# 3. POLYMERS

**Syllabus:** Introduction: polymerization: mechanism of polymerization taking ethylene as an example. Determination of molecular weight of a polymer - numerical problems. Commercial polymers: Plexi glass, Polyurethane and Polystyrene. Polymer composites: Carbon fibre and Epoxy resin – synthesis, properties and applications. Introduction to conducting polymers, mechanism of conduction in polyacetylene and applications.

**Polymer**: A polymer is a large molecule of high molecular weight obtained by the chemical interaction of many small molecules of low molecular weight of one or more type. The process of manufacture of a polymer is called the polymerization.

Examples: Polyethylene, Polyvinyl chloride, Natural rubber, Starch, etc.

Monomers: Small molecules of low molecular weight, which combine to give a polymer, are called monomers.

Degree of Polymerization: The number of monomers used in the process is called degree of polymerization.

Functionality**:** The total number of functional groups or bonding sites present in a monomer molecule is called the functionality of the monomer.

## Polymerization:

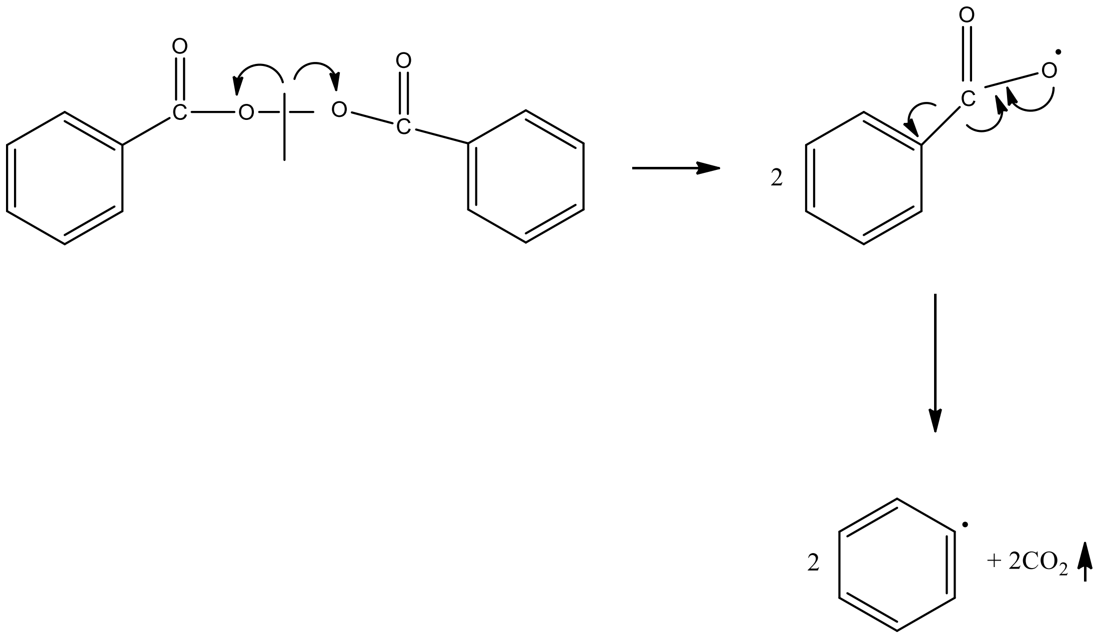
It is the process of conversion of low molecular weight substances into high molecular weight substances with or without the elimination of by products such as HCl, $H_2O$, $NH_3$ etc.

### Mechanism of Free Radical Polymerization:

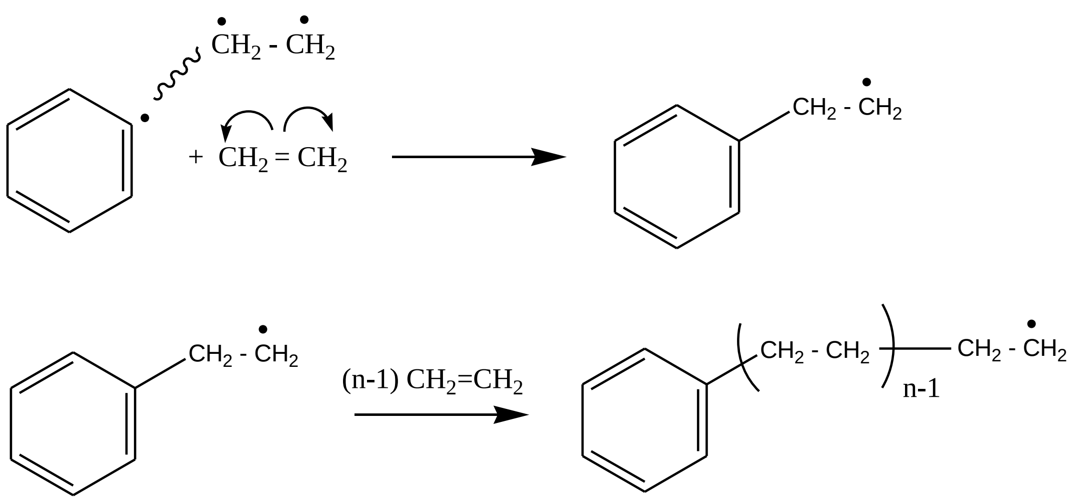
The polymerization of ethylene or ethene monomer by free radical mechanism proceeds in three distinct stages: **1.** Initiation **2.** Propagation **3.** Termination.

$$n\ CH_2{=}CH_2 \xrightarrow{\text{DBP at } 60^{o}C} -(CH_2\text{-}CH_2\text{-})_n$$

**Initiation**: The initiation step involves the production of free radicals by the homolytic dissociation of an initiator such as **dibenzoyl peroxide (DBP)** to yield a pair of radicals. DBP is used as a radical to induce polymerization. These are highly active species. A free radical is an atomic or molecular species having an odd or unpaired electron.



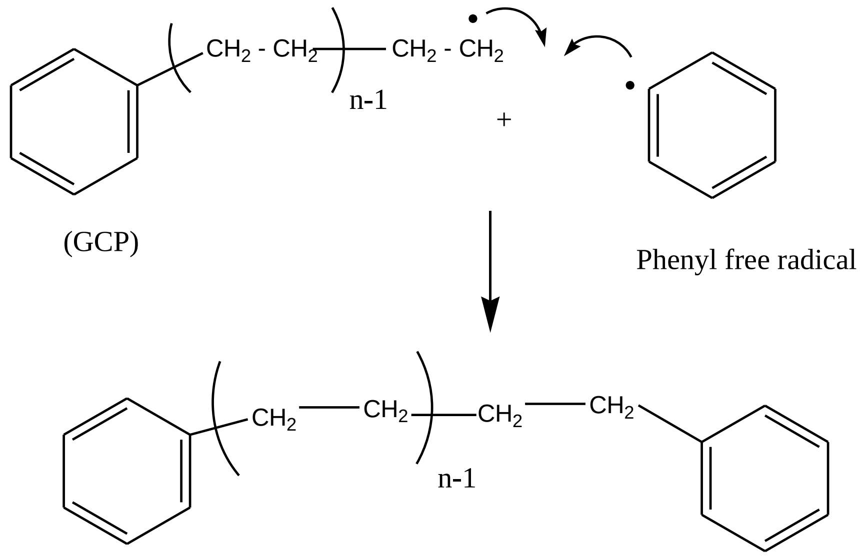

**Propagation:** Phenyl free radical combines ethene to form another free radical. This can combine with n number of ethene molecules to form a molecule called as growing chain polymer (GCP). The process continues as long as ethene is available or until termination occurs.

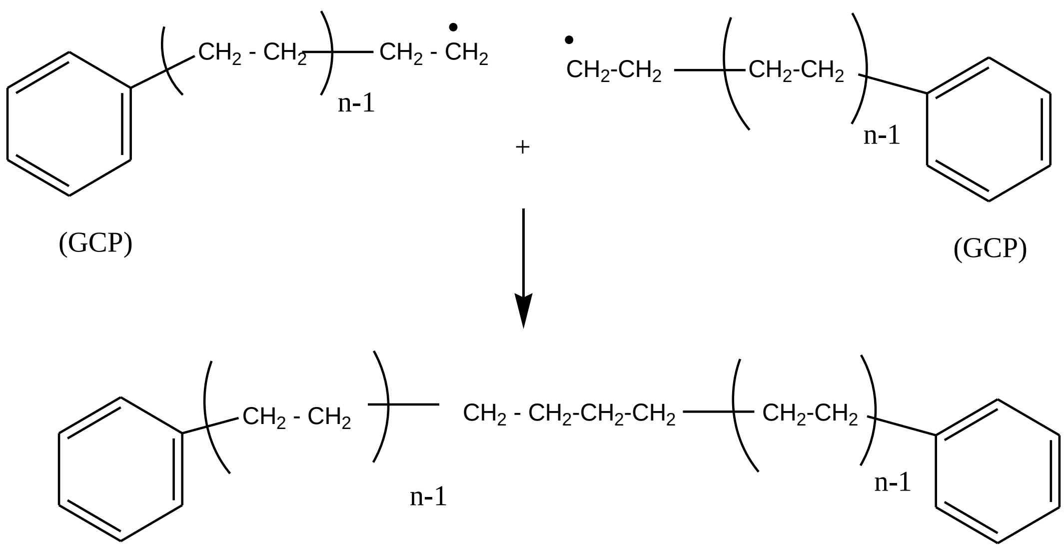



(GCP)

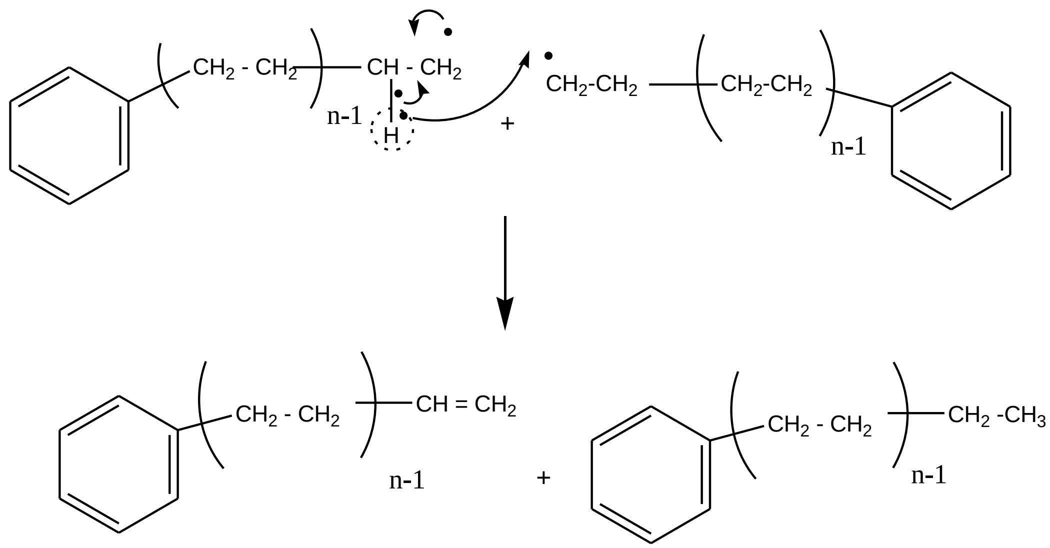
**Termination**: In termination, growing polymer chain is transformed into a dead polymer molecule. Termination of growing chain polymer occurs by one of the following reactions:

**1**. **Coupling or combination:** Two growing polymer chain may react with each other resulting in the formation of a dead polymer chain.




**2. Disproportionation:** Hydrogen atom of one radical center is transferred to another radical center. This results in the formation of two polymer molecules i.e., one saturated and another unsaturated.



Further hydrogenation is carried out to replace phenyl group with hydrogen then the resulting product is purified and used for various applications.

$$CH_3 \left( CH_2 - CH_2 \right)_n CH_3$$

**Degree of Polymerization (DP):** Degree of polymerization is the number of monomer units present in a polymer.

**DP = M / m** where, DP = degree of polymerization
M = molecular weight of the polymer
m = molecular weight of monomer unit

## Molecular Weight of Polymers:

Molecular weight of a polymer influences various properties of a polymer. The low molecular weight polymers are generally soft and gum like substances. The high molecular weight polymers are tougher and more heat resistant. The molecular weight of polymer depends upon the number of monomer units joined together. Polymers may be monodisperse or polydisperse. Hence, it is necessary to take their weight as average molecular weight. There are two types of average molecular weight.

### 1) Number Average Molecular Weight, $\overline{M}n$

It is obtained by dividing the total weight of the dispersed material with the number of molecules present i.e.,

$$\overline{M}_n = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3} = \frac{\sum_{i=1}^{\infty} n_iM_i}{\sum_{i=1}^{\infty} n_i}$$

Where $n_1$, $n_2$, $n_3$ are the number of molecules having masses $M_1$, $M_2$, $M_3$ respectively. The number average molecular weight assumes that each molecule makes an equal contribution to polymer properties regardless of the size or weight.

### 2) Weight Average Molecular Weight, $\overline{M}w$

In this case, molecular weight of polymer not only depends upon the number of monomer units with their masses but also on their size. In the below equation, $n_1$, $n_2$.., denotes the number of molecules having masses $M_1$, $M_2$,.. and $m_1 = n_1M_1$, $m_2 = n_2M_2$.

$$\overline{M}_w = \frac{m_1M_1 + m_2M_2 + m_3M_3}{m_1 + m_2 + m_3} = \frac{\sum_{i=1}^{\infty} n_iM_i^2}{\sum_{i=1}^{\infty} n_iM_i}$$

The molecular weight of the polymer can be determined by using the following methods,

1) Colligative property measurements
2) Light scattering measurements
3) Viscosity measurements
4) Chemical analysis
5) Ultracentrifuge

### Polydispersity Index (PDI):

It is the ratio of weight average molecular weight to the number average molecular weight. For a polymer in which all molecules having identical molecular mass the ratio $\overline{M}w = \overline{M}n$.

$$\text{PDI} = \frac{\overline{M}w}{\overline{M}n}$$

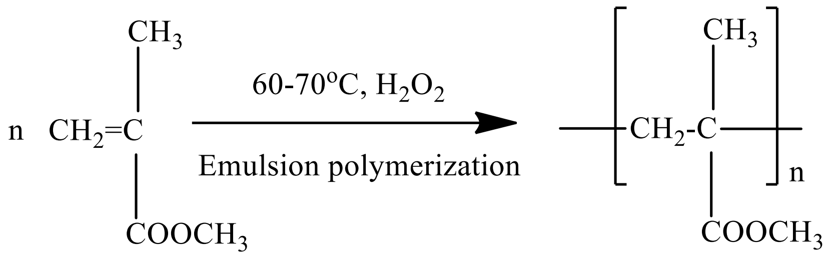
PDI = 1, Polymer is monodisperse and homogeneous

PDI > 1, Polymer is polydisperse and less homogeneous

## Synthesis, Properties and Applications of Few Polymers:

### 1) PMMA (poly methyl methacrylate or plexi glass):

Plexi glass is obtained by the polymerization of methyl methacrylate using hydrogen peroxide as initiator.




MMA

Plexi glass or PMMA

**Properties:**

- Plexi glass is a white transparent thermoplastic (soft on heating and hard on cooling).
- It is amorphous in nature due to bulky pendant groups.
- It has good optical clarity, but has poor scratch resistance.
- It is resistant to water, alkali, and inorganic salts but soluble in many organic solvents.
- Not affected by sunlight.

**Applications:**

- It is used in making protective coatings and plastic jewelry (as it is resistant to action of chemicals)
- It is used for making set of artificial teeth, contact lenses, DVDs, Wash basins etc.
- Used as paint and adhesive.
- Used in the manufacture of automotive lenses, aircraft windows, signal boards (as it has optical clarity).
- Used for making attractive signboards, instruments, artificial eyes.

**2) POLYURETHANES:** Polyurethanes are characterized by the presence of **Urethane linkage** (-HN-CO-O-) in the molecular chains. These are synthesized by the poly addition reaction between **diisocyanate** with **dihydroxy alcohol (diol) or trihydroxy alcohol (triol)**. During the addition, the **H** atom of **OH** group migrates to and adds to **nitrogen atom**.

$$\underset{\text{Diisocyanate}}{n\ O{=}C{=}N{-}R{-}N{=}C{=}O} + \underset{\text{Glycol (diol)}}{n\ HO{-}R'{-}OH} \longrightarrow \underset{\text{Polyurethane}}{\left[ \overset{\overset{\displaystyle O}{\|}}{C} - \overset{H}{N} - R - \overset{H}{N} - \overset{\overset{\displaystyle O}{\|}}{C} - O - R' - O \right]_n}$$

This polymerization is an addition reaction without elimination. The **urethane linkage (-NH-CO-O-)** resembles closely with that of **polyamide linkage (-NH-CO-)**. However, the presence of extra oxygen in urethane linkage offers increased flexibility to the chain. This is the cause for its much lower melting point than polyamides.

**<u>Properties:</u>**

- It has good stretching property.
- It has high tensile strength.
- It is resistant to water, oil and corrosive chemicals.
- It has excellent abrasion resistance.

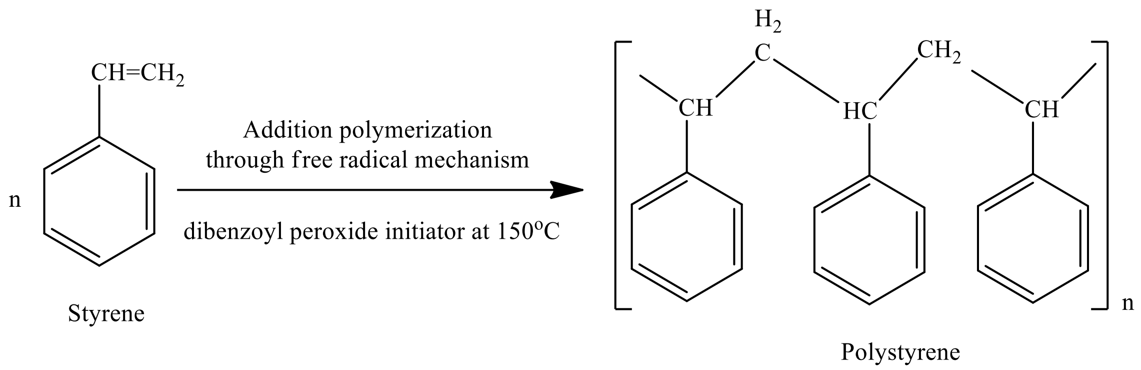
**<u>Applications:</u>** Polyurethanes are commercially available in four different forms:

- As <u>elastomer</u>, they are used in making gaskets, seals, tiers and industrial wheels.
- As <u>fiber</u>, they are used in light weight garments and swimsuits (due to their good stretching property).
- As <u>coating</u>, they are used in floorings of gymnasium, dance floors, seat covers (due to their high abrasion resistance).
- As <u>foam</u>, they are used in computer chairs, automobile seats, furniture cushions (due to their strength, lower density and easy fabrication).

**3) <u>POLYSTYRENE</u>**: PS is a synthetic aromatic hydrocarbon polymer made from the monomer known as styrene. Polystyrene is clear, hard, and brittle. It is an inexpensive resin per unit weight. Polystyrene is one of the most widely used plastics, the scale of its production being several million tonnes per year.

In chemical terms, polystyrene is a long chain hydrocarbon wherein alternating carbon centers are attached to phenyl groups (a derivative of benzene). Polystyrene's chemical formula is $(C_8H_8)_n$.

**<u>Synthesis:</u>** Styrene monomers upon subjecting to addition polymerization interconnect and forms Polystyrene. In the polymerization process, the carbon-carbon π bond of the vinyl group ($H_2C{=}CH_2$) is broken and a new carbon-carbon σ bond is formed, attaching to the carbon of another styrene monomer to the chain. Since only one kind of monomer is used in its preparation, it is a homopolymer. The newly formed σ bond is stronger than the π bond that was broken, thus it is difficult to depolymerize polystyrene. About a few thousand monomers typically comprise a chain of polystyrene, giving a molecular weight of 100,000–400,000 g/mol.




**Properties:**

- It is an amorphous, colorless, and transparent thermoplastic polymer.
- It has low melting point
- It has better resistance towards sunlight and ozone
- Poor conductor of electricity
- Poor conductor of heat
- Remains inert with solvents

**Applications:** Polystyrene can be naturally transparent, but can be colored with colorants.

- Household appliances.
- Consumer electronics products.
- Building and construction.
- Protective packaging (such as packing peanuts, jewel cases, storage of optical discs such as CDs and DVDs).
- Containers, lids, bottles, trays, rollers etc.

## ADHESIVES:

An adhesive is defined as a polymeric substance used to bind together two or more similar or dissimilar materials by surface attachment. They are mainly used to join a variety of substances such as metals, glasses, plastics, paper etc. The process of adhesion is easier, quicker, economical and advantageous compared to soldering, screwing, welding etc.

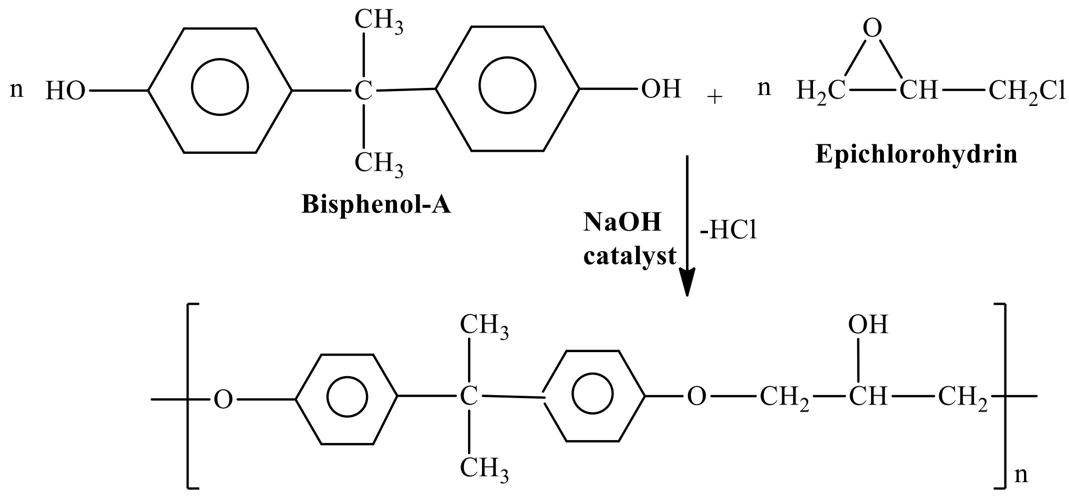
**Types of adhesives**: There are two types of adhesives.

**1**. **Natural adhesives**: These are the natural polymers which have low bond strength. Example: gum, glue, starch etc.

**2. Synthetic adhesives**: These are low molecular weight polymers called resins. These have high strength, resistant to water and corrosion and are unaffected by weather. Example: epoxy resins, phenol-formaldehyde, urea-formaldehyde etc.

## Epoxy Resins [Araldite]:

Epoxy resins are made by condensation polymerization of **Bisphenol-A** and **Epichlorohydrin** in presence of **NaOH as catalyst**.




Epoxy resin

**Properties:**

- Epoxy resins have excellent adhesion to various surfaces.
- Offer good abrasion resistance.
- Possess good electrical insulating properties.
- Excellent chemical resistance.
- High strength and low shrinkage.

**Applications:**

- Used for laminating materials for electrical equipment.
- Impart wrinkle resistance and shrinkage resistance to fabrics.
- Used as structural adhesives.
- Used in the production of aircraft and automobile components.
- Used in industrial flooring, highway surfacing and patching materials.

## POLYMER COMPOSITES:

A composite is a multiphase material made by the combination of two or more materials which exhibits specific properties. The properties of constituents do not dissolve or merge completely into each other but act together, while retaining their individual identities.

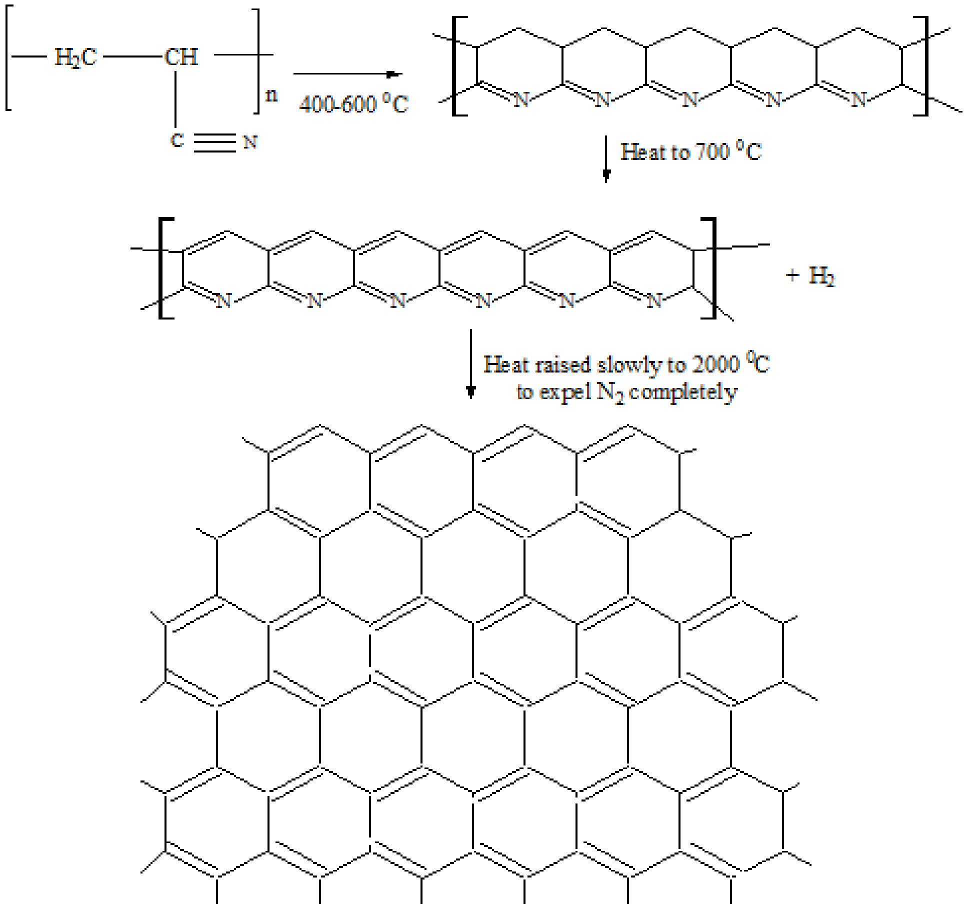
**Example:** Aircraft engineers look for the light weight (low density) materials which possess high strength, stiffness, good abrasion resistance and corrosion resistance. Any single metal, alloy or polymeric material cannot offer the combination of above properties. Hence, composite materials are developed.

A composite containing polymer matrix is known as **polymer composite**. Polymer composites are generally made of two components, namely, **Matrix and Fiber**. The fiber is embedded in the matrix in order to make the matrix stronger. The **matrix** is usually a thermostat material such as epoxy resin or a polyamide and it holds the fibers together. **Fiber** is often glass, but sometimes may be a carbon fiber, Kevlar fiber or polyethylene. Final properties of the composite material depend upon the properties of the constituent phases, their relative amounts and geometry of the fiber.

## CARBON FIBER:

It is a polymer of carbon, consisting of carbon rings. It is prepared by heating **polyacrylonitrile up to 1000 $^oC$** slowly in argon atmosphere. At high temperature, non-carbon atoms expel in the form of water vapor, ammonia, hydrogen and nitrogen. This process is called carbonization. The remaining carbon atoms form tightly bonded carbon crystals that align more or less parallel to the long axis of the fiber. Temperature gradually raised to **2000$^o$C to get wider ribbon like mass**. The temperature of 2000$^o$C is maintained till all the nitrogen is expelled leaving behind wider ribbon like pure carbon fiber in the graphite form.

The carbon fiber is used to make a composite material by using epoxy resin as the matrix. It has tensile strength three times that of steel and almost 4.5 times lighter than steel.




Ribbon like carbon fibre in the graphite form

**Properties**:

- It has high tensile strength almost 3 times greater than that of steel.
- Extremely stiff, strong and light.
- Resistant to chemicals, fire etc.
- These can be reinforced into epoxy resin matrix.

**Applications**:

- In aerospace: wings, antennae, helicopter blades, landing gears, seats, floors rocket motor cases.
- In automobiles: body panels, bumpers, shafts, gears, bearings, automobile brakes, clutches.
- Interior and exterior panels, chairs, tables etc.
- Protective helmets, archery bows, surfboards, fishing rods, diving boards.
- Pipes, tanks, pressure vessels, hoppers, valves, pumps etc.
- Guitar strings, tennis rackets and modern motor bikes.

## CONDUCTING POLYMERS:

Organic polymers having electrical conductivity in the order of a conductor are called as conducting polymers. Conducting polymers are classified as extrinsic and intrinsic conducting polymers.

**Extrinsic conducting polymers** are prepared by mixing polymers with conducting fillers like metal fibers, metal oxides, carbon black etc. Here conductivity is not due to the matrix polymer but due to the added conducting fillers.

**Intrinsic conducting polymers**: In these polymers, conductivity is due to organic polymers themselves which start conducting upon doping with suitable agents. Few polymers which conduct upon doping are polyacetylene, polyaniline, polypyrrole, polyphenylene etc. These polymers in their original form are insulators. But on suitable doping, their conductivity can be increased considerably. The important doping reactions are, Oxidative doping (p-doping), Reductive doping (n-doping), Protonic acid doping.

## Mechanism of conduction in POLYACETYLENE:

**Polyacetylene,** an organic polymer, is a semiconductor on its own, but when doped, its conductivity increases. It can be doped by oxidation with halogen (iodine) called p-doping or by reduction with alkali metal (Na) called n-doping. Oxidative doping is more common.

**Conversion of Polyacetylene into conducting polymers:** Polyacetylene is treated with iodine in presence of $CCl_4$. As a result of oxidation, polaron is generated. Further, repeating the same process, converts polaron into bipolaron. Due to electronic rearrangement, the pi-bonds shifts from one position to other. This movement of charge makes polyacetylene a conducting polymer. On doping, the conductivity of polyacetylene increases from $10^{-5}$ S/cm to $10^{3}$-$10^{5}$ S/cm.

**Mechanism:** When iodine is added as dopant, iodine molecule attracts an electron from the polyacetylene chain and becomes $I_3^-$.

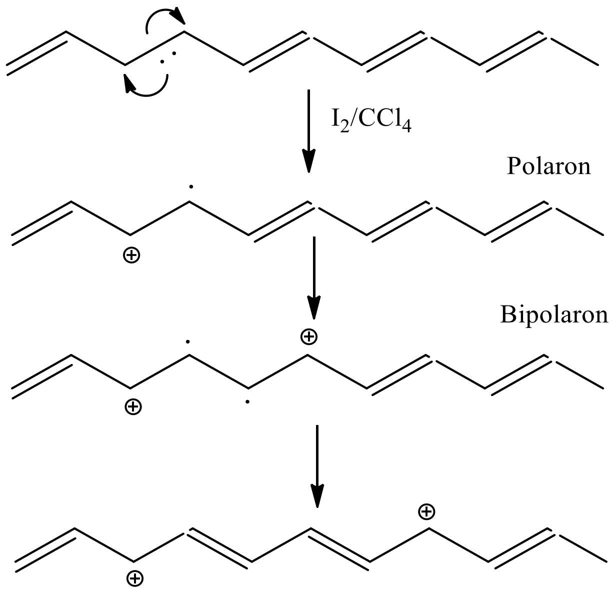
$$(CH)_n + \frac{3x}{2} I_2 \longrightarrow (CH)_n^{x-} + xI_3^-$$

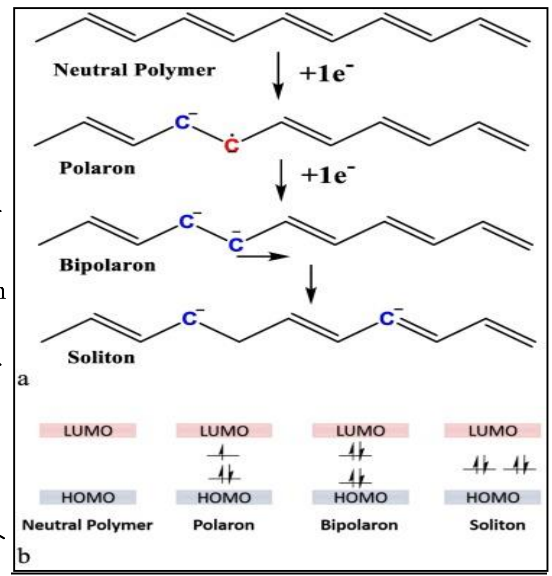
The electron is removed from the top of the polyacetylene valence band creating a **vacancy or hole**. At this stage, polyacetylene is positively charged, is called a **polaron or radical cation**.

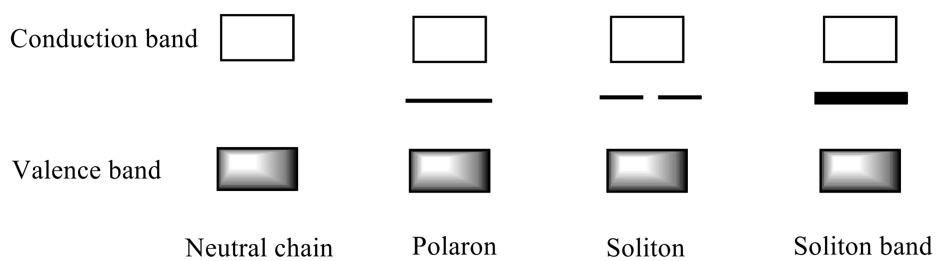
The lone electron of the double bond from which an electron was removed, can move easily. This electron successively moves along the polymer chain and said to be delocalized. The +ve charge, on the other hand, is fixed by electrostatic attraction to the iodide ion, which does not move so readily.

The second oxidation of a chain containing polaron, followed by radical recombination yields **two charge carriers on each chain (bipolaron)**. The positive charge sites on the polymer chains are compensated by anions $I_3^-$ formed by the oxidizing agent during doping.

If polyacetylene is heavily doped (oxidized), **polarons form pairs called solitons**. In polyacetylene, the solitons are delocalized over 12 carbon atoms. Due to the formation of soliton, a new localized electronic state appears in the middle of the energy gap. When doping is high, several charged solitons form soliton band. This band can later merge with edges of valence and conduction bands thus exhibiting conductivity.




**Applications**:

Conducting polymers are used in,

- Used as sensors in humidity sensor, gas sensor, radiation sensor.
- As conductive tracts on printed circuit boards
- Used as an electrode material for rechargeable batteries
- Light emitting diodes
- Information storage devices
- Sign boards or advertisement boards.