k_{21} prefers than k_{22} means $M_2^{\cdot}$ will add preferally to M_1. Therefore copolymer will be richer in M_1 monomer.

④ when $r_1 < 1$ and $r_2 > 1$

In this case copolymer formed will be richer in M_2 monomer

⑤ when $r_1 > 1$ & $r_2 > 1$ $\therefore \frac{k_{11}}{k_{12}} > 1$ & $\frac{k_{22}}{k_{21}} > 1$

Such a system does not usually undergo random copolymerisation.

In this system forms either a mix of a homopolymer or a block copolymer having long sequence of M_1, followed by a long sequence of M_2.

⑥ when r_1 or $r_2 = 0$

$\frac{k_{11}}{k_{12}} = 0$ or $\frac{k_{22}}{k_{21}} = 0$

Such a system usually results in a copolymer with a particular azeotropic composition

⑨ If mole fraction of the monomer with a zero reactive ratio is below the azeotropic Composition. Then the azeotropic copolymer along with homopolymer, will be formed.

⑩ If mole fraction of monomer is higher than the azeotropic composition than alone azeotropic composition then azeotropic copolymer will be formed.

⑦ when $r_1 < 1$ & $r_2 < 1$

$\frac{k_{11}}{k_{12}} < 1$ and $\frac{k_{22}}{k_{21}} < 1$

In this case, type 12 & 21 are prefered. chain ending with M_1 will add on M_2 and chain ending with M_2 will add on M_1

(a) when $r_1 = r_2$

The copolymer formed will be richer in M_1 upto $N_1 = 0.5$

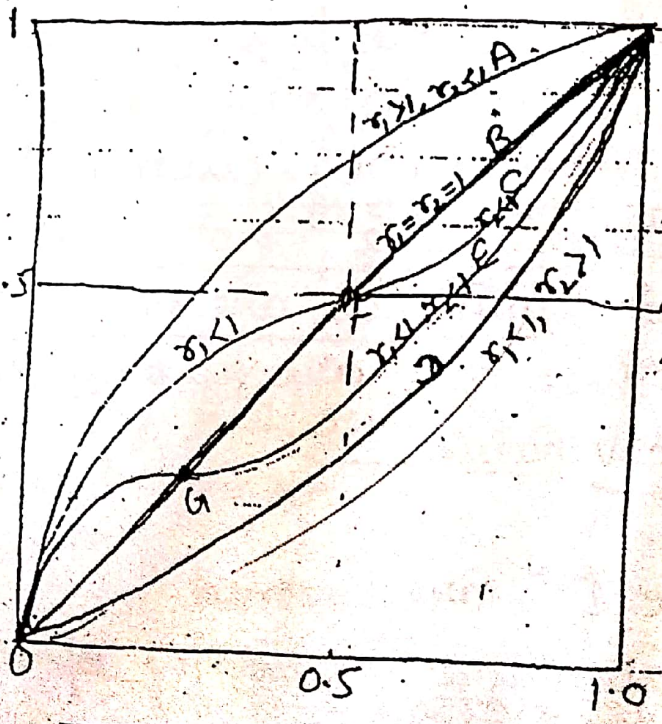
then onwards the copolymer richer will be in M_2 at $N_1 = 0.5$

(b) when $r_1 < r_2$ then azeotropic composition decreases from 0.5 value

(c) when $r_1 > r_2$ there is increase in azeotropic composition

The value of N_1 for the azeotropic composition can be arrived at from following eq.

$$N_1 = \frac{1 - r_2}{2 - r_1 - r_2}$$



(c) Block-Copolymers ⇒ Linear copolymers in which the like monomeric units occur in relatively long sequences are called block co-polymers.

Ex: -A-A-A-B-B-B-B-A-A-A-A-B-B-B-B-

Block copolymers

Block copolymers may be produced by the following four tech.

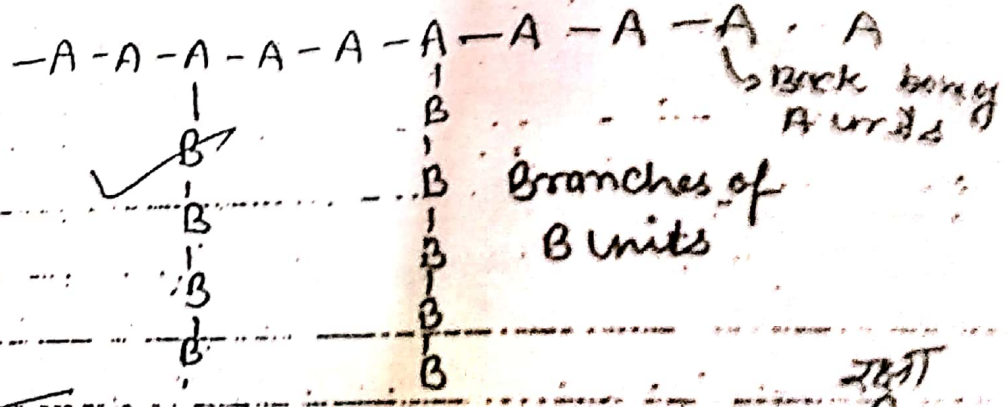
(i) Utilise reactive end groups.

(ii) Activate end gps

(iii) Fragment a chain to produce active end gps

(iv) Transport reactive end gps into a diff. medium

(d) Graft copolymer ⇒ These are branched copolymer in which the branches have diff. chemical st. to that of main chain.



The importance of the block and graft co-polymer is that the resultant material tends to exhibit the properties of each homopolymer

They also have same unique property arising from the chemical linkage b/w the homopolymer sequence.

Eg: Pure polystyrene is quite brittle, whereas polymerisation of about 5% of Rubber produced material which is strong and tough

90 part of vinyl chloride & 10 part of vinyl acetate, the random co-polymerisation

formed has toughness of polyvinyl chloride, thermal stability of polyvinyl acetate. * These Combination of properties makes it useful as a paint.

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