DID YOU EVER WONDER... how bulletproof glass works?

Bulletproof glass, such as that used in armored vehicles, consists of several sheets of glass sandwiched between transparent polymer sheets. The resulting material is comprised of many layers, and the outer layers are capable of absorbing the impact of the bullet, thereby preventing it from penetrating the inner layers. The ability of the glass to resist bullets depends on many factors, including the type of polymer used, the thickness of the glass, the number of layers sandwiched together, the type of bullet, and the range from which the bullet is fired. For this reason, the glass is generally described as “bullet resistant” rather than “bulletproof.”

This chapter will focus on the preparation, classification, and properties of a variety of synthetic polymers, including those found in bullet-resistant glass as well as a large variety of other applications.
27.1 Introduction to Synthetic Polymers

Over the past century, our society has become heavily reliant on polymers. Coffee cups, soft-drink bottles, synthetic fabrics for clothing, CDs and DVDs, trash bags, artificial heart valves, and automobile parts are all manufactured from polymers. Polymers represent a multibillion-dollar industry, with more than 50 trillion pounds of synthetic polymers being manufactured each year in the United States alone.

Recall that polymers are comprised of repeating units that are constructed by joining monomers together.

![Monomers to Polymer Diagram]

Polymers are drawn most efficiently by placing brackets around the repeating unit, where the subscript “n” indicates that the polymer is constructed from a large number of repeating units. Polymers have been discussed many times throughout this textbook, as indicated in Table 27.1.

| TABLE 27.1 REFERENCES TO PRIOR DISCUSSIONS OF POLYMERS IN THIS TEXTBOOK |
|-----------------------------|------------------|
| TOPIC                      | SECTION |
| Introduction to polymers   | 4.5     |
| Cationic polymerization     | 9.3     |
| Conducting organic polymers | 10.1    |
| Radical polymerization      | 11.11   |
| Polymers from dienes        | 17.5    |
| Polysters and polyamides    | 21.12   |
| Polysaccharides             | 24.8    |
| N-Glycosides (DNA and RNA)  | 24.10   |
| Proteins                   | 25.1    |

Polymers can be divided into two major categories: synthetic polymers and biopolymers. The former are prepared by scientists in the laboratory or in factories, while the latter are produced by living organisms. Biopolymers include polysaccharides, DNA, RNA, and proteins, all of which were discussed in the previous chapters. This chapter will focus exclusively on synthetic polymers.

27.2 Nomenclature of Synthetic Polymers

IUPAC has established rules for assigning systematic names to polymers, but these names are rarely used by scientists. An alternative and more common system, also recognized by IUPAC,
involves naming the polymer based on the monomers from which it was derived, as shown in the following examples:

![Monomer structures for Polyethylene, Polypropylene, Styrene, and Polystyrene](image)

When writing the name of a polymer whose monomer contains two words, parentheses are used around the name of the monomer. Thus, polymerization of vinyl chloride yields poly(vinyl chloride).

Polymers are also often called by their trade name, such as Teflon and Kevlar. Table 27.2 provides a list of many common polymers and their uses.

### Table 27.2 Several Common Polymers and Their Uses

<table>
<thead>
<tr>
<th>Name of Polymer</th>
<th>Monomer Structure</th>
<th>Polymer Structure</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
<td>Bottles and trash bags</td>
</tr>
<tr>
<td>Polypropylene</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
<td>Carpet fibers, appliances, car tires</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
<td>Caulks and sealants, bicycle inner tubes, basketballs</td>
</tr>
<tr>
<td>Polystyrene</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
<td>Foam insulation, televisions, radios</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
<td>Water pipes, vinyl plastics</td>
</tr>
<tr>
<td>Poly(methyl-α-cyanoacrylate)</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
<td>Superglue</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
<td>Nonstick coating for frying pans (Teflon)</td>
</tr>
</tbody>
</table>
CONCEPTUAL CHECKPOINT

27.1 Draw and name the polymer that results when each of the following monomers undergoes polymerization:

(a) Vinyl acetate
(b) Vinyl bromide
(c) α-Butylene

27.2 Sodium polyacrylate is a synthetic polymer used in diapers, because of its ability to absorb several hundred times its own mass of water. This extraordinary polymer is made from another polymer, poly(methyl acrylate), via hydrolysis of the ester groups. Draw and name the monomer used to make poly(methyl acrylate).

27.3 Copolymers

The polymers discussed thus far are all called homopolymers. A homopolymer is a polymer constructed from a single type of monomer. In contrast, polymers constructed from two or more different types of monomers are called copolymers. A common example of a copolymer is Saran, which is made from vinyl chloride and vinylidene chloride.

Copolymers often have different properties than either of their corresponding homopolymers. A list of some common copolymers and their applications is presented in Table 27.3. Copolymers are often classified based on the order in which the monomers are joined together. Alternating copolymers contain an alternating distribution of repeating units, while random copolymers contain a random distribution of repeating units.

The precise distribution of any copolymer is dependent on the conditions of its formation. In practice, however, even alternating copolymers will exhibit regions in which the repeating units are distributed randomly.
### Table 27.3 Some Common Copolymers and Their Uses

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Copolymer Name</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl</td>
<td>Saran</td>
<td>Food packaging</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinylidene Chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHPh</td>
<td>SAN</td>
<td>Dishwasher-safe kitchenware and battery cases</td>
</tr>
<tr>
<td>Styrene</td>
<td>Acrylonitrile</td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>Acrylonitrile</td>
<td></td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>ABS</td>
<td>Crash helmets, luggage, and car bumpers</td>
</tr>
<tr>
<td>Styrene</td>
<td>Acrylonitrile</td>
<td></td>
</tr>
<tr>
<td>Butyl rubber</td>
<td></td>
<td>Inner tubes, balls, sporting goods</td>
</tr>
<tr>
<td>Isobutylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isoprene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexafluoropropylene</td>
<td>Viton</td>
<td>Gaskets, seals, and automotive fuel lines</td>
</tr>
<tr>
<td>Vinylidene Fluoride</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Copolymers comprised of homopolymer subunits are classified as either block copolymers or graft copolymers.

![Block copolymer](image1)

![Graft copolymer](image2)

In a **block copolymer**, the different homopolymer subunits are connected together in one chain. In contrast, a **graft copolymer** contains sections of one homopolymer that have been grafted onto a chain of the other homopolymer. Block copolymers and graft copolymers are formed by controlling the conditions under which polymerization occurs.

### Conceptual Checkpoint

**27.3** Draw a region of an alternating copolymer constructed from styrene and ethylene.

**27.4** Draw a region of a block copolymer constructed from propylene and vinyl chloride.

**27.5** Identify the monomers required to make the following alternating copolymer:

![Monomers](image3)
27.4 Polymer Classification by Reaction Type

Polymers can be classified in a variety of ways. Common classification schemes focus on either the type of reaction used to make the polymer, the mode of assembly, the structure, or the properties of the polymer. We will explore each of these classification schemes, beginning with the type of reaction used to make the polymer.

Addition Polymers

As seen in previous chapters, addition reactions involving π bonds can occur through a variety of mechanisms, including cationic addition, anionic addition, and free-radical addition. In much the same way, monomers can join together to form polymers via cationic addition, anionic addition, or free-radical addition. Polymers formed via any one of these processes are called addition polymers. A mechanism for radical polymerization was first discussed in Section 11.11 and is reviewed in Mechanism 27.1.

In the initiation steps, a radical initiator is formed and then couples to one of the monomers, forming a carbon radical. This highly reactive intermediate then undergoes a propagation step in which it couples with another monomer. This process repeats itself, causing the polymer chain to grow. The process ends with a termination step in which two radicals couple together. Since the concentration of radicals is quite low at all times, the probability of two radicals coupling is rather small. As a result, thousands of monomers can be strung together in a single polymer chain before a termination step occurs. In this way, ethylene can be converted into polyethylene in the presence of a radical initiator. In fact, most derivatives of ethylene will also undergo radical polymerization under suitable conditions.
In contrast, cationic addition is only efficient with ethylene derivatives that contain an electron-donating group, such as the following examples:

<table>
<thead>
<tr>
<th>Electron-donating group</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDG</td>
<td>Me</td>
</tr>
<tr>
<td></td>
<td>OMe</td>
</tr>
<tr>
<td></td>
<td>NR₂</td>
</tr>
</tbody>
</table>

A mechanism for cationic polymerization was first discussed in the Practically Speaking box in Section 9.3 and is reviewed here in Mechanism 27.2.

**MECHANISM 27.2 CATIONIC POLYMERIZATION**

**Initiation**

The π bond of a monomer is protonated, generating a carbocation intermediate.

**Propagation**

The π bond of a monomer acts as a nucleophile and attacks the carbocation. This process is repeated, building up the polymer chain.

**Termination**

The polymerization process is terminated when either a base deprotonates the carbocation or a nucleophile attacks the carbocation.

The cationic polymerization process is initiated in the presence of an acid, which transfers a proton to the π bond of a monomer, thereby generating a carbocation. The acid catalyst most often used is formed by treating BF₃ with water.

The carbocation generated during the initiation stage is then attacked by another monomer in a propagation step, and the process repeats itself, enabling the polymer chain to grow. The function of the electron-donating group is to stabilize the carbocation intermediate that is formed after the addition of each monomer to the growing polymer chain. For example, isobutylene readily undergoes cationic polymerization because a tertiary carbocation intermediate is formed during each propagation step.
In contrast, ethylene does not readily undergo cationic polymerization, because the process would involve formation of a primary carbocation, which is not sufficiently stable to form at an appreciable rate.

For monomers that undergo cationic polymerization, the process is terminated when the carbocation intermediate is deprotonated by a base or attacked by a nucleophile, as seen in Mechanism 27.2.

Unlike cationic addition, anionic addition is only efficient with ethylene derivatives that contain an electron-withdrawing group, such as the following examples:

Electron-withdrawing groups were first discussed in Chapter 19, and a list can be found in Section 19.10. Anionic polymerization is believed to proceed via Mechanism 27.3.
Anionic polymerization is initiated in the presence of a highly reactive anion, such as butyl lithium. The anion functions as a nucleophile and attacks the π bond of a monomer, thereby generating a new carbanion. The carbanion generated during the initiation stage then functions as a Michael donor and attacks another monomer, which functions as a Michael acceptor:

This propagation step is repeated, enabling the polymer chain to grow. The function of the electron-withdrawing group is to stabilize the carbanion intermediate that is formed after the addition of each monomer to the growing polymer chain.

For monomers that undergo anionic polymerization, the process continues until all of the monomers have been consumed. But even after all of the monomers have been exhausted, the process is not actually terminated until a suitable acid (such as water) or electrophile (such as CO₂) is added to the reaction mixture. In the absence of a suitable acid or electrophile, the end of each polymer chain will possess a stabilized carbanion site, and the polymerization process can continue if more monomers are added to the reaction mixture. For this reason polymers generated through this process are often called living polymers.

Superglue is a common example of a monomer that readily polymerizes via an anionic addition process. Superglue is a pure solution of methyl-α-cyanoacrylate, which is a monomer containing two electron-withdrawing groups.

With two electron-withdrawing groups, the compound is so reactive toward anionic polymerization that even a weak nucleophile, such as water, will initiate the polymerization process. When superglue is applied to a metal surface, the moisture on the surface of the metal is sufficient to catalyze polymerization, which then occurs very rapidly. In fact, the water and other nucleophiles present in your skin will initiate the polymerization process, explaining why superglue bonds to skin so tightly. In some cases, doctors utilize compounds like superglue to close wounds, instead of using stitches. These compounds are structurally very similar to superglue, except that the methyl group of the ester is replaced with a slightly larger alkyl group. For example, Dermabond, a cyanoacrylate ester with a 2-octyl group, was developed to replace stitches in certain situations.
**SKILLBUILDER**

**27.1 DETERMINING THE MORE EFFICIENT POLYMERIZATION TECHNIQUE**

**LEARN the skill**
Determine whether preparation of the following polymer would be best achieved via cationic addition or anionic addition:

\[
\text{CHO} \quad \text{CHO} \quad \text{CHO} \quad \text{CHO}
\]

**SOLUTION**
First identify the repeating units in the polymer structure.

Next identify the monomer necessary to prepare a polymer with those repeating units.

Now determine whether the group attached to the vinyl position is an electron-withdrawing group or an electron-donating group, as first described in Section 19.10. In this case, the necessary monomer has a carbonyl group, which is an electron-withdrawing group because it can stabilize a negative charge via resonance. We therefore expect this monomer to polymerize most efficiently under basic conditions.

**PRACTICE the skill**
27.6 Determine whether preparation of each of the following polymers would best be achieved via cationic addition or anionic addition:

(a) \[
\text{CN} \quad \text{CN} \quad \text{CN} \quad \text{CN}
\]

(b) \[
\text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe}
\]

(c) \[
\text{CCl}_3 \quad \text{CCl}_3 \quad \text{CCl}_3 \quad \text{CCl}_3
\]

(d) \[
\text{OAc} \quad \text{OAc} \quad \text{OAc} \quad \text{OAc}
\]

(e) \[
\text{NO}_2 \quad \text{NO}_2 \quad \text{NO}_2 \quad \text{NO}_2
\]

(f) \[
\text{CCl}_3 \quad \text{CCl}_3 \quad \text{CCl}_3 \quad \text{CCl}_3
\]
27.4 Polymer Classification by Reaction Type

27.7 Arrange the following monomers in order of reactivity toward cationic polymerization:

\[ \text{OAc} \quad \text{NO}_2 \quad \text{CH}_3 \]

27.8 Arrange the following monomers in order of reactivity toward anionic polymerization:

\[ \quad \text{NO}_2 \quad \text{Cl} \quad \text{O} \]

27.9 Many monomers that readily undergo cationic polymerization, such as isobutylene, will not readily undergo anionic polymerization. Styrene, however, can be effectively polymerized via cationic, anionic, or radical addition. Explain.

27.10 A tube of superglue will harden if it remains open too long in a humid environment. Draw a mechanism that shows how superglue polymerizes in the presence of atmospheric moisture. When drawing your mechanism, make sure to draw the initiation step, at least two propagation steps, and a termination step involving water as the acid.

Condensation Polymers

As seen in previous chapters, the term “condensation” is used to characterize any reaction in which two molecules undergo addition accompanied by the loss of a small molecule such as water, carbon dioxide, or nitrogen gas. Throughout this book, we have seen many condensation reactions. One such example is the Fischer esterification process, as seen in Section 21.10.

\[
\text{R-OH} + \text{H-O-R} \xrightarrow{[\text{H}^+]} \text{R-O}\text{R} + \text{H}_2\text{O}
\]

In this reaction, a carboxylic acid is treated with an alcohol in the presence of an acid catalyst, forming an ester and a water molecule. This process is considered to be a condensation reaction because the reactants undergo addition accompanied by the loss of a water molecule.

Now consider the condensation reactions that can occur when a diacid is treated with a diol. Each compound is capable of reacting twice, enabling formation of a polymer. As an example, consider the formation of poly(ethylene terephthalate), also known simply as PET, which is used to make soft-drink bottles.
As shown, PET is prepared by successive Fischer esterification reactions. Since the polymer is generated via condensation reactions, it is called a **condensation polymer**. Because PET has repeating ester groups, the polymer is also classified as a polyester. Like PET, nylon 6,6 is also prepared via condensation reactions and is also a condensation polymer. Nylon 6,6 is a polyamide, which is prepared from adipic acid and 1,6-hexanedianime.

**Looking Back**
For a review of polyesters and polyamides, see the Practically Speaking box in Section 21.12.

**Conceptual Checkpoint**

27.11 Draw the mechanism of formation of PET in acidic conditions. It might be helpful to first review the mechanism for the Fischer esterification process.

27.12 Draw the polymer that would be generated from the acid-catalyzed reaction between oxalic acid and resorcinol.

Polycarbonates are similar in structure to polyesters, but with repeating carbonate groups instead of repeating ester groups:

![Carbonate group](image)

![Ester group](image)

Carbonates can be formed from the reaction between phosgene and an alcohol.
Polycarbonates are formed in a similar way, by treating phosgene with a diol. As an example, consider the reaction between phosgene and bisphenol A.

\[
\text{Phosgene} + \text{Bisphenol A} \rightarrow \text{Lexan} + \text{HCl}
\]

The resulting polymer is a condensation polymer sold under the trade name Lexan. It is a lightweight, transparent polymer with high impact strength and is used to make bicycle safety helmets, bullet-resistant glass, and traffic lights. Lexan is also used in the production of safety goggles, because it is both lightweight and shatterproof. In recent years, polycarbonates have also become quite popular for the production of CDs and DVDs.

**SKILLBUILDER**

**27.2 IDENTIFYING MONOMERS FOR A CONDENSATION POLYMER**

**LEARN the skill**

Determine which monomers you would use to prepare the following condensation polymer:

\[
\text{RCOOH} + \text{ROH} \rightarrow \text{RCONH}_2 + \text{H}_2\text{O}
\]

**SOLUTION**

First identify the type of functional group that repeats itself:

A polyester

In this case, the repeating functional group is an ester group, so this condensation polymer is a polyester. Recall that ester groups can be prepared from the reaction between a carboxylic acid and an alcohol via a Fischer esterification process.

\[
\text{RCOOH} + \text{ROH} \rightarrow \text{RCONH}_2 + \text{H}_2\text{O}
\]

Preparing a polymer that exhibits repeating ester groups requires reactants that are difunctional; specifically, a suitable diacid and diol must be selected. To determine the starting diol and diacid, it is best to work backward from the structure of the polyester; that is, imagine hydrolyzing each ester group (the reverse of a Fischer esterification).
Inspection of the individual monomers reveals that two different monomers are required. The following diacid and diol can be used to prepare the desired polymer.

\[
\begin{align*}
\text{HO} & \quad \text{O} \\
\text{O} & \quad \text{HO} \\
\end{align*}
\]

27.13 Kevlar is a condensation polymer used in the manufacture of bulletproof vests. Identify the monomers required for the preparation of Kevlar.

27.14 Identify the monomers required to make each of the following condensation polymers:

(a)

(b)

27.15 Identify the condensation polymer that would be produced when phosgene is treated with 1,4-butanediol.

27.16 Nylon 6 is a polyamide used in the manufacture of ropes. It can be prepared via hydrolysis of ε-caprolactam to form ε-aminocaproic acid followed by acid-catalyzed polymerization.

(a) Draw the structure of Nylon 6.

(b) Compare the structure of Nylon 6 with the structure of Nylon 6,6 (shown just before Conceptual Checkpoint 27.11). Which polymer exhibits a smaller repeating unit?

27.5 Polymer Classification by Mode of Assembly

Chain-Growth Polymers

Polymers are also often classified as either chain-growth or step-growth polymers. These terms are used to signify the way in which the polymers are assembled. Chain-growth polymers are formed under conditions in which the monomers do not react directly with each other, but rather, each
monomer is added to the growing chain one at a time. The growing polymer chain generally has only one reactive site, called a growth point, and the monomers attach to the chain at the growth point.

All of the addition reactions seen earlier in this chapter (radical, cationic, and anionic polymerization) are examples of chain-growth processes. Polymers created by any of these addition processes are chain-growth polymers. In contrast, most condensation polymers are not chain-growth polymers, but instead belong to a class called step-growth polymers.

**Step-Growth Polymers**

*Step-growth polymers* are formed under conditions in which the individual monomers react with each other to form oligomers (compounds constructed from just a few monomers), which are then joined together to form polymers.

This mode of assembly occurs when difunctional monomers are used, just as we saw with condensation polymers in the previous section. In such a case, all monomers and oligomers have two growth points instead of just one. As an example, consider the formation of PET.

In general, step-growth polymers are usually condensation polymers, while chain-growth polymers are usually addition polymers, but there are exceptions, such as polyurethanes. **Polyurethanes** are made up of repeating urethane groups, also sometimes called carbamate groups.
Urethanes can be prepared by treating an isocyanate with an alcohol.

\[
\text{R} - \text{N} = \text{C} = \text{O} + \text{ROH} \rightarrow \text{R} - \text{N} = \text{C} = \text{O} - \text{OR}
\]

Polyurethanes can be prepared by treating a diisocyanate with a diol. In preparing polyurethanes, the diols most commonly used are small polymers that bear hydroxyl ends.

This process is not a condensation, because it does not involve the loss of a small molecule. Polyurethanes are technically addition polymers, but nevertheless, they are step-growth polymers because the growing polymer chain has two growth points rather than one. This example illustrates that step-growth polymers cannot always be classified as condensation polymers. Polyurethanes are used for insulation in the construction of homes and portable coolers.

**CONCEPTUAL CHECKPOINT**

27.17 Would these pairs of monomers form chain-growth or step-growth polymers?

(a) \(\text{Cl} = \text{C} = \text{O} + \text{H_2N-C}_2\text{H}_5\text{NH}_2\)

(b) \(\text{Cl} + \text{C} = \text{N}\)

27.18 Should this polymer be classified as a chain-growth polymer or a step-growth polymer?

**27.6 Polymer Classification by Structure**

**Branched Polymers**

Polymers are also often classified by their structure. Branched polymers contain a large number of branches connected to the main chain of the polymer.
Branching occurs when the location of a growth point is moved during the polymerization process. For example, during radical addition, a hydrogen abstraction step can produce a growth point in the middle of an existing chain:

Branching is very common and is observed during many polymerization processes. Polymers can be differentiated from each other based on the extent of branching. Some polymers are highly branched, while other polymers have only a minimal amount of branching or no branching at all. The former are called branched polymers, while the latter are called **linear polymers**. The synthesis of linear polymers often requires the use of special catalysts, described in the following section.

**Linear Polymers**

The field of polymer chemistry was revolutionized in 1953 with the development of Ziegler-Natta catalysts. These catalysts are organometallic complexes that can be prepared by treating an alkyl aluminum compound, such as Et₃Al, with TiCl₄. The development of Ziegler-Natta catalysts enabled scientists to control the polymerization process in the following ways:

1. **Extent of branching.** Free radicals are not involved as intermediates when Ziegler-Natta catalysts are employed, and therefore very little branching occurs. Polymers produced with these catalysts are generally linear polymers, which have very different properties than branched polymers. Without a Ziegler-Natta catalyst, ethylene polymerizes to form a polymer that exhibits about 20 branches per thousand carbon atoms. The resulting polymer chains cannot effectively pack, giving rise to a material with a relatively low density (~0.92 g/cm³) called low-density polyethylene, or LDPE. However, in the presence of a Ziegler-Natta catalyst, ethylene polymerizes to form a polymer that exhibits about five branches per thousand carbon atoms. The resulting polymer chains can pack more efficiently, giving rise to a material with a relatively high density, ~0.96 g/cm³, called high-density polyethylene, or HDPE. LDPE is used to make trash bags, while HDPE has greater strength and is used to make plastic squeeze bottles and Tupperware.

2. **Stereochemical control.** When polymerization is performed using monosubstituted ethylenes as monomers, the resulting polymer has a large number of chirality centers. The relative configurations of these chirality centers are classified as isotactic, syndiotactic, or atactic.
The term **isotactic** is used when all of the chirality centers have the same configuration, **syndiotactic** is used when the chirality centers have alternating configuration, and **atactic** is used when the chirality centers are not arranged in a pattern (they have random configurations). Isotactic, syndiotactic, and atactic polymers exhibit different properties, and all three can be made with the appropriate Ziegler-Natta catalyst.

**CONCEPTUAL CHECKPOINT**

27.19 Polyisobutylene cannot be described as isotactic, syndiotactic, or atactic. Explain.

27.20 Polyethylene is used to make Ziploc bags and folding tables. Identify which of these applications is most likely to be made from HDPE and which is most likely to be made from LDPE.

**Cross-Linked Polymers**

In the Practically Speaking box at the end of Section 17.5, we discussed natural and synthetic rubbers. Recall from that discussion that the vulcanization process introduces disulfide bridges between neighboring chains within the polymer.

The resulting polymer is said to be a **crossed-linked polymer**, which markedly affects the properties of the polymer. Disulfide bridges are not the only way for chains to cross-link. For example, chains can also be cross-linked with branches.

The conditions of polymer formation can be controlled so as to favor either a greater or lesser amount of cross-linking. This difference can have a profound impact on the properties of the resulting polymer, as we will see in the next section.
Crystalline vs. Amorphous Polymers

Many polymers contain regions, called **crystallites**, in which the chains are linearly extended and close in proximity to one another, resulting in van der Waals forces that hold the chains close together.

The regions that are not crystalline are called **amorphous** regions. Crystalline regions render a polymer hard and durable, while amorphous regions render a polymer flexible. The degree of crystallinity of a polymer, and therefore its physical properties, greatly depends on the steric requirements of the substituent(s) present in the repeating unit of the polymer. For example, compare the structures of polyethylene and polyisobutylene.

![Polyethylene and Polyisobutylene](image)

Linear polyethylene (HDPE) exhibits a high degree of crystallinity because there are no substituents to prevent the chains from closely packing. In contrast, polyisobutylene exhibits a low degree of crystallinity, because there are two methyl groups that provide steric bulk, preventing the chains from closely packing.

When highly crystalline polymers like HDPE are heated, the crystalline regions become amorphous at a specific temperature called the **melt transition temperature** ($T_m$). When noncrystalline polymers like polyisobutylene are heated, they become very soft. The temperature at which this transition takes place is called the **glass transition temperature** ($T_g$).

27.7 Polymer Classification by Properties

Polymers are also sometimes classified by their properties. The four most common categories are thermoplastics, elastomers, fibers, and thermosetting resins.

**Thermoplastics**

Thermoplastics are polymers that are hard at room temperature but soft when heated; that is, they exhibit a high $T_g$. Polymers in this category are very useful because they can be easily molded and are commonly used to make toys and storage containers. For example, PET is a thermoplastic used in the manufacture of soft-drink bottles. Other examples of thermoplastics include polystyrene, polyvinyl chloride (PVC), and low-density polyethylene.

Many thermoplastics become brittle at room temperature, which severely limits their utility. This is true of PVC. Pure PVC is highly susceptible to cracking at room temperature and is therefore useless for most applications. To avoid this problem, the polymer can be prepared in the presence of small molecules called **plasticizers**. These molecules become trapped between the polymer chains where they function as lubricants. Common plasticizers are dialkyl phthalates, such as di-2-ethylhexyl phthalate used in vinyl upholstery, raincoats, shower curtains, inflatable boats, and garden hoses. Some plasticizers evaporate slowly with time, and the polymer ultimately returns to a brittle
Elastomers

Elastomers are polymers that return to their original shape after being stretched. Elastomers are typically amorphous polymers that have a small degree of cross-linking. Natural rubber (described in Section 17.5) is one of the most common examples of an elastomer. A more contemporary example is Spandex, which is a polyurethane with a small degree of cross-linking. Spandex fibers are used to make bathing suits and athletic gear, among other applications.

Chewing gum is a complex mixture of polymers, many of which are elastomers. The polymer mixture, called the gum base, serves as a delivery vehicle for the flavors that are present in the mixture. Most gum manufacturers do not reveal the identity of the polymers present in their gum base, as this information is regarded as a trade secret. One thing is certain though: When you chew gum, you are chewing on a glob of synthetic polymers.

Fibers

Fibers are generated when certain polymers are heated, forced though small holes, and then cooled. The resulting fibers exhibit crystalline regions that are oriented along the axis of the fiber, which endow the fibers with significant tensile strength. Examples include Nylon, Dacron, and polyethylene, all of which have the appropriate degree of crystallinity to form fibers.

Thermosetting Resins

Thermosetting resins are highly cross-linked polymers that are generally very hard and insoluble. One such example is Bakelite, first produced in 1907 from the reaction between phenol and formaldehyde.

Phenol functions as a nucleophile, and formaldehyde (activated by protonation) functions as an electrophile in an electrophilic aromatic substitution reaction. The resulting alcohol then functions as an electrophile (again activated by protonation) and reacts with phenol in another electrophilic aromatic substitution reaction.

This process continues and can occur at the ortho and para positions of each ring.

Thermosetting resins can generally withstand high temperatures and are often used in high-temperature applications, such as missile nose cones.
Automobile windshields are specifically designed so that they do not create free shards of glass when broken. This is accomplished in very much the same way that bullet-resistant glass is manufactured, as described in the chapter opener. Two sheets of glass are pressed together with a thin layer of polymer between them. The polymer most often used is poly(vinyl butyral), often called PVB.

The PVB layer is generally prepared by treating polyvinyl alcohol with butyraldehyde.

The carbonyl group of butyraldehyde reacts with two hydroxyl groups to form a cyclic acetal. The resulting polyacetal adheres to both sheets of glass. In the event of a collision, the glass breaks, but the individual pieces remain stuck to the polymer interlayer, thereby preventing the pieces of glass from causing injury. Bullet-resistant glass is very similar, but multiple sheets of glass are used, rather than just two. Alternatively, bullet-resistant glass can also be made using thicker polycarbonate interlayers such as Lexan.

27.8 Polymer Recycling

Polymers have certainly increased our quality of life in countless ways, but their preparation and use have caused serious environmental concerns. Specifically, most synthetic polymers are not biodegradable, which means that they persist and accumulate in the environment. To address this growing problem, many polymers can be recycled. Some polymers are recycled with greater ease than others, depending on the identity of the polymer. For example, in the recycling of soft-drink bottles (made from PET) the bottles are chopped into small chips that are washed to remove the labels and adhesives, then treated with aqueous acid. A reaction occurs in which the polymer chips are broken down into the corresponding...
monomers. This process is essentially the reverse of the polymerization process that formed PET in the first place. The ester groups undergo hydrolysis to produce terephthalic acid and ethylene glycol.

These monomers are purified and then used as feedstock for the production of new PET. PET is somewhat unique in its ease of recycling, because the polymer can be converted back into monomers. As of yet, there is no way to break down addition polymers, such as polyethylene or polystyrene, into their corresponding monomers. These polymers can be melted down and remolded into a new shape or they can be broken down into smaller fragments in a process that is similar to the cracking of petroleum.

There are many logistical problems that limit the effectiveness of polymer recycling, most significantly the collection and sorting of used polymer products. Different kinds of polymers must be recycled in different ways. When recycling PET, a small amount of a different polymer present in the batch will interfere with the recycling process. As such, polymer recycling requires that polymer products be sorted by hand. To facilitate the sorting process, most polymer products are labeled with recycling codes that indicate their composition. These codes (1–7) indicate the type of polymer used and are arranged in order of ease with which the polymer can be recycled (1 being the easiest and 7 being the most difficult). Table 27.4 indicates the seven recycling codes, the polymers that correspond
with each code, and several uses for the recycled products. In many cases, the recycled polymer can be contaminated with adhesives and other materials that may have survived the washing stage. Therefore, recycled polymers cannot be used for food packaging.

CONCEPTUAL CHECKPOINT

27.21 Propose a mechanism for the acid-catalyzed hydrolysis of PET to regenerate the monomers terephthalic acid and ethylene glycol.

Another, more promising, method of reducing the accumulation of polymers in the environment is to develop polymers that are biodegradable and can be recycled by natural processes. **Biodegradable polymers** are polymers that can be broken down by enzymes produced by soil microorganisms. Much research is directed at the development of such polymers, and many have already been developed. Most biodegradable polymers exhibit ester or amide groups, which can be hydrolyzed by enzymes. Examples include a class of compounds called polyhydroxyalkanoates (PHAs), which are polymers of \(\beta\)-hydroxy carboxylic acids.

\[
\begin{align*}
\text{A \(\beta\)-hydroxy carboxylic acid} & \quad \text{A polyhydroxyalkanoate (PHA)} \\
\end{align*}
\]

There are many different PHAs, depending on the identity of the R group. The salient feature in all PHAs is the presence of the repeating ester groups, which are readily hydrolyzed. These ester groups serve as the “weak link” in the polymer. Much research has been devoted to creating polymers with weak links that render the polymers biodegradable. The decades to come are likely to see the emergence of new biodegradable polymers with properties that will rival the properties of traditional, nonbiodegradable polymers.

**REVIEW OF REACTIONS**

**Reactions for Formation of Chain-Growth Polymers**

**Radical Addition**

\[
\begin{align*}
\text{Heat or light} & \quad \text{ROOR} \\
\end{align*}
\]

**Anionic Addition**

\[
\begin{align*}
1) \text{BuLi} & \quad 2) \text{H}_2\text{O or CO}_2 \\
\end{align*}
\]

**Cationic Addition**

\[
\begin{align*}
\text{BF}_3, \text{H}_2\text{O} & \\
\end{align*}
\]

**Reactions for Formation of Step-Growth Polymers**

**Fischer Esterification**

\[
\begin{align*}
\text{ClCl} & \quad \text{HOR} \\
\end{align*}
\]

**Carbonate Formation**

\[
\begin{align*}
\text{HCl} & \\
\end{align*}
\]

Phosgene An alcohol A carbonate
CHAPTER 27 Synthetic Polymers

REVIEW OF CONCEPTS AND VOCABULARY

SECTION 27.1
- Polymers are comprised of repeating units that are constructed by joining monomers together.
- Synthetic polymers are prepared by scientists in the laboratory or in factories, while biopolymers are produced by living organisms.

SECTION 27.2
- The names of polymers are most commonly based on the monomers from which they are derived.

SECTION 27.3
- A homopolymer is a polymer made up of a single type of monomer. Polymers made from two or more different types of monomers are called copolymers.
- Alternating copolymers contain an alternating distribution of repeating units, while random copolymers contain a random distribution of repeating units.
- In a block copolymer, different homopolymer subunits are connected together in one chain. In a graft copolymer, sections of one homopolymer have been grafted onto a chain of another homopolymer.

SECTION 27.4
- Monomers can join together to form addition polymers by cationic, anionic, or free-radical addition.
- Most derivatives of ethylene will undergo radical polymerization under suitable conditions.
- Cationic addition is only efficient with derivatives of ethylene that contain an electron-donating group.
- Anionic addition is only efficient with derivatives of ethylene that contain an electron-withdrawing group, and polymers generated through this process are often called living polymers.
- Polymers generated via condensation reactions are called condensation polymers.
- Polycarbonates are similar in structure to polyesters, but with repeating carbonate groups instead of repeating ester groups.

SECTION 27.5
- Chain-growth polymers are formed under conditions in which each monomer is added to the growing chain one at a time. The monomers do not react directly with each other.
- Step-growth polymers are formed under conditions in which the individual monomers react with each other to form oligomers, which are then joined together to form polymers.
- In general, step-growth polymers are usually condensation polymers, while chain-growth polymers are usually addition polymers, but there are exceptions, such as polyurethanes.

SECTION 27.6
- Branched polymers contain a large number of branches connected to the main chain of the polymer, while linear polymers have only a minimal amount of branching.
- Polymers produced with Ziegler-Natta catalysts are generally linear polymers.
- When polymerization is performed using monosubstituted ethylenes as monomers, isotactic, syndiotactic, or atactic polymers can be formed, depending on the catalyst used.
- Crossed-linked polymers contain disulfide bridges or branches that connect neighboring chains.
- Most polymers contain some degree of cross-linking, and the conditions of polymer formation can be controlled so as to favor either more or less cross-linking.
- Many polymers contain regions called crystallites in which the chains are linearly extended and close in proximity to one another. The regions that are not crystalline are said to be amorphous.
- Crystalline regions become amorphous at the melt transition temperature ($T_m$).
- Noncrystalline polymers become soft at the glass transition temperature ($T_g$).

SECTION 27.7
- Thermoplastics are polymers that are hard at room temperature but soft when heated. They are often prepared in the presence of plasticizers to prevent the polymer from being brittle.
- Elastomers are polymers that return to their original shape after being stretched.
- Fibers are generated when certain polymers are heated, forced through small holes, and then cooled.
- Thermosetting resins are highly cross-linked polymers that are generally very hard and insoluble.

SECTION 27.8
- Most synthetic polymers persist and accumulate in the environment.
- For recycling purposes, polymer products are labeled with recycling codes that indicate their composition.
- Biodegradable polymers can be broken down by enzymes produced by microorganisms in the soil.
SKILLBUILDER REVIEW

27.1 DETERMINING WHICH POLYMERIZATION TECHNIQUE IS MORE EFFICIENT

**STEP 1** Identify the repeating units.

**STEP 2** Identify the monomer necessary to make this polymer.

**STEP 3** Determine whether the monomer bears an electron-withdrawing group or an electron-donating group:

- **EDGs**
  - Me
  - OMe
  - NR₂

- **EWGs**
  - CN
  - CHO
  - CO₂R

**STEP 4** If EWG, then use anionic addition. If EDG, then use cationic addition.

Try Problems 27.6–27.10, 27.27, 27.28, 27.34, 27.38–27.40

27.2 IDENTIFYING THE MONOMERS REQUIRED TO PRODUCE A DESIRED CONDENSATION POLYMER

**STEP 1** Identify the functional group that repeats itself.

**STEP 2** Identify the type of reaction that will produce the desired functional group.

**STEP 3** Identify the two difunctional monomers necessary to form the desired condensation polymer.

Try Problems 27.13–27.16, 27.23, 27.30a,b,d, 27.31, 27.32

PRACTICE PROBLEMS

Note: Most of the Problems are available within WileyPLUS.

27.22 Draw and name the polymer that results when each of the following monomers undergoes polymerization:

(a) Nitroethylene  
(b) Acrylonitrile  
(c) Vinylidene fluoride

27.23 Kodel is a synthetic polyester with the following structure:

(a) Identify what monomers you would use to make Kodel.  
(b) Would you use acidic conditions or basic conditions for this polymerization process?

27.24 Draw the structures of the monomers required to make the following alternating copolymer:

\[
\text{Ph} \quad \text{CH}_2 \quad \text{Cl} \quad \text{H} \quad \text{Ph} \quad n
\]

27.25 Draw a region of a block copolymer constructed from isobutylene and styrene.

27.26 Draw a region of an alternating copolymer constructed from vinyl chloride and ethylene.

27.27 Identify which of the following monomers would be most reactive toward cationic polymerization:

\[
\text{OAc} \quad \text{CN} \quad \text{Cl}
\]

27.28 Identify which of the following monomers would be most reactive toward anionic polymerization:

\[
\text{OAc} \quad \text{CN} \quad \text{CH}_3
\]
27.29 Identify the repeating unit of the polymer formed from each of the following reactions and then determine whether the polymer is a chain-growth or a step-growth polymer.

\[
\begin{align*}
\text{(a)} & \quad \text{CO}_2\text{H} \quad \text{NH}_2 \\
\text{(b)} & \quad \text{OH} \quad \text{O} \quad \text{Cl} \\
\text{(c)} & \quad \text{OH} \quad \text{OH} \\
\end{align*}
\]

27.30 Quiana is a synthetic polymer that can be used to make fabric that mimics the texture of silk. It can be prepared from the following monomers:

\[
\begin{align*}
\text{(a)} & \quad \text{NH}_2 \quad \text{H}_3 \text{N} \\
\text{(b)} & \quad \text{OH} \quad \text{O} \quad \text{OH}
\end{align*}
\]

27.31 Draw the monomer(s) required to make each of the following condensation polymers:

\[
\begin{align*}
\text{(a)} & \quad \text{N} \quad \text{O} \quad \text{O} \\
\text{(b)} & \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O}
\end{align*}
\]

27.32 Draw the condensation polymer produced when 1,4-cyclohexanediol is treated with phosgene.

27.33 Determine whether the following pairs of monomers would form chain-growth polymers or step-growth polymers.

\[
\begin{align*}
\text{(a)} & \quad \text{HO} \quad \text{O} \quad \text{Cl} \\
\text{(b)} & \quad \text{NO}_2 \quad \text{Ph}
\end{align*}
\]

27.34 Nitroethylene undergoes anionic polymerization so rapidly that it is difficult to isolate nitroethylene without it polymerizing. Explain.

27.35 Explain why vinyl shower curtains develop cracks over time.

27.36 Polyformaldehyde, sold under the trade name Delrin, is a strong polymer used in the manufacture of many guitar picks. It is prepared via the acid-catalyzed polymerization of formaldehyde.

\[
\begin{align*}
\text{(a)} & \quad \text{HO} \quad \text{O} \quad \text{OH} \\
\text{(b)} & \quad \text{Cl} \quad \text{Cl}
\end{align*}
\]

27.37 The following monomer can be polymerized under either acidic or basic conditions. Explain.

\[
\begin{align*}
\text{CN} \quad \text{OMe}
\end{align*}
\]

27.38 Anionic polymerization of para-nitrostyrene occurs much more rapidly than anionic polymerization of styrene. Explain this difference in rate.

27.39 Cationic polymerization of para-methoxystyrene occurs much more rapidly than cationic polymerization of styrene. Explain this difference in rate.

27.40 Cationic polymerization of para-methoxystyrene occurs much more rapidly than cationic polymerization of meta-methoxystyrene. Explain this difference in rate.

27.41 Draw segments of the following polymers, indicating the stereochemistry with wedges and/or dashes.

\[
\begin{align*}
\text{(a)} & \quad \text{Syndiotactic poly(vinyl chloride)} \\
\text{(b)} & \quad \text{Isotactic polystyrene}
\end{align*}
\]

27.42 Consider the structure of the following polymer:

\[
\begin{align*}
\text{(a)} & \quad \text{Draw the monomers you would use to prepare this polymer.} \\
\text{(b)} & \quad \text{Determine whether this polymer is a step-growth polymer or a chain-growth polymer.} \\
\text{(c)} & \quad \text{Determine whether this polymer is an addition polymer or a condensation polymer.}
\end{align*}
\]
INTEGRATED PROBLEMS

27.43 Draw the polymer that is expected when the following monomers react under acidic conditions. You may find it helpful to review Section 20.6.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{H}_2\text{N} & \quad \text{OH} \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O}
\end{align*}
\]

27.44 As described in the Practically Speaking box in Section 27.7, poly(vinyl alcohol) is used as a precursor to make PVB for use in automobile windshields. Poly(vinyl alcohol) can be prepared by polymerizing vinyl acetate and then removing the acetate groups via hydrolysis.

This two-step process is required because poly(vinyl alcohol) cannot be made from its corresponding monomer. Explain why vinyl alcohol will not directly undergo polymerization.

27.45 When a solution of aqueous sodium hydroxide is spilled on polyester clothing, a hole develops in the fabric. Describe how the polyester is destroyed.

CHALLENGE PROBLEMS

27.46 When 3-methyl-1-butene is treated with a catalytic amount of BF₃ and H₂O, a cationic polymerization process occurs, but the expected homopolymer is not formed. Instead, a random copolymer is obtained.

(a) Explain why there are two different repeating units.
(b) Draw a segment of the random copolymer that is formed, clearly showing the two different repeating units.
(c) Would you expect cationic polymerization of 3,3-dimethyl-1-butene to produce a random copolymer as well? Justify your answer.

27.47 When ethylene oxide is treated with a strong nucleophile, the epoxide ring is opened to form an alkoxide ion that can function as a nucleophile to attack another molecule of ethylene oxide. This process repeats itself, and a polymer is formed.

The resulting polymer is called poly(ethylene oxide) or poly(ethylene glycol). It is sold under the trade name Carbowax and is used as an adhesive and a thickening agent.

(a) Draw a mechanism showing the formation of a segment of poly(ethylene oxide).
(b) Ethylene oxide can also be polymerized when treated with an acid. Draw the mechanism of formation of a segment of poly(ethylene oxide) under acidic conditions.

(c) Identify the monomer you would use to prepare the following polymer:

(d) Determine whether you would use basic conditions or acidic conditions to prepare the following polymer. Explain your choice.

27.48 Using vinyl acetate as your only source of carbon atoms, design a synthesis for the following polymer: