15

Synthetic Polymers

boots made of synthetic rubber

Probably no group of synthetic compounds is more important to modern life than synthetic polymers. Unlike small organic molecules, which are of interest because of their chemical properties, these giant molecules—with molecular weights ranging from thousands to millions—are interesting primarily because of their physical properties that make them useful in everyday life. Some synthetic polymers resemble natural substances, but most are quite different from materials found in nature. Such diverse products as plastic bottles, compact discs, rugs, food wrap, artificial joints, Super Glue, toys, weather stripping, automobile body parts, and shoe soles are made of synthetic polymers.

A **polymer** is a large molecule made by linking together repeating units of small molecules called **monomers.** The process of linking them together is called **polymerization.**

$$\underset{\text{monomer}}{n\,\mathrm{M}} \xrightarrow{\text{polymerization}} \underset{\text{polymer}}{-\mathrm{M}-\mathrm{M}-\mathrm{M}-\mathrm{M}-\mathrm{M}-\mathrm{M}-\mathrm{M}-\mathrm{M}-\mathrm{M}-}$$

Polymers can be divided into two broad groups: **synthetic polymers** and **biopolymers.** Synthetic polymers are synthesized by scientists, whereas biopolymers are synthesized by cells. Examples of biopolymers are DNA—the storage molecule for genetic information; RNA and proteins—the molecules that facilitate biochemical transformations; and polysaccharides—compounds that store energy and also function as structural materials. The structures and properties of these biopolymers are presented in other chapters. In this chapter, we will explore synthetic polymers.

Humans first relied on *biopolymers* for clothing, wrapping themselves in animal skins and furs. Later, they learned to spin natural fibers into thread and to weave the thread into cloth. Today, much of our clothing is made of *synthetic polymers* (such as nylon, polyester, and polyacrylonitrile). It has been estimated that if synthetic polymers were not available, all the arable land in the United States would have to be used for the production of cotton and wool for clothing.

A **plastic** is a polymer capable of being molded. The first commercial plastic, celluloid, was invented in 1856. It was used in the manufacture of billiard balls and piano keys, replacing scarce ivory and providing a reprieve for many elephants. Celluloid was also used for motion picture film until it was replaced by cellulose acetate, a more stable polymer.

The first synthetic fiber was rayon. In 1865, the French silk industry was threatened by an epidemic that killed many silkworms. Louis Pasteur determined the source of the disease, but it was his assistant, Louis Chardonnet, who accidentally discovered the starting material for a synthetic substitute for silk when, while wiping up some spilled nitrocellulose from a table, he noticed long silk-like strands adhering to both the cloth and the table.

The first synthetic rubber was synthesized by German chemists in 1917, in response to a severe shortage of raw materials as a result of blockading during World War I.

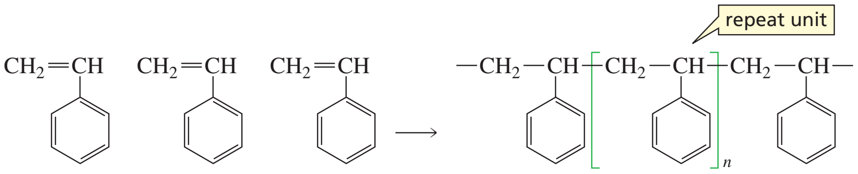
Polymer chemistry is part of the larger discipline of **materials science,** which involves the creation of new materials with improved properties to add to the metals, glass, fabrics, and woods we currently have. Polymer chemistry has evolved into a trillion-dollar industry. Approximately 30,000 polymer patents are currently in force. We can expect scientists to develop many more new materials in the years to come.

15.1 THERE ARE TWO MAJOR CLASSES OF SYNTHETIC POLYMERS

Synthetic polymers can be divided into two major classes: chain-growth polymers and step-growth polymers. **Chain-growth polymers** are made by **chain reactions**—the addition of monomers to the end of a growing chain. The end of a growing chain is reactive because it is a radical, a cation, or an anion. Polystyrene—used for hot drink cups, egg cartons, and insulation, among other things—is an example of a chain-growth polymer. Polystyrene is pumped full of air to produce the material used for insulation in house construction.

Chain-growth polymers are also called addition polymers.

Chain-growth polymers are made by chain reactions.



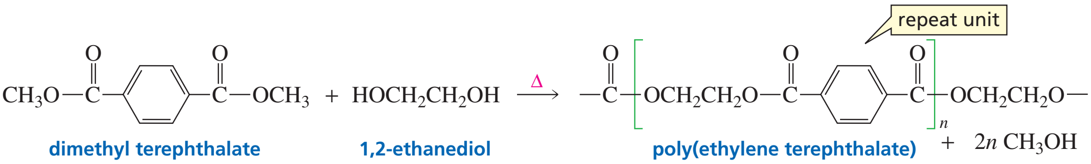
styrene

polystyrene
a chain-growth polymer

Step-growth polymers are also called condensation polymers.

Step-growth polymers are made by linking molecules with reactive functional groups at each end.

Step-growth polymers are made by linking monomers as a result of removing (in most cases) a small molecule, generally water or an alcohol. The monomers have reactive functional groups at each end. Unlike chain-growth polymerization, which requires the individual monomers to add to the end of a growing chain, step-growth polymerization allows any two reactive monomers, dimers, trimers, etc. to be linked. Dacron is an example of a step-growth polymer.



dimethyl terephthalate

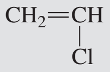
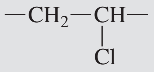
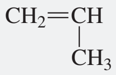
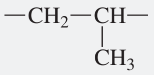
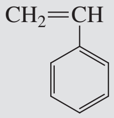
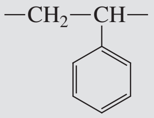
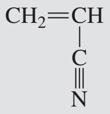
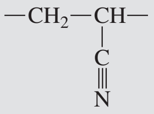
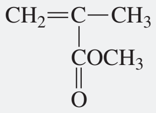
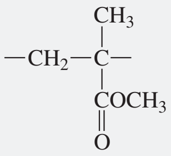
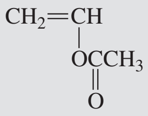
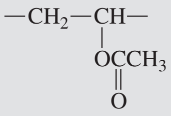
1,2-ethanediol

poly(ethylene terephthalate)
Dacron®
a step-growth polymer

15.2 CHAIN-GROWTH POLYMERS

The monomers used most commonly in chain-growth polymerization are ethylene (ethene) and substituted ethylenes ($CH_2{=}CHR$). Polymers formed from these monomers are called **vinyl polymers.** Some of the many vinyl polymers are listed in Table 15.1.

Table 15.1 Some Important Chain-Growth Polymers and Their Uses

Monomer	Repeating unit	Polymer name	Uses
$CH_2{=}CH_2$	$-CH_2-CH_2-$	polyethylene	toys, water bottles, grocery bags
 $CH_2{=}\underset{\displaystyle Cl}{\underset{\vert}{CH}}$	 $-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-$	poly(vinyl chloride)	shampoo bottles, pipe, siding, flooring, clear food packaging
 $CH_2{=}\underset{\displaystyle CH_3}{\underset{\vert}{CH}}$	 $-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-$	polypropylene	molded caps, margarine tubs, indoor/ outdoor carpeting, plastic chairs
		polystyrene	compact disc jackets, egg cartons, hot drink cups, insulation
$CF_2{=}CF_2$	$-CF_2-CF_2-$	poly(tetrafluoroethylene) Teflon	nonstick surfaces, liners, cable insulation
 $CH_2{=}CH-C{\equiv}N$	 $-CH_2-\underset{\displaystyle C{\equiv}N}{\underset{\vert}{CH}}-$	poly(acrylonitrile) Orlon, Acrilan	rugs, blankets, yarn, apparel, simulated fur
 $CH_2{=}C(CH_3)-\overset{\displaystyle O}{\overset{\Vert}{C}}OCH_3$	 $-CH_2-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle \underset{\Vert}{C}OCH_3}{\underset{\vert}{C}}}}-$	poly(methyl methacrylate) Plexiglas, Lucite	shatter-resistant alternative to glass
 $CH_2{=}CH-OCCH_3$	 $-CH_2-\underset{\displaystyle OCCH_3}{\underset{\vert}{CH}}-$	poly(vinyl acetate)	white glue, adhesives

Chain-growth polymerization proceeds by one of three mechanisms: **radical polymerization, cationic polymerization,** or **anionic polymerization.** Each mechanism has three distinct phases: an *initiation step* that starts the polymerization, *propagation steps* that allow the chain to grow, and *termination steps* that stop the growth of the polymer chain. We will see that the mechanism for a given chain-growth polymerization reaction depends on the structure of the monomer and on the initiator used to activate the monomer.

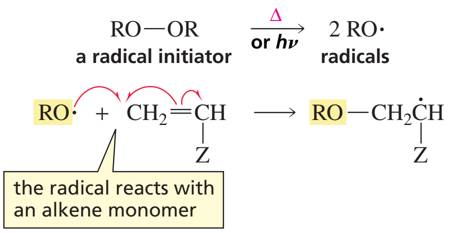
Radical Polymerization

The chain-initiating, chain-propagating, and chain-terminating steps that occur in *radical polymerization* are similar to the steps that take place in the radical reactions discussed in Section 14.2.

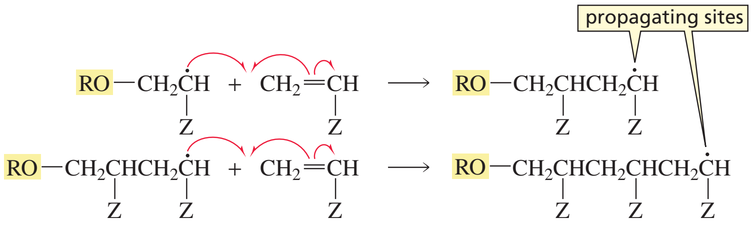
Radical polymerization requires a radical initiator. The radical initiator can be any compound with a weak bond that readily undergoes homolytic cleavage by heat or light to form radicals sufficiently energetic to convert an alkene into a radical.

MECHANISM FOR RADICAL POLYMERIZATION

initiation steps



propagation steps

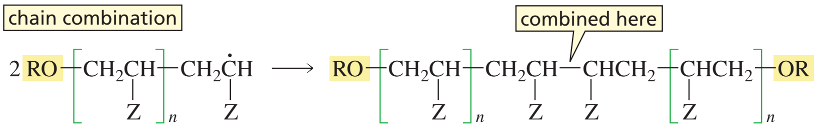


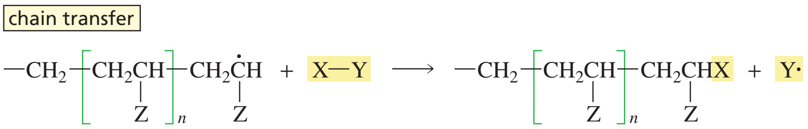
- The initiator breaks homolytically into radicals, and each of these radicals can react with a monomer, creating a monomer radical.
- In the first propagation step, the monomer radical reacts with another monomer, converting it into a radical.
- This radical reacts with another monomer, adding a new subunit to the chain. Notice that the unpaired electron is at the end of the unit most recently added to the chain. This is called the **propagating site.**

Hundreds or even thousands of alkene monomers can add, one at a time, to the growing chain. Eventually, the chain reaction stops because the propagating sites are destroyed in a termination step. Propagating sites are destroyed when

- two chains combine at their propagating sites (chain combination).
- a chain undergoes chain transfer.

termination steps

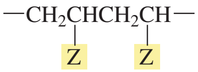


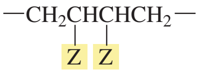


In **chain transfer,** the growing chain reacts with a molecule XY in a manner that allows X· to terminate the chain, leaving behind Y· to initiate a new chain. Molecule XY can be a solvent, a radical initiator, or any molecule with a bond that can readily be cleaved homolytically. Chain transfer can be used to control the molecular weight of the polymer.

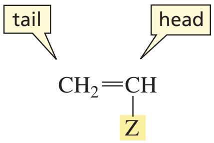
As long as the polymer has a high molecular weight, the groups (RO and X) at the ends of the polymer chains—arising from initiation and chain transfer—are relatively unimportant in determining its physical properties and are generally not even specified; it is the rest of the molecule that determines the properties of the polymer.

Chain-growth polymerization exhibits a marked preference for **head-to-tail addition,** in which the head of one monomer is attached to the tail of another. (Notice that head-to-tail addition of a substituted ethylene results in a polymer in which every other carbon bears a substituent.)


$$-CH_2\underset{Z}{CH}CH_2\underset{Z}{CH}-$$
head-to-tail

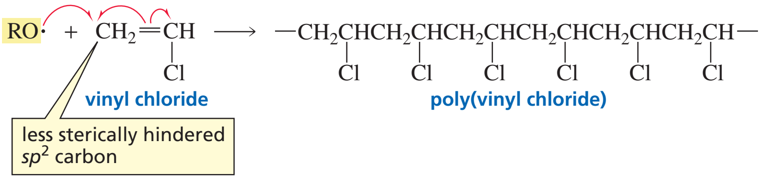

$$-CH_2\underset{Z}{CH}\underset{Z}{CH}CH_2-$$
head-to-head


$$-\underset{Z}{CH}CH_2CH_2\underset{Z}{CH}-$$
tail-to-tail

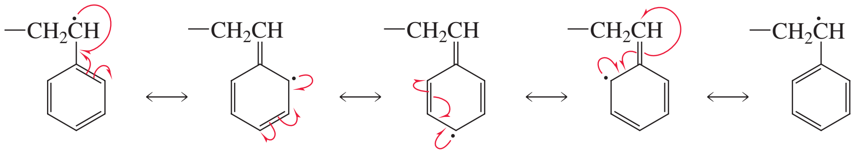


$$CH_2{=}\underset{Z}{CH}$$

Two factors cause head-to-tail addition to be favored. First, there is less steric hindrance at the unsubstituted sp^2 carbon of the alkene; therefore, the propagating site attacks it preferentially.

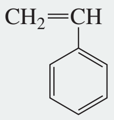
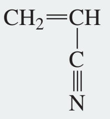
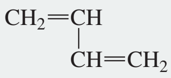
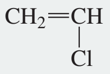
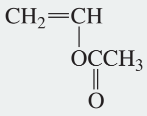
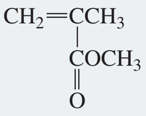


Second, radicals formed by addition to the unsubstituted sp^2 carbon can be stabilized by the substituent attached to the other sp^2 carbon. For example, when Z is a phenyl substituent, the benzene ring stabilizes the radical by electron delocalization.



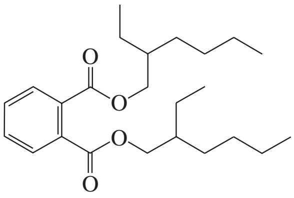
Monomers that most readily undergo chain-growth polymerization by a radical mechanism are those in which the substituent Z is a group able to stabilize the growing radical species by electron delocalization and/or is an electron-withdrawing group.

Table 15.2 Examples of Alkenes That Undergo Radical Polymerization

 styrene	 acrylonitrile	 1,3-butadiene
 vinyl chloride	 vinyl acetate	 methyl methacrylate

Radical polymerization of methyl methacrylate forms a clear plastic known as Plexiglas. The largest window in the world, made of a single piece of Plexiglas (54 ft long, 18 ft high, and 13 in. thick), houses the sharks and barracudas in the Monterey Bay Aquarium.


Plexiglas windows



di-2-ethylhexyl phthalate
a plasticizer

A plasticizer can be dissolved into a polymer to make it more flexible. The **plasticizer** decreases the attractions between the polymer chains, thereby allowing them to slide past one another. The most widely used plasticizer, di-2-ethylhexyl phthalate, is added to poly(vinyl chloride)—normally a brittle polymer—to make products such as vinyl raincoats, shower curtains, and garden hoses.

An important property to consider in choosing a plasticizer is its permanence—that is, how well the plasticizer remains in the polymer. The "new-car smell" appreciated by car owners is the odor of the plasticizer that has vaporized from the vinyl upholstery. When a significant amount of the plasticizer has evaporated, the upholstery becomes brittle and cracks.

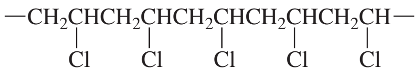
Teflon: An Accidental Discovery

Teflon is a polymer of tetrafluoroethylene (Table 15.1). In 1938, a scientist needed some tetrafluoroethylene for the synthesis of what he hoped would be a new refrigerant. When he opened the cylinder of tetrafluoroethylene, no gas came out. He weighed the cylinder and found that it weighed more than an identical empty cylinder. In fact, it weighed the same as what a cylinder full of tetrafluoroethylene would weigh. Wondering what the cylinder contained, he cut it open and found a slippery polymer. Investigating the polymer further, he found that it was chemically inert to almost everything and could not be melted. In 1961, the first frying pan with a nonstick Teflon coating—"The Happy Pan"— was introduced to the public. Teflon is also used as a lubricant to reduce friction and in pipework that carries corrosive chemicals.

PROBLEM 1♦

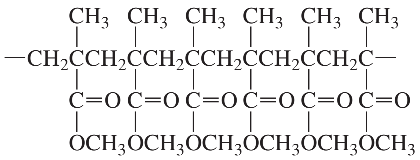
What monomer would you use to form each of the following polymers?

a.



$$-\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}-$$

b.



$$-\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\underset{\mathrm{OCH_3}}{\mathrm{C{=}O}}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\underset{\mathrm{OCH_3}}{\mathrm{C{=}O}}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\underset{\mathrm{OCH_3}}{\mathrm{C{=}O}}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\underset{\mathrm{OCH_3}}{\mathrm{C{=}O}}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\underset{\mathrm{OCH_3}}{\mathrm{C{=}O}}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\underset{\mathrm{OCH_3}}{\mathrm{C{=}O}}}{\mathrm{C}}}-$$

c. $-\mathrm{CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2}-$

PROBLEM 2

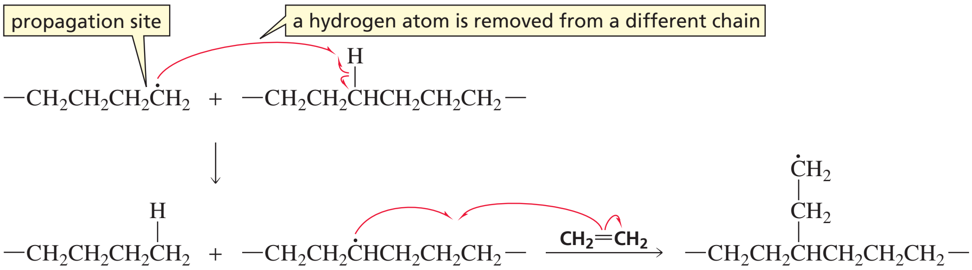
Draw a segment of polystyrene that contains two head-to-head, two tail-to-tail, and two head-to-tail linkages.

PROBLEM 3

Show the mechanism for the formation of a segment of poly(vinyl chloride) that contains three units of vinyl chloride and is initiated by hydrogen peroxide.

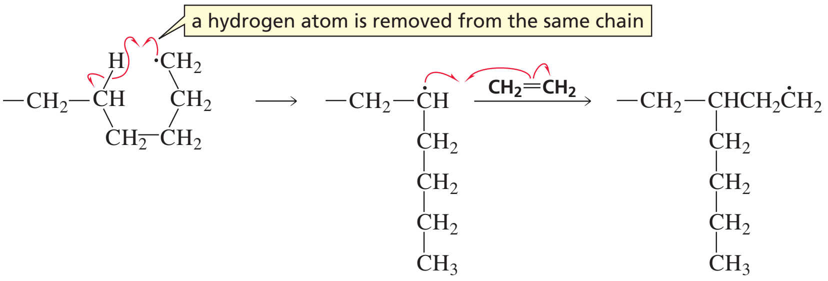
Branching of the Polymer Chain

If the propagating site removes a hydrogen atom from a chain, a branch can grow off the chain at that point. The propagating site can remove a hydrogen atom from a different polymer chain or from the same polymer chain.

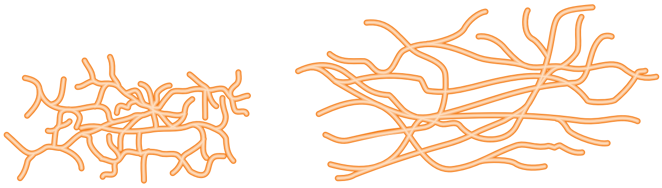


propagation site

a hydrogen atom is removed from a different chain



Removing a hydrogen atom from a carbon near the end of a chain leads to short branches, whereas removing a hydrogen atom from a carbon near the middle of a chain results in long branches. Short branches are more likely to be formed than long ones because the ends of the chain are more accessible.


chain with short branches

chain with long branches

Branched polymers are more flexible.

Branching greatly affects the physical properties of the polymer. Unbranched chains can pack together more closely than branched chains can. Consequently, linear polyethylene (known as high-density polyethylene) is a relatively hard plastic, used for the production of such things as artificial hip joints; whereas branched polyethylene (low-density polyethylene) is a much more flexible polymer, used for trash bags and dry-cleaning bags.

Recycling Symbols

When plastics are recycled, the various types must be separated from one another. To aid in the separation, many states require manufacturers to place a recycling symbol on their products to indicate the type of plastic it is. You are probably familiar with these symbols, which are often embossed on the bottom of plastic containers. The symbols consist of three arrows around one of seven numbers; an abbreviation below the symbol indicates the type of polymer from which the container is made. The lower the number in the middle of the symbol, the greater is the ease with which the material can be recycled: 1 (PET) stands for poly(ethylene terephthalate), 2 (HDPE) for high-density polyethylene, 3 (V) for poly(vinyl chloride), 4 (LDPE) for low-density polyethylene, 5 (PP) for polypropylene, 6 (PS) for polystyrene, and 7 for all other plastics.

recycling symbols

PROBLEM 4

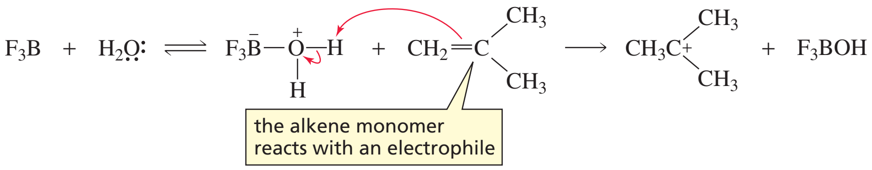
Polyethylene can be used for the production of beach chairs as well as beach balls. Which of these items is made from more highly branched polyethylene?

Cationic Polymerization

In cationic polymerization, the initiator is an electrophile (generally a proton) that adds to the monomer, causing it to become a carbocation. The initiator cannot be an acid such as HCl because its conjugate base (Cl^-) will be able to react with the carbocation. Thus, the initiator often used in cationic polymerization is a compound with an incomplete octet, such as BF_3, and water. Notice that the reaction follows the rule that governs electrophilic addition reactions—that is, the electrophile (the proton initiator) adds to the *sp*^{2} carbon bonded to the most hydrogens (Section 6.3).

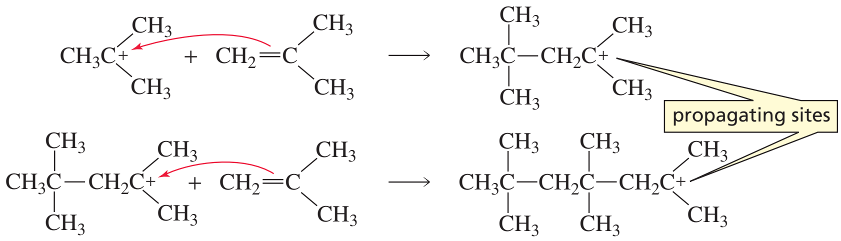
MECHANISM FOR CATIONIC POLYMERIZATION

initiation steps



the alkene monomer reacts with an electrophile

propagating steps



propagating sites

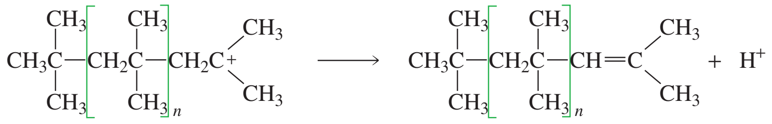
- The cation formed in the initiation step reacts with a second monomer, forming a new cation that reacts in turn with a third monomer. As each subsequent monomer adds to the chain, the new positively charged propagating site is at the end of the most recently added unit.

Cationic polymerization can be terminated by

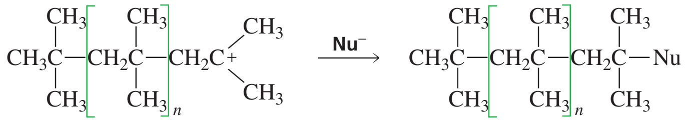
- loss of a proton;
- addition of a nucleophile to the propagating site;
- a chain-transfer reaction with the solvent (XY).

termination steps

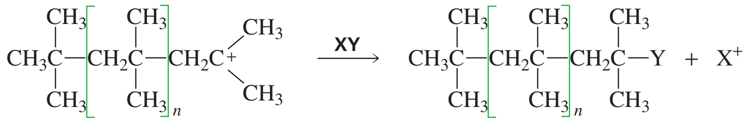
loss of a proton



reaction with a nucleophile

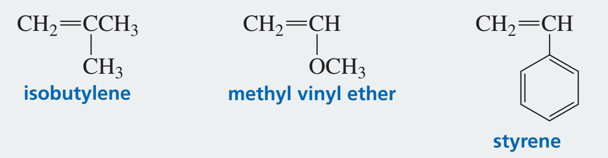


chain-transfer reaction with the solvent



Monomers that are best able to undergo polymerization by a cationic mechanism are those with substituents that can stabilize the positive charge at the propagating site either by hyperconjugation (the first compound in Table 15.3; Section 6.2) or by donating electrons by resonance (the other two compounds in the table; Section 7.9).

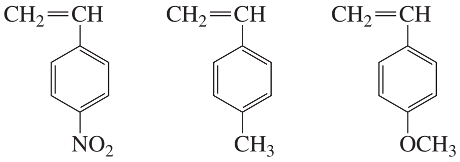
Table 15.3 Examples of Alkenes That Undergo Cationic Polymerization



PROBLEM 5♦

List the following groups of monomers in order from most able to least able to undergo cationic polymerization:

a.



b.

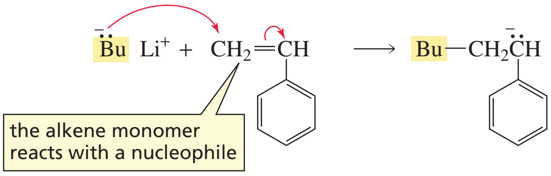
$CH_2{=}C(CH_3)CH_3 \qquad CH_2{=}CHOCH_3 \qquad CH_2{=}CH\overset{O}{\overset{\|}{C}}OCH_3$

Anionic Polymerization

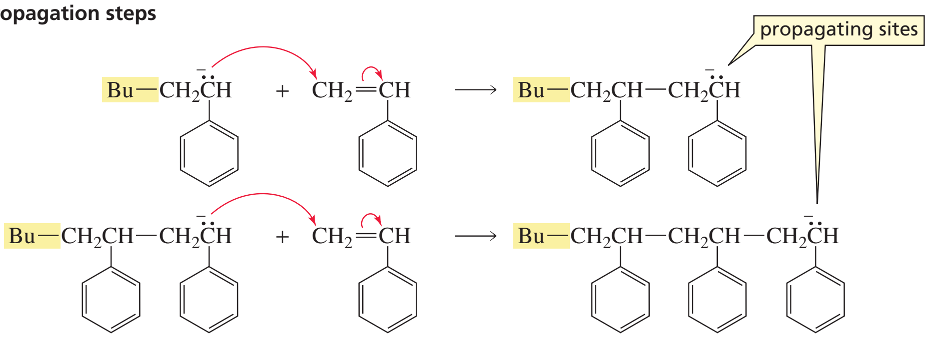
In anionic polymerization, the initiator is a nucleophile that reacts with the monomer to form a propagating site that is an anion. Nucleophilic attack on an alkene does not occur readily because alkenes are themselves electron rich. Therefore, the initiator must be a very good nucleophile, such as sodium amide or butyllithium ($Bu^- \ Li^+$), and the alkene must contain a substituent that can withdraw electrons by resonance, which will decrease the electron density of the double bond.

MECHANISM FOR ANIONIC POLYMERIZATION

initiation step



propagation steps

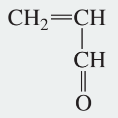


The chain can be terminated by reaction with an impurity in the reaction mixture. If all impurities are rigorously excluded, chain propagation will continue until all the monomer has been consumed. At this point, the propagating site will still be active, so the polymerization reaction will continue if more monomer is added to the system. Such nonterminated chains are called **living polymers** because the chains remain active until they are terminated ("killed").

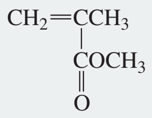
Living polymers are most common in anionic polymerization because the chains cannot be terminated by proton loss from the polymer (as they can in cationic polymerization) or by chain combination (as they can in radical polymerization).

Alkenes that undergo polymerization by an anionic mechanism are those that can stabilize the negatively charged propagating site by resonance electron withdrawal (Table 15.4).

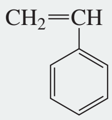
Table 15.4 Examples of Alkenes That Undergo Anionic Polymerization


$CH_2{=}CH{-}CH{=}O$

acrolein

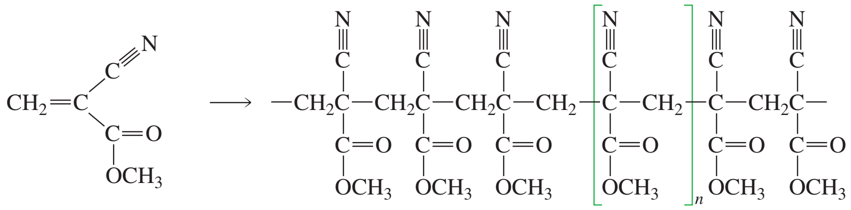

$CH_2{=}C(CH_3){-}C({=}O)OCH_3$

methyl methacrylate



styrene

Super Glue is a polymer of methyl α-cyanoacrylate. Because the monomer has two electron-withdrawing groups, it requires only a moderately good nucleophile to initiate anionic polymerization, such as surface-absorbed water. You may well have experienced this reaction if you have ever spilled a drop of Super Glue on your fingers. A nucleophilic group on the surface of the skin initiates the polymerization reaction, with the result that two fingers can become firmly glued together.



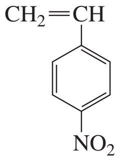
methyl α-cyanoacrylate **Super Glue®**

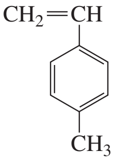
The ability to form covalent bonds with groups on the surfaces of the objects to be glued together is what gives Super Glue its amazing strength. Polymers similar to Super Glue—namely, butyl, isobutyl, or octyl esters rather than methyl esters—are used by surgeons to close wounds.

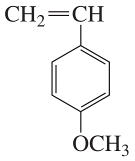
PROBLEM 6♦

List the following groups of monomers in order from most able to least able to undergo anionic polymerization:

a.







b. $CH_2{=}CHCH_3$ $CH_2{=}CHCl$ $CH_2{=}CHC{\equiv}N$

What Determines the Mechanism?

We have seen that the substituent attached to the alkene determines the mechanism for chain-growth polymerization. Alkenes with substituents that can stabilize radicals readily undergo radical polymerization, alkenes with electron-donating substituents that can stabilize cations undergo cationic polymerization, and alkenes with electron-withdrawing substituents that can stabilize anions undergo anionic polymerizations.

Some alkenes undergo polymerization by more than one mechanism. For example, styrene can undergo polymerization by radical, cationic, and anionic mechanisms because the phenyl group can stabilize benzylic radicals, benzylic cations, and benzylic anions. The mechanism followed for its polymerization depends on the nature of the initiator chosen to start the reaction.

PROBLEM 7

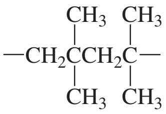
Explain, using resonance structures, why Super Glue is formed by anionic polymerizarion.

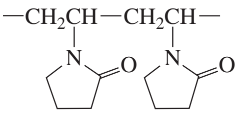
PROBLEM 8♦

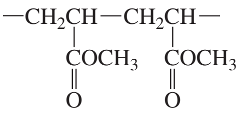
Why does methyl methacrylate not undergo cationic polymerization?

PROBLEM 9♦

Which monomer and which type of initiator would you use to synthesize each of the following polymers?

a.

$-CH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2\underset{CH_3}{\overset{CH_3}{C}}-$

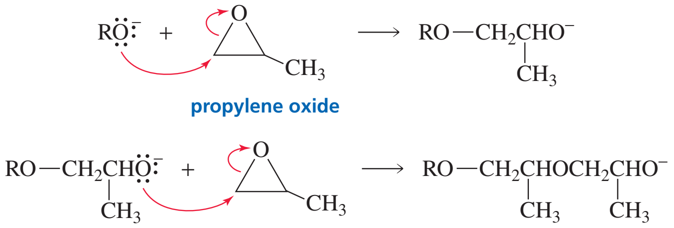
b.


c.

$-CH_2\underset{\substack{|\\ COCH_3\\ \|\\ O}}{CH}-CH_2\underset{\substack{|\\ COCH_3\\ \|\\ O}}{CH}-$

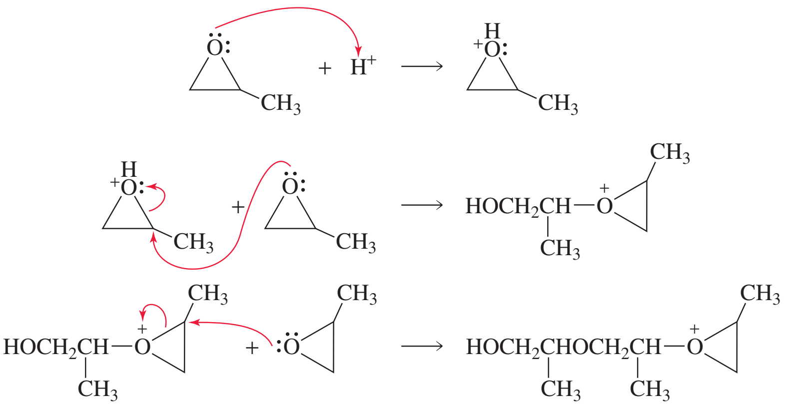
Ring-Opening Polymerizations

Although ethylene and substituted ethylenes are the monomers most commonly used for the synthesis of chain-growth polymers, other compounds can polymerize as well. For example, epoxides can undergo chain-growth polymerization via a ring-opening reaction. Polymerization reactions that involve ring-opening reactions are called **ring-opening polymerizations.**

If the initiator is a nucleophile, polymerization occurs by an anionic mechanism. From what you know about the reactions of epoxides, you should not be surprised that the nucleophile attacks the less sterically hindered carbon of the epoxide (Section 9.8).



If the initiator is an acid, epoxides are polymerized by a cationic mechanism. Notice that under acidic conditions, the nucleophile attacks the more substituted carbon of the epoxide (Section 9.8).



PROBLEM 10

Explain why, when propylene oxide undergoes anionic polymerization, nucleophilic attack occurs at the less substituted carbon of the epoxide, but when it undergoes cationic polymerization, nucleophilic attack occurs at the more substituted carbon.

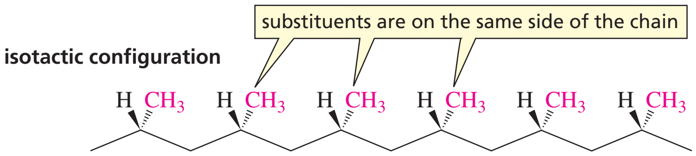
PROBLEM 11

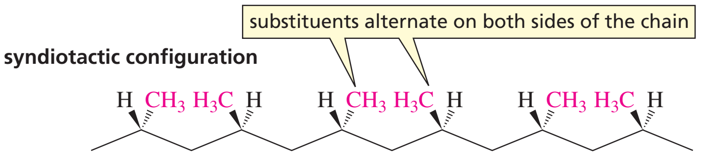
Show the polymerization of 2,2-dimethyloxirane by

a. an anionic mechanism. **b.** a cationic mechanism.

15.3 STEREOCHEMISTRY OF POLYMERIZATION • ZIEGLER–NATTA CATALYSTS

Polymers formed from monosubstituted ethylenes can exist in three configurations: isotactic, syndiotactic, and atactic. An **isotactic polymer** has all of its substituents on the same side of the fully extended carbon chain. (*Iso* and *taxis* are the Greek terms for "the same" and "order," respectively.) In a **syndiotactic polymer** (*syndio* means "alternating"), the substituents regularly alternate on both sides of the carbon chain. The substituents in an **atactic polymer** are randomly oriented.



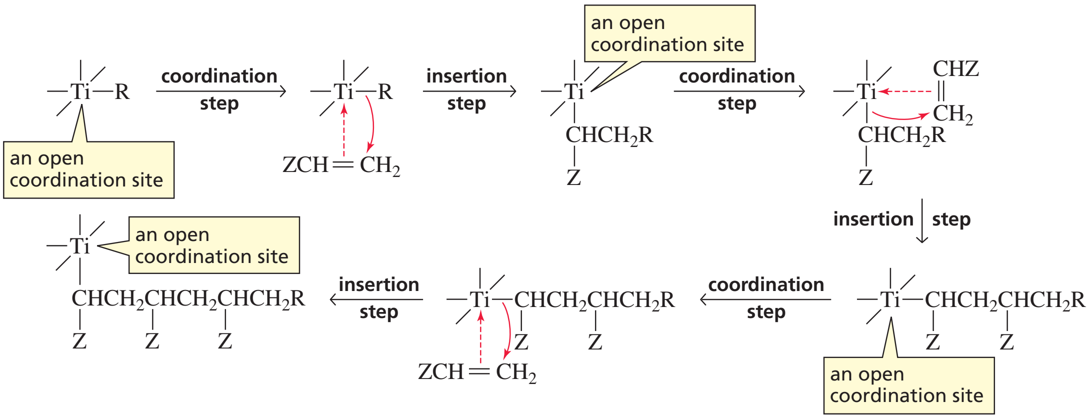


The configuration of the polymer affects its physical properties. Polymers in the isotactic or syndiotactic configuration are more likely to be rigid solids, because positioning the substituents in a regular order allows for a more regular packing arrangement. Polymers in the atactic configuration are more disordered and cannot pack together as well, so these polymers are less rigid and, therefore, softer.

In 1953, Karl Ziegler and Giulio Natta found that the configuration of a polymer could be controlled if the growing end of the chain and the incoming monomer were coordinated with an aluminum–titanium initiator. These initiators are now called **Ziegler–Natta catalysts.** Whether the chain is isotactic or syndiotactic depends on the particular catalyst employed. These catalysts revolutionized the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers that have greater resistance to cracking and heat.

A proposed mechanism for Ziegler–Natta-catalyzed polymerization of a substituted ethylene is shown here.

MECHANISM FOR ZIEGLER–NATTA-CATALYZED POLYMERIZATION OF A SUBSTITUTED ETHYLENE



- The monomer forms a complex with titanium (dotted arrow) at an open coordination site—that is, a site available to accept electrons.
- The coordinated alkene is inserted between the titanium and the growing polymer (R), thereby lengthening the polymer chain.
- Because a new coordination site opens up during insertion of the monomer, the process can be repeated over and over.

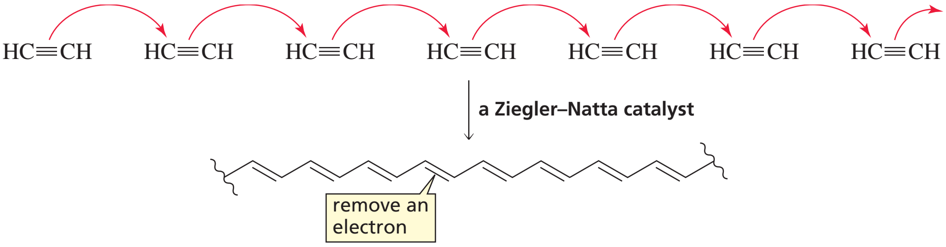
Polyacetylene is another polymer prepared by a Ziegler–Natta process. It can be converted to a **conducting polymer** because the conjugated double bonds in polyacetylene allow electron transport down its backbone after several electrons are removed from or added to the backbone (Section 15.4).

$$\mathrm{HC{\equiv}CH} \xrightarrow{\text{a Ziegler–Natta catalyst}} -\mathrm{CH{=}CH}-\!\left[\mathrm{CH{=}CH}\right]_n\!-\mathrm{CH{=}CH}-$$

acetylene **polyacetylene**

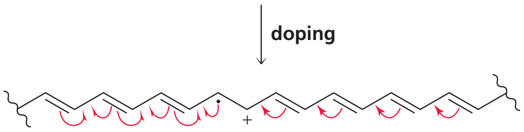
15.4 ORGANIC COMPOUNDS THAT CONDUCT ELECTRICITY

In order for an organic compound to conduct electricity, its electrons must be delocalized so that they can move through the compound just like electrons can move along a copper wire. The first organic compound able to conduct electricity was prepared by polymerizing acetylene using a Ziegler–Natta catalyst.



polyacetylene

The electrons in polyacetylene are not able to move along the length of the chain easily enough to conduct electricity well. However, if electrons are removed from or added to the chain (a process called "doping"), then the electrons can move down the chain and the polymer (with some refinements) can conduct electricity as well as copper can.



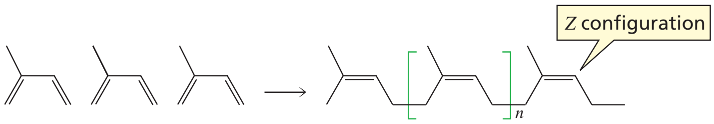
Polyacetylene is very sensitive to air and moisture, which limits its technological applications. However, many other conducting polymers have been developed; they all have a chain of conjugated double bonds.

An important property of conducting polymers is that they are very light. As a result, they are used to coat airplanes to prevent lightning from damaging the interior of the aircraft. The buildup of static electricity can be prevented by coating an insulator with a thin layer of conducting polymer. Conducting polymers are also used in LED (light emitting diode) displays. LEDs emit light in response to an electric current—a process known as electroluminescence. LEDs are used for full color displays in flat-screen TVs, cell phones, and the instrument panels in cars and airplanes. Continued research should lead to many more applications for conducting polymers. One such area is the development of "smart structures," such as golf clubs that will adapt to the golfer's swing. Smart skis (that do not vibrate while skiing) have already been created.

15.5 POLYMERIZATION OF DIENES • NATURAL AND SYNTHETIC RUBBER

When the bark of a rubber tree is cut, a sticky, white liquid oozes out. This same liquid is found inside the stalks of dandelions and milkweed. In fact, more than 400 plants produce this substance. The sticky material is *latex*, a suspension of rubber particles in water. Its biological function is to protect the plant after an injury by covering the wound like a bandage.

Natural rubber is a polymer of 2-methyl-1,3-butadiene, also called isoprene. On average, a molecule of rubber contains 5000 isoprene units.



isoprene units

(*Z*)-poly(2-methyl-1,3-butadiene)
natural rubber

latex being collected from a rubber tree

All the double bonds in natural rubber have the *Z* configuration. Rubber is a waterproof material because its tangled hydrocarbon chains have no affinity for water. Charles Macintosh was the first to use rubber as a waterproof coating for raincoats.

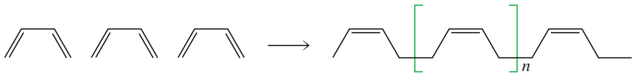
Gutta-percha (from the Malaysian words *getah*, meaning "gum," and *percha*, meaning "tree") is a naturally occurring isomer of rubber in which all the double bonds have the *E* configuration. Like rubber, gutta-percha is exuded by certain trees, but it is much less common. It is also harder and more brittle than rubber. Gutta-percha is the filling material that dentists use in root canals. At one time, it was used for the casing of golf balls. It is no longer used because it becomes brittle in cold weather and tends to split on impact.

PROBLEM 12

Draw a short segment of gutta-percha.

By mimicking nature, scientists have learned to make synthetic rubbers with properties tailored to meet human needs. These materials have some of the properties of natural rubber, including being waterproof and elastic, but they have some improved properties as well; they are tougher, more flexible, and more durable than natural rubber.

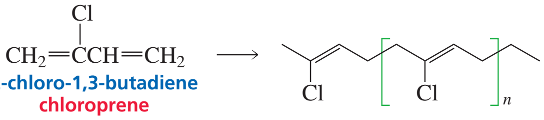
One synthetic rubber, in which all the double bonds are cis, is formed by polymerizing 1,3-butadiene.



1,3-butadiene monomers

(*Z*)-poly(1,3-butadiene)
a synthetic rubber

Neoprene is a synthetic rubber that is made by polymerizing 2-chloro-1,3-butadiene. It is used to make wet suits, shoe soles, tires, hoses, and coated fabrics.



2-chloro-1,3-butadiene
chloroprene

neoprene

A problem common to both natural and most synthetic rubbers is that the polymers are soft and sticky. However, they can be hardened by *vulcanization*. Charles Goodyear discovered this process while looking for ways to improve the properties of rubber. He accidentally spilled a mixture of rubber and sulfur on a hot stove. To his surprise, the mixture became hard but flexible. He called the heating of rubber with sulfur vulcanization, after Vulcan, the Roman god of fire.

Heating rubber with sulfur causes **cross-linking** of the separate polymer chains through disulfide bonds (Figure 15.1). Thus, the vulcanized chains are covalently bonded to each other in one giant molecule. Because the chains have double bonds, they have bends and kinks that allow them to stretch. When the rubber is stretched, the chains straighten out in the direction of the pull. The cross-linking prevents rubber from being torn when it is stretched; moreover, the cross-links provide a reference framework for the material to return to when the stretching force is removed.

The greater the degree of cross-linking, the more rigid is the polymer.

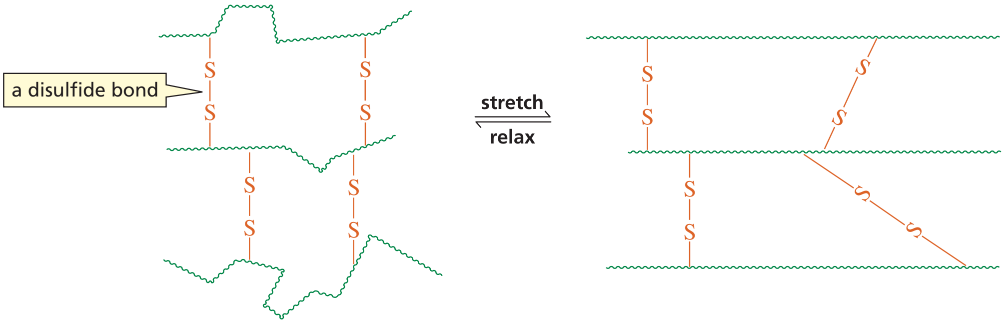


Figure 15.1 The rigidity of rubber is increased by cross-linking the polymer chains with disulfide bonds. When rubber is stretched, the randomly coiled chains straighten out and orient themselves along the direction of the stretch.

The physical properties of rubber can be controlled by regulating the amount of sulfur used in vulcanization. Rubber made with 1%–3% sulfur is soft and stretchy and is used to make rubber bands. Rubber made with 3%–10% sulfur is more rigid and is used in the manufacture of tires. Goodyear's name can be found on many tires sold today. The story of rubber is an example of a scientist taking a natural material and finding ways to improve its properties for useful applications.

PROBLEM 13

a. Draw three segments of the polymer that would be formed from 1,4-polymerization of 1,3-butadiene in which all the double bonds are trans.

b. Draw three segments of the polymer that would be formed from 1,2-polymerization of 1,3-butadiene.

15.6 COPOLYMERS

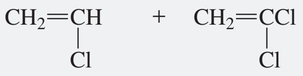
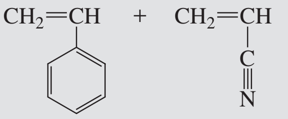
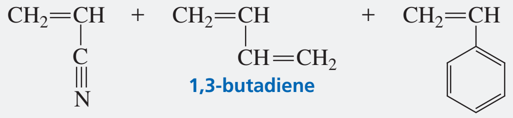
The polymers we have discussed so far are **homopolymers**—they are formed from only one type of monomer. Often, two or more different monomers are used to form a **copolymer.** Increasing the number of different monomers used to form a copolymer dramatically increases the number of different copolymers that can be formed. Even if only two kinds of monomers are used, copolymers with very different properties can be prepared by varying the amounts of each monomer. Both chain-growth polymers and step-growth polymers can be copolymers. Many of the synthetic polymers used today are copolymers. Table 15.5 shows some common copolymers and the monomers from which they are synthesized.

There are several types of copolymers. In an **alternating copolymer,** the two monomers alternate. A **block copolymer** consists of blocks of each kind of monomer. A **random copolymer** has a random distribution of monomers. A **graft copolymer** contains branches derived from one monomer grafted onto a backbone derived from another monomer. These structural differences extend the range of physical properties available to the scientist designing the copolymer.

an alternating copolymer	ABABABABABABABABABABABA
a block copolymer	AAAAABBBBBAAAAABBBBBAAA
a random copolymer	AABABABBABAABBABABBAAAB

a graft copolymer

Table 15.5 Some Examples of Copolymers and Their Uses

Monomers	Copolymer name	Uses
 $CH_2{=}CHCl + CH_2{=}CCl_2$ vinyl chloride vinylidene chloride	Saran	film for wrapping food
 styrene acrylonitrile	SAN	dishwasher-safe objects, vacuum cleaner parts
 acrylonitrile 1,3-butadiene styrene	ABS	bumpers, crash helmets, golf-club heads, luggage
 $CH_2{=}C(CH_3)CH_3 + CH_2{=}C(CH_3)CH{=}CH_2$ isobutylene isoprene	butyl rubber	inner tubes, balls, inflatable sporting goods

Nanocontainers

Scientists have synthesized block copolymers that form micelles (Section 20.3). These spherical copolymers are currently being investigated for their possible use as nanocontainers (10–100 nanometers in diameter) for the delivery of non-water-soluble drugs to target cells. This strategy would allow a higher concentration of a drug to reach a cell than would occur in the natural aqueous milieu. In addition, targeting the drug to the required cells would lower the required dosage of the drug.

PROBLEM 14

Draw four segments of SAN, an alternating copolymer.

15.7 STEP-GROWTH POLYMERS

Step-growth polymers are formed by the intermolecular reaction of molecules with a functional group at each end. When the functional groups react, in most cases a small molecule such as H_2O, alcohol, or HCl is lost. This is why these polymers are also called *condensation polymers* (Section 13.6).

A step-growth polymer can be formed by the reaction of a single bifunctional compound with two different functional groups, A and B. Functional group A of one molecule reacts with functional group B of another molecule to form the compound (A—X—B) that undergoes polymerization.

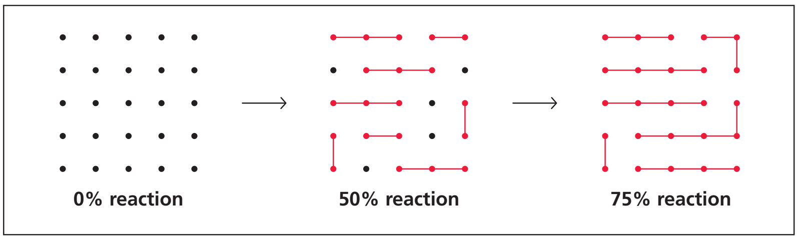
A——B A——B ⟶ A——X——B

A step-growth polymer can also be formed by the reaction of two different bifunctional compounds. One contains two A functional groups and the other contains two B functional groups. Functional group A reacts with functional group B to form the compound (A—X—B) that undergoes polymerization.

Step-growth polymers are made by combining molecules with reactive groups at each end.

A——A B——B ⟶ A——X——B

The formation of step-growth polymers, unlike the formation of chain-growth polymers, does not occur through chain reactions. Any two monomers (or short chains) can react. The progress of a typical step-growth polymerization is shown schematically in Figure 15.2. When the reaction is 50% complete (12 bonds have formed between 25 monomers), the reaction products are primarily dimers and trimers. Even at 75% completion, no long chains have been formed. This means that if step-growth polymerization is to lead to long-chain polymers, very high yields must be achieved. We will see that the reactions involved in step-growth polymerizations are relatively simple (ester and amide formation). However, polymer chemists expend a great deal of effort to arrive at synthetic and processing methods that will result in high-molecular-weight polymers.



0% reaction

50% reaction

75% reaction

▲ **Figure 15.2**

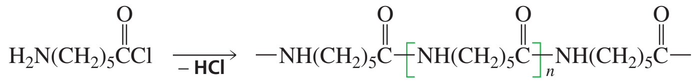
Progress of a step-growth polymerization.

15.8 CLASSES OF STEP-GROWTH POLYMERS

Polyamides

Nylon 6 is an example of a step-growth polymer formed from a monomer with two different functional groups. The acyl chloride group of one monomer reacts with the amino group of another monomer to form an amide (Section 11.7). Thus, nylon is a **polyamide.**

This particular nylon is called nylon 6 because it is formed from the polymerization of 6-aminohexanoyl chloride, a compound that contains six carbons.

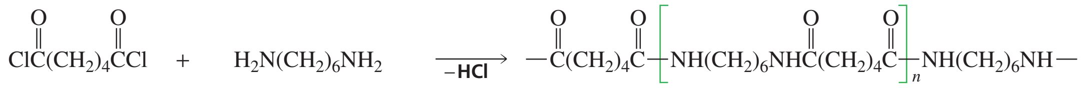


$$H_2N(CH_2)_5\overset{\overset{O}{\|}}{C}Cl \xrightarrow[-\,HCl]{} -NH(CH_2)_5\overset{\overset{O}{\|}}{C}\left[NH(CH_2)_5\overset{\overset{O}{\|}}{C}\right]_n NH(CH_2)_5\overset{\overset{O}{\|}}{C}-$$

6-aminohexanoyl chloride

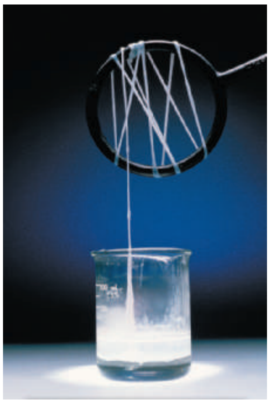
nylon 6
a polyamide

A related polyamide, nylon 66, is an example of a step-growth polymer formed by two different bifunctional monomers—adipoyl chloride and 1,6-hexanediamine. It is called nylon 66 because the two starting materials each have 6 carbons.



$$Cl\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}Cl + H_2N(CH_2)_6NH_2 \xrightarrow[-HCl]{} -\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}\left[NH(CH_2)_6NH\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}\right]_n NH(CH_2)_6NH-$$

adipoyl chloride **1,6-hexanediamine** **nylon 66**



Nylon is pulled from a beaker of adipoyl chloride and 1,6-hexanediamine.

Nylon first found wide use in textiles and carpets. Because it is resistant to stress, it is also used for such things as mountaineering ropes, tire cords, and fishing lines, and as a substitute for metal in bearings and gears. The usefulness of nylon precipitated a search for more new "super fibers" with super strength and super heat resistance.

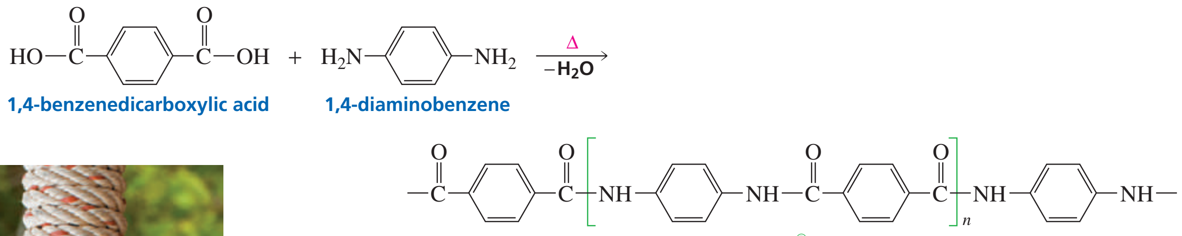
PROBLEM 15♦

a. Draw a short segment of nylon 4. **b.** Draw a short segment of nylon 44.

PROBLEM 16

Write an equation that explains what will happen if a scientist working in the laboratory spills an aqueous solution of sulfuric acid on her nylon 66 hose.

Kevlar is called a super fiber because of its strength; it is an aromatic polyamide. Aromatic polyamides are called **aramides.**

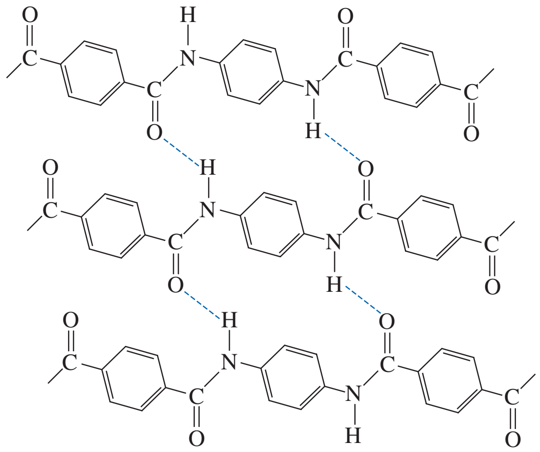


1,4-benzenedicarboxylic acid **1,4-diaminobenzene**

Kevlar®
an aramide

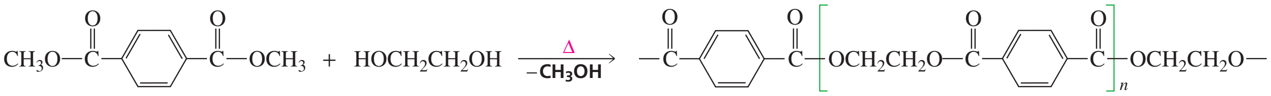
nylon rope

Kevlar owes its strength to the way the individual polymer chains interact with each other. The chains are hydrogen bonded, forming a sheet-like structure. Kevlar is five times stronger than steel on an equal weight basis. Army helmets are made of Kevlar, which is also used for lightweight bullet-resistant vests, automobile parts, high-performance skis, the ropes used on the Mars Pathfinder, and high-performance sails used in the America's Cup. Because it is stable at very high temperatures, it is used in the protective clothing worn by firefighters.



Polyesters

Dacron is the most common of the group of step-growth polymers known as **polyesters**—polymers containing many ester groups. Polyesters are used for clothing and are responsible for the wrinkle-resistant behavior of many fabrics. Dacron is made by the transesterification of dimethyl terephthalate with ethylene glycol (Section 11.8). The durability and moisture resistance of this polymer contribute to its "wash-and-wear" characteristics. Because PET is lightweight, it is also used for transparent soft drink bottles.



dimethyl terephthalate

1,2-ethanediol
ethylene glycol

poly(ethylene terephthalate)
PET
Dacron®
a polyester

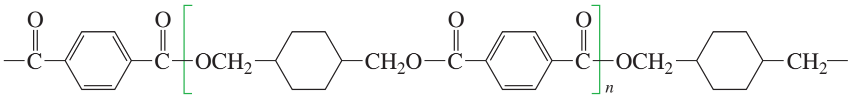
Poly(ethylene terephthlate) can also be processed to form a film known as Mylar. Mylar is tear resistant and, when processed, has a tensile strength nearly as great as that of steel. It is used in the manufacture of magnetic recording tape and sails. Aluminized Mylar was used to make the Echo satellite that was put into orbit around Earth as a giant reflector of microwave signals.

Kodel polyester also is formed by a transesterification reaction. The stiff polyester chain causes the fiber to have a harsh feel that can be softened by blending it with wool or cotton.

Mylar balloons

dimethyl terephthalate

1,4-di(hydroxymethyl)cyclohexane
(cis and trans)



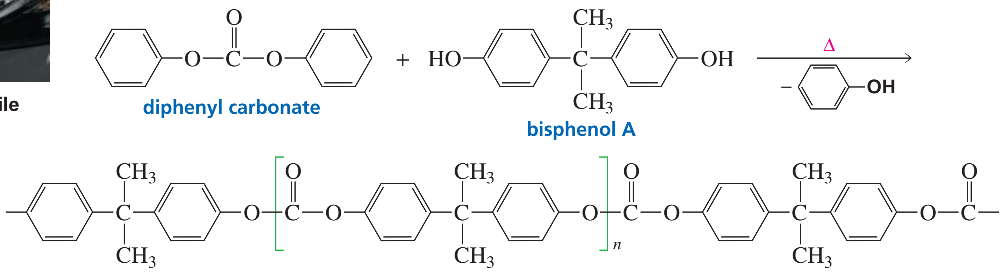
Kodel®

PROBLEM 17

What happens to polyester slacks if aqueous NaOH is spilled on them?

Lexan lens in an automobile

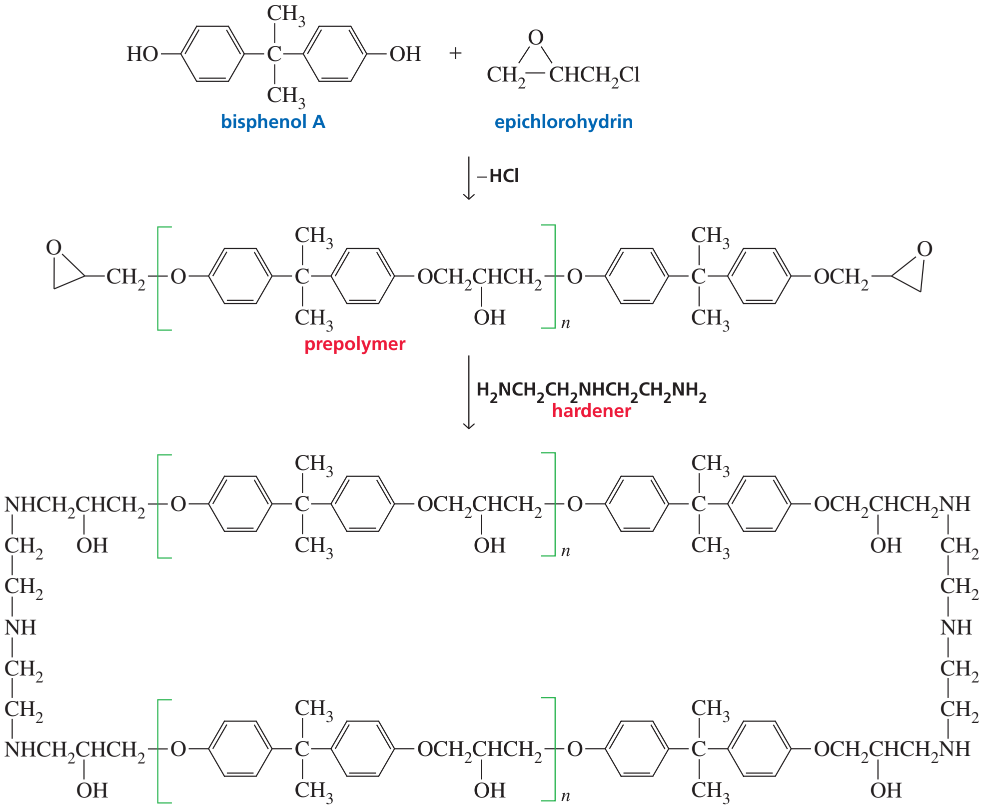
Polyesters with two OR groups bonded to the same carbon are known as **polycarbonates.** Lexan, a polycarbonate produced by the transesterification of diphenyl carbonate with bisphenol A, is a strong, transparent polymer used for motor vehicle headlight lenses, bullet-proof windows, and traffic-light lenses. In recent years, polycarbonates have become important in the automobile industry as well as in the manufacture of compact discs.



Lexan®
a polycarbonate

Epoxy Resins

Epoxy resins are the strongest adhesives known; they are extensively cross-linked systems. They can adhere to almost any surface and are resistant to solvents and to extremes of temperature. Epoxy cement is purchased as a kit consisting of a low-molecular-weight *prepolymer* (the most common is a copolymer of bisphenol A and epichlorohydrin) and a *hardener* that react when mixed to form a cross-linked polymer.



an epoxy resin

Health Concerns: Bisphenol A and Phthalates

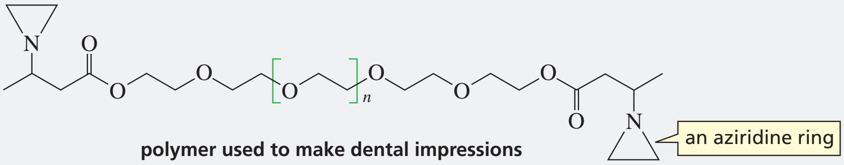
Animal studies have raised concerns about human exposure to bisphenol A and phthalates. Pregnant rats exposed to bisphenol A have been found to have a three to four times higher incidence of precancerous lesions in their mammary ducts. Bisphenol A (BPA) is used in the manufacture of polycarbonates and epoxy resins. Although there is no evidence that bisphenol A has an adverse impact on humans, most manufacturers of polycarbonates have stopped using the compound, and BPA-free water bottles are now found in stores.

Phthalates have been found to be endocrine disruptors—that is, they can alter the proper balance of hormones. Therefore, the primary risk they pose is to a developing fetus. It is difficult to avoid phthalates because of the numerous items (for example, the linings of most aluminum food and beverage cans) that contain them.

Designing a Polymer

Today, polymers are being designed to meet ever more exacting and specific needs. A polymer used for making dental impressions, for example, must be soft enough initially to be molded around the teeth but must become hard enough later to maintain a fixed shape.

The polymer commonly used for dental impressions contains three-membered aziridine rings that react to form cross-links between the chains. Because aziridine rings are not very reactive, cross-linking occurs relatively slowly, so most of the hardening of the polymer does not occur until the polymer is removed from the patient's mouth.



polymer used to make dental impressions

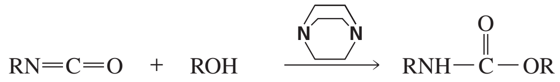
PROBLEM 18

a. Propose a mechanism for the formation of the prepolymer formed by bisphenol A and epichlorohydrin.

b. Propose a mechanism for the reaction of the prepolymer with the hardener.

Polyurethanes

A **urethane**—also called a carbamate—is a compound that has an OR group and an NHR group bonded to the same carbonyl carbon. Urethanes can be prepared by treating an isocyanate with an alcohol, in the presence of a catalyst such as a tertiary amine.

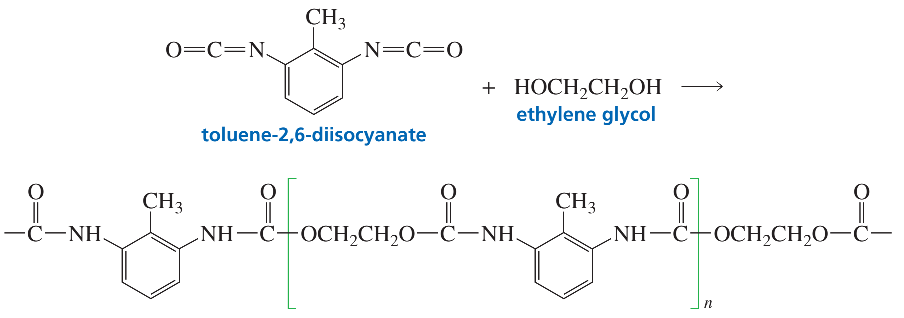


$$\underset{\text{an isocyanate}}{RN{=}C{=}O} + \underset{\text{an alcohol}}{ROH} \xrightarrow{\text{N(CH}_2\text{CH}_2)_3\text{N}} \underset{\text{a urethane}}{RNH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR}$$

an isocyanate an alcohol a urethane

One of the most common **polyurethanes**—polymers that contain urethane groups—is prepared by the polymerization of toluene-2,6-diisocyanate and ethylene glycol. If the reaction is carried out in the presence of a blowing agent, the product is a polyurethane foam. Blowing agents are gases such as nitrogen or carbon dioxide. Polyurethane foams are used for furniture stuffing, bedding, carpet backings, and insulation. Notice that polyurethanes prepared from diisocyanates and diols are the only step-growth polymers we have seen in which a small molecule is not lost during polymerization.

polyurethane foam



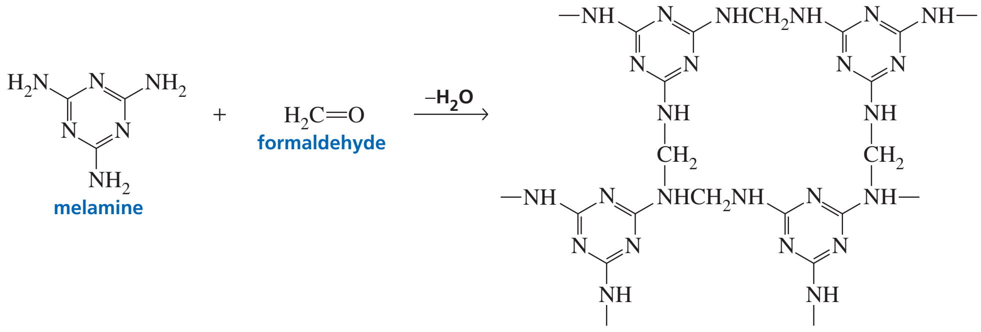
a polyurethane

One of the most important uses of polyurethanes is in fabrics with elastic properties, such as Lycra—known generically as spandex. These fabrics are block copolymers in which some of the polymer segments are polyurethanes, some are polyesters, and some are polyethers; they are always blended with cotton or wool. The blocks of polyurethane are rigid and short, enabling it to be a fabric; the blocks of polyesters and polyethers are flexible and long, providing the elastic properties. When stretched, the soft blocks, which are cross-linked by the hard blocks, become highly ordered. When the tension is released, they revert to their previous state.

Cross-Linked Polymers

Very rigid materials can be obtained if the polymer chains are cross-linked. The greater the degree of cross-linking, the more rigid is the polymer. After they are hardened, they cannot be remelted by heating because the cross-links are covalent bonds, not van der Waals forces. Crosslinking reduces the mobility of the polymer chains, causing the polymer to be relatively brittle.

Melmac, a highly cross-linked polymer of melamine and formaldehyde, is a hard, moisture-resistant material. Because it is colorless, Melmac can be made into materials with pastel colors. It is used to make counter surfaces and lightweight dishes.

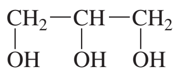


PROBLEM 19

Propose a mechanism for the formation of Melmac.

PROBLEM 20

Explain why, when a small amount of glycerol is added to the reaction mixture of toluene-2,6-diisocyanate and ethylene glycol during the synthesis of polyurethane foam, a much stiffer foam is obtained.



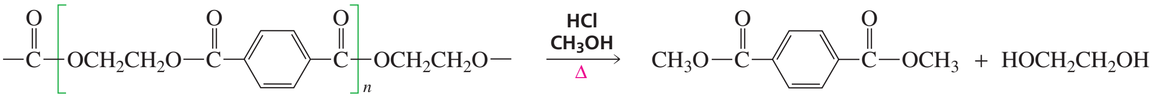
$$\underset{\displaystyle OH}{CH_2}-\underset{\displaystyle OH}{CH}-\underset{\displaystyle OH}{CH_2}$$

glycerol

15.9 RECYCLING POLYMERS

We saw in Section 15.2 that polymers are assigned a number from 1 to 6 that indicates the ease with which that kind of polymer can be recycled—the lower the number, the easier it can be recycled. Unfortunately, only polymers with the two lowest numbers PET (1)—the polymer used to make soft drink bottles—and HDPE (2)—the denser polymer used for juice and milk bottles—are recycled to any significant extent. This amounts to less than 25% of all polymers. The others are found in landfills.

PET is recycled by heating the polymer in an acidic solution of methanol. This transesterification reaction (Section 11.8) is the reverse of the transesterifcation reaction that formed the polymer (page 545). Because the products of recycling PET are the monomers used to make it, the products are recycled to make more PET.



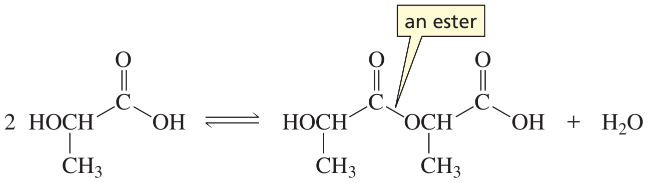
poly(ethylene terephthalate)
PET

dimethyl terephthalate

1,2-ethanediol

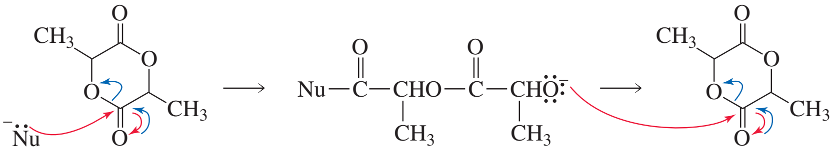
15.10 BIODEGRADABLE POLYMERS

Biodegradable polymers are polymers that can be degraded by microorganisms such as bacteria, fungi, or algae. Polylactide (PLA), a biodegradable polymer of lactic acid, has found wide use. When lactic acid is polymerized, a molecule of water is lost that can hydrolyze the new ester bond, reforming lactic acid.



lactic acid

However, if lactic acid is converted to a cyclic dimer, the dimer can form a polymer without the loss of water by ring-opening polymerization. (The red arrows show formation of the tetrahedral intermediate; the blue arrows show the subsequent elimination from the tetrahedral intermediate.)

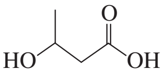


cyclic dimer of lactic acid

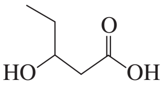
Because lactic acid has an asymmetric center, there are several different forms of the polymer. The polymer's physical properties depend on the ratio of *R* and *S* enantiomers used in its synthesis. Polylactides are currently being used in nonwrinkle fabrics, microwavable trays, food packaging, and in several medical applications such as sutures, stents, and drug-delivery devices. They are also used for cold drink glasses. Unfortunately, hot drinks cause the polymer to liquify. Although polylactides are more expensive than nonbiodegradable polymers, their price is falling as their production increases.

glasses made of PLA

Polyhydroxyalkanoates (PHAs) are also biodegradable polymers. These are step-growth polymers of 3-hydroxycarboxylic acids. Thus, like PLA, they are polyesters. The most common PHA is PHB, a polymer of 3-hydroxybutyric acid; it can be used for many of the things that polypropylene is now used for. Unlike polypropylene, which floats, PHB sinks. PHBV, a PHA marketed under the trade name Biopol, is a copolymer of 3-hydroxybutyric acid and 3-hydroxyvaleric acid. It is being used for such things as wastepaper baskets, toothbrush holders, and soap dispensers. PHAs are degraded by bacteria to CO_2 and H_2O.



3-hydroxybutyric acid



3-hydroxyvaleric acid

PROBLEM 21

a. Draw the structure of a short segment of PHB.
b. Draw the structure of a short segment of PHBV with alternating monomers.

SOME IMPORTANT THINGS TO REMEMBER

- A **polymer** is a giant molecule made by covalently linking repeating units of small molecules called **monomers.** The process of linking them is called **polymerization.**
- Polymers can be divided into two groups: **synthetic polymers,** which are synthesized by scientists, and **biopolymers,** which are synthesized by cells.
- Synthetic polymers can be divided into two classes: **chain-growth polymers** and **step-growth polymers.**
- Chain-growth polymers are made by **chain reactions,** which add monomers to the end of a growing chain.
- The chain reactions take place by one of three mechanisms: **radical polymerization, cationic polymerization,** or **anionic polymerization.**
- Each mechanism has an initiation step that starts the polymerization, propagation steps that allow the chain to grow at the **propagating site,** and termination steps that stop the growth of the chain.
- The choice of mechanism depends on the structure of the **monomer** and the initiator used to activate the monomer.
- In radical polymerization, the initiator is a radical; in cationic polymerization, it is an electrophile; and in anionic polymerization, it is a nucleophile.
- Chain-growth polymerization exhibits a preference for **head-to-tail addition.**
- Branching affects the physical properties of the polymer because unbranched chains can pack together more closely than branched chains can.
- Nonterminated polymer chains are called **living polymers.**
- The substituents are on the same side of the carbon chain in an **isotactic polymer,** alternate on both sides of the chain in a **syndiotactic polymer,** and are randomly oriented in an **atactic polymer.**
- The structure of a polymer can be controlled with **Ziegler–Natta catalysts.**
- Natural rubber is a polymer of 2-methyl-1,3-butadiene. Synthetic rubbers have been made by polymerizing dienes other than 2-methyl-1,3-butadiene.
- Heating rubber with sulfur to cross-link the chains is called **vulcanization.**
- **Homopolymers** are made of one kind of monomer; **copolymers** are made of more than one kind.
- **Step-growth polymers** are made by combining two molecules with reactive functional groups at each end.
- Nylon is a **polyamide. Aramides** are aromatic polyamides. Dacron is a **polyester.**
- **Polycarbonates** have two alkoxy groups bonded to the same carbonyl carbon. A **urethane** is a compound that has an OR and an NHR group bonded to the same carbonyl carbon.
- The greater the degree of cross-linking, the more rigid the polymer.
- **Biodegradable polymers** can be degraded by microorganisms.