

Kinetics of Vinyl Free Radical Polymerization in Simple Systems

Chain polymerization of vinyl monomers by radical mechanism involves four elementary steps, namely:

(i) Initiation process which involves the production of primary radicals from initiators, and this is carried out in three possible ways (a) Irradiation (photolysis or radiolysis) (b) Thermal homolysis and (c) Oxidation-reduction reactions.

(ii) The propagation of the primary radical by the addition of a large number of monomer molecules in a chain mechanism.

(iii) Chain transfer, the growing chain may be involved in a chain transfer reaction with solvent, polymer molecule, monomer, initiator or chain transfer agent...etc.

(iv) The termination process which occurs either by combination or disproportionation.

Initiation process:

This may be presented by the following steps:-



[I] : initiator R_c^\bullet : primary radical

The starting of the growing chain occurs as follows:-



(R_1^\bullet)

Where $CH_2 = CHX$: vinyl monomer, X is the substituted functional group such as $-C_6H_5$, $-COOCH_3$, $-CONH_2$, Cl , $-C \equiv N$, ... etc.

Propagation process :

In propagation process $R\bullet_1$ radical reacts with another monomer molecule to give $R\bullet_2$ which contains two monomer units:-



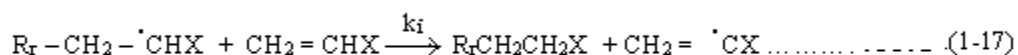
In general, the propagation reaction is presented by the following equation:-



where ($R_r\bullet$): is the polymer radical containing a large number of monomer units (r).

Chain transfer :

The transfer reaction involves transfer of small atoms such as(H or Cl) from a molecule to a propagating radical. Radicals are therefore converted into complete polymeric molecules; at the same time another radical is generated from the molecule providing the atom. In simplest case, the transfer reaction to a monomer may be presented as follows:-

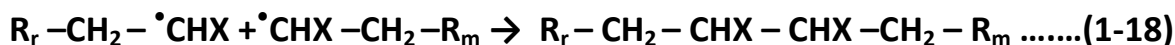


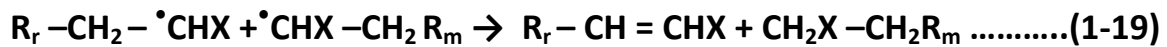
The transfer could occur to polymeric chains, solvent, initiator, monomer molecules, or any other molecules in the system which has a labile atom (e.g CCl_4 or CBr_4) or mercaptans (RSH).

Termination process:

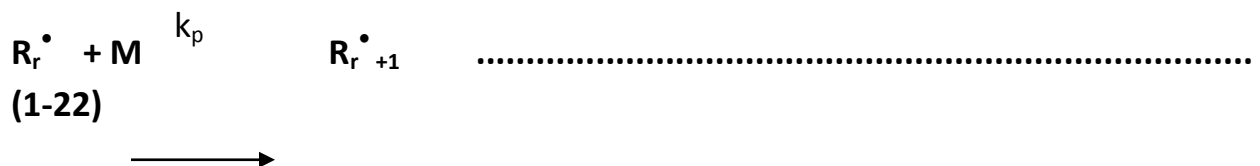
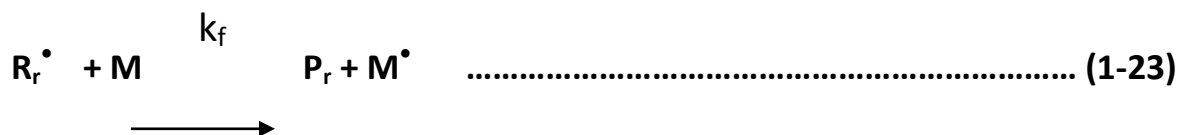
The termination step can take place in two possible ways:-

(i) Combination :-

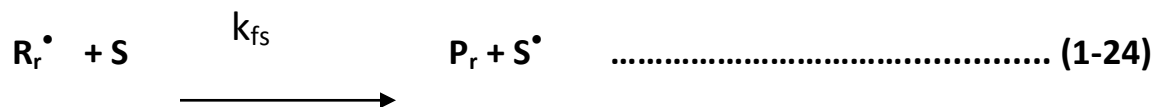


(ii) Disproportionation:-

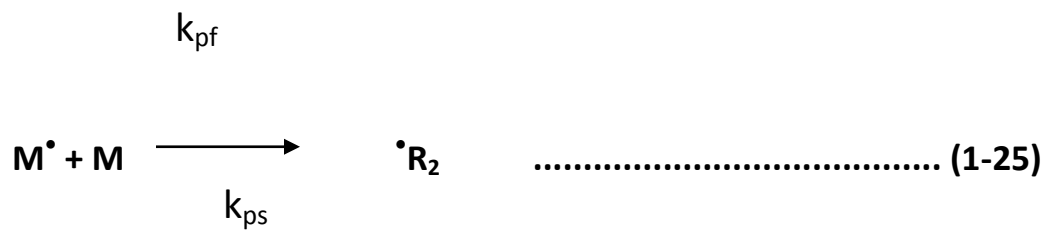
It was described by the following elementary steps, which may be used to illustrate the fundamentals of the kinetics of free radical polymerization in uninhibited, unretarded system.

Initiation**Propagation****Transfer to monomer**

Transfer to solvent



Reinitiation of radicals formed by transfer



Termination By Combination



Or by Disproportionation





Where R_r^\bullet , R_m^\bullet = growing macro- free radicals and

P_r , P_m = polymer molecule with r and s monomer respectively .

M^\bullet, S^\bullet = radical derived from monomer and solvent molecule respectively,

k = are the rate constant for the elementary steps.

This represents an idealized free radical polymerization.

In order to develop a useful kinetic treatment, it is necessary to make simplifying assumptions these are :-

First: Radical reactivity is generally taken to be independent of radical size This means that reaction does not depend on the number of monomer: that growing radical consists of: $k_{p1} = k_{p2} = k_{pn}$.Thus single velocity constant . could be written for propagation (k_p), transfer (k_f) and termination (k_t)•

Second: According to the long chain assumption, the rate of consumption of monomer in the propagating reaction is much greater than the rate of reaction of monomer in initiation or transfer reactions.

Finally: The steady state hypothesis may be applied to all the radical concentrations,

$$-\frac{d[R^\bullet_r]}{dt} \rightarrow 0 \dots\dots\dots (1-29)$$

Equation (1-29) does not mean that $d[\bullet R_r] / dt$ is exactly zero i.e. at steady state the rate of change of radical concentration is small compared either to the rate of formation of radicals or their rate of disappearance. Therefore, the following steady state equations may be derived:-

$$\frac{d[R^\bullet]}{dt} = j - k_f[M][R^\bullet] + k_{pf}[M^\bullet][M] + k_{ps}[S^\bullet][M] - k_{fs}[R^\bullet][S] - (k_{tc} + k_{td})[R^\bullet]^2 = 0 \dots\dots\dots (1-30)$$

$$\hat{j} = f k_d [I] \text{ \textbackslash where } [I] = \text{initiator concentration}$$

k_d = decomposition constant of initiator (giving one radical).

f = initiator efficiency.

$$\frac{d[S^\bullet]}{dt} = k_{fs}[S][R^\bullet] - k_{ps}[M][S^\bullet] = 0 \dots\dots\dots (1-31)$$

$$\frac{d[M^\bullet]}{dt} = k_f[M][R^\bullet] - k_{pf}[M^\bullet][M] = 0 \dots\dots\dots (1-32)$$

In these equations $[R^\bullet] = \sum [R_r]$ is equal to total Propagating radical concentration . By addition of equations (1-30), (1-31) , and (1-32) the following equation is obtained: -

$$[R^\bullet] = \frac{j^{\frac{1}{2}}}{(k_{tc} + k_{td})^{\frac{1}{2}}} \dots\dots\dots (1-33)$$

According to the previous second assumption for long chain, and assuming the solvent, and the monomer radicals are not involved in termination reaction:

$$\frac{-d[M]}{dt} = k_p [M] [R^\bullet] \dots\dots\dots (1-34)$$

Thus the rate of polymerization (ω) is obtained from equations(1-33) and (1-34)

$$\omega = \frac{-d[M]}{dt} = \frac{k_p}{(k_{tc} + k_{td})^{\frac{1}{2}}} [M] j^{\frac{1}{2}} \dots\dots\dots (1-35)$$

Therefore, the rate of radical polymerization is directly proportional to the square root of rate initiation at constant monomer concentration .

This means that kinetic chain length $\bar{\nu}$: is defined as the average number of monomer molecules consumed per each chain started.

$$\bar{\nu} = -\frac{1}{j} \cdot \frac{d[M]}{dt} = \frac{k_p [M]}{(k_{tc} + k_{td})^{\frac{1}{2}} j^{\frac{1}{2}}} \dots\dots\dots (1-36)$$

The average number degree of polymerization D_p : is the average number of monomer molecules consumed per inactive polymer molecule formed.

$$\bar{D}_p = \frac{\text{rate of consumption of monomer}}{\text{rate of formation of polymer}} = \frac{-d[M]/dt}{d[p]/dt}$$

$$\bar{D}_p = \frac{k_p[R^\bullet][M]}{k_f[R^\bullet][M] + k_{fs}[R^\bullet][S] + \left[\frac{k_{tc}}{2} + k_{td}\right][R^\bullet]^2} \dots\dots\dots(1-37)$$

From equation (1-33) :

$$\bar{D}_p = \frac{k_p[M]}{k_f[M] + k_s[S] + \left[\frac{k_{tc}}{2} + k_{td}\right]\left[\frac{j}{k_{tc} + k_{td}}\right]^{\frac{1}{2}}} \dots\dots\dots(1-38)$$

Equation (1-38) is valid for a system in which termination occurs both by combination and disproportionation processes. When termination is mainly by disproportionation, $k_{tc} = 0$

$$\bar{D}_p = \frac{k_p[R^\bullet][M]}{k_f[M] + k_{fs}[S] + (k_{td}j)^{\frac{1}{2}}} \dots\dots\dots(1-39)$$

If the termination is by combination only: i. e., $k_{td} = 0$

$$\bar{D}_p = \frac{k_p[M]}{k_f[M] + k_{fs}[S] + (1/2)(k_{tc}j)^{\frac{1}{2}}} \dots\dots\dots(1-40)$$

If the rate of initiation is high [at higher initiator concentration] in comparison with transfer, then ;

$$\bar{D}_p = \frac{k_p[M]}{(k_{td}j)^{\frac{1}{2}}} = \bar{v} \dots \dots \dots (1-41)$$

$$\bar{D}_p = \frac{k_p[M]}{(1/2)(k_{tc}j)^{\frac{1}{2}}} i.e \quad \bar{D}_p = 2\bar{v} \dots \dots \dots (1-42)$$

If rate of initiation is very low, transfer to solvent or monomer becomes dominating and \bar{D}_p is determined only by transfer; \bar{D}_p has the highest value obtainable, i.e highest molecular weight of polymer.

$$(\bar{D}_p)_{\max} = \frac{k_p[M]}{k_f[M] + k_{fs}[S]} \dots \dots \dots (1-43)$$

$$\frac{1}{\bar{D}_p} = \frac{k_f}{k_p} \cdot \frac{k_{fs}}{k_p} \cdot \frac{[S]}{[M]} + \left[\frac{2+Y}{2(1+Y)} \right] \frac{k_t}{k_p^2[M]^2} \dots \dots \dots (1-44)$$

$$Y = \frac{k_{tc}}{k_{td}} \quad k_t = k_{tc} + k_{td}$$

Equation (1-44) was first derived by Mayo,

from equations (1-35) and (1-36) and assuming $k_t = k_{tc} + k_{td}$

$$k_p / k_t^{\frac{1}{2}} = \frac{1}{[M]} (\omega \bar{v})^{\frac{1}{2}} \dots \dots \dots (1-45)$$

From equation (1-36) if termination is completely by combination , then :

$$\bar{\nu} = \frac{\bar{D}_p}{2} \dots\dots\dots(1-46)$$

Therefore :

$$k_p / k_{t/2} = \frac{1}{[M]} \left[\omega \cdot \frac{\bar{D}_p}{2} \right]^{\frac{1}{2}} \dots\dots\dots(1-47)$$

If termination occurs partially by combination then:

$$k_p / k_t^{1/2} = \frac{1}{[M]} \left[\omega \cdot \bar{D}_p \left[\frac{2+Y}{2(1+Y)} \right] \right]^{\frac{1}{2}} \dots\dots\dots(1-48)$$

The value of $k_p / k_t^{1/2}$ is a characteristic for a given monomer at certain temperature and it does not depend on the type of initiator or mechanism of initiation(see table (1-1)).From the value of $k_p / k_t^{1/2}$ one can know whether the polymerization involves some complications, such as: inhibition, retardation ... etc.

Quantum Yield of photo polymerization Process

The overall quantum yield of photopolymerization (Φ_p) is defined by equation (1-49):-

$$\phi_p = \frac{\text{rate of polymerization}}{\text{quantum input}} = \frac{\omega}{I_{abs}} \dots\dots\dots(1-49)$$

I_{abs} = Intensity of light absorbed by the initiated system and this is governed by Beer-Lamber's law

$$I_{\text{abs}} = I_0(1 - e^{-\epsilon \ell c}) \quad \text{ein} \cdot \text{l}^{-1} \cdot \text{S}^{-1} \dots\dots\dots(1-50)$$

where: I_0 = is the intensity of incident light

ℓ = path length, $[C]$ = concentration of initiator, (ϵ) molar extinction coefficient.

The primary quantum yield with respect to initiation is therefore given by:

$$\phi_i = \frac{j}{I_{\text{abs}}} \dots\dots\dots(1-51)$$

Φ_i = quantum yield of initiation

\hat{j} = is the rate of initiation

Moreover, the energy of the absorbed quantum exceeds the bond energy of the photolyzable linkage; the higher will be the value of the quantum yield of initiation.