

POLYMERS

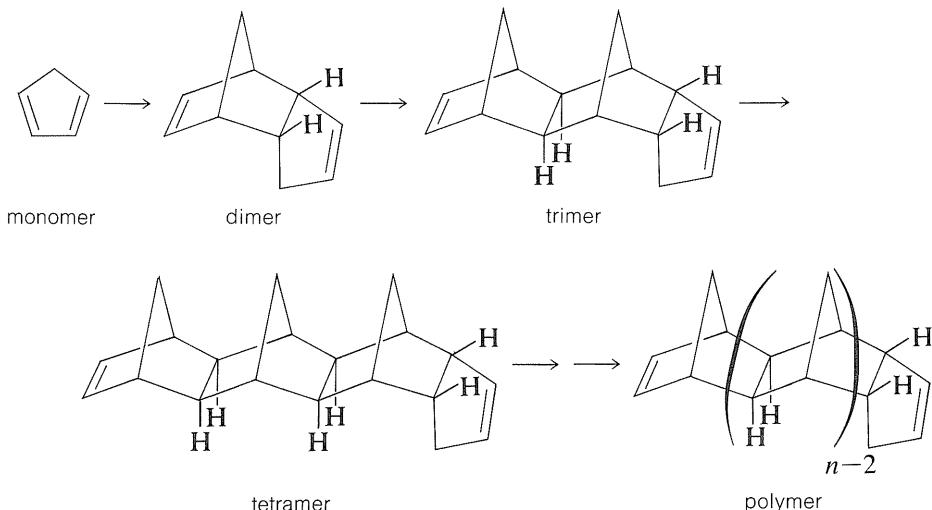
Polymers are substances made up of recurring structural units, each of which can be regarded as derived from a specific compound called a **monomer**. The number of monomeric units usually is large and variable, each sample of a given polymer being characteristically a mixture of molecules with different molecular weights. The range of molecular weights is sometimes quite narrow, but is more often very broad. The concept of polymers being mixtures of molecules with long chains of atoms connected to one another seems simple and logical today, but was not accepted until the 1930's when the results of the extensive work of H. Staudinger, who received the Nobel Prize in Chemistry in 1953, finally became appreciated. Prior to Staudinger's work, polymers were believed to be colloidal aggregates of small molecules with quite non-specific chemical structures.

The adoption of definite chemical structures for polymers has had far-reaching practical applications, because it has led to an understanding of how and why the physical and chemical properties of polymers change with the nature of the monomers from which they are synthesized. This means that to a very considerable degree the properties of a polymer can be tailored to particular practical applications. Much of the emphasis in this chapter will be on how the properties of polymers can be related to their structures. This is appropriate because we already have given considerable attention in previous chapters to methods of synthesis of monomers and polymers, as well as to the mechanisms of polymerization reactions.

The special technical importance of polymer's can be judged by the fact that half of the professional organic chemists employed by industry in the United States are engaged in research or development related to polymers.

29-1 A SIMPLE ADDITION POLYMERIZATION. THE PARTS OF A POLYMER

The thermal polymerization of 1,3-cyclopentadiene by way of the Diels–Alder addition is not an important polymerization, but it does provide a simple concrete example of how a monomer and a polymer are related:



The first step in this polymerization is formation of the dimer, which involves 1,3-cyclopentadiene acting as both diene and dienophile. This step occurs readily on heating, but slowly at room temperature. In subsequent steps, 1,3-cyclopentadiene adds to the relatively strained double bonds of the bicyclo[2.2.1]heptene part of the polymer. These additions to the **growing chain** require higher temperatures (180–200°). If cyclopentadiene is heated to 200° until substantially no further reaction occurs, the product is a waxy solid having a **degree of polymerization** n ranging from two to greater than six.

Polycyclopentadiene molecules have two different kinds of double bonds for **end groups** and a complicated **backbone** of saturated fused rings. The polymerization is reversible and, on strong heating, the polymer reverts to cyclopentadiene.

There are two commonly used and numerically different ways of expressing the *average* molecular weight of a polymer such as polycyclopentadiene. One is the **number-average** molecular weight, \bar{M}_n , which is the total weight of a polymer sample, m , divided by the total number of moles of molecules it contains, ΣN_i . Thus

$$\bar{M}_n = \frac{m}{\Sigma N_i} = \frac{\Sigma (N_i M_i)}{\Sigma N_i}$$

in which N_i is the number of moles of a single kind of molecular species, i , and M_i is the molecular weight of that species.

An alternative way of expressing the molecular weight is by the **weight average**, \overline{M}_w , which can be computed by summing up the contribution (as measured by the weight fraction w_i) of each molecular species i and its molecular weight M_i :

$$\overline{M}_w = \Sigma(w_i M_i)$$

The reason for using the two different molecular weights is that some properties, such as freezing points, vapor pressure, and osmotic pressure of dilute solutions, are related directly to \overline{M}_n , whereas other properties, such as light-scattering, sedimentation, and diffusion constants, are related directly to \overline{M}_w .

Exercise 29-1 Write a reasonable mechanism for the thermal *depolymerization* of 1,3-cyclopentadiene tetramer. How could one chemically alter the tetramer to make thermal breakdown more difficult? Explain.

Exercise 29-2 Suppose a bottle of 1,3-cyclopentadiene were held at a temperature at which polymerization is rapid, but depolymerization is insignificant. Would the polymerization result in conversion of all of the 1,3-cyclopentadiene into essentially one gigantic molecule? Why or why not? How would you carry on the polymerization so as to favor formation of polymer molecules with high molecular weights?

Exercise 29-3* Calculate a number-average and a weight-average molecular weight for a low-molecular-weight sample of poly-1,3-cyclopentadiene having the following composition:

n	Weight %	n	Weight %
2	30	8	4
3	20	9	3
4	15	10	2
5	11	11	1
6	8	≥ 12	~ 0
7	6		

Under what circumstances would you expect \overline{M}_n to be equal to \overline{M}_w ? Suppose one were to determine a molecular weight for a sample of poly-1,3-cyclopentadiene by quantitative hydrogenation of the terminal double bonds. Would the resulting molecular weight be equal to \overline{M}_n , \overline{M}_w , or neither of these?

29-2 TYPES OF POLYMERS

Polymers can be classified in several different ways—according to their structures, the types of reactions by which they are prepared, their physical properties, or their technological uses.

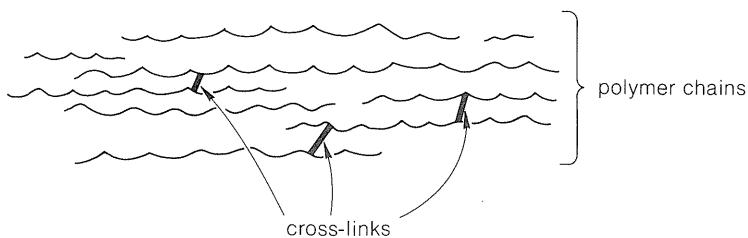


Figure 29-1 Schematic representation of a polymer with a few cross-links between the chains

From the standpoint of general physical properties, we usually recognize three types of solid polymers: **elastomers**, **thermoplastic** polymers, and **thermosetting** polymers. Elastomers are rubbers or rubberlike elastic materials. Thermoplastic polymers are hard at room temperature, but on heating become soft and more or less fluid and can be molded. Thermosetting polymers can be molded at room temperature or above, but when heated more strongly become hard and infusible. These categories overlap considerably but are nonetheless helpful in defining general areas of utility and types of structures.

The structural characteristics that are most important to determining the properties of polymers are: (1) the degree of rigidity of the polymer molecules, (2) the electrostatic and van der Waals attractive forces between the chains, (3) the degree to which the chains tend to form crystalline domains, and (4) the degree of **cross-linking** between the chains. Of these, cross-linking is perhaps the simplest and will be discussed next.

Consider a polymer made of a tangle of molecules with long linear chains of atoms. If the intermolecular forces between the chains are small and the material is subjected to pressure, the molecules will tend to move past one another in what is called **plastic flow**. Such a polymer usually is soluble in solvents that will dissolve short-chain molecules with chemical structures similar to those of the polymer. If the intermolecular forces between the chains are sufficiently strong to prevent motion of the molecules past one another the polymer will be solid at room temperature, but will usually lose strength and undergo plastic flow when heated. Such a polymer is thermoplastic. A **cross-link** is a chemical bond between polymer chains other than at the ends. Cross-links are extremely important in determining physical properties because they increase the molecular weight and limit the translational motions of the chains with respect to one another. Only *two cross-links* per polymer chain are required to connect all the polymer molecules in a given sample to produce one gigantic molecule. Only a few cross-links (Figure 29-1) reduce greatly the solubility of a polymer and tend to produce what is called a **gel polymer**, which, although insoluble, usually will absorb (be swelled by) solvents in which the uncross-linked polymer is soluble. The tendency to absorb solvents decreases as the degree of cross-linking is increased because the chains cannot move enough to allow the solvent molecules to penetrate between the chains.

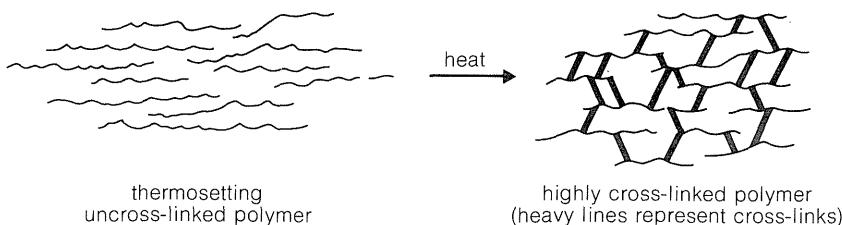
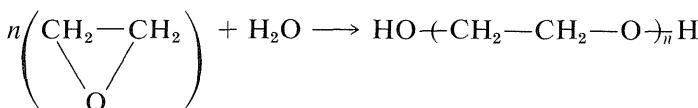
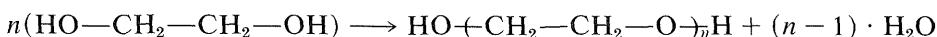


Figure 29-2 Schematic representation of the conversion of an uncross-linked thermosetting polymer to a highly cross-linked polymer. The cross-links are shown in a two-dimensional network, but in practice three-dimensional networks are formed.

Thermosetting polymers normally are made from relatively low-molecular-weight, usually semifluid substances, which when heated in a mold become *highly cross-linked*, thereby forming hard, infusible, and insoluble products having a *three-dimensional network* of bonds interconnecting the polymer chains (Figure 29-2).

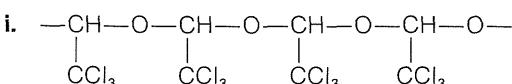
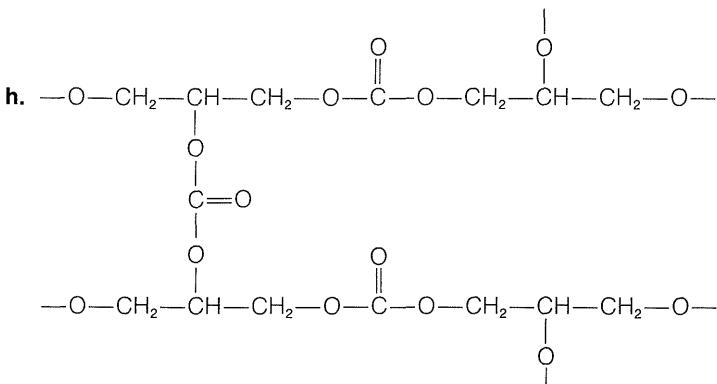
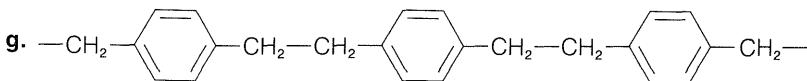
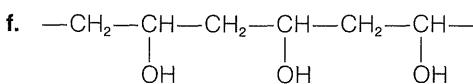
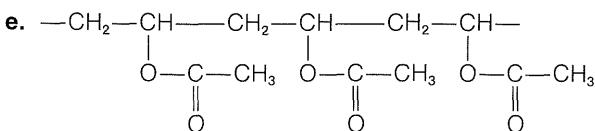
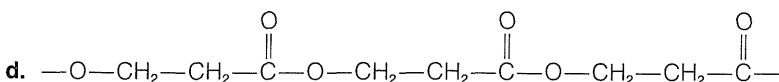
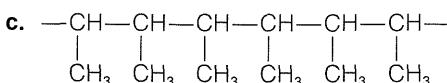
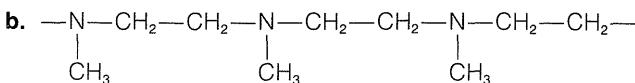
Polymers usually are prepared by two different types of polymerization reactions—*addition* and *condensation*. In addition polymerization all of the atoms of the monomer molecules become part of the polymer; in condensation polymerization some of the atoms of the monomer are split off in the reaction as water, alcohol, ammonia, or carbon dioxide, and so on. Some polymers can be formed either by addition or condensation reactions. An example is polyethylene glycol, which, in principle, can form either by dehydration of 1,2-ethanediol (ethylene glycol), which is condensation, or by addition polymerization of oxacyclop propane (ethylene oxide):¹



Other addition polymerizations were discussed previously, including poly-1,3-cyclopentadiene, alkene polymers (Section 10-8), polyalkadienes (Section 13-4), polyfluoroalkenes (Section 14-7D), and polymethanal (Section 16-4B).

¹ Regardless of whether the *same* polymer would be obtained by polymerization starting with different monomers, the products usually are named to correspond to the starting material. Thus polyethylene glycol and polyethylene oxide would not be used interchangeably for $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_n\text{H}$.

Exercise 29-4 Show how each of the following polymer structures may be obtained from suitable monomers either by addition or condensation. More than one step may be required.



Physical Properties of Polymers

29-3 FORCES BETWEEN POLYMER CHAINS

Polymers are produced on an industrial scale primarily, although not exclusively, for use as structural materials. Their physical properties are particularly important in determining their usefulness, be it as rubber tires, sidings for buildings, or solid rocket fuels.

Polymers that are not highly cross-linked have properties that depend greatly on the forces that act between the chains. By way of example, consider a polymer such as polyethene which, in a normal commercial sample, will be made up of molecules having 1000 to 2000 CH_2 groups in continuous chains. Because the material is a mixture of different molecules, it is not expected to crystallize in a conventional way.² Nonetheless, x-ray diffraction shows polyethene to have very considerable crystalline character, there being regions as large as several hundred angstrom units in length, which have ordered chains of CH_2 groups oriented with respect to one another like the chains in crystalline low-molecular-weight hydrocarbons. These crystalline regions are called *crystallites* (Figure 29-3). Between the crystallites of polyethene are amorphous, noncrystalline regions in which the polymer chains are essentially randomly ordered with respect to one another (Figure 29-4). These regions constitute crystal defects.

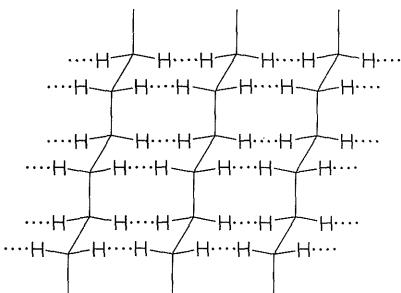


Figure 29-3 Representation of attractive interactions between the hydrogens in a crystallite of polyethene. This drawing is incomplete in that it does not show the interactions of the depicted chains with the other chains in front and behind.

²Quite good platelike crystals, about 100 Å thick, have been formed from dilute solutions of polyethene. In these crystals, CH_2 chains in the *anti* conformation (Section 5-2) run between the large surfaces of the plates. However, the evidence is strong that when the CH_2 chains reach the surface of the crystal they do not neatly fold over and run back down to the other surface. Instead, the parts of a given chain that are in the crystalline segments appear to be connected at the ends of the crystallites by random loops of disordered CH_2 sequences, something like an old-fashioned telephone switchboard.

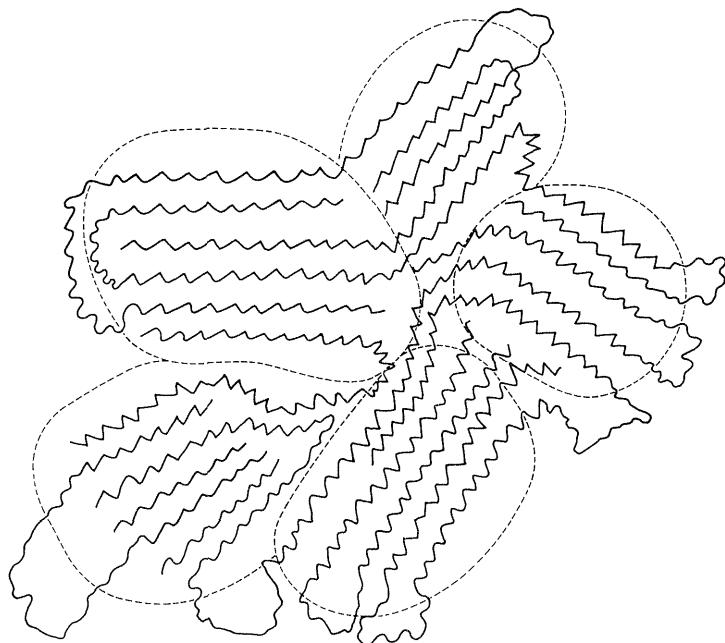


Figure 29-4 Schematic diagram of crystallites (enclosed by dashed lines) in a largely crystalline polymer

The forces between the chains in the crystallites of polyethene are the so-called **van der Waals** or **dispersion** forces, which are the same forces acting between hydrocarbon molecules in the liquid and solid states, and, to a lesser extent, in the vapor state. These forces are relatively weak and arise through synchronization of the motions of the electrons in the separate atoms as they approach one another. The attractive force that results is rapidly overcome by repulsive forces when the atoms get very close to one another (see Figure 12-9, which shows how the potential energy between a pair of atoms varies with the internuclear distance). The attractive intermolecular forces between pairs of hydrogens in the crystallites of polyethene are only about 0.1–0.2 kcal per mole per pair, but for a crystalline segment of 1000 CH₂ units, the *sum* of these interactions could well be greater than the C–C bond strengths. Thus when a sample of the crystalline polymer is stressed to the point at which it fractures, carbon–carbon bonds are broken and radicals that can be detected by esr spectroscopy (Section 27-9) are generated.

In other kinds of polymers, even stronger intermolecular forces can be produced by hydrogen bonding. This is especially important in the polyamides, such as the nylons, of which nylon 66 is most widely used (Figure 29-5).

The effect of temperature on the physical properties of polymers is very important to their practical uses. At low temperatures, polymers become hard and glasslike because the motions of the segments of the polymer chains with

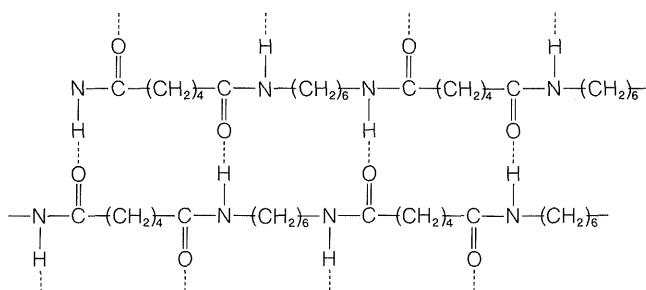


Figure 29-5 Possible hydrogen-bonded structure for crystallites of nylon 66, an amide-type polymer of hexanedioic acid and 1,6-hexanediamine

relation to each other are slow. The approximate temperature below which glasslike behavior is apparent is called the **glass temperature** and is symbolized by T_g . When a polymer containing crystallites is heated, the crystallites ultimately melt, and this temperature is usually called the **melting temperature** and is symbolized as T_m . Usually, the molding temperature will be above T_m and the mechanical strength of the polymer will diminish rapidly as the temperature approaches T_m .

Another temperature of great importance in the practical use of polymers is the temperature at which thermal breakdown of the polymer chains occurs. Decomposition temperatures obviously will be sensitive to impurities, such as oxygen, and will be influenced strongly by the presence of inhibitors, antioxidants, and so on. Nonetheless, there will be a temperature (usually rather high, 200° to 400°) at which *uncatalyzed scission* of the bonds in a chain will take place at an appreciable rate and, in general, one cannot expect to prevent this type of reaction from causing degradation of the polymer. Clearly, if this degradation temperature is comparable to T_m , as it is for polypropene-nitrile (polyacrylonitrile), difficulties are to be expected in simple thermal molding of the plastic. This difficulty is overcome in making polypropene-nitrile (Orlon) fibers by dissolving the polymer in *N,N*-dimethylmethanamide and forcing the solution through fine holes into a heated air space where the solvent evaporates.

Physical properties such as tensile strength, x-ray diffraction pattern, resistance to plastic flow, softening point, and elasticity of most polymers can be understood in a general way in terms of crystallites, amorphous regions, the degree of flexibility of the chains, cross-links, and the strength of the forces acting between the chains (dispersion forces, hydrogen bonding, etc.). A good way to appreciate the interaction between the physical properties and structure is to start with a rough classification of properties of solid polymers according to the way the chains are disposed in relation to each other.

1. An **amorphous** polymer is one with no crystallites. If the attractive forces between the chains are weak and if the motions of the chain are not in

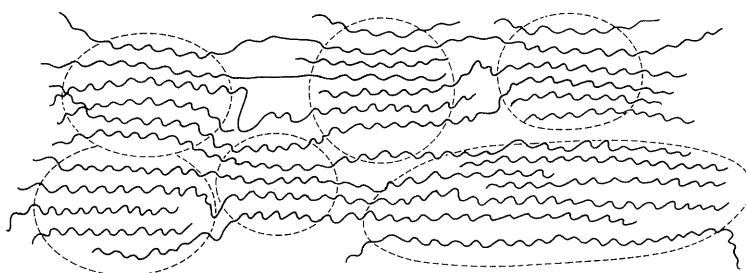


Figure 29-6 Schematic representation of an oriented crystalline polymer produced by drawing the polymer in the horizontal direction. The crystalline regions are enclosed with dashed lines.

some way severely restricted as by cross-linking or large rotational barriers, such a polymer would be expected to have low tensile strength and when stressed to undergo plastic flow in which the chains slip by one another.

2. An **unoriented crystalline** polymer is one which is considerably crystallized but has the crystallites essentially randomly oriented with respect to one another, as in Figure 29-4. When such polymers are heated they often show rather sharp T_m points, which correspond to the melting of the crystallites. Above T_m , these polymers are amorphous and undergo plastic flow, which permits them to be molded. Other things being the same, we expect T_m to be higher for polymers with stiff chains (high barriers to internal rotation).

3. An **oriented crystalline** polymer is one in which the crystallites are oriented with respect to one another, usually as the result of a **cold-drawing** process. Consider a polymer such as nylon, which has strong intermolecular forces and, when first prepared, is in an unoriented state like the one represented by Figure 29-4. When the material is subjected to strong stress in one direction, usually above T_g so that some plastic flow can occur, the material elongates and the crystallites are drawn together and oriented along the direction of the applied stress (Figure 29-6).

An oriented crystalline polymer usually has a much higher tensile strength than the unoriented polymer. Cold drawing is an important step in the production of synthetic fibers.

4. **Elastomers** usually are amorphous polymers. The key to elastic behavior is to have highly flexible chains with either sufficiently weak forces between the chains or a sufficiently irregular structure to be unstable in the crystalline state. The tendency for the chains to crystallize often can be considerably reduced by random introduction of methyl groups, which by steric hindrance inhibit ordering of the chains. A useful elastomer needs to have some kind of cross-linked regions to prevent plastic flow and flexible enough chains to have a low T_g . The structure of a polymer of this kind is shown schematically in Figure 29-7; the important difference between this elastomer and the crystalline polymer of Figure 29-4 is the size of the amorphous regions. When tension is applied and the material elongates, the chains

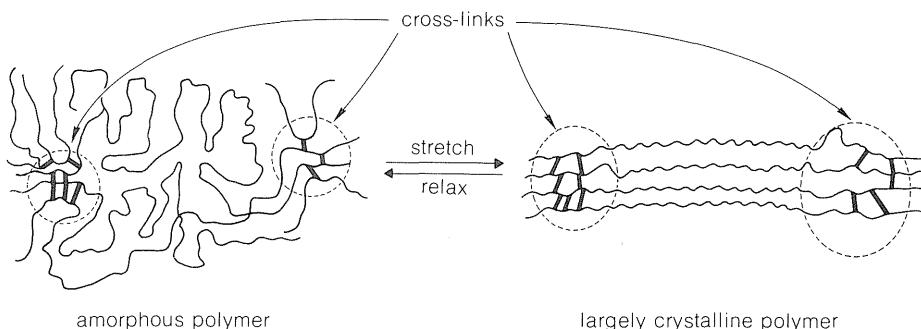
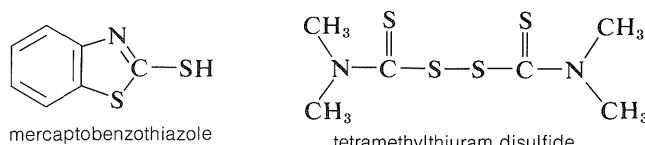


Figure 29-7 Schematic representation of an elastomer in relaxed and stretched configurations. Many elastomers do not crystallize when elongated.

in the amorphous regions straighten out and become more nearly parallel. At the elastic limit, a semicrystalline state is reached, which is different from the one produced by cold drawing of a crystalline polymer in that it is stable only while under tension. The forces between the chains are too weak to maintain the crystalline state in the absence of tension. Thus when tension is released, contraction occurs and the original, amorphous polymer is produced. The entropy (Section 4-4B) of the chains is more favorable in the relaxed state than in the stretched state.

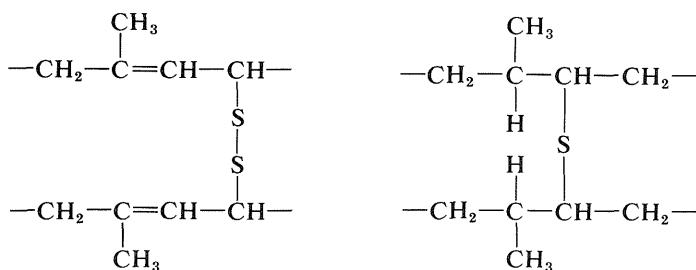
A good elastomer should not undergo plastic flow in either the stretched or relaxed state, and when stretched should have a “memory” of its relaxed state. These conditions are best achieved with natural rubber (*cis*-poly-2-methyl-1,3-butadiene, *cis*-polysisoprene; Section 13-4) by curing (*vulcanizing*) with sulfur. Natural rubber is tacky and undergoes plastic flow rather readily, but when it is heated with 1–8% by weight of elemental sulfur in the presence of an *accelerator*, sulfur cross-links are introduced between the chains. These cross-links reduce plastic flow and provide a reference framework for the stretched polymer to return to when it is allowed to relax. Too much sulfur completely destroys the elastic properties and produces hard rubber of the kind used in cases for storage batteries.

The chemistry of the vulcanization of rubber is complex. The reaction of rubber with sulfur is markedly expedited by substances called *accelerators*, of which those commonly known as mercaptobenzothiazole and tetramethylthiuram disulfide are examples:



Clearly, the double bonds in natural rubber are essential to vulcanization because hydrogenated rubber (“hydrorubber”) is not vulcanized by sulfur. The

degree of unsaturation decreases during vulcanization, although the decrease is much less than one double bond per atom of sulfur introduced. There is evidence that attack occurs both at the double bond and at the adjacent hydrogen (in a manner similar to some halogenations; Section 14-3A) giving cross-links possibly of the following types:



The accelerators probably function by acting as sulfur carriers from the elemental sulfur to the sites of the polymer where the cross-links are formed.

29-4 CORRELATION OF POLYMER PROPERTIES WITH STRUCTURE

The properties of many of the commercially important thermoplastic and elastic polymers can be understood in terms of their chemical structures by using the concepts developed in the preceding section. Thus the simple linear polymers, polyethene $\text{—CH}_2\text{CH}_2\text{—}_n$, polymethanal $\text{—CH}_2\text{—O—}_n$, and polytetrafluoroethene $\text{—CF}_2\text{—CF}_2\text{—}_n$, with regular chains and low barriers to rotation about the bonds in the chain tend to be largely crystalline with rather high melting points and low glass temperatures (see Table 29-1). The situation with polychloroethene (polyvinyl chloride), polyfluoroethene (polyvinyl fluoride), and polyethenylbenzene (polystyrene) as usually prepared is quite different. These polymers are much less crystalline and yet have rather high glass temperatures, which suggests that there is considerable attractive force between the chains. The low degree of crystallinity of these polymers is the result of their having a low degree of regularity of the stereochemical configuration of the chiral carbons in the chain. The discovery by G. Natta in 1954 that the stereochemical configurations of chiral centers in polymer chains could be crucial in determining their physical properties has had a profound impact on both the practical and theoretical aspects of polymer chemistry. Natta's work was done primarily with polypropene and this substance provides an excellent example of the importance of stereochemical configurations.

What properties would we expect for polypropene? If we extrapolate from the properties of polyethene, $\text{—CH}_2\text{—CH}_2\text{—}_n$, $T_m = 130^\circ$ and $T_g = -120^\circ$, and poly-2-methylpropene $\text{—CH}_2\text{—C(CH}_3)_2\text{—}_n$, which is amorphous with

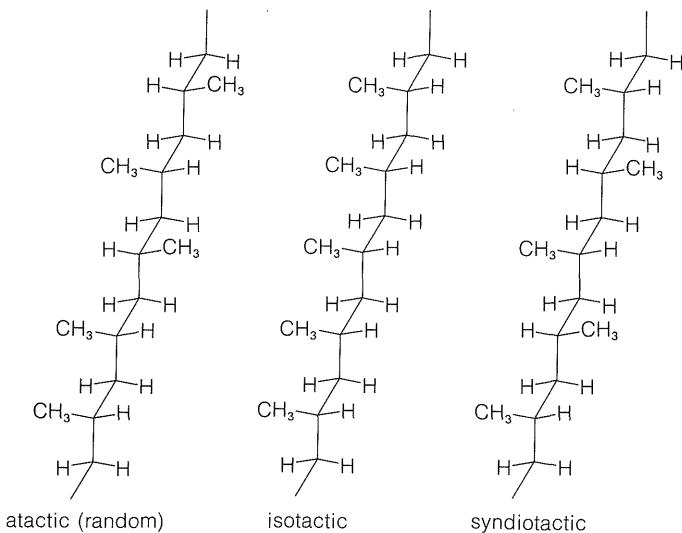


Figure 29-8 Configuration of atactic, isotactic, and syndiotactic polypropene. These configurations are drawn here to show the stereochemical relationships of the substituent groups and are not meant to represent necessarily the stable conformations of the polymer chains.

$T_g = -70^\circ$, we would expect that polypropene would have a low melting point and possibly be an amorphous polymer. In fact, *three* distinct varieties of polypropene have been prepared by polymerization of propene with Ziegler catalysts (Section 10-8D). Two are highly crystalline and one is amorphous and elastic. These polymers are called, respectively, **isotactic**, **syndiotactic**, and **atactic** polypropene. The differences between their configurations are shown in Figure 29-8. If we could orient the carbons in the polymer chains in the extended zig-zag conformation of Figure 29-8, we would find that the atactic form has the methyl groups randomly distributed on one side or the other of the main chain. In contrast, isotactic polypropene has a *regular* structure with the methyl groups all on the *same side* of the chain. Many other kinds of regular structures are possible and the one of these that has been prepared, although not in quantity, is the syndiotactic form, which has the methyl groups oriented *alternately* on one side or the other of the polymer chain.

There are striking differences in physical properties between the atactic and isotactic forms. The atactic material is soft, elastic, somewhat sticky, and rather soluble in solvents such as 1,1,2,2-tetrachloroethane. Isotactic polypropene is a hard, clear, strong crystalline polymer that melts at 175° . It is practically insoluble in all organic solvents at room temperature, but will dissolve to the extent of a few percent in hot 1,1,2,2-tetrachloroethane. That the difference between the atactic and isotactic polymers arises from differences in the configurations of the methyl groups on the chains is shown in a

Table 29-1Representative Synthetic Thermoplastic and Elastic Polymers and Their Uses^a

Monomer(s)	Formula	Type of polymerization	Physical type	T _g , °C	T _m , °C	Trade names	Uses
ethene	CH ₂ =CH ₂	radical (high pressure) Ziegler	semi-crystalline crystalline	<<0	110	polyethylene, Alathon, Hi-fax, Dylan	film, containers, piping, etc.
chloroethene	CH ₂ =CHCl	radical	atactic, semi-crystalline	-120	130		
fluoroethene	CH ₂ =CHF	radical	atactic, semi-crystalline	80	180	polyvinyl chloride, Geon Tedlar	film, insulation, piping, adhesives, etc. coatings ^b
chloroethylene 1,1-dichloroethene chlorotrifluoroethylene	CH ₂ =CHCl CH ₂ =CCl ₂ CF ₂ =CFCI	radical radical	crystalline crystalline	<<0	210	Saran Kel-F	tubing, fibers, film gaskets, insulation ^c
tetrafluoroethylene	CF ₂ =CF ₂	radical	crystalline	<-100	330	Teflon	gaskets, valves, insulation, filter felts, film coatings ^d fibers, molded articles
propene	CH ₂ =CHCH ₃	Ziegler	isotactic, crystalline	-20	175		
ethene propene 1,4-hexadiene hexafluoropropene 1,1-difluoroethene 2-methylpropene	CH ₂ =CH ₂ CH ₂ =CHCH ₃ CH ₂ =CHCH ₂ CH=CHCH ₃ CF ₂ =CFCF ₃ CF ₂ =CH ₂ CH ₂ =C(CH ₃) ₂	Ziegler radical cationic	amorphous amorphous amorphous	-55 -23 -70	Nordel Viton Vistanex, Oppanol	rubber articles rubber articles ^e pressure-sensitive adhesives	
2-methylpropene 2-methyl-1,3-butadiene	CH ₂ =C(CH ₃) ₂ CH ₂ =C(CH ₃)CH=CH ₂	cationic	amorphous				inner tubes

2-chloro-1,3-butadiene	$\text{CH}_2=\text{C}(\text{Cl})\text{CH}=\text{CH}_2$	radical	amorphous	-40		Neoprene	rubber articles ^e
2-methyl-1,3-butadiene	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	Ziegler, Li	amorphous (<i>cis</i> -1,4)	-70	28	natural rubber Ameripol, Coral rubber	rubber articles
ethenylbenzene	$\text{CH}_2=\text{CHC}_6\text{H}_5$	radical	atactic, semi-crystalline	85	<200	Styron Lustron	molded articles, foam
ethenol	$(\text{CH}_2=\text{CHOH})^f$	hydrolysis of polyvinyl ethanoate	crystalline		dec.	polyvinyl alcohol	water-soluble adhesives, paper sizing
1,1-diethenoxy- butane	$\left(\begin{array}{c} \text{OCH}=\text{CH}_2 \\ \\ \text{C}_3\text{H}_7\text{CH}-\text{CH}-\text{OCH}=\text{CH}_2 \end{array} \right)^f$	polyvinyl alcohol and butanal	amorphous			polyvinyl butyral	safety-glass laminate
methanal	$\text{CH}_2=\text{O}$	anionic	crystalline		179	Delrin	molded articles
propenenitrile	$\text{CH}_2=\text{CHCN}$	radical	crystalline	100 ^g	>200	Orlon	fiber
methyl 2-methyl- propenoate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$	radical	atactic amorphous	105		Lucite, Plexiglas	coatings, molded articles
		anionic	isotactic crystalline	115	200		
		anionic	syndiotactic crystalline	45	160		
benzene-1,4-dicar- boxylic acid	$\left. \begin{array}{c} \text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H} \\ \text{HOCH}_2\text{CH}_2\text{OH} \end{array} \right\}$	ester interchange between dimethyl 1,4- benzenedicarboxylate and 1,2-ethanediol	crystalline	56	260	Dacron, Mylar, Cronar, Terylene	fiber, film
1,2-ethanediol							
aza-2-cycloheptanone (caprolactam)	$(\text{CH}_2)_5\text{CONH}$	anionic	crystalline	50	225	Perlon	fibers, molded articles
1,6-hexanediamine hexanedioic acid	$\left. \begin{array}{c} \text{NH}_2(\text{CH}_2)_6\text{NH}_2 \\ \text{HO}_2\text{C}(\text{CH}_2)_4\text{CO}_2\text{H} \end{array} \right\}$	anionic condensation	crystalline	50	270	nylon, Zytel	fibers, molded articles

^aInformation on these and related polymers is given in books listed on page 1459.

^bExceptional outdoor durability.

^cUsed where chemical resistance is important.

^dExcellent self-lubricating and electrical properties.

^eUsed particularly where ozone resistance is important.

^fThese monomers are not the starting materials used to make the polymers, which actually are synthesized from polyvinyl alcohol.

^g T_g is 60° when water is present.

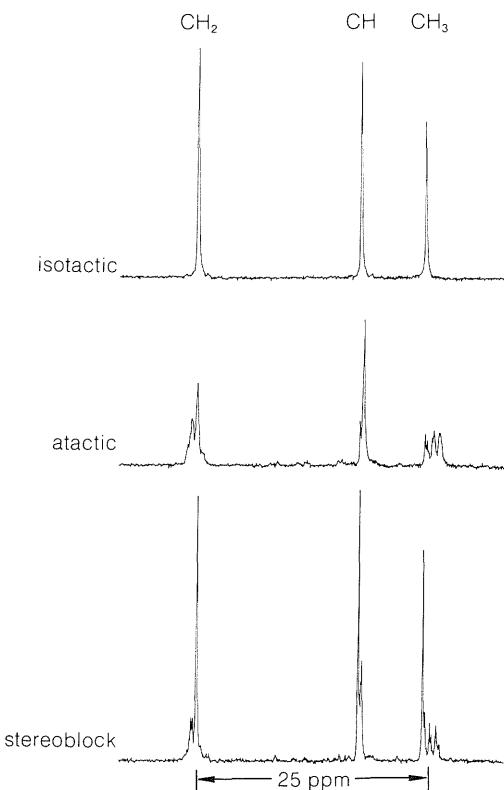


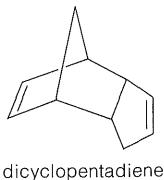
Figure 29-9 Proton-decoupled ^{13}C spectra of different polypropene samples taken in $\text{CHCl}_2\text{CHCl}_2$ solution at 150° at 15.9 MHz. The upper spectrum is of a highly isotactic polypropene, which shows only the faintest indication of lack of stereoregularity. The middle spectrum is of atactic polypropene, which shows a variety of chemical shifts for the CH_3 groups as expected from the different steric interactions generated by random configurations of the methyl groups. The lower spectrum is of a sample of so-called "stereoblock" polymer, which is very largely isotactic. The ^{13}C spectrum of syndiotactic polypropene looks exactly like that of the isotactic polymer, except that the CH_3 —peak is about 1 ppm upfield of the position of the isotactic CH_3 peak and the CH_2 peak is about 1 ppm downfield of the isotactic CH_2 peak.

striking way by ^{13}C nmr spectra (Figure 29-9). The differences in these spectra result from differences in the interactions between the methyl groups for the different configurations, in the same way as we have shown you earlier for axial and equatorial methyl groups on cyclohexane rings (Section 12-3D).

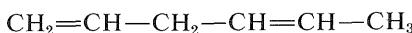
Why should polypropene melt so much higher than polyethene (175° vs. 110°)? The answer lies in the differences between the way the polymers crystallize. Polyethene crystallites have extended zig-zag chains that have very low barriers to rotation about the C-C bonds. Because of interferences between the methyl groups, polypropene does not crystallize in extended

zig-zag chains but instead forms a *helix*, something like the α helix (Section 25-8A), with the chain carbons on the inside and the methyl carbons on the outside. These coils are more rigid than the extended CH₂ chains in polyethene and have stabilizing interchain H ··· H interactions so that a higher temperature is required for melting. Polypropene can be cold drawn to form fibers that resemble nylon fibers although, as might be expected, these fibers do not match the 270° melting point of nylon and, because of their hydrocarbon character, are much more difficult to dye.

Although both linear polyethene and isotactic polypropene are crystalline polymers, ethene-propene *copolymers* prepared with the aid of Ziegler catalysts are excellent elastomers. Apparently, a more or less random introduction of methyl groups along a polyethene chain reduces the crystallinity sufficiently drastically to lead to an amorphous polymer. The ethene-propene copolymer is an inexpensive elastomer, but having no double bonds, is not capable of vulcanization. Polymerization of ethene and propene in the presence of a small amount of dicyclopentadiene or 1,4-hexadiene gives an unsaturated heteropolymer, which can be vulcanized with sulfur in the usual way.



dicyclopentadiene



1,4-hexadiene

The rationale in using these particular dienes is that only the strained double bond of dicyclopentadiene and the terminal double bond of 1,4-hexadiene undergo polymerization with Ziegler catalysts. Consequently the polymer chains contain one double bond for each molecule of dicyclopentadiene or 1,4-hexadiene that is incorporated. These double bonds later can be converted to cross-links by vulcanization with sulfur (Sections 13-4 and 29-3).

Polychloroethene (polyvinyl chloride), as usually prepared, is atactic and not very crystalline. It is relatively brittle and glassy. The properties of polyvinyl chloride can be improved by copolymerization, as with ethenyl ethanoate (vinyl acetate), which produces a softer polymer ("Vinylite") with better molding properties. Polyvinyl chloride also can be **plasticized** by blending it with substances of low volatility such as tris-(2-methylphenyl) phosphate (tricresyl phosphate) and dibutyl benzene-1,2-dicarboxylate (dibutyl phthalate) which, when dissolved in the polymer, tend to break down its glasslike structure. Plasticized polyvinyl chloride is reasonably flexible and is widely used as electrical insulation, plastic sheeting, and so on.

Table 29-1 contains information about a number of representative important polymers and their uses. Some similar data on other polymers already have been given (Section 13-4 and Table 10-4). The important use of modified polymers as ion-exchange resins is discussed in Section 25-4C.

Exercise 29-5 High-pressure polyethylene (Section 10-8C) differs from polyethylene made with the aid of Ziegler catalysts (Section 10-8D) in having a lower density and lower T_m . It has been suggested that this is due to branches in the chains of the high-pressure material. Explain how such branches may arise in the polymerization process and how they would affect the density and T_m .

Exercise 29-6 Radical-induced chlorination of polyethylene in the presence of sulfur dioxide produces a polymer with many chlorine and a few sulfonyl chloride ($—SO_2Cl$) groups, substituted more or less randomly along the chains. Write suitable mechanisms for these substitution reactions. What kind of physical properties would you expect the chlorosulfonated polymer to have if substitution is carried to the point of having one substituent group to every 25 to 100 CH_2 groups? How may this polymer be cross-linked? (A useful product of this general type is marketed under the name of Hypalon.)

Exercise 29-7 When polyethylene (and other polymers) are irradiated with x rays, cross-links are formed between the chains. What changes in physical properties would you expect to accompany such cross-linking? Would the polyethylene become more flexible? Explain.

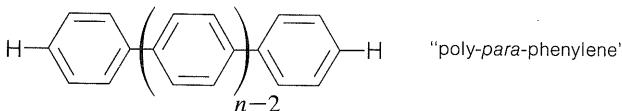
Suppose polyethylene were cross-linked by irradiation at a temperature above T_m . What would happen if it were then cooled?

Exercise 29-8 Answer the following questions in as much detail as you can, showing your reasoning:

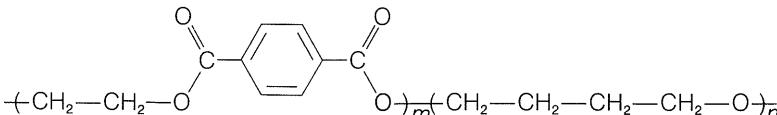
- a. Why is atactic polymethyl 2-methylpropenoate not an elastomer?
- b. How may one make a polyamide that is an elastomer?
- c. What kind of physical properties are to be expected for *isotactic* polyethenylbenzene (polystyrene)?
- d. What would you expect to happen if a piece of high-molecular-weight polypropenoic acid, $(CH_2—CHCO_2H)_n$, were placed in a solution of sodium hydroxide?



- e. What kind of properties would you expect for high-molecular-weight "poly-*para*-phenylene"?



- f. Are the properties, listed in Table 29-1, of polychloroprene produced by radical polymerization of 2-chloro-1,3-butadiene such as to make it likely that *trans*-1,4-addition occurs exclusively?
- g. A very useful oil-resistant commercial polymer called "Hytrel" is a block copolymer, having repeating units of the following basic structure:



The length of the blocks is determined by m and n , and the overall molecular weight by $m+n$. With appropriate average values, the material is a "thermoplastic elastomer," which means that it is elastic and can be stretched without plastic flow at ordinary temperatures but when heated becomes fluid enough to be easily molded. What physical properties would you expect for polymers of this type having $m+n$ large, but with $m = 1, n = 200; m = 30, n = 200; m = 200, n = 200; m = 200, n = 30$ and $m = 200, n = 1$? Which composition would you expect to correspond to Hytrel?

h. Millions of light, strong soft-drink bottles were made from a recyclable 75% ethenyl-benzene-25% propenenitrile copolymer. The mechanical strength of the polymer is increased significantly in the operation of blowing a polymer bubble to fit the mold. Why should this be so?

Exercise 29-9 The material popularly known as "Silly Putty" is a polymer having an $-\text{O}-\text{Si}(\text{R})_2-\text{O}-\text{Si}(\text{R})_2-\text{O}-$ backbone. It is elastic in that it bounces and snaps back when given a quick jerk, but it rapidly loses any shape it is given when allowed to stand. Which of the polymers listed in Table 29-1 is likely to be the best candidate to have anything like similar properties? Explain. What changes would you expect to take place in the properties of Silly Putty as a function of time if it were irradiated with x rays (see Exercise 29-7)?

Exercise 29-10* Suppose one had a sample of completely isotactic polypropene prepared from nonoptically active substances with the structure $\text{H}-\overset{\text{C}}{\underset{\text{CH}_2}{\text{---}}} \text{CH}(\text{CH}_3)-\text{CH}_2-\overset{\text{C}}{\underset{\text{CH}_2}{\text{---}}} \text{CH}_3=\text{CH}_2$.

- a.** Would the material theoretically cause a net rotation of the plane of polarized light? Explain.
- b.** Suppose one could make this polypropene with all D orientations of the CH_3- groups. Would the resulting material have an optical rotation theoretically? Practically?

Preparation of Synthetic Polymers

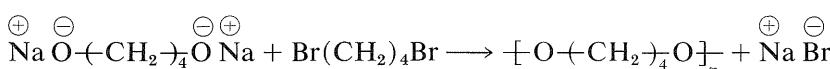
A prevalent but erroneous notion is that useful polymers, such as those given in Table 29-1, can be, and are, made by slap-dash procedures applied to impure starting materials. This is far from the truth; actually, the monomers used in most large-scale polymerizations are among the purest known organic substances. Furthermore, to obtain uniform commercially useful products, extraordinary care must be used in controlling the polymerization reactions. The reasons are simple—namely, formation of a high-molecular-weight polymer

requires a reaction that proceeds in very high yields, and purification of the product by distillation, crystallization, and so on, is difficult, if not impossible. Even a minute contribution of any side reaction that stops polymer chains from growing further will seriously affect the yield of high polymer.

In this section, we shall discuss some of the more useful procedures for the preparation of high polymers, starting with examples involving condensation reactions.

29-5 CONDENSATION POLYMERS

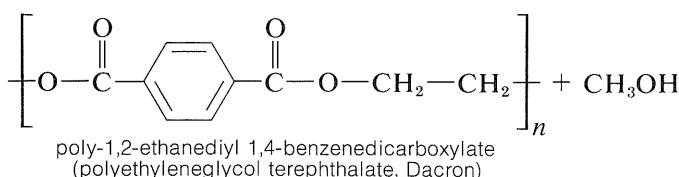
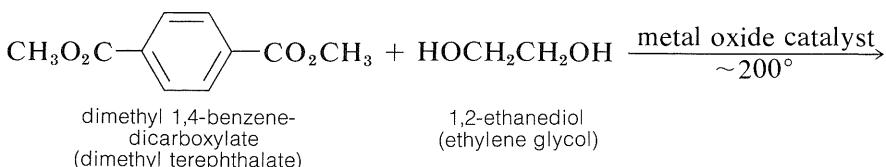
There is a very wide variety of condensation reactions that, in principle, can be used to form high polymers. However, as explained above, high polymers can be obtained only in high-yield reactions, and this limitation severely restricts the number of condensation reactions having any practical importance. A specific example of an impractical reaction is the formation of poly-1,4-butanediol by reaction of 1,4-dibromobutane with the disodium salt of the diol:

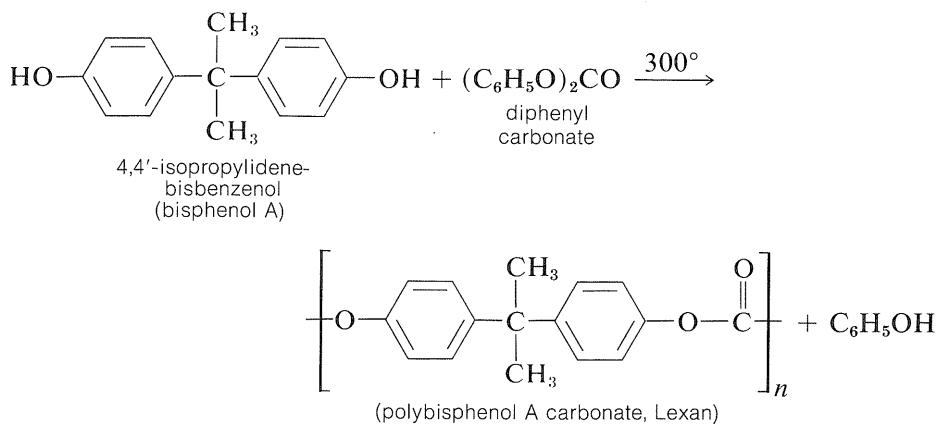


It is unlikely that this reaction would give useful yields of any very high polymer because E2 elimination, involving the dibromide, would give a double-bond end group and prevent the chain from growing.

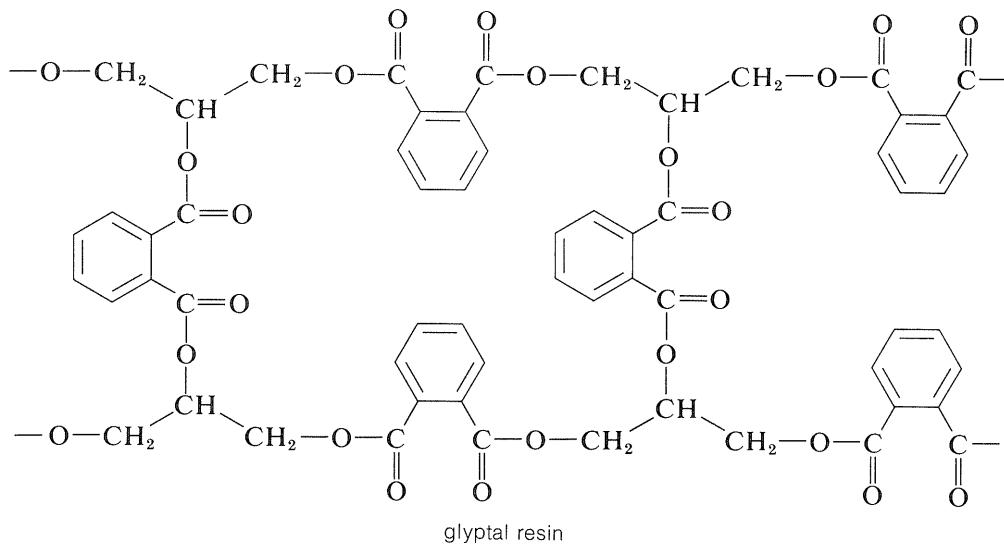
29-5A Polyesters

A variety of polyester-condensation polymers are made commercially. Ester interchange (Section 18-7A) appears to be the most useful reaction for preparation of linear polymers:

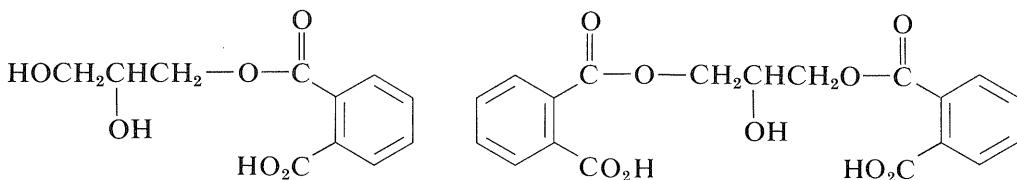




Thermosetting space-network polymers can be prepared through the reaction of polybasic acid anhydrides with polyhydric alcohols. A linear polymer is obtained with a bifunctional anhydride and a bifunctional alcohol, but if either reactant has three or more reactive sites, then formation of a three-dimensional polymer is possible. For example, 2 moles of 1,2,3-propanetriol (glycerol) can react with 3 moles of 1,2-benzenedicarboxylic anhydride (phthalic anhydride) to give a highly cross-linked resin, which usually is called a **glyptal**:

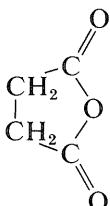


The first stage of the reaction involves preferential esterification of the primary hydroxyl groups with the anhydride to give

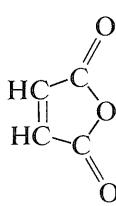


In the next stage, in the formation of the resin, direct esterification occurs slowly, particularly at the secondary hydroxyls. Normally, when the resin is used for surface coatings, esterification is carried only to the point where the polymer is not so cross-linked as to be insoluble. It then is applied to the surface in a solvent and baked until esterification is complete. The product is hard, infusible, and insoluble, being cross-linked to the point of being essentially one large molecule.

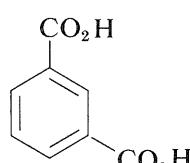
A wide variety of thermosetting polyester (alkyd) resins can be made by similar procedures. The following polybasic acids and anhydrides and polyhydric alcohols are among the other popular ingredients in alkyd formulations:



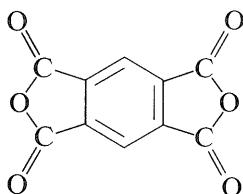
butanedioic
anhydride
(succinic anhydride)



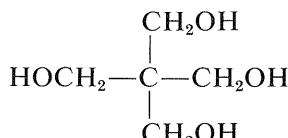
butenedioic
anhydride
(maleic anhydride)



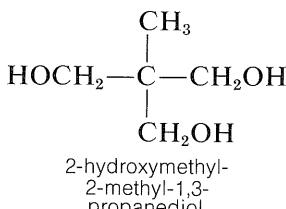
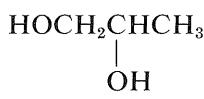
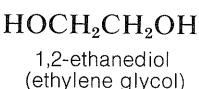
1,3-benzenedicarboxylic
acid
(isophthalic acid)



1,2,4,5-benzene-tetracarboxylic
dianhydride (pyromellitic anhydride)



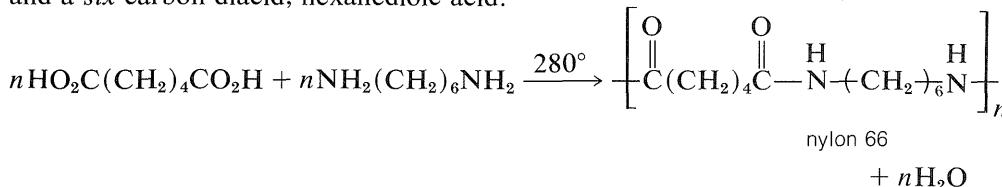
2,2-dihydroxymethyl-
1,3-propanediol
(pentaerythritol)



Articles in which glass fibers are imbedded to improve impact strength often are made by mixing the fibers with an ethenylbenzene (styrene) solution of a linear glycol (usually 1,2-propanediol)-butanedioc anhydride polyester and then producing a cross-linked polymer between the styrene and the double bonds in the polyester chains by a peroxide-induced radical polymerization (Section 29-6E).

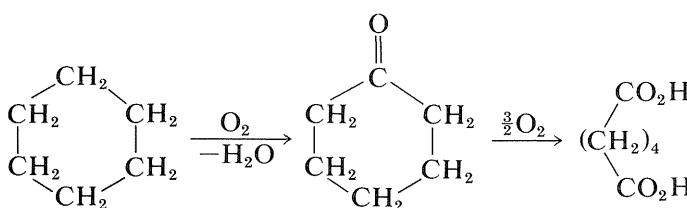
29-5B Nylons

A variety of polyamides can be made by heating diamines with dicarboxylic acids. The most generally useful of these is nylon 66, the designation 66 arising from the fact that it is made from the six-carbon diamine, 1,6-hexanediamine, and a six-carbon diacid, hexanedioic acid:

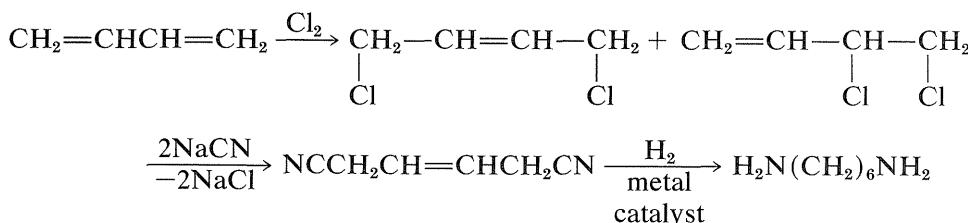


The polymer can be converted into fibers by extruding it above its melting point through spinnerettes, then cooling and drawing the resulting filaments. It also is used to make molded articles. Nylon 66 is exceptionally strong and abrasion resistant.

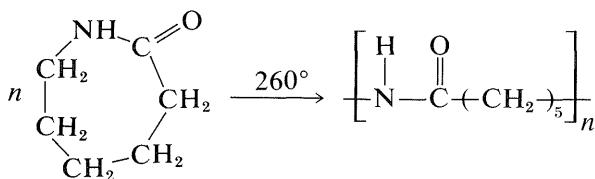
The starting materials for nylon 66 can be made in many ways. Apparently, the best route to hexanedioic acid is by air oxidation of cyclohexanone by way of cyclohexanone:



1,6-Hexanediamine can be prepared in many ways. One is from 1,3-butadiene by the following steps:

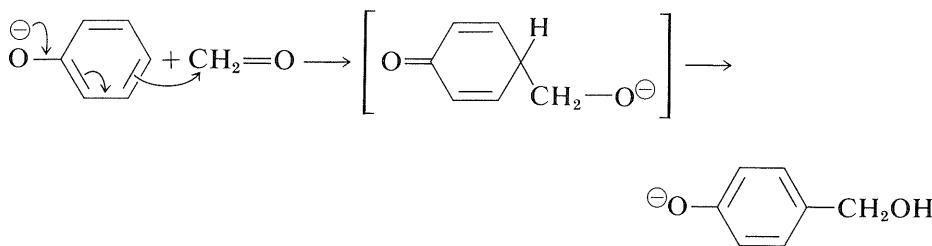


Nylon 6 can be prepared by polymerization of 1-aza-2-cycloheptanone (ϵ -caprolactam), obtained through the Beckmann rearrangement of cyclohexanone oxime (Section 24-3C):

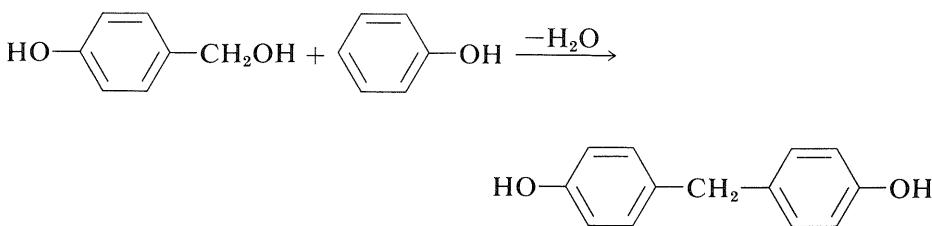


29-5C Bakelite Resins

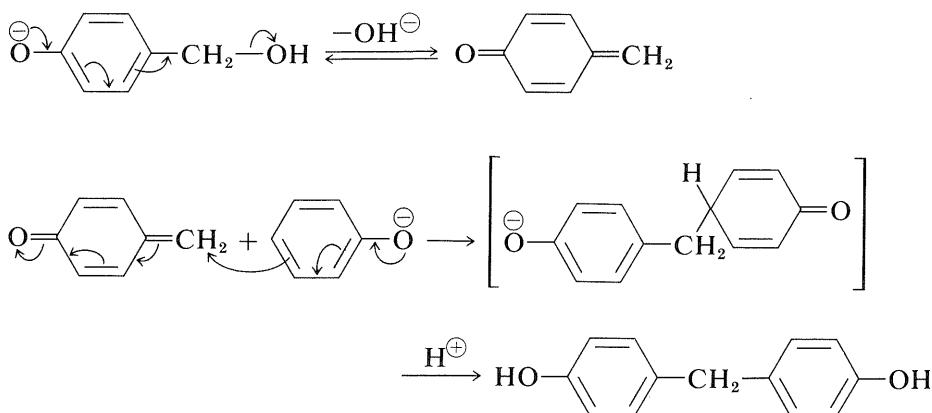
One of the oldest known thermosetting synthetic polymers is made by condensation of phenols with aldehydes using basic catalysts. The resins that are formed are known as **Bakelites**. The initial stage is the base-induced reaction of benzenol and methanal to give a (4-hydroxyphenyl)methanol, and this reaction closely resembles an aldol addition and can take place at either the 2- or the 4-position of the benzene ring:



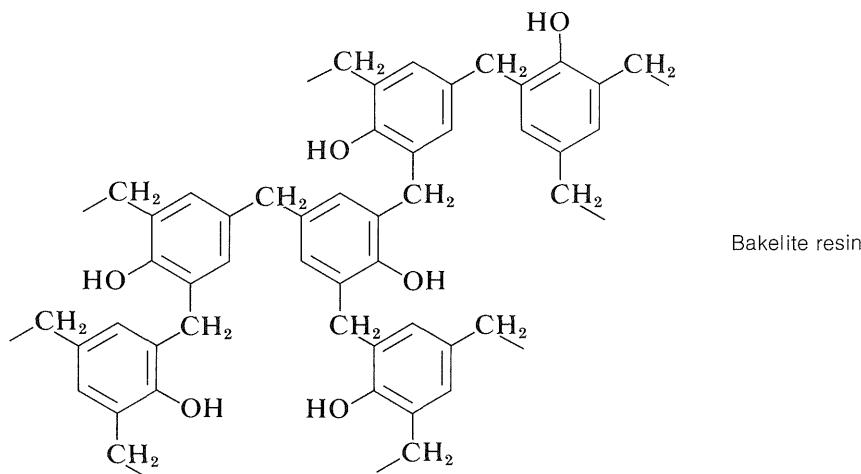
The next step in the condensation is formation of a bis(hydroxyphenyl)-methane derivative, which for convenience is here taken to be the 4,4'-isomer:



This reaction is probably a Michael type of addition to a base-induced dehydrated product of the (4-hydroxyphenyl)methanol:



Continuation of these reactions at the 2-, 4-, and 6-positions of the benzenol leads to the cross-linked three-dimensional Bakelite resin:

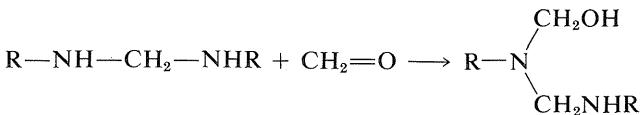


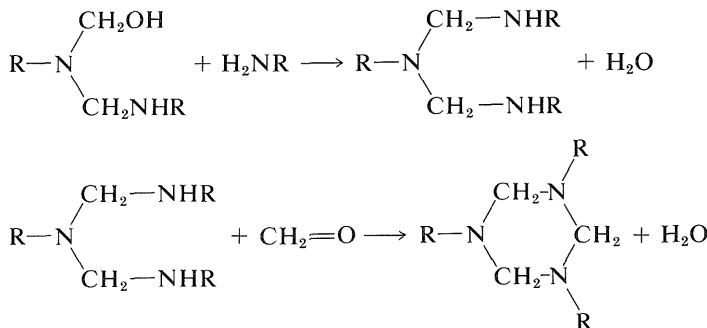
As with the alkyd resins (Section 29-5A), the initial polymerization of a Bakelite resin usually is carried to only a relatively low stage of completion. The low-melting prepolymer (called a **resole**) then is heated in a mold to give the final insoluble, infusible polymer.

Exercise 29-11 What kind of polymer would you expect to be formed if 4-methylbenzenol were used in place of benzenol in the Bakelite process?

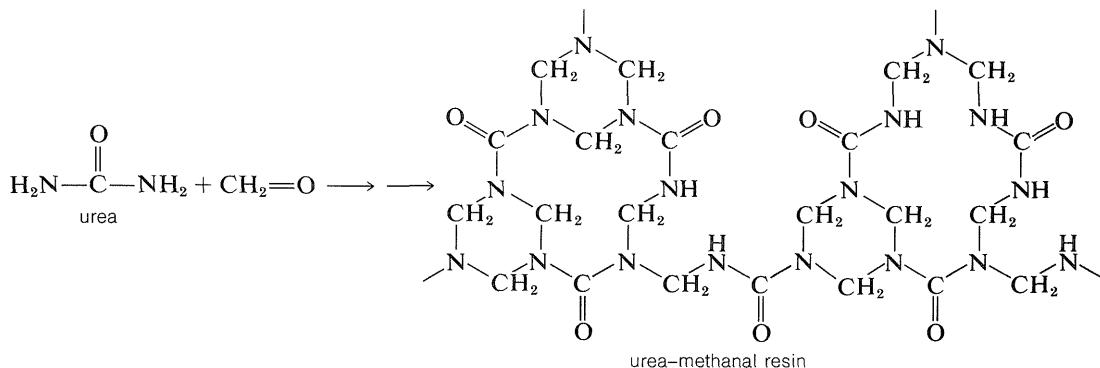
29-5D Urea–Methanal and Melamine Resins

Syntheses of a number of polymers are based on condensation of methanal with amino compounds by mechanisms at least formally analogous to those involved in the preparation of Bakelite resins. The key reactions are:

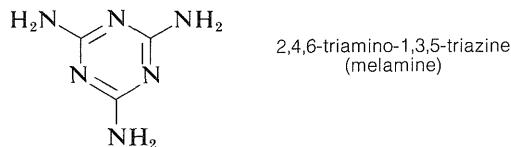




If the amino compound is urea, these types of reactions will lead to a three-dimensional polymer:



A similar polymer is made from 2,4,6-triamino-1,3,5-triazine (melamine) and methanal. It is used for plastic dishes under the name Melmac.



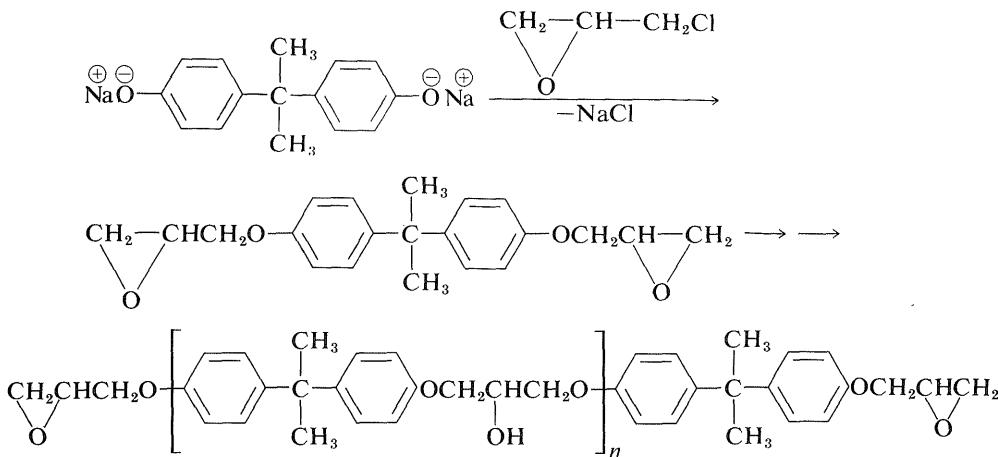
Exercise 29-12 Write a reasonable mechanism for the base-catalyzed condensation of urea with methanal to give bis-methyleneurea, $\text{NH}_2\text{CONHCH}_2\text{NHCONH}_2$.

29-5E Epoxy Resins

A very useful group of adhesives and plastics is based on condensation polymers of bisphenol A and chloromethyloxacyclopropane (epichlorohydrin, $\text{CH}_2-\text{CHCH}_2\text{Cl}$). The first step in the formation of epoxy resins is to form a

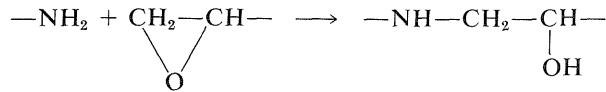


prepolymer by condensation polymerization of the sodium salt of bisphenol A with the epoxide:



The formation of a prepolymer involves two different kinds of reactions. One is an S_N2 -type displacement, and the other is oxide-ring opening of the product by attack of more bisphenol A. Usually, for practical purposes the degree of polymerization n of the prepolymer is small (5 to 12 units).

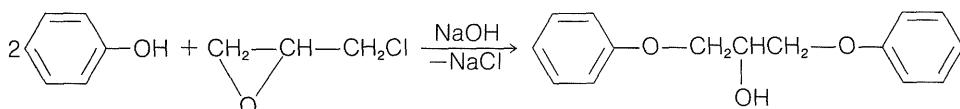
The epoxy prepolymer can be cured, that is, converted to a three-dimensional network, in several different ways. A trifunctional amine, such as $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, can be mixed in and will extend the chain of the polymer and form cross-links by reacting with the oxide rings:



Alternatively, a polybasic acid anhydride can be used to link the chains through combination with the secondary alcohol functions and then the oxide rings.

Exercise 29-13 Show the reaction whereby butenedioic anhydride would be able to cross-link an epoxy prepolymer with $n = 1$.

Exercise 29-14 The terminal carbon of the epoxide ring of epichlorohydrin generally is quite a bit more reactive toward nucleophilic agents than is the carbon bonded to chlorine. Work out a mechanism for the following reaction that takes account of this fact (review Section 15-11D):

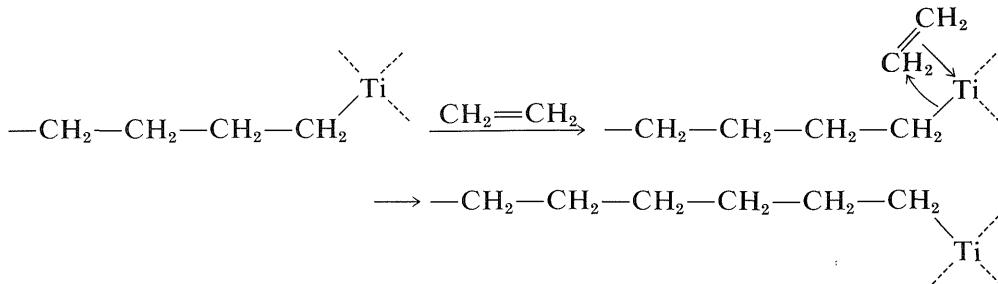


29-6 ADDITION POLYMERS

We have discussed the synthesis and properties of a considerable number of addition polymers in this and previous chapters. Our primary concern here will be with some aspects of the mechanism of addition polymerization that influence the character of the polymer formed.

29-6A Alkene Polymerization

The most important type of addition polymerization is that of alkenes (usually called **vinyl monomers**) such as ethene, propene, ethenylbenzene, and so on. In general, we recognize four basic kinds of mechanisms for polymerization of vinyl monomers—radical, cationic, anionic, and coordination. The elements of the first three of these have been outlined (Section 10-8). The possibility, in fact the reality, of a fourth mechanism is essentially forced on us by the discovery of the Ziegler and other (mostly heterogeneous) catalysts, which apparently do not involve “free” radicals, cations, or anions, and which can and usually do lead to highly stereoregular polymers. With titanium-aluminum Ziegler catalysts, the growing chain has a C-Ti bond; further monomer units then are added to the growing chain by coordination with titanium, followed by an intramolecular rearrangement to give a new growing-chain end and a new vacant site on titanium where a new molecule of monomer can coordinate:

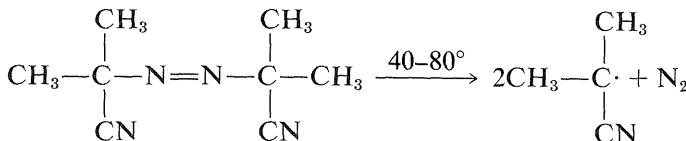
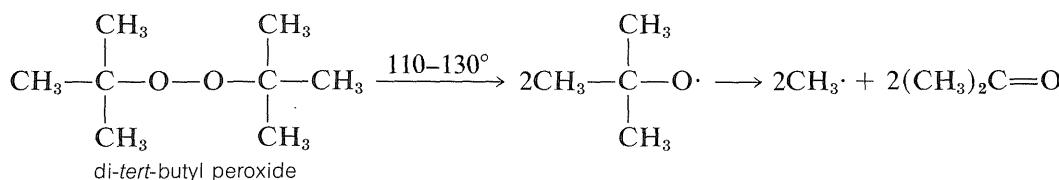
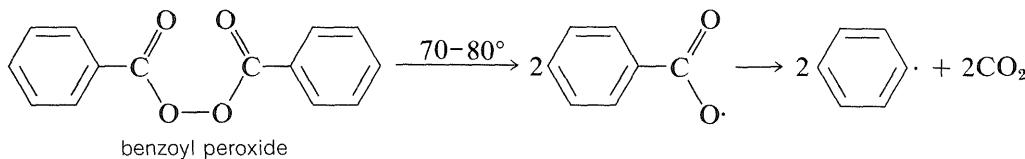


In the coordination of the monomer with the titanium, the metal is probably behaving as an electrophilic agent and the growing-chain end can be thought of as being transferred to the monomer as an anion. Because this mechanism gives no explicit role to the aluminum, it is surely oversimplified. Ziegler catalysts polymerize most monomers of the type $\text{RCH}=\text{CH}_2$, provided the R group is one that does not react with the organometallic compounds present in the catalyst. More reactions of the type that occur in Ziegler polymerizations will be discussed in Chapter 31.

29-6B Radical Polymerization

In contrast to coordination polymerization, formation of vinyl polymers by radical chain mechanisms is reasonably well understood—at least for the kinds

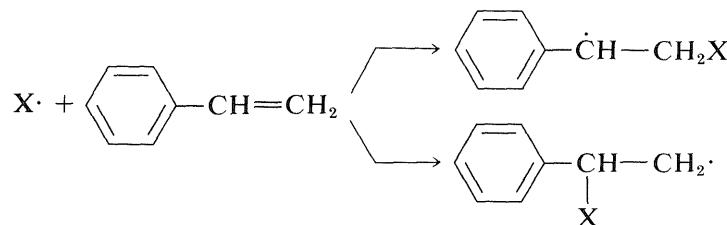
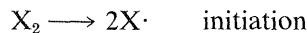
of procedures used on the laboratory scale. The first step in the reaction is the production of radicals; this can be achieved in a number of different ways, the most common being the thermal decomposition of an initiator, usually a peroxide or an azo compound:



di(1-cyano-1-methylethyl)diazene
(azobisisobutyronitrile)

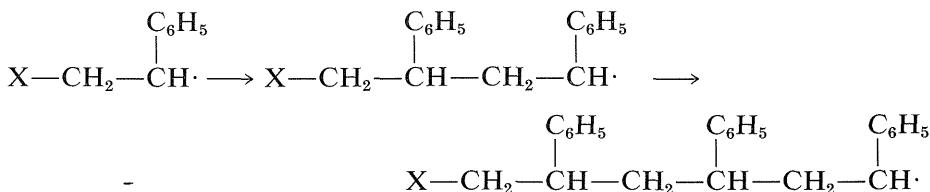
Many polymerizations are carried out on aqueous emulsions of monomers. For these, water-soluble inorganic peroxides, such as ammonium peroxysulfate, often are employed.

Other ways of obtaining initiator radicals include high-temperature decomposition of the monomer and photochemical processes, often involving a ketone as a photosensitizer. Addition of the initiator radicals to monomer produces a growing-chain radical that combines with successive molecules of monomer until, in some way, the chain is terminated. Addition to an unsymmetrical monomer can occur in two ways. Thus for ethenylbenzenes:



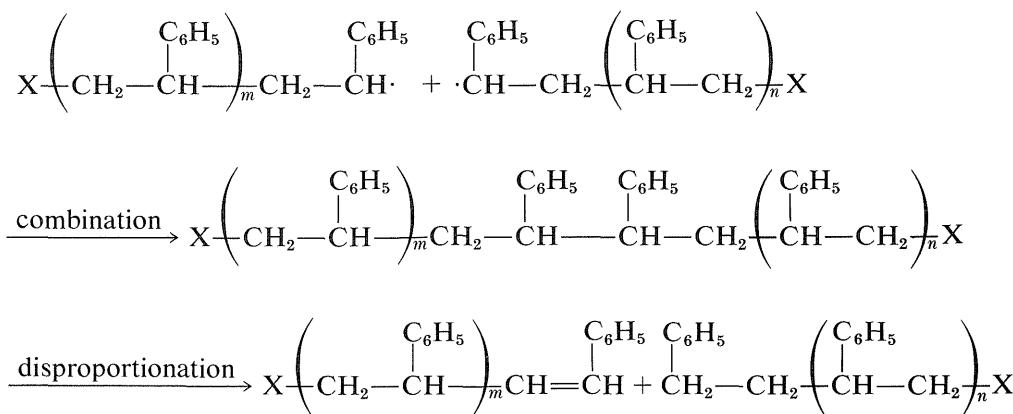
All evidence on addition of radicals to ethenylbenzene indicates that the process by which $X\cdot$ adds to the CH_2 end of the double bond is greatly favored over addition at the CH end. This direction of addition is in accord with the

considerable stabilization of the phenylmethyl radicals relative to the alkyl radicals (see Sections 14-3C and 26-4D). Polymerization then will result in the addition of monomer units to give phenyl groups only on alternate carbons ("head-to-tail" addition):

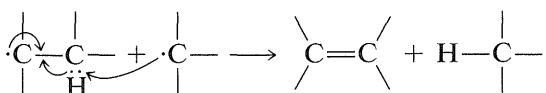


In general, we predict that the direction of addition of an unsymmetrical monomer will be such as to give always the most stable growing-chain radical. Similar considerations were discussed previously (Section 21-11) in respect to how [2 + 2] cycloadditions occur.

The process of addition of monomer units to the growing chain can be interrupted in different ways. One is chain termination by combination or disproportionation of radicals. Explicitly, two growing-chain radicals can combine to form a carbon–carbon bond, or disproportionation can occur with a hydrogen atom being transferred from one chain to the other:

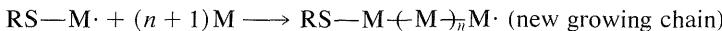
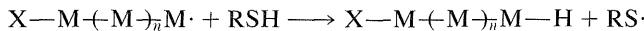


The disproportionation reaction is the radical equivalent of the E2 reaction:



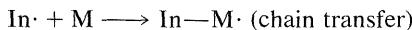
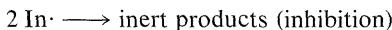
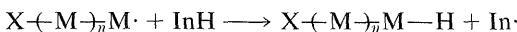
Which mode of termination occurs can be determined by measuring the number of initiator fragments per polymer molecule. If there are two initiator fragments in each molecule, termination must have occurred by combination. One initiator fragment per molecule indicates disproportionation. Apparently, ethenylbenzene polymerizations terminate by combination, but with methyl 2-methylpropenoate, both reactions take place, disproportionation being favored.

Another very important way that a growing chain may be terminated is by chain transfer. This stops the chain but starts a new one. Thiols, such as phenylmethanethiol and dodecanethiol, are efficient chain-transferring agents. The reactions involved are as follows (where M represents monomer and RSH represents the chain-transfer reagent):



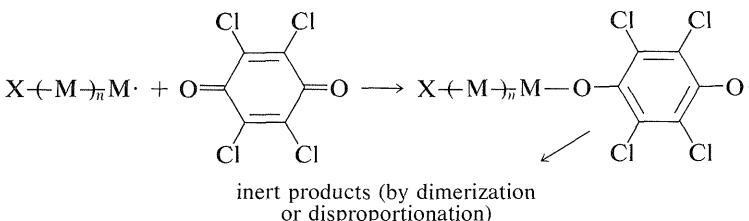
Chain transfer reduces the average molecular weight of the polymer without wasting initiator radicals. Dodecanethiol has considerable use in the manufacture of GRS rubber (Section 13-4) as a regulator to hold down the molecular weight in the emulsion polymerization of 1,3-butadiene and ethenylbenzene.

Polymerization inhibitors stop or slow down polymerization by reacting with the initiator or growing-chain radicals. A wide variety of substances can behave as inhibitors: quinones, hydroquinones, aromatic nitro compounds, aromatic amines, and so on. In cases where the inhibitor is a hydrogen donor (symbolized here by InH), then for inhibition to occur, the radical resulting from hydrogen transfer ($In\cdot$) must be too stable to add to monomer. If it does add to monomer and starts a new chain, chain transfer occurs instead of inhibition. For perfect inhibition, the $In\cdot$ radicals must combine with themselves (or initiator radicals) to give inert products:



Many compounds are known that fall in the intermediate zone between chain transfer and inhibition reagents.

Some inhibitors such as 2,3,5,6-tetrachloro-1,4-benzenedione (tetrachlorobenzoquinone) act as inhibitors by adding to the growing chain radicals to give radicals too stable to continue the chain:



Again, for inhibition to be effective there must be destruction of the stable radicals by dimerization or disproportionation.

The reactive vinyl monomers usually are stabilized against polymerization, while in storage, by addition of 0.1 to 1% of an inhibitor. 1,4-Benzenediol (hydroquinone), 2,6-di-*tert*-butyl-4-methylbenzenol, and 4-*tert*-butyl-1,2-benzenediol are used for this purpose. These substances are especially effective at scavenging $RO\cdot$ radicals, which are formed by oxidation of the monomer with atmospheric oxygen.

Exercise 29-15 Polymerization of methyl 2-methylpropenoate with benzoyl peroxide labeled with ^{14}C in the aromatic ring gives a polymer from which only 57% of the ^{14}C can be removed by vigorous alkaline hydrolysis. Correlation of the ^{14}C content of the original polymer with its molecular weight shows that, on the average, there are 1.27 initiator fragments per polymer molecule. Write mechanism(s) for this polymerization that are in accord with the experimental data, and calculate the ratios of the different initiation and termination reactions.

Exercise 29-16 The radical polymerization of ethenylbenzene gives atactic polymer. Explain what this means in terms of the mode of addition of monomer units to the growing-chain radical.

Exercise 29-17 Polyvinyl alcohol prepared by hydrolysis of polyethenyl ethanoate (polyvinyl acetate; Table 29-1) does not react with measurable amounts of periodic acid or lead tetraethanoate (Sections 16-9A and 20-4A). However, periodic acid or lead tetraethanoate treatment of the polymer does decrease the number-average molecular weight, for a typical sample from 25,000 to 5000. Explain what these results mean in terms of the polymer structures and the mechanism of the polymerization.

Exercise 29-18 Treatment of polychloroethene with zinc in alcohol removed 85% of the chlorine as zinc chloride without formation of unsaturated polymer. What does this result indicate about the polymer structure? Would you have expected that all of the chlorine would be removed by the zinc treatment? Explain. (See Section 14-10C.)

Exercise 29-19 Ozonizations of natural rubber and gutta-percha, which are both poly-2-methyl-1,3-butadienes, give high yields of $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CHO}$ and no $\text{CH}_3\text{-COCH}_2\text{CH}_2\text{COCH}_3$. What are the structures of these polymers?

Exercise 29-20* What conditions would you choose for producing the highest possible yield of (phenylmethylthio)phenylethane by radical-induced addition of phenylmethanethiol to ethenylbenzene? What structure would you expect the product to have? Explain.

Exercise 29-21* The rate of radical polymerization of ethenylbenzene, induced by benzoyl peroxide in mixtures of tetrachloromethane and benzene, is independent of the concentration of tetrachloromethane. At high concentrations of tetrachloromethane, the average molecular weight of the polymer is greatly reduced and chlorine is found in the polymer. Explain.

Exercise 29-22* 2-Propenyl ethanoate with radical initiators gives a rather short-chain polymer in a relatively slow polymerization. Deuterated 2-propenyl ethanoate of the structure $\text{CH}_2=\text{CHCD}_2\text{O}_2\text{CCH}_3$ gives higher-molecular-weight polymer at a faster rate. Explain.

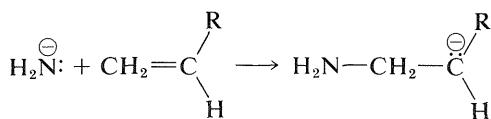
Exercise 29-23 Devise a synthesis of polyethenamine, remembering that ethenamine (vinylamine) itself is unstable.

29-6C Cationic Polymerization

Polymerization by the cationic mechanism is most important for 2-methylpropene (isobutylene), which does not polymerize well by other methods, and was discussed previously in considerable detail (Section 10-8B).

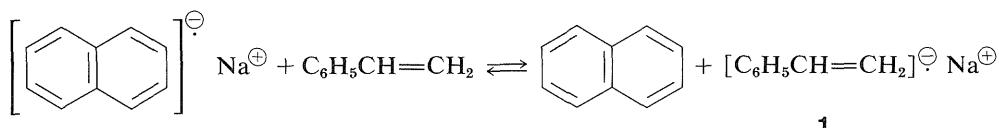
29-6D Anionic Polymerization

In general, we expect that anionic polymerization will be favorable when the monomer carries substituents that will stabilize the anion formed when a basic initiator such as amide ion adds to the double bond of the monomer:

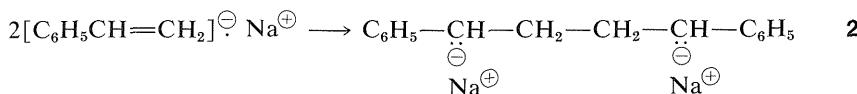


Cyano and alkoxy carbonyl groups are favorable in this respect and propenenitrile and methyl 2-methylpropenoate can be polymerized with sodium amide in liquid ammonia. Ethenylbenzene and 2-methyl-1,3-butadiene undergo anionic polymerization under the influence of organolithium and organosodium compounds, such as butyllithium and phenylsodium.

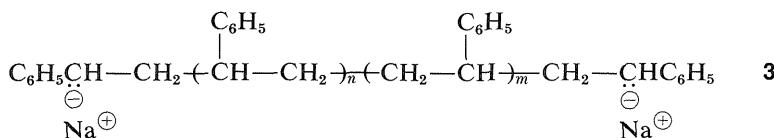
An important development in anionic polymerization has been provided by M. Szwarc's "living polymers." The radical anion, sodium naphthalenide (Section 27-9), transfers an electron reversibly to ethenylbenzene to form a new radical anion, **1**, in solvents such as 1,2-dimethoxyethane or oxacyclopentane:



Dimerization of the sodium naphthalenide radical anion would result in a loss of aromatic stabilization, but this is not true for **1**, which can form a C–C bond and a resonance-stabilized bis-phenylmethyl dianion, **2** (Section 26-4C).



The anionic ends of **2** are equivalent and can add ethenylbenzene molecules to form a long-chain polymer with anionic end groups, **3**:



If moisture and oxygen are rigorously excluded, the anionic groups are stable indefinitely, and if more monomer is added polymerization will continue. Hence the name "living polymer," in contrast to a radical-induced polymerization, which only can be restarted with fresh monomer and fresh initiator, and even then not by growth on the ends of the existing chains.

The beauty of the Szwarc procedure is that the chains can be terminated by hydrolysis, oxidation, carboxylation with CO_2 , and so on, to give polymer with the same kind of groups on each end of the chain. Also, it is possible to form chains in which different monomers are present in blocks. The only requirements are that the different monomers polymerize well by the anion mechanism and contain no groups or impurities that will destroy the active ends. Thus one can start with ethenylbenzene (S), and when the reaction is complete, add methyl 2-methylpropenoate (M) to obtain a block copolymer of the type



The properties of one such polymer are discussed in Exercise 29-8g.

Exercise 29-24* Write an equation for the dimerization of sodium naphthalenide analogous to dimerization of the ethenylbenzene radical anion **1** to give **2**. Show why you may expect that this dimerization would not be as energetically favorable as the dimerization of **1**.

Exercise 29-25* How could you use the living-polymer technique to synthesize $\text{HOCH}_2\text{CH}_2[(\text{C}_6\text{H}_5)\text{CHCH}_2]_2[\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)]_2\text{CH}_2\text{CH}_2\text{OH}$?

29-6E Copolymers

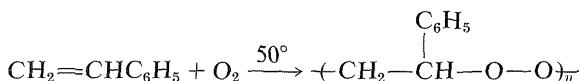
When polymerization occurs in a mixture of monomers there will be competition between the different kinds of monomers to add to the growing chain and produce a copolymer. Such a polymer will be expected to have physical properties quite different from those of a mixture of the separate homopolymers. Many copolymers, such as GRS, ethene-propene, Viton rubbers, and Vinyon plastics are of considerable commercial importance.

The rates of incorporation of various monomers into growing radical chains have been studied in considerable detail. The rates depend markedly on the nature of the monomer being added and on the character of the radical at the end of the chain. Thus a 1-phenylethyl-type radical on the growing chain reacts about twice as readily with methyl 2-methylpropenoate as it does with ethenylbenzene; a methyl 2-methylpropenoate end shows the reverse behavior, being twice as reactive toward ethenylbenzene as toward methyl 2-methylpropenoate. This kind of behavior favors alternation of the monomers in the chain and reaches an extreme in the case of 2-methylpropene and butenedioic anhydride. Neither of these monomers separately will polymerize

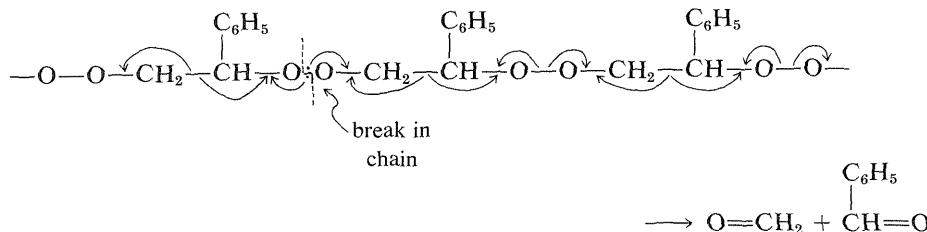
well with radical initiators. Nonetheless, a mixture polymerizes very well with *perfect alternation* of the monomer units. It is possible that, in this case, a 1:1 complex of the two monomers is what polymerizes.

In general however, in a mixture of two monomers one is considerably more reactive than the other and the propagation reaction tends to favor incorporation of the more reactive monomer, although there usually is some bias toward alternation. Ethenylbenzene and 2-methyl-1,3-butadiene mixtures are almost unique in having a considerable bias toward forming the *separate* homopolymers.

One of the more amazing copolymerizations is that of ethenylbenzene and oxygen gas, which at one atmosphere oxygen pressure gives a peroxide with an average molecular weight of 3000 to 4000 and a composition approaching $C_8H_8O_2$:



When heated rapidly in small portions the product undergoes a mild explosion and gives high yields (80% to 95%) of methanal and benzenecarbaldehyde. The mechanism may be a kind of unzipping process, starting from a break in the chain and spreading toward each end:



Another interesting copolymerization is of ethene and carbon monoxide by the radical mechanism. The polymer contains $-CH_2-CH_2-C(=O)-CH_2-CH_2-$

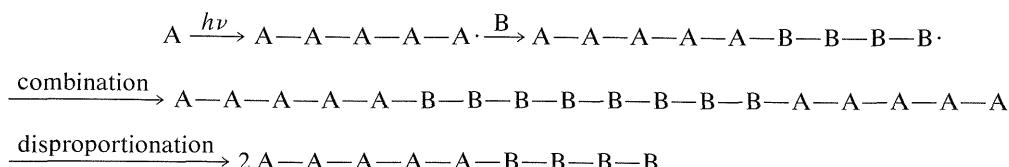
units, which are broken apart at a CH_2-C bond on absorption of ultraviolet light, thereby giving a polymer that has the possibility of degrading in the environment through the action of sunlight (see Section 28-2A).

Exercise 29-26* What physical properties would you expect for a 2-methylpropene-butenedioic anhydride copolymer? (Review Section 29-3.)

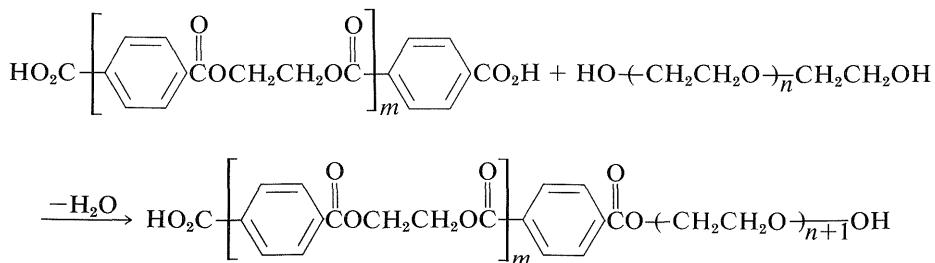
Exercise 29-27* What would be the expected structure of a copolymer of ethenylbenzene and propene made by a Ziegler catalyst if the growing chain is transferred to the monomer as a radical? As an anion?

29-7 BLOCK, GRAFT, AND LADDER POLYMERS

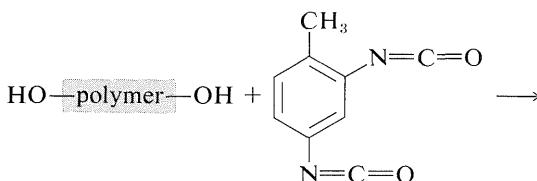
A variation on the usual variety of copolymerization is the preparation of polymer chains made of rather long blocks of different kinds of monomers. A number of ingenious systems have been devised for making such polymers, including the Szwarc method described in Section 29-6D. Another scheme, which will work with monomers that polymerize well by radical chains but not with anion chains, is to irradiate a stream of a particular monomer, flowing through a glass tube, with sufficient light to get polymerization well underway. The stream then is run into a dark flask containing a large excess of a second monomer. The growing chains started in the light-induced polymerization then add the second monomer to give a two-block polymer if termination is by disproportionation, or a three-block polymer if by combination. Thus, with A and B being the two different monomers,

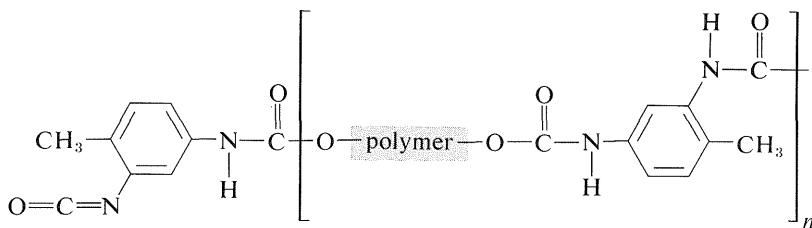


Block polymers also can be made easily by condensation reactions. Thus block polymers similar to the ones described in Exercise 29-8g can be made by esterification:



The very widely used polyurethane foams can be considered to be either block polymers or copolymers. The essential ingredients are a diisocyanate and a diol. The diisocyanate most used is 2,4-diisocyanato-1-methylbenzene, and the diol can be a polyether or a polyester with hydroxyl end groups. The isocyanato groups react with the hydroxyl end groups to form initially an addition polymer, which has polycarbamate (polyurethane) links, and isocyanato end groups:

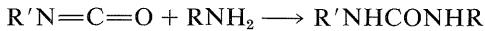




A foam is formed by addition of the proper amount of water. The water reacts with the isocyanate end groups to form carbamic acids which decarboxylate to give amine groups:



The carbon dioxide evolved is the foaming agent, and the amino groups formed at the same time extend the polymer chains by reacting with the residual isocyanate end groups to form urea linkages:

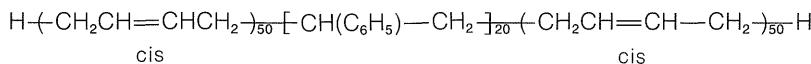
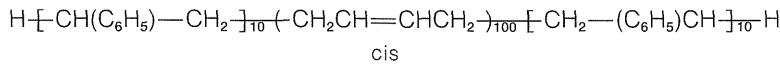


Graft polymers can be made in great profusion by attaching chains of one kind of polymer to the middle of another. A particularly simple but uncontrollable way of doing this is to knock groups off a polymer chain with x-ray or γ radiation in the presence of a monomer. The polymer radicals so produced then can grow side chains made of the new monomer.

A more elegant procedure is to use a photochemical reaction to dissociate groups from the polymer chains and form radicals capable of polymerization with an added monomer.

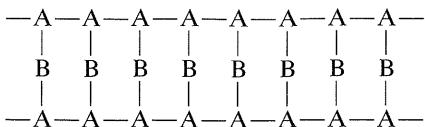
Exercise 29-28* Devise a synthesis of a block polymer with poly-1,2-ethanediol and nylon 66 segments. What kind of physical properties would you expect such a polymer to have?

Exercise 29-29* Suppose one were to synthesize two block copolymers with the following structures:

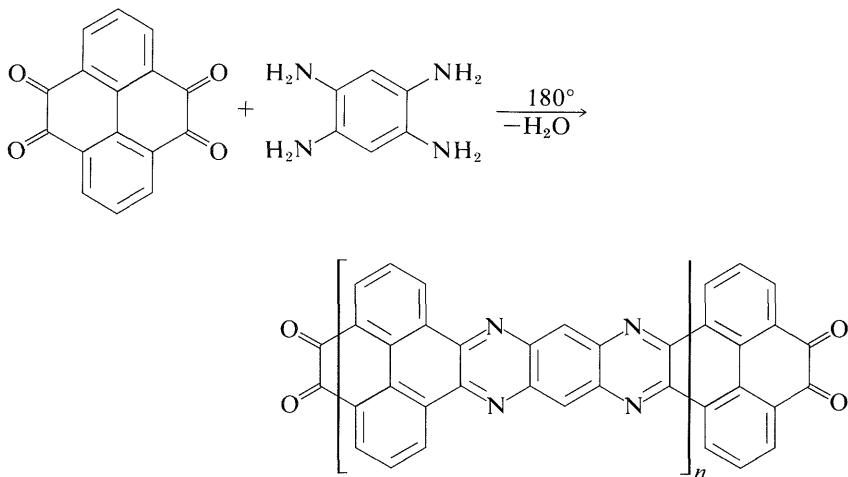


What difference in physical properties would you expect for these two materials? (Review Sections 29-3 and 13-4.)

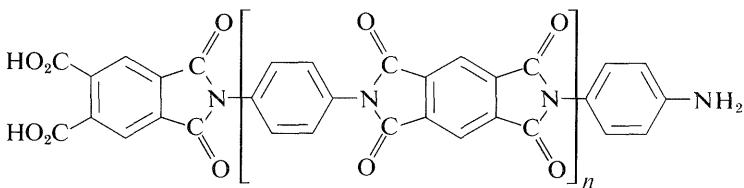
Modern technology has many uses for very strong and very heat-resistant polymers. The logical approach to preparing such polymers is to increase the rigidity of the chains, the strengths of the bonds in the chains, and the intermolecular forces. All of these should be possible if one were to make the polymer molecules in the form of a rigid ribbon rather than a more or less flexible chain. Many so-called **ladder polymers** with basic structures of the following type have been prepared for this purpose:

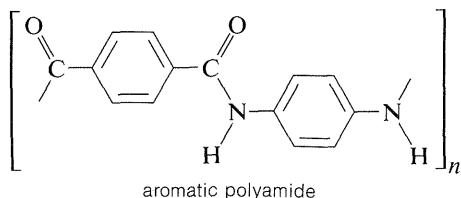


With the proper structures, such polymers can be very rigid and have strong intermolecular interactions. Appropriate syntheses of true ladder polymers in high yield usually employ difficultly obtainable starting materials. An example is

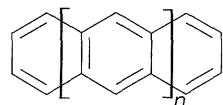


Although there seem to be no true ladder polymers in large-scale commercial production, several **semi-ladder** polymers that have rather rigid structures are employed where high-temperature strength is important. Among these are





Exercise 29-30* What would you expect for the physical and chemical properties of the following ladder polymer?



Exercise 29-31* Fibers made from aromatic polyamides such as from 1,4-benzenediarboxylic acid and 1,4-benzenediamine are at least as strong as steel wire with the same ratio of weight to length. What are the structural features of this kind of polyamide that contribute to the strength?

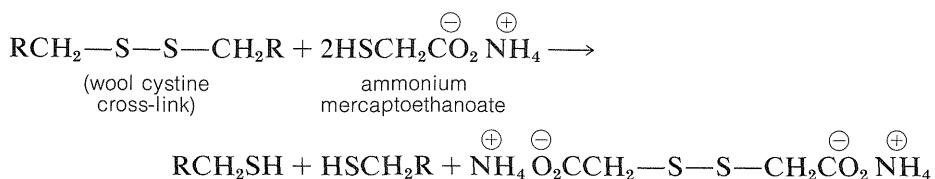
29-8 NATURALLY OCCURRING POLYMERS

There are a number of naturally occurring polymeric substances that have a high degree of technical importance. Some of these, such as natural rubber (Section 13-4), cellulose, and starch (Section 20-7), have regular structures and can be regarded as being made up of single monomer units. Others, such as wool, silk (Section 25-8A), and deoxyribonucleic acid (Section 25-13A) are copolymers. Because we already have considered the chemistry of most of these substances, we shall confine our attention here to wool and collagen, which have properties related to topics discussed previously in this chapter.

29-8A Wool

The structure of wool is more complicated than that of silk fibroin (Figure 25-13) because wool, like insulin (Figure 25-8) and lysozyme (Figure 25-15), contains a considerable quantity of cystine, which provides —S—S— (disulfide) cross-links between the peptide chains. These disulfide linkages play

an important part in determining the mechanical properties of wool fibers because if the disulfide linkages are reduced, as with ammonium mercaptoethanoate solution, the fibers become much more pliable.



Advantage is taken of this reaction in the curling of hair, the reduction and curling being followed by restoration of the disulfide linkages through treatment with a mild oxidizing agent.

Exercise 29-32 The economically important chain reaction, wool + moths \longrightarrow holes + more moths, has, as a key step, scission of the disulfide linkages of cystine in the polypeptide chains by the digestive enzymes of the moth larva. Devise a method of mothproofing wool that would involve chemically altering the disulfide linkages in such a way as to make it unlikely that they would be attacked by the moth enzymes.

29-8B Collagen

The principal protein of skin and connective tissue is called collagen and is primarily constituted of glycine, proline, and hydroxyproline. Collagen is made up of tropocollagen, a substance with very long and thin molecules (14×2900 Å, MW about 300,000). Each tropocollagen molecule consists of three twisted polypeptide strands. When collagen is boiled with water, the

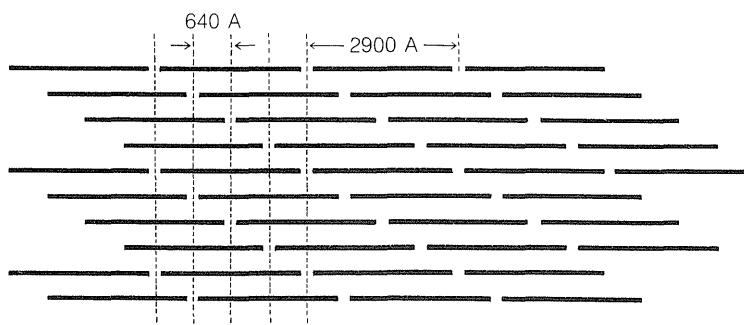


Figure 29-10 Schematic diagram of collagen molecules in a fibril so arranged as to give the 640-Å spacing visible in electron micrographs

strands come apart and the product is ordinary cooking gelatin. Connective tissue and skin are made up of fibrils, 200 Å to 1000 Å wide, which are indicated by x-ray diffraction photographs to be composed of tropocollagen molecules running parallel to the long axis. Electron micrographs show regular bands, 640 Å apart, across the fibrils, and it is believed that these correspond to tropocollagen molecules, all heading in the same direction but regularly staggered by about a fourth of their length (Figure 29-10).

The conversion of collagen fibrils to leather presumably involves formation of cross-links between the tropocollagen molecules. Various substances can be used for the purpose, but chromium salts act particularly rapidly.

Additional Reading

- L. Mandelkern, *An Introduction to Macromolecules*, Springer-Verlag, New York, 1972.
- R. G. Treloar, *Introduction to Polymer Science*, Springer-Verlag, New York, 1970. An excellent and simple introduction to the relationship of polymer physical properties to structure.
- W. J. Burlant and A. S. Hoffman, *Block and Graft Polymers*, Van Nostrand Reinhold Co., New York, 1960.
- A. Ravve, *Organic Chemistry of Macromolecules*, Marcel Dekker, Inc., New York, 1967.
- G. Odian, *Principles of Polymerization*, McGraw-Hill Book Co., New York, 1970.

Polymers in Table 29-1

Much useful information on these and related polymers is given by F. W. Billmeyer, Jr., *A Textbook of Polymer Chemistry*, Wiley-Interscience, New York, 1957; J. K. Stille, *Introduction to Polymer Chemistry*, John Wiley and Sons, Inc., New York, 1962; F. Bueche, *Physical Properties of Polymers*, Wiley-Interscience, New York, 1962; W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Wiley-Interscience, New York, 1961.