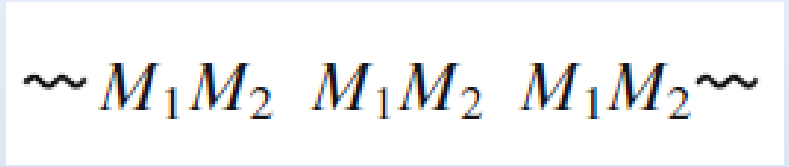
Chain Copolymerization

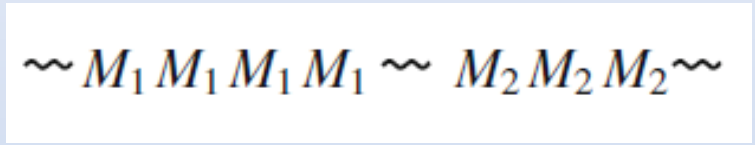
Copolymers contain two or more repeating monomer structures in the polymer chain. The copolymer can be synthesized by chain polymerization using two or more type of monomers. It is called chain copolymerization. The process can be depicted as

$$M_1 + M_2 \rightarrow \sim M_1 M_2 M_2 M_1 M_2 M_1 M_1 M_2 \sim$$

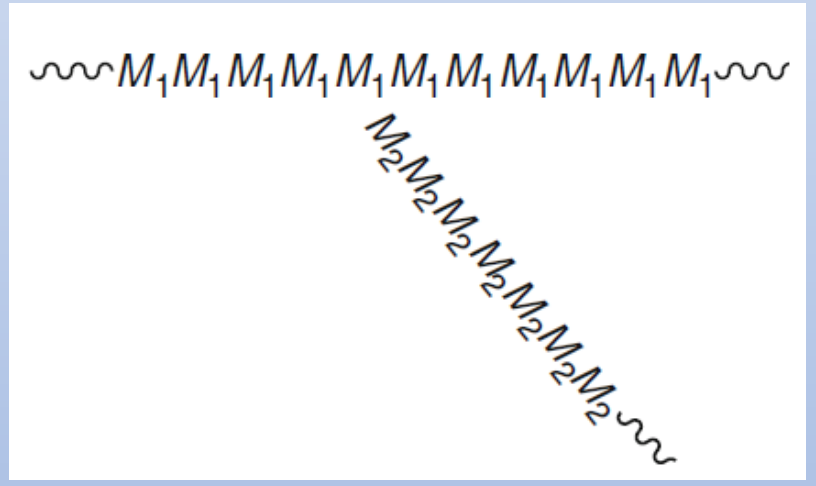
The amount of each monomer in the copolymer is determined by their relative concentration and reactivities. The simultaneous chain polymerization can also be carried out with more than two type of monomers. Such polymerizations are generally referred to as multicomponent copolymerizations; the term terpolymerization is specifically used for systems of three kind of monomers.by

There are three different types of copolymer structures—alternating, block, and graft. The alternating copolymer (I) contains the two monomer units in equimolar amounts in a regular alternating distribution:





While a graft copolymer (III) is a branched copolymer with a backbone of one kind of monomer to which are attached one or more side chains of another monomer,



Reaction Kinetics of Free Radical Copolymerization

The reaction kinetics of free radical copolymerization is similar to the homopolymerization.

However, one needs to consider the variations in reactivity between reacting species. Copolymerization of the two monomers leads to two types of propagating species—one with M1 and the other with M2 at the propagating end and. These can be represented by M1 and M2. If one assumed that the reactivity of the propagating chain is dependent only on the monomer unit at the end of the chain, four propagation reactions are then possible. Monomers M1 and M2 can each add either to a propagating chain ending in M1 or to one ending in M2.

$$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1\cdot$$

$$M_1\cdot + M_2 \xrightarrow{k_{12}} M_2\cdot$$

$$M_2\cdot + M_1 \xrightarrow{k_{21}} M_1\cdot$$

$$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2\cdot$$

where k_{11} is the rate constant for a propagating chain ending in M1 adding to monomer M1, k_{12} is for a propagating chain ending in M1 adding to monomer M2, and so on. The active center of propagating chain is added to same monomer is referred to as homopropagation or selfpropagation;

if it is added to other monomer is referred to as cross-propagation or a crossover reaction. To derive the reaction kinetic equations of copolymerization, we assume the chemical reactivity in a copolymerization is dependent only on the identity of the monomer unit at the

$$-d[M_1]/dt = k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1]$$

$$-d[M_2]/dt = k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2]$$

Dividing the equations yields the ratio of the rates at which the two monomers enter the copolymer, that is, the copolymer composition, as

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1]}{k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2]}$$

In order to remove the concentration terms in M1 and M2 from , a steady-state concentration is assumed for each of the propagating chains M1 and M2 separately. For the concentrations of M1 and M2 remain constant, their rates of interconversion must be equal. In other words, the rates of reactions in equations must be equal:

$$k_{21}[M_2\cdot][M_1] = k_{12}[M_1\cdot][M_2]$$

Equations can be rearranged and combined with other equations to yield

$$\frac{d[M_1]}{d[M_2]} = \frac{\frac{k_{11}k_{21}[M_2\cdot][M_1]^2}{k_{12}[M_2]} + k_{21}[M_2\cdot][M_1]}{k_{22}[M_2\cdot][M_2] + k_{21}[M_2\cdot][M_1]}$$

Dividing the top and bottom of the right side of $k_{21}[M_2\cdot][M_1]$ and combining the result with the parameters r_1 and r_2, which are defined as

$$r_1 = k_{11}/k_{12} \text{ and } r_2 = k_{22}/k_{21}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])}$$

Equation is known as the copolymerization equation or the copolymer composition equation. The copolymer composition, dM1=dM2, is the molar ratio of the two monomer units in the copolymer which is related to the concentrations of the two monomers in the feed, M1 and M2, and the parameters r1 and r2. The parameters r_1 and

The copolymerization equation can also be expressed in terms of mole fractions instead of concentrations. If f1 and f2 are the mole fractions of monomers M1 and M2 in the feed, and F1 and F2 are the mole fractions of M1 and M2 in the copolymer, then

$$f_1 = 1 - f_2 = [M_1]/([M_1] + [M_2])$$

$$F_1 = 1 - F_2 = d[M_1]/(d[M_1] + d[M_2])$$

$$F_1 = \left(r_1 f_1^2 + f_1 f_2\right) / \left(r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2\right)$$

Radical copolymer is more useful than cationic or anionic copolymer, because about all the monomers are reacted in the radical copolymer. Since termination and initiation rate constants are not involved in the copolymer composition equation, the copolymer composition is independent of difference in the rates of initiation and termination. Thus, the particular initiation system used in a radical copolymerization has no effect on copolymer composition. The copolymer composition is also independent on the absence or presence of inhibitions or chain transfer agents. Therefore, under a wide range of conditions, the copolymer composition is independent of the degree of polymerization.

REF: Lecture Notes In Chemistry 82
Principles of Polymer Design and Synth