

## INTRODUCTION

Polymers are the giant molecules produced by the combination of smaller units or molecules. Polymers possess the desirable properties like high strength, light weight, good flexibility, special electrical properties, resistance to chemicals, amenability for quick and mass production and fabrication into complex shapes in a wide variety of colours.

Due to the extraordinary range of properties accessible in polymeric materials, they have come to play an essential and ubiquitous role in everyday life—from plastics and elastomers on the one hand to natural biopolymers such as DNA and proteins that are essential for life on the other. A simple example is polyethylene, whose repeating unit is based on ethylene monomer. Most commonly, as in this example, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms. However, other structures do exist; for example, elements such as silicon form familiar materials such as silicones, examples being silly putty and waterproof plumbing sealant. The backbone of DNA is in fact based on a phosphodiester bond, and repeating units of polysaccharides (e.g. cellulose) are joined together by glycosidic bonds via oxygen atoms.

## HISTORICAL ACCOUNT:

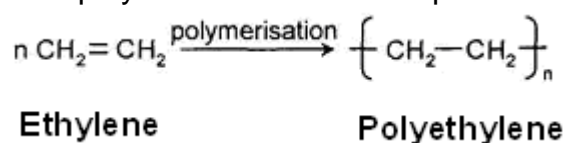
Starting in 1811, Henri Braconnot did pioneering work in derivative cellulose compounds, perhaps the earliest important work in polymer science. The development of vulcanization later in the nineteenth century improved the durability of the natural polymer rubber, signifying the first popularized semi-synthetic polymer. In 1907, Leo Baekeland created the first completely synthetic polymer, Bakelite, by reacting phenol and formaldehyde at precisely controlled temperature and pressure. Bakelite was then publicly introduced in 1909.

## BASIC CONCEPTS

The word polymer is derived from the Greek words polu- meaning "many"; and meros meaning "part". The term was coined in 1833 by Joens Jakob Berzelius.

Many of small molecules (monomers) combine (with covalent bond chains) to form giant molecule(s). This process is called polymerization. During the polymerization process, some chemical groups may be lost from each monomer.

For example, in the polymerization of PET polyester. The monomers are terephthalic acid (HOOC-C<sub>6</sub>H<sub>4</sub>-COOH) and ethylene glycol (HO-CH<sub>2</sub>-CH<sub>2</sub>-OH) but the repeating unit is -OC-C<sub>6</sub>H<sub>4</sub>-COO-CH<sub>2</sub>-CH<sub>2</sub>-O-, which corresponds to the combination of the two monomers with the loss of two water molecules. The distinct piece of each monomer that is incorporated into the polymer is known as a repeat unit or monomer residue.



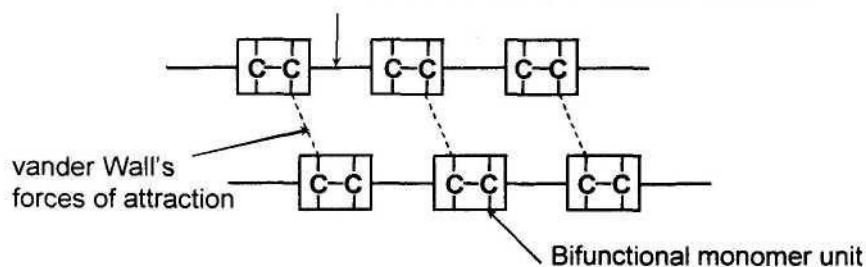
Depending on the degree (No. of Monomer units) of polymerisation, there are two types of polymers.

1. **Oligopolymers:** Those polymers whose degree of polymerisation is less than 600 are called oligopolymers. These polymers do not possess the engineering properties.
2. **Highpolymers:** When the degree of polymerisation of a polymer is more than 600, it is called *high polymer*. High polymers possess the desired engineering properties and widely used.

### Functionality of Monomers:

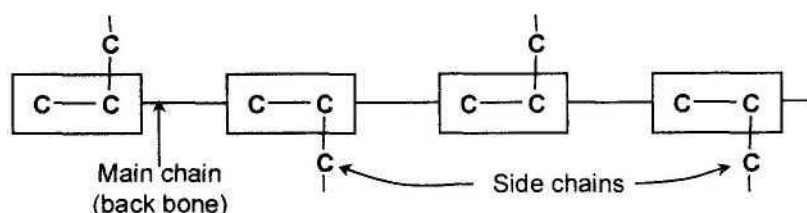
For a substance to act as a monomer, it must have *at least two reactive sites or bonding sites*. The number of reactive sites or bonding sites in a monomer is called *functionality of the monomer*.

If two reactive sites are there in a monomer then it is called *bifunctional*. The two reactive groups are attached on either side of the bifunctional molecule forming a *linear or straight - chain molecule*. The monomer molecules in a linear chain are linked by primary covalent bonds and the different chains are held together by *secondary vander Waal's* forces of molecular attraction. The chain movement is possible only in one direction as shown below.

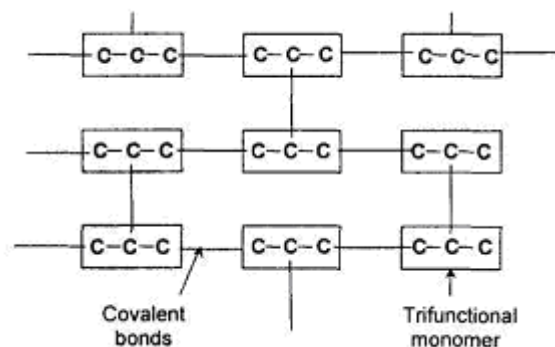


**Bifunctional linear chain molecule**

A trifunctional monomer has three reactive sites. If *three reactive sites* are there in a monomer, then it gives *branched chain polymer*. During the chain growth the side chains may be formed producing branched chain molecules. The chain movement is more restricted in branched chain polymer which is also produced, by mixing trifunctional monomers with bifunctional monomers.



A polyfunctional monomer contains more than three reactive sites. If the number of reactive sites is more than three in a monomer molecule, the three dimensional network of polymer is produced where the movement of the individual molecule is restricted as shown below.



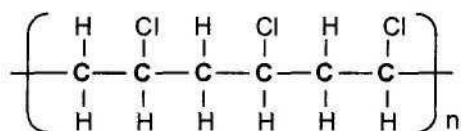
### Nomenclature of polymers:

'Poly' is the term used before the name of monomer or compound, indicating the compound to be a polymer for example *polyethylene* polystyrene, polybutadiene etc.

**Tacticity of polymers** : The arrangement of functional groups on carbon backbone of the polymer is called *tacticity of the polymer*. Depending on the tacticity, there are three different types of polymers.

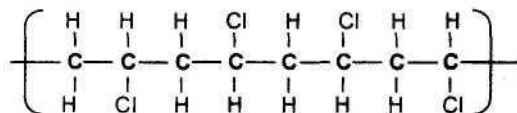
**1. Isotactic polymers (iso-similar):** The polymers in which the functional groups are arranged on the same side are called isotactic polymers.

For example : Poly Vinyl Chloride (PVC)



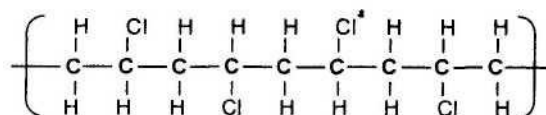
**2. Atactic polymers:** The polymers in which the functional groups are arranged irregularly are called atactic polymers.

For example ■ Poly Vinyl Chloride (PVC)



**3. Syndiotactic polymers:** The polymers with alternate arrangement of functional groups are called syndiotactic polymers.

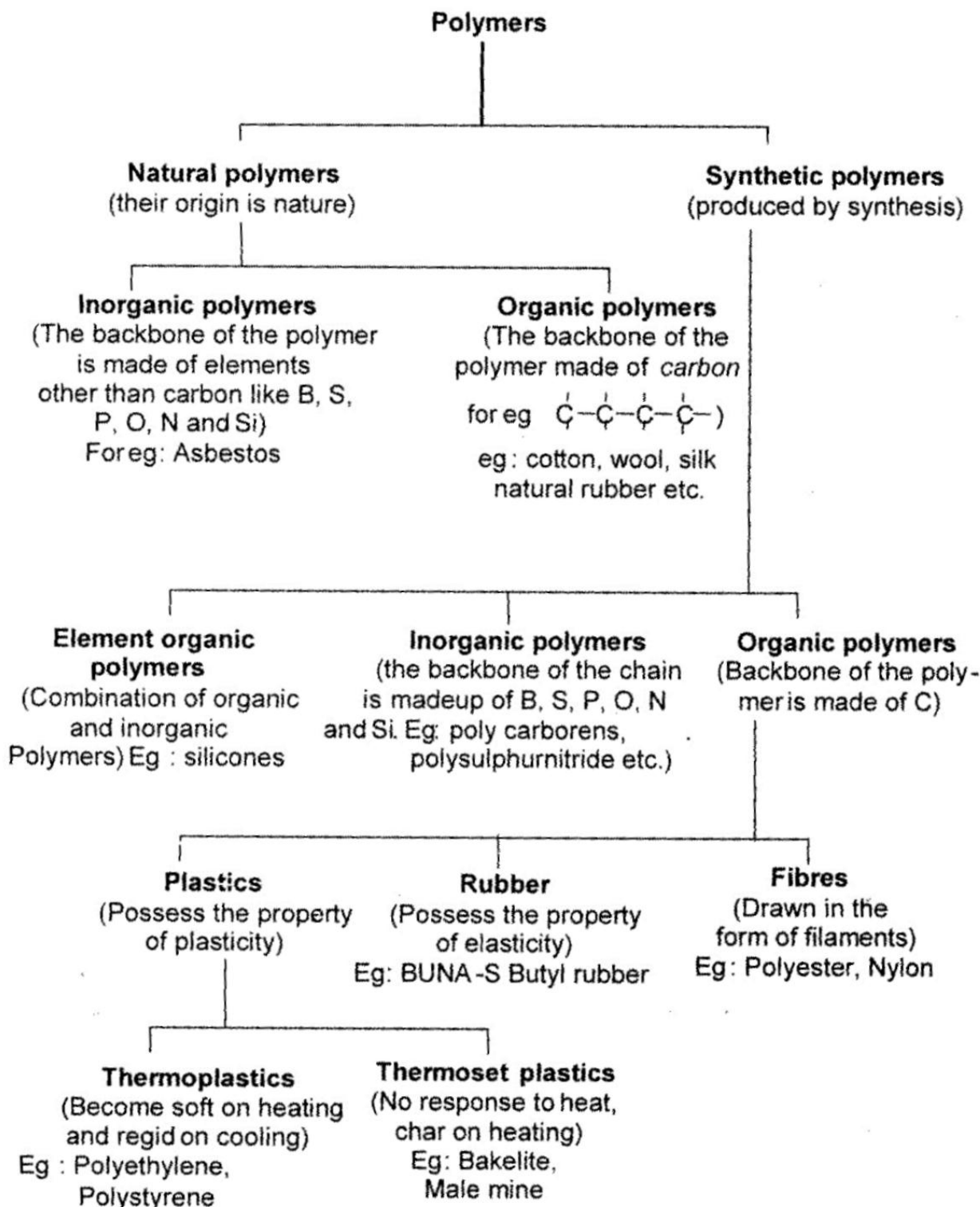
For example : Poly Vinyl Chloride (PVC)



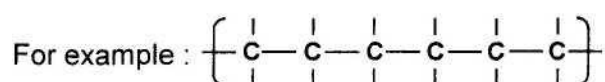
### Classification of the Polymers:

Based on their origin and nature polymers can be classified in the following way

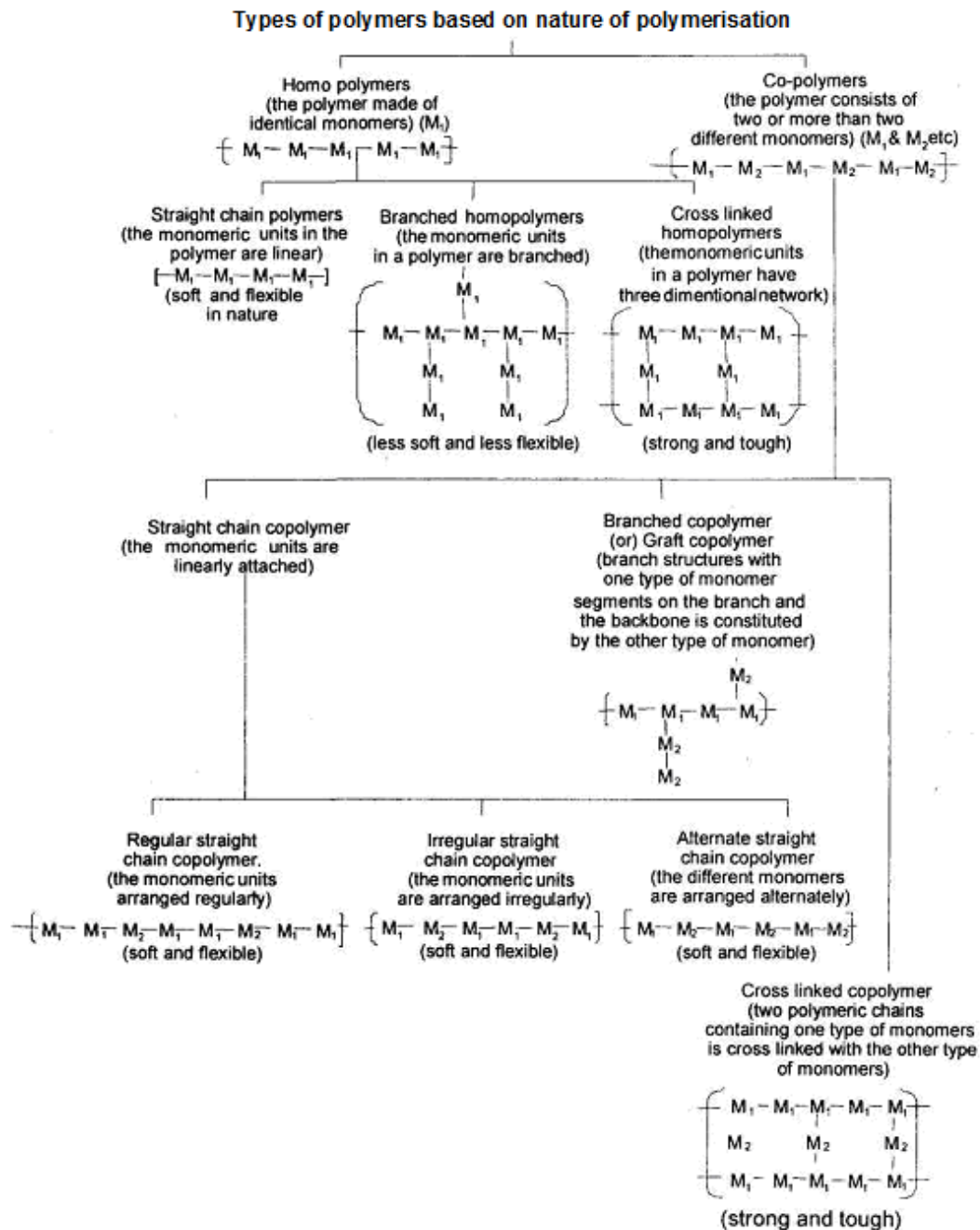
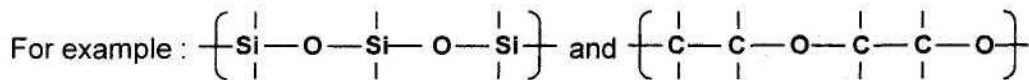
## Classification of Polymers



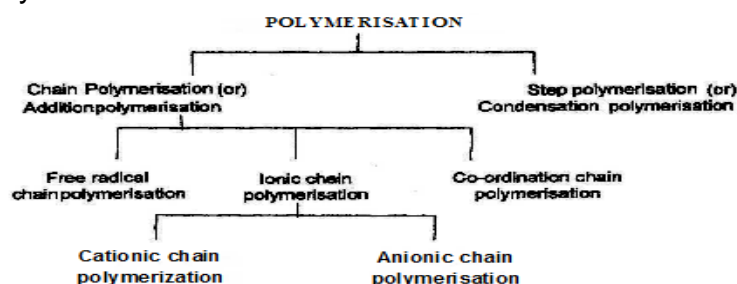
**Homochain polymers:** These polymers whose back bone (main chain) is made up of some type of atoms.



**Heterochain polymers:** These polymers are constituted by two or more than two different types of atoms in their structure.



Mechanism of Polymerisation:



### Chain Polymerisation:

A chain Polymerisation is a reaction that yields a polymer product which is the exact multiple of monomers. Thus the mechanism is also called addition Polymerisation. The following are the characteristics.

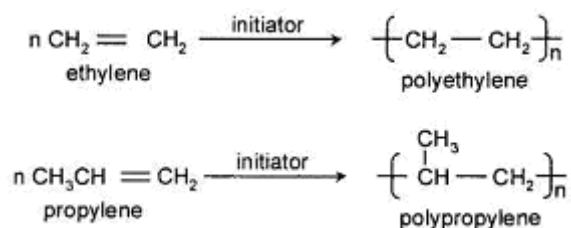
1. The functionality of the monomer is a *double bond* and it is *bifunctional*.
2. The polymerisation takes place by *self-addition* of the monomer molecules to each other. Through a *chain reaction*.
3. No biproducts like H<sub>2</sub>O, CH<sub>3</sub>OH etc., are produced.
4. The polymer has the same chemical composition as that of monomer.
5. The molecular weight of the polymer is the exact multiple of the monomers.
6. The mechanism is carried out in three steps, i.e. initiation, propagation and termination.
7. The mechanism is rapid.
8. The conversion of a *n* bond to a bond takes place during the polymerisation, liberating 20 k.cal/mole of energy. Hence highly exothermic reactions.
9. An initiator is required to start the polymerisation reaction

The compounds containing *double bonds* undergo chain polymerisation.

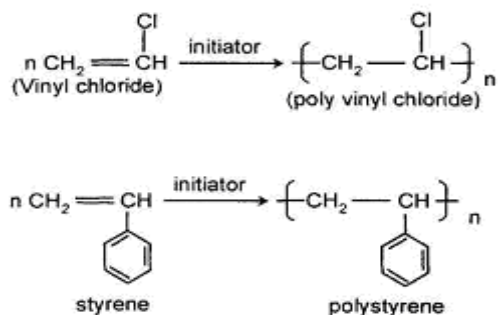
For example :

- 1) olefins
- 2) vinyl
- 3) allyl and
- 4) dienes.

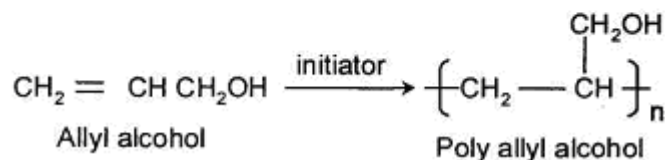
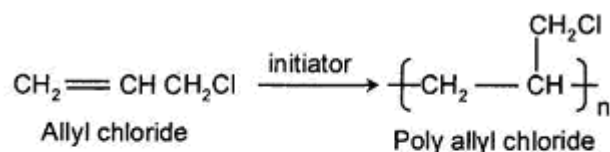
**Olefins:** Olefins like ethylene, propylene, I-butene etc.



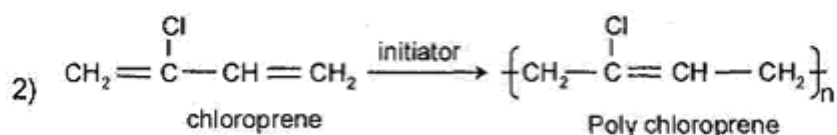
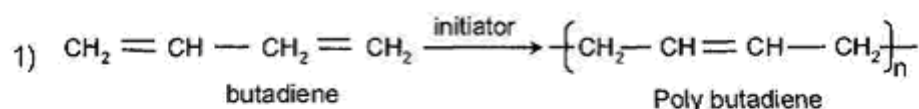
**Vinyl compounds:** The general representation of vinyl compounds is CH<sub>2</sub> = CHX, where X = halide, acid, alcohol, amine, phenyl etc.



**Allyl compounds:** The general formula of allyl compounds is  $\text{CH}_2 = \text{CH} \cdot \text{CH}_2\text{X}$ , where X can be halide, alcohol, ester etc.



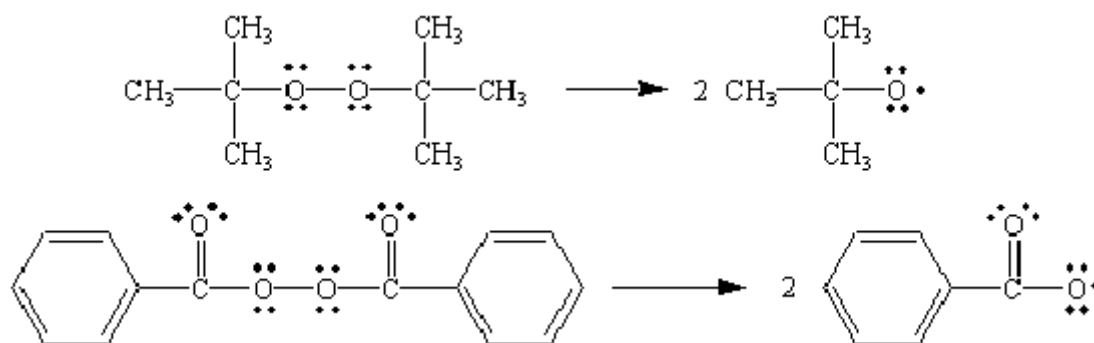
**Dienes:** Dienes has the general formula  $\text{CH}_2 = \text{CH} - \overset{\text{X}}{\underset{|}{\text{C}}} = \text{CH}_2$ , where X = H, halogen or alkyl group.



Chain polymerisation is initiated by Initiators and carried out in three different ways.

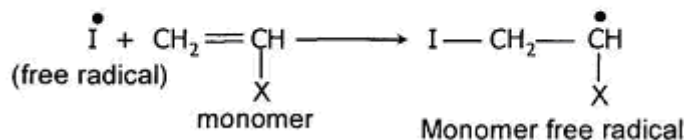
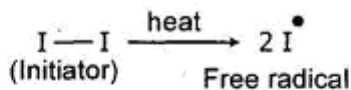
- 1) **Freeradical chain polymerisation:** The freeradical chain polymerisation can be of homolytic fission process or heterolytic fission process.

The *initiator* undergoes homolytic fission to produce *free radicals*, which initiates and propagates (rapid chain growth) the polymerisation reaction as given below. Ex. Bynzoyl peroxide(di-tert-butyl peroxide)

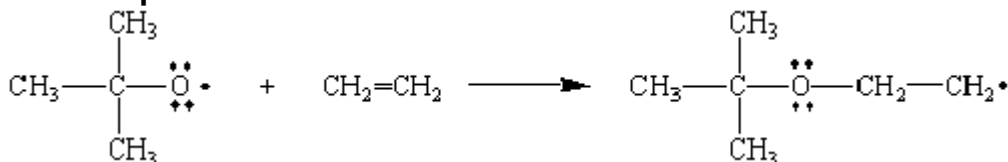


- a. **Initiation:** Initiators are unstable compounds and undergo *homolytic fission* to produce *free radicals* which react with *n* electrons of the monomer to produce *monomer free radical*.

**Theory:**

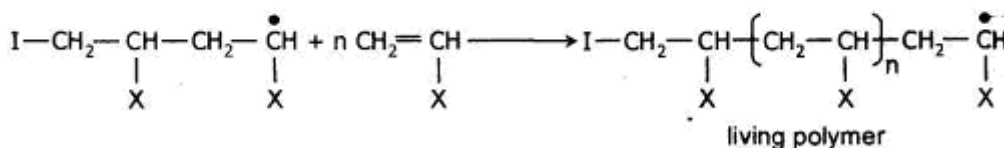
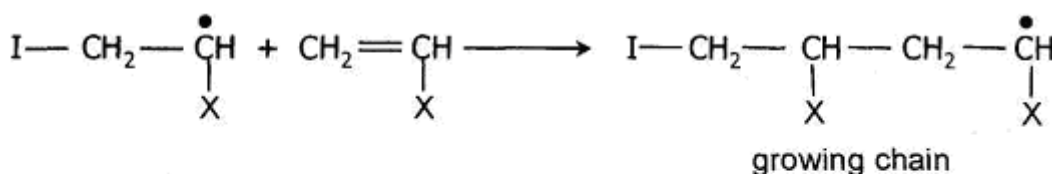


**Example:**

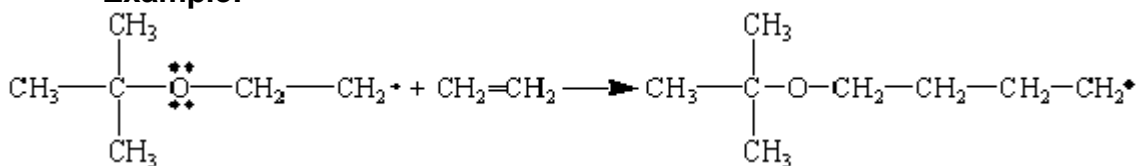


**b. Propagation:** The monomer free radical reacts with a number of monomers rapidly resulting the chain growth with free radical site at the end of the chain producing a *living polymer*. By adding fresh monomers to the living polymer with free radical site, again chain growth starts. Hence it is known as *living polymer*.

**Theory:**

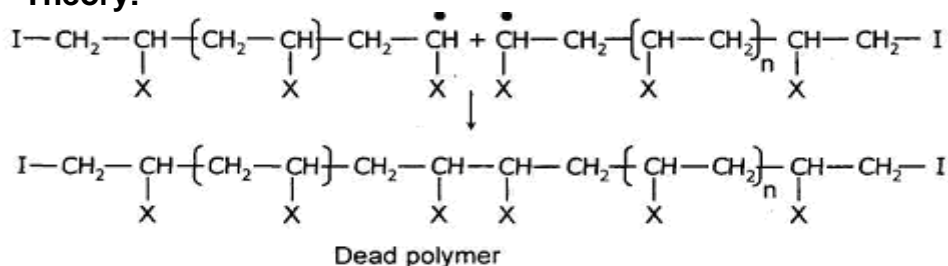


**Example:**



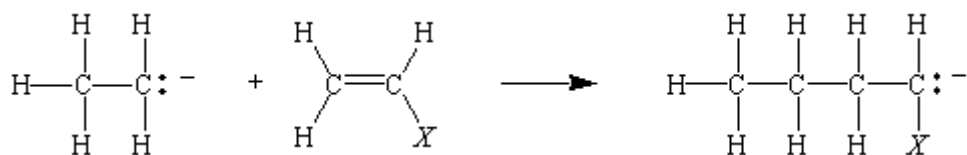
**c. Termination:** Termination (to stop chain growth) of the growing polymer chain is carried by '*coupling*' and '*disproportionation*', resulting the dead polymer. In *coupling*, the collision of two growing chains causes the union of the two chains at their free radical site producing a *dead polymer*.

**Theory:**

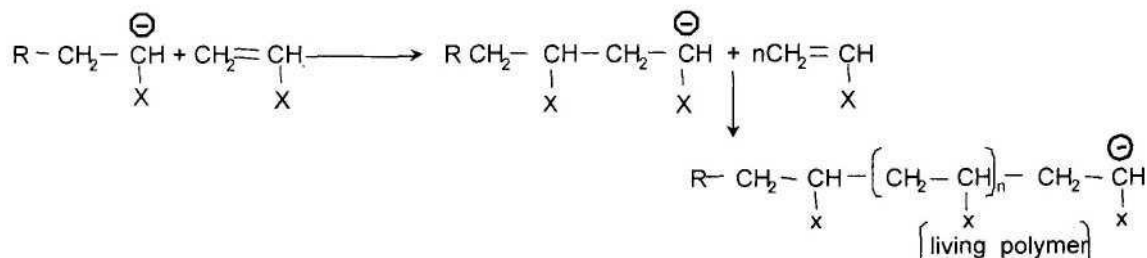




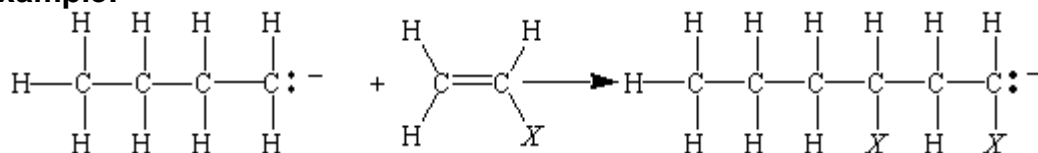




**b) Propagation:** Attack of the monomers by monomer carbanion results in chain growth as shown below.

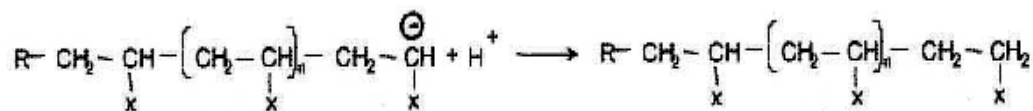


**Example:**

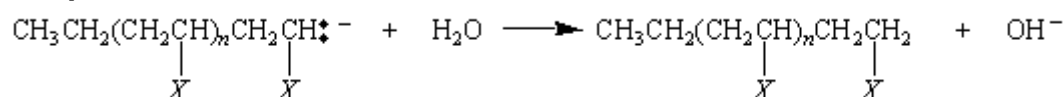


**c) Termination:** Termination of the chain is carried out by a  $\text{H}^+$  ion

**Theory:**



**Example:**

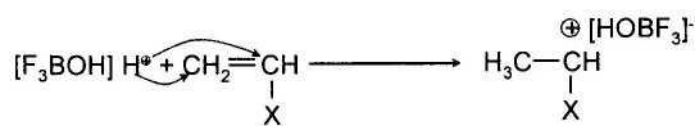


### Cationic chain polymerisation:

The polymerisation that results because of the production of cation due to the initiator attacks the  $n$  electrons of the monomer forming a *monomer carbonium ion* is known as *Cationic Chain Polymerisation*.

**a) Initiation:**

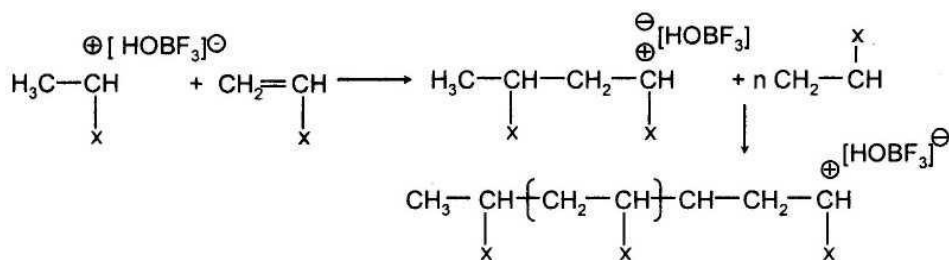
The strong Lewis acids like  $\text{BF}_3$ ,  $\text{AlCl}_3$  etc., (generally called as catalyst) in presence of small amount of water (generally called cocatalyst) initiates the reaction as follows.



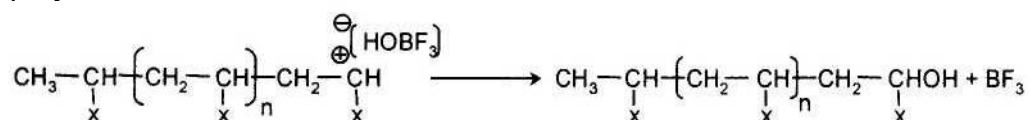
(monomer carbocation)

$[\text{HOBF}_3]^-$  is called *counter ion*, because it is always with carbonium ion of the monomer.

**b) Propagation:** The monomer carbocation attacks the  $n$  electrons of the other monomers resulting the chain growth with carbocation at the end of the chain.



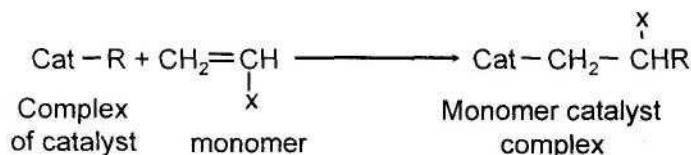
**c) Termination:** Termination of cationic chain polymerisation is done by coupling where the  $\text{OH}^-$  ion from the counter ion terminates the polymerisation.



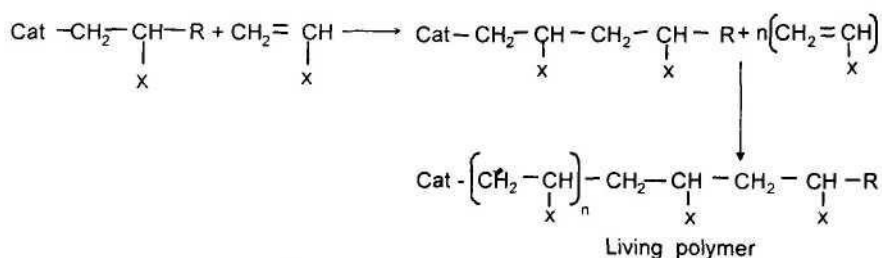
### Co-ordination polymerisation or Zeigler - Natta polymerisation:

Zeigler (1953) and Natta (1955) discovered that in the presence of a combination of transition metal halides like  $\text{TiCl}_4$ ,  $\text{ZnBr}_3$  etc, with an organometallic compounds like triethyl aluminium or trimethyl aluminium, stereospecific polymerisation can be carried out. Combination metal halides and organometallic compounds are called *Zeigler Natta catalysts*. The mechanism of polymerisation is given below.

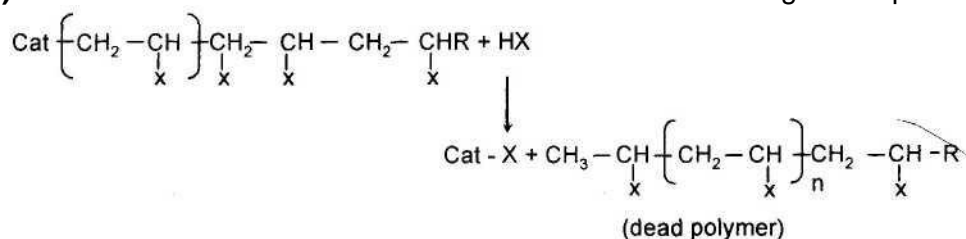
**a) Initiation:** The catalyst form monomer catalyst complexes by reacting with monomer molecule.



**b) Propagation:** The monomer catalyst complex reacts with fresh monomers resulting the chain growth as shown below.



**c) Termination:** Termination is carried out with an active halogen compound.



**PLASTICS, THERMOPLASTIC AND THERMOSET RESINS:**

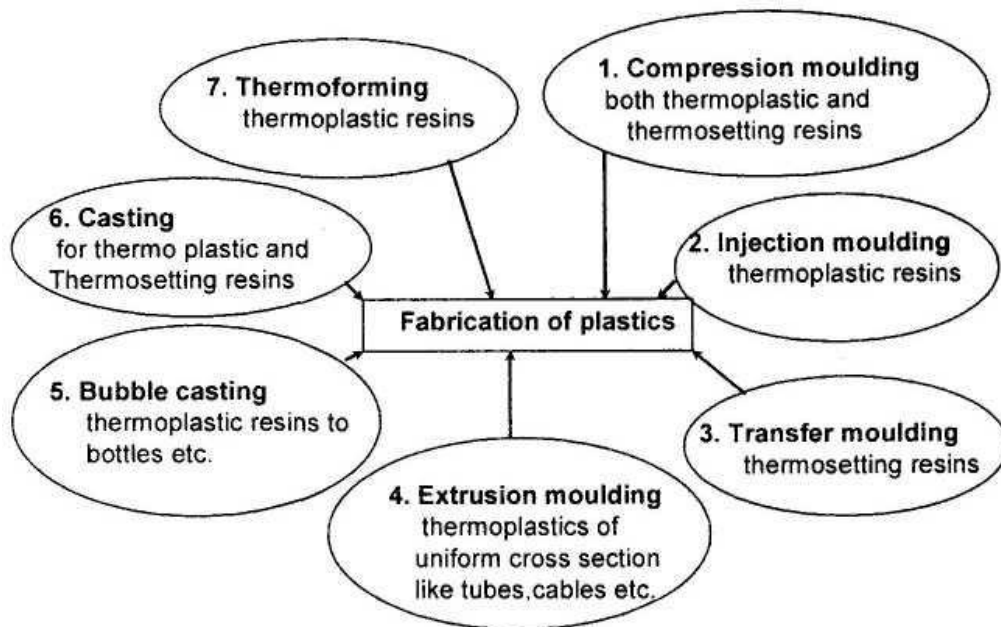
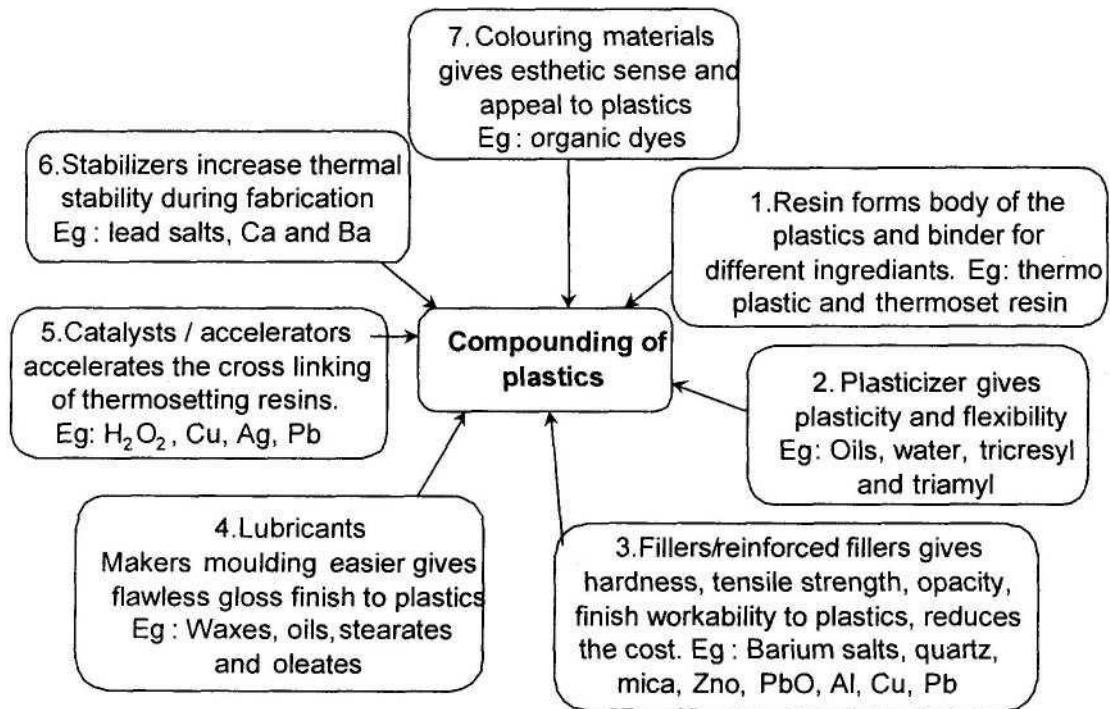
Plastics are the polymers characterised by the property of plasticity (permanent deformation in structure on applying some stress/force), moulded to desired form, when subjected to heat and pressure in presence of catalyst. The term 'plastic' and 'resin' are considered to be synonymous. A resin is the *product of polymerisation* and forms the major part of the plastics. *Plastics* are the materials obtained by the mixing the resin with other ingredients to impart special engineering properties.

Plastics are characterised by light weight, good thermal and electrical insulation, corrosion resistance, chemical inertness, adhesiveness, and easy workability, low fabrication cost, high abrasion resistance, dimensional stability, strength, toughness and impermeability to water.

The plastic resins are broadly classified into two categories thermoplastic resins and thermoset resins. The following are the characteristic differences.

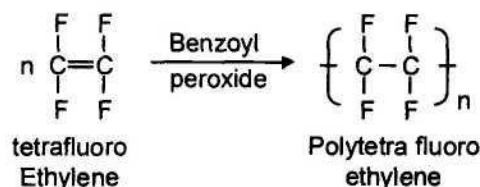
SNO	THERMOPLASTIC RESINS	THERMOSET RESINS
1.	These resins become soft on heating and rigid on cooling.	During fabrication process these resins are moulded. Once moulded or shaped, they can not be softened.
2.	The heating and cooling do not alter the chemical nature of these resins because the changes involved are purely of physical nature.	These resins are permanent setting resins.
3.	Thermoplastic resins are formed by chain polymerisation.	Thermoset resins are formed by step polymerisation.
4.	They consist of long chain linear polymers with weak secondary van der Waals forces of attraction in between.	They have three dimensional network structures.
5.	They are softened on heating readily because the secondary force of attraction between the individual chains can break easily by heat, pressure or both.	The bonds retain their strength on heating hence do not soften on heating.
6.	They can be reshaped.	They cannot be reshaped
7.	These plastics can be reclaimed from waste.	They cannot be reclaimed from waste.
8.	Thermoplastic resins are soft, weak and less brittle.	Thermoset resins are hard, strong and more brittle.
9.	These resins are usually soluble in organic solvents. Eg: Polyethylene, polyvinyl chloride etc.	Due to strong bonds and cross links, they are insoluble in almost all organic solvents. Eg: Bakelite, Nylon etc.

**COMPOUNDING AND FABRICATION OF PLASTICS:**

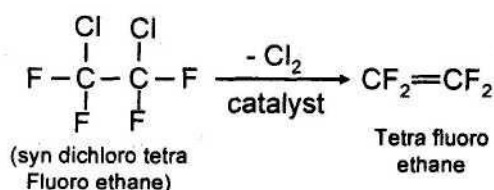


**Some of the useful Plastics:****Teflon(Polytetra fluoro ethylene) or Fluon +CF<sub>2</sub>- CF<sub>2</sub>-}n:**

TEFLON is obtained by the chain polymerisation of tetrafluoro ethylene in presence of benzoyl peroxide as an initiator



Tetra fluoro ethylene is produced by dechlorination of syn dichlorotetrafluoroethane in presence of a catalyst.

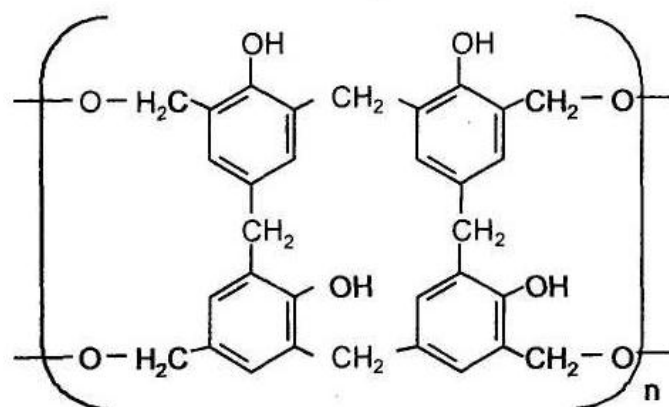
**Properties:**

Due to the presence of highly electronegative fluorine atoms, TEFLON has got

1. High melting point (> 350°C),
2. Exceptionally high chemical resistance (except hot alkali metals and fluorine).
3. High density 2.1 - 2.3 gm/cc
4. It is very strong, hard polymer that can be machined to drilling, punching etc.
5. TEFLON is a very good electrical insulator.
6. It possesses very good abrasion resistance.

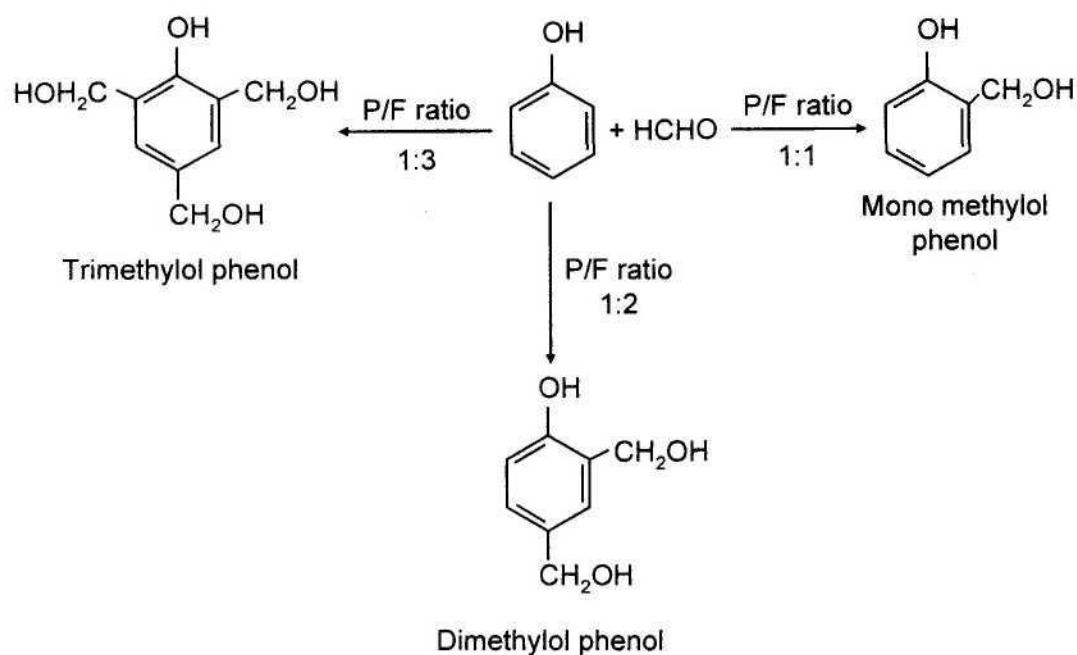
**Engineering uses:**

1. TEFLON is a very good insulating material for motors, transformers, cables, wires, fittings etc.
2. It is used for making gaskets, pump parts, tank linings, tubing etc.
3. Due to its extreme chemical resistance, it is used for making chemical carry pipes.
4. Non - lubricating bearings and non-stick stop cock for burettes are made from TEFLON.
5. It is also used for coating as impregnating glass fiber, asbestos fibers.

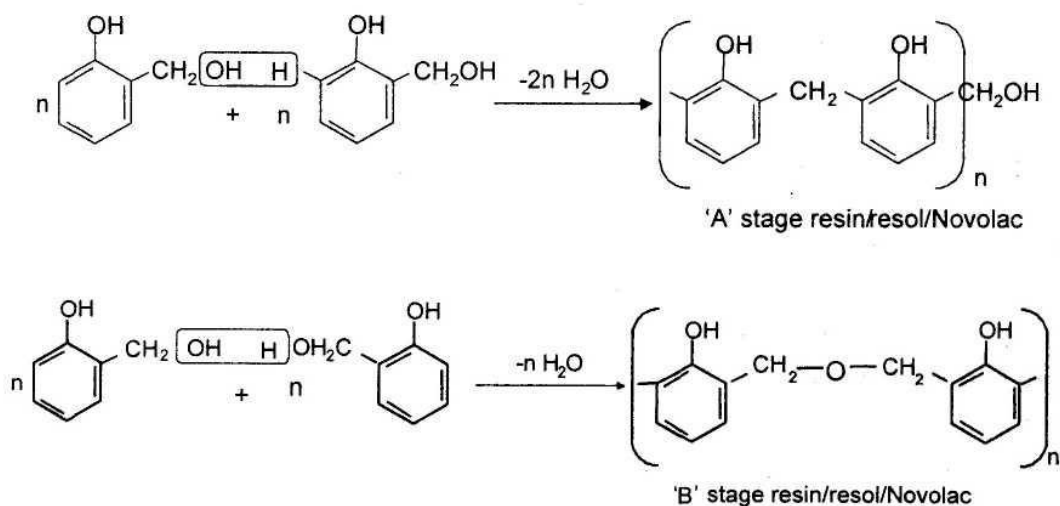
**Bakelite or Phenol - formaldehyde resin:****Bakelite**

Bakelite is an important thermoset resin named after the scientist Bakeland, who synthesised this resin in the year 1909. It is prepared by the step polymerisation of phenol with formaldehyde in presence of an acid or alkali as a catalyst. The polymerisation takes place in three stages.

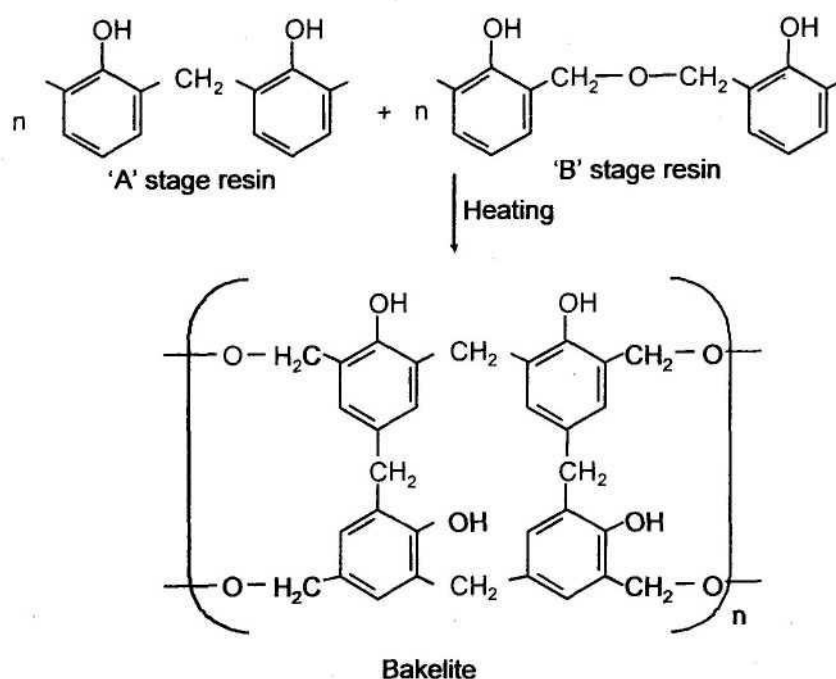
**I stage:** Phenol is made to react with formaldehyde in presence of acid / alkali to produce non - polymeric mono, di, and tri methylol phenols depending on the phenol formaldehyde ratio (P/F ratio).



**II Stage:** The mono, di, and tri methylol phenols are heated to produce two types of straight chain resins by condensation of the methylol group with hydrogen atom of benzene ring or another methylol group.



**III Stage:** This stage of preparation includes heating of 'A' stage resin and 'B' stage resin together, which develops cross linking and bakelite plastic resin is produced.



### Properties :

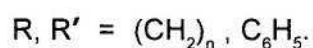
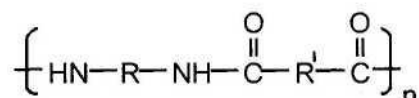
1. Bakelite plastic resin is hard, rigid, and strong.
2. It is a scratch resistant and water resistant polymer.
3. Bakelite has got good chemical resistance, resistant to acids, salts and any organic solvents, but it is attacked by alkalis due to the presence of - OH group.
4. It is a good anion exchanging resin, exchanges - OH group with any other anion.
5. Bakelite is an excellent electrical insulator.
6. It is a very good adhesive.
7. Bakelite has very good corrosion resistance, resistant to atmospheric conditions like  $\text{O}_2$ ,  $\text{CO}_2$ , moisture, light, U.V. radiation etc.



**Engineering applications:** Bakelite is used widely.

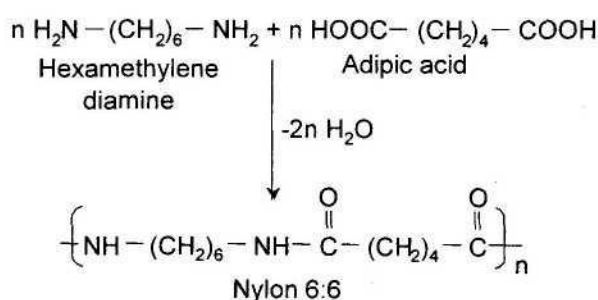
1. For making electrical insulator parts like switches, switch boards, heater handles etc.
2. For making moulded articles like telephone parts, cabinets for radio and television.
3. For making tarpaulins, wood laminates and glass laminates.
4. As an anion exchanger in water purification by ion exchange method in boilers.
5. As an adhesive (binder) for grinding wheels etc.
6. In paints and varnishes.
7. For making bearings used in propeller shafts, paper industry and rolling mills

**Nylon (Poly amide resin):**

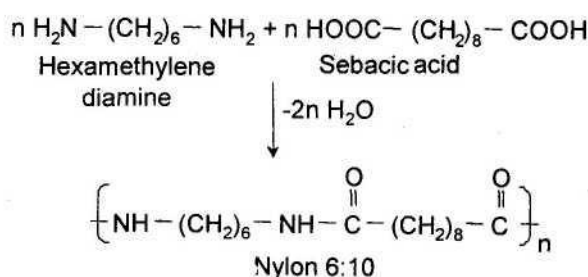


Nylon is a polyamide resin containing recurring amide group in its structure, produced by copolymerisation of diamine with diacid. Depending on the number of carbon atoms in diamine and diacid, there are different types of nylons like nylon 6 : 6, nylon 6 : 10, etc. where the first number indicates the number of carbon atoms in diamine and the second number indicates the number of carbon atoms in diacid.

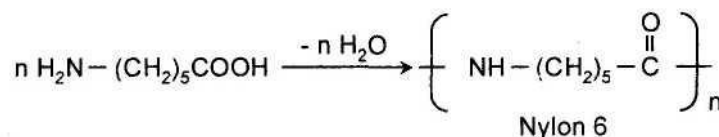
**Nylon 6 : 6 :** Nylon 6 : 6 is produced by the copolymerisation of hexamethylene diamine with adipic acid.



**Nylon 6 : 10:** Nylon 6:10 is synthesised from copolymerisation of hexa methylene diamine with sebacic acid.



**Nylon 6** : Nylon 6 is produced by the homopolymerisation of caprolactum.



**Properties:**

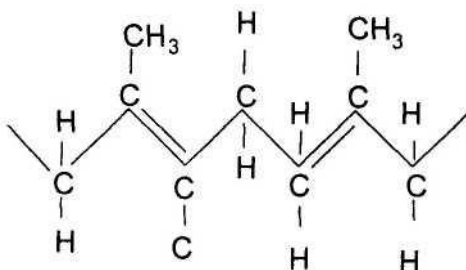
1. Nylons possess high strength, hardness and high melting point. The high melting point of the nylons is due to the hydrogen bonding between the hydrogen atom of the amide group (-NH) and oxygen the C = O group P.
2. Nylons possess high crystallinity, abrasion resistance and good mechanical properties.
3. Nylons possess good chemical resistance,
4. They are good electrical insulators.
5. Nylons possess good resistance to environmental conditions

**Engineering applications:**

1. The major application is in the textile industry.
2. Because of its high thermal and abrasion resistance nylons are used in mechanical engineering applications like gears, bearings, machine parts where greater friction is there.
3. Flexible tubings for conveying petrol etc are made from nylons.
4. Nylons are used as electrical insulators.
5. Nylon 6 is used for making tire cords.
6. Nylons are used in auto mobile industry and telecommunication industry for making radiator parts and coil formers respectively.

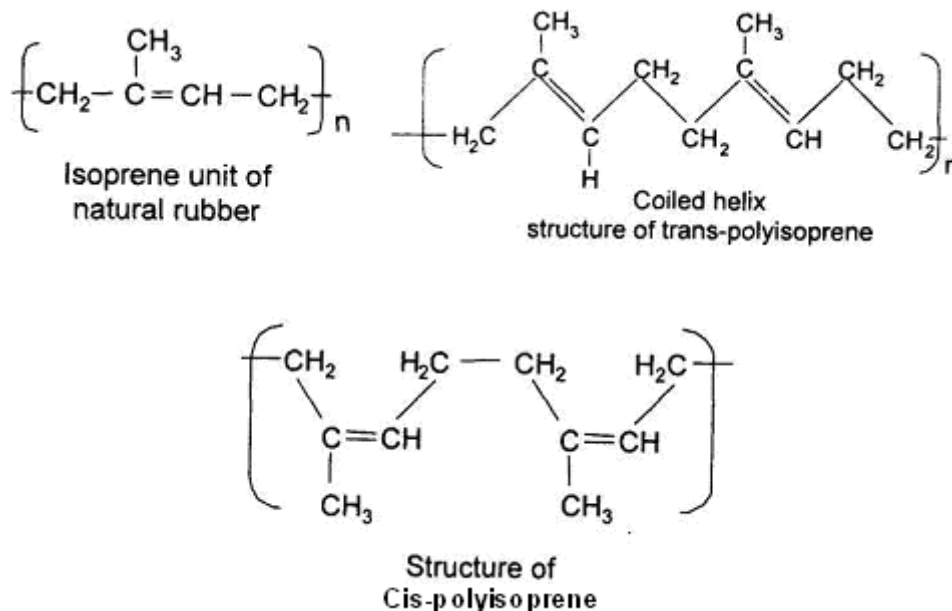
**RUBBER:**

Those polymers which possess the property of elasticity is called rubber. Temporary deformation in structure on applying some stress is more than 600 e.u. when stress is applied, polymer chains get partially aligned with respect to another, thereby causing crystallisation, which makes the polymer stiff. On releasing the stress, the chains get reverted back to their original coiled state. The elasticity of rubber is due to its coiled helix structure, as shown below.



**Natural rubber:**

Natural rubber is processed from the cell sap (latex) of three main types of trees / plants, *Hevea Brasiliensis*, *Guayule*, *Dichopsis percha*, *Palagum gutta* found in tropical and semi-tropical countries. The main composition of natural rubber is polyisoprene, which is in the form of long coiled chains, responsible for the elasticity of natural rubber is shown below.

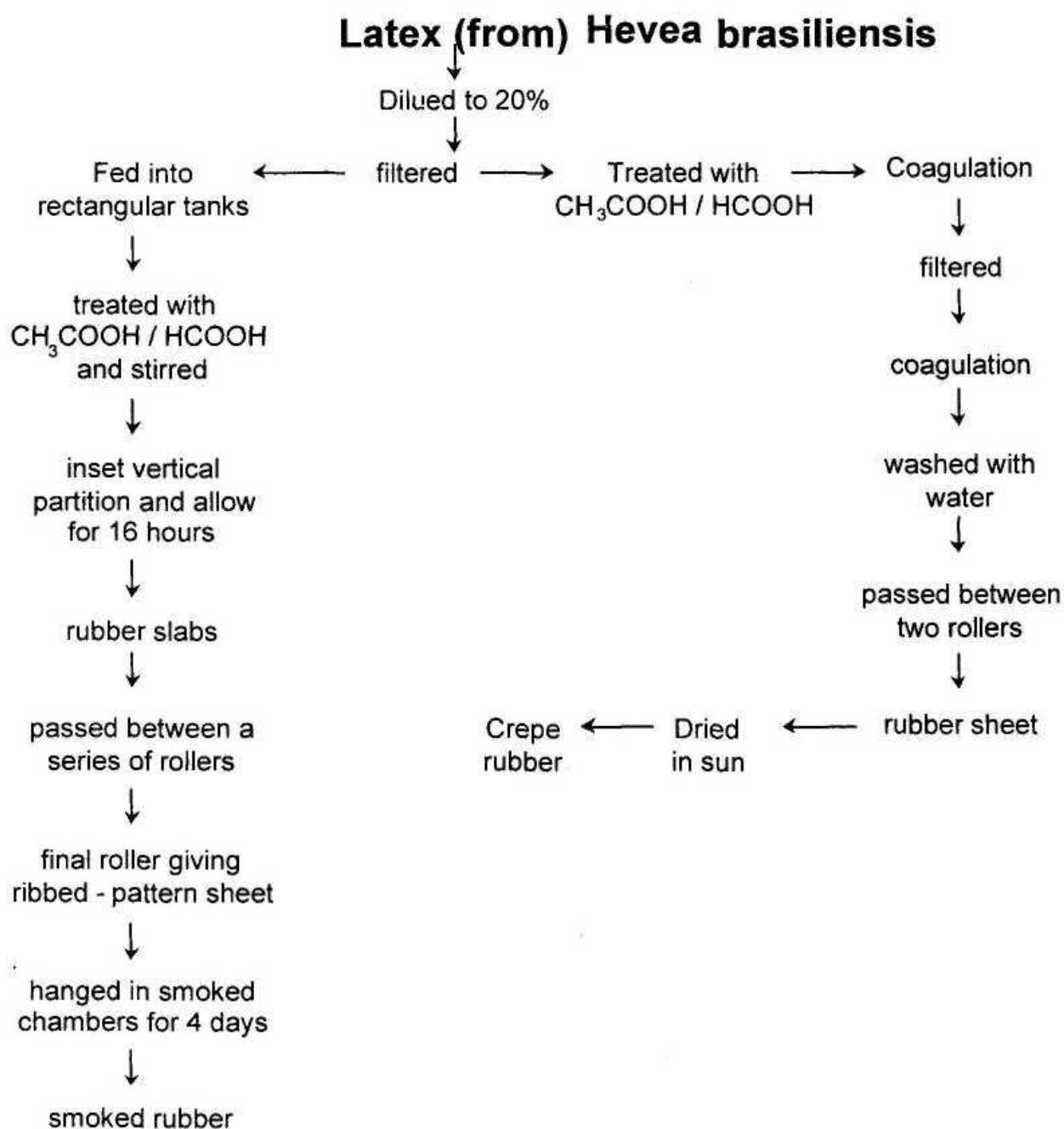


Isoprene in natural rubber exists in two geometrical isomeric forms, cis and trans. Cis-polyisoprene present in *Hevea* rubber and trans - polyisoprene present in *Gayule* and *Percha* rubber.

The processing of natural rubber from *Hevea brasiliensis* starts with tapping of the latex (cell sap flows from the trunk of the tree). Spiral grooves are made on the trunk of the tree and the latex flowing is collected into small vessels, then the latex is emptied into buckets and transferred to the factory for processing tapping is usually done at the intervals of six months.

The latex is diluted to 15 - 20% and filtered to remove suspended impurities like pieces of bark, leaves etc. Then it is taken into tanks and treated with acetic acid or formic acid. The rubber coagulates (precipitates) as *soft white mass* (coagulum) which is filtered and washed with water. The coagulum is passed between two rollers about 3 mm apart and 50 cm wide and extruded in the form of a sheet which resemble the crepe paper, which possess rough surface. The rubber processed by this method is called 'crepe rubber'. The crepe rubber sheet are dried in sun.

In the second type of processing, the filtered latex is fed into long rectangular tanks of 1 m wide and 30 cm deep and treated with acetic acid or formic acid along with constant stirring. Vertical partition plates are inserted and left undisturbed for 16 hours. The coagulum sets in the form of slabs is passed between a series of rollers with decreasing clearance in between them while spraying water on these rollers. The final roller gives ribbed pattern to the rubber sheet which help in quick drying and preventing the adherence of rubber sheets to one another. The sheets are hunged for about 4 days in smoked chambers at 40 - 50°C. This rubber is called *smoked rubber*.



Flow diagram of the processing of Hevea rubber

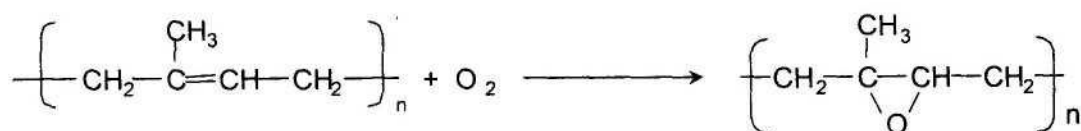
**Processing of Gutta Percha :** Gutta percha is processed from the mature leaves of *Dichopsis gutta* and *Palagum gutta* by solvent extraction process. The mature leaves are ground carefully, heated with water at about  $70^{\circ}\text{C}$  for half an hour time and poured into coldwater. The gutta percha rubber floats on the surface is removed and extracted with carbon tetra chloride. The solvent is evaporated and the rubber is extruded in the form of a sheet by passing between two moving rollers. Gutta percha has transpolyisoprene in its composition.

**Guayule Rubber:** Guayule rubber is processed from guayule shrub, which is a source of natural rubber in North America. This rubber resembles Hevea rubber, as its composition is *cis - polyisoprene*. latex is enclosed in the cells of the shrub. Guayule

shrub is cut into pieces of very small size after removing the leaves and milled in pebble mill with water into a smooth paste. The paste is sent to floatation tanks, where rubber floats on the top is collected. The rubber is extracted with  $\text{CCl}_4$  solvent and extruded in the form of a sheet.

**Vulcanisation of Rubber:** the natural rubber extracted by the above method has got some disadvantages as listed below. Because of the double bond existing in the structure.

1. It is soft and plastic in nature. It becomes *soft at high temperatures and too brittle at low temperature*, containing the temperature range of 10 - 60°C.
2. It swells in water and easily attacked by organic solvents, acids bases and non – polar solvents like mineral oils, benzene and gasoline.
3. It possesses poor tensile strength.
4. Atmospheric oxygen attacks the rubber and produces epoxides which gives bad smell, stick nature to rubber.



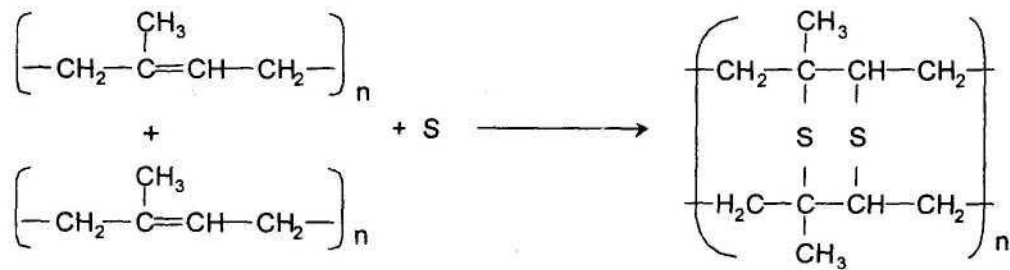
5. The rubber possess tackiness i.e. when two fresh raw rubber sheets were pressed together, they *coalesce* to form a single sheet.
6. When stretched to a great extent, it suffers permanent deformation due to sliding or slippage of some molecular chains over each other.
7. It is attacked by atmospheric  $\text{O}_2$ ,  $\text{CO}_2$ , moisture, light, U.V.radiation etc. and gets less durability.

To improve the properties of rubber, Charles Good in 1839 compounded the raw rubber with some chemicals and heated to 100 - 140°C. Finally the compounded and vulcanised is drawn in the form of a sheet by calendering process.

**Compounding and vulcanisation:** The following are materials added to natural rubber.

#### **Vulcanisers:**

Some chemicals like elemental sulphur, hydrogen sulphide, sulphur dichloride, benzoyl chloride and zinc oxide are added to both natural and synthetic rubbers. The most important vulcaniser is *sulphur* which combines chemically at the *double bonds* of the different chains producing *sulphur cross linkings*, imparting *strength* increases, the brittleness also increases. The percentage of sulphur added is in the range of 0.5 to > 35%. For example the rubber used for making tyres contains 3 to 5% of sulphur and for making battery case the rubber contains 30% of sulphur. If the percentage of sulphur is more than 32, that rubber is called *ebonite* or *vulcanite* or *hard rubber* for some special purposes. The following is the formation of sulphur cross linkings.

**Plasticizers :**

Plasticizers are also called as softners, which impart greater *plasticity* and *adhesion* to the rubber. The most commonly used plasticizers are vegetable oils, waxes rosin etc.

**Accelerators:**

They catalyse the vulcanisation process by reducing the time required for vulcanisation. Most commonly used accelerators are litharge, Magnesia and white lead. Generally 0.5 to 1 % of accelerators are added. *ZnO* is also added which acts as an *activator* Xo accelerators.

**Anti oxidants:**

They retard the deterioration of rubber by light and air. Complex organic amines like phenylnaphthylamine, Phenolic substances and Phosphites are added as antioxidants

**Reinforcing agents :**

They give strength, rigidity, and toughness to the rubber and may form as much as 35% of rubber compound. Commonly used reinforcing agents are ZnO, MgCO<sub>3</sub>, BaSO<sub>4</sub>, and CaCO<sub>3</sub>

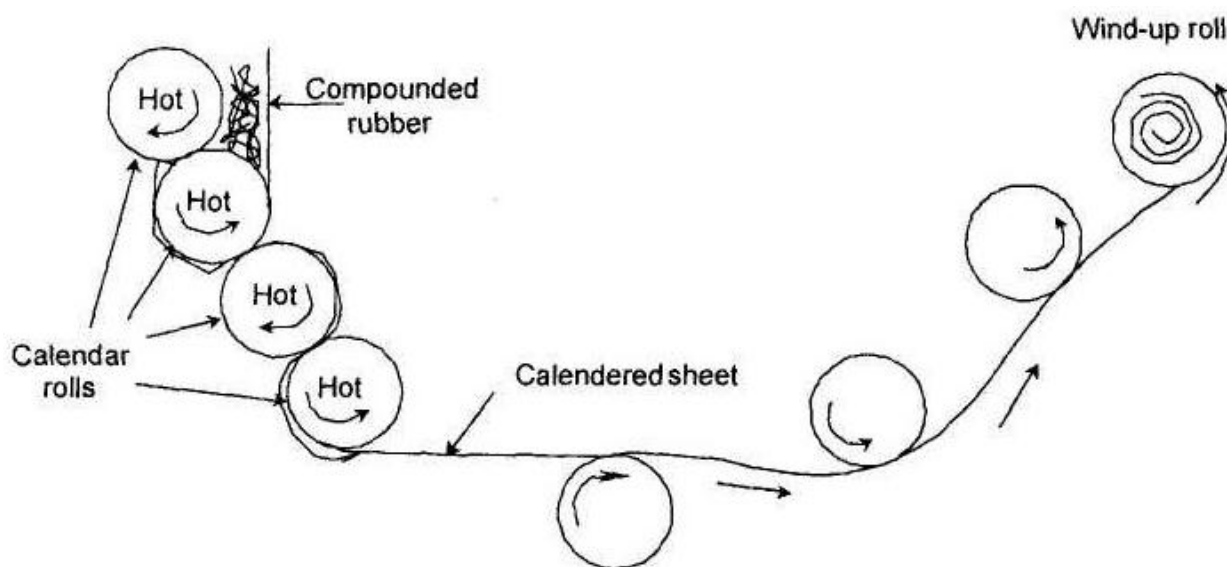
**Colouring agents :**

They impart desired colour to the rubber as follows.

Lithophane, TiO<sub>2</sub> - white,  
Lead chromate - Yellow,  
Caron black - black,

Ferric oxide - red  
Chromium trioxide - green  
Ultra marine – blue

**Calendering** : The natural rubber processed, is mixed with the different compounding and vulcanising material after mastication (subjecting rubber to mashing / grinding) in a Banbury mix and converted to sheets (0.003 to 0.1 inch thickness) by passing between rolls as shown below.



Schematic diagram of a calendaring machine

#### Advantages of vulcanisation:

1. Vulcanised rubber has good tensile strength and load bearing capacity.
2. Vulcanised rubber has good elasticity depending on the extent of vulcanisation.
3. It possesses low water absorption tendency.
4. Vulcanised rubber has higher resistance to oxidation and atmospheric gases like  $O_2$ ,  $CO_2$ , moisture, light and U.V. radiation.
5. Vulcanised rubber is a good electrical insulator and ebonite is a best electrical insulator.
6. The abrasion resistance of natural rubber increases tremendously.
7. The resistance towards organic solvents and chemicals increases.
8. Vulcanised rubber possesses good impact resistance.
9. Vulcanised rubber possesses very good resilience i.e. the article made from it returns to original shape, when the deforming load is removed.

#### Properties of natural rubber:

1. Natural rubber is a strong and tough engineering material.
2. It has very good resilience.
3. Natural rubber is resistant to atmospheric conditions, water, dilute acids and bases.
4. It has got excellent abrasion resistance.
5. Natural rubber is not attacked by organic solvents, petrol,  $CS_2$ ,  $CCl_4$ , turpentine etc.
6. The specific heat and density of raw rubber are 0.502 and 0.934 at  $20^\circ C$ .
7. When rubber is heated with organic sulphonyl chloride or organic sulfonic acid at  $130^\circ C$  it is converted into a thermoplastic resin known as 'thermoprene'.
8. Rubber reacts with chlorine to give chlorinated rubber.

**Applications of natural rubber:**

1. The major application of natural rubber is in the manufacture of tyres.
2. It is used for preparing V belts for power transmission and several types of materials like non - slipping, clean and shock absorbing.
3. The tank linings in chemical plants where corrosive chemicals are stored are prepared from rubber.
4. To reduce machine vibrations, rubber is used for sandwiching between two metal surfaces.
5. Foamed rubber is used for making cushions, mattresses, paddings etc.
6. Toys and sports items are manufactured from natural rubber.
7. Gutta percha rubber is used for making submarine cables, golf ball covers, tissue or adhesive etc.

**ELASTOMERS OR SYNTHETIC RUBBERS:**

After the II world war, due the advancement of automobile industry, the natural rubber sources could not supplement the needs of the automobile industry. An attempt was made to synthesise the rubber but rubber like materials were synthesised to supplement the need of the industries. These materials are called elastomers, because they are characterised by the property of elasticity some of the important elastomers are given below.

**BUNA-S:**

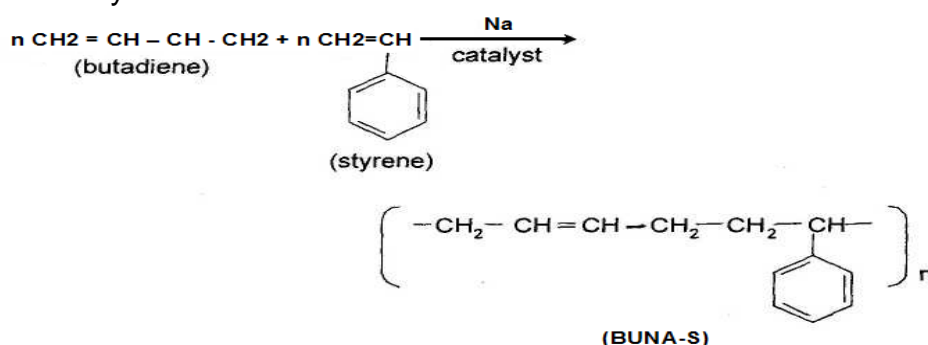
BUNA - S is otherwise called *styrene rubber* or *GRS* (Government Rubber Styrene) or *Ameripol*. BUNA - S stands for the composition of the monomers and catalyst.

BU stands for Butadiene - monomer

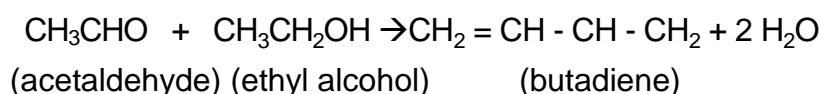
NA stands for Sodium - catalyst

S stands for Styrene - monomer

∴ BUNA - S is produced by the copolymerisation of butadiene with styrene using sodium as a catalyst.

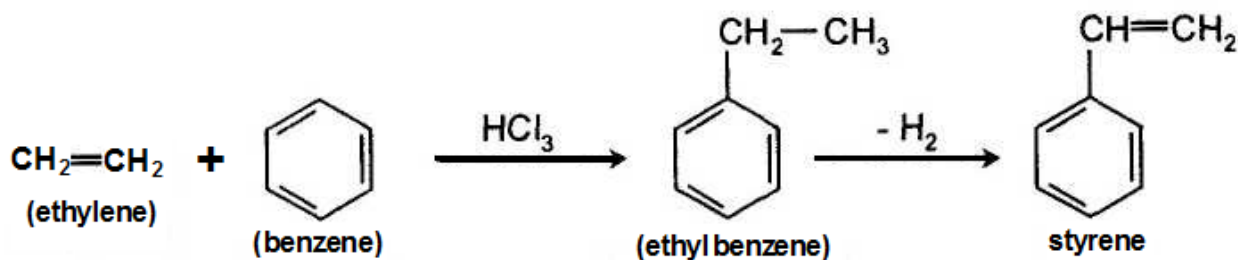


The monomers butadiene and styrene were synthesised in the following way. Butadiene is produced from acetaldehyde and ethyl alcohol as given below.





Styrene is from benzene and ethylene in presence of anhydrous aluminium chloride as catalyst.



### Properties:

1. Styrene rubber is a strong and tough polymer.
2. It is vulcanised by sulphur monochloride ( $\text{S}_2\text{Cl}_2$ ) or sulphur.
3. It resembles natural rubber in processing characteristics and quality of finished products.
4. BUNA - S possess excellent abrasion resistance.
5. It is a good electrical insulator.
6. It is resistant to chemicals but swells in oils and attacked by even traces of ozone, present in the atmosphere.
7. S-tyre rubber possess high load bearing capacity and resilience.

### Applications:

1. Major application of styrene rubber is in the manufacture of tyres.
2. It is used in the footwear industry for making shoe soles and footwear components.
3. It is also used for making wires and cable insulations.
4. The other applications of styrene rubber are for the production of floor files, tank linings in chemical industries and as adhesives.

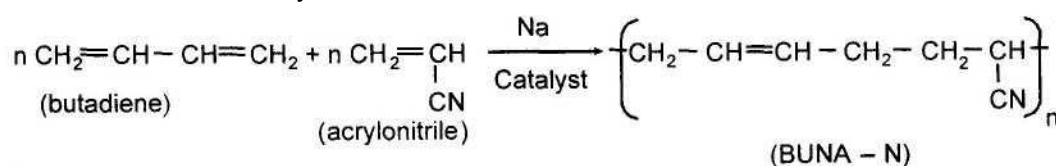
### BUNA - N; GR - A or Nitrile rubber:

Nitrile rubber is a copolymer of butadiene and acrylonitrile where the composition of the monomers and catalyst are in its name.

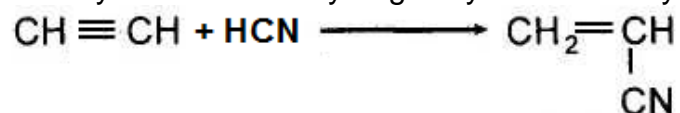
BU stands for butadiene - monomer

NA stands for sodium - catalyst

N stands for acrylonitrile - monomer



Butadiene is prepared from acetaldehyde and ethyl alcohol as described in BUNA - S. Acrylonitrile is prepared by the addition of hydrogen cyanide to acetylene.



### Properties:

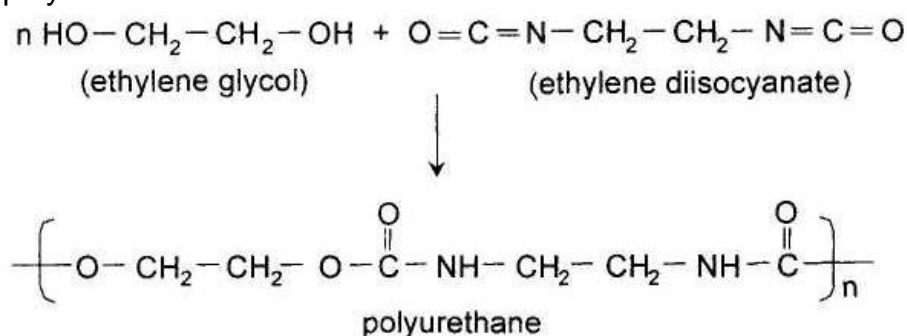
1. Because of the presence of - CN group in the structure BUNA - N possess excellent resistance to heat, sunlight, oils, acids and salts and less resistant to alkalis than natural rubber. It is a strong and tough polymer with lightweight.
2. BUNA - N is also vulcanised with sulphur.
3. It is highly resistant to atmospheric O<sub>2</sub>, CO<sub>2</sub>, moisture, u.v. light and light.
4. BUNA - N is an excellent electrical insulator.
5. Vulcanised BUNA is resistant to ageing and high temperatures.

### Applications of BUNA - N :

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

### Polyurethane rubber or Isocyanate rubber:

The copolymerisation of ethylene diisocyanate and ethylene glycol produces polyurethane rubber by poly addition mechanism.



### Properties:

1. Polyurethanes are highly resistant to oxidation because of their saturated character.
2. Polyurethanes have excellent abrasion resistance and hardness combined with good elasticity.
3. They show good resistance to many organic solvents and oils but attacked by acids, alkalis especially concentrated and hot.
4. Polyurethanes can be foamed to light weight, thermally resistant, chemically resistant an environmentally resistant foams.
5. It is a good electrical and thermal insulator.

### Applications:

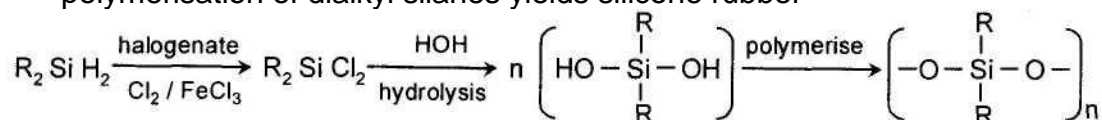
1. Its major utility is as a thermal insulator for refrigerators etc.
2. It is used for surface coatings.

**Silicone rubber (Silastics):**

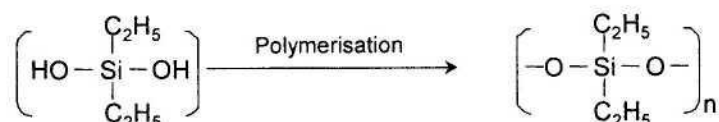
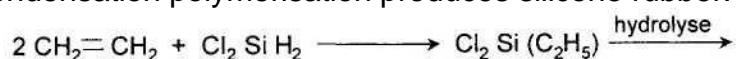
Silicone rubber is a very high molecular weight polymer with siloxane unit [ - O - Si - O - Si - O - ], on back bone along with two alkyl / phenyl linkages to silicon.

They are produced by the following methods.

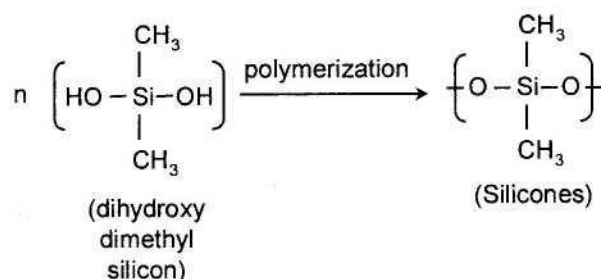
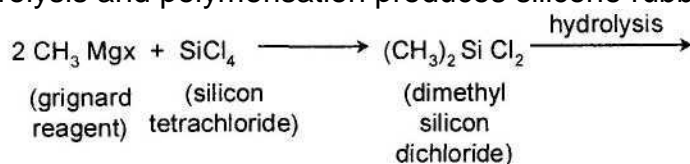
1. By the halogenation of silanes followed hydrolysis and condensation polymerisation of dialkyl silanes yields silicone rubber



2. By the action of ethylene on dialkyl dihydrosilicon, followed by hydrolysis and condensation polymerisation produces silicone rubber.



3. By the action of Grignard reagent on silicon tetra chloride followed by hydrolysis and polymerisation produces silicone rubber.

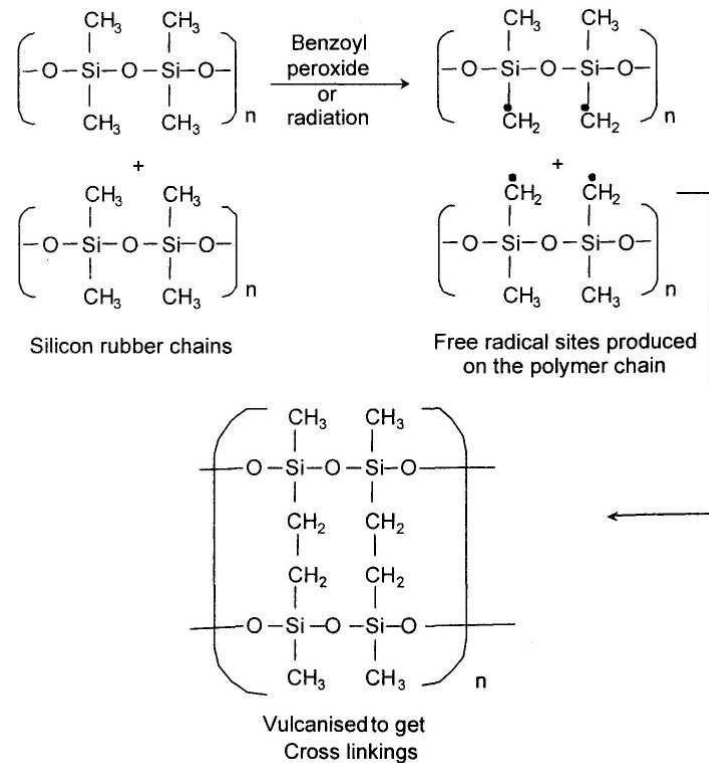
**Applications:**

1. Silicone rubbers find extensive uses as sealing materials, gaskets, diaphragms and rollers.
2. Silicone rubbers are extensively used in aircraft and automobile industry.
3. Domestic oven doors are lined with silicone rubber.

**Properties:**

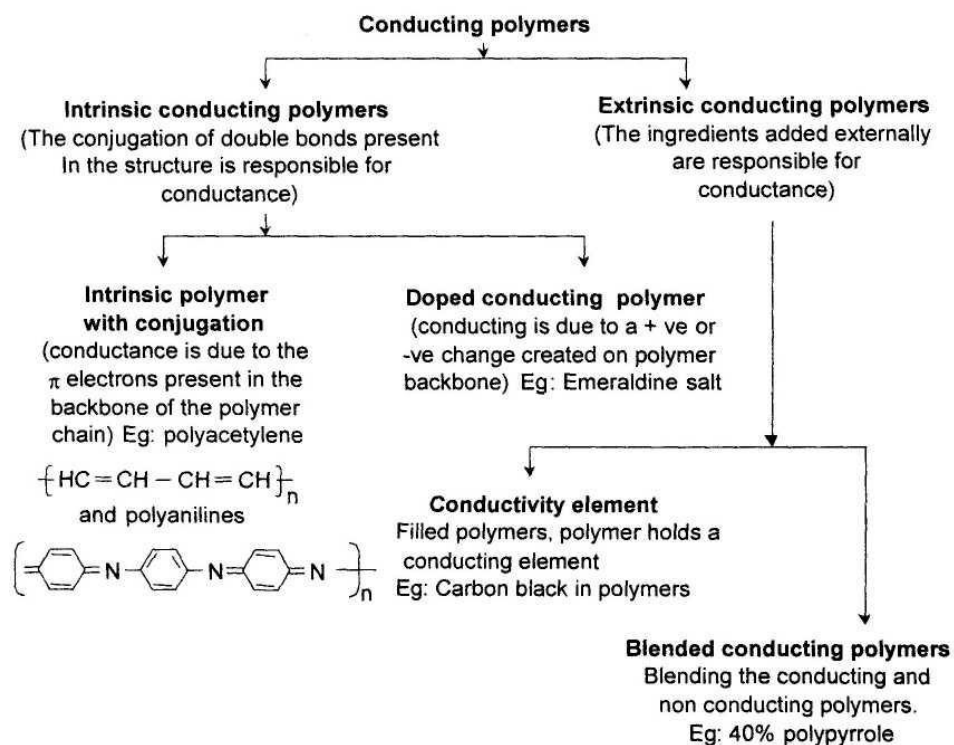
1. Selection of alkyl group on the chain and reinforcing agent during compounding and vulcanisation determine the properties of silicones.
2. Silicone possess strength less than natural rubber.
3. Silicone rubbers are highly resistant to extreme temperatures i.e., - 50 °C to 300 °C, hence good thermal stability.

4. Silicone possess good dielectric strength.
5. Silicone rubber is vulcanised to get cross linkings by free radical mechanism by using benzoyl peroxide as a reagent.



**CONDUCTING POLYMERS:**

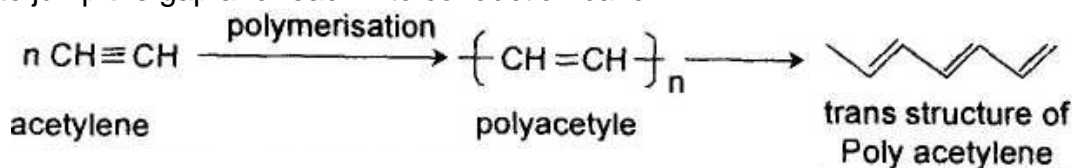
The polymers which conduct electricity are called *conducting polymers*. The conduction of the polymers may be due to unsaturation or due to the presence of externally added ingredients in them. The conducting polymers can be classified in the following way.



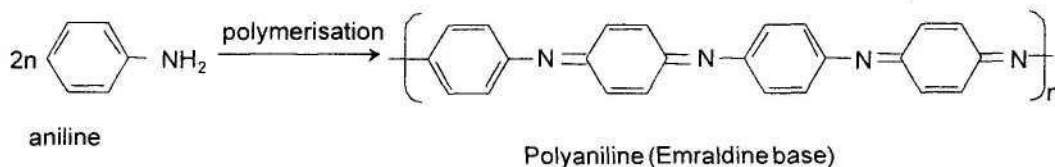
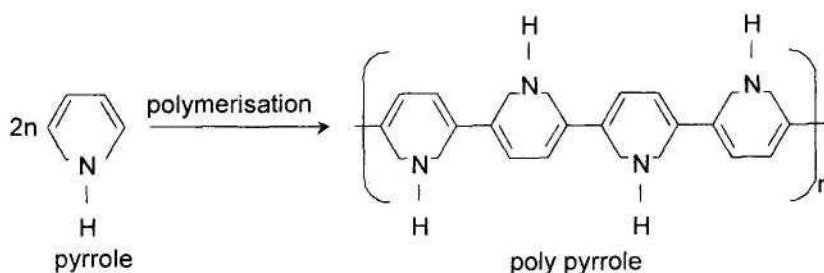
**Intrinsic conducting polymers:**

These polymers are characterised by intensive conjugation of double bonds in their structure i.e. the backbone of the polymer. Again intrinsic conducting polymers are two types as given below.

**Conducting polymers having conjugation:** Such polymers having conjugated double bonds in the backbone possess their conductivity due to π electrons. In π bonding the overlapping of the orbitals is lateral over the entire backbone resulting in the formation of *valence bands* and *conducting bands* which were separated by a significant fermi energy, gap. The electrical conductivity takes place only after thermal or photolytic activation of the electrons, which give them sufficient energy to jump the gap and reach into conduction band.



All these polymers possess conductivities around  $10^{-10} \text{ Scm}^{-1}$  which is sufficient for their use in any engineering applications.



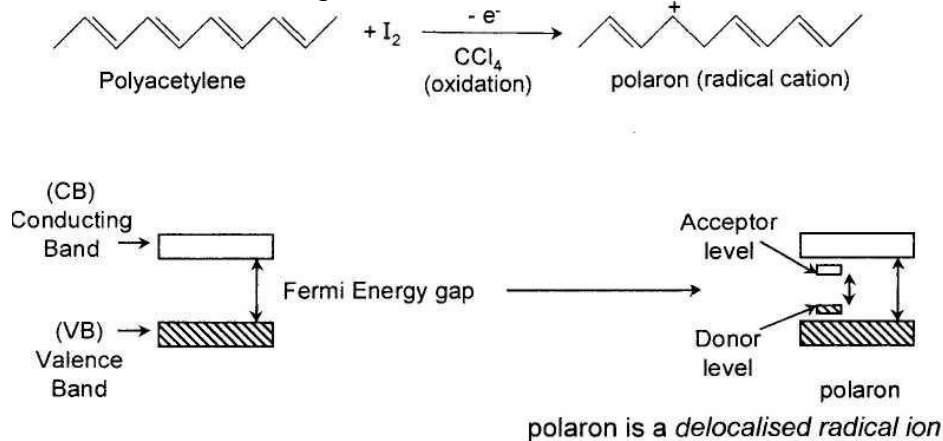
**Doped conducting polymers :** The conducting polymers having π electrons in their backbone can easily be oxidised or reduced because they possess *low ionisation potential* and *high electron affinities*. Hence their conductance can be increased by introducing a positive charge or negative charge on polymer backbone by oxidation or reduction. This process is similar to semiconductor technology and is called *doping*. Doping is again two types.

- 1. Creating a positive site on polymer backbone called *p-doping*
- 2. Creating a negative site on the polymer backbone called *n-doping*.

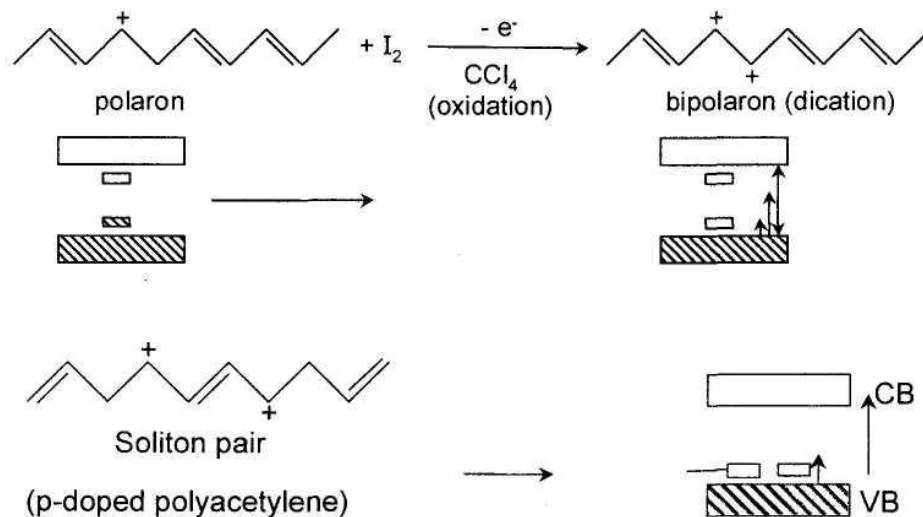
**p - doping:** p - doping is done by oxidation of a conducting polymer like polyacetylene with a Lewice acid or iodine vapour. This is also called *oxidative doping*.



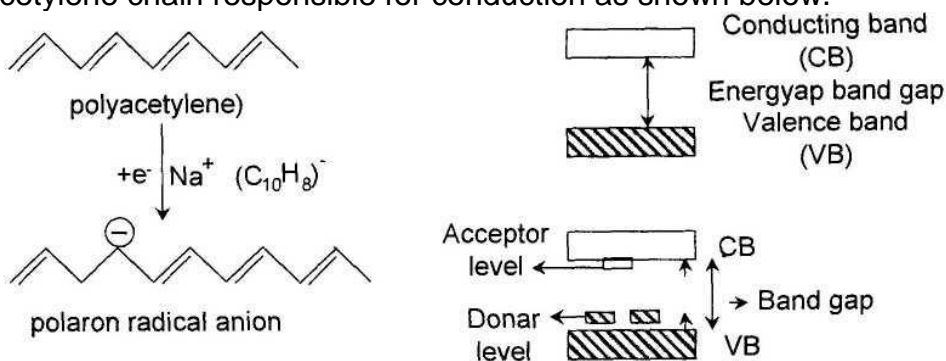
During oxidation process the removal of  $\pi$  electron from polymer back bone lead to the formation of a *delocalised radical ion* called *polaron* having a hole in between valence band and conducting band as shown below.



The second oxidation of the polaron results in two positive charge carriers in each chain called *bipolaron*, which are *mobile* because of delocalisation. These delocalised charge carriers are responsible for conductance when placed in electric field.

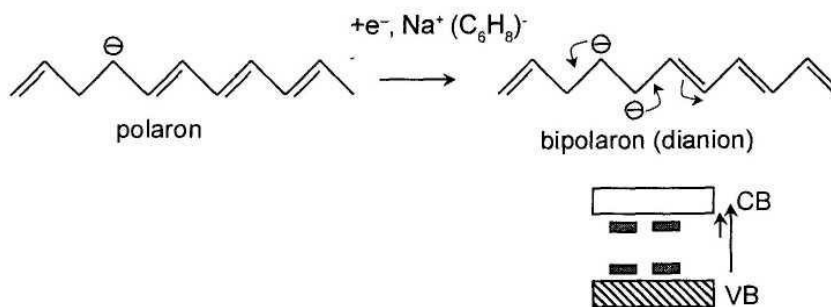


**n - Doping :** n - Doping is carried out by reduction process by the addition of an electron to polymer backbone by using reducing agents like sodium naphthalide Na<sup>+</sup>(C<sub>10</sub>H<sub>8</sub>)<sup>-</sup>. Formation of polaron, bipolaron takes place in two steps, followed by recombination of radicals, which yields two charge carriers on the polyacetylene chain responsible for conduction as shown below.



The electron added to polyacetylene by reductive doping does not go into the conducting band but goes into an intermediate electronic state within the band

gap of radical anion (polaron).



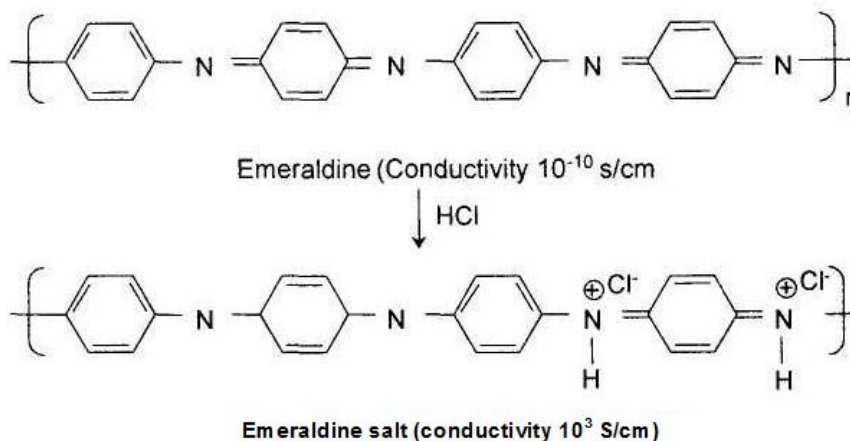
Bipolaron contains electrons in the energy levels residing in the band gap. The Bipolaron lowers its energy by segregating into two negative solitons at the mid gap energy levels. The presence of holes in the band gap allows facile jumps of electrons from valence band into the conduction band. This leads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

In general doping increases the surface conductivity of a polymer to a large extent.

The following conductivities of conducting polymers.

S. No.	Conducting Polymer	Dopants	Conductance (S, cm <sup>-1</sup> )
1.	Trans polyacetylene	I <sub>2</sub> , Na, Br <sub>2</sub> , Li, ASF <sub>5</sub>	10,000
2.	Polyaniline	HCl	1,000
3.	Poly pyrrole	BF <sub>4</sub> <sup>+</sup> ClO <sub>4</sub> <sup>+</sup>	500 - 7500

Polyanilines exist in several oxidation states as far as electrical conductivities are concerned varying from 10<sup>-11</sup> S/cm to > 10<sup>5</sup> S/cm only one form called *emeraldine* salt is *electrically conducting*. The flexible dark blue films of conducting polyaniline is made by protonic doping i.e. *protonation of imine nitrogen* atoms in the backbone. Doping is a reversible process deprotonation can also be done by treatment with alkali *Emeraldine* salt is also known as *synthetic metal* because it possesses metallic conductivity, metallic lusture, metallic sound and poor mechanical strength, less strength and storage ability.



**Advantages of intrinsic conducting polymers:**

The following are the advantages of the intrinsic conducting polymers.

1. These polymers possess good conductivity.
2. They can store a charge
3. Ion - exchange is possible with these polymers.
4. They absorb visible light to give coloured products.
5. They are transparent to x-rays.
6. They can be easily processed with product stability and efficient recycling.

**Disadvantages of intrinsic conducting polymers:**

Their conductivities are inferior to metal conductivities.

For example:

The conductivity of polyacetylene is  $400,000 \text{ S cm}^{-1}$  where as the conductivity of Cu is  $600,000 \text{ S cm}^{-1}$

**Extrinsically Conducting Polymers:**

The conductivity of these polymers is due to the presence of externally added ingredients in them. Again the extrinsically conducting polymers are two types.

1. Conducting element filled polymers.
2. Blended conducting polymers.

**Conducting element filled polymers:**

The polymer acting as a binder to hold the conducting element such as carbon black, metallic fibres, metallic oxides etc. Minimum concentration of conducting filler is added so that the polymer starts conducting. This minimum concentration of conductive filler is called *percolation threshold*. At this concentration of filler, a conducting path is formed in polymeric material. The most preferred filler is the special conducting grade C - black has very high surface area, more porosity and more of a filamentous properties.

**Advantages:**

1. These polymers are low cost polymers.
2. They are light in weight and mechanically durable.
3. These polymers are strong with good bulk conductivity.
4. They are fabricated very easily to any design.

**Applications of conducting polymers:**

1. The conducting polymers are used in *rechargeable batteries*, small in size (button size), and producing current density upto  $50 \text{ mA/cm}^2$ .
2. Conducting polymers are also used for making *analytical sensors* for pH,  $\text{O}_2$ ,  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{NH}_3$  and glucose.
3. The conducting polymers are used for making *ion exchangers*. These membranes made of conducting polymers show selective permeability for ions and gases hence they are used for control release of drug.
4. The conducting polymers are used making *electronic displays* and *optical fibres*.
5. They are used for *electron beam* lithography.
6. The conducting polymers are applicable in photovoltaic devices.



**Blended conducting polymers:**

The conventional polymer is blended with a conducting polymer to improve physical, chemical, electrical and mechanical properties along with the processing properties.

**Examples:** 40% of polypyrrole in a conventional polymer give higher impact strength. These blended polymers are used in electromagnetic shielding.

**Applications:**

These polymers are used in are used in hospitals and operation theatres.

The **disadvantage** of the conducting element filled polymers is that addition of 10% carbon black will drastically decrease the tensile strength, elongation strength and impact strength of the polymer.

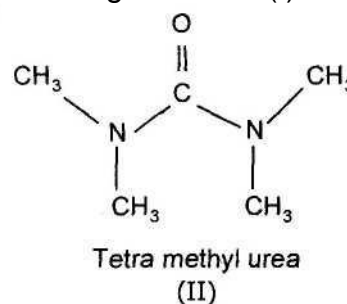
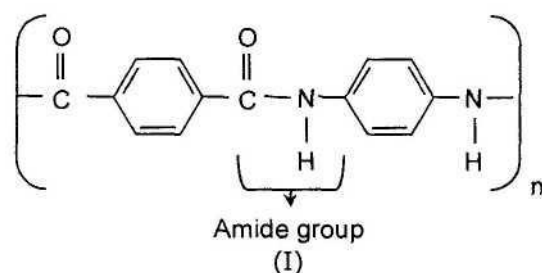
**Factors influencing the conductivity of organic polymers:**

The conductivity of organic polymers is influenced by various factors, listed below.

1. **Conjugation length of the polymer chain:** The conductivity of a polymer increases with increase in chain length or conjugation.
2. **Doping level:** The conductivity increases with increase in doping level, but after some time, it becomes saturated.
3. **Temperature:** The conductivity of conducting polymers increase with increase in temperature. At some high temperature, conductivity becomes constant.
4. **Frequency of current:** The conductivity of these materials also depends on the frequency of current, because dopping is the transport mechanism of these materials.

**LIQUID CRYSTAL POLYMERS (LCP):**

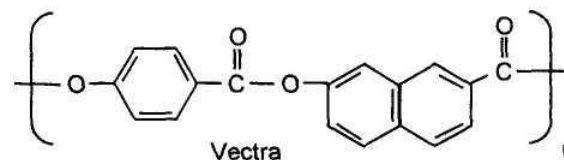
Liquid crystals are materials that behave in some ways like solids and in some ways like liquids. Stephanie kwoiek, a chemist, working at Dupont, had made the first known polymer liquid crystal solution. Kwoiek had invented a new polymer based on the polyamide, named *kevlar* and its repeat unit had this following structure (I).



The macromolecule with the above structure produce very strong fibres. When this polymer dissolved in tetramethyl urea (II) and calcium chloride, the polymer molecules behave strongly. The Kevlar molecular which were long, straight, and stiff, lined up like logs floating down a river, because of the strange opalscent look of the solution. This is unusual because normally molecules in a solution or a pure liquid are not arranged in any orderly fashion. Molecules of solids materials are arranged in orderly fashion called 'crystals'.

Since kevlar solution is a liquid, but its molecules are orderly arranged, the solution is called a 'liquid crystal'. Liquid crystals can be classified into two types.

1. Liquid crystallinity in polymers may occur by dissolving a polymer in a solvent, which are called *lyotropic liquid crystal polymers*. Eg. Kevlar.
2. Liquid crystallinity in polymer may occur by heating a polymer above its glass transition temperature or melting transition point, which are called *thermotropic liquid crystal polymers*. Eg. Vectra having the following structure.



### Properties of liquid crystal polymers:

1. These polymers are capable of forming regions of highly ordered structure while in liquid phase. The degree of order is somewhat less than that of a regular solid crystal.
2. The liquid crystal polymers have high mechanical strength at high temperatures.
3. These liquid crystal polymers possess extreme chemical resistance.
4. They possess inherent flame retardancy and good weatherability.
5. They can be easily fabricated into a variety of forms.
6. LCP can be welded. The lines created by welding are the weak points in the resulting product.
7. LCP has high z - axis coefficient of thermal expansion.
8. LCP resist stress cracking the presence of most chemicals at elevated temperatures.

### Applications of LCP:

LCP are sometimes called '*superpolymers*'. Their wide range of exceptional properties and ease of processing make them design for many demanding applications.

1. LCP thermoplastic fibres possess exceptional strength and residity, suitable for industrial, electronics and also space applications as well as high performance ropes and tennis rackets.
2. LCP finds extensive applications as coatings, composites, and additives.
3. The electrical motor components are made from LCP.
4. LCP finds its applications in electronic industry as LED's and SMT components.
5. LCP has an interesting application like information storage media.