

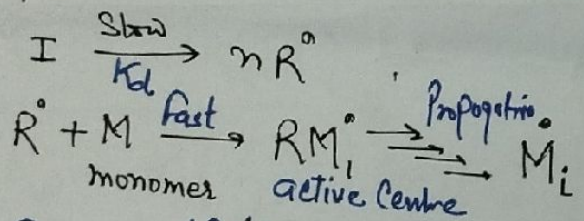
Chain Polymerization (Free radical Polymerization) - in which

L2
P1 One after other. Chain used to be propagate due to formation of Free radical base active Centre and after Consumption of monomers, poly^n used to terminate and yield stable polymer.

Such poly^n follows following Reaction pathway: Initiation \rightarrow Propagation \rightarrow Termination

Initiation : Responsible for formation of free radical active Centre

Initiation may represent as in two steps:

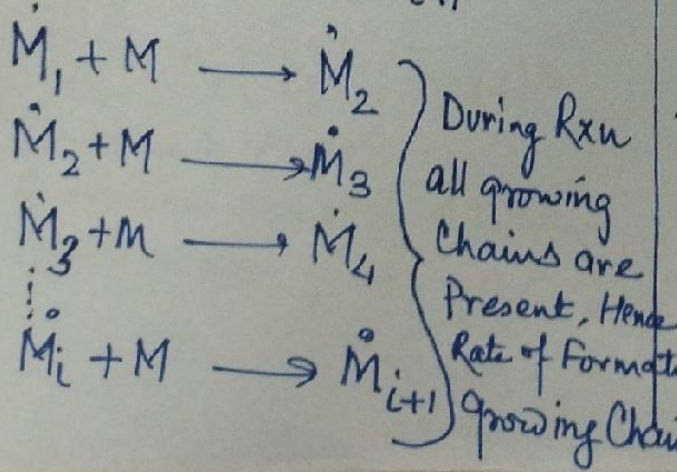
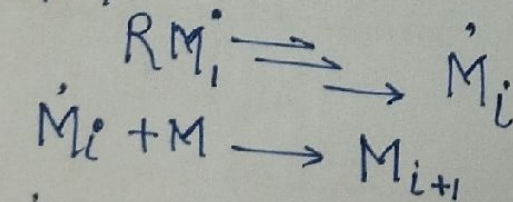


$$R_i = \frac{d[R^\bullet]}{dt} = 2f K_d [I]$$

↑
Rate of formation of active Centre

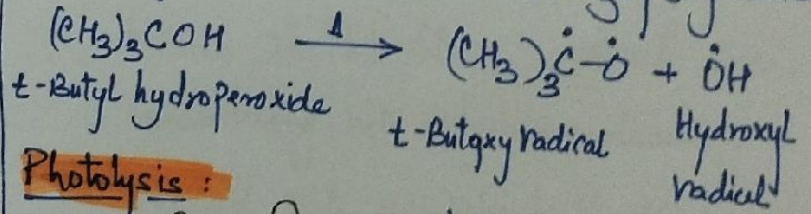
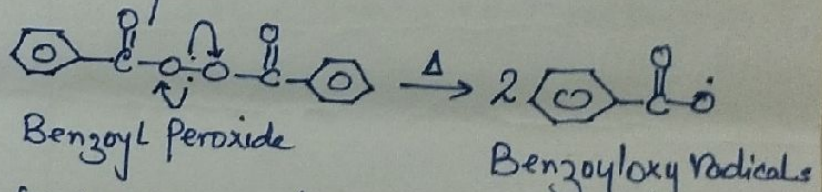
initiator efficiency dissociation constant

Propagation :

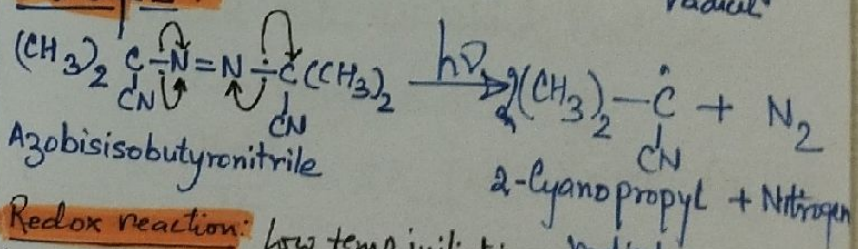


Rxn : Formation of free radical by

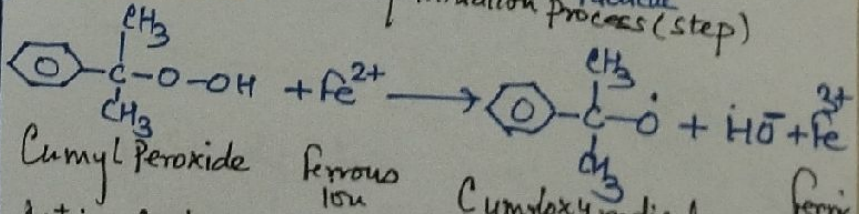
Thermolysis:



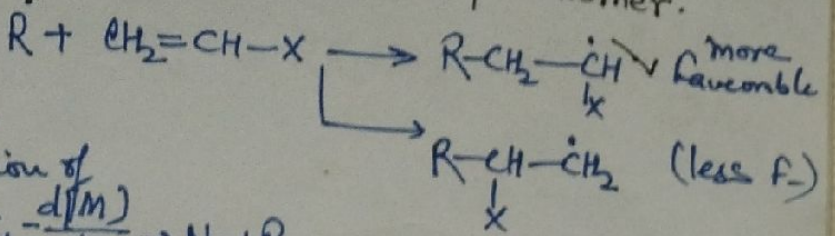
Photolysis :



Redox reaction: low temp initiation process (step)



Active Centre generate when above radicals (R^\bullet) react with π -Bond of molecule of monomer.



L2
P2

$$-\frac{d[M]}{dt} = k_p[M_1][M] + k_p[M_2][M] + \dots + k_p[M_i][M] + \dots$$

or

$$-\frac{d[M]}{dt} = k_p[M]([M_1] + [M_2] + \dots + [M_i] + \dots)$$

$$[\dot{M}] = \sum [M_i]$$

$$R_p = -\frac{d[M]}{dt} = k_p[M][\dot{M}]$$

$$R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{1/2}$$

$$R_p = \left(\frac{k_p}{(2k_t)^{1/2}}\right) R_i^{1/2} [M]$$

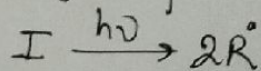
Under Steady State Condⁿ

$$R_i = 2fk_d[I]$$

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2} [M][I]^{1/2}$$

When initiation happened by thermolysis

When initiation is happened through photolysis of an initiator



$$R_i = 2\phi \epsilon I_0 [I]$$

$$R_p = k_p\left(\frac{\phi \epsilon I_0}{k_t}\right)^{1/2} [M][I]^{1/2}$$

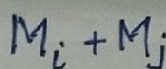
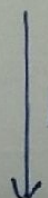
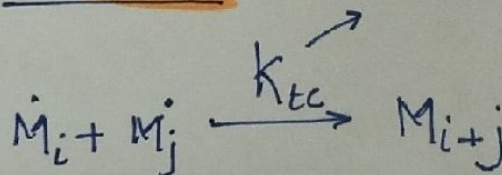
I_0 - intensity of light

ϵ - molar absorptivity of Initiator

ϕ - quantum yield.

Termination

Rate Constant for Combination



k_{td} = Rate Constant for Disproportionation

Hence, in this step, radicals are Consuming into polymer molecule.

Overall rate at which radicals are Consumed is given by:

$$-\frac{d[\dot{M}]}{dt} = 2k_{tc}[\dot{M}][\dot{M}] + 2k_{td}[\dot{M}][\dot{M}]$$

$$= 2k_t[\dot{M}]^2$$

$$k_t = k_{tc} + k_{td}$$

at Steady State

$$\frac{d[R^\bullet]}{dt} = -\frac{d[\dot{M}]}{dt}$$

$$R_i = 2k_t[\dot{M}]^2 \Rightarrow [\dot{M}] = \left(\frac{R_i}{2k_t}\right)^{1/2}$$

Degree of Polymerization (\bar{X}_n) = $\frac{\text{Mole of monomer Consumed in given time}}{\text{Moles of polymer formed in unit time}}$

$$\bar{X}_n = \frac{k_p[M][M']^A}{k_{tc}[M]^2 + 2k_{td}[M]^2}$$

Under steady state : $[M'] = \left[\frac{R_i}{2k_t} \right]^{1/2}$

$$\bar{X}_n = \frac{k_p[M]}{(1 + \frac{k_{td}}{k_t}) k_t^{1/2} (R_i/2)^{1/2}} \quad \text{--- (i)}$$

if termination took place due to disproportionation $\frac{k_{td}}{k_t} = 1$
by combination $q = 0$

$$\bar{X}_n = \frac{k_p[M]}{(1+q)(f k_{td} k_t)^{1/2} [I]^{1/2}} \quad (\text{Thermolysis})$$

$$\bar{X}_n = \frac{k_p[M]}{(1+q)(\phi \epsilon I_0 k_t)^{1/2} [I]^{1/2}} \quad (\text{Photolysis})$$

Hence

$$\bar{X}_n \propto [M][I]^{-1/2}$$

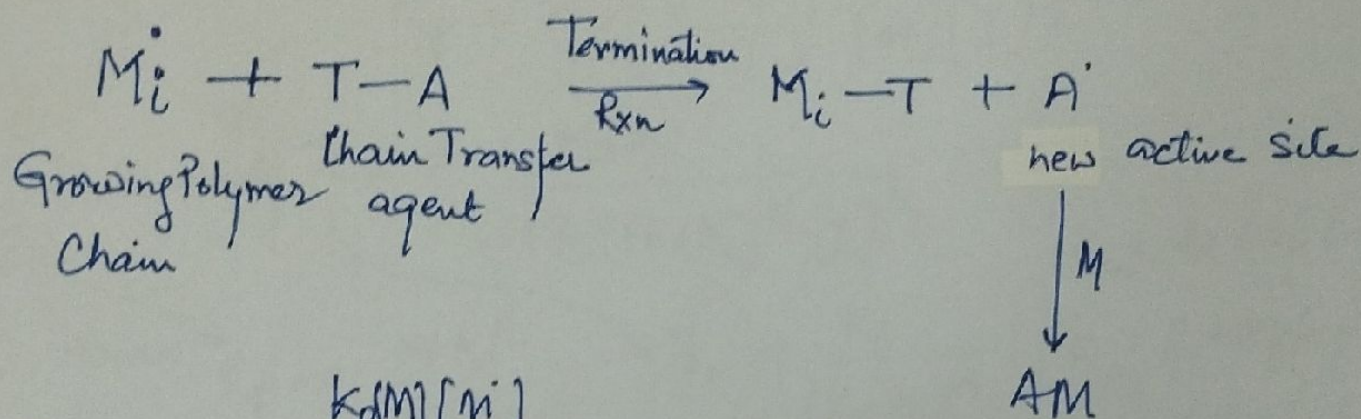
↑
no. average degree of polymerization

Chain Transfer Reaction & its effect on \bar{X}_n

L2
P4

Exp \bar{X}_n is always less than Theoretical \bar{X}_n
due to Chain transfer reaction

$$\bar{X}_n = \frac{k_p[M]}{(1+q)k_t^{1/2}(R_i/2)^{1/2}}$$



$$\bar{X}_n = \frac{k_p[M][M_i]}{K_{tc}[M_i]^2 + 2k_{td}[M_i]^2 + k_{tr}[M_i][M] + k_{trI}[M_i][I] + k_{trs}[M_i][S]}$$

\downarrow Rate constant against Combination \downarrow disproportionation \downarrow Chain transfer Monomer to Monomer \downarrow Chain transfer Monomer to Initiator \downarrow Chain Transfer monomer to Solvent

$$\bar{X}_n = \frac{(1+q)k_t^{1/2}(R_i/2)^{1/2}}{k_p[M]} + \frac{k_{trm}}{k_p} + \frac{k_{trI}[I]}{k_p[M]} + \frac{k_{trs}[S]}{k_p[M]}$$

Mayo-Walling Equation

$$\frac{1}{\bar{X}_n} = \frac{1}{(\bar{X}_n)_0} + C_m + C_I \frac{[I]}{[M]} + C_S \frac{[S]}{[M]}$$

$$\bar{X}_n \propto \frac{k_p}{k_d^{1/2} k_t^{1/2}}$$

Chain transfer Constant

Thermodynamic Consideration:

We understand that rate constant is f^h of Activation Energy E_a

P5
L2

R_p of Chain polyⁿ is already defined as:

$$R_p = k_p \left(\frac{f k_d}{k_t} \right)^{1/2} [M][I]^{1/2}$$

Subsequently $\bar{x}_n = \frac{k_p [M]}{(1+\rho)(f k_d k_t)^{1/2} [I]^{1/2}}$

Hence $R_p \propto \frac{k_p k_d^{1/2}}{k_t^{1/2}}$ and $\bar{x}_n \propto \frac{k_p}{(k_d k_t)^{1/2}}$

$$\frac{d \ln(R_p)}{dT} = \frac{(2E_p + E_d) - E_t}{2RT^2}$$

$$\frac{d \ln(\bar{x}_n)}{dT} = \frac{2E_p - (E_d + E_t)}{2RT^2}$$

$$k_d = A_d \exp(-E_d/RT)$$

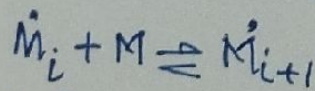
$$k_p = A_p \exp(-E_p/RT)$$

$$k_t = A_t \exp(-E_t/RT)$$

$$k_{tr} = A_{tr} \exp(-E_{tr}/RT)$$

if $E_d \gg E_p > E_t$ then $\frac{d \ln(R_p)}{dT} \rightarrow (+) \text{ive}$

Predicted increase in R_p is based on the assumption that R_p is irreversible in nature



$$\Delta G^\circ = -RT \ln(k_p) \text{ at equilibrium}$$

std Gibbs free energy for Propagation

$$k_p = \frac{[M]_{eq}}{[M^\bullet]_{eq} [M]_{eq}} = \frac{[M]_{eq}}{[M^\bullet]_{eq}}$$

Equilibrium monomer conc.

$$\Delta G_p^\circ = \Delta H_p^\circ - T \Delta S_p^\circ$$

$$\ln[M]_{eq} = \frac{\Delta H_p^\circ}{RT} - \frac{\Delta S_p^\circ}{R}$$

Hence rate of polyⁿ \uparrow with $T \uparrow$

$$\frac{d \ln(\bar{x}_n)}{dT} \rightarrow (-) \text{ive}$$

Hence $\bar{x}_n \downarrow \propto T \uparrow$

It means

$$T \uparrow \propto M \uparrow$$

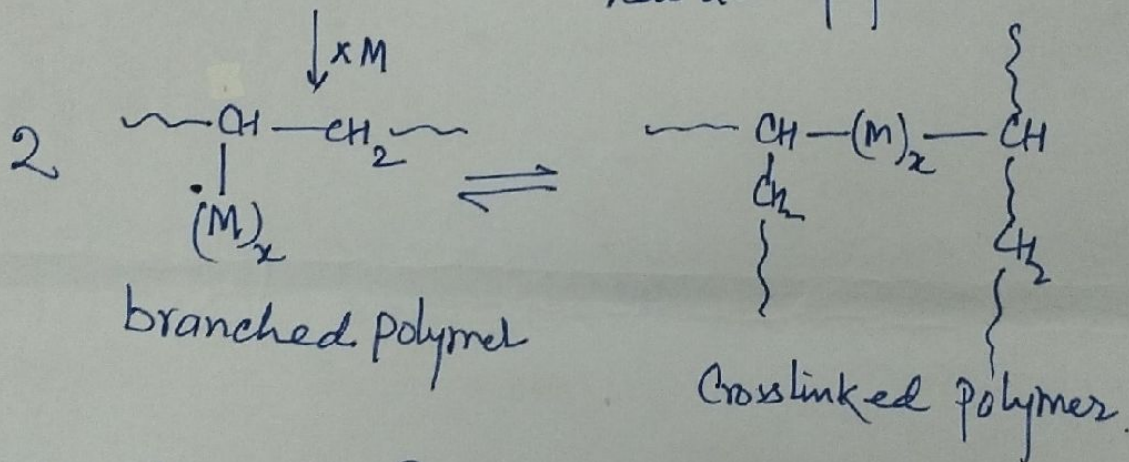
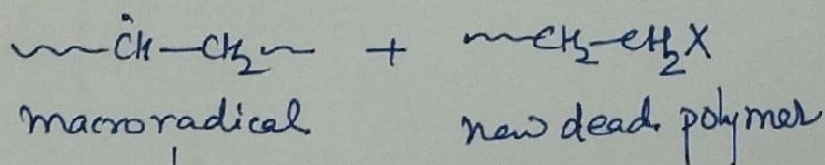
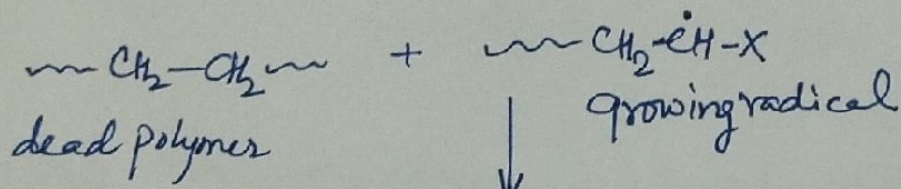
ΔH° = standard enthalpy change for Propagation

ΔS_p° = entropy

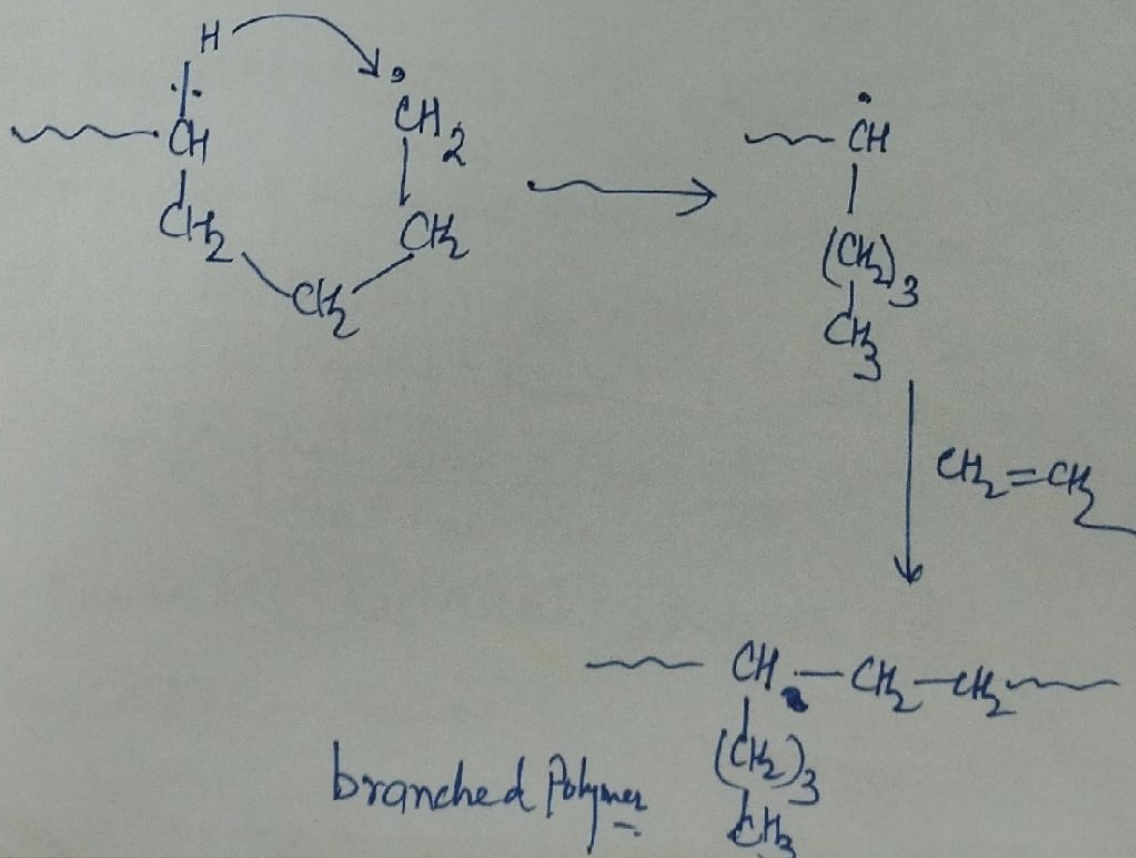
if $\Delta H_p^\circ < 0$ Polymerization is exothermic

Effect of Chain Transfer to Polymers

When dead polymer takes part in chain transfer process then new active centre formed which activate new chain architecture.



back-biting termination Rxn:



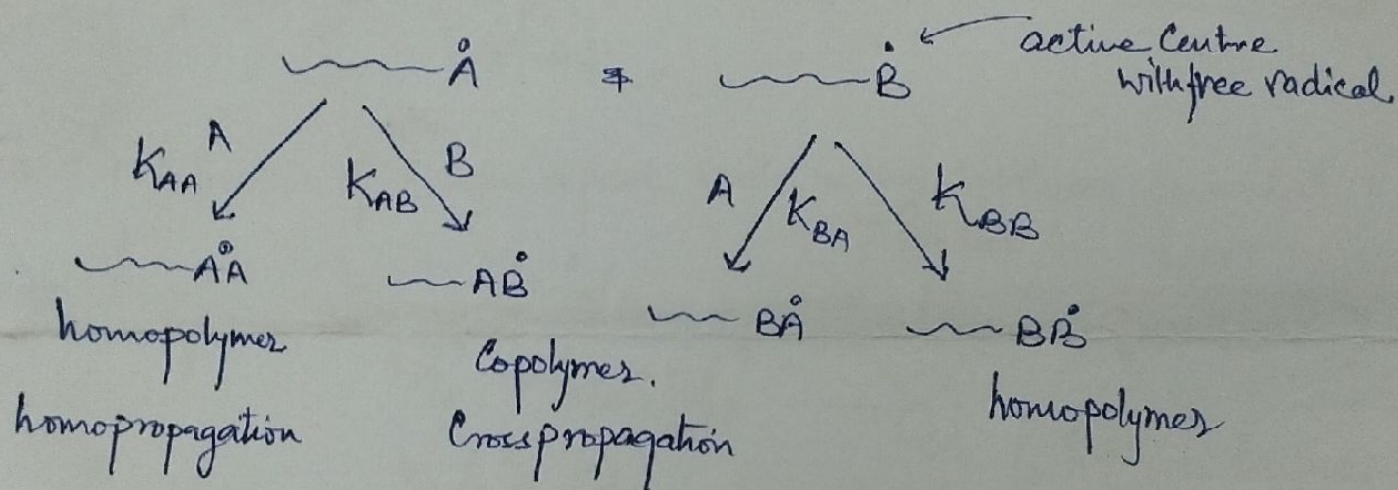
Copolymer Composition prediction at particular instant in time during Chain growth Copolymerization:

Can be analysed
by Terminal Model

(Reactivity of rxn Centre depends only upon terminal monomer unit)

assumption: Consumption of monomer other than propagation is negligible

Possible Active Centres:



$$-\frac{d[A]}{dt} = K_{AA}[A][A] + K_{AB}[A][B] \quad \text{--- (a)} \quad -\frac{d[A]}{dt} = K_{AA}[A][A] + K_{BA}[B][A] \quad \text{--- (b)}$$

$$-\frac{d[B]}{dt} = K_{BB}[B][B] + K_{BA}[A][B] \quad \text{--- (c)} \quad -\frac{d[B]}{dt} = K_{AB}[B][A] + K_{BB}[B][B] \quad \text{--- (d)}$$

At any given time, ratio of the amount of monomer A to monomer B:

$$\frac{d[A]}{d[B]} = \frac{[A] [K_{AA}[A] + K_{BA}[B]]}{[B] [K_{AB}[A] + K_{BB}[B]]} \Rightarrow \frac{[A]}{[B]} \left[\frac{K_{AA} + K_{BA} \frac{[B]}{[A]}}{K_{BB} + K_{AB} \frac{[A]}{[B]}} \right]$$

or $\frac{[A]}{[B]} \left[\frac{K_{AA} \frac{[A]}{[B]} + K_{BA}}{K_{BB} + K_{AB} \frac{[A]}{[B]}} \right] \quad \text{--- (e)}$

Steady State

$$\frac{d[A]}{dt} = K_{BA}[B][A] - K_{AB}[A][B] \quad \left\{ \begin{array}{l} \text{at steady state } \frac{d[A]}{dt} = 0 \\ \frac{d[B]}{dt} = 0 \end{array} \right.$$

$$\frac{d[B]}{dt} = K_{AB}[A][B] - K_{BA}[B][A]$$

$$\Rightarrow \frac{[A']}{[B']} = \frac{K_{BA} [A]}{K_{AB} [B]}$$

in eq (e)

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]} \left(\frac{\frac{K_{AA} \cdot K_{BA} \cdot [A]}{K_{AB}} + K_{BA}}{K_{BB} + \frac{K_{AB} \cdot K_{BA} \cdot [A]}{K_{AB}} \cdot \frac{[A]}{[B]}} \right)$$

mole ratio of A-type to B-type repeat unit at 't'

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]} \left(\frac{r_A [A] + [B]}{r_B [B] + [A]} \right) \quad \text{--- (f)}$$

mole fraction f_A of monomer 'A'

$$\frac{[A]}{[A] + [B]}$$

$$f_B = 1 - f_A$$

in Feed

F_A : Mole fraction of A-type repeat units in the copolymer formed at 't'

→ Product

$$\frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2} = F_A = \frac{d[A]}{d[A] + d[B]} \quad \text{--- (g)}$$

$$F_B = \frac{r_B f_B^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2} \quad \text{--- (h)}$$

Copolymer Composition Equation

Monomer reactivity ratio and Copolymer Composition/Structure

$$r_A = \frac{K_{AA}}{K_{AB}}$$

$$r_B = \frac{K_{BB}}{K_{BA}}$$

$r_A > 1$ \curvearrowright A' prefers to add monomer A.

$r_A < 1$ \curvearrowright A' $\xrightarrow{\quad\quad\quad}$ B

homopolymerization
Copolymerization

$r_A = r_B = 1$ Probability of adding A is same as B monomer

Random Copolymer
($F_A = f_A$)

$r_A > 1; r_B > 1$ no copolymerization

$r_A > 1$ with $r_B < 1$ both type of active centre prefer to add the monomer

$r_A = r_B = 0$ Alternate Copolymer.

Ideal Copolymerization : $r_A > 1, r_B < 1$; $r_A r_B = 1$
 $r_A < 1, r_B > 1$

$$r_A = \frac{1}{r_B}$$

$$\frac{k_{AA}}{k_{AB}} = \frac{k_{BA}}{k_{BB}}$$

$$F_A \neq f_A$$

$$F_A = \frac{r_A f_A}{r_A f_A + f_B}$$

$$r_A r_B \neq 1 \quad r_A r_B < 1 \quad r_A > 1; r_B < 1$$

F_A vs f_A Curve which is similar to ideal Copolymerization but skewed towards Copolymer Composition richer in repeat unit derived from more reactive monomer.

$$r_A/r_B \uparrow$$

↑ longer the sequence of A type repeat units
 ↓ shorter B-type repeat units

$$r_A \gg 1 \quad r_B \ll 1 \rightarrow \text{Homopolymerization}$$

Azeotropic Copolymerization

$$(f_A)_{\text{azeo}} = F_A = f_A$$

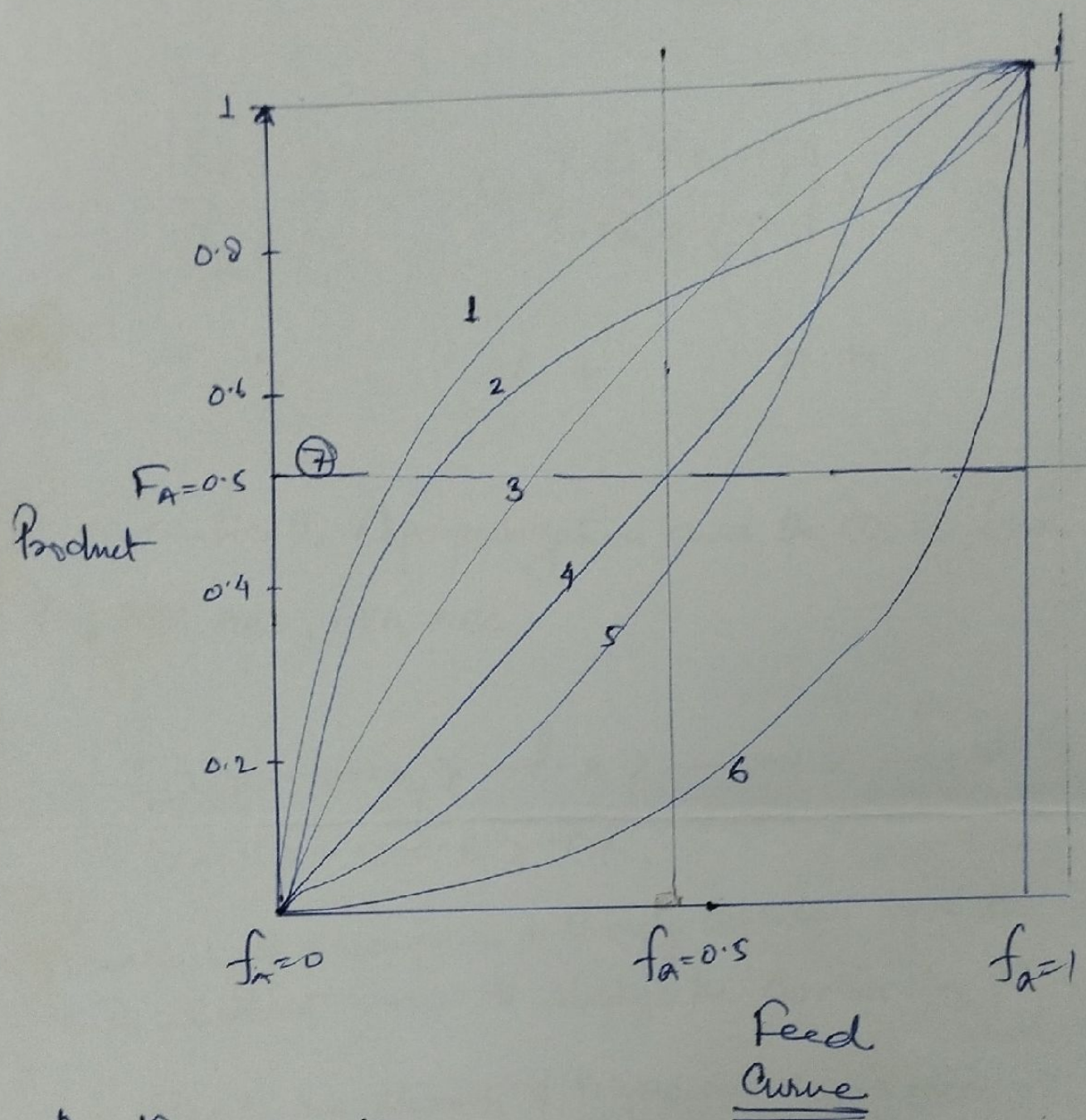
$$r_A < 1 \text{ with } r_B < 1$$

$$r_A < 1 \text{ with } r_B > 1$$

due to change in Condⁿ

$$f_A)_{\text{azeo}} = \frac{1 - r_B}{2 - r_A - r_B}$$

$$r_A r_B \downarrow \text{ with Poly}^n$$



- $r_A = 1.0$ $r_B = 1$
- $r_A = 2$ $r_B = 0.5$
- $r_A = 0.1$ $r_B = 10$
- $r_A = 4$ $r_B = 0.1$
- $r_A = 2$ $r_B = 4$
- $r_A = 0$ $r_B = 0$
- $r_A = 0.5$ $r_B = 0.1$