POLYMERS

Polymers are high molecular weight compounds whose structures are made up of a large number of simple repeating units. The repeating units are usually obtained from low molecular weight simple compounds referred to as monomers. The reaction by which monomers are converted into polymers is known as polymerisation.

For example polyethylene formation from ethylene

$$\longrightarrow \quad n\ CH_2 = CH_2 \quad ^{\text{polymerisation}} \quad -(CH_2\text{-}CH_2)-_{n}$$

Ethylene Polyethylene

The monomer is shown on the left hand side of the equation and products on the right hand side, the repeating polymer unit is enclosed in brackets and lines passing through the brackets show that the chain continues in both directions. The subscript n shows how many times the repeating unit appears.

Degree of polymerisation:-

The size of the polymer molecule is decided by the number of repeating units present in it. The number of repeating units (n) contained in the polymer is known as degree of polymerisation.

$$\longrightarrow \quad n\ CH_2 = CH_2^{\text{polymerisation}}-(CH_2\text{-}CH_2)_n-$$

Ethylene Polyethylene

Where n is degree of polymerisation, it can be 10^4 or more.

Functionality:

The number of bonding sites in a monomer is termed as functionality. For a molecule to act as a monomer it must have at least two reactive sites i.e. its functionality should be two. When the double bond is broken, two single bonds become available for combination.

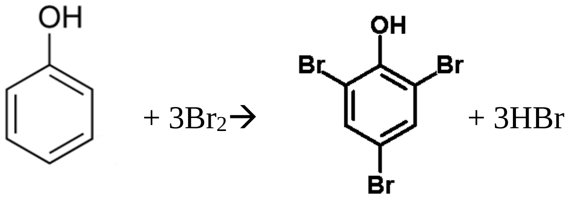
Eg:- 1) Ethylene can add two molecules of hydrogen or halogen.

Hence, it is bi-functional (functionality two)

$$CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$$

Ethylene Ethane

2) Phenol has three reaction sites. Hence, it is tri-functional



Phenol 2,4,6Bromo phenol

3) Acetylene has a functionality of four (tetra functional), as it can react with four atoms of hydrogen or halogen.

$$CH \equiv CH + 2H_2 \rightarrow CH_3 - CH_3$$

ActyleneEthane

Mechanism of Polymerisation:

The process of joining together a large number of simple molecules to form a very big molecule is termed as polymerisation. There are two broad types of polymerisation reactions i.e.

1) Addition Polymerisation (or) Chain Growth Polymerisation
2) Condensation Polymerisation (or) Step Growth Polymerisation

1. Addition Polymerisation: [Chain Growth]

The self addition of monomers to form a large molecule without elimination of any by product is known as ‘Addition Polymerisation’. As no by-product is formed the molecular weight of polymer is sum of molecular weight of monomers.

Addition Polymerisation can be carried out by two mechanisms.

i) Free radical mechanism
ii) Ionic mechanism
iii) Coordination mechanism

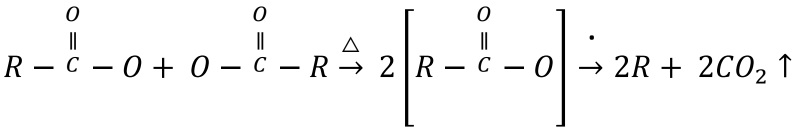
i) Free Radical Mechanism

The initiation of reaction is brought about by the free radicals produced by the initiator which undergo the homolytic fission in the presence of light (or) heat.

Step-1:

1. Chain Initiation

Organic peroxides undergo homolytic fission.



$$R-\overset{\overset{O}{\|}}{C}-O+\ O-\overset{\overset{O}{\|}}{C}-R\xrightarrow{\triangle}2\left[R-\overset{\overset{O}{\|}}{C}-O\right]^{\bullet}\rightarrow 2R+\ 2CO_2\uparrow$$

2. **Chain Propagation:**

$$R + CH_2 \cdot \underline{\frown\frown}\ CH_2 \rightarrow R - CH_2 \overset{\bullet}{-} CH_2$$

$$R - CH_2 \overset{\bullet}{-} CH_2 + n(CH_2 = CH_2) \rightarrow R(CH_2CH_2)nC\overset{\bullet}{H}_2CH_2$$

3. **Chain Termination:**

When two free radicals combine, chain termination takes place.

$$2R(CH_2CH_2)_n\ \overset{\bullet}{C}H_2CH_2 \rightarrow R(CH_2CH_2)_n\ CH_2CH_2 : CH_2CH_2(CH_2CH_2)_nR$$

$$\rightarrow R(CH_2CH_2)_n\ CH_2CH_2\ CH_2CH_2(CH_2CH_2)_nR$$

3) Condensation Polymerisation: [Step growth polymerisation]

In step growth polymerisation, polymers are formed by the stepwise reaction between the functional groups of monomers.

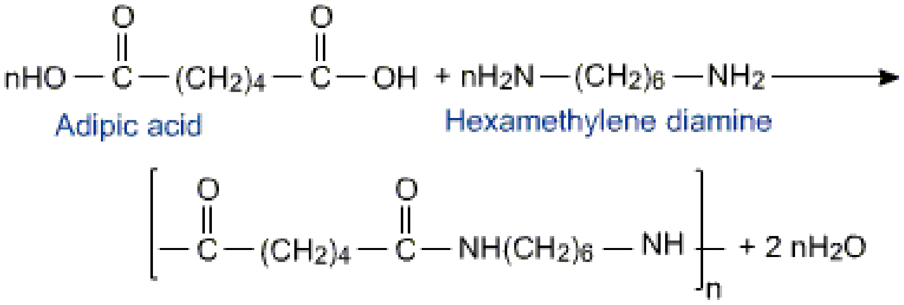
Main Features:

1) Monomers having two (or) more functional groups (-OH, -COOH, -NH_2) can undergo condensation.

2) Polymerisation proceeds through intermolecular condensation.

- Polymer chain growth is slow.
- Polymerisation is catalysed by acids and alkalies.
- Elemental composition of a polymer is different from that of its monomers.

Eg: Nylon 6, 6



$$nHO - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - OH + nH_2N - (CH_2)_6 - NH_2 \longrightarrow \left[- \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - NH(CH_2)_6 - NH - \right]_n + 2\,nH_2O$$

Difference between Addition and Condensation Polymerisation

Addition Polymerisation	Condensation Polymerisation
1) Takes place in monomers having multiple bonds	1) It takes place in monomers having reactive functional group
2) Growth of chain is at one active chain	2) Chain growth occurs minimum at two active centers
3) No by product is formed	3) Generally a byproduct is formed
4) The molecular weight of polymer is sum of molecular weights of monomers.	4) Molecular weight of polymer is not sum of molecular weights of monomers.
Eg: Polyethylene, PVC, Polystyrene	Eg: Bakelite, Urea- Formaldehyde Resin.

Stereo Specific Polymersiation:

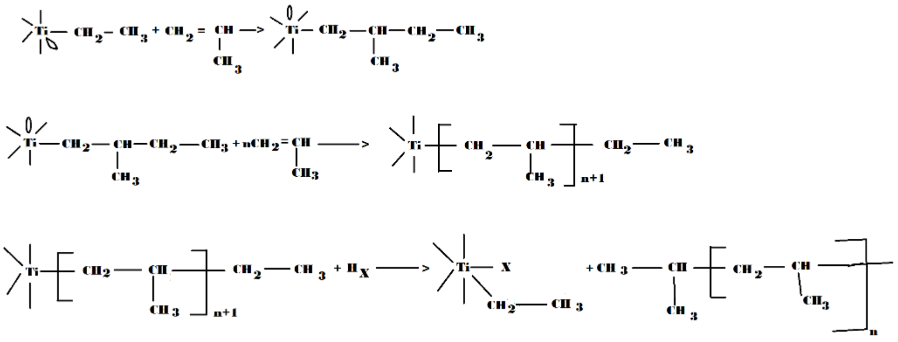
Coordination polymerisation is a form of polymerization that is catalysed by transition metal salts and complexes Known as Ziegler-Natta Catalyst.

Stereospecific polymerization is carried out as:

Initiation: In the initiation step, π – cloud of alkene overlaps with an empty orbital of titanium, then there is insertion of alkene molecule in between the Ti-C bond.

Propagation: As intra molecular rearrangement in carbon chain occurs again generate a vacant site on titanium, each time one monomer molecule can be added.

Termination: It can be done by the addition of molecules containing active hydrogen like hydrogenfluoride.



Individual polymers

A. Polyethylene: It is obtained by the Polymerisation of ethylene

$$nCH_2 = CH_2 \xrightarrow{Polymerisation} -(CH_2 - CH_2) -_n$$

Ethylene Polyethylene

Polyethylene is of two types.

a) Low density polyethylene [LDPE] is polymerized at high pressure of 5000 atmospheres and at a temperature of 250^0 C in presence of oxygen as free radical inhibitors.

$$nCH_2 = CH_2 \xrightarrow[\substack{high\ pressure \\ 250^0C}]{O_2} -(CH_2 - CH_2) -_n$$

b) High density polyethylene [HDPE] is polymerised under 6-7 atmospheric pressure at 60^0C – 70^0C in the presence of ZieglarNatta Catalyst ($Alet_3$ + $Ticl_4$)

Properties:

1) It is a soft flexible polymer.
2) Polyethylene is a good electrical insulator

3) It is resistant to moisture, O_2, CO_2, UV light.

4) It is resistant to acids, alkalies, salts solution at room temperature.

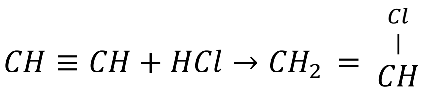
Uses:

1) Used in toys, pipes, bottles and in manufacturing of bags and bottle caps.

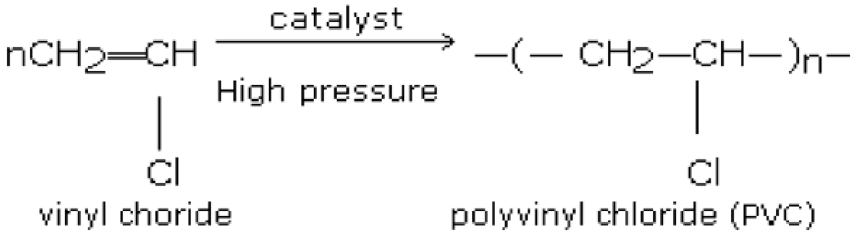
2) Used for wires and cable coatings.

3) Used as packing materials for food and textiles.

B. Polyvinyl Chloride: It is obtained by polymerizing vinyl chloride



$$CH \equiv CH + HCl \rightarrow CH_2 = \overset{Cl}{\overset{|}{CH}}$$



Properties

1) It is colourless, odourless, non-flammable, chemically inert powder.

2) It is resistant to light, atmospheric oxygen, inorganic acids and alkali.

3) It is soluble in hot ethyl chloride.

4) PVC posses a high softening point, greater stiffness and rigidity compared to polyethylene but brittle.

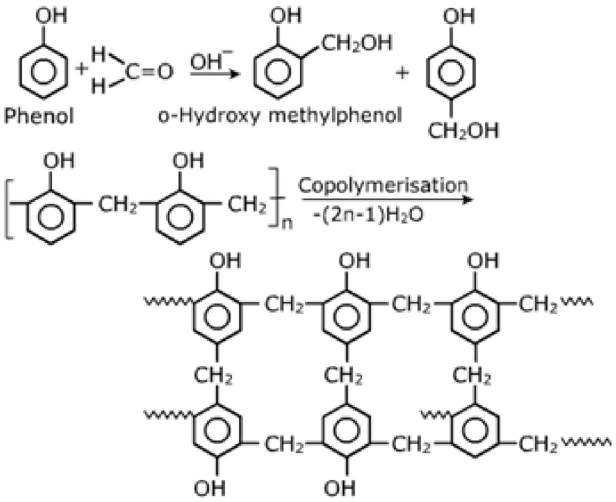
Uses:

1) Rigid PVC is used for making tyres of cycles, motor cycles and mud guards, refrigerator components tank linings of acids, alkalies and safety helmet.

2) Plasticized PVC is used for packing continuous sheets, employed for packing, rain coats, table cloths, curtains, electric insulation, covering electric cables.

C. Bakelite:

It is prepared by condensing phenol with formaldehyde in presence of acidic or alkaline catalyst.



Novolac which on further heating in presence of Hexamethylene tetramine produces Bakelite.

Properties:

1) It is rigid, hard, scratch resistant, infusible, water resistant, insoluble solid.

2) Resistance to non-oxidizing acids (H_2SO_4), salts and many organic salts.

3) They are attacked by alkalies due to presence of free hydroxyl group.

4) They posses excellent electrical insulator.

5) It is a very good adhesive.

Applications:

1) For making electrical insulator parts like switches, switch boarders, etc.

2) For making moulded articles like telephone parts, cabinets for radio and television.

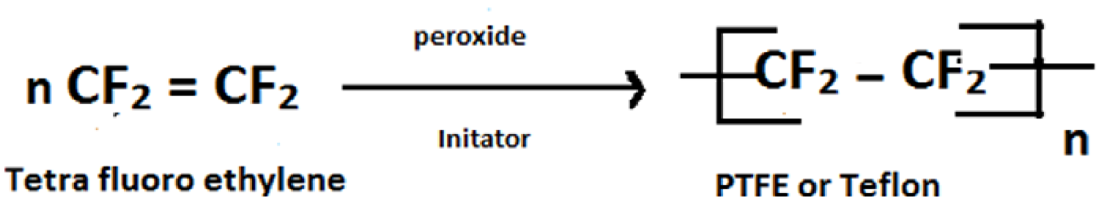
3) In paints and varnishes.

4) As hydrogen exchange resins in water softening

5) Used as adhesives for grinding wheels.

Poly tetra fluoro ethylene (PTFE) or Teflon:

Teflon is obtained by polymerization of tetra fluoro ethylene, under pressure in the presence of benzoyl peroxide as initiator.



Properties:

1. PTFE has extreme toughness, high softening point (327^0 C), high density (2.3 g/cm^2) and strength due to presence of high electronegative fluorine atoms.
2. It has excellent chemical resistance except towards alkali and hot fluorine.
3. PTFE has extreme toughness, high softening point (3270 C), high density (2.3 g/cm2) and strength due to presence of high electronegative fluorine atoms.
4. It has excellent chemical resistance except towards alkali and hot fluorine.

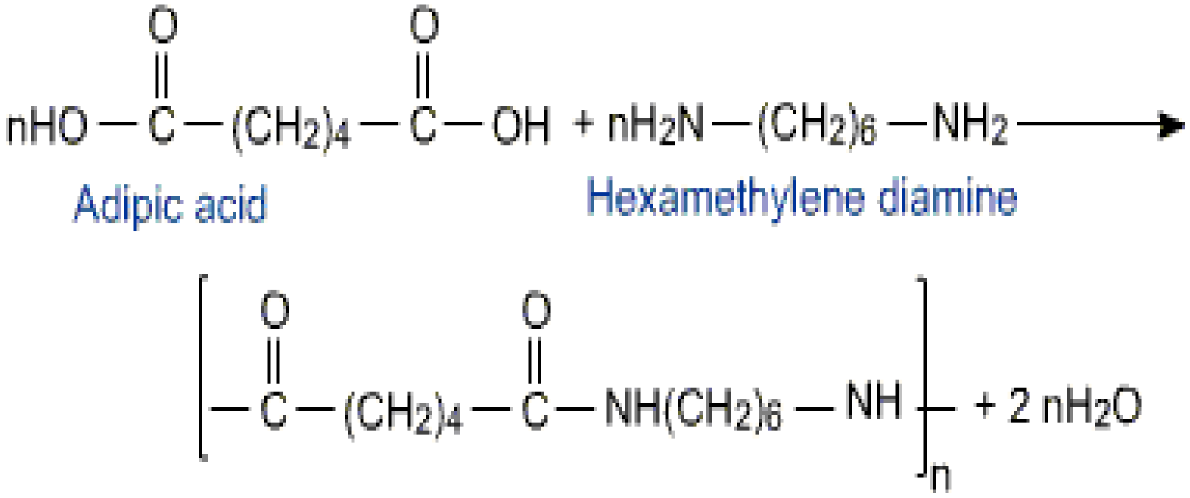
Uses :

1. It is used as non-sticky coating for pans.
2. It is used as insulating material for motors, generators, wires and cables.
3. It is used in non-lubricating bearings.

4. It is used in tank linings, gaskets, magnetic stirrer, coatings etc.

Nylon-6,6:

It is obtained by condensation polymerization of hexamethylene diamine and adipic acid.



$$nHO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + nH_2N-(CH_2)_6-NH_2 \longrightarrow$$

$$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH(CH_2)_6-NH-\right]_n + 2\,nH_2O$$

1. They are translucent, whitish, horny, high melting point (160- 264 ^{0}C).

2. They are resistant to temperature and possess good abrasion resistance.

3.They are insoluble in common organic solvents (benzene, acetone) and soluble in phenol and formic acid.

4.They possess high physical strength and have high lubricating properties.

5.They are flexible and retain original shape after use.

Uses:

1. It is used for fibers which are used in making socks, under garments, dresses ,carpet etc.
2. They are used for making filaments, ropes, bristles of tooth brushes, films etc.
3. They are used in making gears, bearings, electrical mouldings.

Classification of Plastics (Resins):

Plastics are of two types.

1. Thermo Plastic resins are those which can be softened on heating and harden on cooling reversibly.

2. Thermosetting resin does not become soft on heating and they never melt once they set.

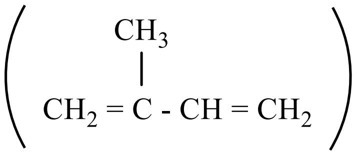
Thermoplastics	Thermosettings
1. They are formed by addition polymerisation only.	1. They are formed by condensation polymerisation.
2. They consists of long chain linear polymers with negligible cross links.	2. They have three dimensional network structures.
3. They soften on heating because secondary forces between the individual chains can break easily by heat, pressure, or both.	3. Their cross links and bonds retain their strength on heating and hence they do not soften on heating.
4. They can be softened, reshaped and reused.	4. They cannot be reshaped and reused.
5. They are usually soft, weak and less brittle.	5. They are usually hard strong and brittle.
6. They are soluble in some organic solvents	6. They are insoluble in almost all organic solvents.
Eg: Polyethylene, Polyvinyl Chloride, Cellulose, Cellulose Derivatives.	Eg: Bakelite, Polyester.

Individual Rubber:

An elastomer is a linear polymer, which exhibits elasticity and other rubber like properties long flexible chains, weak intermolecular forces, occasional cross links are the essential structural requirements of rubber.

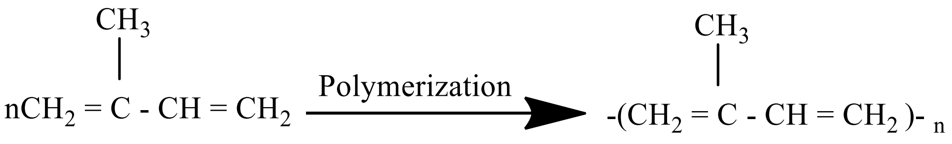
Natural rubber is obtained from rubber trees usually grown in tropical regions. It is obtained from the bark of the tree Heveabrasiliensis .To obtain rubber from these trees incisions are made in the bark. The milky latex that flows out is collected in small vessels and then sent to factories for treatment.

Natural rubber is an addition polymer formed from the isoprene units



$$\left(CH_2 = \overset{\overset{CH_3}{|}}{C} - CH = CH_2 \right)$$

During the treatment, these isoprene molecules polymerize to form long chains of poly isoprene.



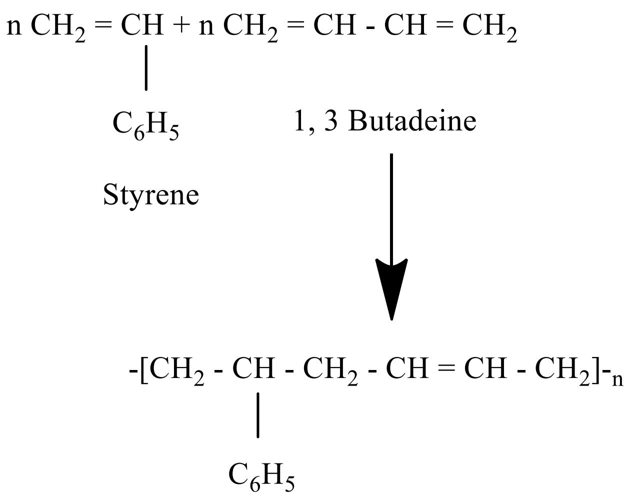
$$nCH_2 = \overset{\overset{CH_3}{|}}{C} - CH = CH_2 \xrightarrow{\text{Polymerization}} -(CH_2 = \overset{\overset{CH_3}{|}}{C} - CH = CH_2)-_n$$

Poly isoprene

Poly isoprene exists in two isomeric forms cis and trans- natural rubber is the cis isomer while the trans isomer is called gutta-percha. The average degree of polymerisation is around 5000. The molecular weight of raw rubber is about 1,00,000-1,50,000.

1. Styrene Rubber or Buna-S:

Butadiene and styrene rubber is obtained from the monomers – styrene, Butadune.



$$n\,CH_2 = \underset{\underset{C_6H_5}{|}}{CH} + n\,CH_2 = CH - CH = CH_2 \longrightarrow -[CH_2 - \underset{\underset{C_6H_5}{|}}{CH} - CH_2 - CH = CH - CH_2]-_n$$

Buna-S

Properties:

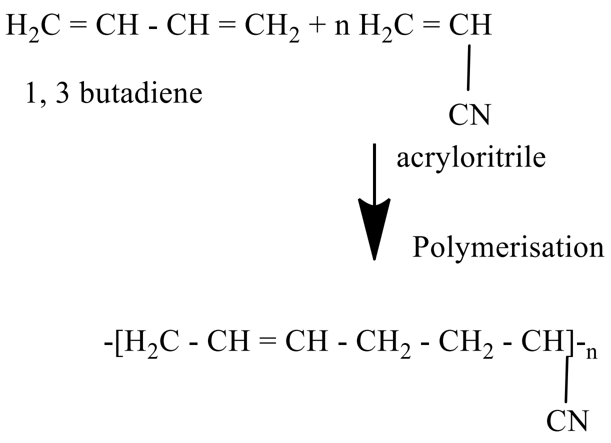
1) It posses high abrasion, resistance, high load bearing capacity and resilience.
2) It gets readily oxidized in presence of traces of ozone.
3) Swells in oils and organic solvents.

Applications:

1) Mainly used for the manufacture of motor tyres.
2) Floor tiles, shoe soles, gaskets etc.
3) Wires and cable insulation and adhesives.

2. Buna-N: (Nitrile Rubber)

It is a copolymer of Butadiene and Acrylonitrile



$$H_2C = CH - CH = CH_2 + n\, H_2C = \underset{\displaystyle CN}{\underset{|}{CH}} \xrightarrow{\text{Polymerisation}} -[H_2C - CH = CH - CH_2 - CH_2 - \underset{\displaystyle CN}{\underset{|}{CH}}]-_n$$

Properties:

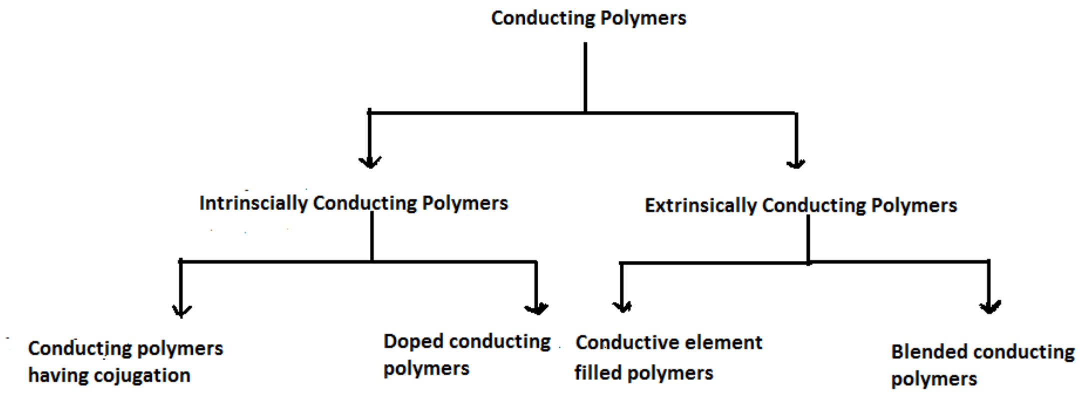
1) It possess excellent resistance to heat, sunlight, oils.
2) Less resistant to alkalis.
3) It is more resistant to ageing than natural rubber.

Uses:

Conveyor belts, high attitude aircraft components, tank linings, hoses, gaskets, printing rollers, adhesives, automobile parts etc.

Conducting Polymers: An organic polymer having linear structure, and extensive conjugation along the polymeric backbone having conductance similar to thatof a conductor is called a conducting polymer. Conducting polymers are usually prepared by doping process. Conducting polymers are preferred over metals in electrical applications due to its light weight, corrosion resistance and greater workability. Examples for conducting polymers are Polyacetylene and polyaniline.

Polymers that conduct electricity are called conducting polymers. They can be classified as follows:



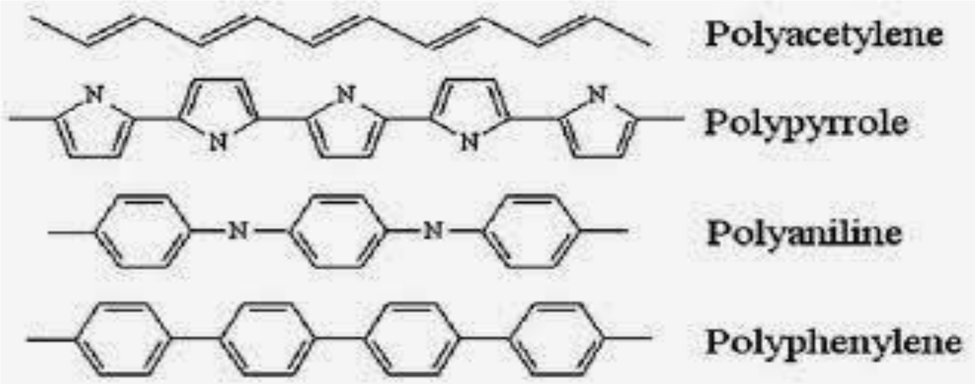
Intrinsic conducting polymers: -

Intrinsic conducting polymers have extensive conjugation (alternate double bonds) in the backbone which is responsible for conduction. They are further divided into two types:

a) Conjugated π electrons conducting polymers: -

The conductivity of these polymers is due to the presence of conjugated π electrons in the backbone. Overlapping of conjugated π electronsover the entire backbone results in the formation of valence band as well as conduction band separated by a significant band gap. Thermal or photolytic activation of polymer gives electrons sufficient energy to jump the gap and reach into lower levels of the conduction band.

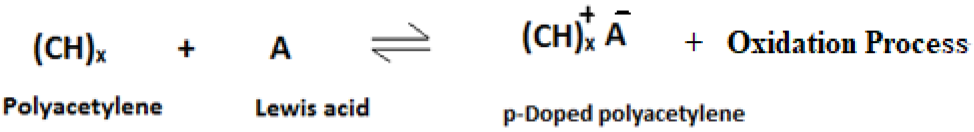
Eg :-



Conductivity of such polymers is of the order 10^{-10} Scm^{-1}. Conductivity of these polymers, having conjugated π- electrons in the backbone is not sufficient for their use in different applications.

b) Doped Conducting polymers: - Intrinsic conducting polymers can be easily oxidized or reduced on account of their low ionization energy and high electron affinities. The conductivity of such polymers can be increased either positive or negative charge on polymer background by oxidation or reduction. Doping can be of two types

i) p-doping: - When the polymer is treated with a Lewis acid, its oxidation takes place and holes (positive charges) are created on the polymer backbone. Commonly used dopants are I_2, $FeCl_3$, Br_2 etc;



$$(CH)_x + A \rightleftharpoons (CH)_x^{+}\bar{A} + \text{Oxidation Process}$$

Eg :- $(C_2H_2)_n + 2FeCl_3 \rightarrow (C_2H_2)_n^+ \ FeCl_4^- + FeCl_2$

Oxidation process (i.e., removal of electrons from the polymer chain backbone) leads to the formation of delocalized radical ion called polaron. On second oxidation of this polaron yields two positive charge carriers on each chain which are mobile. Thus, these delocalized positive charges are current carriers for conduction.

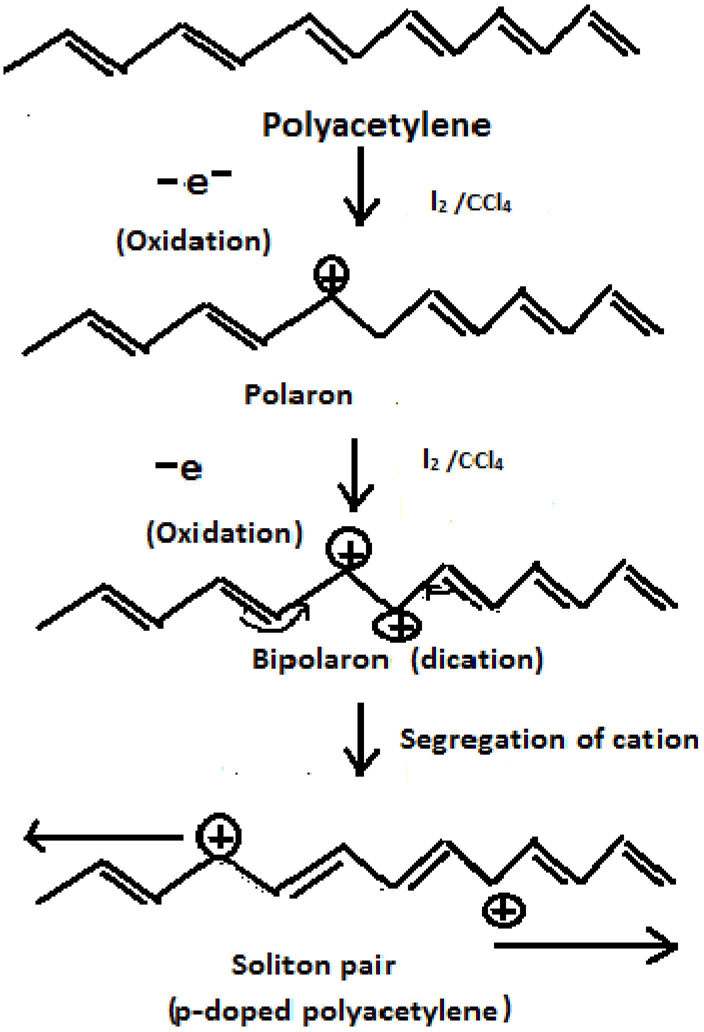
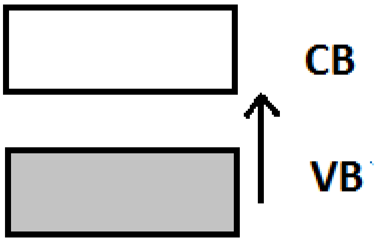


Fig 1.15 Mode of conduction in p-doped conducting polymer

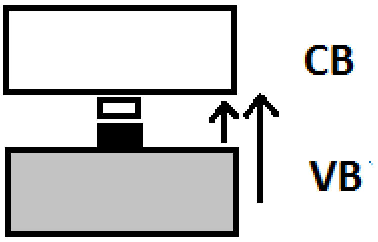
Interpretation of conductivity through band theory: -

1. Valence band (VB) and conduction band (CB) in conjugated polymers are

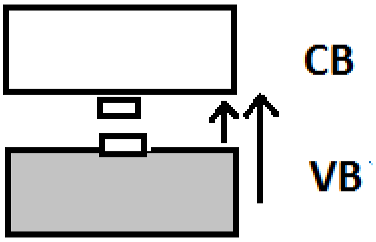
separated by a significant band gap.



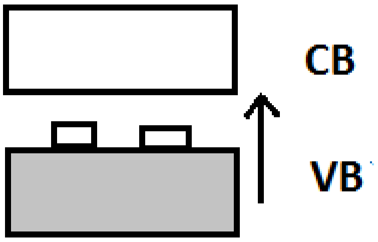
2.Electrons removed by oxidation will lead to the formation of radical .cation (or polaron).It has a hole in between Valence band (VB) and conduction band (CB).



3. Further oxidation will lead to formation of Bi-cation with two holes in Valence band (VB) and conduction band (CB).

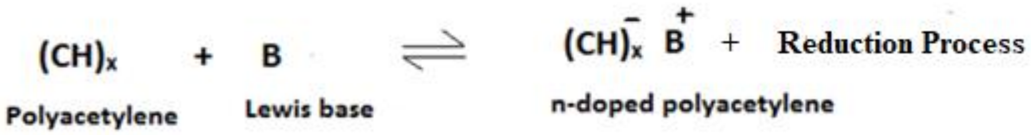


4. Bi-cation lowers its energy by segregation into two positive solitons (i.e two holes in the mid gap energy levels). The presence of holes in the band gap allow facile jump of electrons from valence band into these holes. Thus, holes created in the VB conduct electricity.



b) **n- doping**: -

When the polymer is treated with Lewis base, reduction takes place and negative charges are added on the polymeric chain. Some common n-type dopants are Li, Na naphthylamine, sodium naphthalide ,etc.



$$(CH)_x + B \rightleftharpoons \overset{-}{(CH)_x}\overset{+}{B} + \text{Reduction Process}$$

For example, $(CH)_x + Na^+ (C_{10}H_8)^- \rightarrow Na^+(CH)_x^- + C_{10}H_8$

In n-doping the reduction process (i.e., addition of an electron to the polymer backbone) using a reducing agent like sodium naphthalide, $Na^+(CH)_x^-$leads to the formation of polaron and bipolaron in two steps. This followed by recombination of radicals yields two negative charge carriers formed on each chain of polyacetylene are responsible for conduction.

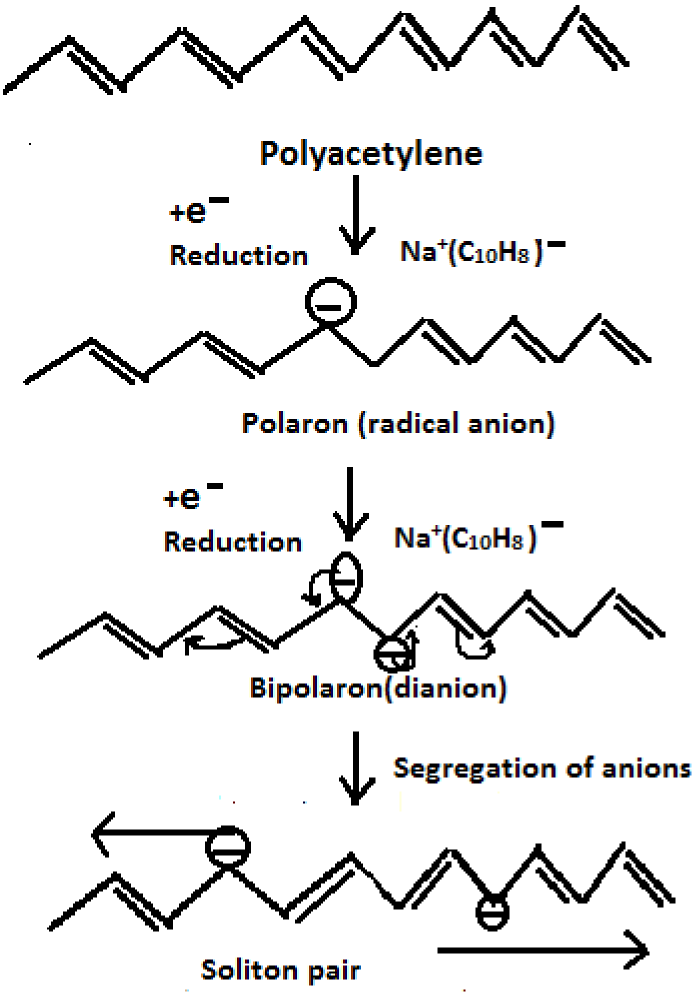
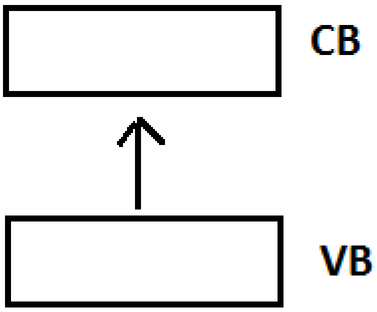


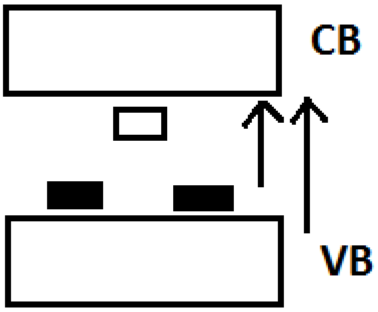
Fig 1.16: Mode of conduction in n-doped conducting polymer

Interpretation of conductivity through band theory: -

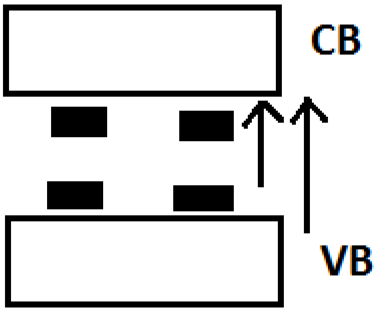
1. Valence band (VB) and conduction band (CB) in conjugated polymers are separated by a significant band gap.



2. Electron added to polymer by reductive doping does not go into the conduction band but into a intermediate electronic state within the band gap of radical anion.

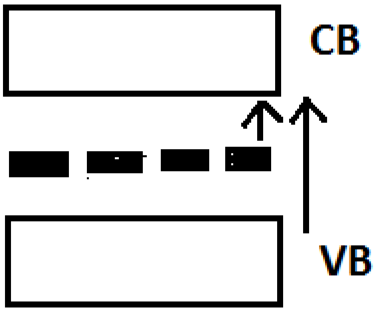


3.Further reduction will lead to the formation of bianion. It contains electrons in the energy levels residing in the band gap.



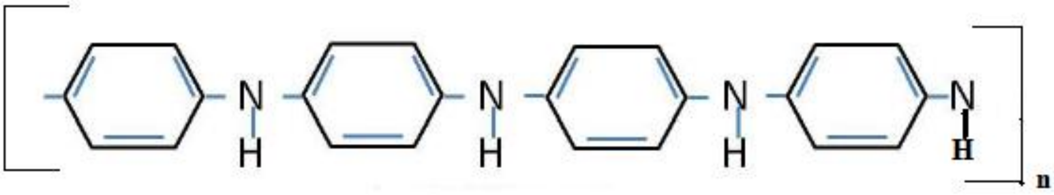
4. Bianion lowers its energy by segregating into two negative solitons at the mid gap

energy levels. Current is carried as the charged soliton and the defect site move along the chain.



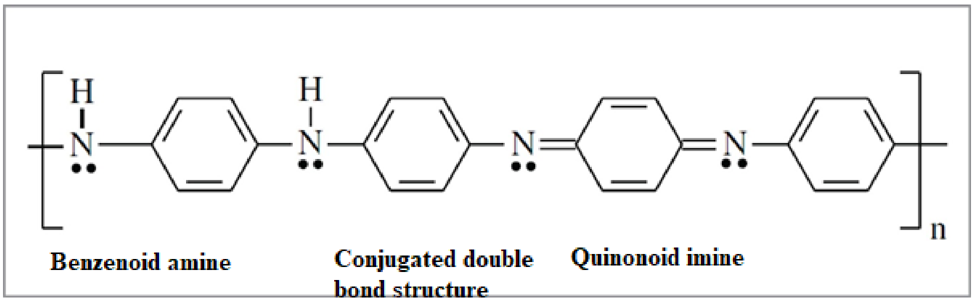
Mechanism of Conduction in Polyaniline:

Among the conducting polymers, polyaniline possess unique properties.



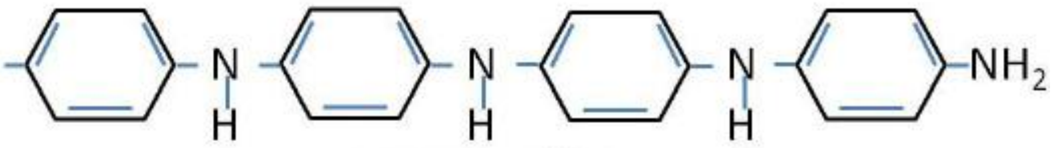
Polyaniline is a conjugated polymer and is reactive. It is transparent in thin layers. In conducting state, it is green, turns red in reducing state and blue in oxidising state. It is a stable conducting polymer and has a wide range of conductivity.

It is the oldest conductive polymer and prepared by the anodic oxidation of aniline in H_2SO_4. Its conductivity is due to conjugated π-bond system formed by the overlapping of carbon p-orbital and alternating C-C bond lengths extending over a large number of recurring monomer units.

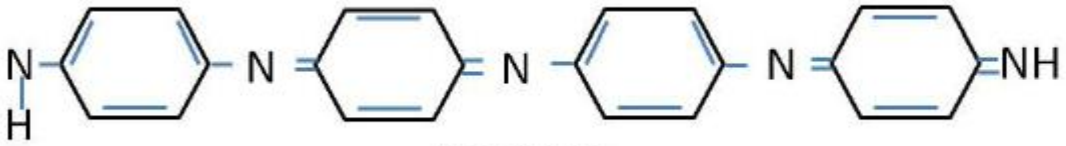


Conjugated double bonds permit the electron mobility throughout the molecule due to delocalised electrons.In addition it has a conjugated double bond structure ,i.e benezenoid ring between the quinonoid imine and the benzenoid amine structure.

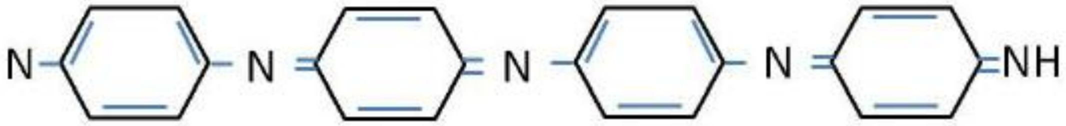
Polyaniline exists mainly in three different forms viz. Leucoemeraldine (LE), Pernigraniline (PE) and Emeraldine Base (EB), out of which the most stable and useful form is EB. On doping with protonic acid (HA) two adjacent imine (=N-) groups of EB gets protonated and thus a bipolaron is formed. The bipolaron then rearranges to form polarons in which the positive charges are delocalised along the polymeric backbone. These positive charges are mobile and hence are responsible for conductivity. The schematic representation is given below.



Leucoemeraldine

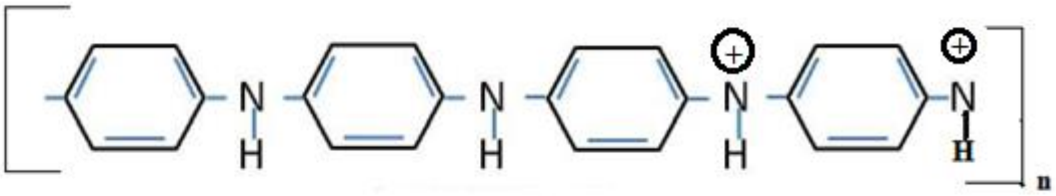


Emeraldine



Pernigraniline

Bipolaron structure of polyaniline



Applications:

1. Polyaniline is used for corrosion protection, sensors , printed circuit boards.
2. It is used for coating of films.
3. It is used as a secondary electrode in rechargeable batteries.

Applications of conducting polymers:

Conducting polymers are widely used because they are light weight, easy to process and have good mechanical properties. Some of the important applications of conducting polymers are:-

i) In rechargeable light weight batteries: - These have perchlorate doped polyacetylene lithium system. These batteries are light in leak proof and small in size.

ii) In electrochemical displays and optical filters: -

Intrinsic conducting polymers can absorb visible light to give coloured products which is useful for electrochromic displays and optical filters (windows with adjustable transparency).

Thus conducting polymers can be used as electrochromic materials (i.e ; the materials which change colour reversibly during the electrochemical processes of charge and discharge).

iii) In electronic devices such as transistors and diodes.

iv) In drug delivery system for human body etc.

v) In photo voltaic devices, e.g; Al/ polymer / Au photovoltaic cells.

vi) In molecular wires and molecular switches.