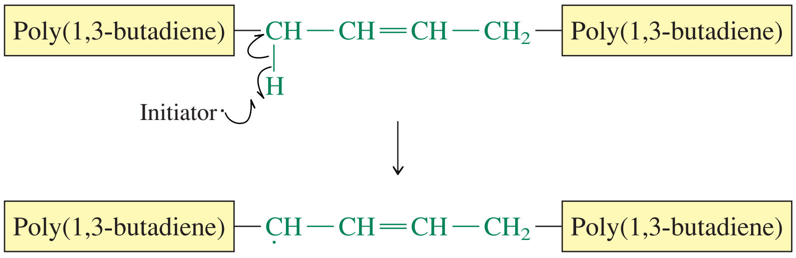
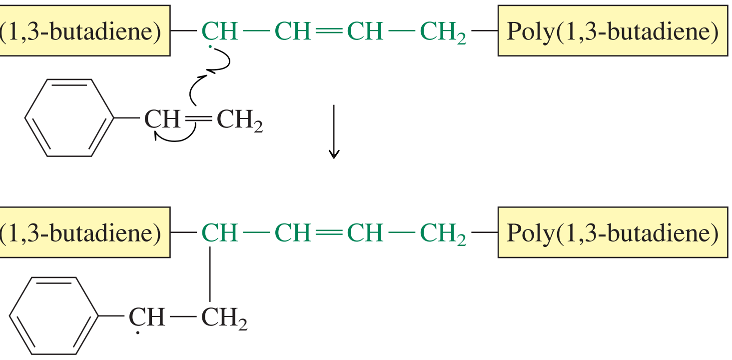
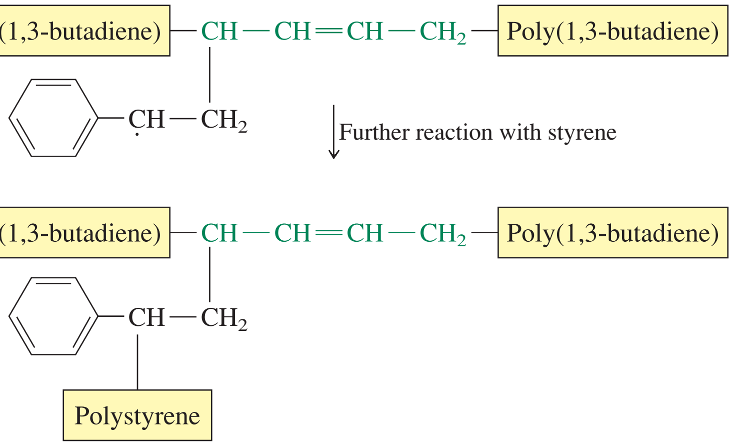
polymerization of styrene in the presence of poly(1,3-butadiene). Instead of reacting with styrene, the free-radical initiator abstracts an allylic hydrogen from poly(1,3-butadiene).



Polystyrene chain growth begins at the allylic radical site and proceeds in the usual way at this and random other allylic carbons of poly(1,3-butadiene).



Polystyrene grafts on a poly(1,3-butadiene) chain are the result.



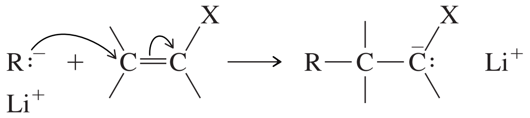
Polystyrene alone is brittle; poly(1,3-butadiene) alone is rubbery. The graft copolymer is strong, but absorbs shock without cracking because of the elasticity provided by its poly(1,3-butadiene) structural units.

29.16 SUMMARY

Section 29.1 Polymer chemistry dates to the nineteenth century with the chemical modification of polymeric natural products. Once the structural features of polymers were determined, polymer synthesis was placed on a rational basis.

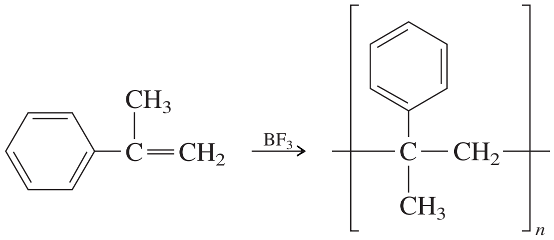
Section 29.2 Polymers are usually named according to the monomers from which they are prepared (*source-based nomenclature*). When the name of the monomer is

Section 29.9 Anionic polymerization of alkenes that bear a carbanion-stabilizing substituent (X) can be initiated by strong bases such as alkyllithium reagents.



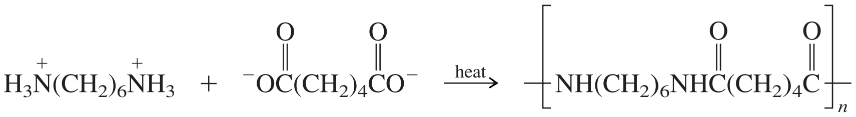
The product of this step is a new organolithium reagent that can react with a second monomer molecule, then a third, and so on. The growing organolithium chain is stable and is called a living polymer.

Section 29.10 Cationic polymerization of alkenes that can form relatively stable carbocations can be initiated by protonation of the double bond or coordination to Lewis acids such as boron trifluoride.



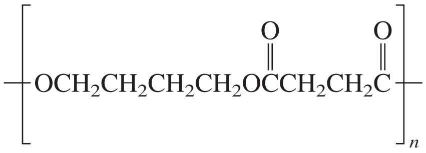
Section 29.11 The key bond-forming process in many polymerizations is a *condensation* reaction. The most common condensations are those that produce polyamides and polyesters.

Polyamide synthesis is illustrated by the preparation of nylon 66, the most commercially successful synthetic fiber.



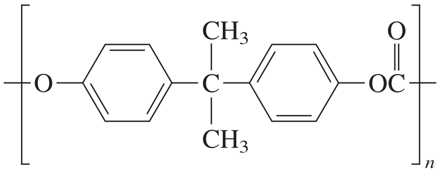
$$H_3\overset{+}{N}(CH_2)_6\overset{+}{N}H_3 + {}^{-}O\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}O^{-} \xrightarrow{\text{heat}} \left[NH(CH_2)_6NH\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}\right]_n$$

Section 29.12 The condensation of a diol and a dicarboxylic acid produces a *polyester.* Poly(tetramethylene succinate) is a biodegradable polyester derived from butanedioic acid and 1,4-butanediol.

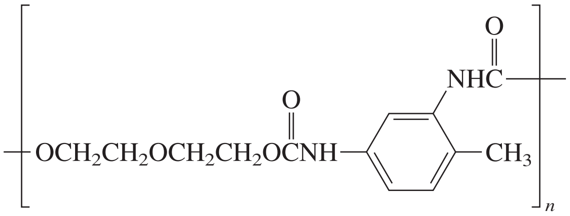


$$\left[OCH_2CH_2CH_2CH_2O\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{C}\right]_n$$

Section 29.13 Most of the applications of *polycarbonates* center on Lexan, a polyester derived from phosgene and bisphenol A.



Section 29.14 Like polycarbonates, *polyurethanes* enjoy wide use even though there are relatively few structural types. Most polyurethanes are made from a mixture of the 2,4- and 2,6-diisocyanate derivatives of toluene and a polymeric diol or triol.



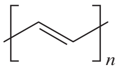
Section 29.15 *Copolymers* are the polymers formed when two or more monomers are present in the mixture to be polymerized. They are classified as random, block, or graft. A *random copolymer* lacks a regular sequence in respect to the appearance of the structural units of the components. A *block copolymer* of monomers A and B is composed of blocks of poly(A) and poly(B). A *graft copolymer* has a main chain of poly(A) to which are grafted branches of poly(B).

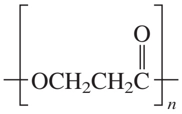
PROBLEMS

29.15 Nylon 11 is a polyamide used as fishing line and is prepared by heating 11-aminoundecanoic acid [$H_2N(CH_2)_{10}CO_2H$]. What is the repeating unit of nylon 11? Is it a condensation or an addition polymer? Chain-growth or step-growth?

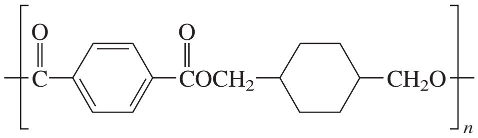
29.16 Is protein biosynthesis as shown in Figure 28.12 (page 1227) step growth or chain growth? Is the protein that results an addition or a condensation polymer? Why?

29.17 *Pseudomonas oleovorans* oxidizes nonanoic acid, then stores the 3-hydroxynonanoic acid produced as a homopolymer. Write the formula for the repeating unit of this polyester.

29.18 From what monomer is the polymer with the repeating unit  prepared? Suggest a source-based name.

29.19 Give the structure of the lactone from which  $\left[\!-\mathrm{OCH_2CH_2}\overset{\displaystyle O}{\overset{\|}{C}}-\right]_n$ is prepared.

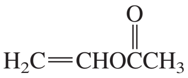
29.20 Kodel fibers are made from the polymer shown. Suggest suitable monomers for its preparation.



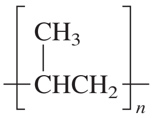
29.21 Of the following monomers which one would undergo cationic polymerization most readily?

$H_2C{=}CHCH_3 \qquad H_2C{=}CHCH{=}CH_2 \qquad H_2C{=}CHC{\equiv}N \qquad H_2C{=}CHCl$

29.22 Of the following monomers which one would undergo anionic polymerization most readily?

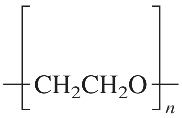
$H_2C{=}CHCH_3$  $H_2C{=}CHO\overset{\displaystyle O}{\overset{\|}{C}}CH_3$ $H_2C{=}CHC{\equiv}N$ $H_2C{=}CHCl$

one word, the polymer is named by simply adding the prefix *poly*-. When the name of the monomer is two words, they are enclosed in parentheses and preceded by *poly*.



$$\left[\begin{array}{c} CH_3 \\ | \\ CHCH_2 \end{array}\right]_n$$

Polypropylene



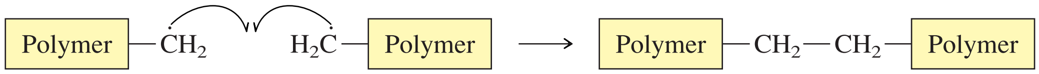
$$\left[CH_2CH_2O\right]_n$$

Poly(ethylene oxide)

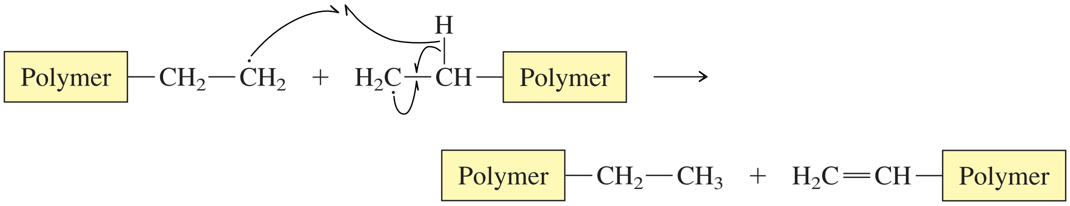
Sections 29.3–29.6 Polymers may be classified in several different ways:

- Reaction type (addition and condensation)
- Chain-growth or step-growth
- Structure (linear, branched, crosslinked)
- Properties (thermoplastic, thermoset, or elastomer)

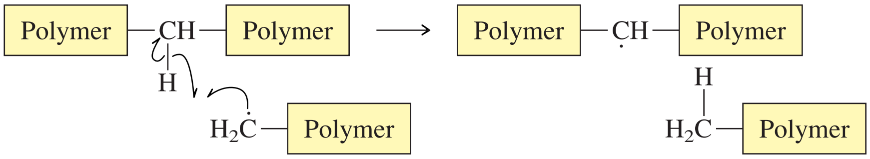
Section 29.7 This section emphasizes initiation and termination steps in alkene polymerization. The main terminating reactions in free-radical polymerization are the coupling of two radicals and disproportionation. *Coupling* of two radicals pairs the odd electrons and stops chain growth.



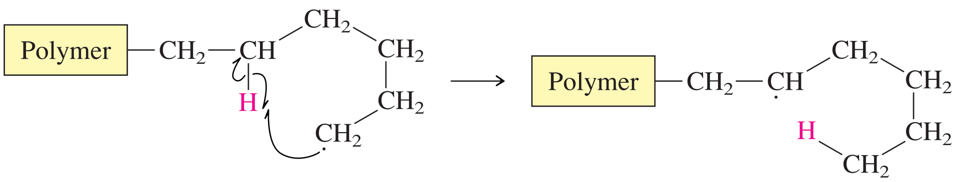
In *disproportionation,* a hydrogen atom is exchanged between two growing chains, terminating one in a double bond and the other in a new C—H bond.



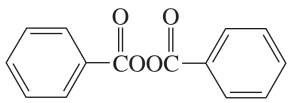
Section 29.8 Free-radical polymerization of alkenes usually gives branched polymers of low crystallinity. The two main mechanisms by which branches form both involve hydrogen atom abstraction by the radical site. In one, a growing chain abstracts a hydrogen atom from a terminated polymer.



The other is an intramolecular hydrogen-atom abstraction. In most cases this reaction proceeds by a six-center transition state and moves the reactive site from the end of the growing chain to inside it.



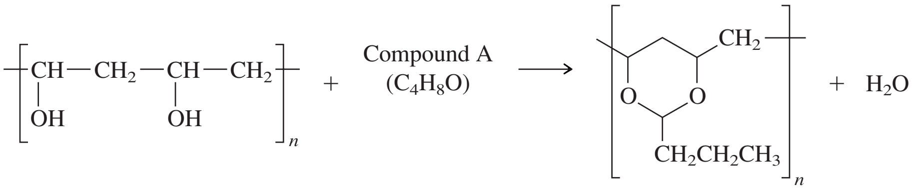
29.23 Polymerization of styrene can occur by a free-radical, cationic, anionic, or coordination complex mechanism. What mechanism will be followed when each of the compounds shown is used to initiate polymerization?

(a) $TiCl_4$, $(CH_3CH_2)_3Al$ (b)  (c) BF_3

29.24 Styrene undergoes anionic polymerization at a faster rate than *p*-methoxystyrene. Suggest an explanation for this observation.

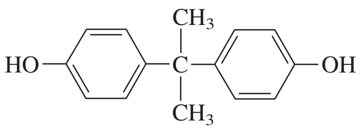
29.25 Given that —C≡N stabilizes carbanions better than phenyl, which monomer would you start with to prepare a copolymer of styrene and acrylonitrile?

29.26 *Poly(vinyl butyral)* is the inner liner in safety glass. It is prepared by the reaction shown. What is compound A?



29.27 *Linear low-density polyethylene* is a copolymer in which ethylene is polymerized under Ziegler–Natta conditions in the presence of a smaller quantity of a second alkene such as 1-hexene. What structural feature characterizes the resulting polymer?

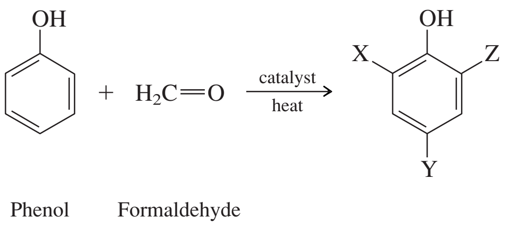
29.28 (a) Bisphenol A is made by the reaction of phenol and acetone. Suggest a mechanism for this reaction. Assume acid (H_3O^+) catalysis.



(b) Bisphenol B is made from phenol and 2-butanone. What is its structure?

29.29 Poly(ethylene oxide) can be prepared from ethylene oxide by either anionic or cationic polymerization methods. Write reaction mechanisms for both processes. Use H_3O^+ as the acid and OH^- as the base.

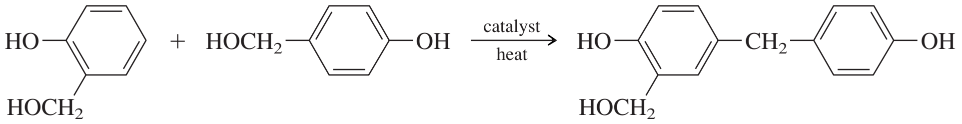
29.30 (a) The first step in the formation of Bakelite from phenol and formaldehyde introduces —CH_2OH groups onto the ring.



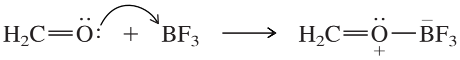
X	Y	Z
H	CH_2OH	H
CH_2OH	H	H
CH_2OH	CH_2OH	H
CH_2OH	H	CH_2OH
CH_2OH	CH_2OH	CH_2OH

Write a mechanism for the formation of *o*-hydroxybenzyl alcohol (X = CH_2OH, Y = Z = H) in this reaction. Assume the catalyst is H_3O^+.

(b) The second step links two of the aromatic rings by a CH_2 group. Write a mechanism for the example shown.



29.31 The first step in the mechanism of cationic polymerization of formaldehyde is:



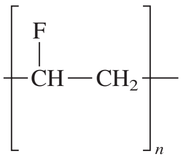
$$\mathrm{H_2C{=}\ddot{O}\!:} + \mathrm{BF_3} \longrightarrow \mathrm{H_2C{=}\underset{+}{\ddot{O}}{-}\overset{-}{B}F_3}$$

Write an equation for the second step using curved arrows to track electron movement.

LEARNING BY MODELING

In Spartan 29.1–29.4 you will use a model of icosane [$CH_3(CH_2)_{18}CH_3$] from the **Database** as a framework for the construction of certain polymers. To reduce the number of operations required, make a model of icosane, replace it with the **Database** model, and save it in a convenient folder. **Minimize** the icosane model and measure the C—C—C bond angles and C—C—C—C dihedral angles.

Spartan 29.1 (a) Substitute the appropriate hydrogens of icosane so as to make a model of syndiotactic poly(vinyl fluoride). **Minimize** the structure and compare its C—C—C bond angles and C—C—C—C dihedral angles with those of icosane.



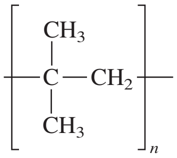
$$\left[\mathrm{\overset{F}{\overset{|}{C}H}{-}CH_2}\right]_n$$

Poly(vinyl fluoride)

(b) Repeat the procedure in (a) for isotactic poly(vinyl fluoride).

(c) One of the polymer chains is more stable than the other. Which one is of lower energy: syndiotactic or isotactic poly(vinyl fluoride)? (Note: The precise *kind* of distortion of polymer chains is not well modeled at our level of calculation. The curvature that you see in the chain is one response to strain, but not the response that the chain actually adopts.)

Spartan 29.2 Make a model of polyisobutylene and **Minimize.** What are the C—CH_2—C bond angles?



$$\left[\mathrm{\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}CH_2}\right]_n$$

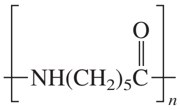
Polyisobutylene

Spartan 29.3 Use the icosane model to make a model of poly(ethylene oxide).

$$\left[\mathrm{CH_2CH_2{-}O}\right]_n$$

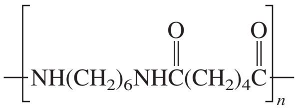
Poly(ethylene oxide)

Spartan 29.4 Modify icosane so as to represent a model of (a) nylon 6, and (b) nylon 66.



$$\left[\mathrm{NH(CH_2)_5\overset{O}{\overset{\|}{C}}}\right]_n$$

Nylon 6



$$\left[\mathrm{NH(CH_2)_6NH\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}}\right]_n$$

Nylon 66