8.6 Reactions of Alkenes

As we saw in Chapter 7, small alkanes can be formed by the process of thermal cracking. This process also produces alkenes and alkynes. In comparison to alkanes, alkenes and alkynes are much more reactive. In fact, alkenes serve as the starting point for the synthesis of many drugs, explosives, paints, plastics and pesticides. Alkanes can undergo five major types of reactions: (1) Combustion Reactions, (2) Addition Reactions, (3) Elimination Reactions, (4) Substitution Reactions, and (5) Rearrangement Reactions. Since combustion reactions were covered heavily in Chapter 7, and combustion reactions with alkenes are not significantly different than combustion reactions with alkanes, this section will focus on the later four reaction types.

Addition Reactions

Most reactions that occur with alkenes are addition reactions. As the name implies, during an addition reaction a compound is added to the molecule across the double bond. The result is loss of the double bond (or alkene structure), and the formation of the alkane structure. The ***reaction mechanism*** of a reaction describes how the electrons move between molecules to create the chemical reaction. Note that in reaction mechanism diagrams, as shown in Figure 8.15, curved arrows are used to show where electrons are moving. The reaction mechanism for a generic alkene addition equation using the molecule X-Y is shown below:

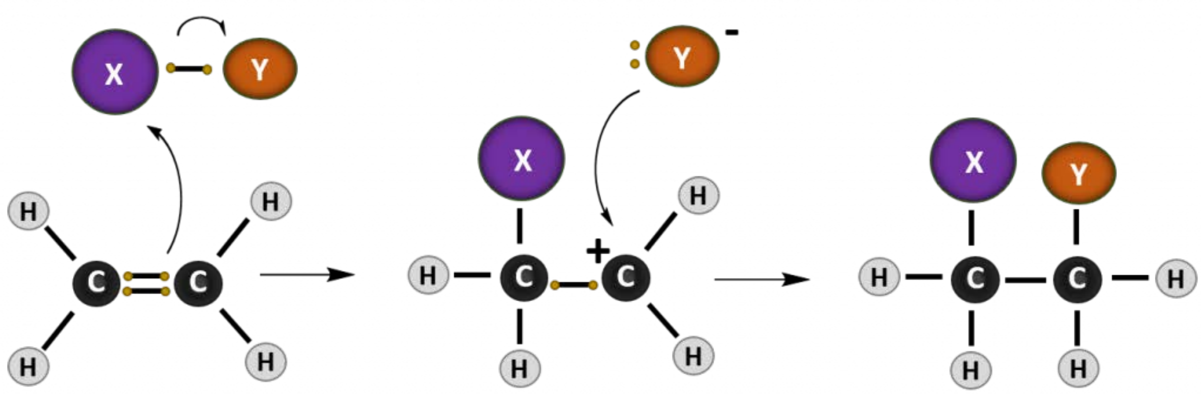


Figure 8.15. Reaction mechanism of a generic addition reaction. In this reaction, an electron from the carbon-carbon double bond of the alkene attacks an incoming molecule (XY) causing the breakage of the carbon-carbon double bond (lefthand diagram) and formation of a new bond between one of the alkene carbons and molecule X. The original electron from X that was participating in the shared bond with Y, is donated to Y causing the breakage of the X-Y bond. In the intermediate state (middle diagram), the alkene is carrying a positively charged carbon ion, called a ***carbocation***, and Y is in a negatively charged anion state. The negative anion is

attracted to the positively charged carbocation and donates the two electrons to form the C-Y bond and complete the product of the addition reaction (righthand diagram).

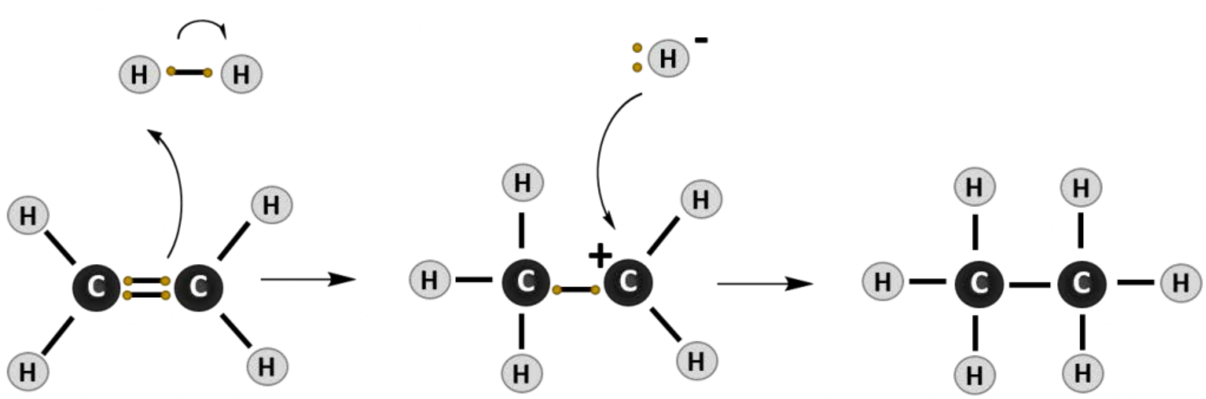
Key Takeaway:

Addition reactions convert an alkene into an alkane by adding a molecule across the double bond.

There are four major types of addition reactions that can occur with alkenes, they include: Hydogenation, Halogenation, Hydrohalogenation, and Hydration.

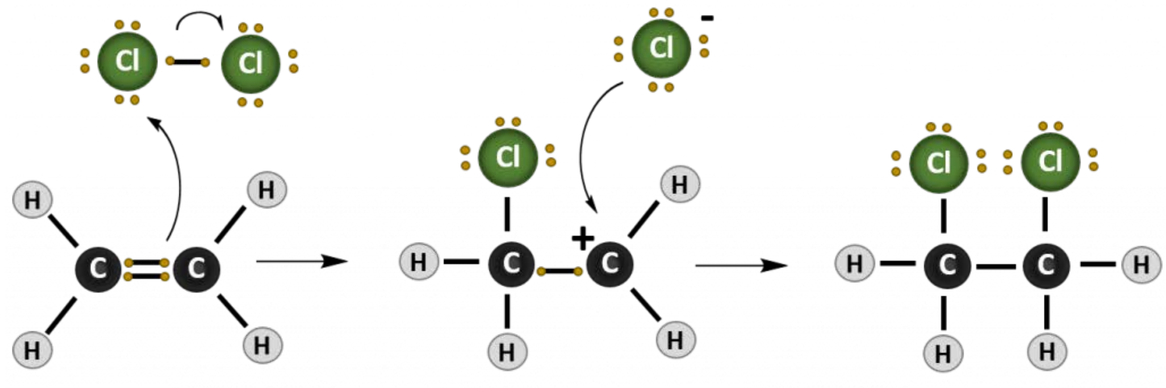
1. Hydrogenation

In a ***Hydrogenation*** reaction, hydrogen (H_2) is added across the double bond, converting an unsaturated molecule into a saturated molecule. Note that the word hydrogen is found in this reaction name, making it easier to remember and recognize: ***Hydrogen****-ation.* In a hydrogenation reaction, the final product is the saturated alkane.



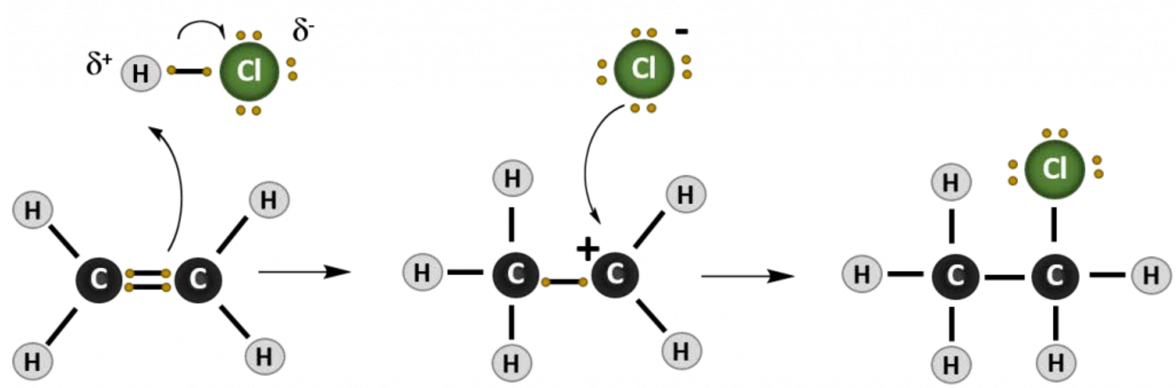
2. Halogenation

In a ***Halogenation*** reaction group 7A elements (the halogens) are added across the double bond. The most common halogens that are incorporated include chlorine (Cl_2), bromine (Br_2), and Iodine (I_2). Notice that the term halogen is found in this reaction name, making it easier to remember and recognize: ***Halogen****-ation.* In halogenation reactions the final product is haloalkane.



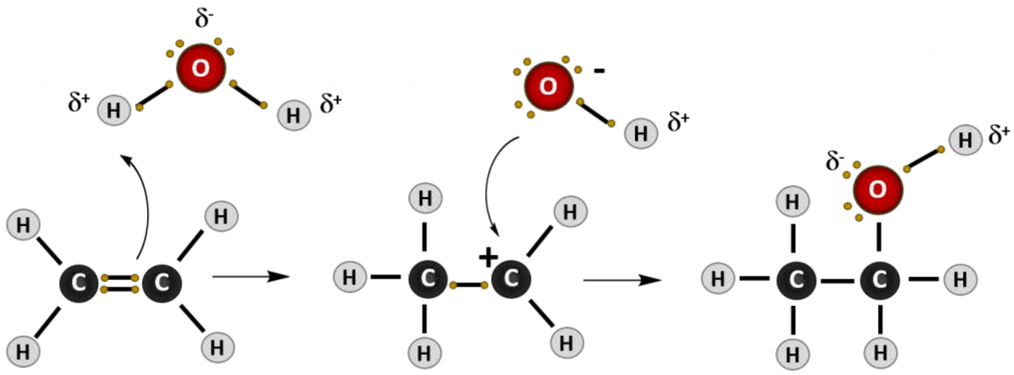
3. Hydrohalogenation

In ***Hydrohalogenation***, alkenes react with molecules that contain one hydrogen and one halogen. Hence the name ***Hydro***-***Halogen***-ation. HCl and HBr are common hydrohalogens seen in this reaction type. In hydrohalogenation, the hydrohalogen is a polar molecule, unlike the nonpolar molecules observed in the halogenation and hydrogenation reactions. In the case of the hydrohalogen, the end of the molecule containing hydrogen is partially positive, while the end of the molecule containing the halogen is partially negative. Thus, when the negatively charged electron from the alkene double bond attacks the hydrohalogen, it will preferentially attack the hydrogen side of the molecule, since the electron will be attracted to the partial positive charge. The halogen will then form the negatively charged anion observed in the intermediate structure and attach second during the addition reaction. The final product is a haloalkane.



4. Hydration

Just like when your are feeling thirsty, the terms ***hydration*** and ***dehydration*** refer to water. ***Hydration*** means the addition of water to a molecule, just like when you feel fully hydrated or full of water, while ***dehydration*** means the removal or elimination of water, just as when you are feeling dehydrated and need some water to drink. Similar to the hydrohalogenation reaction above, water is also a polar molecule. In this case, the water is split into two groups to be added across the double bond of the alkene. It is split into the H- and the -OH components. Similar to the hydrohalogenation reaction, the hydrogen adds first, as it carries the partial positive charge. the OH group forms the negative anion intermediate and is then added to the carbocation to form the final product, which is an alcohol.



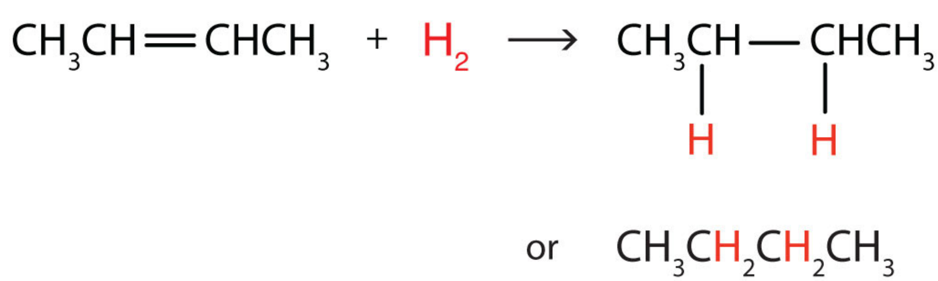
Extra Practice:

Write the equation for the reaction between $CH_3CH{=}CHCH_3$ and each substance.

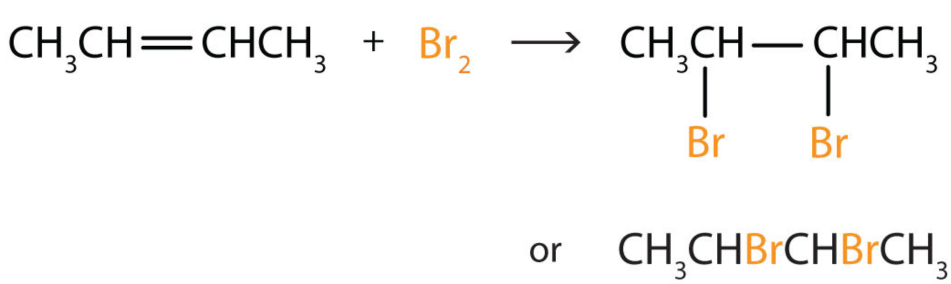
1. H_2
2. Br_2
3. H_2O

Solution

In each reaction, the reagent adds across the double bond.



1.



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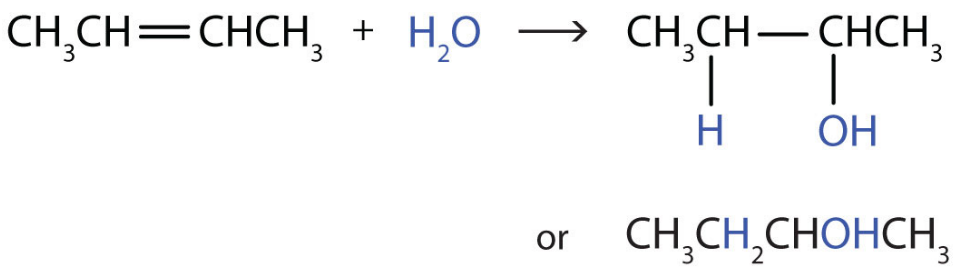


3.

Skill-Building Exercise

Write the equation for each reaction.

1. $CH_3CH_2CH{=}CH_2$ with H_2 (Ni catalyst)
2. $CH_3CH{=}CH_2$ with Cl_2
3. $CH_3CH_2CH{=}CHCH_2CH_3$ with H_2O (H_2SO_4 catalyst)

Concept Review Exercises

1. What is the principal difference in properties between alkenes and alkanes? How are they alike?
2. If $C_{12}H_{24}$ reacts with HBr in an addition reaction, what is the molecular formula of the product?

Answers

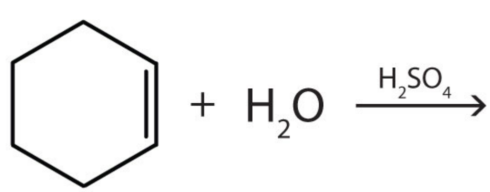
1. Alkenes undergo addition reactions; alkanes do not. Both burn.
2. $C_{12}H_{24}Br_2$

Key Takeaway

- Alkenes undergo addition reactions, adding such substances as hydrogen, bromine, and water across the carbon-to-carbon double bond.

Exercises

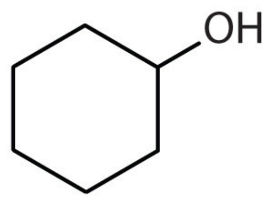
1. Complete each equation.
    1. $(CH_3)_2C{=}CH_2 + Br_2 \rightarrow$
    2. $CH_2{=}C(CH_3)CH_2CH_3 + H_2 \rightarrow Ni CH_2{=}C(CH_3)CH_2CH_3 + H_2 \rightarrow Ni$



    3.
2. Complete each equation.

1. $CH_2{=}CHCH{=}CH_2 + 2H_2 \rightarrow NiCH_2{=}CHCH{=}CH_2 + 2H_2 \rightarrow Ni$
2. $(CH_3)_2C{=}C(CH_3)_2 + H_2O \rightarrow (CH_3)_2C{=}C(CH_3)_2 + H_2O \rightarrow H_2SO_4$
3. 

Answer

1.
    1. $(CH_3)_2CBrCH_2Br$
    2. $CH_3CH(CH_3)CH_2CH_3$
    3. 

2.

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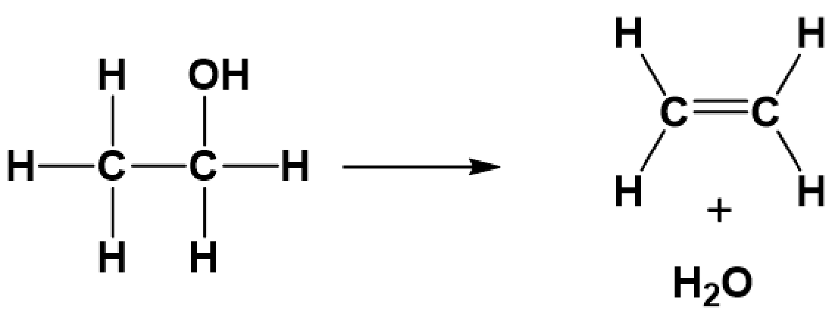
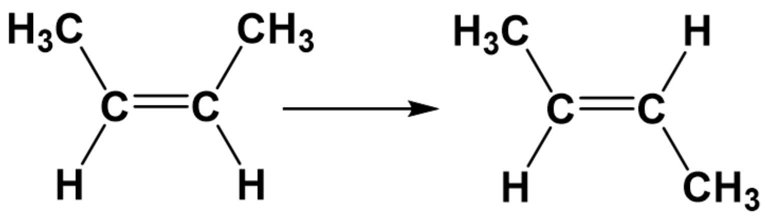
Elimination Reactions

In an elimination reaction a molecule loses a functional group, typically a halogen or an alcohol group, and a hydrogen atom from two adjacent carbon atoms to create an alkene structure. Elimination reactions are essentially the reverse reaction of the hydration and hydrohalogenation addition reactions. Elimination reactions can also occur with the removal of water from alcohol



Rearrangement Reactions

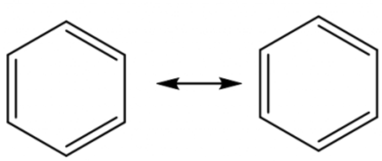
A rearrangement reaction is a specific organic reaction that causes the alteration of the structure to form an isomer. With alkene structures, rearrangement reactions often result in the conversion of a *cis*-isomer into the *trans* conformation.



Cis-conformation *Trans*-conformation

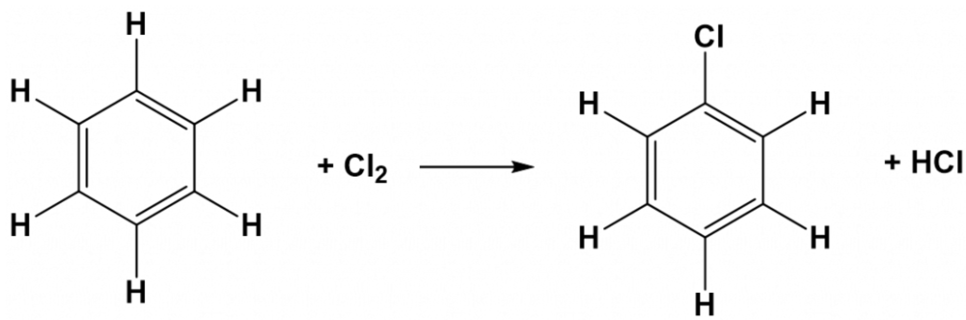
Substitution Reactions

Due to the high reactivity of alkenes, they usually undergo addition reactions rather than substitutions reactions. The exception is the benzene ring. The double-bonded structure of the benzene ring gives this molecule a resonance structure such that all of the carbon atoms in the ring share a continually rotating partial bond structure.



The benzene ring structure is stabilized by resonance. One of the few reactions that benzene rings will undergo are substitution reactions.

Thus, the overall structure is very stable compared to other alkenes and benzene rings do not readily undergo addition reactions. They behave more similarly to alkane structure and lack chemical reactivity. One of the few types of reactions that a benzene ring will undergo is a substitution reaction. Recall from Chapter 7 that in substitution reactions an atom or group of atoms is replaced by another atom or group of atoms. Halogenation is a common substitution reaction that occurs with benzene ring structures. In the diagram below, notice that the hydgrogen atom is substituted by one of the bromine atoms.



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8.7 Alkene Polymers

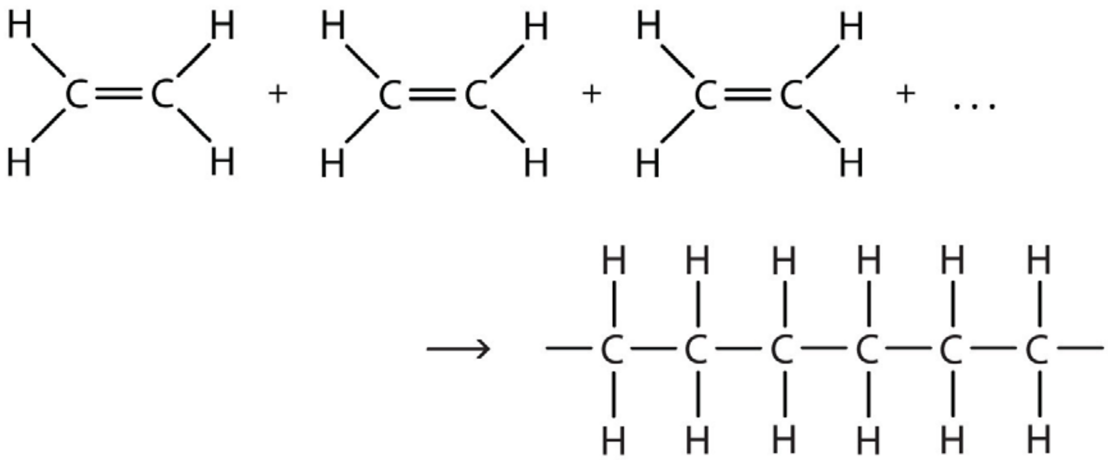
The most important commercial reactions of alkenes are *polymerizations*, reactions in which small molecules, referred to in general as ***monomers***, (from the Greek *monos*, meaning "one," and *meros*, meaning "parts"), are assembled into giant molecules referred to as ***polymers*** (from the Greek *poly*, meaning "many," and *meros*, meaning "parts"). A polymer is as different from its monomer as a long strand of spaghetti is from a tiny speck of flour. For example, polyethylene, the familiar waxy material used to make plastic bags, is made from the monomer ethylene—a gas.

The Production of Polyethene

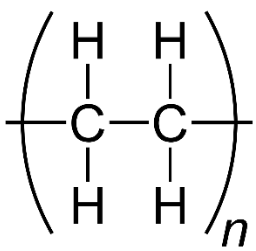
click to see the Royal Society of Chemistry Video on Polyethene Production

Polyethene pellets that are produced in factories can be melted, formed into a giant bubble, and then made into a film that is used in packaging, consumer products, and food services.

There are two general types of polymerization reactions: addition polymerization and condensation polymerization. This section will focus on addition polymerization reactions. (For more information about condensation polymerization, see Chapter 10) In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers. Ethylene molecules are joined together in long chains. The polymerization can be represented by the reaction of a few monomer units:



The bond lines extending at the ends in the formula of the product indicate that the structure extends for many units in each direction. Notice that all the atoms—two carbon atoms and four hydrogen atoms—of each monomer molecule are incorporated into the polymer structure. Because displays such as the one above are cumbersome, the polymerization is often abbreviated as follows, where *n* is the number of repeating units:



Structure from: [Magmar452]

Note

Many natural materials—such as proteins, cellulose and starch, and complex silicate minerals—are polymers. Artificial fibers, films, plastics, semisolid resins, and rubbers are also polymers. More than half the compounds produced by the chemical industry are synthetic polymers.

Some common addition polymers are listed in Table 8.2. Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.

Table 8.2 Some Addition Polymers

Monomer	Polymer	Polymer Name	Some Uses
$CH_2{=}CH_2$	$\sim CH_2CH_2CH_2CH_2CH_2CH_2\sim$	polyethylene	plastic bags, bottles, toys, electrical insulation
$CH_2{=}CHCH_3$	$\sim CH_2\underset{\underset{CH_3}{\vert}}{C}HCH_2\underset{\underset{CH_3}{\vert}}{C}HCH_2\underset{\underset{CH_3}{\vert}}{C}H\sim$	polypropylene	carpeting, bottles, luggage, exercise clothing
$CH_2{=}CHCl$	$\sim CH_2\underset{\underset{Cl}{\vert}}{C}HCH_2\underset{\underset{Cl}{\vert}}{C}HCH_2\underset{\underset{Cl}{\vert}}{C}H\sim$	polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$CF_2{=}CF_2$	$\sim CF_2CF_2CF_2CF_2CF_2CF_2\sim$	polytetrafluoro ethylene	nonstick coatings, electrical insulation

Medical Uses of Polymers

An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about a 250,000 hip joints and 500,000 knees are replaced in US hospitals each year. The artificial ball-and-socket hip joints are made of a special steel (the ball) and plastic (the socket). People crippled by arthritis or injuries gain freedom of movement and relief from pain. Patients with heart and circulatory problems can be helped by replacing worn out heart valves with parts based on synthetic polymers. These are only a few of the many biomedical uses of polymers.

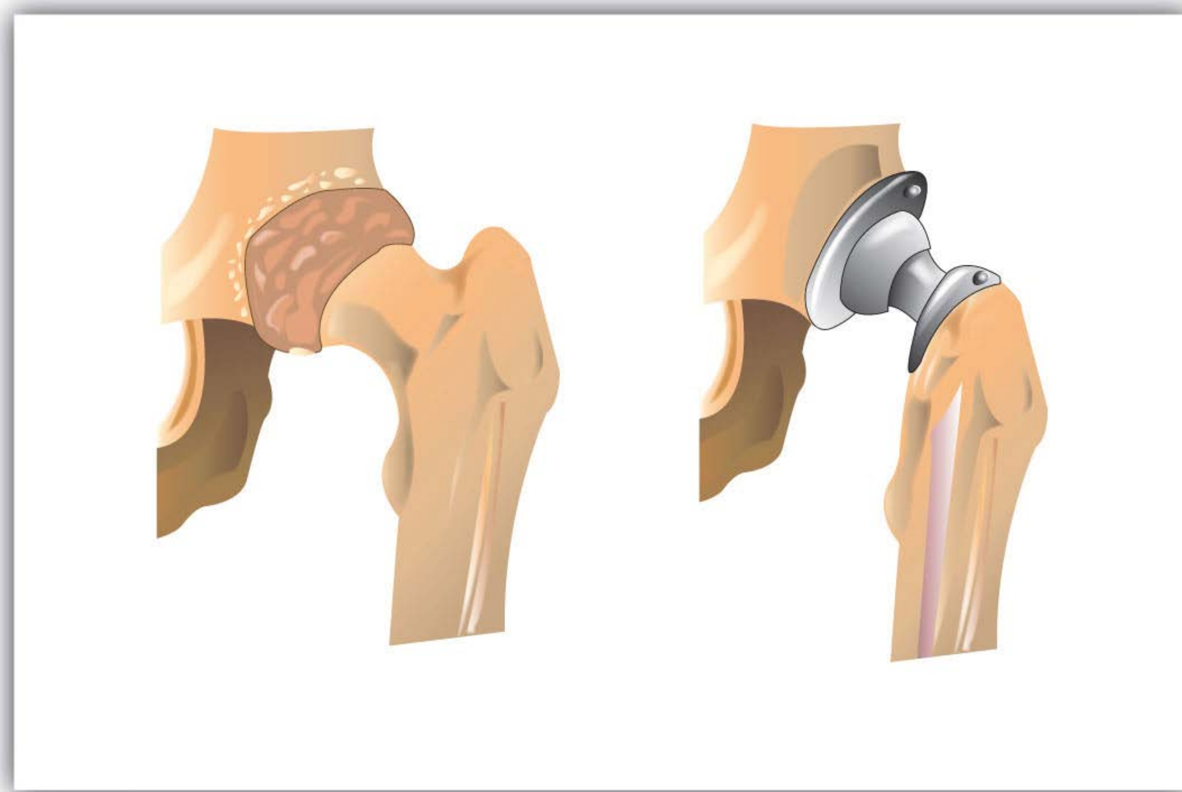


Figure 8.16 Hip Joint Replacement Synthetic polymers are an important part of a hip joint replacement. The hip is much like a ball-and-socket joint, and total hip replacements mimic this with a metal ball that fits in a plastic cup.

Concept Review Exercises

1. What is a monomer? What is a polymer? How do polymer molecules differ from the molecules we have discussed in earlier sections of this chapter?
2. What is addition polymerization? What structural feature usually characterizes molecules used as monomers in addition polymerization?
3. What is the molecular formula of a polymer molecule formed by the addition polymerization of 175 molecules of vinyl chloride (CH_2=CHCl)?

Answers

1. Monomers are small molecules that can be assembled into giant molecules referred to as polymers, which are much larger than the molecules we discussed earlier in this chapter.
2. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers.

3. $C_{350}H_{525}Cl_{175}$

Key Takeaway

- Molecules having carbon-to-carbon double bonds can undergo addition polymerization.

Exercises

1. Write the condensed structural formula of the monomer from which Saran is formed. A segment of the Saran molecule has the following structure: $CH_2CCl_2CH_2CCl_2CH_2CCl_2CH_2CCl_2$.
2. Write the condensed structural formula for the section of a molecule formed from four units of the monomer CH_2=CHF.

Answer

1. H_2C=CCl_2
2.

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