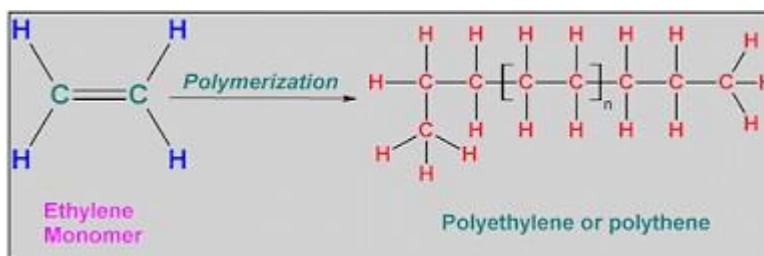


## UNIT V- Materials Chemistry

### ➤ Polymers

**Introduction:** The word polymer is derived from Greek word (*Poly = many; mere = units or parts*). Polymer is a large molecule which is formed by repeated linkage of small molecules, known as monomers. **The process by which monomer molecules are linked is called as polymerization.** Eg. Polyethylene (polythene is a polymer formed by linking together of a large number of ethene ( $C_2H_4$ ) molecules. Thus:



The number of repeating units in the chain is called the —degree of polymerization (D.P). Polymers with high degree of polymerization are called high polymers and those with low degree of polymerization are called oligopolymers.

$$\text{Degree of polymerisation} = \frac{\text{Molecular weight of polymer}}{\text{Molecular weight of monomer}}$$

High polymers have very high molecular weights ( $10^4$  to  $10^6$ ) and hence are called— macromolecules. These polymers have high strength, good flexibility, special electrical properties, resistance to chemicals, fabrication into complex shapes in a wide variety of colors. Polymers can be used for manufacture of strong articles, flexible rubber like masses, soft and resistant foams, smooth and fine fibres, swollen jelly-like food materials to fill cavities, to seal joints, etc.

**Classification of polymers:** There are several ways to classify polymers. The classification is based on several considerations. The source of polymer i.e. natural or synthetic, the type of polymerization process used in the synthesis, nature and type of chain and the solid state behavior of polymer chains etc.

Again polymers may be classified on the basis of the following:

1. Their reaction of stress and temperature.
2. Their mechanical strength and behavior
3. The ways by which they are produced
4. Their molecular arrangement
5. The type of monomer involved in the polymer.

6. The morphology of the polymeric substances.

The different classification schemes can be outlined as follows.

- Natural and synthetic polymers.
- Addition and condensation polymers
- Homochain and Heterochain polymer
- Organic and inorganic polymers and element- organic polymer
- Homo -polymers and co-polymers
- Linear, branched and cross-linked polymers
- Charged or uncharged polymer/ ionic or non- ionic polymer
- Thermoplastics and thermosetting polymers
- Fibers, plastics and Elastomers
- Crystalline and Amorphous polymers.
- Isotactic, syndiotactic and atactic polymers.

**Note:** Polymers with three different type of nonnumeric units are sometimes called as ‘terpolymers’

The repeating units constituting the polymer molecule are called as constitutional repeat units or ‘CRU’.

**Comparison between Thermoplastics and Thermosetting Polymer**  
**Thermoplastics Polymer**

- i. They are often formed by addition polymerization leading to long linear chain polymers with no cross-links.
- ii. They soften readily on heating because secondary forces between the individual chains can break easily by heat, light or pressure.
- iii. They can be reshaped and reused from waste
- iv. These are usually soft, weak and less brittle.
- v. They can be reclaimed from wastes.
- vi. They are usually soluble in suitable solvents.
- vii. Adjacent polymer chains are held together either by vanderwaals forces or dipole- dipole interaction or by hydrogen bonding.
- viii. During molding there is no change in chemical composition occurs.
- ix. These are generally tough materials

Example: PF, PP, PVC, PMMA, PS Nylons etc.

### **Thermosetting Polymer**

- i. They are often formed by condensation polymerization with three dimensional network structures.
- ii. They do not soften on heating and on prolonged heating, however charring of polymers is caused.
- iii. They cannot be reshaped and reused.
- iv. They are usually hard, strong and more brittle.
- v. They cannot be reclaimed from wastes.
- vi. Due to strong bonds having inter and intra-chain cross-linking, these are insoluble in almost all organic solvents.
- vii. Adjacent polymer chains are held together only by strong covalent bonding.
- viii. During molding further polymerization and cross-linking occurs.
- ix. These are brittle materials.

**Example:** Epoxy resins, silicones, Bakelite etc.

### **Natural and Synthetic polymers:**

**Natural polymers:** Obtained from animal and plant origin. Examples--Cellulose, starch, protein, wool, silk, leather.

**Synthetic polymers:** Synthetically prepared in the laboratory. Examples-- Plastics, resins, synthetic fibers like Nylon and Terylene, adhesives, paints etc.

**Homopolymers and Copolymers:** - (i) If a polymer is formed from a single monomer unit, then it is called as a homopolymer.

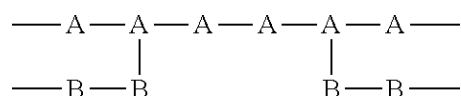
A-A-A-A-A-A-A-A-..

Example: PE, PMMA, PS, PAN ,PVC etc.

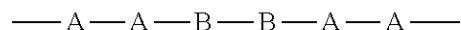
Polymeric compounds which are built up of two different types of monomer units in their chain are called —Copolymers| or —Mixed polymer| polymers with three different types of nonnumeric units are sometimes called as —ter-polymers| copolymers are further classified as alternating copolymers or statistically regular (where both repeating nonnumeric units are joined side by side) and random copolymers or statistically irregular (where there is no regularity in the joining of units of two different monomers)

Copolymers are again classified as block or graft copolymers.

1. Alternating Copolymer ..... ABABABABAB.....
2. Random Copolymer .... ABBABAABAABA.....
3. Block Copolymer ... AAAAABBBBBBAAAA.....
4. Graft Copolymer



Graft Copolymer



Block Copolymer

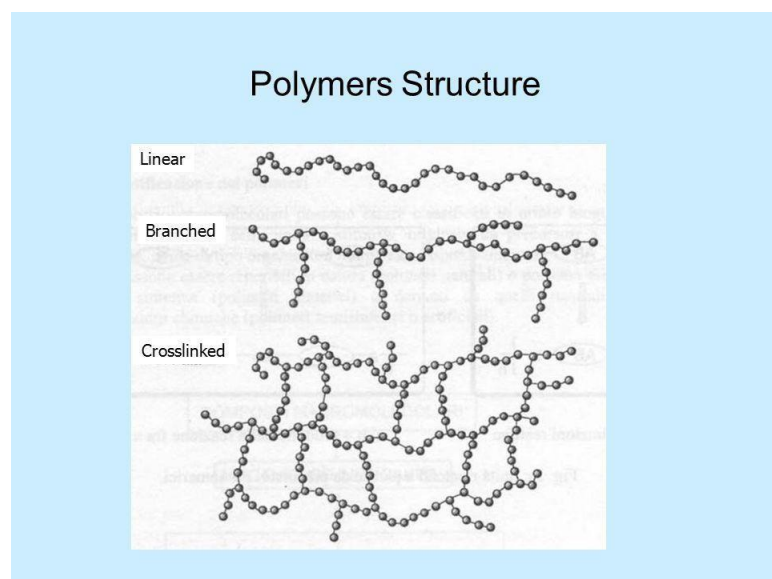
**Oligomers:** The chain like molecules with a few (8-10) structural units are called —oligomers|| aligo means few and mers means parts. These are low molecular weight products. Many organic compounds are of fairly high molecular weight, yet these are not considered as polymers. It is the complexity of their molecules and not the multiple repetitions of the monomers which accounts for their molecular weight and size.

Again polymers can also be classified as linear or cross linked polymers.

Linear polymer

Branched Chain polymer

Cross linked polymer



According to the structure of their main chain, all polymers can be broadly classified as homochain and heterochain polymers. In case of homochain polymers the main chain is made up of linkages between the atoms of same elements. Polymers are divided into two principal classes on the basis of the constitution of the main chain. Homochain polymers are those in which the main chains are constructed from atoms of a single element; heterochain polymers are those in which the main chains are constructed from atoms of two or more elements

Example: Carbon in organic polymers.

**TACTICITY OF POLYMER:** The orientation of monomeric units in a polymer molecule can takes place in an orderly or discordantly fashion with respect to the main chain. This difference in the configuration is known as tactility which affects the physical properties of the polymers.

On the basis of tacticity, the structure of the polymer may be divided into the following categories

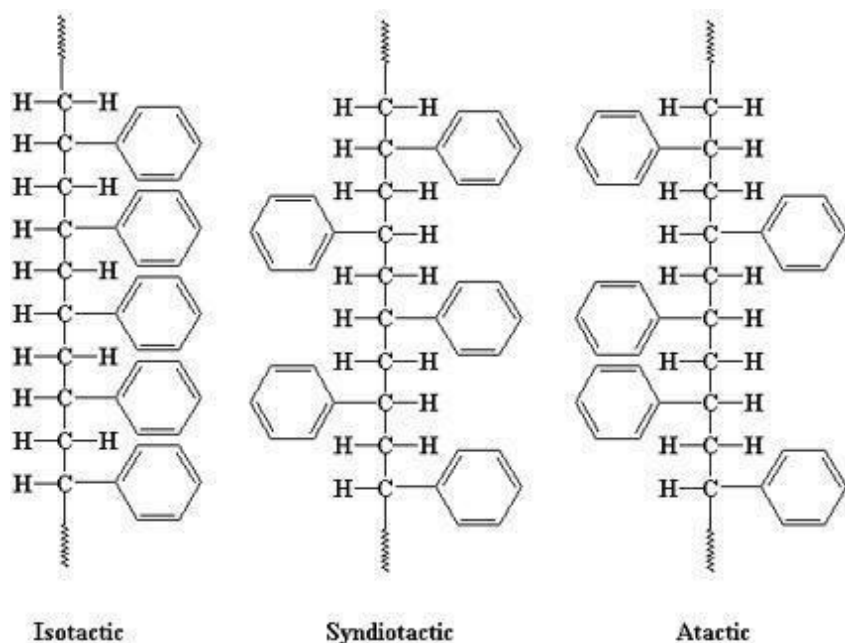
Isotactic (ii) Syndiotactic (iii) Atactic

**Isotactic Polymer:** These polymers consist of chain segments which display a regular repetition of the monomer units with each C atom of the same stereic configuration. In this polymer the substituent group (R) on the polymer lies above or below the plane of the main polymer chain.

**Syndiotactic polymers:** The chains of these polymers consist of regular species of monomer units in which even second C-atoms of the chain possesses opposed stereic configuration. In this polymer the substituent groups (R) lies alternatively above and below the plane of the main chain

**Atactic polymers:** The polymeric chain lacks regularity in the distribution of stereic configuration of the monomer units.

In these polymers there is a random arrangement of substituent groups (R) in the polymer chain



### Functionality:

**Definition:** The average number of the reactive groups on the no of bonds produced per monomer molecule will decide the nature of polymerization. Hence the no of bonding sites on the no. of functional groups present in the monomer is said to be the functionality of the polymer. It is classified into the following categories

**Mono functional compounds:** -Methylene alcohol –  $\text{CH}_3\text{-OH}$  Acetic acid -  $\text{CH}_3\text{-COOH}$  Methyl amine -  $\text{CH}_3\text{-NH}_2$  Acetaldehyde -  $\text{CH}_3\text{-CHO}$

**Bi- functional compounds:** - Ethylene glycol –  $\text{HO – CH}_2\text{- CH}_2\text{- OH}$ , Adipic acid –  $\text{HOOC – (CH}_2)_4\text{ – COOH}$ , Hexamethylenediamine.  $\text{H}_2\text{N- (CH}_2)_6\text{- NH}_2$

**Poly functional compounds:** - Glycerol -  $\text{HO- CH}_2\text{- CH-CH}_2\text{-OH}$ , Tricarboic acid –  $\text{HOOC- CH}_2\text{- CH-CH}_2\text{-COOH}$

Bi-functional monomers containing two functional groups give linear polymers.

Poly-functional compounds with more than two functional groups per molecule of the monomer give branched or cross-linked polymers.

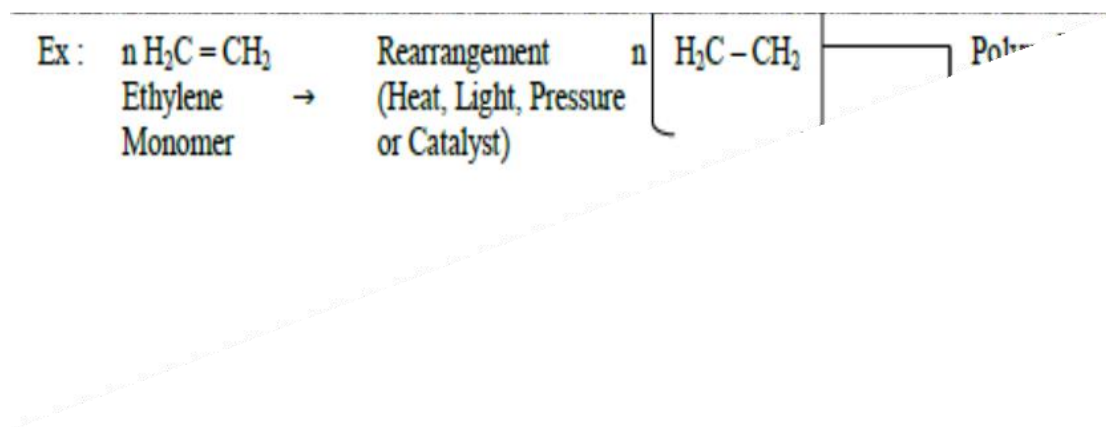
Certain trifunctional monomers may react and produces ring or cyclic polymers.

**Types of Polymerization:** Two types of polymerization are generally distinguished.

(1) Addition or chain polymerization (2) Condensation polymerization or step polymerization

**(1) Addition or chain polymerization:** In such type of polymerization the polymer is formed from monomer without the loss of any molecule (as HCl, H<sub>2</sub>O, NH<sub>3</sub>) and the product is an exact multiple of original monomeric molecule. The monomer usually contains one or more double bonds. In general, such polymerization proceeds by formation of some reactive species initially with the regeneration of reactive feature.

The addition polymerization reaction must be initiated by application of heat, light, pressure or a catalyst for breaking down the double bond of monomers. Eg.:



**2. Condensation or step polymerization:** It is defined as the reaction that occurs between monomers with simple polar group and elimination of small molecules like H<sub>2</sub>O, HCl, NH<sub>3</sub> etc. Eg.

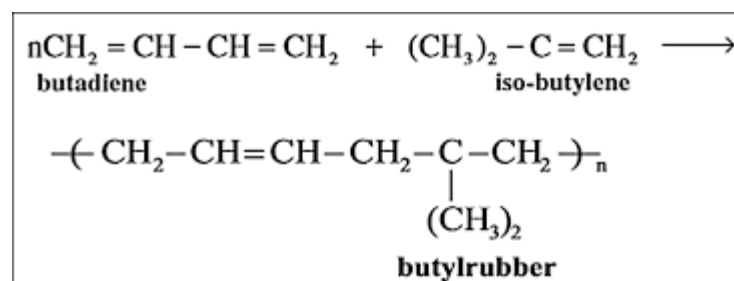
(i) Hexamethylene diamine and adipic acid condense to form a polymer, nylon – 6,6.

### Some industrially Important Polymers: Preparation and Applications

#### Plastics:

**BUTYLRUBBER:** Butyl rubber is a synthetic rubber, a copolymer of isobutylene with isoprene. The abbreviation IIR stands for isobutylene isoprene rubber. Polyisobutylene IS also known as "PIB" or polyisobutene, (C<sub>4</sub>H<sub>8</sub>)<sub>n</sub> is the homopolymer of isobutylene (2-methyl-1-propene) on which butyl rubber is based. Butyl rubber is produced by polymerization of 98% of isobutylene with 2% of isoprene.

Butyl rubber is a great option for shock absorption. But it is not recommended for use when in contact with petroleum oils and fluids. It can be made from the monomer isobutylene [CH<sub>2</sub>=C(CH<sub>3</sub>)<sub>2</sub>] only via cationic addition polymerization.



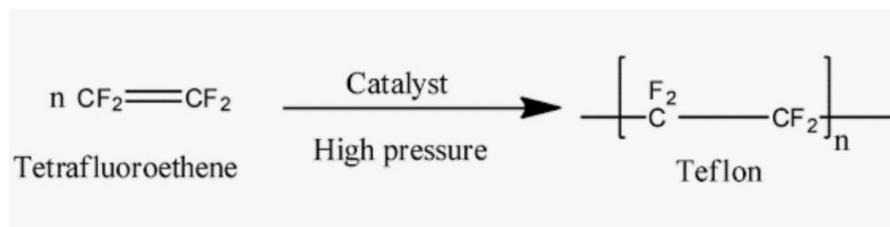
#### Properties:

- It is impermeable to most common gasses.
- It has exceptionally low gas and moisture permeability.
- It possess high damping capabilities
- It is resistant to heat, aging, weather, ozone, chemical attack, flexing, abrasion, and tearing.
- It is resistant to phosphate ester based hydraulic fluids, and has excellent electrical insulation performance.

#### Applications:

- It is used as a sealant for rubber roof repair.
- It is used in tubeless tire liners, inner tubes.
- Stoppers for glass bottles, medicine bottles, and pharmaceuticals.
- It is used as construction sealants, hoses, and in mechanical goods.

**TEFLON (PTFE):** PTFE is produced by free-radical polymerization of tetrafluoroethylene.



**Properties:**

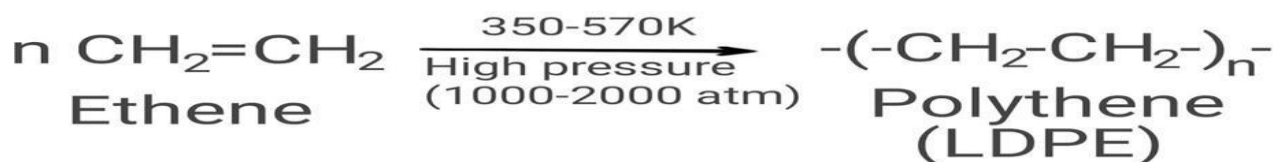
- Teflon is one of the chemically inert substances not affected by strong acids and aqua-regia.
- It is stable at high temperatures.
- It is a thermoplastic polymer that appears as a white solid at room temperature.
- It has density of about  $2200 \text{ kg/m}^3$ . It has a melting point of  $600\text{K}$  ( $327^\circ\text{C}$ ;  $620^\circ\text{F}$ ).
- Alkali metals and most highly reactive fluorinating agents are the only chemicals that can affect its property.
- It has a coefficient of friction of 0.05 to 0.10 which is the third-lowest of any known solid material. It has one of the proficient dielectric properties.

**Applications:**

- PTFE is usually used to coat non-stick frying pans as it has the ability to resist high temperatures.
- It is mostly used as a film interface patch for sports and medical applications due to pressure-sensitive adhesive backing.
- It is used in high friction areas of footwear as in soles.
- It is widely used in medical synthesis, test and many more medicines.

**LDPE**

Preparation: LDPE is prepared from gaseous ethylene under very high pressures (1000-5000 atm) temperatures (up to about  $350^\circ\text{C}$ ) in the presence of oxide initiators.



**Properties:**



- Branched polymer with low crystallinity.
- LDPE is a very flexible material.
- Its melting point is approximately 110 °C (230 °F).

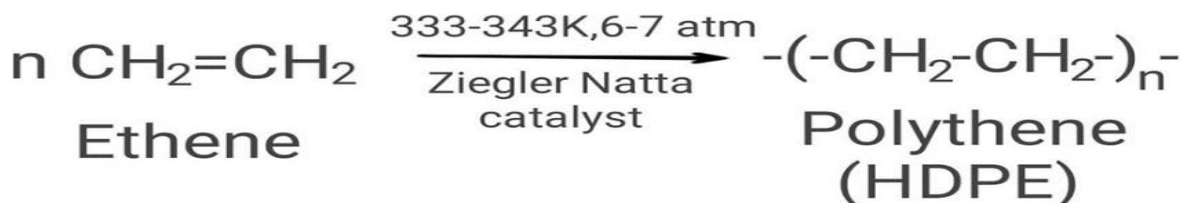
**Applications:**

- Packaging film.
- Trash and grocery bags.
- Wire and cable insulation.
- Squeeze bottles, toys.

## Polyethene

**HDPE:** HDPE can be made by following methods:

1. Using Zeigler- Natta catalyst [ $\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$ ], ethylene is polymerized under 6-7 atm. at 60-70<sup>0</sup> C.



**Properties:**

- a. It has low cost
- b. Impact resistant from -40°C to 90°C
- c. It is moisture resistant and possess good chemical resistance.
- d. It can be readily processed by all thermoplastic methods.

**Applications:**

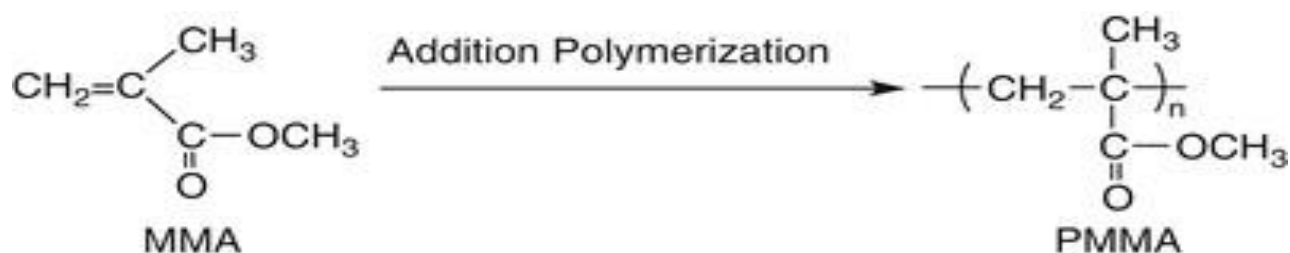
HDPE is resistant to many different solvents and has a wide variety of applications:

- a. It is used in swimming pool installation, 3-D printer filament and banners.
- b. It is used in bottle caps, folding chairs and tables.
- c. Chemical-resistant piping, Coax cable inner insulator
- d. It s used in Food storage containers as well as fuel tanks for vehicles
- e. It is used as corrosion protection for steel pipelines
- f. It is used in Far-IR lenses

## Poly Methyl Methacrylate (PMMA)/Lucite

**Preparation:**

Polymerization of methyl methacrylate (MMA) in the presence of acetyl peroxide or hydrogen peroxide as catalyst



### Properties:

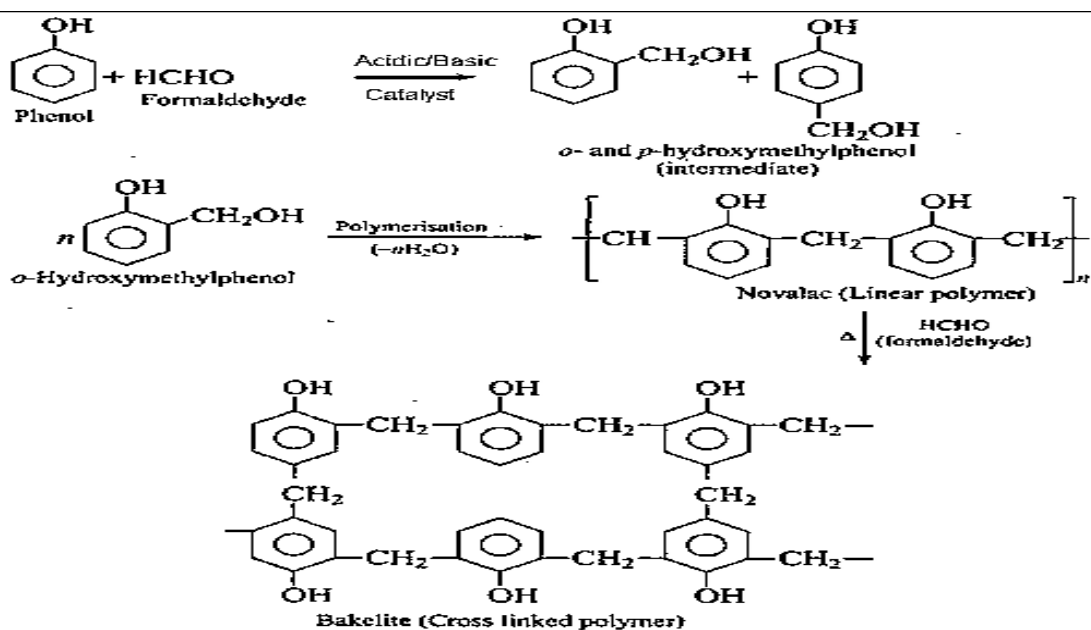
- It is amorphous, colourless, transparent thermoplastic.
- Methyl groups as substituents the carbon atoms restrict chain flexibility.
- Shows excellent weather ability.
- PMMA weighs only one third of glass and can be readily moulded to any desired shape.

### Applications:

- Motor-cycle windscreen
- Wash basins
- Optical fibers
- Light fittings for street lamp housing
- Ceiling lighting for school rooms, factories
- Bubble body of many helicopters

## Bakelite

**Preparation:** Condensation polymerization of Phenol and Formaldehyde



### Properties:

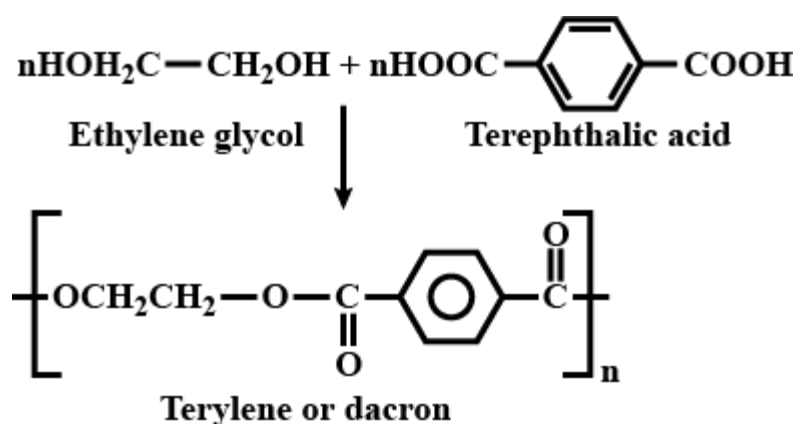
- Dark coloured, pinkish brown.
- These are hard, rigid, and strong materials.
- Shows good heat and moisture resistance.
- They have good chemical resistance, abrasion resistance.
- Good electrical insulation.
- Excellent bonding strength and adhesive properties.

**Applications:**

- Plugs and switches.
- Handles for cooker and saucepans.
- Adhesives for grinding wheels.
- Varnishes, protective coatings.
- Electrical insulation

**Fibres****Polyesters**

**DACRON(PET):** It can be prepared by the condensation of ethylene glycol and terephthalic acid.

**Properties:**

- It is a hard, stiff, strong, dimensionally stable material that absorbs very little water.
- It has good gas barrier properties and chemical resistance except to alkalis (which hydrolyze it).
- Its crystallinity varies from amorphous to fairly high crystalline.

**Applications:**

- It is an excellent water and moisture barrier material used for soft drinks, fruit juice concentrates and sauces and wide-necked jars for coffee.
- It is also used as a substrate in thin film solar cells.
- PET is used for making magnetic recording tape.
- Glass filled PET moldings are used for toasters, coffee machines, car heater and water meter.

**POLYAMIDES [Nylons]**

Polyamides are the polymers, which contain many repeating amide groups in the main polymer chain.

**Nylon – 6, 6:** Nylon – 6;6 is obtained by the polymerization of adipic acid with hexamethylene diamine.



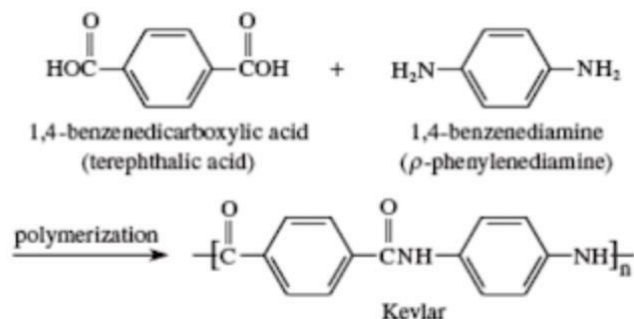
- They are translucent, whitish, high melting ( $160^{\circ}\text{C} - 264^{\circ}\text{C}$ ) polymers.
- They possess high temperature stability and good abrasion resistance.
- They are insoluble in common organic solvents (methylated spirit, benzene and acetone) and soluble in phenol and formic acid.
- Their mouldings and extrusions have good physical strengths (especially high impact strength) and self lubricating properties.
- They absorb little moisture, and are thus drip – dry in nature.
- They are very flexible and retain original shape after use.

### **Applications of Nylon:**

- Nylon 6, 6 is used for making socks, under garments, dresses, carpets, etc.
- Nylon 6 and Nylon 11 are used for moulding purposes for gears, bearings, electrical mountings, etc. Nylon bearings and gears work quietly without any lubrication.
- They are also used for making filaments for ropes, bristles for tooth brushes and films, tyre cords, etc.

### Kevlar Poly (p-phenylene tere phthalamide)

**Preparation:** It is prepared by the condensation polymerisation of terephthalic acid dichloride and 1,4-diaminobenzene.



### Properties:

- Benzene rings are linked to the amide linkage; therefore, Kevlar is very rigid polymer.
- It is in fact, aromatic polyamide so it is also known as aramid polymer.
- There are stronger intermolecular forces between neighbouring chains which make it exceptionally strong.
- It also has high heat stability.
- Extraordinary mechanical properties.
- Kevlar has the ability to be spun into fibers having 5 times the tensile strength of steel.
- High tensile strength is due to extensive H-bonding.
- Extreme chemical inertness.

### Applications:

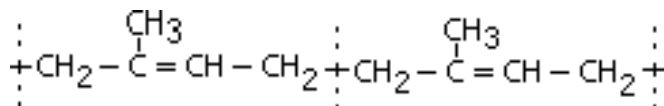
- Tyres, brakes, clutch lining and other car parts
- Bullet-proof vests
- Motor cycle helmets
- Aerospace and air-craft industries

### Elastomers

Polymers that exhibit extreme elastic extensibility when subjected to relatively low mechanical stress. They are also known as rubber. Some elastomers can be stretched by a factor of 10 and yet completely recover to their original shape. Although their properties are quite different from thermosets, they share a similar molecular structure that is different from the thermoplastic.

### Natural Rubber (NR):

Natural rubber is extracted in the form of latex from the bark of the *Hevea* tree.

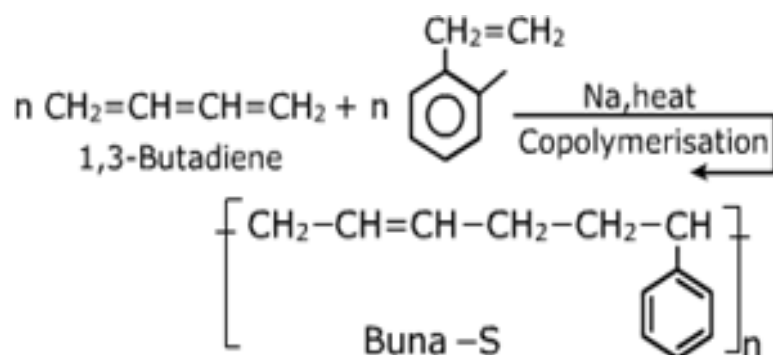


- 99.99% cis Polyisoprene
- Good low temperature flexibility.
- Low Tg (-65 C). Low heat buildup.
- to 400,000 MW. Easy Processing.

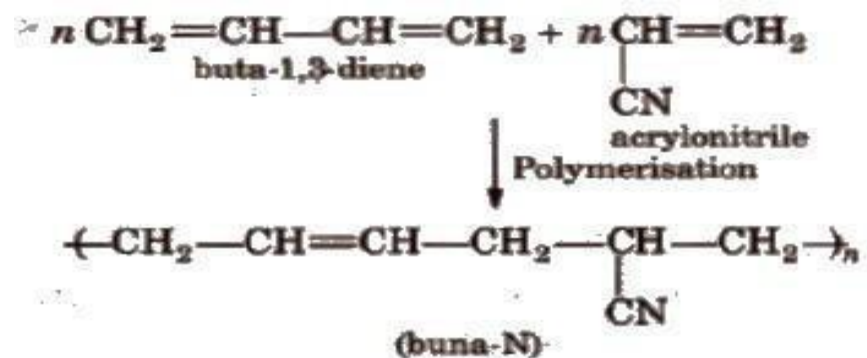
- g. Poor resistance to oxygen, ozone, hydrocarbon solvents and heat.

### **BuNa-S Rubber or Styrene Butadiene Rubber (SBR):**

The rubber obtained is also called Styrene butadiene rubber (SBR). In Buna-S, Bu stands for butadiene and, Na for sodium and S for styrene. It is a polymerized copolymers of styrene and butadiene in 1: 3 ratio. It is vulcanized with sulfur. The rubber is slightly inferior to natural rubber in its physical properties.



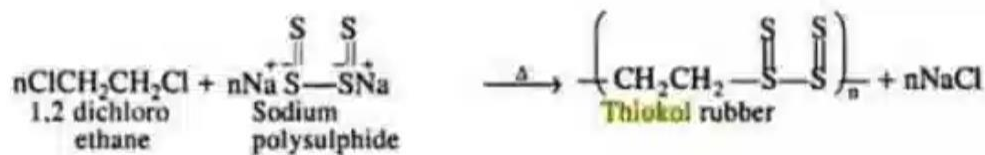
**BuNa–NRubber or Nitrile Rubber (NBR):** Nitrile rubber is the generic name given to emulsion polymerized copolymers of acrylonitrile and butadiene in 1: 1 ratio.



## Thiokols (T) (Polysulfides or Polythioethers)

### Preparation:

They are typically liquid polymers that can be crosslinked by converting the terminal thiol groups (-SH) of the polymer to disulphide (-S-S-) links.



### Properties:

- The typical temperature range for working is  $-45^\circ\text{C}$  to  $105^\circ\text{C}$ . Some grades, however, can withstand temperatures of up to  $150^\circ\text{C}$  /  $170^\circ\text{C}$  (for a short time).
- The properties of the polymer depend on the length of aliphatic groups and the number of sulphur atoms present in it.
- The polymers behave like elastomers when four sulphur atoms or greater are present per monomer; lower amounts of sulphur give a hard, brittle resin
- The elastomer has a high sulphur content, approximately 80% by weight, making it a high-density material with a high resistance to swelling by hydrocarbon oils.
- The low stability of the sulfur-sulfur bond, on the other hand, causes a strong tendency to relax and flow under pressure.
- Thiokol elastomers have low moisture and gas permeability, good flex crack resistance, excellent low temperature flexibility, and resistance to oil, ozone, oxygen and many chemicals such as ethers, ketones, and aromatic hydrocarbons.

### Applications:

- The polymer is most used as a low-molecular weight liquid that cures in place to form an elastomeric sealant
- Thiokols are primarily used in oil-resistant and weather-resistant seals and gaskets.
- They are also used in gasoline hoses and other applications.

## **Polymer Blends**

It is defined as the mixture of at least two macromolecular substances, polymers, or copolymers in which the ingredient content is above 2 wt%.

### **Advantages of blending and properties of blends:**

Blending may **improve** resin or product **performance** by:

- ✓ Producing materials having all desired properties at lowest cost.
- ✓ Extending the engineering resins' performance by incorporation of less expensive polymers.
- ✓ Improvement of specific properties such as:

*Brittleness:* Toughening brittle polymers, thus eliminating the need to use low molecular weight additives plasticizer in the flexible PVC formulations).

*Modulus and Dimensional Stability:* Blending with more rigid and more heat resistant resin.

*Improve Solvent and Chemical Resistance:* Incorporation of semi crystalline polymer into an amorphous resin (e.g., blends of PC with PEST)

*Improve Flame Resistance:* Incorporation of non-flammable resin into a flammable (e.g., styrenics or acrylics with PVC)

*Permanently Anti-Static blends:* Blends with polymers having either –OH or –SH functionality (e.g. ethylene oxide-epichlorohydrin with ABS/PC blend).

*Biodegradability:* Incorporation of a biodegradable resin. Blending makes it possible to produce integrated **multi-layer** structures

- ✓ Providing means for recycling of industrial and/or municipal plastics waste.
- ✓ The blending technology makes it possible to rebuild high molecular weights of partially degraded polymers, thus to produce high performance articles from the plastics waste.

### **Types of polymer blends**

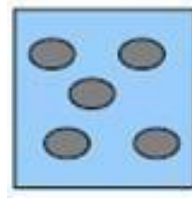
**Miscible polymer blend:** These are homogenous up to the molecular level. They have negative value of free energy of mixing. It is a single –phase structure that has properties values between the values of properties of its components.

**Immiscible polymer blend:** It is a blend that exhibits more than two phases. In this system the two components are phase separated.





**Miscible polymer blend**



**Immiscible polymer blend**

Most compatible blends are immiscible and can be made compatible by a variety of compatibilization techniques.

**Polymer alloy:** When the interface and/or the morphology of an immiscible blend is modified a polymer *alloy* is obtained. These are immiscible, compatible polymer blend with modified interface and morphology.

#### **Comparison between Polymer Blend and Polymer Alloy**

The properties of many plastics can be greatly modified by blending or alloying two or more polymers. Technically, blends are mixtures that are not fully compatible whereas alloys are mixtures that are fully compatible.

Polymer alloy constitutes a specific sub-class of polymer blend; virtually all high performance engineering blends are alloys.

At present polymer alloys, blends and composites consume over 80 wt% of all plastics. This has resulted in:

- Increased scale of production.
- Use of multi-component and multiphase materials.
- New processing methods.

## **Polymer Composites**

Composites can be defined as materials that consist of two or more chemically and physically different phases separated by a distinct interface. Composites are combinations of materials differing in composition, where the individual constituents retain their separate identities. These separate constituents act together to give the necessary mechanical strength or stiffness to the composite part. Composite material is a material composed of two or more distinct phases (matrix phase and dispersed phase) and having bulk properties significantly different from those of any of the constituents. Matrix phase is the primary phase having a continuous character. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it. Dispersed (reinforcing) phase is embedded in the matrix in a discontinuous form. This secondary phase is called the dispersed phase. Dispersed phase is usually stronger than the matrix, therefore, it is sometimes called reinforcing phase.

## **Characteristics of Composites in structural applications**

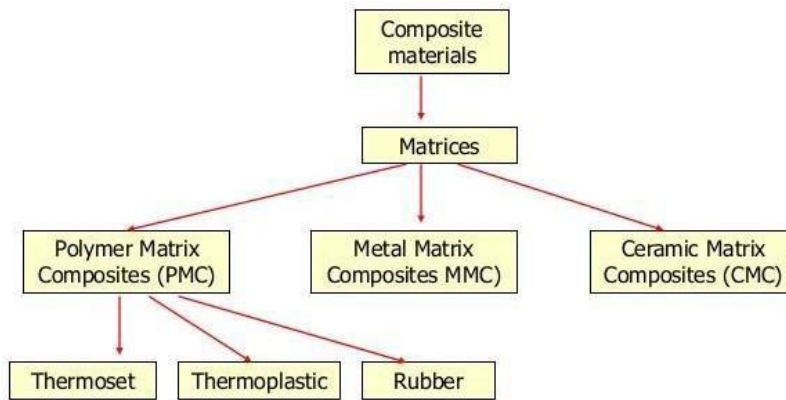
- ✓ They generally consist of two or more physically distinct and mechanically separable materials.
- ✓ They are made by mixing the separate materials in such a way as to achieve controlled and uniform dispersion of the constituents.
- ✓ They have superior mechanical properties and in some cases uniquely different from the properties of their constituents. Wood is a natural composite of cellulose fibers in a matrix of lignin. Most primitive man-made composite materials were straw and mud combined to form bricks for building construction.
- ✓ Most visible applications pave our roadways in the form of either steel and aggregate reinforced Portland cement or asphalt concrete.
- ✓ Reinforced concrete is another example of composite material. The steel and concrete retain their individual identities in the finished structure. However, because they work together, the steel carries the tension loads and concrete carries the compression loads.

## **Classification of Composites**

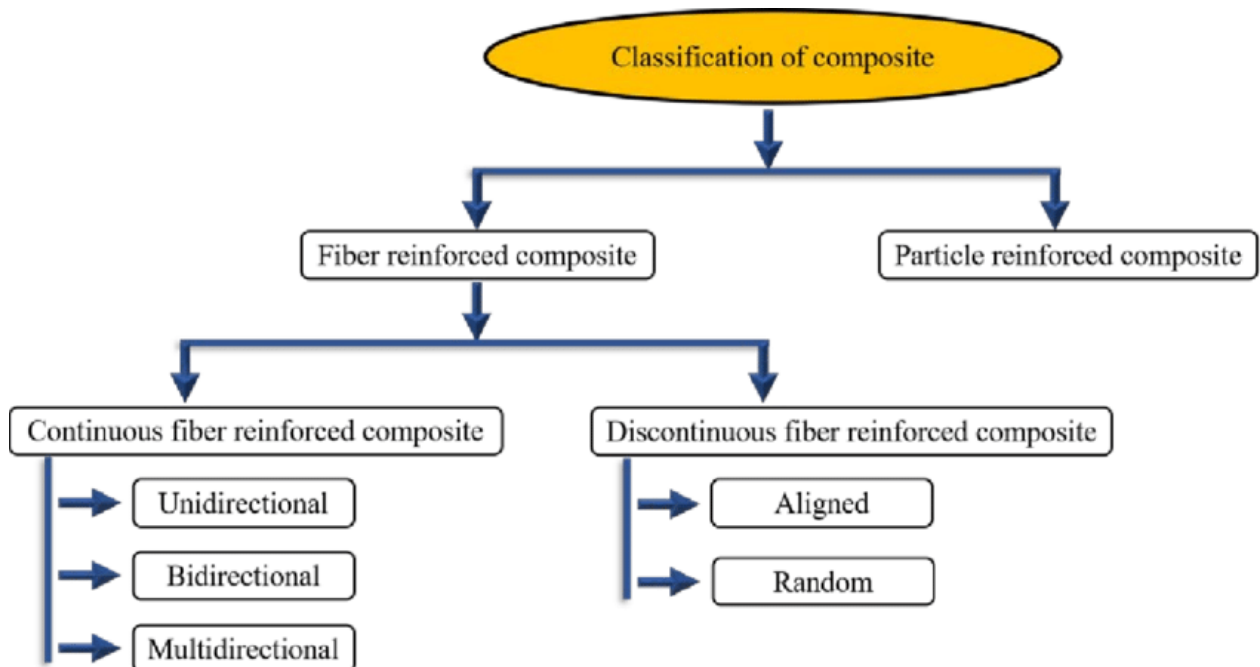
**1 On the basis of matrix phase**, composites can be classified into metal matrix composites (MMCs), ceramic matrix composites (CMCs), and polymer matrix composites (PMCs)

**2 On the basis of reinforcement** composites can be classified into particulate composites (composed of particles), fibrous composites (composed of fibers), and laminate composites.

**1 On the basis of matrix phase**



## 2 On the basis of reinforcement



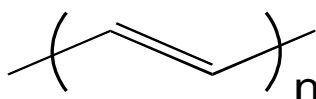
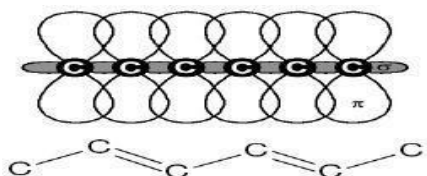
## Conducting Polymers

The polymeric materials, which possess electrical conductivities on par with metallic conductors, are called conducting polymers. Conductivities as high as  $1.5 \times 10^{-1} \text{ ohm}^{-1} \text{ m}^{-1}$  have been attained in these polymeric materials.

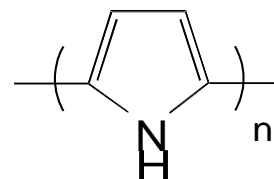
**Different types of conducting polymers are listed below:**

- (1) Intrinsically conducting polymer (ICP) (or) Conjugated – Electrons conducting polymer
- (2) Doped conducting polymer
- (3) Extrinsically conducting polymer
- (4) Coordination conducting polymer (inorganic polymer)

**(1) Intrinsically conducting polymer (ICP) or Conjugated – Electrons conducting polymer** It is a polymer whose backbone or associated groups consist of delocalized electron – pair or residual charge. Such polymers essentially contain conjugated – electrons backbone, which is responsible for electrical charge. In an electric field, conjugated electrons of the polymer get excited, thereby can be transported through the solid polymeric material. Overlapping of orbitals (of conjugated 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 electrons in a polymer increases its conductivity to a larger extent.



Polyacetylene



Polypyrrole

### **(2) Doped conducting polymer**

It is obtained by exposing a polymer to a charged transfer agent in either gas phase or in solution. Intrinsically conducting polymers possess low conductivity 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, called doping. Doping is classified into 2 types.

(a) **p – doping:** P – doping involves treating an ICP with a Lewis acid, there by oxidation process takes place and positive charges on the polymer backbone are created. Some of the common p – dopant used are I<sub>2</sub>, Br<sub>2</sub>, AsF<sub>5</sub>, PF<sub>6</sub>, Naphthylamine, etc, used.

(b) **n – doping:** It involves treating an intrinsically conducting polymer with a lewis base thereby reduction process takes place and negative charges on the polymer backbone are created. Some of the common N – dopant used are Li, Na, Ca, tributyl ammonium, FeCl<sub>3</sub>, etc. for example.

(3) **Extrinsically conducting polymers:** Extrinsically conducting polymers are those polymers whose conductivity is due to the presence of an externally added ingredient in them. These are of the following two types.

(a) **Conductive element filled polymer:** It is a resin or polymer filled with conducting elements such as carbon black, metallic fibres, metal acids, etc. In this, the polymer acts as the binder to hold the conducting elements together in the solid entity.

(b) **Blended conducting polymer:** It is the product obtained by blending a conventional polymer with a conducting polymer either by physical or chemical change.

#### **Applications:**

Some of the important applications of conducting polymers are:

- ✓ In rechargeable light weight batteries based on perchlorate doped polyacetylene – lithium system. These are about 10 times, lighter than conventional lead storage batteries.
- ✓ In optically display devices based on polythiophene. When the structure is electrically based, the optical density of the film changes, i.e., color changes. Such electrochromic systems produce colored displays with faster switching time and better viewing than conventional liquid crystal display devices.
- ✓ It is used in wiring in aircrafts and aerospace components
- ✓ It is used in telecommunication systems
- ✓ It is used in antistatic coatings for clothing.

## Biodegradable polymers

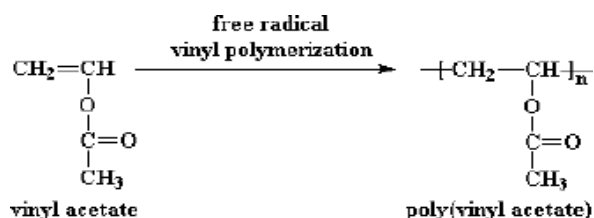
These are those polymers which get decomposed under aerobic or anaerobic conditions, as a result of the action of microorganism/enzymes.

Some biodegradable polymers are listed below

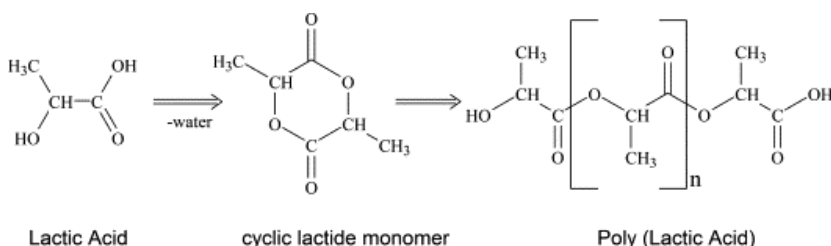
### **Polyvinyl acetate (PVA)**

**Properties:** Polyvinyl acetate is a colorless, transparent material, resistant to water, atmospheric oxygen and chemicals. It is soluble in organic acids and organic solvents. It has a good heat resistance. It harmless if taken orally.

**Uses:** It is used for making records, chewing gums, surgical dresses, paints, plastic emulsions, wrapping papers, leather and textiles etc.

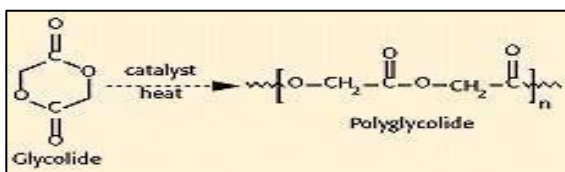


**II. Polylactic acid (PLA):** Polylactic acid (PLA) is obtained by polymerisation of the cyclic dimer of lactic acid or by microbiological synthesis of lactic acid followed by the polycondensation and removal of water by evaporation.



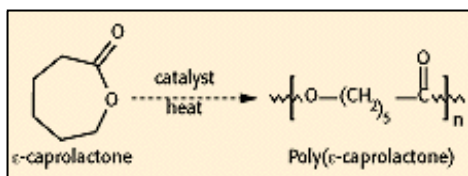
**Applications:** it breaks down in the environment back to lactic acid which can be metabolized which has application in medical field such as sutures, drug delivery systems and wound clips. It has also agriculture applications such as time release coatings for fertilizers and pesticides.

**PGA:** It is used in fishing industry, controlled release of pesticides, egg cartons, Razor handles, toys and in the medical field.



### PCL (Poly caprolactone)

It is thermoplastic biodegradable polyester synthesized by chemical Conversion of crude oil, followed by ring opening polymerisation. PCL has good water, oil, solvent and chlorine resistance. It is manufactured under trade name "Tone Polymer".



## ➤ Organometallics

### Organometallic Compounds

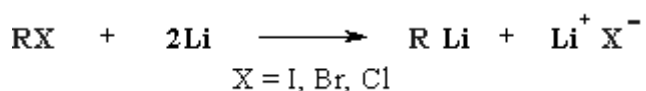
Compounds that contain a metal-carbon bond, **R-M** are known as "*organometallic*" compounds. Organometallic compounds of Li, Mg (Grignard reagents) are amongst some of the most important organic reagents.

Organometallic compounds provide a source of **nucleophilic carbon** atoms which can react with electrophilic carbon to form a new carbon-carbon bond. This is very important for the synthesis of complex molecules from simple starting materials.

To rationalise the general reactivity of organometallics it is **convenient** to view them as ionic, so **R-M = R<sup>-</sup>M<sup>+</sup>**

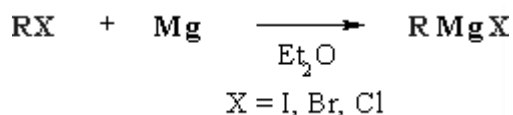
The most important reactions in this chapter are the reactions of organolithiums, **RLi**, and Grignard reagents, **RMgX**, with the carbonyl groups in aldehydes, ketones and esters to give alcohols. However, we will also look at some useful reactions involving Cu, Zn and Hg (mercury).

#### Preparation of Organolithium Reagents



- They are formed by the reaction of alkyl halides with lithium metal.
- Typical solvents are normally anhydrous diethyl ether but pentane or hexane can also be used.
- The alkyl group can be primary, secondary or tertiary.
- Halide reactivity : I > Br > Cl
- **R** can be alkyl, vinyl or aryl
- Other Group I metals (Na, K) can be used instead of Li.

#### Preparation of Organomagnesium Reagents

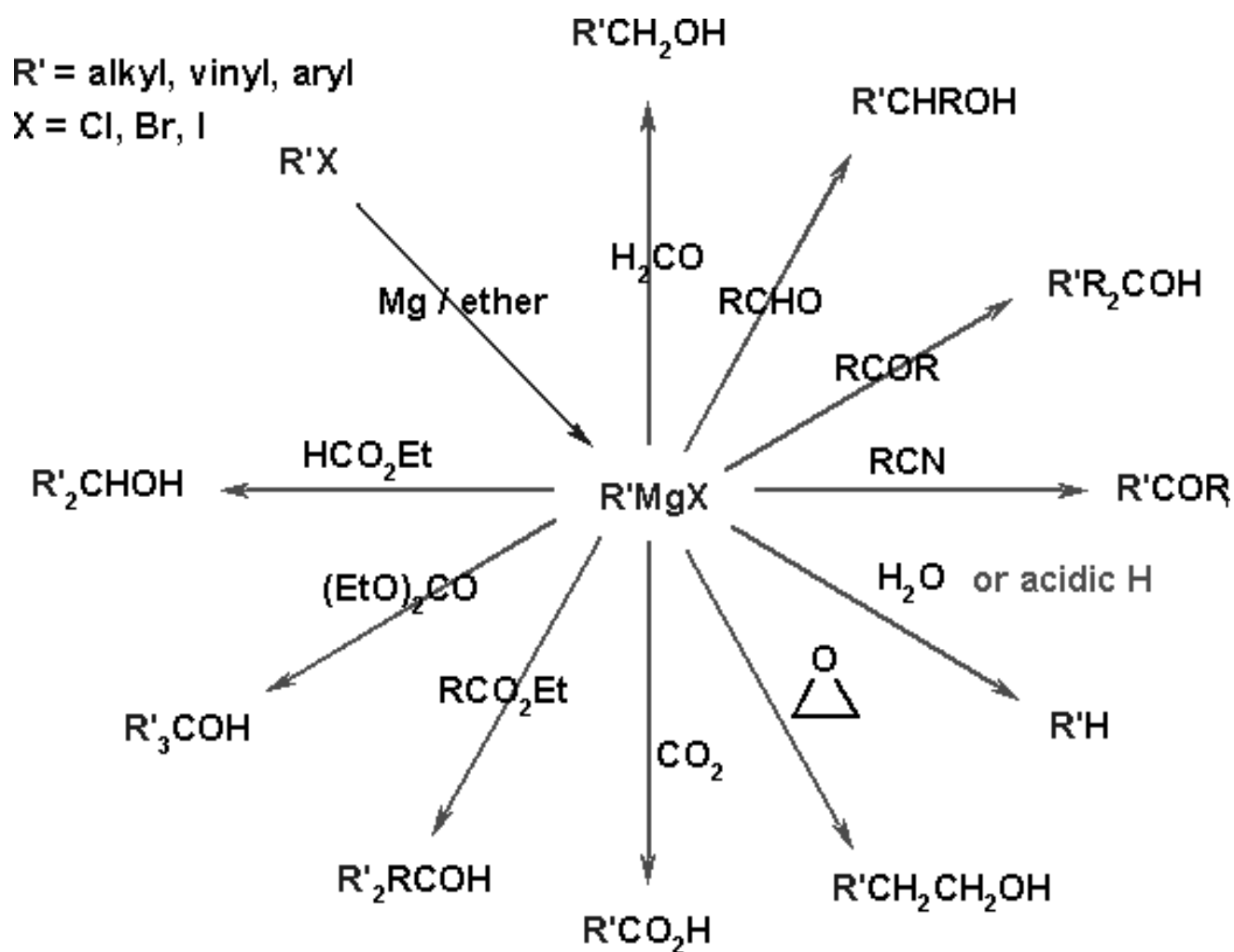


#### Reaction type: oxidation - reduction

Organomagnesiums are formed by the reaction of alkyl halides with magnesium metal.

- Typical solvents are normally anhydrous diethyl ether or tetrahydrofuran.
- The alkyl group can be primary, secondary or tertiary.
- Halide reactivity : I > Br > Cl
- **R** can be alkyl, vinyl or aryl.

### Applications of Grignard Reagent



Typical work-up for these reactions:

1. Dilute aqueous acid or
2. Aqueous ammonium chloride



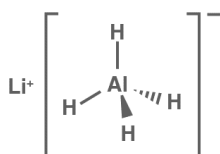
### Lithium Aluminium Hydride – LiAlH<sub>4</sub> (LAH)

LiAlH<sub>4</sub> is a strong reducing agent (because aluminium is less electronegative, and the Al-H bond in LiAlH<sub>4</sub> is more polar) 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.

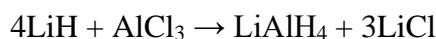
#### Structure of Lithium Aluminium Hydride – LiAlH<sub>4</sub>

- 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 result in its formation.
- Li<sup>+</sup> centres are surrounded by five AlH<sub>4</sub><sup>-</sup> tetrahedra in the structure. A bipyramid arrangement is formed by the Li<sup>+</sup> centres being bonded to one hydrogen atom from each of the surrounding tetrahedra.

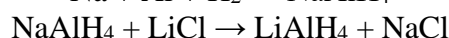
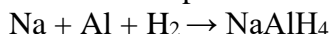


#### Preparation of LiAlH<sub>4</sub>

1. The reaction of lithium hydride and aluminium chloride produces lithium aluminium hydride.



2. In addition to this method, the industrial synthesis requires the initial preparation of sodium aluminium hydride under high pressure and temperature followed by salt metathesis:



*It proceeds in a high yield. Filtration is used to remove LiCl from an ethereal solution of LAH.*

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

1. Lithium aluminium hydride, LAH, is white solid, commercial samples are usually grey due to impurities.
2. It produces hydrogen gas when it reacts violently with water. As a result, it should not be exposed to moisture, and the reactions should take place in inert and dry surroundings.

This reaction can be used to generate hydrogen in the laboratory.



3. The reduction reaction with LiAlH<sub>4</sub> as the reducing agent must be carried out in anhydrous nonprotic solvents such as diethyl ether, THF, and so on.
4. It has a high solubility in diethyl ether. However, due to the presence of catalytic impurities, it may spontaneously decompose in it. Despite its low solubility, THF is the preferred solvent for LAH.
5. Usually, the reactions are carried out with an excess of LiAlH<sub>4</sub>. To remove moisture if any, a small amount of the reagent is added to the solvent.

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

1. LiAlH<sub>4</sub> reduces aldehydes or ketones to the corresponding primary or secondary alcohols. Acetaldehyde, for example, is reduced to ethyl alcohol, while acetone is reduced to isopropyl alcohol.

2. Lithium aluminium hydride is used to reduce carboxylic acids, esters, and acid halides to their corresponding primary alcohols.

For example, LiAlH<sub>4</sub> reduction of acetic acid, methyl acetate, and acetyl chloride yield the same ethyl alcohol.

## Questions

**Marks. 2**

1. What are monomers and polymers? Give suitable examples.
2. Define the term polymerization.
3. Define the term functionality.
4. What do you mean by copolymer and give two examples?
5. What do you mean by Tacticity of polymers.
6. Write name of monomers of the following polymers and classify them as addition or condensation polymers: Teflon, Bakelite, Natural rubber.
7. Why is Bakelite a thermosetting polymer?
8. Write down the addition polymerization and condensation polymerization.
9. Discuss the preparation and uses of PTFE.
10. Discuss the preparation and uses of PMMA.

**Marks. 7**

11. What is a biodegradable polymer? Give example of a biodegradable polymer.
12. Write about the various polymers related to natural rubber with emphasis on their preparation, properties and uses.
13. Differentiate between synthetic rubber over natural rubber.
14. Differentiate between condensation and addition polymerisation.
15. Differentiate between thermoplastic and thermosetting polymers.

**Marks. 9**

16. Define Fibers. Also discuss the preparation, properties and applications of Nylon 6,6 Nylon 6 and Polyester.
17. Define Elastomer. Discuss the preparation, properties and applications of Buna-N, Buna- S.
18. Define plastics. Discuss the preparation, properties, and applications of any one thermoplastic and one thermosetting.
19. Discuss the classification and applications of Conducting polymers.
20. What are Composite materials? Give its classification and application.
21. Illustrate the preparation and properties of Grignard Reagent. Also give its application for the synthesis of 1<sup>o</sup>, 2<sup>o</sup> and 3<sup>o</sup> alcohols by taking suitable examples.
22. Discuss biodegradable polymers with suitable examples and potential applications.
23. Discuss the preparation, properties and applications of Teflon, Dacron, PMMA.
24. Give synthesis of Lithium Aluminium Hydride. How will you synthesize primary, secondary, and tertiary amine with the help of LiAlH<sub>4</sub>?
25. What are speciality polymers. Write short notes on:
  - a. Dendrimers
  - b. Polynucleotides
26. What are polymer blends and its types? Also give the properties and advantages of blending.