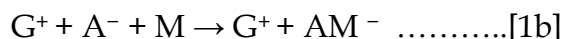


Kinetics of Anionic Polymerization

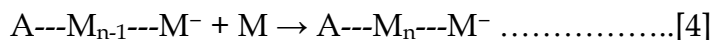
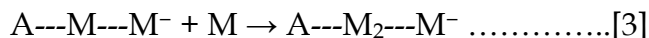
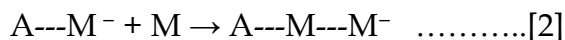
Simple kinetics are found when an ionic polymerization initiator is completely dissociated before the polymerization begins. If we represent the undissociated initiator by GA, then we can assume, for the present that in the polymerization medium the dissociation reaction [1a] is instantaneous and complete.



A monomer molecule must add to A^- , to complete the initiation of a polymerization



Depending on the solvent, the propagating anion may behave as a free ion, AM^- , or as ion pair, AM^-G^+ , or as both. For simplicity we will consider only one type (i.e., free ions) for the present kinetic treatment. The propagation reactions may then be written



It is assumed that the positive ion G^+ is always in the vicinity of the negative chain centre at each step. The extent of charge separation depends on the dielectric constant of the solvent. In the absence of impurities or of substances added deliberately for the purpose of chain termination, no termination reactions exist in this special case. The polymerization ceases only when the monomer is consumed. It begins again if more monomer is added. For this reason, the polymers produced in this special case are so called "living polymers."

In such a situation the kinetics are especially simple because no initiation reaction takes place during the polymerization.

Rate of polymerization

The rate of polymerization is given below-----

$$r_p = \frac{-d[M]}{dt} = k_p [A^-] [M] \quad [5]$$

where, $[A^-]$ is the total concentration of anions of all degrees of polymerization. It is constant and is given by the concentration of the initiator before dissociation, namely $[GA]_0$. Hence,

$$r_p = \frac{-d[M]}{dt} = k_p [GA]_0 [M] \quad [6]$$

Integration of the first order rate equation gives the time dependence of the monomer concentration as

$$[M] = [M]_0 e^{-k_p [GA]_0 t} \quad [7]$$

Rates of anionic polymerization are measured experimentally. From the experimental measurements and a knowledge of $[GA]_0$, k_p may be determined either by [6] or [7].

Average kinetic chain length

Since no termination step exists in a true “living” polymerization, the kinetic chain growth is ended only when the monomer is completely consumed. The average kinetic chain length by definition is

$$v = \frac{\text{monomer consumed}}{\text{number of chain centres}} = \frac{[M]_0 - [M]}{[GA]_0} \quad [8a]$$

which on substitution of $[M]$ from [7] becomes a function of time as given by [8b].

$$v = \frac{[M]_0}{[GA]_0} (1 - e^{-k_p [GA]_0 t}) \quad [8b]$$

According to [8b], in the limit of $t \rightarrow \infty$, or in other orders, at the completion reaction,

$$v_\infty = \frac{[M]_0}{[GA]_0} \quad [8c]$$

Average degree of polymerization

The average degree of polymerization is given by the number of monomer molecules polymerized per polymer molecule formed. The number of polymer molecules formed is equal to the number of chain centers, or initiators, so that the following equation is obtained.

$$\overline{DP} = \frac{[M]_0 - [M]}{[GA]_0} = \frac{[M]_0}{[GA]_0} (1 - e^{-k_p[GA]_0 t}) = v \quad [9]$$

In some cases it is necessary to make a simple modification of [9] to account for the fact that dianions are involved. For example, in the sodium naphthalenide initiated polymerization of styrene. In this case, the number of polymer molecules is half (1/2) of the number of chain centers or initiators. The degree of polymerization is given by

$$\overline{DP} = \frac{[M]_0 - [M]}{1/2 [GA]_0} = 2 \frac{[M]_0}{[GA]_0} (1 - e^{-k_p[GA]_0 t}) = 2v \quad [10]$$