II.1. Introduction:

The definition of polymerization is the process in which small molecules, called monomers, combine together to form long-chain polymers. Polymers are built from simple molecules of the same kind, and monomers are known as basic units of polymers. The name polymer was taken from the Greek word 'Polymeres'. What does polymerization mean? It is the process of formation of polymers, where polymers mean "having many parts".

Two types of polymerization reactions:

- **Step-growth polymerization:**

macromolecules formed by step-wise reactions between reactive chemical groups carried by monomer or polymer molecules. Each molecule can grow by reacting with any other molecule (mono-, di-, tri-, tetra-, etc-mer).

- **Chain-growth polymerization:**

a single initial active center (ion, radical, or organometallic complex) from an initiator allows the formation of a polymer chain. The chain can only grow by the reaction of a monomer with the reactive chemical group located at the end of the growing chain.

II.2. Step-growth polymerization:

Polymers formed by successive reactions between two chemical groups (X, Y,...) carried by molecules containing at least two chemical groups. The reactions occur by simple heating or in the presence of a catalyst, and stop when the active medium is cooled or when one of the initial reactants is completely consumed. Examples: polyesters, polyamides (nylon), polyurethanes, epoxy resins, phenoplasts. Two types of step-growth polymerization:

II.2.1. Polycondensation:

Condensation polymers are formed by a reaction between two different bifunctional or tri-functional monomer units. These monomeric units undergo a condensation reaction to form polymers and small molecules of simple compounds like HCl (Hydrogen chloride), H_2O (Water), alcohol, etc. are eliminated. Silicon, Bakelite, Nylon, etc. are some of the examples of condensation polymers.

a) Synthesis of linear molecules by step-growth polymerization of bifunctional molecules (Thermoplastics).

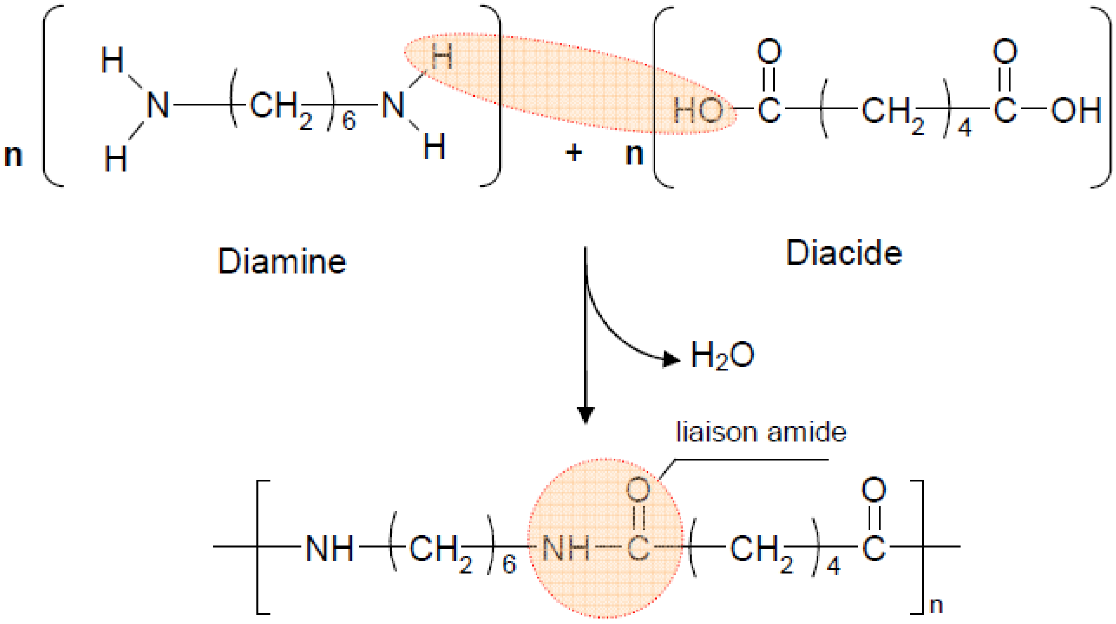
1) 2 monomères possédant chacun un type de fonction chimique (X, Y)

X--- A--- X + Y ---B--- Y ⟶ X--- A--- B--- Y + X--- Y

Monomère	monomer	bifunctional dimer
Dimer	monomer	trimer
dimer	dimer	tetramer
n-mer	m- mer	(n+m)-mer

Synthesis of nylon by polycondensation (elimination of a water molecule).

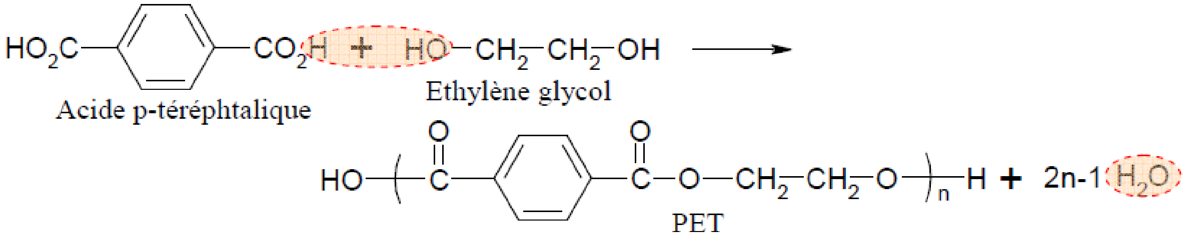
One of the monomers has 2 amine functions (-NH_2), the other monomer contains 2 carboxylic acid functions (-CO_2H).



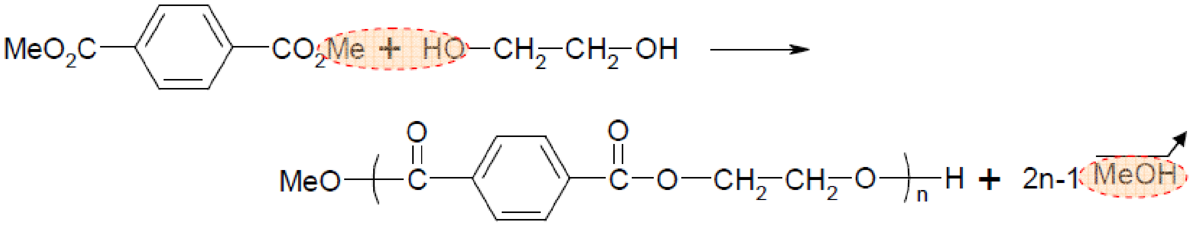
Polyamide 6,6 « *nylon* »

Other examples of polycondensation: polycondensation has great industrial importance, as mechanical properties are improved even though molecular weights are generally lower than with other polymerization techniques.

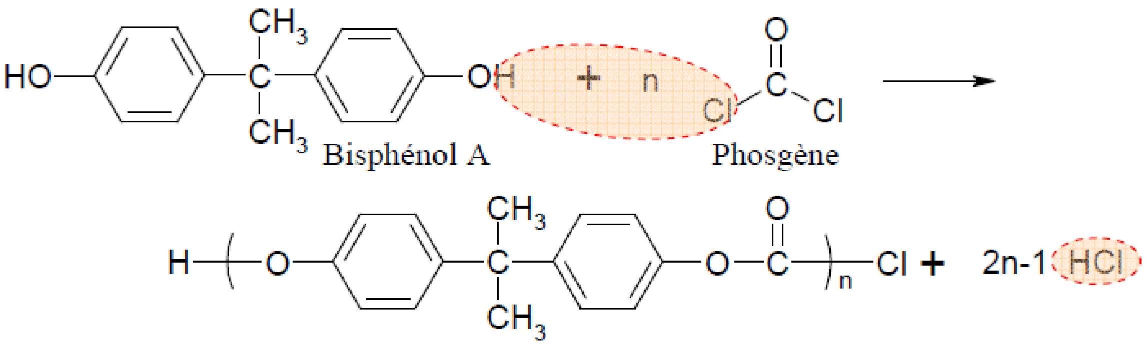
Polyester (Tergal)



The industrial process uses transesterification to easily remove MeOH and shift the equilibrium towards polymer formation.



If the alcohol has a functionality greater than 3, cross-linking (3D network) occurs. This is the case with alkyds (paints)



The degree of polymerization (DP) rarely exceeds 500 (ρ = 0.998), and the molecular weight ($\overline{Mn}$) is less than 5.10^{-4} g.mol-1 due to by-products formed during the reaction, such as oxidation, decarboxylation, and anhydride formation.

To increase the molar mass: increase the purity of the reactants, perfect equimolarity of reactants.

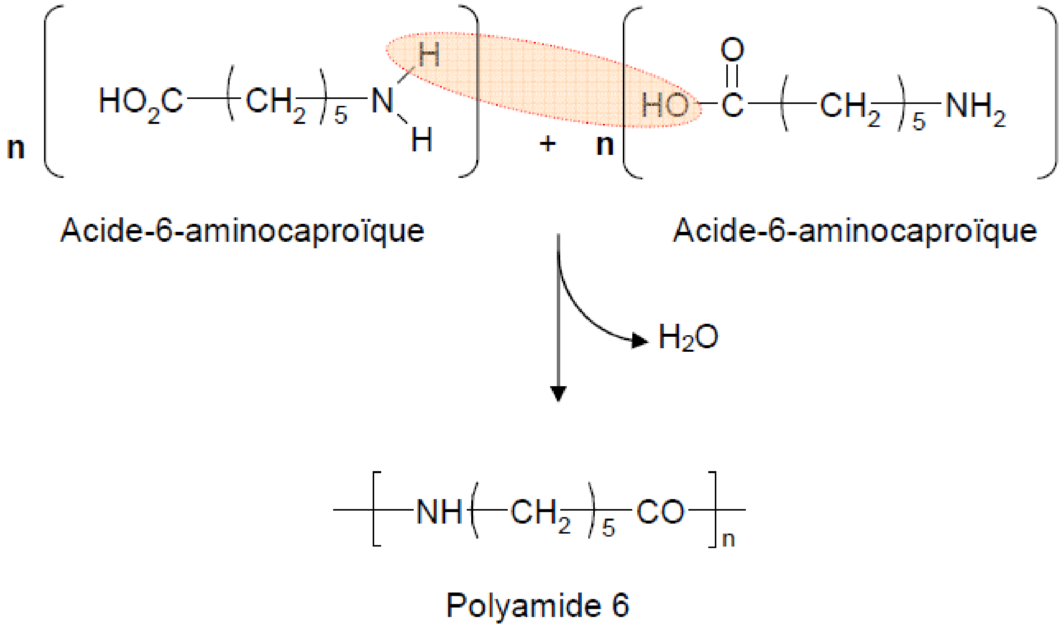
2) <u>1 single monomer with 2 types of chemical function (X, Y)</u>

X--- A--- Y + X--- A---Y ⟶ X--- A--- A--- Y + X Y

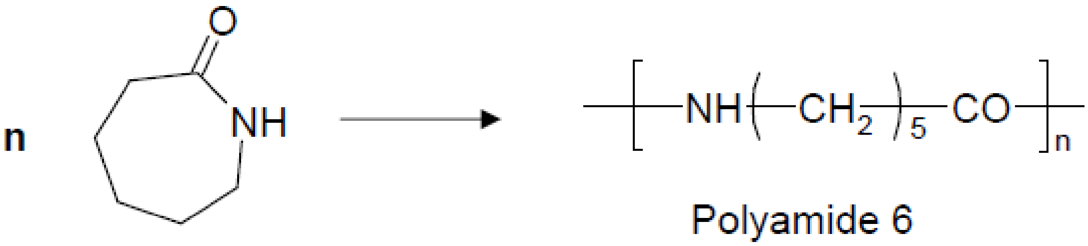
Monomère	monomer	bifunctional dimer
Dimer	monomer	trimer
dimer	dimer	tetramer
n-mer	m- mer	(n+m)-mer

Synthesis of nylon by polycondensation of 6-aminocaproic acid.

The monomer has an amine function ($-NH_2$) and a carboxylic acid function ($-CO_2H$)

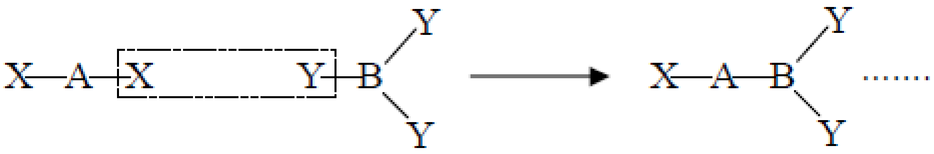


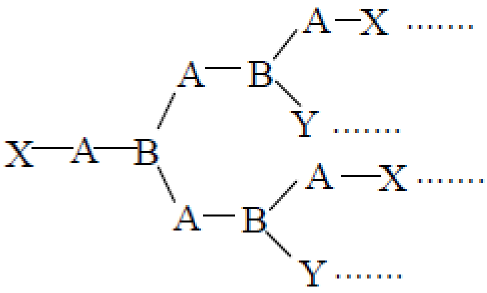
Synthesis of nylon by polyaddition of caprolactam.



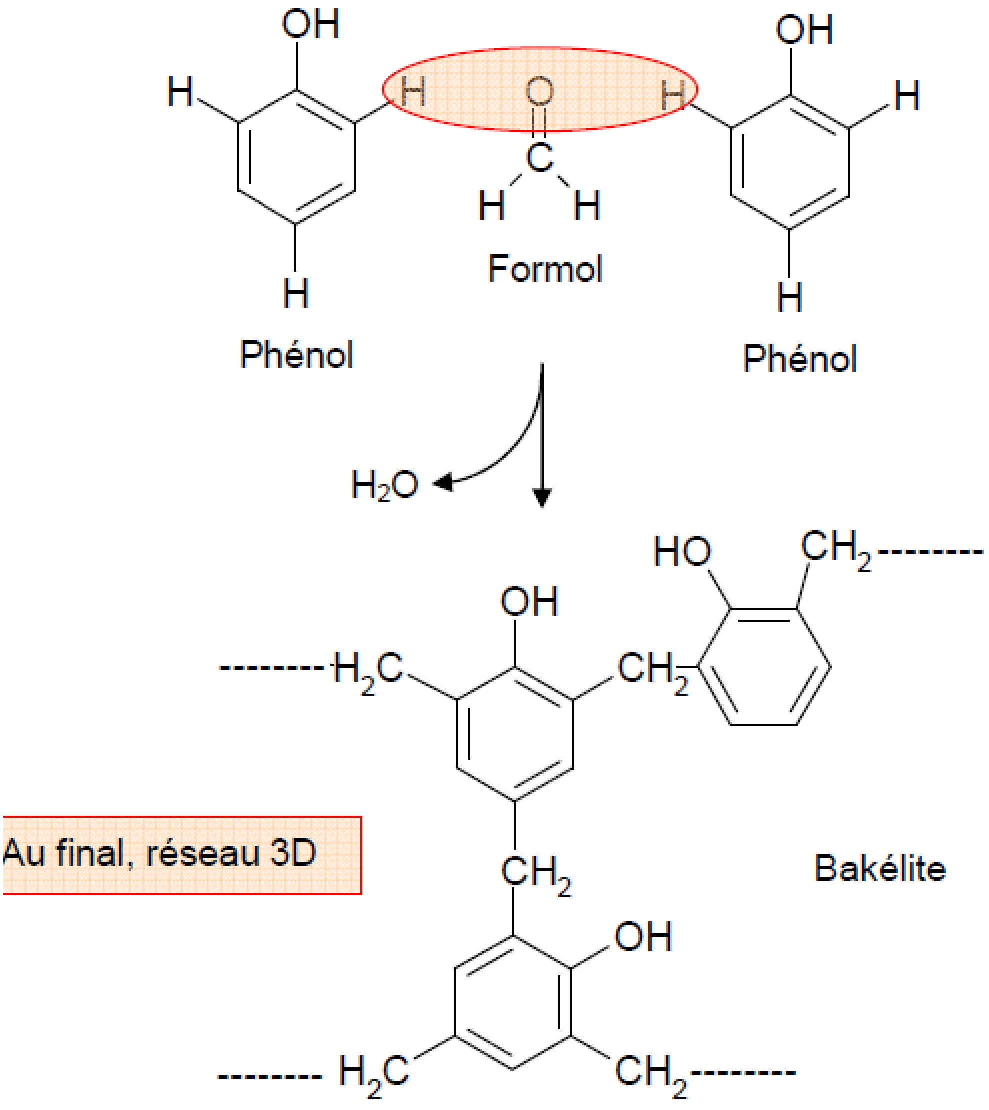
b) Synthesis of three-dimensional molecules by step-growth polymerization of molecules with more than two functions (Thermosetting).

In general, at least one bifunctional monomer and one trifunctional monomer are required. However, the system can be more complicated.





Synthesis of Bakelite: polycondensation from phenol and formaldehyde. Belongs to the family of phenol-formaldehyde resins (phenoplasts).

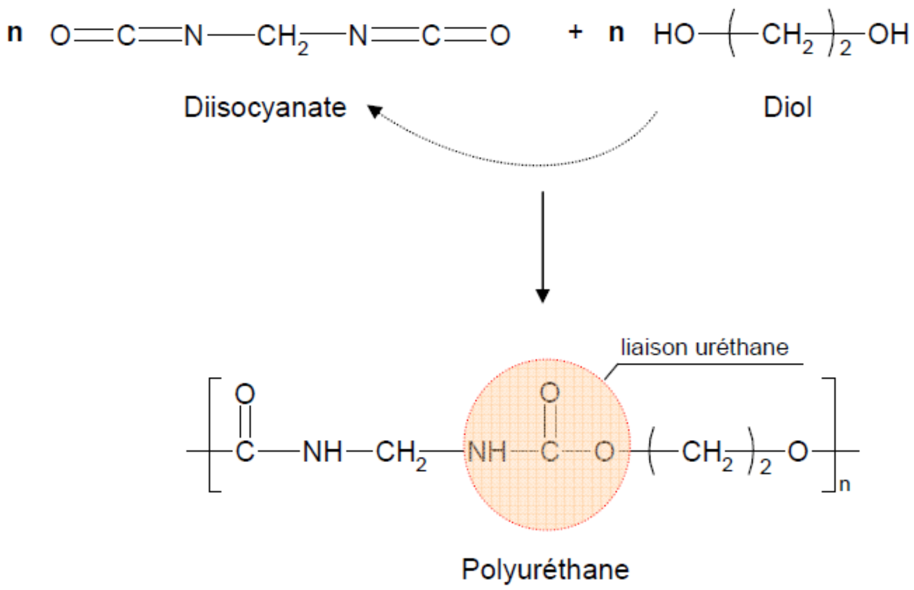


II.2.2. Polyaddition:

In case of addition polymerisation, double or triple bond monomers are repeatedly added to form a polymer. In this type of reaction, no by-products are formed. For instance, propene (C_3H_6) helps in the formation of poly-propene ($(C_3H_6)n$) and polythene ($(C_2H_4)n$) is formed by the addition reaction of ethene (C_2H_4) molecules.

Example:

Synthesis of polyurethane by polyaddition.



Remarks on polyurethanes:

- Polyols are generally of the polyether or polyester type. They provide flexibility to the PU. Triols => three-dimensional network.
- Diisocyanates: Toluene diisocyanate (TDI) is the most commonly used. Methylene-bis-4-phenylisocyanate (MDI) is also widely used for rigid foams. They make up the rigid segments of PU. Triisocyanates => three-dimensional network.
- Amines react with isocyanates to form urea bonds
- –R-N=C=O + R'-NH2 ⟶ R-NH-CO-NH-R', which allow for chain extension or cross-linking.

II.3. Chain Polymerization

II.3.1. Generalities

A chain reaction is a reaction during which a monomer molecule M is added to an active center carried by the growing chain.

If we call n M* a chain consisting of n building blocks and equipped with an active center, the polymerization can be schematized as:

$$M_n^* + M \text{ ----------------- } M^*_{n+1}$$

The point indicates the site of an unpaired electron located on the molecular chain with which a new bond can be formed to increase the size of the chain. The atom on the chain with this unpaired electron constitutes the active center.

Chain reactions occur in 3 steps:

- Initiation (or triggering)
- Propagation (or growth)
- Termination.

Depending on the nature of the active center that triggers the addition of the constituent (parent) units, chain polymerization is classified into one of the following groups:

- Radical polymerization
- Ionic polymerization.

II.3.2. Radical Polymerization:

II.3.2.1. Initiation

This step refers to the formation of an active center on a monomer molecule M. It occurs in 2 steps:

- Formation of a free radical R* from an initiator molecule I.

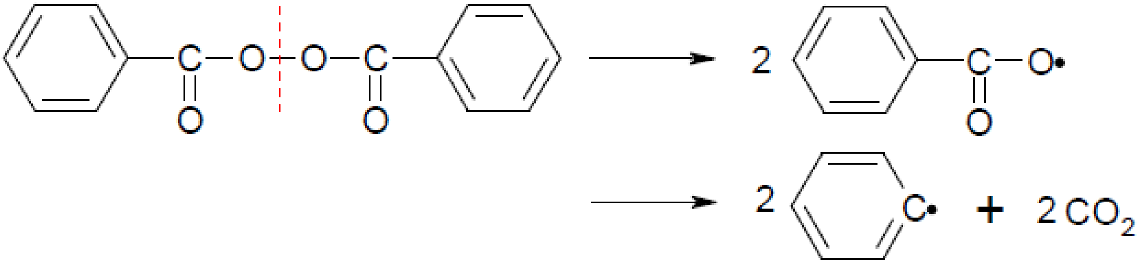
  I ---------n R* (with n = 1 ou 2)
- Addition of the free radical to a mole of monomer M, which then carries an active center.

  R* + M ------------ RM*

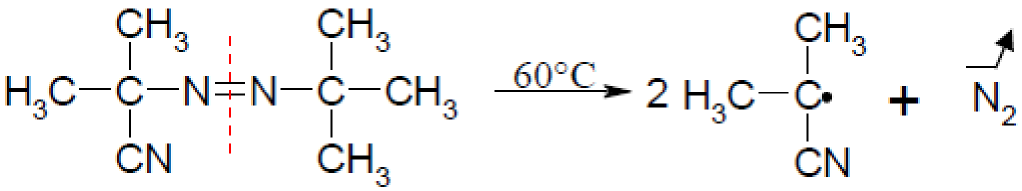
The most common initiators are referred to as "initiating agents".

- **Radicals**

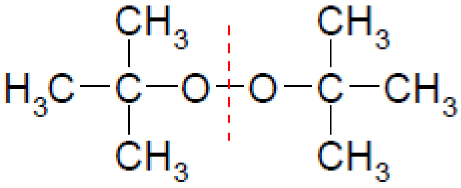
Benzoyl peroxide



AIBN



Peroxyde de tBu



- **Redox**

$H_2O_2 + Fe^{2+} \longrightarrow HO^{*} + OH^{-} + Fe^{3+}$

- **Radiation $\gamma, \beta, h\nu$**

$RH \longrightarrow R^{*} + H^{*}$

II.3.2.2. Propagation:

This is the step where a large number of successive additions of monomer molecules M occur on the formed active center. The time required to add a monomer is very brief, on the order of milliseconds. As a result, several thousand additions can occur in a matter of seconds.

$RM^* + M \longrightarrow RMM^*$

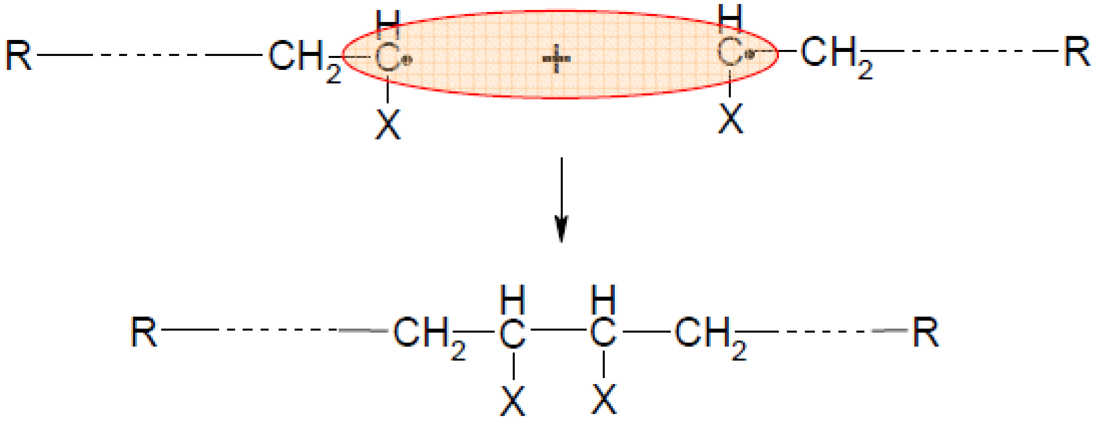
$RMM^* + M \longrightarrow RM\ M^*$

$R\ M\ M^* + M \longrightarrow R\ (M_{n+1})\ M^*$

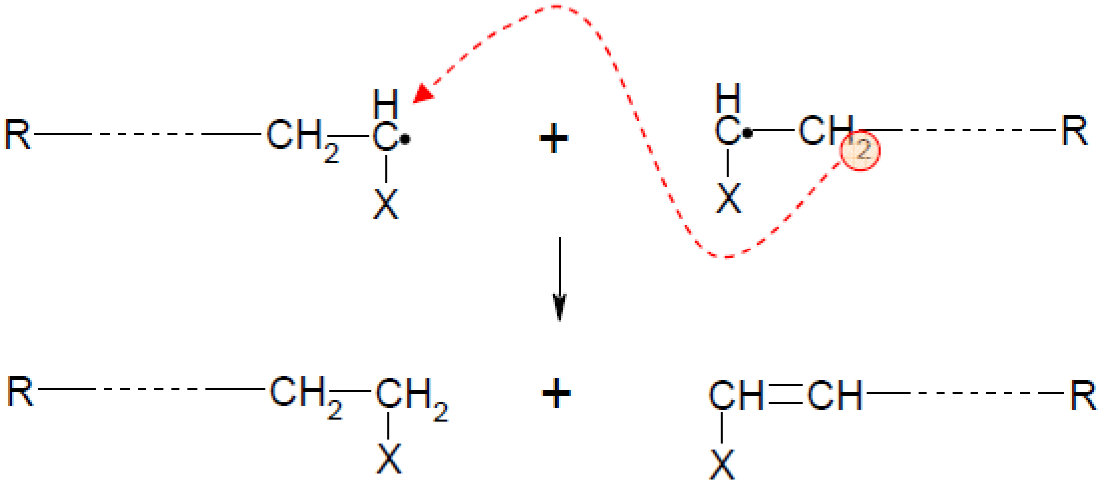
II.3.2.3. Termination:

At this stage, the growth of the polymer chain stops. The active center disappears. Termination reactions are bimolecular involving 2 growing molecules. The mechanism is:

- **Combination:**



- **Disproportionation**: transfer of an H atom.

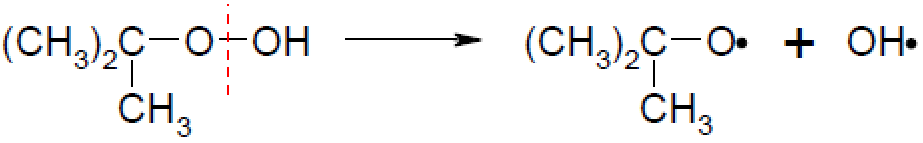


$$R\text{------}CH_2-\overset{H}{\underset{X}{C^\bullet}} + \overset{H}{\underset{X}{C^\bullet}}-CH_2\text{------}R \longrightarrow R\text{------}CH_2-\underset{X}{CH_2} + \underset{X}{CH}=CH\text{------}R$$

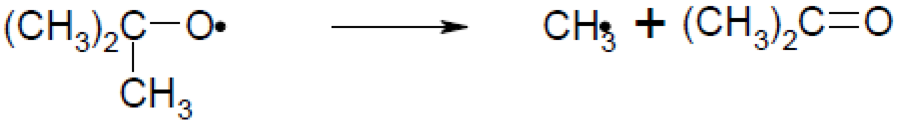
Example of radical polymerization: vinyl monomer, 2 different initiators.

1- initiation

-by breaking a covalent bond (O-O) of the initiator



$$(CH_3)_2\underset{CH_3}{C}-O-OH \longrightarrow (CH_3)_2\underset{CH_3}{C}-O^\bullet + OH^\bullet$$

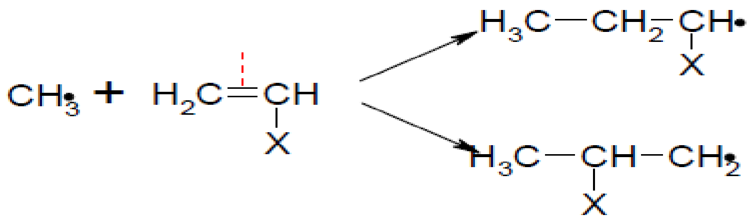


$$(CH_3)_2\underset{CH_3}{C}-O^\bullet \longrightarrow CH_3^\bullet + (CH_3)_2C=O$$

-by oxidation-reduction reaction

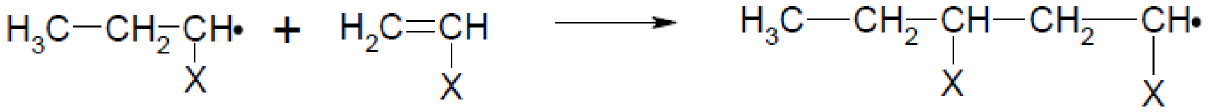
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^\bullet$$

Then addition of the free radical to the vinyl monomer CH2=CHX and creation of an active center on the molecule.



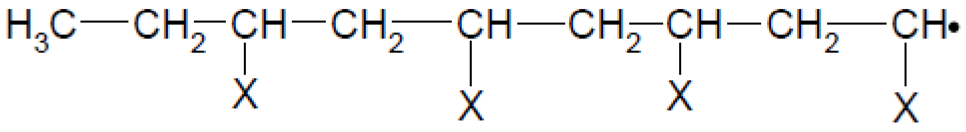
$$CH_3^\bullet + H_2C=\underset{X}{CH} \rightarrow H_3C-CH_2-\underset{X}{CH}^\bullet \quad \text{or} \quad H_3C-\underset{X}{CH}-CH_2^\bullet$$

2- **Propagation**



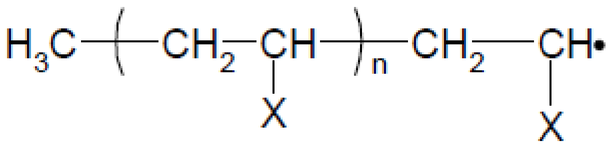
$$H_3C-CH_2-\underset{X}{CH}^\bullet + H_2C=\underset{X}{CH} \longrightarrow H_3C-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}^\bullet$$

Then addition of other monomers......



$$H_3C-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}^\bullet$$

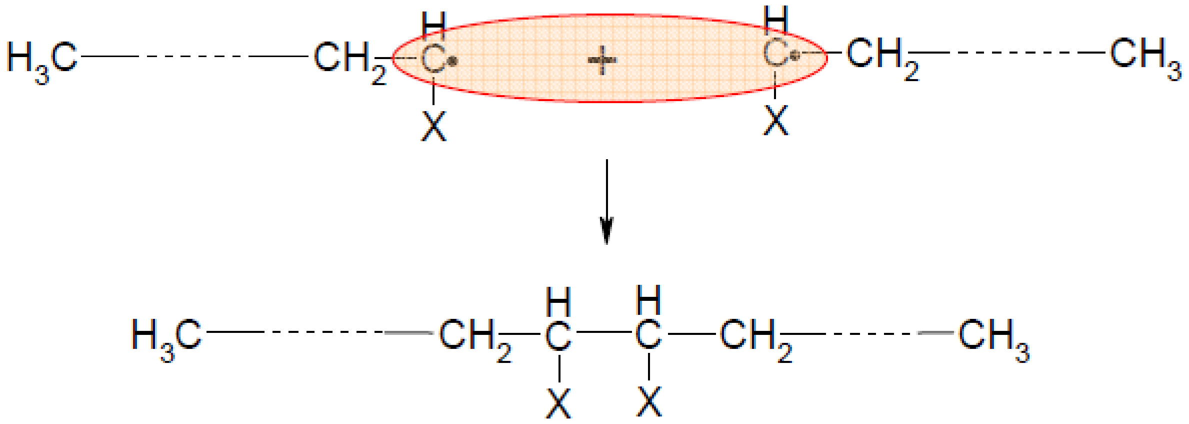
Our



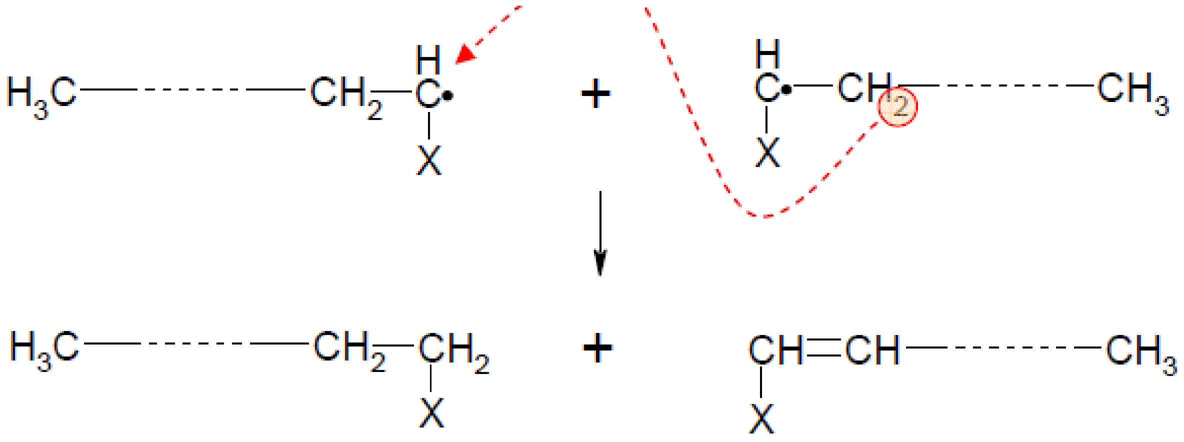
$$H_3C\left(CH_2-\underset{X}{CH}\right)_n CH_2-\underset{X}{CH}^\bullet$$

3- termination

- **by combination**



- by disproportionation



II.4. Radical Polymerization Kinetics:

a- Initiation

Benzoyl peroxide and AIBN decompose into two radicals R*

$$A - A \xrightarrow{k_d} 2A^{\cdot}$$

kd is the dissociation constant of [A].

$$Vd= 2\ Kd[A]\ .f$$

$$A^{\cdot} + M \xrightarrow{k_a} A - M^{\cdot}$$

ka is the polymerization initiation constant.

$$Va = Ka[M][A^*]$$

vd is the limiting velocity because it is the slowest. Overall, we have:

$$Va = 2f\ K_d\ [A]$$

b- propagation

$$A\text{-}M^* + M \text{-----------------} A\text{-}M\text{-}M^*$$

There is equi-reactivity of active centers regardless of the length of the chain carried by the monomer. (AM^*---$AMMM^*$---$A(M)_nM^*$)

$$M^{\cdot} + M \xrightarrow{k_p} M^{\cdot}$$

kp is the propagation constant of the polymer.

$$Vp=Kp[M][M^*]$$

Determining [M*] is difficult because any chain carrying M* can be written as M*.

C- Termination

$$M^* \text{-------------} M$$

There will be deactivation of the radical monomer. In this case, we observe two scenarios:

The first scenario is a recombination reaction.

/\/\/\/\/\/\/\/\/\- $M^{\cdot}$ + $M^{\cdot}$ -/\/\/\/\/\/\/\/\/\ □ /\/\/\/\/\/\/\/\/\-M-M-/\/\/\/\/\/\/\/\/\

In this case, we statistically have a doubling of the mass.

The second scenario is a disproportionation reaction.

/\/\/\/\/\/\/\/\/\-CH_2-$C^{\cdot}H$ -X + X- $HC^{\cdot}$ -/\/\/\/\/\/\/\/\/\ □ /\/\/\/\/\/\/\/\/\-CH=CH-X + \/\/\/\/\/\/\/\/\-CH_2-CH_2-X

In this case, we have two inactive species. This reaction does not have much influence on the masses.

$$M^{\cdot} + M^{\cdot} \xrightarrow{k_t} 2\,M$$

We then have the termination speed Vt

$$Vt = 2\ Kt\ [M^*]^2$$

The 2 does not have a real significance but is rather there by convention.

Note:

The quasi-steady state assumption (QSS) is the state where, at any given moment, there are as many active centers.

destroyed active centers as formed ones. So we have: $\frac{dM*}{dt}$ =0 and therefore:

$$Va=Vt \text{ et donc } f\,K_d[A] = Kt[M^*]^2 .$$

From this, we can deduce [M*] because Kd is stable, f is known, [A] is chosen and Kt is measured.

So we have : [M*] : $[M^*]= \sqrt{\frac{f\ Kd\ [A]}{Kt}}$

We then substitute this into Vp = Kp [M] [M*] and we obtain:

$$Vp = Kp\ [M] \times \sqrt{\frac{f\ Kd\ [A]}{Kt}}$$

Thus, generally, we equate Vp, the propagation rate, to the polymerization rate.

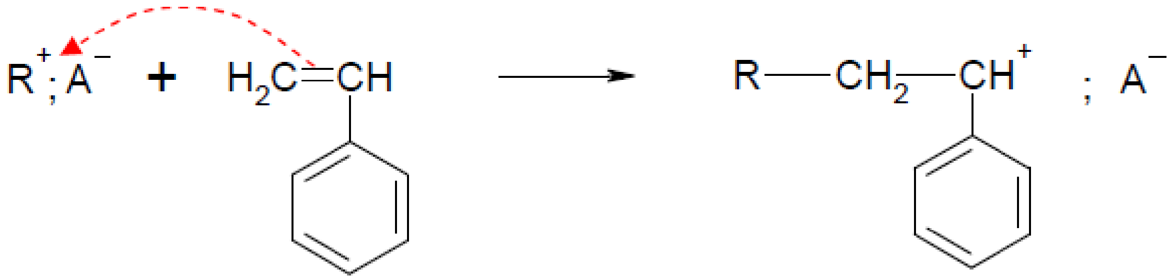
d- Ionic polymerization

The active center is formed by an ion instead of a free radical. There are two types of ion polymerization reactions:

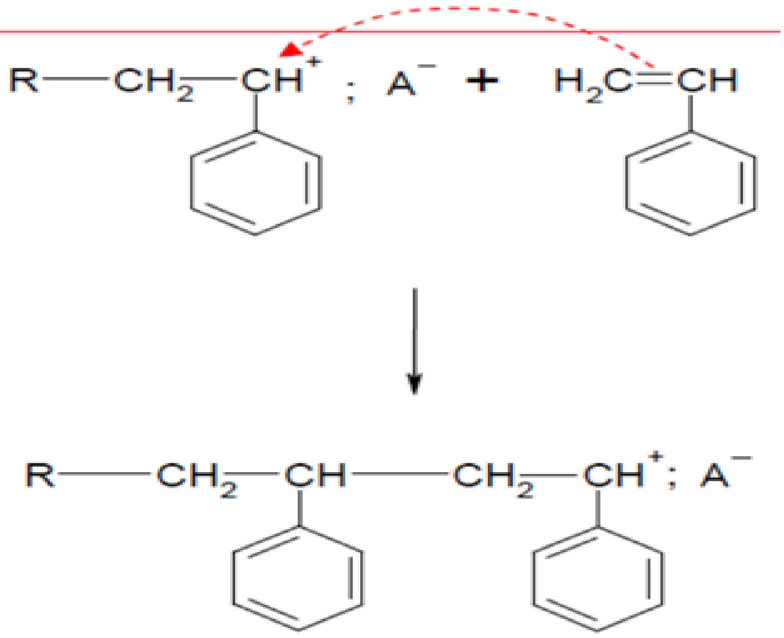
- Cationic polymerization: the carbon of the active center of the growing chain carries a positive charge
- Anionic polymerization: the carbon of the active center of the growing chain carries a negative charge

II.5. Cationic Polymerization: Example of polystyrene synthesis.

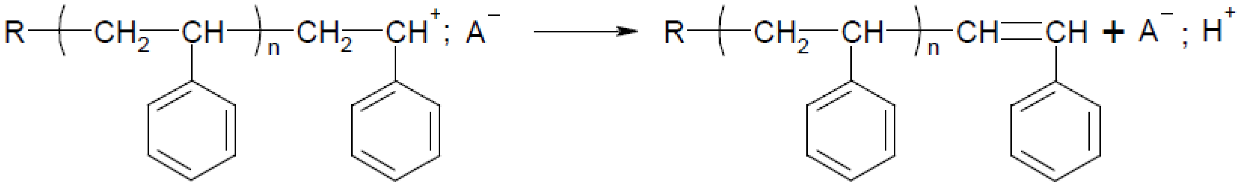
a. Initiation



b. Propagation



c. Termination



Note: by cooling or in certain cases (THF), termination and transfer reactions can be limited, and a living polymer can be obtained.

II.5.1. Kinetics:

For the purpose of establishing the kinetics of generalized cationic polymerization, let A represent the catalyst and RH the cocatalyst, M the monomer, and the catalyst–cocatalyst complex $H^+ AR^-$. Then the individual reaction steps can be represented as follows:

$$A + RH \xrightarrow{K} H^+ AR^-$$

$$H^+ AR^- + M \xrightarrow{Ki} HM^+ AR^-$$

$$HM^+n\ AR^- + M \xrightarrow{Kp} HM^+_{n+1} AR^-$$

$$HM^+n\ AR^- \xrightarrow{Kt} Mn + H^+ AR^-$$

$$HM^+n\ AR^- + M \xrightarrow{Ktr} Mn + HM^+ AR^-$$

The rate of initiation Ri is given by:

$$Ri = Ki\,[H^+ AR^-]\,[M] = ki\,K\,[A]\,[RH]\,[M]$$

The termination step is first order

$$Rt = Kt\,[M^+]$$

where $[M^+]$ is the concentration of all the chain carriers $[HM^+n\ AR^-]$. The retention of the terminating agent AR^- in the vicinity of the chain carrier is responsible for the primary difference between the kinetics of cationic polymerization and that of free-radical polymerization. Assuming that steady state holds, then Ri = Rt and

$$[M^+] = \frac{KKi}{Kt}\,[A]\,[RH]\,[M]$$

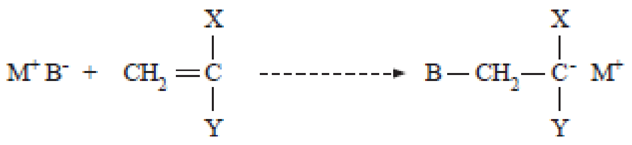
The overall rate of polymerization, Rp is given by

$$Rp = Kp\,[M+]\,[M] = K\,\frac{KiKp}{Kt}\,[A]\,[RH]\,[M]^2$$

II.6. Anionic polymerization:

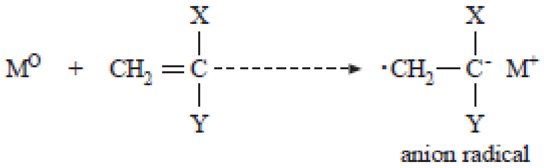
Monomers with electronegative substituents polymerize readily in the presence of active centers bearing whole or partial negative charges. For example, a high-molecular-weight polymer is formed when methacrylonitrile is added to a solution of sodium in liquid ammonia at –75°C. Typical electronwithdrawing substituents that permit the anionic polymerization of a monomer include –CN, –COOR, –C6H5, and –CH› CH2. The electronegative group pulls electrons from the double bond and consequently renders the monomer susceptible to attack by an electron donor. Catalysts for anionic polymerization include Grignard reagents, organosodium compounds, alkali metal amides, alkoxide, and hydroxides.

- Initiation may occur in two ways:
  a direct attack of a base on the monomer to form a carbanion.



$$M^+B^- + CH_2{=}\overset{X}{\underset{Y}{C}} \dashrightarrow B{-}CH_2{-}\overset{X}{\underset{Y}{C^-}}\ M^+$$

or by transfer of an electron from a donor molecule to the monomer to form an anion radical.

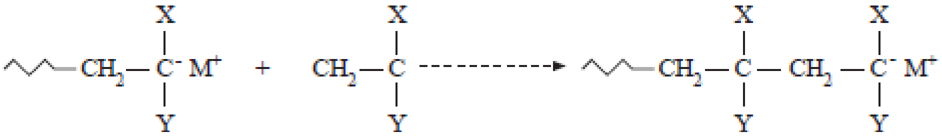


$$M^{0} + CH_2=\underset{Y}{\overset{X}{C}} \dashrightarrow \cdot CH_2-\underset{Y}{\overset{X}{C^{-}}}\ M^{+}$$

M^+B^- may be a metal amide, alkoxide, alkyl, aryl, and hydroxide depending on the nature of the monomer.

The effectiveness of the catalyst in the initiation process depends on its basicity and the acidity of the monomer.

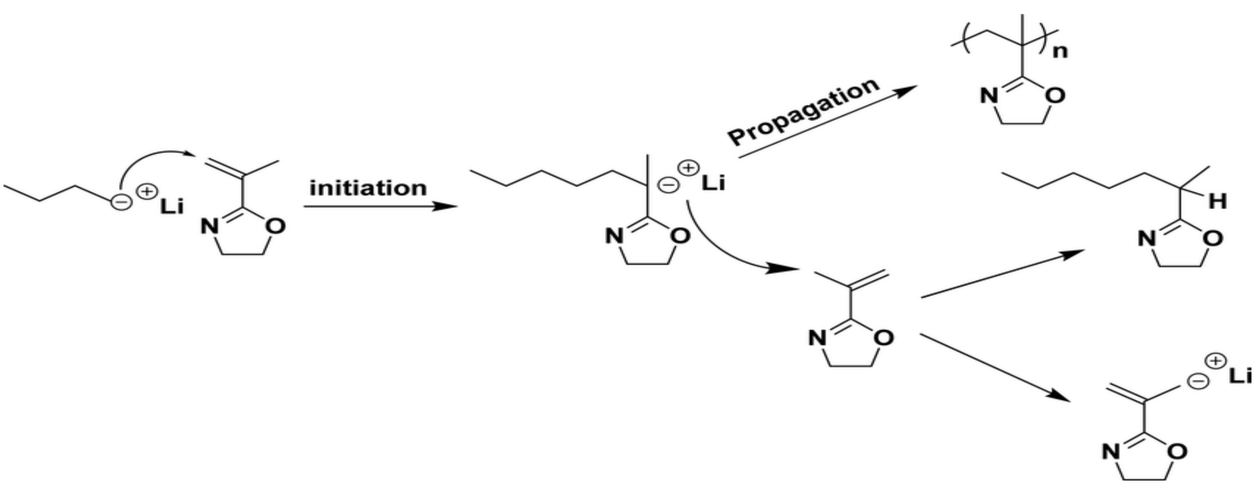
- Propagation in anionic polymerization proceeds according to the following reactions:



$$\sim CH_2-\underset{Y}{\overset{X}{C^{-}}}\ M^{+} + CH_2-\underset{Y}{\overset{X}{C}} \dashrightarrow \sim CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C^{-}}}\ M^{+}$$

Here, M^+ represents a counterion that accompanies the growing chain. In most cases, M^+ is an alkali metal ion, whereas X and Y are either electron-withdrawing groups or unsaturated groups capable of resonance stabilization of the negative charge.

Example:



The termination reaction can be due to a compound capable of reacting with a carbanion (proton generator), present as an impurity or intentionally introduced. In the absence of such a compound, anionic polymerization can be living: no termination reaction occurs and the chains retain their active ends after complete consumption of the monomer.

II.6.1. Kinetics:

Available kinetic data for the polymerization of styrene by potassium amide in liquid ammonia support the following steps in the mechanism of anionic polymerization.

$KNH_2 \xrightarrow{K} K^+ + NH_2$

$NH^-_2 + M \xrightarrow{Ki} NH_2M^-$

$NH_2\ M^-n + M \xrightarrow{Kp} NH_2M$

$NH_2M^-n + NH_3 \xrightarrow{Ktr} NH_2MnH + NH^-_2$

Considering the relatively high dielectric constant of the liquid ammonia medium, the countering K^+ can be neglected. Assuming steady-state kinetics:

$$Ri = Ki\,[NH_2^-]\,[M]$$

$$Rt = tr\,[NH_2\,Mn^-]\,[NH_3]$$

II.7. Heterogeneous polymerization:

Heterogeneous polymerization is a polymerization method that involves the presence of a solid phase, usually a solid catalyst, in the reaction medium. Unlike homogeneous polymerization where the catalyst is dissolved in the liquid phase, heterogeneous polymerization allows for easier recovery of the catalyst and better control of the polymerization.

Heterogeneous polymerization can be performed by different methods, including suspension polymerization, emulsion polymerization, and bulk polymerization.

- **Suspension polymerization** is used for the production of polymers such as polystyrene, PVC, and polyacrylonitrile. In this method, the monomer is dispersed in an aqueous medium with a surfactant to form monomer particles. The catalyst is then added and the reaction is initiated, resulting in the formation of polymer chains inside the particles. The resulting polymer particles remain suspended in the reaction medium and are separated from it once the reaction is complete.

- **Emulsion polymerization** is used for the production of polymers such as polyvinyl acetate and latex. In this method, the monomer is emulsified in an aqueous medium with a surfactant to form monomer droplets. The catalyst is then added and the reaction is initiated, resulting in the formation of polymer chains inside the droplets. The resulting polymer droplets are kept in suspension in the reaction medium and are separated from it once the reaction is complete.

- **Bulk polymerization** is used for the production of polymers such as expanded polystyrene and cross-linked polyethylene. In this method, the monomer is directly mixed with the solid catalyst in a reactor. The polymerization reaction is initiated and the polymer chains are formed inside the bulk monomer. The final product is then extracted from the reactor and can be processed to obtain the desired final form.

Heterogeneous polymerization offers advantages such as better recovery of the catalyst and greater ability to control the polymerization, but it also has disadvantages such as greater difficulty in controlling the chain size distribution and a tendency to form polymer aggregates that can be difficult to disperse uniformly.