

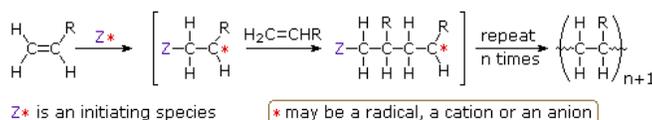
## 9.17: RADICAL CHAIN-GROWTH POLYMERIZATION

### Learning Objective

- predict the polymer/specify the monomer for radical, chain-growth polymers of alkenes

### INTRODUCTION

All the monomers from which addition polymers are made are alkenes or functionally substituted alkenes. 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.



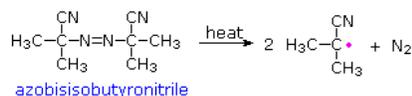
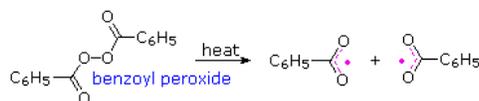
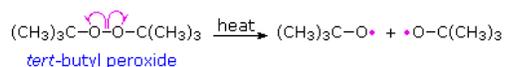
It is useful to distinguish four polymerization procedures fitting this general description.

- 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.

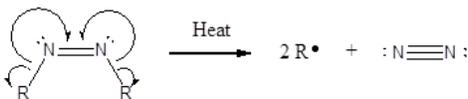
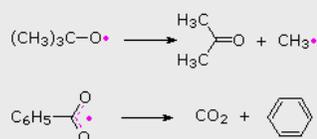
### RADICAL CHAIN-GROWTH POLYMERIZATION

Virtually all of the monomers described above are subject to radical polymerization. Since this 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



#### Subsequent Reactions



By using small amounts of initiators, a wide variety of monomers can be polymerized. One example of this radical 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.



