

POLYMERS / MACROMOLECULES

PART- II

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Sem V Honours

Kinetics of condensation polymerization reactions



$$-\frac{dC_{\text{CO}_2\text{H}}}{dt} = k \cdot \underbrace{C_{\text{CO}_2\text{H}} \cdot C_{\text{OH}} \cdot C_{\text{CO}_2\text{H}}}_{\text{reactants}} + k_A \underbrace{C_{\text{CO}_2\text{H}} \cdot C_{\text{OH}} \cdot C_A}_{\text{reactants}}$$

autocatalyst **external catalyst**

we assume, $C_{\text{CO}_2\text{H}} = C_{\text{OH}} = c$

Thus,
$$-\frac{dc}{dt} = kc^3 + k_A c^2 c_A$$

CASE 1: AUTOCATALYSIS

$$-\frac{dc}{dt} = kc^3$$

$$\Rightarrow -\int_{c_0}^{c_t} \frac{dc}{c^3} = k \int_0^t dt$$

$$\Rightarrow \left[\frac{1}{2c^2} \right]_{c_0}^{c_t} = [kt]_0^t$$

$$\Rightarrow \frac{1}{2c_t^2} - \frac{1}{2c_0^2} = kt$$

$$\Rightarrow \frac{1}{c_t^2} - \frac{1}{c_0^2} = 2kt$$

C_0 = initial concentration
 C_t = concentration at time t

$$\text{Now, } p = \frac{N_0 - N_t}{N_0}$$

$$\Rightarrow p = 1 - \frac{N_t}{N_0}$$

$$\text{Similarly, } \frac{c_t}{c_0} = 1 - p$$

$$\text{Thus, } c_t = c_0(1 - p)$$

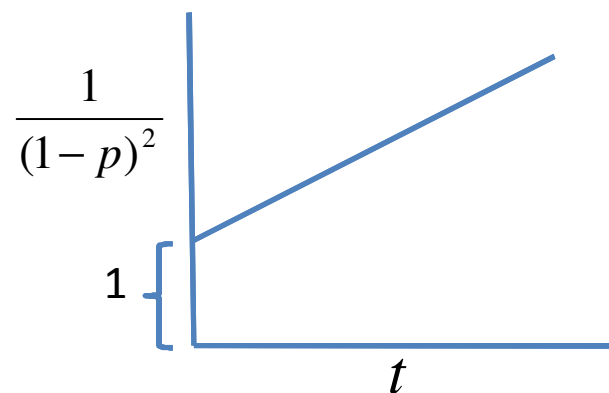
$$\text{Therefore, } \frac{1}{c_0^2(1-p)^2} - \frac{1}{c_0^2} = 2kt$$

$$\Rightarrow \frac{1}{(1-p)^2} = 1 + 2kc_0^2t$$

p = extent of polymerisation reaction

N_0 = initial number of functional groups

N_t = no. of functional groups present at time t



CASE 2: AN EXTERNAL CATALYST (SAY, A MINERAL ACID)

$$-\frac{dc}{dt} = kc^3 + k_A c^2 c_A$$

$$-\frac{dc}{dt} = c^2 (kc + k_A c_A)$$

If a strong mineral acid is used then,

$$kc \ll k_A c_A$$

As c_A is the conc. of the external catalyst so its conc. may be assumed to be constant throughout the reaction.

$$-\frac{dc}{dt} = c^2 k_A c_A$$

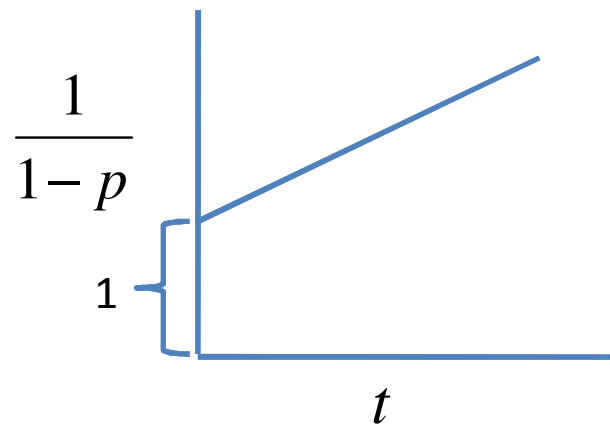
$$-\int_{c_0}^{c_t} \frac{dc}{c^2} = k_A c_A \int_0^t dt$$

$$\Rightarrow \frac{1}{c_t} - \frac{1}{c_0} = k_A c_A t$$

$$\Rightarrow \frac{1}{c_0(1-p)} - \frac{1}{c_0} = k_A c_A t$$

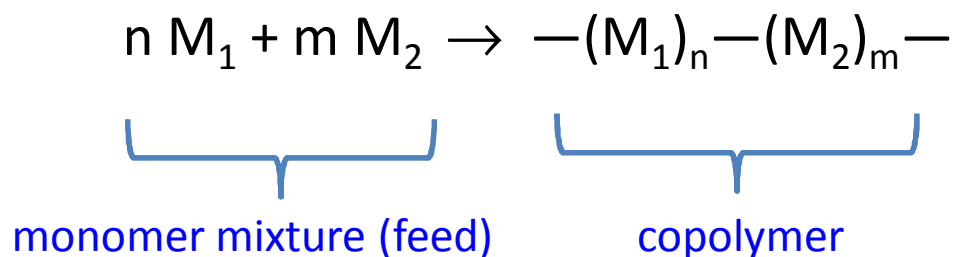
$$\Rightarrow \frac{1}{1-p} = 1 + k_A c_A c_0 t$$

$$\Rightarrow \frac{1}{1-p} = 1 + k' c_0 t$$



Kinetics of copolymerization reaction

- A polymer whose chain contains more than one type of repeating units is called a **copolymer**.
- A case of binary copolymerization involving the two monomers M_1 and M_2 may be represented as,



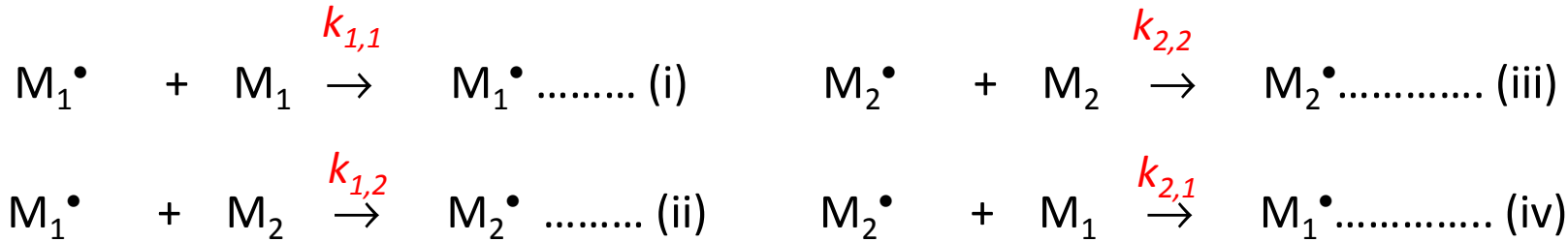
In a binary copolymerization:

- ✓ two different chain radicals can be identified i.e. M_1^\bullet and M_2^\bullet



- ✓ each radical is capable of adding both the monomers
- ✓ the system is characterized by four simultaneously propagation reactions
- ✓ the reactivity of any growing chain depends only on the end monomer unit carrying the free radical site and not on the number or type of monomer units already added to the chain.

chain propagation.....



The rates of consumption of the two monomers during propagation is given by,

$$\begin{aligned} -\frac{d[M_1]}{dt} &= k_{1,1}[M_1^\bullet][M_1] + k_{2,1}[M_2^\bullet][M_1] \\ -\frac{d[M_2]}{dt} &= k_{1,2}[M_1^\bullet][M_2] + k_{2,2}[M_2^\bullet][M_2] \end{aligned}$$

Assuming a steady state, the rate of a particular chain (say, M_1^\bullet) disappearing must be equal to rate of formation of same kind of chain and thus, from (ii) and (iv),

$$k_{1,2} [M_1^\bullet] [M_2] = k_{2,1} [M_2^\bullet] [M_1]$$

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{1,1}[M_1^\bullet][M_1] + k_{2,1}[M_2^\bullet][M_1]}{k_{1,2}[M_1^\bullet][M_2] + k_{2,2}[M_2^\bullet][M_2]}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{1,1} \frac{k_{2,1}[M_2^\bullet]}{k_{1,2}[M_2]} [M_1]^2 + k_{2,1}[M_2^\bullet][M_1]}{k_{1,2} \frac{k_{2,1}[M_2^\bullet][M_1]}{k_{1,2}[M_2]} [M_2] + k_{2,2}[M_2^\bullet][M_2]}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{\frac{k_{1,1} \cdot k_{2,1}}{k_{1,2}} \frac{[M_1]}{[M_2]} + k_{2,1}}{k_{2,1} \frac{[M_1]}{[M_2]} + k_{2,2}}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{\frac{k_{1,1}}{k_{1,2}} \frac{[M_1]}{[M_2]} + 1}{\frac{[M_1]}{[M_2]} + \frac{k_{2,2}}{k_{2,1}}}$$

dividing by $k_{2,1}$

- $d[M_1]/d[M_2]$ is the instantaneous relative molar increment of the two monomers in the copolymer.

- This may be taken as the molar ratio of the two monomer units incorporated in the copolymer i.e. $([M_1]/[M_2])_{copolymer}$.

- $[M_1]/[M_2]$ on R.H.S. of the equation relates to the feed monomer ratio i.e. molar ratio of the two monomers in the feed monomer mixture, $([M_1]/[M_2])_{feed}$.

$$k_{1,1}/k_{1,2} = r_1 \quad \text{and} \quad k_{2,2}/k_{2,1} = r_2$$

- r_1 and r_2 are called reactivity ratios for any given pair of monomers M_1 and M_2 .
- They indicate whether a growing chain carrying a free-radical on a particular monomer unit would prefer to add to its own monomer species or co-monomer species.
- $r_1 > 1$ means that the chain radical M_1^\bullet has a preference to add the like monomer, i.e. M_1 over the unlike monomer M_2 .
- Thus, the composition of the copolymer formed at any given instant is dependent not only on the concentration of the monomer species present in the system at that instant, but also on the reactivity ratios.
- r_1 and r_2 are purely dependent on the nature of the monomers, temperature and mechanism of chain propagation. It is independent of the nature of the solvent.

Five cases can arise:

- $r = 0 \Rightarrow$ the rate constant of homopolymerization is zero. The growing end only adds to the unlike polymer.
- $r < 1 \Rightarrow$ The active species adds on both monomers, but preferentially the unlike monomer.
- $r = 1 \Rightarrow$ The rate constants for both homopropagation and cross propagation are equal; like and unlike monomers are added with equal preference
- $r > 1 \Rightarrow$ The active species adds on both monomers, but preferentially the like monomer.
- $r = \infty \Rightarrow$ Only homopolymerization takes place, and no copolymerization.

$$\left(\frac{[M_1]}{[M_2]} \right)_{\text{copolymer}} = \left(\frac{[M_1]}{[M_2]} \right)_{\text{feed}} \frac{r_1 \left(\frac{[M_1]}{[M_2]} \right)_{\text{feed}} + 1}{r_2 + \left(\frac{[M_1]}{[M_2]} \right)_{\text{feed}}}$$

$$\left(\frac{[M_1]}{[M_2]} \right)_{\text{copolymer}} = \left(\frac{[M_1]}{[M_2]} \right)_{\text{feed}} \frac{r_1 [M_1] + [M_2]}{r_2 [M_2] + [M_1]}$$

copolymer composition equations

- $[M_1]$ and $[M_2]$ on R.H.S. stand for molar concentrations of the monomers M_1 and M_2 in the reactant or feed monomer mixture.

- Using copolymer and monomer compositions as mole fractions instead of mole ratios, the equation becomes,

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

- F_1 and F_2 mole fractions of the monomer segments M_1 and M_2 respectively in the copolymer formed. Thus, $F_1 = 1 - F_2$.

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Ideal copolymerization

- $r_1 r_2 = 1$

- $\frac{k_{1,2}}{k_{1,1}} = \frac{k_{2,2}}{k_{2,1}}$ M_1^\bullet & M_2^\bullet show same tendency to add to M_1 & M_2

- Co-polymer composition equation,

$$\left(\frac{[M_1]}{[M_2]} \right)_{\text{copolymer}} = \left(\frac{[M_1]}{[M_2]} \right)_{\text{feed}} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}$$

$$\left(\frac{[M_1]}{[M_2]} \right)_{\text{copolymer}} = r_1 \left(\frac{[M_1]}{[M_2]} \right)_{\text{feed}} \frac{r_1[M_1] + [M_2]}{r_1[M_1] + [M_2]}$$

[as, $r_1 = 1/r_2$]

$$\left(\frac{[M_1]}{[M_2]} \right)_{\text{copolymer}} = r_1 \left(\frac{[M_1]}{[M_2]} \right)_{\text{feed}}$$

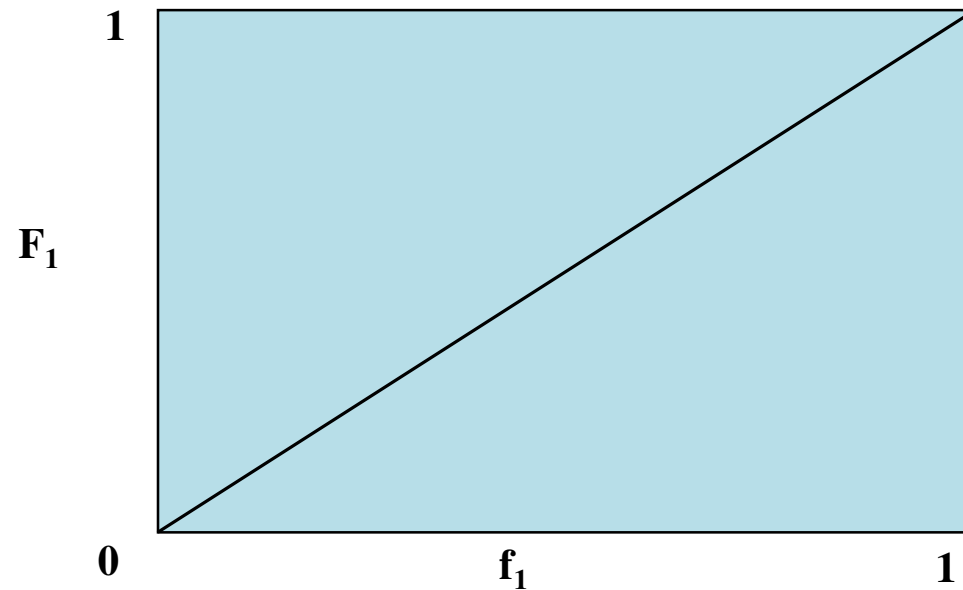
- And $F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2}$

Case I: $r_1 = r_2 = 1$

Copolymer composition is the same as feed monomer composition.

Case II: $r_1 > 1, r_2 < 1$

It is increasingly difficult to prepare copolymers having significant amount of both the monomers as the difference in reactivities of the two monomers increases.



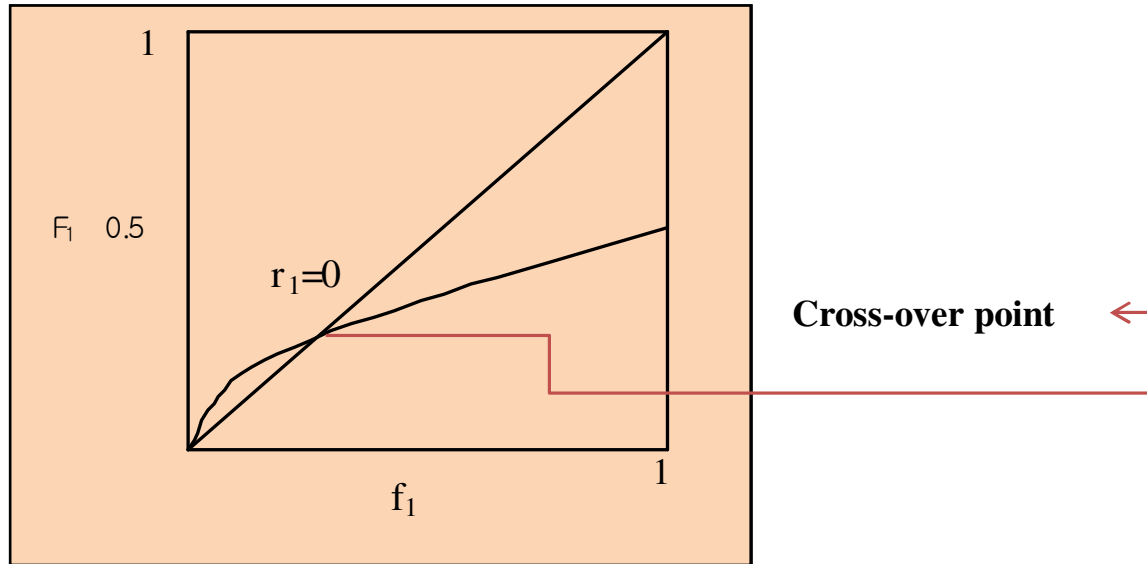
Alternate copolymerization

- $r_1 r_2 = 0$
or
- $r_1 = r_2 = 0$ [Perfect alteration!!]

If $r_1 = r_2 = 0$

- ❖ Neither monomer will react with its own radical but with the radical of the other monomer.
- ❖ Co-polymer composition equation becomes, $\left(\frac{[M_1]}{[M_2]} \right)_{copolymer} = 1$
- ❖ and $F_1 = 0.5$
- ❖ The copolymer composition is fixed irrespective of the feed monomer composition.
- $-M_1-M_2-M_1-M_2-M_1-M_2-M_1-M_2-M_1-M_2-$

If $r_1 < 1$ and $r_2 < 1$ then plots cross line representing $F_1 = f_1$



❖ At these crossover points the copolymer and feed compositions are the same and copolymerization occurs without a change in the feed composition.

❖ Such copolymerizations are termed **Azeotropic copolymerizations**.

❖ Conditions of Azeotropic copolymerization:

$$\left(\frac{[M_1]}{[M_2]} \right)_{\text{copolymer}} = \left(\frac{[M_1]}{[M_2]} \right)_{\text{feed}} \qquad \left(\frac{[M_1]}{[M_2]} \right)_{\text{feed}} = \frac{r_2 - 1}{r_1 - 1}$$