Chapter 3

Engineering Materials

3.1 Polymers

3.1.1 Introduction

Polymer:- In Greek poly = many, mers = units or parts

Small molecules combine with each other to form big molecules. The big molecules are called **polymers**. Polymers are macro molecules or giant molecules of high molecular masses.

Ex:- Poly Ethylene

$$\underset{\text{Ethylene}}{nCH_2=CH_2} \longrightarrow \underset{\text{Polyethylene}}{-\!\left[CH_2-CH_2 \right]_n\!-}$$

Monomer

Reactant molecules in the formation of polymers are called **monomers.**

Ex:- Ethylene is the monomer in the formation of poly ethylene.

$$\underset{\text{Ethylene (Monomer)}}{nCH_2=CH_2} \longrightarrow \underset{\text{Polyethylene}}{-\!\left[CH_2-CH_2 \right]_n\!-}$$

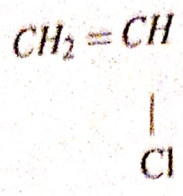
Functionality

In polymerization, the monomers are linked to each other through covalent bonds. So the monomer should have at least two reactive sites (or) bonding sites.

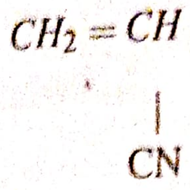
The number of active bonding sites of a monomer is known as **Functionality.**

1. **Bi functional monomers:-** Bifunctional monomers contain two reactive sites.

$CH_2=CH_2$
Ethylene



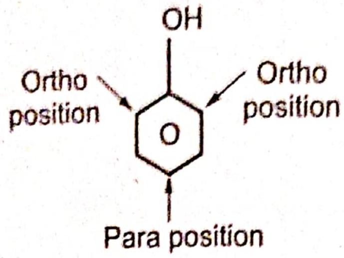
$CH_2=CH(Cl)$



$CH_2=CH(CN)$

Vinyl chloride Acrylonitrile

2. **Tri functional monomers:-** Tri functional monomers contain three reactive sites.



Phenol (2 Ortho positions and 1 para position)

3. **Poly functional monomers:-** A poly functional monomer contains more than three reactive sites. If the numbers of reactive sites are more than 3 in a monomer molecule, the three dimensional network polymer is produced.

   Opening of one double bond gives 2 reactive sites; opening of another double bond gives 2 more reactive sites.

$$H-C\equiv C-H$$

Repeating unit

The unit which is repeated in the polymer is known as **repeating unit.**

Ex:- Ethylene

$$\underset{\text{Ethylene}}{nCH_2=CH_2} \longrightarrow \underbrace{-\!\!\!\left[CH_2-CH_2 \,|\, CH_2-CH_2 \,|\, CH_2-CH_2 \right]_n\!-}_{\text{Repeating Unit}}$$

Polymerization

The phenomenon of the formation of the polymers is known as **polymerization.**

Ex:- Poly Ethylene

$$\underset{\text{Ethylene}}{nCH_2=CH_2} \longrightarrow \underset{\text{Polyethylene}}{-\!\!\left[CH_2-CH_2 \right]_n\!-}$$

Degree of polymerization

The number of repeating units in the formation of polymers is known as **Degree of polymerization**. It is denoted by **Dp**.

$$Dp = \frac{\text{Total molecular weight of the polymer}}{\text{Molecular weight of monomeric unit}}$$

Ex:- If 100 molecules of ethylene on polymerization give polymeric chain, the degree of polymerization of the polymer is 100.

3.1.2 Classification of polymers

Polymers can be classified in a number of ways,

Classification on the basis of source

On the basis of source of the polymers are divided into 2 types.

A. Natural polymers

B. Synthetic polymers

A. **Natural polymers;** The polymers which are found in nature from animals and plants are called **Natural polymers.**

Ex:- Starch (a polymer of α-D-Glucose),Cellulose(a polymer of β-D-Glucose), Proteins (polypeptides and polyamides), Nucleic acids, Natural rubber (a polymer of C is isoprene) & Guttapercha (a polymer of Trans isoprene).

B. **Synthetic polymers:**

The polymers which are synthesized in the Laboratory are known as **Synthetic polymers.**

Ex:- Poly ethylene (PE), Poly styrene (PS), Poly vinyl chloride (PVC), Nylon, Terelene, Bakelite etc.

Classification on the basis of structure

On the basis of structure of polymers are divided into 3 types.

A. Linear polymers

B. Branched chain polymers

C. Three-dimensional network polymers

A. **Linear polymers:** Polymers in which monomeric units are joined in the form of long straight chains are known as **Linear polymers**. These polymers posses high M.P, density and tensile strength due to close packing of polymer chains.

Ex:- High Density Poly Ethylene (HDPE), Nylons, Poly ester.

B. **Branched chain polymers:** The polymers which are mainly linear in nature, but also poses some branches along the main chain are called **Branched chain polymers**. These polymers possess low M.P, density and tensile strength compared to linear polymers, due to poor packing of polymer chains in presence of branches.

Ex:- Low Density Poly Ethylene (LDPE), Glycogen, Amylopectin etc.

C. **Cross linked (or) Three-dimensional network polymers:** The polymers which contain monomer molecules connected to each other by only covalent bonds are called **Cross linked (or) three dimensional network polymers**. They are gaint molecules in which movement of individual monomeric units is prevented by strong cross links. Due to presence of strong cross links they are hard, rigid, and brittle and do not melt, but burn on strong heating.

Ex:- Bakelite, Urea-Formaldehyderesin, Melamine-Formaldehydeetc.

Classification on the basis of their methods of synthesis

Based on the methods of synthesis, the polymers have been classified into two groups.

A. Addition polymers

B. Condensation polymers

A. **Addition polymers:** Polymers are obtained by the repetitive addition of monomers to yield long chains are known as **Addition polymers**.

Ex:- Poly Ethylene (PE), Poly Styrene (PS), PVC etc.

B. **Condensation polymers:** Polymers are obtained in the condensation reaction by the elimination of small molecules like H_2O, NH_3, etc. are known as **condensation polymers**.

Ex:- Nylon-6 (From adipic acid and hexamethylenediamine),

Bakelite (From phenol and formaldehyde),

Polyester (From terephthalic acid and ethylene glycol) etc.

Classification on the basis of growth polymer chain

Based on the growth of polymer, polymers are classified into two groups.

A. Chain growth polymers

B. Step growth polymers

A. **Chain growth polymers:** Polymers are formed by the successive addition of monomer units to the growing chain carrying a reactive intermediate are known as **chain growth polymers.**

Ex:- PE, PS, PVC etc.

Mechanism:-

$$(RCOO)_2 \xrightarrow{\Delta} 2RCOO^{\bullet} \longrightarrow 2R^{\bullet} + 2CO_2$$

Peroxide (initiator) Free radical

$$R^{\bullet} + CH_2 = CH_2 \rightarrow R - CH_2 - \overset{\bullet}{C}H_2 \xrightarrow{CH_2=CH_2} R - CH_2 - CH_2 - CH_2 - \overset{\bullet}{C}H_2$$

$$\downarrow (n-2)CH_2 = CH_2$$

$$R-(-CH_2-CH_2-)_nCH_2-\overset{\bullet}{C}H_2$$

$$R-(CH_2-CH_2)_n-CH_2-\overset{\bullet}{C}H_2+\overset{\bullet}{C}H_2-CH_2-(CH_2-CH_2)_n-R$$

$$\downarrow$$

$$R-(CH_2-CH_2)_n-CH_2-CH_2-CH_2-CH_2-(CH_2-CH_2)_n-R$$

Dead polymer

B. **Step growth polymers:** Polymers are formed through a series of independent reactions involving bond formation (condensation) between two different monomers with the loss of small molecules like H_2O, HCl, NH_3, etc.

Ex:- Nylon-6, Bakelite, Polymer etc.

Mechanism:-

$$A-X+B-Y \longrightarrow A-B+XY$$

$$A-B+A-B \longrightarrow A-B-A-B \text{ (or) } (A-B)_2$$

$$(A-B)_2+A-B \longrightarrow (A-B)_3$$

$$(A-B)_2+(A-B)_2 \longrightarrow (A-B)_4 \longrightarrow (A-B)_n$$

Classification based on molecular forces

On the basis of the Magnitude of intermolecular forces present in polymers, they are classified into 4 Categories.

A. Thermoplastic polymers
B. Thermo setting polymers
C. Elastomers (synthetic rubbers)
D. Fibers

A. **Thermoplastic polymers:** Those polymers are liner, long chain polymers, which can be softened on heating and hardened on cooling reversibly, i.e, are known as **thermoplastic polymers**. Their hardness is a temporary property, subject to change with rise or fall of temperature. Thus, they can be processed again and again.

Ex:- PE, PS, PVC, Nylons, Teflon etc.

B. **Thermo setting polymers:** Those polymers, which during moulding by heating get hardened and once they have solidified, they cannot be softened, are called **thermo setting polymers**. They are permanent setting polymers. Such polymers during moulding acquire three dimensional cross linked structures, with predominately strong covalent bonds. Thus, a thermo setting polymers once moulded cannot be reprocessed.

Ex:- Polyester (Terelene), Epoxy - resin (Araldite), Melamine etc.

C. .**Elastomers (synthetic rubbers):** Any rubber - like plastic polymer, which can be stretched to at least thrice of its original length, but it returns to its original shape and dimensions as soon as stretching force is released, is known as "**Elastomers**"

The elastic deformation in an elastomer arises from the fact that in an unstressed condition, an elastomer molecular chain is in the form of a coil and consequently, it can be stretched like a spring. The chains revert back to their original coiled state as the deforming stress is released. Thus, elasticity of an elastomer is caused by the lengthening and shortening of their polymeric chain springs.

Ex:- BUNA-S, BUNA-N, Butyl rubber

D. **Fibers:** These polymers whose chains are held by strong intermolecular forces like hydrogen bonding are known as **Fibers**". They are crystalline in nature and of high tensile strength, due to strong inter molecular forces.

Ex:- Nylon, Polyester etc.

3.1.3 Types of Polymerization

The polymerization is of four types

1. Addition polymerization
2. Condensation polymerization
3. Co-polymerization
4. Co-ordination polymerization (or) Ziegler-Natta polymerization

Addition (or) Chain Growth Polymerization

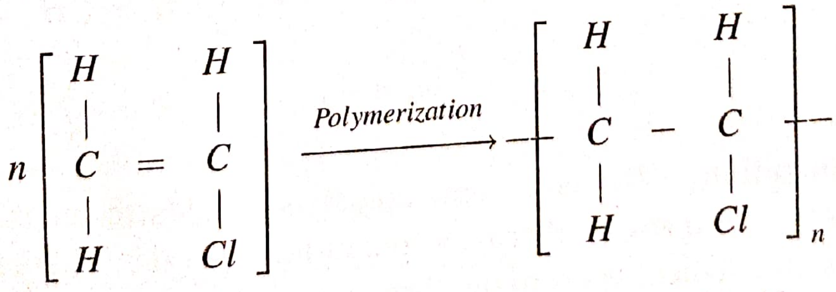
In the polymerization, the polymers are formed without the loss of any material, and the product is an exact multiple of the original monomeric molecule such type of polymerization is known as Addition polymerization. The addition polymerization reaction must be instigated by the application of heat, light, pressure (or) a catalyst for breaking down the double bonds of monomers.

Ex:-

1. Polyethylene

$$\underset{\text{Ethylene}}{n\,CH_2=CH_2} \longrightarrow \underset{\text{Polyethylene}}{-\!\!\left[\, CH_2-CH_2 \,\right]_n\!\!-}$$

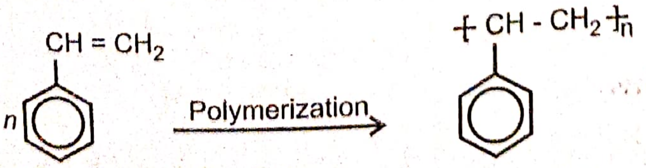
2. Poly vinyl chloride (PVC)



$$n\begin{bmatrix} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & Cl \end{bmatrix} \xrightarrow{Polymerization} -\!\!\begin{bmatrix} H & & H \\ | & & | \\ C & - & C \\ | & & | \\ H & & Cl \end{bmatrix}_n\!\!-$$

Vinyl chloride Polyvinyl chloride

3. Polystyrene



Styrene Polystyrene(PS)

Mechanism of Addition (or) Chain polymerization

Addition polymerization reactions proceed by a chain reaction mechanism consisting of three important steps,

(i) Initiation (or) the formation of an active centre,

(ii) Propagation (or) the formation of a polymer having the active centre, and

(iii) Termination (or) removal of the active centre.

The three different active centers have been found to be formed during the addition polymerization. They are Free radical, Carbonium ion, and Carbanion. So the mechanisms involving these reactive species in polymerization constitute the mechanism of addition polymerization. Let us take one by one.

Free radical addition polymerization

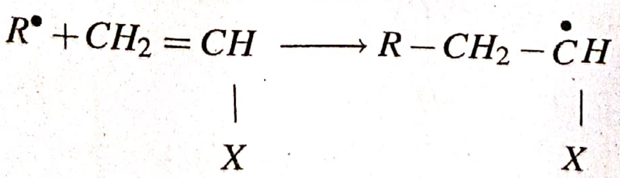
It involves three steps, these steps will form only linear molecules.

(i) **Initiation:-** A reagent that is either itself a free radical, such as oxygen molecule, or that easily decomposes to form free radicals, such as organic peroxides, is used to initiate the reaction.

$$R-O \vdots O-R \rightarrow 2RO^\bullet$$

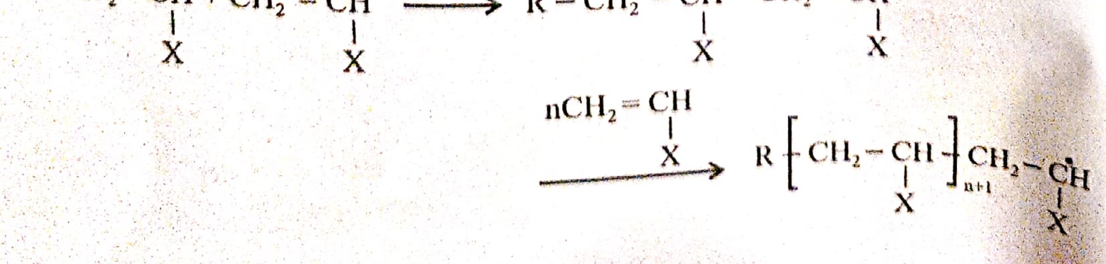
$$2R-O^\bullet \rightarrow 2R^\bullet + O_2$$

The radical now adds to the monomer to form a new free radical, e.g., it adds on vinyl chloride in the following way.



$$R^\bullet + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow R-CH_2-\underset{X}{\underset{|}{\overset{\bullet}{C}H}}$$

(ii) **Propagation:-** The new free radical now adds to another molecule of monomer to form another new free radical like this addition of monomers to the free radical leads to the formation of large free radical.

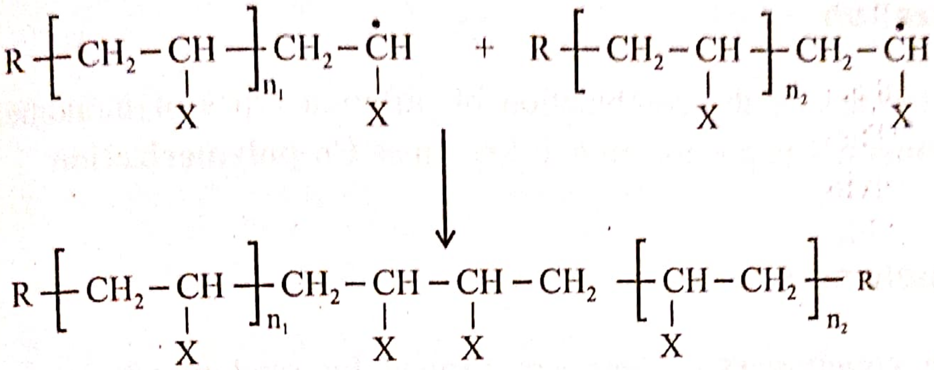


$$R-CH_2-\underset{X}{\underset{|}{\dot{C}H}} + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow R-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

$$\xrightarrow{nCH_2=\underset{X}{\underset{|}{CH}}} R\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_{n+1}CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

(iii) **Termination:-** Termination takes place by the addition of growing free radical polymer with other growing free radical polymer (or)The growing free radical chain reacts with the monomer molecule which involves the transference of a proton either from the monomer molecule to the free radical or vice versa.

Combination:



$$R\left[CH_2-\underset{X}{CH}\right]_{n_1}CH_2-\underset{X}{\dot{C}H} + R\left[CH_2-\underset{X}{CH}\right]_{n_2}CH_2-\underset{X}{\dot{C}H}$$

$$\downarrow$$

$$R\left[CH_2-\underset{X}{CH}\right]_{n_1}CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2\left[\underset{X}{CH}-CH_2\right]_{n_2}R$$

Condensation (or) Step Growth Polymerization

The polymerization reaction, in which the polymers are formed by step by step with the elimination of small molecules like HCl, H_2O, NH_3, etc., is known as condensation polymerization.

Condensation polymerization is an intermolecular 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 may give rise to a cross-linked structure polymer.

Mechanism

$$A-X+B-Y \rightarrow A-B+XY$$

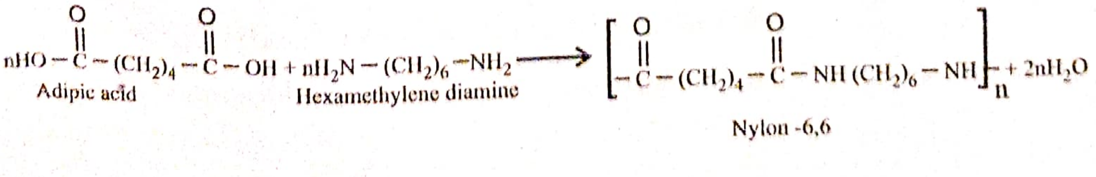
$$A-B+A-B \rightarrow A-B-AB \text{ (or) } (A-B)_2$$

$$(A-B)_2+A-B \rightarrow (A-B)_3$$

$$(A-B)_2+(A-B)_2 \rightarrow (A-B)_4 \rightarrow (A-B)_n$$

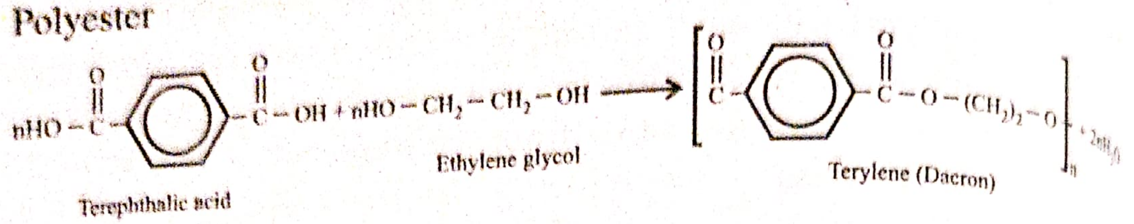
Ex:-

1. Nylon 6,6



$$nHO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + nH_2N-(CH_2)_6-NH_2 \longrightarrow \left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH(CH_2)_6-NH\right]_n + 2nH_2O$$

2. Polyester



Co-polymerization

Polymers are formed by the combination of different types of monomers are called **Co-polymers**. The phenomenon is known as **Co-polymerization**.

Types of Copolymers

1. **Random copolymers:-** These are formed by random arrangement of monomeric units in the chain.

$$A-B-A-A-B-A-B-B-B-A-A-$$

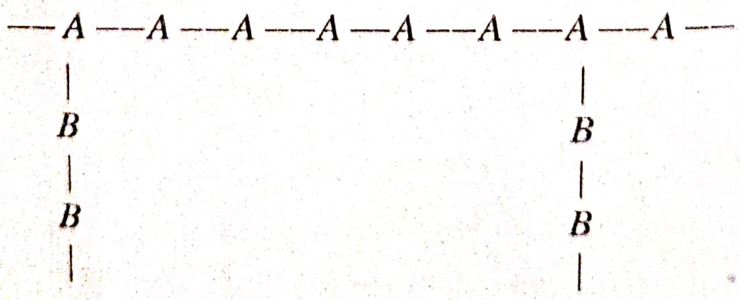
2. **Alternate copolymers:-** These are formed by alternative arrangement of monomeric units in the chain.

$$-A-B-A-B-A-B-A-B-A-$$

3. **Block copolymer:-** It consists of blocks of repeating units of one type alternating with blocks of another type.

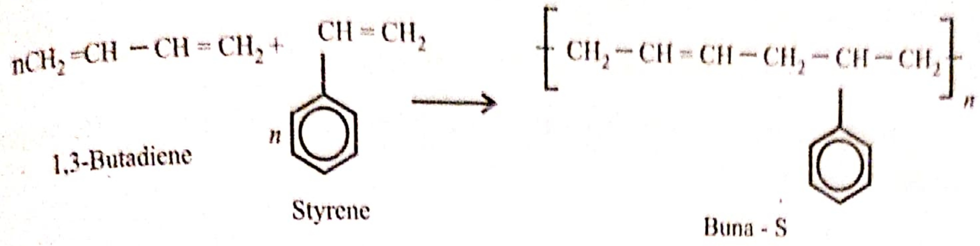
$$-A-A-A-A-B-B-B-B-A-A-A-A-$$

4. **Graft copolymer:-** It consists of a linear polymer chain of one type to which the side chain of a different type has been grafted.

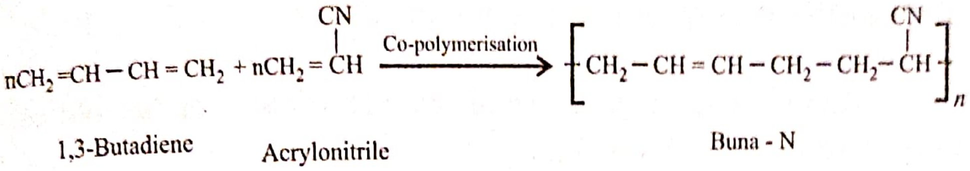


Ex:-

1. BUNA-S



2. BUNA-N



$$nCH_2{=}CH-CH{=}CH_2 + nCH_2{=}\overset{CN}{\overset{|}{CH}} \xrightarrow{\text{Co-polymerisation}} \left[CH_2-CH{=}CH-CH_2-CH_2-\overset{CN}{\overset{|}{CH}} \right]_n$$

3.2 Plastics

The Word Plastics is derived from Greek Word 'Plastikos' meaning capable of being moulded [or] shaped.

"Organic materials of high molecular weight, which can be moulded into any desired form, when subjected to heat and pressure in the presence of catalyst are known as plastics."

Plastics can be moulded [or] pressed [or] casted [or] extruded into various shapes like plates, tubes, bottle, boxes, fibers etc.

3.2.1 General Properties of Plastics

1. Density of plastics is very low as compared to metals.
2. Strength of plastics is sufficient to make low weight, high strength machine parts.
3. Antifriction and self- lubricating properties of plastics enables it to be a good replacement of metal parts.
4. Plastics components offer noiseless operation of moving parts, corrosion resistance, water proofing, leak proof joints, etc.
5. Its production is very easy due to low melting point and excellent flow ability in liquid state into the mold cavity.
6. Low cost of manufacturing in case of plastics.
7. Plastics exhibits insulation for heat and electricity.
8. Plastics are chemically stable when subjected to solvents, oxidizing agents, gases, etc.

9. Plastics are less brittle than glass, yet they can be made equally transparent and smooth.
10. They possess good toughness.
11. Plastics can be easily molded to desired shape.
12. They having very good damping characteristics, colour ability, deformability and weather ability.

3.2.2 Plastics as Engineering materials

Advantages of plastics over other engineering materials.

1. Low fabrication cost, low thermal & electrical conductivities, high resistance to corrosion & solvents.
2. The stress - strain relationship of plastics is similar to that of the metals.
3. Plastics reduce noise & vibration in machines
4. Plastics are bad conductors of heat are useful for making handles used for hot objects, most plastics are inflammable.
5. Plastics are electrical insulators & find large scale use in the electrical industry.
6. Plastics are resistance to chemicals.
7. Plastics are clear & transparent so they can be given beautiful colours.

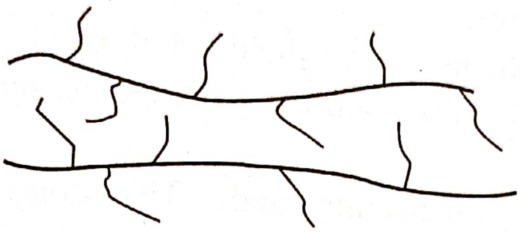
3.2.3 Types of plastics

On the basis of their physical characteristics, plastics are usually divided into three types.

1. Thermo Plastics
2. Thermosets
3. Elastomers

1. **Thermo Plastics:** Thermoplastics have a linear or branched molecular structure which determines their strength and thermal behavior; they are flexible at ordinary temperature. At approx 120-180°C, thermo plastics become a pasty/liquid mass. The service temperature range for thermo plastics is considerable lower than that for thermo sets.
   - These are prepared in single step process.
   - These plastic are generally amorphous (or) crystalline.

- These are linear (or) branched polymers with weak intermolecular attractive forces.
- These plastics become soft on heating and stiffen on cooling at any time.
- They may be remoulded, reshaped, reused and recycled.

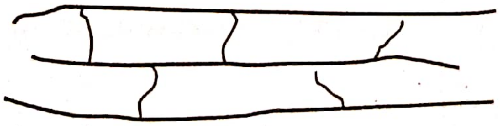


Thermoplastics

Ex: - PE, PS, PVC, Nylons, Teflon etc.

2. **Thermosets:** Thermo sets are hard and have a very tight meshed, branched molecular structure. Curing proceeds during shaping, after which it is no longer possible to shape the material by heating. Further shaping may then only be performed by machining.

- These are normally produced.
- These are cross linked, three dimensional structures.
- Once a product is prepared by heating and moulding, it can't be changed by further heating.
- On excess heating materials undergoes destruction but not become soft.



Thermosettings

Ex:- Bakelite

3. **Elastomers:** Elastomers also have a cross-linked structure; they have a looser mesh than thermo sets, giving rise to a degree of elasticity. Once shaped, elastomers also cannot be reshaped by heating. Elastomers are used, for example,

Ex:- to produce automobile tires.

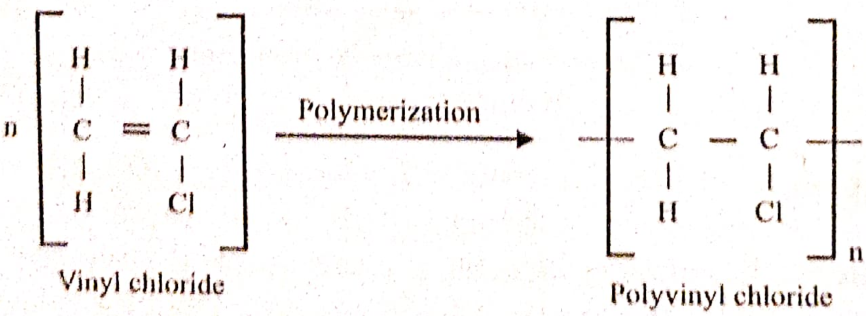
3.2.4 Differences between Thermo Settings and Thermo Plastics

S.No.	Thermo Plastics	Thermo Settings
1.	Formed by either addition (or) condensation polymerisation.	Formed by condensation polymerisation.
2.	They are linear (or) branched linked structures.	They are cross linked (or) three dimensional structures.
3.	Polymers chains are held together by weak attractive forces.	Polymers chains are held together by covalent cross links.
4.	They soften on heating and stiffen on cooling.	They don't soften on heating.
5.	They are soluble.	They are not soluble.
6.	They can be remoulded, reshaped and reused.	They cannot be remoulded.
7.	They can be recycled.	They cannot be recycled.
8.	They are tough.	They are brittle.
9.	They have low melting points.	They have high melting points.
10.	These have usually linear structures. Ex. Polyethylene, PVC, teflon.	These have three dimensional cross linked structures. Ex. Bakelite, urea-formaldehyde, resin

3.3 Preparation, Properties & Uses of the Following Polymers

3.3.1 Poly vinyl chloride (PVC)

Preparation:- PVC is prepared by polymerization of vinyl chloride.



$$n\,\mathrm{CH_2{=}CHCl} \xrightarrow{\text{Polymerization}} \left[-\mathrm{CH_2-CHCl}-\right]_n$$

Properties

1. PVC is a colourless, non-inflammable and chemically inert powder.

2. It has specific gravity 1.33 and melting point 148°C.
3. Resistant to atmospheric condition
4. PVC is strong and brittle.
5. It is resistant to atmospheric conditions like O_2, CO_2 and moisture.
6. PVC is not stable to heat and UV radiations. It undergoes degradation.

Application

1. PVC treated with plasticizers is called plasticized
2. PVC used for electrical insulations, injection moulding articles like tool handles.
3. It is used radio, telephone components, chemical containers, and foams used in buildings.
4. Unplasticized PVC is rigid, highly resistant to chemicals and brittle.
5. PVC is used for making safety helmets, refrigerator components, tyres, cycle and motor cycle mudguards.

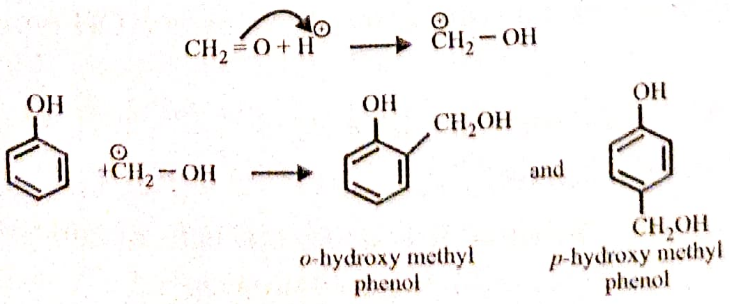
3.3.2 Bakelite (Phenol-formaldehyde Resin)

Preparation

Bakelite is prepared by condensing phenol with formaldehyde in presence of acidic/alkaline catalyst.

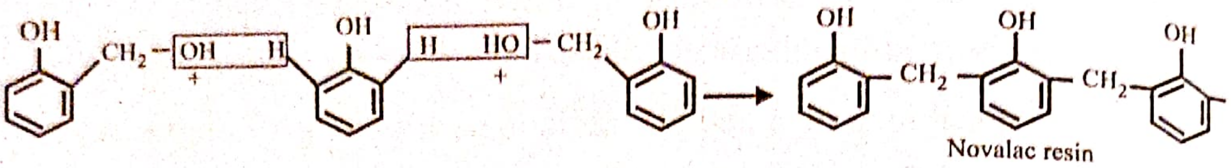
Step-I:-

Phenol reacts with formaldehyde produce O-Hydroxy methyl Phenol & P-Hydroxy methyl Phenol.



Step-II:-

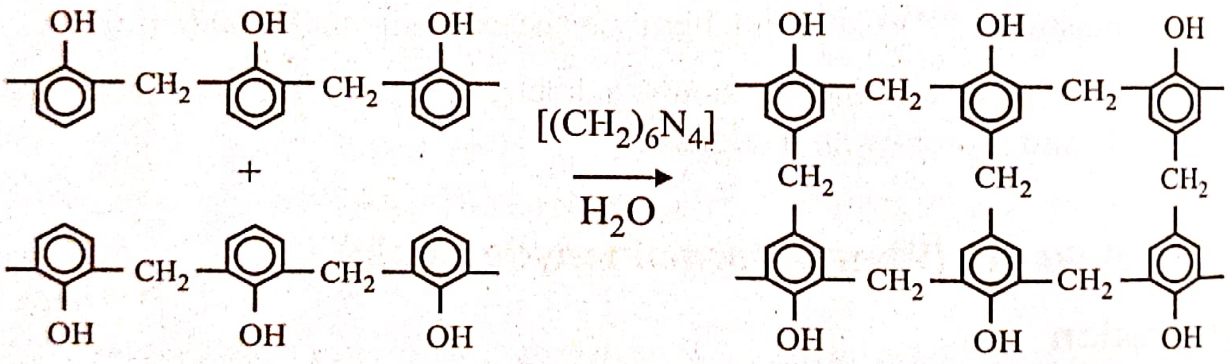
O-Hydroxy methyl Phenol & Phenol, which reacts to form linear polymer Novalac resin.



Step-III:-

During moulding, catalyst Hexa methylene tetra amine $[(CH_2)_6N_4]$ is added. Addition of this catalyst provides excess of formaldehyde, which converts the soluble and fusible Novalac resin into hard, infusible & insoluble solid of cross-linked polymer Bakelite.

$$[(CH_2)_6N_4] + H_2O \rightarrow 6CH_2O + 4NH_3$$



Properties

1. It is hard, rigid & strong.
2. It is a scratch resistant and water resistant polymer.
3. Bakelite has got good chemical resistance, resistant to acids, salts and many organic solvents, but it is attacked by alkalis due to the presence of –OH groups.
4. It is a good anion exchanging resin, exchanges –OH group with any other anion.
5. It is an excellent electrical insulator.
6. It is a very good adhesive.
7. It has very good corrosion resistance, resistant to atmospheric conditions like O_2, CO_2, moisture, light, UV radiation etc.

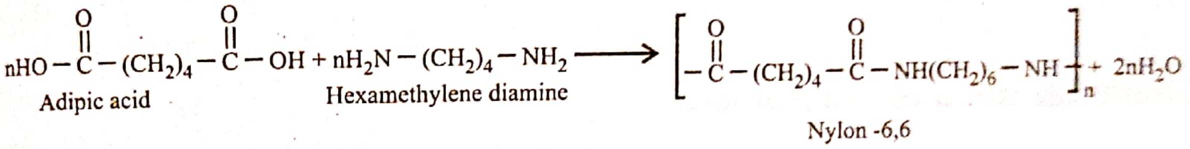
Engineering applications

1. For making Switches, switch boards, heater handles etc.
2. For making moulded articles like Telephone parts, cabinets for radio and television.
3. As an adhesive (binder) for grinding wheels etc.
4. It is used in paints and varnishes.
5. For making bearings used in propeller shafts, paper industry and rolling mills.

3.3.3 Nylon-6,6

Preparation

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



$$\underset{\text{Adipic acid}}{nHO-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Hexamethylene diamine}}{nH_2N-(CH_2)_4-NH_2} \longrightarrow \underset{\text{Nylon -6,6}}{\left[-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-NH(CH_2)_6-NH-\right]_n} + 2nH_2O$$

Properties of Nylon

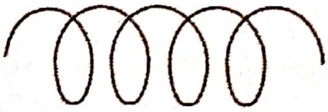
1. They are translucent, whitish, horny, high melting (160 to 264°C) polymers.
2. They possess high temperature stability and good abrasion resistance.
3. They are insoluble in common organic solvents (like methylated spirit, benzene and acetone) and soluble in phenol and formic acid.
4. Their mouldings and extrusions have good physical strength) and self-lubricating properties.

Uses of nylons

1. Nylon-6:6 is primarily used for fibers, which find use in making socks, ladies hoses, under-garments, dresses, carpets, etc.
2. Nylon bearings and gears work quietly without any lubrication.
3. They are also used for making filaments for ropes, bristles for tooth - brushes and films, tyre-cords, etc.

3.4 Elastomers

Rubbers (also known as Elastomers) are high polymers, which have elastic properties in excess of 300 percent. Thus, a rubber-band can be stretched to 4 to 10 times its original length and as soon as the stretching force is released, it returns to its original length. The elastic deformation in an elastomer arises from the fact that in the unstressed condition, an elastomer molecule is not straight chained, but in the form of a coil and consequently, it can be stretched like a spring. The unstretched rubber is amorphous. As stretching is done, the macro molecules get partially aligned with respect to another, thereby causing crystallization and consequent, stiffening of material. On releasing the deforming stress, the chains get reverted back to their original coiled state and the material again becomes amorphous.



Characteristics of Elastomers:

1. Elastomers regain original shape after removing stress.
2. Elastomers are sticky at higher temperatures.
3. Elastomers exist at above glass transition (Tg) temperature.
4. Elastomers absorb moisture.
5. Elastomers have less chemical resistance.
6. Elastomers have weak intermolecular attractions.
7. Elastomers have coiled structures.

3.4.1 SBR (Buna-S or Styrene-Butadiene Rubber)

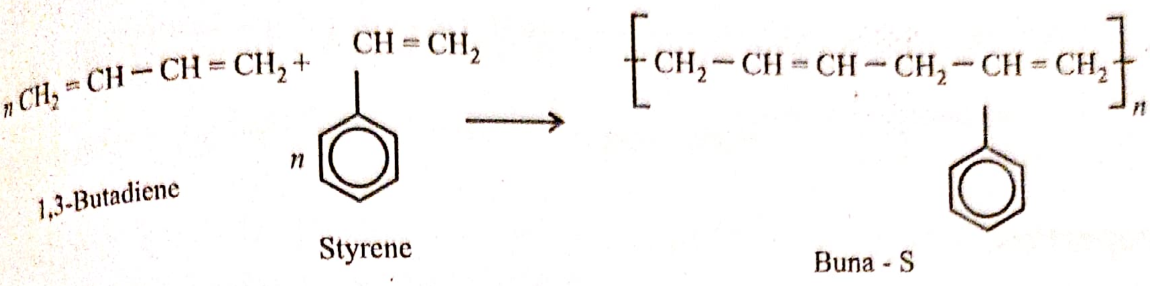
Buna-S is also called as Styrene rubber or GR-S(Government Rubber styrene) Ameripol. Buna-S stands for the composition of the monomers and catalyst.

Bu stands for Butadiene-Monomer

Na stands for Sodium-Catalyst

S stands for Styrene-Monomer

Buna-S is produced by the copolymerization of butadiene with styrene usin sodium as catalyst.



Properties

1. Styrene rubber is a strong and tough polymer.
2. It is vulcanized by sulphur mono chloride (S_2Cl_2) or Sulphur.
3. It resembles natural rubber in processing characteristics and quality of finished products.
4. Buna-S possesses 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.

Engineering applications (Uses)

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 files, tank linings in chemical industries and as adhesives.

3.4.2 Buna-N or Nitrile Rubber (NBR)

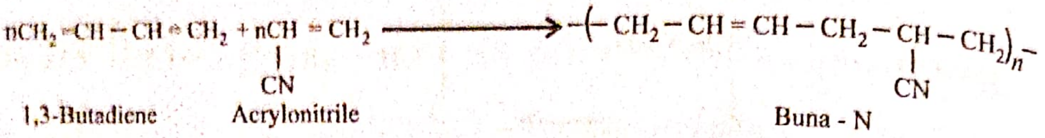
Buna-N is also called as Nitrile rubber or GR-A.Nitrile rubber is a copolymer of butadiene and acrylonitrile where the composition of the monomers and catalyst are in its name.

Bu stands for butadiene - Monomer

Na stands for sodium - Catalyst

N stands for acrylonitrile - Monomer

Buna-N is produced by the copolymerization of butadiene with acrylonitrile using sodium as catalyst.



$$n\,CH_2{=}CH-CH{=}CH_2 + n\,\underset{CN}{\underset{|}{CH}}{=}CH_2 \longrightarrow -\!\left(CH_2-CH{=}CH-CH_2-\underset{CN}{\underset{|}{CH}}-CH_2\right)_n\!-$$

Properties:

1. Because of the presence of -CN group in the structure Buna-N possess excellent resistance to heat, sunlight, oils, acids and salts and less resistant to alkalis than natural rubber. It is a strong and tough polymer with light weight.
2. Buna-N is also vulcanized with Sulphur.
3. It is highly resistant to atmospheric O_2, CO_2, moisture, U.V light and light.
4. Buna-N is an excellent electrical insulator.
5. Vulcanized Buna-N is resistant to ageing and high temperatures.

Engineering applications (Uses):

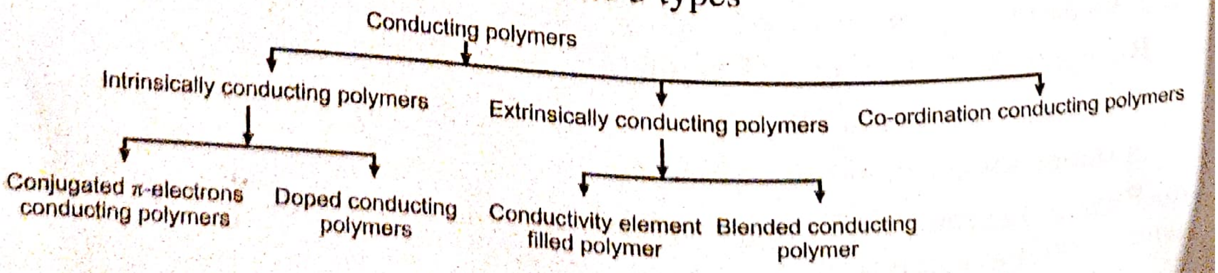
1. Buna-N is used for making conveyors belts, high altitude aircraft components and automobile parts because of its strength and light weight.
2. It is used for making tank linings and pipes for chemical industries.
3. It is also used for making gaskets, oil resistant foams, adhesives and printing rollers.

3.5 Conducting Polymers

Most polymeric materials are poor conductors of electricity, because of the non-availability of large number of free electrons in the conduction process.

"Polymeric materials have been synthesized which possess electrical conductivities on par with metallic conductors. Such polymers are known as **Conducting polymers**".

Conducting polymers are divided into 3 types

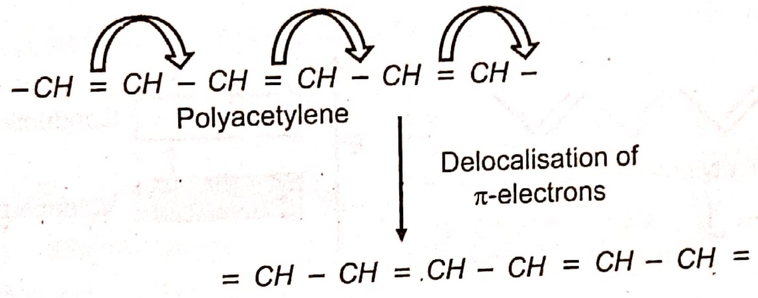


3.5.1 Intrinsically Conducting Polymer (ICP)

Conjugated π-electrons conducting polymer:

"A polymer whose backbones or associate groups consists of delocalized electron pair or residual charge is known as **ICP**".

This type of polymers essentially contain conjugated π-electrons backbone, which is responsible for electrical charge. In an electric field, conjugated π-electrons of polymer get excited; thereby can be transported through the solid polymeric material. Overlapping of orbital's (of conjugated π-electrons) over the entire backbone results in the formation of valence bands as well as conduction bands, which extends over the entire polymer molecule. Presence of conjugated π-electron in a polymer increases its conductivity to a large extent.



Ex:- Poly acetylene polymers, Poly aniline, Poly pyrrole etc.

Doped conducting polymers:

It is obtained by exposing a polymer to a charge transfer agent in either gas phase or in solution.ICPs possess low conductivity ($\approx 10^{-10}$ ohm^{-1} cm^{-1}), but these possess low ionization potential and high electron affinities, so these can be easily oxidized or reduced. Consequently, the conductivity of ICP can be increased by creating either positive or negative charges on the polymer backbone by oxidation or reduction. This technique is called. Doping (an analog with semiconductor). Doping is of two types,

i) P-doping

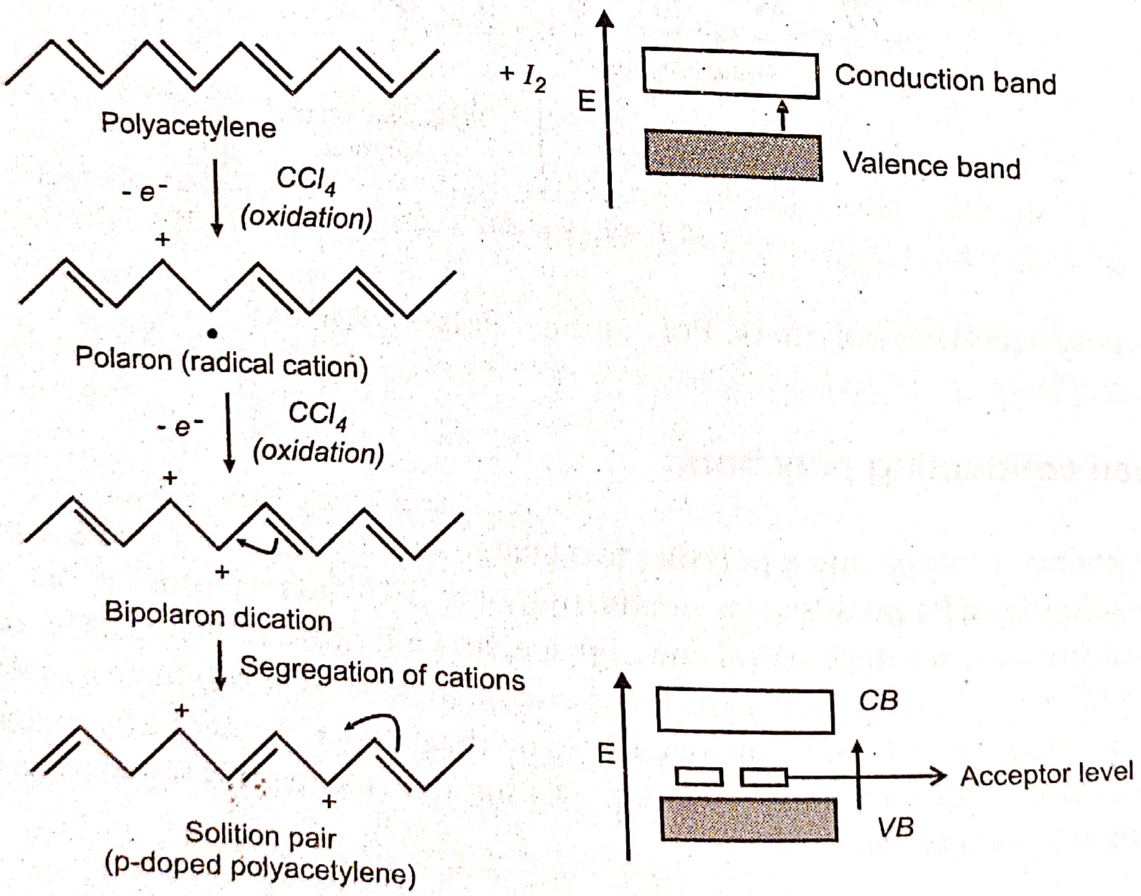
P-doping involves treating an ICP with Lewis acid, thereby oxidation process takes place and positive charges on the polymer backbone are created. Some of the p-dopant used are I_2, Br_2, AsF_5, PF_6, etc.

$$\underset{\text{Polyacetylene}}{(C_2H_2)_n} + 2FeCl_3 \xrightarrow{\text{Oxidation}} (C_2H_2)_n^+ \, FeCl_4^- + FeCl_2$$

$$2\underset{\text{Polyacetylene}}{(C_2H_2)_n} + 3I_2 \xrightarrow{\text{Oxidation}} 2\left[(C_2H_2)_n^+ \, I_n^-\right]$$

During oxidation process the removal of π-electron from polymer backbon lead to the formation of a delocalized radical ion called polaron having a hol in between valence band and conduction band. The second oxidation of th polaron results in two positive charge carriers in each chain called bipolaro which are mobile because of delocalization. These delocalized charge carrie are responsible for conductance when placed in electric field.

The second oxidation of the polaron results in two positive charge carriers each chain called bipolaron, which are mobile because of delocalization. The delocalized charge carriers are responsible for conductance when placed in electi field.



ii) N-doping

N-doping involves treating an ICP with Lewis base thereby reduction pro takes place and negative charges on the polymer backbone are created. S of the common N-dopant used are Li, Na, Ca, Tetrabutyl ammonium, $FeCl_3$,

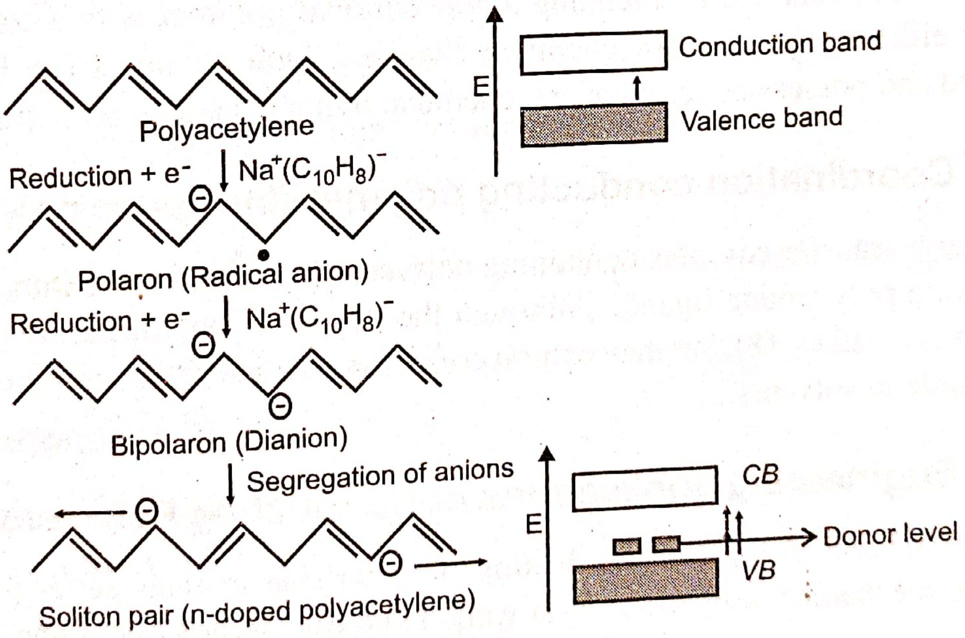
$$\underset{\text{Poly acetylene}}{(C_2H_2)_n} + \underset{\text{lewis base}}{B} \longrightarrow (C_2H_2)_n^- B^+$$

$$\underset{\text{Poly acetylene}}{(C_2H_2)_n} + \underset{\text{Naphthylamine}}{C_{10}H_7NH_2} \longrightarrow (C_2H_2)_n^- NH^+ + \underset{\text{Naphthalene}}{C_{10}H_8}$$

The electron added to polyacetylene by reductive doping does not go into the conducting band but goes into an intermediate electronic state within the bandgap of radical anion(polaron). Bipolaron contains electrons in the energy levels residing in the band gap.

The dianion lowers its energy by segregating into two negative solitons at the midgap energy levels. The presence of holes in the band gap allows facile jumps of electrons from valance band into conduction band. This leads to the generation of conduction pathways. As a consequence the conductivity increases significantly.

Formation of polaron, bipolaron takes place in two steps, followed by recombination of radicals, which yields two charge carriers on the polyacetylene chain responsible for conduction as shown below.



3.5.2 Extrinsically Conducting Polymers (ECP)

Those polymers whose conductivity is due to the presence of "externally" added ingredient in them are known as ECPs. These are of the following two types,

i) Conductive element-filled polymer

This is a resin or polymer filled with conducting elements such as carbon black, metallic fibres, metal oxides, etc.In this, the polymer act as the binder to hold the conducting elements together in the solid entity. These polymers possess reasonably good bulk conductivity, and are generally, low in cost, light in weight, mechanically durable and strong, and easily processable in different forms, shapes and sizes.

Generally, special grade conducting carbon black is used as a filler, due to its

a) Very high surface area (1000 m/g)
b) High porosity, and
c) Filamentous properties

Minimum concentration of conductive filler in the polymer to start the conduction process is known as percolation threshold.

ii) Blended conducting polymer

This product is obtained by blending a conventional polymer with a conducting polymer either by physical or chemical change. Such polymers can be easily processed and possess better physical, chemical and mechanical properties.

3.5.3 Coordination conducting polymer (inorganic polymer)

It is a charge transfer complex containing polymer obtained by combining a metal atom with a polydentate ligand. Although the degree of polymerization in such polymers is small (≤ 18), yet they exhibit corrosion characteristics, and are usually in doubtable in solvents.

3.5.4 Engineering applications of Conducting Polymers

There are several utilities of conducting polymer due to their better physical, chemical, mechanical properties, light weight and easy to process. Some of them are:

1. To make rechargeable light weight batteries.
2. In making of analytical sensors for pH, O_2, NO_2, SO_2, NH_3, glucose.
3. Making of ion-exchangers.
4. In electronic devices such as transistors and diodes.
5. Making of solar cells.
6. In photovoltaic devices.

3.6 Biomaterials

3.6.1 Introduction

A definition for biomaterial has been difficult to formulate, a widely accepted definition for biomaterial is that:

A material derived from biological organisms like plants, animals, bacteria, fungi and other life forms is known as biomaterial.

(or)

A biomaterial is any material, natural or man-made, that comprises whole or part of a living structure or biomedical device which performs, auguments, or replaces a natural function.

3.6.2 Preparation, properties and applications of polylactic acid

Polylactic acid (PLA)Poly(lactic acid) or polylactide (PLA) is a thermoplastic aliphatic polyester commonly made from a-hydroxy acids, derived from renewable resources, such as

- corn starch (in the United States),
- tapioca products (roots, chips or starch mostly in Asia) or
- sugarcanes (in the rest of world).

It can biodegrade under certain conditions, such as the presence of oxygen, and is difficult to recycle.

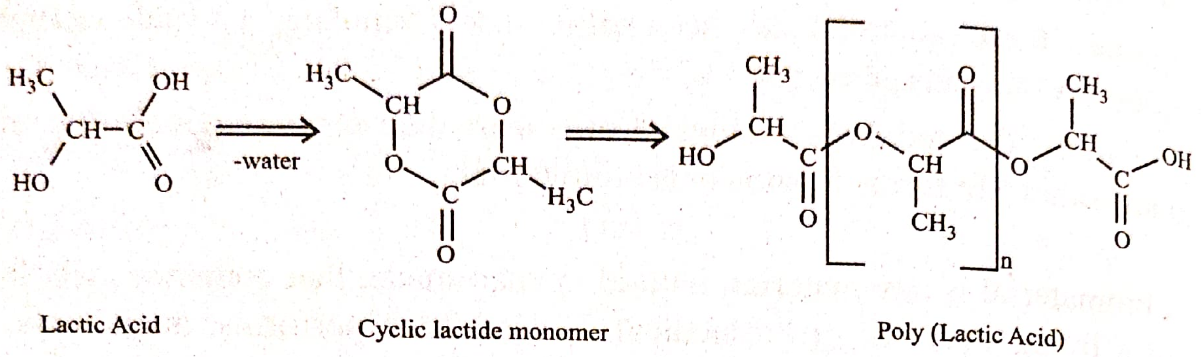
Preparation:

Lactic acid is the starting material for the PLA production process. The polymer is formed either by

1. Direct condensation of lactic acid or
2. Via the cyclic intermediate dimer (lactide), through a ring opening process

- Bacterial fermentation is used to produce lactic acid from corn starch or cane sugar.
- Two lactic acid molecules undergo a single esterfication and then catalytically cyclized to make a cyclic lactide ester.
- PLA of high molecular weight is produced from the dilactate ester by ring-opening polymerization in the presence of Stannous octonate Or tin(II) chloride.

- Polymerization of a racemic mixture of L- and D-lactides usually leads to the synthesis of poly-DL-lactide (PDLLA) which is amorphous.



Applications of PLA in various fields

1. Industrial Applications:-

- Food packaging
- Disposable tableware

2. Agricultural applications:-

- Mulch film made of polylactic acid
- Compostable bags

3. Apparel applications:-

- Activewear
- Shoe linings
- Sport
- Underwear

4. Home furnishing textile:-

- Pillows
- Comforters
- Mattresses
- Duvets
- Outdoor furniture

5. Medical applications:-

- Wound dressing
- Stents
- Wipes
- Dialysis
- Diapers

6. Advanced applications:-

- Prosthetic implants
- Bone surgery
- Controlled-release systems
- Orthopedics
- Drug carriers
- Facial fracture repair
- Tissue engineering
- Antimicrobial agents
- Antitumor
- Ureteral stents
- Biomaterials