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

$$n_1 = \frac{[M_1]\left(r_1(M_1) + (M_2)\right)}{[M_1]\left[r_1[M_1] + [M_2]\right] + M_2\left[r_2[M_2] + [M_1]\right]} \quad -(14)$$

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

$$n_1 = \frac{\frac{M_1}{M_1+M_2}\left(r_1\frac{(M_1)}{(M_1)+M_2]} + \frac{(M_2)}{(M_1)+(M_2)}\right)}{\frac{(M_1)}{(M_1)+(M_2)}\left(r_1\frac{(M_1)}{(M_1)+(M_2)} + \frac{(M_2)}{(M_1)+(M_2)}\right) + \frac{M_2}{M_1+M_2}\left(r_2\frac{M_2}{(M_1)+(M_2)} + \frac{M_1}{(M_1)+(M_2)}\right)} \quad -(15)$$

Whereas $N_1 = \frac{M_1}{M_1+M_2}$ & $N_2 = \frac{M_2}{(M_1)+(M_2)}$

then eq (16) becomes

$$n_1 = \frac{N_1(r_1 N_1 + N_2)}{N_1(r_1 N_1 + N_2) + N_2(r_2 N_2 + N_1)} \quad -(16)$$

$$n_1 = \frac{r_1 N_1^2 + N_1 N_2}{r_1 N_1^2 + N_1 N_2 + r_2 N_2^2 + N_1 N_2}$$

$$n_1 = \frac{r_1 N_1^2 + N_1 N_2}{r_1 N_1^2 + 2N_1 N_2 + r_2 N_2^2}$$

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

Reactivity Ratio & Co-polymerization behaviour

⇒ Composition of ~~of~~ copolymer 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 where $r_1 = r_2 = 0$:

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

Means system has low value of K_{11} & K_{22}

So propapation reaction (PR) type 11 & PR type 22 are not possible.

This means $RM_1^{\cdot}$ will add only M_2

$RM_2^{\cdot}$ will add only M_1

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

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

$n\,\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} + SO_2 \longrightarrow$

② $r_1 = r_2 = 1$: $r_1 = \frac{K_{11}}{K_{12}} = ~~0~~$ or $K_{11} = K_{12} = 1$

$r_2 = \frac{K_{22}}{K_{21}} = 1$ or $K_{22} = K_{21} = 1$

$\xrightarrow{K_{12}} R^{\cdot}M_1$ — PR — 12

$\xrightarrow{K_{21}} R^{\cdot}M_2$ PR — 21

$R^{\cdot}M_2 + M_2 \xrightarrow{K_{22}} R^{\cdot}M_2M_2$ PR — 22

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

$RM_1^{\cdot} \longrightarrow$ on $\left\langle \begin{matrix} M_1 \\ M_2 \end{matrix} \right.$

$RM_2^{\cdot} \longrightarrow$ on $\left\langle \begin{matrix} M_1 \\ M_2 \end{matrix} \right.$

The probability of M_1 or M_2 adding to the radicals ($M_1^{\cdot}$ & $M_2^{\cdot}$) 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 initial monomer feed ratio is called ideal co-polymer.

Azeotropic Polymerisation

Imp — Since the feed composition and copolymer composition remains constant through out the course of polymerisation. This type of copolymerisation is also called the Azeotropic copolymerisation

③ When $r_1 > 1$ and $r_2 < 1$:

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

Means K_{11} prefers than K_{12}

means that $M_1^{\cdot}$ will add preferally to M_1