

Mechanism and Kinetics of Co-polymerization

If two different monomers, M_1 and M_2 , are polymerized together, the following structures result, shown in **Fig. 1**.

In the case of copolymers, we are not dealing with mixtures of the individual homopolymers but instead with products in which both monomers are covalently incorporated in the individual molecules. Although alternating and statistical copolymers can indeed be produced by polymerizing two different monomers together (simultaneously), the syntheses of block and graft copolymers require special methods. To differentiate the products, the following nomenclature has emerged:

- Statistical copolymer: Poly(M_1 -stat- M_2)
- Alternating copolymer: Poly(M_1 -alt- M_2)
- Block copolymer: Poly(M_1 -block- M_2)
- Graft copolymer: Poly(M_1 -graft- M_2)

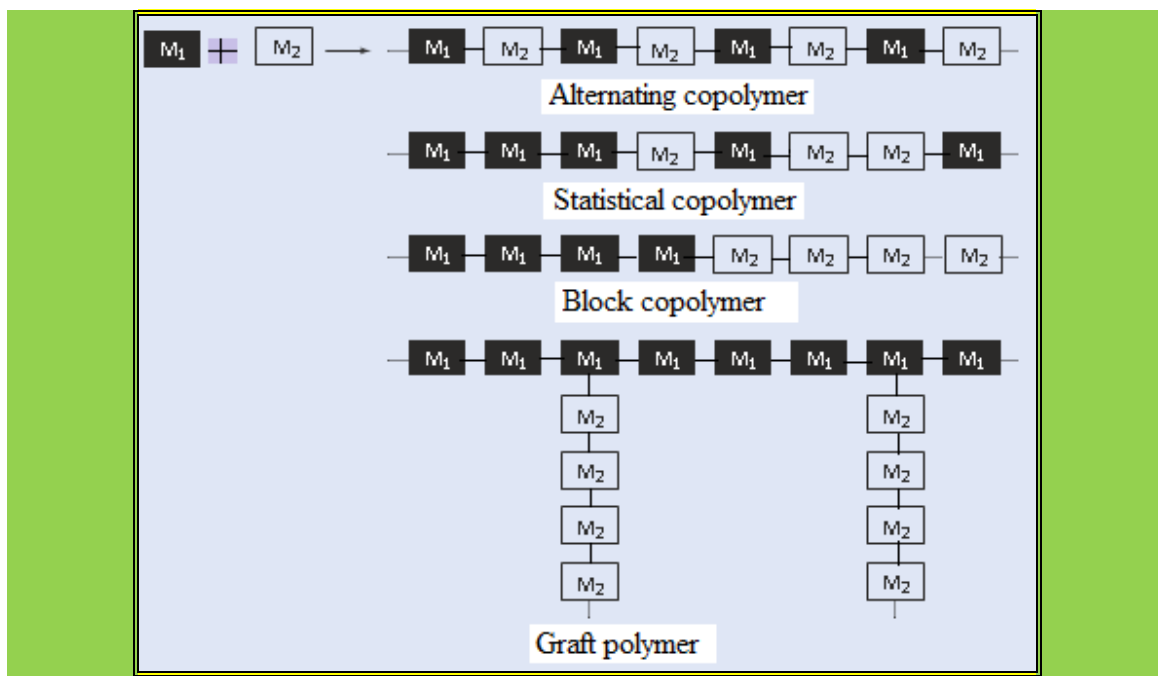


Fig. 1: Structures of alternating, statistical, block, and graft copolymers

If it is not intended to distinguish the specific copolymer architecture, the general term is poly(M_1 -co- M_2).

Copolymerization allows us to synthesize a virtually infinite number of different products. The possible combinations of two different monomers increases by a large multiple if we vary the mixtures between 1 mol% and 99 mol% and take into account that for each monomer combination

there are various possible copolymer architectures. When copolymers are formed of more than two building blocks, the number of combinations reaches vast proportions. An example of a group of copolymers that have become industrially very important is ABS—terpolymers of acrylonitrile, butadiene, and styrene. Copolymerization has the great advantage that the attributes of the homopolymers can be deliberately combined. Taking the example of polystyrene, which is brittle and hard and has only moderate solvent resistance, it can be seen how, by introducing comonomers into the polymer, the service range of polymers based on styrene can be expanded. Copolymers with styrene as comonomer can be thermoplasts [e.g., poly(styrene-co-acrylonitrile), SAN] or elastomers [poly(styrene-co-butadiene) SBR, and poly(styrene-block-butadiene-block styrene), SBS]. For example, by incorporating acrylonitrile, the strength and ductility of SAN-polymers is improved and the resistance against aliphatic hydrocarbons and mineral oils is enhanced compared with polystyrene. SAN polymers with a wide variation in composition are available commercially.

Mayo-Lewis Equation of Copolymerization

The compositions of statistical copolymers are determined by the monomer composition and the relative reactivity of the co-monomers. In the following, the corresponding rules are derived using the example of radical copolymerization.

Deduction of the Mayo-Lewis Equation of Copolymerization

If the radical polymerization is initiated in the presence of two different monomers, M_1 and M_2 , the polymerization goes through all the individual phases of a radical polymerization; that is, the polymerization is initiated by the disintegration of the initiator, the primary radical reacts with the monomer (M_1 or M_2), and the chains grow until they terminate.

Other than in the polymerization with only one monomer M_1 , in the case of copolymerization, four different phases of growth, rather than one, need to be distinguished. A growing chain end derived from M_1 can react with either M_1 or M_2 . Two further possibilities of growth emerge when the growing chain ends are derived from M_2 (**Fig. 2**).

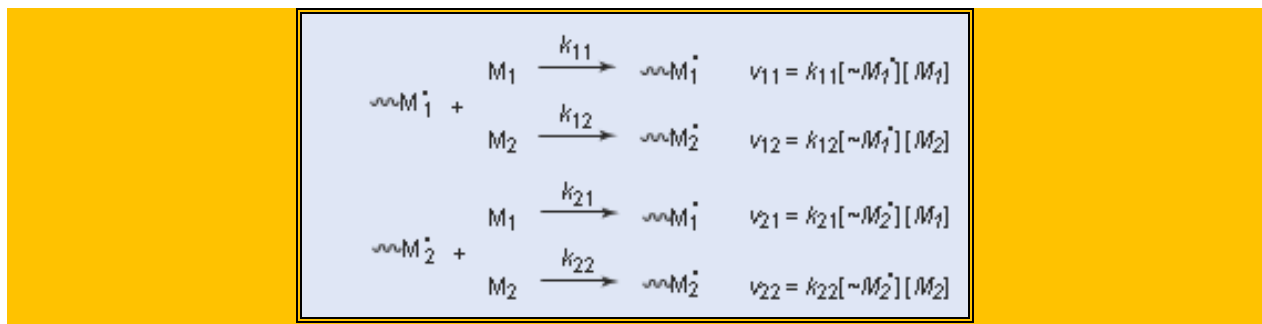


Fig. 2 Chain growth during a radical polymerization of two monomers M_1 and M_2

As the monomers are only consumed by chain growth, the following equations can be formulated for monomer consumption.

$$-\frac{d[M_1]}{dt} = K_{11} [^{\bullet}M_1] [M_1] + K_{21} [^{\bullet}M_2] [M_1] \quad [1]$$

$$-\frac{d[M_2]}{dt} = K_{22} [^{\bullet}M_2] [M_2] + K_{12} [^{\bullet}M_1] [M_2] \quad [2]$$

Furthermore, assuming a stationary state with respect to the number of radicals, it follows that

$$K_{12} [^{\bullet}M_1] [M_2] = K_{21} [^{\bullet}M_2] [M_1] \quad [3]$$

$$\text{and } [^{\bullet}M_1] = \frac{K_{21} [^{\bullet}M_2] [M_1]}{K_{12} [M_2]} \quad [4]$$

The division of [1] by [2] yields

$$\begin{aligned} \frac{d[M_1]}{d[M_2]} &= \frac{K_{11} [^{\bullet}M_1] [M_1] + K_{21} [^{\bullet}M_2] [M_1]}{K_{22} [^{\bullet}M_2] [M_2] + K_{12} [^{\bullet}M_1] [M_2]} \\ &= \frac{[M_1]}{[M_2]} \frac{K_{11} [^{\bullet}M_1] + K_{21} [^{\bullet}M_2]}{K_{22} [^{\bullet}M_2] + K_{12} [^{\bullet}M_1]} \end{aligned} \quad [5]$$

The expression $d[M_1]/d[M_2]$ is a measure of the rate at which the monomers M_1 and M_2 are incorporated into the growing polymer chains at any moment during the polymerization. Thus, this expression describes the chemical composition of the copolymers formed at any one moment in time. Introducing [4] into [5] gives

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{k_{11} \cdot \frac{k_{21} [^{\bullet}M_2] [M_1]}{k_{12} [M_2]} + k_{21} [^{\bullet}M_2]}{K_{22} [^{\bullet}M_2] + k_{12} \cdot \frac{K_{21} [^{\bullet}M_2] [M_1]}{k_{12} [M_2]}} \quad [6]$$

This can be simplified to

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{k_{11} \cdot \frac{k_{21}}{k_{12}} \cdot \frac{[M_1]}{[M_2]} + k_{21}}{k_{22} + k_{21} \cdot \frac{[M_1]}{[M_2]}} \quad [7]$$

By multiplying the second quotient in [7] by $[M_2]/k_{21}$ and simplifying one obtains

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

$$= \frac{[M_1]}{[M_2]} \cdot \frac{\frac{k_{11}}{k_{12}} \cdot [M_1] + [M_2]}{\frac{k_{22}}{k_{21}} [M_2] + [M_1]} \quad [8]$$

Equation [8] can be further simplified by introducing the so-called *copolymerization parameters* r_1 and r_2 . These are defined as follows:

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$

The copolymerization parameters, the reactivity ratios r_1 and r_2 , are very important parameters. They describe the relative reactivity of the radicals towards the monomers M_1 and M_2 . If $r_1 > 1$, then a polymer radical derived from M_1 preferably reacts with the monomer M_1 . In this case, homo-polymerization is favored over hetero-polymerization. Moreover, only these two parameters are necessary to describe the copolymerization instead of the four rate constants. By inserting the parameters r_1 and r_2 into [8] one obtains the Mayo–Lewis copolymerization equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1 [M_1] + [M_2]}{r_2 [M_2] + [M_1]} \quad [9]$$

m_1	Concentration of M_1 in the newly formed polymer ^a
m_2	Concentration of M_2 in the newly formed polymer
$[M_1]$	Concentration of M_1 in the reaction mixture
$[M_2]$	Concentration of M_2 in the reaction mixture
r_1, r_2	Copolymerization parameters

Equation [9] describes the composition of the polymer formed at any one time as a function of the monomer composition at that time. During most co-polymerizations, as the reaction progresses, and depending on the reactivity of the individual co-monomers, a more or less

^aThe proportion of M_1 and M_2 incorporated into the polymer at any one time cannot be determined simply from the composition of the polymer. However, if the copolymerization is prematurely stopped at conversions $p < 5\%$, the difference between the composition at the time of stopping the reaction and the integral, experimentally obtained, copolymer is negligible. It should be noted that all the concentrations mentioned here are molar concentrations.

dramatic change in the proportion of the co-monomers in the reaction mixture occurs. Thus, the copolymers produced after different reaction times, i.e., at different conversions, may be chemically different. Only at extremely low conversions of less than 5 % can the relative monomer concentrations be assumed to be approximately constant; at this stage, [9] gives a good first approximation of the copolymer composition.

If a copolymerization is allowed to continue to complete conversion, the average composition of all the polymer chains naturally corresponds to the initial monomer composition. However, in this case the product also contains a large number of chemically different macromolecules.