◇ SECOND EDITION ◇

Contemporary Polymer Chemistry

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◇ CHAPTER 1 ◇

The Scope of Polymer Chemistry

INTRODUCTION

During the past 40 years, polymer chemistry has had a marked and very direct practical impact on the way of life of people in nearly every region of the earth. Before the beginning of World War II, relatively few materials were available for the manufacture of the articles needed for a civilized life. Steel, glass, wood, stone, brick, and concrete accounted for most of the construction and manufacturing needs of the population, while cotton, wool, jute, and a few other agricultural products provided the raw materials for clothing or fabric manufacture.

The rapid increase in the range of manufactured products following World War II resulted directly from the development of a broad range of new fibers, plastics, elastomers, adhesives, and resins. These new materials are polymers, and their impact on our present way of life is almost incalculable. Products made from polymers are all around us—clothing made from synthetic fibers, polystyrene cups, Fiberglas boats, nylon bearings, plastic bags, polymer-based paints, epoxy glue, polyurethane foam cushions, silicone heart valves, Teflon-coated cookware—the list is almost endless.

It is not surprising, therefore, that more than 50% of all chemists and chemical engineers, large numbers of physicists and mechanical engineers, and nearly all materials scientists and textile technologists are involved with research or development work with polymers. Add to this the fact that biochemistry, biophysics, and molecular biology are fields in which polymer chemistry plays a paramount role, and it is clear why the study of macromolecules is one of the most important and rapidly growing branches of science.

Polymer chemistry is not a specialized side branch of traditional chemistry. Instead, it is a uniquely broad discipline that *encompasses* the whole of chemistry and several other fields as well. Areas of science have always prospered when research

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workers trained in one specialized area turn their attention to a related area. This has been and still is especially true in polymer research. The challenge in polymer chemistry is the application of fundamental chemical and physical techniques and ideas to large and complex molecules. This is a demanding task, and it requires the very best approaches that traditional chemistry can provide.

It will be clear that polymer chemistry, perhaps more than any other research area, cuts across the traditional lines of organic, inorganic, physical, and analytical chemistry; physics; engineering; biology; and even medicine. A newcomer to polymer science needs to be able to blend together knowledge from all these fields. It is to assist in that process that this book has been written.

DEFINITIONS

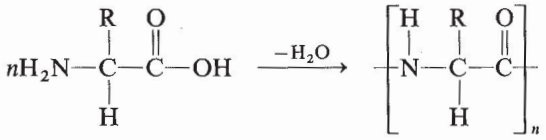
Many of the terms and definitions used in polymer chemistry are not encountered in conventional chemical textbooks, and for this reason the following summary of terminology is given. Some of these definitions will seem fairly obvious, but others will need explanation.

Monomers

A monomer is any substance that can be converted into a polymer. For example, ethylene is a monomer that can be polymerized to polyethylene (reaction 1). An

$$CH_2{=}CH_2 \longrightarrow -CH_2-CH_2-CH_2-CH_2-CH_2- \qquad (1)$$

amino acid is a monomer which, by loss of water, can polymerize to give polypeptides (reaction 2). The term *monomer* is used very loosely—sometimes it applies to dimers or trimers if they, themselves, can undergo further polymerization.

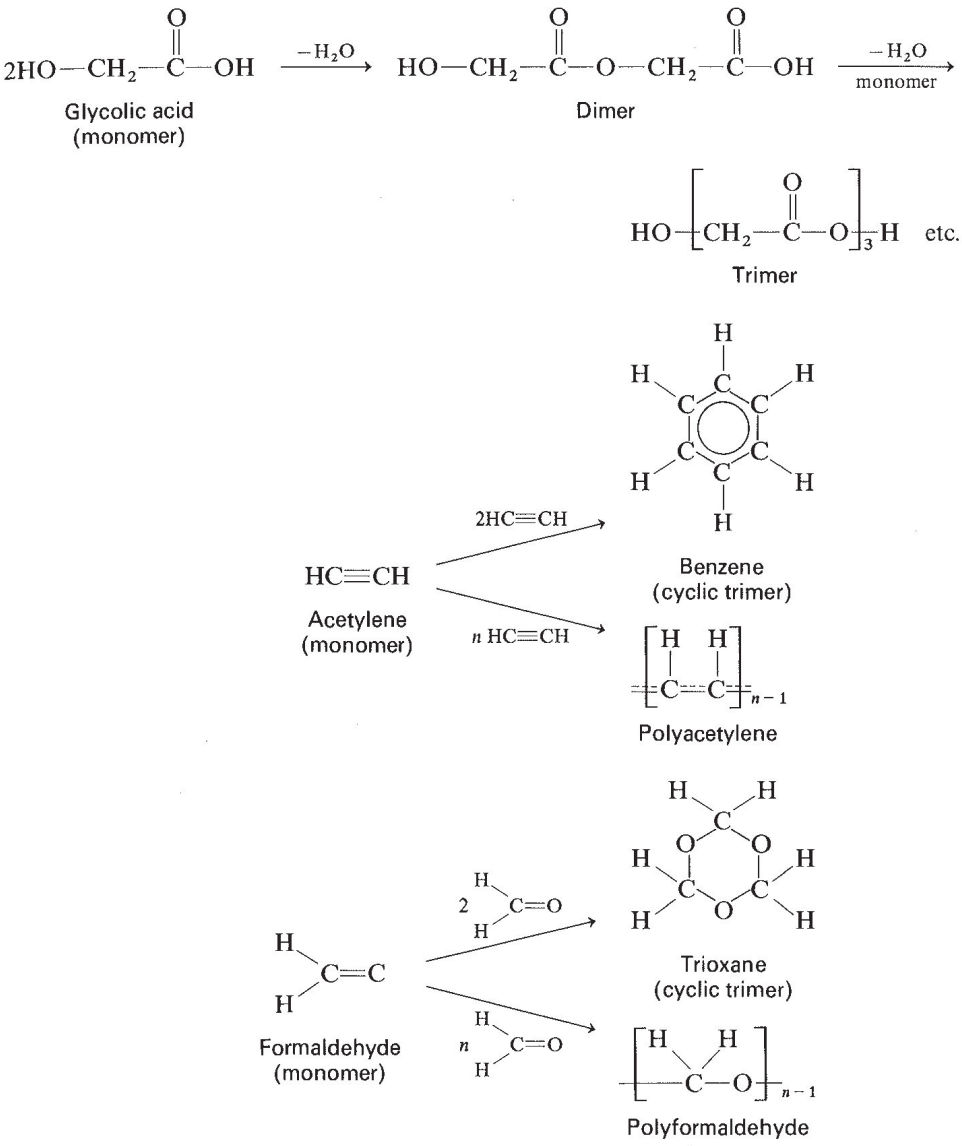


(2)

Dimers, Trimers, and Oligomers

The polymerization of a monomer often occurs in a sequential manner. In other words, two monomer molecules first react together to form a *dimer*. The dimer may then react with a third monomer to yield a *trimer*, and so on. Dimers are usually linear molecules, but trimers, tetramers, pentamers, and so on, can be linear or cyclic. The reactions outlined in schemes (3) to (5) illustrate the relationship between monomers, dimers, and trimers for three systems. Low-molecular-weight polymerization products, for example, dimers, trimers, tetramers, pentamers, and so on—cyclic or linear—are known as *oligomers*. Some care should be taken to avoid use of the term "polymer" to describe materials that are really oligomers, because these two types of products have very different properties.

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Polymers

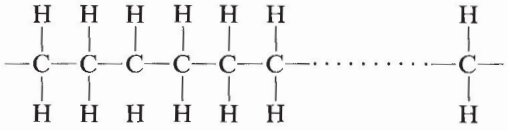
The term *polymer* is used to describe *high-molecular-weight substances.* However, this is a very broad definition and in practice it is convenient to divide polymers into subcategories according to their molecular weight and structure. Although there is no general agreement on this point, in this book we will consider *low polymers* to have molecular weights below about 10,000 to 20,000 and *high polymers* to have molecular weights between 20,000 and several million. Obviously, this is a rather arbitrary dividing line, and a better definition might be based on the number of repeating units in the structure. For example, since polymer properties become almost independent of molecular weight when more than 1000 to 2000 repeating units are

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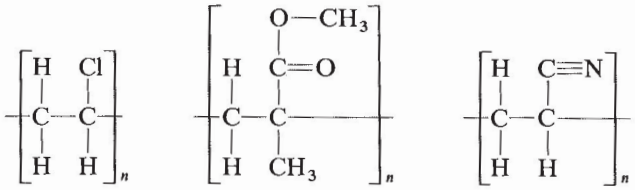
present, this point could also constitute a satisfactory dividing line between low and high polymers.

Linear Polymers

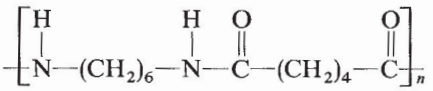
A *linear polymer* consists of a long chain of skeletal atoms to which are attached the substituent groups. Polyethylene (**1**) is one of the simplest examples. Linear polymers are usually *soluble* in some solvent, and in the solid state at normal temperatures they exist as elastomers, flexible materials, or glasslike thermoplastics. In addition to polyethylene, typical linear-type polymers include poly(vinyl chloride) or PVC (**2**), poly(methyl methacrylate) (also known as PMMA, Lucite, Plexiglas, or Perspex) (**3**), polyacrylonitrile[1] (Orlon or Creslan) (**4**), and nylon 66 (**5**).



1



2 **3** **4**



5

Branched Polymers

A *branched polymer* can be visualized as a linear polymer with branches of the same basic structure as the main chain. A branched polymer structure is illustrated in Figure 1.1. Branched polymers are often soluble in the same solvents as the corresponding linear polymer. In fact, they resemble linear polymers in many of their properties. However, they can sometimes be distinguished from linear polymers by their lower tendency to crystallize or by their different solution viscosity or light-scattering behavior. Heavily branched polymers may swell in certain liquids without dissolving completely.

[1] Note that parentheses are not normally used in the name of a polymer if the monomer has a one-word name. The parentheses simply avoid ambiguity.

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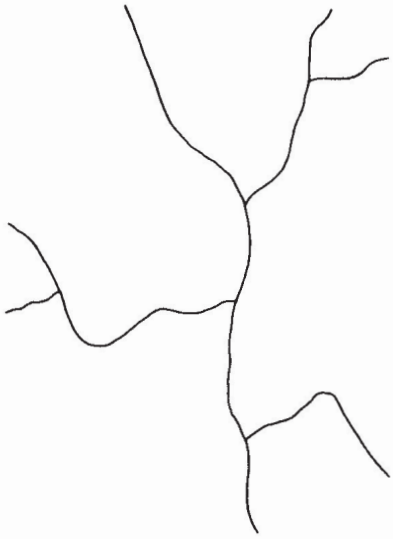


Figure 1.1 Branched polymer.

Crosslinked Polymers

A *crosslinked* or *network polymer* is one in which chemical linkages exist between the chains, as illustrated in Figure 1.2. Such materials are usually swelled by "solvents," but they *do not dissolve.* In fact, this insolubility can be used as a cautious criterion of a crosslinked structure. Actually, the amount by which the polymer is swelled by a liquid depends on the density of crosslinking: the more crosslinks present, the smaller is the amount of swelling. If the degree of crosslinking is high enough, the polymer may be a rigid, high-melting, unswellable solid, such as diamond. Light crosslinking of chains favors the formation of rubbery elastomeric properties.

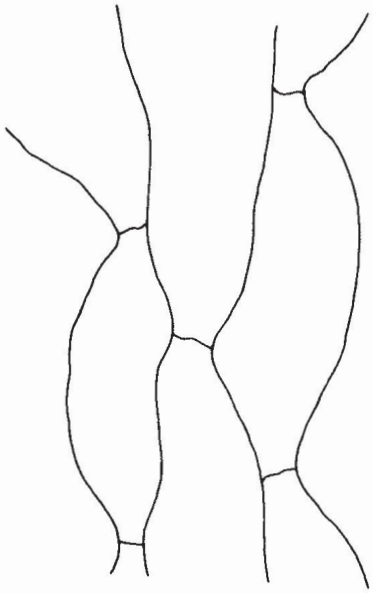
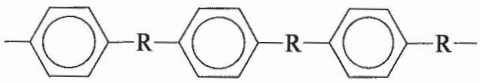


Figure 1.2 Crosslinked macromolecule.

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Cyclolinear Polymers

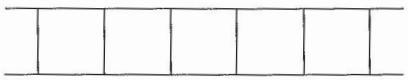
Cyclolinear polymers are a special type of linear polymer formed by the linking together of ring systems. Benzene rings are often incorporated into polymers of this type (**6**), but heterocyclic and inorganic rings can also be utilized in the same way. The properties of cyclolinear polymers resemble those of conventional linear polymers, except that the solubility of the cyclolinear species is often low. The tendency for crystallization may be very high.



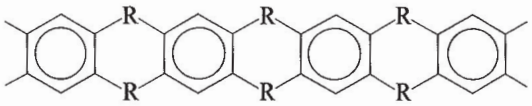
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Ladder Polymers

As the name suggests, a *ladder polymer* consists of linear molecules in which two skeletal strands are linked together in a *regular* sequence by crosslinking units, as illustrated diagramatically in **7.** In practice, aromatic rings may constitute the linking units (**8**) or, in ladder-type silicone polymers, silicon–oxygen units serve the same function (see Chapter 9). As might be expected, ladder polymers have a more rigid molecular structure than do conventional linear polymers, and they are often much less soluble. However, they frequently display very good thermal stability, because molecular-weight decreases must be preceded by the cleavage of two bonds at each cleavage site. Spiropolymers of the type shown in Figure 1.3 are sometimes included in the ladder polymer classification.



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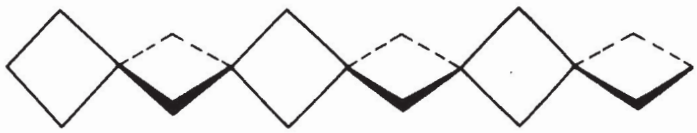
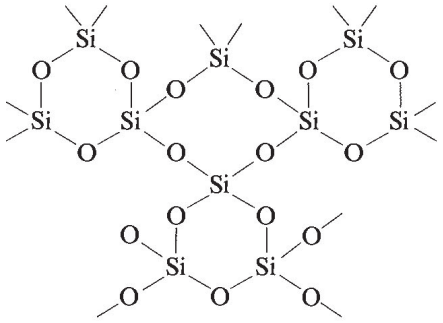


Figure 1.3 Schematic representation of a spiropolymer structure.

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Cyclomatrix Polymers

Many polymer systems are known in which ring systems are linked together to form a three-dimensional matrix of connecting units. These materials are known as *cyclomatrix polymers.* Organic and inorganic rings can be incorporated into such systems, and typical examples are provided by the structures found in some silicate minerals and silicone resins (**9**). Since a three-dimensional network of bonds is formed in these systems, the polymers are highly insoluble, rigid, very high melting, and usually stable at elevated temperatures. Structures of this type are often found in thermosetting resins (see page 11) and in heat-resistant wire coatings.

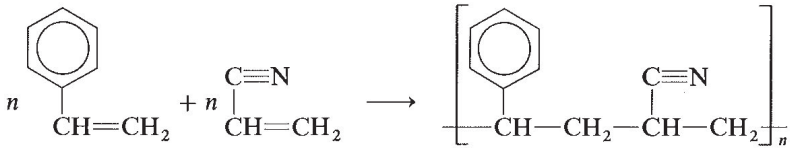


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Graphite is a special example of a cyclomatrix polymer. It has a structure made up of sheets of fused aromatic rings. Individual sheets or layers are sandwiched between the neighboring layers and are held in place by weak van der Waals forces.

Copolymers

A *copolymer* is a polymer made from two or more different monomers. For example, if styrene and acrylonitrile are allowed to polymerize in the same reaction vessel, a copolymer will be formed which contains both styrene and acrylonitrile residues (reaction 6). Many commercial synthetic polymers are copolymers. It should be noted that the sequence of monomer units along a copolymer chain can vary according to the method and mechanism of synthesis. Three different types of sequencing arrangements are commonly found.



Copolymer (6)

1. *Random copolymers.* In random copolymers, no definite sequence of monomer units exists. A copolymer of monomers A and B might be depicted by the

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arrangement shown in **10.** Random copolymers are often formed when olefin-

—A—B—B—B—A—A—B—A—A—A—A—B—A—B—B—B—

10

type monomers copolymerize by free-radical-type processes (see Chapter 3). The properties of random copolymers are usually quite different from those of the related homopolymers.

2. *Regular copolymers.* As the name implies, regular copolymers contain a regular alternating sequence of two monomer units (**11**). Olefin polymerizations that

—A—B—A—B—A—B—A—B—

11

take place through ionic-type mechanisms (see Chapter 4) can yield copolymers of this type. Again, the properties of the copolymer usually differ markedly from those of the two related homopolymers.

3. *Block copolymers.* Block copolymers contain a block of one monomer connected to a block of another, as illustrated in sequence **12.** Block copolymers are

—A—A—A—A—A—A—A—A—B—B—B—B—B—B—B—

12

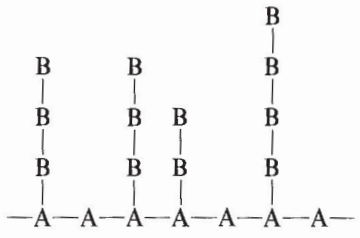
usually formed by ionic polymerization processes. Unlike other copolymers, they retain many of the physical characteristics of the two homopolymers.

Terpolymers

A *terpolymer* contains three different monomer units. These can be sequenced randomly or in blocks.

Graft Copolymers

A *graft copolymer* is usually prepared by linking together two different polymers. For example, a homopolymer derived from monomer A may be induced to react with a homopolymer derived from monomer B to yield the graft copolymer shown in **13.** Graft polymers of this type can often be prepared by the gamma or X-irradiation of a mixture of the two homopolymers, or even by mechanical blending of the



13

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two homopolymers. Alternatively, a graft copolymer may be prepared by the *polymerization* of monomer B from initiation sites along the chain of polymer A. Graft copolymers often display properties that are related to those of the two homopolymers.

Thermoplastics

Basically, a *thermoplastic* is any material that softens when it is heated. However, the term is commonly used to describe a substance that passes through a definite sequence of property changes as its temperature is raised. In Figure 1.4 the thermoplastic characteristics of amorphous, crystalline, and liquid-crystalline polymers are compared. An amorphous polymeric material contains randomly entangled chains. A microcrystalline (usually abbreviated to "crystalline") material contains domains in which the polymer chains are packed in an ordered array. These "crystalline" domains are embedded in an amorphous polymer matrix.

Both amorphous and crystalline thermoplastics are glasses at low temperatures, and both change from a glass to a rubbery elastomer or flexible plastic as the temperature is raised. This change from glass to elastomer usually takes place over a fairly narrow temperature range (2 to 5°C), and this transition point is known as the *glass transition temperature* (T_g). For many polymers, the glass transition temperature is the most important characterization feature. It can be compared to the characteristic melting point of a low-molecular-weight compound, although care should be taken to remember that T_g is definitely *not* a melting temperature in the

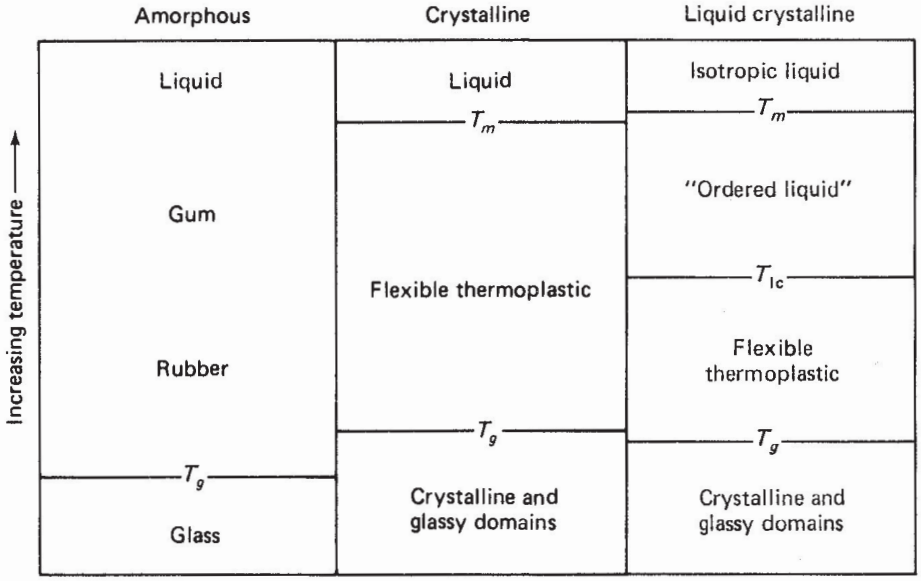


Figure 1.4 Comparison of the thermal behavior of amorphous, crystalline, and liquid crystalline polymers. The main property differences exist in the middle temperature range, where an amorphous polymer is an elastomer or a gum, a crystalline polymer is a tough, flexible material, and a liquid crystalline system shows an ordered liquid state.

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accepted sense of the word. It is more a measure of the ease of torsion of the backbone bonds rather than of the ease of separation of the molecules.

At temperatures above T_g, amorphous polymers behave in a different manner from crystalline polymers. As the temperature of an amorphous polymer is raised, the rubbery elastomeric phase *gradually* gives way to a soft, extensible elastomeric phase, then to a gum, and finally to a liquid. No sharp transition occurs from one phase to the other, and only a gradual change in properties is perceptible.

Crystalline polymers, on the other hand, retain their rubbery elastomeric or flexible properties above the glass transition, until the temperature reaches the melting temperature (T_m). At this point the material liquefies. At the same time, melting is accompanied by a loss of the optical birefringence and crystalline X-ray diffraction effects that are characteristic of the crystalline state.

Some polymers show an additional phase transition between the glass transition temperature and the formation of a true isotropic liquid. These are the so-called *liquid-crystalline* polymers. A liquid-crystalline polymer, when heated, passes through the normal glass and microcrystalline phases but undergoes a quasi melting transition (T_{lc}) at a temperature below the final liquefaction point (T_m). Between T_{lc} and T_m the polymer has some characteristics of a molten material (it flows, for example), but physical techniques reveal the retention of some structural order. Side groups may be loosely stacked in this phase, or skeletal segments may retain some alignment. Only at the highest temperature transition (T_m) is all structure lost, and the material then becomes an isotropic liquid.

The amorphous, crystalline, and liquid crystalline behavior described above is characteristic of linear and branched polymers, copolymers, or cyclolinear polymers. In general, these characteristics are not shown by heavily crosslinked polymers or cyclomatrix materials. These latter substances retain their rigidity when heated. Melting phenomena occur only when the crosslink units or backbone bonds become thermally broken. Lightly crosslinked polymers show many of the conventional thermoplastic properties, with the exception that the true liquid phase may not be formed.

Elastomers

In view of the information just given, it will be clear that an *elastomer* is a polymer that is in the temperature range between its glass transition temperature and its liquefaction temperature. In practice, elastomeric properties become more obvious if the polymer chains are lightly crosslinked. In particular, the liquefaction temperature may be raised by crosslinking, and the polymer may exhibit elastomeric properties over a wider temperature range.

Elastomeric properties appear when the backbone bonds can readily undergo torsional motions to permit uncoiling of the chains when the material is stretched (Figure 1.5). Crosslinks between the chains prevent the macromolecules from slipping past each other and thus prevent the material from becoming permanently elongated when held under tension. An important question connected with elasticity is this: Why do the chains revert to the highly coiled state when the tension on the elastomer is released? The answer lies in the fact that a highly coiled polymer system has a higher degree of disorder and, therefore, a higher entropy than a stretched, oriented

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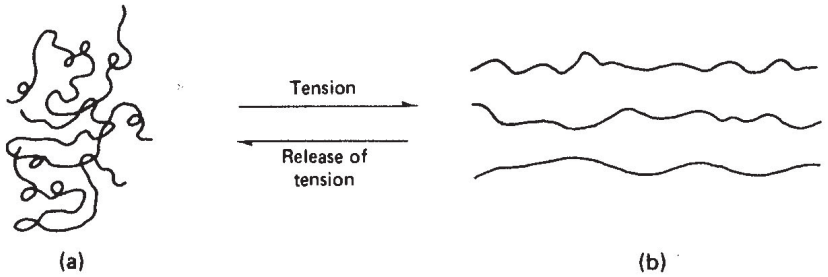


Figure 1.5 Rubbery elastomeric properties result from the stress-induced uncoiling and recoiling of polymer chains. (a) Relaxed: high entropy. (b) Stretched: ordered—low entropy.

sample. Thus, the elastic behavior is a direct consequence of the tendency of the system to assume spontaneously a state of maximum entropy. Since free energy, enthalpy, and entropy are related by the usual expression, $\Delta G = \Delta H - T\Delta S$, a stretched rubber band immediately held to the lips is warm, and the same material appears cold immediately after contraction.

Plasticizers

Many pure polymers are too rigid for use as flexible films. Poly(vinyl chloride) in the pure state is a rather rigid material. Only when this polymer is softened by the addition of liquids, such as phthalate esters, can it be used as a flexible-film or Tygon tubing. Such liquid additives are known as *plasticizers.*

Thermosetting Resin

The term *thermosetting polymer* refers to a range of systems which exist initially as liquids but which, on heating, undergo a reaction to form a solid, highly crosslinked matrix. A typical example is provided by the condensation of methylol melamine to give the hard, tough, crosslinked melamine resin (see Chapter 2). Partly polymerized systems which are still capable of liquid flow are called *prepolymers.* Prepolymers are often preferred as starting materials in technology. In practical terms, an uncrosslinked thermoplastic material can be re-formed into a different shape by heating: a *thermosetting* polymer cannot.

Polymer Blends

When two or more polymers are mixed together mechanically, the product is known as a *polymer blend.* Many polymer blends display properties that are different from those of the individual polymers. Polymer blends can be of two main types, miscible or immiscible. Superimposed on these alternatives are three additional classifications: (1) simple cellular domain mixtures of the polymers, (2) interpenetrating coils of macromolecules that are randomly mixed at the molecular level, and (3) secondary

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block or graft copolymers formed by the physical breaking of bonds, followed by bonding between the different polymeric fragments. The latter type of process can occur when two or more polymers are milled or masticated together. The mechanical shearing can result in the homolytic cleavage of bonds, followed by cross-recombination.

Tacticity

Olefin molecules that contain one unique side group, such as propylene, $CH_2{=}CH(CH_3)$, or styrene, $CH_2{=}CH(C_6H_5)$, yield polymers that possess an asymmetric center at each monomer residue. The tacticity of a polymer describes the sequencing of these asymmetric centers along the chain. Three primary possibilities exist, called isotactic, syndiotactic, or atactic (heterotactic) sequencing. This subject is discussed in more detail in Chapters 4 and 17. Here it is sufficient to note that the tacticity of a polymer markedly affects the bulk physical properties. For example, an isotactic polymer may form a microcrystalline solid that has greater strength and rigidity than its atactic counterpart.

DIFFERENT TYPES OF POLYMERS

It is convenient to classify polymers according to the types of reactions involved in their synthesis. The three main polymerization reaction types are (1) condensation reactions, (2) addition reactions, and (3) ring-opening polymerizations. As will be shown later, this classification is an oversimplification, but it provides a useful starting point for an understanding of the field.

Condensation Polymers (Step Reactions)

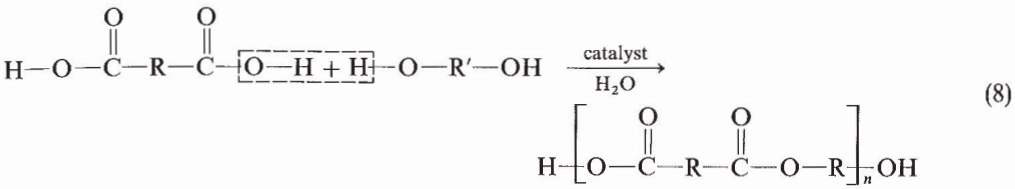
Condensation processes take place when two or more molecules react with each other with the concurrent loss of water or ammonia. This type of reaction is used as a basis for the synthesis of many important polymers, such as nylon, polyesters, phenol–formaldehyde, and urea–formaldehyde resins. It is also the basis for the laboratory formation of silicates and polyphosphates.

Nylon is a condensation polymer formed by the reaction of a diamine with a dicarboxylic acid. In particular, nylon 66 is made by the condensation of hexamethylenediamine with adipic acid as shown in equation (7).

$$H_2N{-}(CH_2)_6NH_2 + HOC{-}(CH_2)_4{-}COH \longrightarrow \text{1:1 Salt} \xrightarrow{H_2O} H{-}\left[NH(CH_2)_6NHC(CH_2)_4C\right]_n{-}OH \qquad (7)$$

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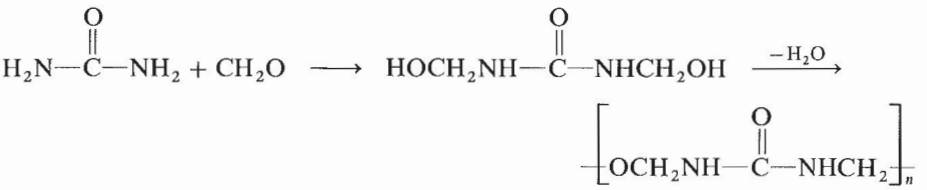
Polyesters, such as Dacron, Terylene, or Mylar, are made by the condensation of a dicarboxylic acid with a diol (reaction 8)(typically, R═C_6H_4 and R′═CH_2CH_2). The water formed in this reaction is removed by distillation. A variant of this synthesis is the use of the methyl ester of the diacid and the removal of methanol. Typical products are made from terephthalic acid (R═C_6H_4) and ethylene glycol (R′═CH_2CH_2). Alkyd paint resins are manufactured from phthalic anhydride and glycerol, and the trifunctionality of the latter reagent ensures the formation of a crosslinked structure (see Chapters 2 and 11).



(8)

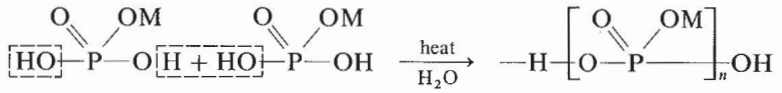
Phenol–formaldehyde (*Bakelite*) *resins* are hard, rigid polymers made by alkylation-condensation reactions between phenols and formaldehyde as discussed in Chapter 2.

Urea–formaldehyde resins are formed by the "methylolation" reaction between urea and formaldehyde, and condensation of the methylol units yields the polymer shown in reaction (9).



(9)

Inorganic condensation polymers, such as polysilicate glasses and polyphosphates, are formed by removal of water from the appropriate di-, tri-, or tetrahydroxy monomer, as illustrated by reaction (10).



(M = An alkali metal) Polyphosphate

(10)

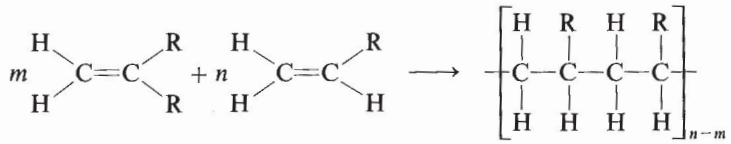
Biological condensation polymerizations, such as those involved in enzyme-catalyzed condensation reactions, are responsible for the polymerization of some amino acids to proteins: for the condensation of sugars to polysaccharides such as starch, cellulose, and glycogen, and for the synthesis of nucleic acids such as DNA and RNA. A separate chapter (Chapter 8) is devoted to a consideration of biological polymers. From the viewpoint of fundamental polymer chemistry it should be remembered that the physiological properties of biological macromolecules are often determined as much by the *molecular conformation* as by the chemical composition.

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This aspect is discussed in Chapters 8 and 18. It should also be noted that many naturally occurring condensation polymers, particularly proteins and cellulose, are chemically modified before they are used in technology. This subject is covered in Chapter 8.

Addition Polymers

Addition polymers are macromolecules formed by the addition reactions of olefins, acetylenes, aldehydes, or other compounds with "unsaturated" bonds. These reactions are summarized by the scheme shown in (11). Many well-known thermo-plas-



(11)

tics are addition-type polymers, the differences between the various materials being associated primarily with the presence of different substituent groups attached to the main chain. For example, high polymers are known (and manufactured on a large scale) in which Cl, CN, C_6H_5, $CH_3OC(O)$—, CH_3, and a variety of other units are present as side groups to the main chain. The equations and names shown in (12) to (21) illustrate some addition polymerization processes.

(a) $n CH_2{=}CH_2 \longrightarrow {+}CH_2{-}CH_2{+}_n$ Polyethylene (12)

(b) $n CH_2{=}CH(Cl) \longrightarrow {+}CH_2{-}CH(Cl){+}_n$ Poly(vinyl chloride) (PVC) (13)

(c) $n CH_2{=}CH(C{\equiv}N) \longrightarrow {+}CH_2{-}CH(C{\equiv}N){+}_n$ Polyacrylonitrile (acrylic fiber, Creslan) (14)

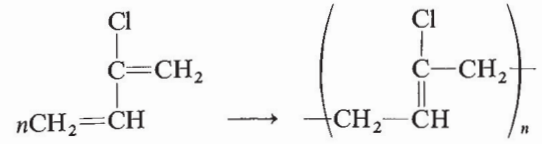
(d) $n CH_2{=}CH(C_6H_5) \longrightarrow {+}CH_2{-}CH(C_6H_5){+}_n$ Polystryrene (15)

(e) $n CH_2{=}C(CH_3)_2 \longrightarrow {+}CH_2{-}C(CH_3)_2{+}_n$ Polyisobutylene (butyl rubber) (16)

(f) $n CH_2{=}CH{-}C(CH_3){=}CH_2 \longrightarrow {+}CH_2{-}CH{=}C(CH_3){-}CH_2{+}_n$ *trans*-1,4-Polyisoprene (17)

(g) $n CH_2{=}CH{-}CH{=}CH_2 \longrightarrow {+}CH_2{-}CH{=}CH{-}CH_2{+}_n$ *trans*-1,4-Polybutadiene (18)

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(h) 

trans-1,4-Polychloroprene (neoprene rubber) (19)

(i) $n CF_2{=}CF_2 \longrightarrow \text{-}(CF_2{-}CF_2)\text{-}_n$ Poly(tetrafluoroethylene) (Teflon[1]) (20)

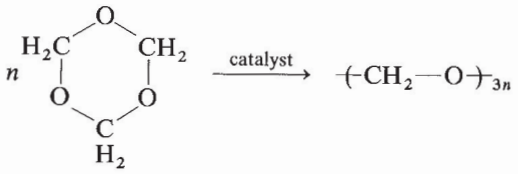
(j) $n CH_2{=}O \longrightarrow \text{-}(CH_2{-}O)\text{-}_n$ Polyformaldehyde (polyoxymethylene, Delrin[2]) (21)

It should be recognized that polymers such as polyacrylonitrile, polybutadiene, and polychloroprene contain additional unsaturation that can be utilized in subsequent high-temperature or crosslinking reactions. Addition polymerizations are considered in more detail in Chapters 3, 4, 5, 12, and 13.

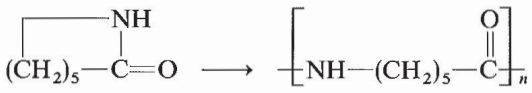
Ring-Opening Polymerizations

The treatment of some cyclic compounds with catalysts brings about cleavage of the ring followed by polymerization to yield high-molecular-weight polymers.

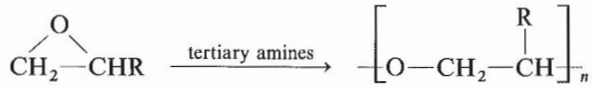
For example, as shown in reaction (22), trioxane polymerizes to yield polyformaldehyde (polyoxymethylene). Caprolactam polymerizes to nylon 6 (reaction 23), and expoxides undergo ring-opening reactions to yield polyethers (24).



(22)

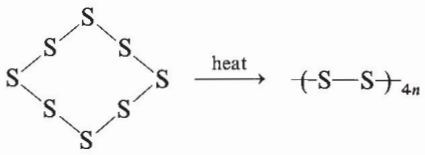


(23)



(24)

A number of inorganic ring systems also polymerize by ring-opening reactions. Rhombic sulfur, cyclic siloxanes, and cyclic chlorophosphazenes behave in this way (reactions 25 to 27).

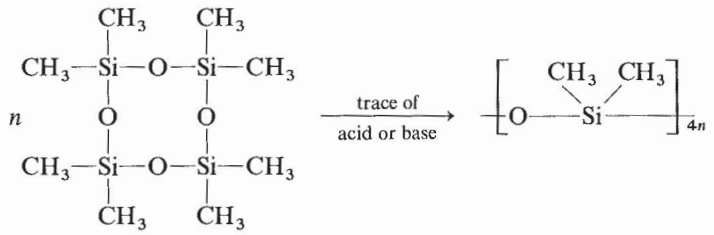


(25)

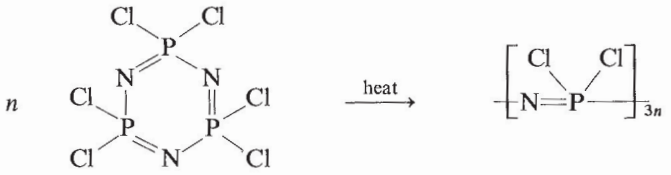
Rhombic sulfur Plastic sulfur

[1] Du Pont's registered trademark for its fluorocarbon resins.
[2] Du Pont's registered trademark for its acetal resins.

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Octamethylcyclotetrasiloxane — Poly(dimethylsiloxane) (26)



Hexachlorocyclotriphosphazene — Poly(dichlorophosphazene) (inorganic rubber) (27)

Ring-opening polymerizations will be considered further in Chapters 6, 9, and 10.

Initiators

A few polymerization reactions take place spontaneously, but most require the addition of small quantities of compounds called *initiators.* As the name suggests, these species start the polymerization process. Many of them are not catalysts in the true sense of that word, because they are changed chemically as they trigger the start of the chain growth process. Different initiators are required for different types of polymerization processes. For example, peroxides, azo compounds, Lewis acids, organometallic species, or high-energy irradiation are used to initiate different addition-type polymerizations. Dehydration or dehydrohalogenation reagents may be needed to induce condensation reactions, and so on. The search for improved initiators has been and still is a major research area in polymer chemistry.

HISTORICAL OVERVIEW

The Macromolecular Hypothesis

Although natural polymers have been used by human beings since antiquity, their structure was not understood, even in elementary terms, until the late nineteenth century. The problem encountered by the earliest investigators was a general unwillingness on the part of the scientific community to believe that giant covalently bonded molecules could exist. Indeed, the physical tools for the measurement of molecular weights in solution (based on the work of Raoult and van't Hoff) did not exist until the 1800s. In 1888, Brown and Morris used a cryoscopic technique to estimate the molecular weight of a starch hydrosylate at about 30,000. The same

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technique was used by Gladstone and Hibbert to estimate that the molecular weight of rubber was between 6000 and 12,000, or perhaps even higher.

However, the demonstration that materials such as starch, rubber, or proteins had high molecular weights did not convince the scientific community that these materials had polymeric structures. On the contrary, it was generally assumed that the high values for the molecular weights resulted from defects in the cryoscopic method, or were due to association of smaller molecules. This view persisted even as the rubber industry prospered after 1839 and synthetic polymers came into limited use. Evidence about the structure of polymers began to accumulate between 1890 and 1919 from the work of Emil Fischer on proteins. However, it was not until 1920 that Staudinger put forward the idea of covalently bonded macromolecular structures for polystyrene, rubber, and polyoxymethylene and began the process of providing convincing evidence in favor of this structure. Even in the following 10 years, this hypothesis was subjected to intense criticism.

Structural Work

The application of physics and physical chemistry to macromolecular systems dates back to the early attempts made in the late nineteenth century to understand the unusual properties of natural polymers, such as rubber, polysaccharides, and proteins. However, it was not until the 1920–1930 period that Meyer and Mark in Germany began to establish the structure of cellulose and rubber with the use of X-ray diffraction techniques. Explanations of rubbery elasticity in terms of polymer conformations were put forward by Kuhn, Guth, and Mark between 1930 and 1934, Kuhn, in particular, was the first to apply statistical methods to the study of macromolecules.

The application of light scattering to macromolecular systems was made by Debye during World War II. It was also during this period that Flory began a series of investigations into the applications of statistical methods, conformational analysis, and other fundamental physicochemical techniques, to polymer science. During the early 1950s, Watson, Crick, Wilkins, Franklin, Kendrew, and Hodgkin successfully applied X-ray diffraction analysis to the structure determination of biological polymers, such as DNA, hemoglobin, and insulin.

Single crystals of polyethylene were first reported by Keller and Till in 1957. Increasingly, during the period 1960–1980, nuclear magnetic resonance (NMR) analysis of polymers in solution has proved to be a vital physical tool. The introduction of solid-state NMR methods in the 1980s has had a major impact on polymer structural analysis. In addition, the use of lasers in light-scattering experiments, the development of Fourier transform infrared analysis, and the introduction of surface probe analysis techniques have been responsible for major advances in our understanding of polymer structures.

Synthetic Polymers

The synthesis of polymers can be traced to the years 1838 and 1839 when the photochemical polymerization of vinyl chloride was observed, styrene was found to polymerize to a glass, and the sulfur-induced vulcanization (crosslinking) of natural

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rubber was discovered. This last discovery by MacIntosh and Hancock in Britain and Goodyear in the United States provided a commercial incentive for the study of polymeric materials, since it led to the widespread use of rubber in tires and rainwear.

As shown in Table 1.1 a number of important new polymers were prepared and commercialized in the period between 1890 and 1930, many of which were based on the use of chemical reactions (acetylation, nitration) carried out on cellulose. It is perhaps astonishing to realize that most of these technological developments occurred during a time when the polymeric nature of these products was not recognized or believed.

The 15 years between 1930 and 1945 represent the springboard for the development of modern synthetic polymer chemistry. By 1930, the macromolecular hypothesis was beginning to be accepted. Moreover, in 1929, Carothers at the Du Pont Company began his classical series of attempts to prepare high polymers from well-characterized, low-molecular-weight compounds. The success of these studies provided a final verification of the macromolecular theory. The work also led to the

TABLE 1.1 APPROXIMATE SEQUENCE OF POLYMER SYNTHESIS DEVELOPMENTS

1838, 1839	Polymerization of vinyl chloride and styrene. Vulcanization of rubber.
1868	"Celluloid" (cellulose nitrate plus camphor).
1893	Rayon (regenerated cellulose).
1910	Styrene-diene copolymers. Phenolic resins.
1914	Cellulose acetate as aircraft "dope."
1920	Cellulose nitrate lacquers (automobiles).
1924	Cellulose acetate fibers.
1927	Cellulose acetate plastics. Poly(vinyl chloride) manufacture.
1929	Urea-formaldehyde resins.
1930	General acceptance of the macromolecular hypothesis.
1931	Poly(methyl methacrylate).
1936	Poly(vinyl acetate) and poly(vinyl butyrate) in laminated safety glass. Nylon 66 manufacture.
1937	Polystrene manufacture.
1939	Melamine-formaldehyde resins. Neoprene rubber. Polysulfide rubber (Thiokol).
1939–1945	Manufacture of polyethylene (U.K.). Polybutadiene rubber (Germany). Acrylonitrile-butadiene rubber (Germany). Polyurethanes (Germany). Styrene-butadiene rubber (U.S.A.). Polyisobutylene (butyl rubber) (U.S.A.).
1945–1960	Epoxy resins, acrylonitrile-butadiene-styrene (ABS) polymers, polyesters, polyacrylonitrile, polysiloxanes (silicones), linear polyethylene, polypropylene, "living" anionic polymerizations, cationic polymerizations, polyoxymethylene, polycarbonates, polyurethane foams, fluorocarbon polymers.
1960–1980s	cis-Polyisoprene rubber, cis-polybutadiene rubber, ethylene-propylene rubber, polyimides, poly(phenylene oxides), polysulfones, styrene-butadiene block copolymers, aromatic polyamides, aromatic ladder polymers, group-transfer polymerization, cyclopolymerizations, olefin metathesis polymerization, polyphosphazenes, polysilanes. . . .

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synthesis of polyamides and polyesters. Nylon 66 was, in fact, produced commercially in 1938. Much of the spadework in polymer synthesis that was to form the foundation of the subject as we know it today was done during this period. Moreover, the technological emergencies generated by World War II provided the stimulus for a massive effort by chemists to synthesize new macromolecular materials. For example, the development of polyethylene as an insulator for radar equipment and the large scale synthesis of replacements for natural rubber took place during this time.

The development of polymer synthesis in the period 1945–1960 was accelerated by the large-scale availability of new monomers from the petrochemicals industry, coupled with a series of key scientific discoveries. These include the pivotal development by Ziegler and Natta of organometallic compounds as initiators for the polymerization of ethylene and catalysts for the stereoregular polymerization of other olefins. The recognition of nonterminated ("living") polymers by Szwarc also occurred during this period, as did many other synthetic advances (Table 1.1).

Many additional discoveries have emerged since the 1960s (Table 1.1), and most of these have transformed polymer science and its related technologies. However, by the late 1980s it was already evident that polymer science was entering a new phase.

This most recent phase of synthetic polymer chemistry has involved a subtle shift in emphasis. Many of the most accessible (and inexpensive) "commodity" polymers have been studied in detail and their applications have been developed extensively. Interest is now focused on the synthesis and study of entirely new polymers that have specialized, high-performance properties, such as very high strength, low-temperature flexibility, electrical conductivity, flame resistance, high-temperature stability, oil and fuel resistance, biomedical compatibility, or suitability for pyrolysis to ceramics. Newer methods of synthesis, such as the macromolecular substitution route to polyphosphazenes, group transfer polymerization, and the use of metathesis-type initiators, are providing access to a wide range of specialty polymers with unique combinations of properties. Aromatic ladder polymers are receiving considerable attention, as are main-chain liquid crystalline polyamides and polyesters. Polymers are now being used as stationary substrates for the binding of transition metal catalysts or enzymes. This trend toward the synthesis of new polymers with specialized properties for critical applications will probably continue in the foreseeable future.

Engineering and Materials Science

Polymer chemistry is a highly developed science in the sense that all the classical perspectives now exist, from synthesis and molecular structural work, through theoretical physics and physical chemistry, to engineering. Polymers have always been used in technology because of their engineering advantages (strength, elasticity, light weight, corrosion resistance, low cost). As will be evident from some of the later chapters, few polymers are used technologically in their chemically pure form. Thus, much of the current research and development work connected with polymers involves studies of the ways in which pure polymers can be modified to make them more suitable for specific applications. Such modifications can involve attempts to physically modify the crystallinity of a polymer, or result from the addition of

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plasticizers, reinforcement agents, or even the addition of other polymers. This interface between polymer chemistry, engineering, rheology, and solid-state science is often described under the general umbrella term of *materials science.* The period since the mid-1960s has seen a striking growth of interest in the materials science aspects of polymer science as investigators seek to improve the properties of well-known synthetic polymers. This type of work is likely to become even more important as technology continues to demand new materials with improved properties at a time when most of the readily available organic polymers have already been commercialized. It seems clear that the technological future of polymer science will require a close interaction between synthetic chemists on the one hand and physical chemists and materials scientists on the other.

STUDY QUESTIONS

1. Refer to an organic chemistry textbook and suggest synthetic routes that could be used to produce monomers such as vinyl chloride, tetrafluoroethylene, styrene, ethylene glycol, and terephthalic acid from petroleum.
2. What types of "crash programs" can you foresee being implemented if the supply of monomers from oil were to be interrupted for several years as a result of international upheavals?
3. Excluding the specific reactions mentioned in this chapter, suggest examples, based on your own prior experience and study, of an addition polymerization, a condensation polymerization, a ring-opening polymerization, and a biological condensation polymerization.
4. How would you distinguish experimentally between an amorphous, a crystalline, and a crosslinked polymer?
5. Devise several reactions that might lead to the synthesis of cyclolinear, ladder, and spiro polymers. After you have spent 10 minutes on this problem, refer to Chapter 2 and reassess your ideas.
6. Based on your intuitive knowledge of chemistry or physics, suggest why rubber is an elastomer at room temperature but glass is not.
7. Without referring to later chapters, suggest ways in which a graft copolymer might be prepared.
8. Before starting to read the next chapter, spend 30 minutes scanning the rest of the book to obtain some perspective of its contents. Glance at the section headings, structural formulas. figures, and the questions at the end of each chapter. Then study individual chapters in detail.

SUGGESTIONS FOR FURTHER READING

P. J. FLORY, *Principles of Polymer Chemistry.* Ithaca, N.Y.: Cornell University Press, 1953, Chap. 1.

H. MORAWETZ, *Polymers: The Origins and Growth of a Science.* New York: Wiley, 1985.

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