UNIT-IV

POLYMERS

The word polymer is derived from Greek words “**poly”** means “many” and “**mer**” means “unit” or “part.

Polymers are generally macromolecules formed by the repeated linking of large number of small molecules.

Polymers are widely used in automobiles, defence, electrical goods and computer components etc.

CLASSIFICATION OF POLYMERS

Polymers are classified based on source and applications as follows. I .**Classification of polymers based on source**

Based on source, polymers are broadly classified into two types

1. Natural polymers.
2. Synthetic polymers.

1. Natural polymers

The polymers obtained from nature (plants and animals) are called natural polymers.

Example :Starch ,Cellulose,Proteins,Nucleic acids,Natural rubber,Biopolymers.

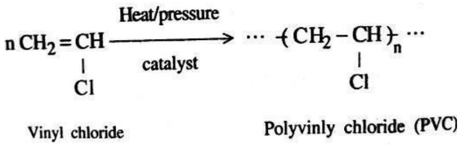
2. Synthetic polymers

The polymers which are prepared in the laboratories, are called synthetic polymers. These are also called man- made polymers.

Example: PVC, polyethylene, nylon, teflon, bakelite, terylene, etc

$$n\ CH_2=CH_2 \xrightarrow{\text{Heat/pressure}} -(CH_2-CH_2-)_n-$$

Ethylene **Polyethylene (PE)**



$$n\,\underset{\underset{Cl}{|}}{CH_2=CH} \xrightarrow[\text{catalyst}]{\text{Heat/pressure}} \cdots\left(CH_2-\underset{\underset{Cl}{|}}{CH}\right)_n\cdots$$

Vinyl chloride Polyvinly chloride (PVC)

II. CLASSIFICATION BASED ON CHEMICAL COMPOSITION

(a) **Organic Polymers**:These are polymers containing apart from carbon atoms, hydrogen, oxygen, nitrogen, sulfur and halogen atoms.

Examples :Polyethylene, Polyvinyl alcohol, PVC, Epoxy polymers, Polyurethane.

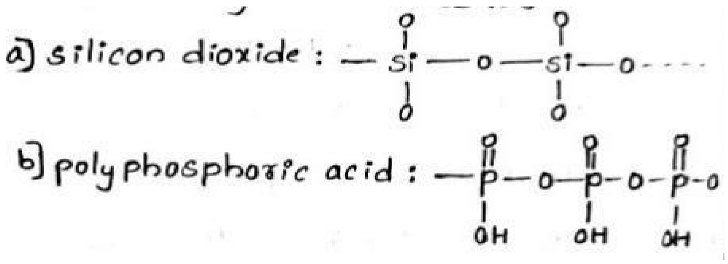
(b) Elemento-organic (or) Hetero-organic Polymers:

These are polymers composed of carbon atoms and hetero-atoms (like N, S & O). The main chains consists of carbon atoms and whose side groups contain hetero atoms linked directly to the C atoms in the chain.

Examples: Polysiloxanes, polytitoxanes.

(c) Inorganic Polymers

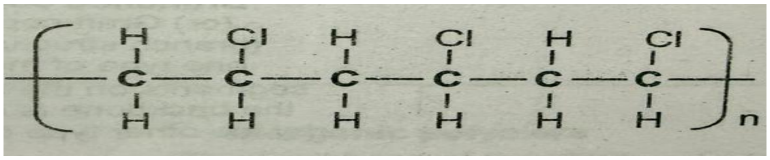
These are polymers containing no carbon atoms. The chains of these polymers are composed of different atoms joined by chemical bonds. Examples



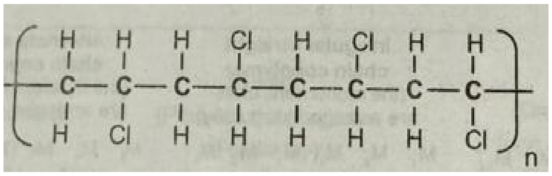
Tacticity: Based on the classification

- Arrangement of functional groups on the backbone of the polymer chain.
- There are 3 types based on tacticity.

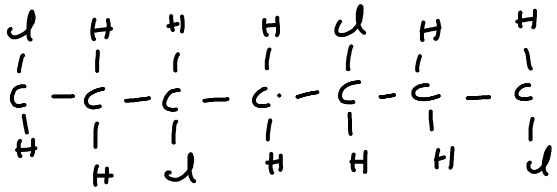
Isotactic polymers: functional groups are arranged on the same side of the polymer.



Atactic polymers: no regular arrangement of functional groups on the backbone of polymer chain.



Syndiotactic polymers: alternate arrangement of functional groups on the polymer chain



POLYMERISATION

Polymerisation is a process in which large number of small molecules (called monomers) combine to give a big molecule (called a polymer) with or without elimination of small molecules like water.

Degree of Polymerisation (DP)

The number of repeating units (n) in a polymer chain is known as degree of polymerisation. It is represented by the following relationship.

$$\text{Degree of polymerisation (n)} = \frac{\text{Molecular weight of the polymeric network}}{\text{Molecular weight of the repeating unit}}$$

Example : 5 (CH2=CH2) → -CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-

In this example, 5 repeating units are present in the polymer chain. So, the degree of polymerisation is 5.

Oligomers

Polymers with low degree of polymerization **(dp)** are known as Oligomers, their molecular weight ranges from 500-5000.

High polymers

Polymers with high degree of polymerization **(dp)** are known as High polymers, their molecular weight ranges from 10,000 2,00,000

TYPES OF POLYMERISATION

Polymerisation reactions may be carried out by any one of the following methods.

1. Addition (or) chain growth polymerisation .
2. Condensation (or) step-wise polymerization.

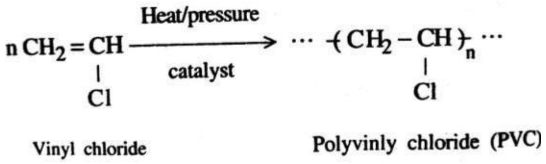
1. *Addition (or) chain growth polymerisation:*

- Polymerisation in which monomers are linked together to form polymers without elimination of simple molecules is called Addtion polymerisation and polymers are called called Addition polymers.
- Unsaturated compounds undergo Addtion polymerisation.The number of monomeric units in polymer is equal to number of monomers. The Monomer must have atleast one multiple bond.In this polymerisation new monomers are added to growing chain of polymer,Hence this polymerisation also called chain growth polymerisation.These polymers are linear in shape and have low moleculer weight.

Examples :**1**.Polyethylene is produced from ethylene. **2**.PVC is produced from vinyl chloride.

$$\text{n CH2=CH2} \xrightarrow{\text{Heat/pressure}} \text{-(CH2-CH2-)n-}$$

Ethylene **Polyethylene (PE)**

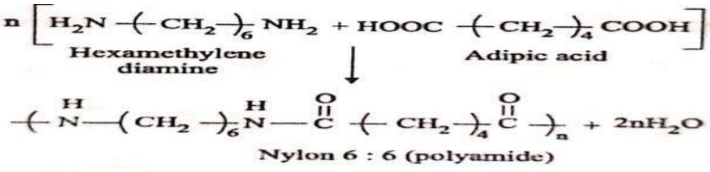


$$\text{n}\,\underset{\text{Cl}}{\text{CH}_2=\underset{|}{\text{CH}}} \xrightarrow[\text{catalyst}]{\text{Heat/pressure}} \cdots\!\left(\text{CH}_2-\underset{\text{Cl}}{\underset{|}{\text{CH}}}\right)_n\!\cdots$$

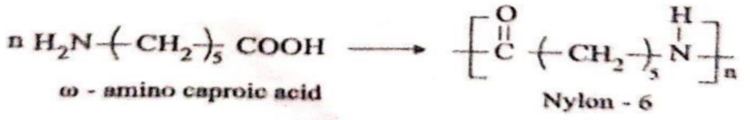
2. *Condensation (or) Step-growth polymerisation*

- Polymerisation in which monomers are added together to form polymers with elimination of simple molecules such as H2O, HCI, CH3OH etc.. is called **Condensation polymerisation** and polymers are called called Condensation polymers . and also called step-growth polymerisation.
- The monomers involved in Condensation polymerisation must have atleast two different functional groups.Ex: NH2(CH2)5COOH.
- The number of monomeric units in polymer is less than the monomers involved.

Examples **1**.Hexamethylene diamine and adipic acid condense to form a polymer, Nylon 6:6 (polyamide).



$$n\left[H_2N-(CH_2)_6-NH_2 + HOOC-(CH_2)_4-COOH\right] \longrightarrow -\!\left(\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right)_n\!- + 2nH_2O$$



$$n\,H_2N-(CH_2)_5-COOH \longrightarrow \left[\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}}\right]_n$$

2.Polymerisation of amino caproic acid to form(add terylene)

In some cases condensation polymerization takes place with out the elimination of small molecule like H2O,HCl etc...

ADDITION/CHAIN POLYMERISATION	**CONDENSATION /STEPPOLYMERIZATION**
The Monomer must have atleast one multiple bond. Example: Acetylene: CH CH	The monomer must have atleast two different functional groups. Ex: $NH_2(CH_2)_5COOH$.
By products are not formed.	By products such as H_2O,HCl,CH_3OH are formed.
Numbers of monometric units increases steadily throughout the reaction.	Monomers are disappear at the early stage of reaction.
Molecular weight of the polymer is multiple of molecular weight of monomer.	Molecular weight of the polymer need not to be multiple of the monomer.
High molecular weight polymer is formed at once.	Molecular weight of the polymer increases through out the reaction.
Longer reaction time give higher yield.	Longer reaction times are need to get high molecular weight.
Thermoplastics are produced Ex: Polyethylene,PVC,etc…	Thermosetting plastics are produced. Ex: Bakelite,Nylon – 6.
Homo-chain polymer is obtained.	Hetero-chain polymer is obtained.

MECHANISM OF ADDITION POLYMERISATION

Mechanism of addition polymerisation can be explained by the Free radial mechanism

Free radical mechanism (or) Free radial polymerisation

Free radical polymerisation occurs in three major steps.

1. **INITIATION**
2. **PROPAGATION**
3. **TERMINATION**

1. **INITIATION**

Initiation involves two reactions.

(a) .***First reaction***

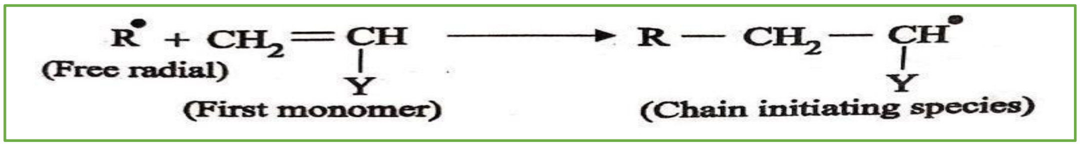
First reaction involves production of free radicals by homolytic dissociation of an initiator (or catalyst) to yield a pair of free radicals ($R^\bullet$)

$$R\text{-}R \longrightarrow 2\,R^{\cdot}$$

Initiator **Free radicals**

(b). ***Second reaction***

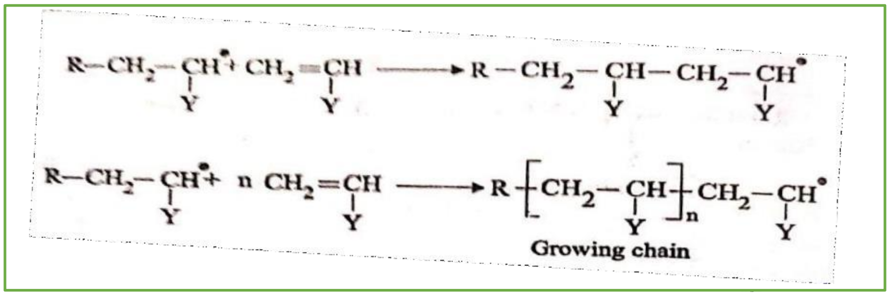
Second reaction involves addition of this free radical to the first monomer to produce chain initiating species



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

2. PROPAGATION

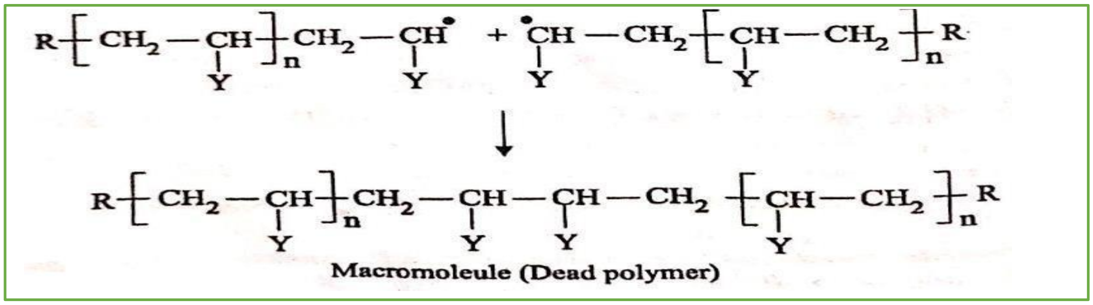
It involves the growth of chain initiating species by the successive addition of large number of monomers.



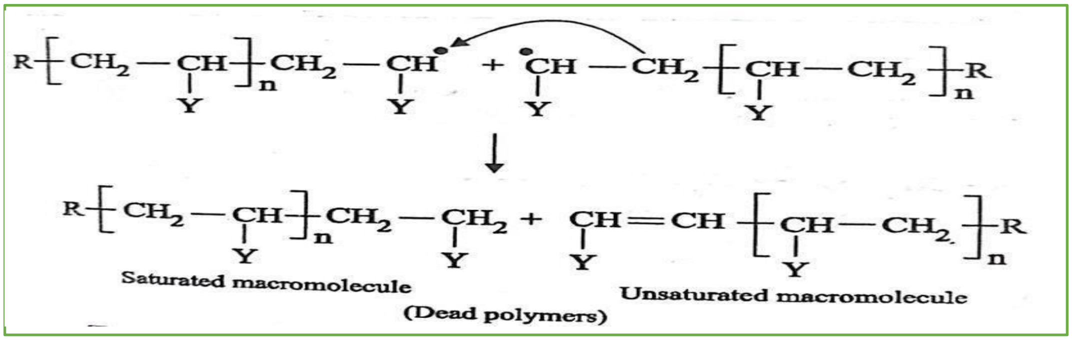
3. TERMINATION

- Termination of the growing chain of the polymer occurs either by coupling reaction or disproportionation (a).***Coupling (or) combination***:

It involves coupling of free radical of one chain end to another free radical to form macromolecule (dead polymer).



(b).Disproportionation



- It involves transfer of a hydrogen atom of one radical center to another radical center forming two macromolecules, one saturated and another unsaturated.
- The products of addition polymerisation is known as Dead polymers.

PLASTICS

Plastics are, A high molecular weight polymer, that can be moulded into any desired shape by the applying of heat and pressure in the presence of a catalyst.

Advantages of plastics over other materials

1. They are light in weight.
2. They possess low melting point.
3. They can be easily moulded and have excellent finishing.
4. They possess very good strength and toughness.
5. They possess good shock absorption capacity.
6. They are corrosion resistant and chemically inert
7. They are very good water-resistant and possess good adhesiveness.

Disadvantages of plastics

1. They are highly soft.
2. They undergo embrittlement at low temperature.
3. They undergo deformation under load.
4. They possess low heat-resistant and poor ductility.
5. Combustibility is high.
6. They undergo degradation upon exposure to heat and UV- radiation.
7. They are Non bio-degradable.

Classification of Plastics

Based on the structure and type of resin used for the manufacture of plastics, plastics are classified into two main types.

1. **THERMOPLASTICS.**
2. **THERMOSETTING PLASTICS.**

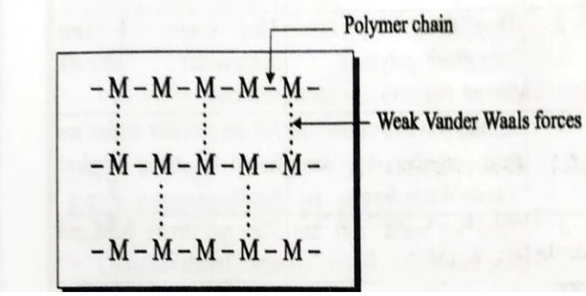
1.Thermoplastics: Examples: (i) Polyethylene (ii) Polyvinyl chloride

2.Thermosetting plastics:Examples: (i) Bakelite (ii) Polyester

Resin:Resin is a basic binding material, present in plastics, Which undergoes polymerization reaction during moulding.

1.*Thermoplastic resins:*

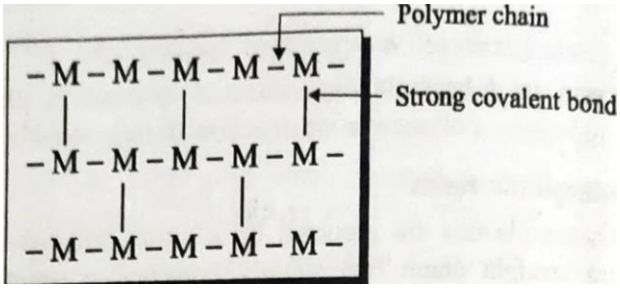
- Thermoplastics are prepared by addition polymerisation.
- They are straight chain (or) slightly branched polymers and various chains are held together by weak Vander Waal's forces of attraction.
- Thermoplastics can be softened on heating and hardened on cooling. They are generally soluble in organic solvents.



Examples:Polyethylene, Polyvinyl chloride.

2. *Thermosetting resins*

- Thermosetting plastics are prepared by condensation polymerisation. Various polymer chains are held together by strong covalent bonds (called crosslinks).



- Thermosetting plastics get harden on heating and once harden, they cannot be softened again. They are almost insoluble in organic solvents.

ExamplesBakelite, Polyester.

Characteristics (or) Properties of Engineering Plastics

Engineering Plastics possess

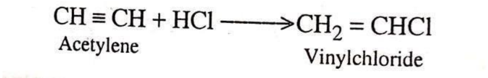
1. High load bearing characteristics,
2. High mechanical strength,
3. High dielectric constants,
4. Readily mouldable properties into complicated
5. High abrasion resistance,
6. Very good rigidity,
7. Good dimensional stability,
8. Fairly good thermal stability,
9. Light weight,
10. High performance properties ie., they can be same manner as metals, alloys and ceramics.

POLYVINYL CHLORIDE (PVC):

Preparation

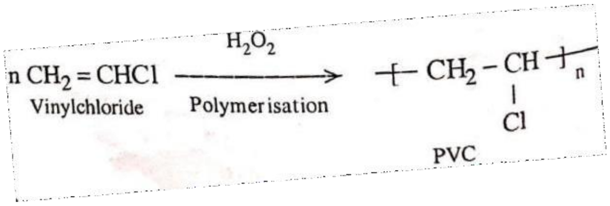
Preparation of PVC involves the following two steps

Step 1: Vinyl chloride is prepared by treating acetylene with hydrogen chloride at 60-80°C in the presence of metal chloride as catalyst.



$$\underset{\text{Acetylene}}{CH \equiv CH} + HCl \longrightarrow \underset{\text{Vinylchloride}}{CH_2 = CHCl}$$

Step 2: Polyvinyl chloride is obtained by heating water emulsion of vinyl chloride in presence of benzoyl peroxide (or) hydrogen peroxide under pressure

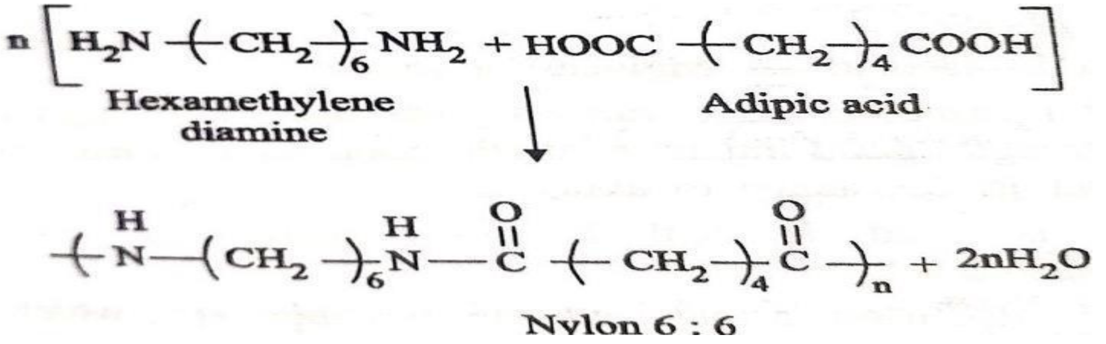


$$n\,\underset{\text{Vinylchloride}}{CH_2 = CHCl} \xrightarrow[\text{Polymerisation}]{H_2O_2} \underset{\text{PVC}}{\left[CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} \right]_n}$$

PREPARATION OF IMPORTANT FIBRES

a.Nylon-6:6

- Nylon-6:6 is prepared by polymerisation of condensing **hexamethylene diamine** and **adipic acid** in toluene solvent at higher temperature in an inert atmosphere.



$$n\left[\underset{\text{Hexamethylene diamine}}{H_2N - (CH_2)_6 - NH_2} + \underset{\text{Adipic acid}}{HOOC - (CH_2)_4 - COOH}\right] \downarrow$$

$$\underset{\text{Nylon 6 : 6}}{\left[\overset{H}{N} - (CH_2)_6 - \overset{H}{N} - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} \right]_n} + 2nH_2O$$

Properties of Nylon 6:6

1. It is a horny translucent material
2. Its melting point is high (264°C)
3. Nylon 6.6 is a less soft and stiff material when compared to nylon 6.
4. It is insoluble in common organic solvents, but soluble in formic acid and cresol.
5. Both fibre and plastic have high tensile strength and dimensional stability.
6. It shows good impact strength due to the large number Of flexible groups.
7. As l/d ratio of the polymer filament is very high and there is high intermolecular attraction between the Molecules due to H-bonds between the carbonyl and Amide -NH- group it can act as a very good fibers.
8. Both nylon fibre and plastic are resistant to abrasion. 9. It does not absorb water and hence can be dried easily.

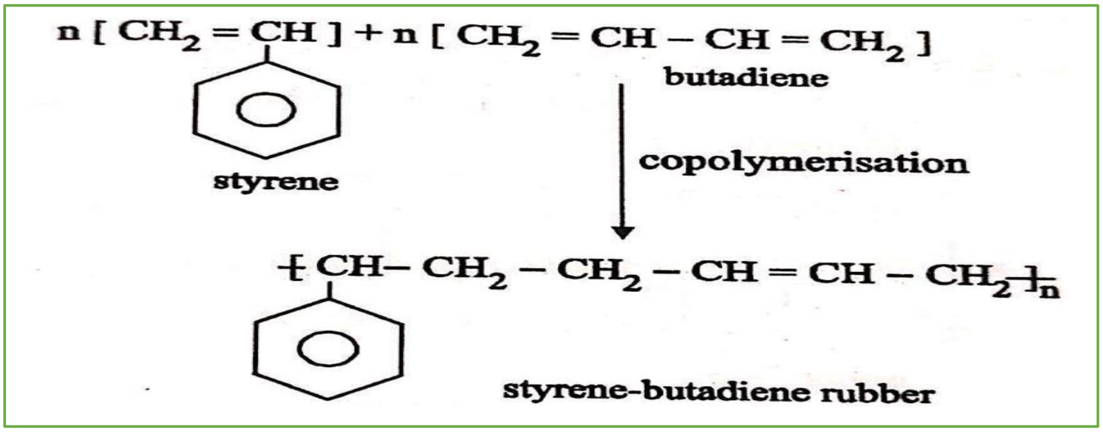
PREPARATION OF IMPORTANT SYNTHETIC RUBBERS (ELASTOMERS)

1.SBR (Styrene-butadiene rubber) (or) Buna-S rubber

Buna-S is the polymer of about 75% butadiene and 25% Styrene.

Preparation

- Buna-S rubber is produced by copolymerization of mixture of 75% butadiene, 25% styrene .



PROPERTIES:

1. Buna-S is resistant to abrasion and possess high load bearing capacity.
2. It undergoes oxidation readily, when traces of ozone is present in the atmosphere.
3. It requires less sulfur for vulcanization when compared to natural rubber.
4. Tensile strength and flexibility of SRB are inferior to those of natural rubber.

Uses

1. Buna-S is used for making light duty tyres, belts hoses And gaskets.
2. It is also used in footwear industry.
3. It is used as an adhesives and in electrical insulation.

S.no	**THERMOPLASTICS**	**THERMOSETTING PLASTICS.**
1	These are formed by Addition polymerisation	These are formed by Codensation polymerisation
2	They are consist of Linear chain polymers	They are consist of Three dimentional structure
3	Polymer chains held together by weak vander wallas forces	Polymer chains held together by strong covalent bonds
4	They are weak,soft and less brittle	They are strong,hard and more brittle
5	They soften on heating and hard on cooling	They donot soften on heating
6	They can be remoulded	They can not be remoulded
7	They have higher moleculer weights	They have lower moleculer weights
8	They are soluble organic solvents	They are insoluble in organic solvents
9	Ex:Polyethylene,PVC etc…	Ex:Bakelite,Nylon- 6.6 etc..

Fibre Reinforced Plastics (FRP)

The fire reinforced pistics composites constitute more than 90% (by weight) of the total composites used in various industries. The advantages of using polymer in structural composites is the ease of fabrication of complex structural shapes. It can be easily manufactured.

The resin matrix commonly used in FRP are polyesters, epoxy, phenolic, silicone, and polyamide polymer resins.

General Characteristics (or) Properties of FRP

1. It possess superior properties like higher yield strength,Fracture strength and fatigue life.

2. Since fibre prevents slip and crack propagation, the mechanical properties of FRP gets increased.
3. possess high corrosion resistance and heat resistance

The properties of FRP mainly depends on nature of the resin matrix .

RESIN	**REASON**
1.Polyester resin.	To provide very good strength and mechanical properties.
2.Epoxy resin.	To provide very good strength and mechanical properties.
3.Silicone resins.	To import good mechanical properties.
4.Phenotic resins.	To withstand high temperatures.
5.Thermoplastics (polyamide,PET,etc…)	Because of its repeatability and repairability

Types of FRP:

Name of FRP	Properties	Applications
1.Glass-FRP	(i)Lower densities, dielectric constants. (ii)Higher tensile strengths and impact resistance. (iii)Excellent corrosion resistance, chemical resistance, Non-flammability.	Automobile parts, storage tanks, plastic pipes, flourings, transportation industries, etc.,
2.Boron-FRP	(i)Excellent stiffness and compressive strength. (ii)Manufacturing of B-FRP is difficult.	Horizontal and vertical tail in aeroplane, stiffening spares, ribs, etc.,
3.Carbon-FRP	(i)Lighter density. (ii)Excellent resistance to corrosion. (iii)Retention of desired properties even at elevated temperatures.	Structural components of air craft and helicopters, recreational equipments, sports materials, Antenna disc, solar panal etc.,
4.Aramid-FRP	They are metal – like ductile and respond non-catastrophically to compressive stresses (because, capable of absorbing energy).	Structural component in aircraft, helicopter parts.
5.Alumina-FRP	Good abrasion resistance, creep resistance and dimensional stability.	Components of engine parts in automobile industry, and components of turbine engine.

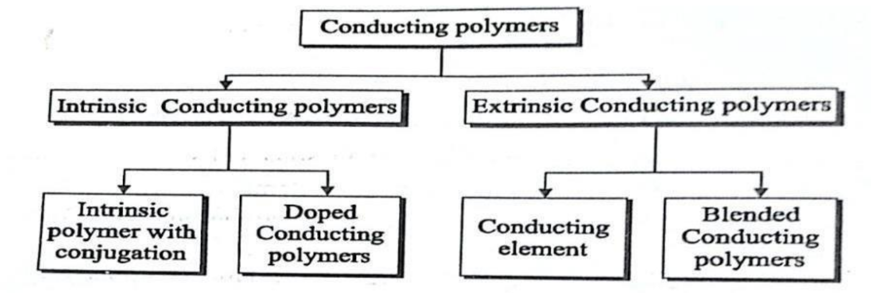
CONDUCTING POLYMERS

Those polymers, which are conduct electricity are called conducting polymers. The conduction in the polymers is mainly due to the

1. Presence of unsaturated conjugated double bonds in the polymer.
2. Addition (or) removal of electrons (doping) into the polymer.

Classification of conducting polymers

The conducting polymers are classified into Two types.



1. *Intrinsic conducting polymers*

- Conduction is mainly due to the conjugated double bond present in the polymer structure.

(a).Intrinsic polymer with conjugation

Conduction is due to the electrons present in the polymer backbone.

(b).Doped conducting polymers

Conduction is due to + ve (or) ve charge created on the polymer backbone.

2.Extrinsic conducting polymers

Conduction is mainly due to the presence of externally added ingredients in

the polymer structure. (a).Conducting element

These polymers act as a binding material and hold conducting elements like carbon black, metallic fibre, metallic oxides, etc..

(b).Blended conducting polymers

Ordinary polymer is blended with a conducting polymer to improve the electrical and mechanical properties.

<u>Doped conducting polymers:</u>

- The conducting polymers obtained by exposing the polymer to a charged transfer agent are called *doped conducting polymers.*
- Doping is the process by which conductivity of the polymers may be increased by creating negative or positive charge on the polymer backbone by oxidation or reduction.

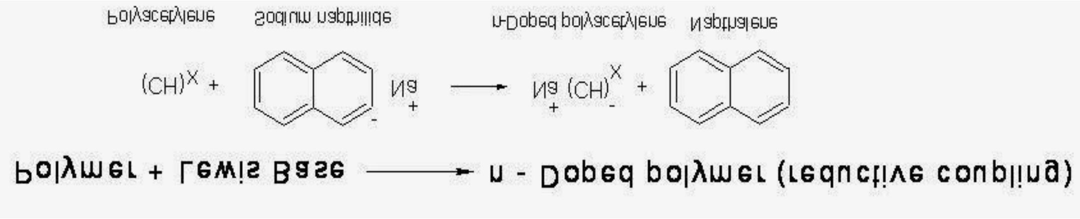
Doping is of two types:

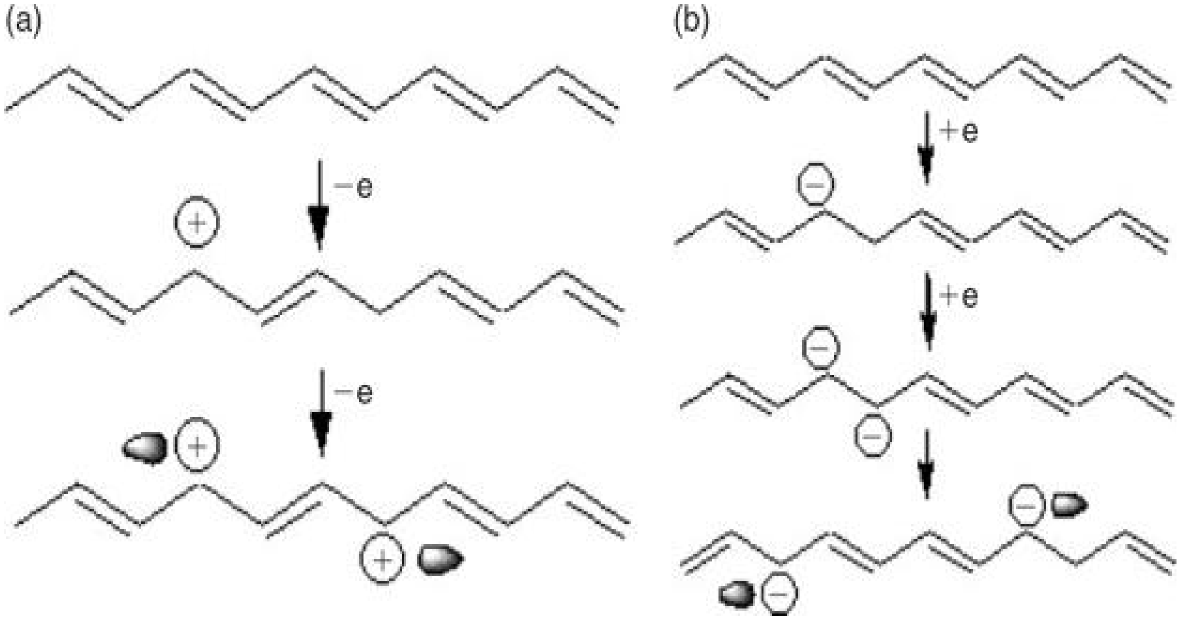
- **p-Doping :** It is done by oxidation process. In this process, the conducting polymer is treated with a Lewis acid.

$$(C_2H_2)_n \quad + \quad 2FeCl_3 \text{ ----------}\rightarrow (C_2H_2^+)_n\,.FeCl_3^- \; + FeCl_2$$

Polyacetylene L.A. +vely charged backbone

- **n-Doping :** It is done by reduction process. In this process, the conducting polymer is treated with a Lewis base.





Applications of Conducting Polymer

1. Conducting polymers are used in solar cells.
2. It is used in telecommunication systems.
3. It is also used as a very good electrode material for Rechargeable batteries.
4. Conducting polymers are used in antistatic coatings for clothing.

5. It is used as a membrane film for gas separations.
6. These are used as electrocatalytic materials in fuel cells..
7. It is used for making analytical sensors.
8. It is used for making ion exchangers.

BIO-DEGRADABLE POLYMERS

Biodegradable polymers are polymers which undergo degradation by the naturally occurring micro-organisms like algae, fungi and bacteria.

The basic requirements of bio-degradable polymers are

1. It should produce non-toxic products.
2. It should undergo controlled rate of biodegradation
3. It should be capable of maintaining good mechanical integrity until degradation.

Factors affecting degradation

The following factors play an important Role in Controlling the rate of degradation.

1. Molecular weight of the polymer.
2. Amount of crystallinity of polymer
3. Hydrophobicity of polymer.

Advantages of Bio-degradable Polymer

1.It is cheaper than normal polymers.	6. It is good to the environment
2.It does not generate as much toxic run-off	7.These are not toxic
3.The emission of CO, is reduced	8.It is easy to recycle
4.It takes less time to break down.	9.It require less energy to produce
5.These polymers are renewable.	

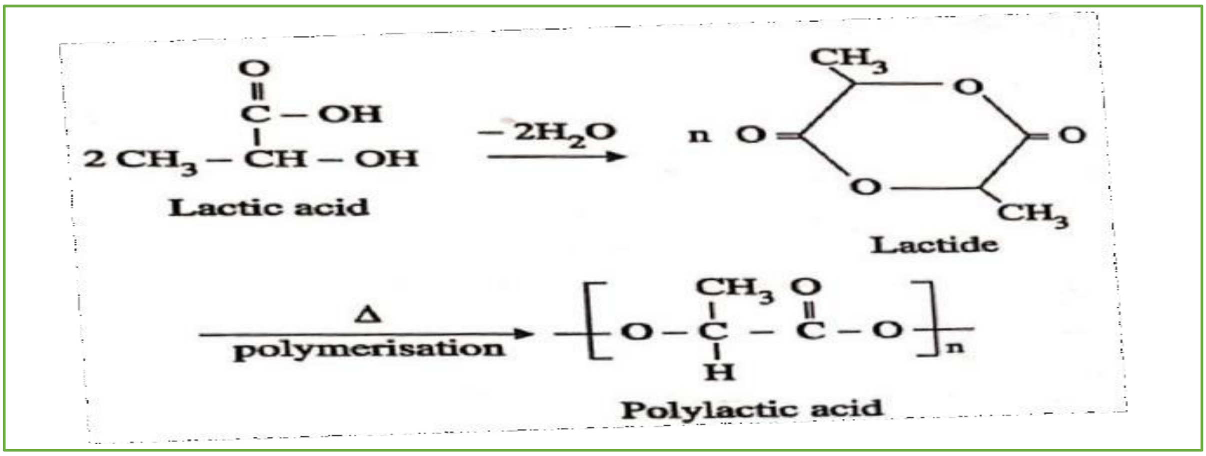
IMPORTANT BIO-DEGRADABLE POLYMERS

1. *Polylactic Acid (PLA)*

Polylactic acid is a biodegradable aliphatic thermoplastic polymer. It is derived from renewable sources such as starch, sugarcane, etc.,

Preparation

- It is prepared by the catalytic dimerisation of lactic acid resulting in the formation of lactide monomer.
- Polymerisation of lactide monomer, in presence of stannous octate, to give polylactic acid.



Properties of PLA	Applications of PLA
1.PLA possess good bio-compatibility, processability, high Strength.	1.PLA is used for making medical implants like, screws, pins, anchors, etc.
2.D-isomer of PLA is crystalline and L-isomer is amorphous.	2.It is used in a number of biomedical applications like drug delivery devices and dialysis media.
3.Biodegradation of D-isomer is slower than L-isomer.	3.It is used in the preparation of bioplastics for packing food and disposable tableware.
	4.It is also used for making compostable packing materials,Food packing, etc.,