

# POLYMER

## **High-Molecular Mass Compound and Polymer.**

The term high-molecular mass and polymer are used at present to denote substance with molecular mass over 5,000 (and upto many millions) as distinct from low-molecular mass substances, whose molecular masses` comparatively rarely run into the hundreds.

## **Macromolecules & its chemistry.**

The molecules of polymers are called macromolecules, and their chemistry is known as macromolecular or polymer chemistry.

## **Polymerization**

Polymerization is the combination of several simple molecules.

## **CLASSIFICATION OF POLYMERS**

Polymers may be classified on the basic of following points

### **(1) On the basis of reaction to stress and temperature:**

#### **(a) Thermoplastic or Thermoplasts:**

These polymers can be repeatedly given shapes by heat and pressure. Hence once used for a particular form, they can again be formed into a different shape or found.

#### **(b) Thermosets:**

These polymers, once subjected to heat and pressure to give a particular form, can't be formed again like the thermoplasts.

#### **(c) Rubbers:**

These polymers, when subjected to heat and pressure, behave at first like the thermoplastics and subsequently become highly elastic. Their elasticity may be arrested at an intermediate stage and the process of doing so is called vulcausation or curing.

### **(2) On the basis of mechanical strength & behavior**

#### **a. Elastomers:**

These are elastic in nature. Their extensibility is reversible and sometime may be as high as 1000%.

Their elasticity is directly proportional to the temperature within a particular range. When the temperature in decreased, the extensibility also decreases and at a temperature called the brittle point they become brittle.

### b. Plastic or elastomers:

Compared to elastomers, these are less elastic and less extensible. When they are deformed, a part of the deformation is found to be permanent while a part is reversible. They have extensibility ranging from 100 to 200%. The extensibility, viscosity and elastic modulus are direct function of temperature.

### c. Fibers:

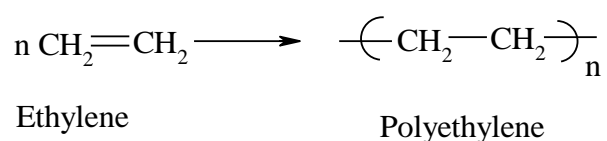
They have low extensibility ranging from 10-20% only. When subjected to deformation, most of the deformation is found to be permanent and the rest is reversible and the reversibility is partly instantaneous and partly delayed.

## (3) On the Basis of methods of polymerization

**(a). Addition or chain reaction polymers :** These polymers are produced by process called addition or chain reaction polymerization. In this process, a simple, low molecular weight molecule (monomer) which possesses at least one double bond, is induced to break. Its double bond resulting in the free valences which then link up with other similar molecules to give the polymer.

Also in this process there is no by product and the monomer retains its identity in the polymer unit.

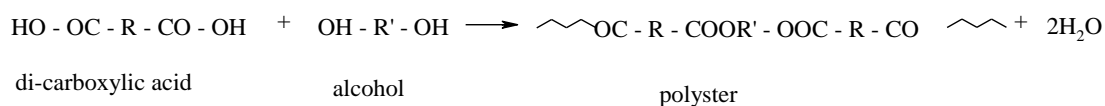
**Eg.**



**(b). Condensation polymers:** These polymers are produced by the method of condensation polymerization. This process is different from the addition process on three counts.

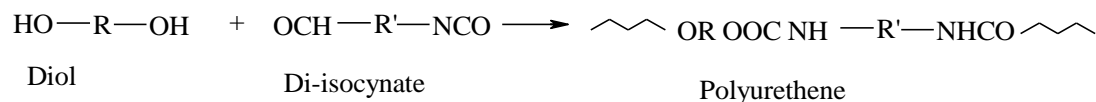
- (i) In condensation polymerization the monomers need not contain a double bond.
- (ii) The monomer does not retain its characteristic molecular formula, in the monomer.
- (iii) A small molecule is essentially given out and hence the resulting molecule is condensed in the process.

### Example



Condensation polymers are sometimes called rearrangement polymers.

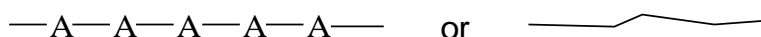
Eg.



#### 4. Molecular arrangement :

(a) **Linear** : All the identifying units are arranged linearly.

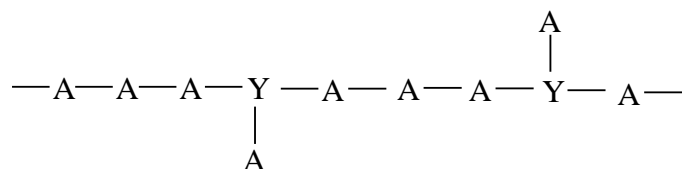
Eg.



Usually bivalent molecules (mesomers) gives linear polymers.

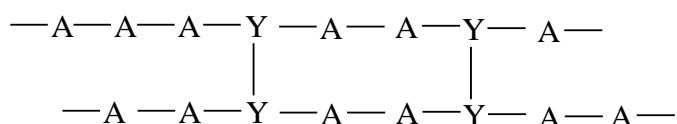
(b) **Branched** : The chain includes some molecules which have valencies of more than two. As a result, branch originates in the linear chains.

Eg.



(c) **Cross - linked** : In this type of polymer. The branched chains reacts with one another & form closed networks.

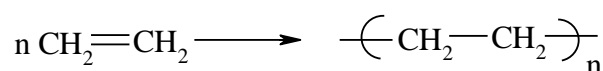
Eg.



#### (5) On the basis of type of mesomer involved in the polymers.

(a) **Homopolymers**: These are composed of only one type of mesomer.

Eg.



(b) **Hetero polymers**: These are composed of more than one type of monomers. These are called copolymers.



**(6) On the basis Morphology of the substance :**

**(a) Crystalline :** A crystalline state of a polymer is one in which the chains are very closely packed.

These polymer are more opagued.

**(b) Amorphous:** An amorphous state of a polymer is one in which the chains are more loosely held.

These polymers are more transparent.

## NOMENCLATURE OF POLYMERS

⇒ Nomenclature of carbon- chain polymers (Homopolymers)

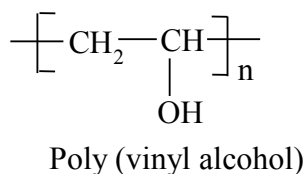
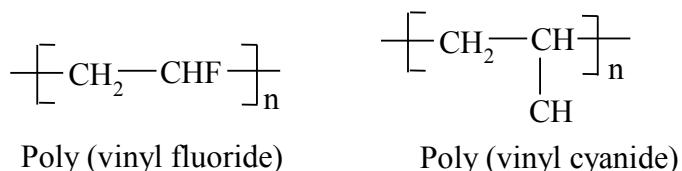
- The name of carbon chain polymers are usually derived by adding the prefix poly to the name of the monomer which forms the monomeric unit.
- If the name of the monomer consists of more than one word it is enclosed in parentheses.

**Eg.**

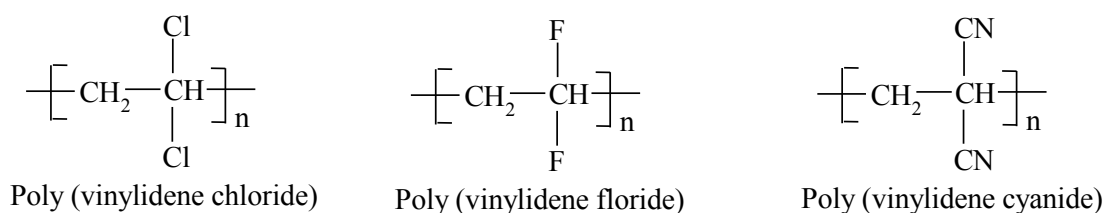
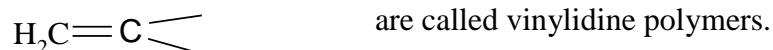
<u>Monomers</u>	<u>Name of Polymers</u>
Vinyl chloride	Poly(vinyl chloride)
Ethylene	Polyethylene
Chloroprene	polychloroprene

- Polymers obtained from monosubstituted ethylene derivatives containing the vinyl radical,  $\text{CH}_2=\text{CH}-$ , are combined under the (general) generic name of vinyl polymers.

This group of polymers includes.



- Polymers obtained from ethylene 1,1-disubstitutes containing the vinylidene radical



- **All the carbon chain polymers can be named on the basis of organic chemistry.**

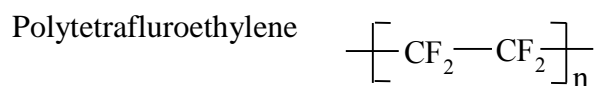
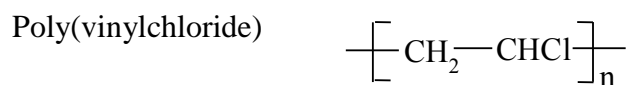
These are as follows.

## Saturated hydrocarbons and their derivatives :

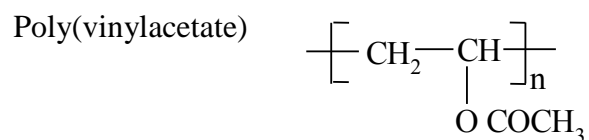
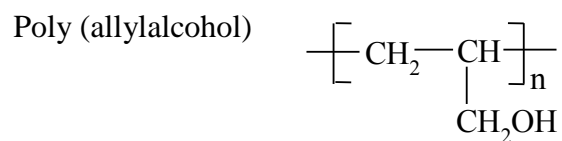
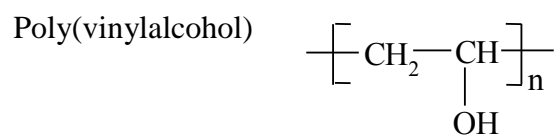
### Saturated Hydrocarbons



### Halo Derivatives

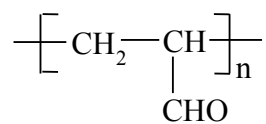


### Alcohols & Esters

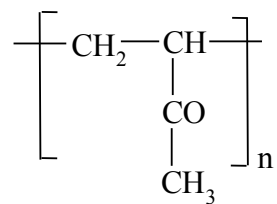


### Aldehydes & lactones

Polyacrolein

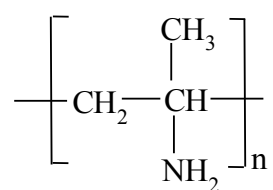


Poly(vinylmethyl ketone)



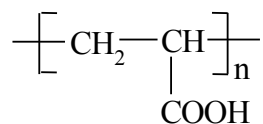
### Amines

Poly(vinylmethylamine)

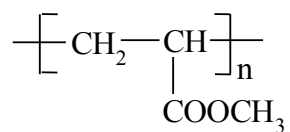


### Acids and derivatives

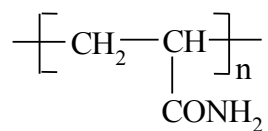
Poly(acrylic acid)



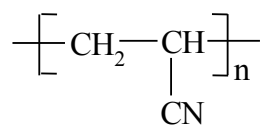
Poly(methyl acrylate)



Poly(acrylamide)

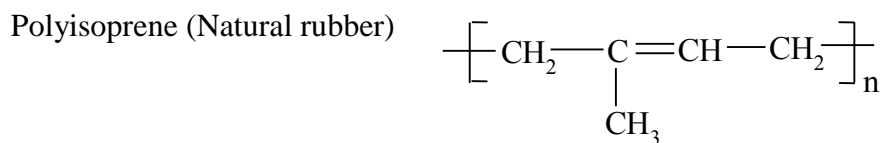
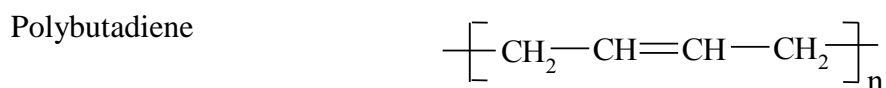


Poly(acrylonitrile)



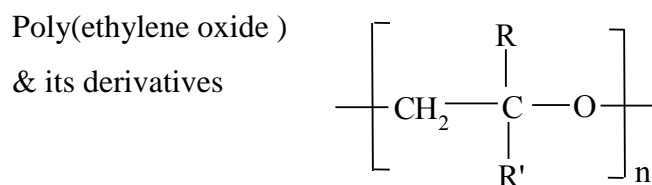


### Unsaturated hydrocarbons & their derivatives: -

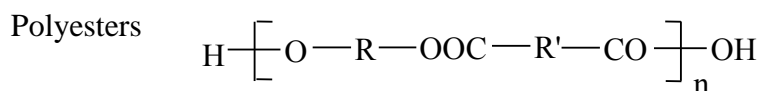
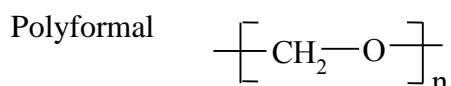


- Depending on the heteroatom present in the main chain, heterochain polymer falls into oxygen, nitrogen and sulphur containing & organo element polymers.

Eg.

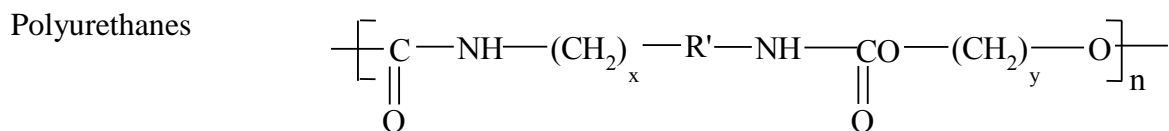
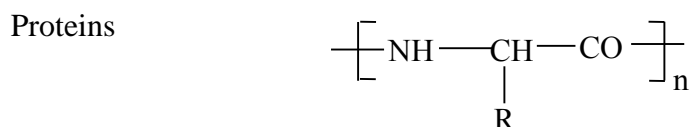


### Polyacetats



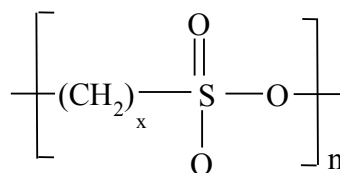
R-glycol radical & R' is a radical of unsaturated/aromatic dibasic acid.

### Nitrogen containing



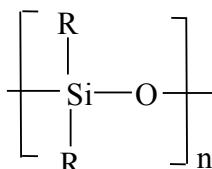
## Urea formaldehyde & Melamine formaldehyde polymers

Sulphur containing



## Polymers with Inorganic Main Chain :-

Polysiloxanes

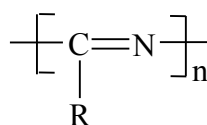


- The name of classes of heterochain polymer are derived from the name of the class of compounds in question, to which is added the prefix poly,

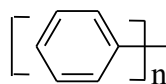
**Eg.** Polyesters, polyamide, polyurethanes etc.

- **Conjugated Bond Polymers** : - These includes both some carbon chain, & some heterochain polymers. Following are some conjugated bond polymers without dividing them into chemical group.

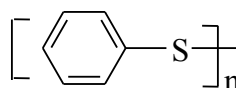
Polynitriles



Polyphenylenes



Poly(phenylene sulphides)



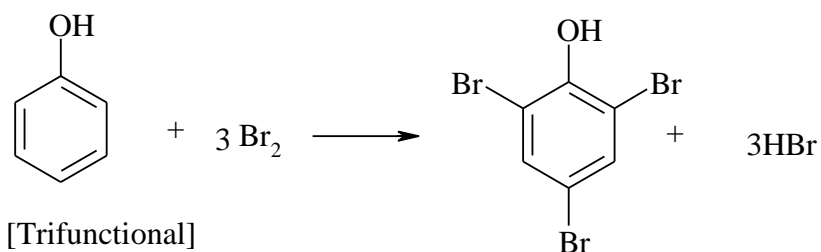
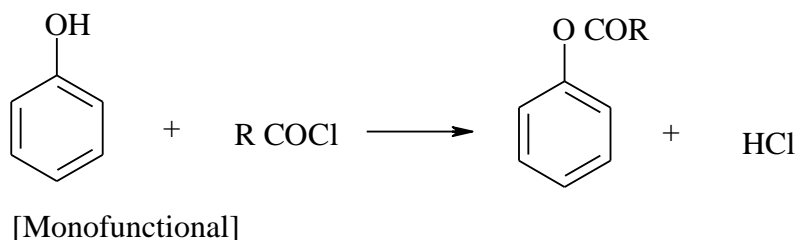
## SYNTHESIS OF POLYMER

The starting materials for the synthesis of polymers are low molecular mass substances (monomers) and, in some cases, oligomers.

A high molecular mass compound can be synthesized, if the monomer can react with at least two other molecular. i.e., if the monomer is at least bifunctional.

⇒ Functionality of a substance also depends on the presence in its molecular of double or triple bonds or mobile hydrogen atoms in its molecule.

**Eg.**



⇒ **Steric (special) factors :**

In some cases the synthesis of high molecule mass compounds is hindered by steric factors.

Steric hindrances are especially characteristics of the polymerization of unsaturated hydrocarbon derivative containing substituting atoms or r. with large rohman.

The functionality of substance is the number of functional groups contains per molecule.

Compounds may be monofunctional or poly functional (bi, tri, tetra, etc.)

Mono functional     $\text{CH}_3\text{—COOH}$     Acetic acid

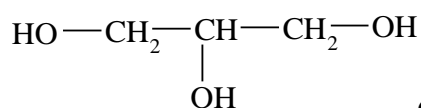
$\text{CH}_3\text{—OH}$     Methyl alcohol

Bifunctional     $\text{HO—CH}_2\text{—CH}_2\text{—OH}$   
Ethylene glycol



Adipic acid

Trifunctional



Glycerol

⇒ Four main methods of synthesizing polymers.

- i. **Chain polymerization**
- ii. **Polycondensation**
- iii. **Step polymerization**
- iv. **Ring scission (ring opening) polymerization.**

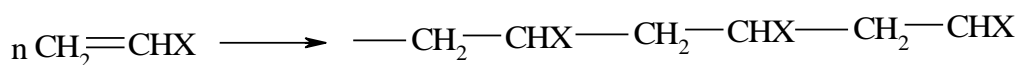
\*[Some authors use the terms addition polymerization to denote any polymerization in which no low-molecular weight by product is formed, and by other to denote chiefly chain polymerization.]

**(i) Chain Polymerization:**

Chain polymerization is one of the commonest methods of synthesizing macromolecular compounds. Almost all carbon. Chain polymers used in engineering synthetic rubbers and polyesters for plastic fibers are made by this method.

This polymerization is the combination of several simple molecules without, the formation of product and, hence incurring no change in the elementary composition of the reactants.

**Example**



Polymerization is always composed by a decrease in unsaturation of the reactants, a reduction in the total number of molecules and an increase in average molecular mass.

- Macromolecules obtained by chain polymerization are usually very long, with their molecular masses in the hundreds of thousands or even millions.
- The molecular mass or find degree of polymerization of a polymer formed by this reaction is obtained almost instantly.
- The kinetics of the reaction is a decisive factor for average molecular mass, degree of polymerization & nature of polydispersity.

Step :

**1. Initiation :** (formation active centre):-

Requires a high activation energy & proceeds slowly.

**2. Propagation :** low activation energy & very high rate

Heat effect is also always positive.

**3. Termination :**

Required small activation energy & has a fairly large reaction rate.

⇒ It is evident that the higher the rate of propagation compared to the rate of elimination, the longer will be the reaction chain and the larger the molecular mass of polymers.

Depending on the nature of active centres, chain polymerization fall into free radical polymerization & ionic polymerization.

**1. Free Radical Polymerization :**

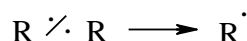
The initiation of the polymer chain growth is brought about by free-radical produced by the decomposition of compounds called initiators.

**Initiators:** They are thermally unstable compounds and decompose into product called free radicals.

Free radical of initiators can be formed thermally, by ultraviolet light or by catalysts.

**Methods of initiating free-radical polymerization:**

1. In thermal polymerization free radical are generated by heating.

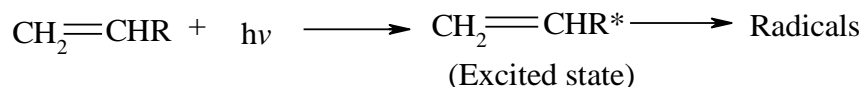


Many monomers practically do not polymerize in the absence of Impurities.

**E.g.** Vinyl acetate, acrylonitrile, vinyl chloride will not polymerize if heated without oxygen.

Other like methyl methacrylate polymerizes fairly rapid on heating.

2. In photo polymerization, the monomer- absorbs a photon and becomes excited.



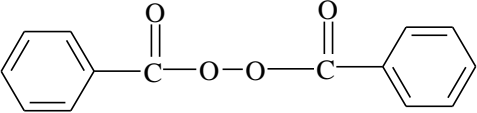
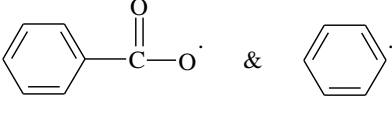
$h\nu$  is the energy of one quantum of light.

Eg. Vinylidene chloride can be polymerized by UV light at 35<sup>0</sup>C , but it will not polymerize in the absence of initiator even if heated.

3. In radiation polymerization the action of high energy radiations (r- rays, x- rays & accelerated electrons) on the monomer also results into free radical.
  4. Initiated polymerization, the radicals may be added in the free state or as compounds which decomposes readily during the polymerization to form free-radical.
- Initiators can also be induced to decompose into free-radical by using suitable catalyst.
  - E.g. Benzoyl peroxide can be decomposed at room temperature with an aromatic tertiary amine.

Hydrogen peroxide and hydroperoxide can be decomposed by ferrous ion & cobaltous ions respectively.

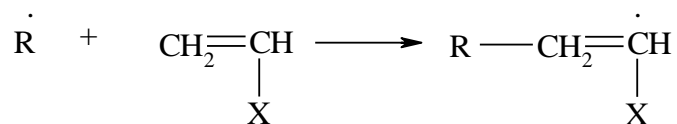
Some initiators and there produced radicals are as follows :

Name	Structure	Free radical found
(AIBN) Azobic- isobutyro-nitrile	$\begin{array}{c} \text{CN} \qquad \qquad \text{CN} \\   \qquad \qquad   \\ \text{H}_3\text{C}-\text{C}-\text{N}=\text{N}-\text{C}-\text{CH}_3 \\   \qquad \qquad   \\ \text{CH}_3 \qquad \qquad \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CN} \\   \\ \text{H}_3\text{C}-\text{C}\cdot \\   \\ \text{CH}_3 \end{array}$
BPO Benzoylperoxide		
Hydrogen Peroxide	$\text{HO}-\text{OH}$	$\text{OH}\cdot$
Peracetic acid	$\begin{array}{c} \text{O} \\    \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{OH} \end{array}$	$\text{CH}_3\text{COO}\cdot \quad \cdot\text{CH}_3 \quad \& \quad \cdot\text{OH}$
Potassium Persulphate	$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\    \qquad \qquad    \\ \text{KO}-\text{S}-\text{O}-\text{O}-\text{S}-\text{OK} \\    \qquad \qquad    \\ \text{O} \qquad \qquad \text{O} \end{array}$	$\text{K}^+ \text{O}^- \text{S}(\text{O})_2 \text{O}\cdot$
Tert. Butyl peroxide	$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\   \qquad \qquad   \\ \text{H}_3\text{C}-\text{C}-\text{OC}-\text{O}-\text{C}-\text{CH}_3 \\   \qquad \qquad   \\ \text{CH}_3 \qquad \qquad \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{C}-\text{O}\cdot \\   \\ \text{CH}_3 \end{array} \quad \& \quad \cdot\text{CH}_3$

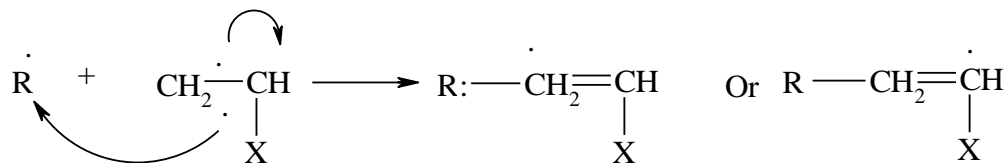
### Initiation :

A free radical contains a unpaired electron. A unpaired electron try to couple with another unpaired electron and get stabilized.

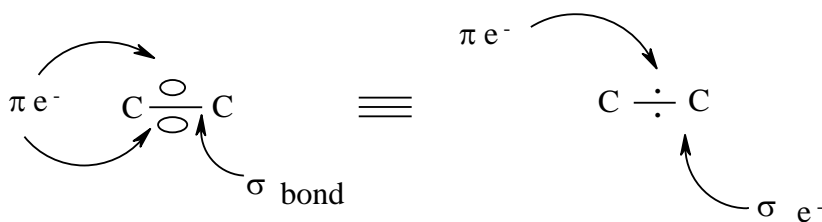
In the initiation free radical e.g. R' attacks the double bond in the monomer molecule, reacting in the following chemical change.



**Mechanical :**



- In the double bond one pair of electron exist as sigma (  $\sigma$  ) electrons, while the other, not so close to nucleolus , exist as pi (  $\pi$  ) electrons.



In the initiation free radical formed from initiator's decomposition interferes with one of  $\pi$  electrons which are not very close to nucleus, so are susceptible to be attacked.

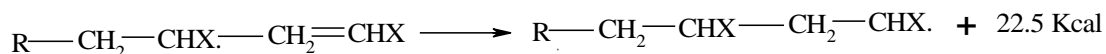
The free radical forms a  $\sigma$  type bond / pair of electron, with one of the electron and so the remaining transfer to the other end forming the radical at the other end.

Free radical attack is an exothermic process, whereas its formation by initiator, decomposition is endothermic.

### PROPAGATION :

Propagation is the process of moving radical from one end to the next molecules end.

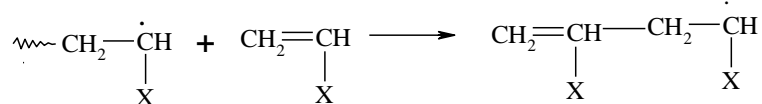
Propagation results in a change of  $\pi$  bonds into  $\sigma$  bonds . This reaction always proceeds with the liberation of heat due to the difference in energies between  $\pi$  &  $\sigma$  bonds.



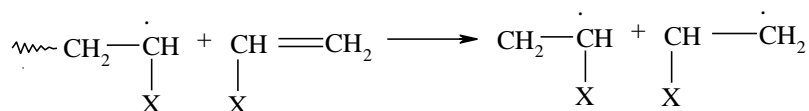
This step results in the linking up of the second monomer unit to the first and transfer of the radical site from the first monomer unit to the second.

The addition of incoming monomer to the growing chain can be of four types.

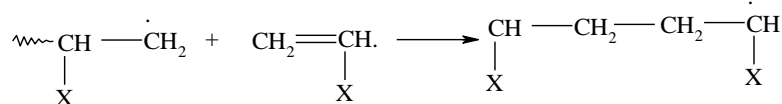
(i) Head to Tail



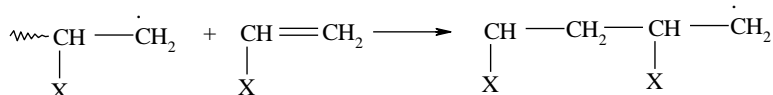
(ii) Tail to Tail



(iii) Head to Head

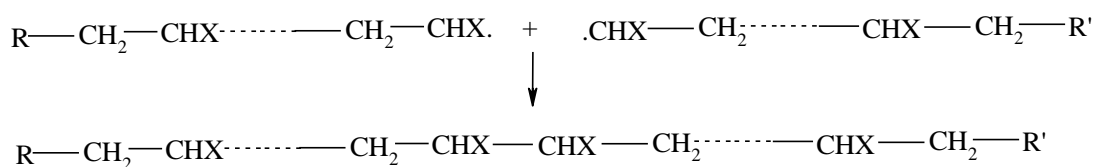


(iv) Tail to Head

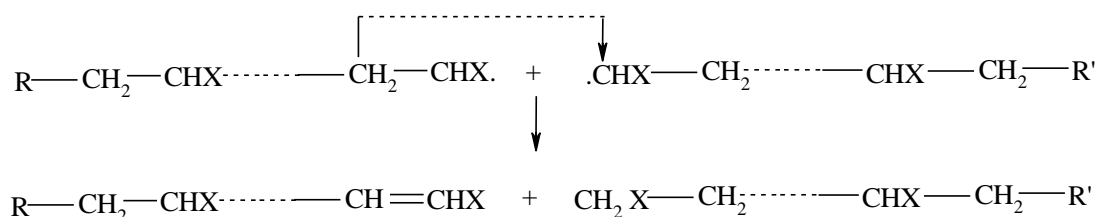


### Termination :

Chain termination must be related to disappearance of the unpaired electron. Therefore, as a such termination occurs as a result of interaction of two radicals. In the simplest case this may be recombination (coupling) of free radicals.



### or Disproportion



- In the first case, the two growing chains unite by the coupling of the electrons present in each chain to form an electron pair and, thus, nullify their reactivity.
- In second case, one H from one growing chain is abstracted by the other growing chains and utilized by the lone electron for getting stabilized, while the chain, which has donated the H, gets stabilized by the formation of a double bond.

There is yet another method of chain termination, which takes place by transfer reaction.



### CHAIN TRANSFER :

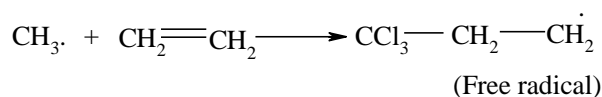
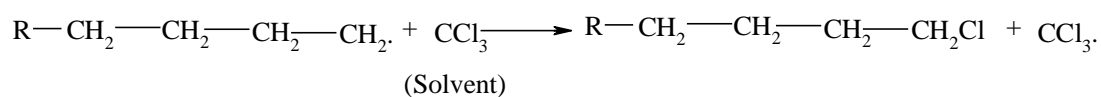
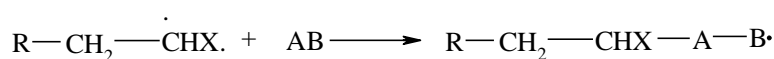
In termination brought about by coupling or disproportionation, the products formed or 'dead' or 'non-reactive, and , hence, no further chain propagation is possible.

In case of ' transfer – reaction' , however, while of growth of polymer chain is stopped, there is a simultaneous generation of a new free-radical capable of initiating a fresh polymer chain growth.

Usually it takes place as a result of interaction of an active centre or a growing chain with an impurity or with the solvent.

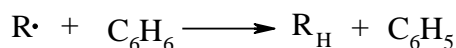
e.g.

If the growing chain ( the free polymer radical) possesses sufficient energy to break the A – B, a saturated molecule's bond, collision of such will result in termination of the chain & generation of new radical.



- Chain transfer in a Non-polar solvent ( H / C ) :

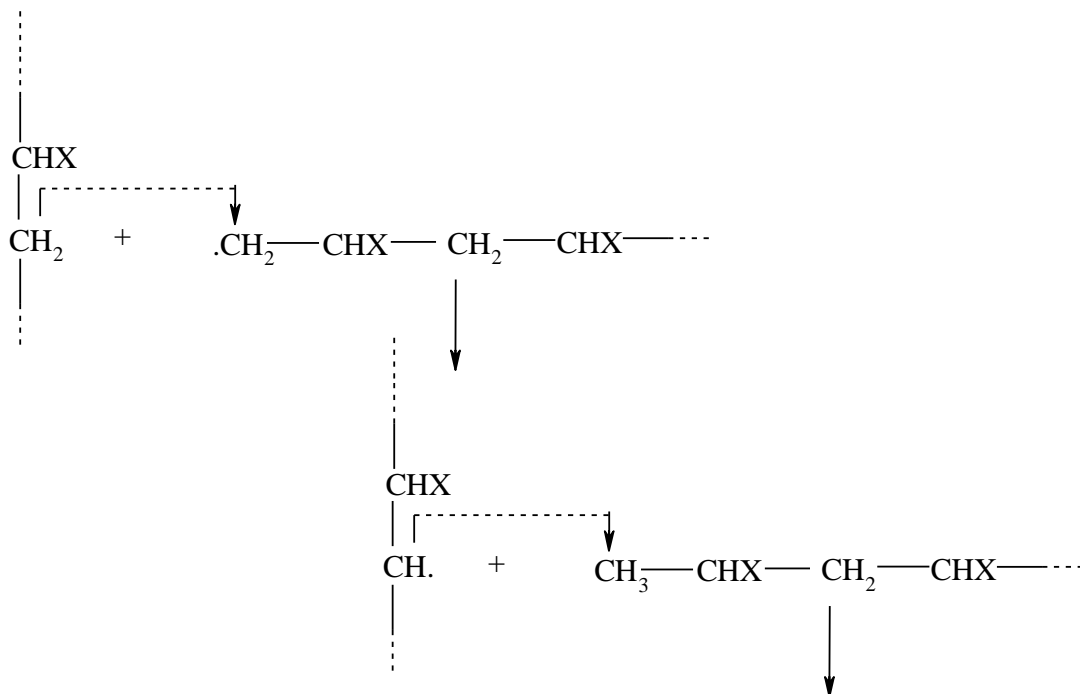
Eg. In benzene , with the formation of phenyl radical



On colliding of with the monomer this radical may start a new chains.

### Scheme :

During chain transfer to a macromolecule the latter loses, say, a hydrogen atom to the growing chain it collides with and turns into a macroradical as follows :



By adding transfer agents to the reaction system one can control the average molecular mass of polymer and obtain polymers with lower degree of polydispersion and branching.

Such agents are called regulators.

Following are used as polymerization regulators.

- (1) chlorinated hydrocarbons ( $\text{CCl}_4$ ,  $\text{Cl}_2\text{C}=\text{CCl}_2$ ,  $\text{Cl}_3\text{C}-\text{CCl}_3$ )
- (2) Mercaptans

The amount of regulators added ranges from 2 to 6 % of the weight of monomer.

### INHIBITORS:

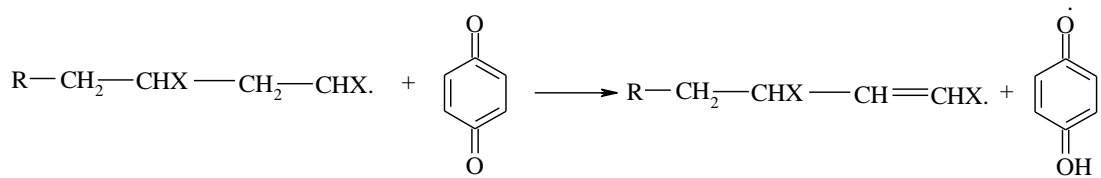
These are chemical substances capable of inhibiting or killing the chains growth by cobbling with the active free radicals and forming either stable products or inactive free radicals.

If the formed radical has low activity radical is incapable of further growth and adds on to a polymer radical and terminates the chains.

e.g.

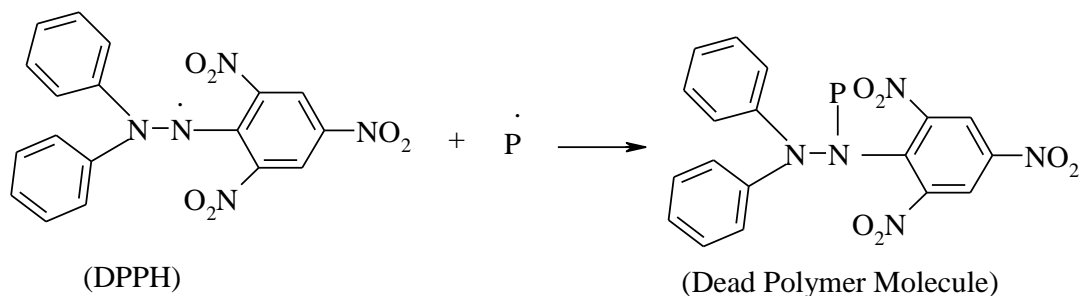
Quinones, nitrobenzene, dinitrobenzene, polyatomic phenols, (Hydroquinone etc) aromatic amine sulphur, iodine etc.

⇒ Quinone removes hydrogen from a growing chain changing it into semiquinone.



Because of conjugation the activity of semiquinone is low and it adds to the growing chains & terminal it.

- Depending on whether a substance entirely stops or only shows down polymerization it is called as inhibitor or a retarder respectively.
- Some inhibitors such as diphenyl picryl hydrazide (DPPH) exist in the form of stable free radicals which can easily stop the chain growth by direct coupling.



The atmospheric oxygen is a good inhibitor.

This is why polymerization is generally carried out under a nitrogen atmosphere.

In industrial practice, however, they are killed by adding further, quantities of initiators to the monomer.

#### • KINETICS :

Kinetics of this type of polymerization can be derived by using Bodenstein's steady state assumption, which is essentially as follows :

- At a certain moment of time the system begins to generate active centres at the rate  $v_a$  and the concentration of these centres ( $n$ ) increase continuously. Simultaneously active centres disappear at the rate  $v_t$  as a result of chain termination, the rate of which increases with the concentration of active centres  $[n]$ .
- After some time the concentration of active centres in the systems becomes constant.
- i.e. the rate at which active centres are formed becomes equal to the rate at which they are used up :

$$v_a = v_t \quad \text{-----(1)}$$

On the basis of the steady state assumption ( i.e. assuming the rates of active centre formation & termination to be equal) dependence between rate & degree of polymerization and other process variable can be found.

The rate of termination may be expressed as :

$$v_t = K_1 [n]^2 \text{ -----(2)}$$

where  $[n]$  = Steady-state concentration of active centre.

$K_1$  = termination rate constants

Then for steady state conditions

$$v_a = K_1 [n]^2 \text{ -----(3)}$$

- Chain propagation occurs through interaction of an active centre with a monomer molecule and therefore the rate of this reaction may be evaluated from the equation.

$$v_p = K_2 [n][m] \text{ -----(4)}$$

Where  $[m]$  is monomer concentration &

$K_2$  = the propagation rate constant

- The overall polymerization rate  $v$  under steady state conditions is equal to the rate of propagation.

$$v = v_p = K_2 [n][m] \text{ -----(5)}$$

- Substituting in this equation the expression for  $[n]$  from equation (3) we have.

$$v = \frac{K_2}{\sqrt{K_1}} [m] \sqrt{v_a} \text{ -----(6)}$$

- The average degree of polymerization of the resulting polymer is determined by the ratio between the propagation and termination rates.

$$\bar{P} = \frac{v_p}{v_t} \text{ -----(7)}$$

substituting the value of equation (3) and (4),

$$\bar{P} = \frac{K_2}{\sqrt{K_1}} \frac{m}{\sqrt{v_a}} \text{ -----(8)}$$

- In initiated polymerization the overall reaction rate and the average degree of polymerization of the resulting polymer can be formed as function of the initiator concentration  $[i]$  by assuming rate of active centre generation is equal to the initiator concentration.

From equation (6)

$$v_a = K_3 [i] \text{ -----(9)}$$

where  $k_3$  = the rate constant of active centre formation,

we get,

$$v = \frac{K_2 \sqrt{K_3}}{\sqrt{K_1}} [m] \sqrt{[i]}$$

Assuming [ m ] to be constant and replacing all the constant by k, the overall polymerization rate :

$$v = K \sqrt{[i]} \text{-----(10)}$$

Thus the overall rate of polymerization is proportional to the square root of initiator concentration.

- Substituting in Eq. (8 ) the value of  $v$  a from Eq. (9) one obtains.

$$\bar{P} = \frac{K_2}{\sqrt{K_1}} \frac{[m]}{\sqrt{K_3} \sqrt{[i]}}$$

Assuming [ m ] to be constant, and representing all the constants by  $K^1$  , we obtain

$$\bar{P} = K' \frac{1}{\sqrt{[i]}}$$

Hence, the average degree of polymerization varies inversely as the square root of the initiator concentration.

*Note : The higher the activation energy of a reaction, the greater will be the effect of temperature.*

#### ❖ Effect of initiator concentration :

Number of free radical formed by decomposition of initiator increases with initiator concentration.

#### ❖ Effect of monomer concentrations :

If carried out in solvent, rate of polymerization and molecular mass increases with monomer concentration.

#### ❖ Effect of pressure :

High and extremely high pressure ( 3,000 to 5,000 atm and more) speeds up reaction  
Pressure of several atmosphere or even tens of atm has practically no effect.

## IONIC POLYMERIZATION

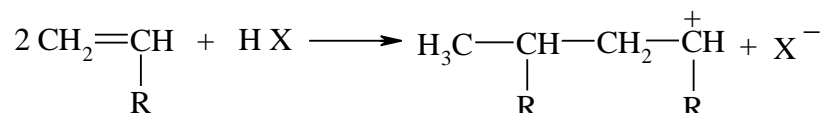
In contrast to radical polymerization, which proceeds by transfer of an unpaired electron along the chain, ionic polymerization involves the formation of a carbonium ion or a carbonion and subsequent transfer of a positive or negative charge along the chain.

Depending on the catalyst used, and the sign of the charge formed ionic polymerization is distinguished between cationic and anionic polymerization.

### 1. Cationic polymerization :

Cationic polymerization occurs in the presence of acids and friedel craft catalyst (  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$  etc.) Being electron acceptors, these catalysts add on to the monomer forming a carbonium ion.

Reaction may be represented schematically as follows :

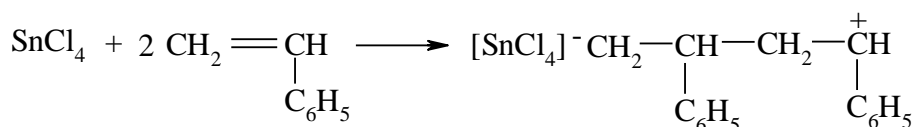


Chain propagation is accompanied by transfer of a positive charge along the chain.

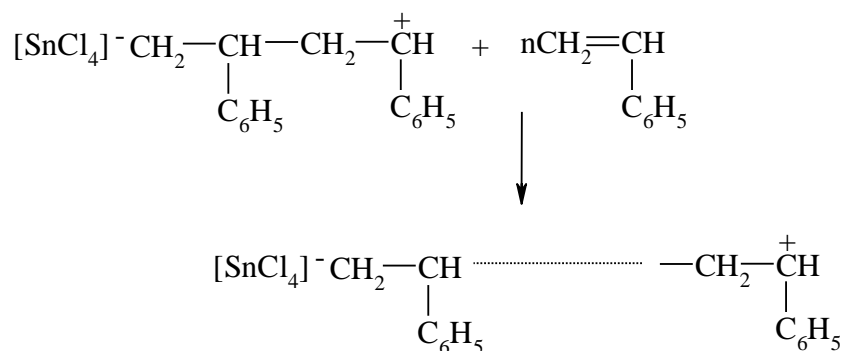
Chain terminator evidently occurs as a result of proton elimination.

The mechanism of olefin polymerization under the action of metal halogenides can be exemplified by the polymerization of styrene in the presence of tin tetrachloride.

- When styrene reacts with tin tetrachloride, a complex is formed at first which reacts with the next styrene molecule to form a carbonium ion active centre :



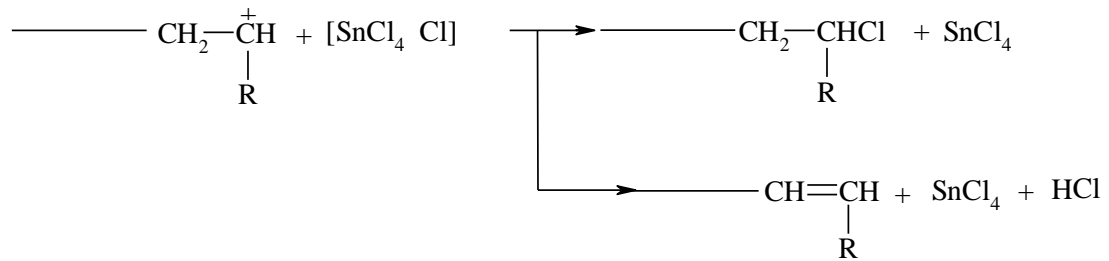
- Chain propagation consists in the addition of monomer molecules with regeneration of the carbonium ion at the end of the chain.



Apparently in this case, collision between the opposite ends of the growing ion results in monomolecular chain termination with elimination of the catalyst and formation of a double bond in one of the end units of the macromolecule :



HCl as co-catalyst :



- Addition of the co-catalyst in an amount not exceeding the stoichiometric ratio with respect to the catalyst increases the rate of polymerization and decrease the molecular mass of the polymer.
  - Only the co-catalyst molecules that combine with catalyst take part in the reaction. The part played by the co-catalyst depends on the mediums.
  - In polar solvent HCl accelerates polymerization where as in non-polar solvent, such as CCl<sub>4</sub> rate of polymerization decreases.

### KINETICS :

Assuming monomolecular mechanism of chain termination, the rates of the elementary reactions of cationic polymerization can be expressed by the following equations.

$$v_a = K_3 [m][b] \quad v_p = K_2 [m][n] \quad v_t = K_1 [n]$$

where, [b] = catalyst concentration

- Making use of steady state assumption, one can find dependence of the average degree of polymerization  $\bar{P}$  and the overall rate of reaction  $v$  on the catalyst concentration.

$\bar{P}$  is determined by the equation :

$$\bar{P} = \frac{v_p}{v_t} = \frac{K_2 [m][n]}{K_1 [n]}$$

$$\bar{P} = K'[m]$$

i.e. the average degree of polymerization is directly proportional to the monomer concentration and is independent of the catalyst concentration.

- The overall rate of polymerization can be formed from the equation.



$$v = v_a \bar{P} = K_3 [m][b]K'[m]$$

If the monomer concentration [ m ] is constantly this equation becomes.

$$v = Kb$$

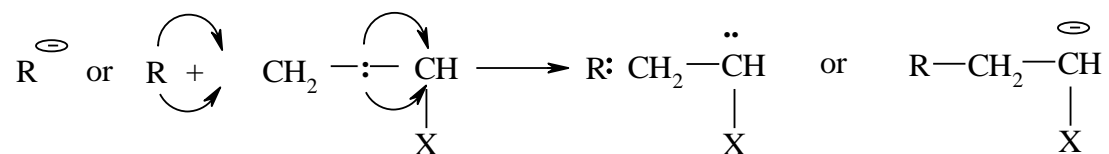
i.e. the overall rate of cationic polymerization is directly proportional to the catalyst concentration.

## 2. Anionic polymerization :

In anionic polymerization the attack on  $\pi$  electron pair of the monomer is done by a negatively charged ion i.e. an anion.

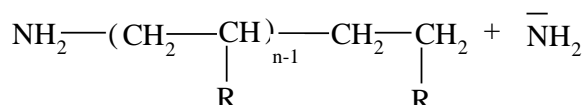
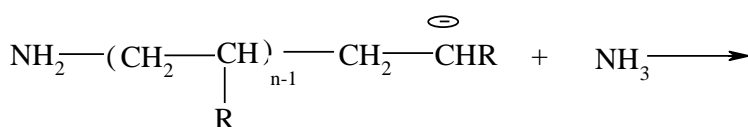
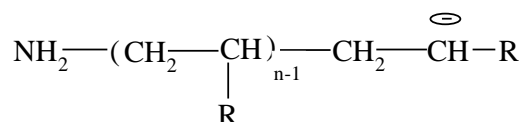
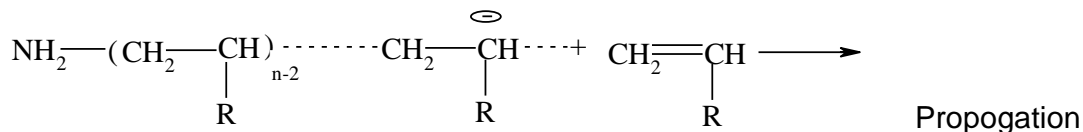
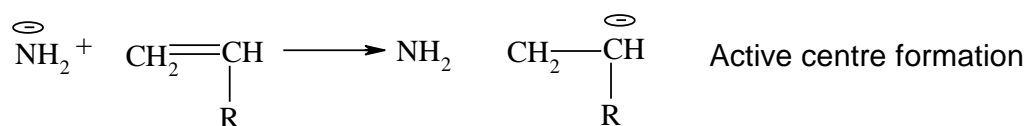
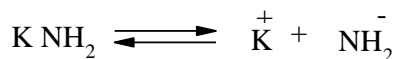
- Such a system has extra electrons and the resultant negative charge attacks the  $\pi$  electron pair, pushing it, as far as possible, that is, to the end of the molecule.

At the same time, it forms a sigma bond with the monomer molecule, The electron pair pushed to the end of the molecule results in the formation of a carbanion.



This carbanion thus formed propagates the chain.

- The mechanism can be exemplified by the polymerization of unsaturated compounds in the presence of potassium amide (  $\text{KNH}_2$  ) in liquid ammonia solution.



Examples : In case of polymerization of styrene in the presence of potassium amide in liquid ammonia molecular mass of polymer is independent of the catalyst concentration.

- And is directly proportional to the concentration of monomer and the molecular mass of polymer decreases with increase in temperature.
- The rate of polymerization is proportional to the square of monomer concentration and to the square root of catalyst concentration.
- Other monomer such as acrylic acid derivatives methyl methacrylate, acrylonitrile, and methacrylonitrile – also polymerize with alkali amide.
- The general type of initiators used in this type of polymerization are organo – alkali compounds such as butyl lithium, triphenyl methyl potassium and ethyl sodium.
- In ionic polymerization, chain propagation involves the participation of a carbanion or an ionic pair; here the end group of growing polymer molecule is highly active, but fairly stable.

That is why anionic polymerization can often proceed without chain termination (because of absence of impurities) until monomer is completely used up.

Such polymerization result in polymers whose macromolecular contain active centres and are capable of initiating polymerization.

These polymers are called “living polymers.”

Block copolymers can be produced by adding other species to “living” polymers.

- In presence of org. alk. compounds polymerization proceeds differently.
- The distinguishing feature of this polymerization is the bi-functional addition of the monomer.

### CO-CORDINATION POLYMERIZATION:

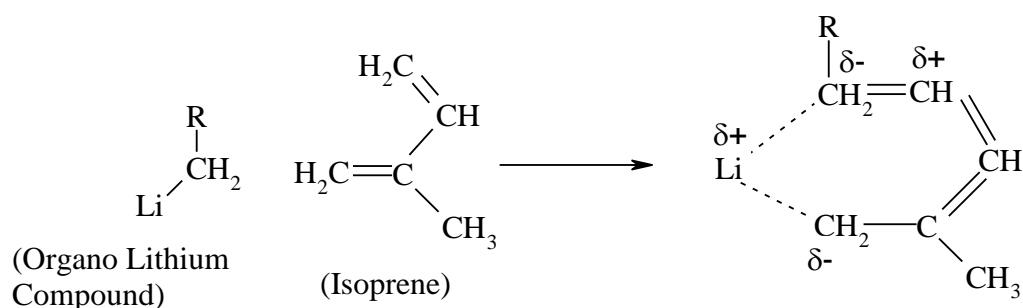
Anionic polymerization is often subdivided into anionic polymerization proper and anion – co ordination polymerization or simply co-ordination polymerization.

- Co-ordination polymerization includes polymerization in the presence of organo metallic compounds which proceeds through a stage of formation of an intermediate catalyst complex, this being a monomer with the catalyst linked to it by co-ordination bond.
- In the polymerization catalyzed by organo metallic compounds two catalyst centres participate in the chain propagation reaction, namely, the metal and the alkyl ( two – centre polymerization mechanism).

### MECHANISM :

It is thought that addition of the monomer molecule is proceed by formation of catalyst complex.

For example, on polymerization of isoprene in the presence of an organolithium compound.



Since the metal is joined to the monomer by a co-ordination bond, polymerization involving the formation of such complexes are called co-ordination polymerization.

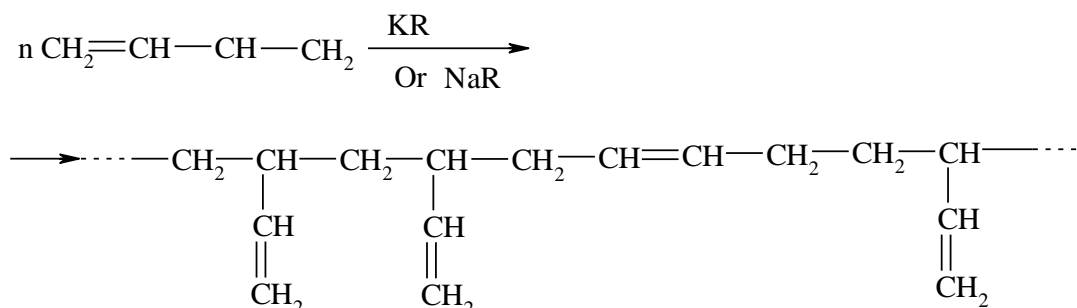
- The structure of the intermediate complex and the spatial arrangement of the monomer molecule in it and so in polymer depend on polarity of the metal carbon bond in the catalyst and the medium in which the polymerization is carried out.

The degree of bond polarity in the organic compounds of alkali metal is :

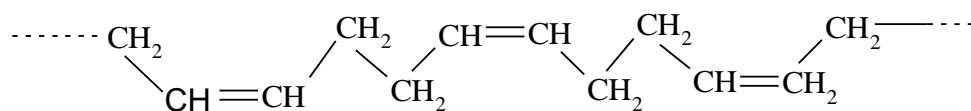


The more polar the bond in the catalyst, the more the mechanism of polymerization approaches that of the pure anionic mechanism (due to formation of free ions).

- Thus polymerization of butadiene in the presence of organo sodium, or organo potassium compounds results in a polymer of predominantly 1,2-structure .



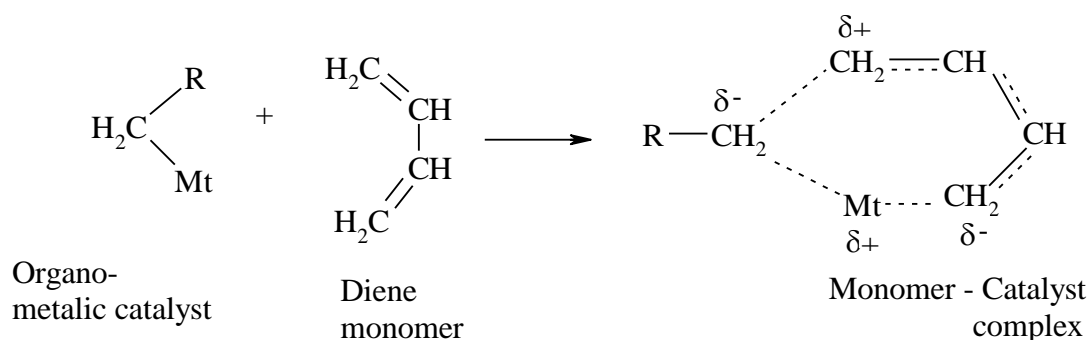
Whereas in the presence of organo lithium compounds with HC as solvents the structure is 90 % 1,4 and the resulting polymer is a stereo regular cis- 1,4 polybutadiene.



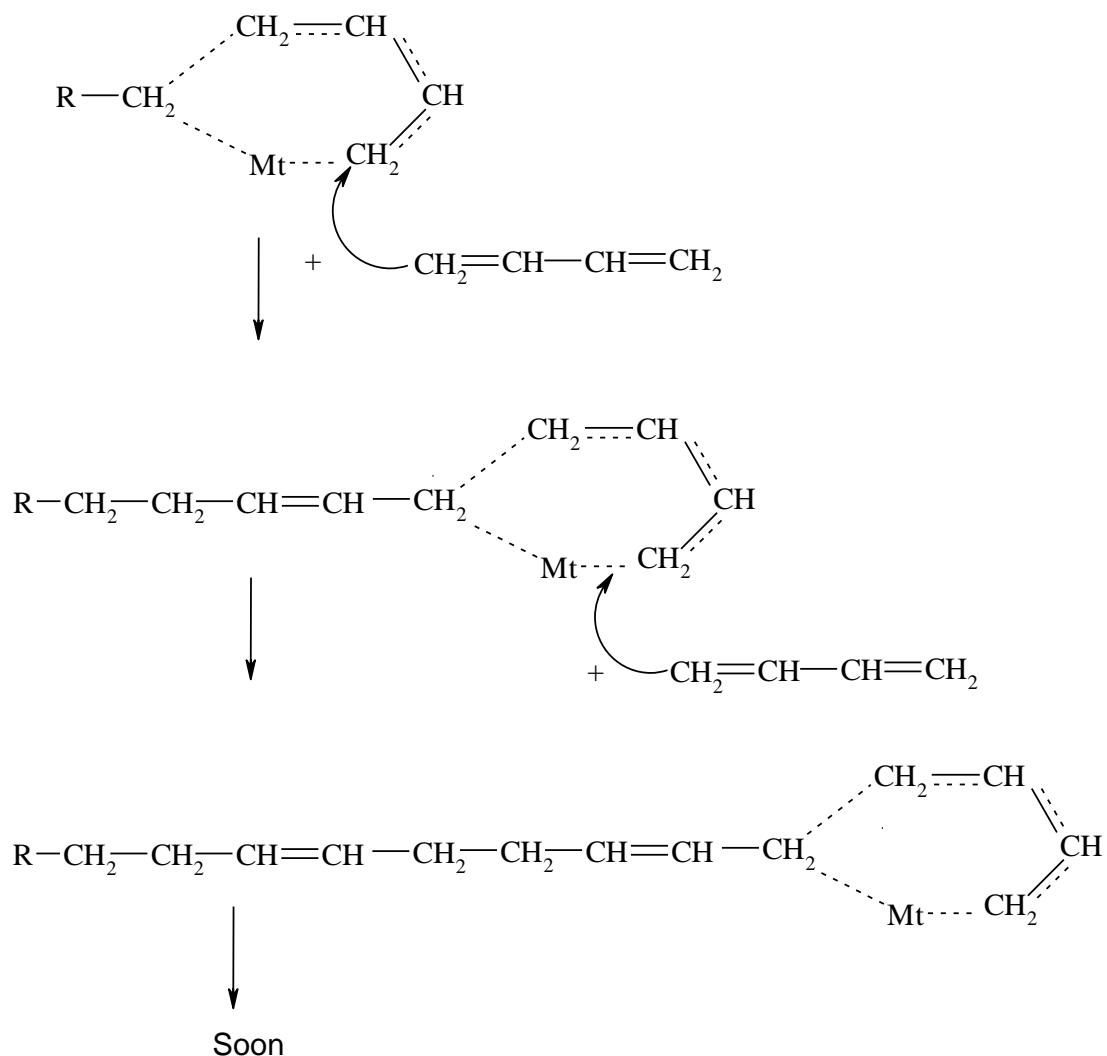
- If this polymerization is carried out in polar solvents, the effect of the catalyst metal on the reaction is weakened considerably due to the formation of a metal solvent complex the polymerization mechanism then approaches the anionic.
- The constitution of the alkyl group of the catalyst evidently also has some effect on the structure of the polymers formed.

“Stereo regular polymers do not form if the alkyl group of the organo lithium compounds contains less than four carbon atom.”

In the other type of example for the same mechanism propagation of chain is as follows.



Where Mt represents transition metals such as Ti, Mo, Cr, V, Ni, etc.



In co-ordination polymerization, the catalyst monomer complex is a heterogeneous system. The monomer is inserted between the metal ion and the carbanion with the result that the polymer chain formed is pushed out from the solid catalyst surface.

For this reason, this polymerization is also known as insertion polymerization.

By choosing a proper catalyst / solvent system, the co-ordination mechanism can be used to formulate highly stereo regular polymers. The well known Ziegler – Natta catalysts belong to this category.

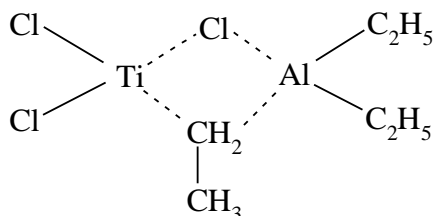
- **ZIEGLER - NATTA CATALYSTS :**

These catalysts contain organo metallic compounds of I – III groups metals and chlorides of IV – VII group metals with transition valence.

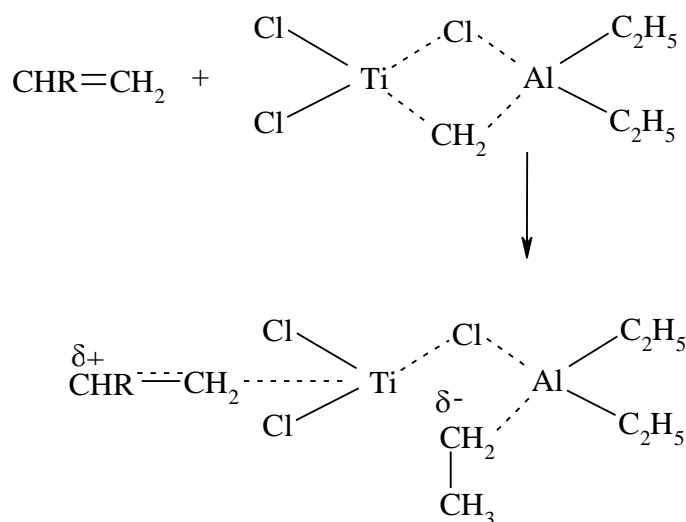
- The most commonly used are organo aluminium compounds and titanium chlorides.
- Since the alkyl derivatives of aluminium possess electro – acceptor properties and metals of transition valence are electron donors, they form co-ordination bonds readily.

It is thought that the active catalyst must have an alkyl group included in its co-ordination bond.

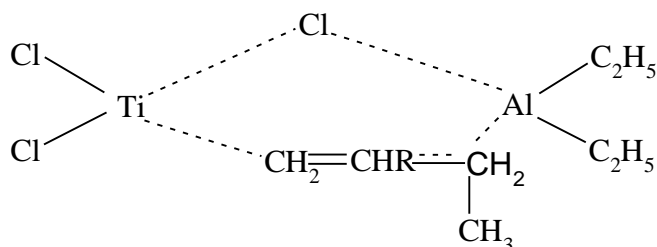
**Mechanism:** According to this idea the catalyst consisting of  $\text{Al}(\text{C}_2\text{H}_5)_3$  and  $\text{TiCl}_3$ , used in industry for the production of polypropylene, evidently has the following structures :



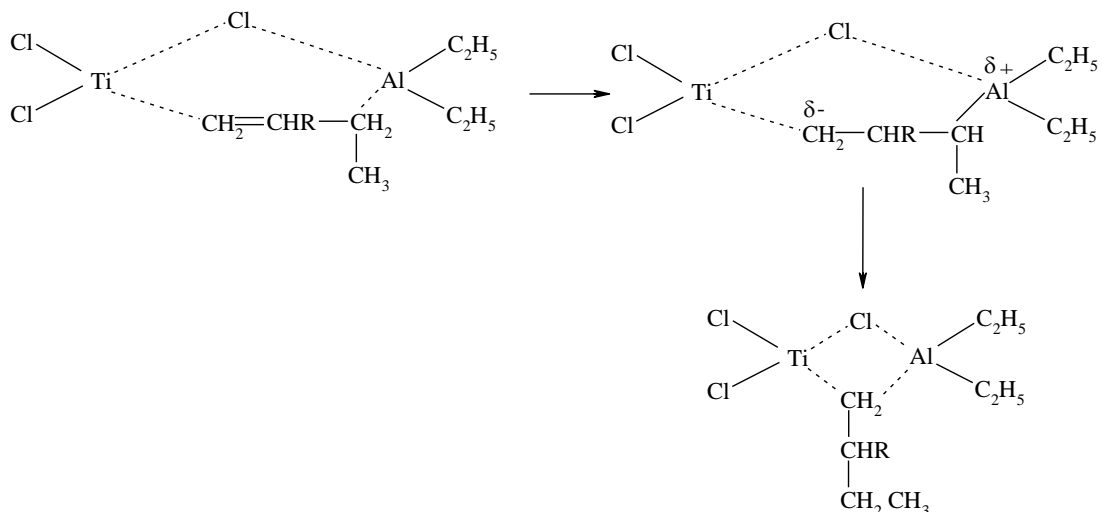
The  $\pi$  electron of the monomer interacts with the 3d electron of titanium, opening the bond between titanium and the ethyl group carbon and forming a co-ordination bond between titanium and the methylene group carbon of the monomer.



with subsequent closing of the cycle.



When the monomer  $\pi$  bond opens and a  $\sigma$  – bond forms with the catalyst ethyl group carbon the co-ordination bond between aluminium and the ethyl group carbon is broken and a bond is formed between the aluminium and the monomer carbon:



The resulting complex serves as an active centre for polymerization.

- Since Ziegler – Natta – catalyst are insoluble, polymerization in which they are involved proceed by heterogeneous catalyst.
- The stereo regularity of polymers is affected greatly by the chemical structure of the catalyst.

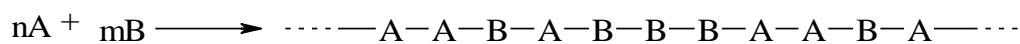
Thus, ethylene polymerization with the Ziegler Natta catalyst [  $\text{Ti Cl}_4 + \text{Al} ( \text{C}_6 \text{H}_5 )_3$  ] results in a linear crystalline polyethylene, but when  $\alpha$  - olefins are polymerized with this catalyst polymer with high content of atactive structures are obtained.

- The stereo regularity of the polymer is sharply reduced by the impurities present in the reaction medium, and decreases with increasing temperature of polymerization.

### CO-POLYMERIZATION:

Copolymerization is the joint polymerization of two or more monomer species.

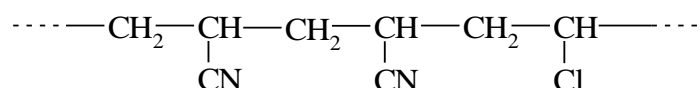
High molecular mass compounds obtained by copolymerization are called copolymers. The copolymerization of two monomer can be described by the equation:



By using different initial species and by varying their ratios, copolymers of various compositions and properties can be obtained.

Most copolymers are irregular in structure; the different monomeric units are randomly arranged in their molecular chains and therefore no repeating section of the chain can be singled out.

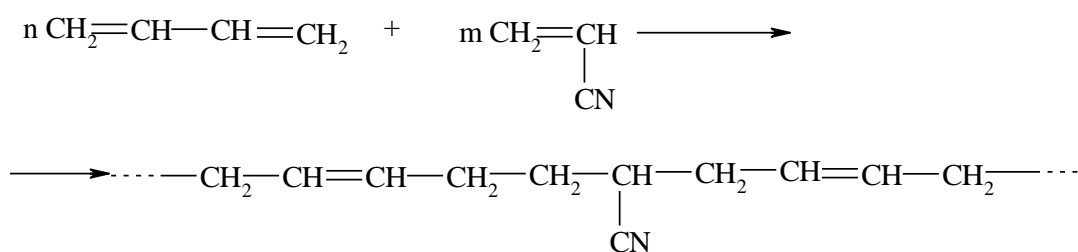
Copolymerization has found extensive practical usage because it enable variation of the properties of high molecular mass compounds over a wide range. For instance, the copolymer of acrylonitrile and vinyl chloride.



Is readily soluble in acetone, whereas polyacrylonitrile and poly(vinyl chloride) are soluble only in high-boiling and difficulty available solvents.

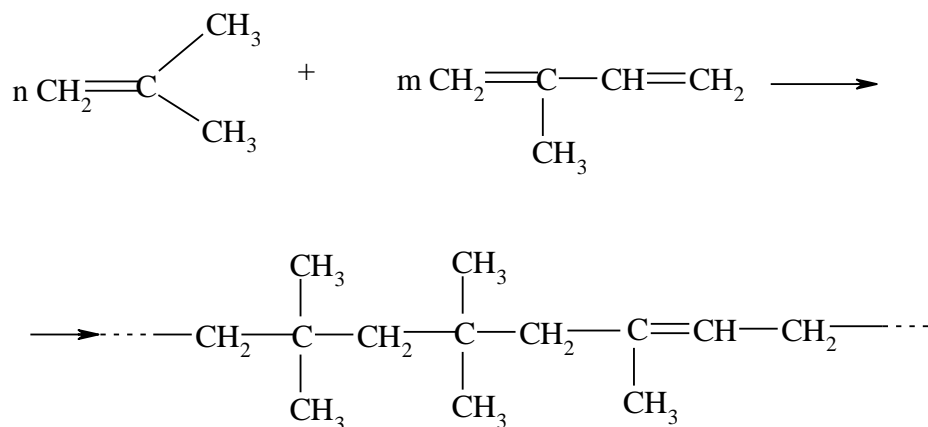
Copolymerization is widely used in the synthetic rubber industry.

Copolymerization of butadiene with acrylonitrile results in a butadiene nitrile rubber known as SKN.



which possess good oil and petrol resistance.

⇒ Copolymerization of isobutene with a small amount of isoprene gives butyl rubber.



Noted for its high gas impermeability.

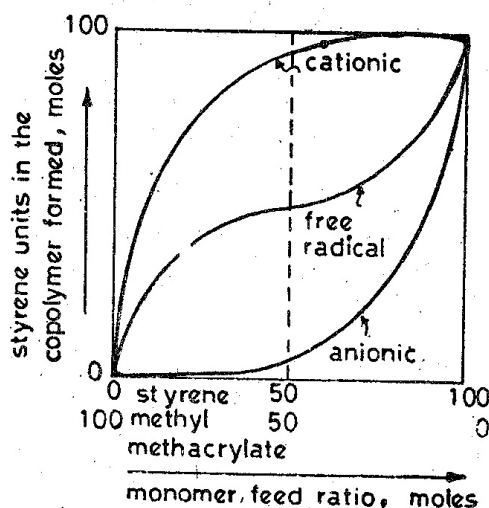
Copolymerization can be brought about by many types of polymerization reactions.

The majority of the commercially important copolymers, however, are made by free radical, ionic or polycondensation polymerization.



### Effect of different techniques of polymerization on copolymers.

The well – known example is the copolymerization of the monomer pair methyl methacrylate styrene , whose composition curves are given below.



At an initial equimolar ratio of styrene to methyl methacrylate (broken line), the free-radical polymerization using benzoyl peroxide yields a copolymer containing roughly 50 % of styrene; A cationic polymerization initiated by borontrifluoride etherate gives a copolymer containing more than 95 % styrene, while the anionic polymerization with triphenyl methyl sodium results in a copolymer having less than 5 % styrene.

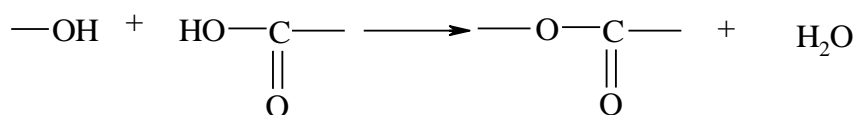
### POLY CONDENSATION:

Poly condensation is a reaction of combination of several molecules accompanied by elimination of simple by products such as water, alcohol, ammonia or HCl.

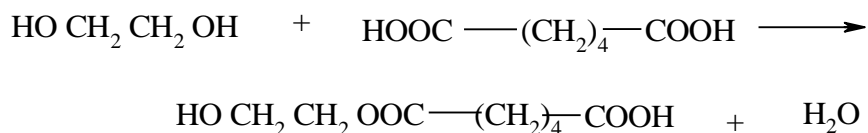
As distinct from polymerization products, the elemental composition of a condensation polymer does not coincide with that of its initial monomers.

Poly condensation is characteristics of compounds containing functional groups. Whereas these groups interact the molecule of a simple compound is evolved and a new group is formed which binds the residues of the reacting molecules.

For examples the reaction between a hydroxyl group and a carboxylic group, giving an ester and a water molecules.

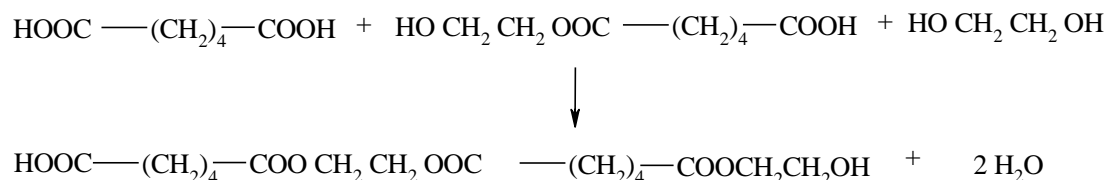


Another example can be taken of is poly condensation of ethylene glycol (EG) and adipic acid.



Apart from non-reactive ester group, this product also contains two reactive groups at the ends.

This can further react with another molecule of E.G. and adipic acid as follows :



The resultant molecules contains reactive group at the ends and hence if more quantities of E.G. and adipic acid are made available, it is capable of reacting further.

The following conclusions from the study of poly condensation are drawn:

- i. Monomer should have two reactive functional groups for polymerization to proceed.
- ii. Polymerization proceeds by step-wise reaction between reactive functional groups.
- iii. Only one type of reaction (i.e. condensation) is involved.
- iv. Polymer formed still contains both the reactive functional groups at its chain ends.

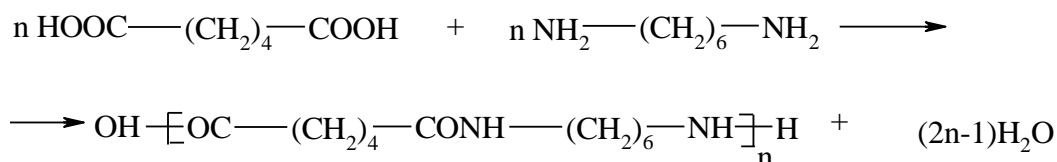
Chain growth may occur by interaction of either a monomer with polymer molecular or of polymer molecule with one another.

A poly condensation involving molecules of one species is called Homopolymerization.

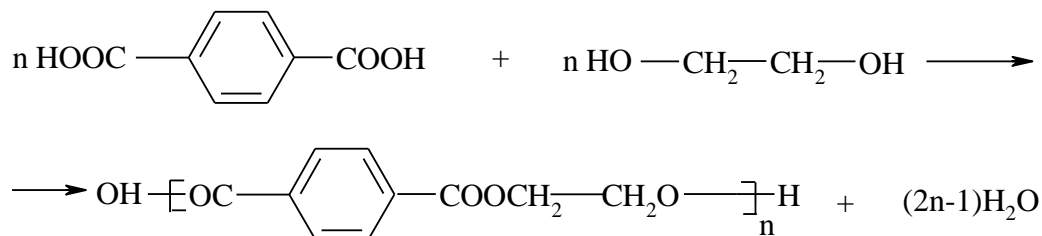
Example is poly condensation of amino acids.

A poly condensation involving different species of molecules is termed as co-poly condensation.

An example is the poly condensation of adipic acid with hexamethylene diamine to form poly hexamethylene diamide.



and the poly condensation of terephthalic acid with ethylene glycol, resulting in poly (ethylene terephthalate).



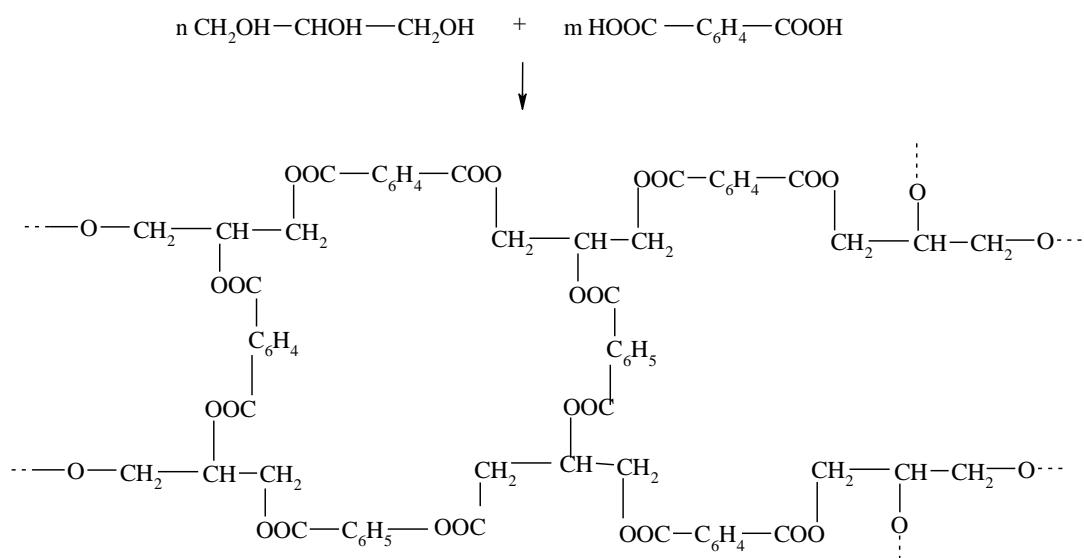
If the reactants are taken in an equimolecular ratio, co-poly condensation proceeds similarly to homo poly condensation.

If the reactants are taken in an equimolecular ratio. co - poly condensation proceeds similarly to homo - polymerization.

Poly condensation of bi functional compounds gives linear polymers.

Poly condensation of compounds having functionality higher than two results in polymers of branched and three-dimensional structure, the number of functional group of the macromolecule increasing as the reaction progress.

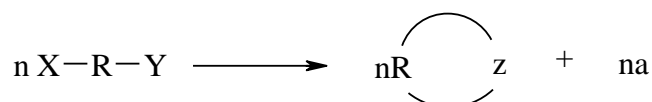
This process may be illustrated by the poly condensation of glycerol and phthalic acid.



### Reaction route of poly functional compounds:

If a molecule contains two or more functional groups, the reaction may proceed inter molecularly or intra molecularly (as shown below).

Intra molecular reaction gives rings formation.



Ring formation and linear poly condensation are competing reactions, and the yields of the cyclic monomer dimer, trimer or polymer depends on the ratio between the rates of these reactions.

⇒ **EFFECTS :**

### 1. Effect of Monomer Concentration on Direction of Reaction :

Decreasing the monomer concentration in the reaction medium lowers the probability of intermolecular interaction, but leaves the probability of intra molecular reaction unchanged.

The time  $t_1$  during which some part  $x$  of the total amount  $a$  of the initial substance reacts intramolecularly can be determined from the kinetic equation of a first order reaction.

$$t_1 = \frac{1}{K_1} \ln \frac{a}{a-x}$$

and is independent of the concentration of the substance.

The time  $t_2$  during which the same part of the initial substance reacts intermolecularly is determined by the kinetic equation of a second order reaction.

$$t_2 = \frac{1}{K_2} \frac{x}{a(a-x)}$$

i.e.,  $t_2$  is inversely proportional to the initial concentration of the substance.

Thus, decreasing the concentration of the initial substance promotes ring formation.

### 2. Effect of temperature on Reaction Routes :

- The second factor determining the rate of reaction is the temperature, which is related to the reaction rate constant by the Arrhenius equation :

$$K = Ae^{-E/RT}$$

- The ratio of reaction rate constants of poly condensation  $K_p$  and cyclization  $K_c$  determines the ratio of yields of poly condensation product and cyclic monomer at constant temperature  $T_i$  :

$$L_1 = \frac{K'_p}{K'_e} = \frac{A'_p}{A'_e} e^{\frac{E_c - E_T}{RT}} = \frac{A_p}{A_e} e^{\frac{\Delta E}{RT}}$$

If the temperature is raised to  $T_2$ , the yield ratio of the cyclic monomer and the polymer will be determined by the following equation:

$$\frac{L_1}{L_2} = \frac{A'_p A''_e}{A'_e A''_p} e^{\frac{E_c - E_T}{RT} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

Since the pre-exponential factor A is independent of the temperature to the first approximation,

$$\frac{L_1}{L_2} = e^{\frac{E_c - E_p}{RT} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

If the activation energy of both, reactions are equal ( $E_c = E_p$ ),  $\frac{L_1}{L_2} = 1$  and the temperature does not affect the direction of the reaction.

But if  $E_c > E_p$  the ratio  $L_1/L_2$  becomes greater than unity with increasing temperature and the (yields of the cyclic) monomer with rising temperature.

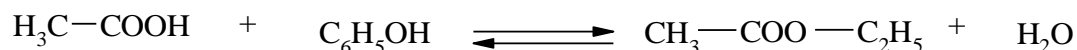
Hence the effect of the temperature on the route of the reaction depends on the differences of activation energies of the cyclization and poly condensation reactions, and greater is this difference, the greater will be the effect.

### KINETICS:

It may be thought that in condensation reactions the molecular mass of polymer should grow indefinitely and in the limiting case all the monomer should turn into a single joint molecule i.e. macromolecule.

Actually polymers obtained in this way have a limited molecular mass. This is due to the fact that, like all condensation reactions poly condensation is an equilibrium reaction.

Consider, by way of a simple example, the formation of ethyl acetate.



If water is not removed from the system, the reaction will not go to completion but will stop as soon as the concentration of the reactants reaches a certain value depending on the equilibrium constant.

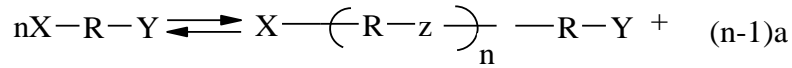
$$K = \frac{C_{\text{CH}_3\text{COOC}_2\text{H}_5} \cdot C_{\text{H}_2\text{O}}}{C_{\text{CH}_3\text{COOH}} \cdot C_{\text{C}_2\text{H}_5\text{OH}}}$$

- The quantity K, characteristic of a given reaction, determines the final state of the system.
- The equilibrium constant differs for different reacting functional groups, but is independent of the species of radical.
- Shifting the equilibrium by removing the condensation by product say from the sphere of reaction will promote the formation of a polymer with a higher molecular mass.
- Assuming that the equilibrium constants K are invariable at all stages of the poly condensation reaction, one can find the dependence between the maximum degree of

polymerization P, the equilibrium constant K, and the number of molecules of the by – product involved.

- Since the total number of reacting groups remains invariable in the course of the reaction, the concentrations of these groups can be replaced by their number.
- We can use the following notations.

Reaction:



No: number of the initial bi-functional compound, equal to the number of X groups and the number of Y groups.

N: number of macromolecules, equal to the number of X groups and the number of Y groups at the end of the reaction.

Na : number of molecules of the by product at equilibrium.

Nz: No –N<sub>v</sub> number of Z bond formed.

If all the bonds in the poly- condensation product are equivalent and the equilibrium constant during this formation is invariable.

$$K = \frac{n_2 \cdot na}{n_1 \cdot n_1} = \frac{n_3 \cdot na}{n_1 \cdot n_2} = \dots = \frac{n_n \cdot na}{n_{n-1} \cdot n} \dots \dots \dots (1)$$

Where,

n<sub>1</sub> = mole fraction of the monomer

n<sub>2</sub>, n<sub>3</sub> ----- n<sub>n</sub> = mole fractions of their dimmer, trimer etc., up to n-mer.

Than,

$$K = \frac{(N_0 - N)Na}{N^2} \dots \dots \dots (2)$$

Dividing the numerator and denominator of the right side of the above equation by No, we get :

$$K = \frac{\left(\frac{N_0 - N}{N_0}\right) \frac{Na}{N_0}}{\left(\frac{N}{N_0}\right)^2} \dots \dots \dots (3)$$

Here,

$$\frac{N_a - N}{N_0} = n_z = \text{mole fraction of bonds per monomeric unit of the polymer}$$

$$\frac{N}{N_0} = n_a = \text{number of moles of by product liberated per monomeric unit of the polymer}$$

$$\frac{N_o}{N} = \bar{P} = \text{average degree of polymerization of the resulting polymer.}$$

Substituting these values into Equation (3) we obtain:

$$K = \frac{n_z \cdot n_a}{\left(\frac{1}{P}\right)^2} \text{-----(4)}$$

Transforming the above equation we get :

$$\bar{P} = \sqrt{\frac{K}{n_a}} \cdot \frac{1}{\sqrt{n_z}} \text{-----(5)}$$

If the molecular mass of the poly condensation product is sufficiently large, the value of  $N_z$  approaches unity, because.

$$n_z = \frac{N_z}{N_0} = \frac{N_0 - N}{N_0} = 1 - \frac{N}{N_0}, \quad \frac{N}{N_0} \text{ being very small}$$

Equating  $\sqrt{n_z} = 1$  we, get the approximate expression of the dependence of the average degree of polymerization on the equilibrium constant and the constant of the by product liberated during the reaction.

$$\bar{P} = \sqrt{\frac{K}{n_a}}$$

“The degree of polymerization of a poly condensation product is directly proportional to the square root of the equilibrium constant and inversely proportional to the square root of the molar fraction of the by-product liberated during the reaction.

⇒ **Effect of Monomer concentration on Rate of poly condensation and molecular mass of polymer.**

- The equilibrium constant is independent of the monomer concentration because dilution changes the concentration of all the components participating in the reaction proportionally,.

- When the reaction is conducted to equilibrium, the molecular mass of polymer is also independent of the monomer concentration. But the rate of poly condensation is proportional to the concentration of the reactants.
- Increasing monomer concentration reduces the time needed to reach equilibrium and obtain a polymer with maximum mass.

⇒ **Effect of temperature on Rate of poly condensation and molecular mass of polymer.**

The rate of poly condensation increases with temperature.

The heat effect of the reaction by isochore (isobar) equation :

$$\ln \frac{K_1}{K_2} = -\frac{Q}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

⇒ It follows from the equation that with rising temperature the equilibrium constant increases in endothermal reactions and decreases in exothermal reactions. The maximum mol. Mass of polymer varies in accordance with the value of the equilibrium constant.

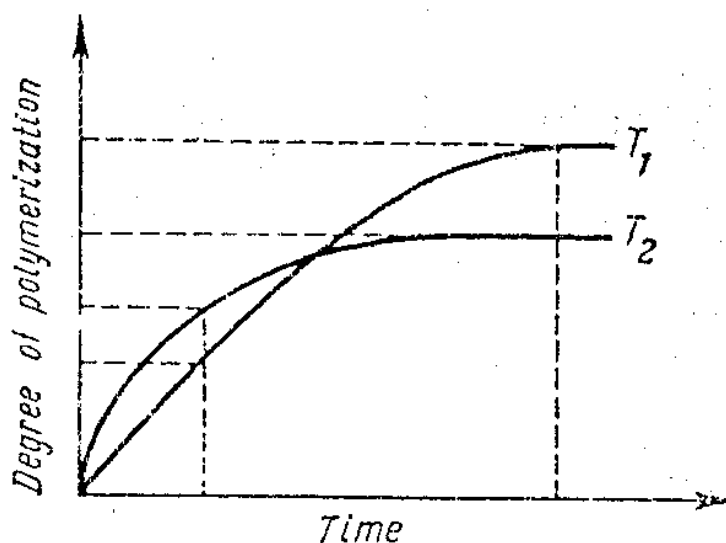


Fig. Dependence of the degree of polymerization of a poly condensation product on the temperature ( $T_2 > T_1$ ).

Increasing the temperature often facilitates removal of the by product, which shifts the equilibrium and results in the formation of higher – molecular mass polymers.

### **POLYMER DEGRADATION :**

**Definition :** Degradation reactions are reactions involving breakage of bonds in the main molecular chain and resulting in a decrease in molecular mass of polymer without altering its chemical composition. (End group May be neglected).



- Degradation is a very important reaction the chemistry of high molecular mass compounds. It is used for determining the structure of polymeric compounds, and for obtaining valuable low – molecular mass substances from natural polymers e.g. glucose from cellulose and starch.
- The splitting of polymeric macromolecular to form free macro radicals is employed for synthesizing modified polymers.
- Degradation of polymers may occur under the action of chemical agents (water acids, alcohols, oxygen etc) or as a result of physical influences (low, light, high energy radiation etc.).
- Chemical degradation is the most characteristic type in the case of hetero chain polymers and involves selective rupture of the carbon – hetero atom bond; the ultimate product of chemical degradation is the monomer.
- Chemical degradation of carbon chain polymers is possible only under very vigorous conditions.
- Degradation of polymers by physical influences is usually non – selective, because the energy characteristics of all chemical bonds are quite close.

⇒ **Methods of Determining Extent of Degradation :**

- These methods are based on determining the number average or the mass –average molecular mass of polymers. The kinetic investigations of polymer degradation one determines the change in number –average molecular mass per unit time because the change in number of particles (molecules) on degradation of the polymer is proportional to the number of bonds ruptured, and is independent of the initial molecular mass of the polymer.
- The number of bonds ruptures can be established directly by the number of functional groups formed on degradation, i.e. by determining the molecular mass.

Other methods of determining the number average molecular mass may also be used.

**Types of Degradation :**

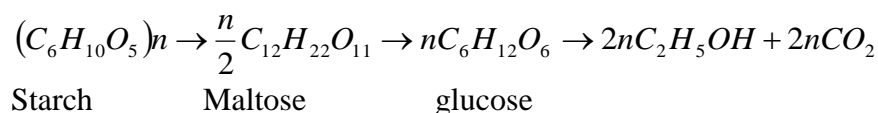
**1. Chemical Degradation:** Chemical degradation proceeds under the action of polar substances such as water, acids, amines, alcohols or oxygen.

**Hydrolysis and Alcoholysis:** Hydrolysis is the most common type of chemical degradation of polymers . Cleavage of a chemical bond with addition of a water molecule.

Hydrolysis is catalyzed by hydrogen or hydroxyl ions. Hydrolysis of a polymer depends on the nature of the functional groups and bonds it is composed. The end group of the newly formed molecules do not differ in nature from those of the initial polymer.

Of great practical importance is the hydrolysis of natural polyacetals poly saccharides.

Complete hydrolysis of starch and cellulose gives glucose.



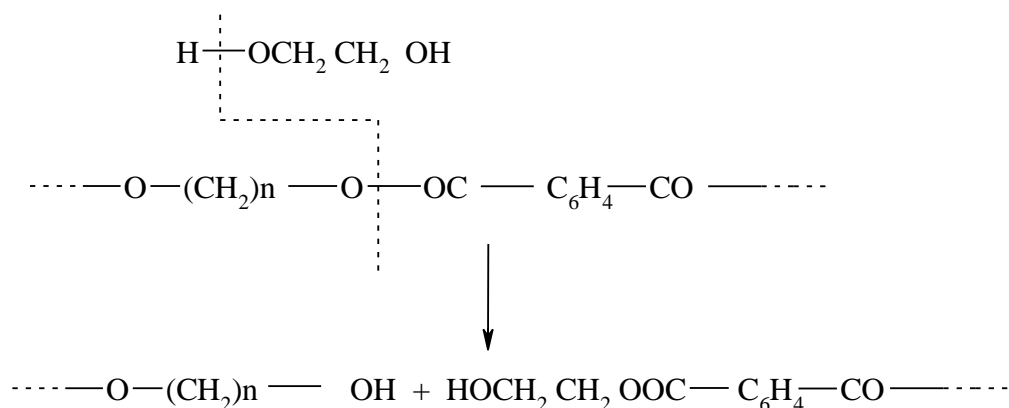
In recent years cellulose containing waste of plant materials are used instead of foodstuff for making alcohol.

Polyester also hydrolyze in the presence of acids and alkalis, hydrolytic cleavages of the ester bond results in alcoholic and acidic end groups.

Poly (ethylene terephthalate) is synthesized from ethers of the acid rather than from the free acid.

Hence, it is more expedient to split up the waste by alcoholysis ( glycoholysis) than by hydrolysis.

Thus, treatment of the PET with boiling ethylene glycol results in a diglycolic ester of terephthalic acid.

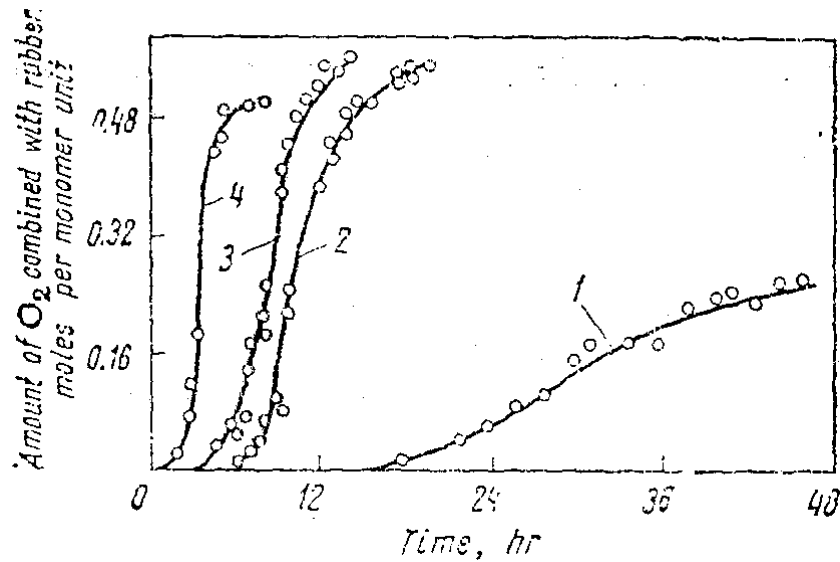


## 2. Oxidative Degradation :

- Though oxidative degradation is a chemical cleavage process, it proceeds much less selectively than other types of chemical degradation.
- Oxidative degradation is characteristics not only of heterochains but, also of homochains polymers.
- The oxidation of paraffin hydrocarbon involving opening of a bond between carbon atoms and the formation of oxygen containing compounds ( acids, aldehydes and alcohols) with a smaller number of carbon atoms.
- This process is used for the commercial production of higher fatty acids.

- The rate of oxidative degradation of polymers increases considerably in the presence of substances which break down readily into free radicals, and also in the presence of in significance quantities of metals of variable valence, such as Fe, Cu, Mn and Ni.

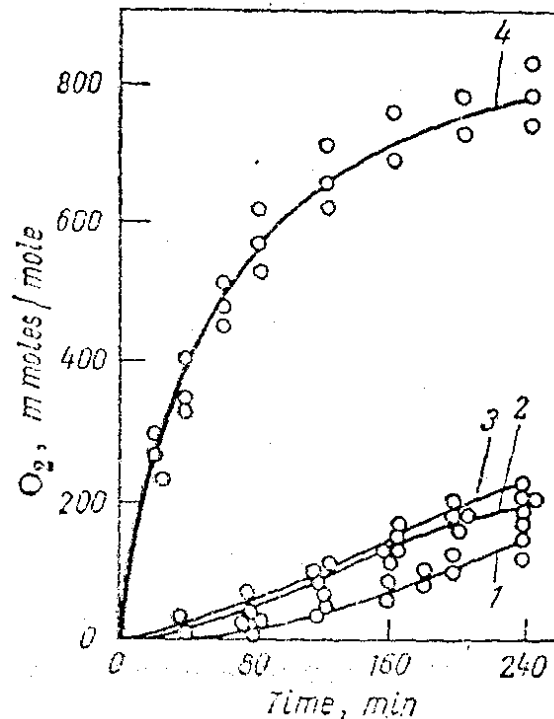
Thus, the presence of iron stearate considerably increases the rate of oxidation of natural number (figure. A) .



(Fig. a) Effect of iron stearate on rate of oxidation of refined natural rubber at 120 °C.

1. without catalyst
2. 0.5 percent iron stearate
3. 1 % iron stearate
4. 1.5 % iron stearate.

- In the presence of inhibitors of free- radical chain processes the rate of oxidation and degradation of polymer increases considerably.  
After the inhibitor is used up, the oxidation proceeds at almost the same rate as without the inhibitor.
- The effect of the chemical structure of a polymer on its resistance to oxidative degradation is already fairly clear.
- In the H/C series this dependence can be observed by competing the rate of oxidative degradation of poly ethylene and poly propylene (figure – b).



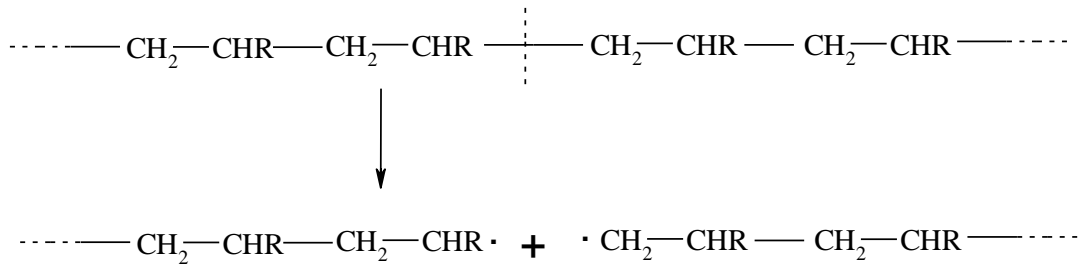
(Figure-B). Absorption of oxygen by various poly olefins at 150 °C (initial O<sub>2</sub> press 600 mm<sub>hg</sub> fig.).

1. High pressure polyethylene (PE)
2. Low pressure PE
3. Ethylene propylene copolymer
4. Polypropylene

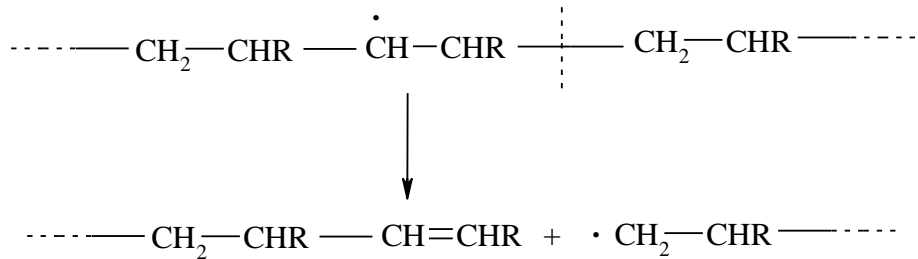
The presence of tertiary carbon atom in polypropylene sharply lowers its resistance to oxidative degradation.

### 3. Degradation by Physical Influences :

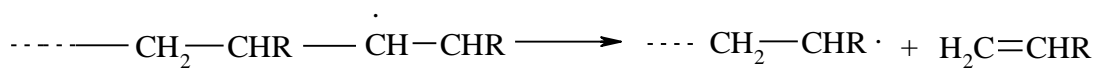
- The degradation of polymers under the action of luminous energy high energy radiation, and mechanical or thermal energy proceeds according to a chain mechanism with the intermediate formation of free radicals.
- The rate of individual steps of the chains process vary depending on the kind of energy used , involving a change in structure of the polymer can either ( 1 ) be completely depressed or ( 2 ) made predominant.
- In the first case the reaction results in a decreased in molecular mass of polymer, in the latter ease, all its physicochemical and mechanical properties are changed.
- The first step / stage of the chain process which develops in the polymer under the action of some kind of energy is the appearance of free radicals.



- Conversion of macromolecule to macro radical may result in rupture of an adjacent carbon carbon bond with the formation of a new free radical.

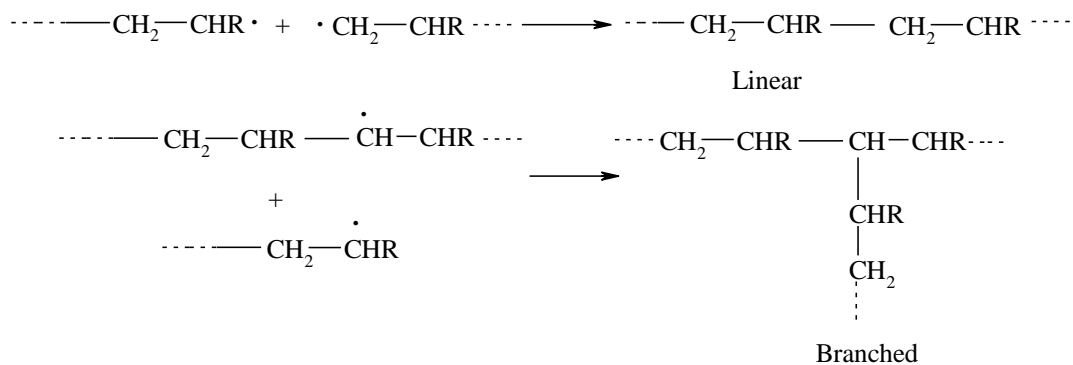


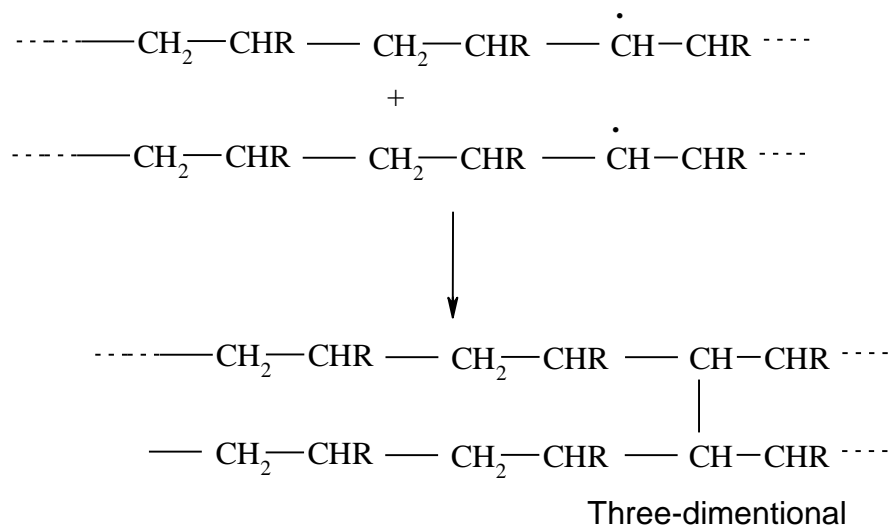
- Transfer of the unpaired electron (chain propagation) may also occur intramolecularly with elimination of a monomer molecule.



- At chain termination step the reaction may be accompanied by a change in structure of polymer.

This may involve combination of the radicals to form linear, branched, and three dimensional polymers.





⇒ **Photo chemical Degradation :**

- Reaction occurring upon irradiation of polymers play an important part in ageing processes , and often determine the life time of natural and synthetic fibers, rubber goods etc.
- The chief process causing the change in properties of the polymer is in most cases the photo chemical chain reaction of scission of its molecular chain, activated by atmospheric oxygen.

The intensity of processes occurring depends on the wave length and intensity of irradiation, the presence of initiators, and the nature of polymer.

e.g. At an elevated temperature (150 °C) U.V. light causes depolymerization (photolysis) of rubber with the liberation of isoprene. The rate increases sharply in the presence of atmospheric oxygen.

- Light weathering decomposes polyethylene in 2 or 3 years, whereas in the dark at ordinary temperature it does not decomposes at all in the same period of time.
- The addition of carbon black to rubbers and polyethylene increases their resistance to ageing.
- Light of wavelength less than 2 to 4 comes only photo degradation in cellulose, but light of a greater wavelength causes oxidative degradation and hydrolysis as well as photodegradation.
- Cellulose ester and polyamides are also degraded by U.V. light.
- Stabilization of polymers to photo chemical degradation is based on addition to the polymer of compounds like benzophenone and its derivative, which readily absorb luminous energy and transform it so that it is radiated by than in quanta of lower energy which are harmless to the polymer.

### Action of High Energy Radiations :

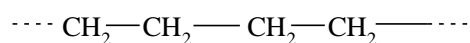
Under the influence of ionizing radiations polymer undergo profound chemical and structural changes affecting all its physiochemical and mechanical properties as well.

Irradiated PE possesses very high resistance to heat and chemical agents, as well as other valuable properties.

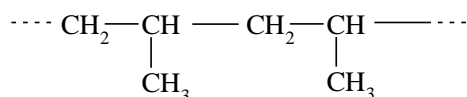
Irradiation of polymers is accompanied by the formation of double bonds. Degradation and formation of 3-dimensional structures always occurs simultaneously when polymers are irradiated, but some polymers are completely degraded by high energy radiations, while in other cross linking of macromolecules predominates.

Example of polymers that are cross linked and degraded on irradiation are given below :

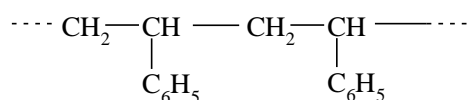
#### Polymers that form 3-dimensioned Structure



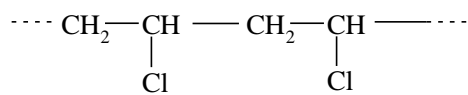
Polyethylene



Polypropylene

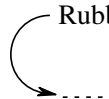


Polystyrene

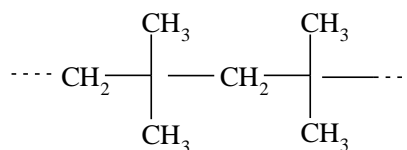


Poly(vinylchloride)

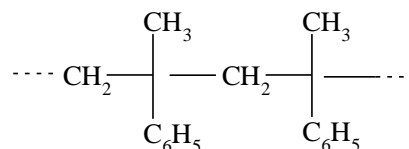
Rubber Polyamides etc



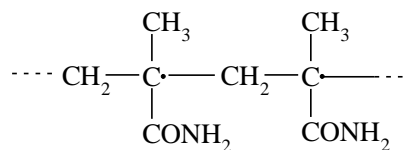
#### Polymer that undergo degradations



Polyisobutane



Poly- $\alpha$ -methylstyrene



Polymethacrylamide

- Fluorine containing polymers
- Cellulose
- Cellulose ester

### Thermal degradation:

- The stability of polymers to heating, the rate of their thermal decomposition, and the natures of the resulting products depend on their chemical structure of the polymer.
- Like any other chain reaction, thermal degradation is accelerated by substances which decompose readily into free radicals, and is slowed down in the presence of substances which are free radical acceptors.

- Besides lowering the average molecular mass and changing the structure of the polymer, thermal degradation causes elimination of monomer depolymerization.

The monomer yields depends on the kind of polymer and on the conditions of its synthesis and thermal splitting.

e.g. When polystyrene is depolymerized at approximately 300 °C., the monomer yields is 60-65 %. Under the same conditions poly(methyl methacrylate) depolymerises to an extent of 90 – 95 % whereas heating poly ( methyl acrylate) gives a very small yield of monomers.

## • **TECHNIQUES / METHODS OF POLYMERISATION :**

Generally polymerizations are studied and practiced by four different techniques.

### **1. Bulk Polymerization : (Mass polymerization)**

This is the homogeneous types of polymerization. But this term is used for only to the initial reaction conditions and not to the subsequent conditions.

In this types, only the monomer, with or without an initiators, is taken in a batch reactor, which may be a glass-lined, mild steel or S.S. jacketed reaction kettle (or an autoclave) with the facility to mechanically agitate the content.

A typical charge will include a monomer, an initiator and a chain transfer agent.

The entire batch is in a single phase. An example of this type of polymerization is that of styrene to polystyrene.

Polymerization is carried out while water is circulated through the jacket to maintain the reaction temperature. But most of the polymerization reactions being exothermic.

Efficient stirring is must for mass polymerization because the reaction mass is essential to maintain uniform quality of the product. For very viscous reaction mass an anchor type stirrer is used.

### **Advantages :**

1. This method gives the purest possible product
2. No subsequent separation purification & recovery steps are involved.
3. It gives the largest possible yields per reactor volume.



**Disadvantages :**

1. Heat removal problem for exothermal reaction is acute.
2. As reaction goes on agitation becomes progressively more and more difficult.
3. Non-uniformity of the reaction leads to broader distribution of products molecular weight.
4. Gases and volatiles may easily get entrapped in the very viscous mass.
5. Removal of last traces of un reacted monomer becomes extremely difficult.

**2. Solution Polymerization :**

In this process monomer is dissolved in a non – reactive solvent and catalyzed. Heat is controlled by dilution, the reaction rate is slowed.

Solution polymerization is useful when the polymer can be utilized in solution.

Mol. Wt. of the polymers ranges from low to medium.

The solvent reduces the viscosity gain with conversion, allows more efficient agitation or stirring of the medium, thus effecting better heat transfer and heat dissipation.

Solution polymerization may be carried out in batch or continuous process.

**Advantages:**

1. Heat removal is easier
2. Tracking the reaction is easy. Hence design of reactor becomes easy through known kinetics.
3. Readymade polymer solution is directly available. This is useful in application as lacquers and adhesives.

**Disadvantages:**

1. Use of solvent lower monomer concentration, hence the rate of polymerization.
2. Solvents involved bring in toxicity, flammability and higher cost.
3. Recovery of used solvent requires additional technology and increases the cost of production.
4. Yields per reactor volume are less then bulk polymerization.

#### **4. Emulsion Polymerization :**

This type of polymerization is very much suited to addition reaction system.

In this process, besides the main two components viz. the dispersed medium and the dispersion mechanism, several other components are added for specific reasons.

Dispersion medium may be any solvents, but most often water is there, where the dispersed medium is monomeric substances to be polymerized.

Size of dispersion droplets are about  $1 \mu (10^4 \text{ \AA})$

These droplets are stabilized by emulsifying agents so that stable emulsion forms.

Emulsifying agents which are soap like materials, include common soaps or salts of carboxylic and sulphonic acid etc.

They may include ( 1 ) surface tension regulators added in the concentration of 0.5 % (e.g. aliphatic alcohols) ( 2 ) Protective colloids such as polyvinyl alcohol, carboxymethyl (cellulose etc to prevent precipitation of monomer or polymer emulsion.

##### **Advantages:**

1. The reaction is easy to control because of efficient heat dissipation.
2. High rate of polymerization and high average chain length are possible.
3. The latex products are often directly usable
4. Process can be continuous.

##### **Disadvantages:**

1. The large surface area of the tiny particles of polymers provides plenty of room for impurities to be adsorbed.
2. The product obtained is less pure because of the several additives.
3. Considerable technology is needed to recover the solid polymer.
4. Use of large quantities of water lowers the yields per reactor volume.

#### **5. Suspension Polymerization :**

This process was developed to overcome some of the disadvantages of emulsion process, in particular the tendency to adsorb impurities due to the large surface area.

Here the average particle size of the suspended phase is between 1 and 10 microns initially.

Unlike an emulsion, a physical suspension of polymerizing drops or beads coalesce rapidly upon stopping the agitation.

The agents added are an initiator and a suspension stabilizer. Water or inert organic solvents can be used provided the monomer and the polymer are insoluble in it.

Each bead or pearl of the monomer acts as a minute, discrete mass polymerization system.

A protective colloid is also added to increase the viscosity of the continuous phase. It has to be inert. The insoluble protective colloid such as  $\text{MgCO}_3$ , collects at the droplet-water interface by surface tension and prevents coalescence of droplet upon collision.

E.g. PMMA ( poly methyl methacrylate) is manufactured by this process.

**Advantages:**

1. Heat is easily removed and controlled.
2. The polymer is obtained in small, granular form which is convenient and easily handled.

**Disadvantages:**

1. Yield per reactor volume is low.
2. It gives a polymer less pure than can be obtained by the mass polymerization process.
3. Process can not be run in a continuous manner.