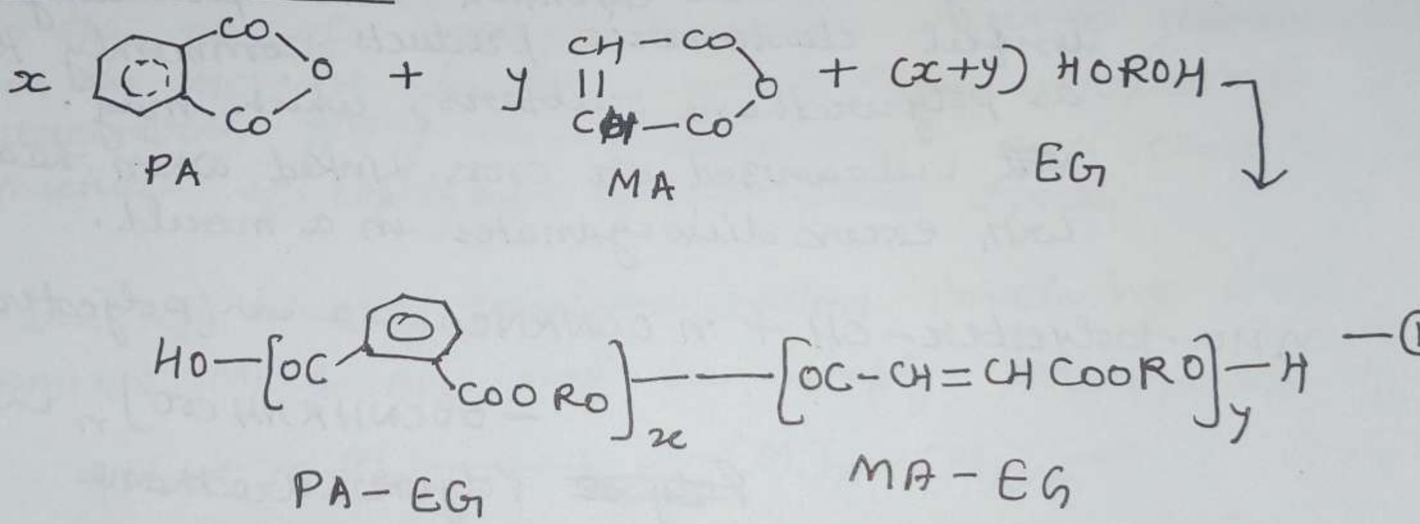
Book = Polymer Science by Premamoy Ghosh (1)

Copolymerization

Copolymerization concept ⇒ A polymer whose chain molecules are composed of more than one kind of repeating chemical units is commonly called a copolymer.

Example — The linear unsaturated polyester formed by intermolecular Condensation of mixture of Phthalic acid (PA) and maleic acid (MA) with a given diol, example ethylene glycol (EG)

Chemical reaction



In eq (1), there is two types of repeating chemical units, (PA-EG) and (MA-EG) in a simplified manner. In actual copolymer two types of distinguishable chemical units would normally appear at random fashion. So the overall composition of the copolymer depend upon the relative values of x & y

The step growth copolymerization involve the formation of copolymer structures with a specific interunit linkage such as amide (−CONH−), ester (−COO−), urethane (−NHCOO−), etc, as in eq(1). It may also involve chain extension and cross linking reaction introducing similar or different kinds of interunit linkages using low molecular weight linear or branched polymers.

Ex ⇒ Polyester urethanes or Polyether urethanes (using low molecular weight preformed linear polyesters or Polyethers with hydroxyl end groups and allowing them to further react with each other through diisocyanates leading to chain extension and producing useful elastomeric products commonly known as polyurethane rubbers, which may ~~be~~ vulcanized or cross linked when heated with excess diisocyanates in a mould.

n HO−polyester−OH + n OCNRNCO ⟶ ~[polyester−OOCNHRNHCOO]$_n$~

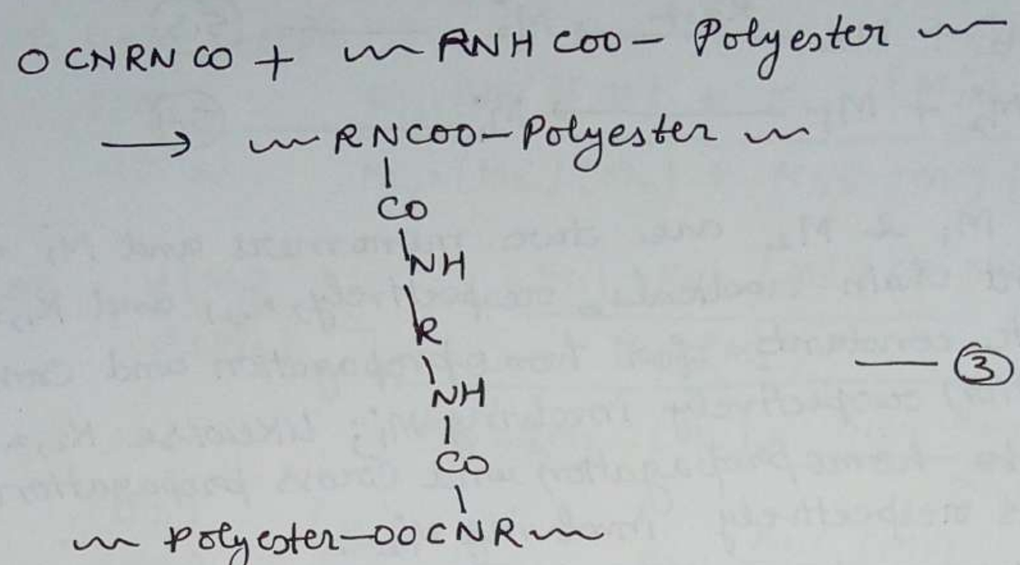
~~Polyester~~ Polyester urethane

— (2)

n HO−polyether−OH + n OCNRNCO ⟶

~[Polyether−OOCNHRNHCOO]$_n$~

Polyurethane



The number of reactions to be necessarily considered to describe the copolymerization of more than one monomer increases geometrically with the increase in the no of involved monomer increases geometrically with the increase in the number of participating monomers, giving varied increasingly and complicated structure of copolymer at the same time.

A case of binary copolymerization involving two monomers M_1 & M_2 may be simply represented as

$$nM_1 + mM_2 \longrightarrow \sim(M_1)_n-(M_2)_m\sim \quad — (4)$$

The structure of the vinyl copolymer in eq (4) however, the two monomer units appear in the copolymer structure in a random way in general.

Kinetics of Chain propagation in binary copolymerization and copolymer composition

The four chain propagation reactions in a binary copolymerization given by the following reactions

$$M_1^\bullet + M_1 \xrightarrow{K_{1,1}} M_1^\bullet \quad — (5.1)$$

$$M_1^\bullet + M_2 \xrightarrow{K_{1,2}} M_2^\bullet \quad — (5.2)$$

$$M_2^{\bullet} + M_2 \xrightarrow{k_{2,2}} M_2^{\bullet} \quad \text{——— (5.3)}$$

$$M_2^{\bullet} + M_1 \longrightarrow M_1^{\bullet} \quad \text{——— (5.4)}$$

Where M_1 & M_2 are two monomers and $M_1^{\bullet}$ & $M_2^{\bullet}$ represent chain radicals, respectively, $K_{1,1}$ and $K_{1,2}$ are the rate constants for homopropagation and cross-propagation respectively involving $M_1^{\bullet}$; likewise $K_{2,2}$ & $K_{2,1}$ refer to homopropagation and cross propagation rate constants respectively involving $M_2^{\bullet}$.
For given rate constant, the first numeral is indicative of the reacting chain radical and the second numeral indicates the reacting monomer.
Homopropagation → the reaction between like radical and monomer and cross propagation relates to reaction between unlike radical and monomer.

The rates of consumption of two monomers are written as

$$-\frac{d[M_1]}{dt} = K_{1,1}[M_1^{\bullet}][M_1] + K_{2,1}[M_2^{\bullet}][M_1] \quad \text{— (6)}$$

$$-\frac{d[M_2]}{dt} = K_{1,2}[M_1^{\bullet}][M_2] + K_{2,2}[M_2^{\bullet}][M_2] \quad \text{— (7)}$$

By elimination of the radical concentration terms using steady state concept for each chain radical & then combining (6) & (7). Under steady state, the conc of $M_1^{\bullet}$ & $M_2^{\bullet}$ remaining constant, rates of interconversion of chain radicals must be equal, which prescribes that the rates of reactions (5.2) & (5.4) are equal i.e.

$$K_{1,2}[M_1^{\bullet}][M_2] = K_{2,1}[M_2^{\bullet}][M_1] \quad \text{— (8)}$$

Now combining (6) & (7) and expressing $[M_1^{\bullet}]$ in terms of $[M_2^{\bullet}]$ (or vice versa) with the help of eq (8) one can obtain

$$\frac{d[M_1]}{d[M_2]} = \frac{K_{1,1}[M_1^\bullet][M_1] + K_{2,1}[M_2^\bullet][M_1]}{K_{2,2}[M_2^\bullet][M_2] + K_{1,2}[M_1^\bullet][M_2]} \quad (9)$$

or

$$\frac{d[M_1]}{d[M_2]} = \frac{\dfrac{K_{1,1}\cdot K_{2,1}[M_2^\bullet][M_1]^2}{K_{1,2}[M_2]} + K_{2,1}[M_2^\bullet][M_1]}{K_{2,2}[M_2^\bullet][M_2] + \dfrac{K_{1,2}\cdot K_{2,1}[M_2^\bullet][M_1][M_2]}{K_{1,2}[M_2]}}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} = \frac{K_{2,1}\dfrac{K_{1,1}}{K_{1,2}}\dfrac{[M_1]}{[M_2]} + K_{2,1}}{K_{2,2} + K_{2,1}\dfrac{[M_1]}{[M_2]}} \quad (10)$$

Dividing numerator and denominator of the right hand side of eq (10) by $K_{2,1}$, one should get

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\cdot\frac{\dfrac{K_{1,1}}{K_{1,2}}\dfrac{[M_1]}{[M_2]} + 1}{\dfrac{K_{2,2}}{K_{2,1}} + \dfrac{[M_1]}{[M_2]}} \quad (11)$$

In eq (11), the left hand side represents relative molar increment of the two monomers in the copolymer. For copolymerization to low conversions this may be taken as the molar ratio of the two monomer units incorporated in the copolymer i.e. $([M_1]/[M_2])_{copolymer}$, while the ratio $[M_1]/[M_2]$ on the right hand side of the equation relates to the feed monomer ratio i.e, molar ratio of the two monomers in the feed monomer mixture $([M_1]/[M_2])_{feed}$. Expressing the ratio of the rate cons by the parameters r_1 and r_2 as shown below

$$\frac{K_{1,1}}{K_{1,2}} = r_1 \quad \text{and} \quad \frac{K_{2,2}}{K_{2,1}} = r_2$$

eq ⑪ becomes

$$\left(\frac{[M_1]}{[M_2]}\right)_{copolymer} = \left(\frac{[M_1]}{[M_2]}\right)_{feed} \cdot \frac{r_1 \left(\frac{[M_1]}{[M_2]}\right)_{feed} + 1}{r_2 + \left(\frac{[M_1]}{[M_2]}\right)_{feed}} \quad (13)$$

eq ⑬ is known as the copolymer composition equation. It expresses that the copolymer composition is dependent on the molar ratio of two monomers in the feed and on the kinetic parameters r_1 & r_2 i.e. the monomer reactivity ratios.

The copolymer equation may also be expressed as

$$\left(\frac{[M_1]}{[M_2]}\right)_{copolymer} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}$$

The copolymer equation may also be alternatively expressed using copolymer and monomer compositions as mole fractions instead of mole ratios.
If F_1 & F_2 are the mole fractions of the monomer segments M_1 and M_2 respectively in the copolymer formed ($F_1 = 1 - F_2$) and if f_1 and f_2 are the mole fractions of the monomers M_1 and M_2 in the reactant monomer mixture ($f_1 = 1 - f_2$) then one obtains from eq ⑪ or eq ⑬

the following expression

$$F_1 = \frac{(r_1 f_1^2 + f_1 f_2)}{(r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2)}$$

Reference → ① Polymer science by Premamoy Ghosh

② Polymer science by willsmeyer