


31

Synthetic Polymers

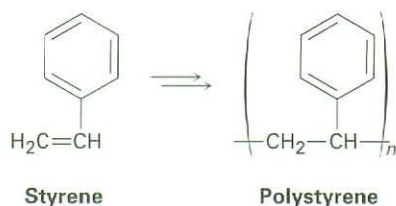
Organic KNOWLEDGE TOOLS

ThomsonNOW Throughout this chapter, sign in at www.thomsonedu.com for online self-study and interactive tutorials based on your level of understanding.

 Online homework for this chapter may be assigned in Organic OWL.

Polymers are a fundamental part of the modern world, showing up in everything from coffee cups to cars to clothing. In medicine, too, their importance is growing for purposes as diverse as cardiac pacemakers, artificial heart valves, and biodegradable sutures.

We've seen on several occasions in previous chapters that a polymer, whether synthetic or biological, is a large molecule built up by repetitive bonding together of many smaller units, or monomers. Polyethylene, for instance, is a synthetic polymer made from ethylene (Section 7.10), nylon is a synthetic polyamide made from a diacid and a diamine (Section 21.9), and proteins are biological polyamides made from amino acids. Note that polymers are often drawn by indicating their repeating unit in parentheses. The repeat unit in polystyrene, for example, comes from the monomer styrene.



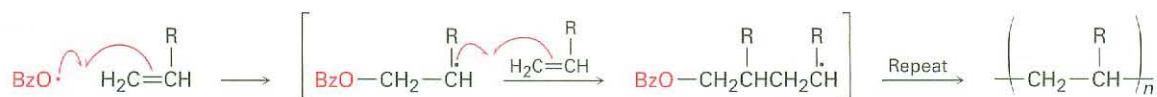
WHY THIS CHAPTER?

Our treatment of polymers has thus far been dispersed over several chapters, but it's now time to take a more comprehensive view. In the present chapter, we'll look further at how polymers are made, and we'll see how polymer structure correlates with physical properties. No course in organic chemistry would be complete without a look at polymers.

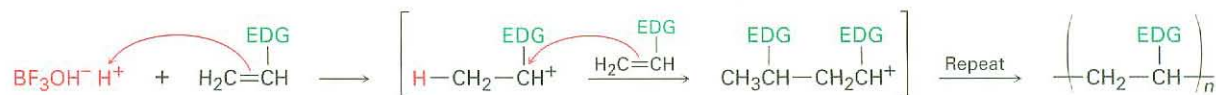
31.1 Chain-Growth Polymers

Synthetic polymers are classified by their method of synthesis as either *chain-growth* or *step-growth*. The categories are somewhat imprecise but nevertheless provide a useful distinction. **Chain-growth polymers** are produced by chain-reaction polymerization in which an initiator adds to a carbon-carbon double bond of an unsaturated substrate (a *vinyl monomer*) to yield a reactive intermediate. This intermediate reacts with a second molecule of monomer to yield a new intermediate, which reacts with a third monomer unit, and so on.

The initiator can be a radical, an acid, or a base. Historically, as we saw in Section 7.10, radical polymerization was the most common method because it can be carried out with practically any vinyl monomer. Acid-catalyzed (cationic) polymerization, by contrast, is effective only with vinyl monomers that contain an electron-donating group (EDG) capable of stabilizing the chain-carrying carbocation intermediate. Thus, isobutylene (2-methylpropene) polymerizes rapidly under cationic conditions, but ethylene, vinyl chloride, and acrylonitrile do not. Isobutylene polymerization is carried out commercially at $-80\text{ }^{\circ}\text{C}$, using BF_3 and a small amount of water to generate $\text{BF}_3\text{OH}^- \text{H}^+$ catalyst. The product is used in the manufacture of truck and bicycle inner tubes.

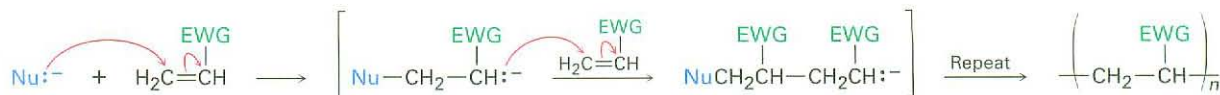


where $\text{BzO}\cdot = \text{Benzoyloxy}, \text{PhCO}_2\cdot$



where **EDG** = an electron-donating group

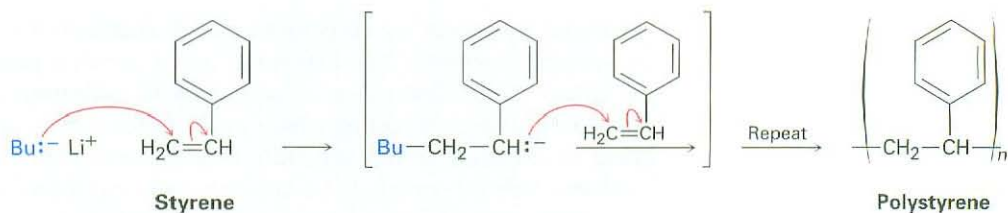
Vinyl monomers with electron-withdrawing substituents (EWG) can be polymerized by basic (anionic) catalysts. The chain-carrying step is conjugate nucleophilic addition of an anion to the unsaturated monomer (Section 19.13).



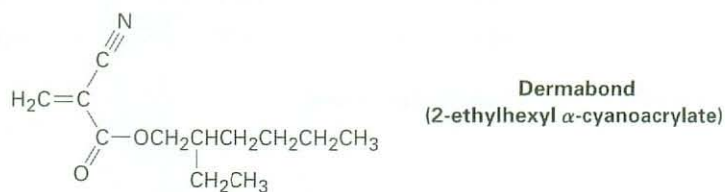
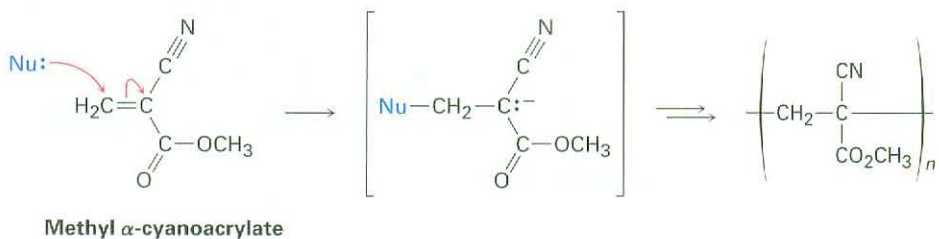
where **EWG** = an electron-withdrawing group

Acrylonitrile ($\text{H}_2\text{C}=\text{CHCN}$), methyl methacrylate [$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$], and styrene ($\text{H}_2\text{C}=\text{CHC}_6\text{H}_5$) can all be polymerized anionically. The polystyrene

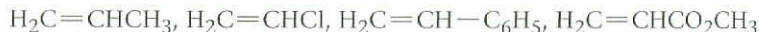
used in foam coffee cups, for example, is prepared by anionic polymerization of styrene using butyllithium as catalyst.



An interesting example of anionic polymerization accounts for the remarkable properties of “super glue,” one drop of which can support up to 2000 lb. Super glue is simply a solution of pure methyl α -cyanoacrylate, which has two electron-withdrawing groups that make anionic addition particularly easy. Trace amounts of water or bases on the surface of an object are sufficient to initiate polymerization of the cyanoacrylate and bind articles together. Skin is a good source of the necessary basic initiators, and many people have found their fingers stuck together after inadvertently touching super glue. So good is super glue at binding tissues together that related cyanoacrylate esters such as Dermabond are used in hospitals in place of sutures to close wounds.



Problem 31.1 Order the following monomers with respect to their expected reactivity toward cationic polymerization, and explain your answer:



Problem 31.2 Order the following monomers with respect to their expected reactivity toward anionic polymerization, and explain your answer:

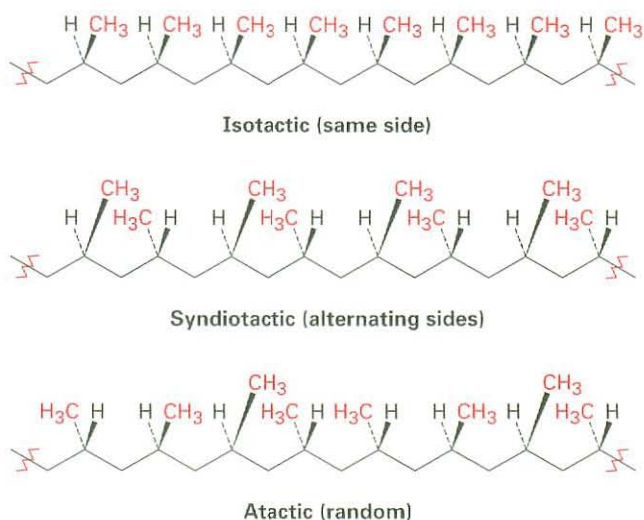


Problem 31.3 Polystyrene is produced commercially by reaction of styrene with butyllithium as an anionic initiator. Using resonance structures, explain how the chain-carrying intermediate is stabilized.

31.2 Stereochemistry of Polymerization: Ziegler–Natta Catalysts

Although we didn't point it out previously, the polymerization of a substituted vinyl monomer can lead to a polymer with numerous chirality centers in its chain. For example, propylene might polymerize with any of the three stereochemical outcomes shown in Figure 31.1. The polymer having all methyl groups on the same side of the zigzag backbone is called **isotactic**, the one in which the methyl groups alternate regularly on opposite sides of the backbone is called **syndiotactic**, and the one having the methyl groups randomly oriented is called **atactic**.

Figure 31.1 Isotactic, syndiotactic, and atactic forms of polypropylene.



Karl Ziegler

Karl Ziegler (1889–1973) was born in Helsa, near Kassel, Germany. After receiving his Ph.D. at the University of Marburg in 1923, he held professorships at several universities, including Heidelberg (1927–1936), before becoming director of the Kaiser Wilhelm Institute for Coal Research at Mülheim-an-der-Ruhr, Germany. He was the first to show the usefulness of organolithium reagents, and he discovered the so-called Ziegler–Natta process for making polyethylene. He received the 1963 Nobel Prize in chemistry for his work on polymerization reactions.

Giulio Natta

Giulio Natta (1903–1979) was born in Imperia, near Genoa, Italy, and received his Ph.D. in chemical engineering at Milan Polytechnic in 1924. After holding positions at the universities of Pavia, Rome, and Turin, he returned to Milan in 1938 as professor of industrial chemistry. For his work on developing methods of polymer synthesis, he shared the 1963 Nobel Prize in chemistry with Karl Ziegler.

The three different stereochemical forms of polypropylene all have somewhat different properties, and all can be made by using the right polymerization catalyst. Propylene polymerization using radical initiators does not work well, but polymerization using *Ziegler–Natta catalysts* allows preparation of isotactic, syndiotactic, and atactic polypropylene.

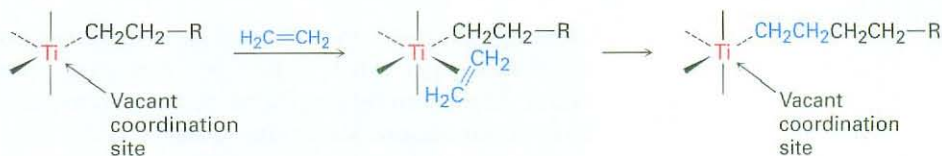
Ziegler–Natta catalysts—there are many different formulations—are organometallic transition-metal complexes prepared by treatment of an alkylaluminum with a titanium compound. Triethylaluminum and titanium tetrachloride form a typical preparation.



Following their introduction in 1953, Ziegler–Natta catalysts revolutionized the field of polymer chemistry because of two advantages: the resultant polymers are linear, with practically no chain branching, and they are stereochemically controllable. Isotactic, syndiotactic, and atactic forms can all be produced, depending on the catalyst system used.

The active form of a Ziegler–Natta catalyst is an alkyltitanium intermediate with a vacant coordination site on the metal. Coordination of alkene monomer

to the titanium occurs, and the coordinated alkene then inserts into the carbon–titanium bond to extend the alkyl chain. A new coordination site opens up during the insertion step, so the process repeats indefinitely.



The linear polyethylene produced by the Ziegler–Natta process, called *high-density polyethylene*, is a highly crystalline polymer with 4000 to 7000 ethylene units per chain and molecular weights in the range 100,000 to 200,000 amu. High-density polyethylene has greater strength and heat resistance than the branched product of radical-induced polymerization, called *low-density polyethylene*, and is used to produce plastic squeeze bottles and molded housewares.

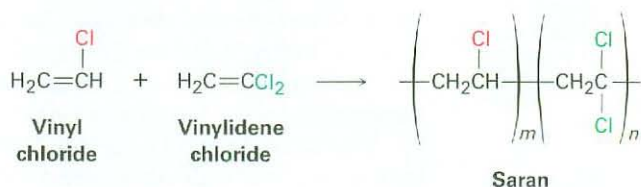
Polyethylenes of even higher molecular weights are produced for specialty applications. So-called high-molecular-weight (HMW) polyethylene contains 10,000 to 18,000 monomer units per chain (MW = 300,000–500,000 amu) and is used for pipes and large containers. Ultrahigh-molecular-weight (UHMW) polyethylene contains more than 100,000 monomer units per chain and has molecular weights ranging from 3,000,000 to 6,000,000 amu. It is used in bearings, conveyor belts, and bulletproof vests among other applications requiring unusual wear resistance.

Problem 31.4 Vinylidene chloride, $\text{H}_2\text{C}=\text{CCl}_2$, does not polymerize in isotactic, syndiotactic, and atactic forms. Explain.

Problem 31.5 Polymers such as polypropylene contain a large number of chirality centers. Would you therefore expect samples of isotactic, syndiotactic, or atactic polypropylene to rotate plane-polarized light? Explain.

31.3 Copolymers

Up to this point we've discussed only **homopolymers**—polymers that are made up of identical repeating units. In practice, however, **copolymers** are more important commercially. **Copolymers** are obtained when two or more different monomers are allowed to polymerize together. For example, copolymerization of vinyl chloride with vinylidene chloride (1,1-dichloroethylene) in a 1:4 ratio leads to the polymer Saran.



Copolymerization of monomer mixtures often leads to materials with properties quite different from those of either corresponding homopolymer, giving the polymer chemist a vast amount of flexibility for devising new materials. Table 31.1 lists some common copolymers and their commercial applications.

Table 31.1 Some Common Copolymers and Their Uses

Monomers	Structures	Trade name	Uses
Vinyl chloride Vinylidene chloride	$\begin{array}{c} \text{H} & & \text{Cl} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array} + \begin{array}{c} \text{H} & & \text{Cl} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{Cl} \end{array}$	Saran	Fibers, food packaging
Styrene 1,3-Butadiene	$\begin{array}{c} \text{H} & & \text{C}_6\text{H}_5 \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array} + \begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	SBR (styrene-butadiene rubber)	Tires, rubber articles
Hexafluoropropene Vinylidene fluoride	$\begin{array}{c} \text{F} & & \text{CF}_3 \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{F} & & \text{F} \end{array} + \begin{array}{c} \text{H} & & \text{F} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{F} \end{array}$	Viton	Gaskets, seals
Acrylonitrile 1,3-Butadiene	$\begin{array}{c} \text{H} & & \text{CN} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array} + \begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	Nitrile rubber	Adhesives, hoses
Isobutylene Isoprene	$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{CH}_3 \end{array} + \begin{array}{c} \text{H}_3\text{C} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	Butyl rubber	Inner tubes
Acrylonitrile 1,3-Butadiene Styrene	$\begin{array}{c} \text{H} & & \text{CN} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array} + \begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	ABS (monomer initials)	Pipes, high-impact applications

Several different types of copolymers can be defined, depending on the distribution of monomer units in the chain. If monomer A is copolymerized with monomer B, for instance, the resultant product might have a random

distribution of the two units throughout the chain, or it might have an alternating distribution.



Random copolymer



Alternating copolymer

The exact distribution of monomer units depends on the initial proportions of the two reactant monomers and their relative reactivities. In practice, neither perfectly random nor perfectly alternating copolymers are usually found. Most copolymers have many random imperfections.

Two other forms of copolymers that can be prepared under certain conditions are called *block copolymers* and *graft copolymers*. **Block copolymers** are those in which different blocks of identical monomer units alternate with each other; **graft copolymers** are those in which homopolymer branches of one monomer unit are “grafted” onto a homopolymer chain of another monomer unit.



Block copolymers are prepared by initiating the polymerization of one monomer as if growing a homopolymer chain and then adding an excess of the second monomer to the still-active reaction mix. Graft copolymers are made by gamma irradiation of a completed homopolymer chain in the presence of the second monomer. The high-energy irradiation knocks hydrogen atoms off the homopolymer chain at random points, thus generating radical sites that can initiate polymerization of the added monomer.

Problem 31.6 Draw the structure of an alternating segment of butyl rubber, a copolymer of isoprene (2-methyl-1,3-butadiene) and isobutylene (2-methylpropene) prepared using a cationic initiator.

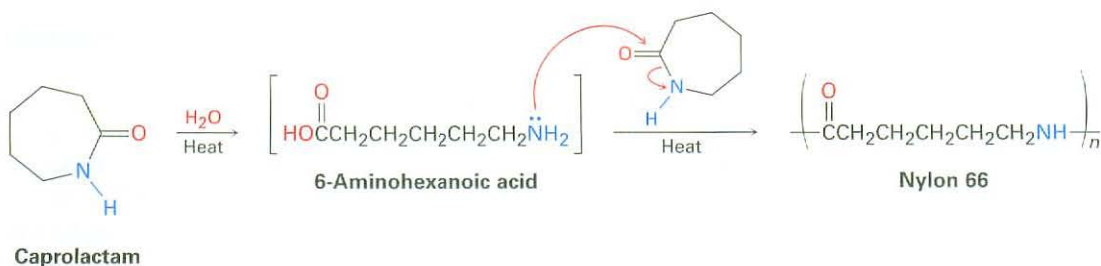
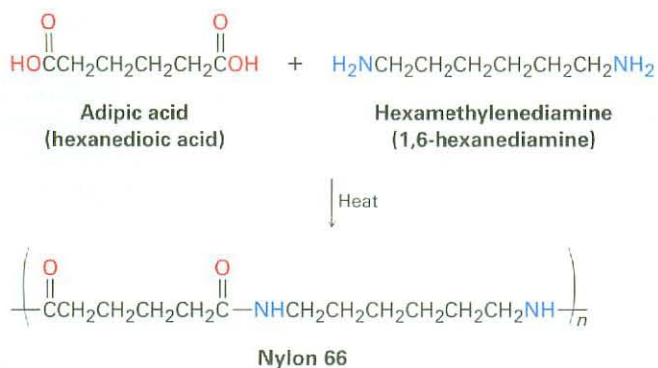
Problem 31.7 Irradiation of poly(-1,3-butadiene), followed by addition of styrene, yields a graft copolymer that is used to make rubber soles for shoes. Draw the structure of a representative segment of this styrene-butadiene graft copolymer.

31.4 Step-Growth Polymers

Step-growth polymers are produced by reactions in which each bond in the polymer is formed stepwise, independently of the others. Like the polyamides (nylons) and polyesters that we saw in Section 21.9, most step-growth polymers

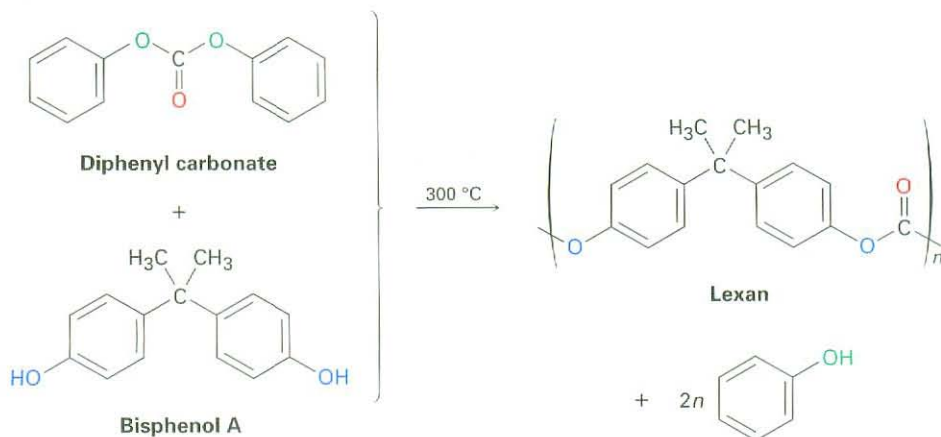
ThomsonNOW Click *Organic Interactive* to predict products from simple polymerization reactions.

are produced by reaction between two difunctional reactants. Nylon 66, for instance, is made by reaction between the six-carbon adipic acid and the six-carbon hexamethylenediamine (1,6-hexanediamine). Alternatively, a single reactant with two different functional groups can polymerize. Nylon 6 is made by polymerization of the six-carbon caprolactam. The reaction is initiated by addition of a small amount of water, which hydrolyzes some caprolactam to 6-aminohexanoic acid. Nucleophilic addition of the amino group to caprolactam then propagates the polymerization.



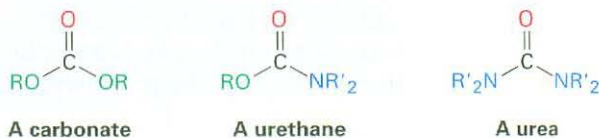
Polycarbonates

Polycarbonates are like polyesters, but their carbonyl group is linked to two -OR groups, [O=C(OR)₂]. Lexan, for instance, is a polycarbonate prepared from diphenyl carbonate and a diphenol called bisphenol A. Lexan has an unusually high impact strength, making it valuable for use in machinery housings, telephones, bicycle safety helmets, and bulletproof glass.

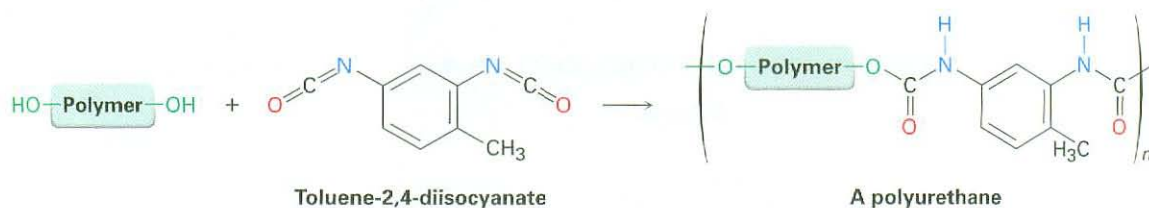


Polyurethanes

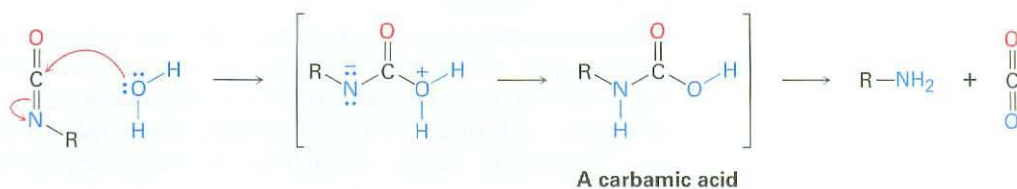
A *urethane* is a carbonyl-containing functional group in which the *carbonyl* carbon is bonded to both an $-OR$ group and an $-NR_2$ group. As such, a urethane is halfway between a carbonate and a urea.



A urethane is typically prepared by nucleophilic addition reaction between an alcohol and an isocyanate ($R-N=C=O$), so a **polyurethane** is prepared by reaction between a diol and a diisocyanate. The diol is usually a low-molecular-weight polymer (MW \approx 1000 amu) with hydroxyl end-groups; the diisocyanate is often toluene-2,4-diisocyanate.



Several different kinds of polyurethanes are produced, depending on the nature of the polymeric alcohol used. One major use of polyurethane is in the stretchable spandex fibers used for bathing suits and athletic gear. These polyurethanes have a fairly low degree of cross-linking, so the resultant polymer is soft and elastic. A second major use of polyurethanes is in the foams used for insulation. Foaming occurs when a small amount of water is added during polymerization, giving a carbamic acid intermediate that spontaneously loses bubbles of CO_2 .



Polyurethane foams are generally made using a *polyalcohol* rather than a diol as the monomer, so the polymer has a high amount of three-dimensional cross-linking. The result is a rigid but very light foam suitable for use as thermal insulation in building construction and portable ice chests.

Problem 31.8 Poly(ethylene terephthalate), or PET, is a polyester used to make soft-drink bottles. It is prepared by reaction of ethylene glycol with 1,4-benzenedicarboxylic acid (terephthalic acid). Draw the structure of PET.

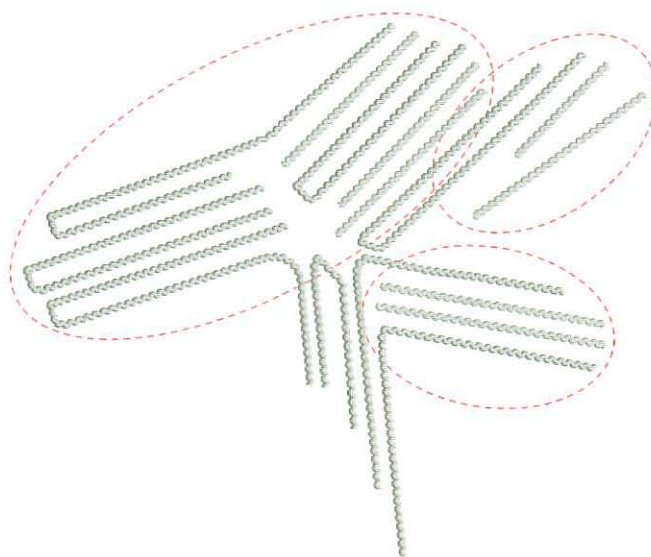
Problem 31.9 Show the mechanism of the nucleophilic addition reaction of an alcohol with an isocyanate to yield a urethane.

31.5 Polymer Structure and Physical Properties

Polymers aren't really that different from other organic molecules. They're much larger, of course, but their chemistry is similar to that of analogous small molecules. Thus, the alkane chains of polyethylene undergo radical-initiated halogenation, the aromatic rings of polystyrene undergo typical electrophilic aromatic substitution reactions, and the amide linkages of a nylon are hydrolyzed by aqueous base.

The major difference between small and large organic molecules is in their physical properties. For instance, their large size means that polymers experience substantially larger van der Waals forces than do small molecules (Section 2.13). But because van der Waals forces operate only at close distances, they are strongest in polymers like high-density polyethylene, in which chains can pack together closely in a regular way. Many polymers, in fact, have regions that are essentially crystalline. These regions, called **crystallites**, consist of highly ordered portions in which the zigzag polymer chains are held together by van der Waals forces (Figure 31.2).

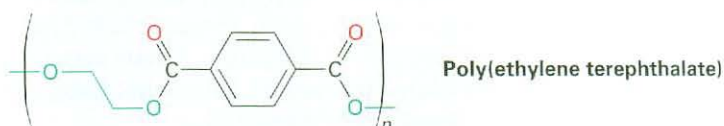
Figure 31.2 Crystallites in linear polyethylene. The long polymer chains are arranged in parallel lines in the crystallite regions.



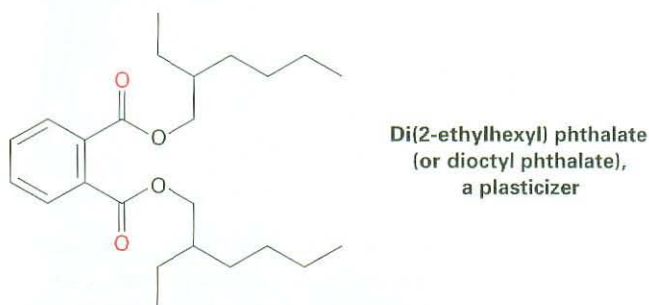
As you might expect, polymer crystallinity is strongly affected by the steric requirements of substituent groups on the chains. Linear polyethylene is highly crystalline, but poly(methyl methacrylate) is noncrystalline because the chains can't pack closely together in a regular way. Polymers with a high degree of crystallinity are generally hard and durable. When heated, the crystalline regions melt at the **melt transition temperature**, T_m , to give an amorphous material.

Noncrystalline, amorphous polymers like poly(methyl methacrylate), sold under the trade name Plexiglas, have little or no long-range ordering among chains but can nevertheless be very hard at room temperature. When heated, the hard amorphous polymer becomes soft and flexible at a point called the **glass transition temperature**, T_g . Much of the art in polymer synthesis lies in finding methods for controlling the degree of crystallinity and the glass transition temperature, thereby imparting useful properties to the polymer.

In general, polymers can be divided into four major categories, depending on their physical behavior: *thermoplastics*, *fibers*, *elastomers*, and *thermosetting resins*. **Thermoplastics** are the polymers most people think of when the word *plastic* is mentioned. These polymers have a high T_g and are therefore hard at room temperature but become soft and viscous when heated. As a result, they can be molded into toys, beads, telephone housings, or any of a thousand other items. Because thermoplastics have little or no cross-linking, the individual chains can slip past one another in the melt. Some thermoplastic polymers, such as poly(methyl methacrylate) and polystyrene, are amorphous and non-crystalline; others, such as polyethylene and nylon, are partially crystalline. Among the better-known thermoplastics is poly(ethylene terephthalate), or PET, used for making plastic soft-drink bottles.



Plasticizers—small organic molecules that act as lubricants between chains—are usually added to thermoplastics to keep them from becoming brittle at room temperature. An example is poly(vinyl chloride), which is brittle when pure but becomes supple and pliable when a plasticizer is added. In fact, most drip bags used in hospitals to deliver intravenous saline solutions are made of poly(vinyl chloride), although replacements are appearing. Dialkyl phthalates such as di(2-ethylhexyl) phthalate (generally called dioctyl phthalate) are commonly used as plasticizers, although questions about their safety have been raised. The U.S. Food and Drug Administration (FDA) has advised the use of alternative materials in compromised patients and infants but has found no evidence of toxicity for most patients.

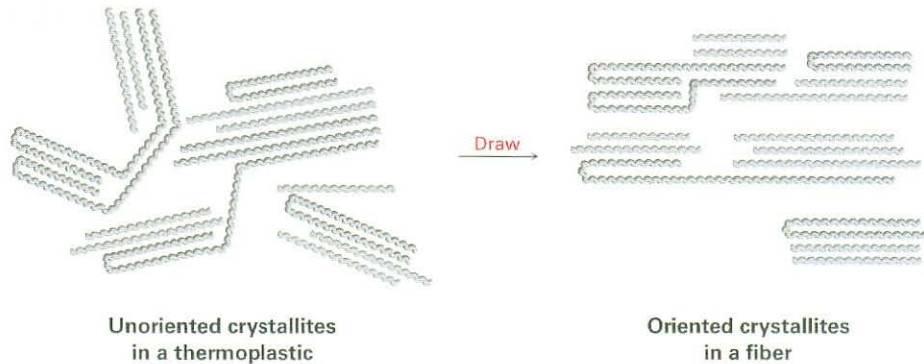


Fibers are thin threads produced by extruding a molten polymer through small holes in a die, or spinneret. The fibers are then cooled and drawn out, which orients the crystallite regions along the axis of the fiber and adds considerable tensile strength (Figure 31.3). Nylon, Dacron, and polyethylene all have the semicrystalline structure necessary for drawing into oriented fibers.

Elastomers are amorphous polymers that have the ability to stretch out and spring back to their original shapes. These polymers must have low T_g values and a small amount of cross-linking to prevent the chains from slipping over one another. In addition, the chains must have an irregular shape to prevent crystallite

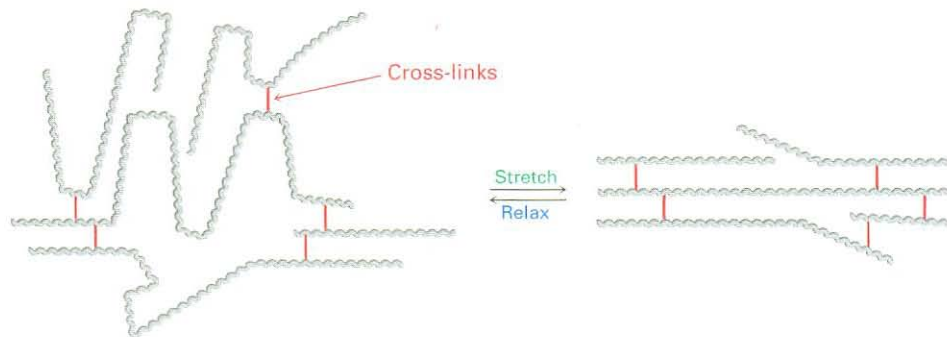
Active Figure 31.3

Oriented crystallite regions in a polymer fiber. Sign in at www.thomsonedu.com to see a simulation based on this figure and to take a short quiz.



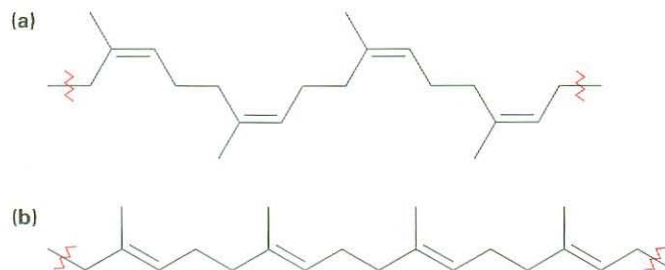
formation. When stretched, the randomly coiled chains straighten out and orient along the direction of the pull. Van der Waals forces are too weak and too few to maintain this orientation, however, and the elastomer therefore reverts to its random coiled state when the stretching force is released (Figure 31.4).

Figure 31.4 Unstretched and stretched forms of an elastomer.



Natural rubber (Chapter 7 *Focus On*) is the most common example of an elastomer. Rubber has the long chains and occasional cross-links needed for elasticity, but its irregular geometry prevents close packing of the chains into crystallites. Gutta-percha, by contrast, is highly crystalline and is not an elastomer (Figure 31.5).

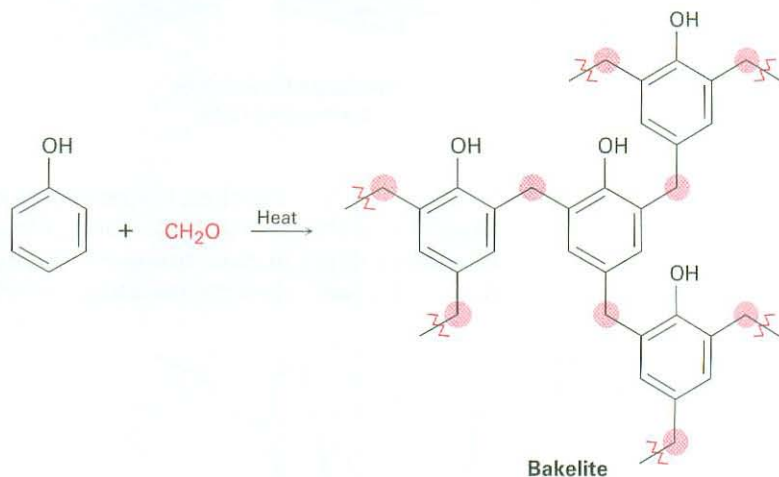
Figure 31.5 (a) Natural rubber is elastic and noncrystalline because of its *cis* double-bond geometry, but (b) gutta-percha is nonelastic and crystalline because its geometry allows for better packing together of chains.



Thermosetting resins are polymers that become highly cross-linked and solidify into a hard, insoluble mass when heated. *Bakelite*, a thermosetting resin first produced in 1907, has been in commercial use longer than any other

synthetic polymer. It is widely used for molded parts, adhesives, coatings, and even high-temperature applications such as missile nose cones.

Chemically, Bakelite is a *phenolic resin*, produced by reaction of phenol and formaldehyde. On heating, water is eliminated, many cross-links form, and the polymer sets into a rocklike mass. The cross-linking in Bakelite and other thermosetting resins is three-dimensional and is so extensive that we can't really speak of polymer "chains." A piece of Bakelite is essentially one large molecule.



Problem 31.10 What product would you expect to obtain from catalytic hydrogenation of natural rubber? Would the product be syndiotactic, atactic, or isotactic?

Problem 31.11 Propose a mechanism to account for the formation of Bakelite from acid-catalyzed polymerization of phenol and formaldehyde.

Focus On . . .



Biodegradable Polymers

The high chemical stability of many polymers is both a blessing and a curse. Heat resistance, wear resistance, and long life are valuable characteristics of clothing fibers, bicycle helmets, underground pipes, food wrappers, and many other items. Yet when those items outlive their usefulness, disposal becomes a problem.

Recycling of unwanted polymers is the best solution, and six types of plastics in common use are frequently stamped with identifying codes assigned by the Society of the Plastics Industry (Table 31.2). After being sorted by type, the

(continued)



© Jiny Fera

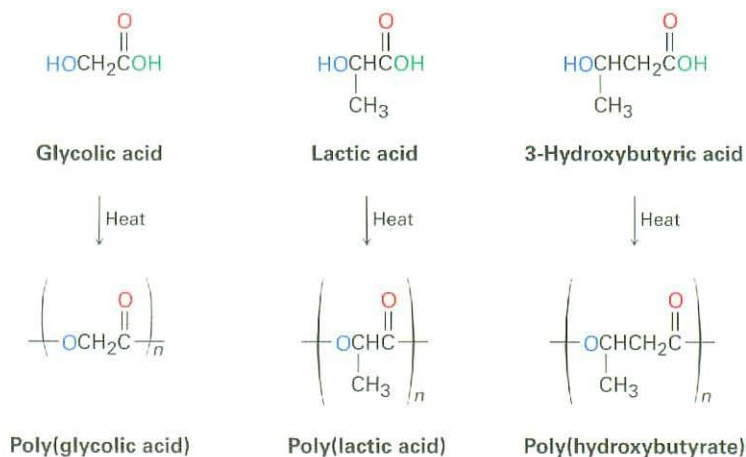
What happens to the plastics that end up here?

items to be recycled are shredded into small chips, washed, dried, and melted for reuse. Soft-drink bottles, for instance, are made from recycled poly(ethylene terephthalate), trash bags are made from recycled low-density polyethylene, and garden furniture is made from recycled polypropylene and mixed plastics.

Table 31.2 Recyclable Plastics

Polymer	Recycling code	Use
Poly(ethylene terephthalate)	1—PET	Soft-drink bottles
High-density polyethylene	2—HDPE	Bottles
Poly(vinyl chloride)	3—V	Floor mats
Low-density polyethylene	4—DPE	Grocery bags
Polypropylene	5—PP	Furniture
Polystyrene	6—PS	Molded articles
Mixed plastics	7	Benches, plastic lumber

Frequently, however, plastics are simply thrown away rather than recycled, and much work has therefore been carried out on developing *biodegradable* polymers, which can be broken down rapidly by soil microorganisms. Among the most common biodegradable polymers are polyglycolic acid (PGA), polylactic acid (PLA), and polyhydroxybutyrate (PHB). All are polyesters and are therefore susceptible to hydrolysis of their ester links. Copolymers of PGA with PLA have found a particularly wide range of uses. A 90/10 copolymer of polyglycolic acid with polylactic acid is used to make absorbable sutures, for instance. The sutures are entirely degraded and absorbed by the body within 90 days after surgery.



SUMMARY AND KEY WORDS

atactic, 1209
 block copolymer, 1212
 chain-growth polymer, 1207
 copolymer, 1210
 crystallite, 1215
 elastomer, 1216
 fiber, 1216
 glass transition temperature (T_g), 1215
 graft copolymer, 1212
 homopolymer, 1210
 isotactic, 1209
 melt transition temperature (T_m), 1215
 plasticizer, 1216
 polycarbonate, 1213
 polyurethane, 1214
 step-growth polymer, 1212
 syndiotactic, 1209
 thermoplastic, 1216
 thermosetting resin, 1217
 Ziegler–Natta catalyst, 1209

Synthetic polymers can be classified as either chain-growth polymers or step-growth polymers. **Chain-growth polymers** are prepared by chain-reaction polymerization of *vinyl monomers* in the presence of a radical, an anion, or a cation initiator. Radical polymerization is sometimes used, but alkenes such as 2-methylpropene that have electron-donating substituents on the double bond polymerize easily by a cationic route through carbocation intermediates. Similarly, monomers such as methyl α -cyanoacrylate that have electron-withdrawing substituents on the double bond polymerize by an anionic, conjugate addition pathway.

Copolymerization of two monomers gives a product with properties different from those of either homopolymer. **Graft copolymers** and **block copolymers** are two examples.

Alkene polymerization can be carried out in a controlled manner using a **Ziegler–Natta catalyst**. Ziegler–Natta polymerization minimizes the amount of chain branching in the polymer and leads to stereoregular chains—either **isotactic** (substituents on the same side of the chain) or **syndiotactic** (substituents on alternate sides of the chain), rather than **atactic** (substituents randomly disposed).

Step-growth polymers, the second major class of polymers, are prepared by reactions between difunctional molecules, with the individual bonds in the polymer formed independently of one another. **Polycarbonates** are formed from a diester and a diol, and **polyurethanes** are formed from a diisocyanate and a diol.

The chemistry of synthetic polymers is similar to the chemistry of small molecules with the same functional groups, but the physical properties of polymers are greatly affected by size. Polymers can be classified by physical property into four groups: **thermoplastics**, **fibers**, **elastomers**, and **thermosetting resins**. The properties of each group can be accounted for by the structure, the degree of crystallinity, and the amount of cross-linking they contain.

EXERCISES

Organic KNOWLEDGE TOOLS

ThomsonNOW Sign in at www.thomsonedu.com to assess your knowledge of this chapter's topics by taking a pre-test. The pre-test will link you to interactive organic chemistry resources based on your score in each concept area.



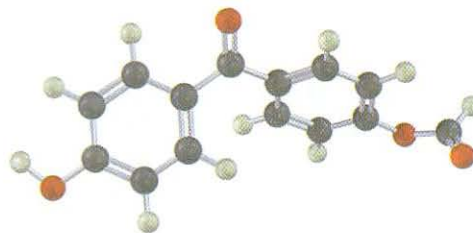
Online homework for this chapter may be assigned in Organic OWL.

■ indicates problems assignable in Organic OWL.

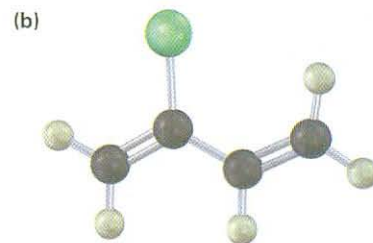
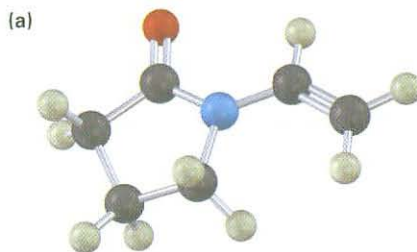
VISUALIZING CHEMISTRY

(Problems 31.1–31.11 appear within the chapter.)

31.12 Identify the structural class to which the following polymer belongs, and show the structure of the monomer units used to make it:

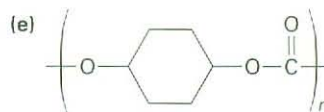
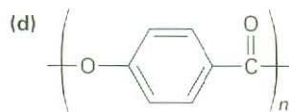
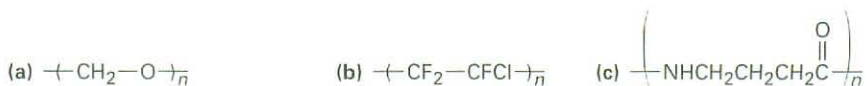
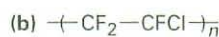
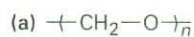


31.13 ■ Show the structures of the polymers that could be made from the following monomers (yellow-green = Cl):



ADDITIONAL PROBLEMS

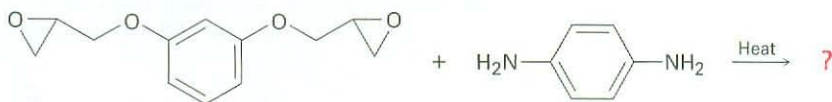
31.14 ■ Identify the monomer units from which each of the following polymers is made, and tell whether each is a chain-growth or a step-growth polymer.



- 31.15** Draw a three-dimensional representation of segments of the following polymers:
 (a) Syndiotactic polyacrylonitrile (b) Atactic poly(methyl methacrylate)
 (c) Isotactic poly(vinyl chloride)
- 31.16** ■ Draw the structure of Kodol, a polyester prepared by heating dimethyl 1,4-benzenedicarboxylate with 1,4-bis(hydroxymethyl)cyclohexane.



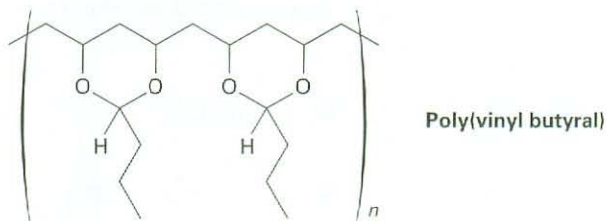
- 31.17** Show the structure of the polymer that results from heating the following diepoxide and diamine:



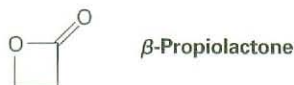
- 31.18** Nomex, a polyamide used in such applications as fire-retardant clothing, is prepared by reaction of 1,3-benzenediamine with 1,3-benzenedicarbonyl chloride. Show the structure of Nomex.
- 31.19** Nylon 10,10 is an extremely tough, strong polymer used to make reinforcing rods for concrete. Draw a segment of nylon 10,10, and show its monomer units.
- 31.20** 1,3-Cyclopentadiene undergoes thermal polymerization to yield a polymer that has no double bonds in the chain. On strong heating, the polymer breaks down to regenerate cyclopentadiene. Propose a structure for the polymer.
- 31.21** When styrene, $C_6H_5CH=CH_2$, is copolymerized in the presence of a few percent *p*-divinylbenzene, a hard, insoluble, cross-linked polymer is obtained. Show how this cross-linking of polystyrene chains occurs.
- 31.22** ■ Poly(ethylene glycol), or Carbowax, is made by anionic polymerization of ethylene oxide using NaOH as catalyst. Propose a mechanism.



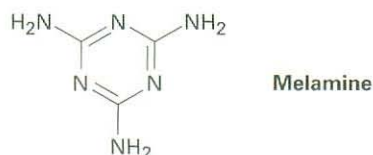
- 31.23** ■ Nitroethylene, $H_2C=CHNO_2$, is a sensitive compound that must be prepared with great care. Attempted purification of nitroethylene by distillation often results in low recovery of product and a white coating on the inner walls of the distillation apparatus. Explain.
- 31.24** Poly(vinyl butyral) is used as the plastic laminate in the preparation of automobile windshield safety glass. How would you synthesize this polymer?



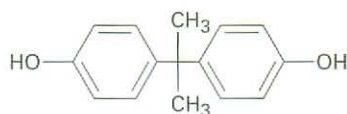
- 31.25 ■ What is the structure of the polymer produced by anionic polymerization of β -propiolactone using NaOH as catalyst?



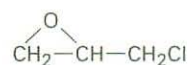
- 31.26 Glyptal is a highly cross-linked thermosetting resin produced by heating glycerol and phthalic anhydride (1,2-benzenedicarboxylic acid anhydride). Show the structure of a representative segment of glyptal.
- 31.27 Melmac, a thermosetting resin often used to make plastic dishes, is prepared by heating melamine with formaldehyde. Look at the structure of Bakelite shown in Section 31.5, and then propose a structure for Melmac.



- 31.28 Epoxy adhesives are cross-linked resins prepared in two steps. The first step involves S_N2 reaction of the disodium salt of bisphenol A with epichlorohydrin to form a low-molecular-weight prepolymer. This prepolymer is then "cured" into a cross-linked resin by treatment with a triamine such as $H_2NCH_2CH_2NHCH_2CH_2NH_2$.

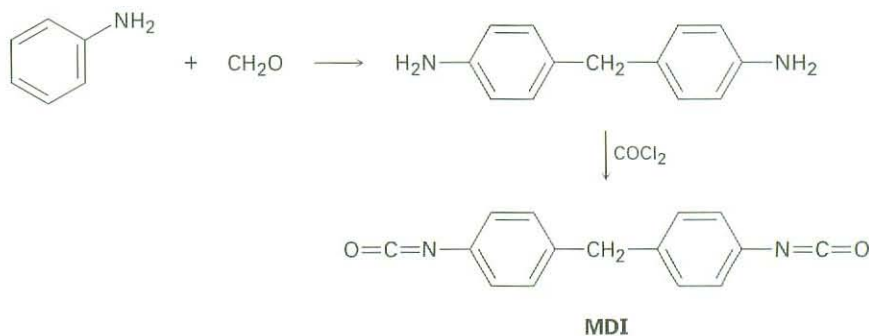


Bisphenol A

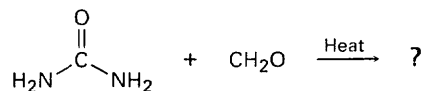


Epichlorohydrin

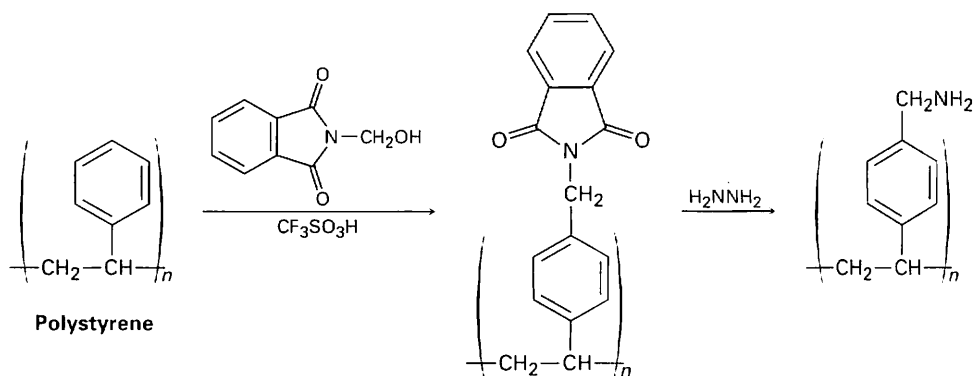
- (a) What is the structure of the prepolymer?
 (b) How does addition of the triamine to the prepolymer result in cross-linking?
- 31.29 The polyurethane foam used for home insulation uses methanediiphenyl-diisocyanate (MDI) as monomer. The MDI is prepared by acid-catalyzed reaction of aniline with formaldehyde, followed by treatment with phosgene, $COCl_2$. Propose mechanisms for both steps.



- 31.30** Write the structure of a representative segment of polyurethane prepared by reaction of ethylene glycol with MDI (Problem 31.29).
- 31.31** The smoking salons of the Hindenburg and other hydrogen-filled dirigibles of the 1930s were insulated with urea-formaldehyde polymer foams. The structure of this polymer is highly cross-linked, like that of Bakelite (Section 31.5). Propose a structure.



- 31.32** The polymeric resin used for Merrifield solid-phase peptide synthesis (Section 26.8) is prepared by treating polystyrene with *N*-(hydroxymethyl)phthalimide and trifluoromethanesulfonic acid, followed by reaction with hydrazine. Propose a mechanism for both steps.



- 31.33** 2-Ethyl-1-hexanol, used in the synthesis of di(2-ethylhexyl) phthalate plasticizer, is made commercially from butanal. Show the likely synthesis route.