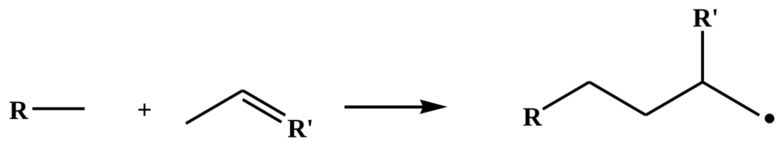
Mechanisms of Polymerization:

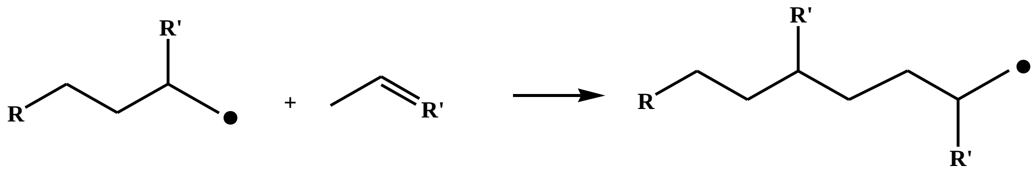
Polymers can be classified into various ways. One the basis may be the mode of preparation of the polymers. **Addition Polymers** are mainly synthesized by reactions initiated by free radicals while **Step Growth polymers chains** are built up step by step via condensation reaction.

Addition Polymers

Olefinic compounds such as ethylene and styrene usually form addition polymers. There are various mode of initiation of the polymerization reaction. Atoms or free radicals are introduced to an unsaturated monomer which adds to the double bond:



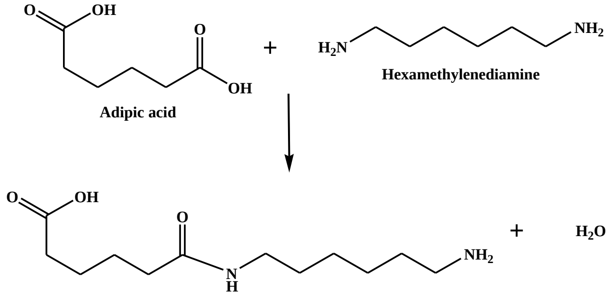
The reaction generates another radical which adds to another molecule of monomer.



This process continues forming larger radicals and at the end two large radicals combine to generate polymer molecule. The radical R which initiates the polymerization process can be introduced to the monomer thermally, or by the application of catalyst, photochemically or radiochemical methods.

Step growth Polymerization

Step growth polymerization occurs by condensation mechanism for example reaction between Adipic acid and Hexamethylene Diamine to produce Nylon 6,6.



Since the product has functional groups –COOH and –NH_2 so that chain can propagate in both the directions for further polymerization. This initiation can be brought up by simply using acid or bases or certain catalysts.

Ionic Polymerizations:

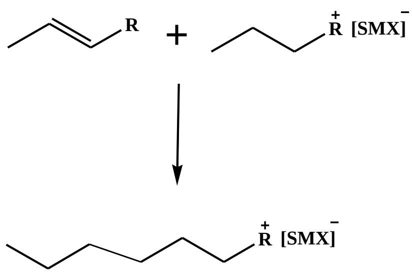
Polymerization processes in solution occurs by mechanism in which intermediates are ions. These processes are catalysed by acidic or basic substances and the rate of polymerization varies with the dielectric constant of the solvent. They can be classified into cationic or anionic depending on the initiating species.

For example in isobutene polymerization is initiated by HCl, $AlCl_3$, iodine etc. the electron acceptors represented as MX form an ion pair with solvent SH

$$MX + SH \rightleftharpoons \overset{+}{H}[SMX]^{-}$$

This ion pair adds to monomer to form another ion pair as

The reaction further proceeds via carbocation that adds to other olefin molecule.



The reaction continues until the monomer is consumed and the chain terminates as stable polymer molecule.

Similar mechanism follows for **Anionic polymerization** which propagates via carbanion **(TRY TO STUDY AND SOLVE BY YOURSELF) such as** using strong bases such as potassium amide in case of styrene to polystyrene synthesis.

- ✓ **Anionic polymers are also called LIVING Polymers. Find out why?**

Kinetics of Polymerization

Free radical polymerization

The general mechanism for the free radical polymerization can be represented as follows:

1. Initiation: Generation of radical

$$R_1 \longrightarrow R_1^{\bullet}$$

2. Chain propagation:

$$R_1^{\bullet} + \text{M (Monomer)} \longrightarrow R_2^{\bullet}$$

$$R_2^{\bullet} + \text{M (Monomer)} \longrightarrow R_3^{\bullet}$$

$$R_3^{\bullet} + \text{M (Monomer)} \longrightarrow R_4^{\bullet}$$

$$R_4^{\bullet} + \text{M (Monomer)} \longrightarrow R_5^{\bullet}$$

$$\vdots$$

$$R_{n-1}^{\bullet} + \text{M (Monomer)} \longrightarrow R_n^{\bullet}$$

3. Termination:

$$R_n^{\bullet} + R_m^{\bullet} \longrightarrow M_{n+m}$$

Assuming the rate of reaction to be v_1 during the initiation and rate constants for the propagating steps to be same denoted by k_p and rate constant for the termination step to be k_T, the steady state approximation for the generation of radicals can be given by

$$v_1 - k_p[R_1][M] - k_T[R_1]([R_1] + [R_2] \dots) = 0 \tag{1}$$

The general formula for R_n being

$$k_p[R_{n-1}][M] - k_p[R_n][M] - k_T[R_n]\sum_{n=1}^{\infty}[R_n] = 0 \tag{2}$$

For infinite number of such equations and sum of all of them is:

$$v_i - k_T\left(\sum_{n=1}^{\infty}[R_n]\right)^2 = 0 \tag{3}$$

The equation simply states that rate of initiation is equal to the sum of the rates of all the termination processes which should be true for steady state.

The rate of disappearance of monomer is the sum of all the propagation reactions,

$$-\frac{d[M]}{dt} = k_p[M]\sum_{n=1}^{\infty}[R_n]$$

From the equation (3) it can deduced that

$$\sum_{n=1}^{\infty} R_n = \left(\frac{v_i}{k_T}\right)^{1/2}$$

And therefore the rate of disappearance of monomer can be given as

$$-\frac{d[M]}{dt} = k_p \left(\frac{v_i}{k_T}\right)^{1/2} [M]$$

For thermal initiation mode of radical generation is by heating the monomer, the initial radical formation may be second order in monomer.

$$v_i = k_i[M]^2$$

Therefore the rate of polymerization for heat initiated reaction can be given by

$$-\frac{d[M]}{dt} = k_p \left(\frac{k_i}{k_T}\right)^{1/2} [M]^2$$

Hence the process follows second order reaction. However if there is a catalyst initiation may follow second order reaction between monomer and catalyst C,

$$v_i = k_i[M][C]$$

The rate of polymerization being

$$-\frac{d[M]}{dt} = k_p \left(\frac{k_i}{k_T}\right)^{1/2} [M]^{3/2}[C]^{1/2}$$

For photochemically initiated reaction the light of intensity I is absorbed expressed in einsteins per second

$$v_i = I$$

The rate of polymerization is then given by

$$-\frac{d[M]}{dt} = k_p \left(\frac{I}{k_i}\right)^{1/2} [M]$$