

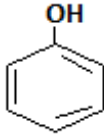
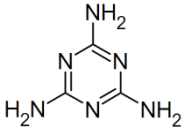
### Unit-III Polymeric Materials

**Monomers:** The small individual molecules which combine with each other to form large molecules are called monomers.

**Examples:** Ethylene, vinyl chloride, styrene, etc.

**Functionality of Monomer:** *“The Number of bonding sites present in a monomer” is called functionality of monomer.*

**Examples:**

Name of Monomer	Structure	Functionality
Ethene	$\text{CH}_2=\text{CH}_2$	2
1,3- butadiene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	2
Ethylene glycol	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	2
Phenol		2 or 3
Melamine		3

Note: The small molecules to act as a monomer, their functionality should be at least two.

**Polymers:** (Poly = many; Mers = Part):

Polymers are high molecular weight giant molecules formed by linking together of small molecules, **monomers**, by means of covalent bond/chemical bond.

**Examples:** poly ethylene, poly (vinyl chloride), Bakelite, etc.

**Polymerization:** The process of joining together of small molecules by means of covalent bonds to form extremely large molecule is called polymerization.

Or

Any chemical process which leads to the formation of polymer is called polymerization.

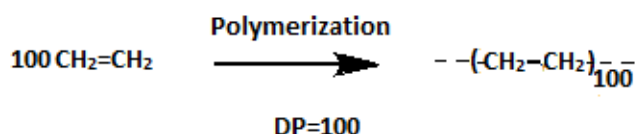
Examples:



### Degree of polymerization:

Number of monomers/repeat units present in the polymer is called "Degree of polymerization".

Example:



### Nomenclature of polymers:

- ✓ Most of the polymers are known by the trivial or trade names. Polymers derived from one type of monomer are denoted by prefixing poly to name of the monomer.

**Examples:** polythene, polypropene etc.

- ✓ If a monomer has substituent or has a multi worded name, then the name of the monomer is enclosed in parenthesis after the prefix poly.

**Examples:** poly (vinyl chloride).

### **Types of polymerizations:**

**chain growth Polymerisation:** In chain growth, the polymer chain always grows one monomer at a time. Chain growth results in a steady increase in chain length with every coupling step.

**Step-growth polymerization:** It refers to a type of polymerization mechanism in which **bi-functional or multifunctional monomers react to form first dimers**, then trimers, longer oligomers and eventually long chain polymers. In step growth, **the polymer chain doubles with each step**.

**Differences between chain growth and step growth polymerisation:**

<u>Chain growth polymerisation</u>	<u>Step growth polymerisation</u>
*Concentration of monomers disappears early in the reaction.	* Concentration of monomers decreases steadily throughout the reaction

*Reaction is fast and polymer is formed at once.	*The polymer is formed in gradual steps.
*There is very little change in the molecular mass throughout the reaction.	*The molecular mass of polymer increases throughout the reaction.
*Increase in reaction time increases the yield but molecular weight is affected a little.	*Long reaction time is required to get high molecular mass polymer.
*Only one repeating unit is added at a time.	Any two species present can react.
*Reaction mixture contains only a monomer, polymer and growing chain.	*All molecular species are present at any stage.

### Preparation, Properties & Applications of the polymers:

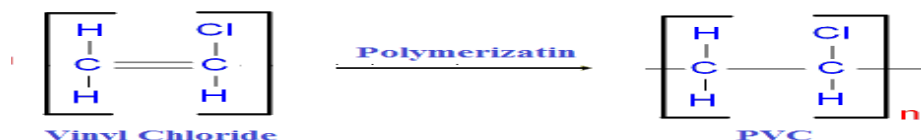
**Plastics:** The polymers which can be shaped into hard and tough utility articles are known as plastics.

Examples: 1. PVC      2. Bakelite:

### 1. 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:

- It is very good insulator for DC & low frequency AC current
- 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.

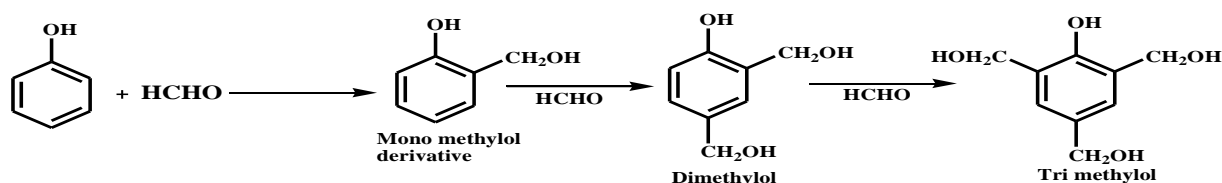
### 2.Bakelite:

It is the condensation polymer of phenol and formaldehyde. It is also known as phenoplast and PF resin.

**Preparation:** Bakelite preparation involves the following steps:

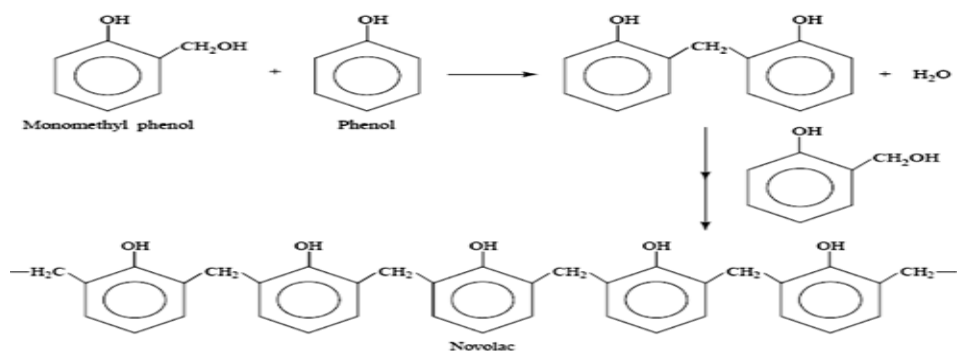
#### Step (i):

Phenol and formaldehyde react to form methylol derivatives which act as monomers for subsequent polymerization.



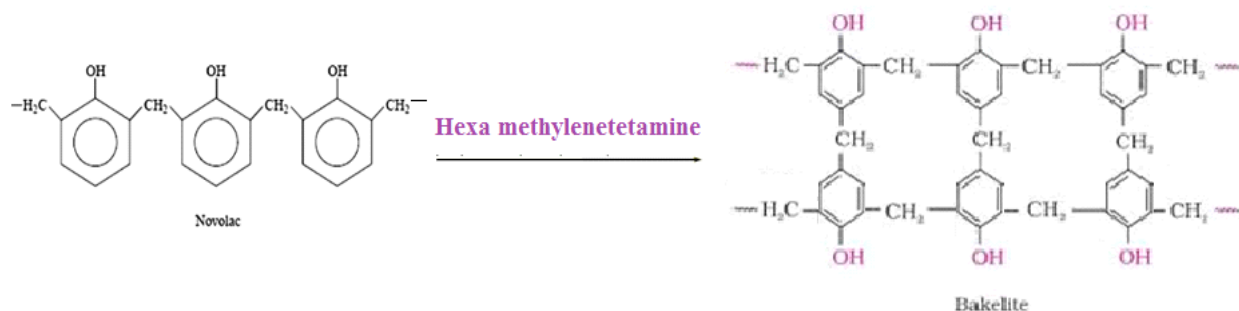
**Step (ii):** In presence of acid catalyst when mole ratio P/F>1.

The methylol derivatives condense with phenol to form dihydroxy diphenyl methane. These on further condensation give low molecular weight linear polymers which are fusible , soluble and are known as “Novalacs”.



#### Step (iii):

Further heating of Novalac in presence of hexamethylenetetramine [(CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>] as curing agent produces a hard, rigid , insoluble and infusible 3-D cross linked polymer known as “Bakelite”.



#### Properties:

- Bakelite is hard, infusible and insoluble strong material.
- They have excellent heat, chemical resistance, but are affected by strong caustic alkalis.
- They have good electrical insulation characteristics.
- They have good abrasion resistance.

#### Uses:

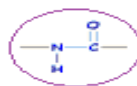
- For making electrical insulating parts like switches, plug etc.
- For making telephone parts, cabinets for radio & television.
- In paints and varnishes.
- As ion exchange resin in softening of water by ion-exchange method.

#### 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.

E.g.: Nylon, Polyester etc.,

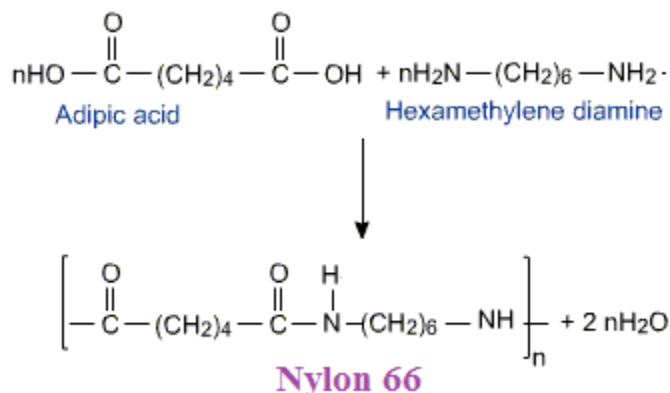
**Polyamides:** The polymers which consists of amide group.



Polyamides occur both naturally and artificially. Examples of naturally occurring polyamides are proteins, such as wool and silk. Examples of artificially made polyamides such as nylons, Kevlar, etc.,

#### Nylon 66:

**Preparation:** It is prepared by the condensation polymerization of adipic acid with hexamethylene diamine.



**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 protects the electrical insulation.

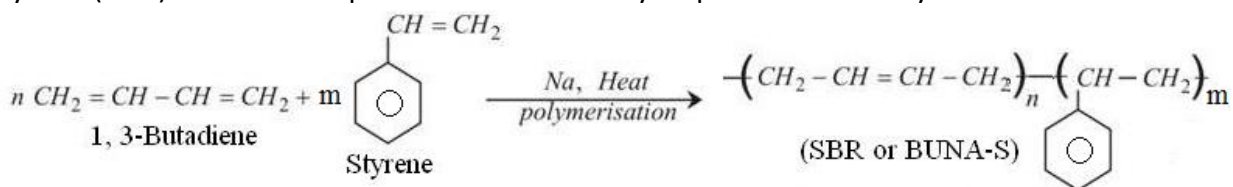
**Elastomers:** Rubber-like solids with elastic properties are called elastomers. Polymer chains are held together in these materials by relatively weak intermolecular bonds, which permit the polymers to stretch in response to macroscopic stresses.

**Example:** Natural Rubber

**Artificial /synthetic rubbers:**

**Styrene Rubber (GR-S or Buna-S or SBR)**

SBR is a copolymer which is prepared by the co-polymerization of 1, 3-butadiene (75%) and styrene (25%) at 5 °C in the presence of cumene hydroperoxide as catalyst.



SBR is also called as cold rubber. SBR can also be vulcanized in the same way as natural rubber either by sulphur or sulphur monochloride. However, the amount of sulphur required for vulcanization is less.

**Properties:** Buna-S has the following properties,

- High abrasion resistance and load bearing capacity.
- Good Resilience.

- It swells in oils and solvents.
- It gets readily oxidized due to the presence of unsaturation.

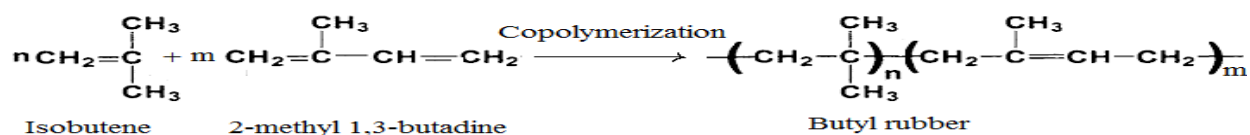
**Uses:** SBR is used for making,

- Automobile tyres, foot wear components.
- Insulation for electrical wires.
- Conveyor belt, tank lining.

### Butyl Rubber (GR-I):

#### Preparation:

Butyl rubber is a copolymer which is prepared by copolymerization of isobutene and small amount of isoprene. It also known as IIR, IIR stands for Isobutylene Isoprene Rubber.



Small amount of isoprene is added to make resultant rubber vulcanizable.

#### Properties:

1. It is quite resistant to oxidation due to low degree of unsaturation.
2. Though it can be vulcanized cannot be hardened much because of low degree of unsaturation.
3. Being non –polar, it has good electrical insulation properties.
4. Compared to natural rubber it possesses low permeability to air and other gases.
5. It is soluble in hydrocarbon solvents like benzene but has excellent resistant to polar solvents like alcohol, acetone and resistant to chemicals like HCl, HF, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, etc.,

**Uses:** It is used for,

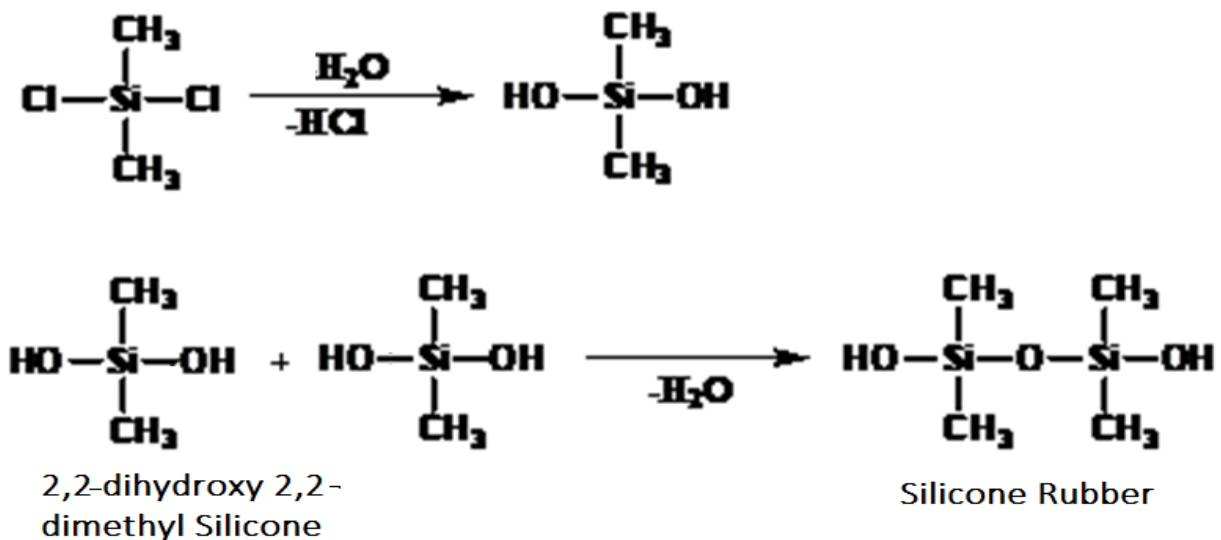
1. Insulation of high voltage wires and cables;
2. Inner tubes of automobile tyres;
3. Conveyor belts for food other materials ;
4. Lining of tanks
5. Hoses etc.

### Silicone Rubber/Silicones :

These polymers contain Siloxane (-Si-O-Si-O-) units with each tetravalent Si atom linked to one or two organic groups.

#### Preparation:

2, 2- dichloro 2,2- dimethyl silicone which on hydrolysis gives dihydroxy silicone compound which is monomer of silicone rubber.



**Properties:**

- They are very stable at high temperature.
- They are resistant to sunlight, oils, acids and alkalis.
- They are flexible between the temperature range of 90-250 °C.

**Uses:**

Silicone rubbers are used as,  
Sealants, lubricants, paints, adhesives, insulation material in electrical fittings and air craft tyres.

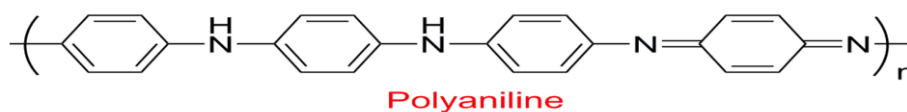
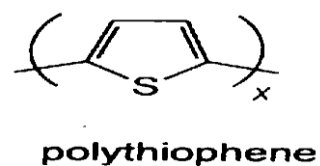
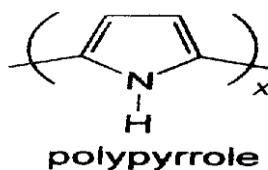
-----Portion for 1st internal test upto Silicone Rubbers-----  
-----

## Conducting Polymers:

The polymers which can conduct electricity due to extensive conjugation are called as conducting /conductive polymers.

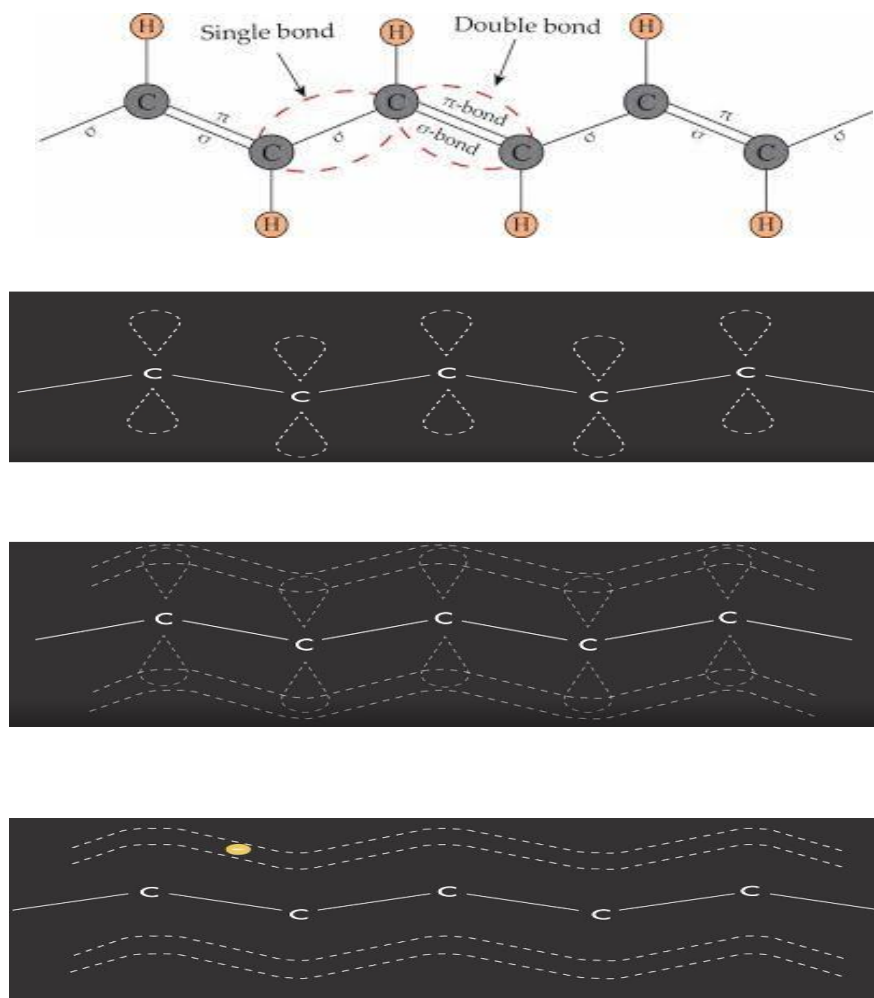
Usually, the extensive conjugation present in the polymer backbone is responsible for conduction of electricity.

**Examples:**

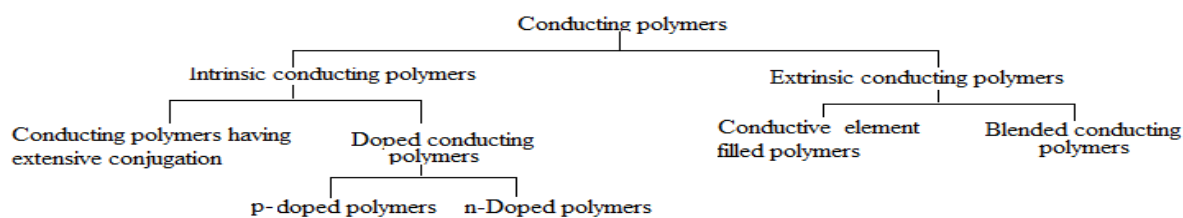




## Conduction mechanism in poly acetylene



Conducting polymers are classified as follows;



### **Intrinsically conducting polymers:**

These polymers have extensive conjugation in the backbone which is responsible for conductance.

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

These polymers contain conjugated  $\pi$  - electrons in the backbone which increases their conductivity to a large extent. This is because, overlapping of conjugated  $\pi$  – electrons over the entire backbone results in valance and conduction bands. These bands are separated by a significant band gap. The electrical conduction occurs only after thermal or photolytic activation of electrons to give them sufficient energy to jump the gap and reach into the lower levels of the conduction band.

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

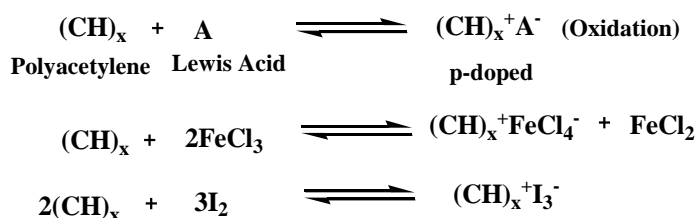
The conducting polymers with high conjugation can be easily oxidised or reduced as they have low ionisation potential. Their conductivities can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction.

Doping is two types:

**Doping** is “addition of impurities or creation of positive or negative charge.

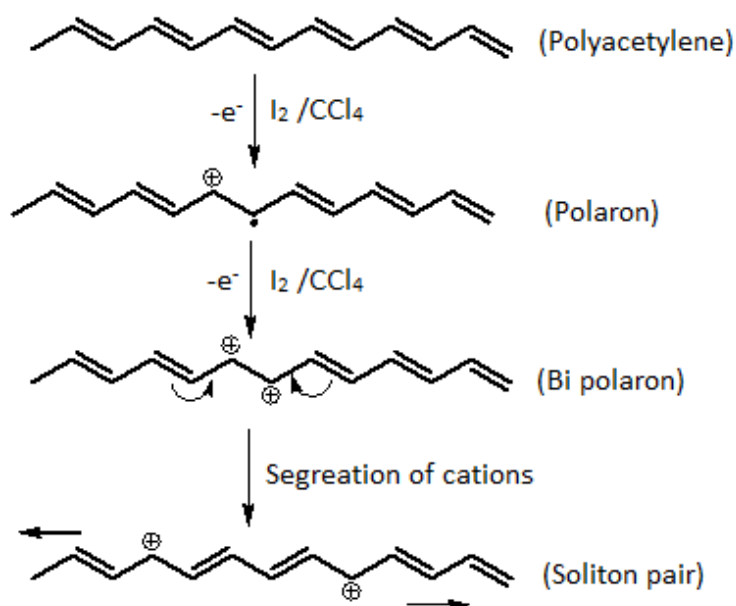
#### **P-Doping (Oxidative doping):**

It is done by oxidation process. Conducting polymer having conjugation is treated with Lewis acids or  $I_2$  vapour of  $I_2$  in  $CCl_4$ .



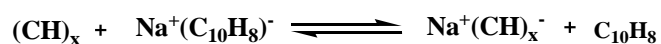
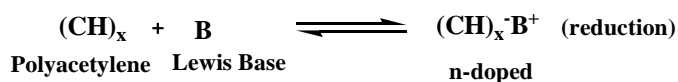
#### **P-Doping of polyacetylene:**

In p-doping, conducting polymer having conjugation is partially oxidised using a suitable oxidising agent which leads to the formation of delocalised radical ion called, **Polaron**. A second oxidation of this Polaron, followed by radical recombination yields two positive charge carriers on each chain which are mobile. Thus, these delocalised positive charges are current carriers for conduction.



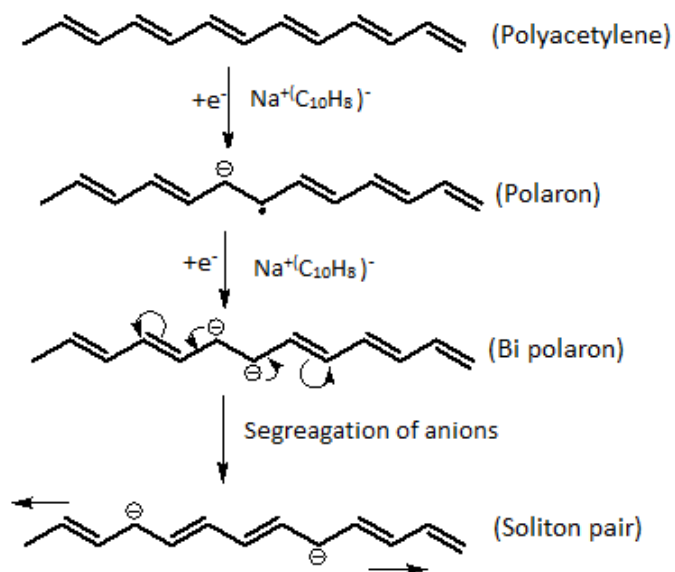
### N-Doping (Reductive doping):

It is done by reduction process. Conducting polymer is treated with Lewis bases or reducing agents.

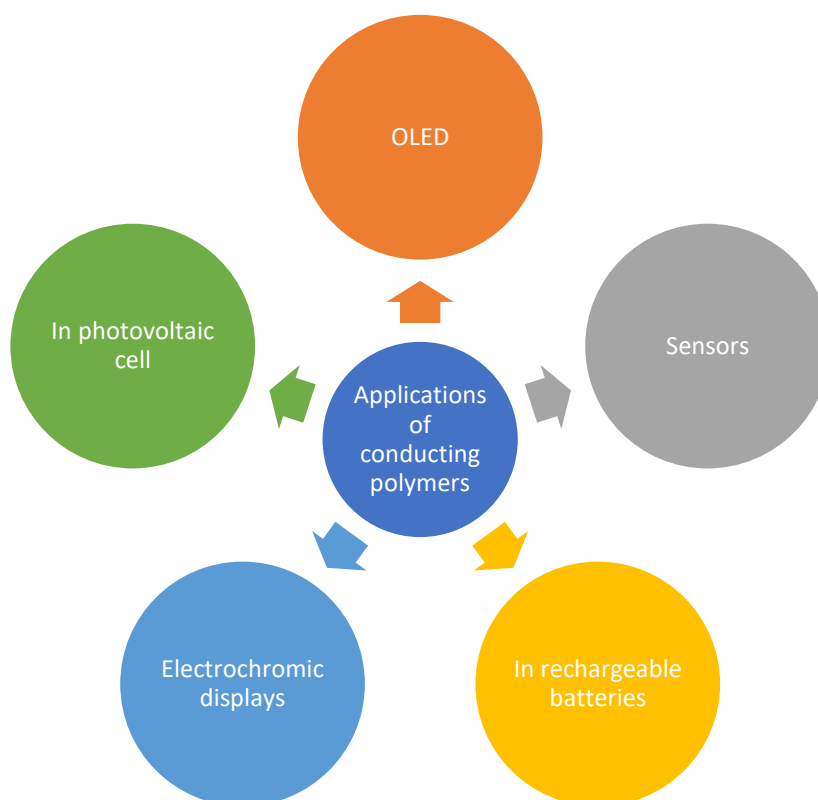


### N-Doping of polyacetylene:

In n-doping, the reduction process leads to formation of Polaron and bi polaron in two steps. This followed by recombination of radical ion yields two negative charge carriers on each chain of polyacetylene which are responsible for conduction.



**Applications of Conducting Polymers:** Conducting polymers are used in the following applications,

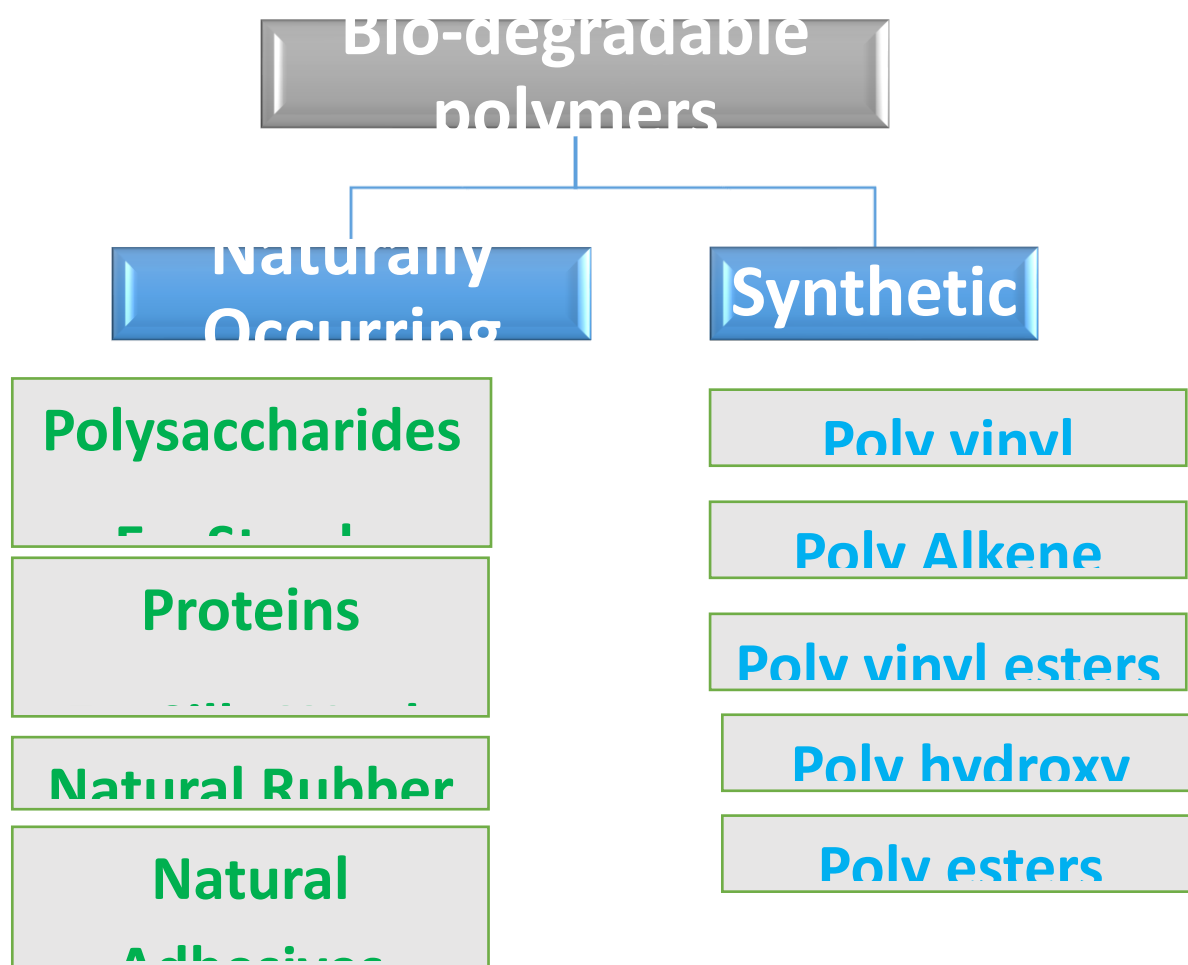


**Biodegradable polymers:**

**Biodegradable polymers are defined as** “the polymeric materials that undergo degradation by environmental factors like sunlight, temperature changes or by the action of micro organisms like algae, fungi and bacteria”

Example: Polylactic acid.

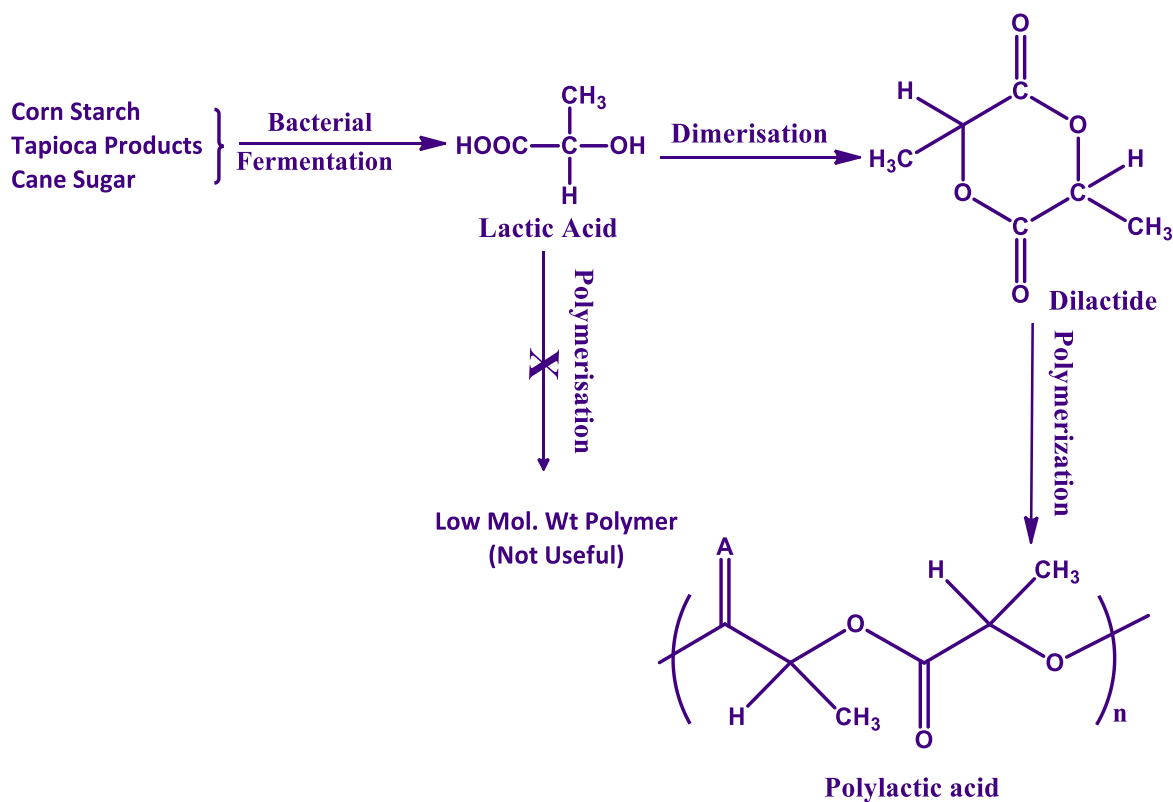
**Classification of Polylactic acid:**



## Polylactic acid:

It is biodegradable thermo plastic, aliphatic polyester derived from renewable resources such as corn starch (in USA), Tapioca products (roots, starch, mostly in Asia) and sugar cane in rest of the world.

### Preparation/Synthesis:



### Properties:

- ✓ PLLA has glass transition temperature between 60-65<sup>0</sup>C, melting temperature between 173-178<sup>0</sup>C and tensile modulus between 2.7-16 Gpa
- ✓ PLA can be processed like most thermoplastics into fibre (using conventional melt spinning process) and films.
- ✓ Heat deflection temperature of PLLA can be increased from 60-190 <sup>0</sup>C by physically blending with PDLA.
- ✓ PDLA & PLLA form highly regular stereo complex with increased crystallinity.
- ✓ Bio-degradation of PDLA is slower than PLLA due to higher crystallinity of PDLA.
- ✓ PDLA has useful property of being optically transparent.

### Applications:

- \* **Cups**
- \* **Packaging**
- \* **Containers, Food**
- \* **Food Service Applications**
- \* **Bottles**
- \* **Tableware, Disposable**
- \* **Outdoor Applications**
- \* **Biomedical Applications**



**PLA Pellets**



### Bio-Medical Applications of Polylactic acid:

