

Putting the value of $d(M_1)$ and $d(M_2)$ from eq (12) in eq (13)

$$\eta_1 = \frac{[M_1] (\gamma_1 [M_1] + [M_2])}{[M_1] (\gamma_1 [M_1] + [M_2]) + M_2 (\gamma_2 [M_2] + [M_1])} \quad (14)$$

Dividing numerator and denominator from $(M_1 + M_2)$ of the equation

$$\eta_1 = \frac{M_1}{M_1 + M_2} \left(\gamma_1 \frac{[M_1]}{[M_1] + [M_2]} + \frac{[M_2]}{[M_1] + [M_2]} \right) \quad (15)$$

$$\frac{[M_1]}{[M_1] + [M_2]} \left(\gamma_1 \frac{[M_1]}{[M_1] + [M_2]} + \frac{[M_2]}{[M_1] + [M_2]} \right) + \frac{M_2}{M_1 + M_2} \left(\gamma_2 \frac{M_2}{[M_1] + [M_2]} + \frac{M_1}{[M_1] + [M_2]} \right)$$

Whereas $N_1 = \frac{M_1}{M_1 + M_2}$ & $N_2 = \frac{M_2}{[M_1] + [M_2]}$

then eq (16) becomes

$$\eta_1 = \frac{N_1 (\gamma_1 N_1 + N_2)}{N_1 (\gamma_1 N_1 + N_2) + N_2 (\gamma_2 N_2 + N_1)} \quad (16)$$

$$\eta_1 = \frac{\gamma_1 N_1^2 + N_1 N_2}{\gamma_1 N_1^2 + N_1 N_2 + \gamma_2 N_2^2 + N_1 N_2}$$

$$\eta_1 = \frac{\gamma_1 N_1^2 + N_1 N_2}{\gamma_1 N_1^2 + 2 N_1 N_2 + \gamma_2 N_2^2}$$

By knowing r_1 & r_2 and monomers
ratio we can calculate the molar
ratio of polymer copolymerisation.

Reactivity Ratio & Co-polymerization behaviour

⇒ Composition of ~~the~~ co polymer formed not only depend on concentration of monomer but also on there reactivity ratio.

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

① When $r_1 = r_2 = 0$

$$r_1 = \frac{k_{11}}{k_{12}} = 0, \quad r_2 = \frac{k_{22}}{k_{21}} = 0$$

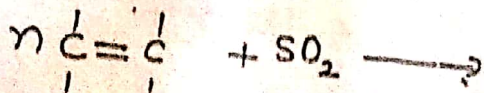
✓ Means system has low value of k_{11} & k_{22}
 So propagation reaction (PR) type 11 & PR type 22 are not possible.

This means RM_1 will add only M_2 ✓

RM_2 will add only M_1 ✓

So the co-polymer formed will have equal No. of M_1 & M_2 which are arranged alternately. So the alternating copolymer will be formed. And it can not form homopolymer.

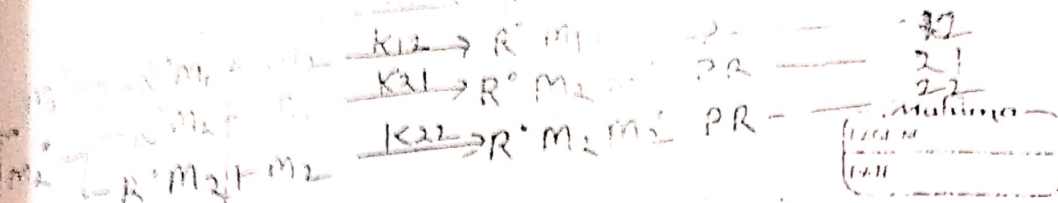
Exa: copolymer of sulphur dioxide and certain olefins, cycloolefins, vinyl compound,



② ✓ $r_1 = r_2 = 1$:

$$r_1 = \frac{k_{11}}{k_{12}} = 1 \quad \text{or} \quad k_{11} = k_{12} = 1$$

$$r_2 = \frac{k_{22}}{k_{21}} = 1 \quad \text{or} \quad k_{22} = k_{21} = 1$$



In this case all the four types of propagation reactions are equally possible.



The probability of M_1 or M_2 adding to the radicals depends purely on the monomer concentration. This type of polymerisation is called ideal or Azeotropic co-polymerisation.

Ideal Co-polymerisation

monomer ratio = monomer feed ratio

imp - Since the copolymer composition can be ideally controlled by adjusting the initially monomer feed ratio, it is called ideal co-polymerisation.

Azeotropic Polymerisation

imp - Since the feed composition and copolymer composition remains constant throughout the course of polymerisation. This type of copolymerisation is also called the Azeotropic copolymerisation.

③ When $r_1 > 1$ and $r_2 < 1$:

$$\frac{k_{11}}{k_{12}} > 1 \quad , \quad \frac{k_{22}}{k_{21}} < 1$$

Means k_{11} prefers than k_{12}

means that M_1 will add preferably to M_1