [Billmeyer, 1984; Mark et al., 1993; Sperling, 2001]. High secondary forces (due to high polarity or hydrogen bonding) lead to strong crystalline forces requiring high temperatures for melting. High secondary attractive forces also decrease the mobility of amorphous polymer chains, leading to

high T_g . Decreased mobility of polymer chains, increased chain rigidity, and high T_g are found where the chains are substituted with several substituents as in poly(methyl methacrylate) and polytetrafluoroethylene or with bulky substituents as in polystyrene. The T_m values of crystalline polymers produced from such rigid chains would also be high. The effects of substituents are not always easy to understand. A comparison of polypropene, poly(vinyl chloride), and poly(vinyl fluoride) with polyisobutylene, poly(vinylidene chloride), and poly(vinylidene fluoride), respectively, shows the polymers from 1,1-disubstituted ethylenes have lower T_g and T_m values than do those from the monosubstituted ethylenes. One might have predicted the opposite result because of the greater polarity and molecular symmetry of the polymers from 1,1-disubstituted ethylenes. Apparently, the presence of two side groups instead of one separates polymer chains from each other and results in more flexible polymer chains. Thus, the effects of substituents on T_g and T_m depend on their number and identity.

The rigidity of polymer chains is especially high when there are cyclic structures in the main polymer chains. Polymers such as cellulose have high T_g and T_m values. On the other hand, the highly flexible polysiloxane chain (a consequence of the large size of Si) results in very low values of T_g and T_m .

Although T_g and T_m depend similarly on molecular structure, the variations in the two transition temperature do not always quantitative parallel each other. Table 1-3 shows the various polymers listed in order of increasing T_g values. The T_m values are seen to generally increase in the same order, but there are many polymers whose T_m values do not follow in the same exact order. Molecular symmetry, chain rigidity, and secondary forces do not affect T_g and T_m in the same quantitative manner. Thus polyethylene and polyoxymethylene have low T_g values because of their highly flexible chains; however, their simple and regular structures yield tightly packed crystal structures with high T_m values. An empirical consideration of ratio T_g/T_m (Kelvin temperatures) for various polymers aids this discussion. The T_g/T_m ratio is approximately 1/2 for symmetric polymers [e.g., poly(vinylidene chloride)], but the ratio is closer to 3/4 for unsymmetric polymers (e.g., poly[vinyl chloride]). This result indicates that T_m is more dependent on molecular symmetry, while T_g is more dependent on secondary forces and chain flexibility.

It should be evident that some of the factors that decrease the crystallization tendency of a polymer also lead to increased values of T_m (and also T_g). The reason for this is that the extent of crystallinity developed in a polymer is both kinetically and thermodynamically controlled, while the melting temperature is only thermodynamically controlled. Polymers with rigid chains are difficult or slow to crystallize, but the portion that does crystallize will have a high melting temperature. (The extent of crystallinity can be significantly increased in such polymers by mechanical stretching to align and crystallize the polymer chains.) Thus compare the differences between polyethylene and poly(hexamethylene adipamide). Polyethylene tends to crystallize easier and faster than the polyamide because of its simple and highly regular structure and is usually obtained with greater degrees of crystallinity. On the other hand, the T_m of the polyamide is much higher (by $\sim 130^\circ\text{C}$) than that of polyethylene because of the much greater secondary forces.

1-6 APPLICATIONS OF POLYMERS

1-6a Mechanical Properties

Many polymer properties such as solvent, chemical, and electrical resistance and gas permeability are important in determining the use of a specific polymer in a specific application. However, the prime consideration in determining the general utility of a polymer is its

mechanical behavior, that is, its deformation and flow characteristics under stress. The mechanical behavior of a polymer can be characterized by its *stress-strain* properties [Billmeyer, 1984; Nielsen and Landel, 1994]. This often involves observing the behavior of a polymer as one applies tension stress to it in order to elongate (strain) it to the point where it ruptures (pulls apart). The results are usually shown as a plot of the stress versus elongation (strain). The stress is usually expressed in newtons per square centimeter (N cm^{-2}) or megapascals (MPa) where $1 \text{ MPa} = 100 \text{ N cm}^{-2}$. The strain is the fractional increase in the length of the polymer sample (i.e., $\Delta L/L$, where L is the original, unstretched sample length). The strain can also be expressed as the percent elongation, $\Delta L/L \times 100\%$. Although N cm^{-2} is the SI unit for stress, psi (pounds per square inch) is found extensively in the literature. The conversion factor is $1 \text{ N cm}^{-2} = 1.450 \text{ psi}$. SI units will be used throughout this text with other commonly used units also indicated.

Several stress-strain plots are shown in Fig. 1-10. Four important quantities characterize the stress-strain behavior of a polymer:

1. *Modulus*. The resistance to deformation as measured by the initial stress divided by $\Delta L/L$.

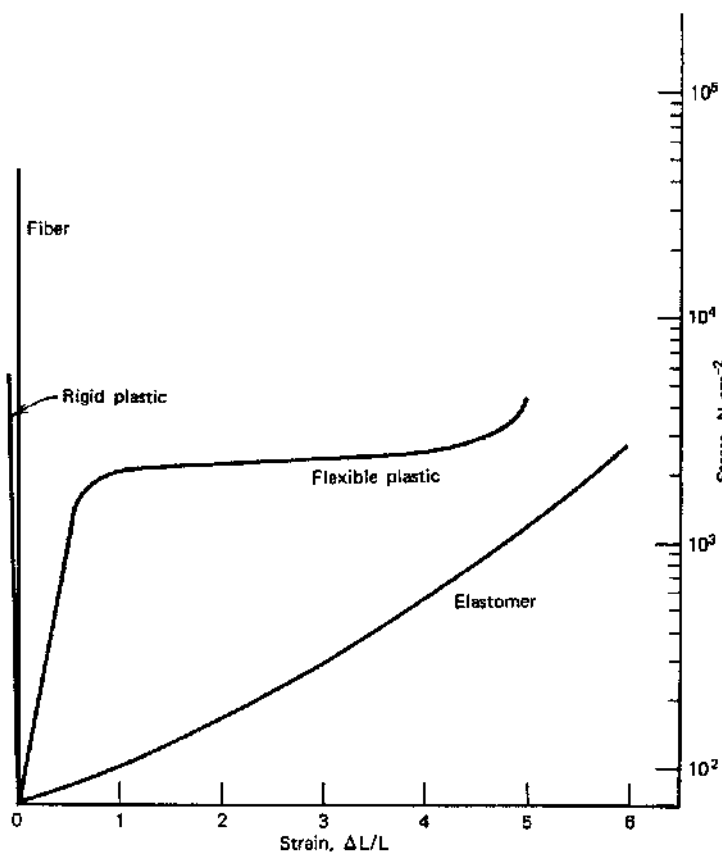


Fig. 1-10 Stress-strain plots for a typical elastomer, flexible plastic, rigid plastic, and fiber.

2. *Ultimate Strength or Tensile Strength.* The stress required to rupture the sample.
3. *Ultimate Elongation.* The extent of elongation at the point where the sample ruptures.
4. *Elastic Elongation.* The elasticity as measured by the extent of reversible elongation.

Polymers vary widely in their mechanical behavior depending on the degree of crystallinity, degree of crosslinking, and the values of T_g and T_m . High strength and low extensibility are obtained in polymers by having various combinations of high degrees of crystallinity or crosslinking or rigid chains (characterized by high T_g). High extensibility and low strength in polymers are synonymous with low degrees of crystallinity and crosslinking and low T_g values. The temperature limits of utility of a polymer are governed by its T_g and/or T_m . Strength is lost at or near T_g for an amorphous polymer and at or near T_m for a crystalline polymer.

An almost infinite variety of polymeric materials can be produced. The polymer scientist must have an awareness of the properties desired in the final polymer in order to make a decision about the polymer to be synthesized. Different polymers are synthesized to yield various mechanical behaviors by the appropriate combinations of crystallinity, crosslinking, T_g , and T_m . Depending on the particular combination, a specific polymer will be used as a *fiber*, *flexible plastic*, *rigid plastic*, or *elastomer* (rubber). Commonly encountered articles that typify these uses of polymers are clothing and rope (fiber), packaging films and seat covers (flexible plastic), eyeglass lenses and housings for appliances (rigid plastic), and rubber bands and tires (elastomer). Table 1-4 shows the uses of many of the common polymers. Some polymers are used in more than one category because certain mechanical properties can be manipulated by appropriate chemical or physical means, such as by altering the crystallinity or adding plasticizers (Sec. 3-14c-1) or copolymerization (Sec. 3-14b, Chap. 6). Some polymers are used as both plastics and fibers, other as both elastomers and plastics.

TABLE 1-4 Use of Polymers

Elastomers	Plastics	Fibers
Polyisoprene	Polyethylene	
Polyisobutylene	Polytetrafluoroethylene	
	Poly(methyl methacrylate)	
	Phenol-formaldehyde	
	Urea-formaldehyde	
	Melamine-formaldehyde	
	← Polystyrene →	
	← Poly(vinyl chloride) →	
	← Polyurethane →	
	← Polysiloxane →	
		← Polyamide →
		← Polyester →
		← Cellulosics →
		← Polypropene →
		Polyacrylonitrile

1-6b Elastomers, Fibers, and Plastics

The differences between fibers, plastics, and elastomers can be seen in the stress–strain plots in Fig. 1-10. The modulus of a polymer is the initial slope of such a plot; the tensile strength and ultimate elongation are the highest stress and elongation values, respectively. Elastomers are the group of polymers that can easily undergo very large, reversible elongations (≤ 500 – 1000%) at relatively low stresses. This requires that the polymer be completely (or almost completely) amorphous with a low glass transition temperature and low secondary forces so as to obtain high polymer chain mobility. Some degree of crosslinking is needed so that the deformation is rapidly and completely reversible (elastic). The initial modulus of an elastomer should be very low ($<100 \text{ N cm}^{-2}$), but this should increase fairly rapidly with increasing elongation; otherwise, it would have no overall strength and resistance to rupture at low strains. Most elastomers obtain the needed strength via crosslinking and the incorporation of reinforcing inorganic fillers (e.g., carbon black, silica). Some elastomers undergo a small amount of crystallization during elongation, especially at very high elongations, and this acts as an additional strengthening mechanism. The T_m of the crystalline regions must be below or not significantly above the use temperature of the elastomer in order that the crystals melt and deformation be reversible when the stress is removed. Polyisoprene (natural rubber) is a typical elastomer—it is amorphous, is easily crosslinked, has a low T_g (-73°C), and has a low T_m (28°C). Crosslinked (moderately) polyisoprene has a modulus that is initially less than 70 N cm^{-2} ; however, its strength increases to about 1500 N cm^{-2} at 400% elongation and about 2000 N cm^{-2} at 500% elongation. Its elongation is reversible over the whole elongation range, that is, up to just prior to the rupture point. The extent of crosslinking and the resulting strength and elongation characteristics of an elastomer cover a considerable range depending on the specific end use. The use of an elastomer to produce an automobile tire requires much more crosslinking and reinforcing fillers than does the elastomer used for producing rubber bands. The former application requires a stronger rubber with less tendency to elongate than the latter application. Extensive crosslinking of a rubber converts the polymer to a rigid plastic.

Fibers are polymers that have very high resistance to deformation—they undergo only low elongations (<10 – 50%) and have very high moduli ($>35,000 \text{ N cm}^{-2}$) and tensile strengths ($>35,000 \text{ N cm}^{-2}$). A polymer must be very highly crystalline and contain polar chains with strong secondary forces in order to be useful as a fiber. Mechanical stretching is used to impart very high crystallinity to a fiber. The crystalline melting temperature of a fiber must be above 200°C so that it will maintain its physical integrity during the use temperatures encountered in cleaning and ironing. However, T_m should not be excessively high—not higher than 300°C —otherwise, fabrication of the fiber by melt spinning may not be possible. The polymer should be soluble in solvents used for solution spinning of the fiber but not in dry-cleaning solvents. The glass transition temperature should have an intermediate value; too high a T_g interferes with the stretching operation as well as with ironing, while too low a T_g would not allow crease retention in fabrics. Poly(hexamethylene adipamide) is a typical fiber. It is stretched to high crystallinity, and its amide groups yield very strong secondary forces due to hydrogen bonding; the result is very high tensile strength ($70,000 \text{ N cm}^{-2}$), very high modulus ($500,000 \text{ N cm}^{-2}$), and low elongation ($<20\%$). The T_m and T_g have optimal values of 265 and 50°C , respectively. [The use of polypropene as a fiber is an exception to the generalization that polar polymers are required for fiber applications. The polypropene used as a fiber has a highly stereoregular structure and can be mechanically stretched to yield a highly oriented polymer with the strength characteristics required of a fiber (see Sec. 8-11d).]

Plastics represent a large group of polymers that have a wide range of mechanical behaviors in between those of the elastomers and fibers. There are two types of plastics—flexible plastics and rigid plastics. The flexible plastics possess moderate to high degrees of crystallinity and a wide range of T_m and T_g values. They have moderate to high moduli (15,000–350,000 N cm⁻²), tensile strengths (1500–7000 N cm⁻²), and ultimate elongations (20–800%). The more typical members of this subgroup have moduli and tensile strengths in the low ends of the indicated ranges with elongations in the high end. Thus polyethylene is a typical flexible plastic with a tensile strength of 2500 N cm⁻², a modulus of 20,000 N cm⁻², and an ultimate elongation of 500%. Other flexible plastics include polypropene and poly(hexamethylene adipamide). Poly(hexamethylene adipamide) is used as both a fiber and a flexible plastic. It is a plastic when it has moderate crystallinity, while stretching converts it into a fiber. Many flexible plastics undergo large ultimate elongations—some as large as those of elastomers. However, they differ from elastomers in that only a small portion (approximately <20%) of the ultimate elongation is reversible. The elongation of a plastic past the reversible region results in its permanent deformation, that is, the plastic will retain its elongated shape when the stress is removed.

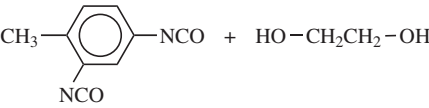
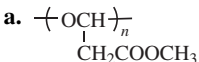
The rigid plastics are quite different from the flexible plastics. The rigid plastics are characterized by high rigidity and high resistance to deformation. They have high moduli (70,000–350,000 N cm⁻²) and moderate to high tensile strengths (3000–8500 N cm⁻²), but more significantly, they undergo very small elongations (<0.5–3%) before rupturing. The polymers in this category are amorphous polymers with very rigid chains. The high chain rigidity is achieved in some cases by extensive crosslinking, for example, phenol–formaldehyde, urea–formaldehyde, and melamine–formaldehyde polymers. In other polymers the high rigidity is due to bulky side groups on the polymer chains resulting in high T_g values, for example, polystyrene ($T_g = 100^\circ\text{C}$) and poly(methyl methacrylate) ($T_g = 105^\circ\text{C}$).

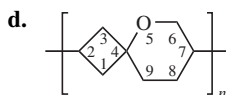
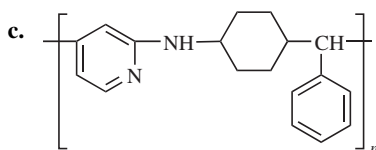
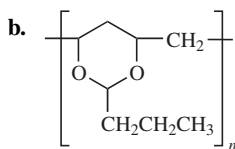
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PROBLEMS

- 1-1** Show by equations the overall chemical reactions involved in the synthesis of polymers from
- $\text{CH}_2=\text{CH}-\text{CO}_2\text{H}$
 - 
 - $\text{H}_2\text{N}-(\text{CH}_2)_5-\text{NH}_2 + \text{ClCO}-(\text{CH}_2)_5-\text{COCl}$
 - $\text{HO}-(\text{CH}_2)_5-\text{CO}_2\text{H}$
 -  + $\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$
 - $\text{CH}_2=\text{CH}-\text{F}$
- 1-2** What is the structure of the repeating unit in each of the polymers in Problem 1-1? Can any other monomer(s) be used to obtain the same polymer structure for any of these polymer?
- 1-3** Classify the polymers as to whether they are condensation or addition polymers. Classify the polymerizations as to whether they are step, chain, or ring-opening polymerizations.
- 1-4** How would you experimentally determine whether the polymerization of an unknown monomer X was proceeding by a step or a chain mechanism?
- 1-5** Name each of the polymers in Problem 1-1 by the IUPAC system. Indicate alternate names where applicable based on the polymer source, non-IUPAC structure system, or trade names.
- 1-6** Name each of the following polymers by the IUPAC system
- 



1-7 A sample of polystyrene is composed of a series of fractions of different-sized molecules:

Fraction	Weight Fraction	Molecular Weight
A	0.10	12,000
B	0.19	21,000
C	0.24	35,000
D	0.18	49,000
E	0.11	73,000
F	0.08	102,000
G	0.06	122,000
H	0.04	146,000

Calculate the number-average and weight-average molecular weights of this polymer sample. Draw a molecular weight distribution curve analogous to Fig. 1-4.

1-8 Indicate how the extent of polymer crystallinity is affected by chemical structure.

1-9 Define T_m and T_g and indicate how they are affected by chemical structure.

1-10 Describe the differences in the properties and uses of flexible plastics, rigid plastics, fibers, and elastomers. What types of chemical structures are typical of each?