MODULE 4
POLYMERS AND GREEN FUELS

Module-4: Polymers and Sustainable Energy	8 Hours
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. **Sustainable Energy:** Introduction, construction, and working of the photovoltaic cell, advantages, and disadvantages. Generation of energy (green hydrogen) by electrolysis of water using PEM Electrolyzer and its advantages.	

The Term “**Polymer**” is derived from the Greek word ‘**Polus**’ (Meaning ‘’Many, Much) and ‘**mero’s** (Meaning ‘parts’), and refers to a molecules whose structure is composed of multiple repeating units. The term was coined in 1833 by **Jones Jacob Berzelius.**

A polymer is defined as a macromolecule formed by the repeated combination of several simple molecules (Monomers) through covalent bonds”

Example: Polyethylene, nylon, PVC, Teflon, polyester, bakelite, etc.

Monomer is defined as a simple molecule with two or more binding sites through which it forms covalent linkages with other monomer molecules to form the macromolecule.

Examples: *Alkenes, vinyl chloride, adipic acid,* **and** glycol **with two bonding sites act as monomers.**

Monomers must have two or functional ends or functionalities.

CH_3OH has one functional group and one functionality (Not a true monomer)

$CH_2=CH_2$ has one functional group and two functionalities (A true monomer)

HO-CH_2-CH_2-OH has two functional groups and two functionalities (A true monomer)

Polymerization: A process by which monomers combine chemically to form a macromolecule is called Polymerization.

a) Addition Polymerization
b) Condensation Polymerization

a) **Addition Polymerization:** a process where monomer units repeatedly add to each other without losing any atoms, resulting in a long chain polymer it is also called as chain growth polymerization.

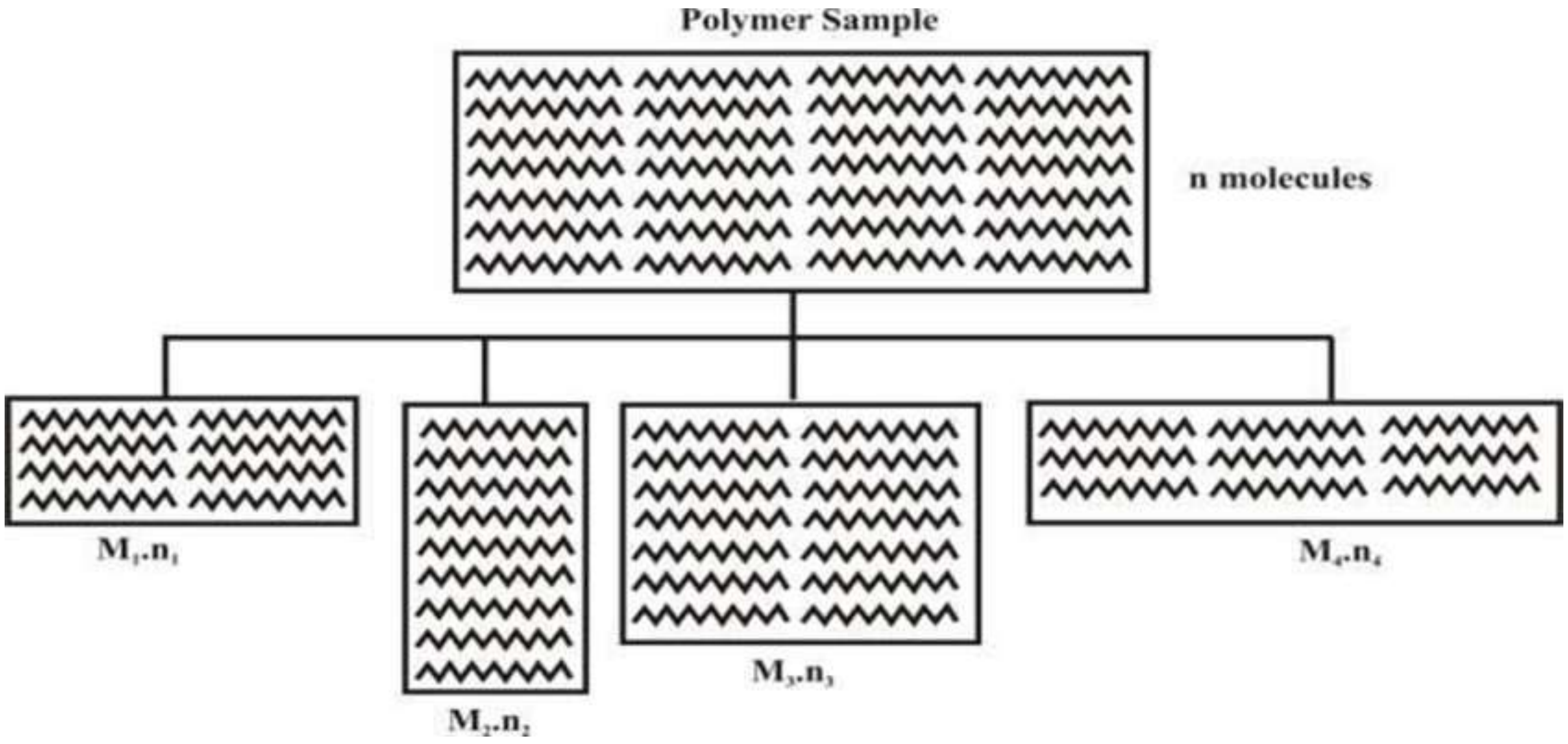
Example: Formation of Polyethylene, Teflon, PVC etc

b) **Condensation Polymerization:** a process where monomers react to form larger structural units (polymers) with the elimination of byproducts usually water, NH_3 and HCL as a by-product.

Example: Nylon6,6 , Polyester, Kevlar, Bakelite etc.

Molecular weight of a Polymer

"Molecular weight of a polymer is defined as sum of the atomic weight of each of the atoms in the molecules, which is present in the polymer"



Number Average Molecular Weight ($\overline{M}n$)

The total weight of all the polymer molecules in a sample, divided by the total number of molecules in a sample.

$$\overline{Mn} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \ldots\ldots}{N1 + N2 + N3 + \ldots\ldots\ldots\ldots\ldots\ldots\ldots}$$

Weight – Average Molecular Weight ($\overline{M}w$)

Sum of the products of total mass of groups of molecules and their respective molecular mass is divided by the total mass of all the molecules.

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

Degree of polymerization (DP): - The no of repeating units or monomer units in the chain of a polymer is called degree of polymerization (DP) . The molecular weight of an addition polymer is the product of the molecular weight of the repeating unit and the degree of polymerization (DP).

$$DP = \frac{Molecular\ weight\ of\ the\ polymer}{Molecular\ weight\ of\ the\ monomer}$$

Poly Dispersity index [PDI]: Index of polydispersity or PDI is used as a measure of molecular weight distribution and is defined as

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

If PDI =1 polymer is mono disperse & Homogeneous.

PDI >1 polymer is poly disperse & less Homogeneous.

Problems

1. A polymer has the following molar mass.

Number of molecules	Molar mass (g/mol)
50	5000
75	6000

Calculate the number average, weight average and PDI

(1) $n_1 = 50, \; m_1 = 5000$

$n_2 = 75, \; m_2 = 6000$

$$\overline{M}_n = \frac{\Sigma n_i M_i}{\Sigma n_i}$$

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$$

$$\overline{M}_n = \cancel{n_1 M} \frac{(50 \times 5000) + (75 \times 6000)}{50 + 75}$$

$$= \frac{250000 + 450000}{125}$$

$$= \frac{700000}{125} = 5600 \text{ g mol}^{-1}$$

$$\bar{M}_w = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i}$$

$$= \frac{50(5000)^2 + 75(6000)^2}{(50 \times 5000) + (75 \times 6000)}$$

$$= \frac{125 \times 10^7 + 270 \times 10^7}{7 \times 10^5}$$

$$= \frac{395 \times 10^7}{7 \times 10^5} = 5642 \ g\,mol^{-1}$$

$$PDI = \frac{\bar{M}_w}{\bar{M}_n} = \frac{5642}{5600} = 1.0075$$

Example 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:

Sl No	No of Molecules(N)	Molecular Mass(M) g/mol
1	$N_1 = 100$	$M_1 = 10^3$
2	$N_2 = 250$	$M_2 = 10^4$
3	$N_3 = 300$	$M_3 = 10^5$

Number average molecular mass ($\bar{\mathbf{M}}$n) is given by:

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

$$\mathbf{\bar{M}}\text{n} = \frac{100 * 10^3 + 250 * 10^4 + 300 * 10^5}{100 + 250 + 300} = 50153\ {}^{g}/_{l}$$

Weight average molecular mass **($\bar{M}$w)** is given by:

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

$$\mathbf{\bar{M}}\text{w} = \frac{100 *) * (10^3) * (10^3) + 250 * (10^4) * (10^4) + 300 * (10^5) * (10^5)}{100 * 10^3 + 250 * 10^4 + 300 * 10^5} = 92794\ {}^{g}/_{l}$$

$$\text{PDI} = \frac{\overline{Mw}}{\overline{\overline{Mn}}} = \frac{92794}{50153} = 1.85$$

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

1. A polymer sample contains 1, 2, 3 and 4 molecules having molecular weights 10^5, $2*10^5$, $3*10^5$ and $4*10^5$, respectively. Calculate the number average and weight average molecular weight of the polymer.

Solution:

Sl No	No of Molecules(N)	Molecular Mass(M) g/mol
1	$N_1 = 1$	$M_1 = 10^5$
2	$N_2 = 2$	$M_2 = 2*10^5$
3	$N_3 = 3$	$M_3 = 3*10^5$
4	$N_4 = 4$	$M_4 = 4*10^5$

Number average molecular mass (**M̅**n) is given by:

$$\bar{\mathbf{M}}\mathrm{n} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + N_{14} M_4}{N_1 + N_2 + N_3 + N_4}$$

$$\bar{\mathbf{M}}\mathrm{n} = \frac{\mathbf{1*(1*10^5) + 2*(2*10^5) + 3*(3*10^5) + 4*(4*10^5)}}{\mathbf{1+2+3+4}}$$

$$\bar{\mathbf{M}}\mathrm{n} = \frac{\mathbf{30*10^5}}{\mathbf{10}}$$

$$\boxed{\bar{\mathbf{M}}\mathrm{n} = 3.0 * 10^5\ g/L}$$

$$\bar{\mathbf{M}}\mathrm{w} = \frac{(1*\mathbf{10^5})*(1*\mathbf{10^5}) + \mathbf{2}*(\mathbf{2}*\mathbf{10^5})*(\mathbf{2}*\mathbf{10^5})+\mathbf{3}*(\mathbf{3}*\mathbf{10^5})*(\mathbf{3}*\mathbf{10^5})+\mathbf{4}*(\mathbf{4}*\mathbf{10^5})*(\mathbf{4}*\mathbf{10^5})}{\mathbf{1}*(\mathbf{1}*\mathbf{10^5})+\mathbf{2}*(\mathbf{2}*\mathbf{10^5})+\mathbf{3}*(\mathbf{3}*\mathbf{10^5})+\mathbf{4}*(\mathbf{4}*\mathbf{10^5})}$$

$$\bar{\mathbf{M}}\mathrm{w} = \frac{(\mathbf{1+8+27+64})*\mathbf{10^{10}}}{(\mathbf{1+4+9+16})*\mathbf{10^5}}$$

$$\bar{\mathbf{M}}\mathrm{w} = 3.3 * 10^5 \mathrm{g/L}$$

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,

Sl No	No of Molecules(N)	Molecular Mass(M) g/mol
1	N_1= 20	M_1= 15000
2	N_2= 35	M_2= 25000
3	N_3= 45	M_3= 20000

The number average molecular mass of the polymer is given by

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

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

The weight average molecular mass of the polymer is given by

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

$$\overline{M_w} = \frac{N_1M_1{}^2 + N_2M_2{}^2 + N_3M_3{}^2}{N_1M_1 + N_2M_2 + N_3M_3}$$

$$\overline{M_w} = \frac{20X\;(15000)^2 + 35X\;(25000)^2 + 45X\;(20000)^2}{20X15000 + 35X\;25000 + 45\,X\;20000} = 21385\,g/mol$$

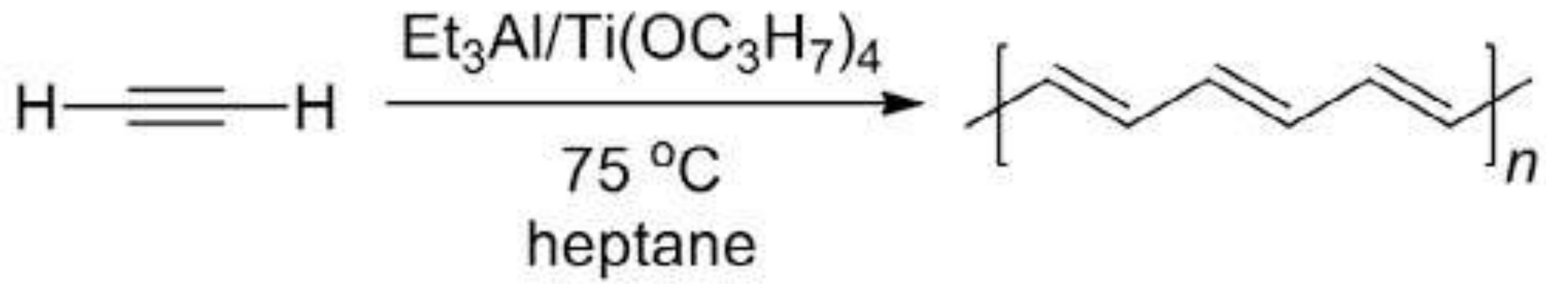
Poly dispersity index, PDI $= \dfrac{\overline{Mw}}{\overline{Mn}} = \dfrac{21385}{20750} = 1.03$

PDI >1 ,the given polymer is less homogeneous and

Conducting polymers

Conducting polymers are polyconjugated organic polymers that conduct electricity because of their conjugated π-bonds.

Synthesis of Polyacetylene



Synthesis of conducting polymer

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

a) Linear Structure

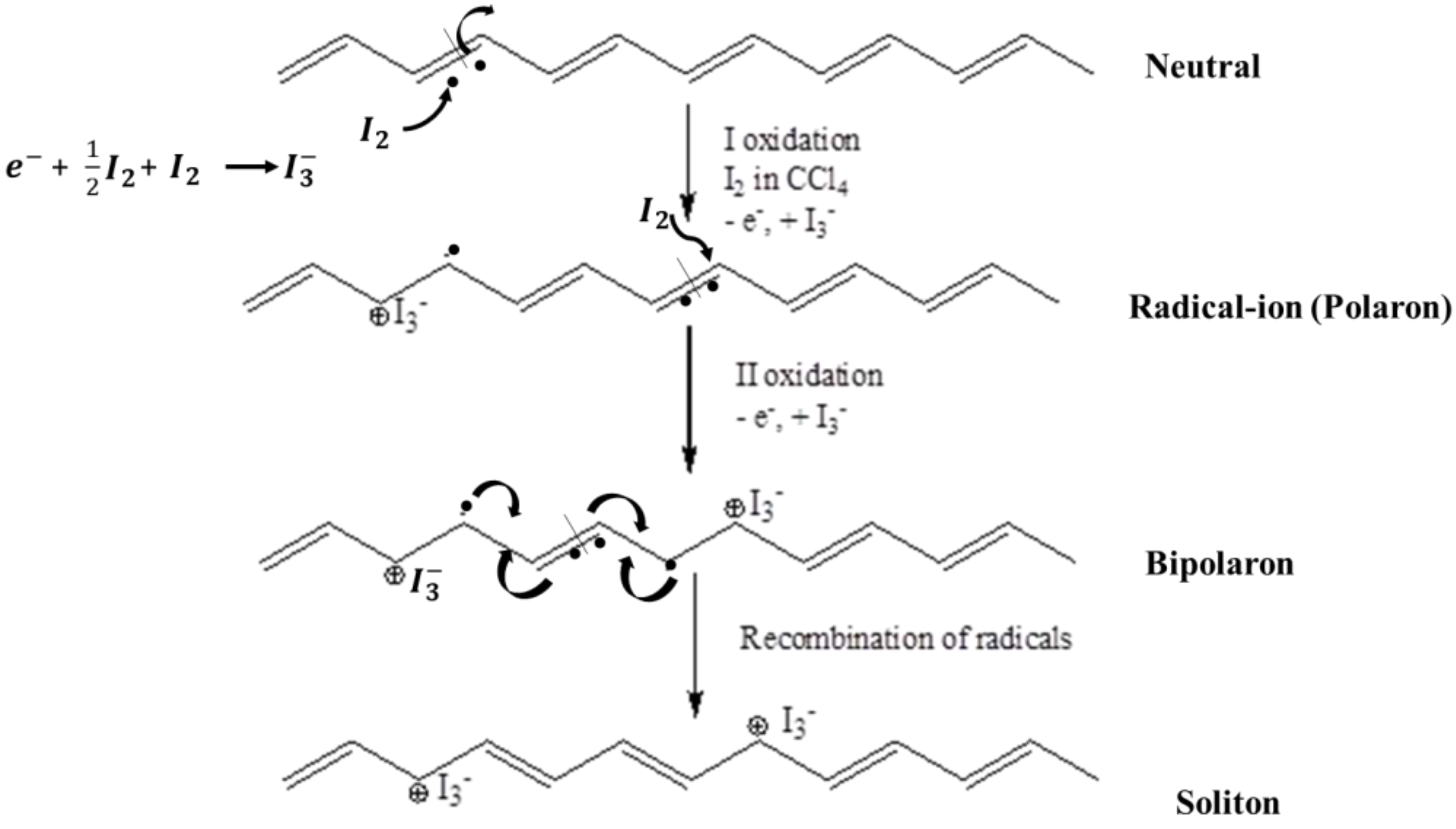
b) Extensive conjugation in polymeric back bone (pi-bond)

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;

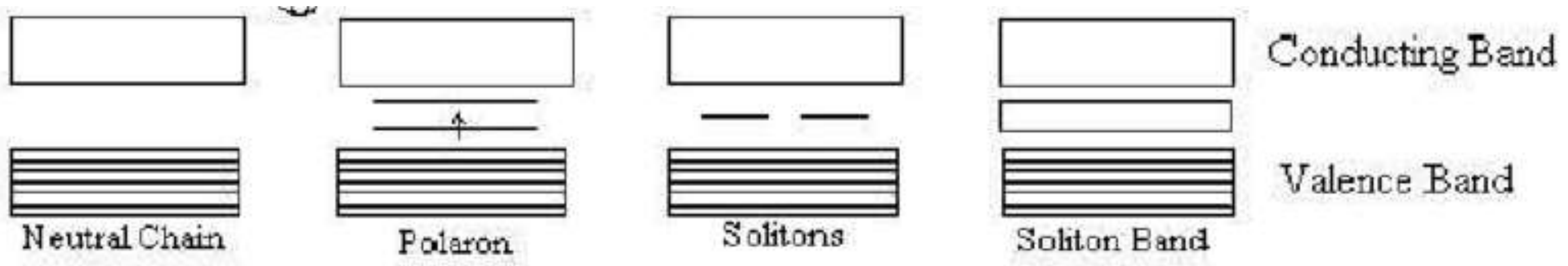
1. Oxidative doping (p-doping)
2. Reductive doping (n-doping)
3. Protonic acid doping (p-doping)

Oxidative doping (p-doping):

Polyacetylene is converted to conducting polyacetylene using oxidizing agent such as iodine in CCl_4.



Reactions of p- doping of polyacetylene

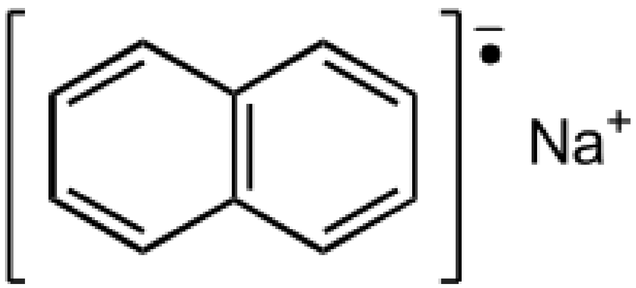

Conducting Band
Valence Band
Neutral Chain
Polaron
Solitons
Soliton Band

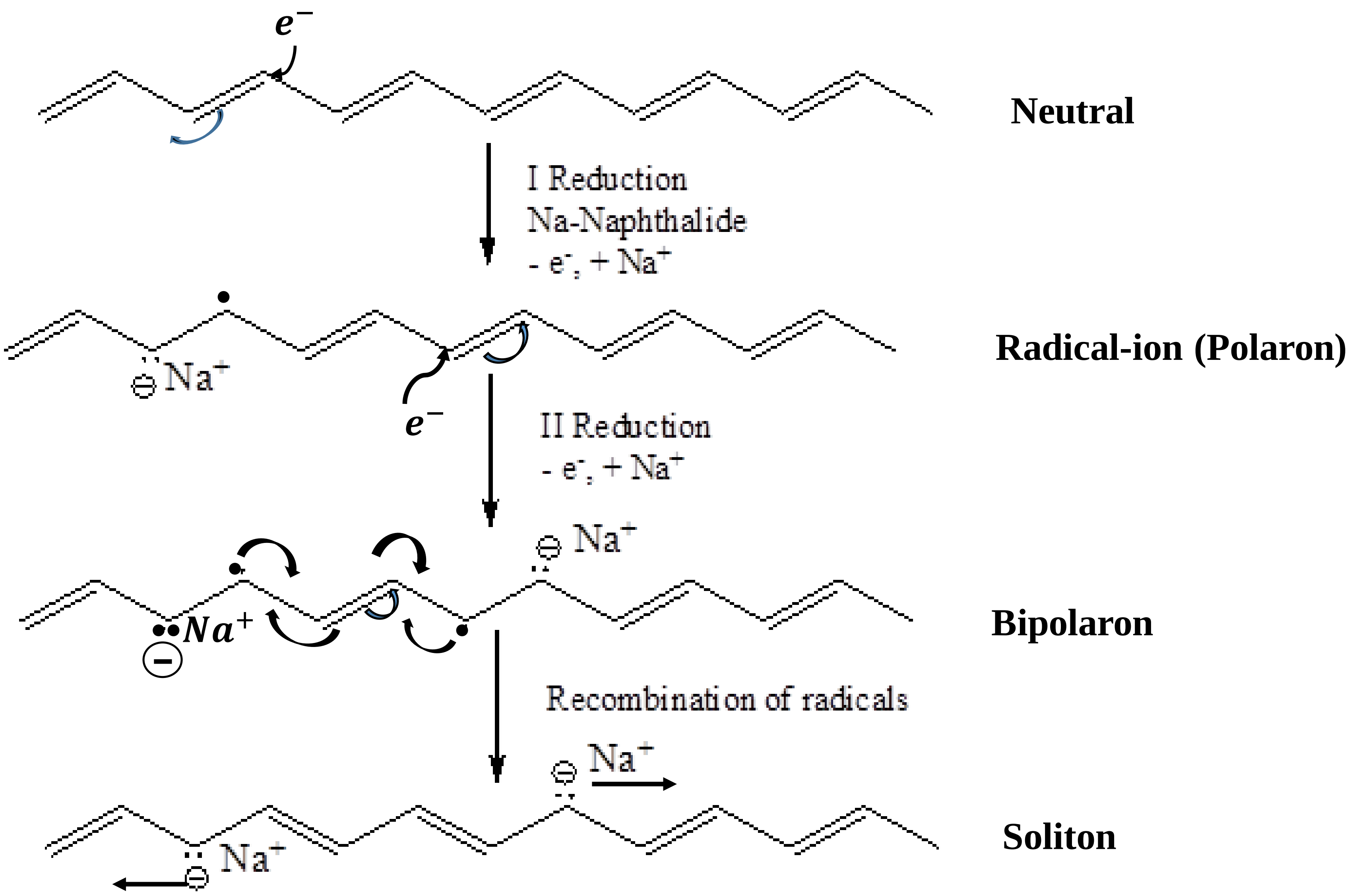
Mechanism of conduction:

- The removal of an electron from the polymer pi-back bone using oxidizing agents to form radical ion called **polaron.**
- A second oxidation of a chain of polaron gives **Bipolaron.**
- Recombination of radicals in Bipolaron gives Soliton.
- The positive charges on Soliton are mobile in two directions and current carriers for conduction.

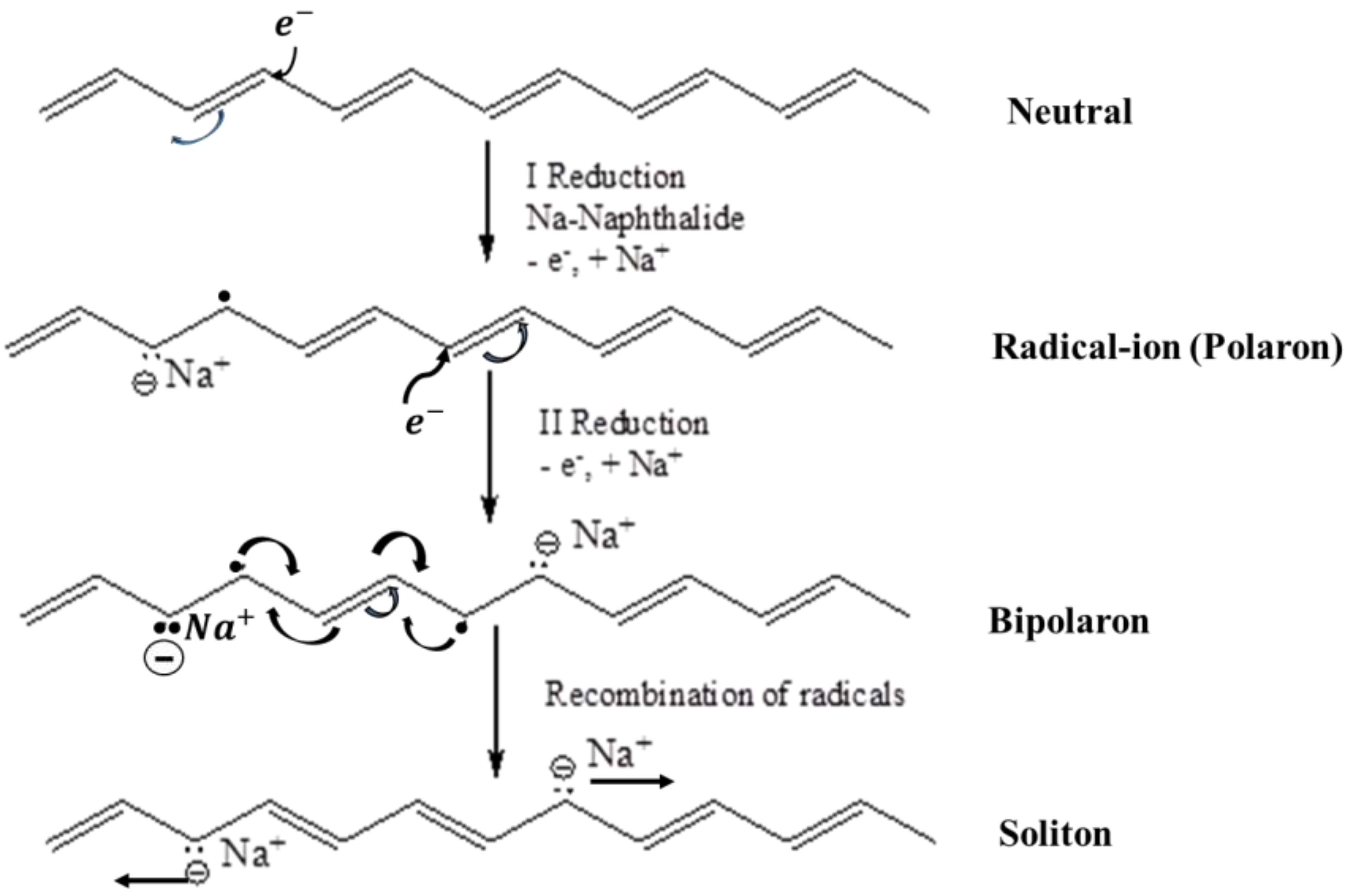
2. Reductive doping (n-doping):

In reductive doping technique, pi-backbone of a polyacetylene is partially reduced using sodium napthalide in tetra hydro furan.





Reactions of n- doping of polyacetylene

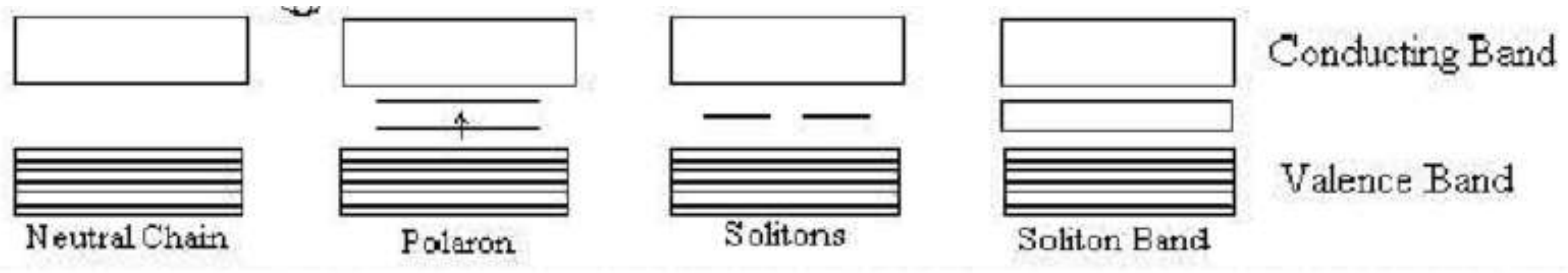


Reactions of n- doping of polyacetylene

Mechanism of conduction:

- The addition of an electron to the polymer back bone by using a reducing agent generates a radical ion or polaron.
- A second reduction of chain containing polaron gives Bipolaron.
- Recombination of radicals of Bipolaron produces Soliton.
- The negative charges on Soliton are mobile in two directions and current carriers for conduction.

Energy Gap diagram



Applications of Conducting Polyacetylene

1. ***Used as electrode material in*** lightweight rechargeable batteries.

2. Used in making Glucose Sensor.

3. Used in making Transistors

4. Light Emitting Diodes

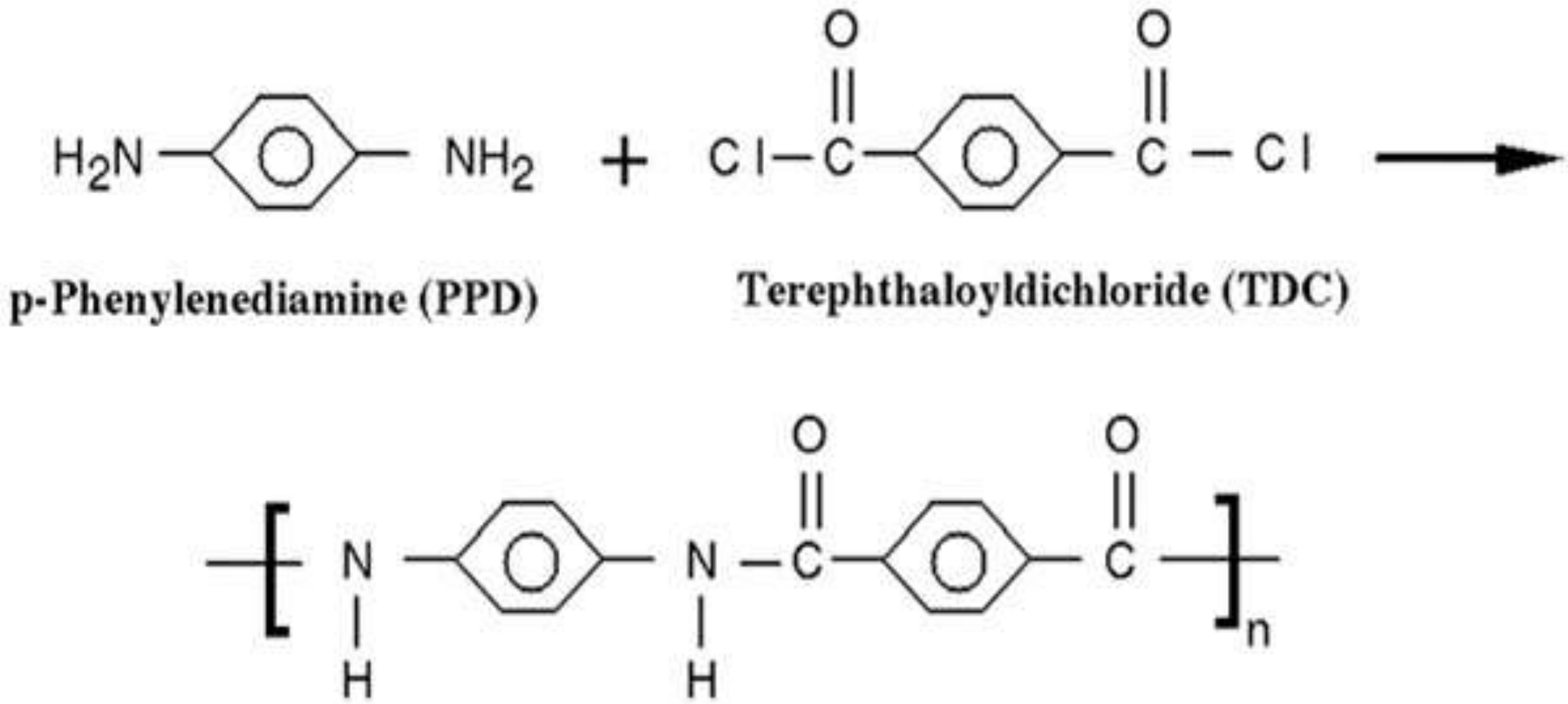
KEVLAR FIBER

Polymer Composite: A polymer composite is a material made of two or more types of polymers with different physical and chemical properties that, when combined, produce a material with characteristics different from the individual components.

Polymer composites are usually made of two components, Fiber and Matrix

Synthesis, Properties and Applications of Kevlar Fibre:

Kevlar is a polyamide, in which all the amide groups are separated by para-phenylene groups. The Chemical composition of Kevlar is poly para phenylene terephthalamide.


p-Phenylenediamine (PPD)
Terephthaloyldichloride (TDC)


KEVLAR FIBER
https://textilelearner.net

Kevlar is fiber embedded in an epoxy resin polymer matrix is called Polymer Composite

Properties of Kevlar

1. *Kevlar is crystalline, lightweight and non-flammable*
2. *Resistant to heat, impact, scratch*
3. *Withstands harsh environmental conditions*
4. *Abrasion and corrosion resistant*
5. *High tensile strength*
6. *Resistant to Chemicals*

Applications

The physical properties of Kevlar make it a suitable material for many applications, such as:

1. It is used in lightweight boat hulls. Aircraft panels, Racecars
2. Bulletproof vests and combat helmets
3. Reinforce material for car tires, bicycle tires, which reduces puncture rate
4. Marine current turbine and wind turbine
5. Ropes and cables
6. Fiber-optic cables for communication, data transmission and ignition

BULLET / STAB
PROOF VESTS

DIVING GLOVES

WALKING BOOTS

MILITARY HELMET

CUT RESISTANT
GLOVES

BICYCLE TYRES

CAR TYRES

FIRE PROOF
CLOTHING

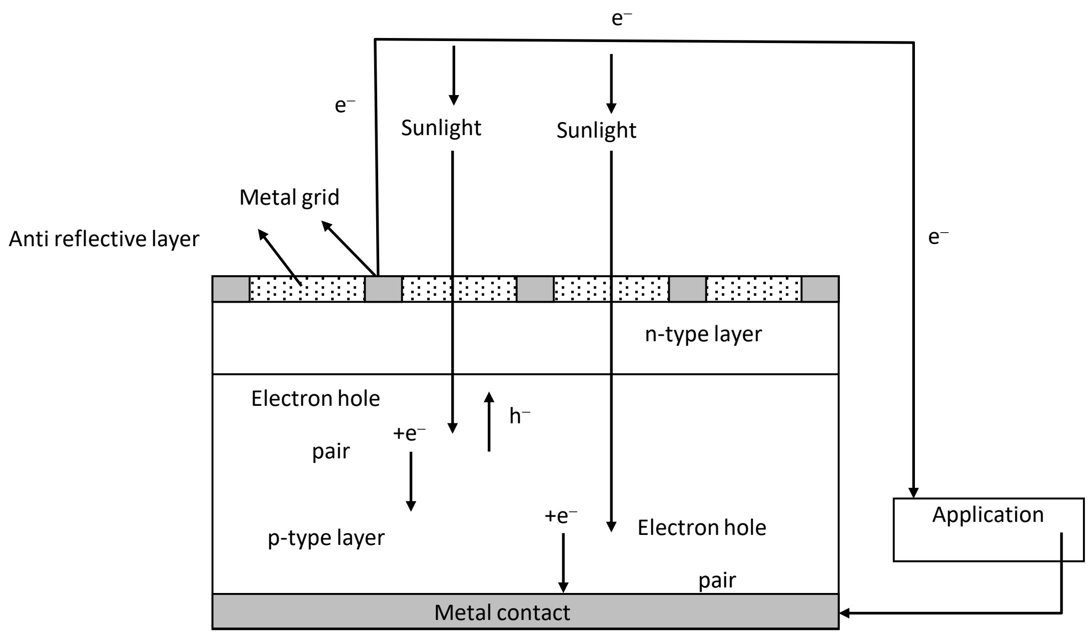
Green Fuels

Hydrogen, Solar Energy and wind energy are called as Green Fuels.

Photovoltaic Cells

Photovoltaic cells or solar cells are semiconductor device that converts sunlight into direct current (DC) electricity.

Construction and working of photovoltaic cells



A typical silicon photovoltaic cell is composed of a thin poly crystalline silicon wafer consisting of an ultra-thin layer of phosphorus doped. (n-type) silicon on top of boron doped (p-type) silicon. Hence a p-n junction is formed. A metallic grid forms one of the electrical current contacts of the diode and allows light to fall on the semiconductor between the grid lines as shown in Fig. An antireflective layer between the grid lines increases the amount of light transmitted to the semiconductor. The cell's other electrical contacts is formed by a metallic layer on the back of the solar cell.

PV cell works on the principle of photoelectric effect E=hγ, When light radiation falls on the p-n junction diode, electron – hole pairs are generated by the absorption of the radiation. The electrons are drifted to and collected at the n-type end and the holes are drifted to p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced.

Applications:

PV can meet the need for electricity for parking meters, temporary traffic signs, emergency phones, radio transmitters, water irrigation pumps, stream-flow gauges, remote guard posts, lighting for roadways, and more.

Advantages of PV cells:

- Fuel source is vast and infinite.
- No emissions, no combustion or radioactive residues for disposal.
- Does not contribute to global warming or pollution.
- Low operating cost and high reliability.

  No moving parts and so no wear and tear.
- No recharging is required.

  They do not corrode.

Disadvantages of PV cells:

- Sunlight is relatively low density energy.
- High installation cost.
- Energy can be produced only during daytime.

Green hydrogen is defined as hydrogen produced by splitting water into hydrogen and oxygen using renewable electricity.

Properties of Green fuel- Hydrogen

1. Clean energy source
2. Obtained by water splitting through electrolysis and unlimited
3. Action of sunlight, wind and water produces Hydrogen
4. It is a renewable source of energy
5. It has high electrochemical reactivity
6. It has high energy density
7. Does not produce harmful byproducts

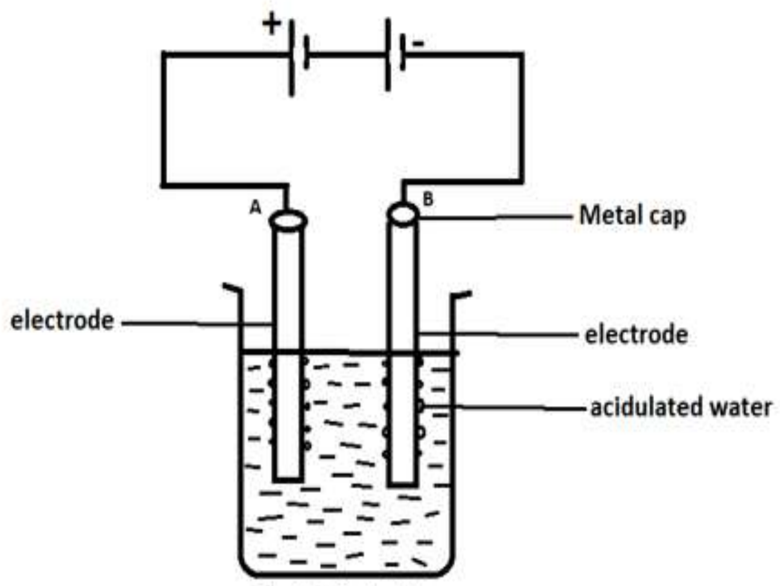
Advantages

1. Use of hydrogen reduces 30% of greenhouse emissions
2. It is an alternative to fossil fuel
3. Produces more energy than fossil fuel therefore referred to as “Energy Bounce”
4. Sustainable energy source because replenished easily by sunlight, wind and water
5. Reduces air pollution

Generation of energy (green hydrogen) by electrolysis of water and its advantages

Green hydrogen is defined as hydrogen produced by splitting water into hydrogen and oxygen using renewable electricity.

Principle of water electrolysis



Electrolysis of water

Water electrolysis unit consists of an anode, a cathode separated with an electrolyte, and a power supply.
A direct current (DC) is applied from the negative terminal of the DC source to the cathode (seat of the reduction reaction), where the hydrogen is produced.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

$$4H^+ + 4e^- \rightarrow 2H_2$$

$$\overline{}$$

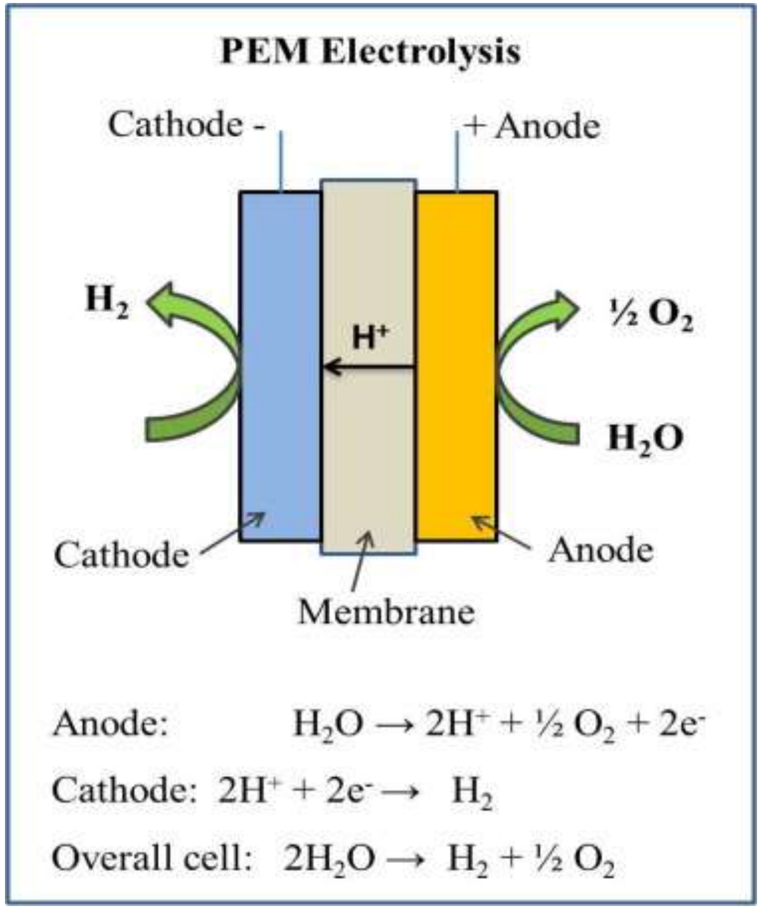
$$2H_2O \rightarrow O_2 + 2H_2$$

The hydrogen can be stored in salt caverns, storage tanks, or the gas grid. Smaller hydrogen quantities can also be stored in metal hydrides

PEM electrolyzer (Polymer electrolyte Membrane)

Noble metals like platinum and iridium oxide as the electro catalysts (anode and cathode).

Polysulfonated membranes was used as a electrolyte or Proton Exchange Membrane



During electrolysis water decomposes at the anode into protons and molecular oxygen.

At anode: $2H_2O \longrightarrow 2H^+ + 2e^- + \frac{1}{2}\mathbf{O_2}$

Protons migrate to the cathode under the effect of the electric field.

At cathode: $2H^+ + 2e^- \longrightarrow H_2$

These proton exchange membranes having many advantages such as

- Lower gas permeability : No mixing of products formed at anode and cathode
- High proton conductivity: Mobility of protons towards cathode is high, quick production of hydrogen gas
- Operated at moderate pressure of 30 bar

Limitations

- Cost of electrodes is too high
- Maintenance cost is high