Module-4 POLYMERS & GREEN FUELS

Polymers: Introduction, Molecular weight - Number average, weight average and numerical problems. Preparation, properties and commercial applications of Kevlar. Conducting polymers–synthesis and conducting mechanism of polyacetylene and commercial applications. Preparation, properties and commercial applications of graphene.
Green Fuels: Introduction, construction and working of solar photovoltaic cell, advantages, and disadvantages. Generation of energy (green hydrogen) by electrolysis of water and its advantages.

POLYMERS

Definition: "Polymers are macro sized molecules of high molecular mass formed by the combination of a large number of simple molecules by covalent bonds".
Ex: Polyethylene, polyacetylene, polystyrene, polyvinyl chloride, natural and synthetic rubbers etc.

Polymerization: "The process by which the monomers are converted into polymers is called Polymerization".

MOLECULAR WEIGHT OF POLYMERS:

Due to the varying chain lengths, a polymer is considered to have average molecular mass. 2 types of average molecular masses have been recognized namely, number average and weight average molecular masses.

Number average molecular mass: It is obtained by dividing the total weight of the monomers with the number of monomer molecules present in polymer i.e.,

$$\overline{M_n} = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3}$$

Where n_1, n_2, n_3 are the number of molecules having masses M_1, M_2, M_3 respectively. The above equation can also be written as, $\overline{M_n} = \frac{\sum niMi}{\sum ni}$

Where M_i is the masses of monomers and n_i is the number of monomers.

Weight average molecular mass: It gives the representation to different molecular species in proportion to their weight in the given polymer molecule.

$$\overline{M_w} = \frac{w_1M_1 + w_2M_2 + w_3M_3}{w_1 + w_2 + w_3}$$

Where w and M represent the weight and molecular masses of each species present in polymers. Since w= nM,

$$\overline{Mw} = \frac{\sum niMi^2}{\sum niMi}$$

Poly Disparity index [PDI]:

$$\text{PDI} = \frac{\overline{Mw}}{\overline{Mn}}$$

If PDI =1 polymer is mono disperse & Homogeneous.
PDI >1 polymer is poly disperse & less Homogeneous.

NUMERICALS

1. In a sample of a polymer, 100 molecules have molecular mass 10^3 g/mol, 250 molecules have molecular mass 10^4 g/mol, and 300 molecules have molecular mass 10^5 g /mol, calculate the number average and weight average molecular mass of the polymer, Calculate PDI and comment on it.

Solution
It is given that,
N_1 =100 & M_1 = 10^3g/mol,
N_2 =250 & M_1 = 10^4 g/mol,
N_3 =300 & M_1 = 10^5 g/mol.
The number average molecular mass of the polymer is given by

$$\overline{Mn} = \frac{\sum NiMi}{\sum Ni}$$

$$= \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N1 + N2 + N3...} = \frac{100\, X\, 10^3 + 250\, X\, 10^4 + 300\, X\, 10^5}{100 + 250 + 300} = 50153 g/mol$$

The weight average molecular mass of the polymer is given by

$$\overline{Mw} = \frac{\sum Ni\, Mi^2}{\sum Ni\, Mi}$$

$$\overline{M_w} = \frac{N_1 M_1{}^2 + N_2 M_2{}^2 + N_3 M_3{}^2}{N_1 M_1 + N_2 M_2 + N_3 M_3}$$

$$\overline{M_w} = \frac{100\, X\, (10^3)^2 + 250\, X\, (10^4)^2 + 300\, X\, (10^5)^2}{100\, X 10^3 + 250\, X\, 10^4 + 300\, X\, 10^5} = 92794\ g/mol$$

Poly dispersity index, PDI $= \frac{\overline{Mw}}{\overline{Mn}} = \frac{92794}{50100} = 1.85$

PDI >1, the given polymer is less homogeneous and poly disperse in nature.

2. In a sample of a polymer, 20% molecules have molecular mass 15000 g/mol, 35% molecules have molecular mass 25000 g/mol, and remaining molecules have molecular mass 20000 g /mol, calculate the number average and weight average molecular mass of the polymer, Calculate PDI and comment on it.

Solution
It is given that,
N_1 =20 & M_1 = 15000g/mol,
N_2 =35 & M_1 = 25000g/mol,
N_3 =45 & M_1 = 20000 g/mol.
The number average molecular mass of the polymer is given by

$$\overline{Mn} = \frac{\sum NiMi}{\sum Ni} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N1 + N2 + N3...}$$

$$= \frac{20 X\, 15000 + 35 X\, 25000 + 45\, X\, 20000}{20 + 35 + 45} = 20750\ g/mol$$

The weight average molecular mass of the polymer is given by

$$\overline{Mw} = \frac{\sum Ni\, Mi^2}{\sum Ni\, Mi}$$

$$\overline{M_W} = \frac{N_1 M_1^{\,2} + N_2 M_2^{\,2} + N_3 M_3^{\,2}}{N_1 M_1 + N_2 M_2 + N_3 M_3}$$

$$\overline{M_W} = \frac{20X\,(15000)^2 + 35X\,(25000)^2 + 45X\,(20000)^2}{20X\,15000 + 35X\,25000 + 45X\,20000} = 21385\,g/mol$$

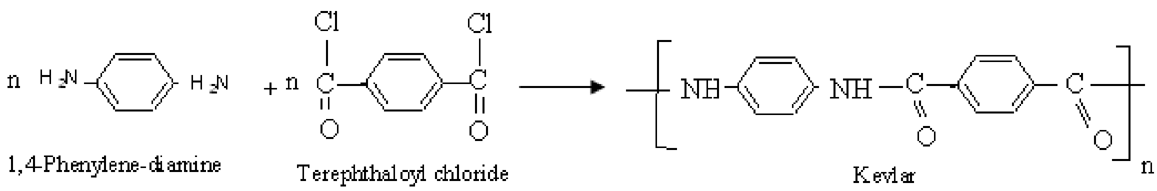
$$\text{Poly dispersity index, PDI} = \frac{\overline{Mw}}{\overline{Mn}} = \frac{21385}{20750} = 1.03$$

PDI >1 ,the given polymer is less homogeneous and poly disperse in nature.

POLYMER COMPOSITES

The combination of two or more distinct components to form a new class of material suitable for structural applications is referred to as composite materials. When one of the components is a polymer, resulting composite called as polymer composite.

Kevlar: Kevlar is synthesized in solution of N-methyl-pyrrolidone & calcium chloride from the monomers 1, 4-phenylene-diamine (para-phenylenediamine) & terephthaloyl chloride through a condensation reaction with liberation of HCl as a byproduct.



Properties:

1. It has very light weight.
2. It has high tensile strength and stiffness.
3. It has very good corrosion resistance.

Applications of Kevlar:

1. It is used to make light weight boat hulls
2. aircraft fuselage panels, pressure vassals, high performance race car, bullet proof vests,
3. Used in puncture resistance bicycle tyres etc.

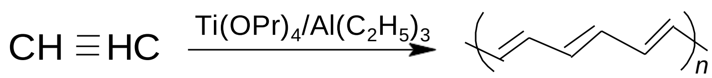
CONDUCTING POLYMERS

Definition: "An organic polymer with highly delocalized pi-electron system having electrical conductance is called conducting polymer".

Ex: Polyacetylene, polypyrrole, polythiophene, polyphenylene, polyaniline, etc.

Synthesis of Polyacetylene:

From Acetylene: In this method polyacetylene is synthesized by using monomer gaseous acetylene in the presence of Ziegler-Natta catalyst such as Titanium isopropaxide ($Ti(OPr))_4$) and triethyl aluminium ($Al(C_2H_5)_3$).



Acetylene Polyacetylene

This polymerization involves metal insertion into the triple bond of the monomer.

Commercial Applications of Polyacetylene:

1. Used in the manufacture of chemical sensors, corrosion inhibitors.
2. Used in compact electronic devices such as polymer based transistors, LEDs etc.

Mechanism of conduction in polyacetylene: Conducting polymers are generally produced by doping an oxidizing or a reducing agent into an organic polymer with conjugated back bone consisting of pi-electron system.

An organic polymer can be converted into a conducting polymer if it has

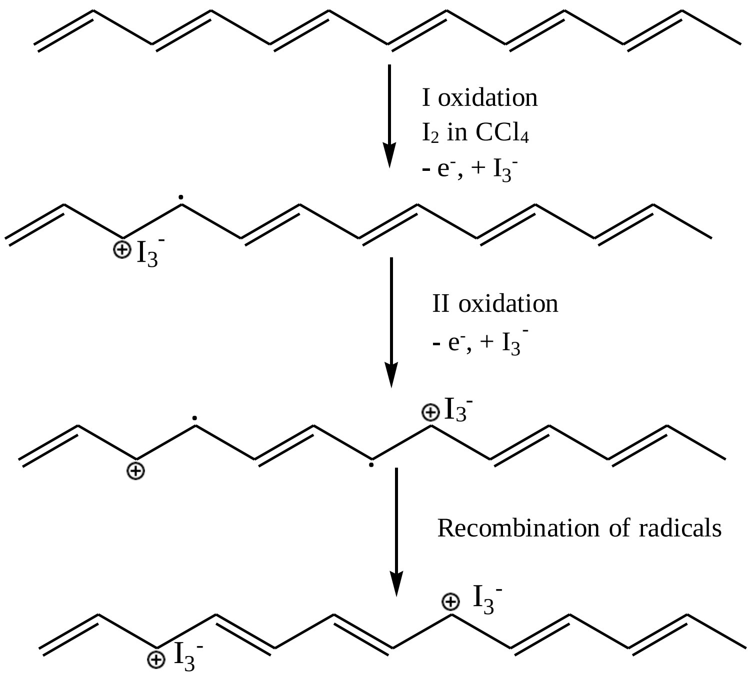
1. Linear structure
2. Extensive conjugation in polymeric back bone (Pi-back bone)

The conducting polymers are synthesized by doping, in which charged species are introduced in organic polymers having pi-back bone. The important doping reactions are;

1. Oxidative doping (p-doping)
2. Reductive doping (n-doping)
3. Protonic acid doping (p-doping)

1. Oxidative doping (p-doping): In this process, pi-back bone of a polymer is partially oxidized using a suitable oxidizing agent. This creates positively charged sites on polymer back bone, which are current carriers for conduction.

The oxidizing agents used in p-doping are iodine vapor, iodine in CCl_4, HBF_4, perchloric acid and benzoquinone.



Reactions of p- doping of polyacetylene

The removal of an electron from the polymer pi-back bone using a suitable oxidizing agents leads to the formation of delocalized radical ion called polaron. A second oxidation of a chain containing polaron followed by radical recombination yields two charge carriers on each chain. The positive charges sites on the polymer chains are compensated by anions I_3^- formed by the oxidizing agent during doping. The delocalized positive charges on the polymer chain are mobile, not the dopant anions.

Thus, these delocalized positive charges are current carriers for conduction. These charges must move from chain to chain as well as along the chain for bulk conduction On doping polyacetylene using iodine in CCl_4, for partial oxidation, the conductivity increases from 10-5 $S.cm^{-1}$ to 10^3-10^5 $S.cm^{-1}$.

Applications:

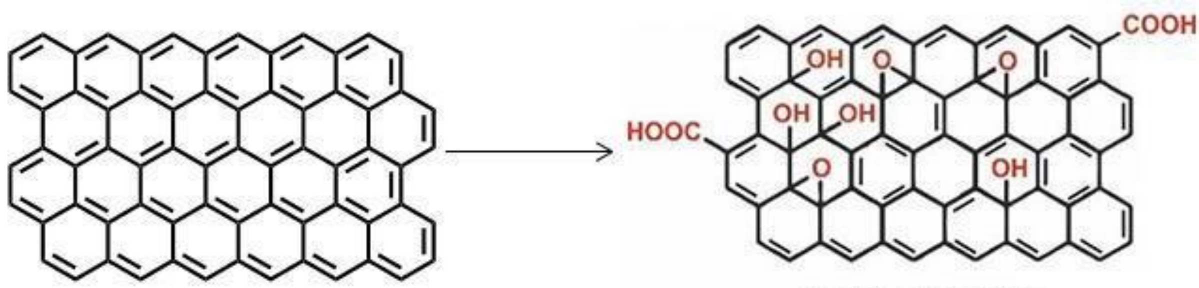
- Fabrication of organic thin transistors.
- Non-volatile memory devices based on organic transistors.
- Fabrication of organic photovoltaic cells.
- Fabrication of organic light-emitting devices (OLED).
- Conducting polymer actuators and Micropumps.
- Focused upon polymer membranes that incorporated electronically conducting polymers and piezoelectric polymers.

GRAPHENE OXIDE:

Graphene oxide (GO) is two-dimensional material formed by the oxidation of graphene. It is a single-atomic-layered material, when stacked together forms graphite oxide. It contains hydroxyl (-OH), alkoxy (C-O-C), carbonyl (C=O), carboxylic acid (-COOH) and other oxygen-based functional groups. These groups are attached to both the sides of a single graphite sheet and overcome the inter-sheet van der Waals force. As a result, interlayer spacing increase causing reduction in its conductivity. It has been using in several applications in electronics, conductive films, electrode materials and nano composites.

SYNTHESIS:

Take 2g graphene and 2g of $NaNO_3$ (catalyst) in 50 ml of $H2SO_4$ bath in 1000 ml volumetric flask kept in an ice bath (0-5 ^oC) with continuous stirring for 2 hours. Then add 6g $KMnO_4$ (oxidizing agent) very slowly at temperature kept below 15 ^oC. After some time, remove the ice bath and allow the mixture for stirring at 35 ^oC for 48 hours. Finally, treat the solution with 10 ml H_2O_2 to terminate the reaction and filter. After filtration, dry it in vacuum at room temperature to get powdered graphene oxide.



graphene graphene oxide

Properties of Graphene Oxide

1. High thermal conductivity and high electrical conductivity.
2. High elasticity and flexibility.
3. High hardness and high resistance
4. Ionizing radiation is not affected.
5. Transparent material.

Commercial Applications of Graphene Oxide

1. Used in electronic and energy storage devices.
2. Used in Bio- sensors and biomedical applications.
3. Used as super capacitors.
4. Used as membranes, catalysts and water purification technology.

GREEN FUELS

Introduction

A fuel derived from biomass is called as green fuel. They are considered as renewable, eco-friendly, relatively less flammable compared to fossil fuel, has better lubricating properties and reduce greenhouse gases up to 65 percent. It can be manufactured from wide range of materials. Most common forms of green fuels are

1. Solar Power 2. Wind Power 3. Hydropower 4. Geothermal Energy 5. Biomass and 6. Biofuels.

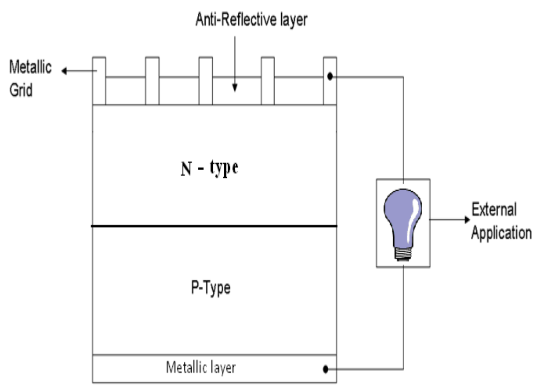
Photovoltaic cells (Solar cells):

The device, which converts solar energy into electrical energy, is called photovoltaic cell and the phenomenon is called photovoltaic effect.

CONSTRUCTION WORKING AND APPLICATIONS OF SOLAR CELLS

Construction:

- The device consists of p-n junction diode coated with anti-reflective layer (TiO_2) at the top.
- Two electrical contacts are provided, one in the form of metallic grid at the top of the junction and the other is a silver layer at the bottom of the cell.
- The antireflective layer coated in between the metallic grids which allow light to fall on the semiconductor.



Working:

- The photons of solar radiations enter n-type semiconductor breaks barrier potential and moves to p-type semiconductor where photons knock the electrons in p type to form electron hole pair.
- The free electrons so formed will travels through the circuit from n-type and recombines with holes again in p-region.
- The movement of electrons from n type to p type generates electric current. The electrical energy produced from the solar cell is used for various applications

Advantages of PV cells:

- ✓ Eco friendly energy conversion device.
- ✓ Do not undergo corrode
- ✓ No moving parts in PV cell, hence no wear and tear.

Disadvantages of PV cells:

- ✓ Installation cost is high.
- ✓ Produced only during the day time.
- ✓ It generates only DC current.

Applications:

- ✓ Used in toys, watches, remote lighting systems
- ✓ Used in water pumping, water treatment.
- ✓ Used in emergency power, satellites. Etc.

HYDROGEN FUEL

Hydrogen fuel is preferred over the other fossil fuels because of the following features.

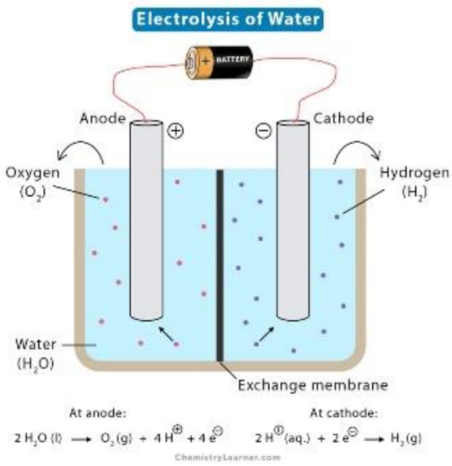
- It is lightest element
- Gas of diatomic molecules having the formula H_2.
- Colourless, odourless and Tasteless
- Non-metallic and non-toxic
- Highly combustible,
- Most abundant chemical substance in the universe.

Generation of hydrogen by electrolysis of water

It is the process of splitting of water into oxygen and hydrogen gas by electrolysis.

- It consists of two electrodes i.e. anode and cathode.
- Both are separated by membranes.
- When electricity is passed, oxidation takes place at anode, it gives H^+ ions and electron, also liberates Oxygen gas.

  At Anode: $2 H_2O(l) \rightarrow O_2(g) + 4 H^+(aq) + 4e^-$
- The H^+ ions move into cathodic compartment through membranes and electrons move from anode to cathode through external circuit.
- At cathode the H^+ ions accepts electrons and forms H_2 gas. This liberated hydrogen gas is used as a fuel
- At Cathode : $4H^+(aq) + 4e^- \rightarrow 2H_2(g)$



Alkaline water electrolysis

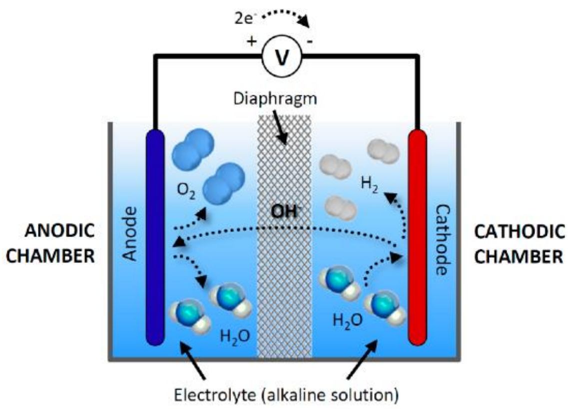
- It consists of two electrodes i.e. anode and cathode.
- Both electrodes are made up of Ni based metal, because it is more stable during the oxygen evolution.
- These electrodes are immersed in KOH solution (25-35%).
- Both electrodes are separated by porous diaphragm prevent gases crossover and allows only hydroxide ions.
- Cell voltage is 1.3 – 2 V
- When electricity is passed, at anode hydroxide ions lose electrons and forms water molecules.

$$\text{Anode: } 2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$$

- At cathode, water molecules accept electrons and liberate hydrogen gas and forms hydroxide ions.
- These hydroxide ions move from cathode to anode through diaphragm and process continues.

$$\text{Cathode: } H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

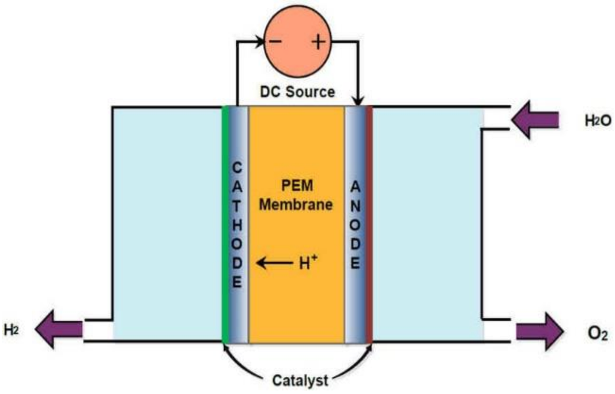
$$\text{Total reaction: } 2H_2O \rightarrow O_2 + 2H_2$$



Advantages

- Low cost and well established technology
- Long Stability and stacks in the megawatt range
- Non-noble catalyst

Proton Exchange Membrane Electrolysis or Polymer electrolyte membrane



- In a polymer electrolyte membrane (PEM) electrolyzer, the electrolyte is a solid specialty plastic material.
- PEM water electrolysis is involving the pumping of water to the anode where it is spilt into oxygen (O_2), protons (H^+) and electrons (e^-).
- Water reacts at the anode to form oxygen and positively charged hydrogen ions (protons).
- The electrons flow through an external circuit and the hydrogen ions selectively moves across the PEM to the cathode.
  At Anode: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4e^-$
  At Cathode: $4\ H^+(aq) + 4e^- \rightarrow 2H_2(g)$

Advantages

- No corrosive and leaking electrolyte
- No acid carryover
- Minimum power requirement per unit of gas generated