

Chain Growth (addition) polymerization

This type of polymerization is a repetitions addition of a similar unit without any side product.

The functional groups within the monomer needed to be polymerized are unsaturated bonds (double or triple) or rings.

The characteristics of chain polymerization process can be listed as below:

- 1-The growth reaction is by adding the repeating units one by one at time to the chain.
- 2- The concentration of the monomer was decreased steadily throughout the reaction (the time is a function of monomer concentration).
- 3- High M.wt. is found at the beginning of the reaction. The molecular weight was changed little or did not changes with the time. (long reaction time give high yields but did not effect on the M.wt.
- 4- Reaction mixture at any time contains only monomer, high M.wt. polymer and about 10^{-8} part of growing chains, so that the molecular weight is very difficult to be controlled.
- 5- the reaction rate is usually fast.
- 6- the temperature will accelerate the reaction.
- 7- To start the reaction , it must be catalyzed with some catalytic reagent known as initiators.

According to the reaction mechanism, there are many types of reactions can be classified to:

- 1- free radical polymerization.
- 2- Ionic polymerization (cationic or anionic)
- 3- coordination polymerization.
- 4- copolymerization.

All these types of reactions are irreversible. The most popular monomers are vinyl monomers, like styrene (ph-CH=CH_2), vinyl alcohol ($\text{CH}_2=\text{CHOH}$) Propylene ($\text{CH}_2=\text{CHCH}_3$), vinyl chloride ($\text{CH}_2=\text{CHCl}$).

Polymerization reaction steps:

Three steps of polymerization reaction;

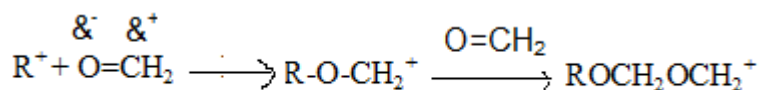
Initiation, Propagation, Termination.

Also some side reactions can be present, such as isomerization and graft polymerization.

The initiation step is the cleavage of the double bond to free radicals or to ions according to the type of the reaction. The chemical structure of the monomers is the dominate factor for choosing the type of the polymerization reaction. e.g. the substituents in the monomer effects on choose the type of reaction (free radical or ionic), whereby the substituents can push or draw the electrons to the double bonds.

Example:

Formaldehyde $\text{CH}_2=\text{O}$ has partial negative charge on O atom and partial positive on C atom. It was very easy to catalyze formaldehyde ionically from O side by attaching with positive moiety or from C side by attaching with negative moiety.



Generally the carbonic double bond can be catalyzed according to the substituents as:

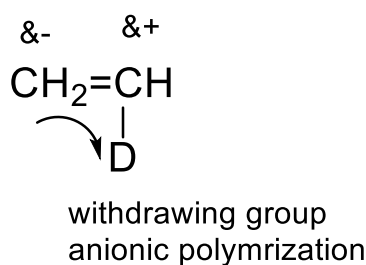
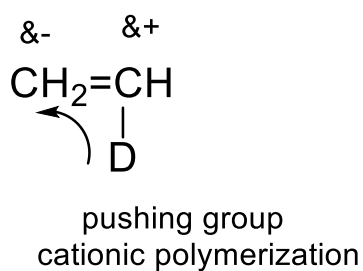


Table : some vinylic monomers and the ability to the type of polymerization (favorite type of polymerization).

| Monomer | Chemical structure | cationic | anionic | radical |
|---------------|--|----------|---------|---------|
| Ethylene | $\text{CH}_2=\text{CH}_2$ | + | + | + |
| 1,3-butadiene | $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ | + | + | + |
| Styrene | $\text{Ph}-\text{CH}=\text{CH}_2$ | + | + | + |
| Acrylonitrile | $\text{CH}_2=\text{CHCN}$ | - | + | + |
| Vinyl ester | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{CH}=\text{CH}_2 \end{array}$ | - | - | + |
| Acryl amide | $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{CH}-\text{C}-\text{NH}_2 \end{array}$ | - | + | + |
| Vinyl ether | $\text{CH}_2=\text{CHOR}$ | + | - | - |
| propylene | $\text{CH}_2=\text{CHCH}_3$ | + | - | - |

Free radical addition polymerization:

The polymerization process is done through free radical polymerization reaction. The free radical was produced from some reagent to confirmed active center in the monomer to which the other monomer molecules are added. The mechanism of the reaction include three steps:

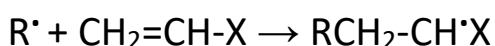
1) Initiation:

In this step a free radical was created chemically or physically in the reaction medium. Physically can be done by many means like:

- a) photoinitiation through exposing the system to some radiation (UV, visible or IR).
- b) exposing to high energy radiation (α , β , or γ) (ionizing light).
- c) mechanical.
- d) thermal.
- e) electricity (electrochemical).

By these means the double bond of the monomer will be cleavage to produce two free radicals.

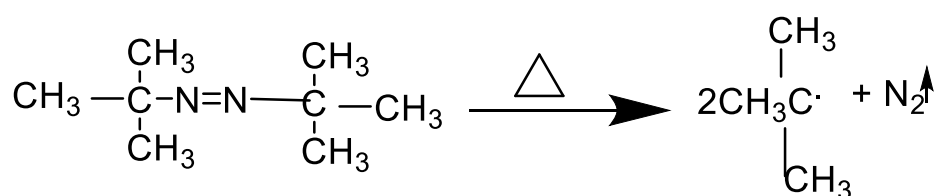
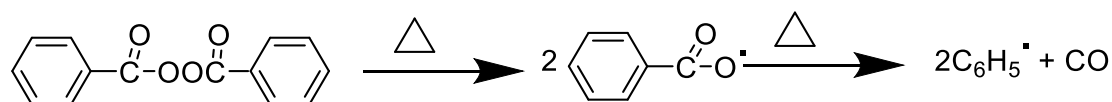
Chemically initiation is by using some chemicals known as initiators which are dissociate and produce free radical disrupt the bonds of the monomer and formed new free radical.



There are many types of initiators:

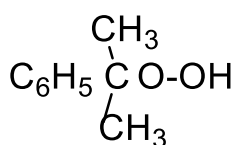
a) these compounds are dissociate thermally to form free radicals which initiate the reaction. Many reagent known in this field as a thermal initiators as peroxide ROOR, azo compounds RN=NR, hydroperoxide ROOH,

per acid $\text{RC}(=\text{O})\text{OOH}$, dibenzoyl peroxide was thermally dissociate:

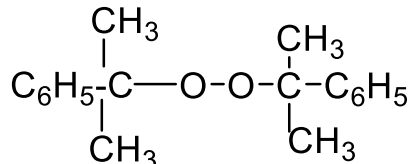


Azobis isobutyronitrile (AIBN)

Another important industrial initiators as:



decumyl hydroperoxid



dicumyl peroxide

Every one of these initiators can be dissociate in specific temperature, so in industry you must know the temperature of processing in order to choose the suitable initiator.

b) Redox initiator

free radical was formed through oxidation- reduction reaction at low temperature (0- 50°C). It was used in emulsion polymerization .

examples

i) metal ion (reducing agent) with peroxide



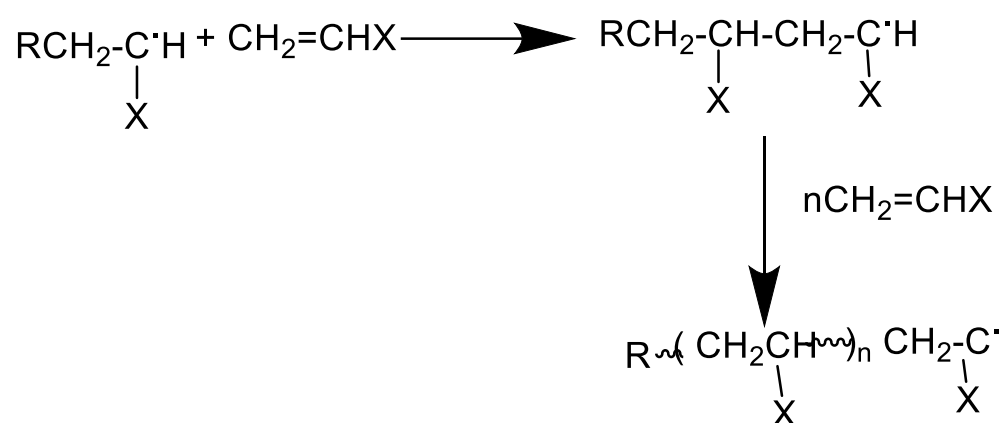
ii) reaction of transition element with halides

iii) system of persulfate with mercaptan



2-Propagation step

In this step, the new free radical produced by attaching the free radical of initiator with the monomer molecule (thermodynamically stable) is capable of adding successive monomers to propagate the chain

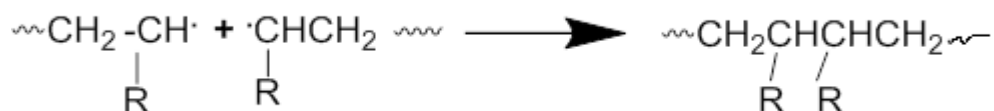


The propagation will continue until the supply of monomer was exhausted and there is no tendency of radicals to react with another monomer.

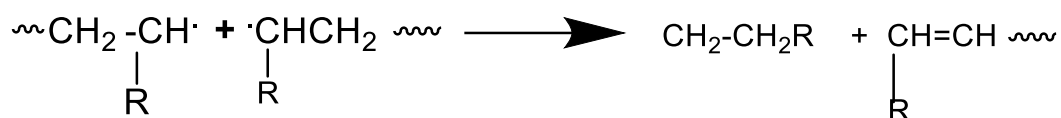
3- Termination step

The growth of the chain was stopped, whereby the free radical was ended by many side reactions as:

a) Coupling or recombination of two free radicals with each other

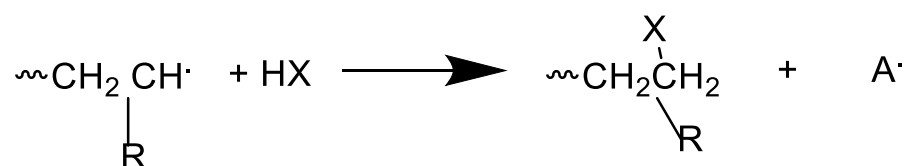


b) Disproportionation by transfer of H atom between two chains

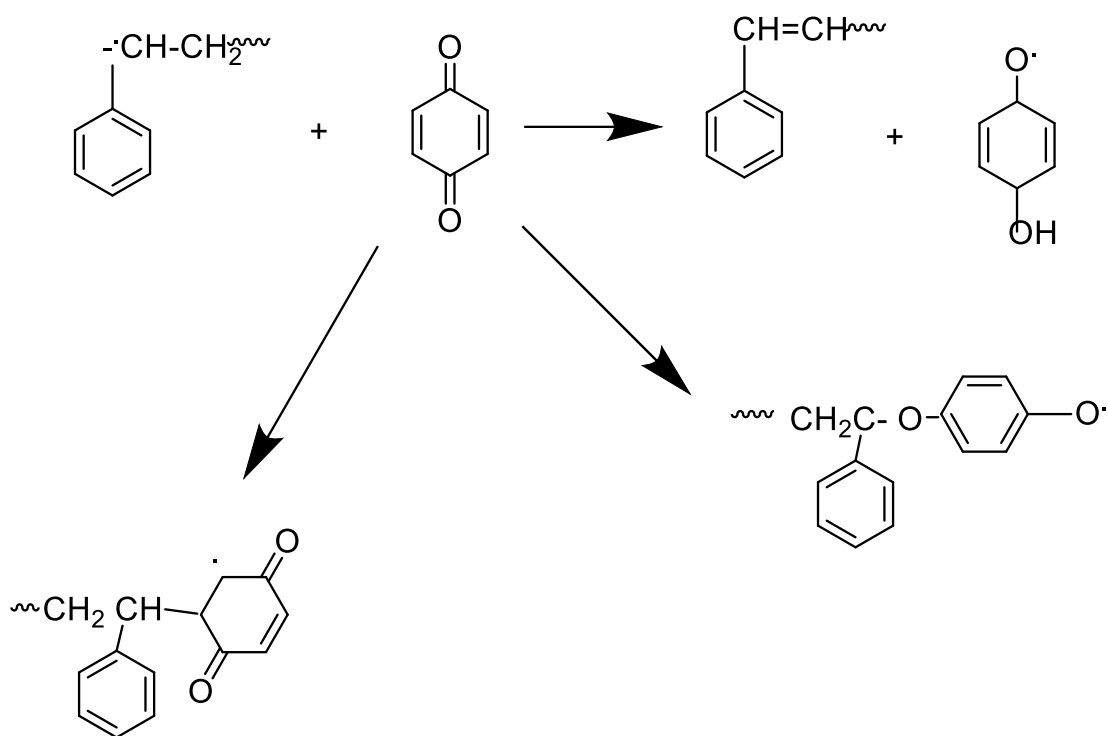


c) Chain transfer

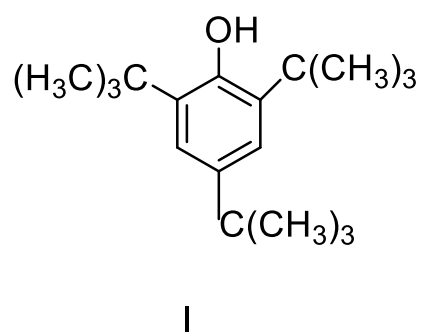
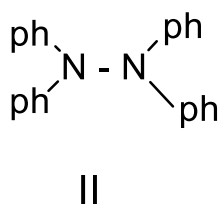
The free radical of the chain was transfer to another molecule in the medium (solvent or monomer)



In some cases reagents are added to the reaction mixture in order to stop the polymerization reaction called (**inhibitors**), or to reduce the reaction rate called (**retardents**). The most known reagents are quinones and hydroquinones. In styrene reaction the benzoquinone was added to stop the polymerization reaction by following the mechanism:



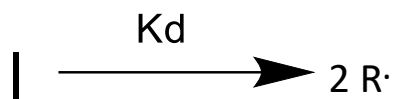
The formed free radical on benzoquinone is unreactive because of the resonance and stop the polymerization reaction. this compound was also added to styrene monomer to prevent the polymerization during the storage. This type is called inhibitor. Tri-t-butyle phenol (I) or tetraphenylhydrozone (II) can be used as retardants. The steric hindrance is used to give stable free radical and reduce the reaction rate.



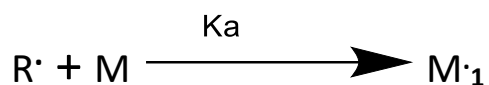
Kinetics of free radical addition polymerization:

The three steps of reaction mechanism of radical polymerization of vinyl monomers can be achieved kinetically as follows:

| the initiator was decompose to liberate free radical R^\cdot

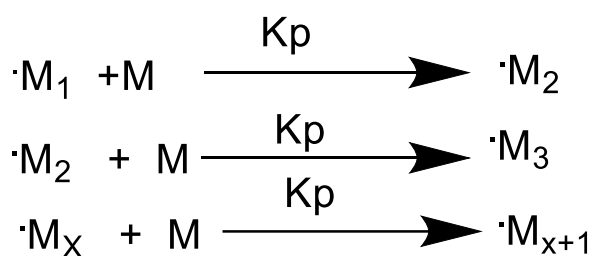


R^\cdot radical was added to the monomer molecule to form a chain radical



K 's are the rate constant for each steps.

The successive steps in propagation

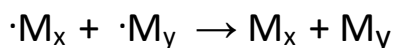


All these steps have the same rate constant K_p , since radical reactivity is presumed to be independent of chain length.

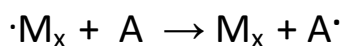
The termination step involves combination (coupling)



Or disproportionation



or chain transfer reactions including the transfer of the free radical to another molecule in the medium (monomer, solvent, or polymer chain)



The rate constant of the termination steps is denoted K_t .

The rate of the three steps can be written in terms of concentration of the species involved and rate constants.

The rate of initiation is

$$R_i = \frac{d[M\cdot]}{dt} = 2f K_i [I] \dots\dots\dots 1$$

(f) is the fraction of radicals which is successful in initiating the chains. while the rate of termination is

$$R_t = - \frac{d[M\cdot]}{dt} = 2 K_t [M\cdot]^2 \dots\dots\dots 2$$

At the steady-state conditions $R_i = R_t$, from equations 1 and 2

$$[M\cdot] = \left(\frac{f K_i [I]}{K_t} \right)^{1/2} \dots\dots\dots 3$$

The rate of propagation R_p is the same as the rate of the disappearance of the monomer

$$R_p = - \frac{d[M]}{dt} = K_p [M][M\cdot] \dots\dots\dots 4$$

Substitution of 3 in 4

$$R_p = K_p \left(\frac{f K_i [I]}{K_t} \right)^{1/2} [M] \dots\dots\dots 5$$

From 5 the rate of polymerization is positively proportional to the square root of the initiator concentration and monomer concentration if f is independent of $[M]$. this is in the case of high efficiency of initiator.

In case of low efficiency of initiator, f may be proportional to $[M]$, R_p is proportional to $[M]^{3/2}$.

Degree of polymerization = $\overline{D_p}$

$$\overline{D_p} = \frac{R_p}{R_t} = \frac{K_p [M]}{(fk_d K_t)^{1/2} [I]^{1/2}}$$