

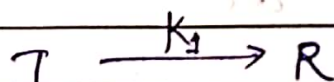
Kinetics of Additional Polymerization $\Rightarrow$

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

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

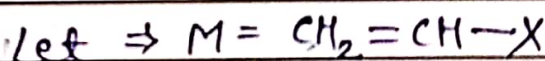
Objective Chemistry

(i) Initiation step $\Rightarrow$

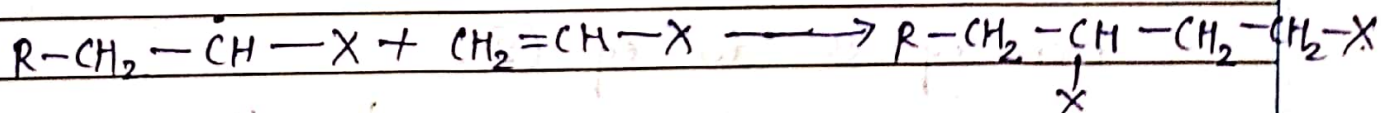
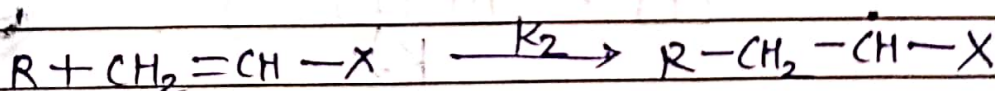


$$\text{Rate of initiation step} = k_1 [I] \quad \text{--- (1)}$$

(ii) Propagation step $\Rightarrow$



Then,



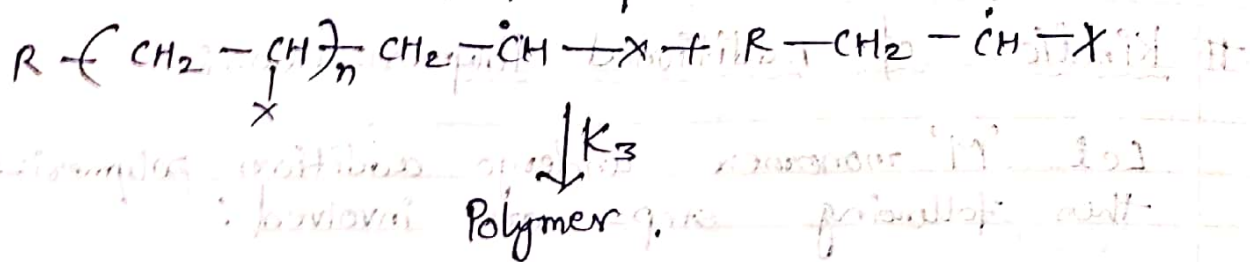
$$\text{Rate of disappearance of monomer} = \frac{-d[M]}{dt}$$

$$\boxed{\frac{-d[M]}{dt} = k_2 [M] [R]}$$

--- (2)

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iii) Termination step $\Rightarrow$ Chain termination takes place when two free radicals combine as:



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

$$\text{Rate of polymerization} = -\frac{d[M]}{dt} = K_2 [M] [R] \quad (1)$$

Using SSA $\rightarrow$

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

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

$$[R] = \frac{K_1^{1/2} [I]^{1/2}}{K_3^{1/2}}$$

Objective Chemistry

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

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

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

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

* Kinetic Chain Length $\Rightarrow (l)$

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

$$l = \frac{-d[M]/dt}{k_1[I]}$$

$$l = \frac{\frac{k_1^{\frac{1}{2}} k_2}{k_3^{\frac{1}{2}}} \times [M][I]^{\frac{1}{2}}}{k_1[I]}$$

$$l = \frac{k_2[M]}{k_1^{\frac{1}{2}} k_3^{\frac{1}{2}} [I]^{\frac{1}{2}}}$$

That means

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

Objective
Chemistry

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Que $\Rightarrow$ For addition polymerization the rate constant for free radical formation is $4 \times 10^{-3} / \text{sec}$.

The initial con. of initiator is 10^{-3} mol/L .

The overall rate of polymerisation is $4 \times 10^{-3} \text{ mol/L/sec}$. Find the kinetic chain length.

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

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

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

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

$$l = 10^3$$

Objective Chemistry