

**TEXTBOOK**

**OF POLYMER SCIENCE**

**Second Edition**

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## Radical Chain (Addition) Polymerization

### *A. Chemistry of Vinyl Polymerization*

The polymerization of unsaturated monomers typically involves a chain reaction. It can be initiated by methods typical for simple gas-phase chain reactions, including the action of ultraviolet light. It is susceptible to retardation and inhibition. In a typical chain polymerization, one act of initiation may lead to the polymerization of thousands of monomer molecules.

The characteristics of chain polymerization listed in Table 8-1 suggest that the active center responsible for the growth of the chain is associated with a single polymer molecule through the addition of many monomer units. Thus polymer molecules are formed from the beginning, and almost no species intermediate between monomer and high-molecular-weight polymer are found. Of several postulated types of active center, three have been found experimentally: cation, anion, and free radical. Free radical polymerization is discussed in this chapter, and the related cases of ionic and coordination polymerization are described in Chapter 10.

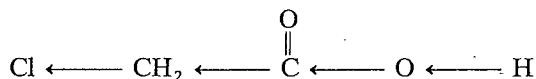
The concept of vinyl polymerization as a chain mechanism is not new, dating back to Staudinger's work in 1920. However, an alternative mechanism of a stepwise reaction involving hydrogen transfer was seriously considered as late as 1936. The controversy was largely settled by Flory's analysis of the kinetics of vinyl polymerization in 1937. He showed conclusively that radical polymerization proceeds by and requires the steps of initiation, propagation, and termination typical of chain reactions in low-molecular-weight species.

#### *Vinyl monomers*

***Electronic structures of organic compounds*** As noted in Chapter 1C, most organic compounds involve covalent or shared-electron bonds. Single covalent bonds have bond electrons which are distributed within a considerable

volume of space between the two nuclei and symmetrically about the line connecting them. In a double bond, the presence of the second pair of electrons destroys the axial symmetry, modifying the volume within which the electrons are found to a ribbonlike band between the nuclei. As a result there is a high energy barrier preventing free rotation, and *cis-trans* isomers become possible. The fact that the second electron pair is held only about 70% as firmly as the first leads to high polarizability and chemical reactivity in unsaturated compounds.

The positions and reactivities of the electrons in unsaturated molecules are subject to several geometrical and electrical influences. *Mesomerism* and *resonance* are used to explain certain facts, such as the equivalence of the reactivity of all the hydrogen atoms in benzene. The presence of strongly electropositive or electronegative groups in a molecule may cause an *inductive shift* of electrons. In chloroacetic acid, e.g., the shift of electrons toward the chlorine atom effectively increases the strength of the acid:



A further effect is purely *electrostatic* in nature: if, e.g., an atom or group of atoms is substituted for a hydrogen atom adjacent to a double bond, the electrostatic force exerted by the electrons of the substituent on those of the double bond affects the reactivity of the molecule.

The end result of these influences is that the reaction of the double bond with a free radical proceeds well for compounds of the type  $\text{CH}_2=\text{CHX}$  and  $\text{CH}_2=\text{CXY}$ , called *vinyl monomers*. (Monomers in which fluorine is substituted for hydrogen may be included in this class.) The polymerization of monomers with more than one double bond is considered in Chapter 12.

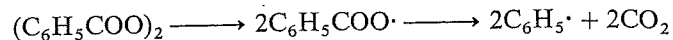
Not all vinyl monomers yield high polymer as a result of radical polymerization. Aliphatic hydrocarbons other than ethylene polymerize only to oils; 1,2-disubstituted ethylenes not at all. Among compounds of the type  $\text{CH}_2=\text{CXY}$ , those in which both groups are larger than  $\text{CH}_3$  polymerize slowly if at all.

#### Mechanism of vinyl radical polymerization

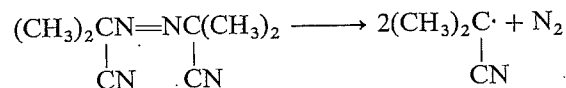
**Generation of free radicals** Many organic reactions take place through intermediates having an odd number of electrons and, consequently, an unpaired electron. Such intermediates are known as *free radicals*. They can be generated in a number of ways, including thermal decomposition of organic peroxides or hydroperoxides (Mageli 1968) or azo or diazo compounds (Zand 1965). Other modes of generation of free radicals, occasionally used to initiate polymerization, include photolytic decomposition of covalently bonded compounds (photoinitiation, Section B); dissociation of covalent

bonds by high-energy radiation (Chapter 12F); oxidation-reduction reactions (redox initiation, Chapter 12B); and electrochemical initiation (Friedlander 1966; Funt 1967).

Two reactions commonly used to produce radicals for polymerization are the thermal or photochemical decomposition of benzoyl peroxide:

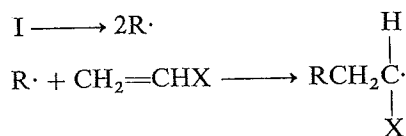


and of azobisisobutyronitrile:



The stability of radicals varies widely. Primary radicals are less stable and more reactive than secondary radicals, which are in turn less stable than tertiary ones. (Some tertiary radicals, such as the triphenylmethyl, can be isolated in the solid state without decomposition.) The phenyl radical is more reactive than the benzyl radical, the allyl radical is quite unreactive, and so on.

**Initiation** When free radicals are generated in the presence of a vinyl monomer, the radical adds to the double bond with the regeneration of another radical. If the radical formed by decomposition of the *initiator* I is designated R·,



The regeneration of the radical is characteristic of chain reactions.

Evidence for the radical mechanism of addition polymerization comes not only from the capability of radicals to accelerate vinyl polymerization but also from the demonstration that the polymers so formed contain fragments of the radicals. The presence of heavy atoms, such as bromine or iodine, or radioactive atoms, in the initiator has been shown many times to lead to polymers from which these atoms cannot be removed.

The efficiency with which radicals initiate chains can be estimated by comparing the amount of initiator decomposed with the number of polymer chains formed. The decomposition of the initiator can usually be followed by analytical methods. The most direct method of finding the initiator efficiency then depends upon analyzing the polymer for initiator fragments. This is not difficult in cases where the initiator leaves a reactive end group on the polymer or is radioactively tagged. In other polymerizations it is more useful to determine the number of polymer molecules formed from the number-average molecular weight of the polymer. Still another alternative, sometimes of doubtful validity, is to react the chain radical stoichiometrically

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