

### Nanomaterials

Materials having the dimension of the order of billionth of a meter or nano meter are called **nanomaterials**.

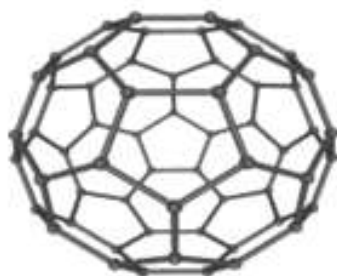
#### Classification:

1. Nano crystalline materials
2. Fullerenes
3. Dendrimer
4. Polyhedral silsesqui oxane
5. Nano intermediates
6. Nano composites
7. Biological nanomaterials

#### Nano crystalline materials:

These are aggregates containing a few hundred to several thousands of atoms which are joined to form crystalline form of matter. Resultant crystalline form of matter is called clusture. So these nanomaterials are called nano crystals. They can be used for getting semiconductor crystals. Their diameter is nearly 1nm. They are used for making very strong and long lasting metallic parts. On mixing nano crystals with plastic we get nano composites.

#### Fullerenes:



These are the molecular form of very pure carbon. They are discovered in 1995. They possess cage like structure of carbon atoms. Most abundant fullerene is buckminsterfullerene (buckminsterfullerene,  $C_{60}$ ). They possess spherical structure of 60 carbon atoms. Fullerenes contain twelve five membered rings and twenty six membered rings and possess a perfect icosahedral geometry. This geometry is similar to that of a soccer football. In fullerene, each carbon atom is bonded to three other carbon atoms and is  $sp^2$  hybridized.

#### **Uses:**

- They are used in drug delivery system.
- They are used in electronic circuits.
- They are used as lubricant in ball bearings.

#### **Dendrimer:**

These are organic nano particles. These are highly branched tree like organic polymers. These are obtained from monomers which are added in discrete steps to get tree like appearance. Highly controlled step wise reactions and purifications are required at each step to control the size, structure and functionality of dendrimer.

Eg. PAMAM Dendrimer (Poly Amido Amine)

#### **Polyhedral silsesquioxane:**

These are inorganic organic hybrid nano particles. They possess unique set of physical and chemical properties such as high solubility, thermal stability, dielectric constant, permeability and optical transparency. The stoichiometry of the compound is  $RSiO_{1.5}$ . That means every silicon atom is bound to an average of one and half oxygen (Silsesquiox) and to a hydrocarbon group (ane). Hence the name polyhedral silsesquioxane.

#### **Nano intermediates:**

They include nano structured films, dispersions, high surface area materials, supramolecular compounds etc. They are used in solar cells, sensors, battery etc.

#### **Nano composites:**

On mixing solid nano particles with plastic resin we get nano composites. They possess more strength. They are lighter and stiffer than thermoplastics. They are less brittle. They possess excellent corrosion resistance. Hence they are used as an anticorrosive material.

#### **Biological nano materials:**

These are nano materials of biological origin.

Properties of biological nano materials:

- Self assembly property
- Specific molecular recognition

Eg. DNA nano particles, nano structured peptides

Self assembled nano particles can be used to release compounds under specific conditions and are used in drug delivery systems.

(\***Self assembly** is a phenomenon where the components of the system assemble themselves spontaneously via an interaction to form larger functional unit.\*)

(\* **Molecular Recognition** is the specific interaction between two or more molecules through non covalent bond.\*)

### **Classification based on dimension**

This is the classification based on the number of dimensions which are not confined to the nanoscale range(<100 nm).

#### 1. Zero dimension (0-D)

Here all the three dimensions are in the nanometric range. Eg. Nano particles

#### 2. One dimension (1-D)

Here one of the dimensions is outside the nanometric range and the other two are within the range. Eg. Nano wires, fibres and tubes.

#### 3. Two dimension (2-D)

Here two of the dimensions is outside the nanometric range and one is within the range. Eg. Nano films, layers and coatings

#### 4. Three dimension (3-D)

Here all the dimensions are outside the nano metric range and one is within the range. Eg. Bundles of nano wires and tubes, multilayers.

### **Nanotubes**

CNT is a tiny hollow cylinder with outside diameter of a nanometer. These are formed spontaneously from carbon atoms. CNT's are sheets of graphene rolled to make a tube. Graphene is one atom thick planar sheets of  $SP^2$  hybridized carbon atoms as in graphite. On aligning in specific manner, their atoms can conduct electricity as effectively as copper. On aligning in a slightly different manner they become electrical semiconductor. They are stronger than steel.

Classification of nano tubes:

On the basis of alignment of carbon atoms, nanotubes are three types.

#### 1. Arm chair nanotube

#### 2. Zig-zag nanotube

#### 3. Chiral nanotube

#### • **Arm chair nanotube:**

If the line of hexagons is parallel to the axis of the nanotube, then the resultant nanotube is called arm chair nanotube.

#### • **Zig-zag nanotube:**

If the line hexagon is arranged in a zig-zag manner, then the resultant nanotube is called zig-zag nanotube.

#### • **Chiral nanotube:**

Line of hexagon exhibit a twist or spiral around the axis of the nanotube which is called chirality. Hence the name chiral nanotube.

On the basis of number of cylindrical structures, nanotubes are of two types.

#### 1. SWCN (Single Walled Carbon Nanotubes)

#### 2. MWCN (Multi Walled Carbon Nanotubes)

#### • **SWCN:**

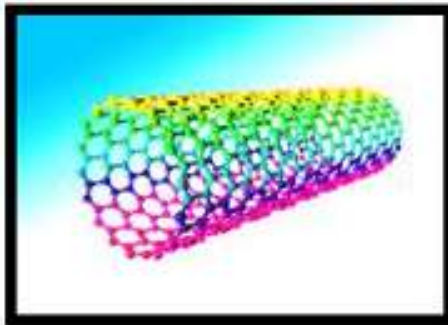
They contain only one nanotube cylinder.

#### • **MWCN:**

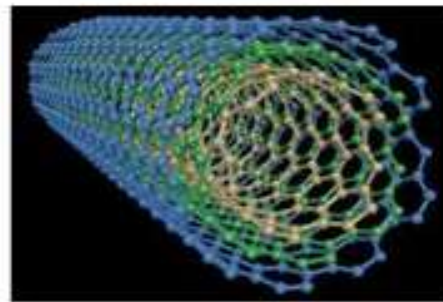
They contain more than one nanotube cylinders.



SWCN



MWCN



### Properties:

- Young's modulus is 10 times more than that of steel.
- They possess excellent magneto resistance.
- They are very stiff, hard to bend. Once they are bent, they are very resilient.
- Their thermal conductivity is more than diamond and is very high.
- They are very good conductors of electricity.

### Uses of nanotubes:

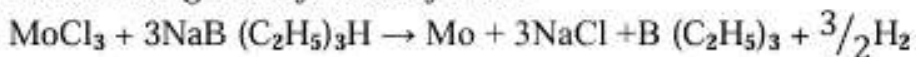
- They can be used as mechanical reinforcement material.
- It can be used a catalyst in many reactions.
- Lithium which is a charge carrier in some of the batteries can be stored inside the nanotube.
- They can be used in field effect transistors.
- They can be used as paper batteries.
- They can be used in solar cells.

### Synthesis of nano materials:

#### 1. Reduction :

##### a) Chemical Reduction:

Molybdenum nano particles can be obtained by reducing molybdenum chloride in toluene using tri ethyl boro hydride.



Tri ethyl lithium boro hydride, sodium boro hydride can also be used as reducing agents.

##### b) Electro reduction:

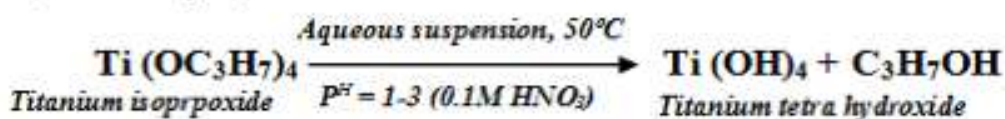
Copper nanoparticles can be prepared by this method. The electro reduction process chamber consists of a copper plating bath containing homogeneous acidified  $\text{CuSO}_4$  solution. The nano particles formed as spongy layers of ball structures at the cathode. These spongy layers of Cu can be easily separated to give fine nano particles.

#### 2. Hydrolysis: Sol- Gel Method or Chemical Solution Deposition

This method is used for the synthesis of nano crystalline titanium powder.

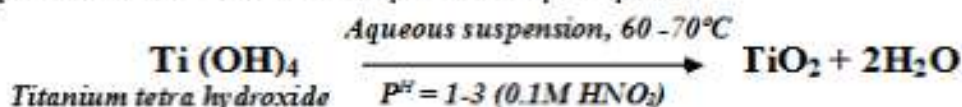
### STEP I:

Nano crystalline  $\text{TiO}_2$  powder is prepared by the hydrolysis of titanium isopropoxide to get a sol(Solid in liquid).



### STEP II:

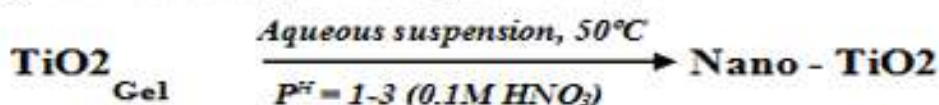
Titanium tetra hydroxide sol will undergo poly condensation by peptisation at a temperature of 60 - 70°C for a period of 18 – 20 hours to produce a precipitate.



Resultant TiO<sub>2</sub> precipitate possesses three dimensional network structure. The precipitate is then washed with ethanol and dried under vacuum conditions for three hours at a temperature of 100°C to get TiO<sub>2</sub> gel(Liquid in solid).

### **STEP III:**

In this step TiO<sub>2</sub> gel is annealed to get Nano crystalline TiO<sub>2</sub>.



### **Scanning Electron Microscopy (SEM)**

SEM is an important surface characterisation technique used in nanotechnology. It is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. This can provide information about topography (surface features), morphology (shape and size of the particles), composition and crystallographic information.

#### **Principle**

SEM scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can give information about the surface topography and composition. Electrons from the top of the column is accelerated down and passed through a combination of lenses to produce a focused beam of electrons which hits the surface of the sample. As a result of the electron sample interaction, signals are produced. These signals are then detected by appropriate detectors. Thus high resolution three dimensional images are produced.

#### **Instrumentation**

SEM provides detailed surface information by tracing a sample with an electron beam. This process begins with an electron gun (electron source) generating a beam of energetic electrons down the column and are then passed through a series of electromagnetic lenses. Usually used electron gun is a tungsten wire. Condenser lens compresses the electrons to a narrow beam and the objective lens focuses the electron beam to the sample chamber. This chamber holds the sample under vacuum to eliminate interference of unwanted particles. When the electrons come in contact with the sample, energetic electrons are released from the surface of the sample. Finally detectors will detect signals from the sample. The signals usually include secondary electrons (SE), back scattered electrons (BSE) and X-rays. BSE are incidental electrons reflected backwards. This comes from the deeper regions of the sample. SE originates from the surface of the sample. Therefore BSE and SE provide different types of information. X-rays emitted from beneath the sample surface can provide element and mineral information. SEM produces black and white three dimensional images. A display monitor can be used for the display of images.



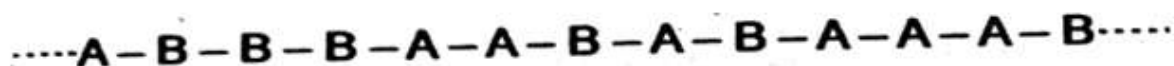
## Co- polymers

Polymers which are formed by the polymerization of two or more different monomers are called co-polymers. (Eg. BS, ABS co-polymers)

Types of co-polymers

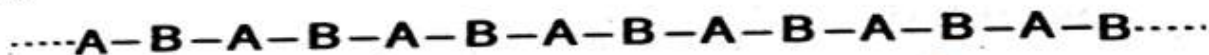
### 1. Random co-polymer:

If the monomeric units are arranged in a random fashion, then the co-polymer is known as random co-polymer.



### 2. Alternating co-polymer

If the monomers are arranged in a regular alternating fashion, then it is called alternating co-polymer.



### 3. Block co-polymer

Co-polymer which can be formed with a long chain of homo polymer followed by a block of another homo polymer chain, then it is called block co-polymer.



### 4. Graft co-polymer

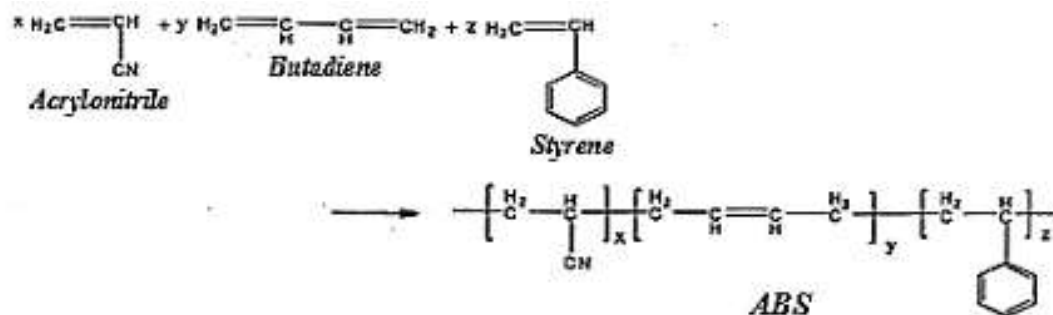
Co-polymers can be formed with homo polymers remaining grafted to the main chain of homo polymer at intervals, and then it is called graft co-polymer.



## ABS (Acrylonitrile Butadiene Styrene)

### Preparation:

It is obtained by dissolving poly butadiene in liquid acrylonitrile and styrene in presence of free radical initiator.



Properties:

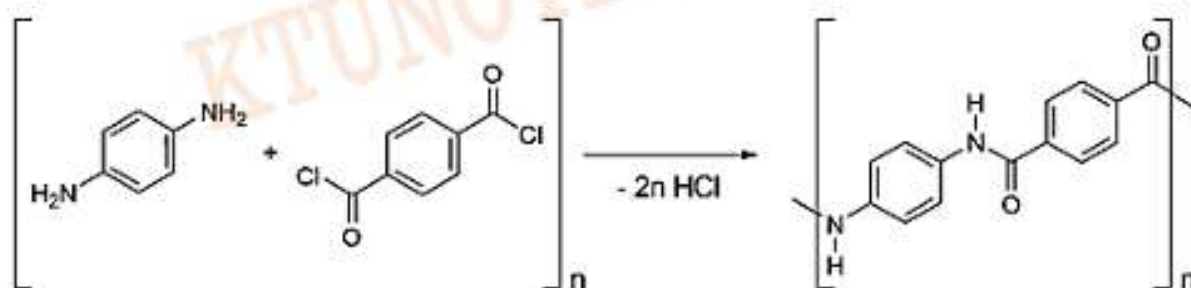
- Very hard, rigid and tough material.
- Resistant to impact, stretch, bent etc.
- Possess high tensile strength.
- Possess stiffness.
- Possess chemical resistance and heat resistance.
- Ductile in nature.

Uses:

- Used for making automobile parts.
- Used for making building materials.
- Used for making house wares such as refrigerator parts, parts of micro wave oven, coffee maker etc.

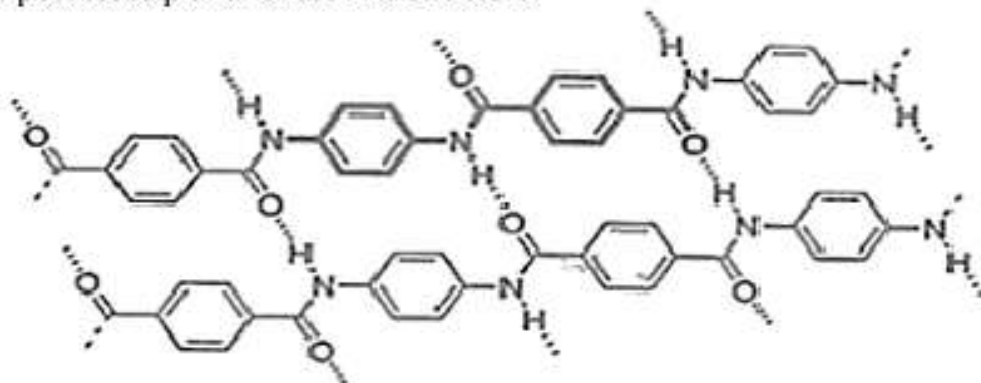
### KEVLAR (PPTA)

KEVLAR is poly para-phenylene terephthalamide. It is obtained by the condensation polymerization of para phenylene diamine and terephthaloyl chloride.



### Structure of KEVLAR

It possesses planar sheet like structure.



Three types of bonding are possible in Kevlar.

1. Covalent bonding

It is the strongest bonding in Kevlar.

## 2. Vander Waals forces of interaction

These are weak bondings. Different chains in the Kevlar structure are held together by Vander Waals forces of interaction.

## 3. Hydrogen bonding

Hydrogen bondings are possible between amide linkages.

Due to the difference in the strength of covalent and Vander waals forces, Kevlar possesses anisotropy.

Properties:

- It is five times stronger than steel.
- Possess high tensile strength and chemical resistance.
- Extremely light weight material.
- Possess heat resistance.

Uses:

- For making bullet proof vests
- For making industrial gloves, helmets, body pads etc.
- For making sports equipments.
- For making industrial hoses.

## Conducting Polymers

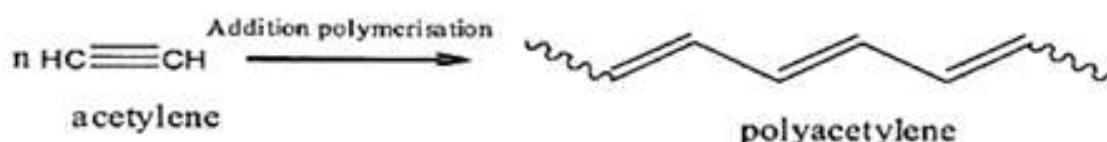
Recently synthesized organic polymers are called organo electronic compounds. They can function as conductor or super conductor. Polymers are usually poor conductors of electricity, because of the absence of free electrons.

Polymers which can conduct electricity is called **conducting polymers**.

Eg. Polyacetylene, polyaniline, polypyrrole etc.

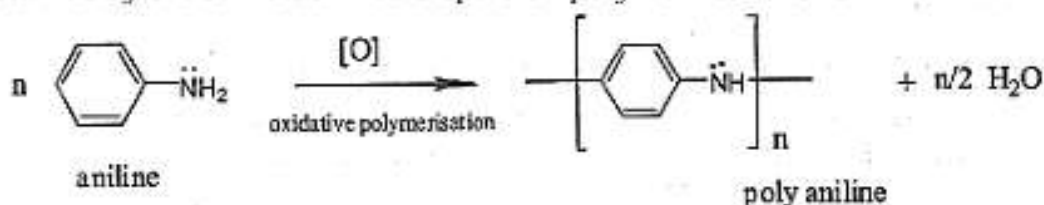
The first widely studied is polyacetylene. Its conductivity can be increased by a factor of  $10^{12}$  by doping it with an electron donor like alkaline earth metal ion or an electron acceptor like  $I_2$  or  $AsF_5$ .

Conductivity increases with decrease in band gap because in that case small amount of energy is required to promote an electron from valence band to the conduction band. In the case of polymeric insulators band gap is very large (1.5-4eV) which obstruct the flow of electrons. But by the careful design of the chemical structure of polymeric back bone it is possible to reduce the band gap as low as possible (0.5-1eV)



### Poly aniline:

Poly aniline is a conducting polymer obtained by the oxidative polymerization of aniline. It is also obtained by the self-stabilized dispersion polymerization of aniline



The conductivity of poly aniline is due to the transfer of electrons along the conjugated system, which is due to the presence of lone pair of electrons on nitrogen. Conductivity of poly



aniline can be increased by protonation. At room temperature its conductivity is  $1000 \text{ Scm}^{-1}$ . It is soluble in organic solvents.

Properties:

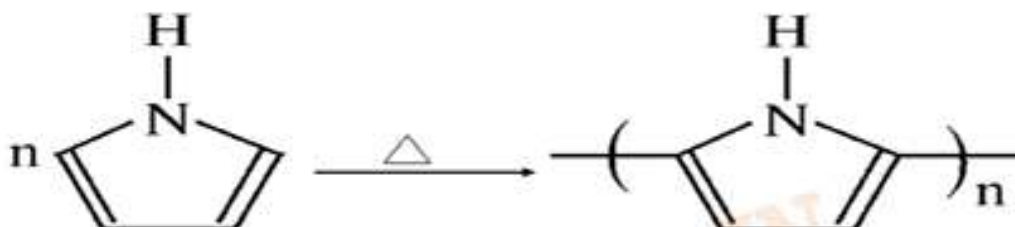
- It is highly flexible
- Possess high strength.
- Low cost material.
- It is stable both in air and water.
- Possess excellent anti-corrosion property.

Applications:

- 1) Used in LED, since the colour changes with the application of particular voltage and chemicals..
- 2) Used as electromagnetic shield and IR absorber.
- 3) Used for making rechargeable batteries.
- 4) Used as a corrosion resistive material.

### Poly pyrrole:

Poly pyrrole is a conducting polymer obtained by the polymerization of pyrrole under the influence of free radical, anionic or cationic initiator.



Poly pyrrole is a conjugated polymer. The conductivity of poly pyrrole is due to the electronic transfer along the conjugated  $\pi$  system.

Properties:

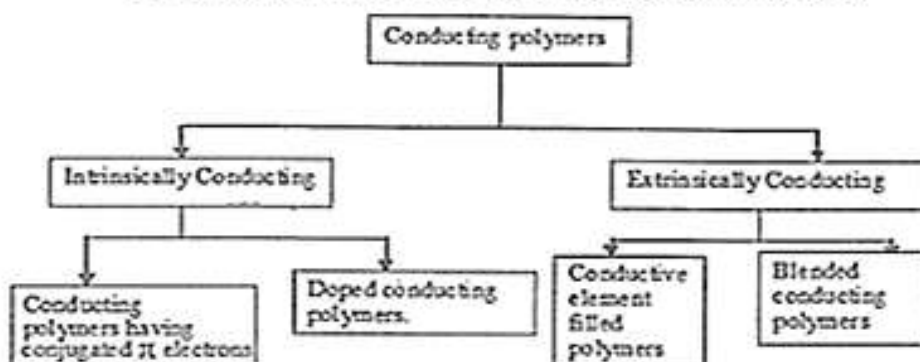
- It has excellent thermal, chemical and mechanical properties.
- It can be processed into any desired shape.
- It has good environmental stability.
- Electrical resistance decreases with increase in temperature. Hence conductivity increases.

Applications:

1. Used for making rechargeable batteries.
2. Used for making chemical carrying pipes.
3. Used as a very good electrical conductor.
4. It can be used as a tissue (cell) support substrate.

### Classification of Conducting Polymers:

Conducting polymers can be classified into following types



Polymers which can conduct electricity are called conducting polymers. Polymers are usually pure conductors of electricity due to the absence of free electrons. In the case of polymers band gap is very large (1.5 – 4 eV). But by the careful design of the chemical structure of polymeric back-bone, it is possible to reduce the band gap as low as possible (0.5 – 1eV). Conducting polymers are classified into

1) Intrinsically conducting polymers

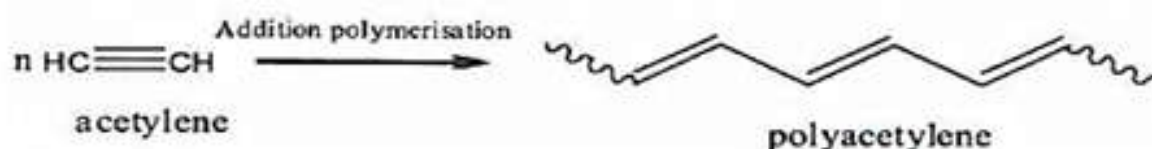
2) Extrinsically conducting polymers

1) Intrinsically conducting polymers

These are conducting polymers which have extensive conjugation in the polymeric back-bone which is responsible for conductance. These are again classified into

a) Conducting polymers containing conjugated  $\pi$  electrons:

These conducting polymers contain conjugated  $\pi$  electrons along the polymeric chain. The orbitals of conjugated  $\pi$  electrons overlap over the entire polymeric back-bone, resulting in the formation of valence band and conduction band, which extends over the entire polymeric back-bone. These bands are separated by a very small band gap. Thus electrical conduction would occur when electrons from valence band are excited to conduction band either thermally or photolytically. Eg. Poly acetylene



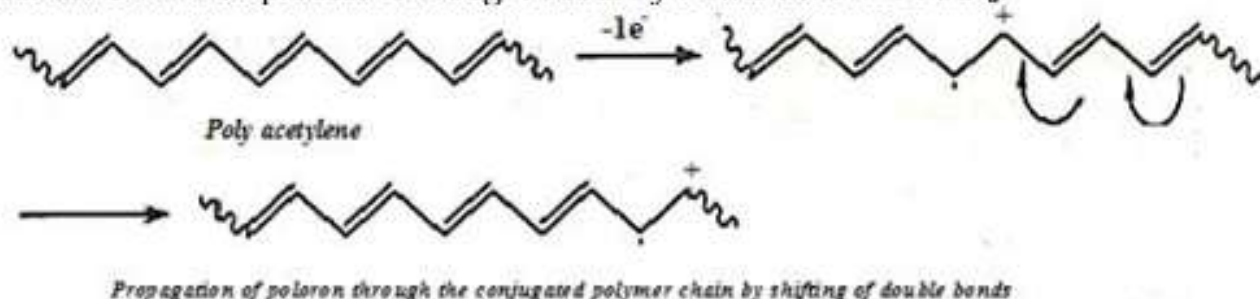
b) Doped conducting polymers:

Conductivity of intrinsically conducting polymers can be increased by creating a positive charge or negative charge by oxidation or reduction. This process is called doping. Conducting polymers obtained by this process is called doped conducting polymers. Doping is of two types.

p – doping & n - doping

#### Mechanism of conduction by p – Doping:

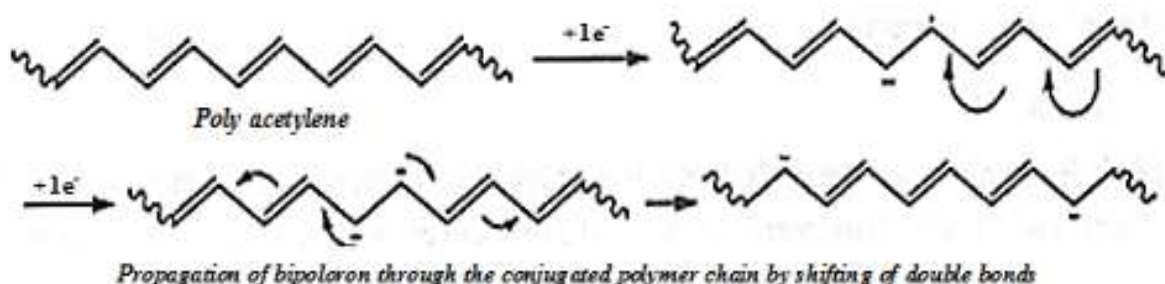
p – Doping is done by oxidation process. In this process some electrons of the  $\pi$ -bonds of the conjugated double bonds are removed and holes are created which can move along the polymer and the polymer becomes electrically conductive. The radical cation produced is called polaron. The polarons are mobile and can move along the polymer chain by the rearrangement of double and single bonds. Oxidation process is brought about by Lewis acid like  $\text{FeCl}_3$ .



#### Mechanism of conduction by n – Doping:

n – Doping is done by reduction process. In this process some electrons are introduced into the polymer having conjugated double bonds. Reduction can be done by using Lewis base like sodium naphthalide. This will lead to the formation of polaron and bipolaron in two steps.





## 2) Extrinsic conducting polymers:

These are conducting polymers whose conductivity is due to the presence of externally added ingredients in them. These are also classified into two.

### a) Conducting element filled conducting polymers.

These are polymers which are filled with conducting elements such as carbon black, metallic fibers, metal oxides etc. Here the polymers act as a binder to hold the conducting elements together. These polymers are low cost, light weight, mechanically durable and strong and can be easily processed into different shapes and sizes.

### b) Blended conducting polymers

These are polymers obtained by blending conducting polymers with conventional polymers. They possess better physical, chemical and mechanical properties.

### Distinguish between p-Doping & n-Doping

p-Doping	n-Doping
<ul style="list-style-type: none"> <li>• Done by Oxidation</li> <li>• Positive charge is created during the process.</li> <li>• Polorons are produced.</li> <li>• Single step process.</li> <li>• Lewis acid like <math>\text{FeCl}_3</math> is used as the reagent.</li> </ul>	<ul style="list-style-type: none"> <li>• Done by reduction</li> <li>• Negative charge is created during the process.</li> <li>• Polorons and bipolarons are produced.</li> <li>• Two step process.</li> <li>• Lewis base like sodium naphthalide is used as reagent.</li> </ul>

### OLED (Organic Light Emitting Diode)

OLED is an advanced form of LED and is made up of conducting polymer like polyaniline. Its thickness is 200 times smaller than human hair.

Parts of OLED:

1. Substrate:
2. Anode
3. Hole Transport Layer (HTL)
4. Electron Transport Layer (ETL)
5. Cathode

#### **Substrate:**

A clear plastic or glass that supports OLED is called substrate.

#### **Anode:**

When current passes through the OLED, it removes electrons and adds holes. Usually used anode is ITO (Indium Titanium Oxide)

#### **HTL:**

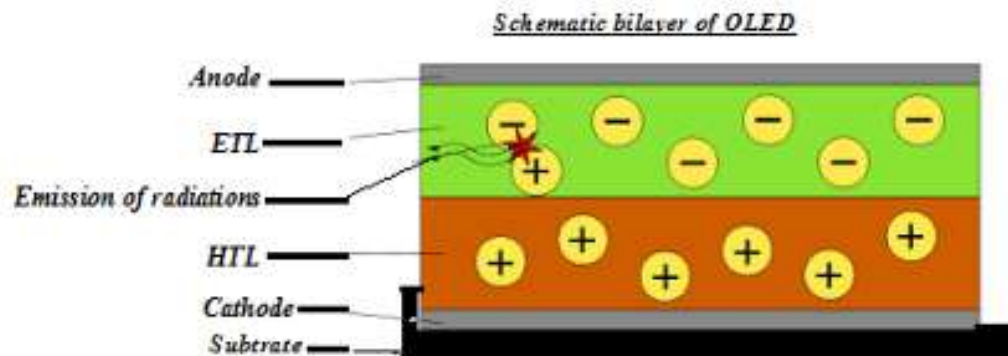
It is the conducting layer made of conducting polymer like polyaniline. It helps for the transport of holes from the anode through the OLED.

**ETL:**

It is the emissive layer made of polyfluorene. Light is produced in the ETL. It helps for the transport of electrons from the cathode through the OLED.

**Cathode:**

It ejects electrons when current flows through the OLED. Al or Ca is used as cathode.

**Working of OLED:**

When a voltage is applied across the OLED, a current of electrons flows from cathode to anode. During this current flow electron hole capture each other by electrostatic force of attraction. Recombination of electrons with holes produces light. The wave length of light produced depends on the band gap of the conducting polymer.

**Properties:**

- It is considered as a cold lighting source. Since no heat is generated during its working.
- Its power consumption is very less.
- It is flexible, very thin and small.
- It generates good quality light.
- More efficient than incandescent lamps and halogen lamps.

**Applications:**

1. They are used for making screens of smart watches, mobile phones, laptops and televisions.
2. They can be used for getting ambient lighting sources.

**Limitation:**

- Life time of the organic polymer is limited.

**Advantages**

- Manufacture OLED is highly economical and efficient.
- No backlight is produced by the device and its power consumption is very less.
- Its response time is less than 0.01 minutes.