1. General Remarks

The process yielding the first species capable of being linked with a monomer molecule by a covalent bond while simultaneously endowing the added monomer unit with the activity associated with the initiator is the initiation of addition polymerization. The addition of an anion $A^-$ to a vinyl monomer $\text{CH}_2=\text{CH}X$ yielding a new $A\cdot\text{CH}_2\overline{\text{CH}}X$ anion is an example of initiation of ionic polymerization. The addition of the next monomer molecule yields the same end-group but attached to a longer tail, i.e. $A\cdot\text{CH}_2\overline{\text{CH}}X\cdot\text{CH}_2\overline{\text{CH}}X$. The sequence of the latter events constitutes the propagation of polymerization.

Propagation perpetuated by a positively charged end-group, or induced by a positive end of a reactive dipole, is known as a cationic, or pseudo-cationic, polymerization. Similarly, an anionic or pseudo-anionic polymerization ensues when a negatively charged end-group, or a negative end of a dipole, constitutes the active, propagating center. On the whole, the initiator, or its fragment, remains associated in some fashion with the active end of an ionically growing macromolecule during the whole period of its growth. For example, the counterion accompanying the initiating anion mentioned in the preceding paragraph becomes now a chaperoon of the newly formed polymer. Hence, the propagation constant, the mode of monomer addition, and the other characteristic features of ionic polymerizations are affected by the nature of the initiator. In this respect ionic propagation differs from radical propagation since the initiator does not affect the rate constant of propagation of the latter polymerization, a point previously stressed in Chapter 1.

The various processes that initiate ionic polymerization may be classified under the headings: the initiations by salts, i.e., by free ions and their...
various aggregates; the initiations by protic and Lewis acids or by Lewis bases; the initiations induced by electron transfer; and the initiations caused by ionizing radiation. The propagation of polymerization, the process resembling the initiation by salts, is discussed in the first section of this chapter, and photochemical initiations are reviewed in the section dealing with electron transfer processes. This classification, although not sharp, helps to systematize the various phenomena observed in this large field of divergent chemical reactions.

Some initiators of ionic polymerizations require activation by reagents either present in the system prior to monomer addition or added subsequently. Such initiations are complex and often result in the establishment of an equilibrium between active and dormant species. Although the latter do not initiate polymerization, they do participate in the reaction, because, due to the dynamic nature of the equilibrium, they are ceaselessly and reversibly converted into the active species.

The simplest mode of initiation of polymerization arises upon the addition of an initiator or its active fragment, denoted by $X$, to a monomer $M$, i.e.,

$$X + M \rightarrow X\cdot M^*.$$  

Such an addition could be reversible and then its rate is given by:

$$-d[X]/dt = k_i[X]\cdot[M]\cdot(k_p[M]/(k_i + k_p[M])),$$

where $k_p$ denotes the rate constant of monomer addition to $X\cdot M^*$, and $k_i$ and $k_{-i}$ are the forward and backward rate constants of the $X$ addition to the monomer. For $k_{-i} << k_p[M]$ this equation yields the rate of initiation, first order in $X$ and $M$. At the other extreme, for $k_{-i} >> k_p[M]$, the $-d[X]/dt$ pertains to the rate of initiator consumption while at equilibrium with the monomer. The consumption is then first order in $X$ but second order in $M$, i.e., $-d[X]/dt = k_pK_e[X]\cdot[M]^2$ with $K_e = k_i/k_{-i}$. The addition is always exothermic, and when its exothermicity exceeds the activation energy of the monomer addition to $X\cdot M^*$ the polymerization speeds up on lowering the temperature and its apparent activation energy is negative.

It is beneficial when the rate of initiation is faster than, or at least equal to, the rate of propagation. Under such conditions polymers of narrow molecular mass distribution could be formed, provided that the system is "living," i.e., the termination and chain-transfer are virtually avoided.

Most of the initiators of ionic polymerization are labile. Attention has to be paid to their integrity; their decomposition or isomerization must be prevented. For example, sodium naphthalenide, an initiator frequently used in anionic polymerization, isomerizes when kept in solution at am-