

# Polymer and Composites

- ❖ Introduction, definition, degree of polymerization ( $D_p$ ), concept of molecular weight (number average, weight average & numerical based on them), glass transition temperature.
  - ❖ Classification of polymers: polymerization mechanism: (step and chain polymers)
  - ❖ Polymerization Reaction: addition and condensation,.
  - ❖ Thermal behavior: Thermoplastic and thermosetting,
  - ❖ types of monomers: linear, branched and cross-linked polymers, homo and copolymers.
- Commercial Polymers: synthesis, properties and application, polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), m phenol Formaldehyde (PF), epoxy resin.
- Specialty polymers: basic concept applications of conductive polymers, biodegradable polymers, recycling of polymers
- Composites: classification, fiber and particle reinforced composites.



## Types of materials



Metals / Alloys



Ceramics



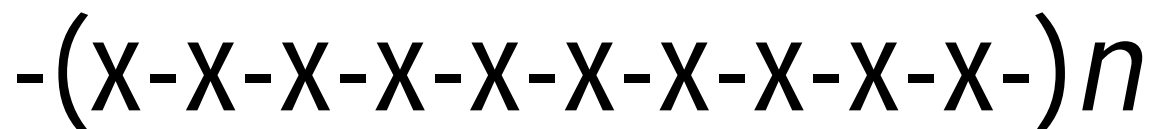
Polymers

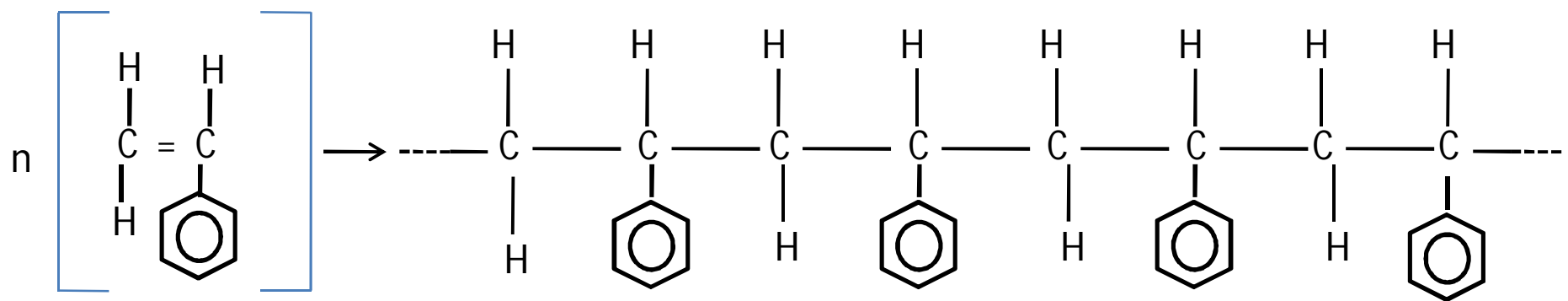
## Introduction

**Polymer**  $\longrightarrow$  **Poly + meros**

Defined as high molecular weight compounds formed by combination of large number of one or more types of molecules of low molecular weight

Polymers are giant molecules of high molecular weight called as macromolecules which are built up by linking together large number of small molecules called as monomers and the reaction by which the monomers combine to form polymers is called as polymerization.





Styrene

Poly styrene (PS)

## Natural Polymers

Cellulose (Present in wood)

Polyphosphates (Present in bones)

DNA

Rubber

## Synthetic Polymers

Polyethylene

Polypropylene

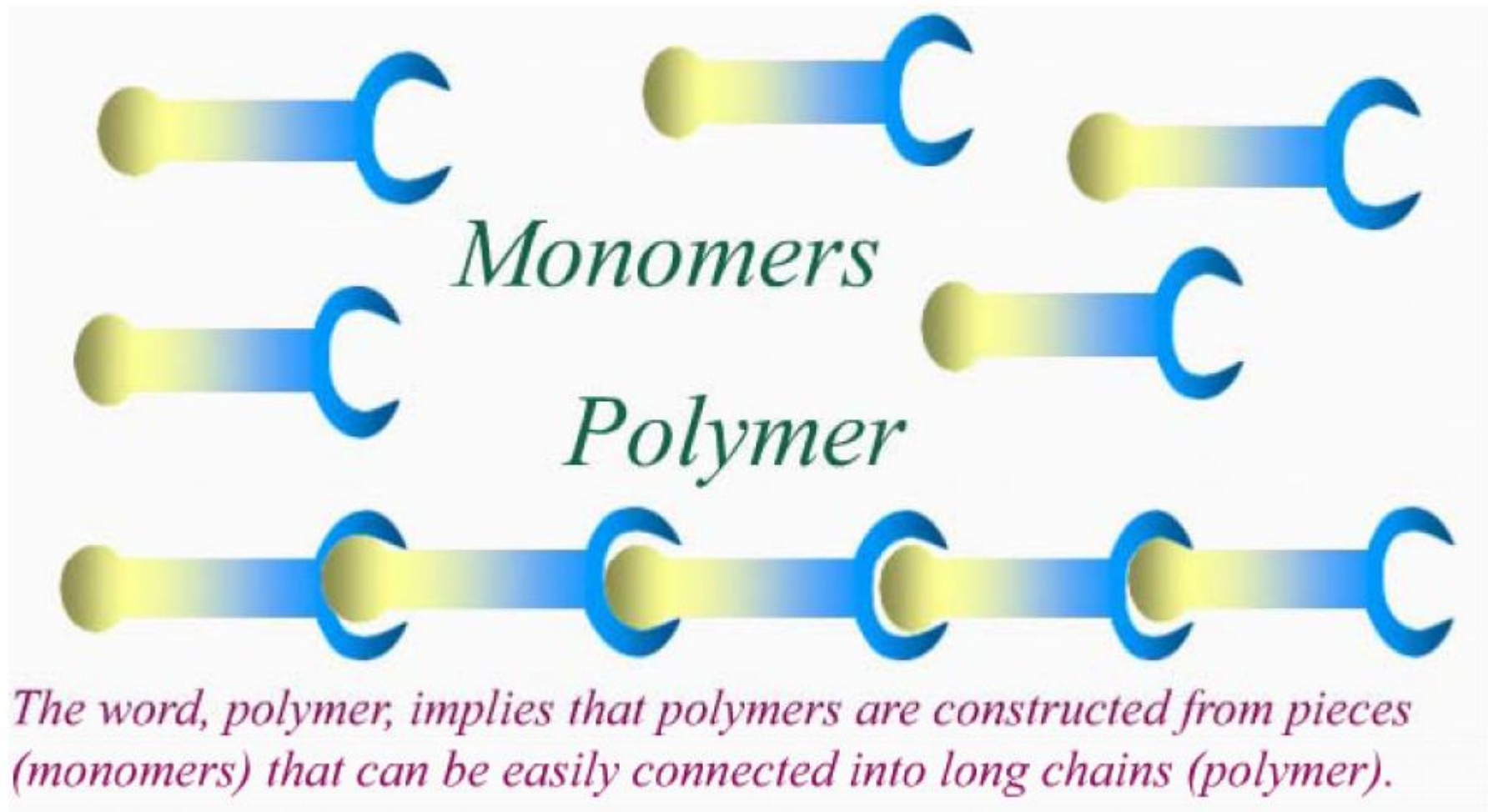
Nylon

Polyesters , PVC

# Polymers

- The earliest synthetic polymer was developed in 1906, called Bakelite.
- The development of modern plastics started in 1920s using raw material extracted from coal and petroleum products (Ethylene). Ethylene is called a building block.
- Polymers are long-chain molecules and are formed by polymerization process, linking and cross linking a particular building block (**monomer**, a unit cell).
- The term polymer means many units repeated many times in a chain-like structure.
- Most monomers are organic materials, atoms are joined in covalent bonds (electron-sharing) with other atoms such as oxygen, nitrogen, hydrogen, sulfur, chlorine,....

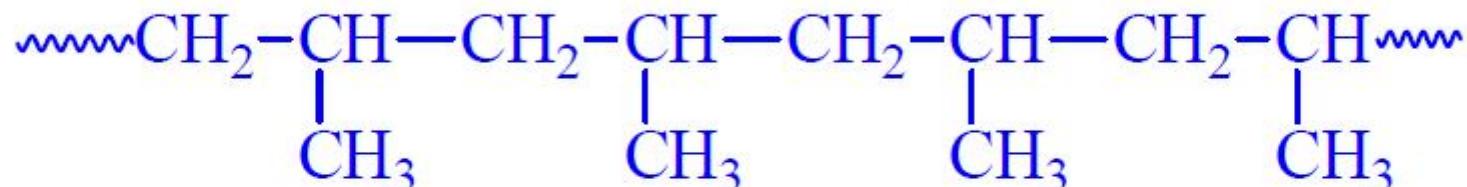
# Monomer to Polymer



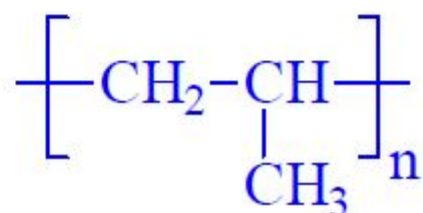


**Structure units** are connected to one another in the polymer molecule, or polymeric structure, by covalent bonds.

**Repeat unit:** The atoms that make up the backbone of a polymer chain come in a regular order, and this order repeats itself all along the length of the polymer chain. For example, look at polypropylene :

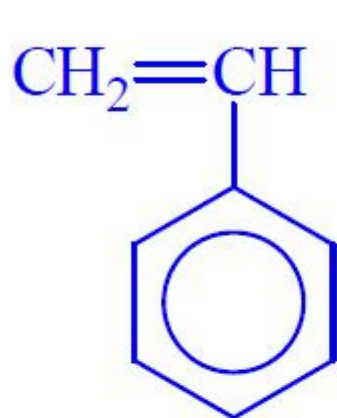


Its backbone chain is made up of just two carbon atoms repeated over and over again. One carbon atom has two hydrogen atoms attached to it, and the other carbon atom has one hydrogen atom and one pendant methyl group ( $\text{CH}_3$ ). This is called the *repeat structure* or the *repeat unit*. To make things simple, we usually only draw one unit of the repeat structure, like this:

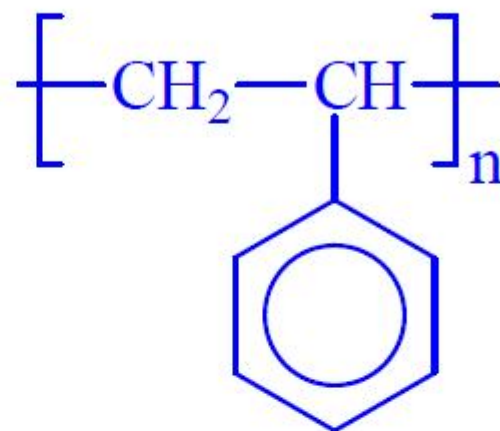




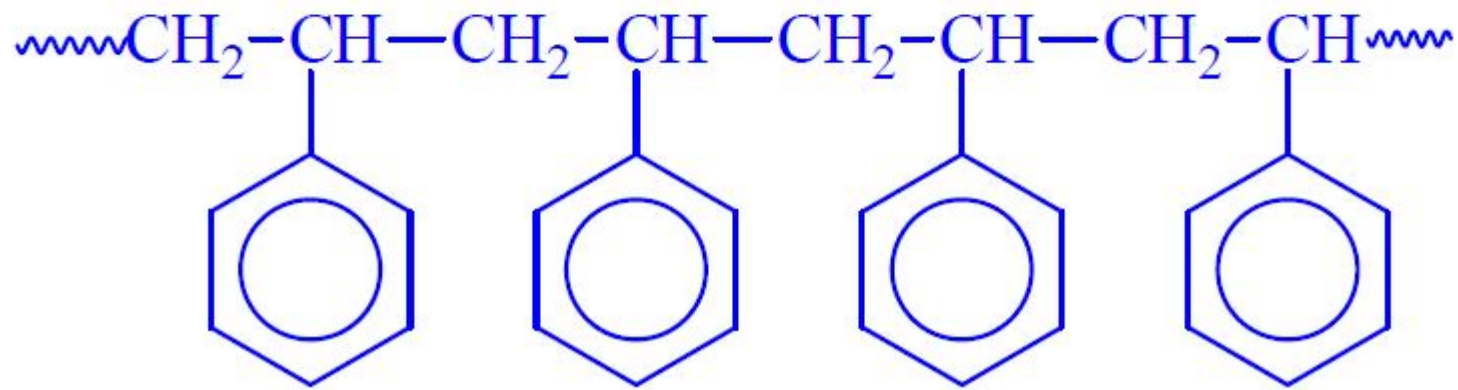
Another **example**: styrene monomers join together to make polystyrene:



Styrene monomer



Polystyrene repeat unit



## Degree of Polymerization

The number of repeating units ( $n$ ) in the polymer chain is known as the degree of polymerization.

Degree of polymerization is related to the molecular weight of the polymer  $[M]$  by the relation

$$D_p = \frac{M}{m} \quad \text{or} \quad D_p \times m = M$$

*Where  $m$  is the molecular weight of the monomer*

*$M$  is the molecular weight of the Polymer*

*$D_p$  is the degree of polymerization*

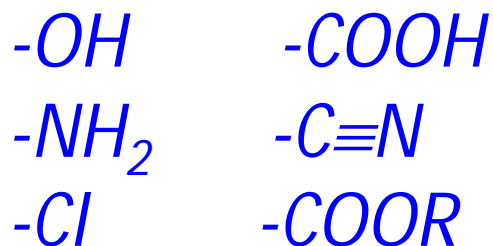
Most of the polymers have molecular weights ranging from 5000-200000

# Functionality of the polymer

## *Reactive Positions in a monomer*

- ❖ These reactive positions are useful for joining large number of monomers to form a polymer.
- ❖ Easily reacting positions present in the form of functional groups or in the form of  $C=C$

*Functional groups present in monomer organic molecules are*

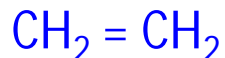


# Functionality of the polymer

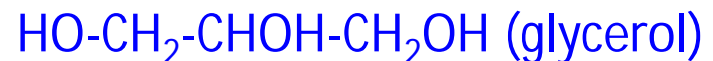
❖ The number of active bonding sites or the number of reactive positions in a monomer is referred to as its functionality.

- ✓ Monomers having 2 reactive positions are called as bifunctional
- ✓ Monomers having 3 reactive positions are called as trifunctional
- ✓ Monomers having 4 reactive positions are called as tetrafunctional

Examples of bifunctional monomers

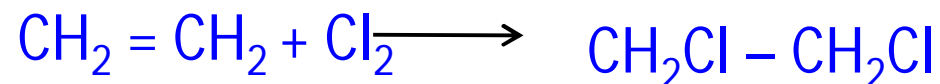
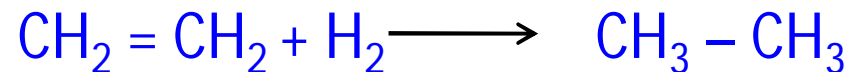


Examples of trifunctional monomers

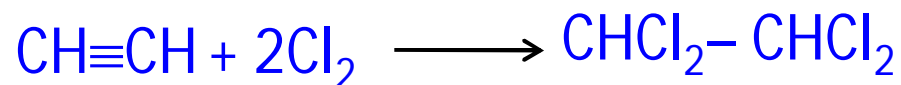
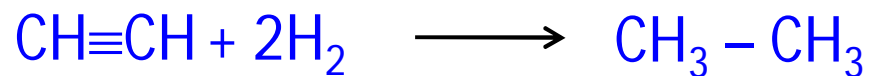


Examples of tetrafunctional monomers





Bifunctional (because Reacting with 2 hydrogen atoms or halogen atoms)



Tetrafunctional (because Reacting with 4 hydrogen atoms or halogen atoms)

## Nomenclature of monomers

- ❖ A polymer may consist of monomer of identical or different chemical structures. They are known as **homopolymers** and **copolymers** respectively.
- ❖ Copolymerization is the combined polymerization of 2 or more monomer species.

**Homopolymer**- only one monomer  
(repeating unit)



**Copolymer** – more than one monomer



Random copolymer: The monomer units are randomly distributed along the polymer chain.

..-A-B-B-A-A-A-A-B-A-A-B-B-B-B-B-A-B... (RANDOM SEQUENCE)

Examples: commercial polymer such as butadiene and styrene, butadiene and acrylonitrile.

Alternate copolymer: The monomer units are arranged in an regular alternating manner.

...-A-B-A-B-A-B-A-B-A-B-A-B..

Examples: Polyesters, polyamides, styrene-acrylonitrile..

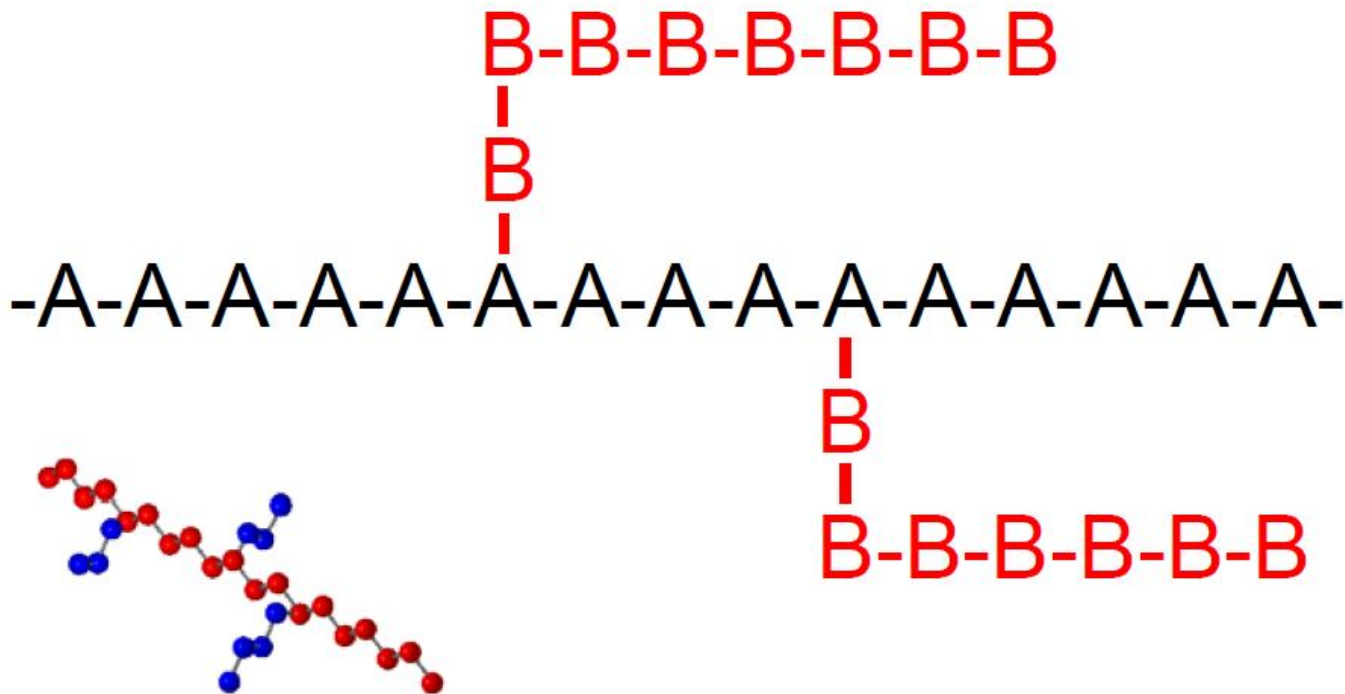
Block copolymer: In this a block of repeating unit of one monomer is followed by a block of repeating unit of another monomer.

..-A-A-A-A-B-B-B-B-A-A-A-A-B-B-B-B-A-A-A-A..

Graft copolymer: The polymer is formed by one type of repeating unit of monomer is grafted on a chain of monomer units of another types acting as backbone of the polymer.

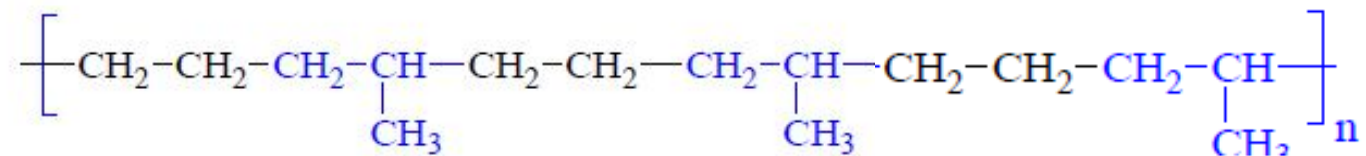
## ■ Graft

Poly(styrene)-*graft*-poly(butadiene)

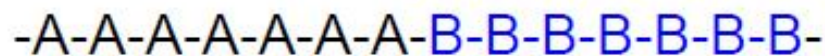
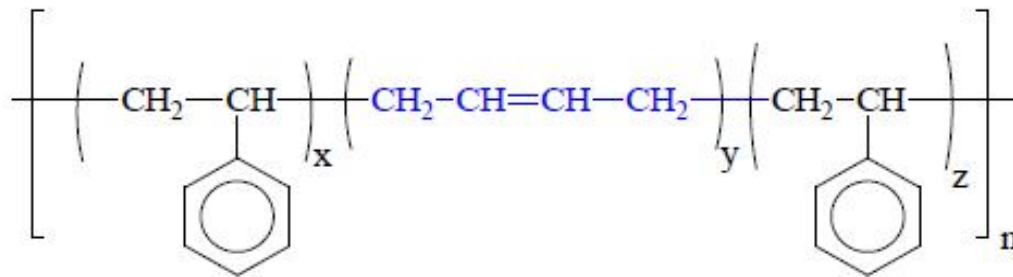


# Copolymers

- Alternating and random



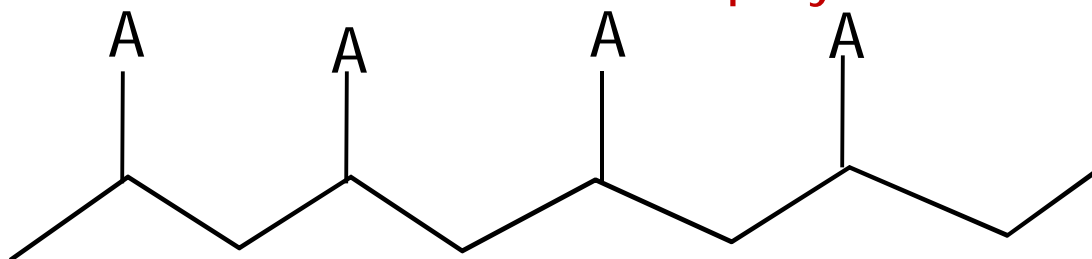
Block



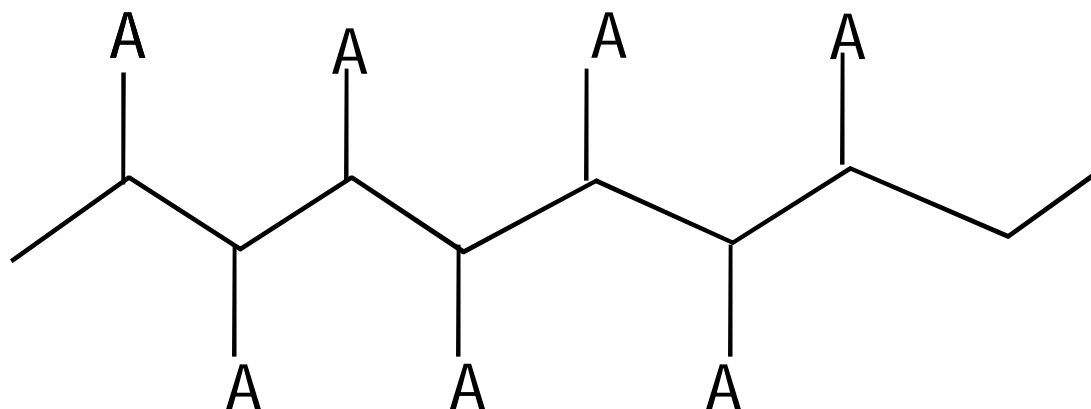
## Tacticity (stereoisomerism) of polymers

The orientation of the monomeric units in a polymer molecule w.r.t. to main chain is called as the tacticity of the polymer.

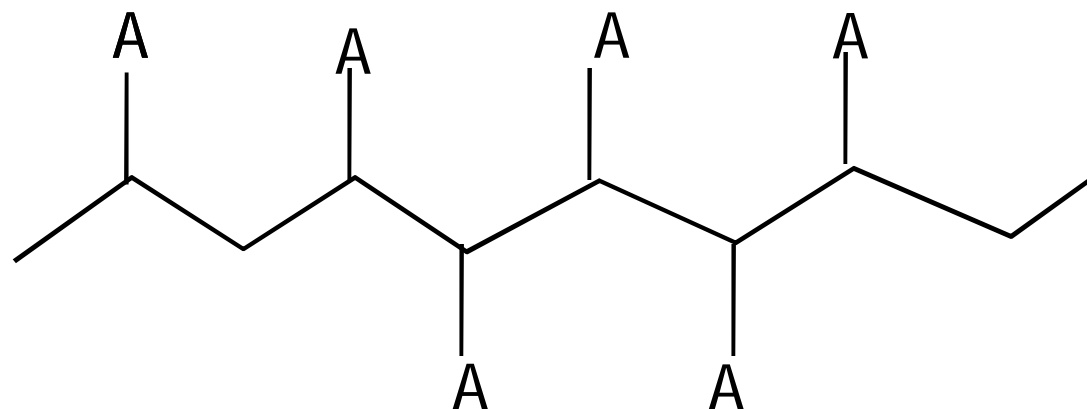
When all the functional groups or side groups are present on the same side of the polymer chain it is called as **isotactic polymer**



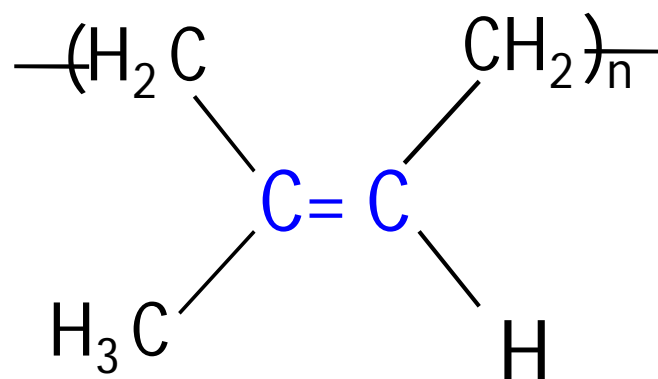
When the functional groups or side groups are present in an alternating manner it is called as **syndiotactic polymer**



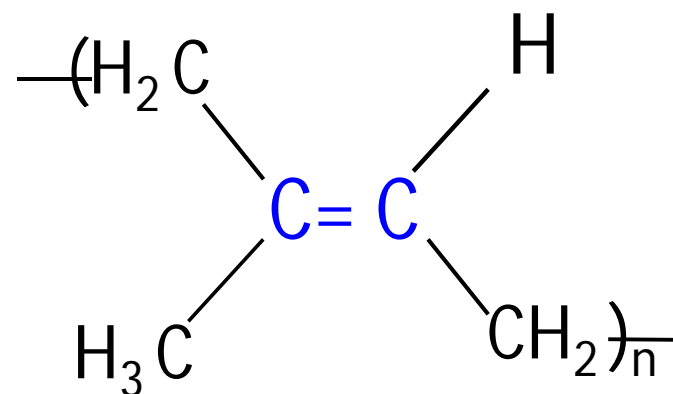
When the functional groups or side groups are present in random manner it is called as **atactic polymer**



## Cis and Trans Isomer



Cis 1,4 polyisoprene (natural rubber)



Trans 1,4 isoprene (synthetic Rubber)

## Molecular Weight of Polymers

- ❖ Most of the properties of polymers such as viscosity, softening temperature, heat resistance, are influenced by the molecular weight.
- ❖ Low molecular weight polymer are soft and gum like resins where as high M.W polymers are tough and exhibit better heat resistance.
- ❖ Thus controlling M.W. is of great importance for industry and research.
- ❖ However in the polymerization process all the polymer chains do not grow to same size.
- ❖ The process of chain growth termination is random process and hence the chains have different molecular weights.



## Molecular Weight of Polymers

As the polymer formed is of same chemical type but have different degree of polymerization (D.P) size and molecular weight, the average value of their molecular weight is taken.

- ❖ Number average molecular weight
- ❖ Weight average molecular weight

Lets say that the total number of molecules in a polymer is **N**

If  $N_1$  molecules in the polymer have molecular weight  $M_1$

$N_2$  molecules have molecular weight  $M_2$

$N_3$  molecules have molecular weight  $M_2$  and so on

$$\therefore \text{Total number of molecules} = N = N_1 + N_2 + N_3 + \dots + N_i$$

The molecular weight of  $N_1$  molecules will be  $N_1 M_1$

The contribution by  $N_1$  molecules will be 
$$= \frac{N_1 M_1}{\sum N_i}$$

Similarly the molecules with different molecular weights  $N_2, N_3 \dots$

$$\overline{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots + N_i M_i}{\sum n_i} = \frac{\sum N_i M_i}{\sum N_i}$$

## ❖ Number average molecular weight ( $\overline{M}_n$ )

It is defined as the total mass ( $M_i$ ) of all the molecules ( $N_i$ ) in a sample divided by the total number of molecules present.

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

Determined by measurement of colligative properties such as

- ❖ Freezing point depression
- ❖ Boiling point elevation
- ❖ Osmotic pressure etc.

# Weight average molecular weight

Lets consider a polymer of molecular weight  $W$

Let  $W_1$  = the weight of the  $N_1$  polymer molecules having molecular weight  $M_1$

$W_2$  = the weight of the  $N_2$  polymer molecules having molecular weight  $M_2$

$W_n$  = the weight of the  $N$  polymer molecules having molecular weight  $M_n$

The total weight of the polymer is  $W = W_1 + W_2 + W_3 + W_4 + W_5 \dots W_i$   
 $= \sum W_i$

The weight fraction of  $W_1$  Weight =  $W_1/W$

The molecular weight contribution of  $W_1 = W_1 M_1 / W$

Similarly the contributions from others will be  $W_2 M_2 / W$ ,  $W_3 M_3 / W$

$$\begin{aligned} \text{The average molecular weight } \overline{M_w} &= \frac{W_1 M_1 + W_2 M_2 + W_3 M_3 + \dots}{\sum W_i} \\ &= \frac{\sum W_i M_i}{\sum W_i} \quad (1) \end{aligned}$$

If the weight  $W_1$  contains  $N_1$  molecules of molecular weight  $M_1$  then

$$W_1 = N_1 \times M_1$$

**Similarly  $W_i = N_i \times M_i$**

Substituting for  $W_i$  in equation 1 becomes,

The average molecular weight  $M_w = \frac{\sum N_i \times M_i \times M_i}{\sum N_i M_i}$

$$\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

If a polymer sample has population of  
25 molecules of molecular weight each = 15000  
20 molecules of molecular weight each = 20000  
5 molecules of molecular weight each = 25000

Calculate its number average and weight average molecular mass and find Mw/Mn ratio.

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

$$\overline{M}_n = \frac{[25 \times 15000 + 20 \times 20000 + 5 \times 25000]}{50}$$

$$\overline{M}_n = \frac{375000 + 400000 + 125000}{50} = \frac{900000}{50} = 18,000$$



$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$\overline{M}_w = \frac{[25 \times (15000)^2 + 20 \times (20000)^2 + 5 \times (25000)^2]}{[25 \times 15000 + 20 \times 20000 + 5 \times 25000]}$$

$$\overline{M}_w = \frac{5625 \times 10^6 + 8000 \times 10^6 + 3125 \times 10^6}{900000}$$

$$\overline{M}_w = \frac{1.675 \times 10^{10}}{900000} = 18611.1$$

$$M_w/M_n = 18611 / 18000 = 1.033$$

# Polymerization Types

- ❖ Addition or Chain Growth Polymerization.
- ❖ Condensation or Step Growth Polymerization.

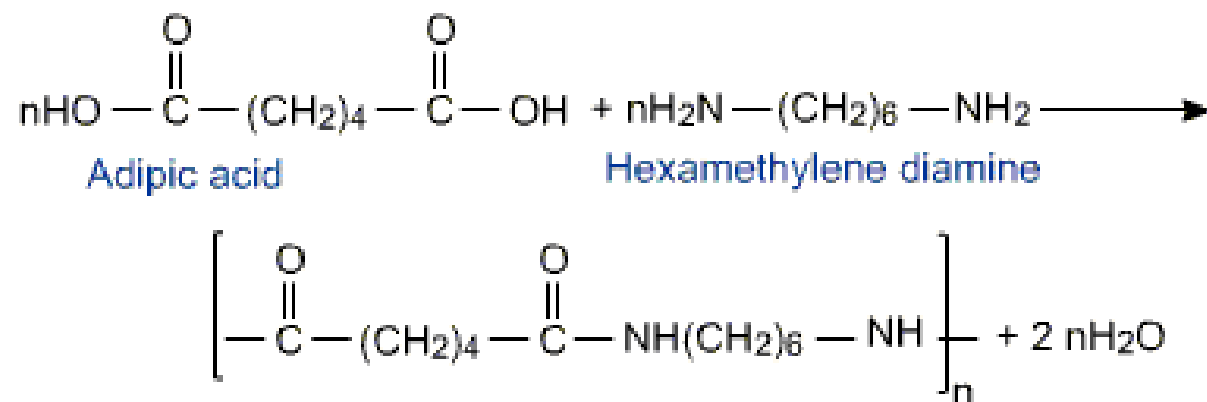
## Addition Polymerization

- ❖ In this type of polymerization simple addition of monomers takes place to form a polymer.
- ❖ The formed polymer is exact multiple of the monomer molecules.
- ❖ Usually double or triple bond containing monomers undergo this type of polymerization.
- ❖ The process of polymerization takes place by application of heat, light pressure or a catalyst. During the polymerization process opening of double or triple bond takes place and the monomers are linked to each other.
- ❖ Addition polymerization is quick and rapid process.

Polymers like PVC, polyethylene, polystyrene are prepared by addition polymerization

# Condensation Polymerization

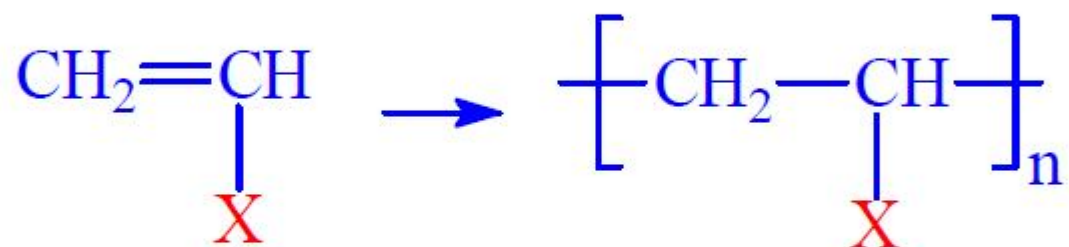
- ❖ The monomers involved in the polymerization undergo condensation reaction.
- ❖ The monomers have 2 or more functional groups.
- ❖ Two or more monomers react together undergoing polymerization reaction with elimination of small molecules like water, HCl, NH<sub>3</sub> etc.
- ❖ It's a slow process.
- ❖ Polymers like polyesters, polyurethane, nylon 6,6 are formed by condensation polymerization.



<b>Addition or chain polymerization</b>	<b>Step or condensation polymerization</b>
The polymer grows by sequential addition of monomers to a reactive site.	Any two molecular species can react.
Chain growth is linear.	Chain growth is exponential.
Maximum molecular weight is obtained early in the reaction.	Maximum molecular weight is obtained late in the reaction.
Longer reaction time has a little effect on molecular weight.	To obtain high molecular weight longer reaction time is essential.
E.g PE, PP, PS, PVC	E.g. Polyester, Nylon 6,6, Bakelite, Polycarbonate

# Addition Polymerisation mechanism

- ❖ Reactions in which monomers combine without the elimination of a small molecule.



- ❖ Usually involves the breaking of a double bond.



# Mechanism of Addition polymerization.

It requires a  
catalyst or initiator like free radical  
or reactive cation or anion  
or coordination catalyst.

- ❖ It is an exothermic process utilizing  $C=C$  in the monomer which opens and forms linked polymers.
- ❖ The composition of the polymer is same as that of the monomer involved.
- ❖ No by products are formed.

## Step I : Initiation

In this step the monomer interacts with the initiator for its activation and generates active monomer molecule.



## Step II : Propagation

In this step the reactive monomer  $M^*$  interacts with other monomer molecules leading to propagation of polymer chain.



## Step III : Termination

It is the process in which addition to the polymer chain is stopped or the chain growth is arrested.

Termination can take place by following ways

- ❖ Termination by coupling or combination
- ❖ Termination by disproportionation
- ❖ Termination by chain transfer

Different types of initiators can be used for chain growth. The reaction proceeds by addition of a monomer unit to a radical initiator or an initiation ion by which the active state is transformed from the initiator to the added monomer.

Examples: peroxides, Hydrogen peroxide, Benzoyl peroxide, Acetyl peroxides etc.

Depending on the nature of the active center addition polymerization is classified as

**A. Free radical Polymerization**

**B. Ionic Polymerization**

1) Cationic Polymerization

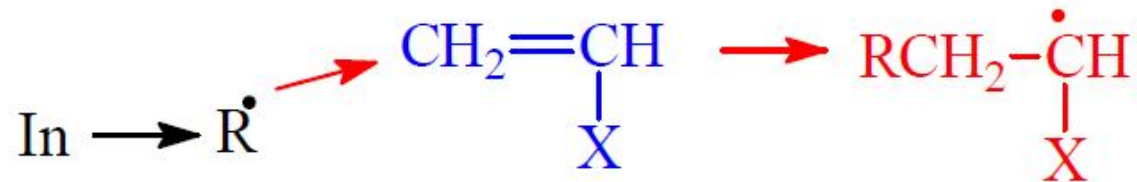
2) Anionic Polymerization

## Free Radical Polymerization

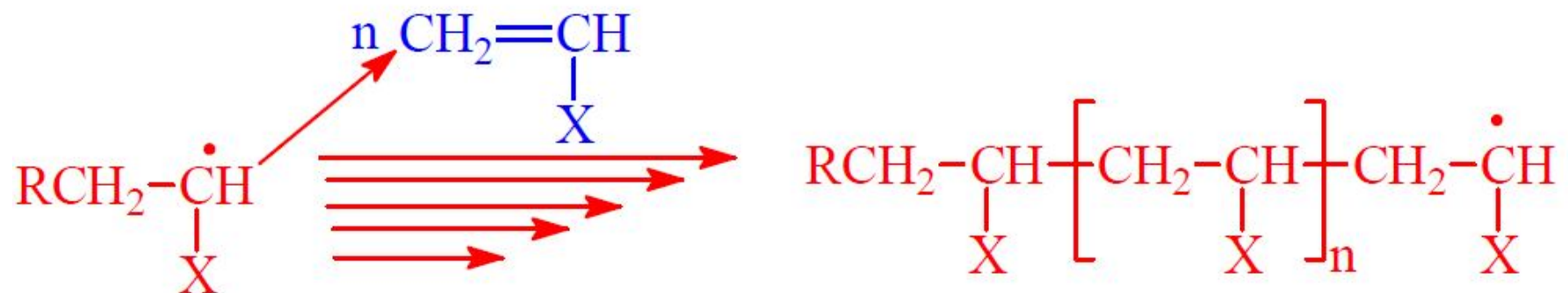
- ❖ In this the monomer is first converted into a free radical by action of heat light or pressure.
- ❖ The free radical is a molecule having an unpaired electron and has high tendency to gain an additional electron thus making it highly reactive.
- ❖ It acts by breaking a bond on other molecule thereby gaining an electron. This leaves an unpaired electron on the other molecules , creating another free radical.
- ❖ This process continues leading to polymer chain growth..
- ❖ The monomers involved in this process are mainly unsaturated having double bonds.

# Radical Polymerisation

- Initiation – Creation of an active site (free radical). [ Initiator: benzoyl peroxide]



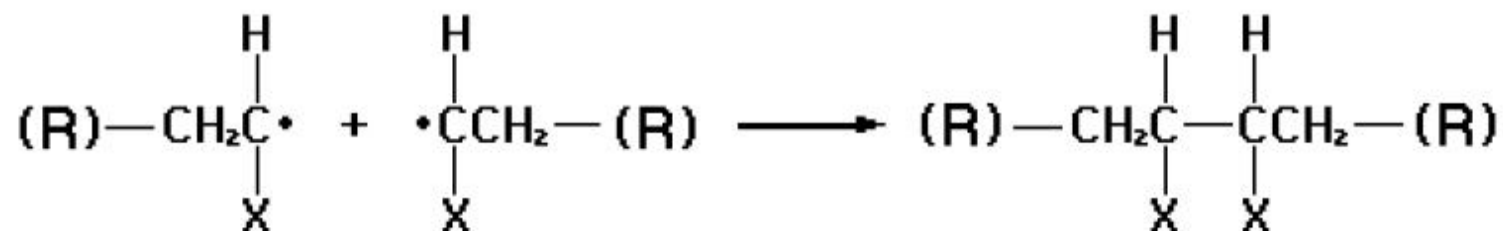
- Propagation – Growth of polymer chain by addition of a monomer to an active site and the creation of a new active site.



## ❖ Termination by Coupling

■ Termination – Growth of chain stops.

□ Combination – Two growing chains collide.



## ❖ Termination by disproportionation

Hydrogen atom on one radical centre is transferred to another radical centre resulting in Formation of one saturated and one unsaturated polymer molecule



## Ionic Polymerization.

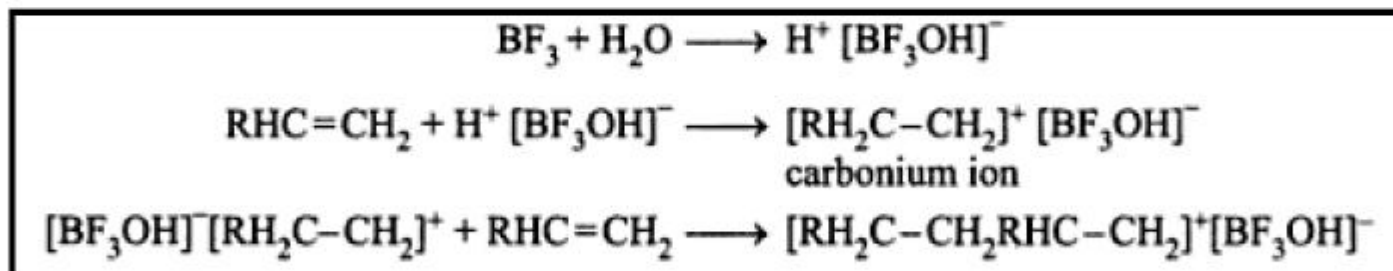
- ❖ Cationic Polymerization when electron donating groups such as methyl are present
- ❖ Anionic polymerization when electron withdrawing groups are present.



# Cationic Polymerisation

Addition polymerisation can be initiated by cations (cationic polymerisation) or by anions (anionic polymerisation).

*Cationic polymerisation* Cationic initiators such as Bronsted acids (e.g., HCl, H<sub>2</sub>SO<sub>4</sub> etc.) and Lewis acids (e.g., AlCl<sub>3</sub>, BF<sub>3</sub>, etc.) form carbonium ions (ion containing a trivalent carbon with a positive charge) which function as chain carriers in the polymerisation of substituted ethylenes. Lewis acids require the presence of a co-catalyst usually water to act as a proton donor. Proton from Bronsted acids or obtained by the reaction between a Lewis acid and water initiates the polymerisation.



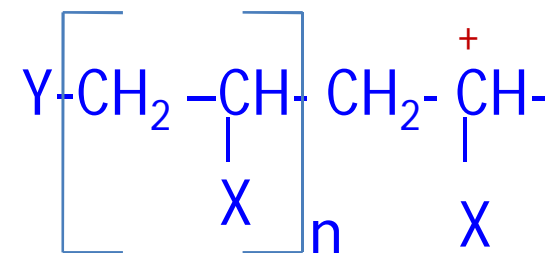
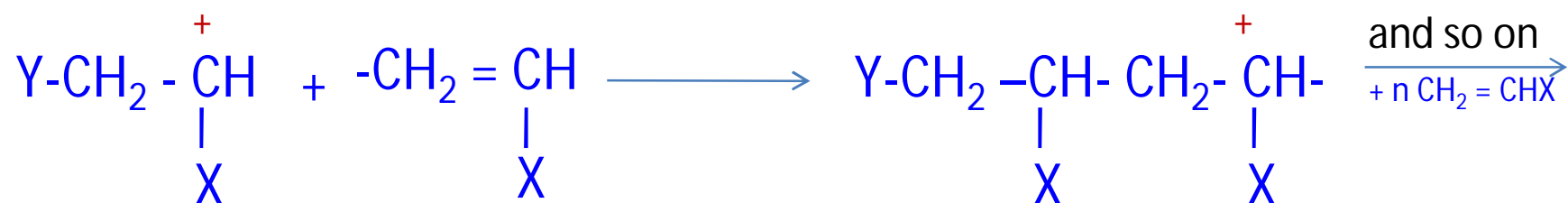
An alkene monomer with an electron releasing substituent favours the formation of carbonium ion and hence cationic polymerisation. A well known example of cationic polymerisation is the copolymerisation of 2-methyl propene (isobutylene) with a small amount of 2-methyl-1, 3-butadiene (isoprene) to give butyl rubber.

## Mechanism of Cationic Polymerization

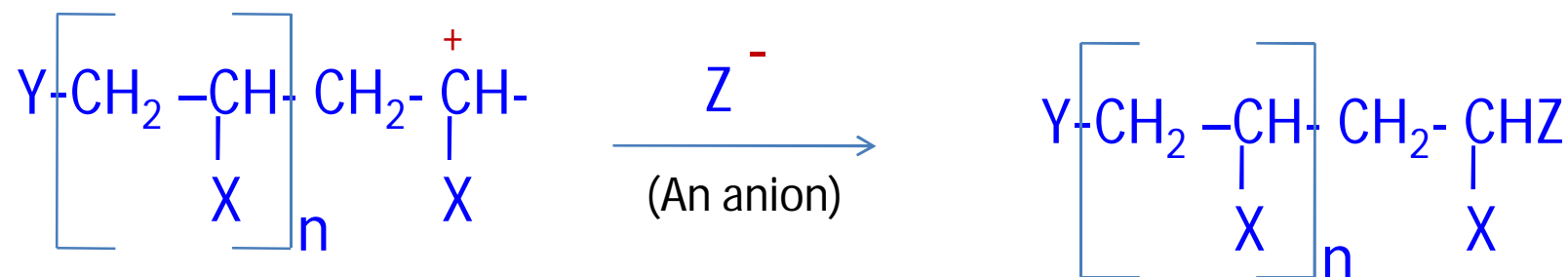
Initiation



propagation



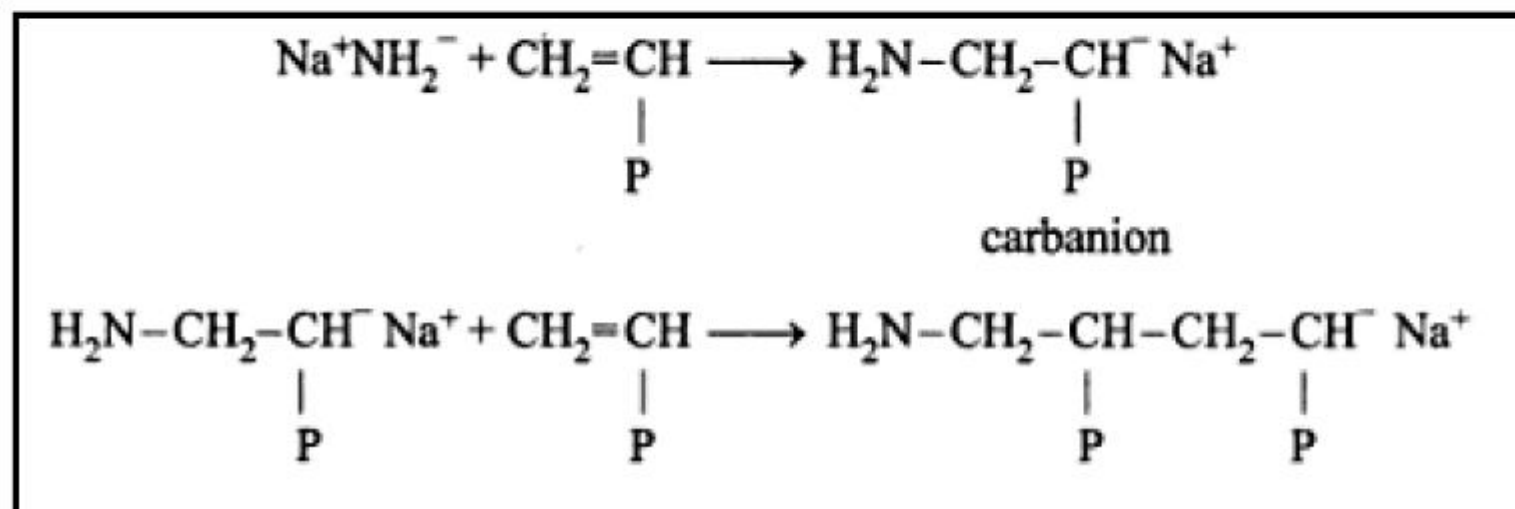
Termination



Polymer

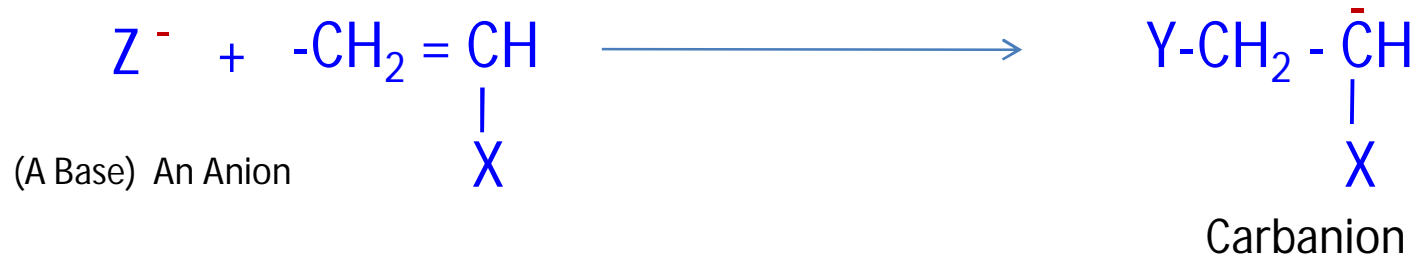
# Anionic Polymerisation

*Anionic polymerisation* Electron donors such as alkali metal amides (e.g.,  $\text{NaNH}_2$ ) and alkali metal alkyls (e.g., *n*-butyl lithium) attack an electrophilic site of an alkene monomer such as acrylonitrile or methyl methacrylate resulting in a carbanion (ion containing a trivalent carbon with a negative charge) which propagates the chain polymerisation. The electron withdrawing pendant or substituent groups in the alkene monomer facilitate the formation of carbanions. The growing chain remains an anion as the negative charge is transferred along the chain.

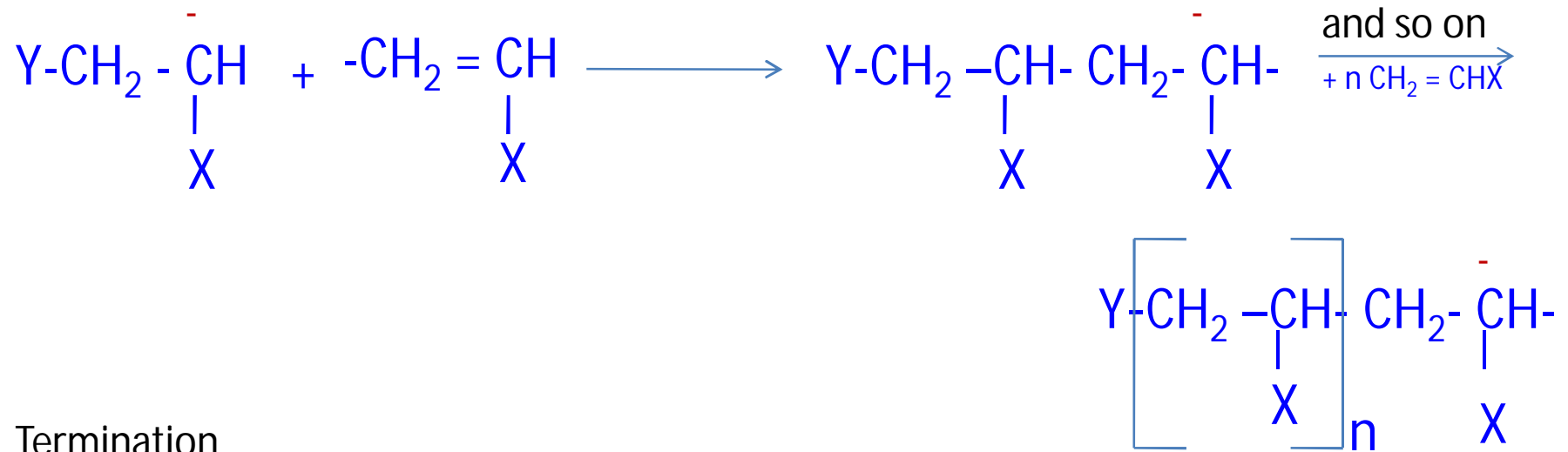


## Mechanism of Anionic Polymerization

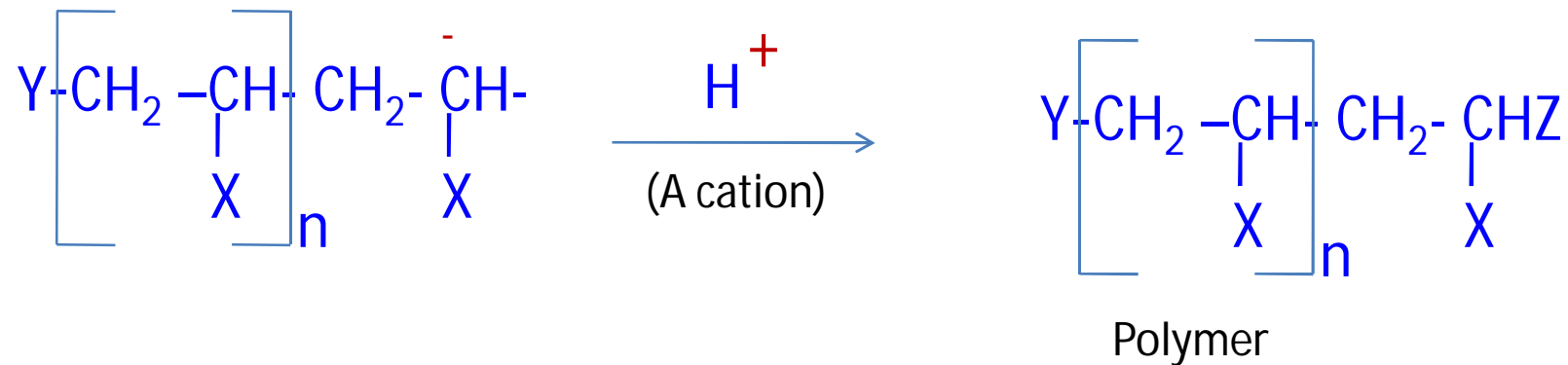
Initiation



propagation



Termination



## Condensation or Step Growth Polymerization.

- ❖ In this type of polymerization bifunctional or multifunctional monomers react to first form dimers, then trimers, longer oligomers and eventually long chain polymers.
- ❖ The chain growth is in a step wise manner and therefore it's a relatively slow process.
- ❖ The polymer chain growth may follow different paths as follows.
  - ❖ Monomer + Monomer  $\longrightarrow$  Dimer
  - ❖ Dimer + Monomer  $\longrightarrow$  Trimer
  - ❖ Dimer + Dimer  $\longrightarrow$  Tetramer
  - ❖ Dimer + Trimer  $\longrightarrow$  Pentamer.....

Depending on the thermal response polymers can be classified as

## Thermoplastic Polymers

- ❖ These polymer can be softened or plasticized repeatedly on heating without much changes in the properties.
- ❖ In other words these polymers can be softened on heating and hardened on cooling reversibly.
- ❖ This indicated that their hardness is a temporary property which can change with increasing or decreasing temperature.
- ❖ Thus thermoplastic polymers can be processed repeatedly.
- ❖ Examples: Polythene, polypropylene, Polyvinyl chloride (PVC), Polystyrene , Nylons etc. They are soluble and fusible after many cycles of heating and cooling.

## Thermosetting Polymers

- ❖ These polymer are obtained in soluble and fusible form in early stages of their synthesis
- ❖ But after moulding or heating they get hardened and once they have solidified they can not be softened again.
- ❖ This hardening happens because of chemical reactions leading to further growth and cross linking polymer chains having strong covalent bonds.
- ❖ In other words these polymers are permanently setting polymers.
- ❖ Thus thermosetting polymers can not be processed repeatedly.
- ❖ Examples: Bakelite, Phenolic resins, Urea/melamine resins, epoxy resins, urea formaldehyde.

Thermoplastic Polymers	Thermosetting Polymers
They softened on heating easily.	They do not soften on heating. On continuous heating they burn.
They are long chain linear polymers. <b>Van der Waal's forces of attraction.</b>	They have three dimensional network structure having strong <b>covalent bonds.</b>
They are formed by addition polymerization.	They are formed by condensation polymerization.
They are soft, weak and less brittle.	They are hard, strong and more brittle.
By heating to a suitable temperature they can be softened and reshaped and thus reused.	They can not be reshaped and reused on heating.
They are they are usually soluble in organic solvents  <b>Example PVC</b>	They are they are usually insoluble in almost all organic solvents because of their strong bonds and cross linking.  <b>Example Bakelite</b>



# Glass Transition Temperature

- ❖ The glass transition occurs in amorphous polymers in which during cooling the polymer, the crystallization does not take place.
- ❖ That means the polymer chains are not able to arrange themselves in a three dimensional long range ordered structure.
- ❖ Upon cooling the glass transition leads to an increase in viscosity and there is a gradual transition from liquid to a rubberlike state to a rigid solid.

# Glass Transition Temperature

The temperature at which the polymer experiences a transition from a rubbery to rigid state is called as the glass transition temperature ( $T_g$ )

The melting and glass transition temperatures are of importance because they determine the upper and lower temperature limits for various applications.

# Melting and Glass Transition Temperature

- Melting of a crystalline polymer
  - transforming solid with an ordered structure to a viscous liquid with a highly random structure
- Amorphous glass transitions
  - transformation from a rigid material to one that has rubberlike characteristics
  - temperature has large effect on chain flexibility
- Below glass transition temperature,  $T_g$ 
  - polymers are usually brittle and glass-like in mechanical behavior
- Above glass transition,  $T_g$ ,
  - polymers are usually more elastic and will show deformation

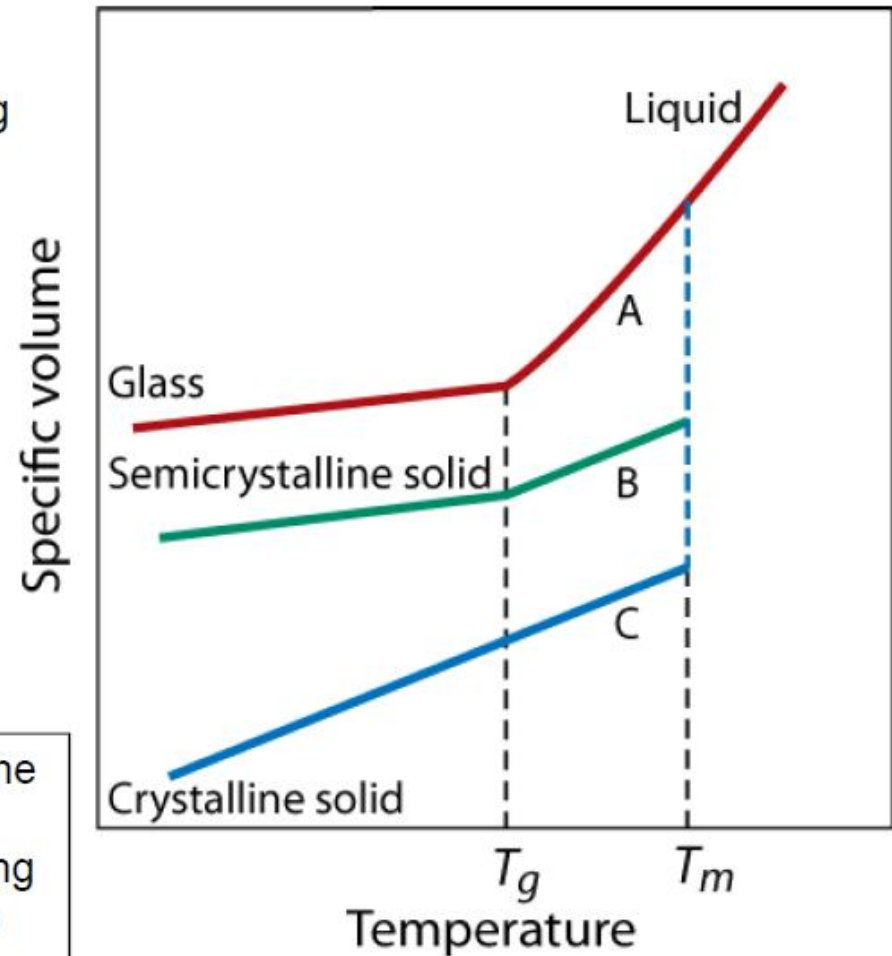
**Meaning-** Bond rotations are “freezing” which means chains can’t slip past each other so polymer becomes brittle, (no plastic deformation)

# Melting vs. Glass Transition Temperature

Factors affecting  $T_m$  and  $T_g$

- Both  $T_m$  and  $T_g$  increase with increasing chain stiffness
- Chain stiffness increased by
  - ✓ Bulky side groups (e.g methyl, phenyl, naphthyl groups)
  - ✓ Polar groups or sidegroups (e.g -OH, -CN, Cl)
  - ✓ Double bonds or aromatic chain groups
- Regularity – effects  $T_m$  only

❖ The value of  $T_g$  depends on the mobility of the polymer chain - the more immobile the chain, the higher the value of  $T_g$ . In particular, anything that restricts rotational motion within the chain should raise  $T_g$ .

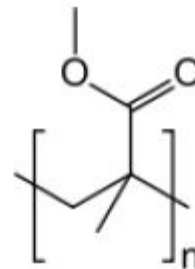


Semicrystalline polymers have true **melting temperatures ( $T_m$ )** at which the ordered regions break up and become disordered. In contrast, the amorphous regions soften over a relatively wide temperature range (always lower than  $T_m$ ) known as the **glass transition ( $T_g$ )**.

Fully amorphous polymers do not exhibit  $T_m$ , of course, but all polymers exhibit  $T_g$ . Above these temperatures, polymers are liquids.

**Examples of amorphous polymers:**

Polyimide, Polystyrene,  
poly(methyl methacrylate) etc.



**PMMA**

**Examples of semicrystalline polymers:**

Linear polyethylene, PET (polyester),  
isotactic polypropylene



## $T_g$ and $T_m$ values of some polymers

<i>Material</i>	<i>Glass Transition Temperature [°C (°F)]</i>	<i>Melting Temperature [°C (°F)]</i>
Polyethylene (low density)	-110 (-165)	115 (240)
Polytetrafluoroethylene	-97 (-140)	327 (620)
Polyethylene (high density)	-90 (-130)	137 (279)
Polypropylene	-18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Polyester (PET)	69 (155)	265 (510)
Poly(vinyl chloride)	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)

$T_g$  values are always lower than  $T_m$

# Composite Materials





## Definition

A composite material is defined as a material system consisting of a mixture of two or more macro constituents which are mutually insoluble, differing in form and /or composition and forming distinct phases/.

Example: Wood ( cellulose fibers+ lignin )

Bone ( Collagen + apatite)

Insulating tape

Water Proof material

Reinforced concrete etc

## Characteristics of composites materials

- ❖ Higher specific strength
- ❖ Higher specific stiffness
- ❖ Higher strength
- ❖ High temperature stability
- ❖ Better toughness
- ❖ Better impact and thermal shock resistance
- ❖ Lower thermal expansion coefficient
- ❖ Better corrosion resistance
- ❖ Cheap and easy to fabricate

## Applications of composites

1. Industrial Applications : Automobile industries, transportation industries, turbine engines, wire drawing dies, valves, vacuum pump parts, spray nozzles, sport goods, etc.
2. Marine applications : Propellers, shafts, hulls, spars, and other ship parts.
3. Aeronautical Applications: Rocket components, aircrafts ( business and military), space ships.
4. Communication Antennae, Electronic circuit boards
5. Safety equipments.

## Essential constituents of composites

1. **Matrix Phase:** it is the continuous body constituent, which encloses the composite and gives it a bulk form.

It can be a metal, ceramic or a polymer. Depending on the matrix phase composites are known as, metal matrix composite( MMC), ceramic matrix composite( CMC) and polymer matrix composite(PMC).

### Functions:

1. binds the dispersed phase together
2. Acts a medium to transfer the extremely applied load to the dispersed phase
3. Protects the dispersed phase.
4. Prevents the propagation of brittle cracks due to its plasticity and softness.

**Dispersed Phase:** It is the structural constituent which determines the internal structure of the composite. Important dispersed phase are

1. Fiber: Glass fibers, carbon fibers, aramid fibers.
2. Particulates
3. Flakes
4. Whisker

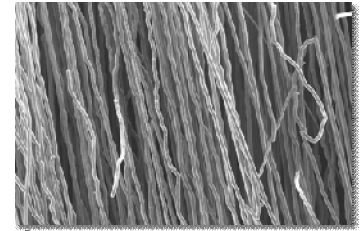
Glass fibers (10  $\mu\text{m}$ ) are prepared by forcing molten glass through small opening followed by cooling.

The performance of glass fibers is enhanced due to

- a. Ready availability
- b. Low cost
- c. High specific strength
- d. Can be economically used to produced glass reinforced polymer composite



Carbon fibers (8  $\mu\text{m}$ ) are prepared by continuous pyrolysis of organic fibers such as cellulose or polyacrylonitrile.



The performance of carbon fibers is enhanced due to

- a. High modulus, specific strength and stiffness at elevated temperatures
- b. Resistance to moisture, acids, bases and other solvents

Aramid Fibers are prepared by spinning liquid aramid oligomers (Kevlar The performance of carbon fibers is enhanced due to

- a. High modulus, specific strength and stiffness at elevated temperatures
- b. Wide temperature range(-200 to 200 °C
- c. Resistance to creep and fatigue failure
- d. Excellent toughness and impact resistance



**Particulates** are small pieces of hard solid material ( metallic or non metallic).

The distribution of particulates in the matrix is random which results in an isotropic material.

**Effects of adding particulates to matrix materials :**

1. Enhancement is surface hardness
2. High performance at elevated temperatures
3. Abrasion resistance is improved
4. Reduction in shrinkage and friction
5. Low cost
6. Thermal and electrical conductivities are modified
7. Enhanced strength

**Flakes:** they are thin solids having two dimensional geometry. E.g. mica sheets.

They impart strength in plane as compared to fibers. The packing of flakes is also more effective as compared to fibers.

**Whiskers** are thin strong filaments or fibers made by growing a crystal. E.g. graphite , Silicon, Silicon nitride. Usually they are several microns in diameter.

High elastic modulus,

High degree of crystallinity

High strength



## Type of composites

1. Fiber Reinforced Composite
2. Particulate Composites
3. Layered Composites

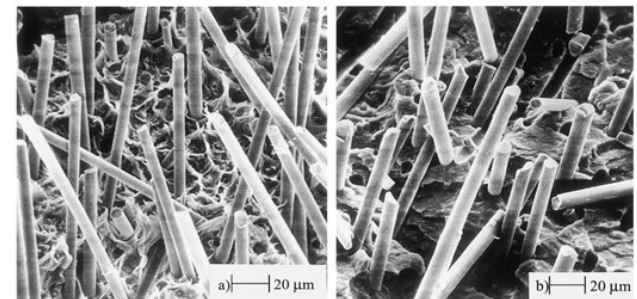
# Fiber reinforced Composites

Properties depend on the following

- Nature and properties of both fibers as well as the matrix phase.
- Their relative volume fraction
- Orientation and distribution of fibers in matrix phase
- Length to diameter ratio ( aspect ratio)

Characteristics of fiber reinforced composites

- High yield strength and modulus
- Excellent mechanical properties
- Enhanced shock resistance
- High fracture strength and fatigue life



# Types of fiber reinforced composites

1. **Glass fiber reinforced polymer composite** : Lower density, higher tensile strength, impact and chemical resistance

**Limitations** : limited temperature range for working and low stiffness and rigidity.

**Uses** : in Automobile parts, storage tanks, plastic pipes etc.

2. **Carbon fiber reinforced polymer composite** : Excellent Corrosion resistance, higher density, high temperature uses

**Limitations** : Higher Cost.

**Uses** : in Automobile parts, storage tanks, plastic pipes etc.

3. **Aramid fiber reinforced polymer composite**

#### 4. Alumina and/or carbon fiber reinforced metal composite :

Improved specific strength, stiffness, abrasion resistance, creep resistance.

Examples are

Matrix-Al alloy, reinforcement with  $\text{Al}_2\text{O}_3$  or carbon fibers.

**Properties:** Low Density, wear resistant, resistance to thermal dissipation

**Applications:** Engine components in automobile industries

Matrix-A Ni or Co based alloy, reinforcement with  $\text{Al}_2\text{O}_3$  or Tungsten.

**Properties:** excellent resistance to impact strength, creep and rupture, and high temperature stability.

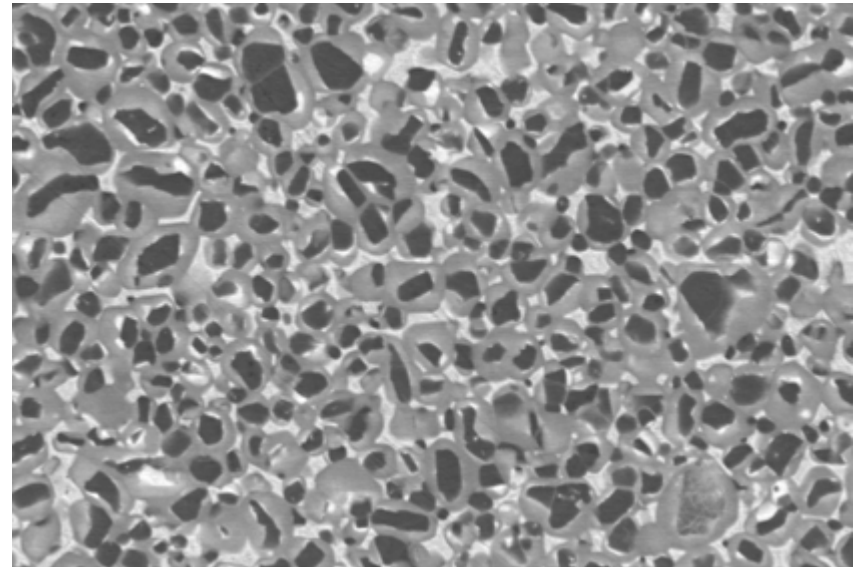
**Applications:** Engine components in automobile industries

## Particulate composites

They are prepared by dispersing the varying size and shape of one material in the matrix of other materials.

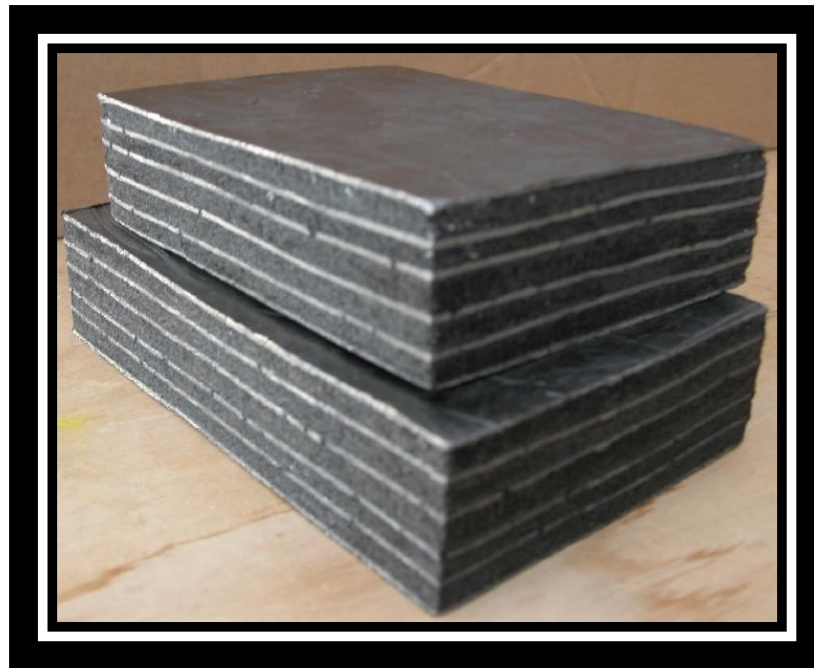
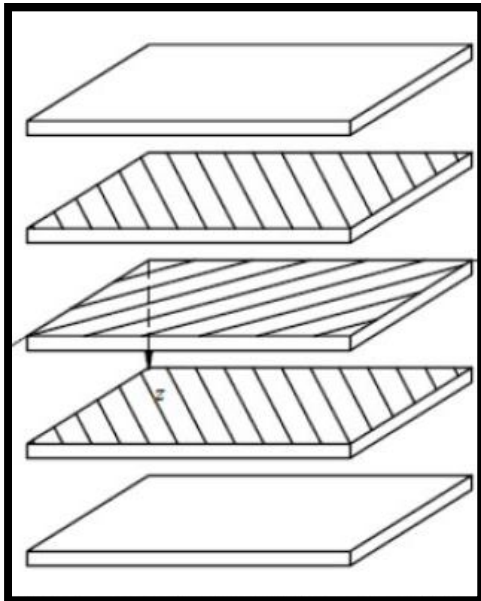
Most important of such composites are cermets. ( Ceramic bonded with metal)

Oxide based cermets (  $\text{Al}_2\text{O}_3 + \text{Cr}$  )  
Carbide based cermets (  $\text{WC} + \text{Co}$  )



## Layered Composites

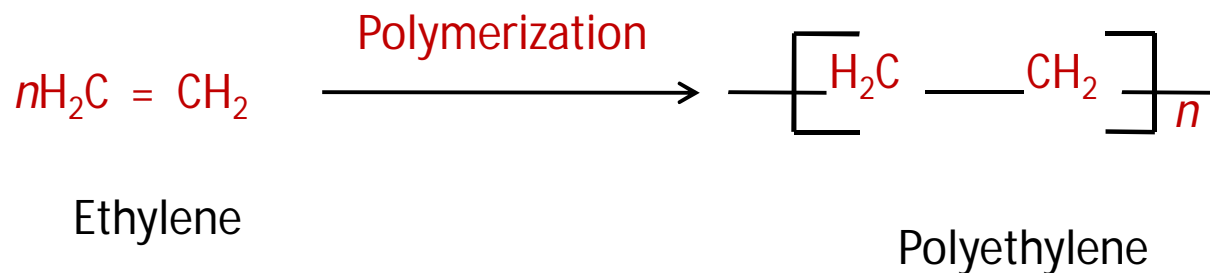
The properties of layered composites depend on the properties of constituents and their geometrical design. Posses high strength, in both directions of reinforcements.



# Polyethylene

## Synthesis

Polyethylene is prepared by polymerization of monomer ethylene



- Ethylene gas is first liquefied under high pressures.
- It is sent to a heated pressure vessel maintained at temperature between 150 to 250 degree Celsius.
- For low density ethylene free radical initiator is used and a pressure of 1000-3000.
- For High density polyethylene ionic catalyst or metal oxide catalysts .

# Properties of Polyethylene

Appearance:

It's a rigid, waxy, white and translucent material.



- ❖ Chemically resistant to strong acids and alkalis and to salt solutions at room temperature .
- ❖ The degree of crystallinity is about 40 to 95 % and depends on the degree of branching of the PE chain.
- ❖ High pressure synthesized polyethylene has branched structure which imparts more flexibility and toughness.
- ❖ Low pressure process results in a completely linear polyethylene which has higher density and better chemical resistance.



# Commercial polyethylene

Type I (Low Density)

0.91 to 0.925 g/cm<sup>3</sup>

Type II (Medium Density)

0.925 to 0.94 g/cm<sup>3</sup>

Type III (High Density)

0.94 to 0.965 g/cm<sup>3</sup>

- ❖ Rigidity is enhanced
- ❖ Completely Linear
- ❖ Chemical resistance is high mainly towards organic solvents
- ❖ High softening temperature

Type of PE	Density (g/cm <sup>3</sup> )	Crystallinity (%)	Softening Point (K)	Tensile strength
LDPE	0.920	55	360	85-136
HDPE	0.955	80	400	204-313

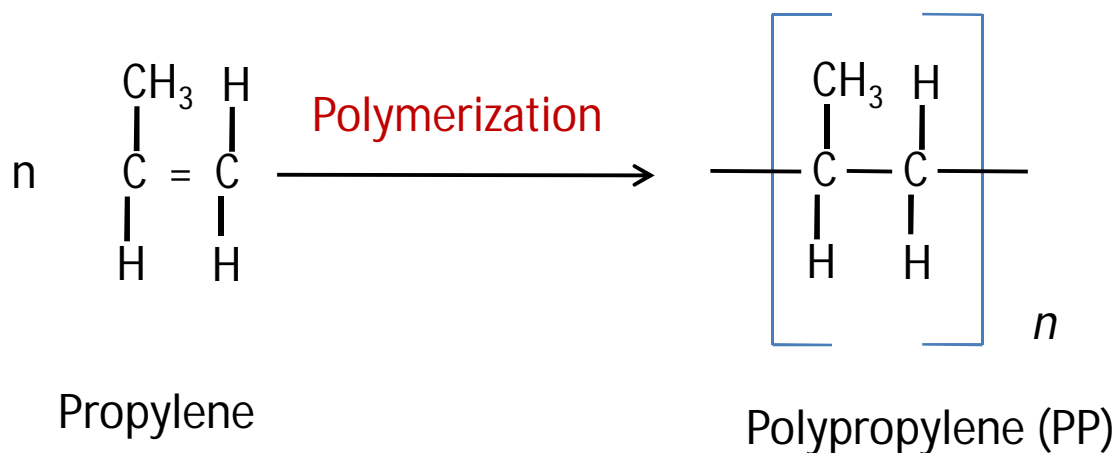
## Applications of Polyethylene

- ❖ LDPE films are used for packing frozen food, textile products.
- ❖ Due to high chemical inertness and high toughness they are used in making high frequency insulator parts, bottle caps, kitchen and domestic appliances.
- ❖ Also finds applications in chemical plants, in packaging, tubes, pipes, coated wires and cables.

# Polypropylene

## Synthesis

Polypropylene is synthesized by polymerization of propylene in the presence of Zeigler-Natta catalyst. ( $\text{AlR}_3\text{-AlCl}_3$ )



## Properties of Polypropylene

- ❖ PP is stereoregular and highly crystalline polymer.
- ❖ It has melting point of 160-170 degree Celsius.
- ❖ It possesses better hardness, stiffness than polyethylene.
- ❖ Also it is more resistant than PE

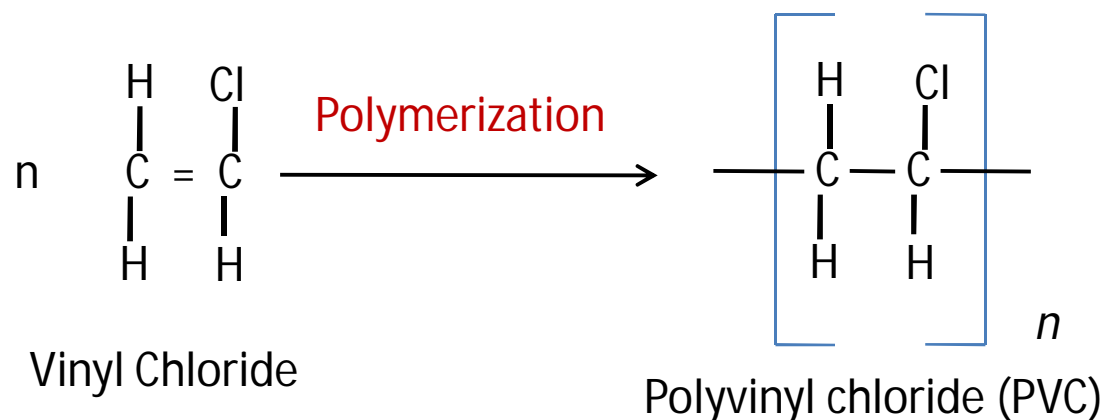
## USES of Polypropylene

- ❖ PP is used in moulded parts and fibers.
- ❖ It is also used in making ropes which have high strength.
- ❖ Carpets, blankets, hand bags, etc are also made by using PP.
- ❖ Waterpipes, washing machine parts, hospital equipments

# Polyvinylchloride

## Synthesis

Polyvinylchloride (PVC) is synthesized by heating water emulsion of vinyl chloride in presence of small amounts of benzyl peroxide or  $\text{H}_2\text{O}_2$  in an autoclave under pressure.



Vinyl chloride is prepared by treating acetylene with  $\text{HCl}$  at 60-80 deg cel in presence of metal chloride as a catalyst.



## Properties of Polyvinylchloride

- ❖ PVC is colorless, odourless, non inflammable and chemically inert powder.
- ❖ It is resistant to light, oxygen, acids and alkalis.
- ❖ It is soluble in hot chlorinated hydrocarbons such as ethyl chloride.
- ❖ It has a softening point of 148 degree Celsius.

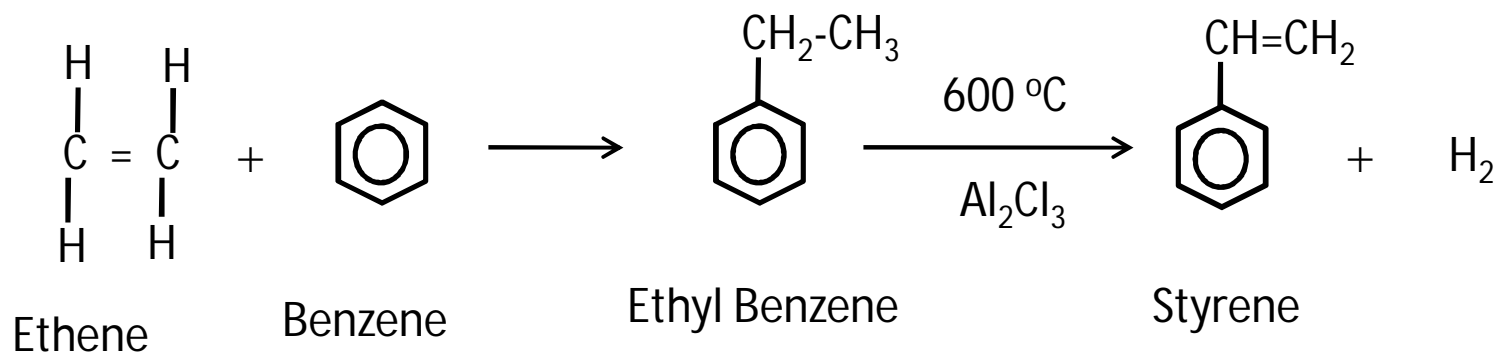
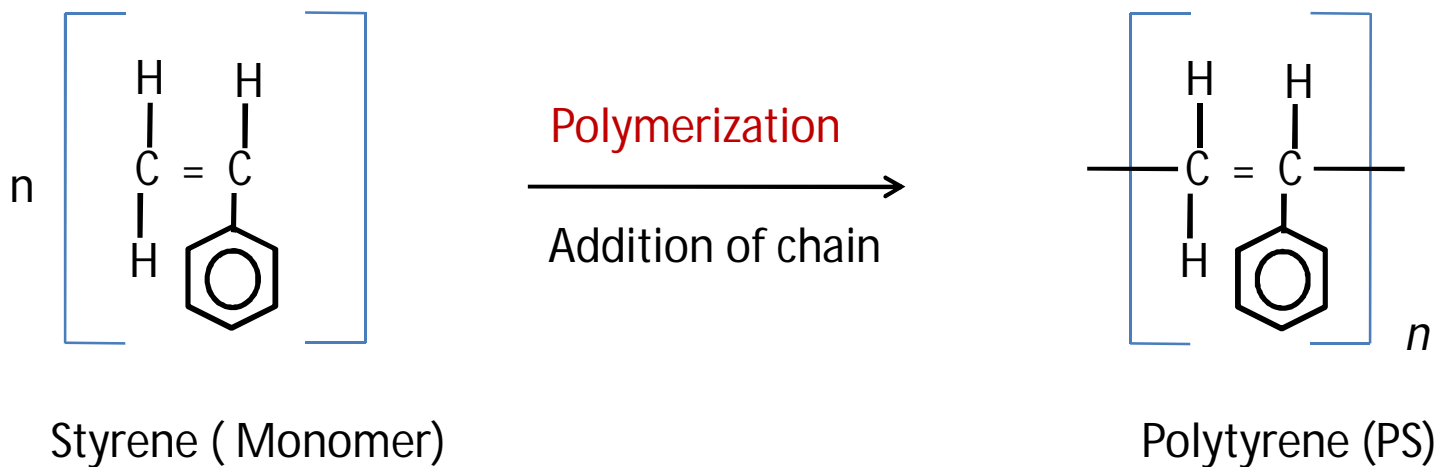
## USES of Polypropylene

- ❖ One of the most widely used plastic.
- ❖ *Rigid or non plasticized PVC* has very high chemical resistance, high rigidity but its brittle.
- ❖ It is used in making sheets used in tank linings, light fittings, safety helmets, refrigerator parts, tyres, cycle and motor cycle mud guards.
- ❖ Also used as pipes and tubes as replacement for non ferrous metals.
- ❖ *Plasticized PVC* is used in making continuous sheets of variable thickness to be used in making of raincoats, table cloths, curtains, electrical insulations for cables.
- ❖ Also used in making of toys , tool handles, toilet goods, radio parts, conveyer belts etc.

# Polystyrene

## Synthesis

Polystyrene is prepared by polymerization of styrene (dissolved in ethyl benzene) in presence of benzoyl peroxide catalyst.





## Properties of Polystyrene

- ❖ PS is transparent, light polymer having light stability and excellent moisture resistance.
- ❖ Eclectically insulating.
- ❖ Has high resistance towards acids.
- ❖ It has good chemical resistance.
- ❖ It can transmit light through curved sections.
- ❖ Softening temperature is 90-100 °C

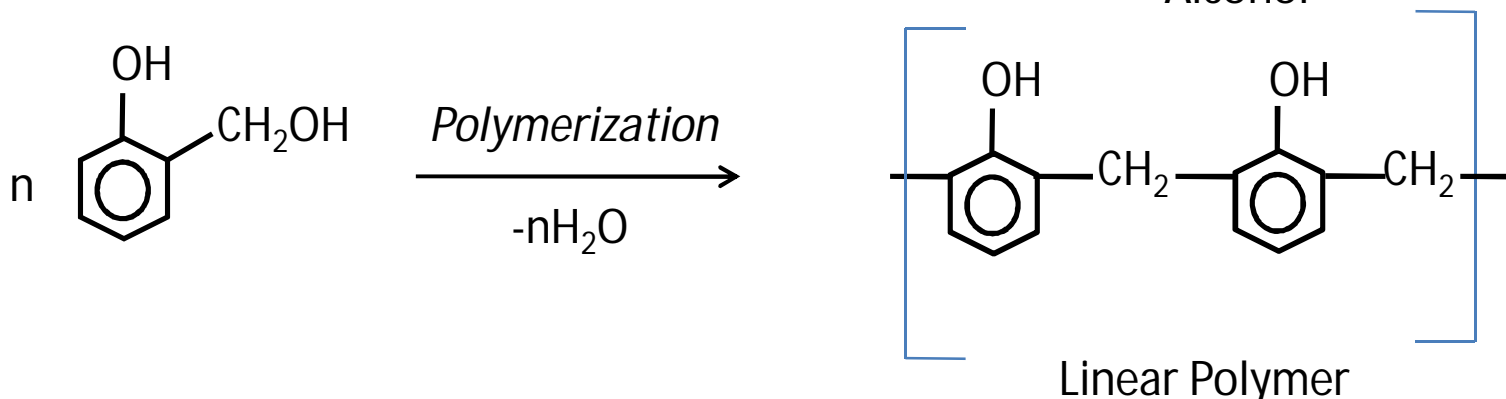
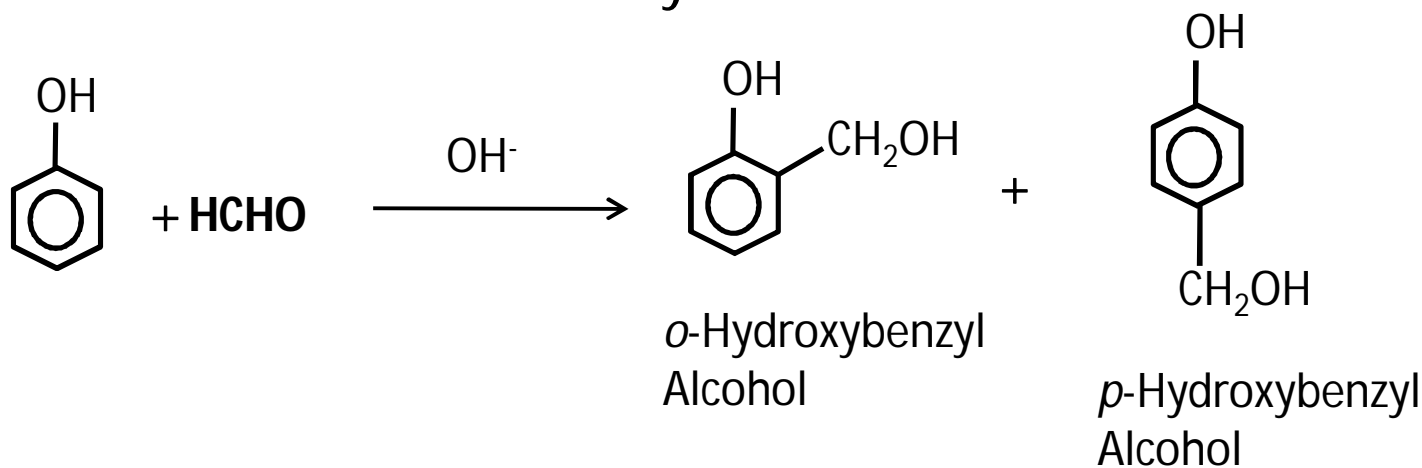
## USES of Polypropylene

Used in moulding of articles like toys, combs, buckles, radio and TV parts, Refrigerator parts, battery cases, high frequency electric insulators, lenses etc.

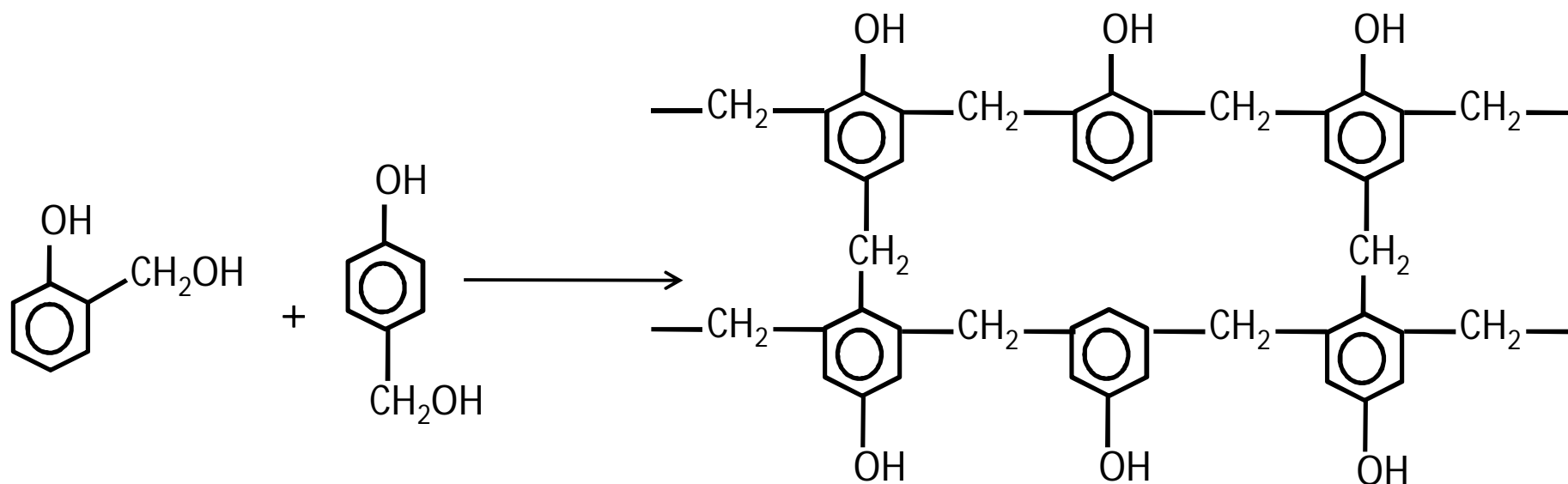
# Phenol Formaldehyde

❖ Its a condensation polymer prepared from Phenol and Formaldehyde in presence of a basic catalyst. It is also known as **Bakelite**.

## Synthesis



Ortho and para substituted phenols undergo polymerization to produce cross linked polymer Bakelite



## Properties of Phenol Formaldehyde

- ❖ Phenolic resins are hard, rigid, scratch resistant, infusible, water resistant insoluble solids.
- ❖ They are resistant to non oxidizing acids, salts and many organic solvents.
- ❖ They are easily attacked by alkalis because of the presence of free hydroxyl groups present in their structures.
- ❖ They exhibit very good electrical insulating behavior.

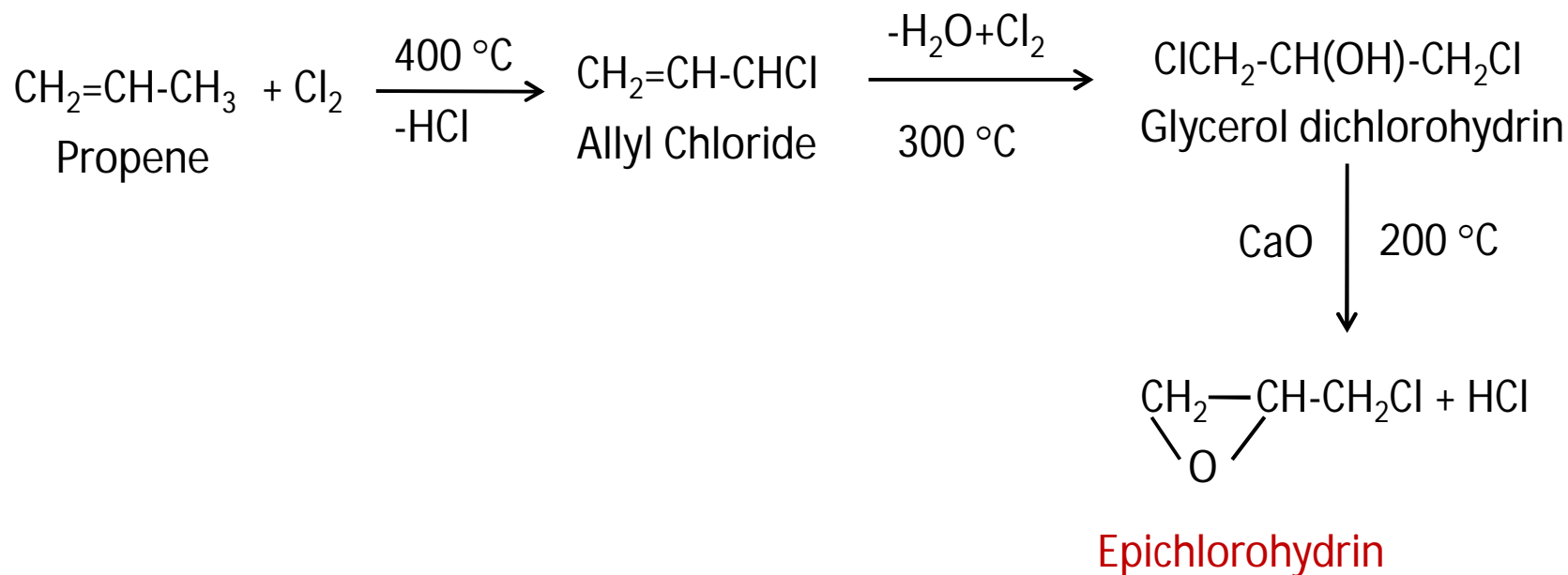
## Uses of Phenol Formaldehyde

- ❖ Used for making electrical insulating parts like switches, plugs, switch boards, heater handles.
- ❖ For making moulded articles like telephone parts.
- ❖ Used for impregnating fabrics, wood and plastics.
- ❖ Used for making bearings which are used in propeller shaft for paper industry and rolling mills.
- ❖ Used as adhesives or binders for grinding wheels.

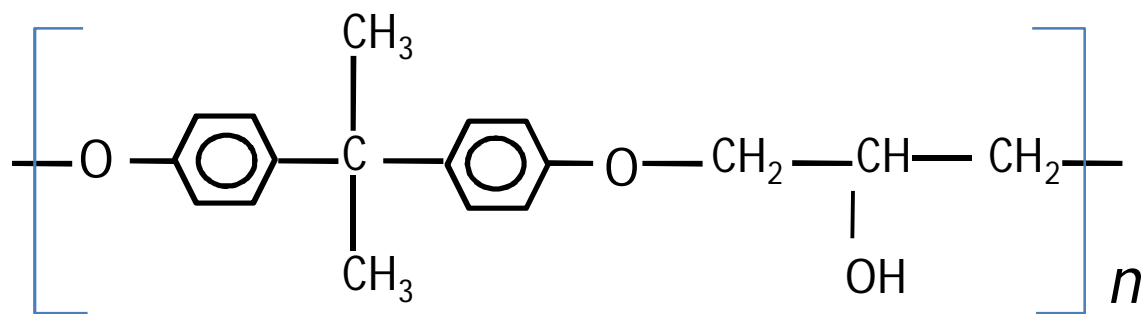
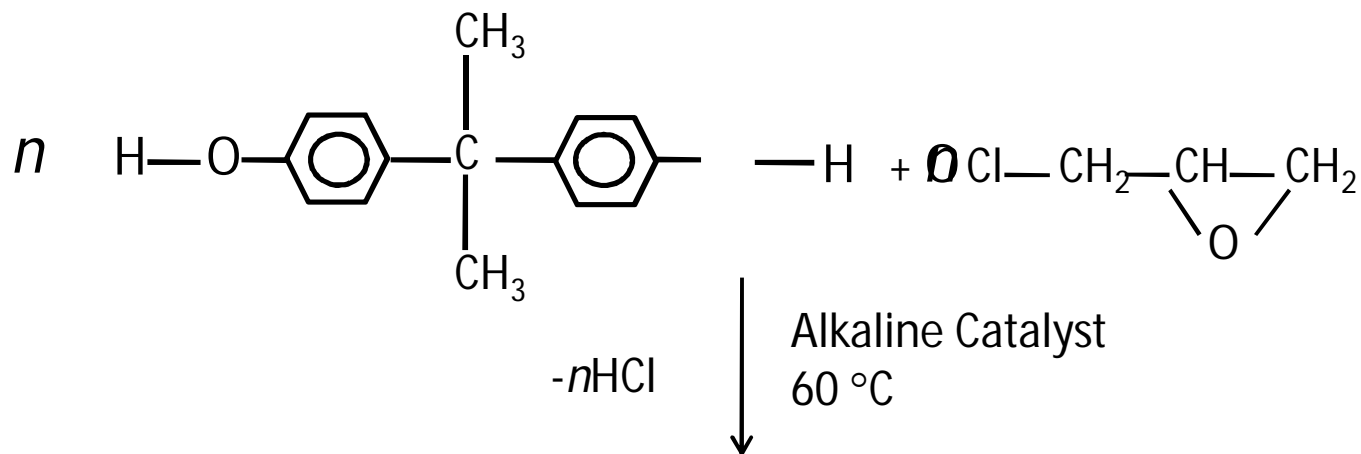
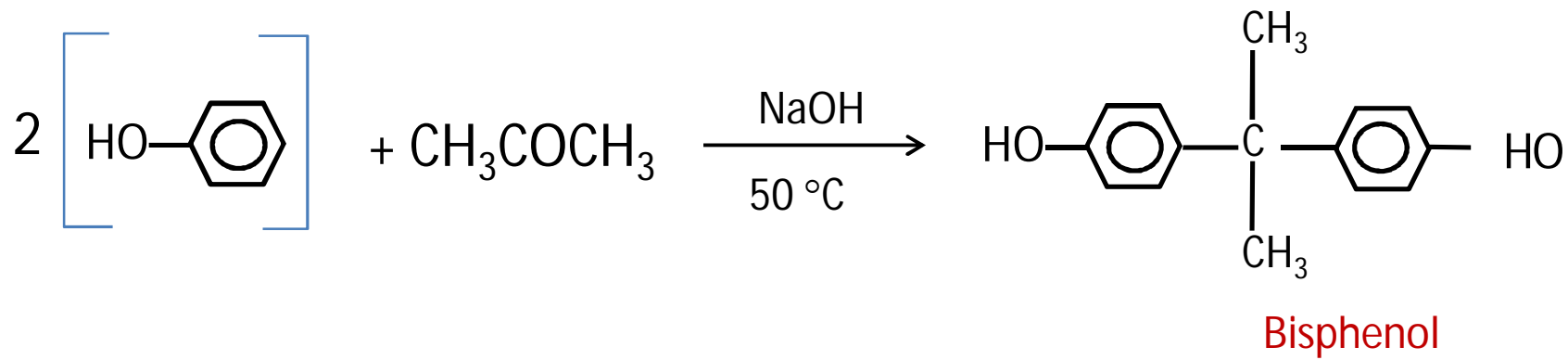
# Epoxy resins

## Synthesis

- ❖ Epoxy resins are synthesized from epichlorohydrin ( an organic epoxide).
- ❖ Epichlorohydrin is a colourless toxic liquid having boiling point 115.2 °C



Bisphenol is prepared by condensation of phenol with acetone



Epoxy Resin

## Properties of epoxy resins

Epoxy resins have high chemical resistance to water, acids, alkalis and other chemicals due to the presence of stable ether linkages.

The reactive groups like epoxide and hydroxyl are widely separated and gives them high flexibility.

The cross linking imparts toughness and heat resistance in cured polymers.

## Applications of epoxy resins

- ❖ Used as adhesives

- ❖ For surface coatings

Used in the production of metal components for aircrafts and automobiles,

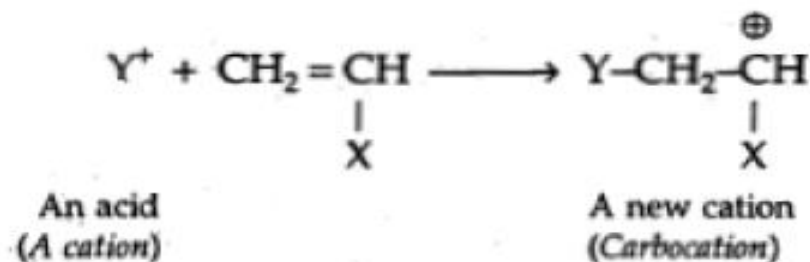
Used as laminating and casting materials.

Used for skid resistant surfaces for highways since it can impart high traction surface under wet and oily conditions, excellent resistance in freezing conditions etc.

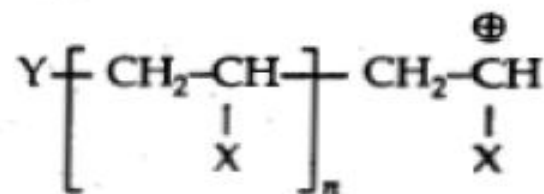
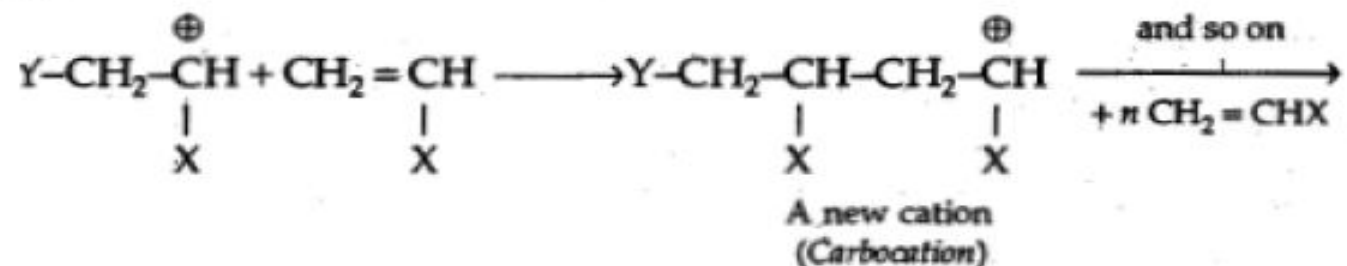
# Mechanism of Cationic Polymerisation

Cationic mechanism of polymerization involves the following steps :

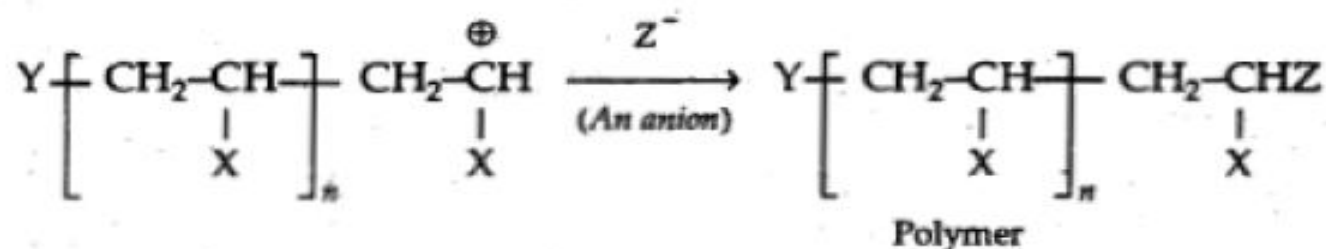
(i) *Initiation* :



(ii) *Propagation* :



(iii) *Termination* :

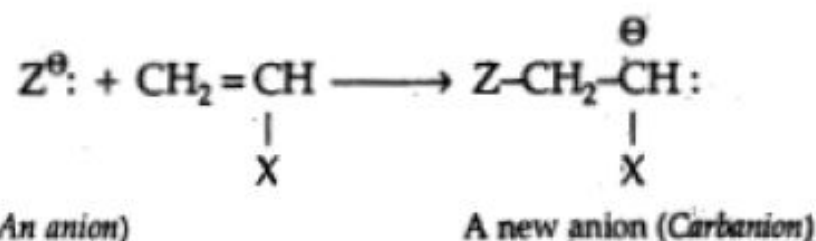




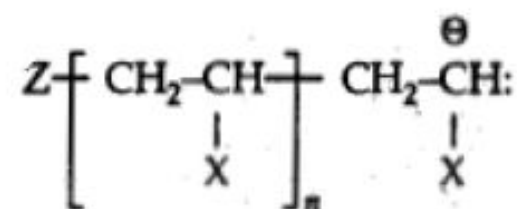
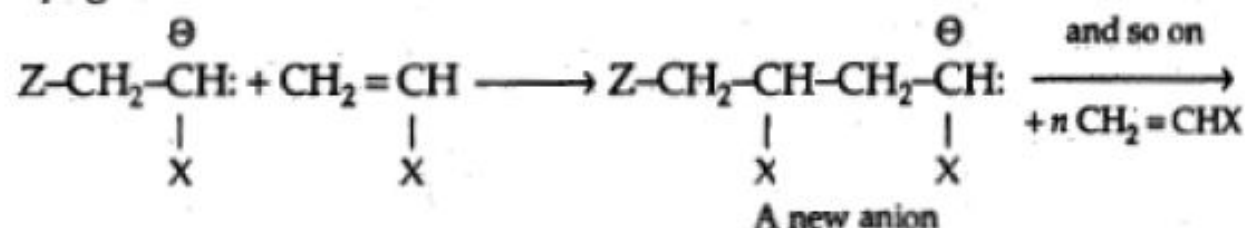
# Mechanism of Anionic Polymerisation

Anionic mechanism of polymerization involves the following steps :

(i) **Initiation :**



(ii) **Propagation :**



(iii) **Termination :**

