

**DR. A.P.J. ABDUL KALAM TECHNICAL UNIVERSITY, LUCKNOW**



**ENGINEERING CHEMISTRY (BAS-102/ 202)**  
**B. TECH. I YEAR**



## COURSE OUTCOMES

<b>CO- 1</b>	Students will be able to explain the formation and stability of homo and hetero di atomic molecules. They will understand the concept of liquid crystals and nanomaterials.
<b>CO-2</b>	Students will be able to apply basic concept of spectroscopy to identify various molecular structures.
<b>CO- 3</b>	Students will be able to apply the concept of Nernst equation, Gibbs Helmholtz equation, EMF and thermodynamic functions to solve various problems based on electrochemistry. They will be able to identify the causes of corrosion and best methods to reduce it as well as to understand the phase rule and apply it to the water system.
<b>CO 4</b>	Students will be able to analyze water sample for its type and amount of hardness. They will be able to analyze coal sample qualitatively and quantitatively.
<b>CO- 5</b>	Students will be able understand the importance of polymers in our day to day life. They will be able to understand how various organic compounds can be synthesized using Grignard's Reagent and LAH.



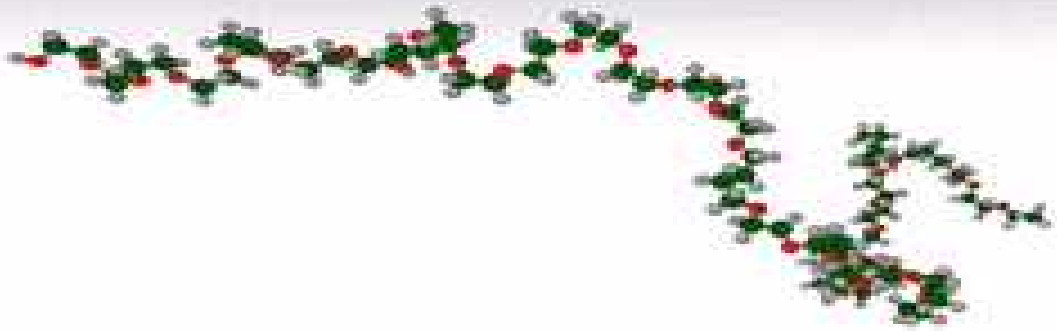
# POLYMERS AND ORGANOMETALLIC COMPOUNDS



## Contents

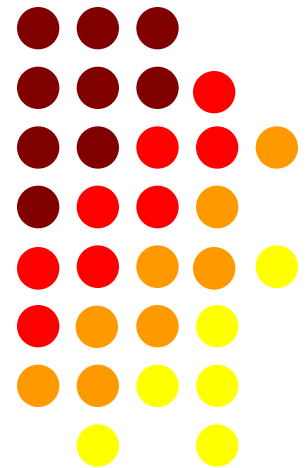
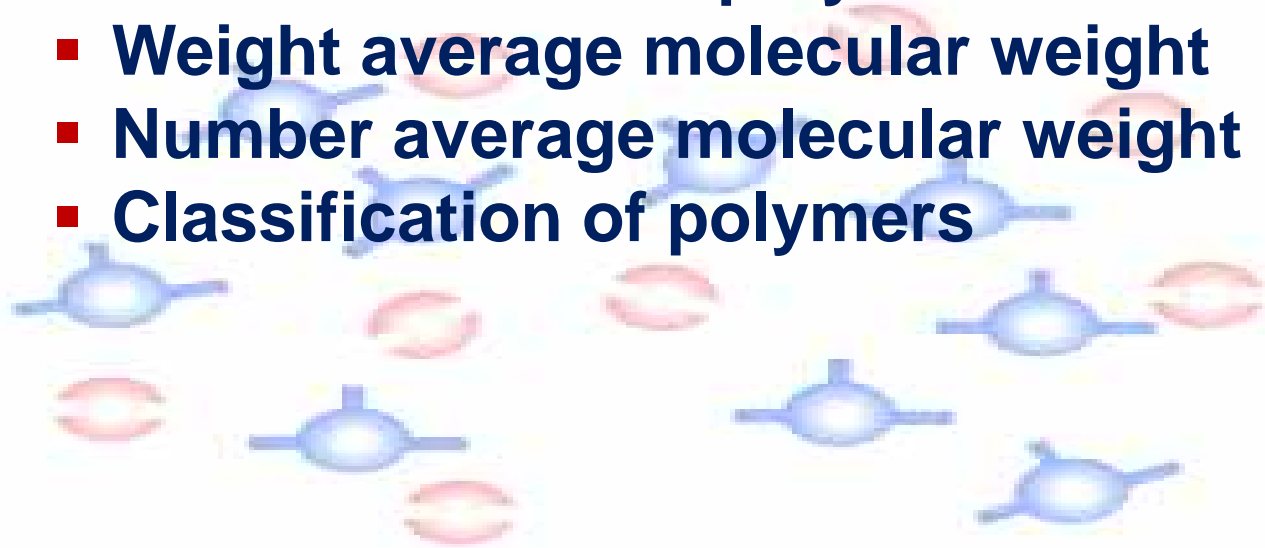
- Basic definitions, characteristics of polymers, Weight average and number average molecular weights, Classification of polymers.
- Preparations and applications of some industrially important polymers (Buna N, Buna S, Nylon 6, Nylon 6,6 , Terylene, Lucite, Teflon, Bakelite, Kevlar, Decron, Thiokol,)
- Conducting polymers and Biodegradable polymers: Preparation, Properties & Applications
- Blends & Composites: Properties & Applications
- Organometallic compounds, their classification and general methods of preparations.
- Grignard Reagent and its applications.
- $\text{LiAlH}_4$  Reagent and its applications.





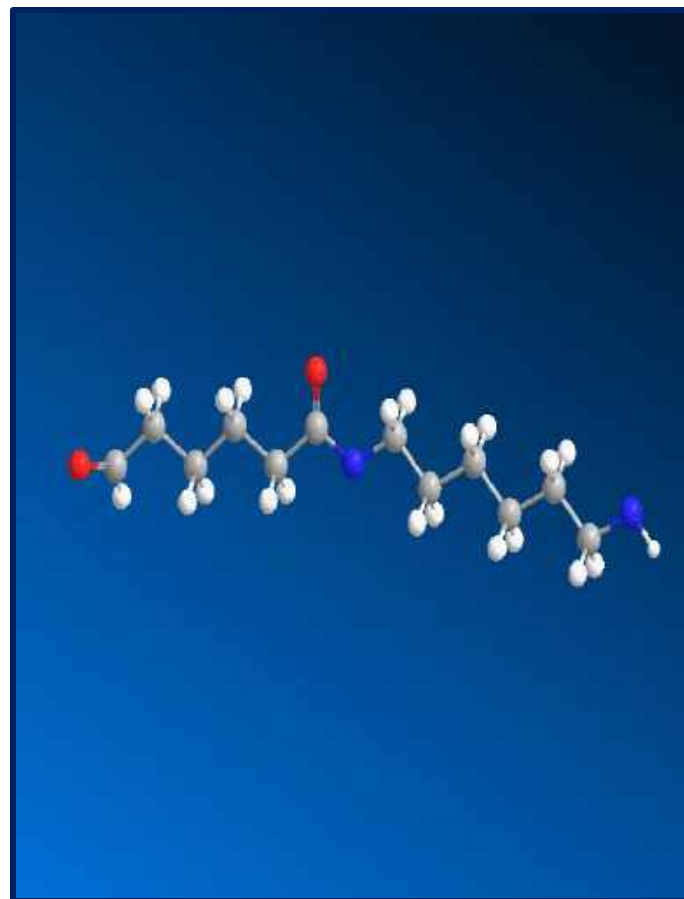
## LECTURE - 34

- **Basic definitions**
- **Characteristics of polymers**
- **Weight average molecular weight**
- **Number average molecular weight**
- **Classification of polymers**



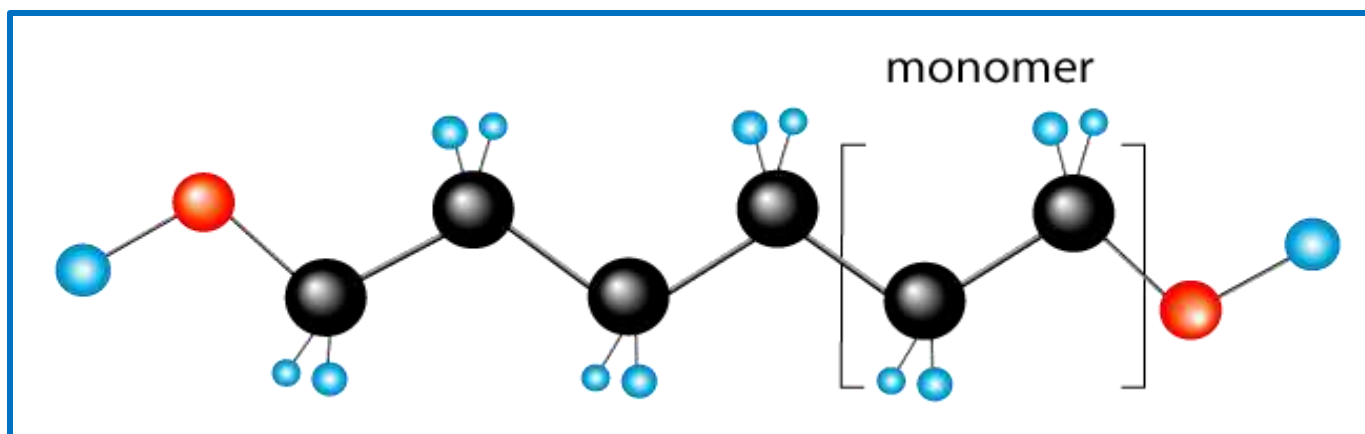
## POLYMER

The word '*polymer*' is coined from two Greek words poly and merose ***poly means many and merose means unit or part.*** The term polymer is defined as macro molecules formed by combination of large number of repeating units. These are also called *macromolecules*.

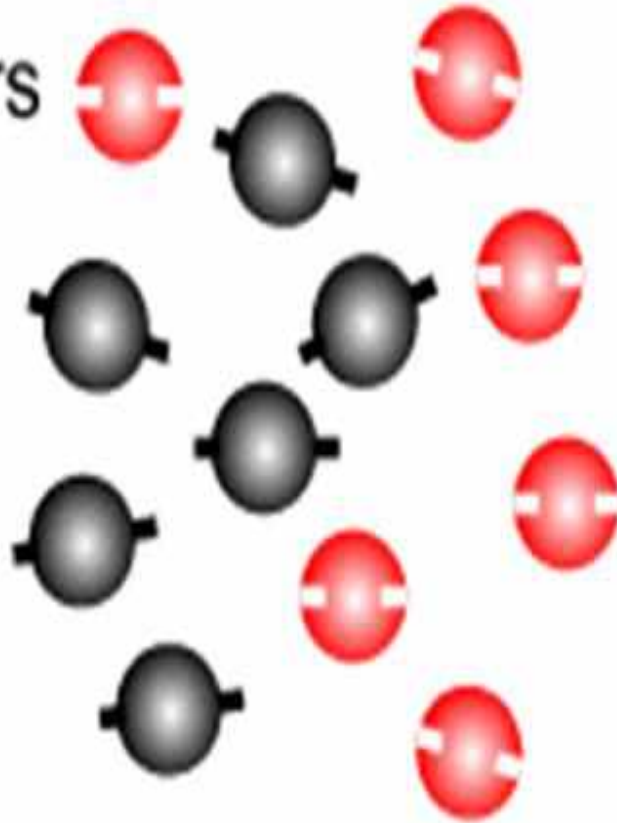


## MONOMER

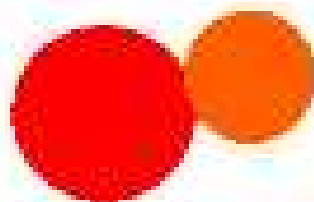
The basic repeating structural units of polymers which are linked to each other by covalent bonds are known as *monomers*. Ex- *Ethene* is the monomer of Polythene, *Vinyl chloride* is the monomer of PVC.



Monomers

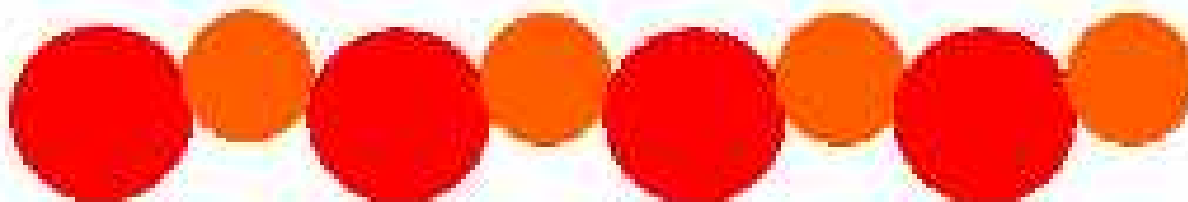


## Monomer

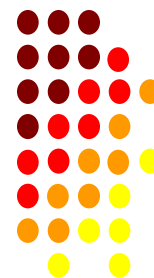


A monomer is a single molecule.

## Polymer

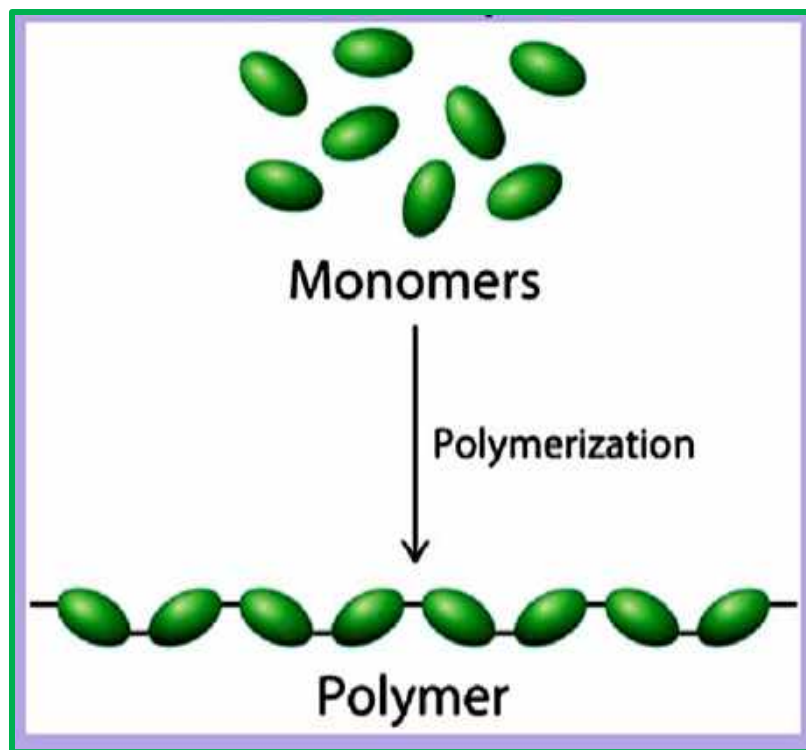


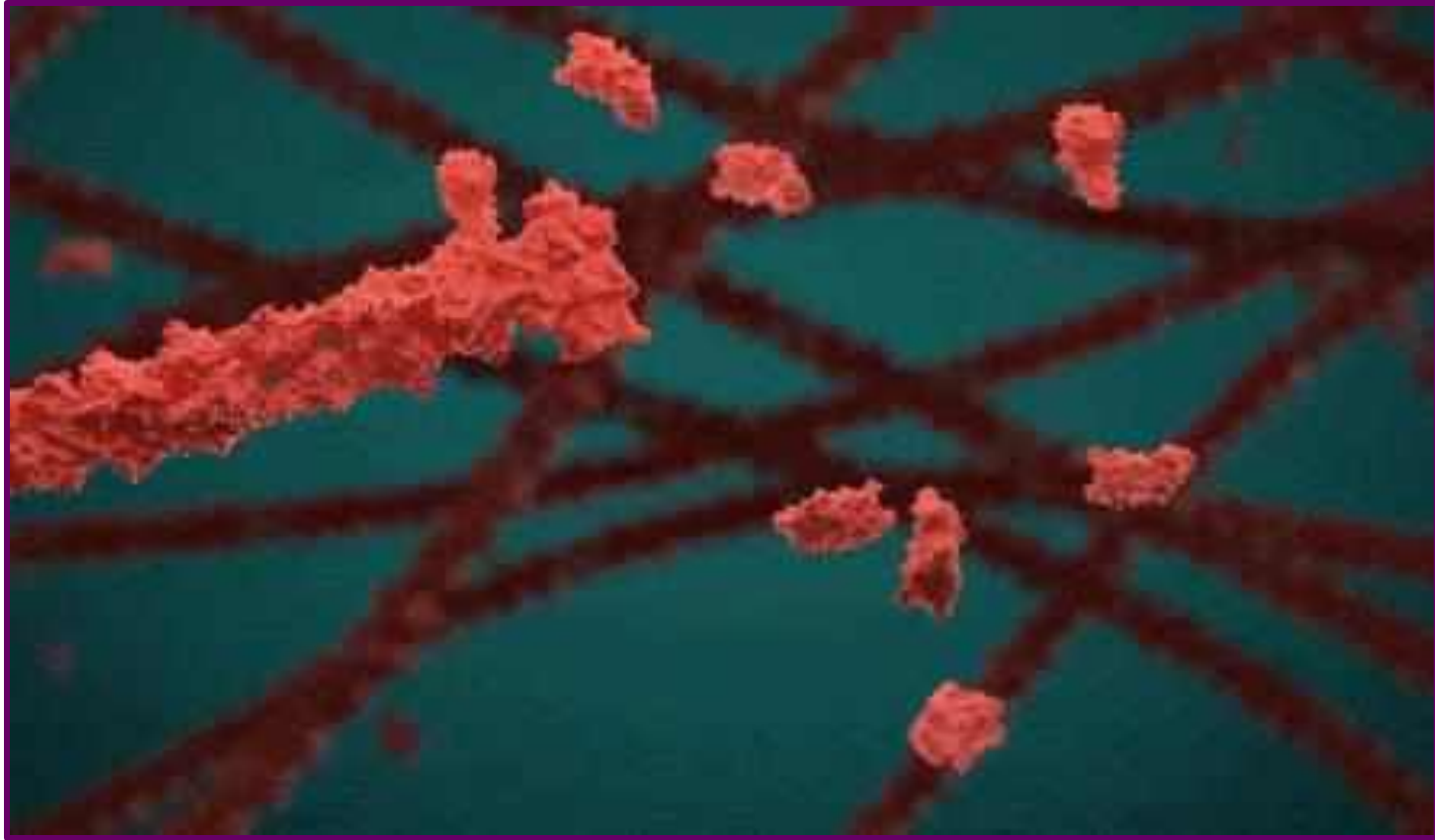
A polymer is a chain of monomers.



# POLYMERIZATION

The process of formation of polymers from respective monomers under specific conditions is called *polymerization*.





# POLYMERIZATION



## DEGREE OF POLYMERISATION (DOP)

The number of monomeric units that combine together in total to form the polymer is known as its ***degree of polymerization***. It is generally represented as 'n'.

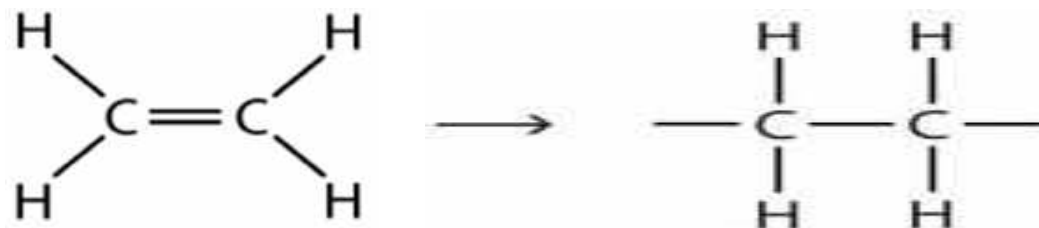


In above case the degree of polymerization (DP) = n, as 'n' monomers (ethene) have joined to form the polymer (polythene).



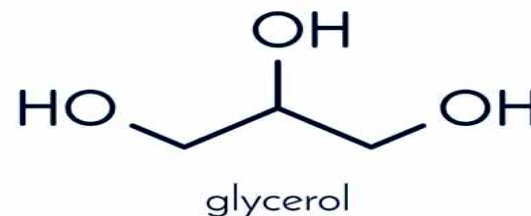
## FUNCTIONALITY

- The functionality of a monomer is the number of binding sites that are available in that monomer.
- ***A molecule can act as a monomer only if it is at-least bifunctional in nature.*** For example, the functionality of ethene is 2, since it can form two new bonds on breaking the existing pi bond.

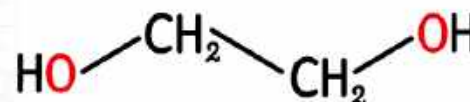


# SIGNIFICANCE OF FUNCTIONALITY

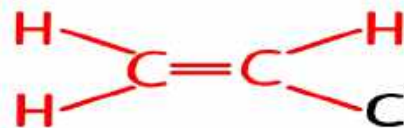
- If,  $f = 2$ , a linear chain polymer is formed. E.G. ethene, ethylene glycol, hexamethylene diamine, adipic acid
- If,  $f > 2$ , branched or cross linked polymers are formed. E.g..... glycerol



Ethylene glycol



Vinyl chloride



## EXAMPLE SHOWING FUNCTIONALITY

Compound	Chemical Formula	No. of Double bonds per molecule	Number of functional gps. present per molecule		Functionality
			-OH	-COOH	
Ethylene Glycol	$C_2H_6O_2$	Nil	2	Nil	Bifunctional
Vinyl Chloride	$C_2H_3Cl$	1	Nil	Nil	Bifunctional
Glycerol	$C_3H_7O_3$	Nil	3	Nil	Trifunctional



## CHARACTERISTICS OF POLYMERS

- All the polymers are macromolecules, but all the macromolecules are not polymers.
- Polymers are semi crystalline material.
- Low tensile strength , easy processibility.
- Low density, high mould ability.
- High resistance to degradation.
- Generally insulators, few are conductors.
- Have average molecular weight.



- Polydisperse in nature.
- Properties of polymers depend on their molecular weight, type of bonds between various chains.
- Primary bonds (backbone) in polymers are covalent bonds whereas the secondary bonds (between chains) can be Vander Waals forces, dipole-dipole interaction or hydrogen bonds.

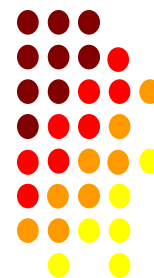


## CONDITIONS FOR POLYMERISATION

There are certain conditions that need to be fulfilled for a polymerization process to occur. Different polymers require different set of conditions which are :

- Particular temperature and pressure.
- Presence of a particular catalyst.
- May or may not require an initiator.

***\*A catalyst alters the rate of reaction where as an initiator is required to start the reaction.***



## Why do polymers have average molecular weight?

- Polymers are ***polydisperse*** in nature that means polymers are not composed of identical molecules.
- When polymerization starts, a number of polymer chains start growing but all of them do not start at the same moment or stop their growth at the same time. Hence ***polymer molecules differ in the number of monomer units joined to have different molecular weights.***



- Therefore the ***polymer molecules in a sample are of same chemical type but of different DP, size and molecular weight.***
- In polymers all the chains have different molecular weight. For example, HDPE is made up of various long carbon chains, but the lengths of the chains may vary by thousands of monomer units. Because of this, polymer molecular weights are usually given as averages.



## MOLECULAR WEIGHT DETERMINATION

There are two ways to calculate the average molecular weight of polymers:

- *Number Average Molecular Weight ( $\bar{M}_n$ )*
- *Weight Average Molecular Weight ( $\bar{M}_w$ )*



## NUMBER AVERAGE MOL. WT.

Number average molecular weight is determined by using the total molecular weight of molecules and total number of molecules.

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

- $M_i$  = molecular weight of molecule.
- $n_i$  = number of molecules.
- $M_n$  = number average molecular weight.



# WEIGHT AVERAGE MOLECULAR WEIGHT

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

- $M_w$  = weight average molecular weight.
- $M_i$  = molecular weight of the molecule.
- $n_i$  = number of monomer molecules.



## POLYDISPERSITY INDEX (PDI)

The dispersity index, or formerly *polydispersity* index (*PDI*), or *heterogeneity index*, or simply *dispersity* ( $\mathcal{D}$ ), is a measure of the distribution of molecular mass in a given polymer sample.

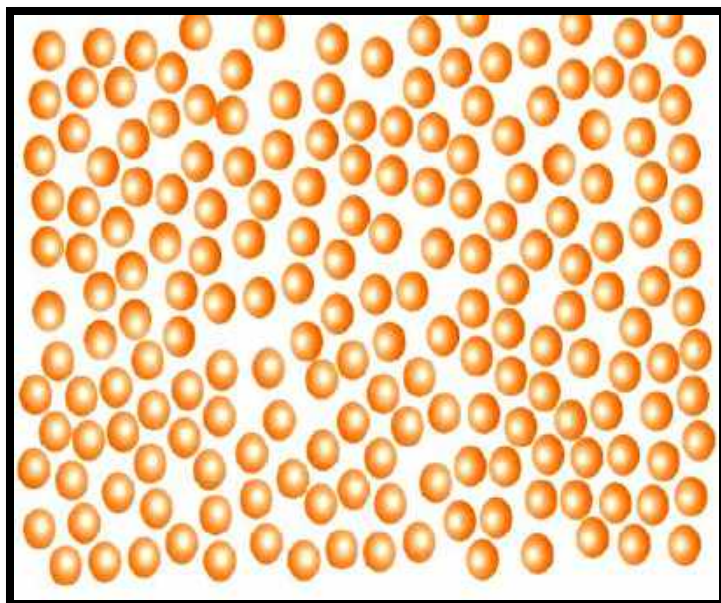
$$PDI = M_w / M_n$$

where,  $M_w$  = weight average molecular weight  
 $M_n$  = number average molecular weight



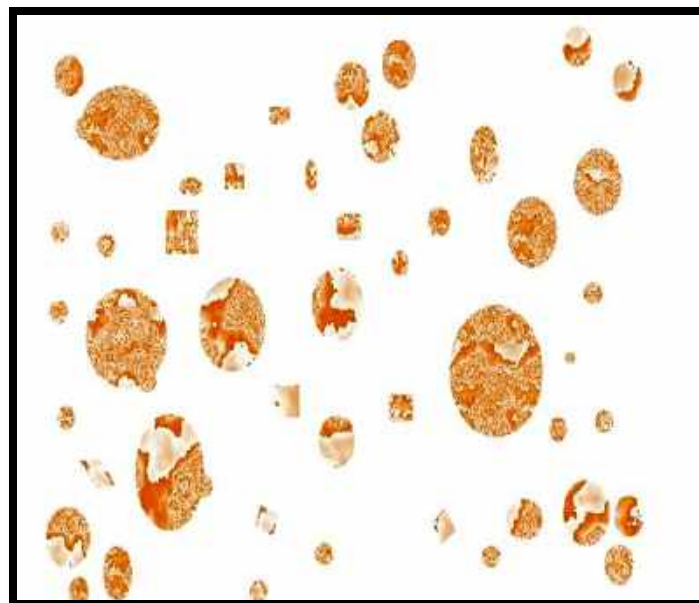
- $M_w$  can only be larger or equal to  $M_n$ , so PDI is always equal to or greater than 1.
- The numerical value of PDI ranges from 0.0 (for a perfectly uniform sample with respect to the particle size) to 1.0 (for a highly polydisperse sample with multiple particle size populations).
- A ***PDI = 1 indicates polymer chain to be mono disperse.*** But, normally it is difficult to synthesize polymer chains of identical  $M_w$  or  $M_n$ . Therefore, ***all polymers will have PDI > 1.***
- The dispersity indicates the distribution of individual molecular masses in a batch of polymers.





**Distribution of components in a monodispersed polymer material**

$$\text{PDI} = 1$$



**Distribution of components in a polydispersed polymer material**

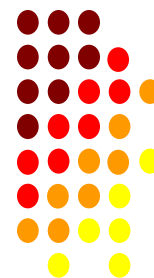
$$\text{PDI} > 1$$



**Q1. In a particular sample of a polymer, 100 molecules have molecular mass  $10^3$  each, 200 molecules have a molecular mass of  $10^4$  each and 200 molecules have molecular mass  $10^5$  each. Calculate the number average and mass average molecular mass.**

**Sol. *Number average molecular mass***

$$\begin{aligned}\overline{M}_n &= \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3} \\ &= \frac{100 \times 10^3 + 200 \times 10^4 + 200 \times 10^5}{100 + 200 + 200} \\ &= 44,200\end{aligned}$$



## Weight average mol. Wt.

$$\begin{aligned} \bar{M}_w &= \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} \\ &= \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2}{N_1 M_1 + N_2 M_2 + N_3 M_3} \\ &= \frac{100 \times (10^3)^2 + 200 \times (10^4)^2 + 200 \times (10^5)^2}{100 \times 10^3 + 200 \times 10^4 + 200 \times 10^5} \\ &= 91,407.23 \end{aligned}$$



**Q2. In a polymer, there are 100 molecules of molecular weight 100, 200 molecules of molecular weight 1000 and 300 molecules of molecular weight 10,000. Find out the number average and weight average molecular weight and polydispersity index.**

**Sol. Number average mol. Wt.**

$$\begin{aligned}
 \overline{M}_n &= \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3} \\
 &= \frac{100 \times 100 + 200 \times 1000 + 300 \times 10,000}{100 + 200 + 300} \\
 &= \frac{10000 + 200000 + 3000000}{600} \\
 &= 3210000 / 600 = 5350
 \end{aligned}$$



## Weight average mol. Wt.

$$\bar{M}_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2}{N_1 M_1 + N_2 M_2 + N_3 M_3}$$

$$= \frac{100 \times 100 \times 100 + 200 \times 1000 \times 1000 + 300 \times 10,000 \times 10,000}{100 \times 100 + 200 \times 1000 + 300 \times 10,000}$$

$$= \frac{3.0201 \times 10^{10}}{3210000} = 9408.4$$

## Poly dispersity index

$$PDI = \bar{M}_w / \bar{M}_n = 9408.4 / 5350 = 1.757$$



# CLASSIFICATION OF POLYMERS

1. By Origin

2. By Monomer

3. By action of heat

4. By Mode Of Polymerization

5. By Structure

6. By Tacticity

7. By Application & Physical Properties



## 1. By origin/occurrence

Polymers can be divided into natural, semi synthetic and synthetic polymers on the basis of their origin.

- **Natural polymers**

Polymers which are isolated from natural materials, are called as '*natural polymers*'. E.g. Cotton, silk, wool, rubber, natural rubber.

- **Synthetic polymers**

Polymers synthesized in laboratories from low molecular wt. compounds, are called as, '*synthetic polymers*'. E. g. polyethylene, nylon, terylene.



## Examples of Natural and Synthetic Polymers

Natural polymers are made by living organisms.

Synthetic polymers are made by chemical reactions in a lab.



DNA



Rubber



Nylon



Polyester



Cellulose



Wool



Teflon



Epoxy

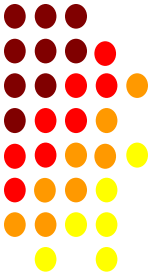


▪ **Semi synthetic polymers**

- Semi synthetic polymers are those which are prepared by making some chemical changes in the *natural products*.
- *They can be obtained by simple chemical treatment of natural polymers to improve their physical properties like lustrous nature and tensile strength.*
- Like Rayon is prepared from the wood pulp and some man made products. *Rayon is the first semi synthetic polymer in the world.*
- Cellulose derivatives as cellulose acetate and cellulose nitrate, etc. are the usual examples of this sub category.



# SEMI-SYNTHETIC POLYMERS

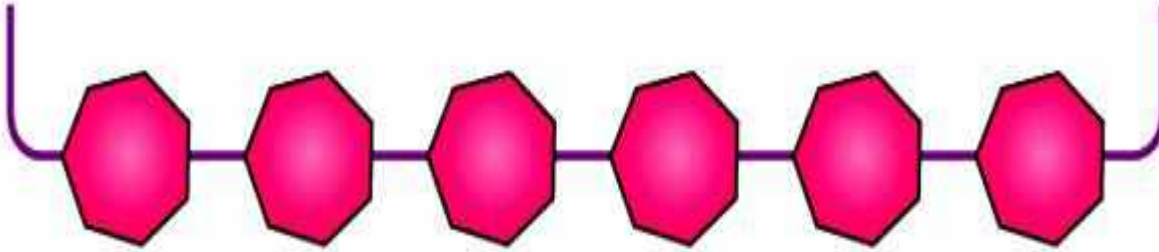


## 2. On the basis of monomers

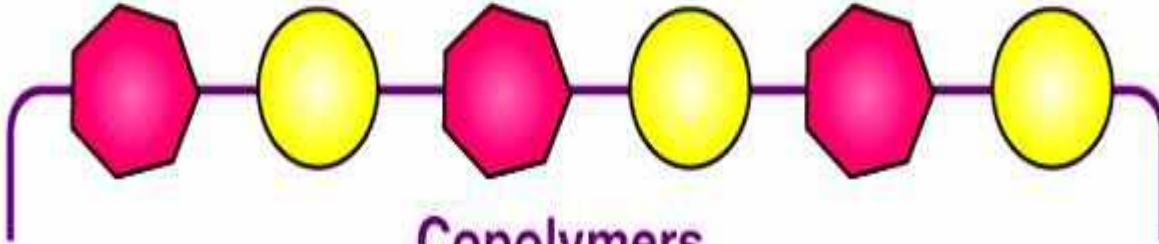
Polymers can be classified as homo-polymers and co-polymers on the basis of monomers.

<b>HOMOPOLYMERS</b>	<b>COPOLYMERS</b>
Polymers made up of same monomer units.	Polymers made up of two or more than two different monomer units.
They have fixed properties.	The desirable properties of a homopolymer can be infused into the copolymer.
Example: Polythene (Ethene), PVC (vinyl chloride)	Example: Buna-S (Butadiene + styrene), Nylon-6,6.(Hexamethylene diamine + adipic acid)





Homopolymers



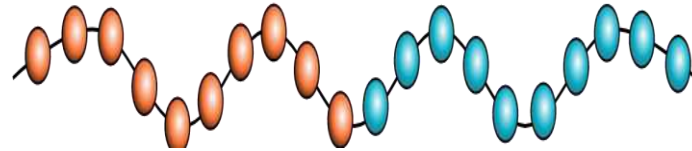
Copolymers





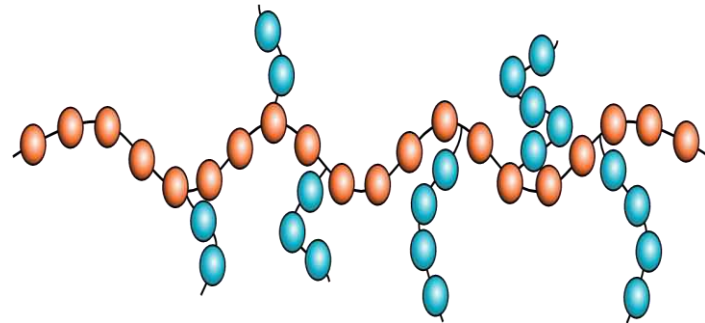
### **c) Block copolymers**

In this block of one type of monomer is followed by the block of other type of monomer. Example: SBS rubber.



### **d) Graft copolymers**

One type of monomer segment is grafted on the backbone chain of another type of monomer segment. Example: High impact poly styrene.



# An overview of homopolymers and copolymers

## Homopolymer



## COPOLYMERS

### Alternating



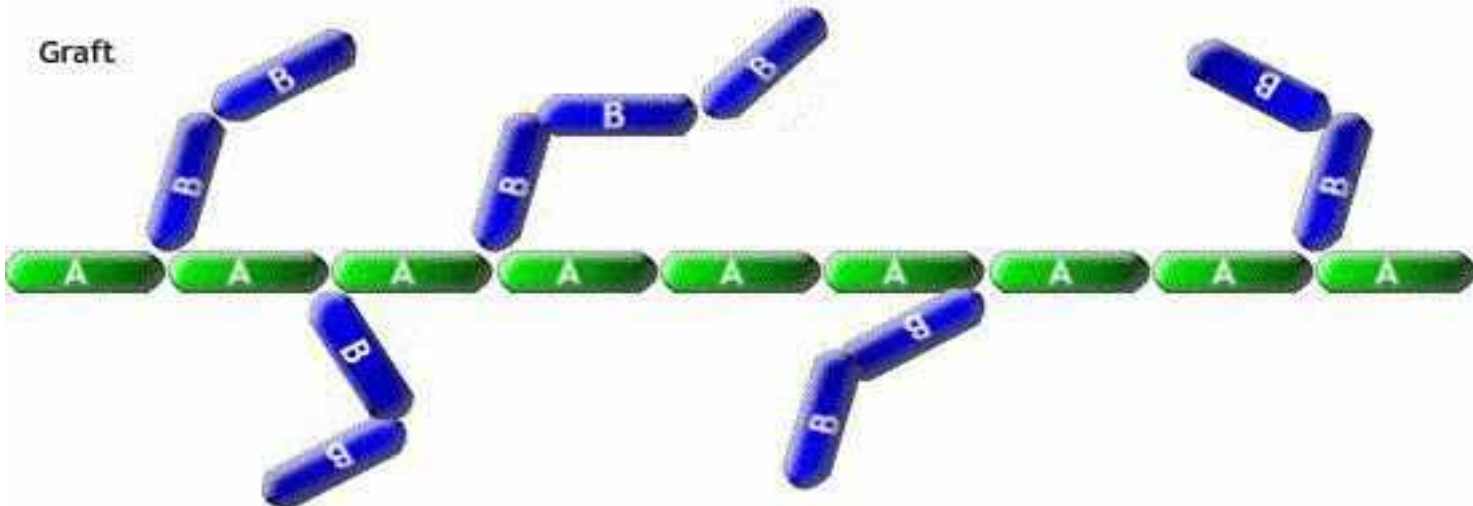
### Block



### Random



### Graft



### **3. On mode of polymerisation**

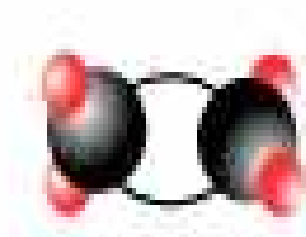
Polymers can be classified on the basis of mode of polymerization into two sub groups.

#### **a) Addition polymers**

- The addition polymers are formed by the repeated addition of unsaturated monomer molecules (possessing double or triple bonds). E.g.: the formation of polythene from ethene and polypropene from propene.
- However, the addition polymers formed by the polymerization of a single monomeric species are known as homo polymers, e.g., polythene.



## HOW ADDITION OCCURS?

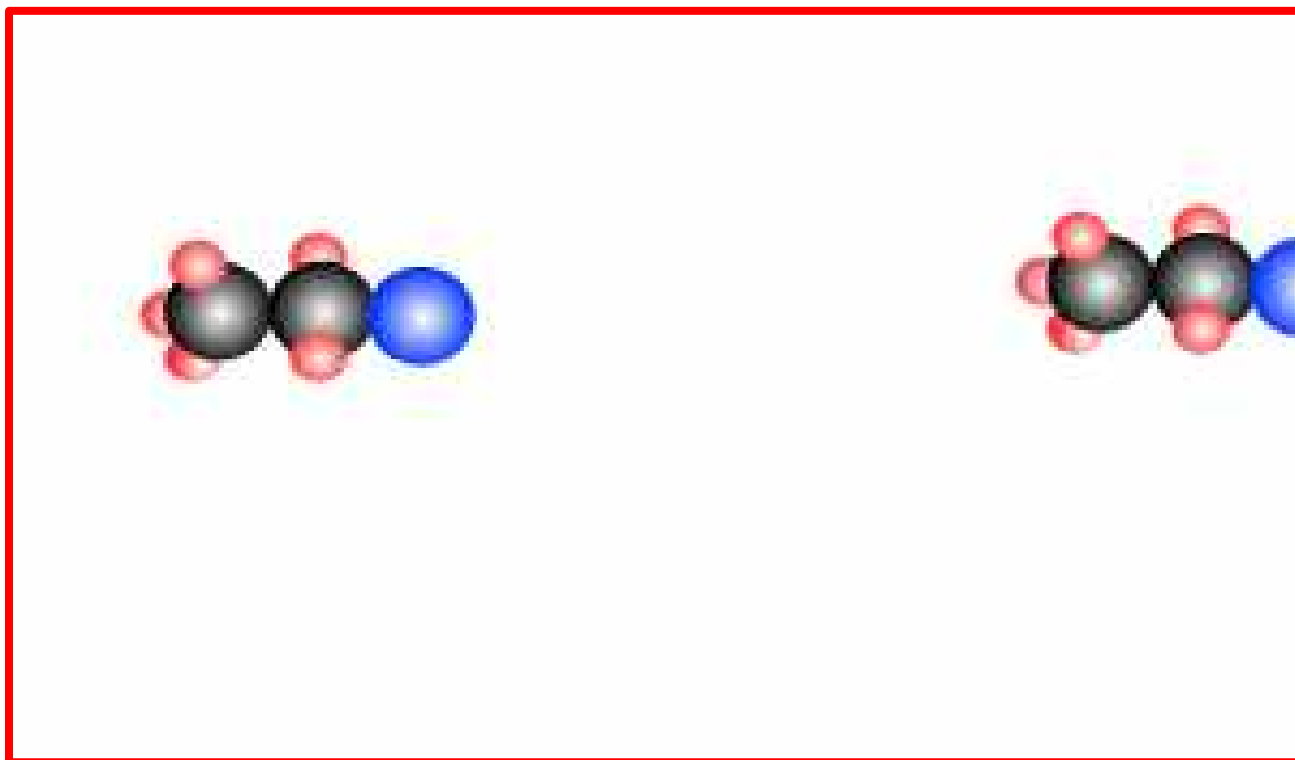


## **b) Condensation polymers**

- The condensation polymers are formed by repeated condensation reactions *between two different or same bi-functional or tri-functional monomeric units*.
- In these polymerization reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place.
- *The examples are terylene (dacron), nylon-6,6, nylon-6 etc.*



## HOW ACTUALLY CONDENSATION HAPPENS



## Necessary condition for condensation polymerisation

- Presence of at-least *two reactive functional groups* in the monomers.
- Condensation of monomers with the *elimination of small molecules* like water,  $\text{CO}_2$ ,  $\text{NH}_3$ .
- These reactions continue in *step wise* manner.

**Example: *Preparation of Nylon-6,6.***



## Differences between condensation and addition polymerisation

<b>Condensation polymerisation</b>	<b>Additional polymerisation</b>
Also known as step growth polymerisation	Also known as chain growth polymerization
It takes place in monomers having reactive functional groups	It takes place in monomers having multiple bonds.
It takes place with elimination of simple molecule like, H <sub>2</sub> O, NH <sub>3</sub> , HCl etc.	No elimination of simple molecule.
Repeat units of monomers are different	Repeat units of monomers are same.
The molecular mass of polymer increases throughout the reaction	There is very little change in the molecular mass throughout the reaction
Product obtained may be thermosetting/thermoplastic	Product obtained are thermoplastic
E.g:- Bakelite, polyester ,polyamides etc.	E. g :-Polyethylene, PVC, poly styrene.



## 4. On the basis of action of heat

On basis of action of heat polymers are classified into thermoplastic and thermosetting polymers.

Such polymer that soften on heating and stiffen on cooling are termed as '**thermoplastic**' polymers. **Ex. Polyethylene, PVC, nylon, sealing wax.**

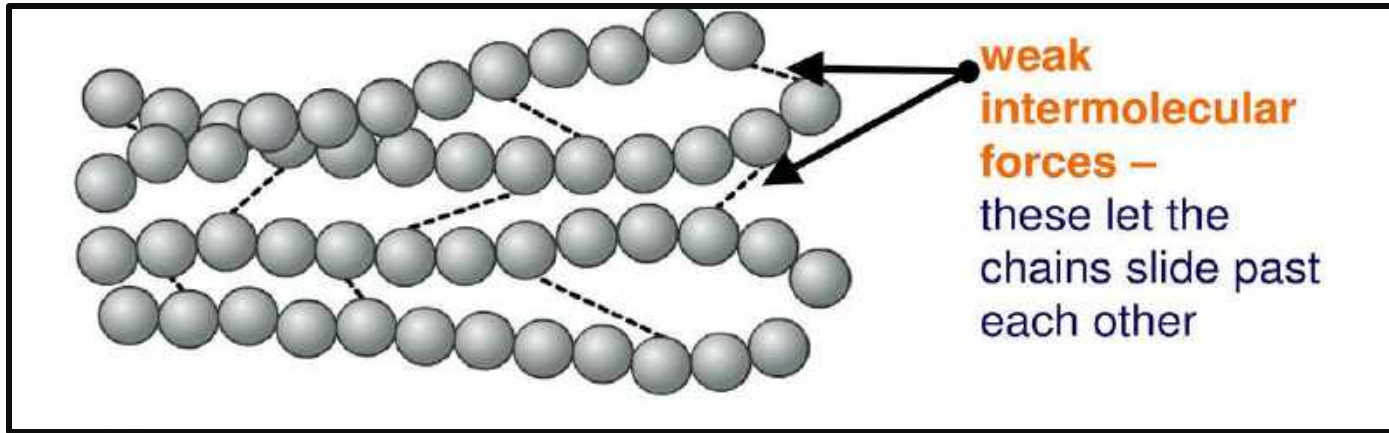
Polymer that becomes an infusible and insoluble mass on heating are called '**thermosetting**' polymers. **Ex. Bakelite, epoxy etc.**



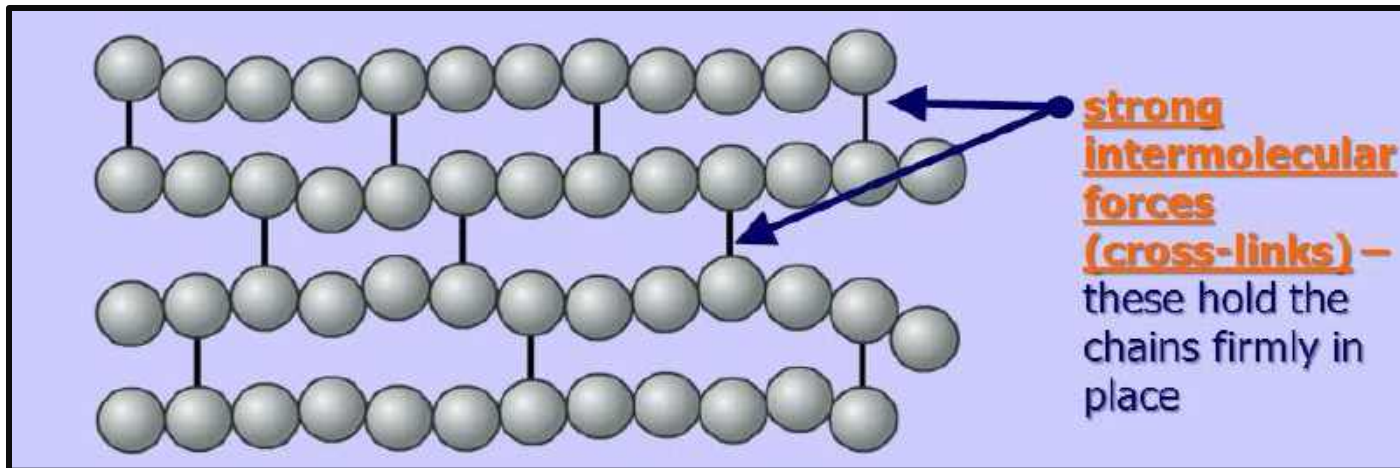
## Differences between Thermoplastic and thermosetting polymers

<b>Thermoplastic Polymers</b>	<b>Thermosetting Polymers</b>
These are produced by additional polymerization	These are produced by condensation polymerization.
The resins are made of long chains attached by weak Vander Waal's force of attraction	The resins have three dimensional network structure connected bonds.
On heating they soften and on cooling become stiff chemical nature won't change	On heating they become stiff & hard. No change on cooling. Chemical nature changes.
They can be remoulded	They cannot be remoulded
Scrap can be used	Scrap cannot be used
The resins are soft, weak and less brittle	The resins are usually hard, strong tough & more brittle
These are easily soluble in organic solvents E.g.:- PVC	Resins are not soluble in organic solvents E.g.:- Bakelite
Contain long chain polymer with no cross linkage.	They have 3D network structure.



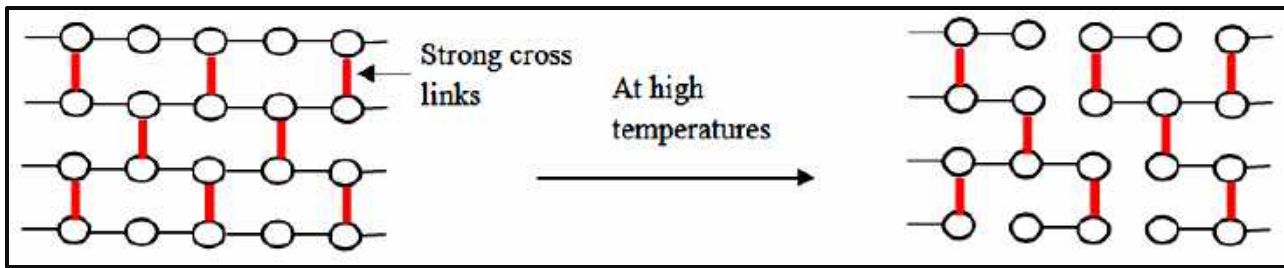
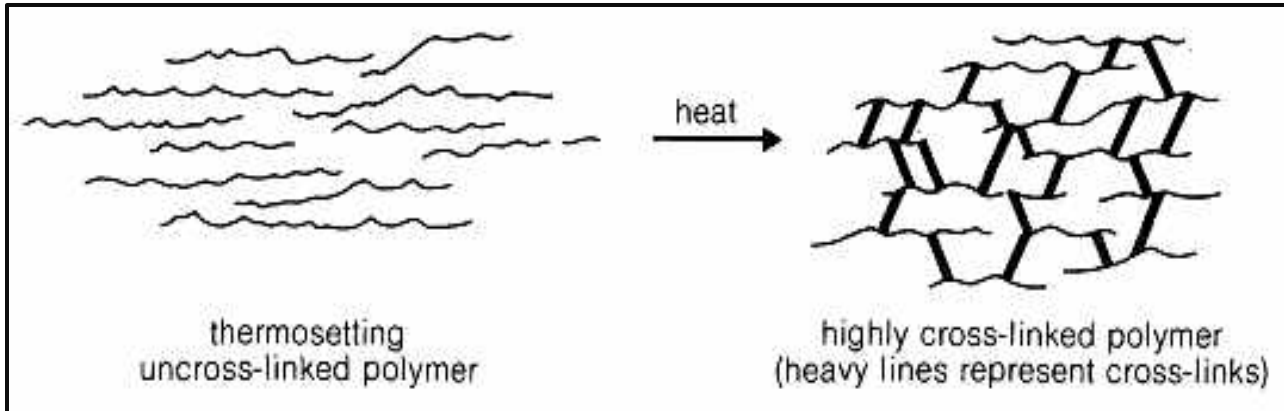
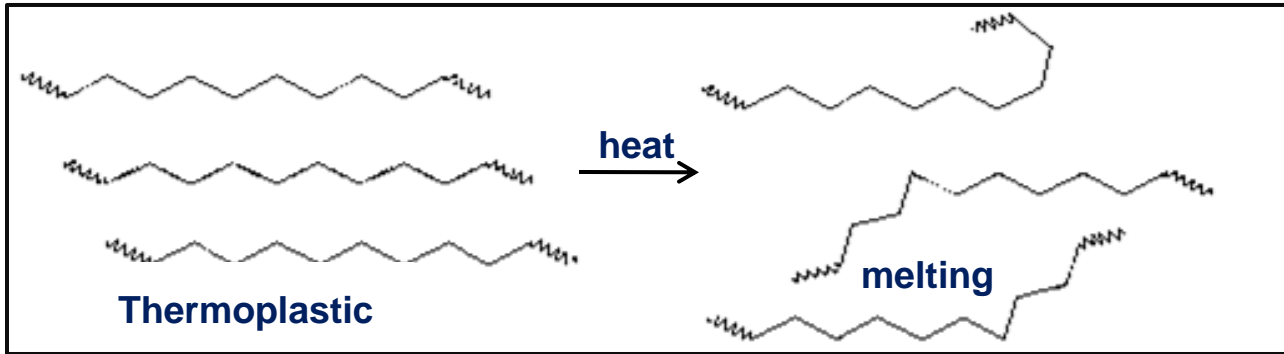


## Thermoplastic polymers



## Thermosetting polymers





**Thermosetting plastic**

**Thermal degradation**



## 5. Classification based on structure

Based on the structure the polymers are classified into linear, branched and cross linked polymers.

- **Linear polymers**

These polymers consist of long and straight chains.

The examples are high density polythene, polyvinyl chloride, etc.

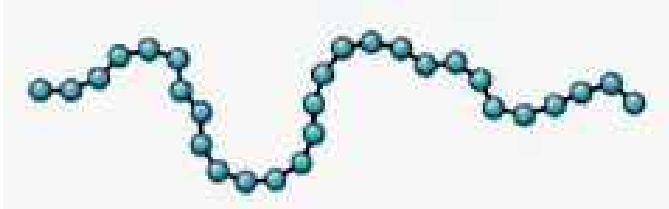
- **Branched polymers**

These polymers contain linear chains having some branches, e.g., low density polythene (LDPE)

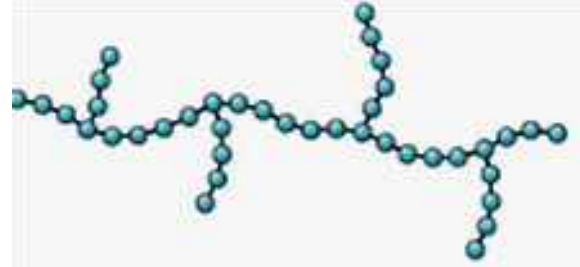


- **Cross linked or network polymers**
  - These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains.
  - These can be loosely cross linked as in elastomers or can be tightly cross linked as in thermosets.
  - These are hard, rigid and brittle due to their network structure. e.g. Bakelite, melamine, etc.

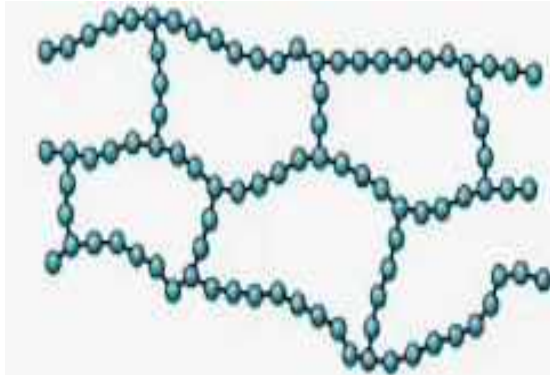




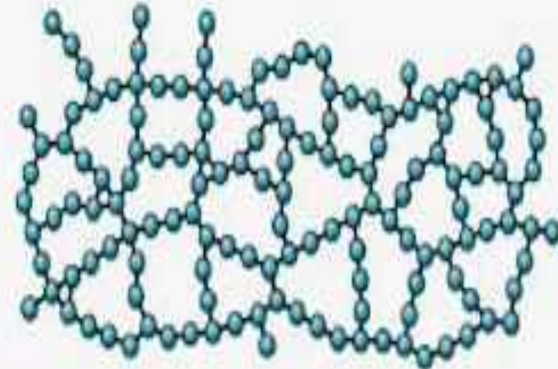
**Linear Polymer**



**Branched Polymer**



**Loosely cross  
linked polymer**



**Tightly cross  
linked polymer**



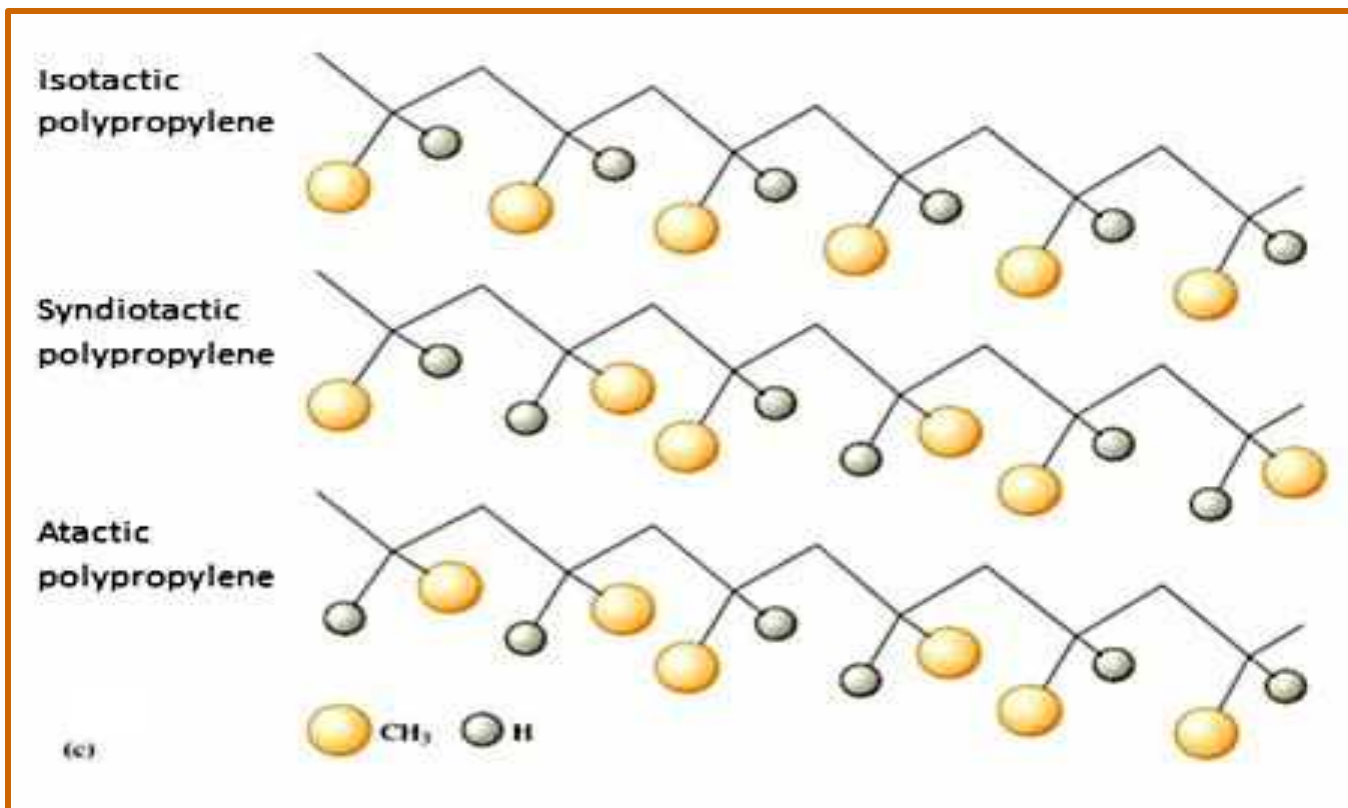
## **6. On the basis of tacticity**

Tacticity is defined as orientation or arrangement of side chains / groups on both the sides of main polymeric chain. On the basis of tacticity there are three types of polymers:

- **Isotactic:** In isotactic polymers functional groups are arranged on the same side (single side) of the main polymeric chain (cis arrangement). Ex: Natural rubber (poly-cis-isoprene).
- **Syndiotactic:** In isotactic polymers functional groups arranged in the alternate fashion on both the sides of the main carbon polymeric backbone. Example: Gutta Purcha (poly-trans-isoprene).



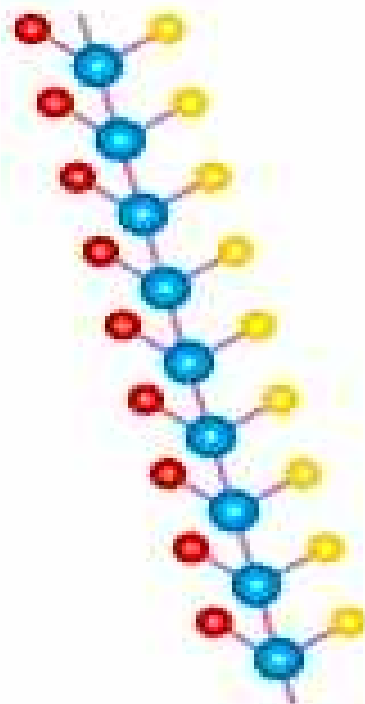
- **A-tactic:** Functional groups arranged in a random manner around the main carbon skeleton. Ex: Poly vinyl chloride.



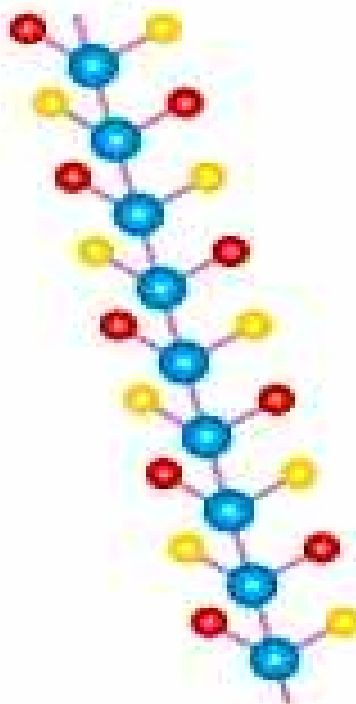
## Tacticity in polypropylene



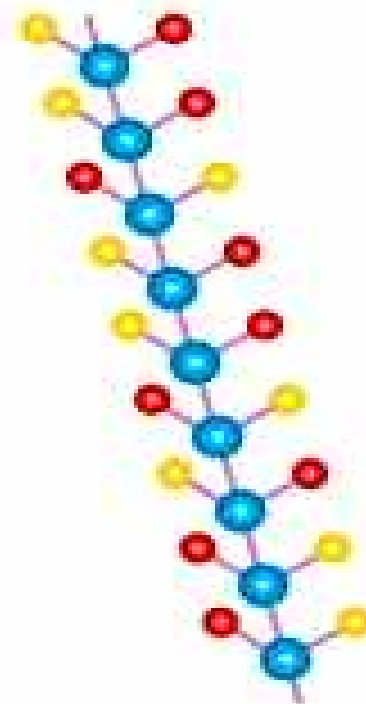
## Tacticity Structures



Isotactic



Syndiotactic



Atactic



Carbon atom



Hydrogen atom



Substituent groups



## **7. Application & physical properties**

On the basis of applications and physical properties polymers are classified as:

### **a) Plastics**

- Plastics are the organic materials of high molecular weight, which can be moulded into any desired form when subjected to heat and pressure in the presence of a catalyst.
- All thermoplastic polymers are called plastics.
- They do not have cross linking between chains.
- Ex- polypropylene (used for fibers and bottles), polystyrene (used to make Styrofoam cups)



# Plastics



## **b) Rubbers (Elastomers)**

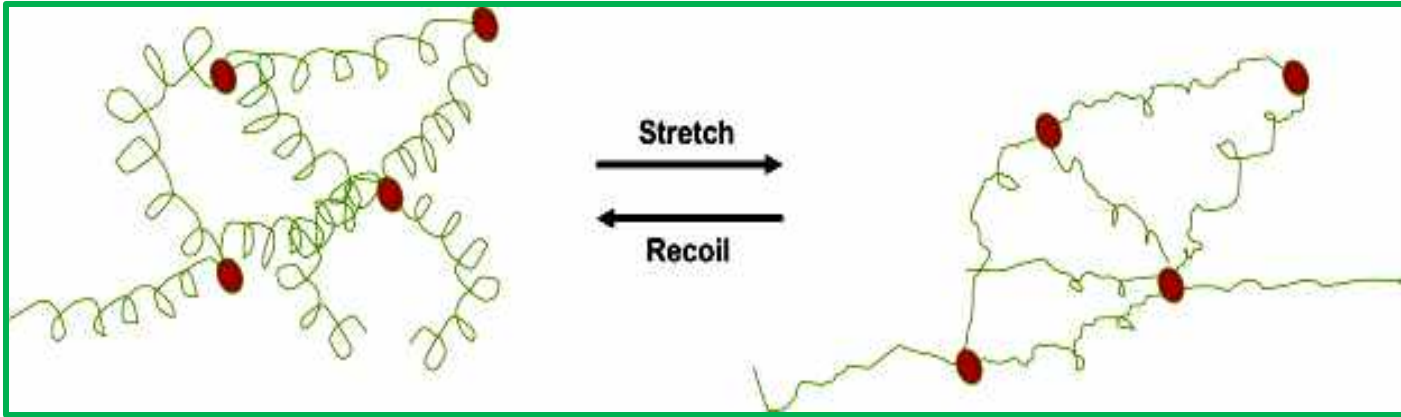
- A polymer that has the ability to regain its original shape after being deformed is known as rubber or elastomer.
- In elastomers, polymer chains are held together by the weakest intermolecular forces.
- They are amorphous polymers with high degree of elasticity.
- These polymers consist of randomly coiled molecular chains having few cross links.
- Ex: Buna-S, Buna-N, neoprene etc.



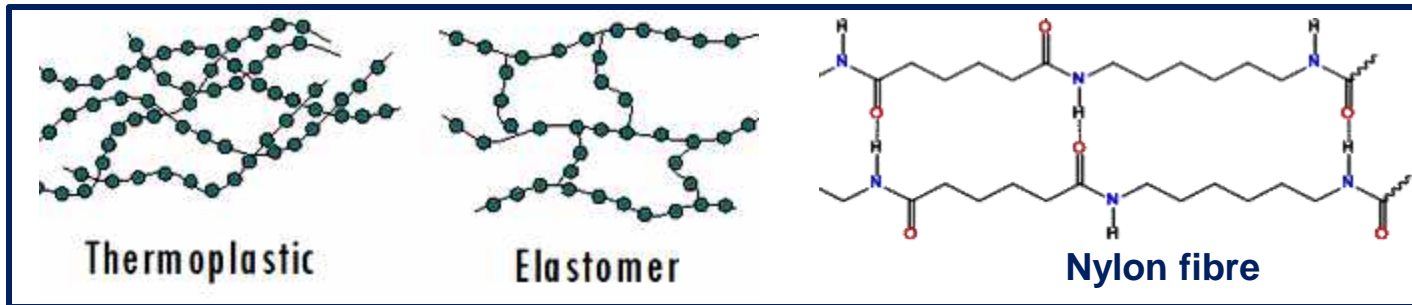
## **C) Fibres**

- Fibers are long filament like material whose length is at least 100 times its diameter.
- They have high tensile strength.
- They have comparatively strong intermolecular forces like hydrogen bonding.
- They are strongest of the three different type of polymers i.e. rubbers, plastics and fibres.
- Ex: polyamides (all the nylons like nylon-6,6, nylon-6, ), polyesters (Terylene), etc.





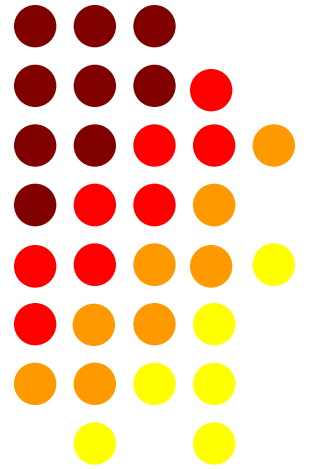
## Elastomer





## LECTURE - 35

# PREPARATION, PROPERTIES AND USES OF SOME INDUSTRIALLY IMPORTANT POLYMERS

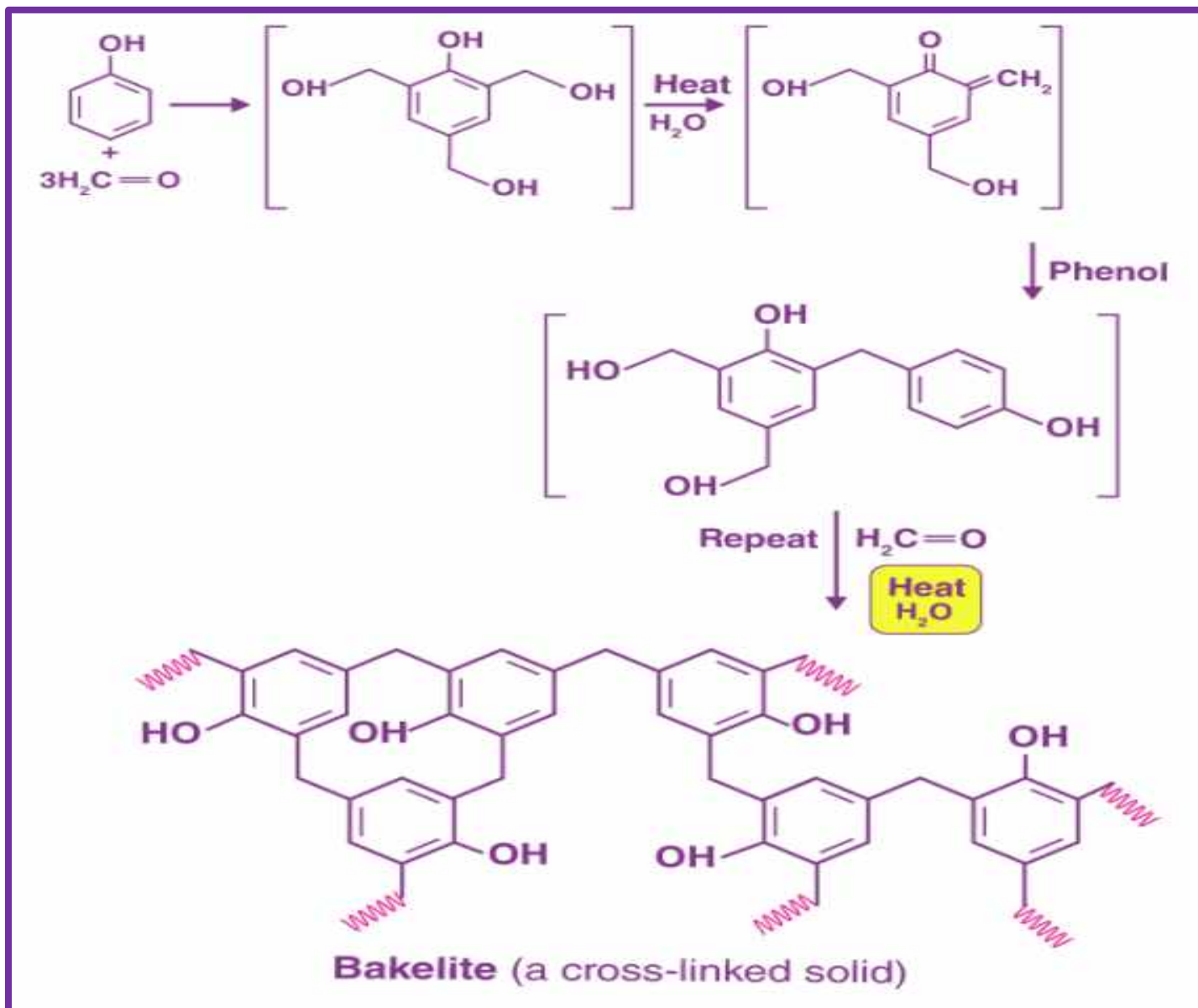


## Bakelite (Phenol- Formaldehyde Resin )

- It is a ***thermosetting polymer*** and was the first plastic made from synthetic components.
- It is prepared by condensing ***phenol*** with ***formaldehyde*** (monomers) in presence of acidic/alkaline catalyst.
- The initial reaction results in the formation of o- and p- hydroxyl methyl phenol which reacts to form linear polymer, ***novolac***.
- During moulding hexamethylene tetramine is added, which converts to insoluble solid of cross-linked structure Bakelite.







## Properties

- It can be molded very quickly, decreasing production time.
- Resistant to non oxidizing acid, salts and organic solvents.
- Resistant to electricity.
- Heat resistant.
- Scratch resistant.
- Water resistant.
- Have lustre (shine).



## Applications

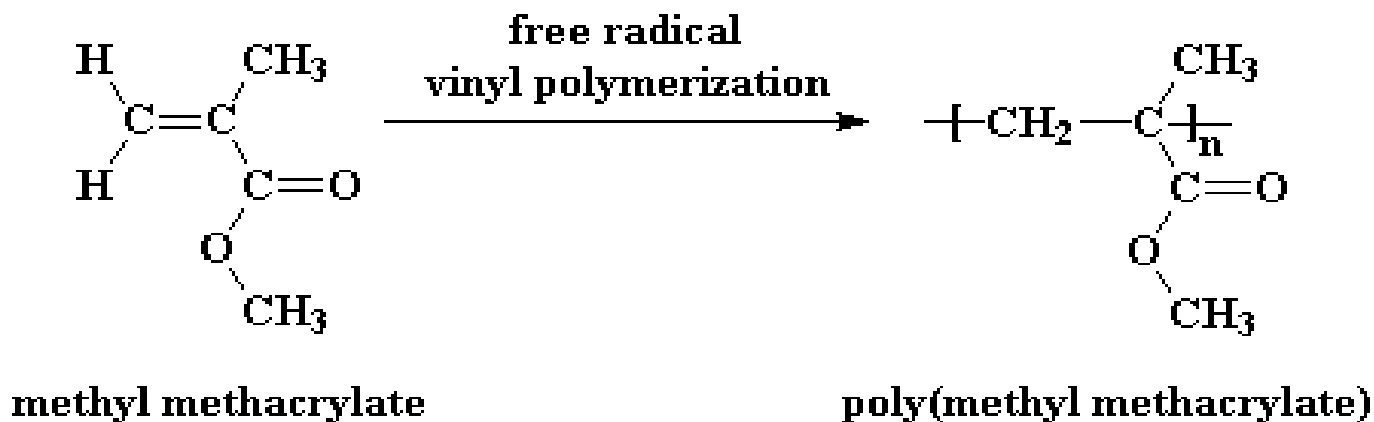
- It is used for making electric insulator parts like switches.
- For making moulded articles like telephone parts, cabinet of radio and television.
- As adhesives.
- In paints and varnishes.
- For making bearings.
- For impregnating fabrics, wood and paper.



# Poly methyl methacrylate (PMMA) or Plexi Glass

## Preparation:

**Methyl methacrylate** (monomer) on polymerization in presence of a peroxide initiator gives poly methyl methacrylate (PMMA)



## Properties

- Plexi glass (PMMA) is a white transparent thermoplastic.
- It has an excellent optical clarity, which is not affected by sunlight or age.
- It is resistant to most of the chemicals but soluble in most of the organic solvents.
- It has poor scratch resistance.



## *Applications*

- Smart phone screens, Car windows
- Sanitary ware (bathtubs), LCD screens
- Used in medical and dental applications
- Used in lenses of exterior lights of automobiles.
- Used in Shatter resistant panels for building windows.
- Used for constructing residential and commercial aquariums.



# Articles made of PMMA

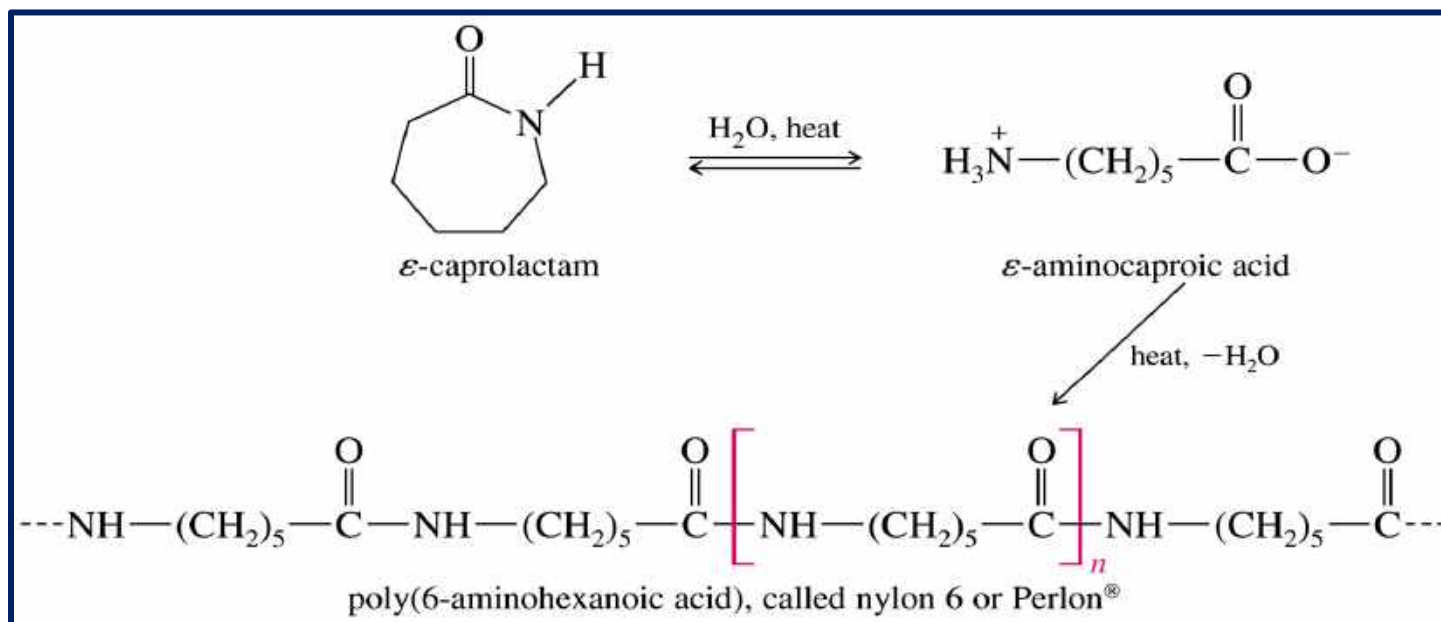


# 1. FIBRES

## a) Nylon-6:

Condensation polymer, Homopolymer, polyamide.

**Preparation:** Nylon-6 can be prepared by ring opening polymerization of **Caprolactam (monomer)**.



## Properties

- Tough
- High tensile strength
- Elastic in nature
- Have lustre (shine).



## Applications

- Gears, fittings, and bearings
- Automotive industry.
- As thread in bristles for toothbrushes, surgical sutures.
- As strings in guitars, sitars, violins etc.
- Making threads, ropes, filaments, nets, and tyre cords

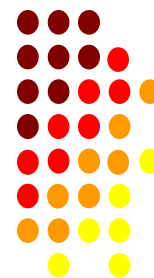
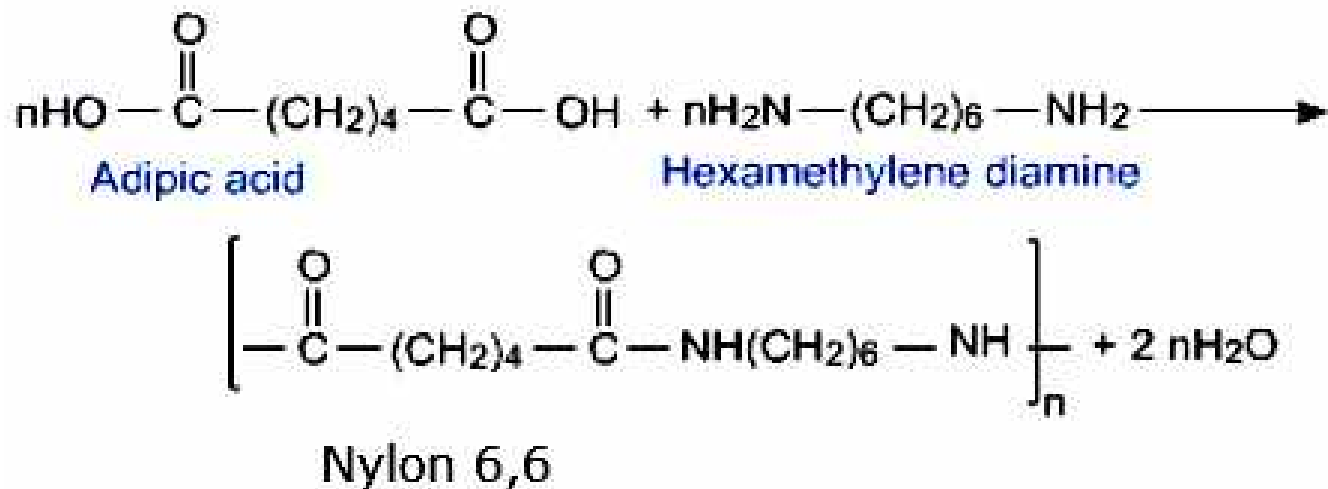


## b) Nylon-6,6

*Condensation polymer, Copolymer, polyamide.*

### Preparation:

It can be prepared by poly-condensation of **Adipic acid** and **Hexamethylene diamine** (monomers).



## Properties

- Light weight
- water resistant
- High melting point.



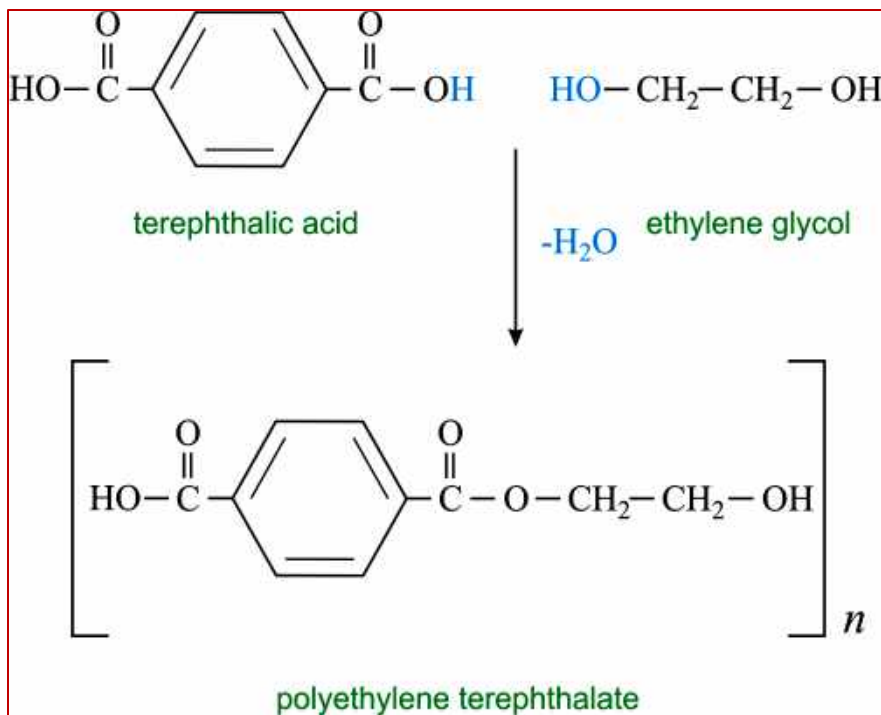
## Applications

- Used to make swim-wears, sleeping bags.
- Used to make machine parts, seat belts.
- Used to make airbags, socks, carpets, ropes etc.
- Used in parachutes.



## c) Dacron or Polyester (or) Terylene (or) Polyethylene Phthalate

Dacron or terylene is a polyester and copolymer. It is prepared by Condensation polymerisation.



### Preparation:

Terylene is made from **ethylene glycol** and **terephthalic acid (monomers)**.



## Properties

- Crease resistant
- Weightless.
- It is highly resistant to mineral & organic acids.
- Water resistant.
- It has high melting point.

## Applications

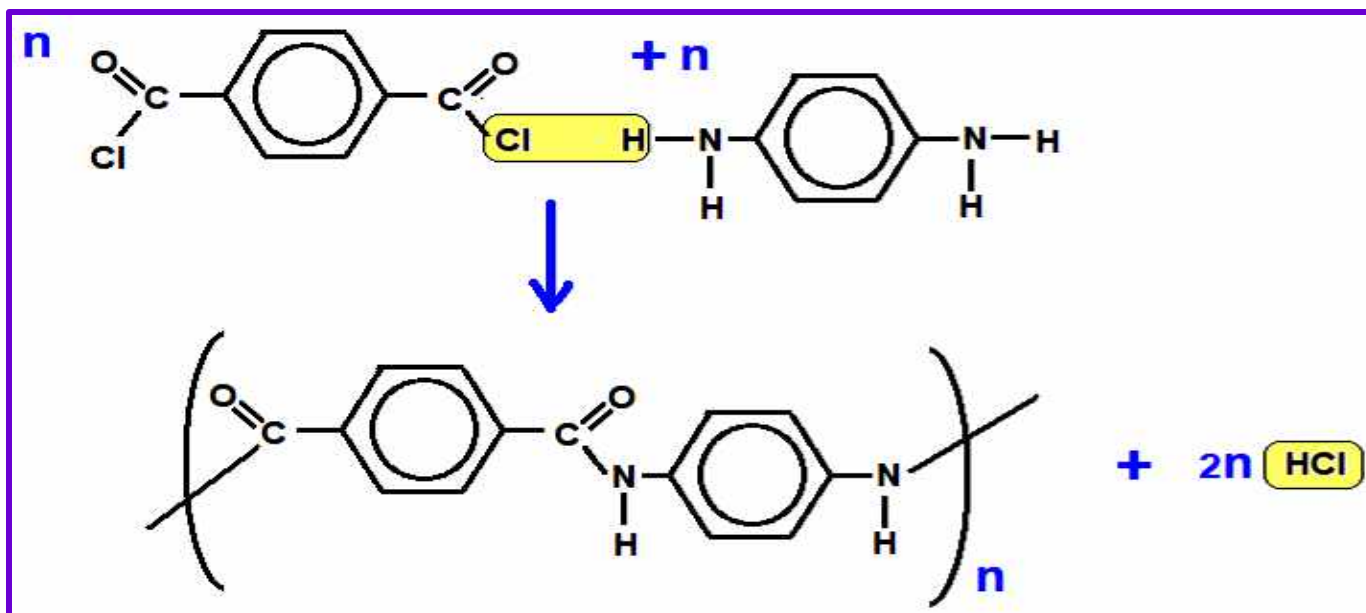
- Ropes
- Nets
- Thread
- Raincoats
- Fleece jackets, Quilts
- Clothing
- Medical textiles



## d) KEVLAR

### Preparation

It is a polyamide, prepared by the condensation polymerization of *para-phenylenediamine* and *terephthaloyl chloride* (monomers).



## Properties

- Kevlar is a very strong material – about five times stronger than steel.
- Possess high tensile strength
- Low weight
- High chemical inertness.
- High cut resistant
- Fracture resistance
- Flame resistance.



## *Applications*

- Component of personal armor such as combat helmets, ballistic face masks and ballistic vests.
- Inner lining for bicycle tyres to prevent punctures.
- Heat- or flame-resistant fabrics
- Bulletproof clothing
- Used for motorcycle safety clothing.



# Applications of kevlar

BULLET / STAB  
PROOF VESTS



DIVING GLOVES



WALKING BOOTS



MILITARY HELMET



CUT RESISTANT  
GLOVES



BICYCLE TYRES



CAR TYRES



FIRE PROOF  
CLOTHING



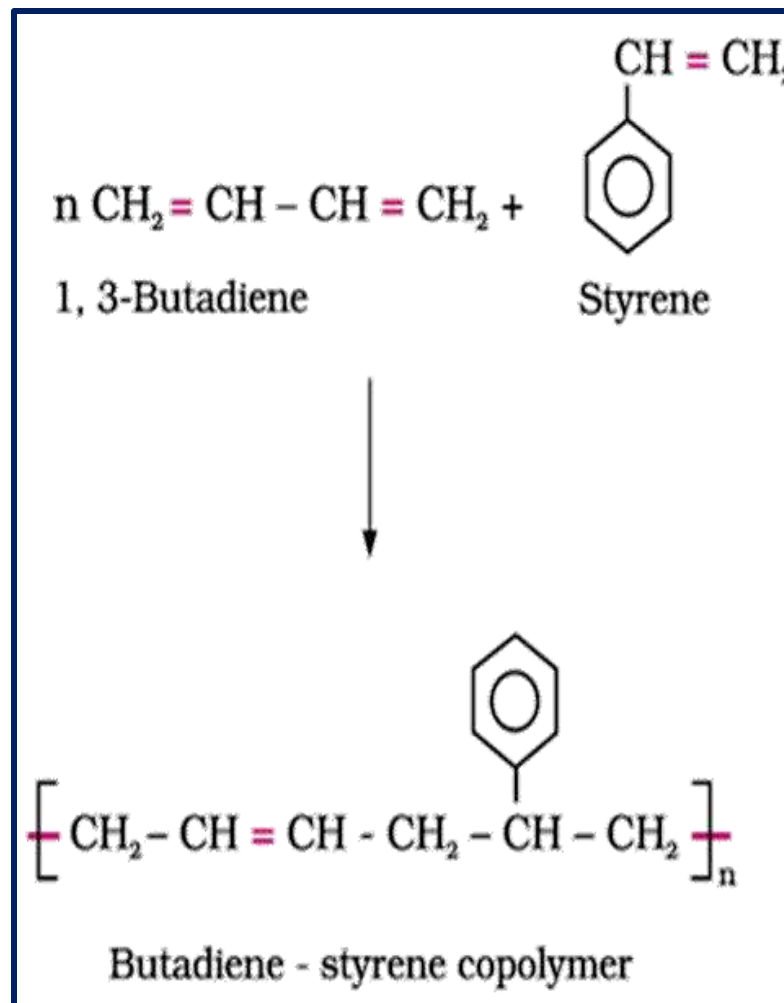
## 2. Rubber

Rubber is an elastomer that is, a polymer that has the ability to regain its original shape after being deformed.

### a) Buna-S or SBR: (Elastomer)

Addition, copolymer of **1,3-Butadiene** (75% by weight) & **styrene** (25% by weight).

#### Preparation:



## Properties

- High abrasion resistance.
- High load bearing capacity.
- Swells in oils and solvents.



## Applications

- Used in shoe heels and soles.
- Used in chewing gum.
- Used in making motor cycle and scooter tyre, cycle tyres and tubes.
- Electrical insulation.

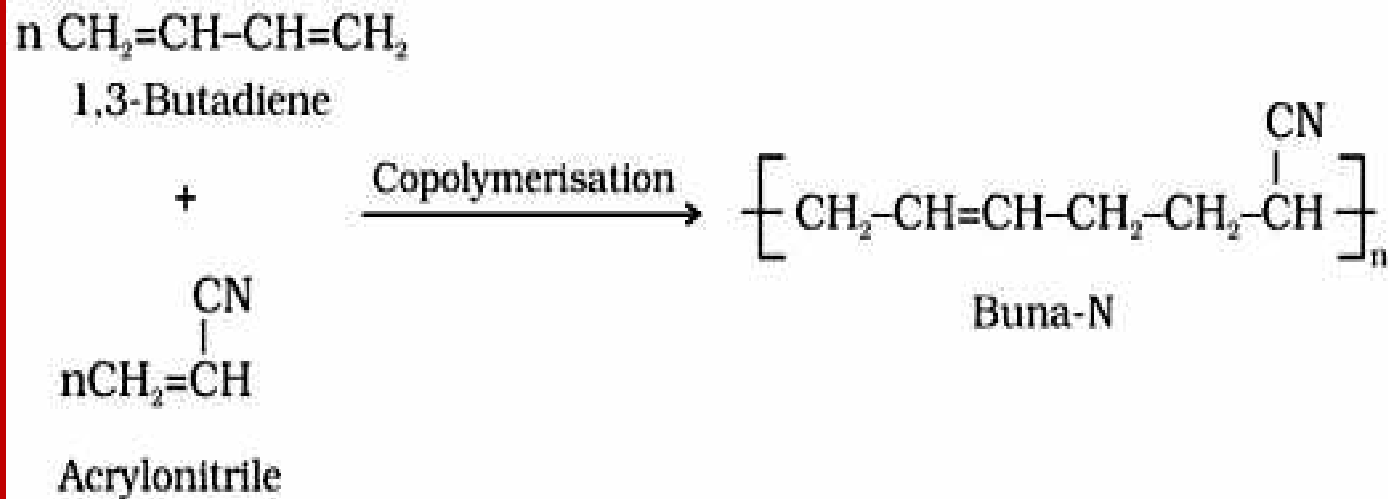


## **b) NBR or Buna-N or nitrile rubber:**

Elastomer, addition polymer

### **Preparation:**

Copolymer of Butadiene (about 75% by weight) and acrylonitrile (25% by weight).



## Properties

- Highly polar
- Oil resistant.

## Applications

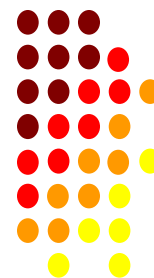
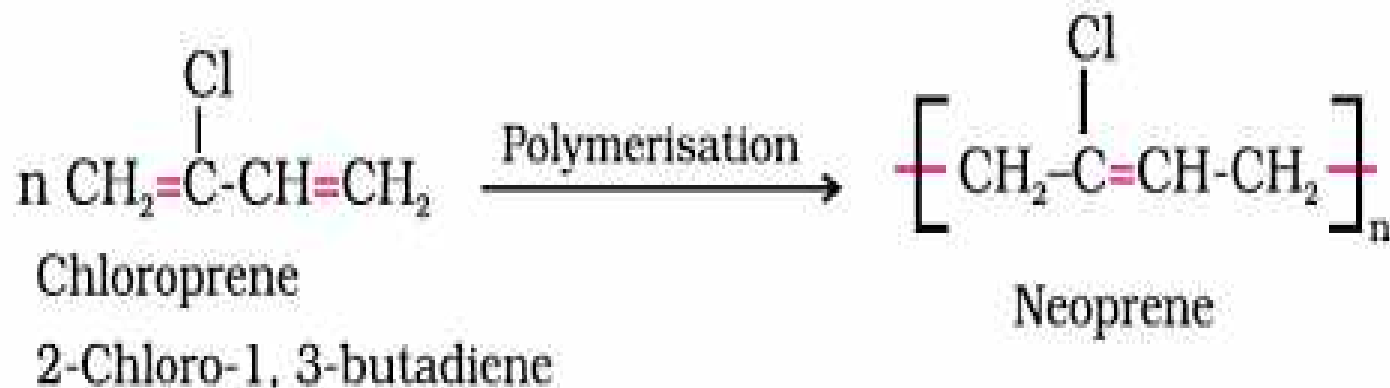
- Conveyor belts.
- Hoses, seals and gaskets.
- Protective gloves in nuclear industry and tank lining.
- Adhesives



## c) Neoprene

Elastomer, Homopolymer made by addition polymerisation.

**Preparation:** made by polymerisation of *chloroprene* (*monomer*).



## Properties

- Inert to chemicals.
- Fire resistant.
- Corrosion resistant.
- Water resistant.



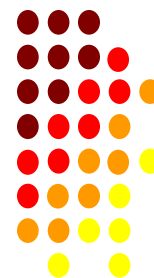
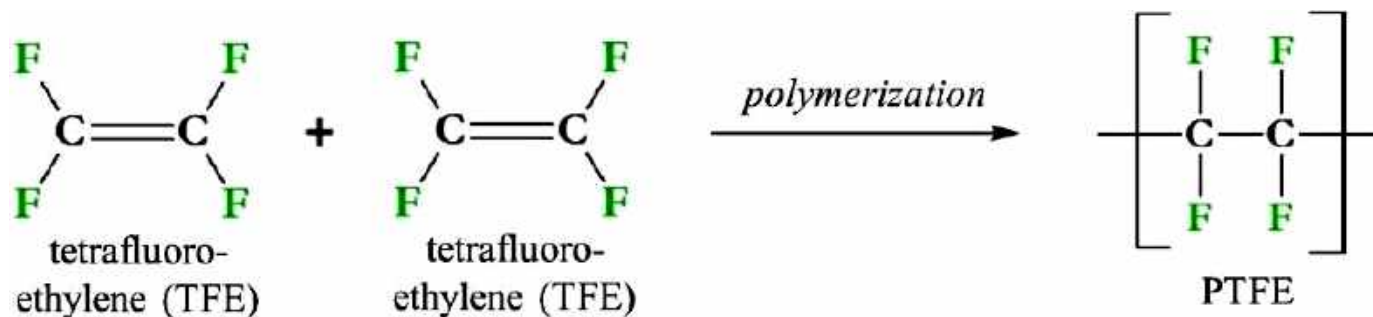
## Applications

- Making gloves and coated fabrics.
- Used in power transformers.
- Used in wet-suits and diving-suits
- Neoprene is also used for Halloween masks.
- Lining of reaction vessels.



## d) TEFLON

- Teflon is obtained by polymerization of ***tetra fluoroethylene (monomer)***, under pressure in presence of benzoyl peroxide as catalyst.
- The compact interlocking of highly electronegative fluorine atoms alongside stronger and stable C-F bonds are the reasons for high heat stability (melting point of 327°C) of PTFE.



## Properties

- Chemical-resistance towards all chemicals
- High density and high heat resistance.

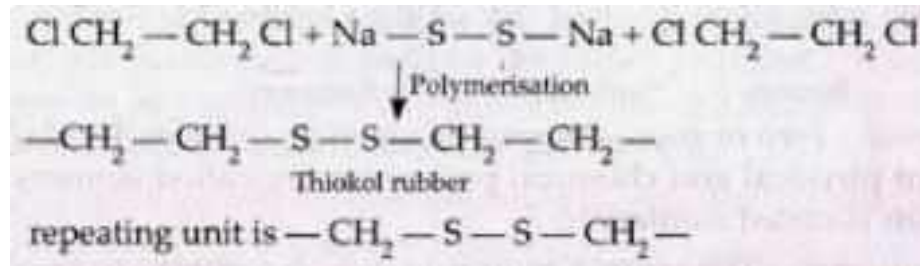
## Applications

- Insulating material for motors.
- For making gaskets, packing material.
- For coating and impregnating glass fibers, non stick coating of pans etc.



# Thiokol

Thiokol also known as polythioethers. It is made by polymerising ethylene chloride and sodium polysulphide.



## Properties:

1. Thiokol elastomer exhibit low moisture and gas permeability.
2. It is good flex crack resistance.
3. It shows outstanding low temperature flexibility as well as good resistance to oil, ozone, oxygen and many chemicals including ethers, ketones and aromatic hydrocarbons.



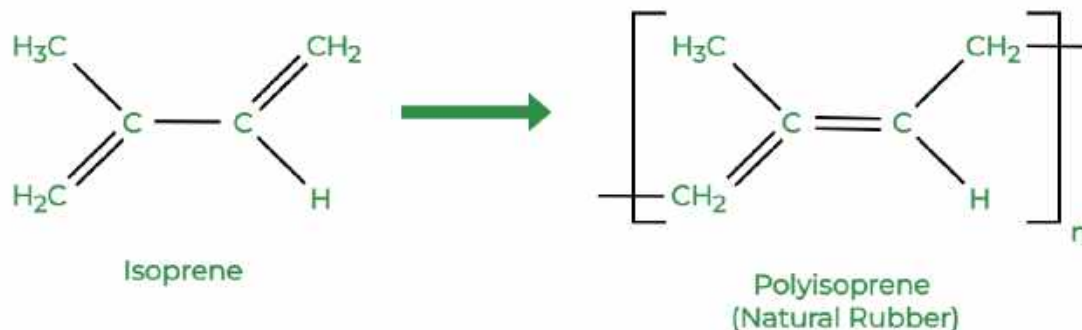
## **Applications:**

1. Thiokol polymers are used as an elastomer in seals and sealants
2. Thiokol mixed with oxidizing agents can be used as a fuel in rocket engines.



## Polyisoprene

- Natural rubber is polyisoprene in which monomer units are of isoprene i.e 2-methyl-1,3 butadiene.



### Uses:-

It is used in medical devices, surgical gloves, aircraft and car tires, pacifiers, clothes, toys,

### Disadvantages:-

The disadvantages of natural rubbers are quite less resistant to attack by organic acid.

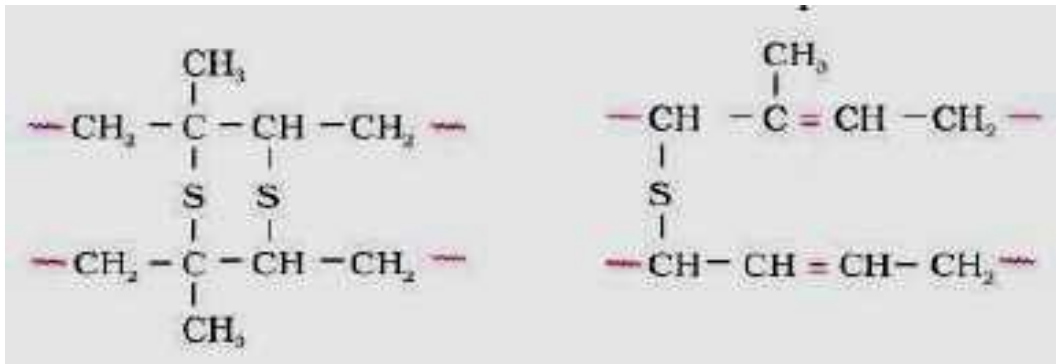
It has little durability.

When stretched to a greater extent, it suffers permanent deformation.



## Vulcanization of rubber:

Vulcanization is a chemical process that involves treating rubber with sulfur or other cross-linking agents to improve its mechanical properties and durability.



The cross-links introduced during vulcanization provide rubber with several important benefits:

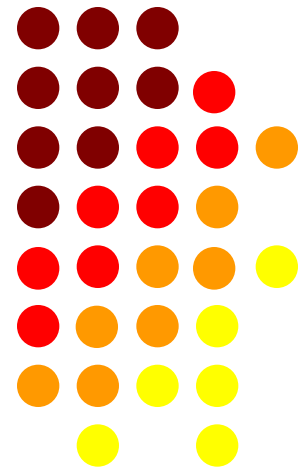
1. Increased strength and durability
2. Improved elasticity and flexibility
3. Improved resistance to heat and chemicals.
4. Reduced tackiness





## LECTURE - 36

- Conducting polymers
- Biodegradable polymers

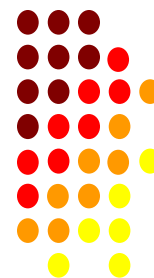


## Conducting Polymers

- Polymers that conduct electricity are known as conducting polymers.
- These polymers show conductivity due to extensive conjugation in their backbone.

### Conditions for a polymer to be conducting

- The polymer chain should contain conjugation (alternate sigma and pi bonds) through out its chain. So that there are resonating and mobile electrons for conduction.
- Polymer should have high planarity in its structure.
- Presence of aromatic rings in the chain with continuous resonance.
- Polymer chain should be linear.



# Classification of conducting polymers

## **CONDUCTING POLYMERS**

**INTRINSICALLY  
CONDUCTING  
POLYMERS**

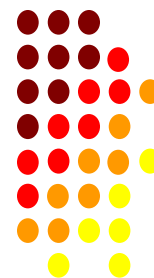
**EXTRINSICALLY  
CONDUCTING  
POLYMERS**

**DOPED  
CONDUCTING  
POLYMERS**

**CONJUGATED  
CONDUCTING  
POLYMERS**

**POLYMERS  
WITH  
CONDUCTING  
ELEMENT**

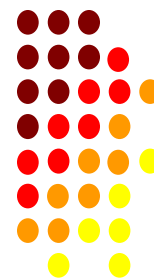
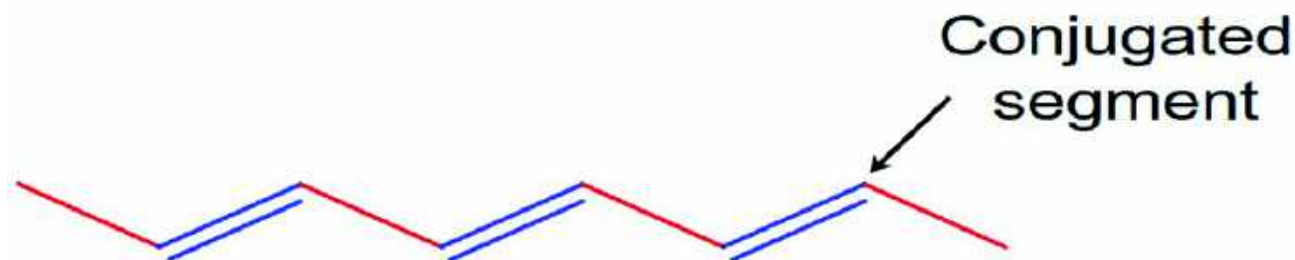
**BLENDED  
CONDUCTING  
POLYMER**



# 1. Intrinsically conducting polymers

These are the polymers which contain extensive pi-conjugation in the main chain and can conduct electricity either normally or on doping. They can be further classified as:

- Conjugated conducting polymers
- Doped conducting polymers

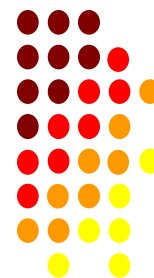
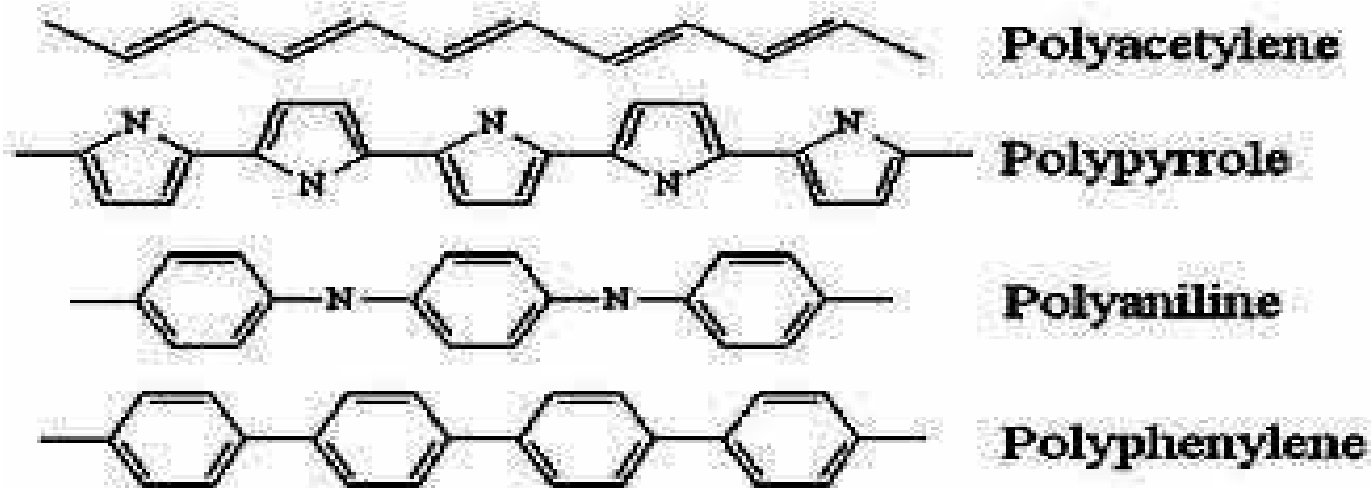


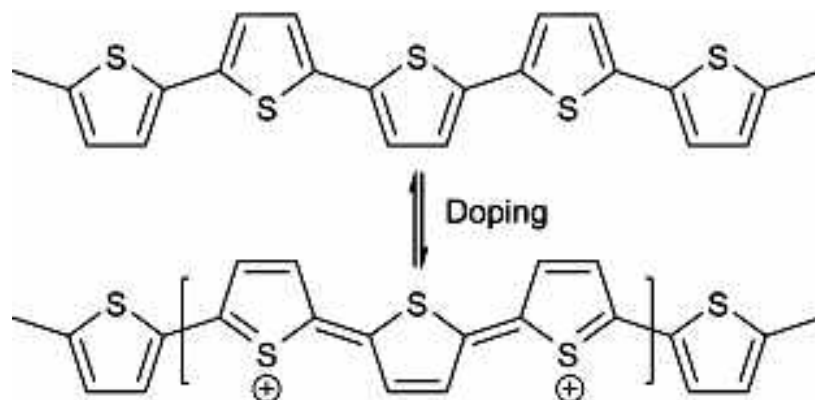
## a) CONJUGATED CONDUCTING POLYMERS

These polymers contain conjugated pi bonds in their main polymeric backbone, which results in the formation of valence band and conduction band.

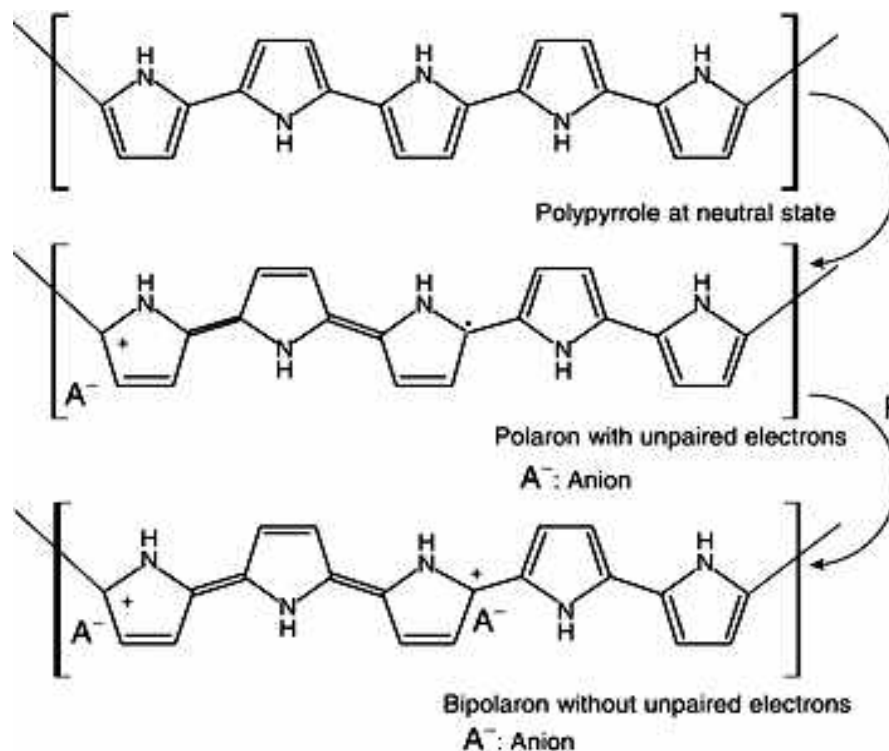
There is movement of electrons due to conjugation making them conducting.

Example: polypyrrole, polythiophene, polyacetylene, polyparaphenylene.

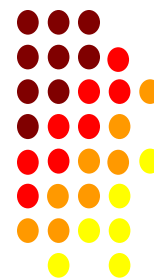




**Conducting polythiophene**



**Conducting polypyrrole**



## **b) DOPED CONDUCTING POLYMERS**

- These are the polymers which have conjugated pi bonds but have gap between valance and conduction band and cannot conduct electricity normally.
- They are doped with electron donor or electron acceptors to make them conducting.

Doping can be done in two ways:

- p-Doping
- n-Doping



### p-doping:

- Done by removal of electron from backbone.
- This is done by using lewis acid as FeCl<sub>3</sub>



### n-Doping:

- Done by addition of electron in the backbone.
- This is done by using Lewis base as Na, Li .



## **2. Extrinsicly conducting polymers**

These are the polymers that do not contain the factors responsible for conduction and are made conducting by adding external ingredients in them.

### **a) Polymers with conducting element:**

- Conductive elements such as carbon black, metal oxide are added to polymer.
- Polymer acts as binder and hold these elements and thus acts as conductive polymer.



**b) Polymers with conducting blend or blended conducting polymer:**

- Blending a conventional polymer with conducting polymer takes place.
- Conventional polymer gains the conducting property.



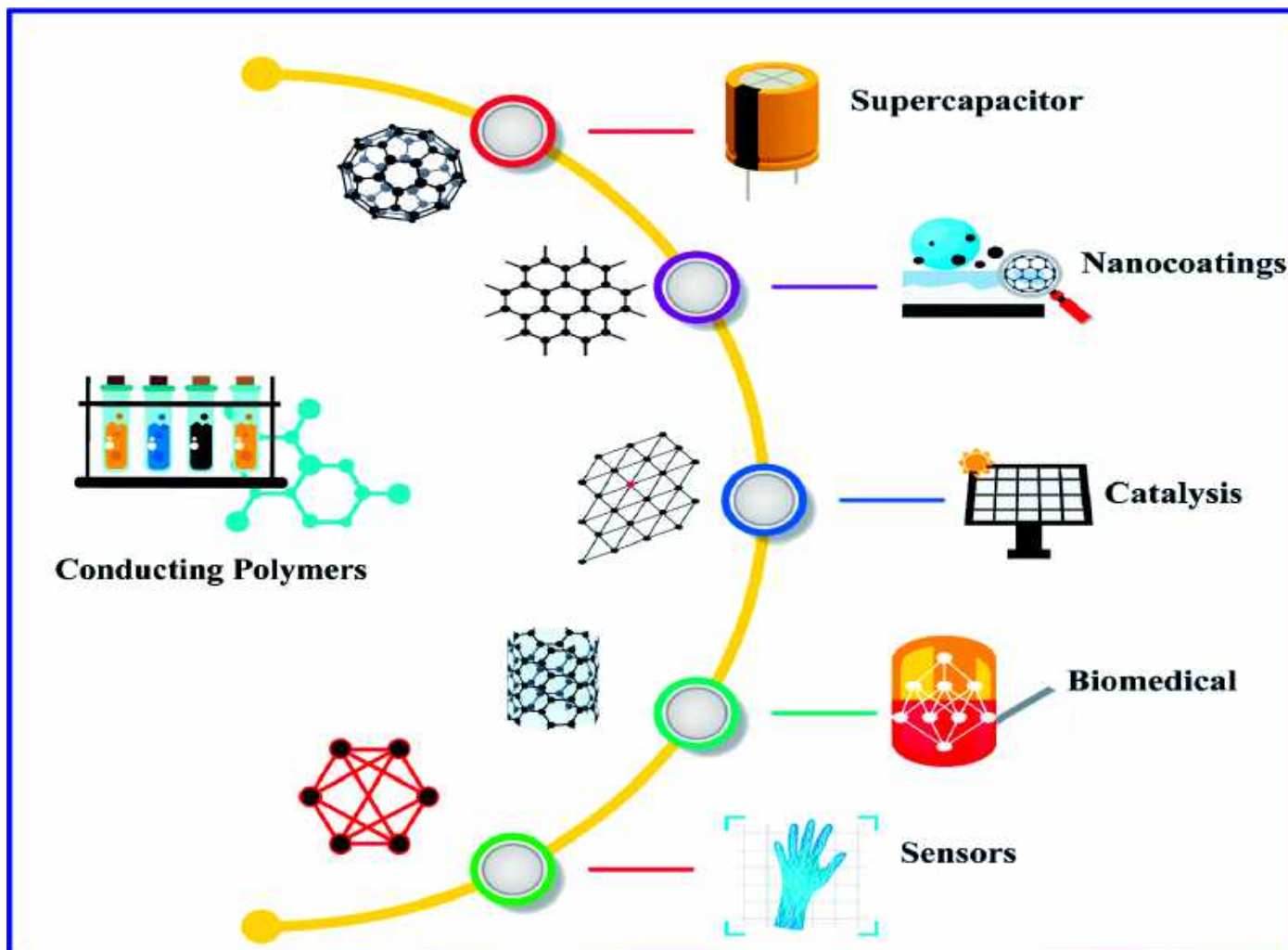
## Applications of conducting polymers

- **Rechargeable batteries:** Doped CP's are used as promising charge storage material. They are small sized, long lasting and can produce high current density ( $50 \text{ mA/cm}^2$ ).
- **As antistatic material:** To avoid static electricity in plastic carpets in offices, theatres, doped polyaniline is used as antistatic material.
- **Optical filters:** Radiations from the screens of computer and other electrical devices can be absorbed by coating of CP's on casing.



- **Sensors:** CP's have chemical properties suitable to use them as sensors for pH, O<sub>2</sub>, NO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub> , glucose, reducing and oxidizing chemicals, for the study of their even low concentrations.
- **In electronics:** They are used for photodiodes, light emitting wall papers, light emitting diodes (LED) and data storage.
- **Photovoltaic cells:** Conducting polymers can be used in construction of photovoltaic cells.
- In molecular wires and molecular switches.
- In electromagnetic screening materials.





## Biodegradable polymers

The polymers which can degrade in nature by the action of enzymes and microbes are known as biodegradable polymers.

Functional Groups generally used in preparation of biodegradable polymers are Ether, Esters, Amides.



## Factors affecting biodegradation

- **Size and shape:** Polymers should not be very large and should not be too much branched.
- **Crystallinity:** Polymers should be semi crystalline. The percentage of crystallinity should be less.
- **Hydrophilicity:** For biodegradation polymers should be water soluble.
- **Presence of functional groups:** Polymers should be having functional groups. Polymers based only on carbon atoms are non-biodegradable.
- **Presence of suitable microorganism**
- **Presence of favourable conditions** like suitable temperature, moisture, pH for proper functioning of micro-organism.



## Biodegradation process

**Step- 1<sup>ST</sup>:** The long polymer molecules are reduced to shorter and shorter lengths and undergo oxidation. The molecules become hydrophilic (water attracting) and small.

**Step 2<sup>ND</sup>:** Biodegradation starts in the presence of moisture and micro-organisms found in environment. The plastic material is completely broken down into the residual products of the biodegradation process.

**Step 3<sup>RD</sup>:** Micro- organisms consume the degraded plastic. Carbon dioxide, water and biomass are produced and returned to nature by way of the bio cycle.



1

Degradation



2

Biodegradation



3

Return to Nature

Photosynthesis



## Importance of biodegradable polymers

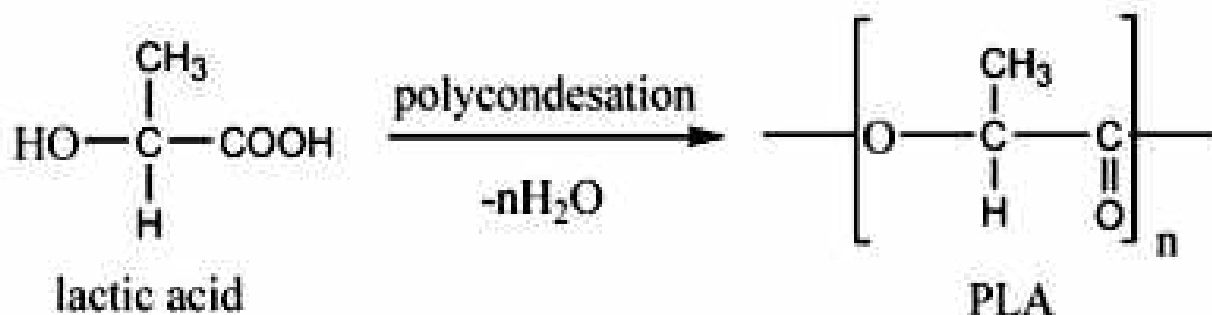
- Produced from renewable resources.
- Used in fields of medicine, agriculture and packaging.
- Able to be recycled, burned without producing toxic products.
- Used in localized delivery of drugs.
- Reduce side effects.
- Controllable degradation rate.



# Formation, properties and uses of some biodegradable polymers

## 1. Poly(lactic acid):

Formed by polymerisation of lactic acid.



### Properties:

- PLA is compostable and biodegradable.
- It is resistant to grease and moisture.



## Uses:

- PLA is used in plastic surgery and surgical sutures.
- It is used in food packaging.
- Used in drug delivery systems.

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

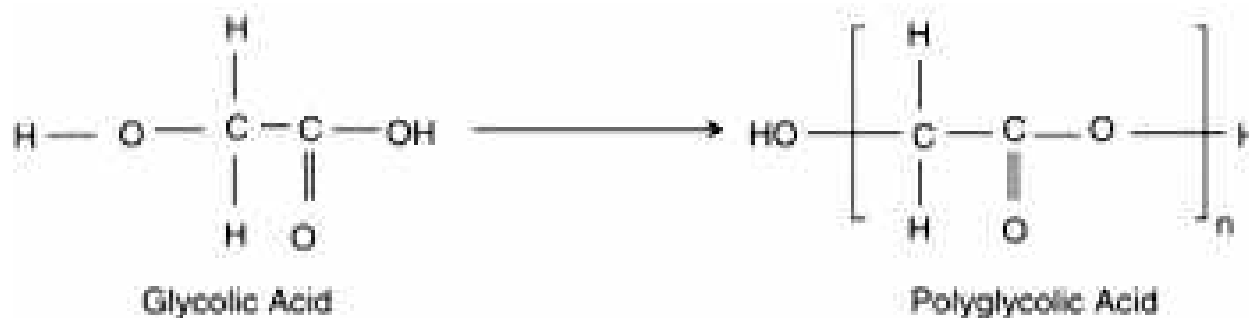


**PLA Pellets**



## 2. Poly glycolic acid

It was the first synthetic absorbable suture.



### Properties:

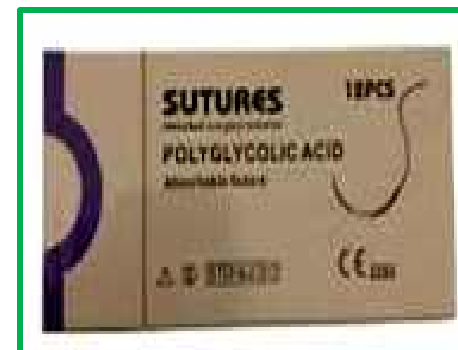
- PGA is highly crystalline.
- It has a high melting point.
- Has low solubility in organic solvents.



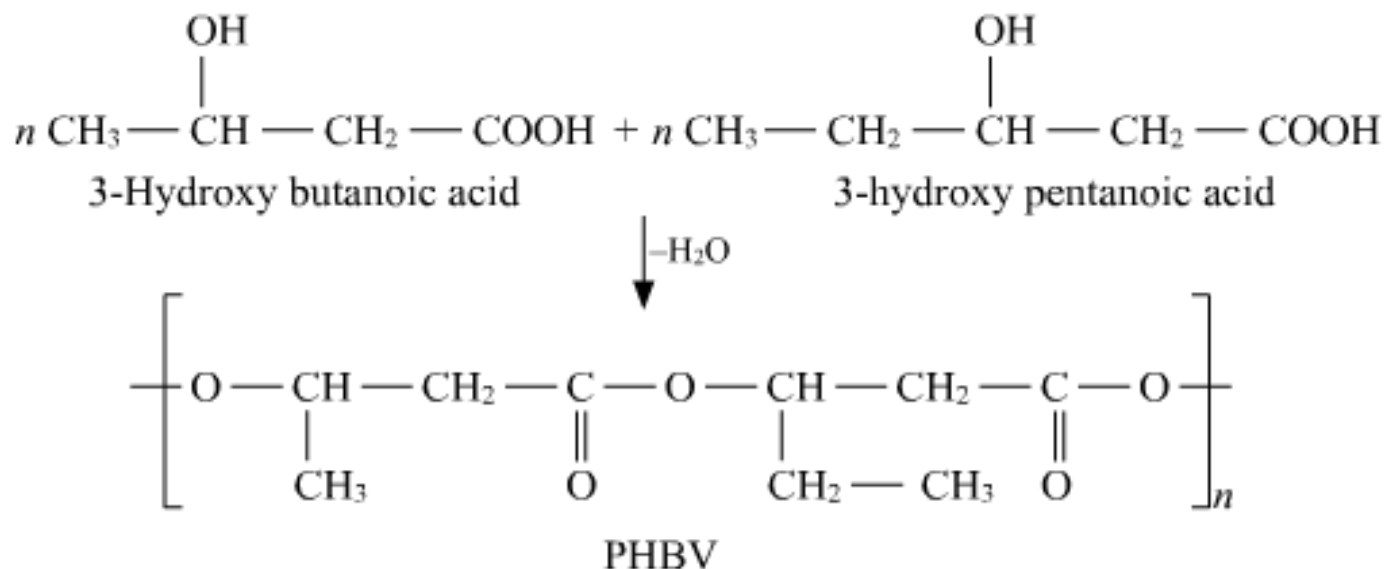
## Uses:

This polymer was used to develop the first synthetic absorbable suture which was marketed under the trade name of Dexon.

- Used in tissue engineering.
- Used in controlled drug delivery
- Used as biodegradable sutures.



### 3. Poly-β-hydroxybutyrate-co- β hydroxyvalerate (PHBV) or (BIOPOL) or (BIOMER-L)



#### Properties:

- PHBV is a thermoplastic polymer.
- It is brittle.

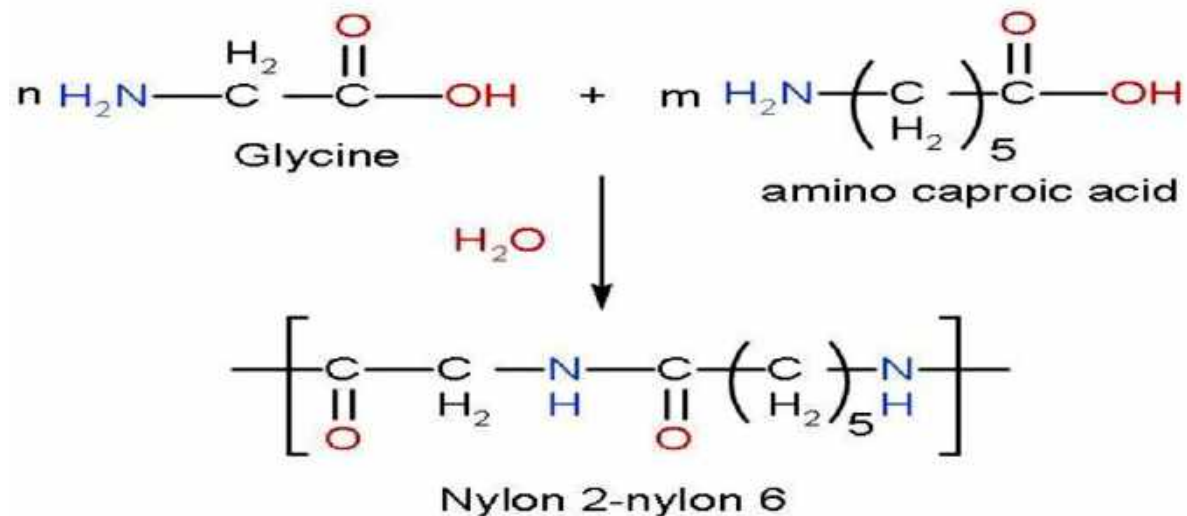


## **Applications:**

- In controlled release of drugs.
- Medical implants and repairs.
- Orthopedic devices.
- Manufacturing bottles of shampoos etc.



## 4. Nylon-2-nylon-6 :



### Properties:

- It is a polyamide and copolymer of glycine (H<sub>2</sub>N-CH<sub>2</sub>-COOH) and amino caproic acid (H<sub>2</sub>N-(CH<sub>2</sub>)<sub>5</sub>COOH).
- It is biodegradable.



## Uses:

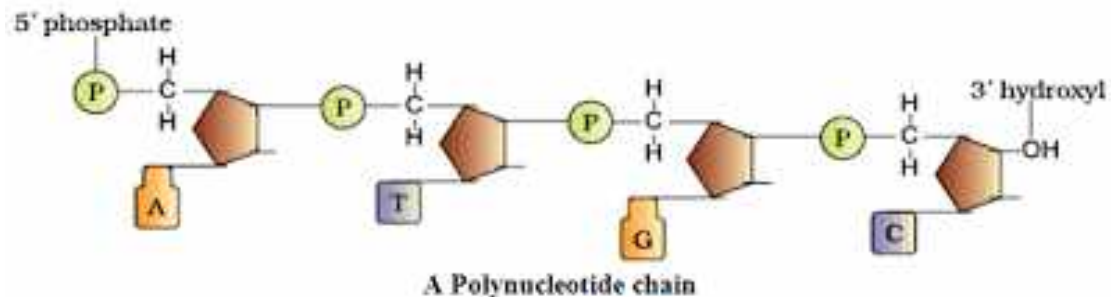
- Used to make ropes and parachutes and tooth brush bristles.
- Nylon is also used as dressing material in shirts etc.



# Polynucleotides

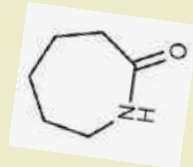
A polynucleotide chain is composed of monomers of nucleotide molecules. The structure of DNA is two nucleotide molecules wound together. Even RNA is made of a single chain of polynucleotides. The design of the DNA and RNA polynucleotide chain are given below:

- Every monomer has three sections, namely a **pentose sugar**, a **nitrogenous base** and a **phosphate group**.
- The **pentose sugar** and the **phosphate groups** are linked by a **phosphodiester linkage**.
- The four nitrogenous bases are **adenine**, **cytosine**, **guanine** and **thymine** or **uracil**.

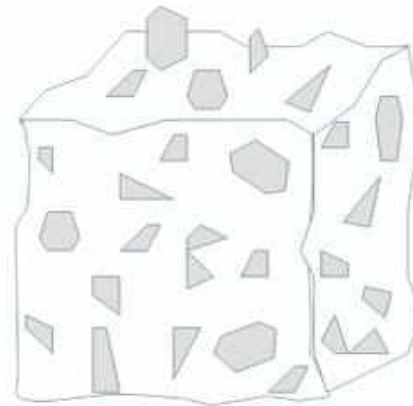
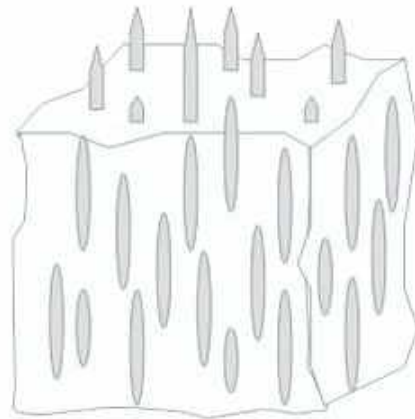
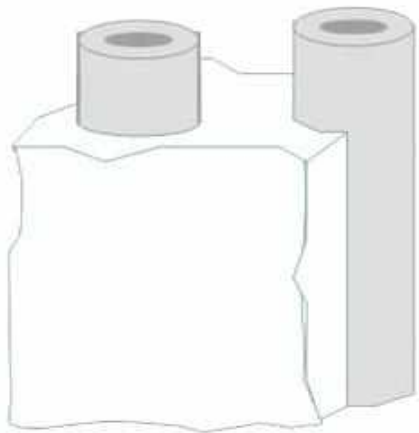


Polymer	Monomer
Polythene	ethylene $\text{CH}_2=\text{CH}_2$
Polyvinylchloride (PVC)	vinyl chloride $\text{CH}_2=\text{CHCl}$
Polytetrafluoroethylene (PTFE), Teflon	tetrafluoroethylene $\text{CF}_2=\text{CF}_2$
Polymethyl methacrylate (PMMA), Plexi Glass, Lucite	methyl methacrylate $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$
Buna-N	acrylonitrile $\text{CH}_2=\text{CHCN}$ butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
Buna-S	styrene $\text{CH}_2=\text{CHC}_6\text{H}_5$ butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
Kevlar	para $\text{ClO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{Cl}$ para $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$



Polymer	Monomer
Nylon-6	caprolactum 
Nylon-66	adipic acid $\text{HO}_2\text{C}-(\text{CH}_2)_4-\text{CO}_2\text{H}$ hexamethylenediamine $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$
Dacron, PET	ethylene glycol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ terephthalic acid para $\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$
Bakelite	formaldehyde $\text{HCHO}$ phenol $\text{C}_6\text{H}_5\text{OH}$
Thiokol	ethylenechloride $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{Cl}$ sodiumpolysulphide $\text{Na}_2\text{S}_2$





# LECTURE -37

c)

Polymer A

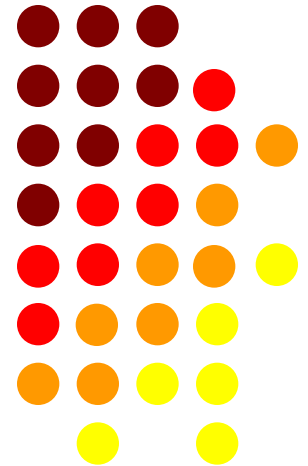
Polymer B

## Polymer blends and composites

Miscible

Partially Miscible

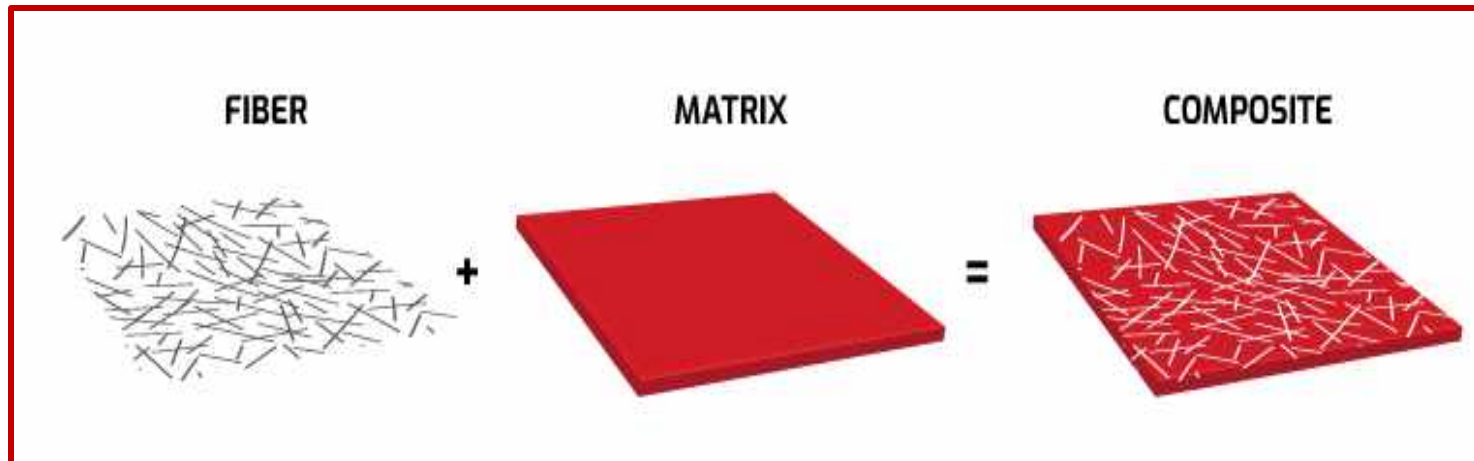
Immiscible

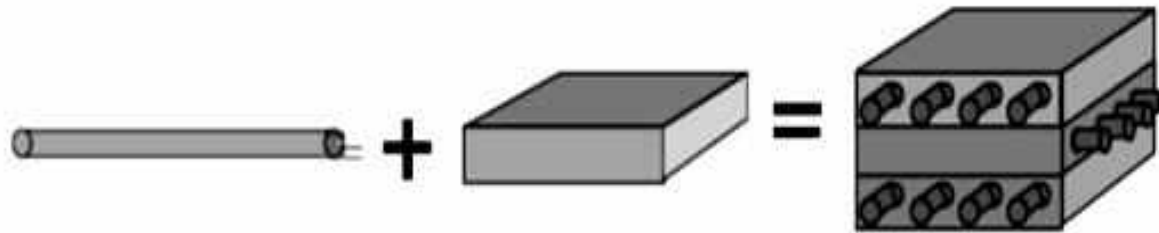


## Composites:

Composite material is a material composed of two or more phases (matrix phase and dispersed phase) and an interface separating them.

Their bulk properties are different from those of any of the constituents.





**Fiber/Filament  
Reinforcement**

- High strength
- High stiffness
- Low density

**Matrix**

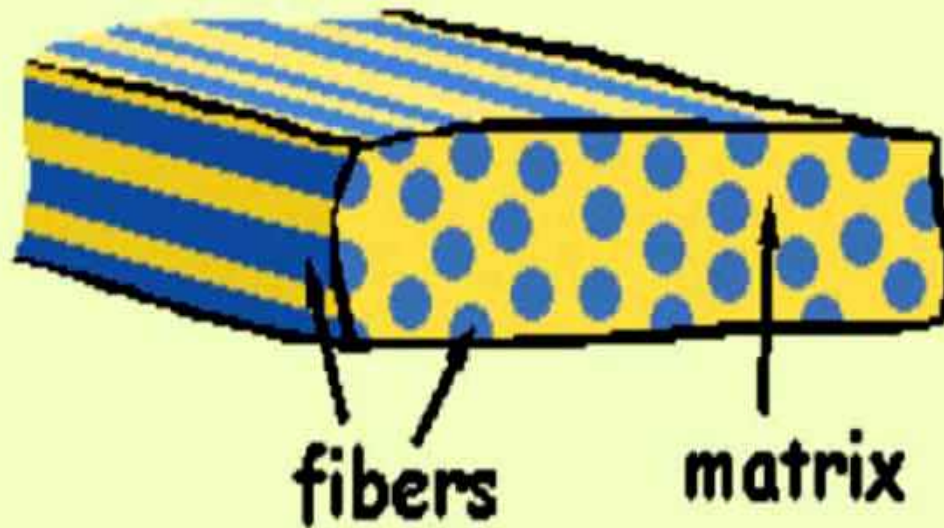
- Good shear properties
- Low density

**Composite**

- High strength
- High stiffness
- Good shear properties
- Low density



a close-up of what  
a composite might  
look like



<b>MATRIX</b>	<b>REINFORCEMENT</b>
It is primary phase.	It is secondary force.
It is in continuous form.	It is in discontinuous form.
It holds the dispersed phase and shares load with it.	It is embedded in matrix.
Weaker than dispersed phase.	Stronger than matrix phase.

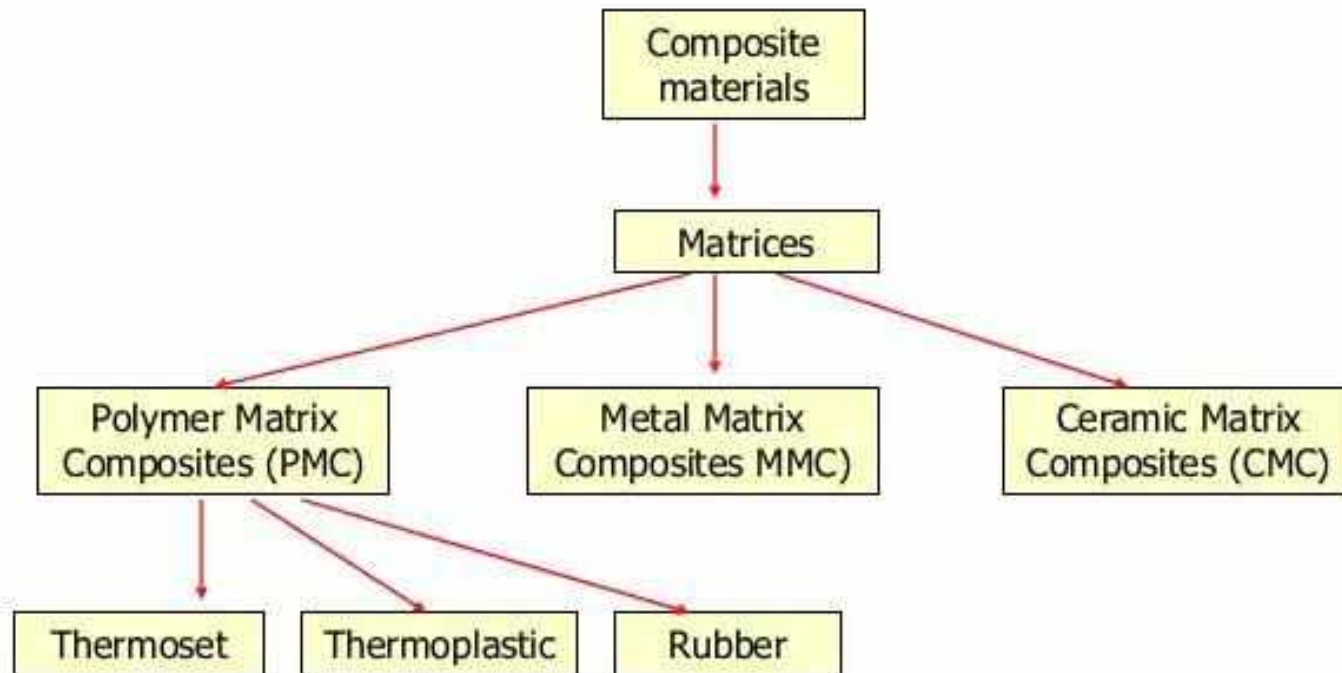
### **Classification of composite materials:**

There are two classification systems of composite materials:

- Based on matrix phase.
- Based on reinforcement phase.



# Classification based on Matrices

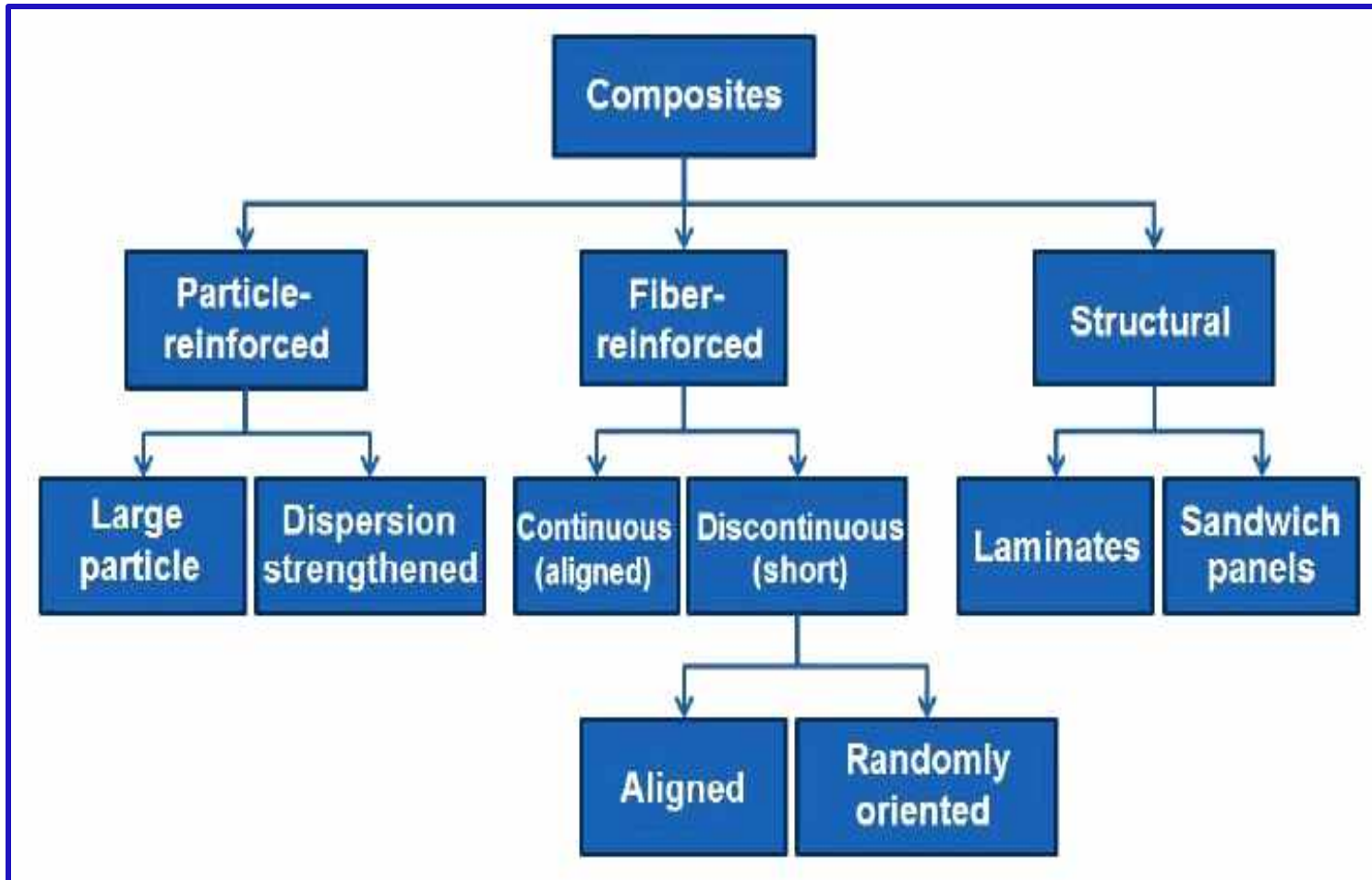


## Properties of polymer matrix, metal matrix and ceramic matrix composites

<b>Polymer matrix composite</b>	<b>Metal matrix composite</b>	<b>Ceramic metal composite</b>
The matrix is made of polymer.	Matrix is made of metal.	Matrix is a ceramic material.
Low cost	High cost	High cost
Low density	High density	High density
Low thermal stability	Resist thermal shock	High thermal stability

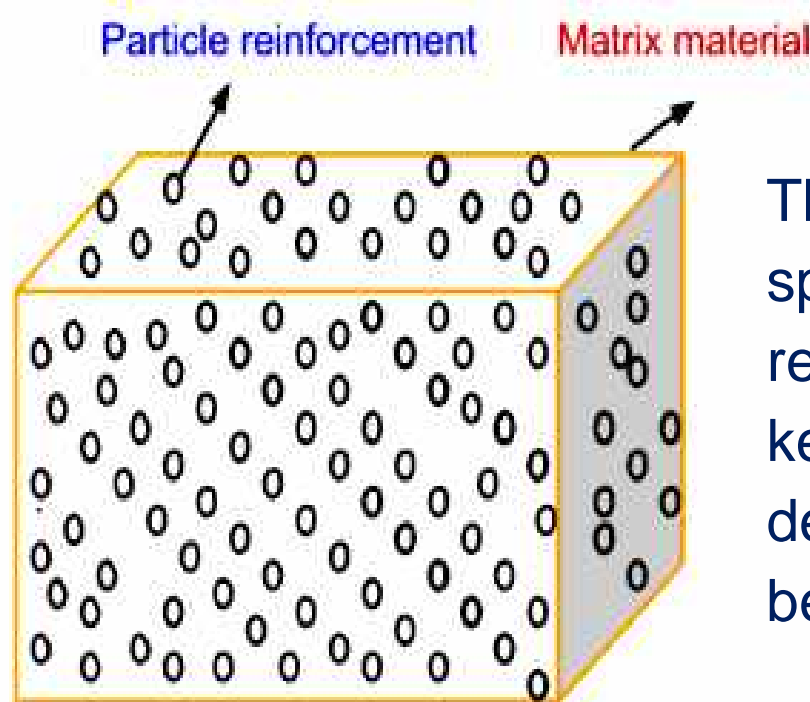


# Classification based on reinforced material



## 1.) Particles as reinforcement (particulate composites)

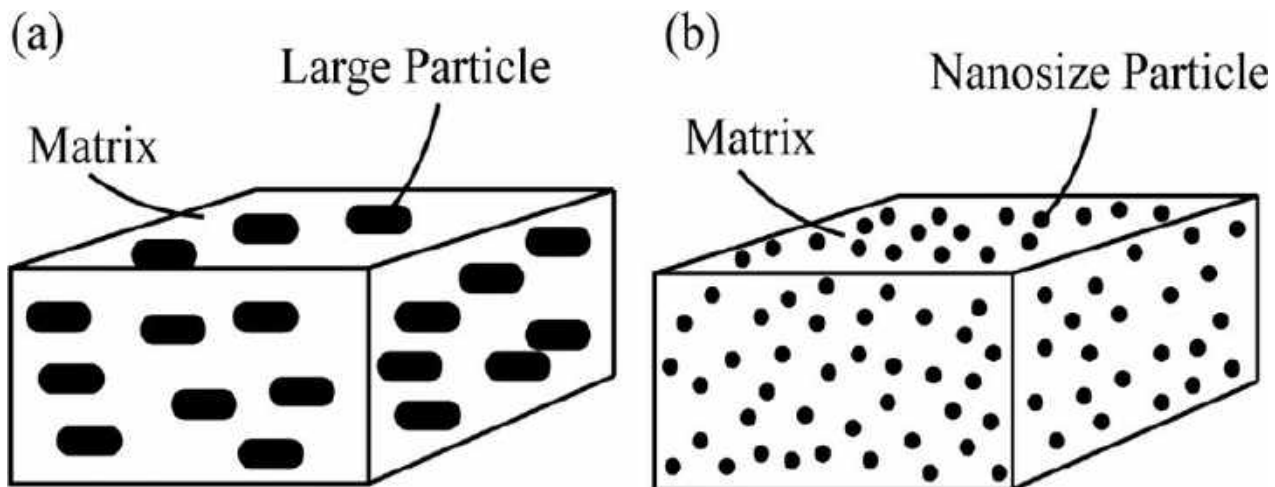
Particulate composites consist of *a matrix reinforced with a dispersed phase* in the form of particles.



The type, shape and spatial arrangement of reinforcing phase are the key parameters in determining mechanical behaviour of composite.



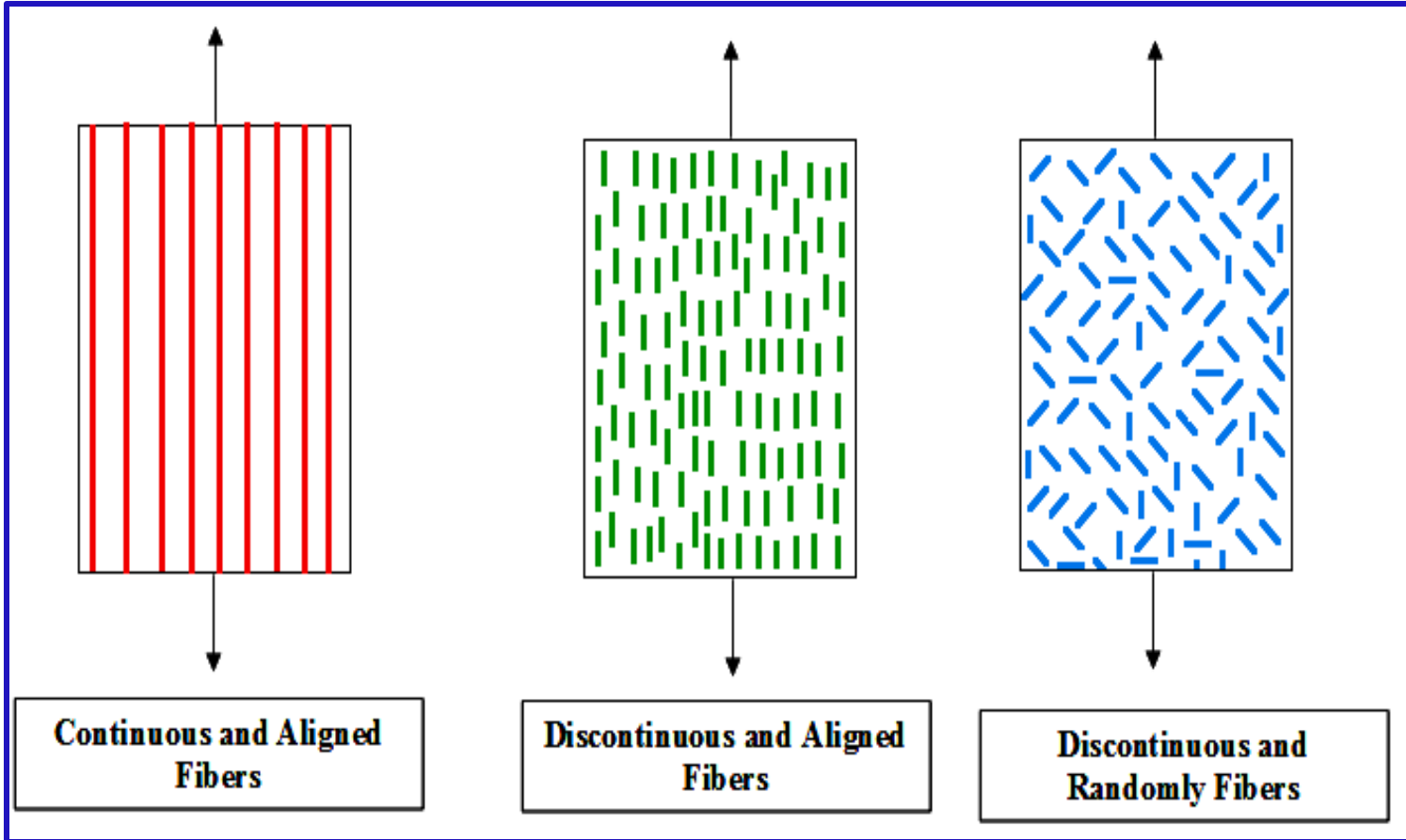
The particles used as reinforcement may be Large or small particles



## **2.) Fibers as reinforcement (fibrous composites)**

- A fiber composite material consists of a filamentary phase embedded in a continuous matrix phase.
- The aspect ratio (i.e., ratio of length to diameter) of the filaments may vary from about 10 to infinity (for continuous fibers).
- The fibres may be continuous, discontinuous or random.





### **3. Structural composites:**

These are engineered products made from plastic, wood, glass, or carbon fiber materials. Types of structural composites. ***These may be Laminar or sandwich panels.***

#### **a. Laminar:**

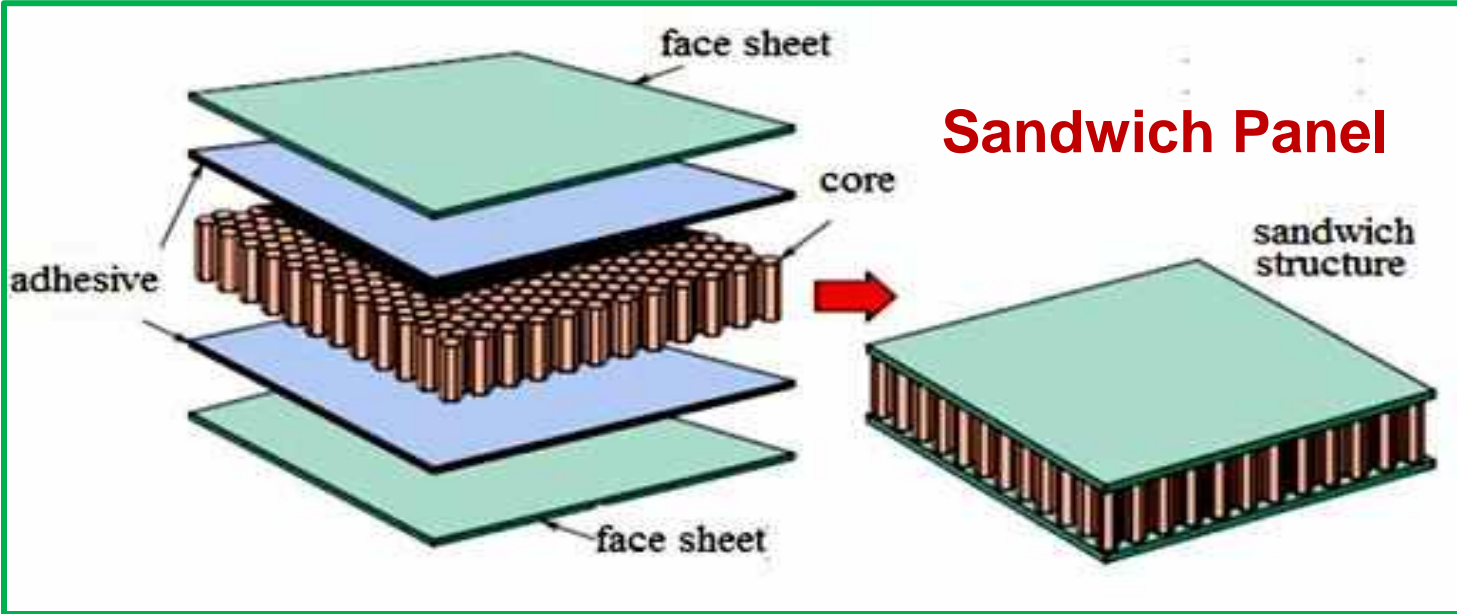
- It is composed of two-dimensional sheets or panels that have a preferred high strength direction such as is found in wood and continuous and aligned fiber-reinforced plastics.
- The layers are stacked and cemented together such that the orientation of the high-strength direction varies with each successive layer.
- One example of a relatively complex structure is modern ski and another example is plywood.



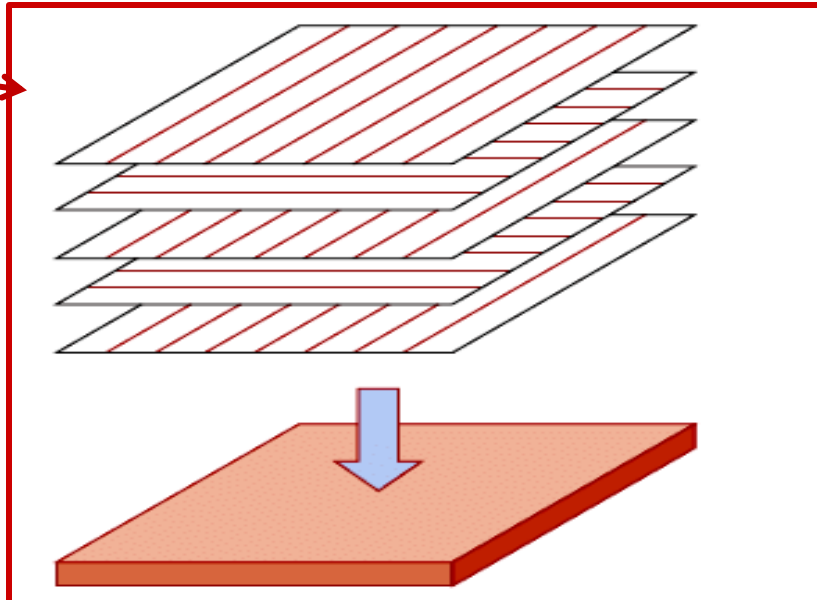
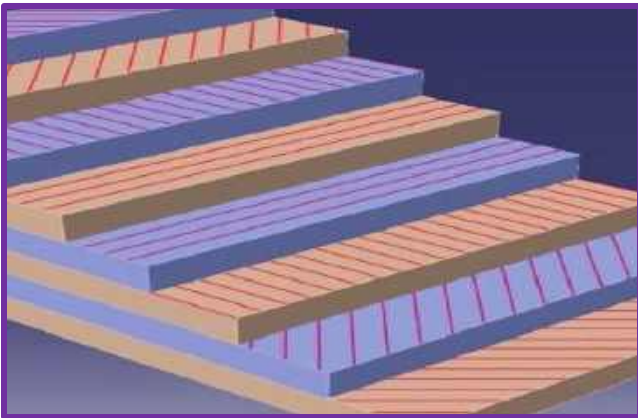
## **b. Sandwich Panels:**

- Consist of two strong outer sheets which are called face sheets and may be made of aluminum alloys, fiber reinforced plastics, titanium alloys, steel.
- Face sheets carry most of the loading and stresses. Core may be a honeycomb structure which has less density than the face sheets and resists perpendicular stresses and provides shear rigidity.
- Sandwich panels can be used in variety of applications which include roofs, floors, walls of buildings and in aircraft, for wings, fuselage and tailplane skins.





### Laminar



# Examples of natural composites



*Wood is an example of a natural composite material.*



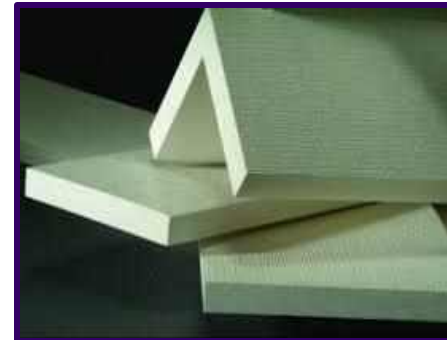
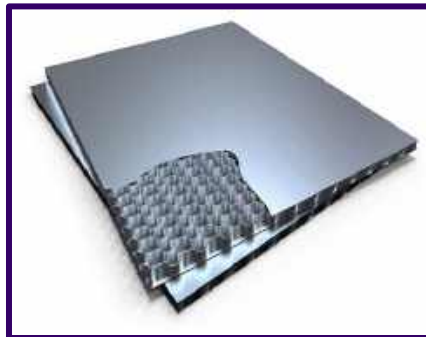
## Advantages of composites

- Light Weight
- High Strength to weight ratio
- Corrosion resistant
- Design flexibility
- Dimensional stability
- Durable
- Chemical resistance
- High performance at elevated temperatures
- Outstanding electrical insulation



## Applications

- These composites make a great building material for airplanes and spacecraft.
- Automotive manufacturing and railway industries in the form of dashboards, car covers, engine covers, car floors, and seats.
- light houses, hydraulic construction, storage tanks, and door and window components.
- For reconstruction and repair infrastructure.



## Polymer blends

- Polymer Blend is a mixture of two or more than two polymers, having physical properties different from the component polymers.
- The components of polymer blend should be friendly with each other.
- Blending is done to improve the properties of components.
- Example: Mixture of wool and terylene forms a polymer blend.
- Wool (-CONH-) + Terylene (-COO-) polymer blend.



## T<sub>g</sub> (Glass Transition Temperature)

Glass Transition Temperature is the point at which a material goes from a hard brittle state to a soft and rubbery state. Amorphous polymers only have a T<sub>g</sub>.

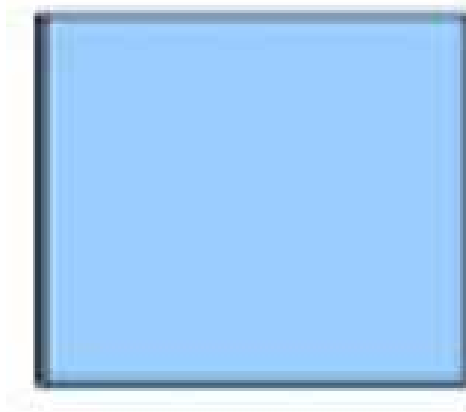
- Some polymers are used above their glass transition temperatures and some are used below.
- Hard plastics like polystyrene and PMMA are used below their glass transition temperatures; that is in their glassy state.
- Rubber elastomers like polyisoprene & polyisobutylene, are used above their T<sub>g</sub>'s, that is, in the rubbery state, where they are soft and flexible.



## Types of polymer blends

### 1. Miscible polymer blend:

- Homogenous
- Negative value of the free energy of mixing
- It is a single –phase structure.
- Has one Tg. (Tg = glass transition temperature).
- Example PS/PPO

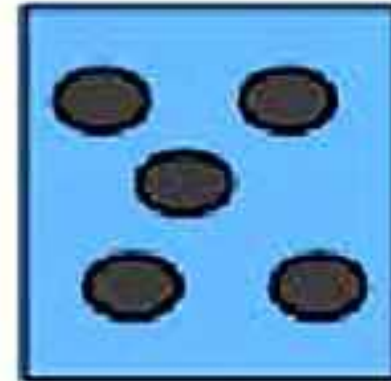


**Miscible Polymer Blend**



## 2. Immiscible polymer blend:

- A blend exhibits more than two phases (Heterogeneous)
- Positive value of free energy of mixing i.e.  $\Delta G_m > 0$ .
- Has two Tg's (glass transition temperature).
- There is poor adhesion between the blend phases.
- The properties of all the components are present in one blend phase. Eg. PA (Polyamide)/PPO (Polyphenylene Oxide), PA (Polyamide) / PP (Polypropylene)



**Immiscible Polymer Blend**



**3. Homologous polymer blend:**

Mixture of same polymers with different molecular weight distribution.(e.g., PP (Polypropylene) / PA-6 (Polyamide-6 or Nylon 6)

**4. Isomorphic polymer blend:**

Polymer blends of two or more different semi-crystalline polymers which are miscible in both crystalline as well as in molten state.

**5. Compatible polymer blend:**

Blends that are miscible in a certain range of composition and temperature, but immiscible in others. Example: PC (Polycarbonate) / ABS (Acrylonitrile buta -diene styrene)



## *Methods of polymer blending*

Generally, blending methods are:

- Mechanical mixing-cheapest
- Melt mixing
- Fine powder mixing
- Use of monomer(s) as solvent for another component, then polymerization.
- Solution mixing



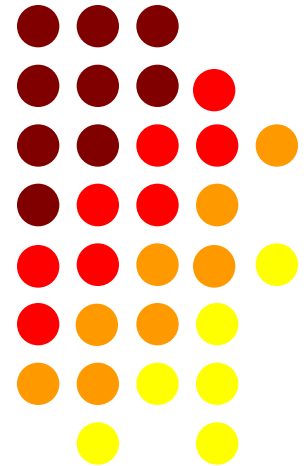
## **Advantages of blending**

- Producing materials having desired properties at lowest cost.
- It improves solvent and chemical resistance.
- It improves flame resistance.
- Recycling of industrial and municipal plastics waste.
- Blending reduces the material cost.
- Enables to produce materials with higher aesthetic value.



# LECTURE - 38

**Step growth and chain growth  
polymerisations,  
Mechanism of polymerisation via free  
radical, ionic intermediates**



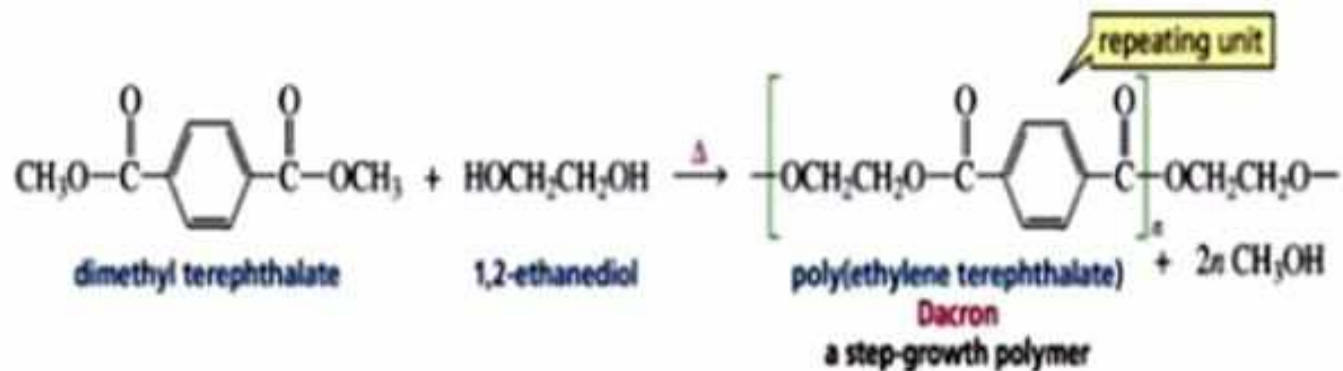


## Step-growth polymerization

- Step-growth polymerization refers to a type of polymerization mechanism in which bi-functional or multifunctional monomers react to form first dimers, then trimers, long oligomers and eventually long chain polymers.
- It is also known as condensation polymerisation.
- Condensation polymerisation is a process that involves repeated condensation reactions between two different bifunctional or tri-functional monomers.
- In condensation polymerisation some product such as  $H_2O$ ,  $NH_3$  etc. are released.



## Step Growth polymerization:



## **Free radical polymerization:**

- Free radical polymerization is a type of addition polymerization that involves the use of free radicals to initiate and propagate the polymerization process. It is one of the most common methods used to produce a wide range of synthetic polymers. Here are the key steps involved in free radical polymerization:
- **Initiation:**  
Initiation begins with the generation of free radicals, which are highly reactive species with unpaired electrons.



- **Propagation:**

The free radicals generated in the initiation step react with monomer molecules, initiating the growth of the polymer chain.

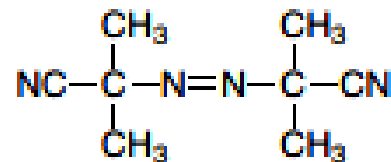
- **Termination:**

Polymerization continues until termination occurs.



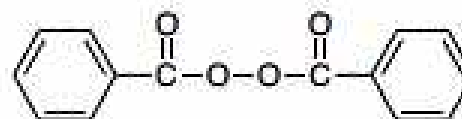
# Examples of compounds used as free radical initiators

- AIBN  $\longrightarrow$  2,2'-azobis(isobutyronitrile)



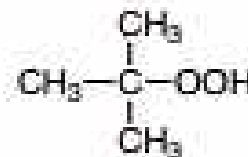
AIBN

- BPO  $\longrightarrow$  Benzoyl peroxides



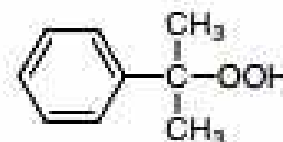
BPO

- TBHP  $\longrightarrow$  tert-butylhydroperoxide



TBHP (70% in Water)

- Cumene Hydroperoxide

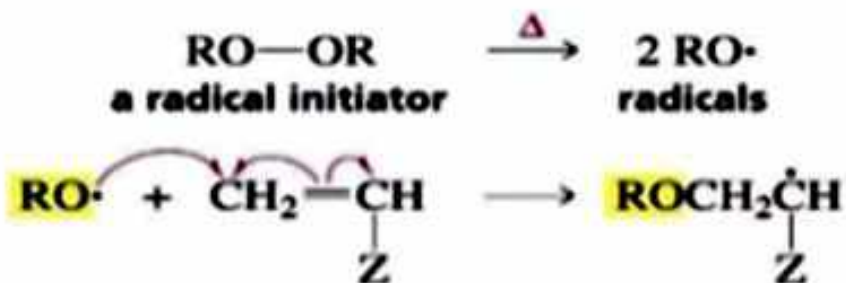


Cumene Hydroperoxide (cont)

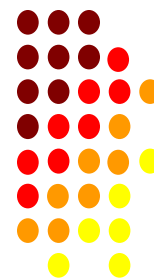
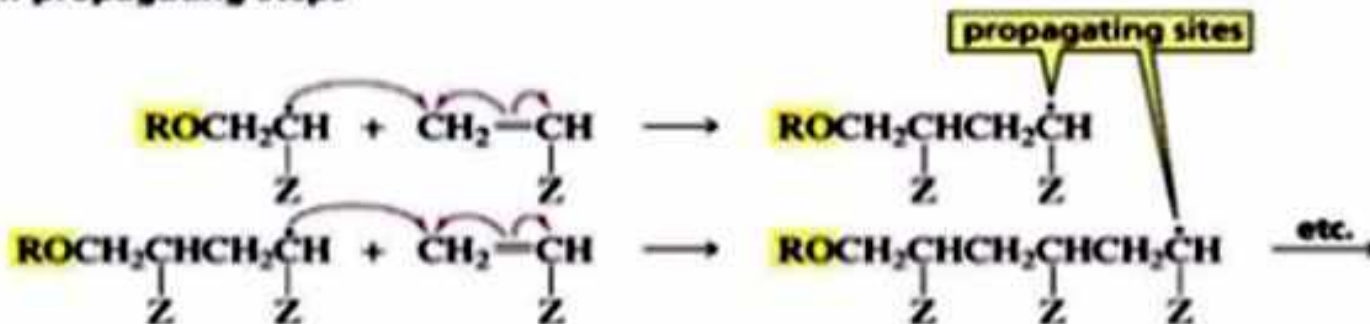


# Mechanism of free radical polymerization:

## chain-initiating steps



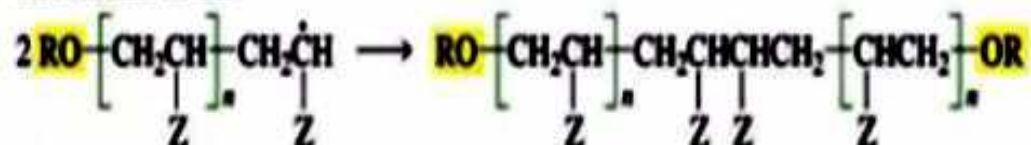
## chain-propagating steps



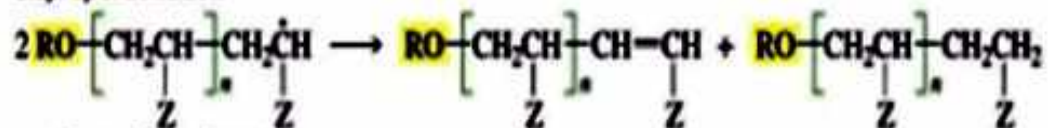
# Mechanism of free radical polymerization:

methods to terminate the chain

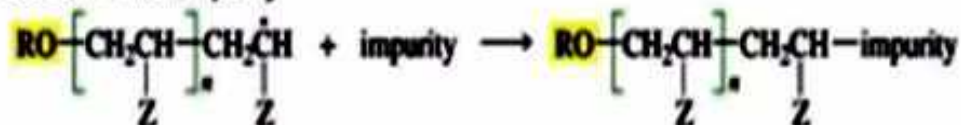
chain combination



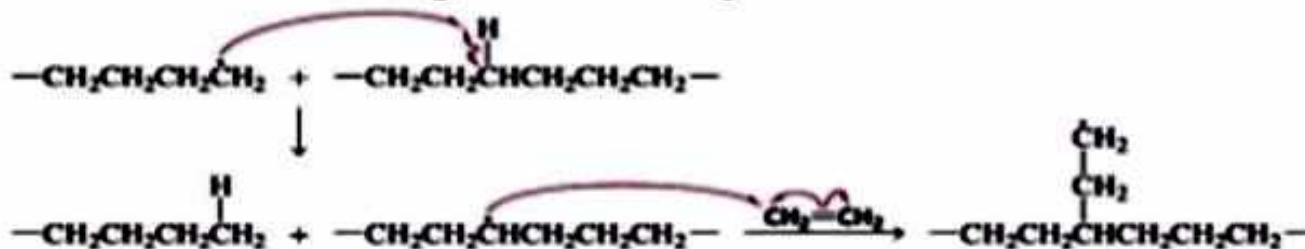
disproportionation



reaction with an impurity

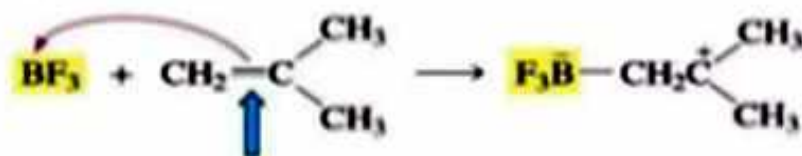


## Branching of the Polymer Chain



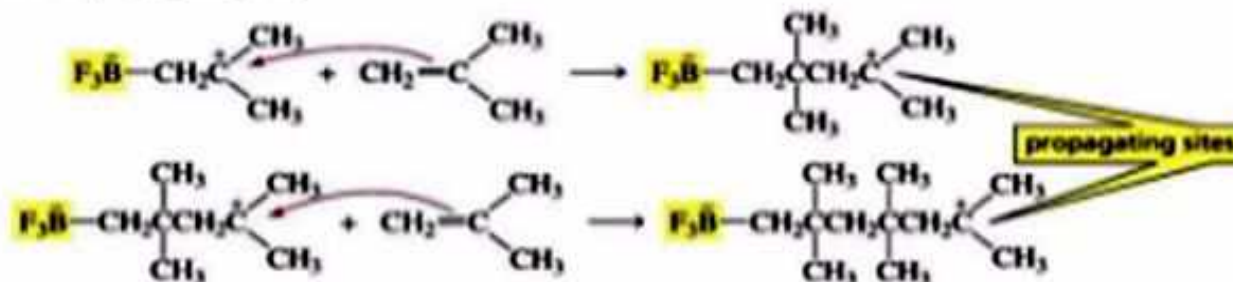
# Mechanism of cationic polymerization:

chain-initiating step



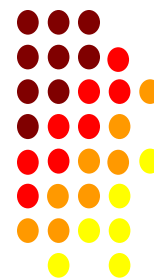
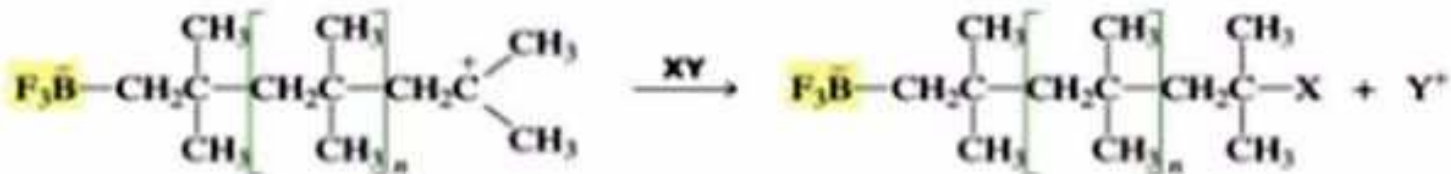
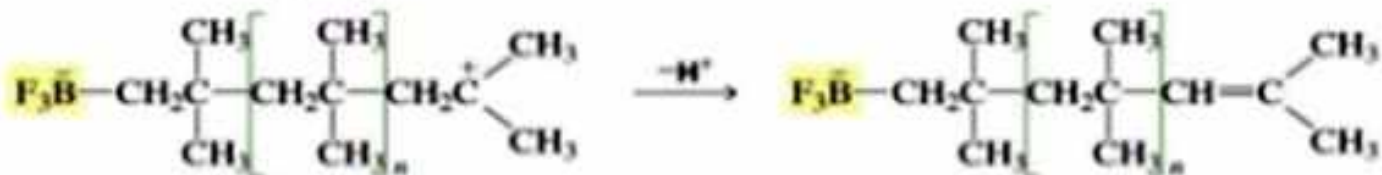
the alkene monomer  
reacts with an electrophile

chain-propagating steps



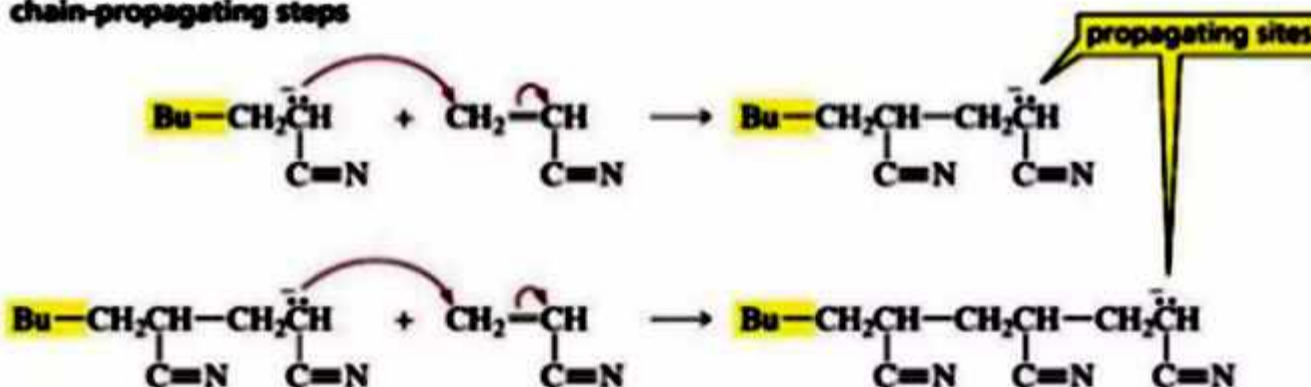
# Mechanism of cationic polymerization:

chain-terminating steps



## Mechanism of anionic polymerization:

chain-propagating steps



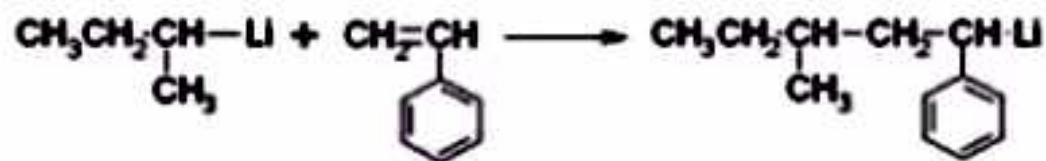
- Non-terminated chains are called living polymers and the chains remains active until they are killed.



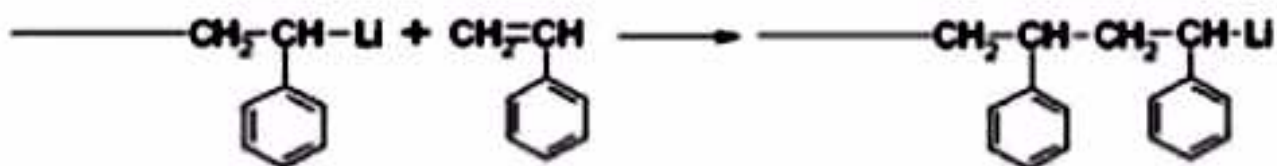
# Mechanism of anionic polymerization:

## Styrene Polymerization

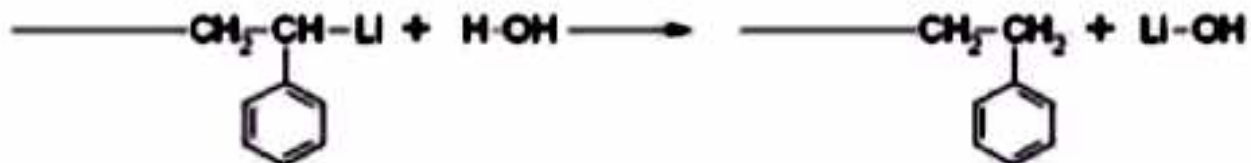
Initiation:



Propagation:

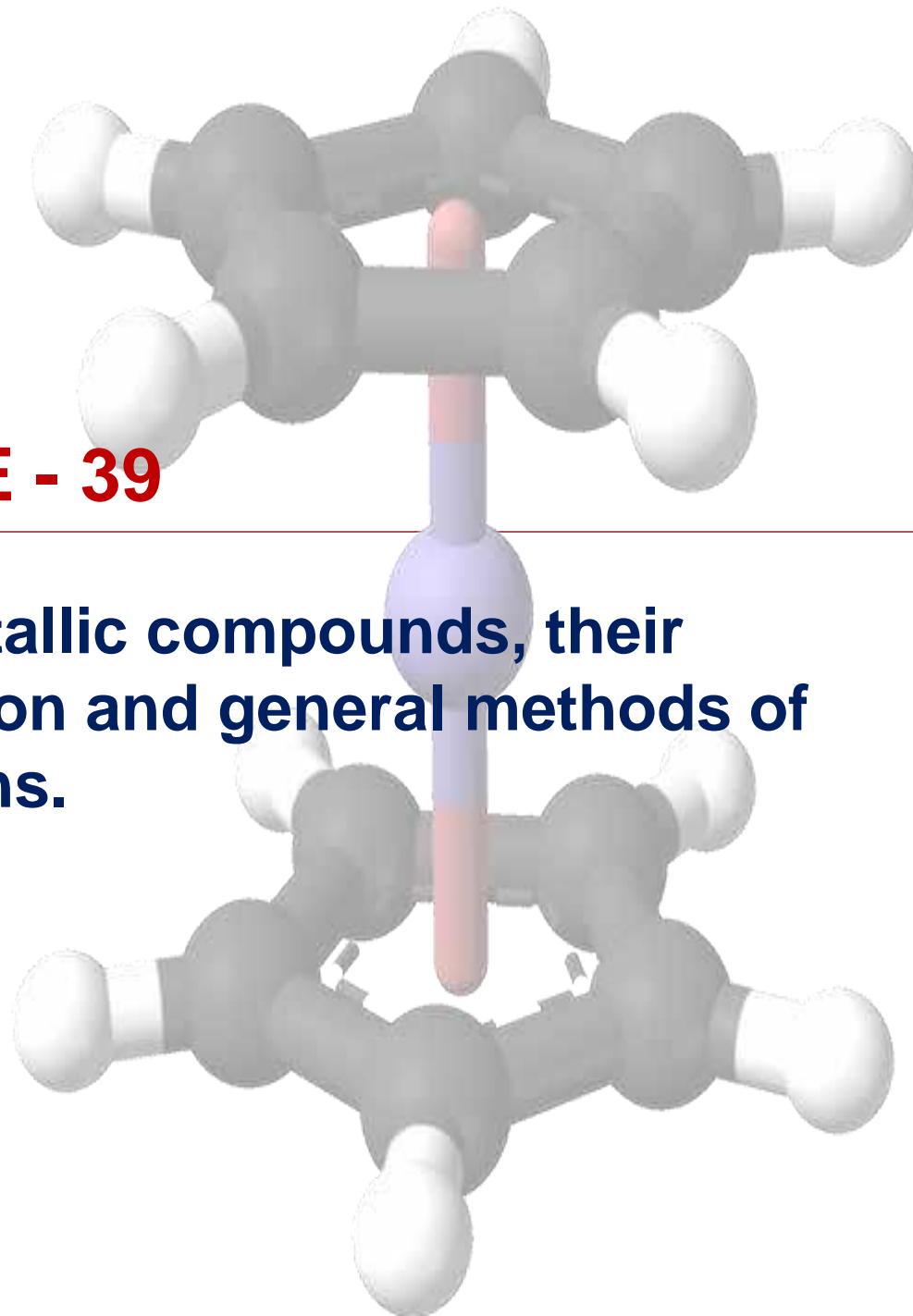
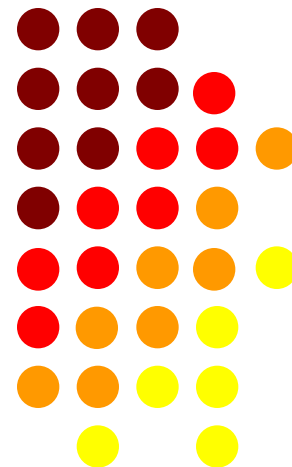


Termination:



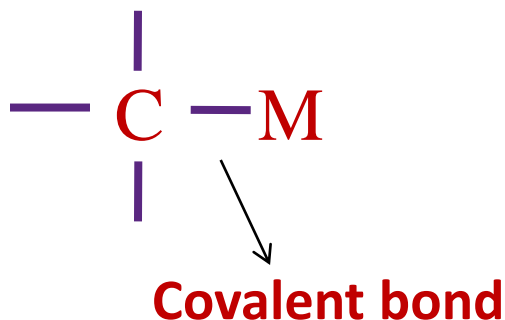
## LECTURE - 39

**Organometallic compounds, their classification and general methods of preparations.**



## ORGANOMETALLIC COMPOUNDS

The compounds in which the carbon atom of the organic group are bonded to metal atom directly are known as organometallic compounds.



Where M = any metal like Mg, Li, Na, Ca, Al etc.



## Properties of OMC

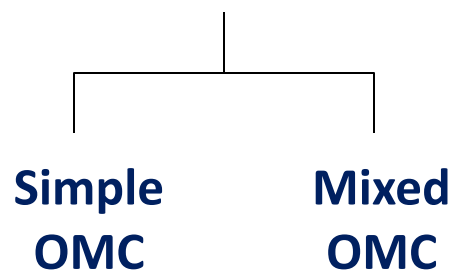
- The compounds consisting of highly electro positive metals such as sodium or lithium are very volatile and can undergo spontaneous combustion.
- These compounds can act as reducing agents, especially the compounds formed by highly electropositive metals. (Grignard reagents reduces aldehydes and Ketones to alcohols).



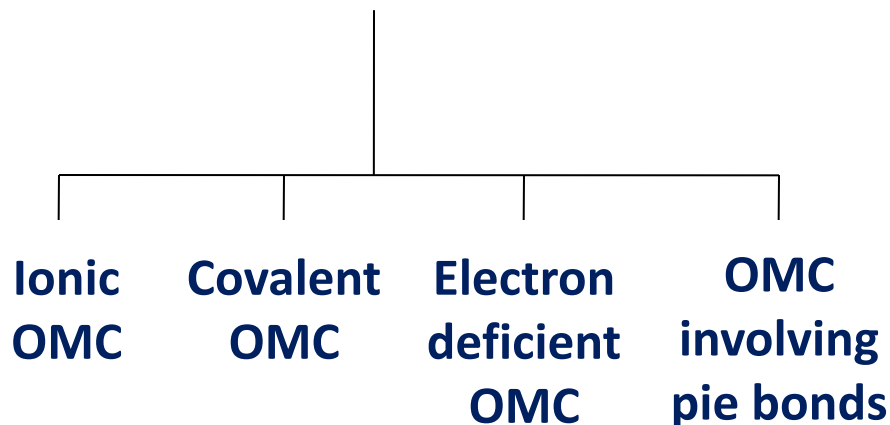
# Classification of Organometallic Compounds

## Organometallic compounds

Based on  
groups attached  
to carbon atom



Based on type  
of C-M bond



# Classification of OMC

## I. Based on groups attached to metal atom

1. **Simple organometallic compounds:** In these compounds the metal atom is bonded to only carbon and hydrogen atoms. E.g.  $(C_2H_5)_4Pb$ . They are of two types:

- ***Symmetrical:*** Metal atom is bonded to same type of groups. E.g.  $(C_2H_5)_2Hg$ .
- ***Unsymmetrical:*** Metal atom is bonded to different hydrocarbon radicals. E.g.  $C_2H_5HgC_4H_9$

2. **Mixed organometallic compounds:** In addition to carbon the metal atom is attached to other groups also. E.g.  $C_2H_5MgBr$



## II. On the basis of type of C-M bond

### 1. Ionic organometallic compound

In these compounds there is ionic bond between metal atom and carbon atom (greater difference of electronegativity). E.g. Organo sodium compounds ( $C_6H_5Na$ ), Organo potassium compounds ( $C_5H_5K$ ).

### 2. Covalent organometallic compounds or sigma bonded compounds

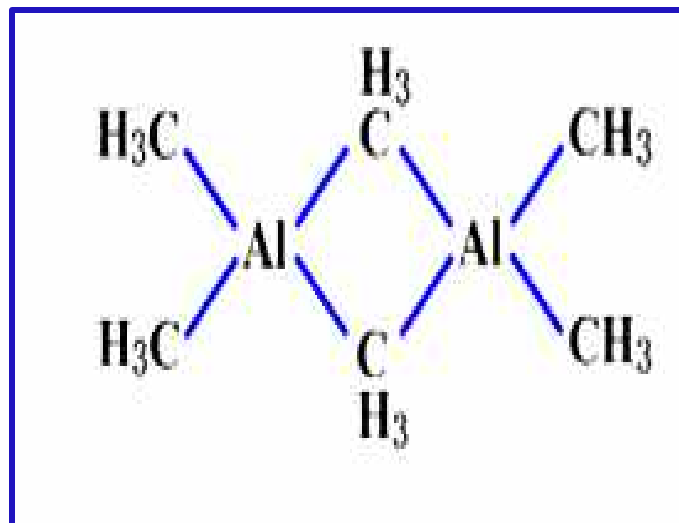
In these compounds the metal atom forms a simple covalent bond with the carbon atom (difference of electronegativity is very low). E.g. Metal alkyl compounds –  $Pb(C_2H_5)_4$ ,  $Zn(C_6H_5)_2$



### 3. Electron deficient organometallic compounds:

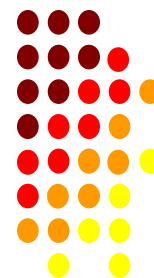
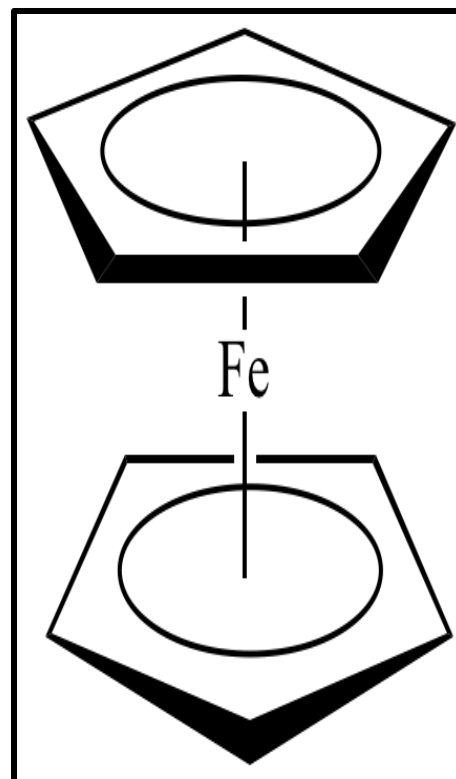
Electron deficient organometallic compounds are generally associated with elements that have less than half-filled valence shells and are designated as such because of an insufficient number of valence electrons to allow all the atoms to be linked by traditional two-electron two-centre bonds.

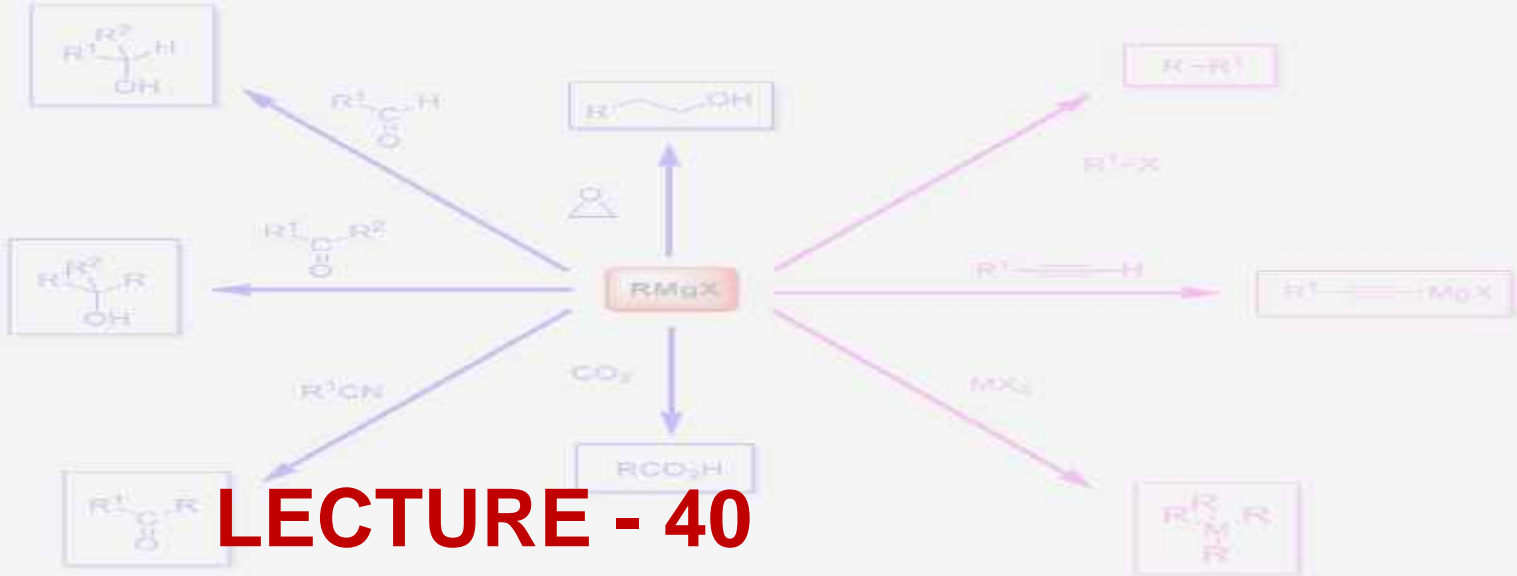
These include the compounds having bridge alkyl groups. e.g. Alkyls of Li, Be, Al. Bonding is multicentre type. e.g. Dimeric trialkyl aluminium  $[Al_2(CH_3)_6]$



#### 4. Organometallics involving $\pi$ bonds

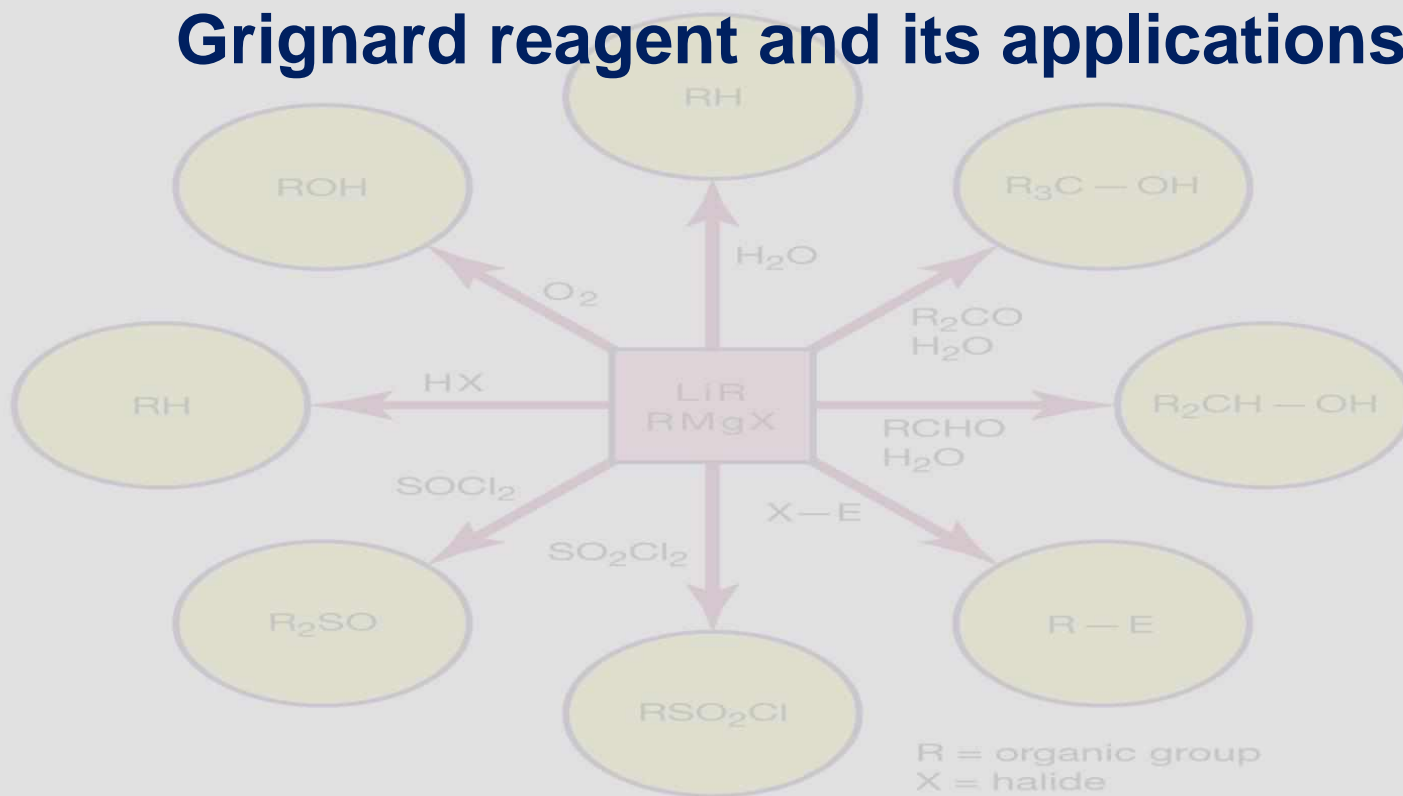
Have metal-ligand bonds between metal and  $\pi$  orbital of organic ligands. Example: Compounds of transition metals with alkenes, alkynes, benzene and other ring systems, such as metallocene. E.g. Ferrocene -  $(C_5H_5)_2Fe$ .



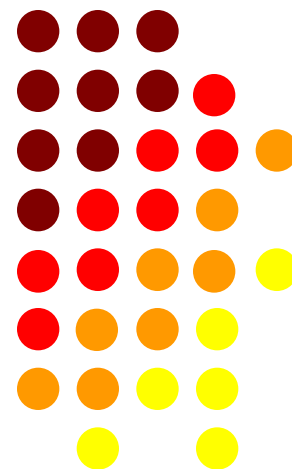


# LECTURE - 40

## Grignard reagent and its applications.



R = organic group  
 X = halide  
 E = B, Si, Ge, Sn, Pb, As, Sb



## GRIGNARD REAGENT

- It is a type of organometallic compound i.e. organo-magnesium compound.
- Grignard reagent has a formula  $\text{RMgX}$  where X is a halogen, and R is an alkyl or aryl (based on a benzene ring) group.
- A typical Grignard reagent might be  $\text{CH}_3\text{CH}_2\text{MgBr}$ .

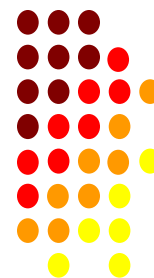


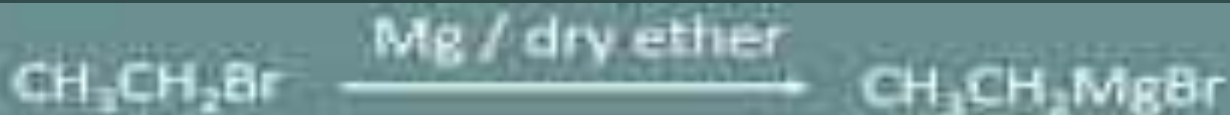
## Preparation of a Grignard reagent

1. Prepared by the action of organic halide and Mg metal in ether or tetra hydro furan.



The reaction is carried out in presence of diethyl ether or tetra hydro furan to avoid the presence of moisture, as G.R. reacts with water to form alkane.





## Characteristics of Grignard reagent

- The bond between C and Mg in Grignard reagent is a polar covalent bond.
- Since carbon is more electronegative in comparison to Mg (electropositive in nature), the shared pair of electron is shifted towards carbon atom.
- Due to this the carbon behaves as a nucleophile.
- So, Grignard reagent shows nucleophilic substitution and nucleophilic addition reactions.



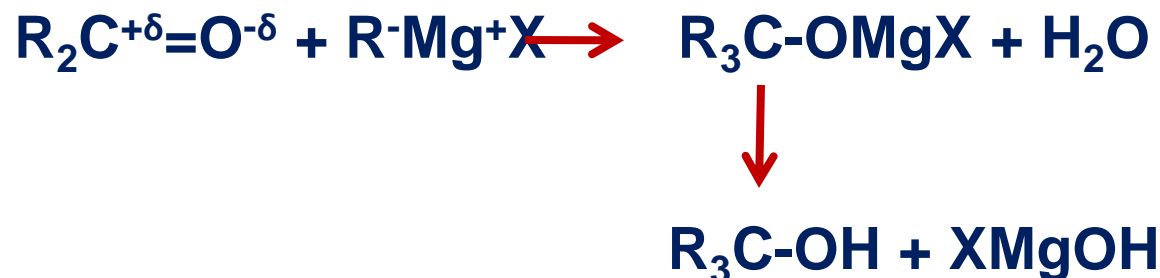
Hence, characteristic reactions of G.R. are:

- Nucleophilic substitution
- Nucleophilic addition

**Nucleophilic Substitution:**



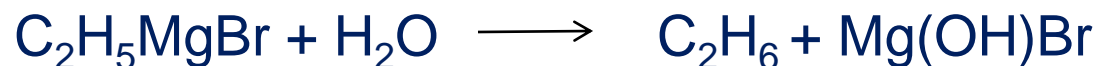
**Nucleophilic Addition:**



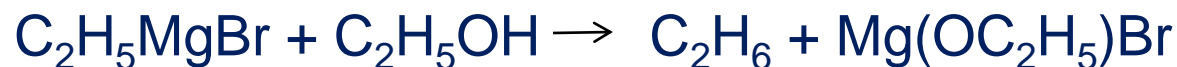
## Applications of Grignard reagent

### 1. Formation of alkanes on reaction with active hydrogen.

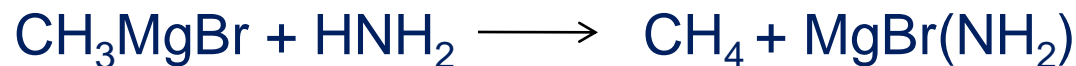
With water:



With alcohol:



With Ammonia:

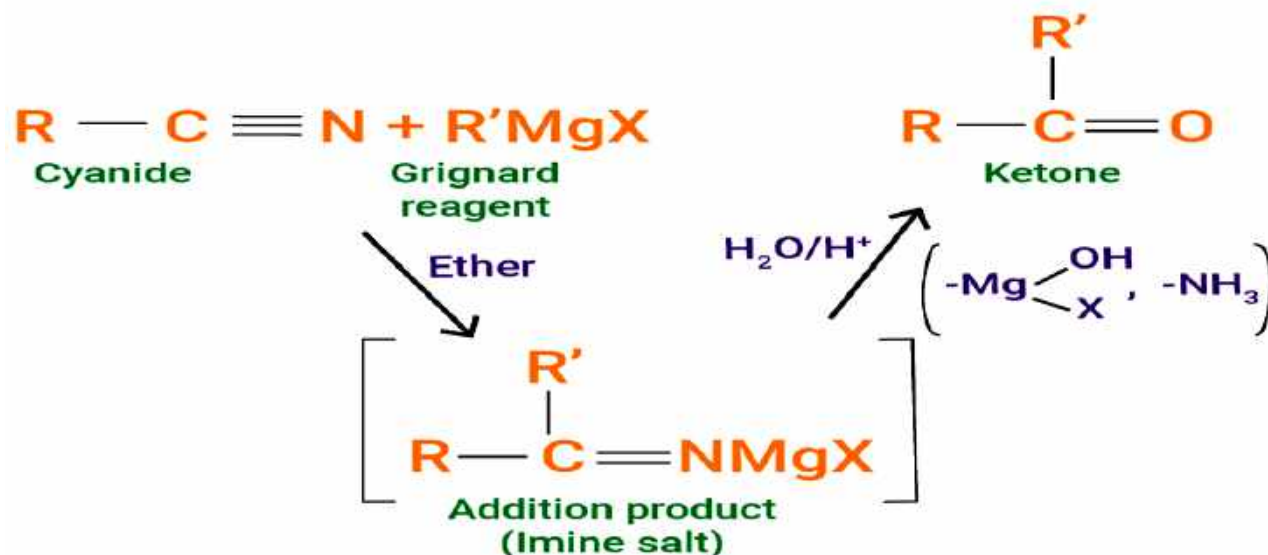


## 2. Formation of amines:

Reaction of G.R. with chloramines

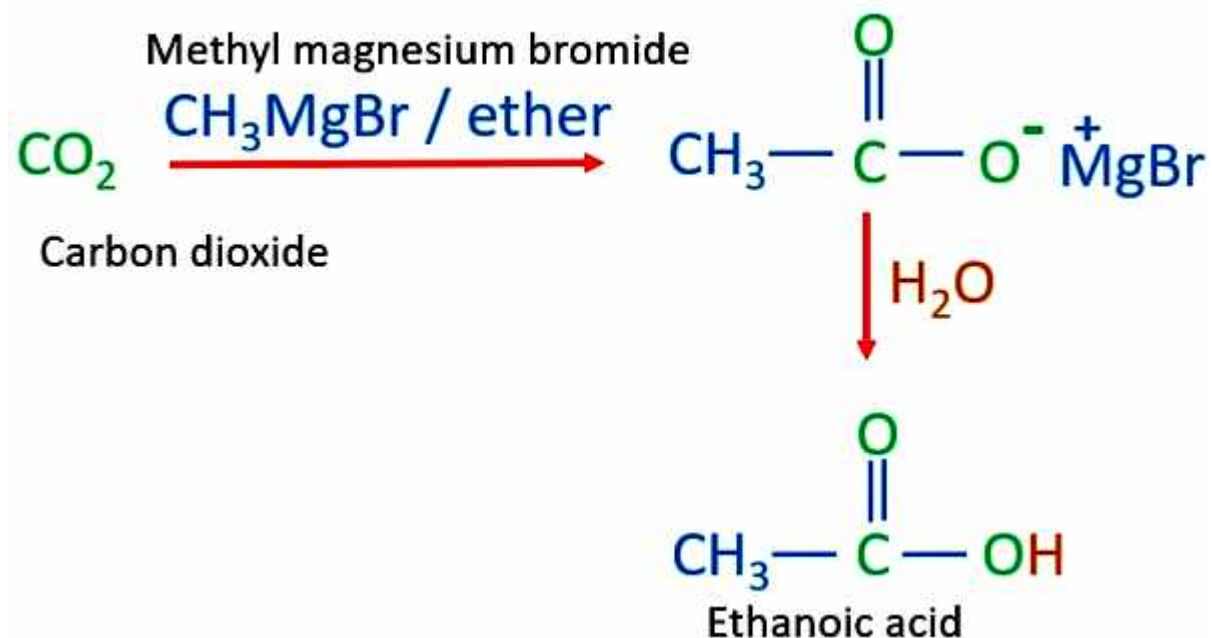


## 3. Formation of ketones: Grignard reagent and cyanides react to give cyanides



## 4. Formation of carboxylic acid

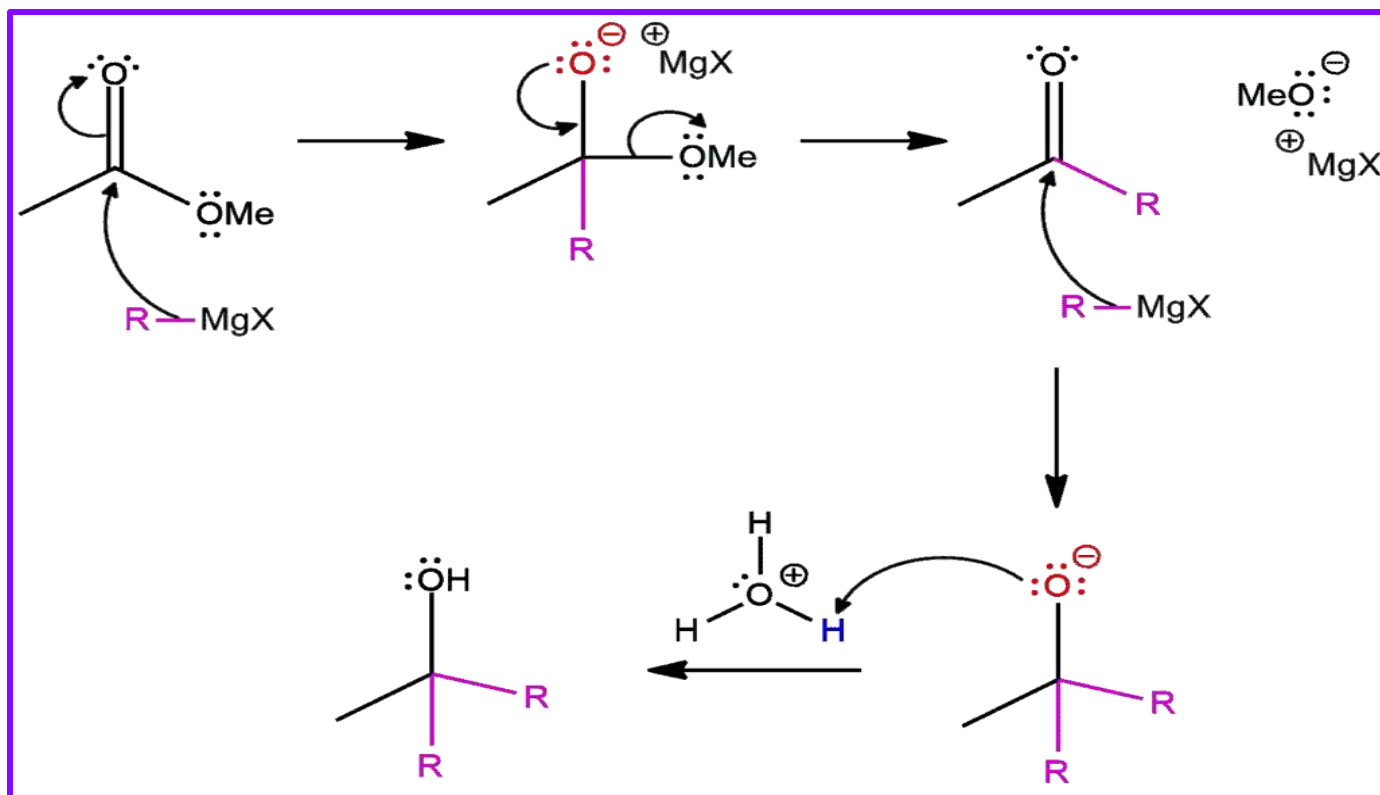
Grignard reagent and  $\text{CO}_2$  reacts to form carboxylic acids.



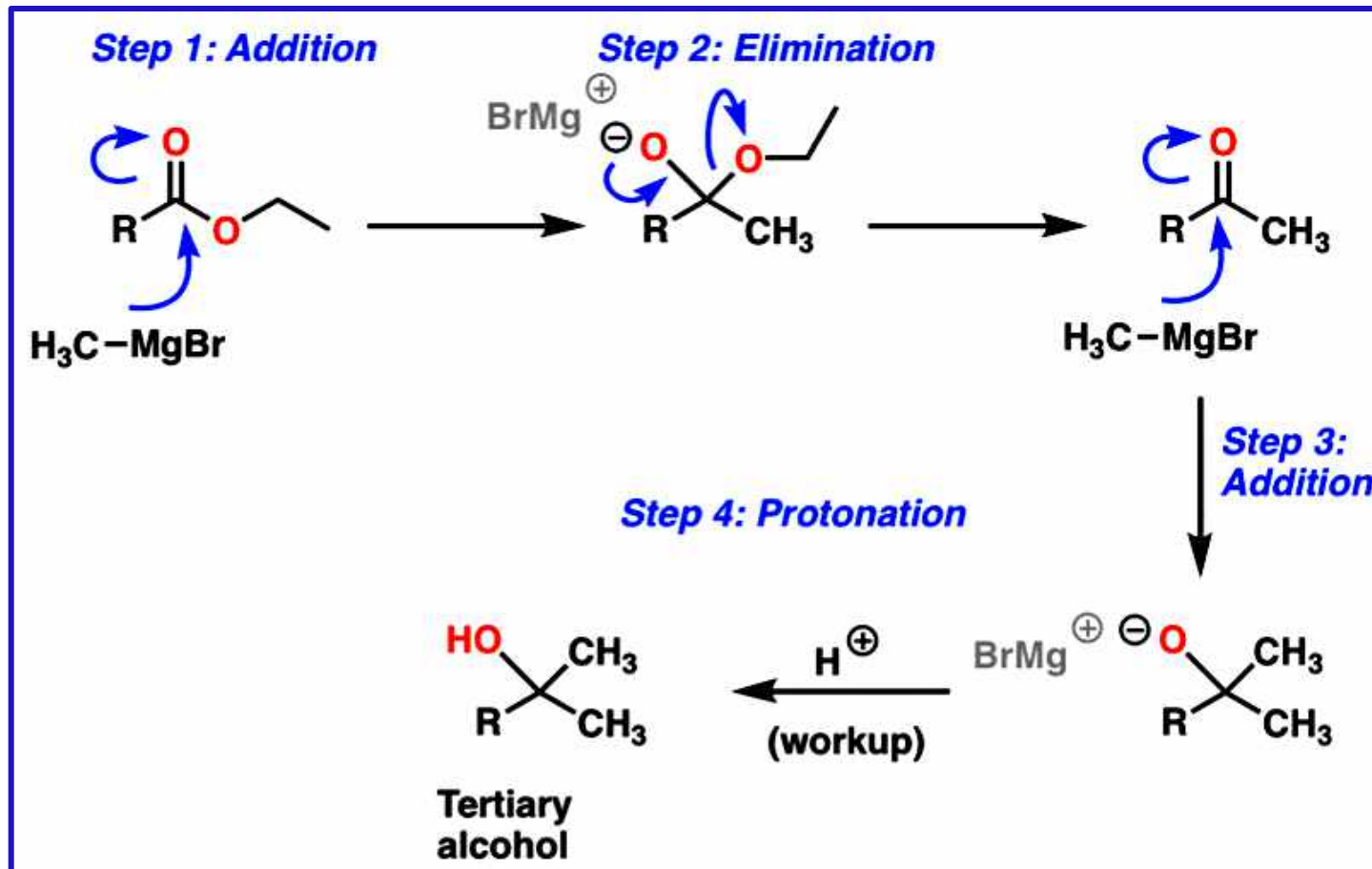


## 7. Reaction with esters:

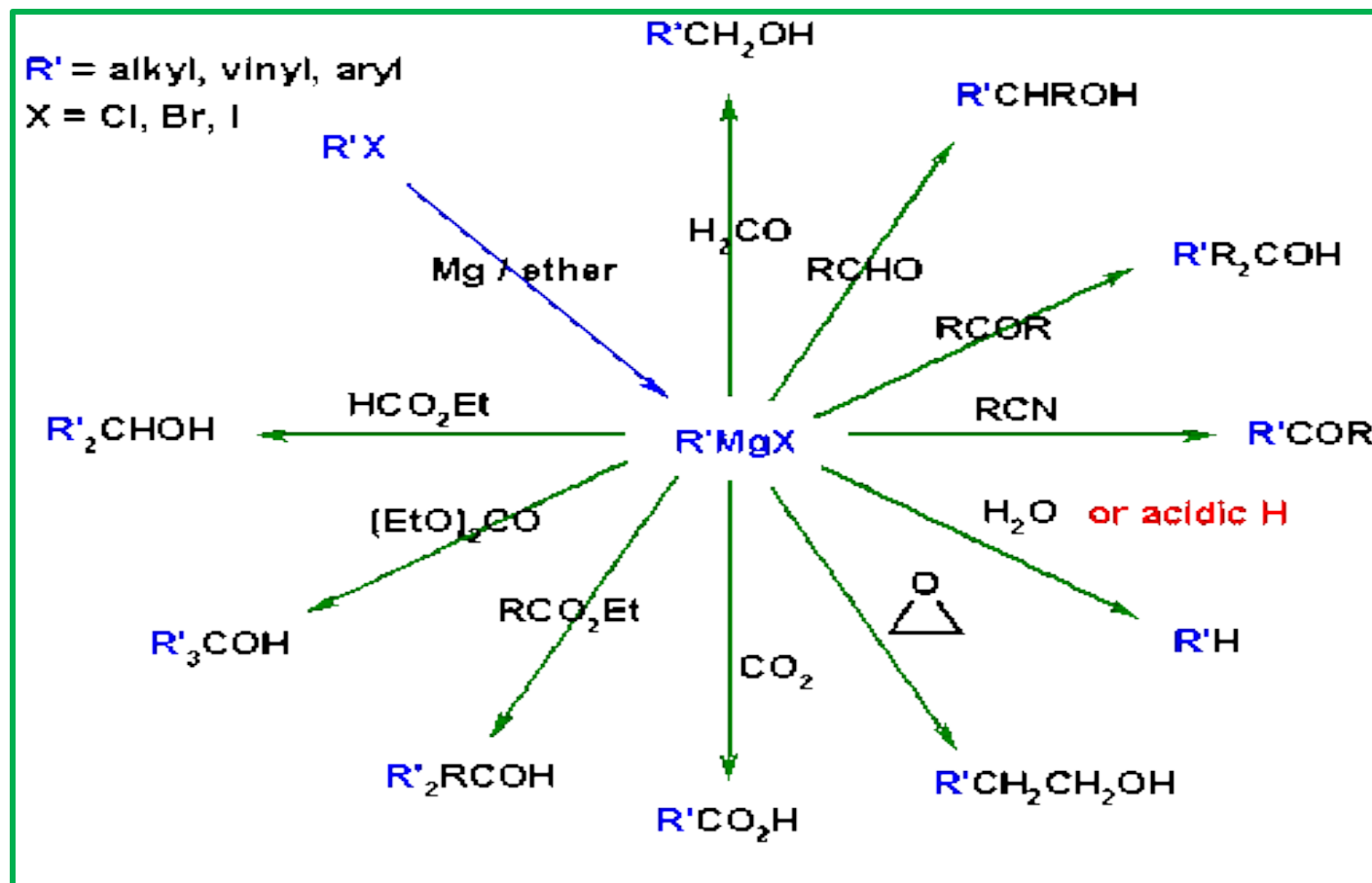
2 molecules of  $\text{RMgX}$  reacts with an ester of formic acid to give secondary alcohol.

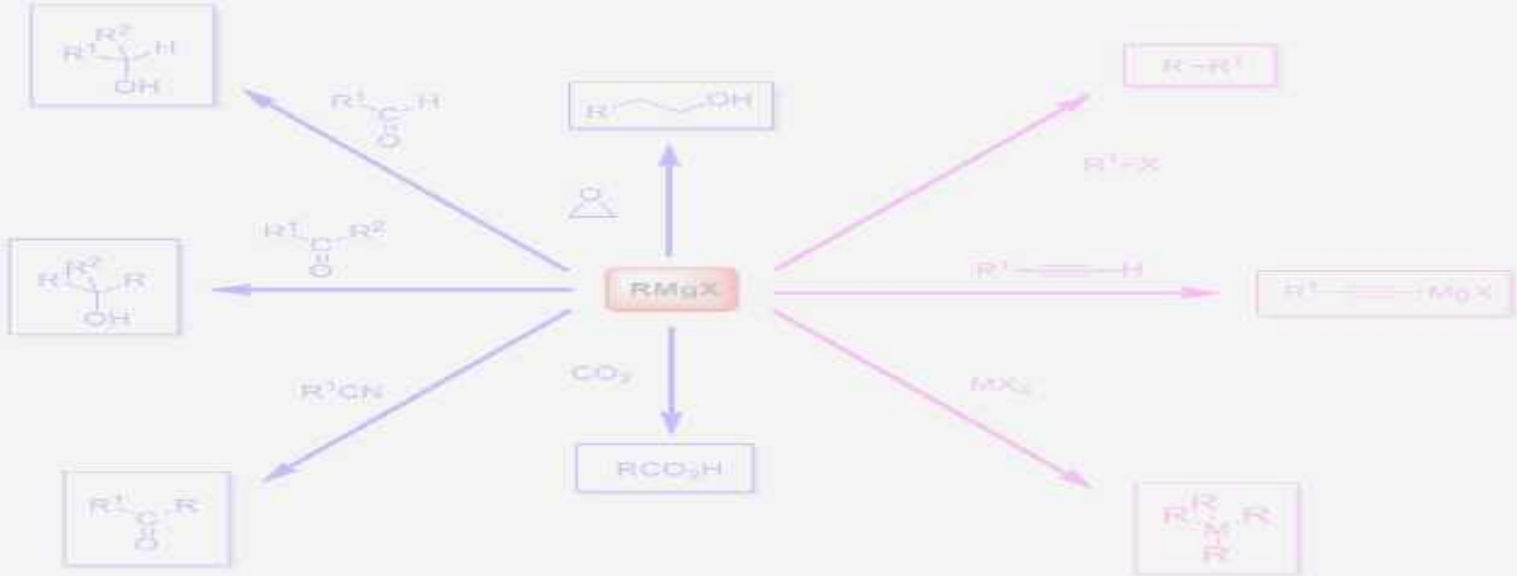


Higher esters react with two molecules of  $\text{RMgX}$  to form tertiary alcohols.

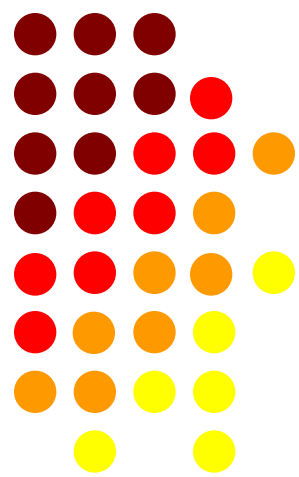
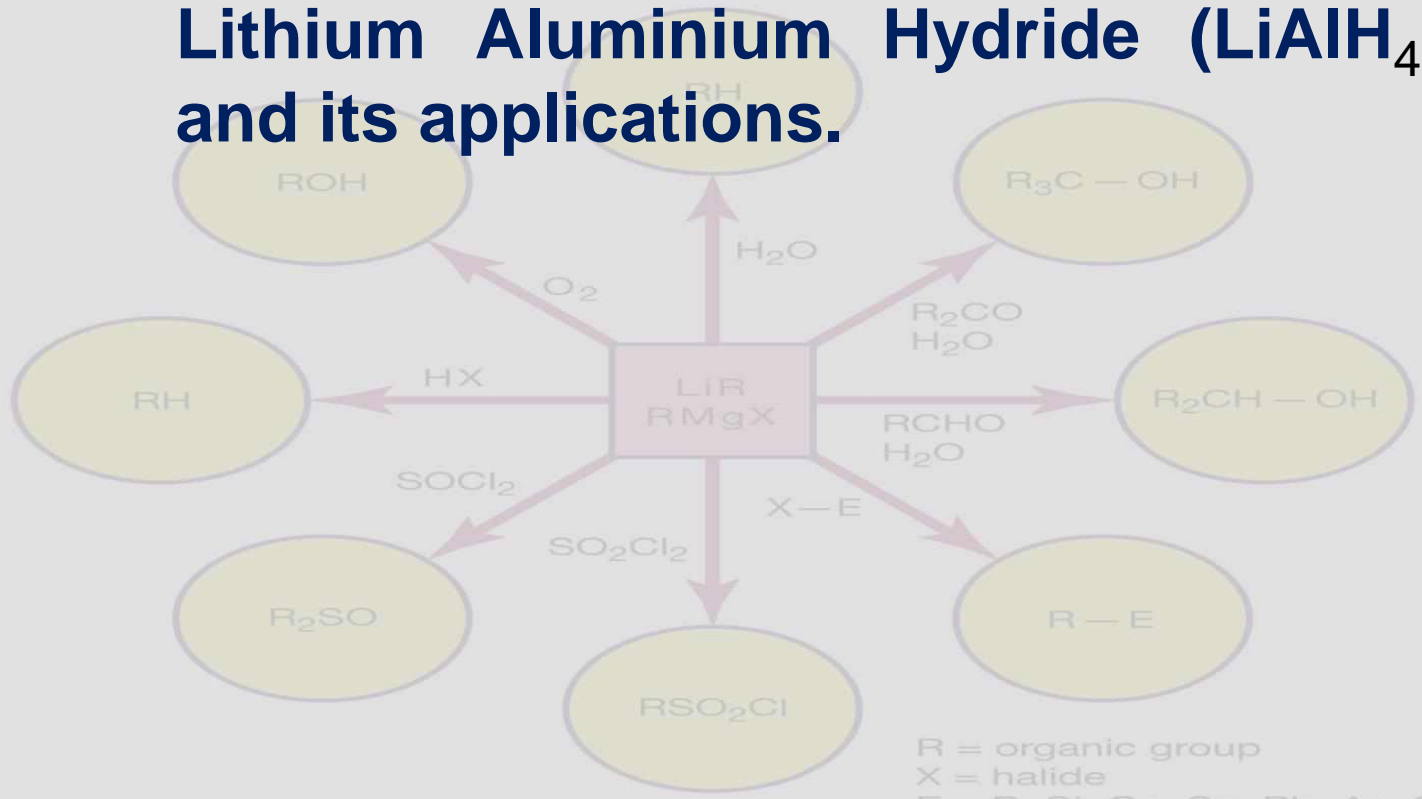


# Summary of reactions of Grignard's reagent with different organic compounds





# Lithium Aluminium Hydride ( $LiAlH_4$ ) and its applications.



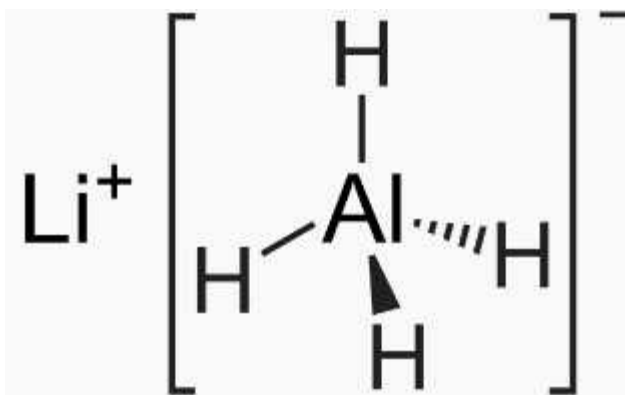
## Lithium Aluminium Hydride ( $\text{LiAlH}_4$ )

- Lithium aluminium hydride,  $\text{LiAlH}_4$ , also abbreviated as LAH, is a reducing agent commonly employed in modern organic synthesis
- It is a nucleophilic reducing agent, best used to reduce polar multiple bonds like  $\text{C}=\text{O}$ .
- $\text{LiAlH}_4$  reagent can reduce aldehydes to primary alcohols, ketones to secondary alcohols, carboxylic acids and esters to primary alcohols, amide and nitriles to amines and epoxides to alcohols.
- Lithium aluminium hydride, LAH reagent cannot reduce an isolated non-polar multiple bond like  $\text{C}=\text{C}$ . However, the double or triple bonds in conjugation with the polar multiple bonds can be reduced.



## Structure of $\text{LiAlH}_4$

- There is a tetrahedral arrangement of hydrogens around  $\text{Al}^{3+}$  in aluminium hydride,  $\text{AlH}_4^-$  ion. It is formed by coordination of hydride,  $\text{H}^-$  ions to  $\text{Al}^{3+}$  ion.
- The hybridization in central Al is  $\text{sp}^3$



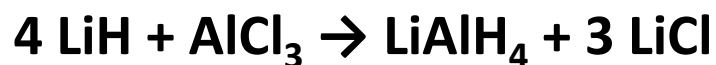
Tetrahedral structure of  $\text{LiAlH}_4$



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

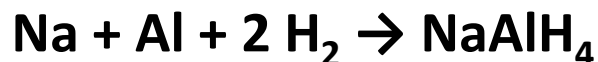
### Method 1: Conventional Method

LiAlH<sub>4</sub> was first prepared from the reaction between lithium hydride (LiH) and aluminium chloride.

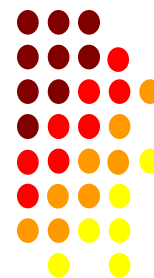


### Method 2: Industrial Method

In addition to above method, the industrial synthesis entails the initial preparation of sodium aluminium hydride from the elements under high pressure and temperature.

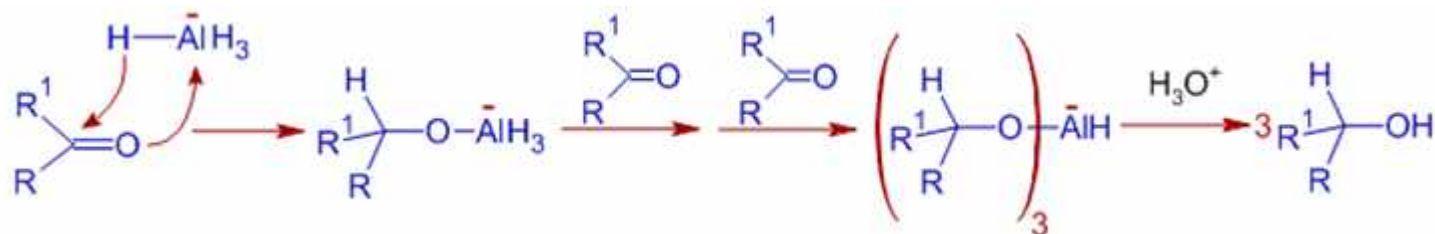


LiAlH<sub>4</sub> is then prepared by a salt metathesis reaction



## Mechanism of reduction by $\text{LiAlH}_4$

Initially, a hydride ion is transferred onto the carbonyl carbon and the oxygen atom coordinates to the remaining aluminium hydride species to furnish an alkoxytrihydroaluminate ion, which can reduce the next carbonyl molecule. Thus three of the hydride ions are used up in reduction.



## Application of $\text{LiAlH}_4$ in organic synthesis

The summary chart of applications of  $\text{LiAlH}_4$  in the reduction of different types of functional groups.

Functional group conversion
<u>Aldehydes, ketones</u> -----> <u>Alcohols</u>
<u>Carboxylic acids</u> -----> <u>Alcohols</u>
<u>Esters, acid halides</u> -----> <u>Alcohols</u>
<u>Amides</u> -----> <u>amines</u>
<u>Nitriles</u> -----> <u>amines</u>
<u>oxiranes (epoxides)</u> -----> <u>alcohols</u>
<u>lactones</u> -----> <u>diols</u>
<u>haloalkanes, haloarenes</u> -----> <u>alkanes, arenes</u>

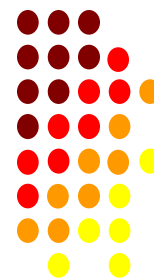
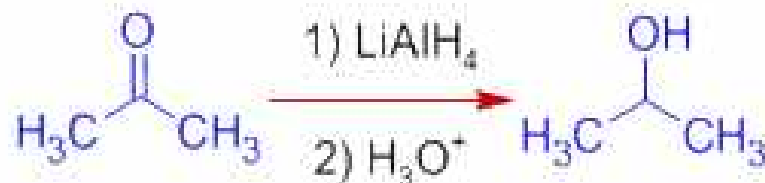
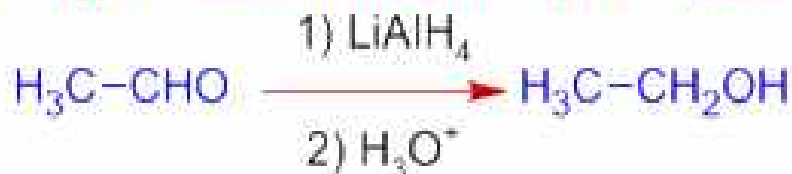


## Reduction of carbonyl compounds using $\text{LiAlH}_4$

1. The aldehydes or ketones are reduced by  $\text{LiAlH}_4$  to the corresponding primary or secondary alcohols respectively.

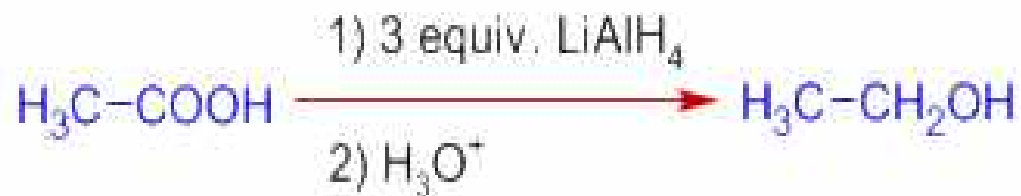
E.g. Acetaldehyde is reduced to ethyl alcohol and acetone is reduced to isopropyl alcohol.

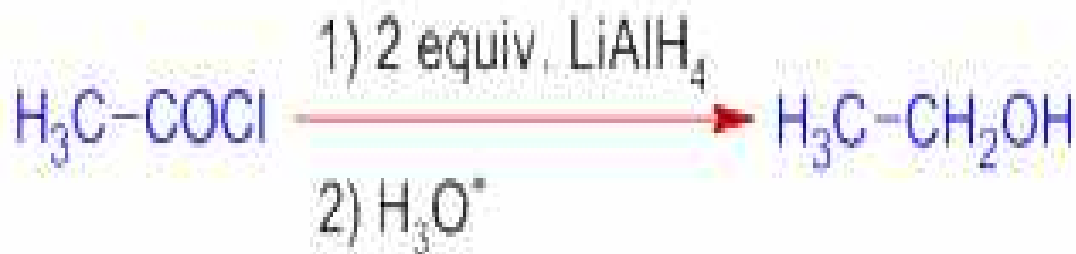
### $\text{LiAlH}_4$ Reduction of carbonyl compounds



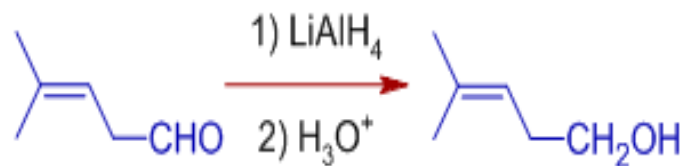
2. The carboxylic acids, esters and acid halides are reduced to corresponding primary alcohols by Lithium aluminium hydride.

E.g. The reduction of Acetic acid, methyl acetate and acetyl chloride by  $\text{LiAlH}_4$  furnish the same ethyl alcohol.



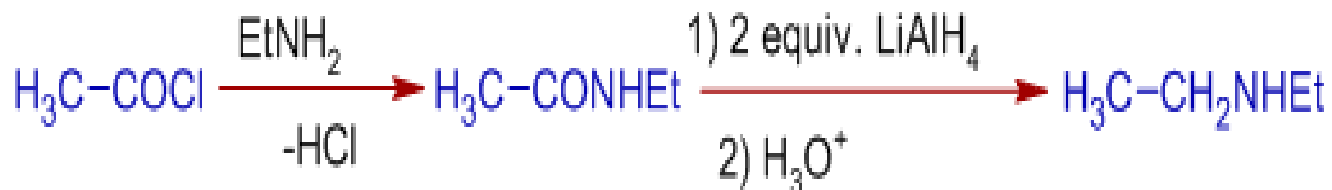


$\text{LiAlH}_4$  does not affect the isolated carbon-carbon double or triple bonds



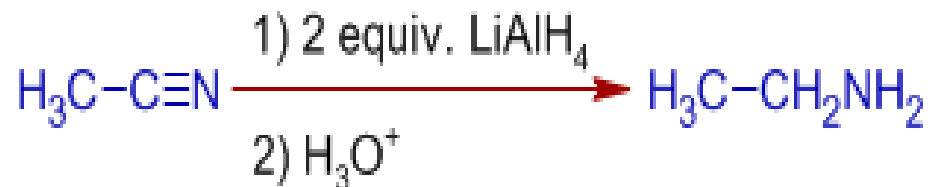
3. The amides are reduced to amines by Lithium aluminium hydride,  $\text{LiAlH}_4$ . Especially this method is used to get secondary amines.

E.g. Diethyl amine can be prepared starting from acetyl chloride as follows:



4. The nitriles are reduced to primary amines by  $\text{LiAlH}_4$ .

E.g. Acetonitrile is reduced to ethyl amine by  $\text{LiAlH}_4$ .



5. The haloalkanes and haloarenes are reduced to corresponding hydrocarbons by Lithium aluminium hydride.

