Kinetics of Radical Polymerization

The following mechanism is used to describe a free-radical polymerization.

$$\text{Initiator (I)} \xrightarrow{k_i} 2R' \quad ; \text{formation of free radical}$$

$$R' + M \xrightarrow{k'} R_1 \quad ; \text{Initiation of chains}$$

$$R_1 + M \xrightarrow{k_{1p}} R_2 \quad ; \text{Propagation of chains}$$

$$R_2 + M \xrightarrow{k_{2p}} R_3 \quad ; \text{Propagation of chains}$$

$$--- \quad --- \quad ---\rightarrow \quad ---$$

$$R_n + M \xrightarrow{k_{np}} R_{n+1} \quad ''\qquad '' \qquad ''$$

$$R_n + R_m \xrightarrow{k_{tnmc}} P_{n+m} \quad \text{Termination of chains}$$

$$R_n + R_m \xrightarrow{k_{tnmd}} P_n + P_m \quad '' \qquad '' \qquad ''$$
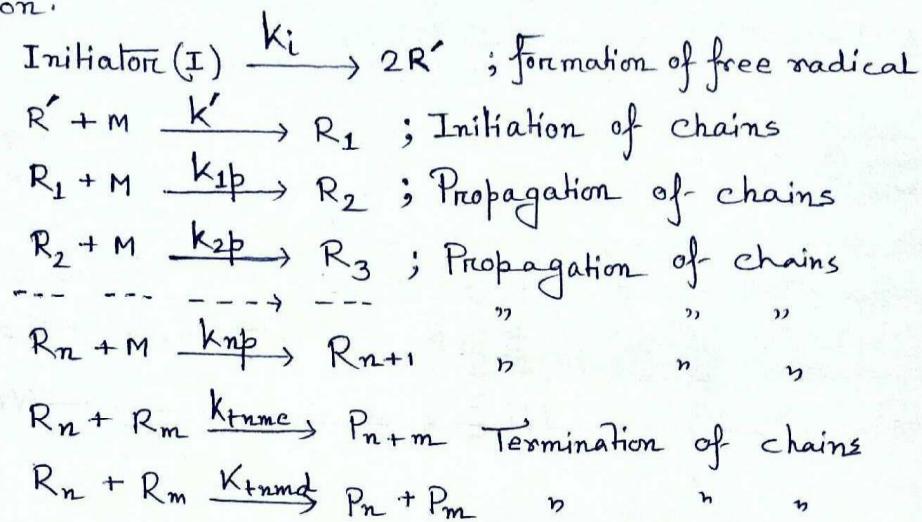
M = monomer molecule, R' = initiating radical, R_n = propagating radical of degree of polymerization n, P_n = polymer molecule of degree of polymerization n, and so on. For simplicity at this state we omit chain transfer reaction from the mechanism.

Approximations:

A rigorous kinetic treatment leads to immense complexities and in order to derive useful and tractable results, it is necessary to introduce some simplifying assumptions and approximations.

Kinetic chain length: It is assumed that the kinetic chain lengths are very large. This means that the number of monomers molecules consumed in the chain initiation process is negligible compared to the number consumed in chain propagation reactions.

The direction of radical addition to the monomer: In the polymerization of $CH_2 = CHX$, the structure of all the propagating radicals is of the type shown below and then there occurs head-to-tail addition.

$$\text{\Large$\mathcal{M}$}-CH_2-\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle X}{|}}{C}}{}^{\bullet}$$
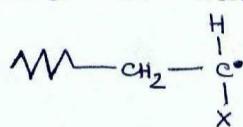
Radical reactivity and size: It is assumed that the reactivity

of the propagating radicals is independent of the size or degree of polymerization of the radical. Therefore the rate constants for propagation, $k_{1p}, k_{2p}, \cdots k_{np}$ are taken to be equal and are written simply as k_p. Similarly, for termination reactions, the rate constants k_{nmc} and k_{nnd} are assumed to be independent of n and m and are written as simply as k_{tc} and k_{td}. k_p is independent of radical size. This will generally be valid approximation except in the initial stages of propagation.

However, the assumption that k_t ($k_t = k_{tc} + k_{td}$) is independent of size is usually less valid. Nevertheless, this assumption must be made in order to obtain tractable results.

The steady-state approximation: All free radicals present in the system are assumed to be at steady-state approximation concentration. This means that the total concentration of propagating radicals (which is the sum of the conc^n of propagating radicals of all degrees of polymerization) is also a steady-state value. Expressed algebrically this means that

$$\frac{d[R']}{dt} = \frac{d[R_n]}{dt} = \frac{d[R]}{dt} = 0 \quad \cdots \cdots (1)$$

Where $[R] = \sum_n [R_n]$

If initial concentration of monomer is $[M]_0$ then

$$[M]_0 = [M] + \sum_n n[P_n] + \sum_n n[R_n] \quad \cdots \cdots (2)$$

By differentiating and rearranging, the above expression is written as

$$-\frac{d[M]}{dt} = \sum_n n\left(\frac{d[P_n]}{dt}\right) + \sum_n n\left(\frac{d[R_n]}{dt}\right) \quad \cdots \cdots (3)$$

Experimentally, it is found that, except in the very earliest stages of the reaction, the loss of monomer is, in fact, accounted quantitatively by the appearance of the polymeric product. Thus, we can write equation (3) as given below

$$-\frac{d[M]}{dt} = \sum_n n\left(\frac{d[P_n]}{dt}\right) \quad \cdots \cdots (4)$$

Steady-state concentrations of the propagating radicals:

If the total concentration, [R] is to be in a steady-state, as assumed by (1), the rate of initiation(r_i) of propagating radicals must be equal to their rate of termination(r_t) or

$$\frac{d[R]}{dt} = r_i - r_t = 0 \quad\text{------------ (5)}$$

the rate of initiation is given by

$$r_i = k'[R'][M] \propto 2K_i[I] \quad\text{---------(6)}$$

Since, some loss of initiating radicals always occurs through side reactions, the rate of initiation is usually written as

$$r_i = 2K_i f[I] \quad\text{--------- (7)}$$

Where f represents the fraction of initiating radicals produced that actually add to monomer to form R_1 (see mechanism).

In considering the rate of termination, r_t, it is necessary to distinguish between the reactions of like radicals and unlike radicals. Thus, for both combination and disproportionation, we must distinguish between the two termination processes.

$$R_n + R_n \xrightarrow{K_{tnn}} \text{Polymer} \quad\text{------- (8)}$$

$$R_n + R_m \xrightarrow{K_{tnm}} \text{Polymer} \quad\text{----- (9)}$$
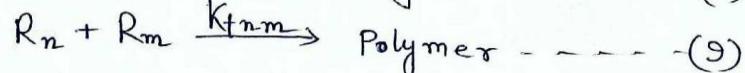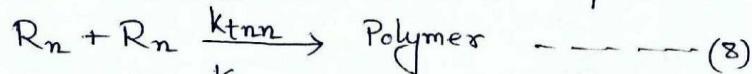
We have assumed that reactivity is independent of size, so the rate constants K_{tnn} and K_{tnm} can differ only by a factor of 2. This is a consequence of the relative collision frequencies of like and unlike species (i.e., $K_{tnm} = 2K_{tnn}$)

Applying the law of mass action to (8) and (9), the termination rate for radicals of degree of polymerization n can be written as

$$r_t(n) = 2K_{tnn}[R_n]^2 + [R_n]\sum_{m \neq n} K_{tmn}[R_m] \quad\text{----(10)}$$

or $$r_t(n) = 2K_{tnn}[R_n]\left\{[R_n] + \sum_{m \neq n}[R_m]\right\}$$

or $$r_t(n) = 2K_{tnn}[R_n]\sum_m[R_m] = 2K_t[R_n][R] \quad\text{---- (11)}$$

Now, the total rate of termination of all radicals is obtained by summation over n as

$$r_t = \sum_n r_t(n) = 2K_t[R]\sum_n[R_n] = 2K_t[R]^2 \quad\text{-------(12)}$$

Substitution of (7) and (12) into (5) gives

$$[R] = \left(\frac{r_i}{2K_t}\right)^{1/2} = \left(\frac{fK_i[I]}{K_t}\right)^{1/2} \text{--------(13)}$$

In the case of photolytic or radiation-induced polymerization, $2K_i[I]$, which is the rate of formation of initiating radical may simply be replaced by $2I_a$. Therefore

$$r_i = 2\varphi I_a \quad \text{where } \varphi \text{ is quantum yield}$$
$$\text{and } I_a = \epsilon I_0[M]$$
$$\epsilon = \text{extinction coefficient, } I_0 = \text{intensity}$$
$$\text{of incident light \& } [M] = \text{monomer conc}^n.$$

So, $r_i = 2\varphi \epsilon I_0[M]$

Rate of polymerization:

Application of the mass action law # to the mechanism gives the theoritical rate of polymerization.

$$r_p = K'[R'][M] + K_{1p}[R_1][M] + K_{2p}[R_2][M] + \text{-----} \quad (14)$$

or $$r_p = [M]\left\{K'[R'] + \sum_n K_{np}[R_n]\right\} \text{----------} (15)$$

According to the "assumption of long chain" made earlier, $K'[R']$ is very much less than $\sum_n K_{np}[R_n]$. Therefore equation (15) is written as

$$r_p = K_p[M]\sum_n [R_n] \approx K_p[M][R] \text{--------}(16)$$

$$\Rightarrow r_p = \left(\frac{K_p^2}{2K_t}\right)^{1/2} r_i^{1/2}[M] = \left(\frac{K_p^2}{2K_t}\right)^{1/2}(2fK_i)^{1/2}[I]^{1/2}[M] \text{-----}(17)$$

This equation predicts that the rate of polymerization at a given temperature should vary with the square root of the initiation rate or initiator concentration and with the first power of the monomer concentration.

Average Kinetic Chain Length:

The average kinetic chain length, v, is defined as the average number of monomer molecules polymerized per chain initiated or equivalently, as the rate of polymerization per unit rate of initiation.

$$v = \frac{r_p}{r_i} = \frac{r_p}{r_t} = \frac{K_p[M][R]}{2K_t[R]^2} = \frac{K_p[M]}{2K_t[R]} \text{----------}(18)$$

Average Degree of polymerization:

The average degree of polymerization, $\overline{DP}$, is defined as the average number of monomers per polymer molecule. The total rate of formation of polymer is defined by the following equation, since termination takes place by two ways combination and disproportionation & disproportionation gives two polymer molecules whereas one is formed by combination.

$$\frac{d[P]}{dt} = \left(k_{tc} + 2k_{td}\right)[R]^2 \quad - - - - - \cdot (19)$$

The instantaneous average degree of polymerization is then given by

$$\overline{DP} = \frac{-\frac{d[M]}{dt}}{\frac{d[P]}{dt}} = \frac{K_p[M]}{\left(K_{tc} + 2K_{td}\right)[R]} \quad - - - - - \cdot (20)$$

We may express $\overline{DP}$ in terms of the average kinetic chain length;

$$\overline{DP} = 2\nu\left(\frac{K_{tc} + K_{td}}{K_{tc} + 2K_{td}}\right) - (21)$$

From equation (18)

$$\frac{k_p[M]}{[R]} = 2K_t \nu$$

$$= 2\nu\left(K_{tc} + K_{td}\right)$$

Often one type of termination predominate. If so the following simplification of (21) can be assumed

1. If termination by combination predominates, $k_{td} \ll K_{tc}$, and
$$\overline{DP} = 2\nu$$

2. If termination by disproportionation predominates, $K_{td} \gg K_{tc}$, and
$$\overline{DP} = \nu$$

Thus, for any free radical chain polymerization in which chain transfer does not occur, $\overline{DP}$ must be between ν and 2ν.