

8.10: RADICAL ADDITIONS TO ALKENES - CHAIN-GROWTH POLYMERS

OBJECTIVES

After completing this section, you should be able to

- write the detailed mechanism for the radical polymerization of an alkene.
- give examples of some common alkene monomers used in the manufacture of chain-growth polymers.
- identify the alkene monomer used to prepare a specific chain-growth polymer, given the structure of the polymer.

KEY TERMS

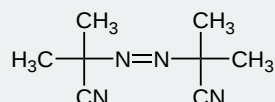
Make certain that you can define, and use in context, the key terms below.

- monomer
- polymer
- vinyl monomer

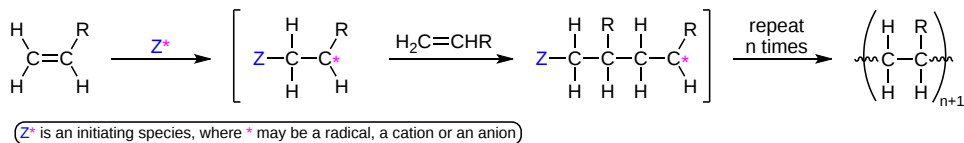
STUDY NOTES

Vinyl monomers are monomers of the type $\text{CH}_2=\text{CHX}$. Recall that the vinyl group is $\text{CH}_2=\text{CH}-$.

Although benzoyl peroxide is commonly used as an initiator in free-radical polymerization reactions, an alternative reagent is azobisisobutyronitrile, shown below.



A polymer is a large molecule built of repeat units of many monomers (smaller molecules). An example of this in the biological world is cellulose, which is a polymer composed of repeating glucose monomer units. A synthetic example would be of polyethylene, which is a polymer with ethylene as the repeating unit for the monomer. The most common and thermodynamically favored chemical transformations of alkenes are addition reactions. Many of these addition reactions are known to proceed in a stepwise fashion by way of reactive intermediates, and this is the mechanism followed by most polymerizations. A general diagram illustrating this assembly of linear macromolecules, which supports the name chain growth polymers, is presented here. Since a pi-bond in the monomer is converted to a sigma-bond in the polymer, the polymerization reaction is usually exothermic by 8 to 20 kcal/mol. Indeed, cases of explosively uncontrolled polymerizations have been reported.



It is useful to distinguish four polymerization procedures fitting this general description.

- **Radical Polymerization** The initiator is a radical, and the propagating site of reactivity (*) is a carbon radical.
- **Cationic Polymerization** The initiator is an acid, and the propagating site of reactivity (*) is a carbocation.
- **Anionic Polymerization** The initiator is a nucleophile, and the propagating site of reactivity (*) is a carbanion.
- **Coordination Catalytic Polymerization** The initiator is a transition metal complex, and the propagating site of reactivity (*) is a terminal catalytic complex.

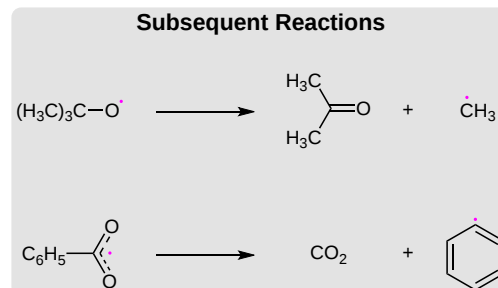
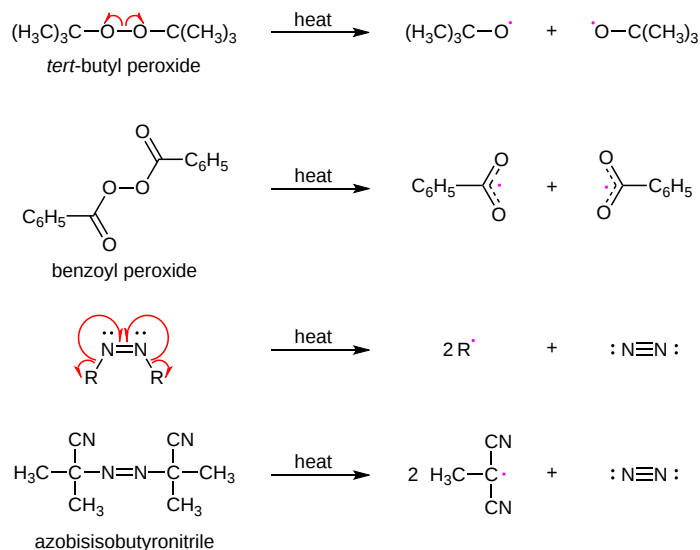
RADICAL CHAIN-GROWTH POLYMERIZATION

Chain-growth polymers are formed in a chain-reaction process. The first step involves an initiator to add to a carbon-carbon double bond in the first monomer, which results in a reactive intermediate. This intermediate reactive intermediate then goes and reacts with a second alkene monomer to yield another reactive intermediate. This process continues to grow the polymer from one monomer to many monomers until the termination step when the radical is consumed.

Note: In radical mechanisms, the arrow showing the movement of the electron looks like a "fish hook" or half-arrow as opposed to a full arrow, which indicates the movement of an electron pair.

Initiation: Virtually all of the monomers described above are subject to radical polymerization. Since radical polymerization can be initiated by traces of oxygen or other minor impurities, pure samples of these compounds are often "stabilized" by small amounts of radical inhibitors to avoid unwanted reaction. When radical polymerization is desired, it must be started by using a radical initiator, such as a peroxide or certain azo compounds. The formulas of some common initiators, and equations showing the formation of radical species from these initiators are presented below.

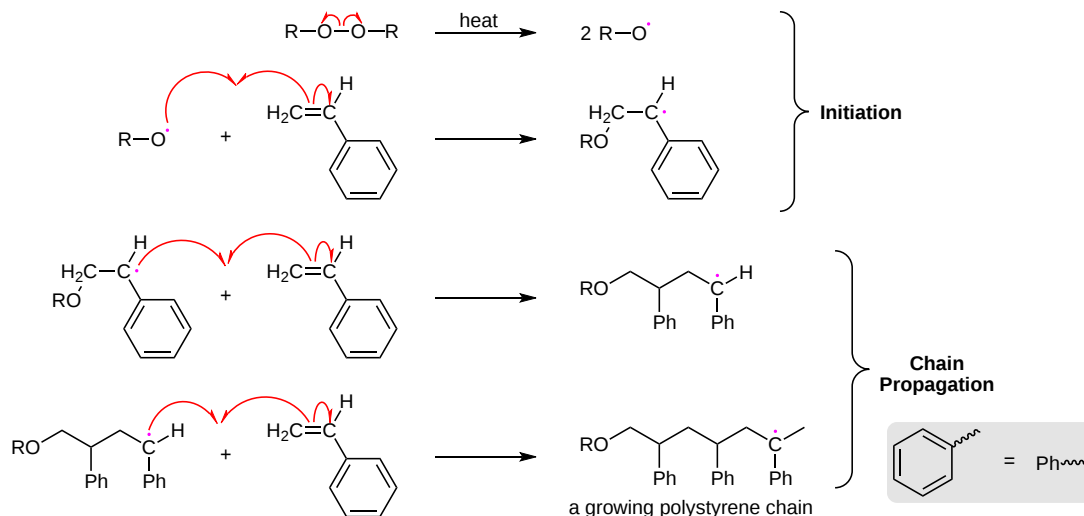
Some Radical Initiators



Propagation: Once the initiator has reacted with the alkene to create the carbon radical intermediate, it adds to another alkene molecule to yield another radical. This process repeats building the polymer chain.

Termination: The chain growing process ends when a reaction that consumes the radical happens. The most common processes are radical combination (two growing chains combine together) and disproportionation.

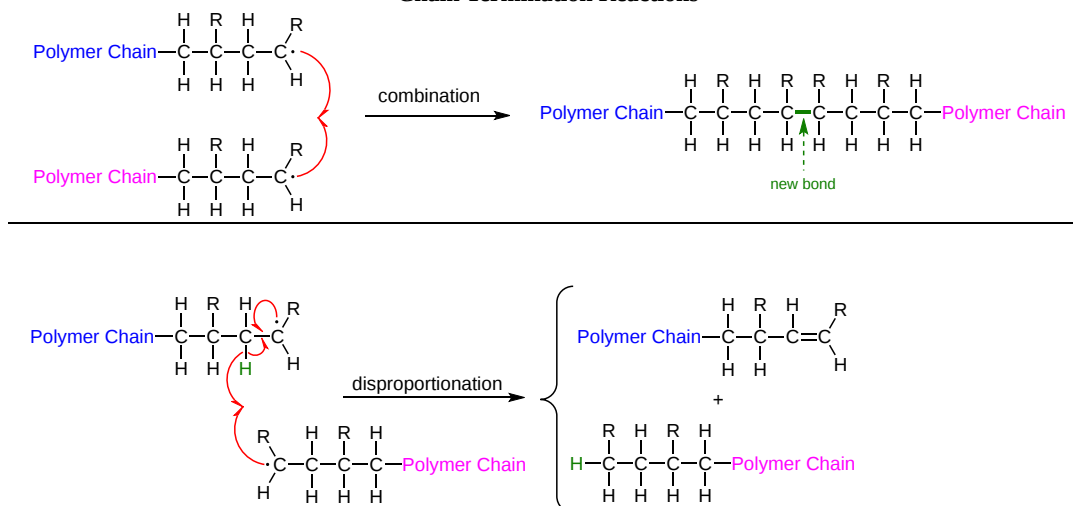
One example of this radical chain-growth polymerization is the conversion of styrene to polystyrene, shown in the following diagram. The first two equations illustrate the initiation process, and the last two equations are examples of chain propagation. Each monomer unit adds to the growing chain in a manner that generates the most stable radical. Since carbon radicals are stabilized by substituents of many kinds, the preference for head-to-tail regioselectivity in most addition polymerizations is understandable. Because radicals are tolerant of many functional groups and solvents (including water), radical polymerizations are widely used in the chemical industry.



In principle, once started a radical polymerization might be expected to continue unchecked, producing a few extremely long chain polymers. In practice, larger numbers of moderately sized chains are formed, indicating that chain-terminating reactions must be taking place. The most common termination processes are Radical Combination and Disproportionation. These reactions are illustrated by the following equations. The growing polymer chains are colored blue and red, and the hydrogen atom transferred in disproportionation is colored green. Note that in both types of termination two reactive radical sites are removed by simultaneous conversion to stable product(s).

Since the concentration of radical species in a polymerization reaction is small relative to other reactants (e.g. monomers, solvents and terminated chains), the rate at which these radical-radical termination reactions occurs is very small, and most growing chains achieve moderate length before termination.

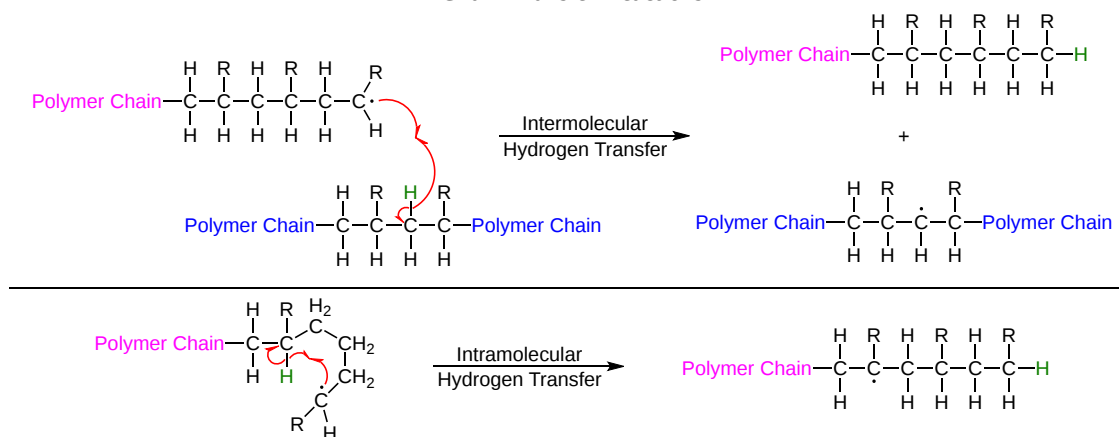
Chain Termination Reactions



The relative importance of these terminations varies with the nature of the monomer undergoing polymerization. For acrylonitrile and styrene combination is the major process. However, methyl methacrylate and vinyl acetate are terminated chiefly by disproportionation.

Another reaction that diverts radical chain-growth polymerizations from producing linear macromolecules is called chain transfer. As the name implies, this reaction moves a carbon radical from one location to another by an intermolecular or intramolecular hydrogen atom transfer (colored green). These possibilities are demonstrated by the following equations

Chain Transfer Reactions



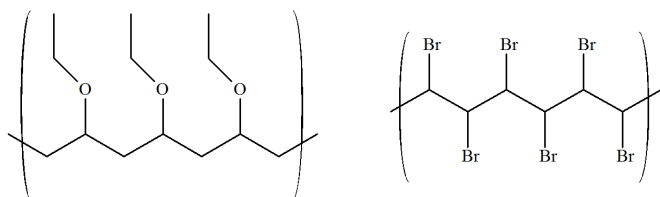
Chain transfer reactions are especially prevalent in the high pressure radical polymerization of ethylene, which is the method used to make LDPE (low density polyethylene). The 1°-radical at the end of a growing chain is converted to a more stable 2°-radical by hydrogen atom transfer. Further polymerization at the new radical site generates a side chain radical, and this may in turn lead to creation of other side chains by chain transfer reactions. As a result, the morphology of LDPE is an amorphous network of highly branched macromolecules.

EXERCISES

QUESTIONS

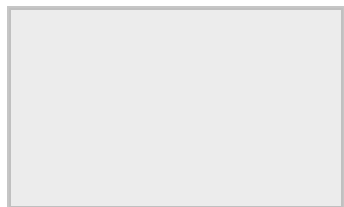
Q8.10.1

Propose the monomer units in the following polymers:



SOLUTIONS

S8.10.1



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