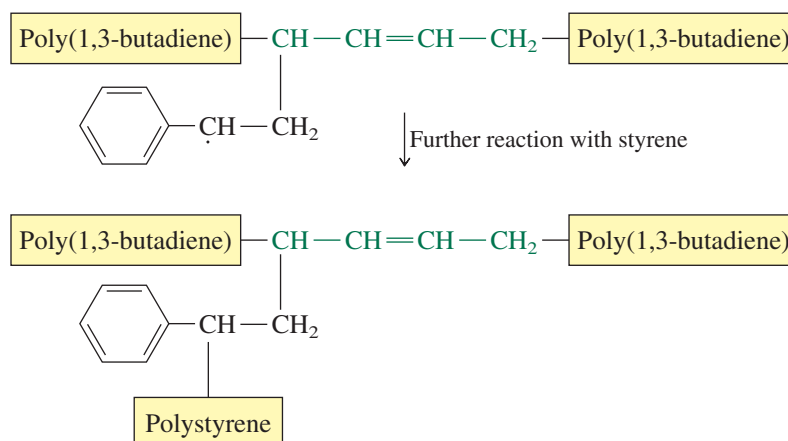


Polystyrene grafts on a poly(1,3-butadiene) chain are the result.

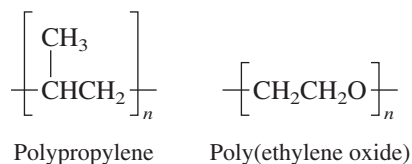


Polystyrene alone is brittle; poly(1,3-butadiene) alone is rubbery. The graft copolymer is strong, but absorbs shock without cracking because of the elasticity provided by its poly(1,3-butadiene) structural units.

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 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*.



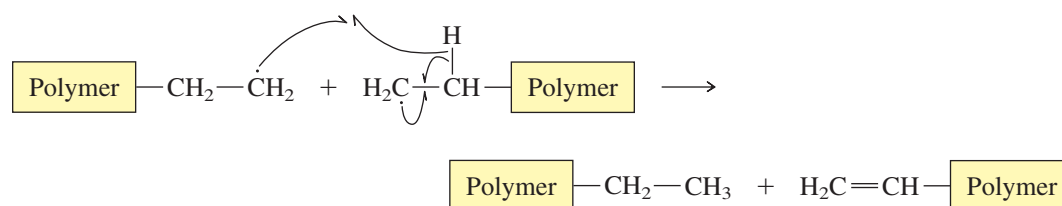
Sections 29.3–29.6 Polymers may be classified in several different ways:

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

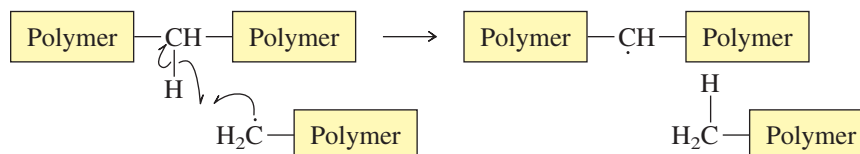
Section 29.7 This section emphasizes initiation and termination steps in alkene polymerization. The main terminating reactions in free-radical polymerization are the coupling of two radicals and disproportionation. *Coupling* of two radicals pairs the odd electrons and stops chain growth.



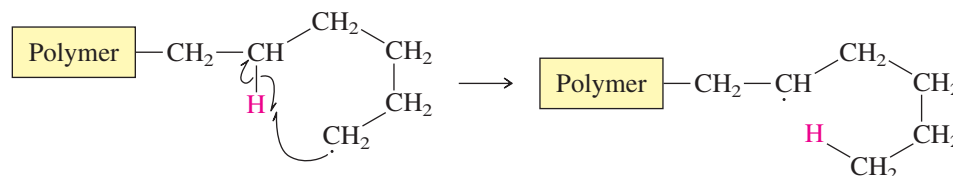
In *disproportionation*, a hydrogen atom is exchanged between two growing chains, terminating one in a double bond and the other in a new C—H bond.



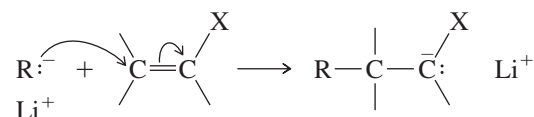
Section 29.8 Free-radical polymerization of alkenes usually gives branched polymers of low crystallinity. The two main mechanisms by which branches form both involve hydrogen atom abstraction by the radical site. In one, a growing chain abstracts a hydrogen atom from a terminated polymer.



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.

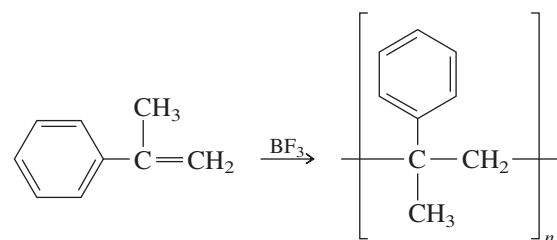


Section 29.9 Anionic polymerization of alkenes that bear a carbanion-stabilizing substituent (X) can be initiated by strong bases such as alkyllithium reagents.



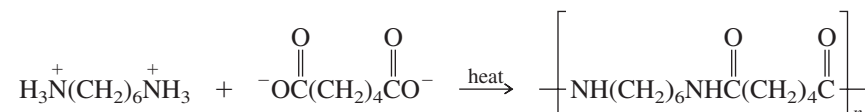
The product of this step is a new organolithium reagent that can react with a second monomer molecule, then a third, and so on. The growing organolithium chain is stable and is called a living polymer.

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.

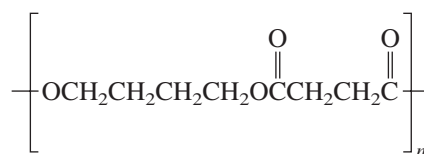


Section 29.11 The key bond-forming process in many polymerizations is a *condensation* reaction. The most common condensations are those that produce polyamides and polyesters.

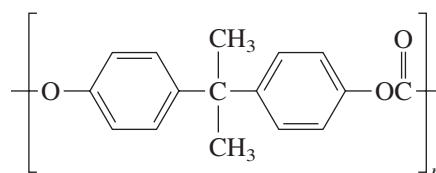
Polyamide synthesis is illustrated by the preparation of nylon 66, the most commercially successful synthetic fiber.



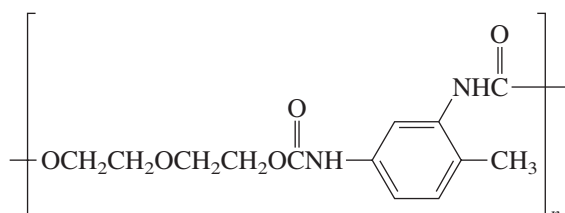
Section 29.12 The condensation of a diol and a dicarboxylic acid produces a *polyester*. Poly(tetramethylene succinate) is a biodegradable polyester derived from butanedioic acid and 1,4-butanediol.



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 [$\text{H}_2\text{N}(\text{CH}_2)_{10}\text{CO}_2\text{H}$]. 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 1183) 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 $\left[\text{CH}_2\text{CH}=\text{CHCH}_2 \right]_n$ prepared? Suggest a source-based name.

29.19 Give the structure of the lactone from which $\left[\text{OCH}_2\text{CH}_2\text{C}(=\text{O}) \right]_n$ is prepared.