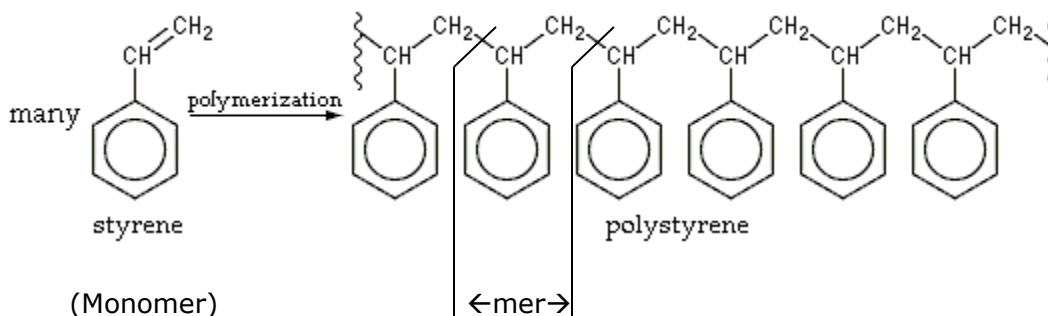


## POLYMERS

**Polymer** : Polymer is a high molecular mass giant molecule formed by linking together of a large number of small molecules of monomers.

Eg : polyethene, Poly styrene, PVC etc.

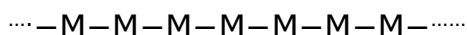
**Monomers** : Small molecules which combine with each other to form polymer molecules are termed as 'monomers'.



**Degree of Polymerisation**: The number of repeating units (n) in chain formed in a polymer is known as the 'degree of polymerisation'. Most of the polymers fall into 5,000 – 2,00,000 molecular mass range.

**Polymerisation**: The process of reacting monomer molecules together in a chemical reaction to form a polymer is known as 'Polymerisation'.

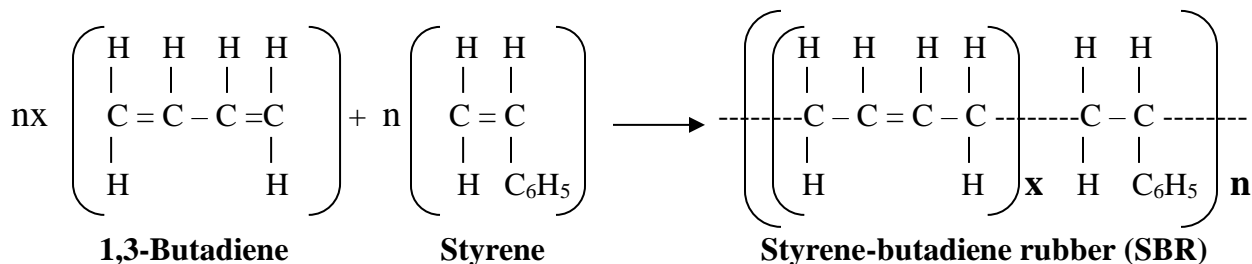
**Homo polymer** : The polymer which consists of identical monomer units are termed as 'homo polymer'



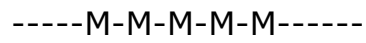
Eg : Polythene, PVC, Poly styrene etc.

**Co-polymer** : The polymer which consists of monomers of different chemical structure is termed as a 'Co polymer'.

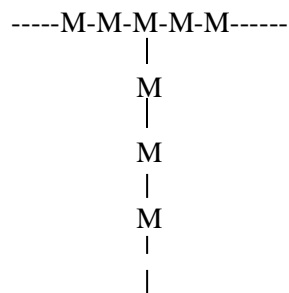
Eg : Buna- S



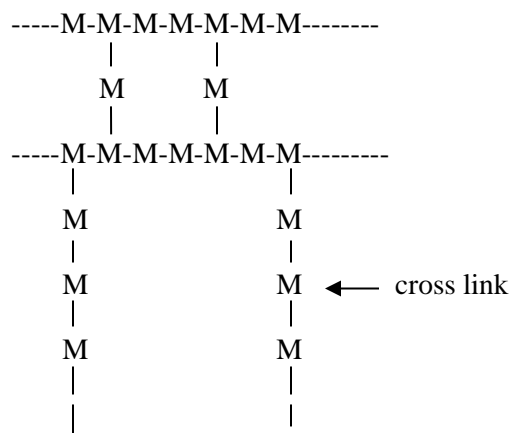
The monomer unit in a polymer may be present in linear, branched or cross-linked structure.



**Linear homopolymer**

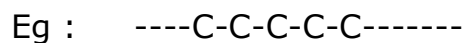


**Branched chain homopolymer**

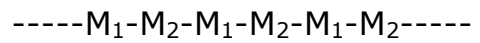
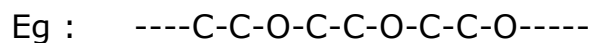


**Cross linked homopolymer**

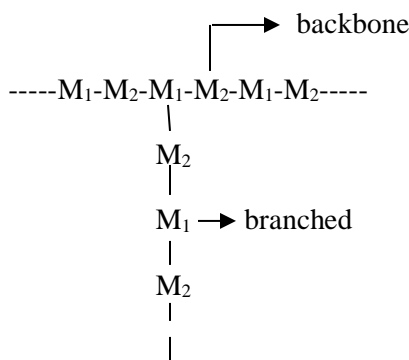
If the main chain is made up of same species of atoms, the polymer is called **'Homo chain polymer'**.



If the main chain is made up of different atoms, then the polymer is called **'Hetero chain polymer'**.

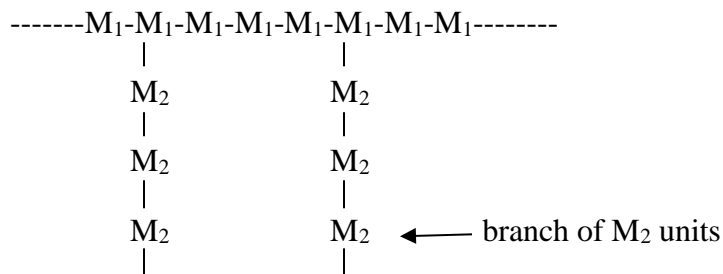


**Linear Copolymer**



**Branched chain Copolymer**

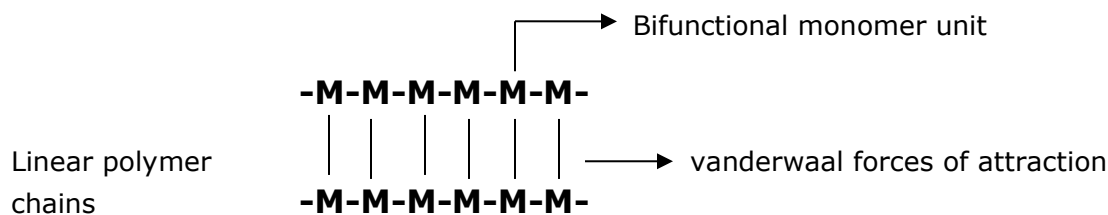
**Graft copolymer :** Graft copolymers are the branched structures in which the monomer segments on the branches and the backbone differ.



Eg : HIPS (High Impact Polystyrene) in which Backbone : Polystyrene & Branched or grafted chain : Polybutadiene

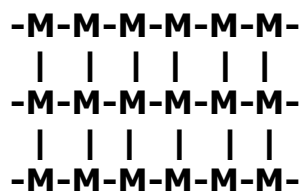
**Functionality of a monomer :** The number of bonding sites or reactive sites present in a monomer is called as its functionality. Every monomer must have minimum two bonding sites for polymerisation process.

**a)** If the functionality of a monomer is two (bifunctional) i.e. two reactive groups attach side by side to each other, linear or straight chain polymers are formed.



eg: Ethylene, styrene, vinyl chloride, adipic acid, hexa methylene diamine, glycol etc.

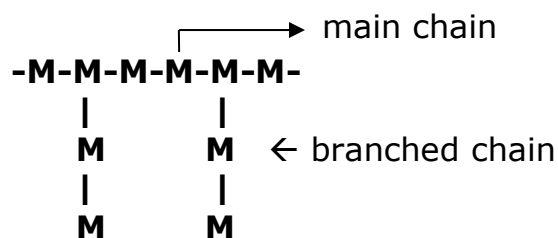
**b)** If the functionality of monomer is three (tri functional), cross linked three dimensional network polymers are formed. The monomeric molecules are joined to each other by covalent bonds and the movement of individual molecules is totally restricted.



eg: Phenol, Melamine, Glycerol etc.

Polymer- Bakelite

c) Mixture of trifunctional monomers in a small amounts of a bifunctional monomers give branched chain polymers.



**TACTICITY:** The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain. This difference in the configuration is known as 'Tacticity'.

### **THERMO PLASTIC POLYMERS:**

These are linear, long chain polymers, which can be softened on heating & hardened on cooling reversibly. Repeated heating & cooling do not alter the chemical nature of these materials. These plastics are formed as a result of addition polymerization

Eg: PVC, PVA, Polystyrene etc

### **THERMO SETTING RESINS**

These are the resins which, during molding process (by heating etc) get hardened and once they have solidified, they cannot be softened i.e. they are permanent setting resins. These are formed as a result of three – dimensional cross – linked structure with strong covalent bonds. These bonds retain their strength, even on heating & on over heating they become charred. These are formed by condensation polymerization.

Eg: Bakelite, Terylene etc

#### **Thermo plastics**

1. These are formed by addition polymerization.
2. These consist of long – chain linear polymers.

#### **Thermo setting resins**

These are formed by condensation polymerization.

These have a three dimensional Cross – linked structure.

- |   |  |
|---|--|
| 3. They soften on heating                             | They do not soften on heating & Charring takes place on prolonged heating. |
| 4. They can be softened, reshaped & reused by heating | They cannot be reshaped & reused by heating.                               |
| 5. They are soft, weak and less brittle.              | They are hard, strong and more Brittle                                     |
| 6. These can be reclaimed from waste                  | These cannot be reclaimed from Wastes                                      |
| 7. They are soluble in some organic solvents          | They are insoluble in almost all Organic solvents.                         |

### **CLASSIFICATION OF POLYMERS:**

Polymers can be classified in many ways.

#### 1. **Classification on the basis of their source:-**

Depending upon the source, polymers are divided into two types.

- Natural polymers:** Polymers which are isolated from Natural materials are called 'Natural Polymers.' Eg: Cotton, Silk, Wool, Natural rubber etc.
- Synthetic polymers:** Polymers which are prepared from low molecular weight compounds are called 'Synthetic Polymers'. Eg: Polythene, PVC, Nylon etc

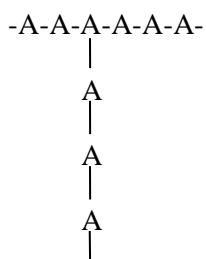
**2. Basing on chemical structure:** Basing on chemical structure polymers (both homo & co-polymers) are classified into 3 types namely linear, branched & cross linked.

#### **Homo polymers**

##### a. **Linear:**



##### b. **Branched:**

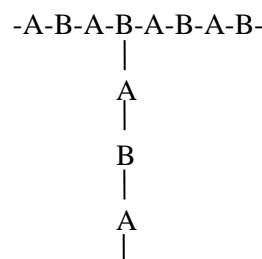


#### **Co polymers**

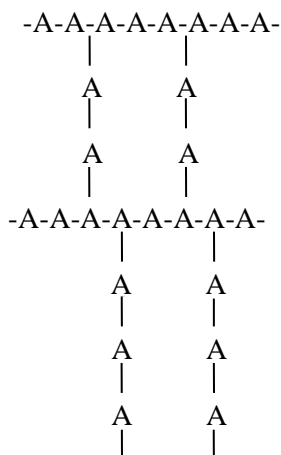
##### a. **Linear:**



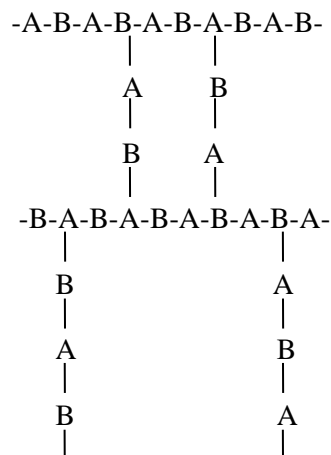
##### b. **Branched:**



c. Cross linked:



c. Cross linked:



### 3. Basing on the Method of synthesis:

They can be classified into two types:

- Addition Polymers:** The polymers which are formed by the addition of smaller molecules without leaving simple molecules are called 'addition polymers'.  
Eg: Polystyrene, polythene, PVC etc
- Condensation polymers:** The polymers which are formed by the addition of smaller molecules with the elimination of simple molecules like H<sub>2</sub>O, HCl, Methanol etc are called 'condensation Polymers'.  
Eg; Polyesters, Nylon 6:6 etc

### 4. Basing on the Nature of Backbone Chain:

Basing on the nature of Backbone Chain, Polymers are classified into two types:

- Organic polymers:** The polymers whose backbone chain is made up of carbon compounds are called 'Organic Polymers'.  
Eg; Polythene, PVC, Nylon 6:6 etc
- Inorganic polymers:** The polymers whose backbone chain is made up of compounds other than carbon compounds are called 'Inorganic polymers'.  
Eg: Polygermanium, Silicone polymers etc.

### 5. Basing on the molecular forces:

On the Basis of the magnitude of intermolecular forces present in polymers, they are classified into four categories:

a. **Thermo Plastic Polymers:** These are linear, long chain polymers, which can be softened on heating & hardened on cooling. Their hardness is a temporary property.

Eg: Polyethylene, PVC, Nylon etc

b. **Thermosetting Polymers:** The polymers which change irreversibly into hard and rigid materials on heating are called 'Thermo setting Polymers'.

Eg; Bakelite, epoxy resins (araldite), Polyester (Terylene) etc

c. **Elastomers (Rubbers):** The polymers which show good strength and elongate on stretching are called 'Elastomers'.

Eg: Synthetic rubbers like Buna-S, Buna-N etc

Natural rubbers like poly isoprene etc

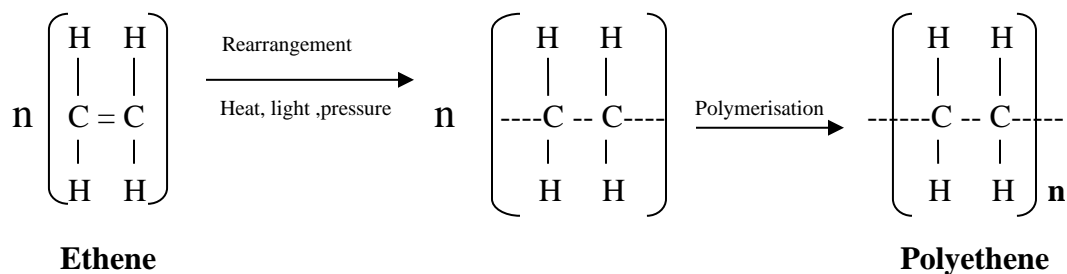
d. **Fibers:** The polymers which can be drawn into filament like materials are called 'fibers'. In this, the chains are held by strong intermolecular forces like hydrogen bonding.

Eg: Nylon 6:6, Polyester etc.

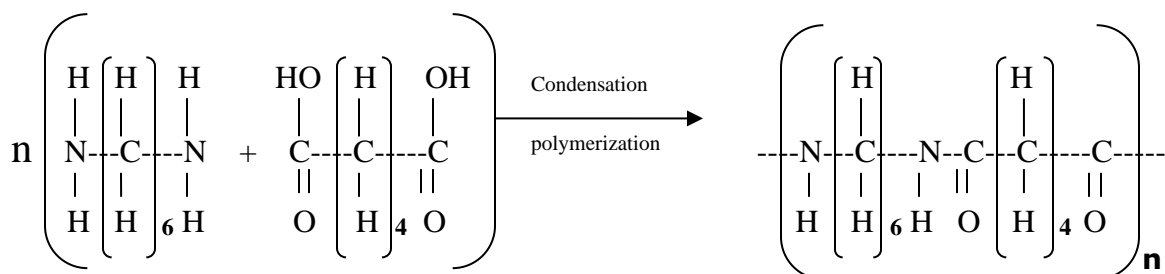
**Polymerisation :** The process of reacting monomer molecules together in a chemical reaction to form a polymer is known as 'Polymerisation' .

### **Types of Polymerisation:**

i) **Addition or Chain Polymerisation:** It is a reaction that yields a product, which is an exact multiple of the original monomer molecule. Such a monomer contains one or more double bonds, which by intermolecular rearrangement, may make the molecule bi functional. It is formed by the application of heat, light, pressure or catalyst.



**ii) Condensation or Step Polymerisation :** It is a reaction occurring between simple polar group containing monomers with the formation of polymer and elimination of small molecules like water, HCl etc. **Eg: Nylon 6:6**



**Hexamethylene  
diamine**

**Adipic acid**

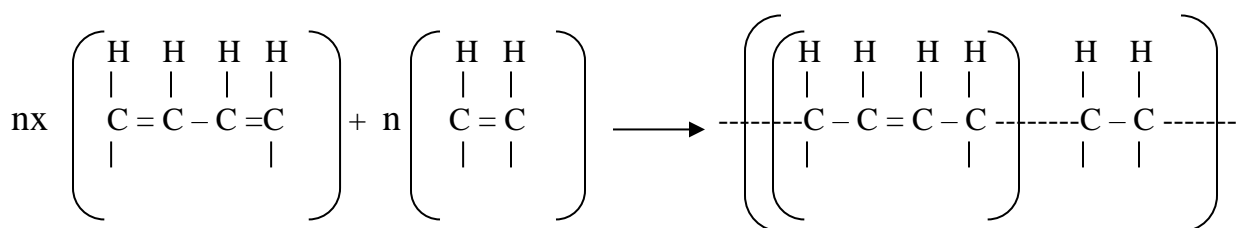
**Nylon 6:6**

The condensation polymerization is an inter molecular combination, and it takes place through the different functional groups (in the monomers) having affinity for each other. When monomers contain three functional groups, it forms a cross-linked structure polymer.

<u>1<sup>st</sup></u>	<u>2<sup>nd</sup></u>	<u>product</u>	<u>example</u>
<b>Hydroxyl</b> -OH	<b>Carboxyl</b> -COOH	<b>Polyester</b> -OOC-	<b>Polyethylene terephthalate</b> ( <b>Terylene</b> )
<b>Amino</b> -NH <sub>2</sub>	<b>Carboxyl</b> -COOH	<b>Polyamide</b> -NH-CO-	<b>Nylon-6:6</b>
<b>Hydroxyl</b> -OH	<b>Isocyanate</b> OCN-	<b>Polyurethane</b> -OC-NH-	<b>Spandex Fibre</b>

**iii) Co-Polymerisation :** It is the joint polymerization of two or more monomer species. High molecular weight compounds obtained by co-polymerisation, are called 'Co-polymers'

**Eg :** Buna- S







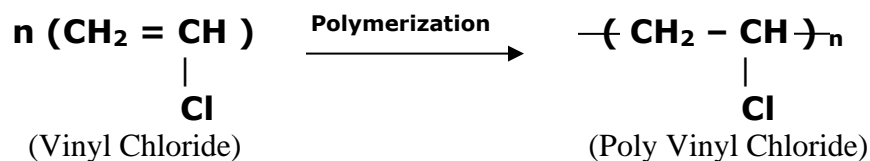
## PLASTICS

Organic materials of high molecular weight which can be molded into any desired shape when subjected to heat and pressure in the presence of a catalyst are called 'Plastics'.

### POLY VINYL CHLORIDE (PVC) :

#### Preparation:

Poly vinyl chloride (PVC) is obtained by heating a water emulsion of Vinyl chloride in presence of benzoyl peroxide or  $\text{H}_2\text{O}_2$  in an auto clave under pressure.



The PVC so obtained is Rigid PVC (unplasticized). It can be softened by adding plasticizers & can be called as 'Plasticized PVC'.

#### Properties of Rigid PVC :

- 1) Rigid PVC is a colourless, odourless and non-inflammable.
- 2) It has excellent oil resistance and resistance to weathering.
- 3) Due to the presence of 'Cl' atoms, hardness and stiffness of the polymer increases.
- 4) It has high chemical resistance, but soluble in ethyl chloride & THF.

#### Uses of Rigid PVC :

- 1) Due to chemical resistance, it can be used as tank linings in acid plants.
- 2) Due to resistance to weathering, it is used in building industry.
- 3) It is also used in making pipes, window frames, edible oil containers, mineral water bottles, safety helmets, mudguards for vehicles etc.

**Plasticized PVC :** Addition of plasticizers like DOP (di octyl phthalate), di butyl phthalate, tri cresyl phosphate etc. to rigid PVC gives plasticized PVC.

Properties of plasticized PVC :

- 1) It is very good insulator for DC & low frequency AC current
- 2) It is flexible and show water proof nature.

Uses of Rigid PVC : It is used for making

- 1) Leather cloth used for car seat, covers etc
- 2) Kitchen upholstery, ladies hand bags, plastic rain coats
- 3) Baby pants, swim suits etc.

**RESINS**

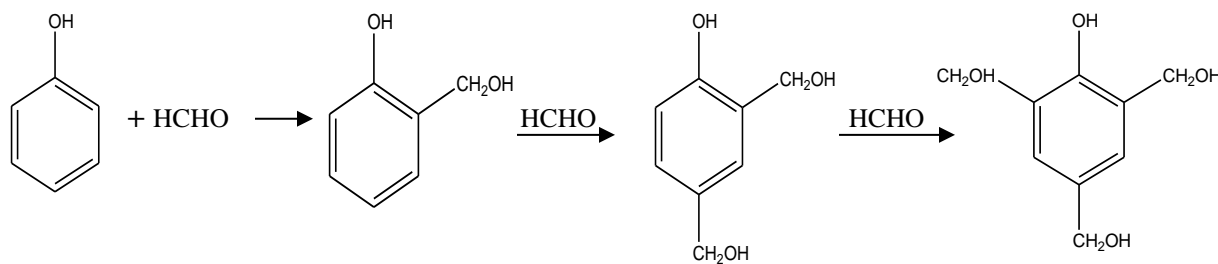
Resins are the basic binding materials, which form a major part of plastics, and which actually has undergone polymerization and condensation reactions, during their preparation.

**BAKELITE:**

It is a thermosetting resin obtained by condensation polymerization of phenol & formaldehyde. These are also called as phenol-formaldehyde resins.

**Preparation:** Preparation of Bakelite involves the following steps.

**Step 1.** Phenol & Formaldehyde react with each other to form methylol derivatives which act as monomers for polymerization.



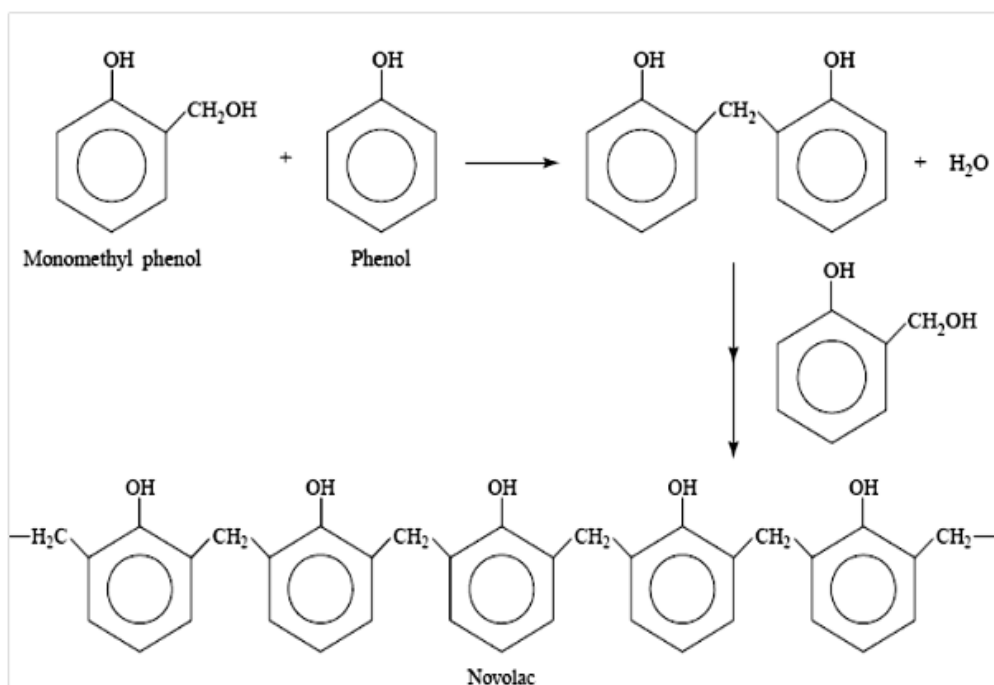
Phenol

Mono Methylol  
Phenol

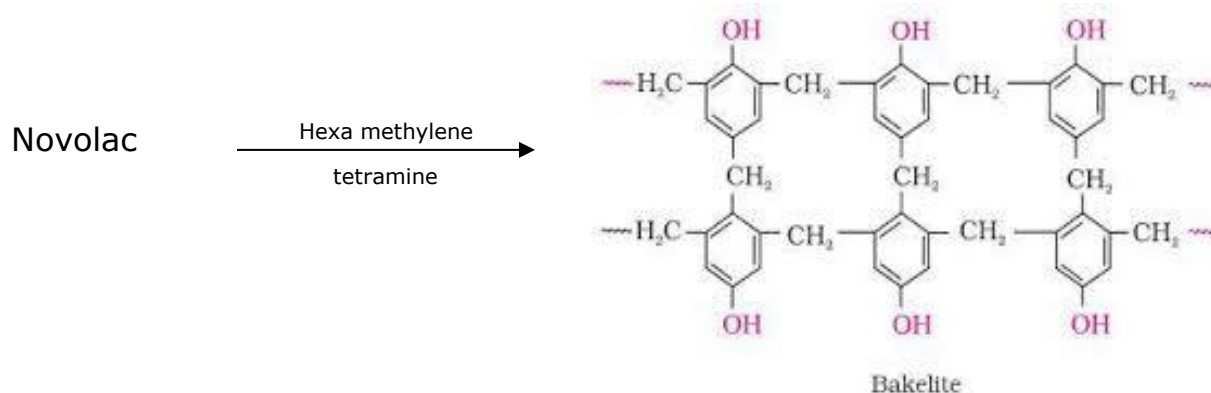
Di Methylol Phenol

Tri Methylol Phenol

**Step :2** Condensation polymerization of phenol (excess) & Formaldehyde in the presence of an acid catalyst gives low molecular weight linear polymer called 'NOVOLAC'. It is fusible & soluble in solvents.



**Step :3** On further heating of NOVOLAC in the presence of hexa methylene tetramine  $\{(CH_2)_6 N_4\}$  produces 3-d cross linked network polymers called 'Bakelite'. It is a hard, rigid and infusible solid.



### **Properties :**

1. Bakelite is hard, rigid and strong material.
2. Phenol formaldehyde resins are heat and moisture resistant.
3. They have good chemical resistance.
4. They have good electrical insulation characteristics

5. Low molecular weight Phenol-formaldehyde resins have excellent bonding strength and adhesive properties.

**Uses :** These are used for preparing

1. Domestic switches & Plugs
2. Handles for cookers & sauce pans
3. Adhesives for grinding wheels & brake linings
4. For preparing ion exchange resins
5. Novolac is used for preparing varnishes, electrical insulation and protective coatings.
6. For impregnating fabrics, wood and paper.

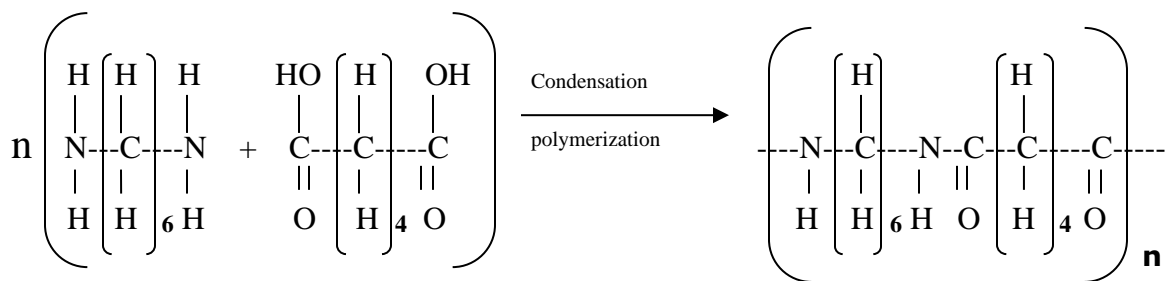
### **FIBERS**

The polymers which can be drawn into filament like materials are called 'fibers'. In the fibers, the polymeric chains are held by strong intermolecular forces like hydrogen bonding.

Eg: Nylon, Polyester etc

### **NYLON-6:6 :**

It is prepared by the condensation polymerization of hexamethylene diamine with adipic acid



**Hexamethylene  
diamine**

**Adipic acid**

**Nylon 6:6**

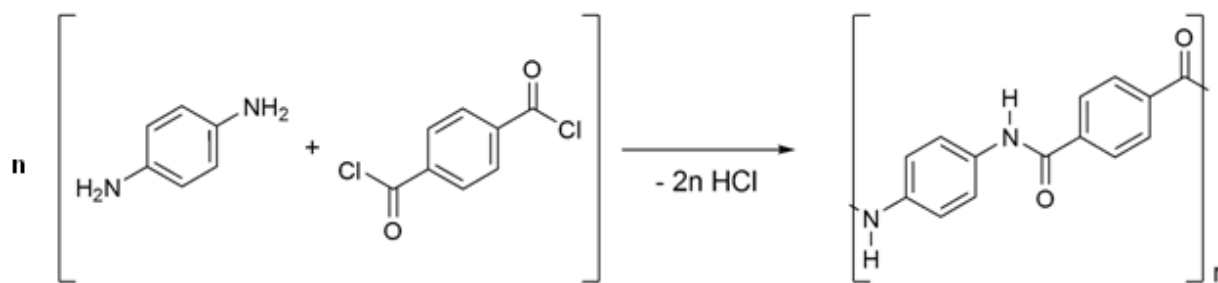
**Properties :** They are translucent, whitish, horny, high melting (160-264°C) polymers. They are resistance to high temperature and abrasion. They are insoluble in benzene and acetone and soluble in phenol, formic acid etc. They have good strength and absorb little moisture.

**Uses of Nylons** : Nylon 6:6 is used for making socks, dresses, carpets etc. It is also used in making gears, bearings, bushes etc. It is used for jacketing electrical ware and protect the electrical insulation.

**KEVLAR** :

It is an aromatic polyamide having benzene rings linked to the amide groups  $-\text{CONH}-$ .

**Preparation** : It is prepared by the condensation polymerization of terephthalic acid dichloride and 1,4-diamino benzene.



1,4-diamino benzene

Terephthalic acid dichloride

Kevlar

**Properties:** Kevlar is exceptionally strong (5 times stronger than steel & 10 times stronger than Al). It has high heat stability and flexibility. The unique properties of Kevlar are due to the benzene rings are linked to the amide linkage & therefore Kevlar is very rigid polymer. As it is an aromatic polyamide, it is also known as 'aramid Polymer'. There are stronger inter molecular forces between neighboring chains, which make it exceptionally strong.

**Applications:** Kevlar has the following potential uses:

- Tyres, brakes, clutch lining and other car parts,
- Bullet proof vests,
- Motor cycle helmets,
- Aerospace and air-craft industries.

**RUBBERS (or) ELASTOMERS** :

Polymers which show good strength and elongate on stretching are called 'Elastomers'.

Eg: Natural & Synthetic rubbers.

**Natural rubber** is obtained from the exudates sample from the bark of the rubber trees like Hevea Brasiliensis, Gauyule etc. These exudates called Latex are processed to get Crude rubber.

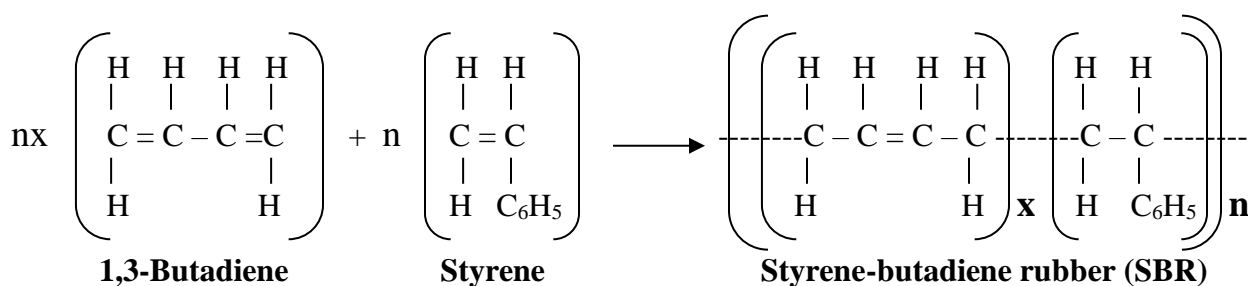
### **SYNTHETIC RUBBERS:**

Any Vulcanisable manmade rubber like polymer which can be stretched to at least twice its length but retains its original shape and dimension as soon as the stretching force is removed is called as 'Synthetic rubber' (or) 'artificial rubber'.

Eg: Buna-S, Buna-N, Butyl rubber, Thiokol etc

### **Buna –S (or) GR – S (or) Styrene Butadiene Rubber:**

**Preparation:** Co – polymerization of Butadiene (75%) and styrene (25%) in the presence of cumene hydro peroxide catalyst gives polystyrene – butadiene rubber.



Since SBR contain double bonds, Vulcanization can be done in the same way as natural rubber either by adding Sulphur (or) Sulphur mono chloride. ( $\text{S}_2\text{Cl}_2$ )

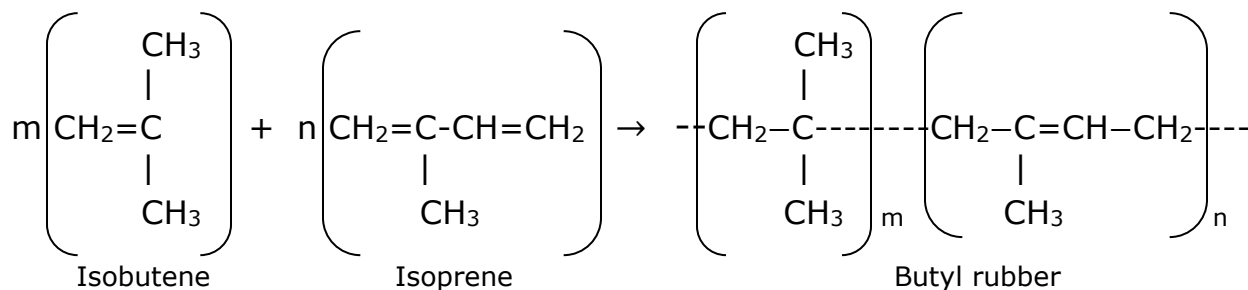
**Properties:** SBR has the following characteristics:

1. High abrasion resistance
2. High load bearing capacity
3. Resilience
4. Swells in oils & solvents
5. Low oxidation resistance i.e. readily gets oxidized, especially in the presence of traces of Ozone in atmosphere.

**Applications:** It is used in the manufacturing of (1) Motor tyres (2) Shoe soles (3) Footwear components (4) Wire & cable insulation (5) carpet backing (6) Adhesives (7) Gaskets (8) Tank lining etc.

## **BUTYL RUBBER or GR-I or Poly Isobutene :**

**Preparation:** Co-Polymerization of isobutene with small amounts of Isoprene (1 to 5%) gives Butyl rubber.



## **Properties :**

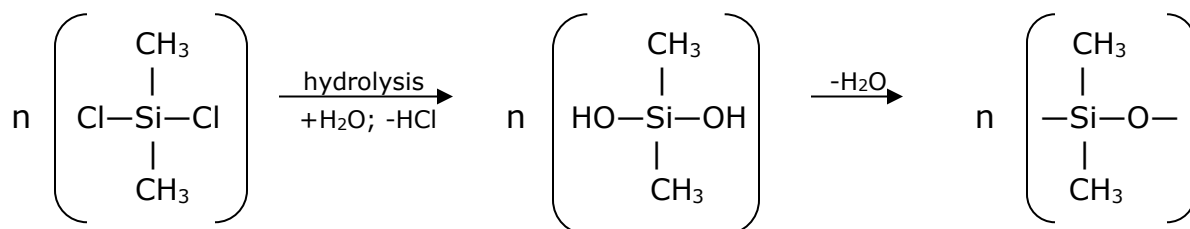
- 1) It has low permeability to air & other gases
- 2) It has excellent resistance to heat, abrasion, chemicals etc.
- 3) It is insoluble in polar solvents but soluble in hydrocarbons like benzene.
- 4) It has resistance to ozone & has good electrical insulating properties.
- 5) It can be vulcanized, but cannot be hardened much due to low unsaturation.

## **Uses :**

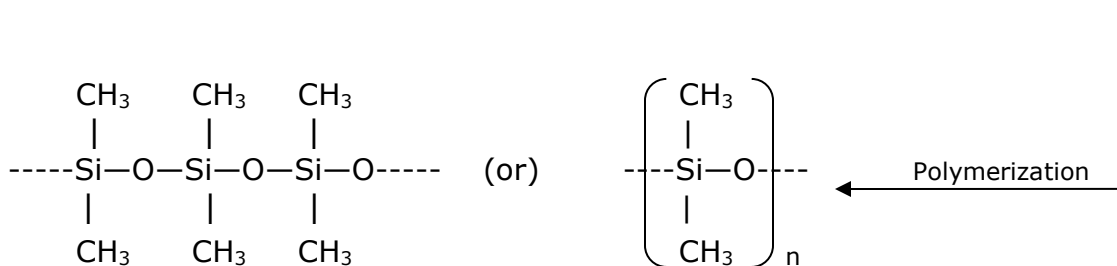
It is used for making cycle, automobile tubes, automobile parts, hoses, conveyer belts for food, in lining of tanks hoses, insulation for high voltage wires & cables etc.

## **SILICONE RUBBERS:**

Silicone rubbers are obtained by the polymerization of di-methyl silicone hydroxide or cyclic Siloxane in to polymer poly Siloxane.

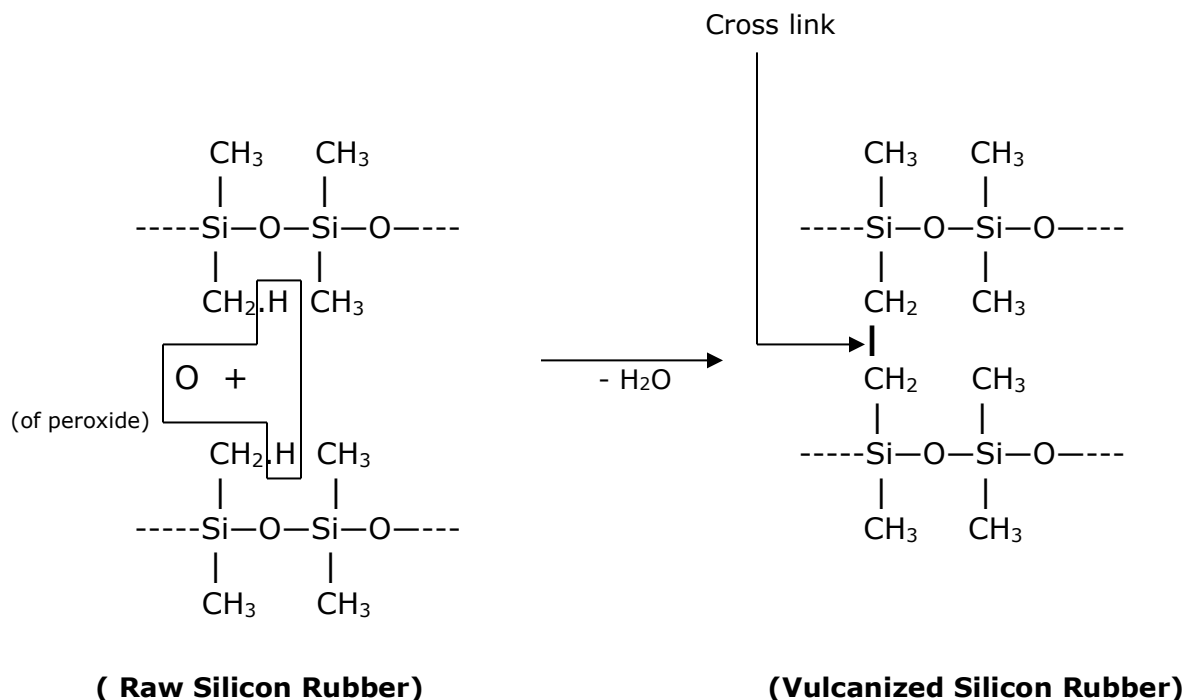


**Dimethyl silicon di chloride** ( Unstable ) **Di hydroxy dimethyl silicone** ( Unstable )



Inter – chain forces in these polymers is extremely weak, so the gum tensile strength of the rubber is very low and can be increased by adding fine Silica Powder.

Due to the un-saturated character, the polymer can be vulcanized by organic peroxides to form cross links between two adjacent chains. Peroxides remove some of the hydrogen atoms from the group on the Silicon atoms and thus allow the carbon atoms of two adjacent chains to couple and form cross links.



**Properties**

1. They possesses excellent resistance to prolonged exposure to sun light, weathering, boiling water, common oils, dilute acids and alkalis.



2. They remain flexible in the temperature range of 90 – 250°C
3. At very high temperature, silicon rubber leaves behind non – conducting silica (SiO<sub>2</sub>) instead of carbon tar.
4. They are resistant to air and ozone over the temperature range of -100 to 500° F.

### **Uses:**

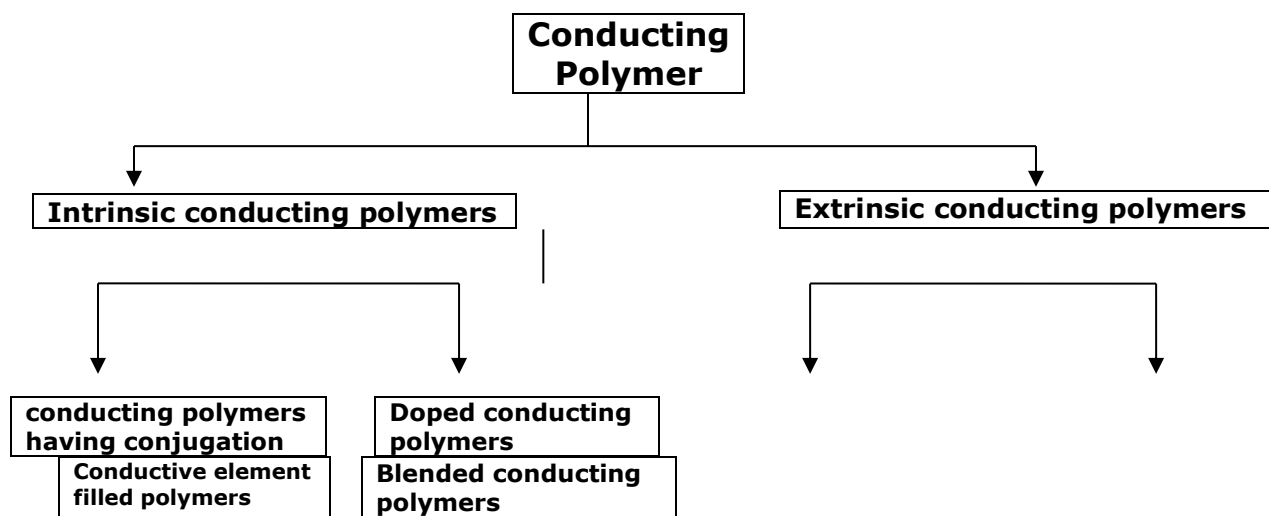
1. They are useful in making tyres for fighter aircrafts as they prevent damage on landing.
2. They are used as sealing materials in search lights & in aircraft engines.
3. For insulating the electrical wiring in ships
4. In making lubricants, paints & protective coatings for fabric finishing and water proofing
5. As adhesive in electronic industry
6. For making boots for use at very low temperature.

## **CONDUCTING POLYMERS**

**Conducting Polymer :** A polymer which can conduct electricity is called as a 'Conducting Polymer' .

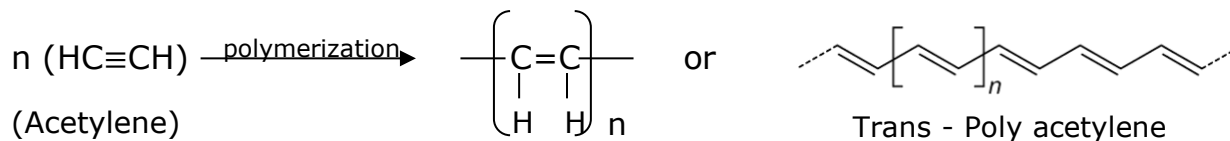
In general, conductivities of polymers are very low ( $10^{-9}$  to  $10^{-17}$  ohm<sup>-1</sup>m<sup>-1</sup>). Later conducting polymers are synthesized, their conductivities are high ( $1.5 \times 10^7$  ohm<sup>-1</sup> m<sup>-1</sup>).

Conducting polymers can be classified in the following way,



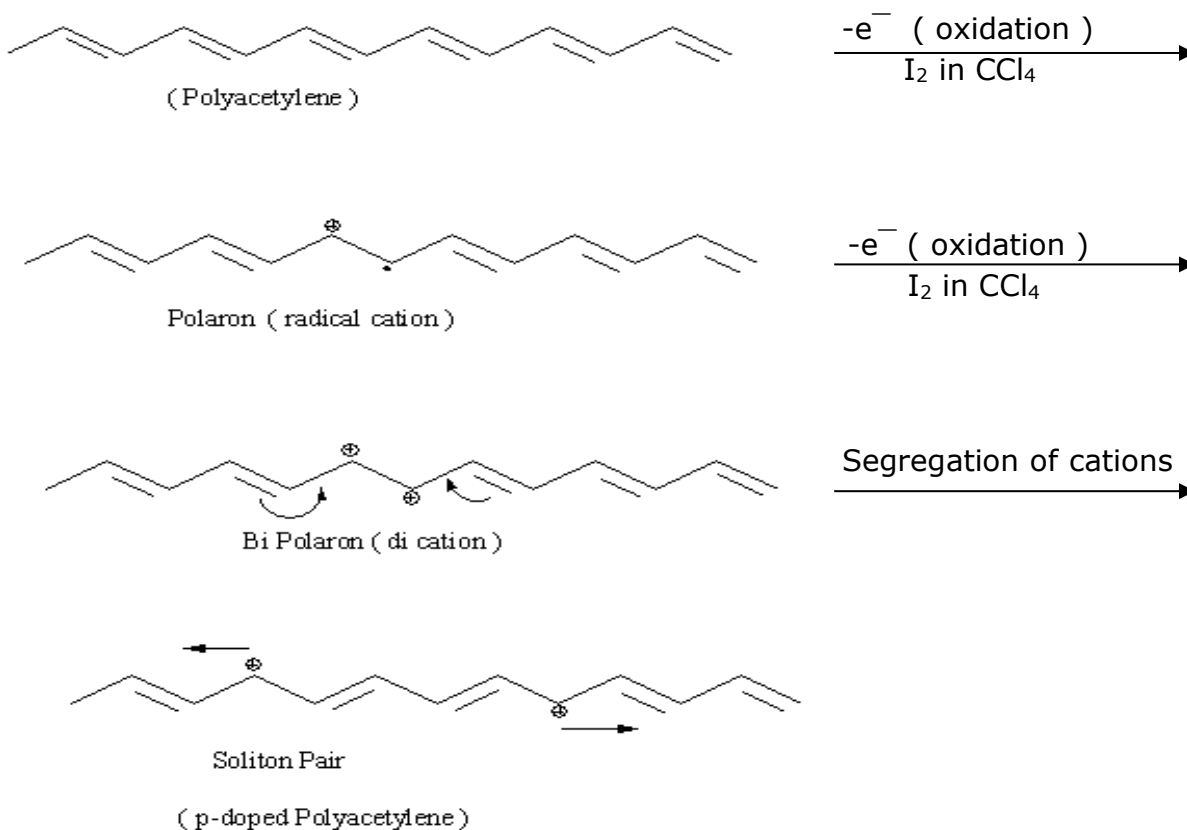
## POLYACETYLENE

Acetylene on polymerization forms Polyacetylene.



p-doping or Oxidative doping : In this process, pi-backbone of a polymer is partially oxidized using a suitable oxidizing agent. This creates positively charged sites on polymer backbone, which are current carriers for conduction. The oxidizing agents used in p-doping are  $\text{I}_2$ ,  $\text{I}_2$  in  $\text{CCl}_4$ ,  $\text{HBF}_4$ ,  $\text{HClO}_4$ , benzoquinone etc.

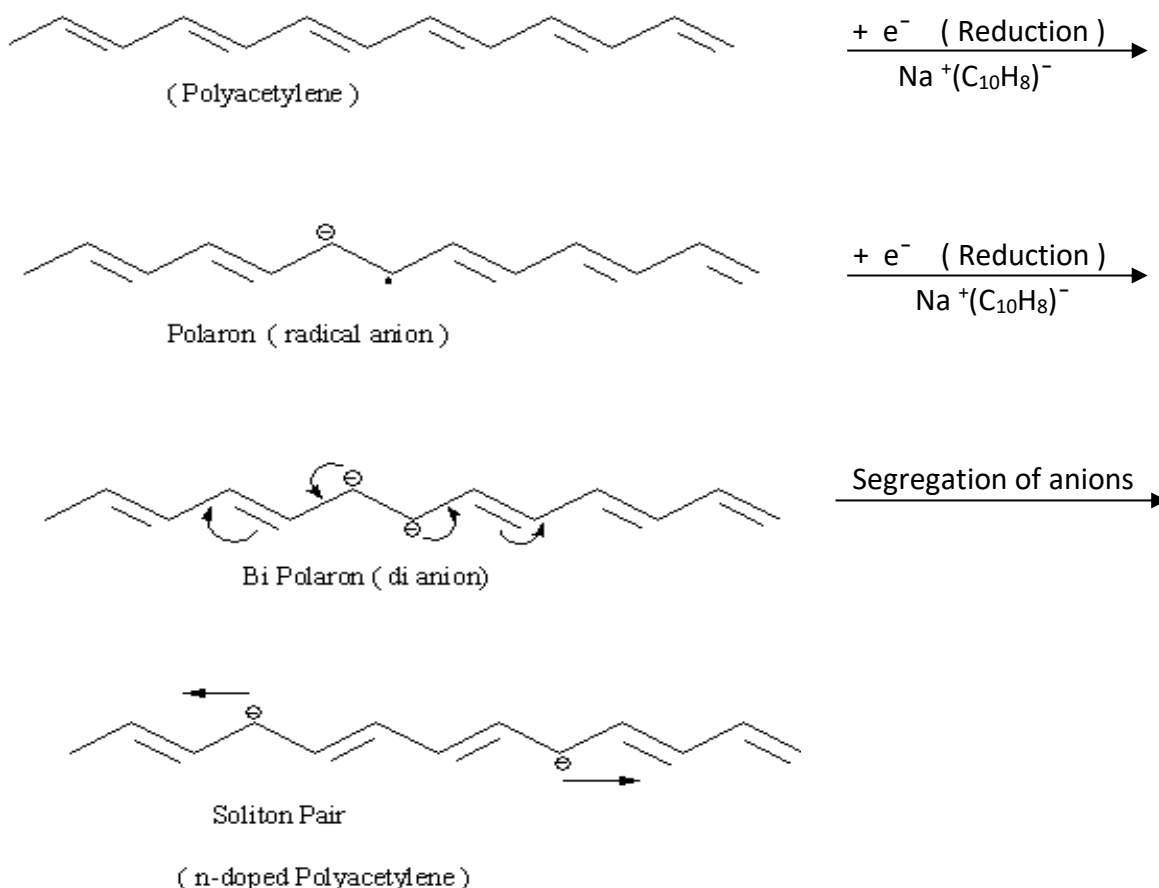
Mechanism of conduction in p-doping : The removal of an electron from the polymer pi-backbone using a suitable oxidizing agents leads to the formation of delocalized radical ion called 'Polaron'.



A second oxidation of a chain containing polaron, followed by radical recombination yields two charge carriers on each chain which are mobile. Thus these delocalized positive charges are current carriers for conduction. These charges must move from chain to chain as well as along the chain for bulk conduction. On doping polyacetylene using  $I_2$  in  $CCl_4$  for partial oxidation, the conductivity increases from  $10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$  to  $10^3\text{-}10^5 \text{ ohm}^{-1} \text{ cm}^{-1}$ .

n-doping or reductive doping : In n-doping , pi-backbone of a polymer is partially reduced by a suitable reducing agent. This creates negatively charged sites on polymer back bone. These negatively charged sites are responsible for the conduction. The most commonly used reducing agent for partial reduction of polymer back bone is a solution of Sodium Naphthalide in tetra hydro furan.

Mechanism of conduction in n-doping : The addition of electron to the polymer back bone by using a reducing agent generates a radical ion or polaron. A second reduction of chain containing polaron, followed by the recombination of the radicals yield two negative charge carriers on each chain of the polyacetylene which are responsible for conduction.



**Applications of Conducting polymers :** Conducting polymers are used

- 1) As electrode material for commercial rechargeable batteries, (coin type).
- 2) As Sensors-humidity sensors, gas sensors, radiation sensor, biosensor for glucose, galactose etc.
- 3) In electro chromic displays and optical filters (windows with adjustable transparency)
- 4) In wiring in aircrafts & aerospace components
- 5) As film membranes for gas separations
- 6) In fuel cells as the electro catalytic materials
- 7) In telecommunication systems
- 8) In photo voltaic devices {eg: **Al** | **conducting polymer** | **Au** photovoltaic cells}
- 9) In Solar cells etc.

### **BIODEGRADABLE POLYMERS**

Biodegradable polymers are the polymers which has the ability of being chemically transformed by the action of biological enzymes or micro organisms into products which themselves are capable of further biodegradation to produce biomass and CO<sub>2</sub>.

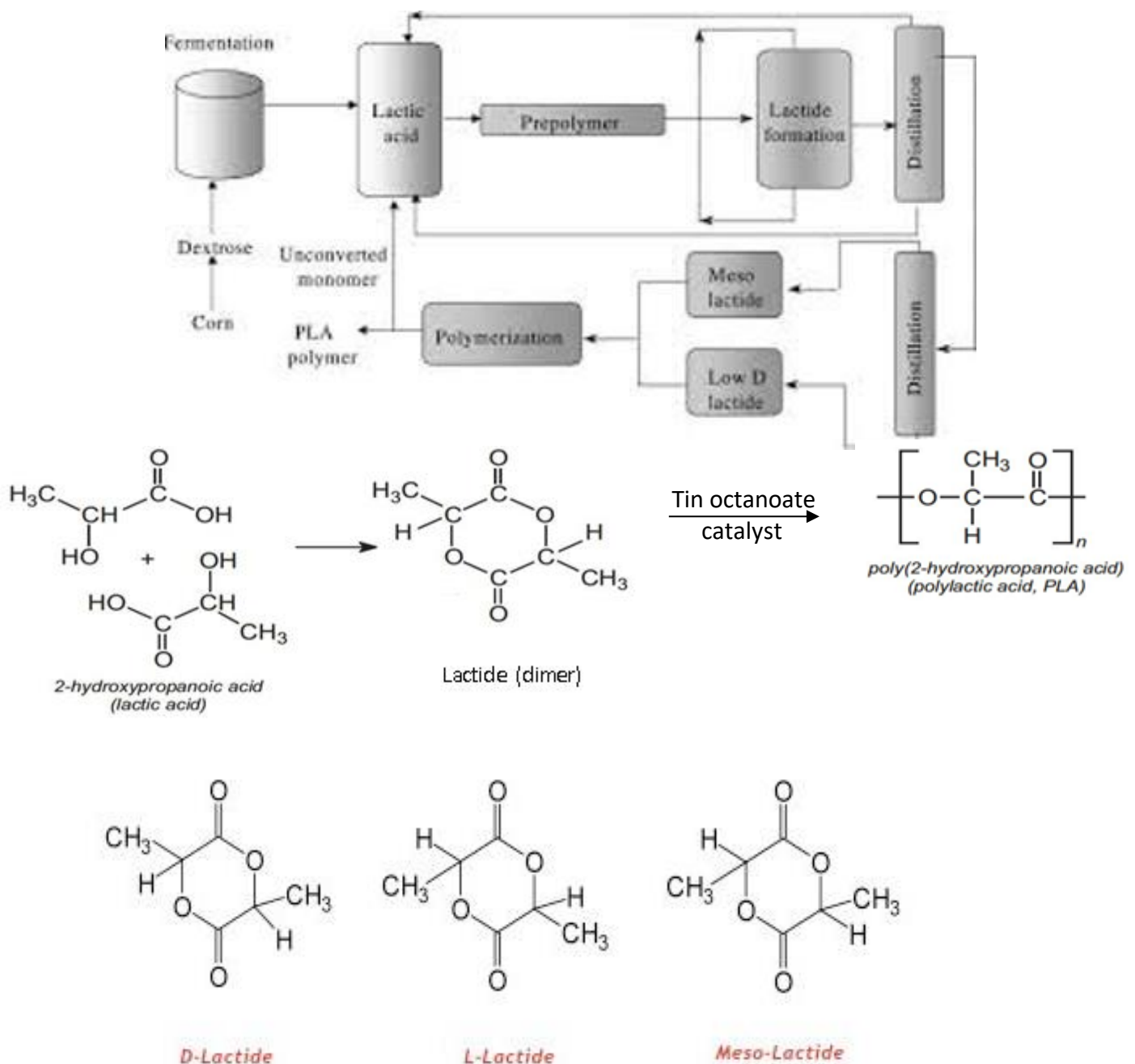
Biodegradable polymers are classified into 2 types:

- i) **Natural biodegradable polymers :** The polymers which are naturally occurred & undergo biodegradation to produce environmentally friendly products, such polymers are known as `Natural biodegradable polymers `.  
**Eg :** Cellulose, Starch, Casein etc.
- ii) **Synthetic biodegradable polymers :** The polymers which are manmade & undergo biodegradation to produce environmentally friendly products, such polymers are known as ` Synthetic biodegradable polymers `.  
**Eg:** Poly glycoside, polylactide, poly amino-triazole etc.

### **POLY LACTIC ACID :**

Poly lactic acid is biodegradable thermo plastic aliphatic polyester derived from lactic acid.

Lactic acid is produced by the fermentation of dextrose (from corn starch or cane sugar) followed by the continuous condensation reaction of aqueous lactic acid to produce low molecular weight PLA pre polymer. Next, the low molecular weight oligomers are converted into a mixture of lactide stereo isomers using a catalyst to enhance the rate & selectivity of intra molecular crystallization reactions. The molten lactide mixture is then purified by vacuum distillation. Finally, PLA high polymer is produced using tin octanoate {Sn(oct)<sub>2</sub>} catalyst, ring opening polymerization in the melt, completely eliminating the use of costly and environmentally unfriendly solvents. After the polymerization is complete, any remaining monomer is removed under vacuum & recycled to the beginning of the process.



**Properties :**

- 1) PLA is insoluble in water. It is moisture and grease resistant.
- 2) It is biodegradable and compostable.
- 3) Requires 20% to 50% less fossil fuels to produce.
- 4) Poly L-lactic acid and poly D-lactic acid also exist.
- 5) It can be processed into a fibre & film.
- 6) Melting point is 40-50°C and it can be increased by blending with PDLA.

**Applications :**

- 1) Disposable plates, cups, film wraps etc.
- 2) Plastic bottling and fast food companies (eg: Micro wovable trays)
- 3) Textile Industry (eg: Woven shirts)
- 4) Paper coatings, clothing fibres, compost bags etc.
- 5) Bio medical purposes such as sutures, drug delivery devices, fractured bone fixation, tissue engineering etc.
- 6) Used as anti microbial food packing purposes etc.
- 7) Disposable table ware diapers.