

# POLYMERIC MATERIALS

## INTRODUCTION

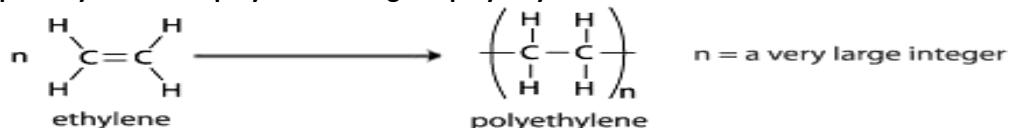
Polymers are the giant molecules produced by the combination of smaller units or molecules. Polymers possess the desirable properties like high strength, light weight, good flexibility, special electrical properties, resistance to chemicals, amenability for quick and mass production and fabrication into complex shapes in a wide variety of colours.

## BASIC CONCEPTS

The word polymer is derived from the Greek words polu- meaning "many"; and meros meaning "part". The term was coined in 1833 by Joens Jakob Berzelius.

Many of small molecules (monomers) combine (with covalent bond chains) to form giant molecule(s). This process is called polymerization. During the polymerization process, some chemical groups may be lost from each monomer.

For example ethylene under polymerization gives polyethylene.



- Write a note on degree of polymerization.

Degree of polymerization:

- ❖ It is defined as the number of monomers units in a homo polymer.
- ❖ Most of the polymers are in the molecular mass range of 5,000 – 2, 00,000.
- ❖ But incase of hetero polymer, degree of polymerization (D.P) is defined as the ratio of total molecular weight of a polymer to molecular weight of each repeating unit.
- ❖ In the above equation, 'n' is the degree of polymerization.

$$D_p = \frac{\text{Total Molecular Weight of the Polymer}}{\text{Molecular Weight of Monomeric Unit}} = \frac{M_n}{M_o}$$

$$M_n = M_o \cdot D_p$$

$$M_n = \text{Total molecular weight of the polymer}$$

$$M_o = \text{Molecular weight of monomeric unit}$$

$$D_p = \text{Degree of Polymerisation}$$

Depending on the degree (No. of Monomer units) of polymerisation, there are two types of polymers.

1. Oligopolymers: Those polymers whose degree of polymerisation is less than 600 are called oligopolymers. These polymers do not possess the engineering properties.

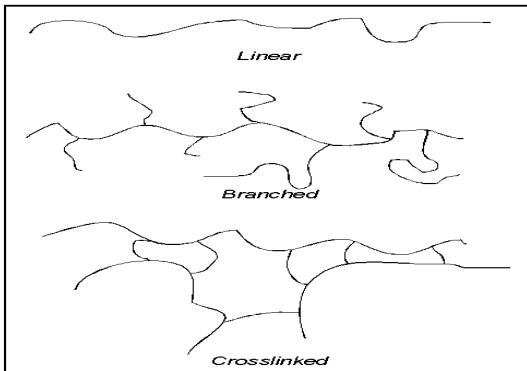
2. Highpolymers: When the degree of polymerisation of a polymer is more than 600, it is called *high polymer*. High polymers possess the desired engineering properties and widely used.

- Write a note on Functionality of polymers.

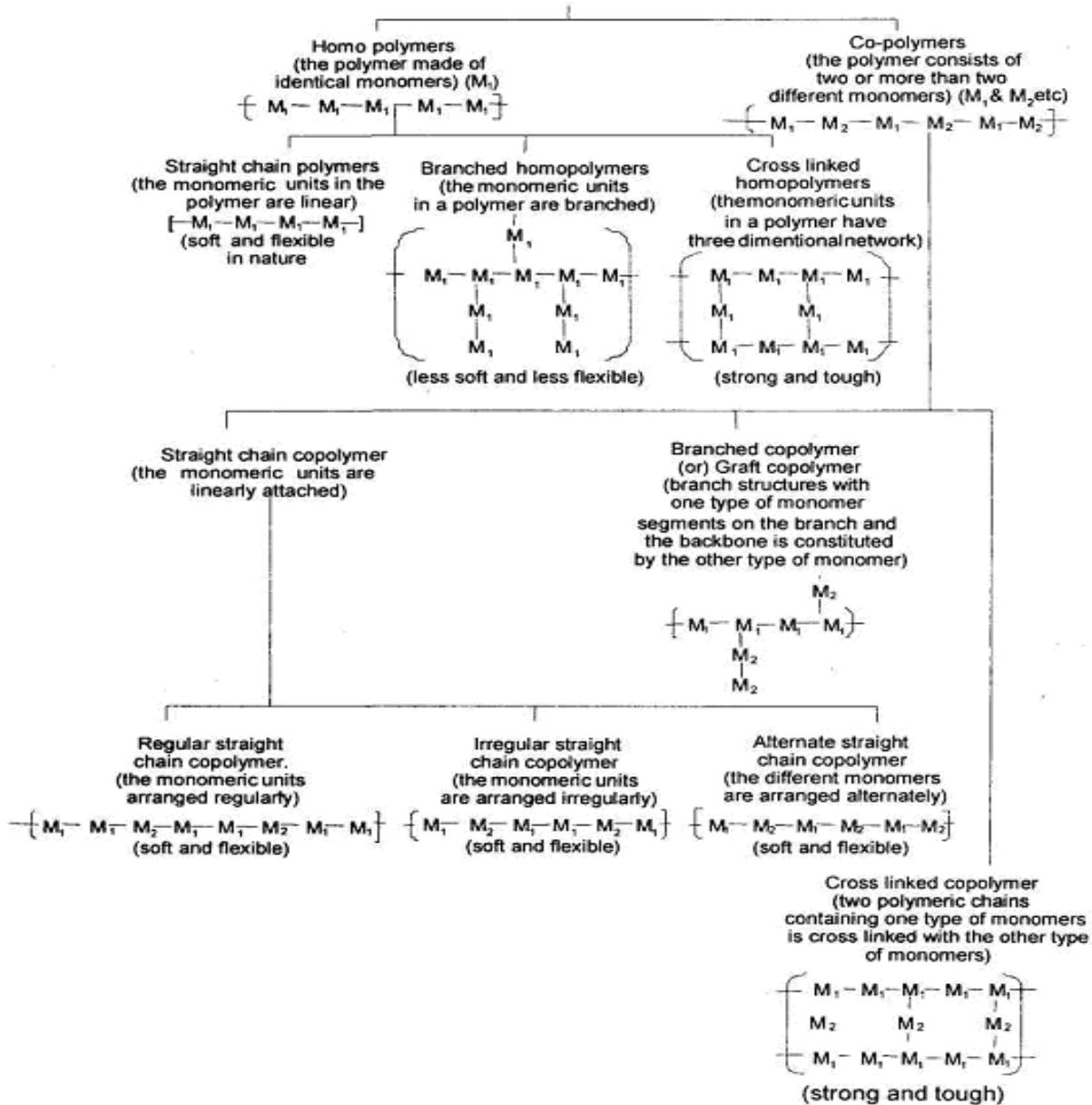
Functionality:

- ❖ The number of active bonding sites of a monomer is referred to as its functionality.
- ❖ So, the monomer should have two reactive sites (or) bonding sites to form a polymer.
- ❖ Different types of polymer structure can be obtained based on the functionality of monomeric units.
- ❖ Case-I:
  - Linear or straight chain molecules are formed by the combination of bifunctional monomers which contain two reactive sites.
  - Linear polymers are obtained by strong covalent bonds. But different chains are held together by secondary weak vanderwaal's forces.
- ❖ Case-II:
  - Branched chain polymers are obtained by the combination of trifunctional monomer and bifunctional monomers.
- ❖ Case-III:

- Three dimensional network polymers are obtained by the combination of polyfunctional monomers.
- In such polymeric molecules, the movement of monomer units is prevented by strong cross links.



#### Types of polymers based on nature of polymerisation

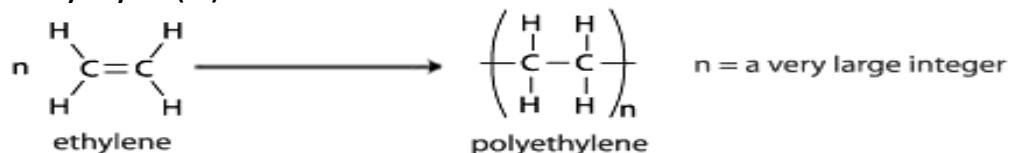


- Write a note on Methods of polymerization (or) • Note on addition and condensation polymerization with examples (or) • Classification of polymers based on methods of polymerization.

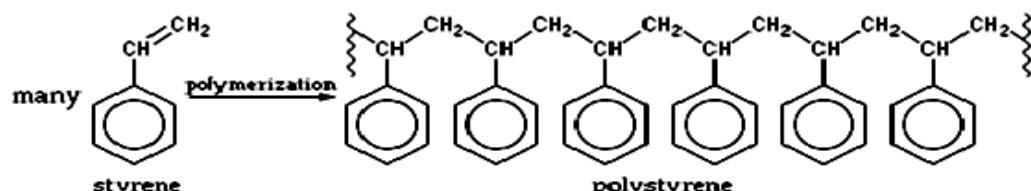
⚡ Based on their methods of synthesis:

## ♠ 1.Addition polymerization:

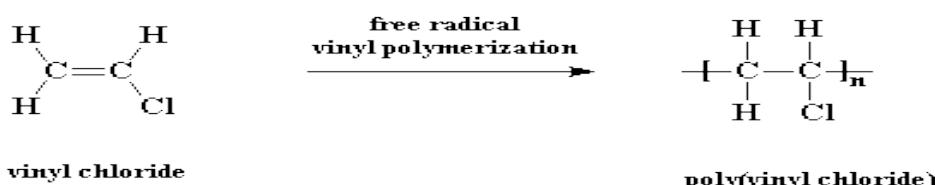
- ◆ In this polymerization process, the monomers add together by repeating addition without formation of byproducts to form polymer.
  - ◆ It can takes place through formation of either radicals or ionic species such as carboanions and carbocations.
  - ◆ Ex:PE, PS, PVC etc.
  - ◆ Ex.1 Polyethylene(PE)



## **Ex.2 Polystyrene**

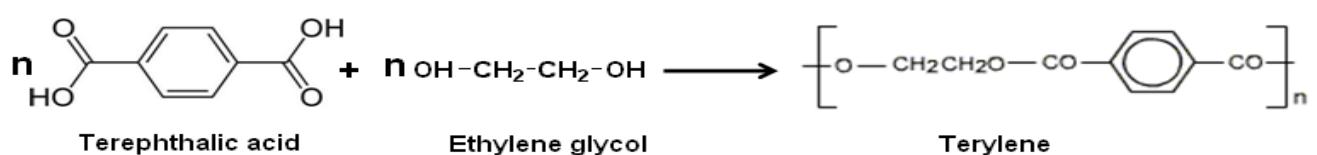


### **Ex.3 Polyvinyl chloride**



#### ♠ 2. Condensation polymerization:

- ◆ When the molecules of same monomers or different monomers simply linked together by the formation of low molecular weight byproducts, this process is called as condensation polymerization.
  - ◆ Ex: Nylon-6, Terylene etc.
  - ◆ Ex: 1.Nylon-6,  
  - ◆ Ex: 1.Terylene



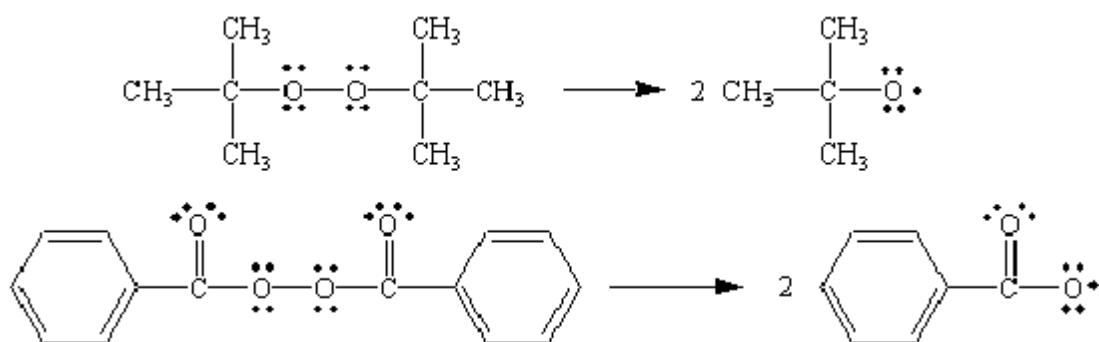
•Differences between Addition & Condensation Polymerisation

Addition Polymerisation	Condensation Polymerisation
1. Polymer is formed by addition of monomers without elimination of small molecules.	1. Polymer is formed by two or more monomers by the elimination of small molecules.
2. No by-products are formed.	2. By products are formed.
3. Homo chain polymers, generally thermo plastic is obtained.	3. Hetero chain polymer either thermo plastic or thermo setting can be obtained.
4. The growth of chain is at one active centre.	4. The growth of chain occurs at minimum of two active centres.

## ❖ Free radical chain polymerisation:

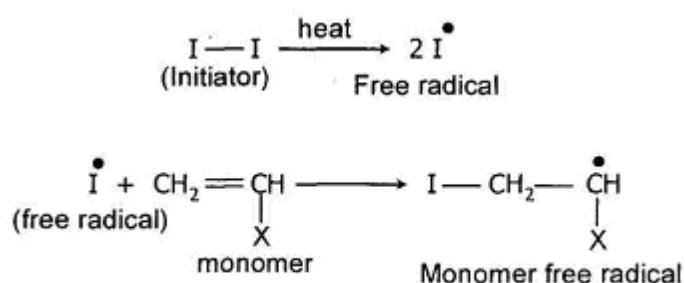
The free radical chain polymerisation can be of homolytic fission process or heterolytic fission process.

The *initiator* undergoes homolytic fission to produce *free radicals*, which initiates and propagates (rapid chain growth) the polymerisation reaction as given below. Ex. Benzoyl peroxide(di-tert-butyl peroxide)



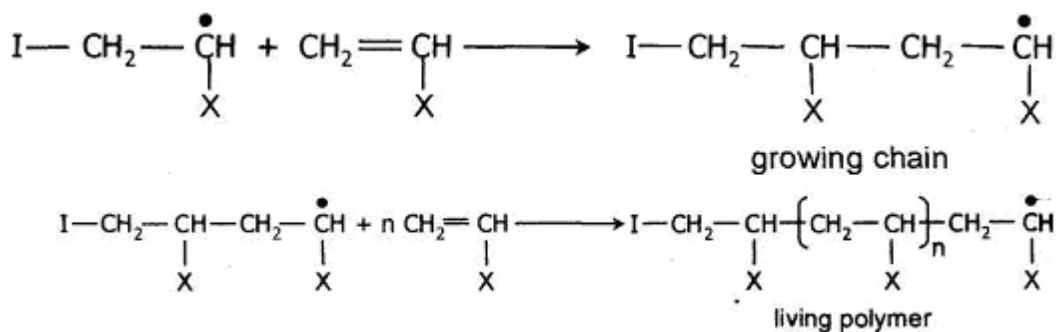
i. **Initiation:** Initiators are unstable compounds and undergo *homolytic fission* to produce *free radicals* which react with  $n$  electrons of the monomer to produce *monomer free radical*.

Theory:



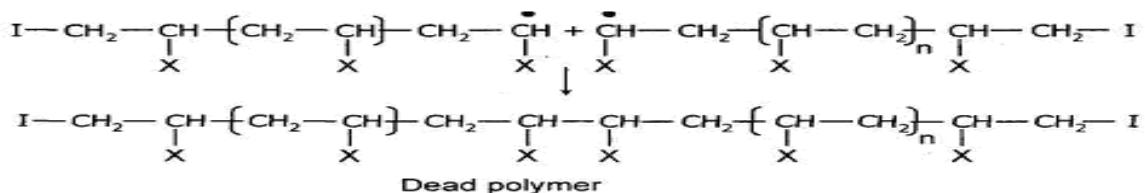
ii. **Propagation:** The monomer free radical reacts with a number of monomers rapidly resulting the chain growth with free radical site at the end of the chain producing a *living polymer*. By adding fresh monomers to the living polymer with free radical site, again chain growth starts. Hence it is known as *living polymer*.

Theory:

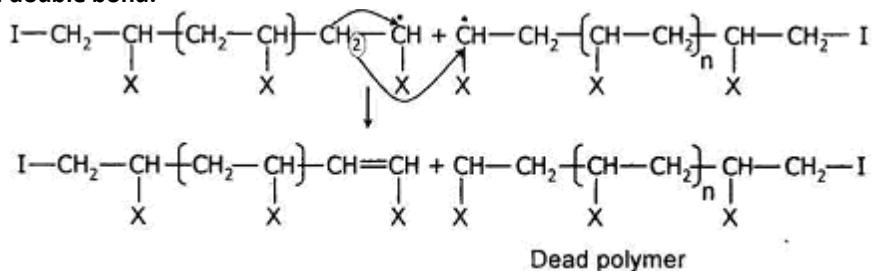


**iii. Termination:** Termination (to stop chain growth) of the growing polymer chain is carried by '*coupling*' and '*disproportionation*', resulting the dead polymer. In *coupling*, the collision of two growing chains causes the union of the two chains at their free radical site producing a *dead polymer*.

Theory:



In termination by disproportionate, H from the growing chain is abstracted by the other growing chain, utilising the lone electron for getting stabilised, while the chain which has donated the H gets stabilised by the formation of a double bond.



## Classification of polymers

(i) Based on structure/shape

Polymer

structure

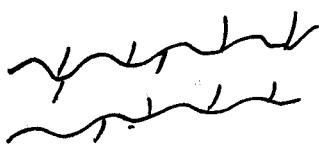
a) Linear



Example

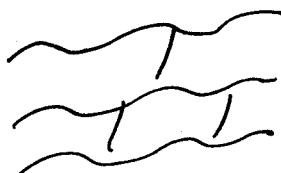
HDPE (High density polyethene)

b) Branched



L.D.PE (Low density polyethene)

c) Cross linked



XLP E  
(Cross-linked polyethene  
Rubbers Thermosets)

(ii) Based on Origin

a) Natural polymers : Carbohydrates, Proteins etc

b) Synthetic polymers : plastics rubbers fibers etc

(iii) Based on Conductance

a) Insulators : Mostly all polymers are insulators

b) Conducting polymers : Polyaniline, Poly Pyrrole

(iv) Based on Number of monomers

a) Homo polymers : Ex polyethene, PVC

b) Co-polymers : BuNa-S, BuNa-N

(v) Based on type of monomers

(a) polar : (PET, Nylon)

(b) non polar : (PE, PP)

(vi) Based on Response to heat.

(a) Thermoplastics [soft on heating & hard on cooling] PE, PVC

(b) Thermosets [no change on heating]

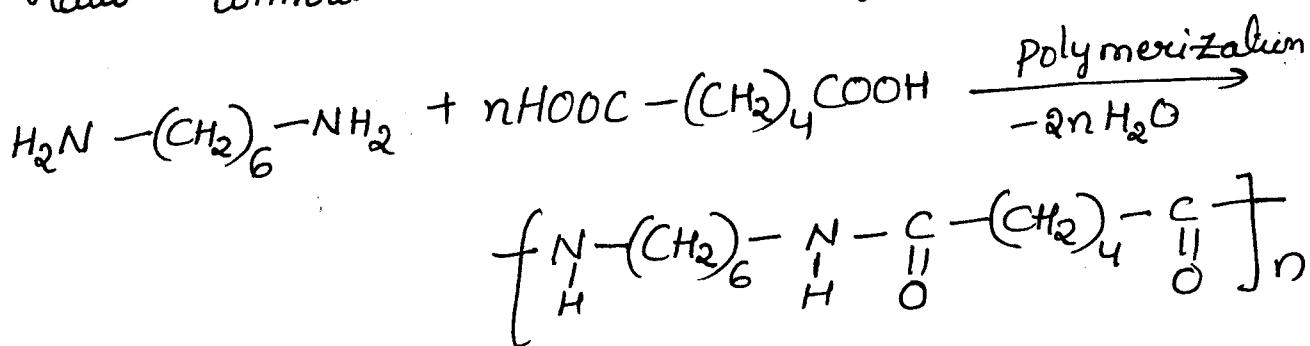
Bakelite,

(vii) Based on Environment friendly nature

Biodegradable :-

Durable :-

Nylon-6:6: It is made by the condensation polymerization of hexamethylene diamine and adipic acid 1:1 molar ratio without an external strong acid.



Nylon 6:6 [or] Poly hexamethylene adipamide]

Properties :

- 1) The structure of nylons are linear
- 2) The molecular chains are held together by Hydrogen bonds. Thus, nylon have high crystallinity,

which imparts high strength, high melting point, elasticity, toughness, abrasion resistance and retention of good mechanical properties upto  $125^{\circ}\text{C}$ .

(3) They are also sterilisable.

(4) Nylons are polar polymers, they have good hydrocarbon resistance.

### Applications

(1) Nylon-6:6 is used as fibers, which find use in making socks, ~~under~~. Carpets etc

(2) Nylon-6:6 is used in mechanical engineering for applications like Gears, Bearings, Bushes, Cams etc

(3) Nylon-6:6 is also used for jacketing electrical wires to provide a tough, abrasion resistant outer cover to protect the primary electrical insulation.

(4) Naty Nylon 6 is mainly used for making tyre cords, filament for soap bristles for tooth brushes.

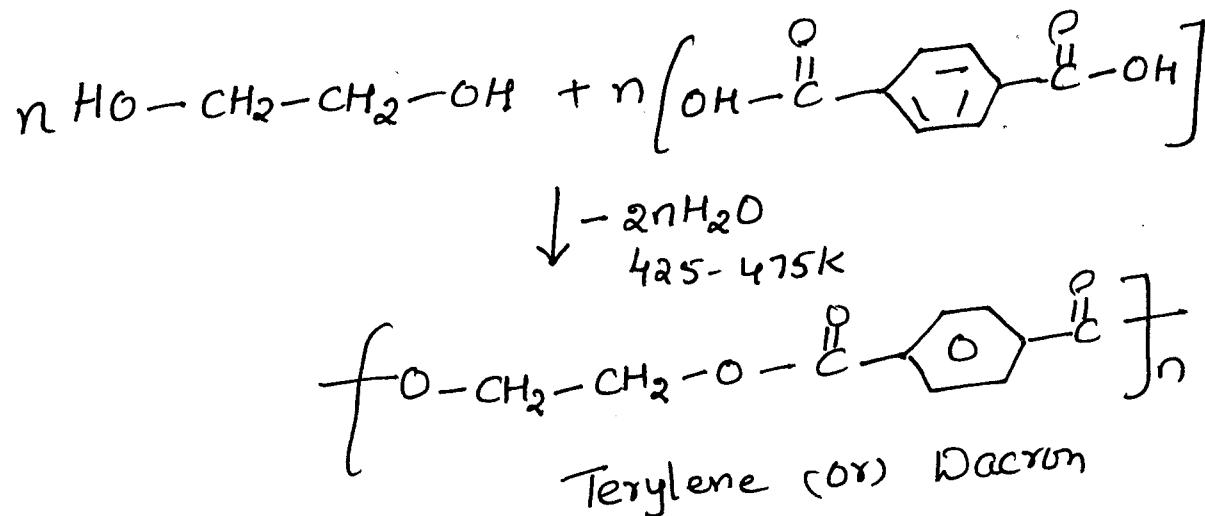
### Terylene [poly ethylene Terephthalate]

Poly ethylene terephthalate is a copolymer and its monomer units are terephthalic acid [Benzene-1,4-dicarboxylic acid] and ethylene glycol [ethane-1,2 diol]

it

(2) It is commercially known as Terylene

4.

Properties

1. It has high mechanical strength and dimension stability.
2. It is a very strong fibre will suffer little loss <sup>in strength</sup> when wet.
3. It is stable in the temperature range of 40-100°C.
4. It is elastic in nature.
5. It shows creep and abrasion resistance and good insulating properties.
6. It shows low water absorption and at room temp, it is resistant to water, dilute acids, salts, aliphatic and aromatic hydrocarbons and alcohols.

Applications of Terylene

1. It is used for making video and audio tapes.
2. It is used in textile industry for making hard wear clothes and other dress materials.
3. It is used for making clear bottles for food and beverages.
4. The fibre may be blended with cotton and wool to form another fabrics, like terycot and terywool.

## PLASTICS:

The word plastic itself comes from the Greek word *plastikos*, which means to be able to be shaped or moulded by heat.

### **Advantages of plastics over other traditional materials (like wood, metals, glass etc):**

- 1) Plastics are available in attractive colours.
- 2) They do not undergo corrosion.
- 3) They are not affected by insects.
- 4) They are light in weight
- 5) They are cheap.
- 6) They can be moulded into any shape easily.
- 7) They are chemically inert.
- 8) They have good abrasion resistance.
- 9) They are good insulators of heat and electricity.

### **Disadvantages:**

1. Recycling of plastic is a costly process.
2. Plastic undergo biodegradation after long time.
3. Incineration of plastic causes pollution.
4. Plastics are derived from petrochemicals and their production causes environmental pollution.
5. Plastics are low heat resistance and brittle. They undergo deformation at low temperatures.

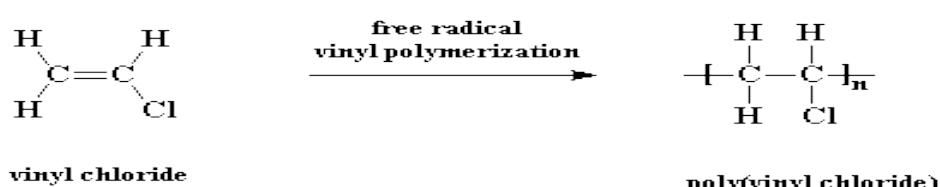
### **Differences between Thermo Plastics & Thermo Setting plastics :**

S.n o	<b>THERMOPLASTIC RESINS</b>	<b>THERMOSET RESINS</b>
1.	These resins become soft on heating and rigid on cooling.	During fabrication process these resins are moulded. Once moulded or shaped, they can not be softened.
2.	Thermoplastic resins are formed by chain polymerisation.	Thermoset resins are formed by step polymerisation.
3.	They can be reshaped.	They cannot be reshaped
4.	These plastics can be reclaimed from waste.	They cannot be reclaimed from waste.
5.	Thermoplastic resins are soft, weak and less brittle.	Thermoset resins are hard, strong and more brittle.
6.	These resins are usually soluble in organic solvents. Eg: Polyethylene, polyvinyl chloride etc.	Due to strong bonds and cross links, they are insoluble in almost all organic solvents. Eg: Bakelite, Nylon etc.

### **Write preparation, properties and applications of i) PVC.**

#### **i)PVC (Poly vinyl chloride):**

**Preparation:** Poly vinyl chloride is produced by heating vinyl chloride in presence of benzoyl peroxide or H<sub>2</sub>O<sub>2</sub>.



**Properties:** PVC is colourless, odourless, non-inflammable and chemically inert powder. Pure resin possesses greater stiffness and rigidity compared to poly ethylene. It is brittle in nature.

**Applications: or Uses:**

1. P.V.C is mainly used as an insulating material.
2. It is used for making table clothes, rain coats, toys, tool handles, radio components, etc.
3. It is used for making pipes, hoses, etc.
4. It is used for making helmets, refrigerator components, etc.
5. It is used in making cycle and automobile parts.

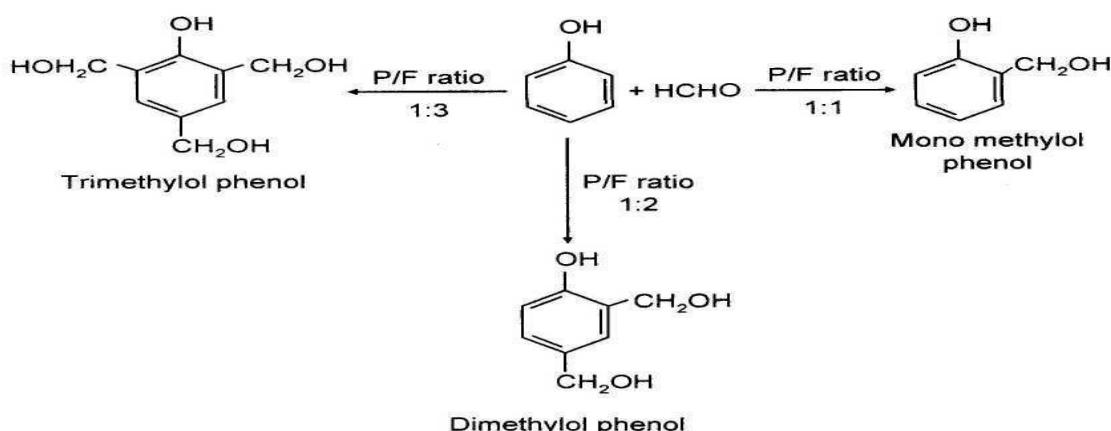
### **Phenol formaldehyde resins or Bakelite :**

Bakelite is a condensation polymer of phenol and formaldehyde

**Preparation :**

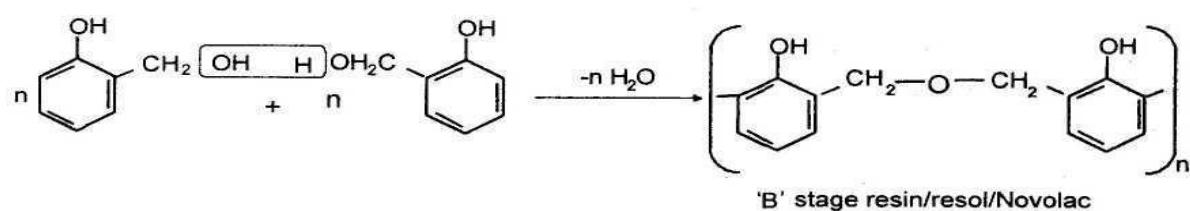
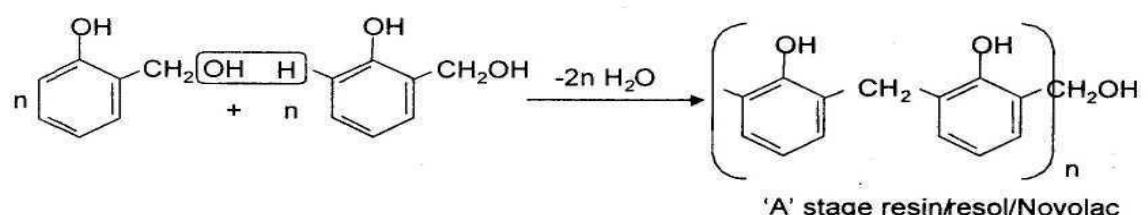
**I) stage:**

Phenol is made to react with formaldehyde in presence of acid / alkali to produce non - polymeric mono, di, and tri methylol phenols depending on the phenol formaldehyde ratio (P/F ratio)

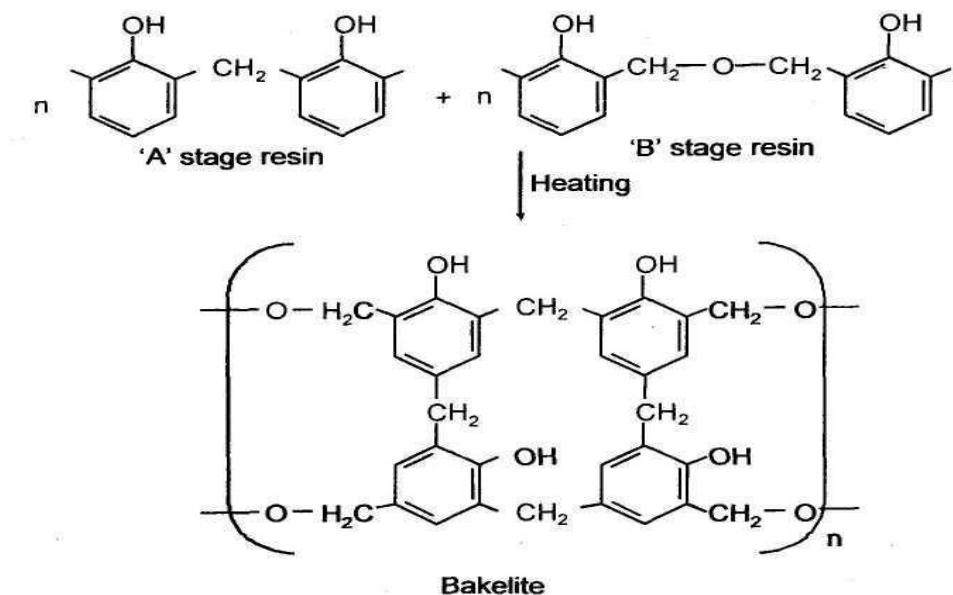


**II) Stage:**

The mono, di, and tri methylol phenols are heated to produce two types of straight chain resins by condensation of the methylol group with hydrogen atom of benzene ring or another methylol group.



**III) Stage:** This stage of preparation includes heating of 'A' stage resin and 'B' stage resin together, which develops cross linking and bakelite plastic resin is produced.



#### Properties:

1. Bakelite plastic resin is hard, rigid, and strong.
2. It is a scratch resistant and water resistant polymer.
3. Bakelite has got good chemical resistance, resistant to acids, salts and any organic solvents, but it is attacked by alkalis due to the presence of - OH group.
4. It is a good anion exchanging resin, exchanges - OH group with any other anion.
5. Bakelite is an excellent electrical insulator.
6. It is a very good adhesive.
7. Bakelite has very good corrosion resistance, resistant to atmospheric conditions like O<sub>2</sub>, CO<sub>2</sub>, moisture, light, U.V.radiation etc.

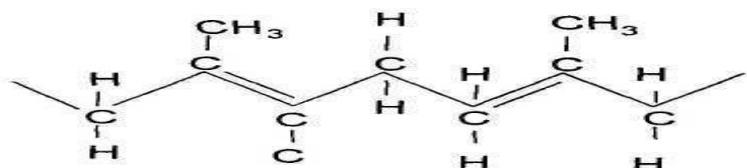
#### Engineering applications: Bakelite is used widely.

1. For making electrical insulator parts like switches, switch boards, heater handles etc.
2. For making moulded articles like telephone parts, cabinets for radio and television.
3. For making tarpaulins, wood laminates and glass laminates.
4. As an anion exchanger in water purification by ion exchange method in boilers.
5. As an adhesive (binder) for grinding wheels etc.
6. In paints and varnishes.
7. For making bearings used in propeller shafts, paper industry and rolling mills.

### **ELASTOMERS:**

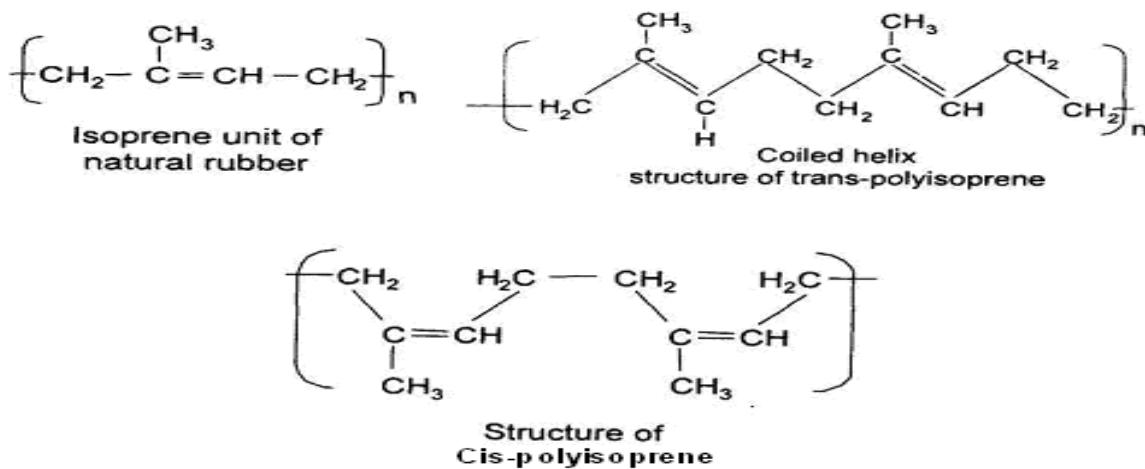
**Definition:** Elastomers are high polymers that undergo very long elongation (500 – 1000%) under stress, yet regain original size fully on release of stress. Those rubbers are therefore referred to as elastomers.

The property of elastomers is known as elasticity. This arises due to the coiled structure of elastomers.



### Natural rubber:

Natural rubber is found in several species of rubber trees grown in tropical countries, of these *Hevea brasiliensis* is the most important source of natural rubber and the rubber obtained from this is known as "Hevea" rubber. Rubber is stored in the form of white fluid called 'latex' behind the bark of the rubber tree.



Natural rubber is a high polymer of isoprene (2-methyl-1,3-butadiene).

Polyisoprene exists in two geometric isomers cis and trans forms.

Natural rubber is soft and has cis-configuration while 'Guttapercha' or, 'Ballata' has trans configuration.

### Defects (or) Disadvantages of natural rubber:

The natural rubber obtained from latex cannot be used in industries because it has some defects.

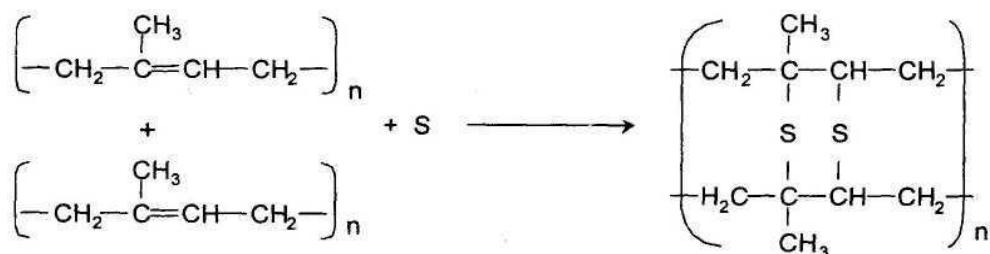
1. It becomes soft and sticky during summer and it becomes hard and brittle during winter.
2. It swells in water and easily attacked by organic solvents, acids bases and non – polar solvents like mineral oils, benzene and gasoline.
3. It possesses poor tensile strength.
4. Atmospheric oxygen attacks the rubber and produces epoxides which gives bad smell, stick nature to rubber.

### Vulcanisation:

Some chemicals like elemental sulphur, hydrogen sulphide, sulphur dichloride, benzoyl chloride and zinc oxide are added to both natural and synthetic rubbers. The most important vulcaniser is *sulphur* which combines chemically at the *double bonds* of the different chains producing *sulphur cross linkings*, imparting *strength* increases, the brittleness also increases.

2 to 4% Sulphur addition gives soft elastic rubber.

When sulphur content is more than 30%, we get hard rubber called 'Ebonite' (or) vulcanite.



**Write preparation, properties and applications of i) Buna-S ii) Thiokol**

**BUNA-S [or] SBR,[or] GRS) Styrene Butadiene Rubber) gov. regulated styrene rubber or Ameripol**

BUNA - S is otherwise called styrene rubber or *GRS* (Government Rubber Styrene) or *Ameripol*.

BUNA - S stands for the composition of the monomers and catalyst.

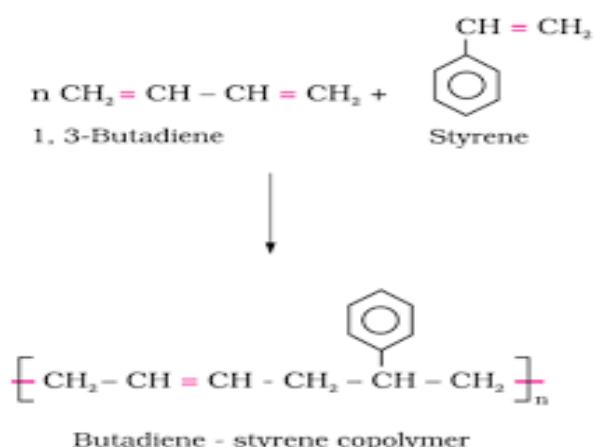
BU stands for Butadiene - monomer

NA stands for Sodium - catalyst

S stands for Styrene - monomer

Buna-S is the most important synthetic rubber it is obtained by the co-polymerization of butadiene and styrene using sodium as a catalyst.

**Preparation :**



**Properties:**

1. Styrene rubber is a strong and tough polymer.
2. It is vulcanised by sulphur monochloride ( $\text{S}_2\text{Cl}_2$ ) or sulphur.
3. It resembles natural rubber in processing characteristics and quality of finished products.
4. BUNA - S possess excellent abrasion resistance.
5. It is a good electrical insulator.
6. It is resistant to chemicals but swells in oils and attacked by even traces of ozone, present in the atmosphere.
7. Styrene rubber possess high load bearing capacity and resilience.

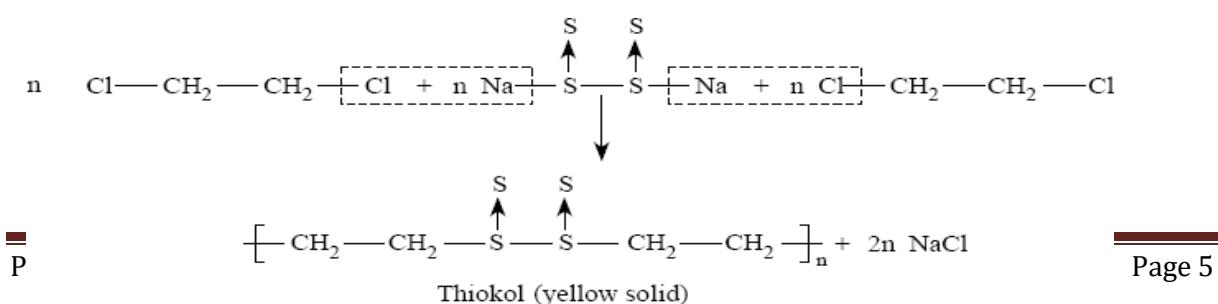
**Applications:**

1. Major application of styrene rubber is in the manufacture of tyres.
2. It is used in the footwear industry for making shoe soles and footwear components.
3. It is also used for making wires and cable insulations.
4. The other applications of styrene rubber are for the production of floor tiles, tank linings in chemical industries and as adhesives.

**Thiokol (Polysulphide Rubber or GR-P):**

Polysulphide rubbers are the condensation product of ethylene dichloride and sodium tetra sulphide.

**Preparation :**



### **Properties:**

Thiokol rubber possess strength and impermeability to gases.

This rubber cannot be vulcanized and it cannot form hard rubber.

Possess good resistance to mineral oils,fuels,oxygen,solvents,ozone and sunlight.

It is also resistant to the action of petrol lubricants and organic solvents

### **Applications:**

Fabrics coated with thiokol are used for barrage balloons,life rafts and jackets.

Thiokols are used for lining for conveying gasolin and oil.

Used for making gaskets and seals for printing rolls.

Thiokol mixed with oxidizing agents in used as a fuel in rocket engine.

## **CONDUCTING POLYMERS:**

A polymer which conducts electricity is called conducting polymer.

Eg :- Polyaniline, polyacetylene, polypyrrole, etc

They are classified into two types :      1) Intrinsically conducting polymers.

    2) Extrinsicly conducting polymers

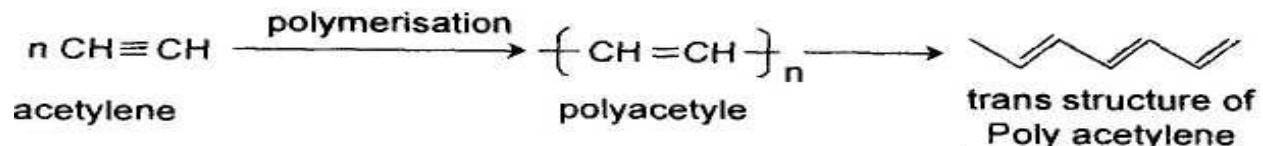
### **1. Intrinsically conducting polymers:**

These have extensive conjugation in the backbone which is responsible for conductance. These polymers can be divided into two :

#### **a) Conducting polymers having conjugated $\pi$ – electrons in the backbone:**

eg :- polyacetylene, polyaniline etc.

These type of polymers due to overlapping of conjugated  $\pi$  – electrons over the entire backbone results in the formation of valence bonds as well as conduction bands, which extends over the entire polymer molecule. But since the valence band and the conduction band are separated by a significant band gap, conductivity of these polymers is not very high.



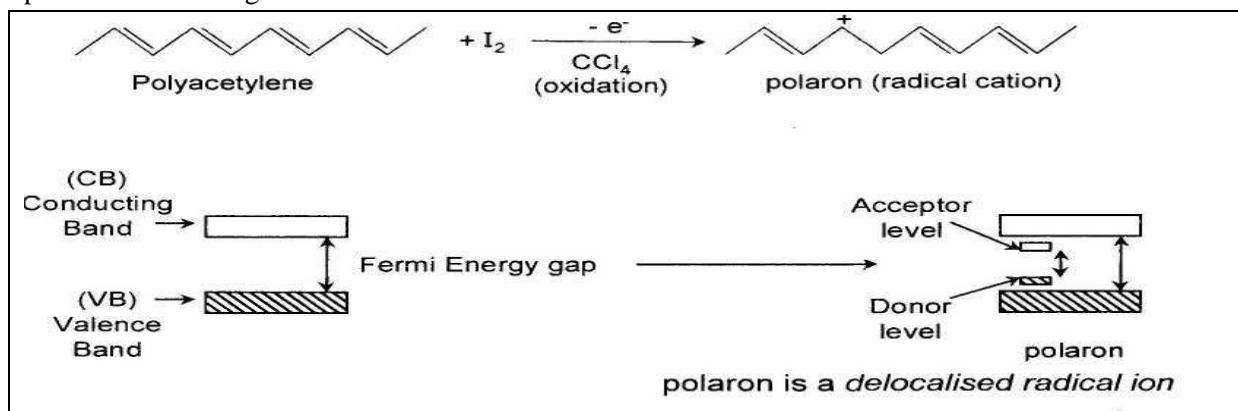
#### **b) Doped conducting polymers:**

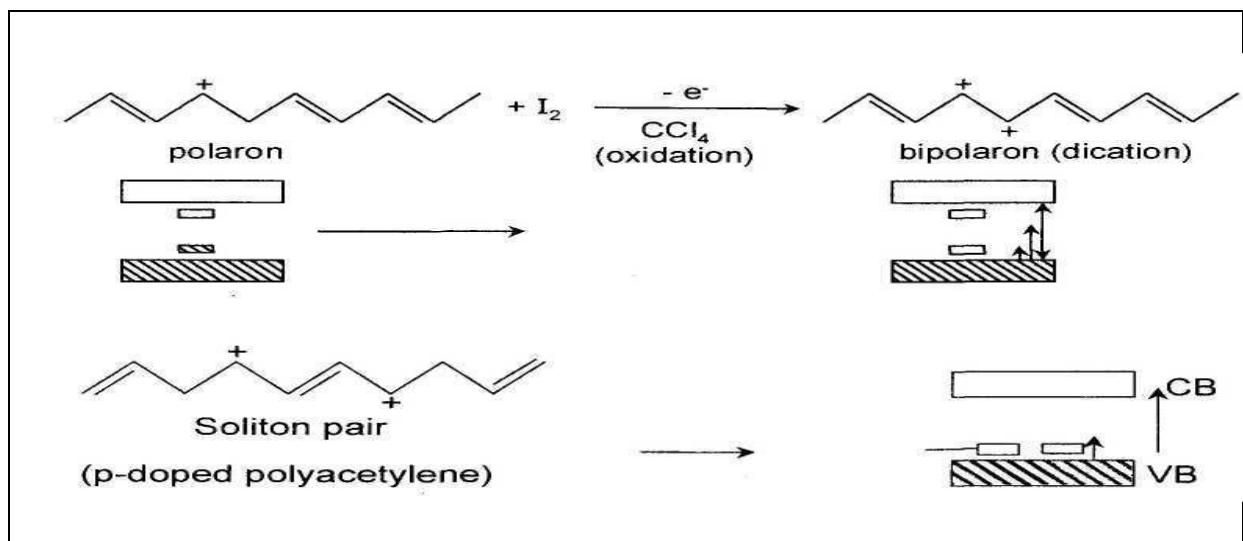
Conductivities of polymers having conjugated  $\pi$  – electrons in the backbone can be increased by creating either +ve or -ve charges on the polymer backbone by oxidation or reduction. This process is called doping.

It can be done in two ways :

##### **i)Oxidative doping (P – doping ):**

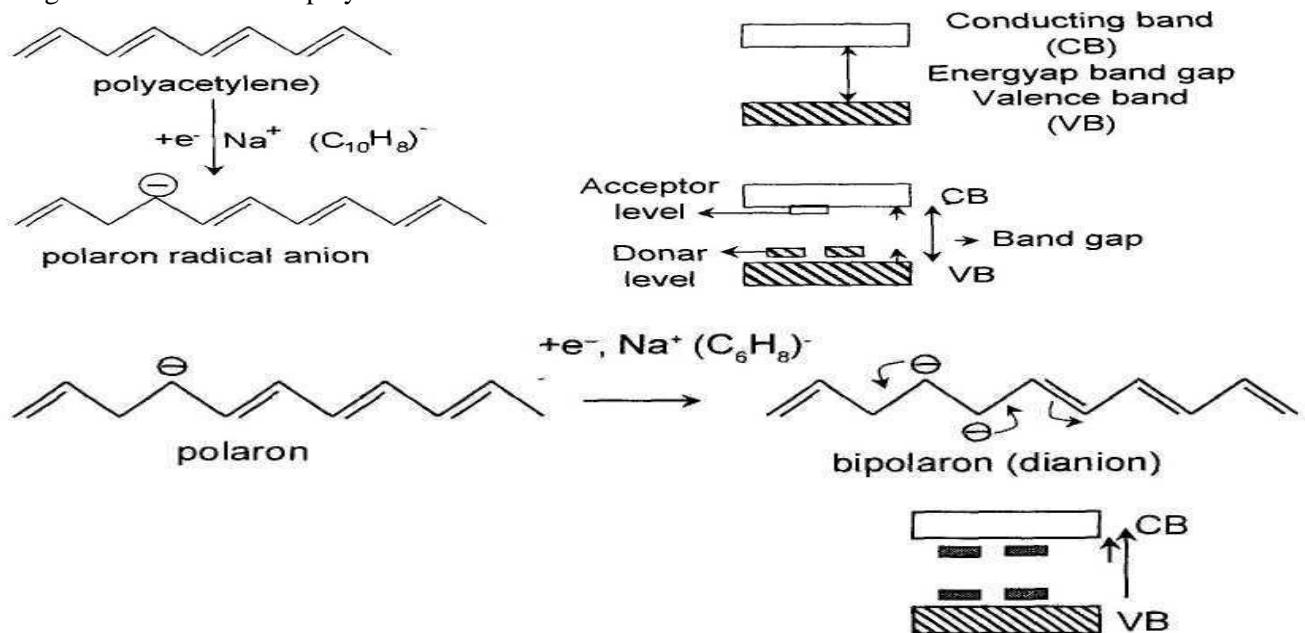
It involves treating the conjugated polymer with a Lewis acid like  $\text{FeCl}_3$  thereby oxidation takes place and +ve charges are created on the back bone.





### ii) Reductive doping (n - doping):

It involves treating the polymer with a Lewis base like  $RNH_2$  thereby reduction takes place and -ve charges are created on the polymer back bone.



## 2.Extrinsically conducting polymers:

Some of the polymers conduct electricity due to externally added ingradients to them. They are of two types.

- a) Polymers with conductive elements filled Polymers. b) Blended conducting polymers.

### a).Polymers with conductive elements filled:

In these polymers, the polymer acts as a 'binder' and holds the conducting element added so that the polymer becomes a conductor. Examples of conductive elements are carbon black, metallic fibers, metallic oxides etc.

Minimum concentration of conductive element to be added so that the polymer becomes a conductor is called percolation threshold. The conductive elements added to create a conducting path in the polymer.

### b).Blended conducting polymers:

These polymers are obtained by blending a conventional polymer with a conducting polymer.

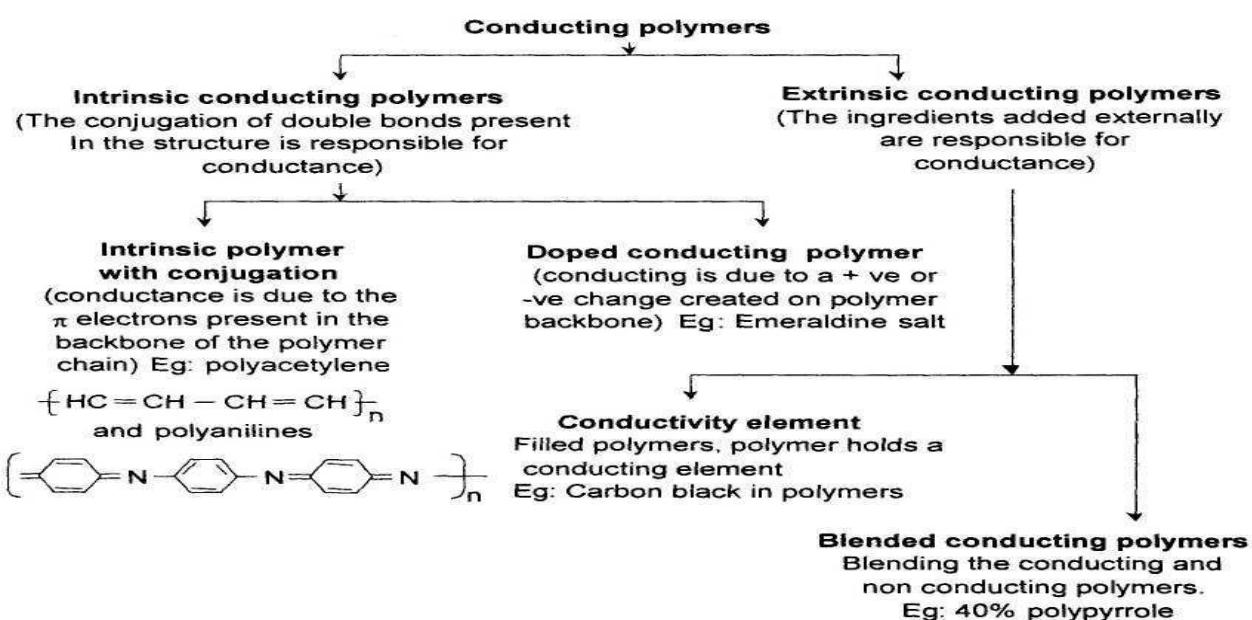
The polymer thus obtained has good chemical, physical, electrical properties and mechanical strength. Ex; 40% pyrrole when blended with a conventional polymer, the combination gives conducting polymer with good impact strength.

### Applications of conducting polymers in biomedical devices:

- ★ Conducting polymers are used in preparation of artificial devices like Heart valves, kidneys, and lungs.
- ★ Poly methyl methacrylate is used as bone cement used for some fracture repairs.
- ★ Poly methyl methacrylate is also used for artificial teeth.
- ★ Used in preparation other medical devices include sutures, pins, screws used during surgery on bones, ankles, hands etc.
- ★ They are used to prepare contact lenses which permit O<sub>2</sub> to the eyes. These lenses are called rigid gas permeable lenses (RGP).

### Applications of conducting polymers in electronics:

- ✉ They are used in rechargeable batteries.
- ✉ They are used in analytical sensors of p<sup>H</sup>, O<sub>2</sub>, NO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub> etc.
- ✉ Used in photo voltaic cells. Ex; Al/polymer/Au.
- ✉ Used in telecommunication systems.
- ✉ Used in transistors and diodes.
- ✉ Used in solar cells.
- ✉ Used as wiring in air crafts and aerospace parts



### **Write a note on Biodegradable polymers.**

- ◆ Biodegradation is the chemical breakdown of materials by physiological environment.
- ◆ Some polymers undergo degradation when exposed to moisture, heat, oxygen, ozone and micro-organism.
- ◆ These agents change the chemical structure of the polymer and lead to change in properties of polymer.
- ◆ Generally materials obtained from plants, animals and other living organism and synthetic materials similar to plant and animal material undergo degradation by microorganisms.

## Bio-degradable polymers:

- Biodegradable polymers are defined as "the polymeric materials that undergo degradation by environmental factors like, sunlight, temperature changes or by the actions of micro-organisms like algae, fungi and bacteria".
- They are easily compostable and recyclable.
- Ex. polyactic acid, poly glycolic acid, poly vinyl alcohol etc.

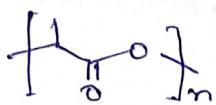
## Types of Bio-degradable polymers:

Based on degradation they are of two types:

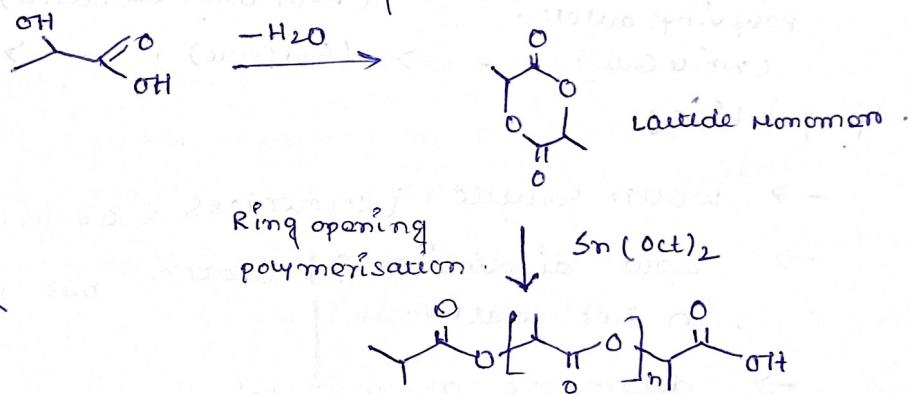
1. Naturally Biodegradable polymers: They are called as bio-polymers.  
Ex. Silk, wool, starch etc.
2. Synthetic Biodegradable polymers: They are of two subtypes:
  - A. Biosynthetic polymers: They are produced by process by microorganisms. Ex. Albumin, Gelatin etc.
  - B. Synthetic: These polymers are derived from petroleum degradation by microorganisms. Ex. Poly vinyl alcohol, PLA etc.

## Poly-Lactic acid (PLA):

It is a biodegradable thermo plastic, aliphatic polyester derived from renewable resources such as corn-straw, tapioca products (roots, starch) and sugar cane.



- (1). Preparation: Oligomerisation and catalytic dimerization of lactic acid results in the formation of lactide monomer, which undergoes polymerization in the presence of stannous octate catalyst to give PLA.



- (2). Advantages:

(1). It is environment friendly.

(2). It has good mechanical and physical properties.

(3). It is biocompatible.

(4). It is nontoxic and can be metabolized by organisms.

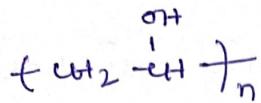
- (3). Applications:

(1). PLA is used in making disposable packing materials, bottles, cups and food containers.

(2). It is widely used in orthopedic medical implants in the form of screws, plates, rods.

(3). Production of biodegradable synthetic garments, hygienic products etc.

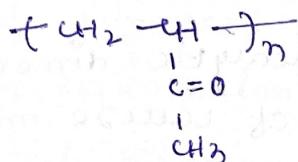
## Poly vinyl alcohol:



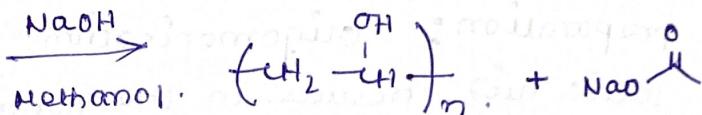
$\Rightarrow$  water soluble synthetic polymer.

$\Rightarrow$  posses excellent mechanical properties.

## (1). Preparation:



(PVAe),  
poly vinyl acetate.  
(white Glue).



hydrolysis. PVA.  
(both acidic & basic).



## (2). Properties:

- $\rightarrow$  water soluble (colourless & odourless).
- $\rightarrow$  slow dissolution in water but rapidly dissolve in hot water.
- $\rightarrow$  decompose above  $150^\circ\text{C}$ .
- $\rightarrow$  It is amorphous & crystalline.

## (3). Applications:

(1). It is used in ~~contact~~ contact lenses.

(2). It is used in food packaging & pharmaceutical applications.

(3). Used in textile industries like paper industry because of high chemical stability.