One of the most important technical reactions of alkenes is their conversion to higher-molecular-weight compounds or polymers (Table 10-4). A polymer is defined as a long-chain molecule with recurring structural units. Thus polymerization of propene gives a long-chain hydrocarbon with recurring units:

\[
\begin{align*}
\text{propane (propylene)} & \quad \text{polypropene (polypropylene)} \\
\text{CH}_3 & \quad \text{CH} = \text{CH}_2 \\
\end{align*}
\]

\[n \times \text{CH}_3\text{CH} = \text{CH}_2 \rightarrow \begin{array}{c} \text{CH}\text{CH}_2 \end{array}_n \quad \Delta H^\circ = -n \times 20 \text{ kcal}
\]

**Table 10-4: Alkene Monomers and Their Polymers**

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Formula</th>
<th>Type of addition polymerization</th>
<th>Polymer or Trade Name</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>CH(\equiv\text{CH}_2)</td>
<td>radical addition polymerization</td>
<td>Polyethylene</td>
<td>Films, extruded, tubing, packaging, fibers, adhesives</td>
</tr>
<tr>
<td>Propene</td>
<td>CH(\equiv\text{CH}_2)</td>
<td>ziegler</td>
<td>Polypropene</td>
<td>Fibers, adhesives, protective coatings</td>
</tr>
<tr>
<td>propylene</td>
<td>CH(_\text{2}\text{CH}_2\text{CH}_3)</td>
<td>radical</td>
<td>Polytetrafluoroethylene</td>
<td>Coatings, bearings, adhesives, fasteners</td>
</tr>
<tr>
<td>styrene</td>
<td>CH(_\text{2}\text{CH} = \text{CH}_2)</td>
<td>nucleophilic addition polymerization</td>
<td>Polystyrene</td>
<td>Filaments, adhesives, paper, plastic, rubber, coatings</td>
</tr>
<tr>
<td>acrylic acid</td>
<td>CH(_\text{2}\text{CH} = \text{CH}_2)</td>
<td>radical</td>
<td>Acrylic</td>
<td>Paints, adhesives, plastics, fibers</td>
</tr>
<tr>
<td>butadiene</td>
<td>CH(_\text{2}\text{CH} = \text{CH}_2)</td>
<td>radical</td>
<td>Butadiene</td>
<td>Rubbers, rubber articles, adhesives</td>
</tr>
<tr>
<td>isoprene</td>
<td>CH(_\text{2}\text{CH} = \text{CH}_2)</td>
<td>radical</td>
<td>Isoprene</td>
<td>Rubber, adhesives, plasticizers, coatings</td>
</tr>
<tr>
<td>tert-butyl acrylate</td>
<td>CH(_\text{2}\text{CH} = \text{CH}_2)</td>
<td>radical</td>
<td>Tertiary butyl acrylate</td>
<td>Adhesives, coatings, plasticizers</td>
</tr>
</tbody>
</table>

Most technically important polymerizations of alkenes occur by chain mechanisms and may be classed as anion, cation, or radical reactions, depending upon the character of the chain-carrying species. In each case, the key steps involve successive additions to molecules of the alkene, the differences being in the number of electrons that are supplied by the attacking agent for formation of the new carbon-carbon bond. For simplicity, these steps will be illustrated by using ethene, even though it does not polymerize very easily by any of them:

\[
\begin{align*}
&\text{R} - \text{CH}_2 - \text{CH}_2 - + \text{CH}_2 = \text{CH}_2 \rightarrow \text{R} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - , \text{ etc.} \\
&\text{R} - \text{CH}_2 - \text{CH}_2 - + \text{CH}_2 = \text{CH}_2 \rightarrow \text{R} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - , \text{ etc.} \\
&\text{R} - \text{CH}_2 - \text{CH}_2 - + \text{CH}_2 = \text{CH}_2 \rightarrow \text{R} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - , \text{ etc.}
\end{align*}
\]

### 10-8A Anionic Polymerization

Initiation of alkene polymerization by the anion-chain mechanism may be formulated as involving an attack by a nucleophilic reagent \(\text{Y}^-\) on one end of the double bond and formation of a carbanion:

\[
\text{Y}^- + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Y} : \text{CH}_2 = \text{CH}_2 :\text{carbanion}
\]
Attack by the carbanion on another alkene molecule would give a four-carbon carbanion, and subsequent additions to further alkene molecules would lead to a high-molecular-weight anion:

$$\text{Y:CH} - \text{CH}_2 - \text{CH} = \text{CH}_2 + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Y:CH}_2 - \text{CH} = \text{CH}_2 - \text{CH} = \text{CH}_2$$

$$\frac{n \times \text{CH} = \text{CH}_2}{\text{Y:CH} = \text{CH} + \text{CH} = \text{CH}_2 + \text{CH} = \text{CH}_2}$$

The growing chain can be terminated by any reaction (such as the addition of a proton) that would destroy the carbanion on the end of the chain:

$$\text{Y:CH}_2 - \text{CH} = \text{CH} + \text{CH} = \text{CH}_2 \rightarrow \text{Y:CH} = \text{CH} + \text{CH} = \text{CH}_2 - \text{CH} = \text{CH}_2$$

$$\frac{\text{H}^+}{\text{Y:CH} = \text{CH} + \text{CH} = \text{CH}_2 + \text{CH} = \text{CH}_2 - \text{CH} = \text{CH}_2}$$

Anionic polymerization of alkenes is quite difficult to achieve because few anions (or nucleophiles) are able to add readily to alkene double bonds (see Section 10-6). Anionic polymerization occurs readily only with alkenes substituted with sufficiently powerful electron-attracting groups to expedite nucleophilic attack. By this reasoning, alkenes should polymerize more readily than alkenes under anionic conditions, but there appear to be no technically important alkyne polymerizations in operation by this or any other mechanism. Perhaps this is because the resultant polymer would be highly conjugated, and therefore highly reactive, and may not survive the experimental conditions:

$$n \times \text{HC} = \text{CH} \rightarrow \text{YHC} = \text{CH} + (\text{CH} = \text{CH})_n \text{CH} = \text{CH}_2$$

Polymerization of an alkene by acidic reagents can be formulated by a mechanism similar to the addition of hydrogen halides to alkene linkages. First, a proton from a suitable acid adds to an alkene to yield a carbocation. Then, in the absence of any other reasonably strong nucleophilic reagent, another alkene molecule donates an electron pair and forms a longer-chain cation. Continuation of this process can lead to a high-molecular-weight cation. Termination can occur by loss of a proton. The following equations represent the overall reaction sequence:

$$\text{H}^+ + \text{CH}_2 = \text{CH}_2 \leftrightarrow \text{CH}_2 = \text{CH}_2 \text{CH}_2 = \text{CH}_2 \text{CH}_2 = \text{CH}_2 \text{CH} = \text{CH}_2$$

$$\frac{n \times \text{CH} = \text{CH}_2}{\text{CH}_2 = \text{CH}_2 + \text{CH}_2 = \text{CH}_2 + \text{CH} = \text{CH}_2}$$

$$\frac{\text{H}^+}{\text{CH}_2 = \text{CH}_2 + \text{CH}_2 = \text{CH}_2 + \text{CH} = \text{CH}_2}$$

Ethene does not polymerize by the cationic mechanism because it does not have sufficiently electron-donating groups to permit easy formation of the intermediate growing-chain cation. 2-Methylpropene has electron-donating alkyl groups and polymerizes much more easily than ethene by this type of mechanism. The usual catalysts for cationic polymerization of 2-methylpropene are sulfuric acid, hydrogen fluoride, or a complex of boron trifluoride and water. Under nearly anhydrous conditions a very long chain polymer called polyisobutylene is formed.
Polyisobutylene fractions of particular molecular weights are very tacky and are used as adhesives for pressure-sealing tapes.

In the presence of 60% sulfuric acid, 2-methylpropene is not converted to a long-chain polymer, but to a mixture of eight-carbon alkenes. The mechanism is like that of the polymerization of 2-methylpropene under nearly anhydrous conditions, except that chain termination occurs after only one 2-methylpropene molecule has been added:

The short chain length is due to the high water concentration; the intermediate carbocation loses a proton to water before it can react with another alkene molecule.

The proton can be lost in two different ways, and a mixture of alkene isomers is obtained. The alkene mixture is known as "diisobutylene" and has a number of commercial uses. Hydrogenation yields 2,2,4-trimethylpentane (often erroneously called "isooctane"), which is used as the standard "100 antiknock rating" fuel for internal-combustion gasoline engines:
10-8C Radical Polymerization

Ethene can be polymerized with peroxide catalysts under high pressure (\((1000 \text{ atm})\) or more, literally in a cannon barrel) at temperatures in excess of \((100^\circ\text{C})\). The initiation step involves formation of radicals, and chain propagation entails stepwise addition of radicals to ethene molecules.

\[
\begin{align*}
\text{initiation:} & \quad R\cdot + \cdot + R \rightarrow 2R\cdot \\
\text{propagation:} & \quad R\cdot + \text{CH}_2=\text{CH}_2 \rightarrow R\cdot: \text{CH}_2-\text{CH}_2 \\
& \quad R\cdot: \text{CH}_2-\text{CH}_2 \rightarrow R\cdot: \text{CH}_2-\text{CH}_2 + n \times \text{CH}_2=\text{CH}_2 \\
& \quad \rightarrow \text{RO}+\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2.
\end{align*}
\]

Chain termination can occur by any reaction resulting in combination or disproportionation of free radicals.

\[
\begin{align*}
\text{termination:} & \quad 2\text{RO}+\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \rightarrow \left[\text{RO}+\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\right]_2 \\
& \quad \text{combining} \\
2\text{RO}+\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \quad \overset{\text{H transfer}}{\rightarrow} \\
& \quad \text{RO}+\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 + \text{RO}+\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \\
& \quad \text{disproportionation}
\end{align*}
\]

The polyethene produced in this way has from 100 to 1000 ethene units in the hydrocarbon chain. The polymer possesses a number of desirable properties as a plastic and is used widely for electrical insulation, packaging films, piping, and a variety of molded articles. Propene and 2-methylpropene do not polymerize satisfactorily by radical mechanisms.

10-8D Coordination Polymerization

A relatively low-pressure, low-temperature ethene polymerization has been achieved with an aluminum-molybdenum oxide catalyst, which requires occasional activation with hydrogen (Phillips Petroleum process). Ethene also polymerizes quite rapidly at atmospheric pressure and room temperature in an alkane solvent containing a suspension of the insoluble reaction product from triethylaluminum and titanium tetrachloride (Ziegler process). Both the Phillips and Ziegler processes produce very high-molecular-weight polyethylene with exceptional physical properties. The unusual characteristics of these reactions indicate that no simple anion, cation, or radical mechanism can be involved. It is believed that the catalysts act by coordinating with the alkene molecules in somewhat the same way that hydrogenation catalysts combine with alkenes (Section 11-2A).

Polymerization of propene by the Ziegler process gives a very useful plastic material. It can be made into durable fibers or molded into a variety of shapes. Copolymers (polymers with more than one kind of monomer unit in the polymer chains) of ethene and propene made by the Ziegler process have highly desirable rubberlike properties and are potentially the cheapest useful elastomers (elastic polymers). A Nobel Prize was shared in 1963 by K. Ziegler and G. Natta for their work on alkene polymerization.

The properties and uses of polymers are discussed in greater detail in Chapters 13 and 29. The most important alkene monomers used in addition polymerizations are listed in Table 10-4 along with some names and uses of the
corresponding polymers.

References