## **Polymer**

Polymers are high molecular weight, large molecular which are formed by combination of small units joined together by covalent bond. The small units in a polymer are called monomers. The process of formation of polymer is called polymerization. For example

$$nCH_2 = CH_2 \rightarrow -(CH_2 - CH_2)_n - Ethene$$
 Polyethene

$$nHOOC - (CH_2)_4 - COOH + nNH_2 - (CH_2)_6 - NH_2 \rightarrow$$
  
Adipic Acid Hexamethylene diamine

O O 
$$|C| = (CH_2)_4 - C - NH - (CH_2)_6 - NH)_n - + 2nH_2O$$
  
Nvlon 6.6

## **Classification of Polymer**

## (A) On the basis of origin

There are two types of polymer:-

- (i) Natural Polymer:- These polymers occur in nature. For example, natural rubber, cellulose, starch etc.
- (ii) Synthetic Polymer:- These polymers are obtained by chemical synthesis. For example, polyvinyl chloride, polystyrene, polyester etc.

## (B) On the basis of chemical composition

There are two types of polymer:-

- (i) Organic Polymer:- In this type of polymer the chain is made up of carbon atom alongwith other atoms like oxygen, nitrogen etc. For example, nylon, polyester, polystyrene, polypropylene etc.
- (ii) Inorganic Polymer:- In this type of polymer, the chain is made up of atoms other than carbon atoms. For example, silicones, poly phosphoric acid.

## (C) On the basis of chemical structure

There are two types of polymer:-

- (i) Homopolymer or homochain polymer:- In this type of polymer, the chain is made up of one type of atom only. For example, polystyrene, polypropylene, polyvinyl chloride etc.
- (ii) Heteropolymer or heterochain polymer:- In this type of polymer, the chain is made up of more than one type of atoms. For example, nylon, polyester, etc.

#### (D) On the basis of chain structure

There are two types of polymer:-

(i) Linear Polymer:- In this type of polymer, the monomer unit is linked with two other monomer units on either side forming a continuous chain.

For example,  

$$nCH_2 = CH_2 \rightarrow -CH_2 - CH_2 - CH_2$$

(ii) Branched Polymer:- These are linear polymer with some branching. For Example,

$$\begin{array}{c} nCH_2 = CH - CH_3 \rightarrow -CH_2 - CH - CH_2 - CH - CH_2 - CH - \\ Propene \\ CH_3 \\ CH_3 \\ CH_3 \end{array}$$

# Polypropylene

(iii) Cross linked Polymer:- In this type of polymer, the linear chains are cross linked together by covalent bond. For Example,

vulcanized rubber

(E) On the basis of Polymerization process

There are two types of polymers:-

- (i) Addition Polymer:- For example, polystyrene, polypropylene, polyvinyl chloride etc.
- (ii) Condensation polymer:- For example, nylon, polyester, etc.
- (F) On the basis of their end use
  - (i) Thermoplastic
  - (ii) Thermosetting
  - (iii) Elastomers
  - (iv) Fibres

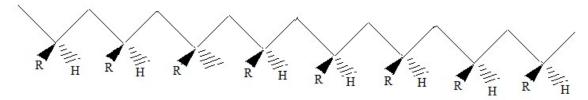
#### **Tacticity in Polymer**

Let us the monomer of type  $CH_2 = CH - R$  which Polymerized as follows:-

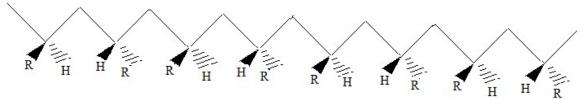
$$nCH_2 = CHR \rightarrow -(CH_2 = CH)_n - R$$

If R is group or atom other than hydrogen, there will be a generation of stereo centres in alternate carbon atom. Depending upon configuration of stereo centres, there are three types of polymers:-

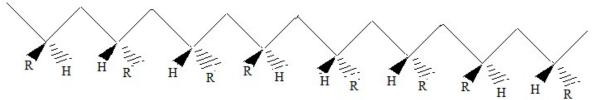
1. **Isotactic:** If the configuration of all the stereocentres are either R or S, then it is said to be isotactic polymer. The isotactic polymer is represented as



**2. Syndiotactic:-** If the configuration of stereocentres are alternatively R and S then it is called syndiotactic polymer. The syndiotactic polymer is represented as



**3. Atactic:-** If the configuration of stereocentres are in random manner then it is called atactic polymer. The atactic polymer represented as



## Characteristic of polymers

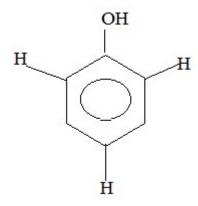
- 1. Polymers are high molecular weight and large molecule. Therefore, it is also called macromolecule.
- 2. Most of the polymers are combustible materials.
- 3. The chemical, electrical, optical, mechanical and thermal properties depend upon:-
  - → shape and size of polymer
  - → the presence or absence of characteristic intermolecular forces
- **4.** Polymers are easily moulded into even complex shape.
- **5.** Polymers have both crystalline as well as amorphous properties.
- **6.** The intermolecular forces in polymers can be Van Der Waal forces, dipole dipole Interactions or hydrogen bonding.

## **Functionality**

Functionality is defined as the number of reactive sites present in the monomers. If the functional group is not present in monomer unit then the functionality of that unit is decided by the presence of double or triple bond. The monomer with double bond shows bi functionality and triple bond shows tetra functionality. The monomer to undergo polymerization must have at least two functional group. For example,

$$HOOC - (CH_2)_4 - COOH$$
 bi functional  $CH_2 - OH$   $CH - OH$   $Tri$  functional  $CH_2 - OH$ 

In some molecule the number of replaceable hydrogen decides its functionality. For example



Tetra functionality

In this case there are three replaceable hydrogens and one OH group. Therefore, it act as tetra functional monomer.

The bi functional monomers always form linear polymer whereas monomers having more than one reactive sites form cross linked polymer.

## Molecular weight of polymer

Molecular weight of polymer increases continuously during the polymerization depending on monomer units joined together form macromolecules. Since the polymerization chain might be broken on various stages and the final product will not have macromolecules of same molecular weight, hence, an average value of molecular weight is taken.

There are two types of molecular weight of polymer:-

(i) Number Average Molecular Weight  $\overline{(M_n)}$ :- The number Average Molecular Weight is defined as

$$\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i}$$

$$\overline{M_n} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 \dots}{N_1 + N_2 + N_3 \dots}$$

Where  $N_i$  = Number of moles of macromolecule

 $M_i$  = Molecular weight of macromolecule

(ii) Weight Average Molecular Weight ( $\overline{M}_w$ ):- The Weight Average Molecular Weight is defined as

$$\overline{\mathbf{M}}_{w} = \frac{\sum \mathbf{N}_{i} \mathbf{M}_{i}^{2}}{\sum \mathbf{N}_{i} \mathbf{M}_{i}}$$

$$\overline{M}_{w} = \frac{N_{1}M_{1}^{2} + N_{2}M_{2}^{2} + N_{3}M_{3}^{2}.....}{N_{1}M_{1}^{2} + N_{2}M_{2}^{2} + N_{3}M_{3}^{2}.....}$$

Where  $N_i$  = Number of moles of macromolecule

M<sub>i</sub> = Molecular weight of macromolecule

**Numerical Problem** 

1. In a particular sample of polymer, 100 molecules have molecular mass  $10^3$  each, 200 molecules have molecular mass  $10^4$  each and 200 molecules have molecular mass  $10^5$  each. Calculate the

number average and weight average molecular mass.

#### **Solution**

$$\begin{split} \overline{M_n} &= \frac{\sum N_i M_i}{\sum N_i} \ = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 \dots}{N_1 + N_2 + N_3 \dots} \\ &= \ \frac{100 \ x \ 10^3 + 200 \ x \ 10^4 + 200 \ x \ 10^5}{100 + 200 + 20} = \textbf{44200} \end{split}$$

Again

$$\overline{M}_{w} = \frac{\sum N_{i}M_{i}^{2}}{\sum N_{i}M_{i}} = \frac{N_{1}M_{1}^{2} + N_{2}M_{2}^{2} + N_{3}M_{3}^{2}....}{N_{1}M_{1} + N_{2}M_{2} + N_{3}M_{3}....}$$

$$= \frac{100 \text{ x } (10^{3})^{2} + 200 \text{ x } (10^{4})^{2} + 200 \text{ x } (10^{5})^{2}}{100 + 200 + 200} = 91000$$

2. In a polymer sample, 30% molecule have molecular mass 40000, 40% have molecular mass 30000 and rest 30% have 60000. Calculate the number average and weight average molecular mass.

#### **Solution**

Since,

$$\overline{M_n} = -\frac{\sum N_i M_i}{\sum N_i} \ = \ \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 \ldots \ldots}{N_1 + N_2 + N_3 \ldots \ldots}$$

$$= \frac{30 \times 20000 + 40 \times 30000 + 30 \times 60000 = 43333}{30 + 40 + 30}$$

Again

$$\begin{split} \overline{M_w} = & \ \, \frac{\sum N_i M_i^2}{\sum N_i M_i} = \ \, \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2 .....}{N_1 M_1 + N_2 M_2 + N_3 M_3 .....} \\ = & \ \, \frac{30 \ x \ (20000)^2 + 40 \ x \ (30000)^2 + 30 \ x \ (60000)^2}{30 \ x \ 20000 + 40 \ x \ 30000 + 30 \ x \ 60000} = \textbf{36000} \end{split}$$

#### **Polymerization**

The process of formation of polymer is called Polymerization. There are two types of Polymerization.

(A) Addition Polymerization or Chain – Growth Polymerization:- In this type of polymerization process the polymer is formed from the monomer without loss of any small molecule. For Example

$$nCH_2 = CHR \rightarrow -(CH_2 = CH)_n - \begin{cases} \\ \\ R \end{cases}$$

The addition polymerization takes place through the formation of either of three intermediates depending upon initiators.

- (i) Free radicals
- (ii) Cations
- (iii) Anions

The general mechanisms for addition polymerization involve three steps:-

Step I Initiation:- This step involve generation of intermediates depend upon initiators

$$nCH_2 = CH + Z \rightarrow Z - CH_2 - ^*CH_2$$

R

Where \* is . or + or -

#### **Initiator**

#### **Intermediate**

Free radical

- (i) Peroxide (e.g. Benzoyl peroxide)
- (ii) Acids

(Mineral acids or Lewis acid)

Cation

(ii) Base

Anion

(Alkali or Lewis base)

**Step II Propagation:-** This step involve successive addition of monomers form long chain species

$$Z-CH_2-{^*CH} + CH_2 = CHR \rightarrow Z-CH_2-CH-CH_2-{^*CH} \xrightarrow{R} R$$

$$Z-CH_2-CH-CH_2-CH-CH_2-{^*CH} \text{ and so on } R$$

$$R$$

$$R$$

$$R$$

$$R$$

#### **Step III Termination:-**

- (a) In case of free radical the reaction is terminated
- (i) by coupling

(ii) by disproportionation

(b) In case of cation the reaction is terminated by addition of base.

(c) In case of anions the reaction is terminated by addition of acid.

(c) In case of anions the reaction is terminated by addition of acid.

$$Z - (CH_2 - CH)_m - CH_2 - {}^+CH \xrightarrow{H_2O/H^+} Z - (CH_2 - CH)_m - CH_2 - CH_2$$

$$R \qquad R \qquad R \qquad R$$

(B) Condensation Polymerization or Step – growth Polymerization:- In this Polymerization chain growth is accompanied with the elimination of small molecule like water, HCl, CH<sub>3</sub>OH, NH<sub>3</sub> etc. depending upon the types of monomer. For Example

$$nHOOC - (CH_2)_4 - COOH + nNH_2 - (CH_2)_6 - NH_2$$
 Adipic Acid Hexamethylene diamine

**Mechanism:-** The condensation Polymerization involve two steps:-

**Step I:-** The two monomers undergo condensation reaction

$$HOOC - (CH_2)_4 - COOH + NH_2 - (CH_2)_6 - NH_2 \rightarrow$$
Adipic Acid Hexamethylene diamine

O O 
$$HO-C-(CH_2)_4-C-NH-(CH_2)_6-NH_2+H_2O$$

Step II:- Successive condensation of monomers give rise to step growth polymer

$$\begin{array}{c} O & O \\ \parallel & \parallel \\ n\,HOOC - (CH_2)_4 - COOH \, + \,HO - C - (CH_2)_4 - C - NH - (CH_2)_6 - NH_2 \\ & + \,nNH_2 - (CH_2)_6 - NH_2 \\ \downarrow & \downarrow \\ O & O \\ - (\,C - (CH_2)_4 - C - NH - (CH_2)_6 - NH)_n - \, + \,nH_2O \\ & Nylon \, 6,6 \end{array}$$

## Difference between Addition and Condensation Polymerization

Addition Polymerization	Condensation polymerization
1. It also known as chain – growth	1. I also known as step – growth
polymerization.	polymerization.
2. It takes place in monomer having multiple bond.	<ul><li>2. It takes place in monomer having atleast two functional group.</li><li>3. It takes place with elimination of small</li></ul>
<b>3.</b> It takes place without elimination of small molecule.	molecule, such as, H <sub>2</sub> O, HCl, NH <sub>3</sub> etc.

- **4.** Products obtained by this polymerization are thermoplastic.
- **5.** High molecular weight polymer is formed very soon.
- **4.** Products obtained by this polymerization are either thermoplastics or thermosetting.
- **5.** The molecular weight of polymer increases steadily throughout the reaction.

**Copolymer:-** Polymers which are made up of at least two different types of monomers are called copolymers. The process of formation of copolymer is known as copolymerization. For example, Nylon 66, Terylene, BUNA – S, BUNA – N etc. There are four types of copolymers:-

1. Alternate copolymer:- In such copolymer, the different monomers are alternate in chain. If X and Y represents two different monomers, the alternate copolymer may be represented as:-

For example, Nylon 66

**2. Block Copolymer:-** In this type, a block of one type of monomer is alternate with block of other type of monomer. For example, BUNA – S. If X and Y represents two different monomers, the block copolymer may be represented as:-

For example, BUNA - S

**3. Random Copolymer:-** In this type of copolymer the monomers are joined together in random manner. If X and Y represents two different monomers, the random copolymer may be represented as:-

**4. Graft Copolymer:-** In this type of copolymer the chain of one monomer is grafted to the chain of other monomer. If X and Y represents two different monomers, the graft copolymer may be represented as follows:-

#### Thermoplastics:-

Thermoplastics are linear polymers which are made up of monomers having bi functional monomers. These are soften on heating and can be moulded into desire shape. For Example, polyethene, polypropylene, polyvinyl chloride, poly styrene etc.

#### Thermosettings:-

Thermosettings are highly cross linked materials. These are become hard infusible mass on heating which cannot be moulded in desire shape. These are formed by monomers having more than two functional groups. For Example, Bakelite, urea – formaldehyde resins etc.

## Differentiate between Thermoplastic and Thermosetting Polymers.

Thermoplastic Polymer	Thermosetting polymer
1. Thermoplastics are linear polymer.	<b>1.</b> Thermosetting polymers are cross – linked polymer.
<b>2.</b> Thermoplastics are generally addition polymer.	<b>2.</b> Thermosettings are generally condensation polymer.
<b>3.</b> On heating they become soft and hard on cooling.	3. On heating they become hard infusible mass
<b>4.</b> These are recyclable.	<b>4.</b> These are non recyclable.
<b>5.</b> They can be remoulded into desire shaped.	5. They cannot be remoulded.

#### **Elastomers**

Elastomers are the materials which are capable of being stretched at least 150% of their original length and regain its original shape after removal of deformation force.

For Example, natural rubber and synthetic rubber (such as, BUNA – S, BUNA – N, neoprene etc.)

## **Natural Rubber**

Natural rubber is a colloidal latex which contain about 45% of rubber. It is obtained from plant called rubber tree. Natural rubber is polymer of isoprene which polymerized with cis - 1,4 – head to tail addition.

$$CH_3$$
  $CH_3$   $CH_3$   $CH_2 = C - CH - CH_2 \rightarrow -(CH_2 - C = CH - CH_2)_n - CH_2$  Isoprene natural rubber

Natural rubber is of little use due to its undesirable properties. The defects are removed by the process called vulcanization.

**Vulcanization:** It consists of heating the raw rubber at 100-140° C with sulphur. The sulphur combines chemically at the double bonds of different rubber springs and provides cross-linking between the chains. This cross-linking during vulcanization brings about a stiffening of the rubber by anchoring and consequently preventing intermolecular movement of rubber springs. The amount of sulphur added determines the extent of stiffness of vulcanized rubber. Vulcanized rubber has good tensile strength and extensibility.

#### Uses of natural rubber

- 1. Rubber is used in manufacturing of toys, sports materials, tyres etc.
- 2. Rubber lined tanks are used in chemical industries to prevent from corrosion.
- 3. It is used in conveyor belt for transmission of several types of materials.
- 4. Foam rubber is used in manufacturing of cushions, mattresses, padding etc.
- 5. Rubber is used for manufacturing of gaskets.

## Synthetic rubber

Synthetic rubber is the term which is used for that rubber like material obtained by chemical synthesis. Synthetic rubbers have been produced by polymerization of conjugated dienes resembling isoprene. The important synthetic rubber are as follows:-

# Styrene – butadiene rubber or SBR or BUNA – S

Styrene – butadiene rubber is the first commercially made synthetic rubber. It is a copolymer obtained by the copolymerization of butadiene (75%) and styrene (25%) by emulsion polymerization at  $50^{\circ}$ C in the presence of peroxide initiator.

Styrene – butadiene rubber having repeating unit of mainly 1-4 addition product. According to the temperature used, two processes have been developed. The hot process at  $(50^{\circ}\text{C})$  and the cold process  $(-18^{\circ}\text{C to }5^{\circ}\text{C})$ . The rubber obtained by hot process called hot rubber and rubber obtained by cold process is called cold rubber. Cold process is more efficient than hot process. Both the rubber can be vulcanized by conventional method using sulphur. A reinforcing filler is added to achieve good physical properties.

## **Properties:**

- 1. High abrasion resistance.
- 2. High load capacity.
- 3. At elevated temperatures SBR almost 2/3 of their tensile strength whereas natural rubber only loses ½th.
- 4. Cold SBR is superior to the standard product because it contain less chain branching and cross linking.
- 5. It swells in oil and solvents.

## **Application:**

SBR is used:-

- 1. In manufacturing of shoe soles and footwear component.
- 2. In making insulation of wires and cables.
- 3. In making carpet backing, adhesive, gaskets and tank lining.
- 4. In making floor tiles.

## Nitrile - Butadiene Rubber or NBR or BUNA - N

The nitrile rubbers are polymer of butadiene and acrylonitrile in the ratio of 1:1 ratio. It is prepared by emulsion polymerization using peroxide initiator.

The vulcanization is done by conventional means by adding sulphur.

#### **Properties:-**

1. Due to presence of cyano group (-CN) it is less resistant to alkali than natural rubber.

- 2. It has good tensile strength and abrasion resistance.
- **3.** It possesses excellent resistance to heat, sunlight acids and salts.
- **4.** The rubber are less resilient than rubber.

#### Uses:-

- 1. The nitrile rubber is used for oil resistance.
- 2. It is used for making conveyer belts, lining of tank and gaskets.
- 3. Automobile parts and high altitude aircraft component.
- 4. It is used for making printing rollers, adhesive and oil resistance foam.

## Neoprene or GR – M rubber

This is also known as poly chloroprene or polychloro butadiene or duprene. Neoprene is prepared by polymerization of chloroprene, takes place through free radical emulsion polymerization.

$$\begin{array}{c|c}
C1 & & C1 \\
 & | & \\
 & | & \\
 & | & \\
 & | & \\
 & CH_2 - C - CH - CH_2 - \\
 & | & \\
 & CH_2 - C - CH - CH_2 - \\
 & | & \\
 & Neoprene
\end{array}$$
Neoprene

The vulcanization of neoprene is different form that of other elastomers because it can be vulcanized by heat alone.

**Properties:-** Neoprene is closely resemble to natural rubber.

- 1. Neoprene has superior resistant to vegetable mineral oils.
- 2. It is superior to natural rubber as far as aging and effects of high temperature are concerned.
- 3. Neoprene is soluble in polar solvents due to the presence of chloro group.
- 4. Vulcanized neoprene have high tensile strength and high resistant to oxidative degradation.
- 5. It has got high oil resistant than natural rubber and SBR.

#### Uses:-

- 1. It is used in oil resistant wire and cable coating, industrial houses and shoe soles.
- 2. Its latex is used for manufacturing of gloves and coated fabrics.
- 3. It is used for making tubings for carrying corrosive gases and oils.
- 4. Used in manufacture of sponges, conveyer belts, lining of reaction vessels etc.

**Fibres:-** The fibres are the material having thread like structure. The examples of fibres are:

**Polyamides:-** Polyamides is a group of polymers which contains the amides (-CONH -) linkage in the main polymer chain. These are synthetic linear polymer which is capable of fibre formation. Polyamides are prepared by polycondensation between dicarboxylic acid and diamines. The general structures is given as follows:-

The typical examples of polyamides are:-

# Nylon 6,6:-

Nylon 6,6 is prepared by the polycondensation of hexamethylene diamine with adipic acid

**Nylon 6:-** The starting material of nylon 6 is cyclohexanone.

# **Properties of Nylons:-**

- 1. They are insoluble in common solvents.
- 2. Nylon are characterized by a combination of high strength, elasticity, toughness and abrasion resistance.
- **3.** They have good moisture resistance.
- **4.** They are very flexible and retain their original shape after use.

#### **Applications:-**

- 1. Nylon is used as a plastics as well as fibre. It is used is manufacture of automobile tire cords, ropes and threads.
- **2.** Nylon is also used to make textiles fibres.
- 3. Nylon being a tough plastic, is used as a substitute for metals in gears and bearing etc.
- **4.** Nylon can be moulded in one piece whereas similar item in metal requires assembling of several parts.
- **5.** Nylon is used as textile fibres.
- **6.** Nylon is used in making brushes and bristle.

**Polyesters:-** Polyesters are the polymers have general formula (- COO -) linkage. The general formula is given as

$$-\left(-O-(R)_{x}-O-C-(R)_{y}-C-(R)_{y$$

Polyesters are the condensation polymers obtained by the reaction by the reaction of an acid and an alcohol each containing atleast bi-functionality. The common example of polyester is Terylene or Dacron.

Terylene

# **Properties:-**

- 1. Depending on its processing and thermal treatment the polyester the polymer exist as an amorphous transparent or semi crystalline material.
- 2. The crystalline polymer has melting point 265°C.
- 3. The glass transition temperature is  $80^{\circ}$ C.
- **4.** It has good mechanical strength upto temperature around 175°C.

#### Uses:-

- 1. It has good fibre forming property with high tensile strength and excellent crease resistant garment.
- **2.** Terycot is a blend of terylene + cotton.
- 3. It is used as a film in the manufacturing of magnetic recording tapes and aluminum sheets.

## Biodegradable polymer

A large number of polymers are quite resistant to the environmental degradation process which are responsible for the accumulation of polymeric material as a solid waste. These solid waste causes acute environmental problem and remain undegrade for a long time. Due to the problem created by polymeric waste, certain new biodegradable synthetic polymers have been developed. These polymers contain functional groups similar to the functional group in bio polymers.

**Biodegradable polymers:** Biodegradable polymers are those polymers which get decomposed by the process of biodegradation. Biodegradation is defined as a process carried out by biological systems (usually fungi or bacteria) wherein a polymer chain is cleaved via enzymatic activity. Some examples of bio polymers are:-

# Requirments for biodegradation

There are following three elements for the biodegradation process which needs to be simultaneous present:-

- 1. **Micro organisms:** The micro organisms must exist with the appropriate biochemical machinery to synthesized enzymes specific for the target polymer to initiate the depolymerization process.
- **2. Environment:** The following environmental factors must require the appropriate environment for the micro organisms for producing the appropriate enzymes to degradation of target polymers:
- (i) Temperature
- (ii) Pressure
- (iii)Moisture

# (iv)Oxygen

**3. Substrate:** Substrate must have essential features, such as, suitable functional group, hydrophilicity, low molecular weight and less crystallinity for biodegradation process to be successful.

# Types of biodegradable polymers:-

There are two types of biodegradable polymers:-

- 1. Natural biodegradable polymer: Natural polymers such as, collagen, lignin, poly  $-\gamma$  glutamic acid are some of the examples natural biodegradable polymers.
- 2. Synthetic biodegradable polymer:- The examples of synthetic biodegradable polymers are:-

## Polyhydroxy valerate

## Polylatic acid

## Polyglycollic acid

$$\begin{array}{c} O \\ || \\ nHO-CH_2-COOH \longrightarrow \\ Glycollic \ acid \end{array} \\ \begin{array}{c} O \\ -(O-CH_2-C)_n - \\ Polyglycollic \ acid \end{array}$$

## **Needs for biodegradable polymers**

The necessity for biodegradable polymer is to solve the problems associated with traditional and non – biodegradable. Some of them are:-

- 1. It may reduce the generation of solid waste based on plastic.
- 2. It reduce the requirement of solid waste disposal management, such as land fillings.
- 3. It reduced the plastic waste problem in seas and oceans.
- **4.** Biodegradable polymers are poised to revolutionize everything from food packaging to medical devices.

#### Uses

- 1. Biodegradable polymers are used mainly for medical goods, such as, controlled drug releasing devices.
- 2. These are also used in agricultural materials, such as, films for seeds coatings, fast food wrappers and film for hygiene products.

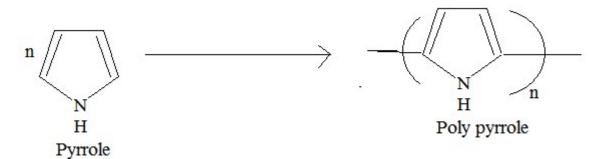
## **Conducting Polymers:-**

Conducting polymers are organic polymers that conduct electricity. Until 1970, all organic polymers were used in electrical, electronic and other applications as insulators, taking advantage of their excellent insulation properties. Thus, organic polymers having electrical conductance of the order of conductors are now called as conducting polymers. Conducting polymers have been classified into two types:

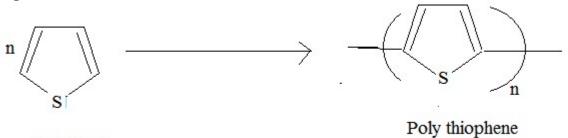
- 1. Extrinsically Conducting Polymers:- Extrinsically Conducting Polymers They are prepared by mixing conducting fillers like metal fibres, metal oxides or carbon black with insulating polymers. These are also called as conductive element filled polymers. Here, insulating polymer forms the continuous phase and added fillers form the conducting network. A minimum concentration of conducting filler has to be added so that the polymer starts conducting. The conductivity in this type of polymer is not due to the matrix polymer but due to conducting fillers which are added.
- **2. Intrinsically Conducting Polymers:** Intrinsically Conducting Polymers In these type of polymers, conductivity is due to the organic polymers themselves. They conduct electricity when doped with oxidizing or reducing agents or protonic acids. The factor responsible for conductance in these polymers are conjugated electrons. Organic polymers with highly delocalized π-electrons having electrical conductance of the order of conductors are called as inherently or intrinsically conducting polymers or synthetic metals. Some important intrinsically conducting polymers are:

# **Polyacetylene**

# **Polypyrrole**



# **Polythiophene**



# Thiophene

These are stable in air, at room temperature and ability to store charge.

## **Major Application**

Conducting polymers are used

- 1. As corrosion inhibitors
- 2. Electromagnetics shields for computers.

- 3. Transistors and LED (Light Emitting Device) based on polythiophene.
- 4. In lasers used in flat televisions
- 5. In solar cells.

# Preparation, Properties and Applications of some important polymers Teflon:-

Teflon is obtained by polymerization of water – emulsion of tetrafluoro ethylene, under pressure in presence of benzoyl peroxide as catalyst.

$$\begin{array}{c} nF_2C = CF_2 & \underline{ \begin{array}{c} benzoyl \ peroxide \\ \end{array} } & - \Big( \underline{ \begin{array}{c} CF_2 - CF_2 - \\ \end{array} } \Big)_{\underline{n}} \end{array}$$
 tetrafluoro ethene

#### **Properties:-**

- 1. It is a white solid compound at room temperature.
- 2. Its density is about  $2200 \text{ kg/m}^3 2.2 \text{ g/cm}^3$
- **3.** Its melting point is 327°C K.
- **4.** It is a chemical resistance compound, the only chemicals that can affect these compounds are alkali metals.
- **5.** It shows good resistance towards heat and low temperature.
- **6.** It has a low water absorption capacity.
- 7. It has an anti-adhesion ability due to which it is used as non-stick kitchen utensils.

#### Uses

- 1. It is used in making waterproof fabric.
- 2. It is used in making non-stick cookware.
- 3. It is used in making an anti-friction device.
- **4.** It is used for coating medical appliances (surgical devices).
- 5. Due to its high resistance to corrosion, it is used for coating the lining of laboratory appliances.

## Lucite or Polymethyl methacrylate (PMMA) or perpex

Lucite is obtained by the polymerization of methyl methacrylate in the presence of acetyl peroxide or hydrogen peroxide.



## **Properties**

- 1. Lucite is hard, fairly rigid material with high softening point.
- 2. It has high optical transparency.
- 3. It has low resistance to hot acids and alkalies.

#### Uses

It is used for making lenses, aircraft light fixture, cockpit canopies, adhesives TV screens etc.

#### Kevlar

Kevlar is an aromatic polyamide similar to nylon. It is prepared by polycondensation between aromatic dichloride and aromatic diamide.

## **Properties**

- 1. Kevlar is exceptionally strong material (5 times stronger than steel).
- 2. It is high thermal stability and flexibility.

#### Uses

It is used in vast applications such as aerospace engineering (such as the body of the aircraft), body armour, bulletproof vests, car brakes, and boats.

#### **Bakelite:**

Bakelite is a condensation polymer of phenol and formaldehyde in presence of acidic/alkaline catalyst. The preparation of Bakelite involve two steps:-

#### Step 1

In the first step formaldehyde reacts with phenol and produces o-hydroxy methyl phenol and p-hydroxy methyl phenol.

## Step II

In this step o-hydroxyl methyl phenol and p- hydroxyl methyl phenol come together and form Bakelite.

#### **Properties**

Some of the important properties of Bakelite are as follows:

- 1. Bakelite is a thermoset or thermosetting plastic.
- 2. It is a non-conductor of electricity, having a dielectric constant of 4.4 to 5.4.
- 3. It is heat-resistant and therefore, non-flammable. Thus, it functions as a good insulator.
- 4. Bakelite is also resistant to any kind of chemical action and hence, is non-destructive.
- 5. It can be very easily and quickly moulded.
- **6.** The mouldings of Bakelite are fairly scratch-resistant.

## **Uses of Bakelite**

- 1. Bakelite is used in the manufacture of a variety of products, including utensil handles, bangles, and vehicle parts.
- 2. It may be dyed into a variety of colours, allowing it to be employed in the creation of vivid and appealing products.
- **3.** Bakelite is a good insulator that is used in the manufacture of non-conducting parts of radio and electric devices such as sockets, wire insulation, switches and automobile distribution caps etc.
- **4.** It is used in the manufacture of clocks, buttons, washing machines, toys, kitchenware, and other items.

#### Kevlar

Kevlar is an aromatic polyamides similar to nylon. It is prepared by polycondensation of aromatic dicarboxylic acid and aromatic diamine.

## **Properties**

- 1. Kevlar is exceptionally strong (5 times stronger than steel) and light weight.
- 2. It has high heat stability and flexibility.
- 3. It has a much higher tensile modulus than steel wire.

#### Uses

It is used in vast applications such as aerospace engineering (such as the body of the aircraft), body armor, bulletproof vests, car brakes, and boats.

## Thiokol

Thiokol is also called polysulphide rubber or Gr - P. it is prepared by the condensation polymerization of sodium polysulphides and ethylene dichloride.

$$nCl - CH_2 - CH_2 - Cl + nNa - S - S - Na$$
  $-2nNaCl$   $-CH_2 - CH_2 - S - S - CH_2 -$ 

# **Properties**

- 1. Polysulphide rubber possesses extremely good resistance to mineral acids, oils, fuels, solvents and sunlight.
- 2. It is also impermeable to gases.
- 3. It cannot be vulcanized.
- **4.** It possesses poor strength and abrasion resistance.

#### Uses

- 1. It is used in preparation of sealants, coatings and other rubber products.
- 2. It is used in solid propellants for rockets.
- 3. It is used for manufacture of oils hoses, chemically resistant tubing and engine gaskets.

#### **Role of Polymers in society**

Role of polymer in the society includes several positive and negative impacts

# Positive impacts of polymer

The positive impacts of polymers are:-

# 1. Medical and biomedical applications:-

Both natural and synthetic polymers are used in medical prosthetic applications like heart valves, dental problems, joints, making of artificial skin, blood vessels, and also in systems for drug delivery.

## 2. Transportation Applications:-

Fuel cell mainly made of polymers has been developed for energy efficiency and to prevent burning of fossil fuel. Natural and synthetic rubbers in equal proportion are used in production of tyres.

## 3. Packaging:-

Low density polyethene (LDPE) blends were made into the reusable bags used for carrying rubbish or groceries. Biopolymers have been used for food packaging application.

## 4. Agriculture:-

Polymers of different grades are used in restrained release of nutrient and pesticides, seed coatings, soil conditioning and plant protection.

#### 5. Communication:-

Polymers are used to provide insulation to underground cables that are used in telecommunication, broadband and radio equipment.

## **Negative impacts of polymer**

The negative impacts of polymers are:-

- 1. Synthetic polymers mainly obtained from petroleum are a major environmental concern.
- 2. Most of the polymers are non biodegradable which create acute problem of plastic based solid waste.
- 3. Burning of plastics leads to production of harmful gases which release into the atmosphere.
- 4. Plastic pollution in oceans leads to disturbance in marine life.

## **Speciality Polymer**

Speciality Polymers are the class of some High Performance Polymers (HPP), including plastics, polymers, fluids, membranes, smart hydrogels and elastomers that are designed to meet the critical requirements that engineers face every day in key industries including, Plastics, Automobiles, Aeronautics, Smart Devices, Healthcare, Pharmacy, Energy Production and Storage.

## **Types of Speciality Polymer**

The different types of speciality polymers are:

# 1. Ionic polymer – metal composites (IPMCs)

Ionic polymers are, either organic or inorganic, having both covalent and ionic bonds in their molecular structure. This is the basic characteristic feature that distinguishes the ionic polymers from their conventional counterparts. Their working principle is that Water molecules pair with cations.

#### 2. Liquid Crystal Polymers (LCPs)

Liquid-crystal polymers (LCPs) polymers, which are extremely inert. They resist stress cracing in the presence of most chemicals at elevated temperatures, including aromatic or halogenated hydrocarbons bases, ketones, and other aggressive industrial substances. Their hydrolytic stability in boiling water is excellent.

#### 3. Synthetic Polymer Membranes

It is a synthetically created membranes which is usually intended for separation purposes in laboratory or in industry. The best known synthetic membrane separation processes are water purification reverse osmosis, dehydrogenation of natural gas, removal of micro – organism from dairy products and dialysis.

## 4. Smart Hydrogels

Materials which adjust their properties in response to environmental factors such as temperature, pH and ionic strength are rapidly evolving and known as smart materials. Hydrogels are hydrophilic polymers that can retain many times their own weight in water. The smart hydrogels are used for producing contact lenses, hygiene and wound dressing.

# 5. Dendritic Polymers

Dendritic polymers are belonging to a special class of macromolecules. They are called "Dendrimers." Similar to linear polymers, they composed of a large number of monomer units that were chemically linked together. Due to their unique physical and chemical properties, dendrimers have wide ranges of potential applications. These include adhesives and coatings, chemical sensors, medical diagnostics, drug high-performance polymers, catalysts, building blocks of supermolecules, separation agents and many more.

## **Polymer Blends**

Polymer blend is a simple physical combination of two or more incompatible polymers. For example, wood is natural blend of more than one polymers.

## **Properties:-**

- **a.** A polymer blend appears as separate phases, when viewed under microscope.
- **b.** Between different polymeric chain, only Van der Waal forces, dipole interaction hydrogen bonding exists.
- **c.** The properties of a polymer blend are closely related to the properties of individual polymer component.
- **d.** Blending usually improves the properties like processability, impact strength, abrasion resistance, flame retardation etc.
- e. Sensitive component of polymer blend may be protected from degradation by blending.

# **Applications of polymer blends**

- **a.** Polycarbonate ABS(Acrylonitrile butadiene styrene) blend is used for making electrical housings and machine parts.
- **b.** Nylon 6 and polycarbonate blend possesses improved toughness and is employed for making sports equipment and transport containers.
- **c.** Polyamide polyphenylene sulphide blend possesses properties of both. It has high temperature resistance. It is used as an insulator and electrical connectors.
- **d.** Polydimethylphenylene polystyrene blend possesses low water absorption, low moulding shrinkage, resistance to hydrolysis and quite good dielectric properties over wide range of temperature. It is used in electrical industries, automobile parts, radio and television parts.
- e. Cotton terylene blend is used in manufacturing of textile for synthetic cloth.

#### **Composites**

A composite material may be defined as a material system consisting of a mixture of two or more micro – constituents, which are mutually insoluble, differing in form and/or composition and forming distinct phases. For examples wood, bone, insulating tapes, reinforced concrete etc.

## **Constituents of composites**

The two essential constituents of composites are:-

- 1. Matrix Phase:- It is continuous body constituent, which encloses the composite and give its bulk form. Matrix phase may be metal matrix composites, ceramics matrix composites or polymer matrix composites. The functions of matrix phase are binds the dispersed phase together, act as a medium to transmit and distribute an externally applied load to the dispersed phase and protect the dispersed phase from chemical action and keep in proper position and orientation during the application of load.
- **2. Dispersed Phase:-** Dispersed phase is the structural constituent, which determines the internal structures of composites. The important dispersed phase of composites are:-
- **a. Fibre:-** It is a long and thin filament of any polymer, metal and ceramic having high length to diameter ratio. Its diameter nears crystal size diameter. If matrix is unidirectional, then the resulting composite is anisotropic. The examples for fibre dispersed phase are glass fibres, carbon fibres and aramid fibre.
- **b. Particulates:-** These are small pieces of hard solid material (metallic or non metallic). The distribution of particles in a given matrix is usually random, thereby, resulting isotropic composites.
- **c.** Flakes:- These are thin solids having a two dimensional geometry. For example, mica flakes.
- **d.** Wishkers:- These are thin strong filaments or fibres made by growing a crystal. For example, graphite, silicon, carbide, sapphire, silicon nitride and aluminum oxide. Usually, they are in several mm in length and several microns in diameter and thickness.

# **Types of composites**

There are mainly three types of composites:-

- **A.** Fibre reinforced composites
- **B.** Particulate composites
- C. Layered composites

# Advantageous characteristics of composites:-

Important advantage of composite material over conventional materials (metals, polymers and ceramics) are:-

- Higher specific strength
- Lower specific gravity
- Higher specific stiffness
- Maintain strength even at high temperature
- Better toughness, impact and thermal shock resistance
- Lower thermal expansion
- Better corrosion and oxidation resistance
- Lower electrical conductivity

## **Applications of composites:-**

- Composites are used in automobile industries, transportation industries, turbine engine, valves, pump parts fabrications of roof and floor, furniture, high speed machinery etc.
- Marine applications like propellers, shafts, hulls, spars and other ship parts.
- Aeronautical applications like components of rockets, aircrafts, helicopters, missiles etc.
- In Communication antennae, electronic circuit boards etc.
- Safety equipment like ballistic protection.

#### Organometallic compounds

Organometallic Compounds are chemical compounds which contain at least one bond between a metallic element and a carbon atom belonging to an organic molecule. Generally, the bond between the metal atom and the carbon belonging to the organic compound is covalent in nature. The examples for organometallic compounds are:-

Where R – alkyl or aryl group

X - Cl, Br or I

(ii) Organolithium

Where R – alkyl or aryl group

(iii) Dialkyl zinc

$$R - Zn - R$$

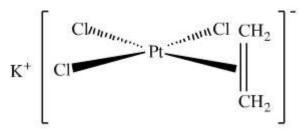
RLi

R – alkyl or aryl group

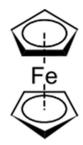
(iv) Wilkinson's catalyst

 $[(C_6H_5)_3P]RhCl$ 

(v) Zeise's Salts



(vi) Ferrocene



# Grignard's Reagent:-

Grignard's Reagent are most important of all organometallic compounds. It is used in the synthesis of large variety of organic compounds.

## Preparation of organometallic compound

Grignard's Reagent are prepared by treatment of alkyl or aryl halide with magnesium in anhydrous ether solvent.

$$RX + Mg \xrightarrow{Dry \text{ ether}} RMgX$$

For example

$$C_2H_5Br + Mg \xrightarrow{Dry ether} C_2H_5MgBr$$

## Synthetic application of Grignard's reagent

## 1. Preparation of Alcohol

# (a) Preparation of primary alcohol

When Grignard's reagent reacts with formaldehyde followed by hydrolysis gives primary alcohol.

$$R^{-}Mg^{+}X + H - C - H \rightarrow H - C - H \xrightarrow{O^{-}Mg^{+}X} \underbrace{H_{2}O/H^{+}}_{1^{0}} \xrightarrow{R - CH_{2} - OH + MgX(OH)}_{1^{0}}$$

#### (b) Preparation of secondary alcohol

When Grignard's reagent reacts with aldehyde other than formaldehyde followed by hydrolysis gives Secondary alcohol.

## (c) Preparation of tertiary alcohol

When Grignard's reagent reacts with ketone followed by hydrolysis gives tertiary alcohol.

# 2. Preparation of Hydrocarbon

Grignard's reagent reacts with water gives hydrocarbon

$$RMgX \ + H_2O \ \rightarrow R - H \ + \ MgX(OH)$$

## 3. Preparation of Carboxylic Acid

When Grignard's reagent reacts with CO<sub>2</sub> (solid ice) followed by hydrolysis gives Carboxylic Acid

#### 4. Preparation of Aldehydes and ketone

#### (a) Preparation of Aldehydes

When Grignard's reagent reacts with HCN followed by hydrolysis gives aldehydes.

#### (b) Preparation of Ketones

When Grignard's reagent reacts with alkyl cyanide followed by hydrolysis gives aldehydes.

#### Lithium Aluminium Hydride (LiAlH<sub>4</sub>)

Lithium aluminium hydride, also known as LAH, is a reducing agent that is commonly used in modern organic synthesis. It is a nucleophilic reducing agent that is best suited for reducing multiple polar bonds such as C=O. The LiAlH<sub>4</sub> reagent is capable of converting aldehydes to primary alcohols, ketones to secondary alcohols, carboxylic acids and esters to primary alcohols, amides and nitriles to amines, epoxides to alcohols, and lactones to diols. The LAH reagent, lithium aluminium hydride, cannot reduce isolated non-polar multiple bonds such as C=C. The double or triple bonds in conjugation with the multiple polar bonds, on the other hand, can be reduced.

#### Structure of LiAlH<sub>4</sub>

In aluminium hydride, AlH<sub>4</sub><sup>-</sup> ion, hydrogens are arranged in a tetrahedral arrangement around Al<sup>3+</sup>. The coordination of hydride, H<sup>-</sup> ions to Al<sup>3+</sup> ions results in its tetrahedral formation. The Li<sup>+</sup> ion form ionic bond with AlH<sub>4</sub><sup>-</sup> ion.

# Preparation of LiAlH4

- 1. The reaction of lithium hydride and aluminium chloride produces lithium aluminium hydride.  $4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl$
- **2.** In addition to this method, the industrial synthesis requires the initial preparation of sodium aluminium hydride under high pressure and temperature:

$$Na + A1 + H_2 \rightarrow NaA1H_4$$

Following that, LiAlH4 is synthesised by reaction as follows:

#### Reactions of LiAlH4

## 1. Reaction with Aldehyde and Ketone

When aldehyde and ketone undergo reduction with LiAlH<sub>4</sub> give primary and secondary alcohol respectively.

$$H_3C$$
 $H_3C$ 
 $H_3C$ 
 $H_3C$ 
 $H_3C$ 
 $H_3C$ 
 $H_3C$ 
 $OH$ 
Ethanol

$$H_3C$$
 $C_2H_5$ 
 $C_2$ 

#### 2. Reaction with Carboxylic acid and esters

Carboxylic acids and esters undergo reduction with LiAlH<sub>4</sub> gives corresponding alcohols.

# 3. Reaction with epoxide

When epoxide undergo reduction with LiAlH<sub>4</sub> gives corresponding alcohol

$$\begin{array}{c|c} O & LiAlH_4 \\ \hline R-CH-CH_2 & \longrightarrow & R-CH_2-CH_2-OH \\ \hline Epoxide & & Primary Alcohol \\ \end{array}$$

## 4. Reaction with nitriles and azides

When amines and azides undergo reduction with LiAlH<sub>4</sub> gives corresponding amines.

$$\begin{array}{c} \text{CH}_3 - \text{N}_3 \\ \text{Methyl azide} \end{array} \xrightarrow{\begin{array}{c} \text{LiAlH}_4 \\ \text{Methyl amine} \end{array}} \text{CH}_3 - \text{NH}_2$$