CHAPTER 29 Synthetic Polymers

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Catchers don’t wear masks anymore. They wear sturdy helmets made of glass-reinforced nylon 6, a polymer made from the compound (caprolactam) shown in the electrostatic potential map.

A polymer is a substance composed of macromolecules, molecules that contain a very large number of atoms and have a high molecular weight. Starch, cellulose, silk, and DNA are examples of naturally occurring polymers. Synthetic polymers include nylon, polyethylene, and Bakelite, among countless others. Polymers need not be homogeneous, and most are not. Even one as simple as polyethylene is a mixture of macromolecules with different chain lengths and different degrees of branching.

This chapter is about synthetic polymers, many of which have been introduced in earlier chapters where we emphasized the connection between the reactions used to prepare polymers and the core reactions of organic chemistry. In this chapter, we will add new polymers and methods to those already introduced and expand our understanding of their synthesis, structure, and properties. As we do so, keep in mind that the reactions used to prepare polymers are the same fundamental reactions that occur with simple organic compounds.

### 29.1 Some Background

The earliest applications of polymer chemistry involved chemical modification designed to improve the physical properties of naturally occurring polymers. In 1839, Charles Goodyear transformed natural rubber, which is brittle when cold and tacky when warm, to a substance that maintains its elasticity over a wider temperature range by heating it with sulfur (vulcanization). The first synthetic fibers—called rayons—were made by chemical modification of cellulose near the end of the nineteenth century.

Leo Baekeland patented the first totally synthetic polymer, which he called Bakelite, in 1910 (Figure 29.1). Bakelite is a versatile, durable material prepared from low-cost materials (phenol and formaldehyde) and was the most successful synthetic material of its kind for many years.

These early successes notwithstanding, knowledge about polymer structure was meager. Most chemists believed that rubber, proteins, and the like were colloidal dispersions of small molecules. During the 1920s Hermann Staudinger, beginning at the Swiss Federal Institute of Technology and continuing at the University of Freiburg, argued that polymers were high-molecular-weight compounds held together by normal covalent bonds. Staudinger’s views received convincing support in a 1929 paper by Wallace H. Carothers of Du Pont who reached similar conclusions.

Vulcanization was summarized in the essay “Diene Polymers” in Chapter 10, p. 404.
Staudinger’s studies of polymer structure and Carothers’ achievements in polymer synthesis accelerated the development of polymer chemistry, especially its shift from chemical modification of natural polymers to the design and synthesis of new materials. Thousands of synthetic polymers are now known; some mimic the properties of natural materials, others have superior properties and have replaced natural materials.

29.2 Polymer Nomenclature

Although the IUPAC has set forth rules for naming polymers according to structure, an alternative IUPAC source-based system that names polymers according to the monomers from which they are prepared is more widely used.

Source-based names are, for example, the ones we are accustomed to seeing for polymers such as polyethylene (Section 6.22) and polystyrene (Section 11.18). When the name of the monomer is a single word, the polymer derived from it is generated by simply adding the prefix poly-. When the name of the monomer consists of two words, both words are enclosed in parentheses immediately following poly. Thus, polycrylonitrile and poly(vinyl chloride) are the polymers of acrylonitrile and vinyl chloride, respectively.

\[
\text{Acrylonitrile} = \begin{array}{c}
H_2C=CH-CN \\
\text{CH}_2=\text{CH} \\
\end{array} \\
\text{Polyacrylonitrile} = \begin{array}{c}
C=\text{N} \\
\text{CH}_2=\text{CH} \\
\end{array} \\
\text{Vinyl chloride} = \begin{array}{c}
H_2C=\text{CH-Cl} \\
\text{CH}_2=\text{CH} \\
\end{array} \\
\text{Poly(vinyl chloride)} = \begin{array}{c}
\text{Cl} \\
\text{CH}_2=\text{CH} \\
\end{array}
\]

The convention for writing polymer formulas is to enclose the repeating unit within brackets, followed by the letter \( n \) to indicate that the number of repeating units is not specified. It is, however, assumed to be large.

**PROBLEM 29.1**

Structural formulas for acrylic and methacrylic acids are shown at the right. Give the names of the polymers requested in (a) and (b) and represent their structures in the bracketed repeating unit format.

(a) The amide of acrylic acid (acrylamide)

(b) The methyl ester of methacrylic acid (methyl methacrylate)

**Sample Solution** (a) Acrylamide is one word; therefore, its polymer is polyacrylamide. The repeating unit follows the pattern illustrated for polyacrylonitrile and poly(vinyl chloride).

\[
\text{Acrylamide} = \begin{array}{c}
H_2C=\text{CHCNH}_2 \\
\text{CH}_2=\text{CH} \\
\end{array} \\
\text{Polyacrylamide} = \begin{array}{c}
\text{CH}_2=\text{CHCNH}_2 \\
\text{CH}_2=\text{CH} \\
\end{array}
\]

Source-based nomenclature does not require that a particular polymer actually be made from the “source” monomer. Both poly(ethylene glycol) and poly(ethylene oxide), for example, are made from ethylene oxide and have the same repeating unit.

\[
\text{CH}_2\text{CH}_2\text{O} \\
\]

The structural difference between the two is that the value of \( n \) is larger for poly(ethylene oxide) than for poly(ethylene glycol). Therefore, their physical properties are different and they are known by different source-based names.

Many polymers are routinely referred to by their common names or trade names. The polymer \( \text{CF}_2\text{CF}_2 \) is almost always called Teflon rather than polytetrafluoroethylene.
29.3 Classification of Polymers: Reaction Type

Structure, synthesis, production, and applications of polymers span so many disciplines that it is difficult to classify them in a way that serves every interest. Figure 29.2 compares some of the different ways. This section describes how polymers are classified according to the type of reaction—addition or condensation—that occurs.

Addition polymers are formed by reactions of the type:

\[ A + B \rightarrow A-B \]

where the product (A—B) retains all of the atoms of the reactants (A + B). In the general equation, A and B are monomers that react to give the polymer. When A = B, the resulting polymer is a homopolymer. Polystyrene is an example of a homopolymer.

When the two monomers are different, the polymer is a copolymer. Saran, used as a protective wrap for food, is a copolymer of vinylidene chloride and vinyl chloride.

Vinylidene chloride + Vinyl chloride \rightarrow \text{Saran}

The two components in a copolymer need not be present in equal-molar amounts. In a typical Saran formulation vinylidene chloride is the major monomer (about 85%), and vinyl chloride the minor one.

Polymers prepared from alkenes (olefins), regardless of whether they are homopolymers or copolymers, are known as polyolefins and are the most familiar addition polymers.
Not all addition polymers are polyolefins. Formaldehyde, for example, polymerizes to give an addition polymer that retains all of the atoms of the monomer.

\[
\text{H}_2\text{C} = \text{O} \rightarrow \left[ \text{CH}_2 - \text{O} \right]_n
\]

Formaldehyde \hspace{1cm} Polyformaldehyde

When monomeric formaldehyde is needed, to react with a Grignard reagent, for example, it is prepared as needed by heating the polymer in order to “depolymerize” it.

**PROBLEM 29.2**

Under certain conditions formaldehyde forms a cyclic trimer (C_3H_6O_3) called trioxane. Suggest a structure for this compound.

Condensation polymers are prepared by covalent bond formation between monomers, accompanied by the loss of some small molecule such as water, an alcohol, or a hydrogen halide. The condensation reaction:

\[
\text{X} - \text{Y} + \text{X} - \text{Y} \rightarrow \text{X} - \text{Y} + \text{X} - \text{Y}
\]

gives a condensation polymer when applied to difunctional reactants. The first condensation step:

\[
\text{X} - \text{Y} + \text{X} - \text{Y} \rightarrow \text{X} - \text{Y} + \text{X} - \text{Y}
\]

gives a product that has reactive functional groups. Condensation of these functional groups with reactant molecules extends the chain.

\[
\text{Y} - \text{Y} + \text{X} - \text{Y} \rightarrow \text{Y} - \text{Y} + \text{X} - \text{Y}
\]

The product retains complementary functional groups at both ends and can continue to grow. The most familiar condensation polymers are polyamides, polyesters, and polycarbonates.

The aramids, polyamides in which the amide bonds join aromatic rings, are one class of condensation polymer. Heating 1,4-benzenediamine and the acyl chloride of benzene-1,4-dicarboxylic acid (terephthalic acid) gives the aramid Kevlar with loss of hydrogen chloride.

\[
\begin{align*}
\text{H}_2\text{N} - \text{C}_6\text{H}_4 - \text{NH}_2 & + \text{O} - \text{C}_6\text{H}_4 - \text{O} - \\
\text{1,4-Benzenediamine} & \rightarrow \text{H}_2\text{N} - \text{C}_6\text{H}_4 - \text{NH} - \text{C}_6\text{H}_4 - \text{C} - \text{C} - \text{O} - \\
\text{Kevlar} & + n\text{HCl}
\end{align*}
\]

Kevlar fibers are both strong and stiff and used to make bulletproof vests and protective helmets as illustrated in Figure 29.3.

**PROBLEM 29.3**

The amide bond between a molecule of 1,4-benzenediamine and a molecule of terephthaloyl chloride is formed by the usual nucleophilic acyl substitution mechanism. Write a structural formula for the tetrahedral intermediate in this reaction.

**29.4 Classification of Polymers: Chain Growth and Step Growth**

Addition and condensation are familiar to us as reaction types in organic chemistry. The terms we apply to the two different ways that macromolecules arise from lower-molecular-weight units are unique to polymer chemistry and are illustrated in Figure 29.4.
In a chain-growth process monomers add one-by-one to the same end of a growing chain (Figure 29.4a). Each chain has only one growth point. The concentration of monomer decreases gradually until it is depleted.

In a step-growth process (Figure 29.4b), chains have at least two growth points. Most of the monomer molecules are consumed early in the process to give a mixture of compounds of intermediate molecular weight called oligomers. These oligomers react together to give longer chains.

**Figure 29.4**
Chain-growth (a) and step-growth (b) polymerization. During chain growth, the amount of monomer remaining decreases gradually. In step growth, most of the monomer is consumed early and the molecular weight of the polymer increases as oligomers combine to form longer chains.

In a chain-growth process monomers add one-by-one to the same end of a growing chain (Figure 29.4a). Each chain has only one growth point. The concentration of monomer decreases gradually until it is depleted.

In a step-growth process (Figure 29.4b), chains have at least two growth points. Most of the monomer molecules are consumed early in the process to give a mixture of compounds of intermediate molecular weight called oligomers. These oligomers react with one another to form the polymer. The molecular weight continues to increase even after all the monomer molecules have reacted.

In general, chain growth is associated with addition polymerization and step growth with condensation polymerization. It is not always so, however. We’ll see an example later in this chapter of an addition polymer in which step growth, not chain growth, characterizes macromolecule formation.

**Problem 29.4**
We can anticipate this “later in the chapter” example by examining the reaction:

$$\text{ROH} + \text{R'N-C-O} \rightarrow \text{ROCNHR'}$$

Is this an addition reaction or a condensation?

**29.5 Classification of Polymers: Structure**

Polymers made from the same compounds can have different properties depending on how they are made. These differences in physical properties result from differences in the overall structure of the polymer chain. The three major structural types—linear, branched, and cross-linked—are illustrated in Figure 29.5. Other, more specialized, structural types—ladders, stars, and dendrimers—have unique properties and are under active investigation.

Linear polymers (Figure 29.5a) have a continuous chain of repeating units. The repeating units within the chain are subject to the usual conformational requirements of organic chemistry. The collection of chains can range from random, much like a bowl...
of spaghetti, to ordered. We describe polymers at the random extreme as amorphous and those at the ordered extreme as crystalline.

Most polymers are a mixture of random tangles interspersed with crystalline domains called crystallites (Figure 29.6). The degree of crystallinity of a polymer, that is, the percentage of crystallites, depends on the strength of intermolecular forces
between chains. For a particular polymer, density increases with crystallinity because randomly coiled chains consume volume, while closer packing puts the same mass into a smaller volume. The efficiency with which the chains can pack together is strongly affected by the extent to which the chain is branched.

**Branched polymers** (Figure 29.5b) have branches extending from the main chain. In general, increased branching reduces the crystallinity of a polymer and alters properties such as density.

Contrast the properties of low-density polyethylene (LDPE) and high-density (HDPE), two of the six polymers familiar enough to have their own identifying codes for recycling (Table 29.1). Both are homopolymers of ethylene, but are prepared by different methods and have different properties and uses. As their names imply, LDPE has a lower density than HDPE (0.92 g/cm³ versus 0.96 g/cm³). LDPE is softer, HDPE more rigid. LDPE has a lower melting point than HDPE. LDPE is the plastic used for grocery store bags; HDPE is stronger and used for water bottles, milk jugs, and gasoline tanks.

The structural difference between the two is that LDPE is more branched, averaging about 20 branches for every thousand carbon atoms compared with about 5 per thousand for HDPE. The greater density of HDPE results from packing more mass into the same volume. Unbranched chains pack more efficiently than branched ones, which translates into stronger intermolecular forces, greater crystallinity, and a tougher, more durable material.

Like HDPE, isotactic polypropylene is highly crystalline with numerous uses, including fibers for rope and carpets. Atactic polypropylene, on the other hand, is much less crystalline and has few applications.

Chains in a **cross-linked** or network polymer (Figure 29.5c) are connected to one another by linking units, which may be long or short and composed of the same repeating units as the main chain or different ones. Vulcanization, for example, uses sulfur to cross-link the hydrocarbon chains of natural rubber. In general, cross-linking increases rigidity by restricting the movement of the polymer chains. Vulcanized rubber is a lightly cross-linked elastomer; Bakelite can be so highly cross-linked as to be considered a single molecule.

### 29.6 Classification of Polymers: Properties

How a polymer responds to changes in temperature is important not only with respect to the conditions under which it can be used, but also in the methods by which it is transformed into a commercial product.

**Thermoplastic** polymers are the most common and are those that soften when heated. At their **glass transition temperature** ($T_g$), thermoplastic polymers change from a glass to a flexible, rubbery state. Past this point amorphous polymers are gradually transformed to a liquid as the temperature is raised. Crystalline polymers undergo a second transition, liquefying only when the **melting temperature** ($T_m$) is reached. Compare the behaviors of atactic, isotactic, and syndiotactic poly(methyl methacrylate) on being heated.

<table>
<thead>
<tr>
<th>Poly(methyl methacrylate)</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>atactic</td>
<td>114</td>
<td>—</td>
</tr>
<tr>
<td>isotactic</td>
<td>48</td>
<td>160</td>
</tr>
<tr>
<td>syndiotactic</td>
<td>126</td>
<td>200</td>
</tr>
</tbody>
</table>

The atactic form of poly(methyl methacrylate) is amorphous and exhibits only one transition temperature ($T_g$). The stereoregular isotactic and syndiotactic forms are partially crystalline and undergo both a glass transition and melting.

The process that takes place at $T_g$ is an increase in the conformational mobility of the polymer chains. At $T_m$, attractive forces in crystallites are broken and individual chains separate.

Melting temperature is an important factor in respect to how polymers are used. The relatively low $T_m$ for low-density polyethylene (115°C) makes it an easy polymer to cast into the desired shape when melted, but at the same time limits its applications. When, for example, a container is required that must be sterilized by heating, the higher $T_m$ of HDPE (137°C) makes it a better choice than LDPE.
### TABLE 29.1 Recycling of Plastics

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Polymer</th>
<th>New</th>
<th>Recycled</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETE</td>
<td>Poly(ethylene terephthalate)</td>
<td>Polyester textile fibers, tire cords, photographic film, soft drink and water bottles, food jars</td>
<td>Carpet fibers, detergent bottles, bathtubs, car parts, audio- and videotapes</td>
</tr>
<tr>
<td>HDPE</td>
<td>High-density polyethylene</td>
<td>Bottles, automobile fuel tanks, milk jugs, bags, cereal box liners</td>
<td>Plastic lumber for exterior uses (picnic tables, mailboxes, decks, trash bins, planters)</td>
</tr>
<tr>
<td>V</td>
<td>Poly(vinyl chloride)</td>
<td>Floor tiles, vinyl siding, plumbing pipe, gutters and downspouts, garden hoses, shower curtains, window frames, blister packs</td>
<td>Many of the uses of recycled poly(vinyl chloride) are the same as those of new material</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low-density polyethylene</td>
<td>Trash bags, packaging, squeezable bottles, grocery bags</td>
<td>Packaging film and bags</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
<td>Indoor–outdoor carpet, rope, medicine bottles, packaging</td>
<td>Indoor–outdoor carpet, rope, fishing nets, tarpaulins, auto parts</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
<td>Television cabinets, luggage, egg cartons, toys, Styrofoam cups, appliances</td>
<td>Styrofoam insulation and packaging, coat hangers, containers</td>
</tr>
<tr>
<td>OTHER</td>
<td>Other (acrylics, nylon, polycarbonates, etc.)</td>
<td>5-Gallon reusable water bottles, automobile bumpers and other parts, tires, telephones, safety helmets</td>
<td></td>
</tr>
</tbody>
</table>

*The uses of new and recycled plastics are often the same, and many products are a mixture of new and recycled material.*
Unlike thermoplastic polymers that soften on heating, thermosetting polymers (also called thermosetting resins) pass through a liquid state then solidify (“cure”) on continued heating. The solidified material is a thermoset. It is formed by irreversible chemical reactions that create cross links as the thermosetting polymer is heated. Bakelite, a highly cross-linked thermoset made from phenol and formaldehyde, is prepared in two stages. In the first stage, condensation between phenol and formaldehyde gives a polymer, which, in its fluid state, is cast in molds and heated, whereupon it solidifies to a hard, rigid mass. The chemical reactions that form the fluid polymer and the solid thermoset are the same kind of condensations; the difference is that there are more cross links in the thermoset. Melamine (used in plastic dinnerware) is another example of a thermoset.

Elastomers are flexible polymers that can be stretched but return to their original state when the stretching force is released. Most amorphous polymers become rubbery beyond their glass transition temperature, but not all rubbery polymers are elastic. Cross links in elastomers limit the extent to which elastomers can be deformed then encourage them to return to their original shape when they are relaxed.

### 29.7 Addition Polymers: A Review and a Preview

Addition polymers are most familiar to us in connection with the polymerization of alkenes.

\[
\begin{align*}
\text{C} &= \text{C} \\
&\rightarrow \left[ \begin{array}{c}
\text{C} \\
\text{C}
\end{array} \right]_n
\end{align*}
\]

Table 29.2 reviews alkene polymerizations that proceed by free radicals and by coordination complexes of the Ziegler–Natta type. Both are chain-growth processes; their propagation steps were outlined in Mechanism 6.12 (page 263) and Mechanism 14.6 (page 609), respectively. The present section examines two other significant factors in alkene polymerization: initiation and termination.

**Initiators of Alkene Polymerization:** Whether free-radical or coordination polymerization occurs depends primarily on the substance used to initiate the reaction. Free-radical polymerization occurs when a compound is present that undergoes homolytic bond cleavage when heated. Two examples include

\[
\begin{align*}
\text{Di-tert-butyl peroxide} &\quad \text{H}_2\text{C} = \text{CHCl} \\
\text{Azobisisobutyronitrile (AIBN)} &\quad \text{N} = \text{C} = \text{C} \cdot \text{H}_3 \cdot \text{CH}_3
\end{align*}
\]

Two 1-cyano-1-methylethyl radicals \( + \) nitrogen

Table 29.2 reviews alkene polymerizations that proceed by free radicals and by coordination complexes of the Ziegler–Natta type. Both are chain-growth processes; their propagation steps were outlined in Mechanism 6.12 (page 263) and Mechanism 14.6 (page 609), respectively. The present section examines two other significant factors in alkene polymerization: initiation and termination.

**Initiators of Alkene Polymerization:** Whether free-radical or coordination polymerization occurs depends primarily on the substance used to initiate the reaction. Free-radical polymerization occurs when a compound is present that undergoes homolytic bond cleavage when heated. Two examples include

\[
\begin{align*}
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\text{Azobisisobutyronitrile (AIBN)} &\quad \text{N} = \text{C} = \text{C} \cdot \text{H}_3 \cdot \text{CH}_3
\end{align*}
\]

Two 1-cyano-1-methylethyl radicals \( + \) nitrogen

**PROBLEM 29.5**

(a) Write a chemical equation for the reaction in which tert-butoxy radical adds to vinyl chloride to initiate polymerization. Show the flow of electrons with curved arrows.

(b) Repeat part (a) for the polymerization of styrene using AIBN as an initiator.

**Sample Solution**  (a) tert-Butoxy radical adds to the CH\(_2\) group of vinyl chloride. The free radical formed in this process has its unpaired electron on the carbon bonded to chlorine.

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{C} &= \text{O} \quad \text{(CH}_3\text{)}_2\text{C} = \text{CHCl} \\
\text{H}_2\text{C} &= \text{CHCl} &\rightarrow \text{2-tert-Butoxy-1-chloroethyl radical}
\end{align*}
\]
Coordination polymerization catalysts are complexes of transition metals. The original Ziegler–Natta catalyst, a mixture of titanium tetrachloride and diethylaluminum chloride, has been joined by numerous organometallic complexes such as the widely used bis(cyclopentadienyl)zirconium dichloride.

![Bis(cyclopentadienyl)zirconium dichloride]

### Table 29.2 Summary of Alkene Polymerizations Discussed in Earlier Chapters

<table>
<thead>
<tr>
<th>Reaction (section) and comments</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Free-radical polymerization of alkenes (Section 6.22)</strong>&lt;br&gt;Many alkenes polymerize when treated with free-radical initiators. A free-radical chain mechanism is followed and was illustrated for the case of ethylene in Mechanism 6.12 (page 263).</td>
<td>Ethylene $\xrightarrow{200^\circ C, 2000$ atm $O_2$ or peroxides} Polyethylene $\left[\text{CH}_2\text{CH}_2\right]_n$</td>
</tr>
<tr>
<td><strong>Free-radical polymerization of dienes (Section 10.14)</strong>&lt;br&gt;Conjugated dienes undergo free-radical polymerization under conditions similar to those of alkenes. The major product corresponds to 1,4-addition.</td>
<td>2-Chloro-1,3-butadiene (Chloroprene) $\xrightarrow{\text{free-radical initiator}}$ Polychloroprene $\left[\text{CH}_2\text{C}==\text{CHCH}_2\right]_n$</td>
</tr>
<tr>
<td><strong>Free-radical polymerization of styrene (Section 11.18)</strong>&lt;br&gt;Styrene can be polymerized under free-radical, cationic, anionic, and Ziegler–Natta conditions. The mechanism of the free-radical polymerization was shown in Mechanism 11.2 (page 445).</td>
<td>Benzyl peroxide $\xrightarrow{-80^\circ C}$ Polystyrene $\left[\text{CH}==\text{CH}_2\right]_n$</td>
</tr>
<tr>
<td><strong>Ring-opening metathesis polymerization (Section 14.16)</strong>&lt;br&gt;The double bonds of strained cyclic alkenes are cleaved by certain carbene complexes of tungsten and, in the process, undergo polymerization.</td>
<td>Bicyclo[2.2.1]-2-heptene (Norbornene) $\xrightarrow{\text{catalyst} - 80^\circ C}$ Polynorbornene $\left[\text{CH}==\text{C}==\text{CH}_2\right]_n$</td>
</tr>
<tr>
<td><strong>Coordination polymerization (Section 14.17)</strong>&lt;br&gt;Organometallic compounds such as bis(cyclopentadienyl)zirconium dichloride ($\text{Cp}_2\text{ZrCl}_2$) catalyze the polymerization of ethylene by the sequence of steps shown in Mechanism 14.6 (page 609).</td>
<td>Ethylene $\xrightarrow{\text{Cp}_2\text{ZrCl}_2, \text{methylalumoxane}}$ Polyethylene $\left[\text{CH}_2\text{CH}_2\right]_n$</td>
</tr>
</tbody>
</table>

**Termination Steps in Alkene Polymerization:** The main chain-terminating processes in free-radical polymerization are combination and disproportionation. In a combination,
In disproportionation, two alkyl radicals react by hydrogen-atom transfer. Two stable molecules result; one terminates in a methyl group, the other in a double bond. The pairing of the odd electron of one growing radical chain with that of another gives a stable macromolecule.

\[
\text{RO} \left[ \text{CH}_2\text{CH}_2 \right]_x \text{CH}_2\text{CH}_2 + \text{H}_2\text{CCH}_2 \left[ \text{CH}_2\text{CH}_2 \right]_y \text{OR} \rightarrow
\]

Two growing polyethylene chains

\[
\text{RO} \left[ \text{CH}_2\text{CH}_2 \right]_x \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \left[ \text{CH}_2\text{CH}_2 \right]_y \text{OR}
\]

Terminated polyethylene

In disproportionation, two alkyl radicals react by hydrogen-atom transfer. Two stable molecules result; one terminates in a methyl group, the other in a double bond.

\[
\text{RO} \left[ \text{CH}_2\text{CH}_2 \right]_x \text{CH}_2\text{CH}_2 + \text{H}_2\text{C} \left[ \text{CH}_2\text{CH}_2 \right]_y \text{OR} \rightarrow
\]

Two growing polyethylene chains

\[
\text{RO} \left[ \text{CH}_2\text{CH}_2 \right]_x \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 + \text{H}_2\text{C} = \text{CH} \left[ \text{CH}_2\text{CH}_2 \right]_y \text{OR}
\]

Methyl-terminated polyethylene Double-bond-terminated polyethylene

Both combination and disproportionation consume free radicals and decrease the number of growing chains. Because they require a reaction between two free radicals, each of which is present in low concentration, they have a low probability compared with chain growth, in which a radical reacts with a monomer. Combination involves only bond making and has a low activation energy; disproportionation has a higher activation energy because bond breaking accompanies bond making. Disproportionation has a more adverse effect on chain length and molecular weight than combination.

PROBLEM 29.6

Other than combination, a macromolecule of the type \( \text{RO} \left[ \text{CH}_2\text{CH}_2 \right]_x \text{CH}_2\text{CH}_2 \left[ \text{CH}_2\text{CH}_2 \right]_y \text{OR} \) can arise by a different process, one which also terminates chain growth. Show a reasonable reaction and represent the flow of electrons by curved arrows.

Among several chain terminating reactions that can occur in coordination polymerization, a common one is an elimination in which a \( \beta \)-hydrogen is transferred to the metal.

\[
\text{Zr} \left[ \text{CH}_2\text{CH}_2 \right]_x \text{CH}_2\text{CH}_2 \rightarrow \text{Zr} + \text{H}_2\text{C} = \text{CHR}
\]

29.8 Chain Branching in Free-Radical Polymerization

Even with the same monomer, the properties of a polymer can vary significantly depending on how it is prepared. Free-radical polymerization of ethylene gives low-density polyethylene; coordination polymerization gives high-density polyethylene. The properties are
Branching in Polyethylene Caused by Intramolecular Hydrogen Transfer

**Overall reaction:**

\[
\text{Polymer} - \overset{\text{CH}_2}{\text{CH}_2} - \overset{\text{CH}_2}{\text{CH}_2} - \overset{\text{CH}_2}{\text{CH}_2} \rightarrow \text{Polymer} - \overset{\text{CH}_2}{\text{CH}_2} - \overset{\text{CH}_2}{\text{CH}_2} - \overset{\text{CH}_2}{\text{CH}_2}
\]

**Mechanism:**

**STEP 1:** The carbon at the end of the chain—the one with the unpaired electron—abstracts a hydrogen atom from the fifth carbon. The transition state is a cyclic arrangement of six atoms.

The resulting radical is secondary and more stable than the original primary radical. Therefore, the hydrogen atom abstraction is exothermic.

**STEP 2:** When the radical reacts with ethylene, chain extension takes place at the newly formed radical site. The product of this step has a four-carbon branch attached to the propagating chain.

**STEP 3:** Reaction with additional ethylene molecules extends the growing chain.
A comparable process cannot occur when Ziegler–Natta catalysts are used because free radicals are not intermediates in coordination polymerization.

**Intermolecular hydrogen atom abstraction (chain transfer):** Mechanism 29.2 shows how a growing polymer chain abstracts a hydrogen atom from a terminated chain. The original growing chain is now terminated, and the original terminated chain is activated toward further growth. Chain growth, however, occurs at the branch point, not at the end of the chain. An already long chain adds a branch while terminating a (presumably shorter) growing chain. Chain transfer not only leads to branching, but also encourages disparity in chain lengths—more short chains and more long branched chains. Both decrease the crystallinity of the polymer and reduce its strength.

As in the case of intramolecular hydrogen abstraction, branching by chain transfer is not a problem when alkenes are polymerized under Ziegler–Natta conditions because free radicals are not intermediates in coordination polymerization.

**PROBLEM 29.7**

Suggest an explanation for the observation that branches shorter or longer than four carbons are found infrequently in polyethylene. Frame your explanation in terms of how $\Delta H$ and $\Delta S$ affect the activation energy for intramolecular hydrogen atom abstraction.

---

**MECHANISM 29.2**

**Branching in Polyethylene Caused by Intermolecular Hydrogen Transfer**

**STEP 1:** A growing polymer chain abstracts a hydrogen atom from a terminated chain. This step terminates the growing chain and activates the terminated one.

**STEP 2:** Reaction of the new chain with monomer molecules produces a branch at which future growth occurs.
29.9 Anionic Polymerization: Living Polymers

Anionic polymerization is a useful alternative to free-radical and Ziegler–Natta procedures for certain polymers. Adding butyllithium to a solution of styrene in tetrahydrofuran (THF), for example, gives polystyrene.

![Mechanism 29.3: Anionic Polymerization of Styrene]

Mechanism 29.3 shows how addition of butyllithium to the double bond of styrene initiates polymerization. The product of this step is a benzylic carbanion that then adds to a second molecule of styrene to give another benzylic carbanion, and so on by a chain-growth process.

Polystyrene formed under these conditions has a narrower range of molecular weights than provided by other methods. Initiation of polymerization by addition of butyllithium to styrene is much faster than subsequent chain growth. Thus, all the butyllithium is consumed and the number of chains is equal to the number of molecules of

### MECHANISM 29.3

### Anionic Polymerization of Styrene

**STEP 1:** Anionic polymerization of styrene is initiated by addition of butyllithium to the double bond. The regioslectivity of addition is governed by formation of the more stable carbanion, which in this case is benzylic.

\[
\text{Styrene} + \text{Butyllithium} \rightarrow \text{Polystyrene}
\]

**STEP 2:** The product of the first step adds to a second molecule of styrene.

**STEP 3:** The product of the second step adds to a third molecule of styrene, then a fourth, and so on to give a macromolecule. Reaction continues until all of the styrene is consumed. At this point the polystyrene exists as an organolithium reagent.

The organolithium reagent is stable, but easily protonated by water to give polystyrene. Alternatively, another monomer can be added to continue extending the chain.
butyllithium used. These starter chains then grow at similar rates to produce similar chain lengths.

**PROBLEM 29.8**

How will the average chain length of polystyrene vary with the amount of butyllithium used to initiate polymerization?

As shown in step 3 of Mechanism 29.3 once all of the monomer is consumed the polymer is present as its organolithium derivative. This material is referred to as a **living polymer** because more monomer can be added and anionic polymerization will continue until the added monomer is also consumed. Adding 1,3-butadiene, for example, to a living polymer of styrene gives a new living polymer containing sections (“blocks”) of polystyrene and poly(1,3-butadiene).

\[
\begin{align*}
\text{CH}_2=\text{CH} &\quad \text{CH} \quad \text{CH}_2 \\
\text{Li}^+ &\text{CH}_2=\text{CH} \quad \text{CH} \quad \text{CH}_2 \quad \text{(CH}_2)_3\text{CH}_3 \\
&+ \quad \text{H}_2\text{C} \quad \text{CH} \quad \text{CH} \quad \text{CH}_2
\end{align*}
\]

“Living” polystyrene

\[
\begin{align*}
\text{Li}^+ :\text{CH}_2 &\quad \text{CH} \quad \text{CH} \quad \text{CH}_2 \\
&\quad \text{CH}_2=\text{CH} \quad \text{CH} \quad \text{CH}_2 \quad \text{(CH}_2)_3\text{CH}_3 \\
&\quad \text{CH} \quad \text{CH}_2 \\
&+ \quad \text{H}_2\text{C} \quad \text{CH} \quad \text{CH} \quad \text{CH}_2
\end{align*}
\]

“Living” styrene-butadiene copolymer

Living polymerizations are characterized by the absence of efficient termination processes. They are normally terminated by intentionally adding a substance that reacts with carbanions such as an alcohol or carbon dioxide.

The kinds of vinyl monomers that are susceptible to anionic polymerization are those that bear electron-withdrawing groups such as \(-\text{C} \equiv \text{N}\) and \(-\text{C} \equiv \text{N}\) on the double bond.

\[\text{H}_2\text{C} \quad \text{CH} \quad \text{C} \equiv \text{N} \quad \text{H}_2\text{C} \quad \text{CH} \quad \text{COCH}_3 \quad \text{H}_2\text{C} \equiv \text{C} \quad \text{C} \equiv \text{N}\]

Acrylonitrile  Methyl acrylate  Methyl 2-cyanoacrylate

When a carbonyl and a cyano group are attached to the same carbon as in methyl 2-cyanoacrylate, the monomer that constitutes *Super Glue*, anionic polymerization can be initiated by even weak bases such as atmospheric moisture or normal skin dampness.

**PROBLEM 29.9**

Write a structural formula for the carbanion formed by addition of hydroxide ion to methyl 2-cyanoacrylate. Accompany this structural formula by a contributing resonance structure that shows delocalization of the negative charge to oxygen, and another to nitrogen.
29.10 Cationic Polymerization

Analogous to the initiation of anionic polymerization by addition of nucleophiles to alkenes, cationic polymerization can be initiated by the addition of electrophiles. The alkenes that respond well to cationic polymerization are those that form relatively stable carbocations when protonated. Of these, the one used most often is 2-methylpropene, better known in polymer chemistry by its common name isobutylene.

\[
\text{H}_2\text{C} = \text{CH}_2 \xrightarrow{\text{acid catalyst}} \left[ \begin{array}{c} \text{CH}_3 \\ \text{C} - \text{CH}_2 \\ \text{CH}_3 \end{array} \right]_n
\]

2-Methylpropene \quad \text{Polyisobutylene}

The mechanism for polymerization of 2-methylpropene is shown in Mechanism 29.4. The usual catalyst is boron trifluoride to which a small amount of water has been added. The two react to give a Lewis acid/Lewis base complex.

\[
\text{H}_2\text{O} + \text{BF}_3 \rightarrow \text{H}_2\text{O} - \text{BF}_3
\]

Water \quad \text{Boron trifluoride} \quad \text{Water/Boron trifluoride complex}

This complex is a strong Bronsted acid and protonates the double bond of 2-methylpropene in step 1 of the mechanism.
Polyisobutylene is the “butyl” in butyl rubber, one of the first synthetic rubber substitutes. Most inner tubes are a copolymer of 2-methylpropene (isobutylene) and 2-methyl-1,3-butadiene (isoprene).

**29.11 Polyamides**

The polyamide nylon 66 takes its name from the fact that it is prepared from a six-carbon dicarboxylic acid and a six-carbon diamine. The acid–base reaction between adipic acid and hexamethylenediamine gives a salt, which on heating undergoes condensation polymerization in which the two monomers are joined by amide bonds.

![Chemical structure of nylon 66](image)

2-Methylpropene

**Cationic Polymerization of 2-Methylpropene**

**STEP 1:** The alkene is protonated, forming a carbocation.

**STEP 2:** The carbocation formed in the preceding step reacts with a molecule of the alkene, forming a new carbocation.

**STEP 3:** The process shown in step 2 continues, forming a chain-extended carbocation.

**STEP 4:** One mechanism for chain termination is loss of a proton.

Polyisobutylene is the “butyl” in butyl rubber, one of the first synthetic rubber substitutes. Most inner tubes are a copolymer of 2-methylpropene (isobutylene) and 2-methyl-1,3-butadiene (isoprene).

**29.11 Polyamides**

The polyamide nylon 66 takes its name from the fact that it is prepared from a six-carbon dicarboxylic acid and a six-carbon diamine. The acid–base reaction between adipic acid and hexamethylenediamine gives a salt, which on heating undergoes condensation polymerization in which the two monomers are joined by amide bonds.

\[
\text{O} \quad \text{O} \\
\text{OC(CH}_2\text{)}_4\text{CO}^- \quad \text{H}_3\text{N(CH}_2\text{)}_6\text{NH}_3^+ \\
\text{Salt of adipic acid and hexamethylenediamine} \quad \text{280–300°C} \quad \text{H}_2\text{O} \\
\text{NH(CH}_2\text{)}_6\text{NHC(CH}_2\text{)}_4\text{O}^- \\
\text{Nylon 66} \\
\]

Nylon 66 was the first and remains the most commercially successful synthetic polyamide (Figure 29.7). Others have been developed by varying the number of carbons in the chains of the diamine and the dicarboxylic acid.
Nylon 66 resembles silk in both structure and properties. Both are polyamides in which hydrogen bonds provide an ordered arrangement of adjacent chains.

A variation on the diamine/dicarboxylic acid theme is to incorporate the amino and carboxylic acid groups into the same molecule, much as Nature does in amino acids. Nylon 6 is a polyamide derived by heating 6-aminohexanoic acid.

\[
\text{H}_2\text{N} \left(\text{CH}_2\right)_5\text{CO} \xrightarrow{\text{heat}} \left[\text{NH} \left(\text{CH}_2\right)_5\text{CH} \right]_n \right) + \text{H}_2\text{O} \\
\text{6-Aminohexanoic acid} \quad \text{Nylon 6} \quad \text{Water}
\]

**PROBLEM 29.10**

Nylon 6 is normally prepared from the lactam derived from 6-aminohexanoic acid, called \(\varepsilon\)-caprolactam. Do you remember what a lactam is? Write the structure of \(\varepsilon\)-caprolactam.

Polyamides derived from aromatic diamines are called *aramids*, are quite strong, and enjoy a number of uses. Protective clothing, including bullet-resistant vests, made from the aramid fiber *Kevlar*, for example, are effective yet light in weight.

**PROBLEM 29.11**

*Nomex* is an aramid fiber used for fire-resistant protective clothing. It is a polyamide prepared by condensation of 1,3-benzenediamine (\(m\)-phenylenediamine) and 1,3-benzenedicarboxylic acid (isophthalic acid). What is the repeating unit of *Nomex*?

**29.12 Polyesters**

The usual synthetic route to a polyester is by condensation of a dicarboxylic acid with a diol. The best known polyester is poly(ethylene terephthalate) prepared from ethylene glycol and terephthalic acid.

\[
\text{O} \quad \text{O} \\
\text{HOC} \left(\text{Benzene-1,4-dicarboxylic acid}\right) + \text{HOCH}_2\text{CH}_2\text{OH} \xrightarrow{200-300^\circ\text{C}} \left[\text{OCH}_2\text{CH}_2\text{O} \right]_n \\
\text{Poly(ethylene terephthalate)}
\]
The popularity of clothing made of polyester-cotton blends testifies to the economic impact of this polymer. Poly(ethylene terephthalate) is the PETE referred to in the recycling codes listed in Table 29.1. Plastic bottles for juice, ketchup, and soft drinks are usually made of PETE, as is Mylar film (Figure 29.8).

**Alkyd resins** number in the hundreds and are used in glossy paints and enamels—house, car, and artist’s—as illustrated in Figure 29.9. Most are derived from benzene-1,2-dicarboxylic acid (o-phthalic acid) and 1,2,3-propanetriol (glycerol). Two of the hydroxyl groups of glycerol are converted to esters of o-phthalic acid; the third is esterified with an unsaturated fatty acid that forms cross links to other chains. With both a hydroxyl group and a carboxylic acid function in the same molecule, glycolic acid and lactic acid have the potential to form polyesters. Heating the α-hydroxy acid gives a cyclic diester, which, on treatment with a Lewis acid catalyst (SnCl$_2$ or SbF$_3$) yields the polymer.

Surgical sutures made from poly(glycolic acid) and poly(lactic acid), while durable enough to substitute for ordinary stitches, are slowly degraded by ester hydrolysis and don’t require a return visit for their removal. Poly(glycolic acid) fibers also hold promise as a scaffold upon which to grow skin cells. This “artificial skin” is then applied to a wound to promote healing.

**PROBLEM 29.12**

Another monomer from which surgical sutures are made is ε-caprolactone. What is the repeating unit of poly(ε-caprolactone)?

Polymers are also used in controlled-release forms of drugs and agricultural products such as fertilizers and herbicides. By coating the active material with a polyester selected so as to degrade over time, the material is released gradually rather than all at once.

### 29.13 Polycarbonates

Polycarbonates are polyesters of carbonic acid. *Lexan* is the most important of the polycarbonates and is prepared from the diphenolic compound bisphenol A.
Lexan is a clear, transparent, strong, and impact-resistant plastic with literally countless applications. It is used in both protective and everyday eyeglasses as illustrated in Figure 29.10. The Apollo 11 astronauts wore Lexan helmets with Lexan visors on their 1969 trip to the moon. CDs and DVDs are Lexan polycarbonate, as are many cell phones, automobile dashpanels, and headlight and taillight lenses.

29.14 Polyurethanes

A urethane, also called a carbamate, is a compound that contains the functional group \(-\text{OCNH}^-\). Urethanes are normally prepared by the reaction of an alcohol and an isocyanate.

\[
\text{ROH} + \text{R'}\text{N}==\text{C}==\text{O} \rightarrow \text{ROCNHR'}
\]

Polyurethanes are the macromolecules formed from a diol and a diisocyanate. In most cases the diol is polymeric and the diisocyanate is a mixture of the “toluene diisocyanate” isomers.

If, for example, only the 2,6-diisocyanate were present, the repeating unit of the resulting polyurethane would be

Because a mixture of diisocyanate isomers is actually used, a random mixture of 2,4- and 2,6-substitution patterns results.
The reaction of an alcohol with an isocyanate is addition, not condensation. Therefore, polyurethanes are classified as addition polymers. But because the monomers are difunctional, the molecular weight increases by step growth rather than chain growth.

A major use of polyurethanes is in spandex fibers. Spandex, even when stretched several times its length, has the ability to return to its original state and is a superior substitute for rubber in elastic garments. Its most recognizable application is in athletic wear (swimming, cycling, running) where it is the fabric of choice for high-performance athletes (Figure 29.11).

Polyurethanes have many other applications, especially in paints, adhesives, and foams. Polyurethane foams, which can be rigid (insulation panels) or flexible (pillows, cushions, and mattresses) depending on their degree of cross linking, are prepared by adding foaming agents to the polymerization mixture. One method takes advantage of the reaction between isocyanates and water.

Although esters of carbamic acid (urethanes) are stable compounds, carbamic acid itself rapidly dissociates to an amine and carbon dioxide. Adding some water to the reactants during polymerization generates carbon dioxide bubbles which are trapped within the polymer.

**29.15 Copolymers**

Copolymers, polymers made from more than one monomer, are as common as homopolymers. The presence of more than one monomer in a chain makes some control of properties possible. Some structural units stiffen the chain, others make it more flexible. Often a second monomer is added to allow cross linking.

Copolymers are classified according to the distribution of monomers in the macromolecule.

1. Random
2. Block
3. Graft

**Random copolymers:** As the name implies, there is no pattern to the distribution of monomer units in a random copolymer.

\[
\text{RN} - \text{C} - \text{O} + \text{H}_2\text{O} \rightarrow \text{RNH} - \text{C} - \text{OH} \rightarrow \text{RNH}_2 + \text{CO}_2
\]

Although esters of carbamic acid (urethanes) are stable compounds, carbamic acid itself rapidly dissociates to an amine and carbon dioxide. Adding some water to the reactants during polymerization generates carbon dioxide bubbles which are trapped within the polymer.

**Styrene–butadiene rubber (SBR) for automobile tires is a random copolymer.** It is prepared by two methods, free-radical and anionic polymerization, both of which are carried out on a mixture of styrene and 1,3-butadiene. Free-radical initiation is essentially nonselective and gives the random copolymer. Anionic initiation is carried out under conditions designed to equalize the reactivity of the two monomers so as to ensure randomness.

**Block copolymers:** The main chain contains sections (blocks) of repeating units derived from different monomers. The sequence:

\[
\text{A} - \text{A} - \text{A} - \text{B} - \text{B} - \text{A} - \text{A} - \text{A} - \text{B} - \text{B} - \text{A} - \text{B} - \text{A} - \text{B}
\]

shows only two blocks, one derived from A and the other from B. A macromolecule derived from A and B can contain many blocks.

The living polymers generated by anionic polymerization are well suited to the preparation of block polymers. Adding 1,3-butadiene to a living polystyrene block sets the stage for attaching a poly(1,3-butadiene) block.
The properties of the block copolymer prepared by anionic living polymerization are different from the random styrene–butadiene copolymer.

**Graft copolymer:** The main chain bears branches (grafts) that are derived from a different monomer.

A graft copolymer of styrene and 1,3-butadiene is called “high-impact polystyrene” and is used, for example, in laptop computer cases. It is prepared by free-radical 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.

**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.

![Free-radical polymerization reaction](image)

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 alkylithium reagents.

![Anionic polymerization reaction](image)

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.

![Cationic polymerization reaction](image)

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.

$$\text{H}_3\text{N(CH}_2\text{)}_6\text{NH}_3^+ + \text{O}^\text{-OC(CH}_2\text{)}_4\text{CO}^\text{+} \xrightarrow{\text{heat}} \left[\text{NH(CH}_2\text{)}_6\text{NH(CCH}_2\text{)}_4\text{C}^\text{+}_n\right]$$
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.

\[
\begin{array}{c}
\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCCH}_2\text{CH}_2\text{C} \\
\end{array}
\]

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

\[
\begin{array}{c}
\text{CH}_3 \\
\end{array}
\]

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.

\[
\begin{array}{c}
\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCNH} \\
\end{array}
\]

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\(_2\)N(CH\(_2\))\(_{11}\)CO\(_2\)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 \[
\begin{array}{c}
\text{O} \\
\end{array}
\]
prepared? Suggest a source-based name.

29.19 Give the structure of the lactone from which \[
\begin{array}{c}
\text{OCH}_2\text{CH}_2\text{C} \\
\end{array}
\]
is prepared.
29.20 Kodel fibers are made from the polymer shown. Suggest suitable monomers for its preparation.

\[
\text{[Image of polymer structure]}
\]

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

- H₂C=CHCH₃
- H₂C=CHCH=CH₂
- H₂C=CHC≡CH
- H₂C=CHCl

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

\[
\text{[Image of polymer structure]}
\]

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) TiCl₄, (CH₃CH₂)₃Al  
(b) \[
\begin{array}{c}
\text{[Image of initiator structure]} \\
\text{O} \\
\text{O}
\end{array}
\]
(c) BF₃

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

29.25 Given that \(-\text{C≡N}\) 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?

\[
\text{[Image of reaction structure]}
\]

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 (shown) is made by the reaction of phenol and acetone. Suggest a mechanism for this reaction. Assume acid (\( \text{H}_3\text{O}^+ \)) 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 \( \text{H}_2\text{O}^- \) as the acid and \( \text{OH}^- \) as the base.

29.30 (a) The first step in the formation of Bakelite from phenol and formaldehyde introduces \(-\text{CH}_2\text{OH}\) groups onto the ring.

\[
\text{[Image of reaction structure]}
\]

\[
\begin{array}{|c|c|c|}
\hline
\text{X} & \text{Y} & \text{Z} \\
\hline
\text{H} & \text{CH}_3\text{OH} & \text{H} \\
\text{CH}_3\text{OH} & \text{H} & \text{H} \\
\text{CH}_3\text{OH} & \text{CH}_3\text{OH} & \text{H} \\
\text{CH}_3\text{OH} & \text{CH}_2\text{OH} & \text{CH}_3\text{OH} \\
\hline
\end{array}
\]
Write a mechanism for the formation of \( \alpha \)-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.

\[
\text{HO-} + \text{HOCH}_2- \xrightarrow{\text{catalyst}} \xrightarrow{\text{heat}} \text{HO-CH}_2- \text{HO}
\]

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

\[
H_2C=\bar{O}^- + BF_3 \rightarrow H_2C=\bar{O}^- BF_3
\]

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

---

**DESCRIPTIVE PASSAGE AND INTERPRETIVE PROBLEMS 29**

**Chemical Modification of Polymers**

Many useful polymers are not themselves the initial products of polymerization but are prepared by chemically modifying the original polymer. Partially fluorinated polyethylene used for protective gloves and to coat automobile gasoline tanks is made by exposing polyethylene to \( F_2 \) diluted with nitrogen.

\[
\text{CH}_2\text{CH}_2\text{CH}_2 + F_2 \rightarrow \text{CH}_2\text{CH}~\text{F} + HF
\]

Partial fluorination gives a polymer that, like polyethylene, is easy to cast into films but with a greater resistance to oxidation and water penetration.

The solid support in Merrifield’s synthesis of ribonuclease (Section 27.18) was prepared by incorporating \( \text{-CH}_2\text{Cl} \) groups into a styrene/\( p \)-divinylbenzene copolymer by electrophilic aromatic substitution.

At the same time that Merrifield was developing his method for the solid-phase synthesis of peptides, Robert Letsinger (Northwestern University) was independently applying the same concept to polynucleotide synthesis. Modern methods for making oligonucleotides are direct descendents of Letsinger’s method.

Today’s chemists can buy Merrifield-type resins with varying degrees of chloromethyl substitution and cross linking tailored for specific purposes. Because the chlorine atom is primary and benzylic, these resins can be further modified by nucleophilic substitution.

\[
\text{PS-CH}_2\text{Cl} + \text{Nu}^- \rightarrow \text{PS-CH}_2\text{Nu} + \text{Cl}^-
\]

(In this and succeeding equations, the blue sphere represents a polymer bead and \( \text{PS} \) stands for polystyrene or a copolymer of polystyrene and \( p \)-divinylbenzene.)

The products of these reactions form the basis for an entire methodology—polymer-supported chemical reactions—wherein the modified polystyrene serves as a reactant, reagent, or catalyst. The reactions are the usual ones of organic chemistry. In the following equation, for example, the modified polystyrene serves as a phase-transfer catalyst (Section 22.5). The main advantage of using a polymer-supported reagent, or in
this case a polymer-supported catalyst, is that it makes isolation of the reaction product easier.

\[
\begin{align*}
\text{CH}_3\text{(CH}_2\text{)}_3\text{CH}_2\text{Br} + \text{KCN} & \xrightarrow{\text{PS}-\text{CH}_3\text{P(Bu)}_3\text{Cl}^-} \text{CH}_3\text{(CH}_2\text{)}_3\text{CH}_2\text{CN} + \text{KBr} \\
\text{(in toluene)} & \quad \text{(in water)} & \quad \text{(in toluene)} & \quad \text{(in water)}
\end{align*}
\]

Cyanide ion from aqueous KCN exchanges with Cl\(^-\) of the polymer-supported phosphonium chloride and reacts with 1-bromooctane on the surface and within channels of the polymer support. When the reaction is judged to be complete, the polymer (insoluble in both toluene and water) is recovered by filtration and the aqueous layer removed. Distillation of the toluene solution of the product furnishes nonanenitrile, the product of nucleophilic substitution of cyanide for bromide.

The number of applications of chemically modified polymers as materials, reagents, and catalysts is extremely large. The following problems give a few examples.

### 29.32

Chemical modification of polymers is not always beneficial. Which of the following polymers will be adversely affected by air oxidation the most?

\[
\begin{align*}
\begin{array}{c}
\text{CF}_2 \xrightarrow{\text{A}} \text{CH}_2 \xrightarrow{\text{B}} \text{CH}_2 \xrightarrow{\text{C}} \text{CH}_2 \xrightarrow{\text{D}} \text{CH}_2
\end{array}
\end{align*}
\]

A. B. C. D.

### 29.33

The living polymer formed by reaction of ethylene with butyllithium can be converted to a long-chain alkyldiphenylphosphine by reaction with compound X. The alkyldiphenylphosphine is used in the preparation of phase-transfer catalysts and as a ligand in polymer-supported organometallic compounds. What is compound X?

\[
\begin{align*}
\text{H}_2\text{C} & \xrightarrow{\text{BuLi}} \text{Bu} \left[ \text{CH}_2\text{CH}_2 \right]_n \xrightarrow{\text{compound X}} \text{Bu} \left[ \text{CH}_2\text{CH}_2 \right]_n \text{P(C}_6\text{H}_5)_2
\end{align*}
\]

\[
\begin{align*}
\text{(C}_6\text{H}_5)_2\text{PH} & \quad \text{(C}_6\text{H}_5)_2\text{PCl} & \quad \text{(C}_6\text{H}_5)_2\text{PLi} & \quad \text{(C}_6\text{H}_5)_3\text{P}
\end{align*}
\]

A. B. C. D.

### 29.34

The alkyldiphenylphosphine formed in the preceding equation was converted to a dialkyldiphenylphosphonium salt for use as a phase-transfer catalyst. Which of the following is a suitable reactant for such a conversion?

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li} & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{ONa}
\end{align*}
\]

A. B. C. D.

### 29.35

A copolymer of styrene and \(p\)-bromostyrene can be transformed into a living polymer as shown. The aryllithium sites then serve to start chain growth when a suitable monomer is added.
29.36 Which of the following is the most suitable for the transformation in the equation?

\[
\text{LiOH} \quad \text{LiCl} \quad \text{LiCu(CH}_3\text{)}_2 \quad \text{Li}
\]

A. \hspace{1cm} B. \hspace{1cm} C. \hspace{1cm} D.

29.37 What is the polymer-containing product of the following reaction?

\[
\begin{align*}
\text{PS} & \quad \text{CH}_2\text{NH}_2 + \text{BrCH}_2(\text{CH}_2)_9\text{COH} + \text{N} = \text{C} = \text{N} \\
\text{PS} & \quad \text{CH}_2\text{NHCH}_2(\text{CH}_2)_9\text{COH} \quad \text{PS} \quad \text{CH}_2\text{NHCC(\text{CH}_2)_9\text{CH}_2\text{Br}}
\end{align*}
\]

A. \hspace{1cm} B.

29.38 The ethyl ester function in the R-BINAP derivative shown was used as the reactive “handle” to bind the chiral unit to polystyrene giving a ligand suitable for ruthenium-catalyzed enantioselective hydrogenation.

Which of the following has the proper functionality to react with this ester by nucleophilic acyl substitution to give a polystyrene-supported ligand?

A. \hspace{1cm} B. \hspace{1cm} C. \hspace{1cm} D.

29.39 The polystyrene-supported quaternary ammonium chloride shown was treated with aqueous sodium hydroxide, then shaken with a solution of compound X and phenol in toluene at 90°C to give butyl phenyl ether in 97% yield. What is compound X?

A. \hspace{1cm} B. \hspace{1cm} C. \hspace{1cm} D.