Copolymerization

It was a polymerization of two or more different monomers. The resulted copolymer have a characteristic of the two monomers. Terepolymerization is specifically used for system of three monomers.

Copolymerization process allows the synthesis of unlimited different products by variations in the nature and relative amount of the used monomers in the produced copolymer. The participation of the monomer in the backbone of the copolymer chain depends on the concentration of the monomers in the reaction mixture (feed) and their reactivity ratios.

Types of copolymers:

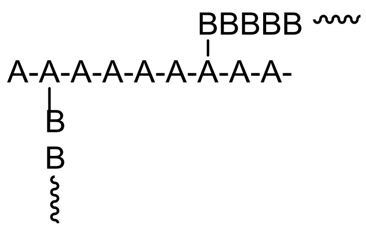
According to their chemical structure and the sequences of the repeating units (monomers) in the copolymer chain, the types of the copolymers can be:

1- Random ---ABBAAABABBAA---

2- Alternate –ABABAB----

3- Block --AAAAABBBBBAAAAAABBBBBB—

4- Graft



In condensation polymers, the copolymers can be alternate or block only.

The copolymerization equations (free radical copolymerization):

The rate of addition of monomer to the growing chain ended with free radical depends only on the nature of the end group of the radical chain. Thus adding monomers M1 or M2 to the growing chain lead to radicals of type $M1^{\bullet}$ or $M2^{\bullet}$. there are four possible ways in which the monomers can be added:

$$\left.\begin{array}{llr} & & \text{rate} = \\ \sim M_1^{\bullet} + M_1 \xrightarrow{K11} \sim M_1^{\bullet} & \text{-------------} & k11[M1^{\bullet}][M1] \\ \sim M_1^{\bullet} + M_2 \xrightarrow{K12} \sim M_2^{\bullet} & \text{-----------} & K12[M1^{\bullet}][M2] \\ \sim M_2^{\bullet} + M1 \xrightarrow{K21} \sim M_1^{\bullet} & \text{-----------} & K21[M2^{\bullet}][M1] \\ \sim M_2^{\bullet} + M2 \xrightarrow{K22} \sim M_2^{\bullet} & \text{----------} & K22[M2^{\bullet}][M2] \end{array}\right) \text{----------} \quad 1$$

At the steady state , concentration of $M1^{\bullet}$ and $M2^{\bullet}$ Must remain constant. The rate of conversion of $M1^{\bullet}$ to $M2^{\bullet}$ Must equal to that of conversion of $M2^{\bullet}$ to $M1^{\bullet}$ Or

$$K12[M1^{\bullet}][M2] = K21[M2^{\bullet}][M1] \text{ ------------- } 2$$

The rate of disappearance of the two types of monomers are given by

$$\left.\begin{array}{l} -\dfrac{d[M1]}{dt} = K11[M1^{\bullet}][M1] + K21[M2^{\bullet}][M1] \\ \\ -\dfrac{d[M2]}{dt} = K21[M1^{\bullet}][M2] + K22[M2^{\bullet}][M2] \end{array}\right\} \text{ ----------- } 3$$

Reactivity ratio is the ratio between the efficiency of reaction of the monomer with itself to the reaction with the second monomer.

$$r_1 = \frac{k11}{k12} \quad , \quad r_2 = \frac{k22}{k21} \qquad r = \text{reactivity ratio}$$

By combining 2 and 3 with r

$$\frac{d[M1]}{d[M2]} = \frac{[M1] \ (r_1[M1] + [M2])}{[M_2] \ (r_2 [M2] + [M1])} \quad \text{-----------} \ 4$$

Equation 4 is called the [**Copolymer equation]**

The meaning of reactivity ratios r_1 and r_2 are the rate constant for a given radical adding its own monomer to that for its adding to the other monomer.

$r_1 > 1$ means radical $M1^{\cdot}$ Prefers to add M1

$r_1 < 1$ means $M1^{\cdot}$ Prefers to add M2

The reactivity ratios did not affected by the presence of inhibitors, chain transfer agents or solvent.

From equation 4 , the rate constants of initiation and termination do not appear, this means that the composition of the copolymer is independent on the overall reaction rate and initiator concentration.

Whereby d[M1]/ d[M2] represent the ratio of monomers within the copolymer chain.

From the value of $r_1$and r_2 we can conclude the type of the copolymer according to the arrangement of the monomers units in the polymer chain as follows:

1-) $r_1 x r_2 = 1$ $\qquad r_1 = 1/ r_2$
or

$$\frac{k11}{k12} = \frac{k21}{k22}$$

The produced copolymer is random and the amount of the units in the chain is affected by the composition of the feed.

The copolymer equation reduced to

$$\frac{d[M1]}{d[M2]} = \frac{r_1[M1]}{[M2]}$$

2-) $r_1=0 \quad r_2= 0$

The copolymer is alternate , this means that each radical prefers to react with the other monomer. The copolymer equation become.

$$\frac{d[M1]}{d[M2]} = 1$$

3-) r_1 and $r_2 < 1$

The copolymer is alternate

4-) $r_1 = r_2 = 1$

The copolymer is random. The activities of each monomer to react with other monomer are equal.

5-) r_1 and $r_2 > 1$

The copolymer is block. Any monomer prefers to react with itself.

6-) $r_1 > 1$, $r_2 < 1$

the copolymer chain consist mainly of M1 and very small amount of M2 or only M1.

Relation between feed composition and copolymer structure:

F_1 and F_2 are the mole fractions of M1 and M2 in the copolymer, f_1 and f_2 are the mole fractions of M1 and M2 in feed.

$$F_1 = 1 - F_2 = \frac{d[M1]}{d([M1] + [M2]} \quad \text{-------------} \; 5$$

$$f_1 = 1 - f_2 = \frac{[M1]}{[M1] + [M2]} \quad \text{----------} \; 6$$

Combine between 4, 5 and 6 become:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f1^2 + 2f1f_2 + r_2 f_2^2} \quad \text{-----------} \; 7$$

From equation 7

$$F_1 \neq f_1$$

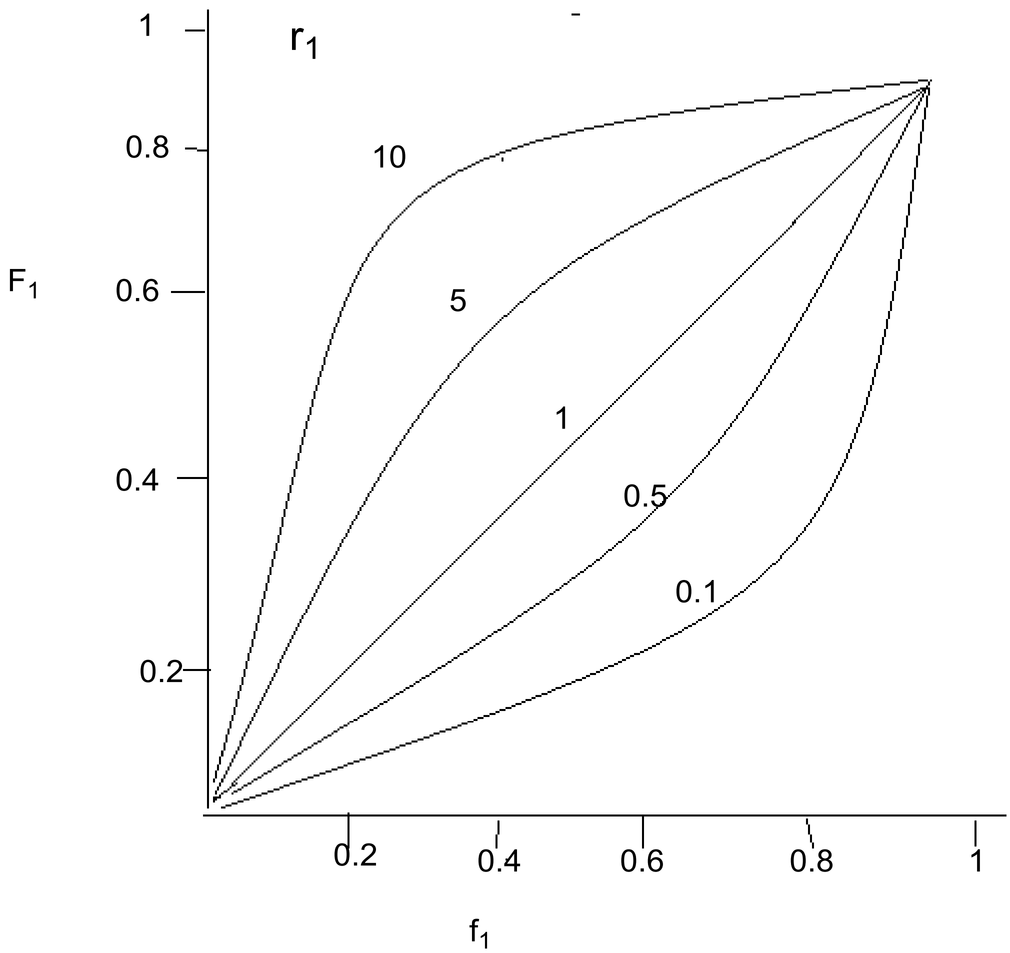
And both f_1 and F_2 changes as polymerization proceeds.

Drawing curves between feed(f_1) vs. instantaneous polymer composition (F_1), four monomer reactivity ratios shows the effect of r_1 and r_2 on the copolymer composition as follows:

1) $r_1 = 1/r_2$ or $r_1 r_2 = 1$ ideal copolymerization

$$F_1 = \frac{r1f1}{r1f1 + f2}$$

The calculate curve is :



As reactivity ratio of monomer M1 increase , its F_1 increase, and when $r_1 = r_2 = 1$ the copolymer contain the appreciable amounts of both components but the copolymer is random.

In case of different r_1 and r_2 as

$r_1 > 1$, $r_2 < 1$ or $r_1 < 1$, $r_2 > 1$

the copolymer contain high percent of monomer with high reactivity ratio more than the other with lower reactivity ratio.

2) $r_1 = r_2$ Alternate copolymerization

The two monomers are in the copolymer with same percent;

$F_1 = 0.5$, whenever the amount of feed, so

$$\frac{d[M1]}{d[M2]} = 1$$

In general $0 < r_1 r_2 < 1$

As $r_1 r_2$ decrease from 1, the copolymer become alternate, at $r_1 r_2 = 0$, the copolymer become complete alternate.

When $F_1 = f_1$, this is known as azeotropic copolymerization and

$$\frac{d[M1]}{d[M2]} = \frac{1 - r_2}{1 - r_1} \quad \text{or}$$

$$f_1 = \frac{1 - r_1}{2 - r_1 - r_2}$$

3) block copolymer produced when $r_1 > 1$ and $r_2 > 1$.

Evaluation of monomer reactivity ratios:

The usual experiment determination of r_1 and r_2 involves polymerization at low conversion for a variety of feed compositions. The formed polymers in every case are isolated and their composition are analysis by any available method. Equation 7 can be rearrangement to

$$\frac{f_1(1 - 2F_1)}{(1 - f_1)\, F_1} = r_2 + \frac{f_1^2(F_2 - 1)}{(1 - f_1)^2\, F_1}\, r_1$$

By plotting

$$\frac{f_1(1 - 2F_1)}{(1 - f_1)\, F_1} \quad \text{vs.} \quad \frac{f_1^2(F_2 - 1)}{(1 - f_1)^2\, F_1}\, r_1$$

Give straight line with slop = r_1 and intercept of r_2.

Another method by rearrangement the equation 4 to the following equation.

$$r_2 = \frac{[M1]}{[M2]} \left[\frac{dM1}{dM2} \left(1 + \frac{[M1]\, r_1}{[M2]} - 1\right) \right]$$

Analysis the copolymer composition to measure dM1 and dM2 for different feed ratios [M1] and [M2] we can calculate r_1 and r_2.

Ionic copolymerization:

The ionic copolymerization differ from radical copolymerization in many points as:

1- There are little number of monomers that can be ionically polymerized because the monomer must have withdrawing or donating groups to be ionic polymerized.

2- the ionic copolymerization is always ideal copolymerization, where r_1r_2 is always (1).

3- the reactivity ratios of the monomers depends on the initiator types and temperature.