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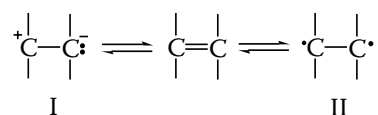
# 3 Free-Radical Addition Polymerization

## 3.1 ADDITION POLYMERIZATION

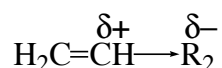
In step-growth polymerization reactions it is often necessary to use multifunctional monomers if polymers with high molar masses are to be formed; this is not the case when addition reactions are employed. Long chains are readily obtained from monomers such as vinylidene compounds with the general structure  $\text{CH}_2=\text{CR}_1\text{R}_2$ . These are bifunctional units, where the special reactivity of  $\pi$ -bonds in the carbon to carbon double bond makes them susceptible to rearrangement if activated by free-radical or ionic initiators. The active center created by this reaction then propagates a kinetic chain, which leads to the formation of a single macromolecule whose growth is stopped when the active center is neutralized by a termination reaction. The complete polymerization proceeds in three distinct stages: (1) *initiation*, when the active center which acts as a chain carrier is created; (2) *propagation*, involving growth of the macromolecular chain by a kinetic chain mechanism and characterized by a long sequence of identical events, namely the repeated addition of a monomer to the growing chain; and (3) *termination*, whereby the kinetic chain is brought to a halt by the neutralization or transfer of the active center. Typically the polymer formed has the same chemical composition as the monomer, i.e., each unit in the chain is a complete monomer, and not a residue as in most step-growth reactions.

## 3.2 CHOICE OF INITIATORS

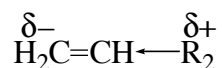
A variety of chain initiators is available to the polymer chemist. These fall into three general categories: *free radical*, *cationic*, and *anionic*. The choice of the most appropriate one depends largely on the groups  $\text{R}_1$  and  $\text{R}_2$  in the monomer and their effects on the double bond. This arises from the ability of the alkene  $\pi$ -bond to react in a different way with each initiator species to produce either heterolytic (I) or



homolytic (II) fission. In most olefinic monomers of interest the group  $\text{R}_1$  is either H or  $\text{CH}_3$ , and for simplicity we can consider it to be H. The group  $\text{R}_2$  is then classifiable as an electron-withdrawing group



or an electron-donating group



Both alter the negativity of the  $\pi$ -bond electron cloud and thereby determine whether a radical, an anion, or a cation will be stabilized preferentially.

In general, electron withdrawing substituents,  $-\text{CN}$ ,  $-\text{COOR}$ ,  $-\text{CONH}_2$ , reduce the electron density at the double bond and favor propagation by an anionic species. Groups that tend to increase the double-bond nucleophilicity by donating electrons, such as alkenyl, alkoxy, and phenyl, encourage attack by cationic initiators and, in addition, the active centers formed are resonance stabilized. Alkyl groups do not stimulate cationic initiation unless in the form of 1,1-dialkyl monomers or alkyl dienes, and then heterogeneous catalysts are necessary. As resonance stabilization of the active center is an important factor, monomers like styrene and 1,3-butadiene can undergo polymerization by both ionic methods because the anionic species can also be stabilized.

Because of its electrical neutrality, the free radical is a less selective and more generally useful initiator. Most substituents can provide some resonance stabilization for this propagating species.