

**B.Sc. Semester-VI
Organic Chemistry
Paper-XIV**

2. Synthetic Polymers

Coverage:

5. Free Radical Vinyl Polymerization: Mechanism and Examples



Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi

5. Addition or Chain-Growth Polymerization

The monomers used most commonly in chain-growth polymerization are ethylene (ethene) and substituted ethylenes. In the chemical industry, monosubstituted ethylenes are known as **alpha olefins**. Polymers formed from ethylene or substituted ethylenes are called **vinyl polymers**. Some of the many vinyl polymers synthesized by chain-growth polymerization are listed in Table 28.1.

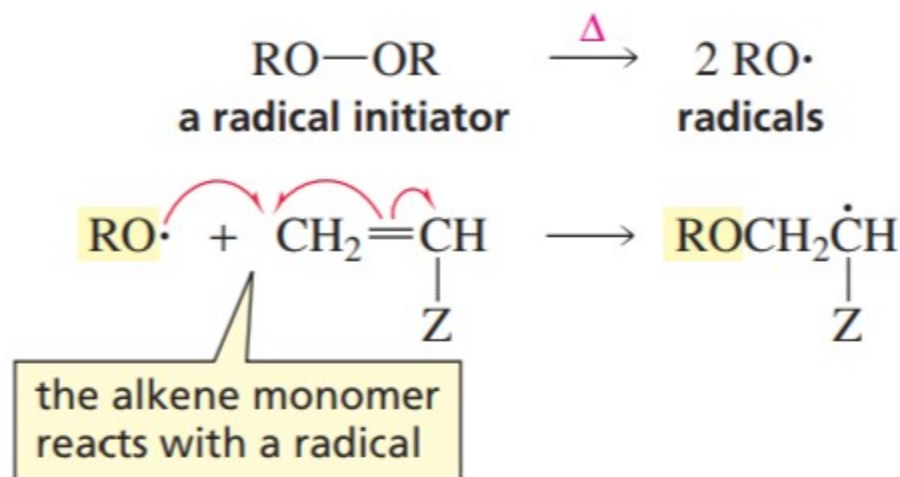
Chain-growth polymerization proceeds by one of three mechanisms: **radical polymerization**, **cationic polymerization**, or **anionic polymerization**. Each mechanism has three distinct phases: an *initiation step* that starts the polymerization, *propagation steps* that allow the chain to grow, and *termination steps* that stop the growth of the chain. We will see that the choice of mechanism depends on the structure of the monomer *and* the initiator used to activate the monomer.

5a. (i) Free Radical Vinyl Polymerization

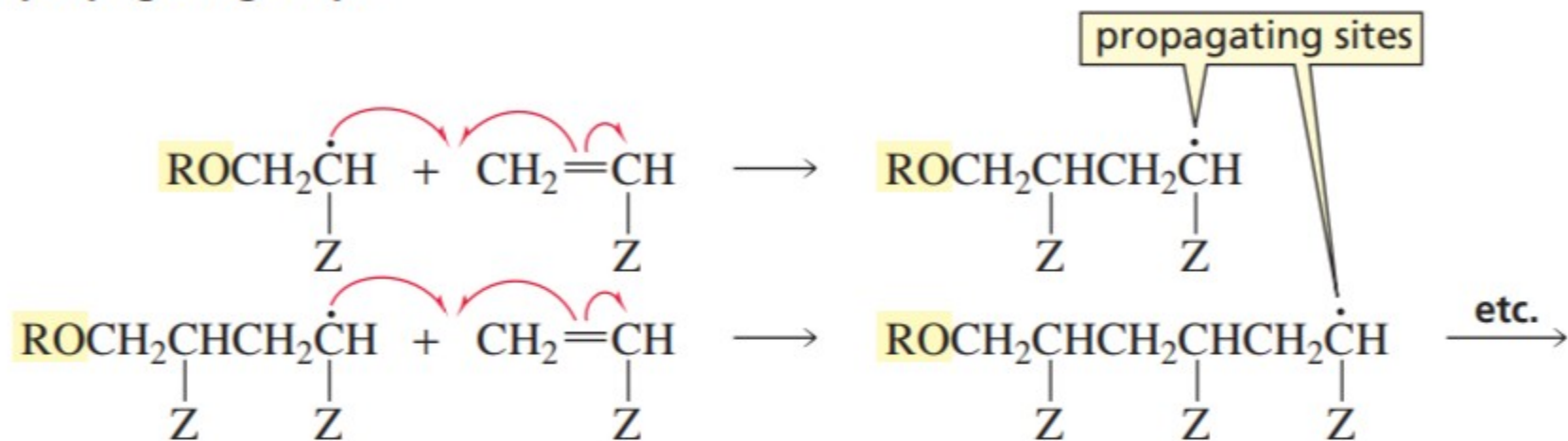
For chain-growth polymerization to occur by a radical mechanism, a radical initiator must be added to the monomer to convert some of the monomer molecules into radicals. The initiator breaks homolytically into radicals, and each radical adds to an alkene monomer, converting it into a radical. This radical reacts with another monomer, adding a new subunit that propagates the chain. The radical site is now at the end of the most recent unit added to the end of the chain. This is called the **propagating site**.

Mechanism:

chain-initiating steps



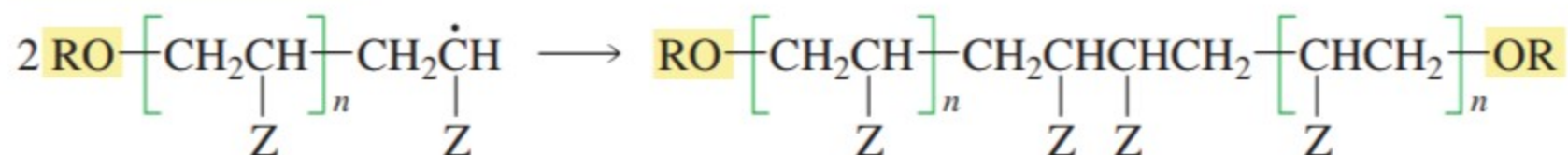
chain-propagating steps



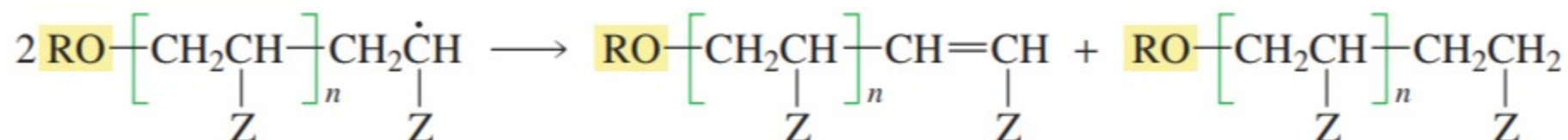
This process is repeated over and over. Hundreds or even thousands of alkene monomers can add one at a time to the growing chain. Eventually, the chain reaction stops because the propagating sites are destroyed. Propagating sites can be destroyed when two chains combine at their propagating sites; when two chains undergo *disproportionation*, with one chain being oxidized to an alkene and the other being reduced to an alkane; or when a chain reacts with an impurity that consumes the radical.

three ways to terminate the chain

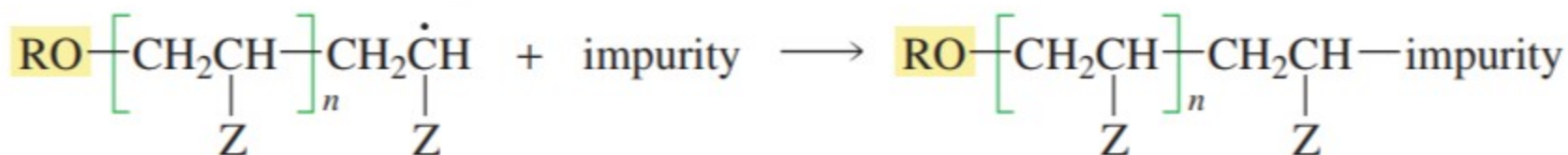
chain combination



disproportionation



reaction with an impurity

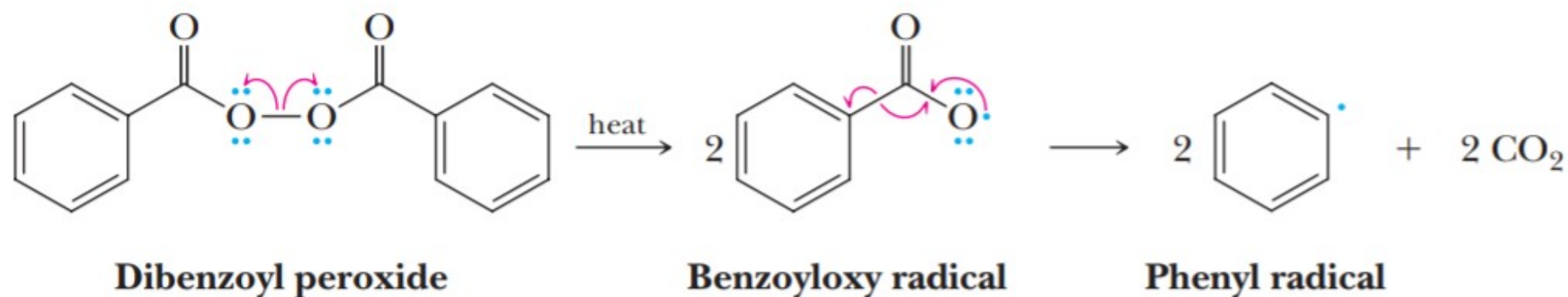


As long as the polymer has a high molecular weight, the groups at the ends of the polymer are relatively unimportant in determining its physical properties and are generally not even specified; it is the rest of the molecule that determines the properties of the polymer.

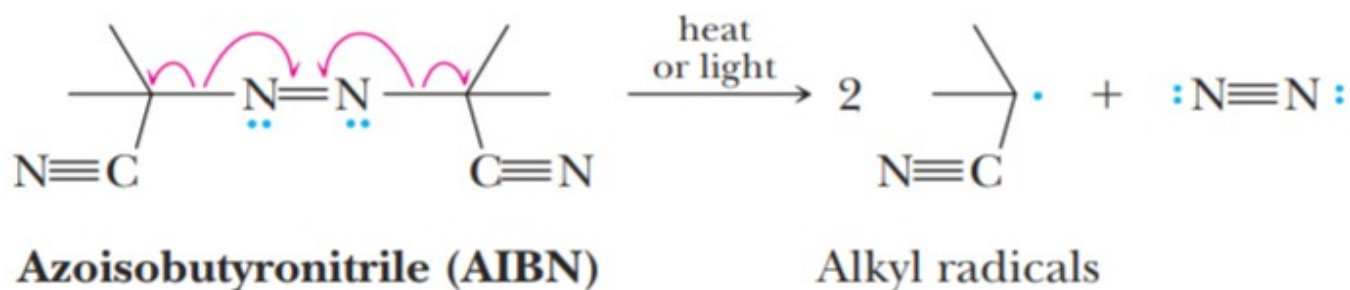
The molecular weight of the polymer can be controlled by a process known as **chain transfer**. In chain transfer, the growing chain reacts with a molecule XY in a manner that allows X• to terminate the chain, leaving behind Y• to initiate a new chain. XY can be a solvent, a radical initiator, or any molecule with a bond that can be cleaved homolytically.



Among the initiators used for radical chain-growth polymerizations are diacyl peroxides, such as dibenzoyl peroxide, which decompose as shown upon heating. In the first step, homolytic cleavage of the weak O—O peroxide bond yields two acyloxy radicals. Each acyloxy radical then decomposes to form an aryl radical and CO₂.

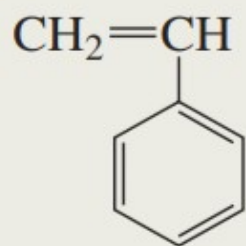


Another common class of initiators used in radical polymerizations is azo compounds, such as azoisobutyronitrile (AIBN), which decompose upon heating or by the absorption of UV light to produce alkyl radicals and nitrogen gas.

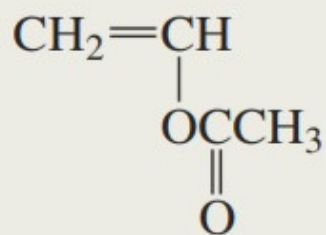


The chain initiation, propagation, and termination steps for radical polymerization of a substituted ethylene monomer are shown for the monomer RCH=CH₂. Dissociation of the initiator produces a radical that reacts with the double bond of a monomer. Once initiated, the chains continue to propagate through successive additions of monomers.

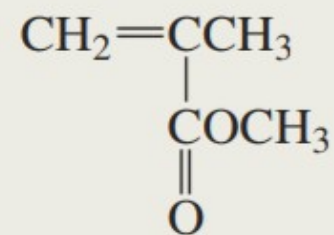
Table 1: Examples of Alkenes That Undergo Radical Polymerization



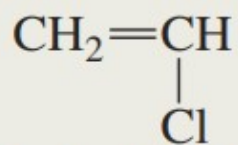
styrene



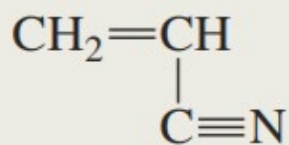
vinyl acetate



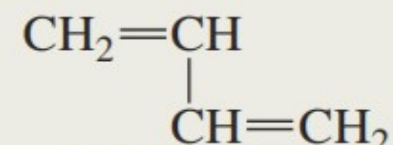
methyl methacrylate



vinyl chloride



acrylonitrile



1,3-butadiene

Any compound that readily undergoes homolytic cleavage to form radicals that are sufficiently energetic to convert an alkene into a radical can serve as an initiator for radical polymerization. Several radical initiators are shown in Table 2.

Table 2: Some Radical Initiators

