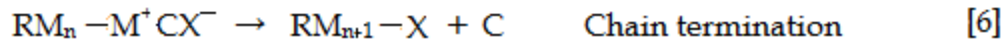
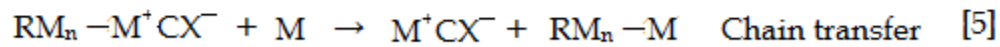
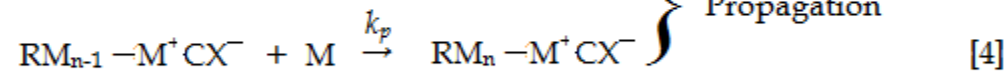
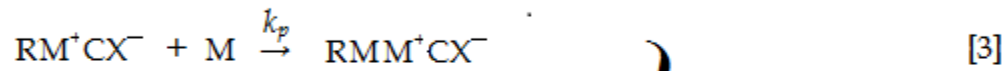
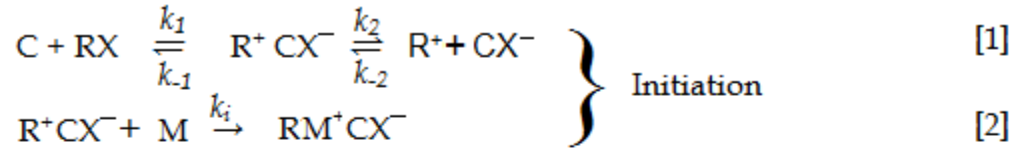


Kinetics of Cationic Polymerization

For discussion of kinetics of cationic polymerization, we may depict this polymerization by the following set of elementary reactions, in which C is the catalyst or initiator, RX is the co-catalyst, and M is the monomer.



In [2] to [6], only the polymerization that involves ion pairs is shown explicitly. It must be kept in mind that a similar polymerization chain carried by free ions, $RM_n -M^+$, may be occurring simultaneously and that an equilibrium involving ion pairs and free ions, such as shown in [1], exists for ion pairs of all sizes.

The rate of polymerization by ion pairs may be written

$$\frac{-d[M]}{dt} = r_p = k_p [M] \sum_{n=0}^{\infty} [RM_n -M^+ CX^-] \quad [7]$$

The rate of termination in a catalyzed ionic polymerization will be first order with respect to the growing chain concentration. This is understandable on the basis of electrostatic considerations. In the media usually employed, the counterion must remain so close to the positive chain centre that the ion pair (or free ions) behaves in a kinetic sense as a single entity. Thus,

$$r_t = k_t \sum_n [M_n -M^+ CX^-] \quad [8]$$

If we assume steady state for the concentration of growing chains, then $r_t = r_i$ and we have from [8],

$$\sum_{n=0}^{\infty} [RM_n - M^+ CX^-] = \frac{r_i}{k_t} \quad [9]$$

Therefore, the rate of polymerization by ion pairs is given by

$$r_p = \frac{k_p}{k_t} [M] r_i \quad [10]$$

with an analogous expression holding for the rate of polymerization by free ions. It is complexity and variety of the kinetic expressions for r_i , the rate of initiation. The rate of initiation at a fixed temperature and in a given solvent will be determined by the equilibria or steady state existing among ion pairs, catalyst, co-catalyst, and monomer. Thus, it is possible to write

$$r_i = f([C], [RX], [M]) \quad \dots\dots\dots[11]$$

but it must be recognized that the function f can take on such a variety of forms that it can be determined with confidence only by actual experiment for any given system.

Degree of polymerization

The degree of polymerization was simply given by the ratio of the rate of depletion of the monomer to the rate of formation of the polymer. Since polymer is formed in both the termination and the transfer reactions, namely [5] and [6], we have

$$\overline{DP} = \frac{r_p}{r_t + r_{tr}} \quad [12]$$

In terms of the cationic mechanism shown in [1] to [6], in which transfer occurs only to monomer, equation [12] becomes

$$\overline{DP} = \frac{k_p [M]}{k_t + k_{tr} [M]} \quad [13]$$

or, in the usual inverted form, known as the Mayo equation.

$$\frac{1}{\overline{DP}} = \frac{k_{Tr,M}}{k_p} + \frac{k_t}{k_p} \frac{1}{[M]} \quad [14]$$

Transfer can occur also to additional substances, often introduced inadvertently into the system as impurities. In such cases, [14] must be transformed to the following equation.

$$\frac{1}{\overline{DP}} = \frac{k_{Tr,M}}{k_p} + \frac{k_t}{k_p} \frac{1}{[M]} + \frac{\sum_x k_{Tr,X}}{k_p} \frac{[X]}{[M]} \quad [15]$$

In contrast to free-radical polymerization, the formation of the polymeric product in cationic polymerization occurs mainly by transfer rather than by termination. Therefore if cationic systems are rigorously freed from all impurities (i.e., $[X] = 0$), equation [15] predicts that when $k_t \ll k_{Tr,M} [M]$, \overline{DP} will be independent of $[M]$ and should be determined only by the value of the ratio $k_p/k_{Tr,M}$. In practice, this is often difficult to achieve because impurities need to be present only at trace levels to decrease \overline{DP} .