Unit IV

Kinetics of: Copolymerisation:

→ when two or more monomers are polymerised it is called as co-polymerisation.

→ Polymer is composed of more than one repeat unit polymerised by free radical, ionic and polycondensation polymerisation

$$nM_1 + mM_2 \longrightarrow \sim\sim(M_1)_n\sim(M_2)_m\sim$$

Types: (i) free Radical copolymerisation

(ii) Ionic copolymerisation.

(iii) Poly condensation.

Exmp: SBR is first commercially made copolymer.

① free-radical co-polymerisation:

(1) (a) Initiation: Let two monomers, M_1 and M_2 be mixed together and polymerised using a free radical Initiator.

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The initiator decompose into free radical and this free radical can attack M_1 or M_2 as follows:

$$\underset{\text{Initiator}}{I} \longrightarrow \underset{\text{free radical}}{R^\bullet + R^\bullet}$$

$$R^\bullet + M_1 \longrightarrow RM_1^\bullet$$

$$R^\bullet + M_2 \longrightarrow RM_2^\bullet$$

(2) (b) Propagation:

$RM_1^\bullet$ Can add to either M_1 or M_2

$RM_2^\bullet$ Can add to either M_1 or M_2

$$RM_1^{\bullet} + M_1 \xrightarrow{k_{11}} RM_1M_1^{\bullet} \quad (\text{PR type } 1,1)$$
$$RM_1^{\bullet} + M_2 \xrightarrow{k_{12}} RM_1M_2^{\bullet} \quad (\text{PR type } 1,2)$$
$$RM_2^{\bullet} + M_1 \xrightarrow{k_{21}} RM_2M_1^{\bullet} \quad (\text{PR type } 2,1)$$
$$RM_2^{\bullet} + M_2 \xrightarrow{k_{22}} RM_2M_2^{\bullet} \quad (\text{PR type } 2,2)$$

** Rate of these four propagation reactions are

$$R_{11} = k_{11}[M_1^{\bullet}][M_1] \quad \text{— (1)}$$
$$R_{12} = k_{12}[M_1^{\bullet}][M_2] \quad \text{— (2)}$$
$$R_{21} = k_{21}[M_2^{\bullet}][M_1] \quad \text{— (3)}$$
$$R_{22} = k_{22}[M_2^{\bullet}][M_2] \quad \text{— (4)}$$

** The rate at which the monomers M_1 and M_2 are consumed during the propagation.

$$-\frac{d(M_1)}{dt} = k_{11}[M_1^{\bullet}][M_1] + k_{21}[M_2^{\bullet}][M_1] \quad \text{— (5)}$$

$$-\frac{d(M_2)}{dt} = k_{12}[M_1^{\bullet}][M_2] + k_{22}[M_2^{\bullet}][M_2] \quad \text{— (6)}$$

Now According to steady state law

Rate of formation of radical = Rate of disappearance of radical

$$k_{12}[M_1^{\bullet}][M_2] = k_{21}[M_2^{\bullet}][M_1] \quad \text{— (7)}$$

$$\frac{[M_1^{\bullet}]}{[M_2^{\bullet}]} = \frac{k_{21}}{k_{12}} \frac{[M_1]}{[M_2]} \quad \text{— (8)}$$

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$$\boxed{M_1^{\cdot} = \frac{k_{21}}{k_{12}} \frac{(M_1)(M_2^{\cdot})}{[M_2]}} \quad — (9)$$

combining equation (5) & (6) or (5)/(6)

$$\frac{d(M_1)}{d(M_2)} = \frac{k_{11}(M_1^{\cdot})(M_1) + k_{21}(M_2^{\cdot})(M_1)}{k_{12}(M_1^{\cdot})(M_2) + k_{22}(M_2^{\cdot})(M_2)} \quad (10)$$

we get - a copolymer equation

$$\cancel{\frac{d(M_1)}{d(M_2)} = \frac{(M_1)}{(M_2)} \cdot k_{11}/k_{12} (M_1]}$$

Put the value of $M_1^{\cdot}$ from eq. (9) we get a copolymer equation.

$$\frac{dM_1}{dM_2} = \frac{\frac{k_{11} \cdot k_{21}}{k_{12}} \cdot \frac{(M_1)^2 (M_2^{\cdot})}{\cancel{M_2}} + k_{21}(M_2^{\cdot})(M_1)}{\frac{\cancel{k_{12}} k_{21}}{\cancel{k_{12}}} \frac{(M_1)(M_2)(M_2^{\cdot})}{\cancel{(M_2)}} + k_{22}(M_2^{\cdot})(M_2)}$$

$$\frac{d(M_1)}{d(M_2)} = \frac{\frac{k_{11} \cdot k_{21}}{k_{12}} \cdot (M_1)^2 \cancel{(M_2^{\cdot})} + k_{21}\cancel{(M_2^{\cdot})}(M_1)(M_2)}{k_{21} \cdot (M_1)\cancel{(M_2^{\cdot})}(M_2) + k_{22}\cancel{(M_2^{\cdot})}(M_2)^2}$$

$$\frac{d(M_1)}{d(M_2)} = \frac{(M_1)}{(M_2)} \frac{\{k_{11} \cdot \cancel{k_{21}}/k_{12} \cdot (M_1) + \cancel{k_{21}}(M_2)\}}{[\cancel{k_{21}}(M_1) + k_{22}(M_2)]} \quad (11)$$

∴ divided by k_{21}

if $r_1 = \frac{k_{11}}{k_{12}}$ & $r_2 = \frac{k_{22}}{k_{21}}$ — r_1 & r_2 are reactivity ratio.

$$\frac{d(M_1)}{d(M_2)} = \frac{M_1}{M_2} \cdot \frac{r_1(M_1) + (M_2)}{r_2(M_2) + (M_1)} \quad \text{—(12)}$$

$$\frac{(m_1)}{(m_2)} = \frac{M_1}{M_2} \cdot \frac{r_1(M_1) + (M_2)}{r_2(M_2) + (M_1)} \quad \text{—(12)(A)}$$

where $\frac{[m_1]}{[m_2]}$ gives the ratio of monomer M_1 & M_2 entered into the copolymer formed.

imp: If we express the monomer components m_1 and m_2 in terms of mole fraction instead of molar concentration, the mole fraction of monomer M_1 in the copolymer can be given by

$$n_1 = \frac{m_1}{m_1 + m_2} = \frac{d(M_1)}{d(M_1) + d(M_2)} = 1 - n_2 \quad \text{—(13)}$$

n_1 & n_2 mole fraction of monomer (M_1 & M_2) in copolymer formed.

The mole fraction of monomer M_1 in the monomer feed can be given by

$$N_1 = \frac{M_1}{M_1 + M_2} = 1 - N_2$$

where N_1 & N_2 are the mole fraction of monomers M_1 and M_2 respectively, in the monomer feed.

$$\frac{K_{11} \cdot K_{21}}{K_{12}}$$