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# Kinetics of Additional Polymerization :→

Let 'M' monomer undergo addition polymerization then following steps are involved :

(i) Initiation Step
(ii) Propagation Step
(iii) Termination Step.

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(i) **Initiation step** :⇒

$$I \xrightarrow{K_1} R$$

Rate of initiation step $= k_1[I]$ —— (1)

(ii) **Propagation step** :⇒

let ⇒ $M = CH_2=CH-X$

Then,

$$R + CH_2=CH-X \xrightarrow{K_2} R-CH_2-\dot{C}H-X$$

$$R-CH_2-\dot{C}H-X + CH_2=CH-X \longrightarrow R-CH_2-\underset{X}{\underset{|}{C}H}-CH_2-\dot{C}H_2-X$$

Rate of disappearance of monomer $= \dfrac{-d[M]}{dt}$

$$\boxed{\frac{-d[M]}{dt} = K_2[M][R]} \quad \text{—— (2)}$$

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(iii) Termination step :- Chain termination takes place when two free radicals combine as :

$$R\text{-}(CH_2 - \underset{X}{\underset{|}{CH}})_n - CH_2 - \dot{C}H - X + R - CH_2 - \dot{C}H - X \xrightarrow{K_3} \text{Polymer}$$

Since Rate of polymerization depends on Rate of disappearance of monomer then.

$$\text{Rate of polymerization} = \frac{-d[M]}{dt} = K_2 [M][R]$$

Using SSA →

$$K_1[I] = K_3 [R]^2$$

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$$[R]^2 = \frac{K_1 [I]}{K_3}$$

$$[R] = \frac{K_1^{1/2} [I]^{1/2}}{K_3^{1/2}} \quad \text{—— (3)}$$

From eq: (3) to eq. (2).

$$\frac{-d[M]}{dt} = K_2 [M] \times \frac{K_1^{1/2} [I]^{1/2}}{K_3^{1/2}}$$

$$\frac{-d[M]}{dt} = \frac{K_1^{1/2} K_2}{K_3^{1/2}} * [M][I]^{1/2}$$

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$$\frac{-d[M]}{dt} \propto [M] \quad \& \quad \frac{-d[M]}{dt} \propto [I]^{1/2}$$

* Kinetic Chain Length :⇒ ($l$)

$$l = \frac{\text{Rate of disappearance of monomer}}{\text{Rate of initiation step.}}$$

$$l = \frac{-d[M]/dt}{K_1[I]}$$

$$l = \frac{K_1^{1/2} K_2}{K_3^{1/2}} \times [M][I]^{1/2} \Big/ K_1[I]$$

$$l = \frac{K_2[M]}{K_1^{1/2} K_3^{1/2} . [I]^{1/2}}$$

That means

$$l \propto [M] \quad \& \quad l \propto \frac{1}{[I]^{1/2}}$$

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Ques → For addition polymerization the rate constant for free radical formation is $4 \times 10^{-3}$/sec. The initial con. of initiator is $10^{-3}$ mol/L. The overall rate of polymerisation is $4 \times 10^{-3}$ mol/L/sec. Find the kinetic chain length.

Solve. Given ⇒ $\frac{-d[M]}{dt} = 4 \times 10^{-3} \text{ mol } L^{-1} \sec^{-1}$

$K_1 = 4 \times 10^{-3} \sec^{-1}$

$[I] = 10^{-3} \text{ mol } L^{-1}$

$$l = \frac{-d[M]/dt}{K_1 [I]} = \frac{4 \times 10^{-3} \text{ mol } L^{-1} \sec^{-1}}{4 \times 10^{-3} \sec^{-1} \times 10^{-3} \text{ mol } L^{-1}}$$

$$\boxed{l = 10^3}$$

Objective chemistry