# UNIT-4 POLYMERS

Definition - Classification of polymers: Based on origin and tacticity with examples – Types of polymerization - Addition (free radical addition mechanism) and condensation polymerization. Plastics, Elastomers and Fibers: Definition and applications (PVC, Buna-S, Nylon-6,6). Differences between thermoplastics and thermosetting plastics, Fiber reinforced plastics (FRP).

**Conducting polymers:** Definition and Classification with examples - Mechanism of conduction in trans poly-acetylene and applications of conducting polymers ,Polylactic acid and its applications.

# UNIT-4 POLYMERS

Polymers : *poly* = many and *mer* = part or unit

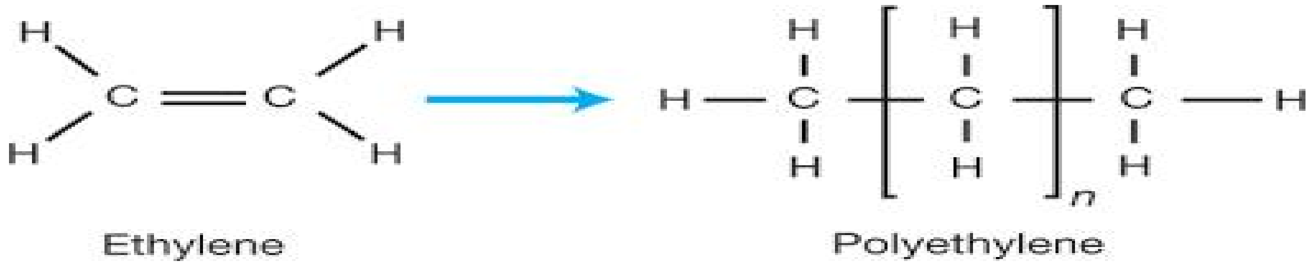
- Polymer is giant molecule of high molecular weight formed by large number of smaller molecules called monomers.
- Eg of natural polymers : Protein, wood, cotton, cellulose

Monomer : Small molecule with at least two reactive sites, that can combine to form polymers.

- Unsaturation or functional groups

Properties of polymers: cheap, high strength, light weight , flexibility , resistance to chemicals , fabrication into desired shape , durability, insulating properties.

Polymerization:The chemical reaction in which number of same or different monomers either with unsaturation or functional groups combine with or without the elimination of functional groups to form homo or hetero polymer is known as polymerization.



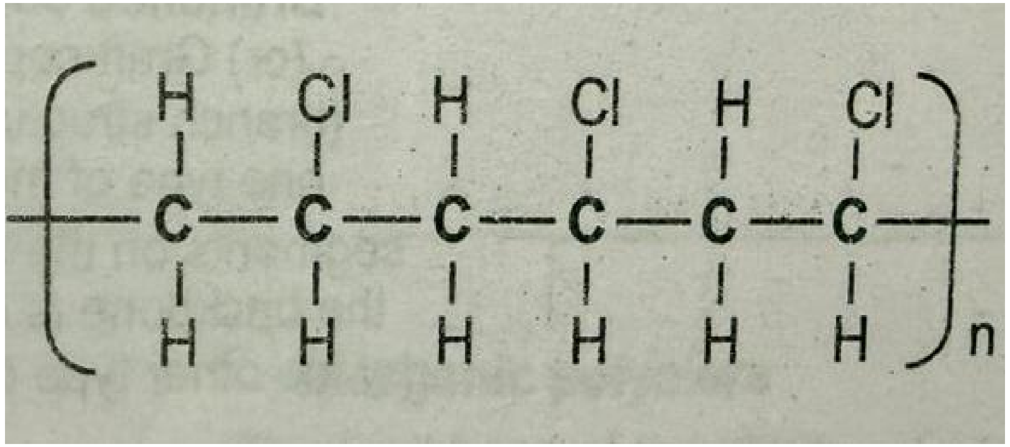

Degree of Polymerization: The number of monomeric units/repeating units in a polymer.

- Oligo polymers – less than 600
- High polymers- more than 600

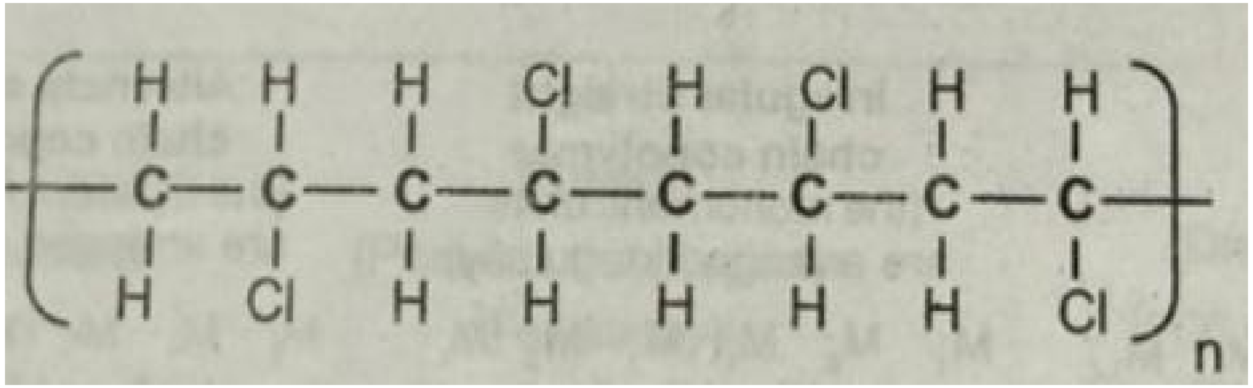
## Tacticity:

- Arrangement of functional groups on the backbone of the polymer chain.
- There are 3 types based on tacticity.

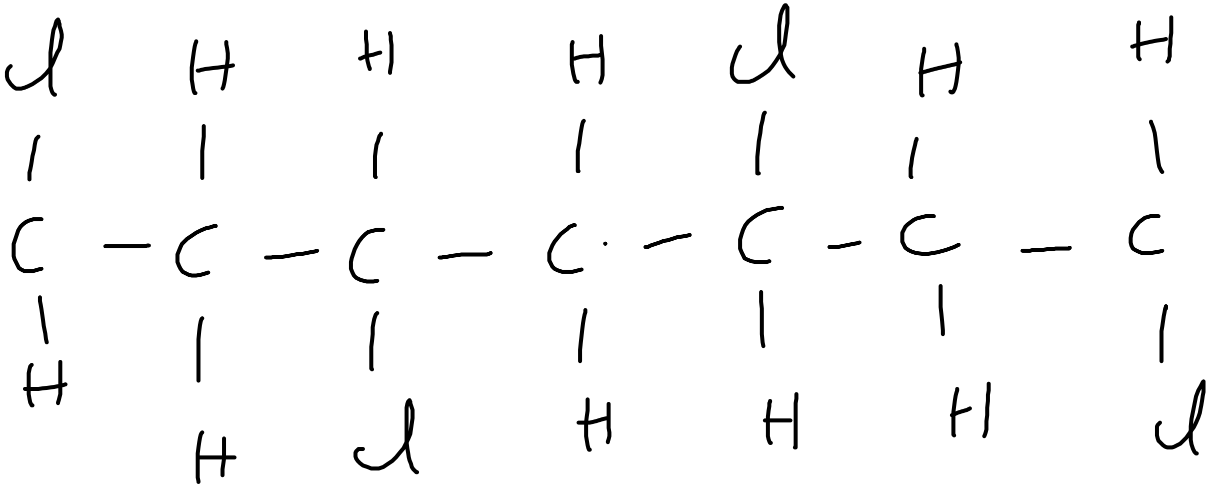
Isotactic polymers: functional groups are arranged on the same side of the polymer.



Atactic polymers: no regular arrangement of functional groups on the backbone of polymer chain.



Syndiotactic polymers: alternate arrangement of functional groups on the polymer chain



Types of polymerization:

1) Addition Polymerization  2) Condensation Polymerization

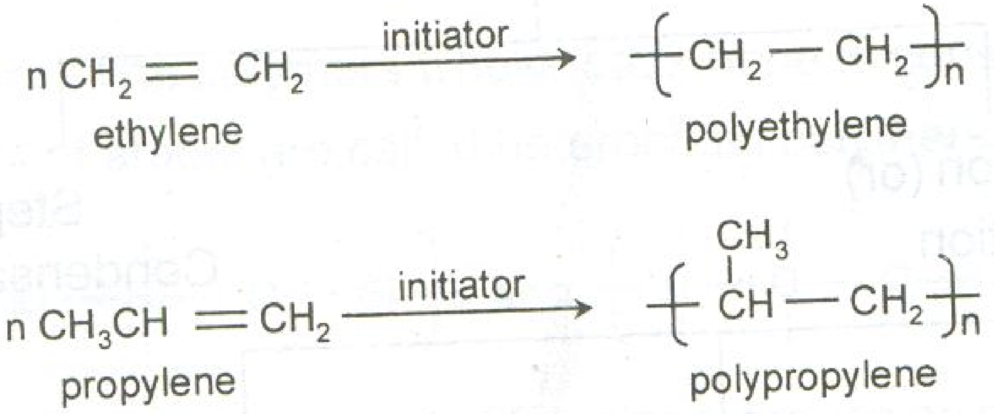
## Addition or chain polymerization:

- The chemical reaction in which number of same or different monomers with unsaturation combine without the elimination of functional groups to form homo or hetero polymer is known as addition polymerization.
- It is also called as chain polymerization.
- It gives polymers which are exact multiple of monomers.

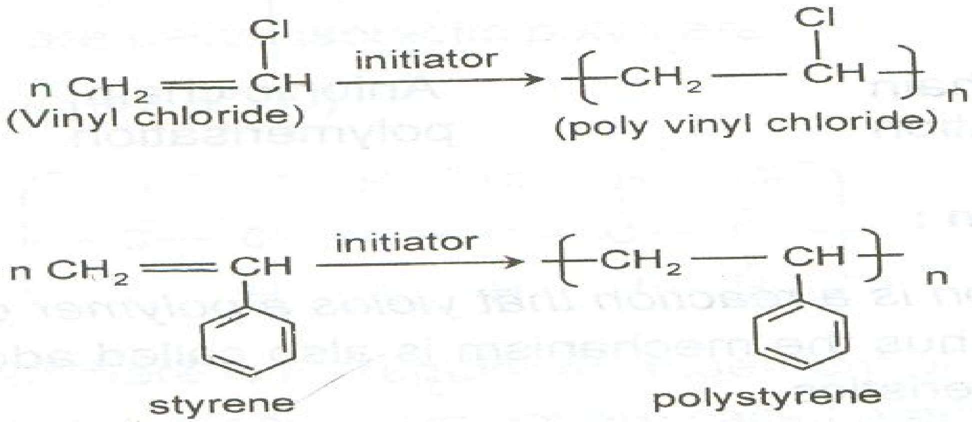
## Characteristics:

- A chain polymerization is a reaction that yields a product which is the exact multiple of monomers.
- The functionality of monomer is a double bond and it is bifunctional.
- It takes place by the self addition of monomer molecules to each other through a chain reaction.
- No byproducts like H2O ,CH2OH are produced.
- The polymer has the same chemical composition as that of monomer.
- The molecular weight of the polymer is in exact multiples of monomers.
- The mechanism occurs in 3 steps. Initiation,propagation and termination.
- The mechanism is rapid.
- It is highly exothermic. The conversion of ∏ to σ bond involves the liberation of 20 kcal/mole of energy.

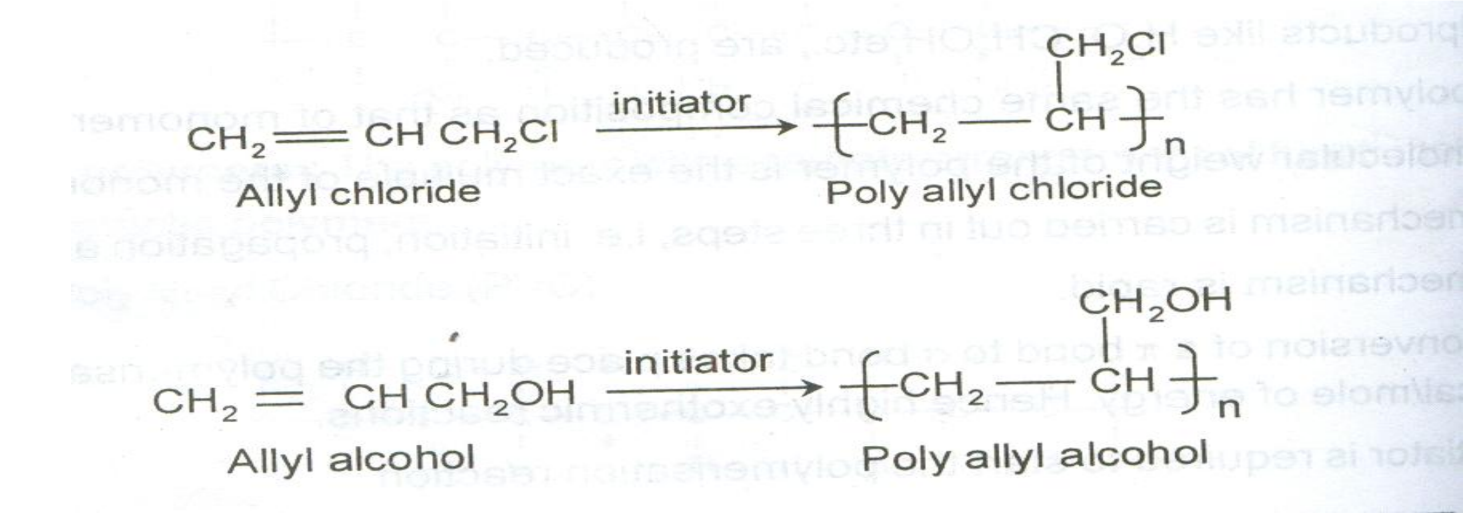
# Eg: olefins



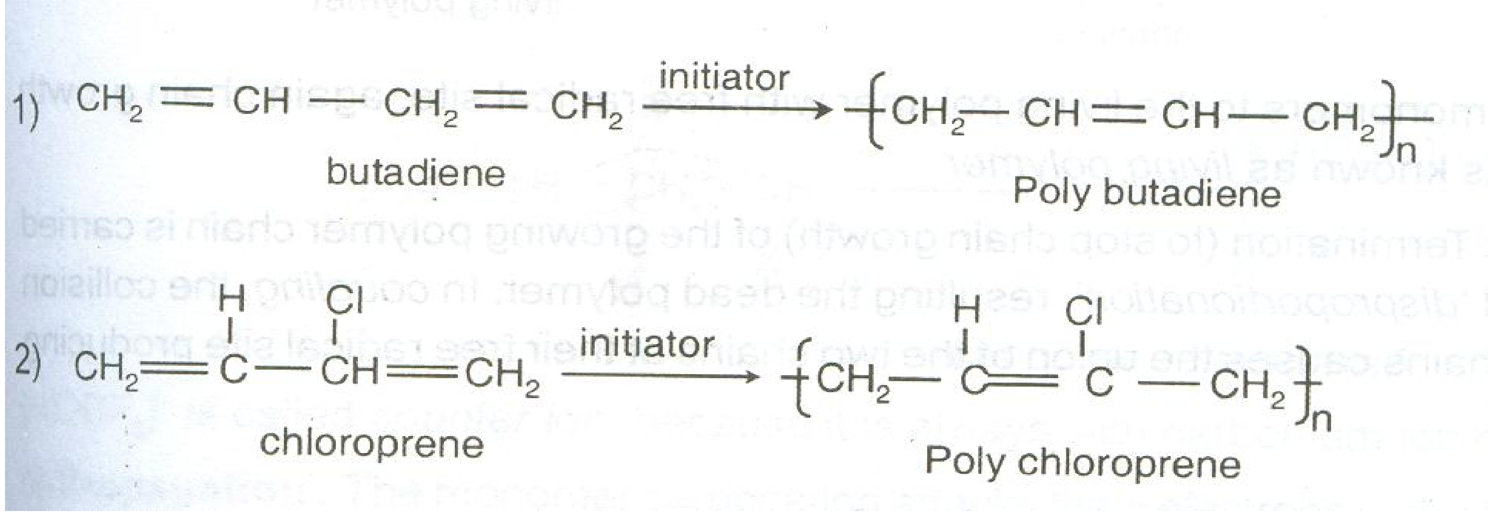

# Vinyl compounds:



# Allyl compounds:

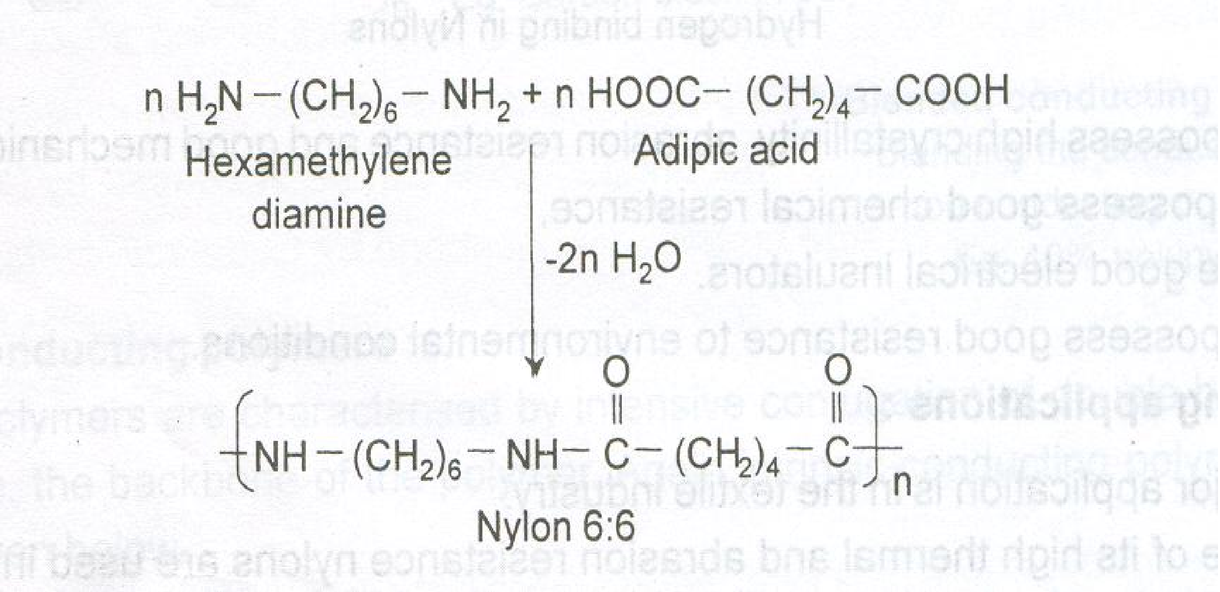


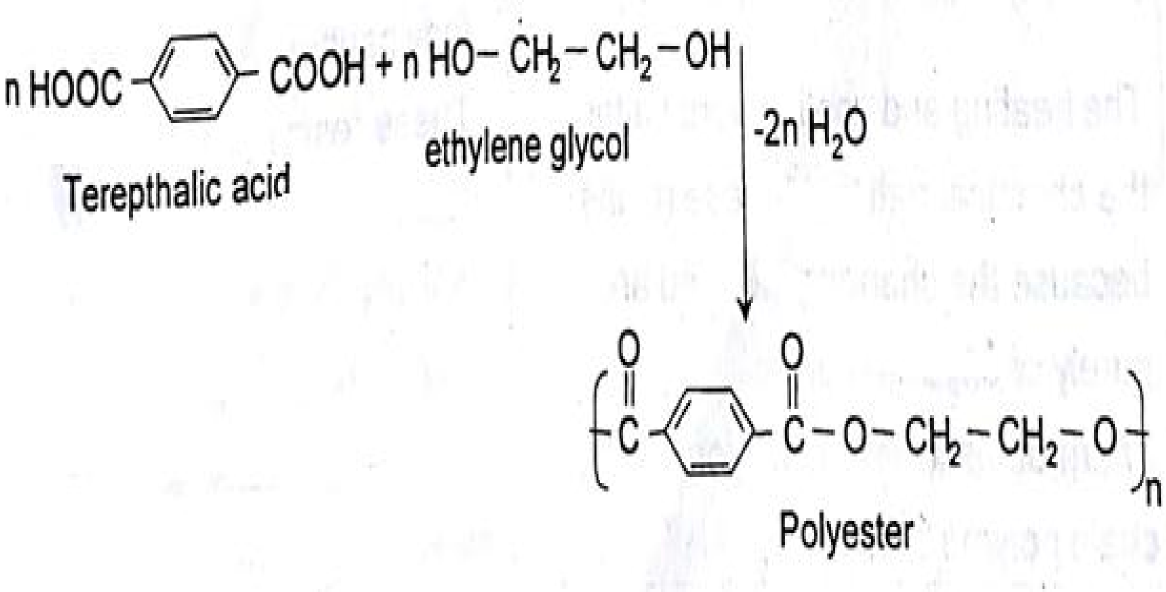

# Dienes:



## Condensation or step polymerization:

The chemical reaction in which number of same or different monomers with functional groups combine with the elimination of functional groups like $H_2O$, NaCl, $CH_3OH$ etc. to form homo or hetero polymer is known as condensation polymerization.



- Condensation polmerisation takes place by the condensation reaction of functional groups of monomers with the elimination of by products like $H_2O$,HCl,$CH_3OH$ .
- The monomers contain the functional groups like –OH,-COOH,-$NH_2$,RCOOR ,halides etc.
- The functionality of the monomers is two or more than two. The monomers must be dibasic acids,diols,diamines etc.
- It occurs in slow step wise manner.
- The reaction involves the elimination of by products like HCl, $H_2O$, $CH_3OH$ etc.
- The reaction is not exothermic.
- The molecular weight of the polymer is not in exact multiples of monomers.
- It is not a three-step mechanism.
- The reactions are catalyzed by a catalyst.

# Plastics:

- Plasticity (permanent deformation)
- Can be molded to any desired shape presence of catalyst, heat or pressure.
- Based on the behavior of plastics upon heating, plastics are classified into two types.
    - Thermoplastics
    - Thermo sets

| Thermoplastic Resin | Thermoset Resins |
|---|---|
| They soften on heating readily and become strong when cooled | Once they are fabricated, can’t be remolded by heating |
| Consists of long chain linear molecules | They have 3 –d network |
| The linear chains are connected by weak wandewaal’s attractive forces | The network structure has covalent bonding. |
| Formed by Addition polymerization | Formed by Condensation polymerization |
| They are soft, weak & less brittle | They are hard, strong and more brittle |
| They can be reclaimed from wastes | Can’t be reclaimed from wastes |
| Usually soluble in some org. solvents | Due to strong bonds & cross linking they are insoluble in all org. solvents |
| Can be remoulded, reused,recycled | They can’t |
| Eg: PE,PVC,PS | Eg: Bakelite, Nylons |

## Polyvinyl chloride:

- Monomer-vinyl chloride
- Vinyl chloride is prepared by treating acetylene with HCl at 60-80 C in the presence of metal oxide catalyst.
- PVC is prepared by heating vinyl chloride in the presence of benzoyl chloride or H2O2 by free radical addition polymerization.

## Properties:

- Colorless , non-inflammable, chemically inert powder
- Specific gravity is 1.33,M.P is 148 C
- Resistant to atmospheric conditions like O2,CO2,moisture.
- Rigid and flexible
- Resistant to light

## Applications:

Rigid or unplasticized PVC: highly resistant to chemicals and brittle.

- safety helmets, refrigerator components, tyres, cycle and motorcycle mudguards.

Plasticized pvc: produced by mixing plasticizers like dibutyl phthalate,

Dioctyl phthalate , tricresyl phosphate etc.

Raincoats , table cloths , handbags , curtains , electrical insulators, shoes, radio and T.V components , chemical containers, cameras, aircrafts etc

## Nylon 6,6:

- polyamide resin with recurring amide groups
- Prepared by the co polymerization of diamine and diacid.
- Depending on the number of carbon atoms in diamine and diacid,there are different types of nylons like nylon 6,6 and nylon 6,10
- The first number indicates no.of carbon atoms in diacid and second number indicates the number of carbon atoms in diamine.

## Properties:

- Translucent,whitish with high M.P (>500 C)
- High temperature resistance and good abrasion resistance
- Good strength
- Insoluble in organic solvents

## Applications:

- Textile industry
- Because of their thermal and abrasion resistance,nylons are used in mechanical engineering applications like gears,bearings,machine parts.
- Flexible tubing for conveying petrol
- Electrical insulators
- In automobile industry and telecommunication industry for making radiator parts and coil formers.
- For making filaments for ropes, bristles for tooth rushes etc

## Buna-S rubber(styrene rubber):

It is produced by the co-polymerization of butadiene of 75% and styrene of 25%

### Properties:

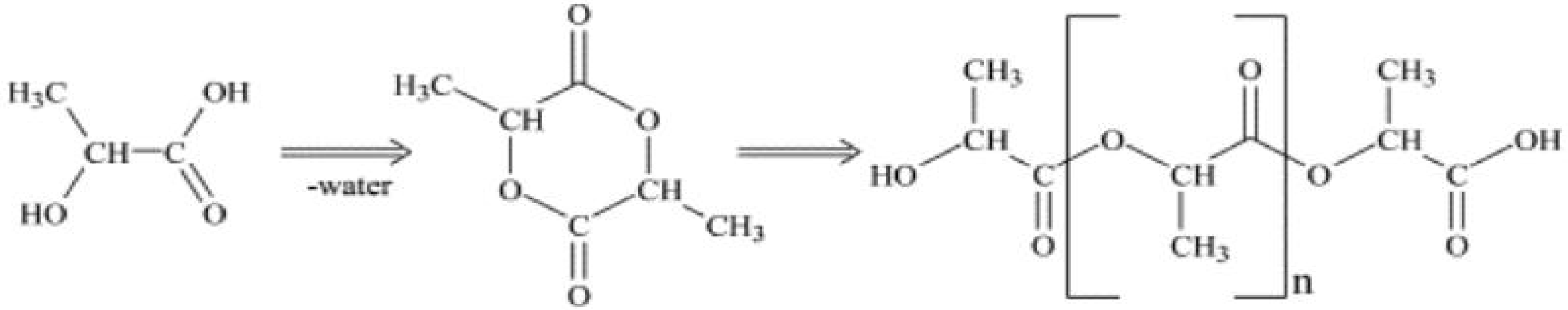
- Strong and tough polymer
- High abrasion resistance
- High load bearing capacity
- Swells in oil and solvents
- Low oxidation resistance
- It can be vulcanized as natural rubber with sulphur or sulphur monochloride.
- Good electrical insulator

## Applications:

- Motor tyres
- Shoe soles
- Foot wear components
- Insulation of wire and cables
- Carpet backing
- Gaskets
- Adhesives
- Tank lining

## Polylactic acid (PLA):

- It is a biodegradable thermoplastic polymer .
- It is derived from renewable resources like corn starch , tapioca roots, starch, sugarcane etc.
- Lactic acid is obtained by the bacterial fermentation of sugarcane or from the starch obtained from corn.
- The catalytic dimerization of lactic acid results in the formation of lactide monomer .
- The obtained lactide undergoes polymerization in the presence of stannous octate to produce polylactic acid.




Lactic Acid cyclic lactide monomer Poly (Lactic Acid)

Properties:

- M.P  173-178 c
- Glass transition temperature 60-150 C
- PLA is a chiral compound and exists as poly l-lactic acid (PLLA)
- Possess biocompatibility, processability and good strength

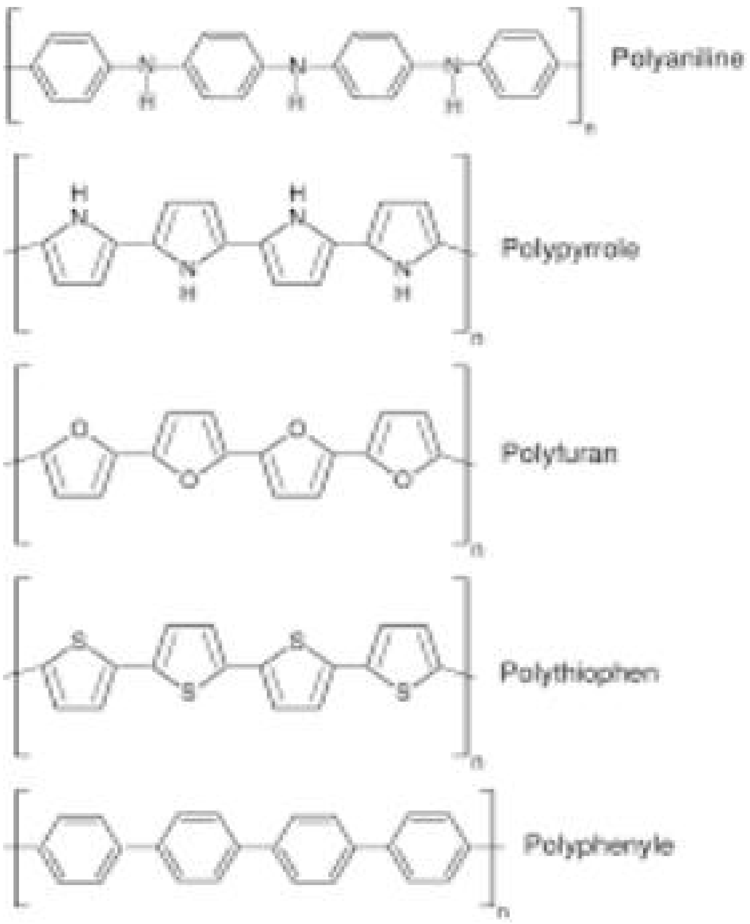
Applications:

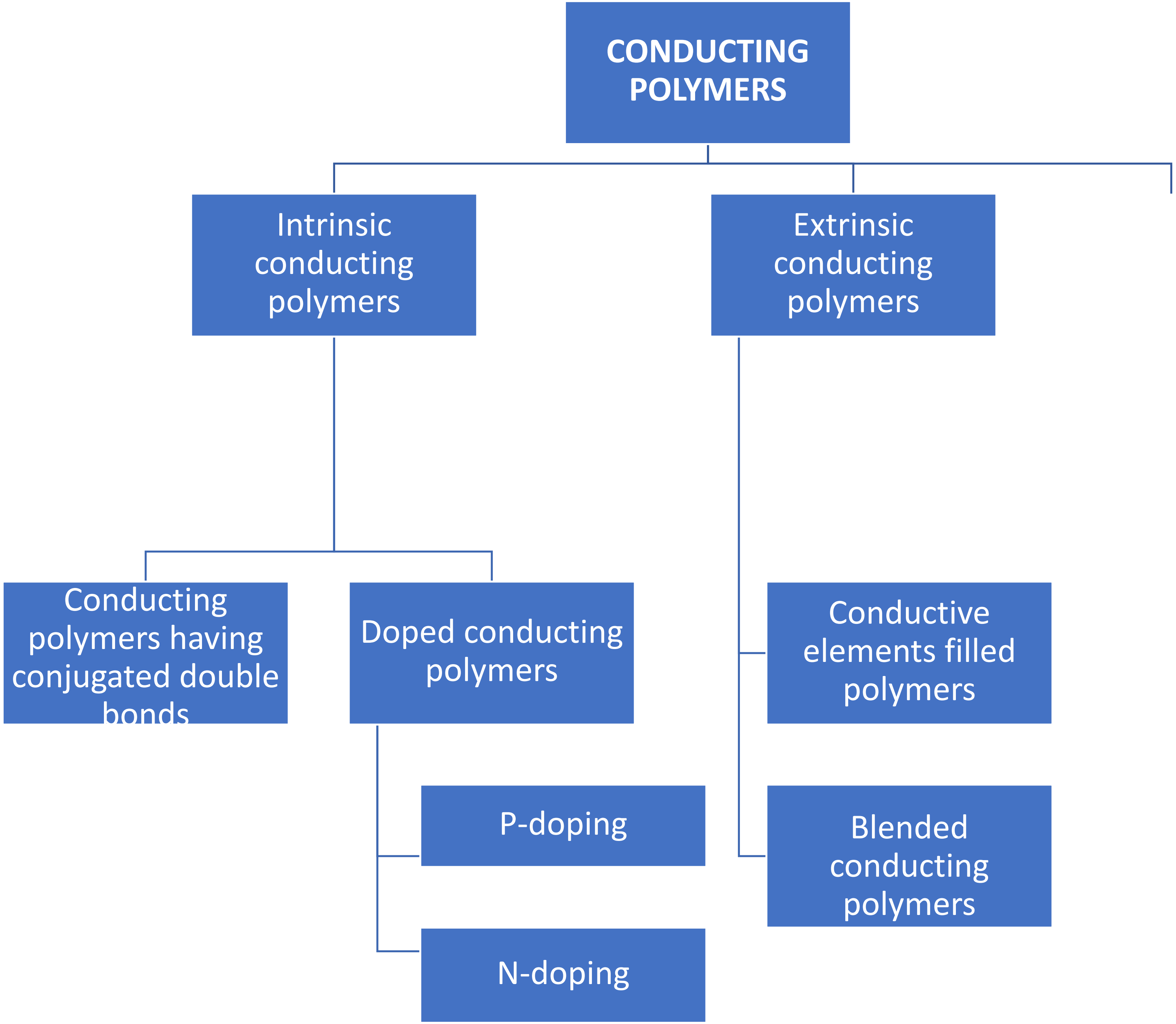
- Used for making medical implants like anchors, screws, pins etc.
- In biomedical applications like sutures, drug delivery devices and dialysis media.
- For making compostable packing material,disposable garments,food packing

# CONDUCTING POLYMERS

- Polymers which can conduct electricity are called conducting polymers.
- Ordinary polymers generally

are insulators



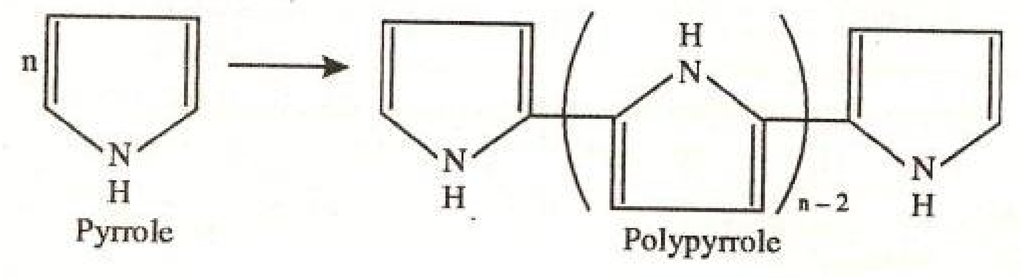

CONDUCTING POLYMERS
Intrinsic conducting polymers
Extrinsic conducting polymers
Conducting polymers having conjugated double bonds
Doped conducting polymers
P-doping
N-doping
Conductive elements filled polymers
Blended conducting polymers

**Intrinsic conducting polymers :**

- These types of polymers have a solid backbone made up of extensive conjugated system, which is responsible for conductance. They are of two types:

**Conducting polymers having conjugated π-electrons in the backbone :**

- These contain a conjugated π-electron backbone responsible for electrical charge.
- Under the influence of electrical field conjugated π -electrons of the polymer get excited, which can then be transported through the solid polymer.
- overlapping of orbitals of conjugated π -electrons over the entire backbone results in the formation of valence bands as well as conduction bands, which extend over the complete polymer molecule.
- The presence of conjugated π -electrons in polymers increases its conductivity, *e.g.,*



**Doped conducting polymers:**

- The conducting polymers obtained by exposing the polymer to a charged transfer agent are called *doped conducting polymers.*
- Doping is the process by which conductivity of the polymers may be increased by creating negative or positive charge on the polymer backbone by oxidation or reduction.

**Doping is of two types:**

- **p-Doping :** It is done by oxidation process. In this process, the conducting polymer is treated with a Lewis acid.

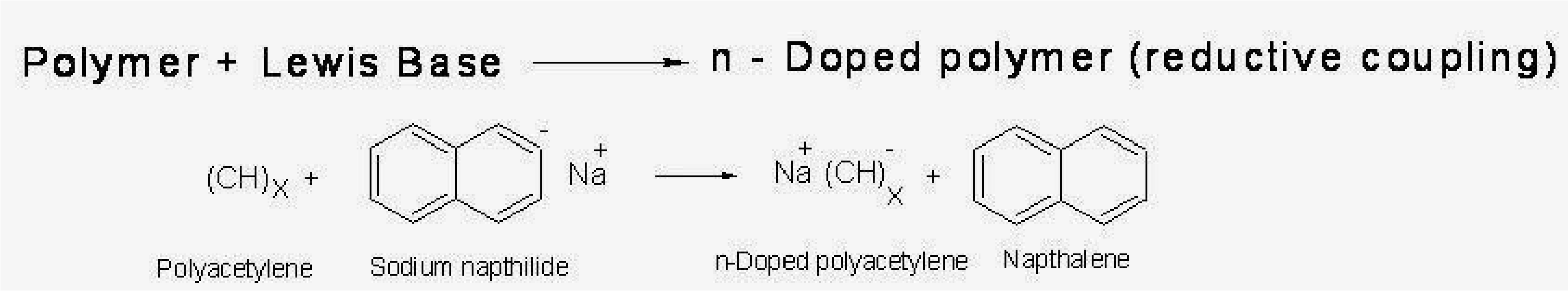
$$\underset{\text{Polyacetylene}}{(CH)_x} + \underset{\text{Lewis acid}}{A} \rightleftharpoons \underset{p\text{-Doped polyacetylene}}{(CH)_x^+ A^-}$$

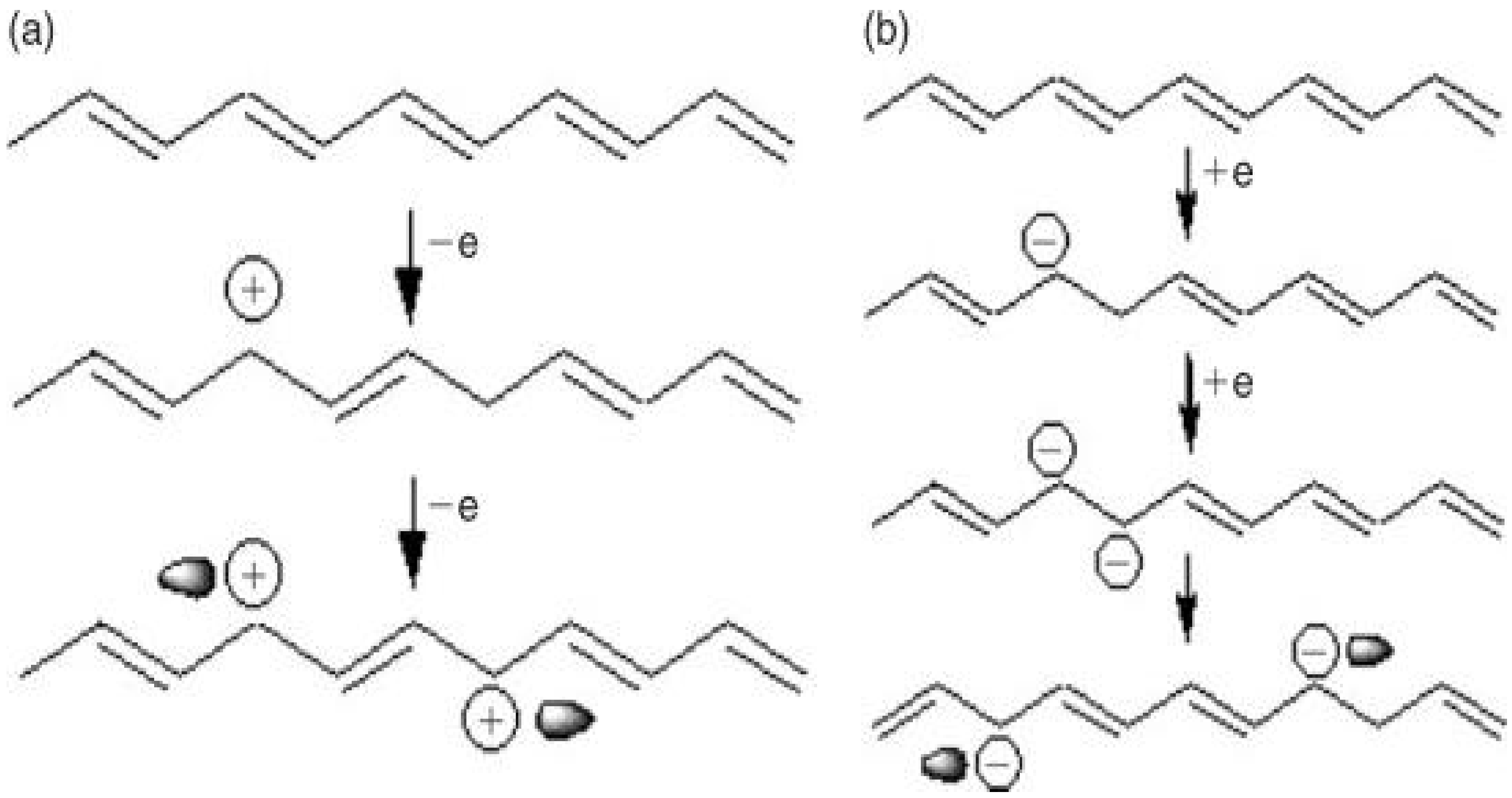
$$\underset{\text{Polyacetylene}}{(C_2H_2)_n} + \underset{\text{L.A.}}{2FeCl_3} \text{-----------}\rightarrow \underset{\text{+vely charged backbone}}{(C_2H_2^+)_n .FeCl_3^-} + FeCl_2$$

- **n-Doping :** It is done by reduction process. In this process, the conducting polymer is treated with a Lewis base.

$$(CH)_x \quad + \quad B \quad \rightleftharpoons \quad (CH)^-_x\, B^+$$

Polyacetylene      Lewis ba      Doped polyacetylene

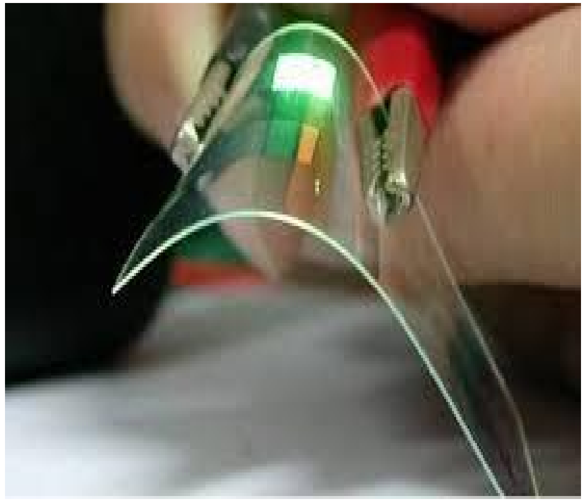





(a)p-doping (b) n-doping

**Applications of conducting polymers:** Conducting polymers are widely used:

1. In rechargeable batteries.
2. In making analytical sensors for pH, $O_2$, $SO_2$, $NH_3$, glucose, etc.
3. In the preparation of ion exchangers.
4. In controlled release of drugs.
5. In optical filters.
6. In photo voltaic devices.
7. In telecommunication systems.
8. In micro-electronic devices.
9. In bio-medical applications.



***Advantages:-***

- Polymers possess good conductivity.
- They can store charge.
- They absorb visible light to give colored complex.

## Fiber Reinforced Plastics(FRP):

- Composite material that consists of a polymer matrix reinforced with high strength fiber material.
- The polymer reinforced with high strength fiber material to impart good mechanical strength and hardness is called FRP.

polymer + fiber material --------→ FRP

- Main reinforcing fibres that are used are glass , graphite, alumina boron , carbon , asbestos etc.
- Produced by bonding fiber material with polymer matrix and curing it under heat and pressure.
- Hardness and strength are imparted by fillers like carborundum , quartz and mica
- Barium salt impervious to X-rays
- Asbestos provide heat & corrosion resistance

Processing techniques:

- Matched metal die molding
- Injection molding
- Hand lay-up
- Spray-up

## Advantages:

- Exceptional strength to weight ratio, ideal for light weight, durable structures in aerospace and automotive applications
- Their corrosion resistance ensures longevity in harsh environments such as acid storage tanks and marine settings
- FRP’s versatility allows complex shapes to be molded for diverse uses from boat hulls to building materials.
- Provide excellent thermal and electrical insulation enhancing safety in various applications.
- Their durability reduce maintenance cost and external service life.
- Their design flexibility supports innovative architectural and engineering solutions.
- Their non-magnetic properties are useful in specialized equipment and environments.

## Applications:

- In space crafts, airplanes ,boat hulls, acid storage tanks , automotive components and construction materials.
- In manufacturing large capacity fuel and chemical storage tanks

Types:

**Glass Fiber-Reinforced Polymer (GFRP)** : Glass Fiber-Reinforced Polymer (GFRP) is a composite material made of glass fibers embedded in a polymer matrix (usually epoxy, polyester, or vinyl ester resin). It combines the strength and flexibility of glass fibers with the lightweight and moldable nature of polymers.

**FEATURES:**

- Lightweight
- High Strength-to-Weight Ratio
- Good Mechanical Properties
- Corrosion and Chemical Resistance
- Thermal and Electrical Insulation
- Cost-Effective
- Ease of Fabrication

**Applications:**

- Boat hulls, water tanks, automotive parts, Chemical storage tanks and pipes, Cable trays and ladders, Cooling tower components, Surfboards, skis, hockey sticks, Playground equipment
- Electrical insulators, Fire-retardant panel, Safety helmets and gears

**Carbon Fiber-Reinforced Polymer (CFRP):** Carbon Fiber-Reinforced Polymer (CFRP) is a high-performance composite material made from a polymer matrix (usually epoxy) reinforced with carbon fibers. It is known for its exceptional strength, stiffness, and lightweight properties.

**FEATURES:**

- High Strength-to-Weight Ratio
- High Stiffness
- Corrosion Resistant
- Thermal stability: CFRP performs well under moderate temperatures but degrades above 250°C (depends on matrix).
- Fatigue Resistant: Can withstand repeated loading and unloading without failure.
- Electrical Conductivity: Carbon fibers are conductive, but the composite as a whole depends on the matrix used.

**Applications**:

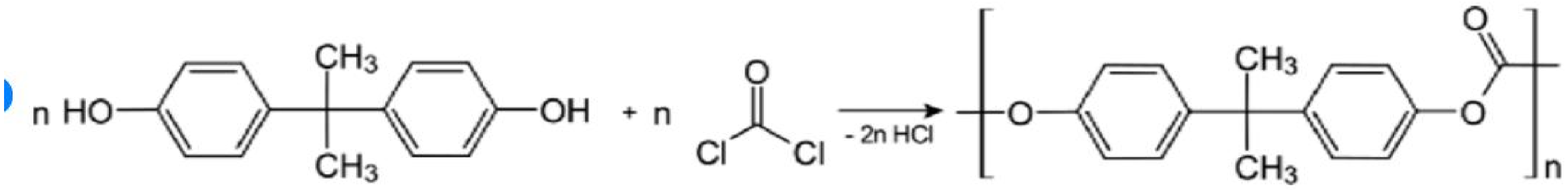
- Aircraft structural components (wings, fuselage panels, tail sections), Satellite parts and drone frames, in automotive industry (body of racing car), in strengthening of buildings and bridges, in medical applications, etc.,

**Aramid Fiber-Reinforced Polymer (AFRP) :** Aramid Fiber-Reinforced Polymer (AFRP) is a composite material made by combining aramid fibers (like Kevlar) with a polymer matrix (usually epoxy or polyester resin). This combination results in a material that is:

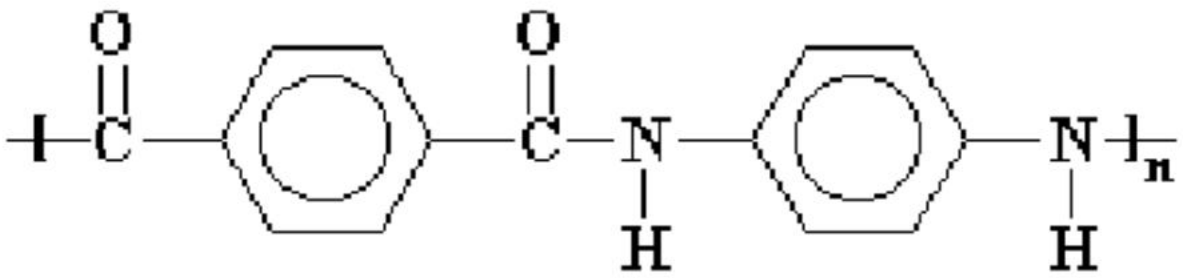
- Exceptionally strong
- Lightweight
- Resistant to impact, heat, and wear
- Non-Conductive
- Corrosion and Chemical Resistance
- Low Density and High strength to weight ratio

**Common Aramid Fibers Used:** Kevlar , Twaron ,Nomex

**Applications:** Bulletproof vests, helmets, body armor, Tires, brake pads, clutch linings, Aircraft fuselage parts, wing edges, Helmets, hockey sticks, canoe paddles, Structural strengthening, Cable protection, insulating sheets.




Bisphenol phosgene polycarbonate




Kevlar