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UNIT-I

HIGH POLYMERS & PLASTICS

POLYMERS

Polymers are made of two Greek words:

"poly" means many and "mers" means unit or part.

*"A polymer is a high molecular weight compound formed by joining of a large number of a small units".

*"The process is joining together of a large number of simple small molecules to form very big molecules is termed as POLYMERISATION".

*Small molecules that combine with each other to form a polymer are known as MONOMERS.

Example: polythene.

$n\ CH_2 = CH_2 \rightarrow [CH_2\text{-}CH_2]_n$

Ethylene polythene

(monomer) (polymer)

*Homo polymer: A polymer that is obtained from only one type of monomer.

*Co polymer: A polymer that is obtained from only one type of monomers.

Eg:

Nylon6,6 (Poly hexamethylene adipate)

Its monomers;

a) Adipic acid ($HOOC\text{-}(CH_2)_4\text{-}COOH$)
b) Hexa methylenediamine($H_2N\text{-}(CH_2)_6\text{-}NH_2$)

Polymerization:

The process of joining together of a large number of simple small molecules to form very big molecules is termed as polymerization.

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TYPES OF POLYMERISATION:

In 1929 W.H. Carothers categorized the polymerization reactions in to two types.

i) Addition polymerization.
ii) Condensation polymerization.

i) Addition polymerization:

Addition polymerization is obtained by linking together the monomer molecules by achain reaction to give a polymer, whose molecular weight is exactly an integral multiple of the monomer. It is also known as 'chain growth polymerization.'

Eg: polythene.

Polythene is obtained by the polymerization of ethylene.

*A single monomer is involved in addition polymerization and hence the polymer is a homo polymer.

* Addition polymerization reaction is usually induced by light, heat or a catalyst, for opening the double bond of monomer and creating the reactive sites.

COPOLYMERISATION:

Addition polymer involving the mixture of two or more suitable monomers gives a copolymer and the process is called copolymerization.

Eg: A synthetic rubber, GR-S rubber, with elastomeric properties is obtained by copolymerization of styrene and 1, 3butadine.

Copolymers have desirable and different properties compared to the corresponding homo polymers.

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***MECHANISM OF ADDITION POLYMERIZATION:**

Addition or chain growth polymer is the linking of molecules having multiple bonds.

Addition or chain growth polymerization proceeds in three important steps:

i) Initiation step: this step involves the formation of reactive particle.
ii) Propagation step: It consists of a growing polymer chain having reactive particles.
iii) Termination step: In this step the growth of chain is finally terminated.

*polymerization of ethylene and its substituted compound (eg:CH_2=CHX) can be carried out by using any of four mechanisms.

i) Free radical polymerization mechanism.

ii) Cationic mechanism of polymerization.

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iii) Anionic mechanism of polymerization.

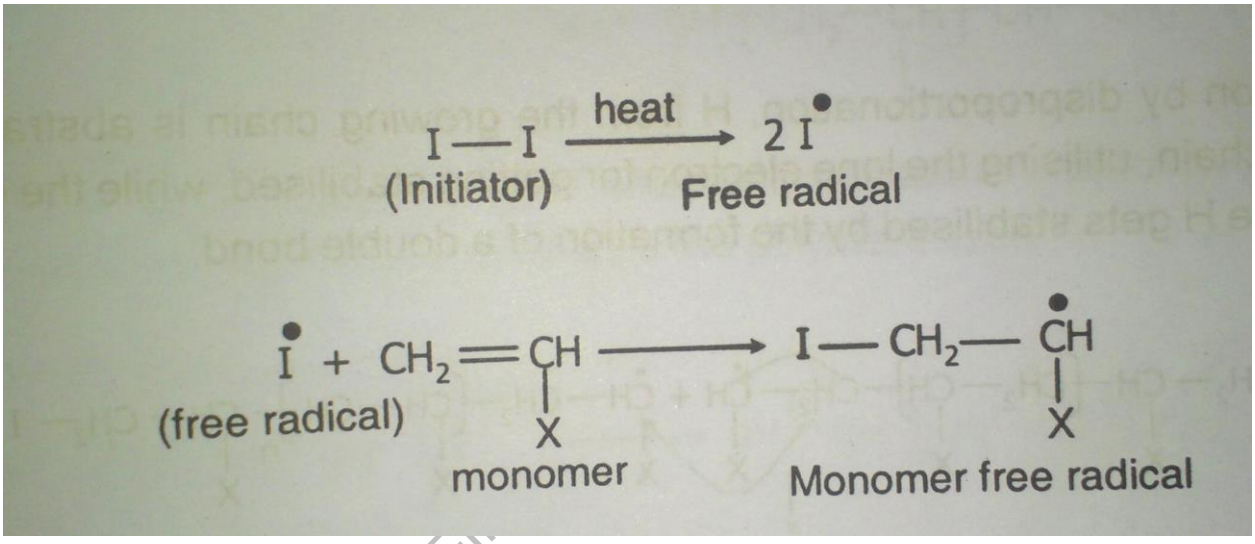
iv)Coordination polymerization or Ziegler-Natta polymerization.

i) FREE RADICALPOLYMERIZATION MECHANISM:

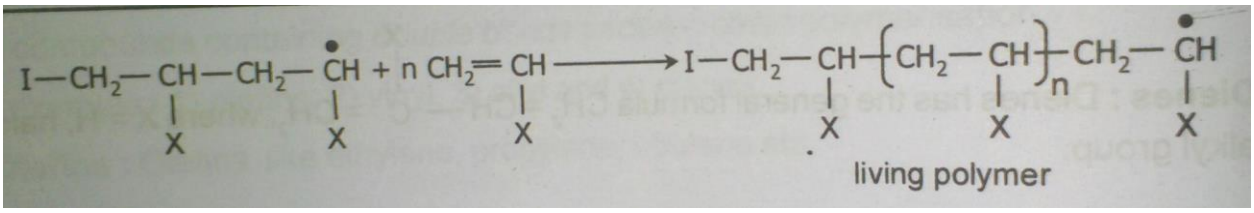
In the frère radical polymerization, monomer is activated by the action of light, heat or by adding chemicals known as initiators.

1) **Initiation step:**
   Initiators are unstable compounds and undergo homolytic fission to produce free radicals which react with π electrons of the monomer to produce monomer free radical.

Benzoyl peroxide, hydrogen peroxide are good initiators for free radical chain polymerization.



2) **progration step:**
   The monomer free radical reacts with a number of monomers rapidly resulting the chain growth with free radical site at the end of the chain producing a living polymer.



By adding fresh monomers to the living polymer with free radical site, again chain growth starts. Hence it is known as living polymer.

3) **Termination step:**Termination (to stop chain growth) of the polymer chain is carried by 'coupling' and 'disproportionation', resulting the dead polymer.

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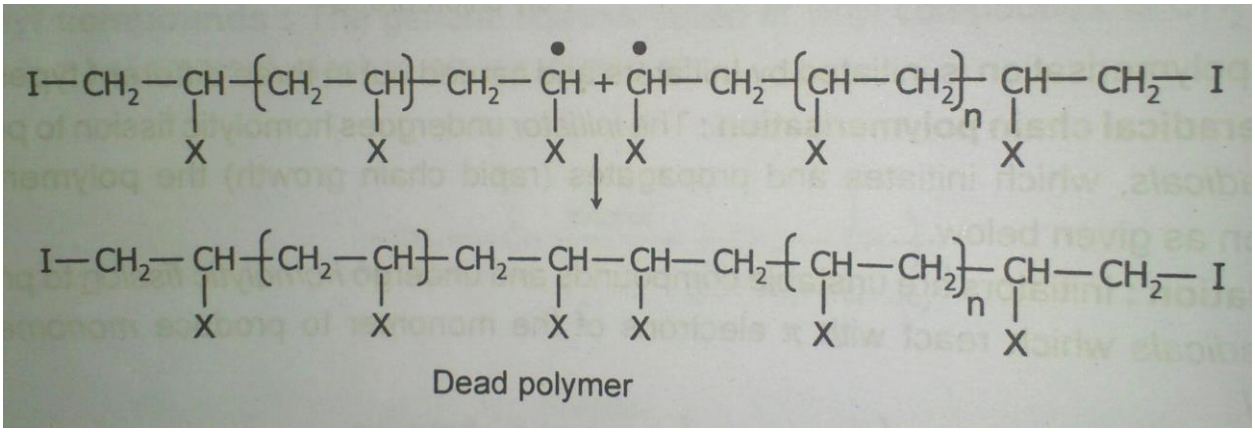
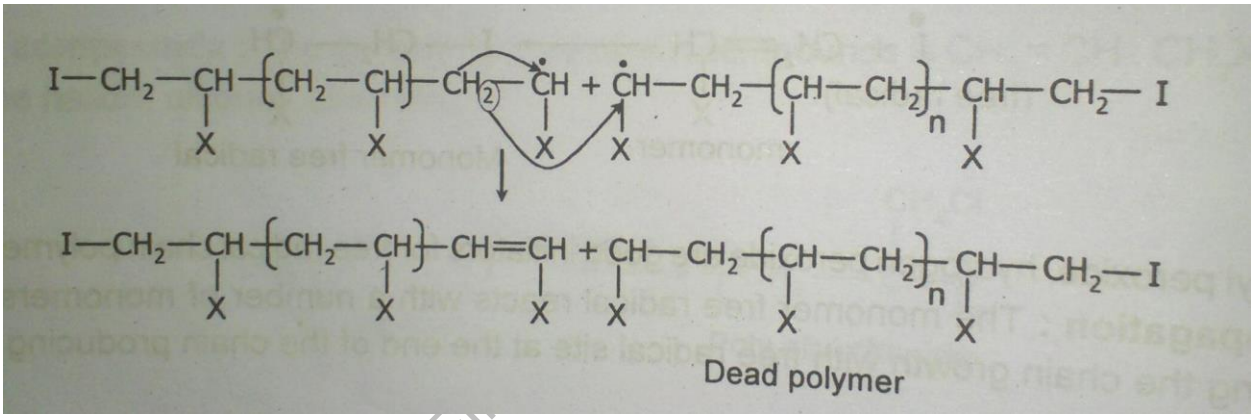
i) **By Coupling Or Combination:** In which , the collision of the two chains at their free radical site producing a dead polymer.



ii) By Disproportionate: In which one hydrogen atom of one radical center is transformed to another radical center .This results in the formation of two polymer molecules, one saturated and one unsaturated. But this step is very rare.



ii) CATIONIC MECHANISM OF POLYMERIZATION:

In cationic polymerization ,the catalysts used are Lewis acids (electron pair acceptors), such as $Sncl_4$, $Ticl_4$,$Alcl_3$,BF_3 and $H2SO_4$.

The polymerization proceeds through the formation of the carbocation and chain growth is accompanied with the transfer of the positive charge along with the polymer chains.

Its mechanism involves the following steps:

1) INITIATION STEP: In cationic chain polymerization the cation produced by the initiator attacks the π electrons of the monomer forming a monomer carbonium ion.

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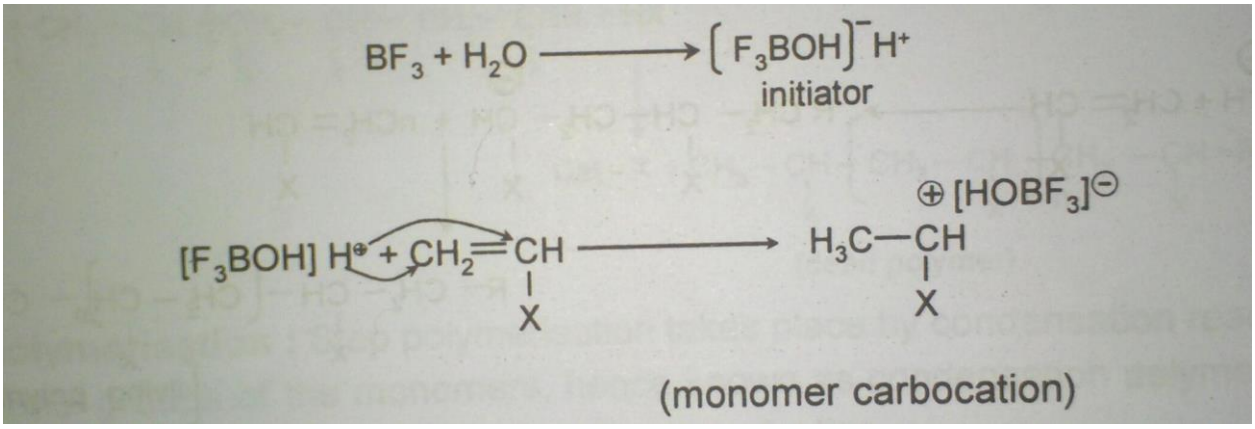
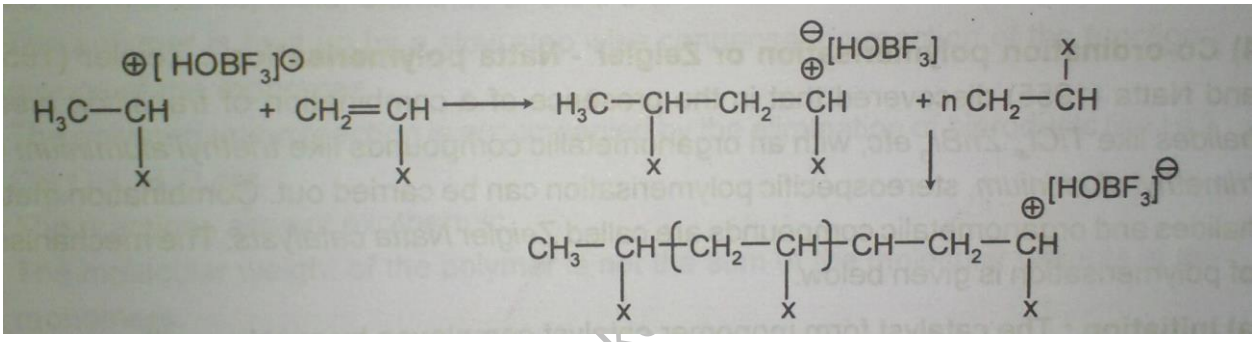
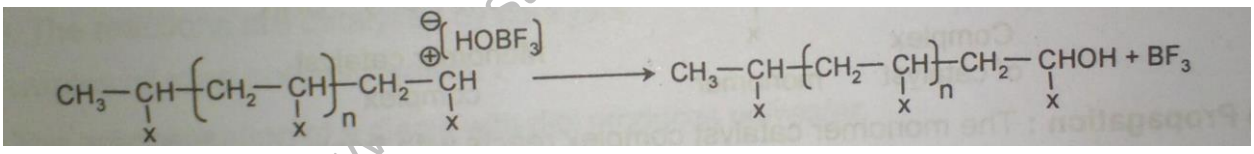


$[HOBF_3]^-$ is called counter ion, because it is always with carbonium ion of the monomer.

2) PROPOGATION STEP: The monomer carbocation attacks the π electrons of the other monomers resulting the chain growth with carbocation at the end of the chain.



3) TERMINATION STEP: Termination of cationic chain polymerization is done by coupling where the OH^- ion the counter ion terminates the polymerization.



iii) ANIONIC MECHANISM OF POLYMERIZATION:

Anionic polymerization involves the formation of carbanion. In these polymerizations, the electron donor catalysts are used.

Eg: alkali metals, amides, Grignard reagents.

Its mechanism involves the following steps:

1) Initialization step: An anion produced by the initiator will react with the monomer to produce monomer carbanion.

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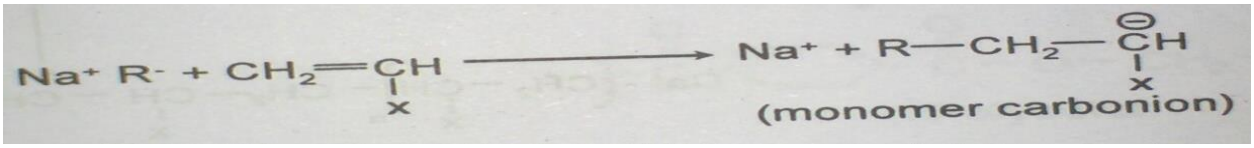
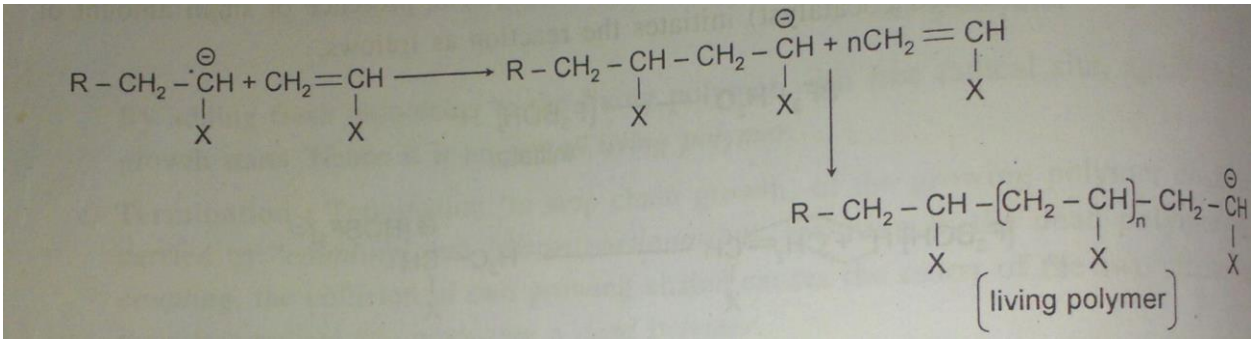
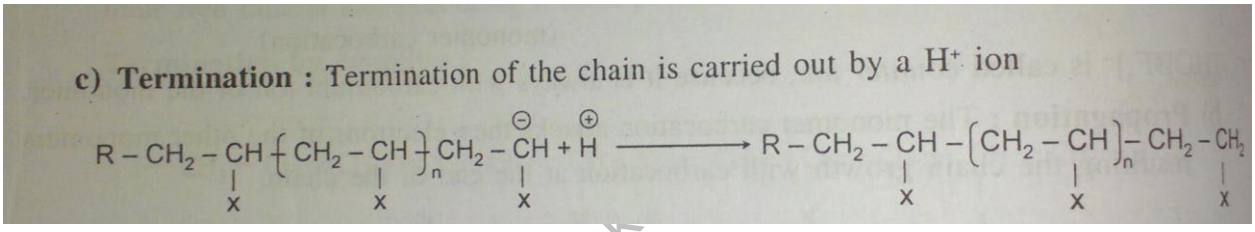


2**) propogation step:** Attack of the monomers by monomer carbanion results in chain growth as shown below.



3) termination step: Termination of the chain is carried out by a H^+ ion.

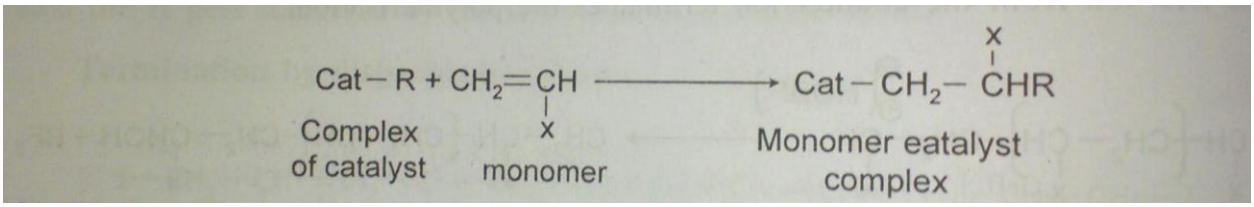


iv) COORDINATION POLYMERISATION:

Ziegler and Natta discovered that in the presence of a combination of a transition metal halide (like $Ticl_4$ or $Ticl_3$, $ZrBr_3$,$Ticl_2$,halides of v , zr ,cr ,mo and w) and an organometallic compound (like triethyl aluminium or trimethyl aluminium), stereospecific polymerization can be carried out.

Its mechanism involves the following steps:

1) **Initialization step:** The catalyst form monomer catalyst complexes by reacting with monomer molecule.



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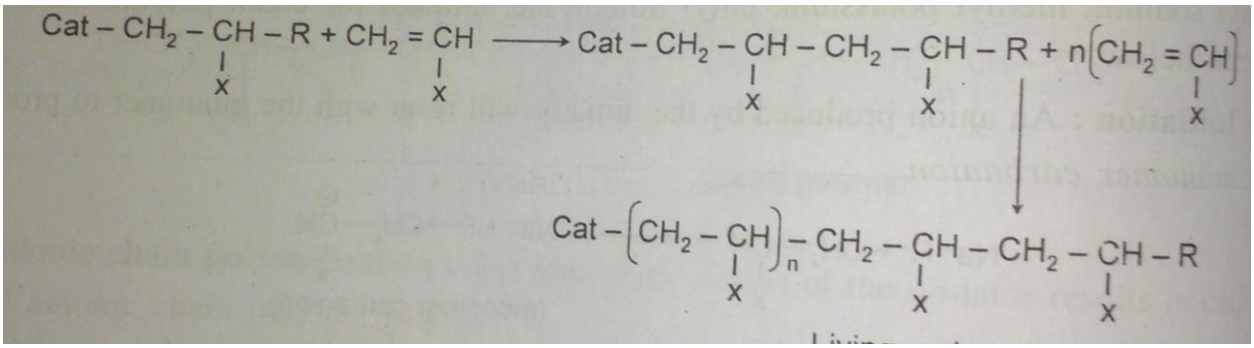
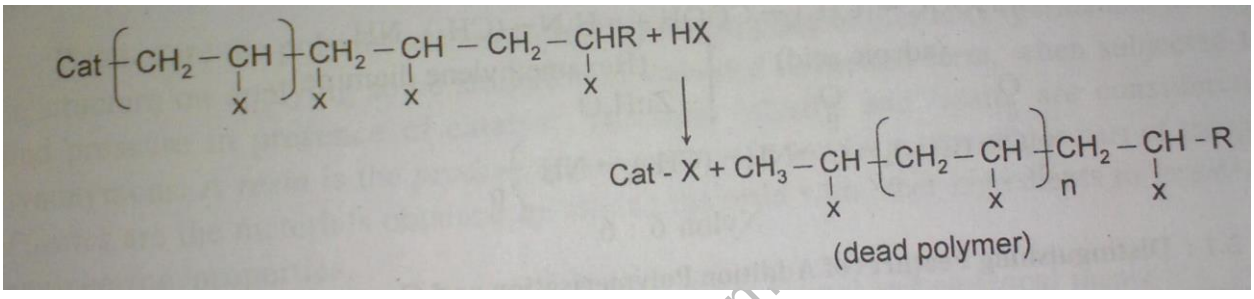
2**) Propagation step:** The monomer catalyst complex reacts with fresh monomers resulting the chain growth as shown below.



3) Termination step: Termination is carried out with an active halogen compound.



Ziegler- natta polymerization is used to prepare polypropylene, polyethylene, polydiene etc,. the importence of this method lies in the fact that stereospecific polymers are obtained.

ii) condensation polymerization:condensation polymerization (or) step growth polymerization or is a reaction occurring between simple polar group contains monomers with the formation of polymer and elimination of small molecules like water, HCL etc.

Example:-

SYNTHESIS OF NYLON -6,6 (Poly hexamethylene adipote,

Its monomers,

(a) adipic acid (HOOC-$(CH_2)_4$-COOH)

(b) Hexamethylene diamine (H_2N-$(CH_2)_6$-NH_2)

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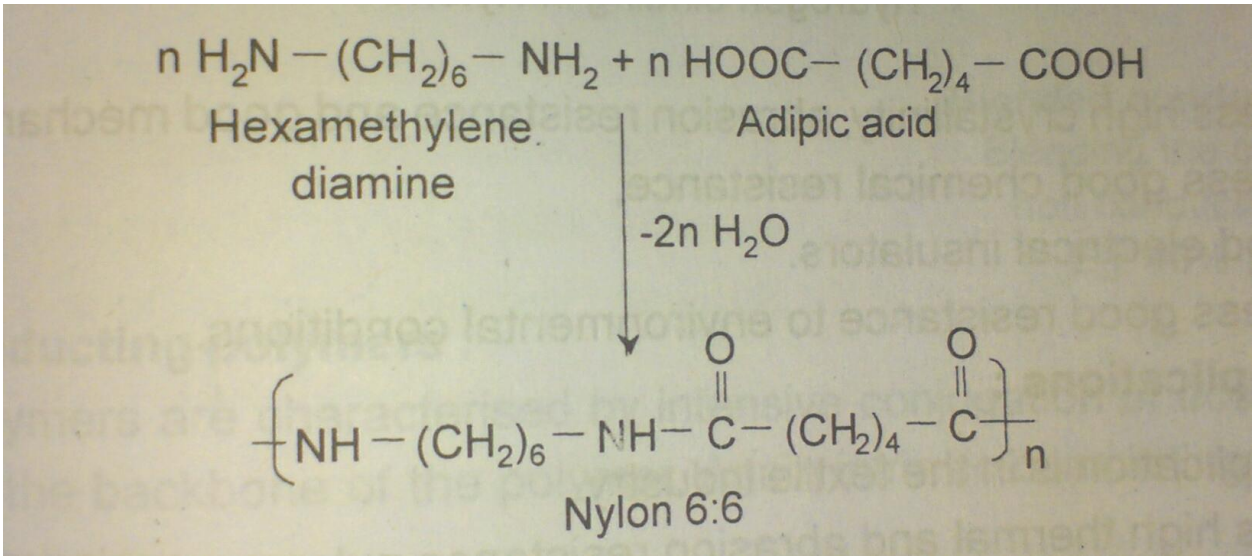

RESIN:- a resin is the product of polymerization. i.e., pure polymerisation product is resin.

PLASTIC:- plastics are the materials obtained by the mixing the resin with other ingredients to impart special engineering properties.

Plastics are the polymers characterized by the property of plasticity, moulded to desired form when subjected to heat and pressure in presence of catalyst

Plastics are characterized by light weight, good thermal and electrical insulation, corrosion resist chemical inertness, adhesiveness, easy workability, low fabrication cost, high abrasion resistance ,dimensional stability,strength,toughness and impermeability to water.

The term plastic and resin are considered to be resins.

*The plastic resins are broadly classified in to two categories, they are:

i) Thermo plastics resins.

ii) Thermoset resins.

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i) Thermo plastics resins:

These resins become soft on heating and rigid on cooling.

ii) Thermoset resins:

During fabrications process these resins are moulded .Once they are solidified, they cannot be softened. Plastics are formed when polymer resins are blended with certain external materials known as compounding or moulding ingredients

These ingredients provide sturdiness and other desired characteristics to polymer resins.

****DIFFERENCE BETWEEN THERMOPLASTIC AND THERMOSET RESINS****

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Thermoplastic Resins :	Thermoset Resins:
*These are prepared by addition or condensation polymerization process . *They have either linear or branched structures. *Adjacent polymer chains are held together by either vandervaal's forces or by dipole-dipole forces or by H-bonds. *They soften on heating and stiffen on cooling. * Low molecular weight thermoplastics are soluble in their suitable solvents. * They can be remoulded ,re-shaped and re-used. * During moulding ,there is no change in their chemical composition. Eg: Polyethylene, PVC	*These are prepared by condensation polymer polymerization process only. * They have three dimensional, cross linked network structure. * Adjacent polymer chains are held together by strong covalent bonds are called cross-link. *They do not soften on heating. *They are not generally soluble in any solvent. *They can't be remoulded and and hence cannot be re-used. *They undergo chemical changes such as further polymerization and cross-linking during moulding. Ex: nylons, Bakelite

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****COMPOUNDING OF PLASTICS****

Compounding or moulding constituents are:

i)resins ii)plasticizers iii) fillers iv)lubricants v)catalysts vi)accelerators vii)coloring matter.

i)RESIN:

a) The product of polymerization is called resin, and this forms the major portion of the body of plastics.

b) this acts as a binder which holds the different constituents together.

Eg: Thermoplastic and thermoset resins.

ii) PLASTISIZERS:

*Plasticizers increase plasticity and flexibility of the polymer.

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*plasticizers neutralize the intermolecular forces of attraction between polymer chains .Plasticizers decrease the strength and chemical resistance.

Eg: vegetables oils, camphor,esters, of steric acid, trycresyl phospate and trivinyl phosphate etc.,

iii) FILLERS:

*Fillers give better hardness , tensile strength, opacity, finish and workability and plastics.

*Fillers reduce the cost of the polymers.

*They reduce the shrinkage of the polymer on setting.

*Fillers reduce the brittleness of polymers.

*Some special types of fillers are added to impart special properties to polymer likebarium salts make polymers impermeable to X-rays and asbestos provides heat and corrosion resistance to polymers.

Eg:

*Wood flour, gypsum, saw dust, marble flour , paper pulp cotton fibres and metallic oxides like ZnO and PbO.

*Reinforced fillers are those which enhance the mechanical strength of the plastics.

iv) LUBRICANTS:

*Lubricants make moulding of plastic easier.

*They impart flawless, glossy, finish to the products.

*Lubricants prevent moulded article from sticking to the fabrication equipment.

Eg: waxes, oils, stearates, oleates, and soaps.

v) CATALYST OR ACCELERATORS:

They accelerate the polymerization of fusible resin during moulding operation in to cross linked infusible form for thermosetting resins.

Eg.Benzoyl peroxide, hydrogen peroxide, acetyl sulphuric acid, metals like silver ,copper & leadand metal oxide like zinc oxide.

vi) STABILIZERS:

*stabilizers improve thermal stability during polymerization.

Eg.White lead, lead chromate, red lead, stearetes, of lead, cadmium and barium.

vii) COLOURING MATERIALS:

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*The coloring agents in the form of organic dyes and opaque inorganic pigments when added to powered plastics, provide pleasing and decorative color.

Name of the pigment used	Imparted colour
Ultramarine	Blue
Carbon black	Black
Calcium carbonate	White
Chromium trioxide	Green
Ferric oxide	Red

FABRICATION OF PLASTICS:-

Depending on the type of resin, whether thermoplastic or thermo set, many methods of fabrication of plastics are used.

Some of them are,

1. Compression moulding
2. Injection moulding.

1. COMPRESSION MOULDING:

This method is applied to both thermo plastic and thermo setting resins. A desired quantity of compounded plastics resin is filled in the cavity present in the bottom mould, the top mould and bottom mould are capable of being moved relative to each other. When heat and pressure are applied according to specifications, the cavities get filled with fluidized plastic. The two moulds are closed tightly and curing is done either by heating in case of thermo set plastic resins or by cooling in case of thermoplastic resins. After curing the moulded article is taken out by opening the mould.

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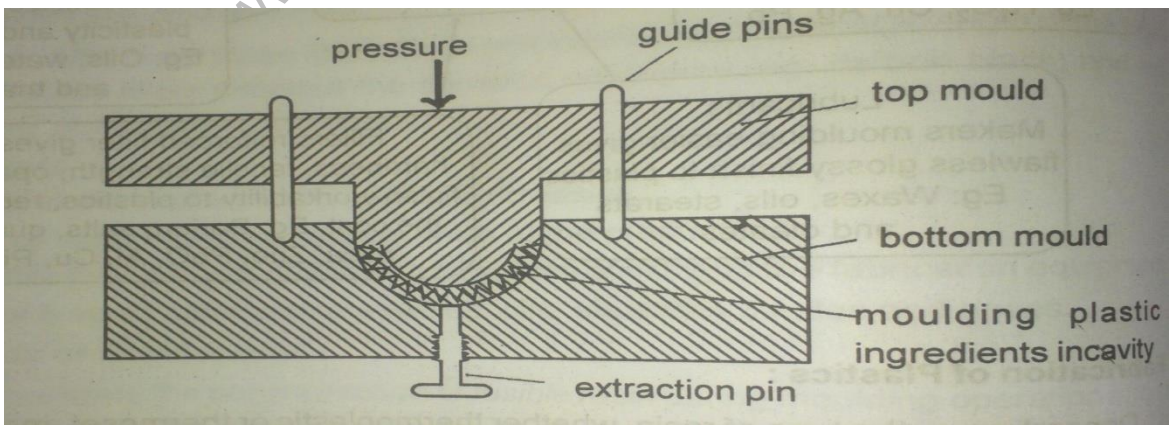

This method is used commonly for manufacture of cylinders, gears handles etc.

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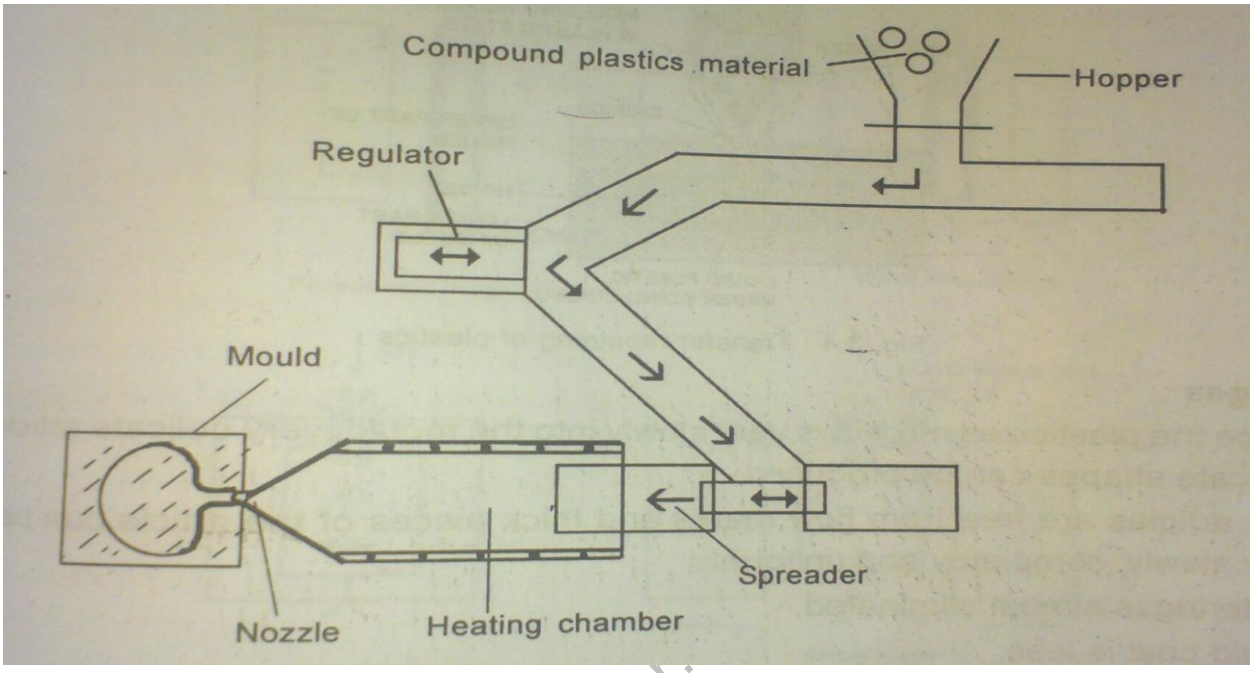
2. INJECTION MOULDING:

Injection moulding is generally carried out for the fabrication of thermoplastic resins. The compounded plastic material is added from a hopper from where they move through a tube having proper dimensions for the accurate quantities to be charged to the lower cylinder as shown in the figure.



The plunger moves to and fro in the cylinder to send the plastics material into the spreader in a heating chamber where the materials are converted to viscous liquid pushed through the nozzle into cold mould maintained at room temperature. The molten thermoplastics material sets in the mould which is sometimes water cooled and proper pressure is maintained. The finished article is taken out by opening the mould.

ADVANTAGES OF INJECTION MOULDING:

1. This method is characterized by high speed production and low mould cost.
2. Loss of materials is less.

PREPARATION, PROPERTIES AND ENGINEERING APPLICATIONS OF PVC, TEFLON AND BAKELITE:

1.POLY VINYL CHLORIDE (PVC):

Poly vinyl chloride is produced by free radical chain polymerization of vinyl chloride in presence of benzoyl peroxide or hydrogen peroxide.

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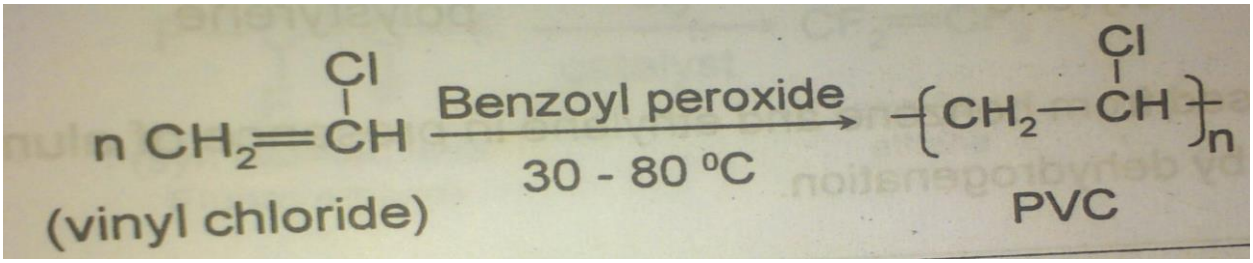


PROPERTIES:

1. PVC is a colourless, non-inflammable and chemically inert powder.
2. It has specific gravity 1.33 and M.P. 148^0C.
3. Resistant to atmospheric conditions.
4. It is strong and brittle.
5. It is resistant to atmospheric conditions like O_2, CO_2 and moisture.
6. PVC is not stable to heat and U.V radiation. It undergoes degradation.

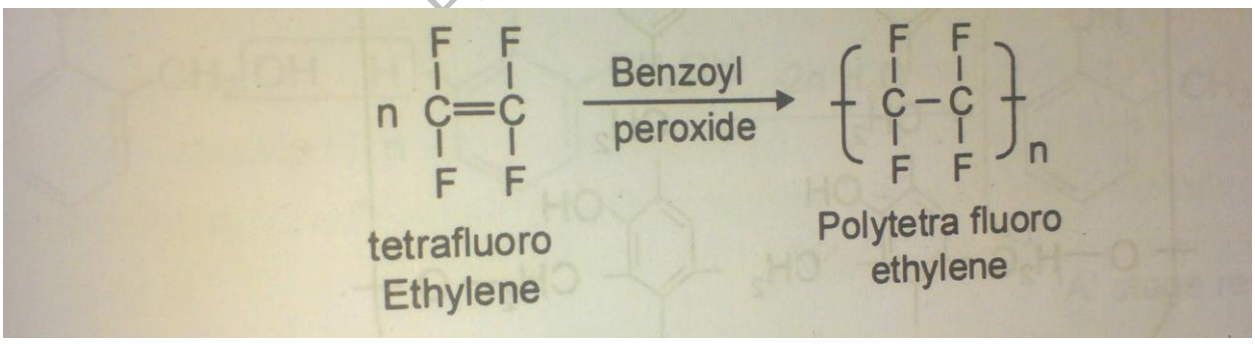
ENGINEERING APPLICATIONS:

PVC treated with plasticizers is called plasticized PVC is used for electrical insulations, injection moulding articles like tool handles, radio and telephone components, chemical containers, and foams used in buildings, cameras and air crafts.

Unplasticized PVC is rigid, highly resistant to chemicals and brittle. It is used for making safety helmets, refrigerator components, tyres, cycle and motor cycle mudguards.

2.TEFLON:

Teflon is obtained by the chain polymerization of tetrafluoroethylene in the presence of benzoyl peroxide as an initiator.



PROPERTIES:

Due to the presence of highly electronegative fluorine atoms, TEFLON has got

1. High M.P. (>350^0C)
2. Exceptionally high chemical resistance (except hot alkali metals and fluorine).
3. High density 2.1 to 2.3 gm/cc.

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4. It is very strong, hard polymer that can be machined to drilling, punching etc.
5. It is a very good electrical insulator.
6. It possess very good abrasion resistance.

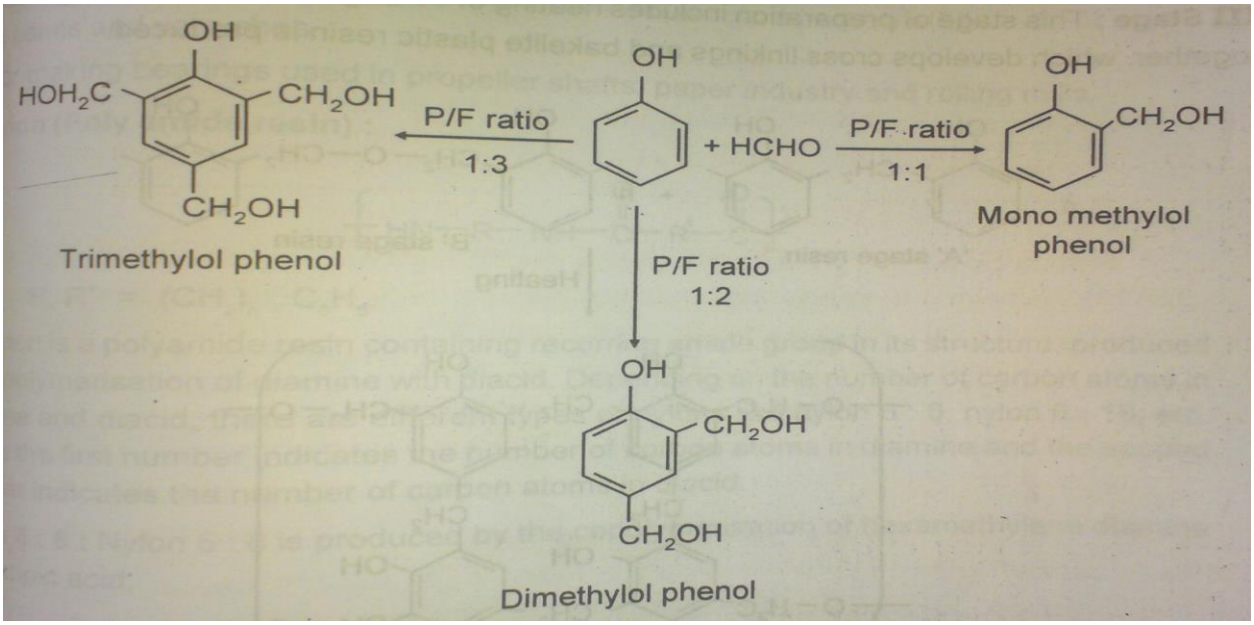
ENGINEERING APPLICATIONS:

1. It is a very good insulating material for motors, transformers, cables, wires etc.
2. It is used for making gaskets, pump parts, tank linings, tubing etc.
3. Due to its extreme chemical resistance, it is used for making chemical carry pipes.
4. Non-lubricating bearings and non-stick stop cock for burettes are made from TEFLON.

3.BAKELITE (OR) PHENOL – FORMALDEHYDE RESIN:

It is an important thermoset resin prepared by the step polymerization of phenol with formaldehyde in presence of an acid or alkali as a catalyst. This polymerization reaction takes place in 3 stages.

Stage 1: phenol is made to react with formaldehyde in the presence of acid / alkali to produce non-polymeric mono, di and tri methylol phenols depending on phenol – formaldehyde ratio (P/F ratio).



Stage 2: The mono, di and tri methylol phenols are heated to produce two types of straght chain resins by condensation of the methylol group with hydrogen atom of benzene ring or another methylol group.

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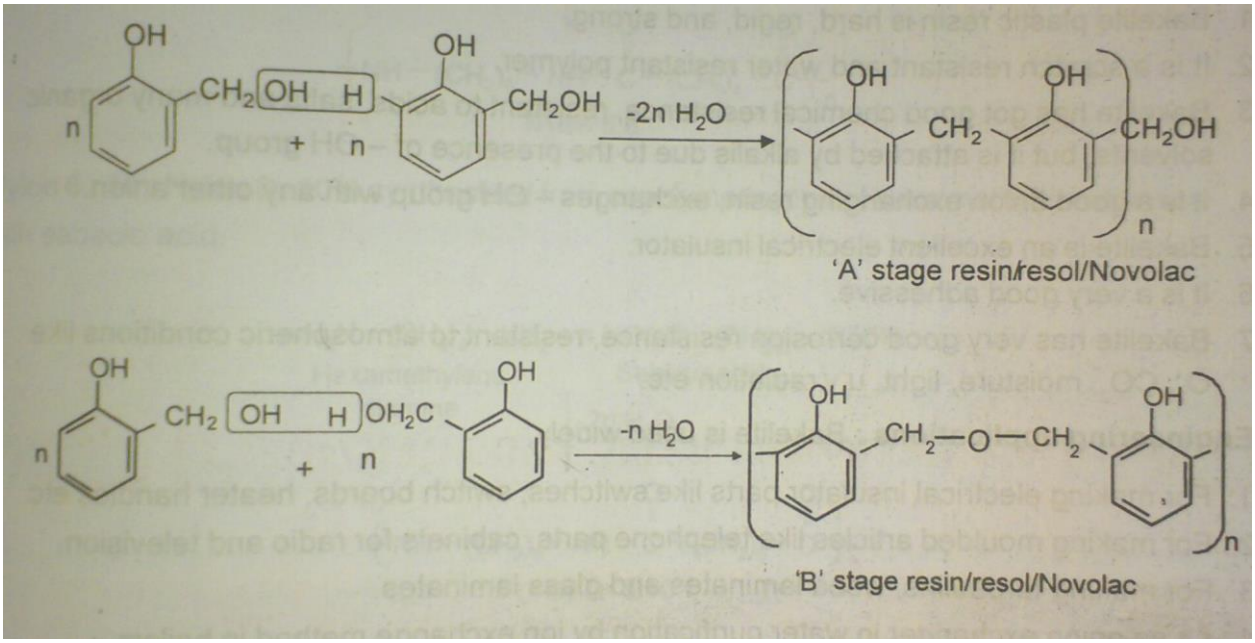
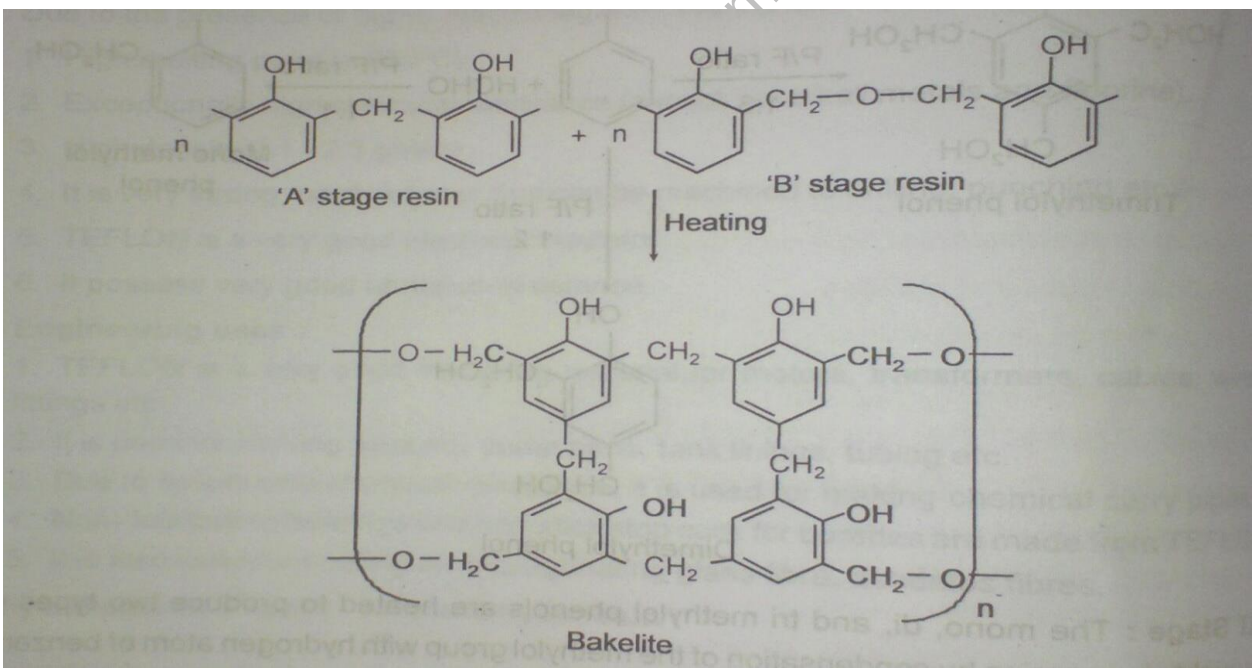


Stage 3: This stage of preparation includes heating of A stage resin and B stage resin together, which develops cross linkings and Bakelite plastic resin is produced.



PROPERTIES:

1. It is hard, rigid and strong.
2. It is a scratch resistant and water resistant polymer.
3. It has got good chemical resistance, resistant to acids, salts and many organic solvents, but it is attacked by alkalies due to the presence of - OH group.

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4. It is a good anion exchange resin.
5. It is an excellent electrical insulator.
6. It is a very good adhesive.

ENGINEERING APPLICATIONS:

Bakelite is used widely,

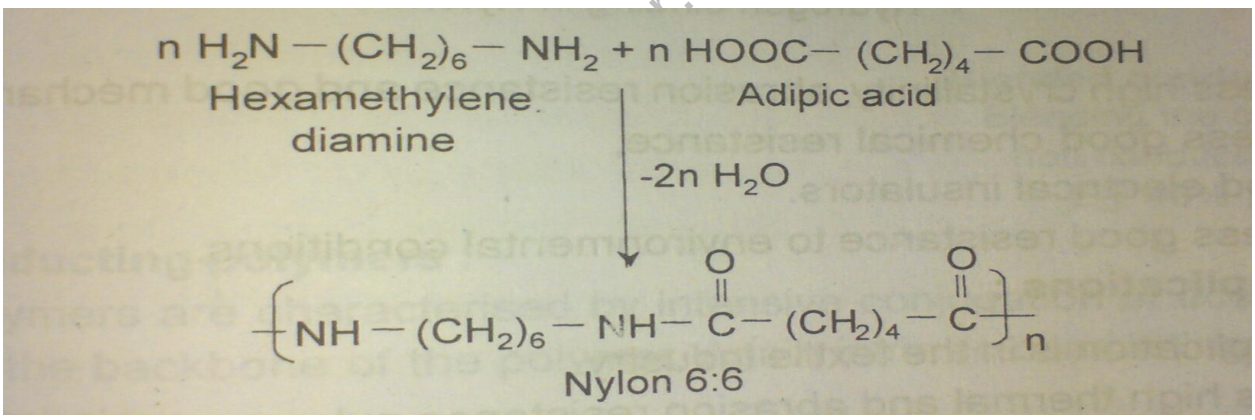
1. For making electrical insulator parts like switches, swtch boards, heater handles etc.
2. For making moulded articles like telephone parts, cabinets for radio and television.
3. For making tarpaulins, wood laminates and glass laminates.
4. As an anion exchanger in water purification by ion exchange method in boilers.
5. As an adhesive (binder) for grinding wheels etc.
6. In paints and varnishes.

FIBERS:

Those polymers which can be drawn in the form of filaments with high tensile strength, rigidity or stiffness and irreversible deformation are called fibers. These fibers possess high crystallisability and high melting points.

1.NYLON -6,6:

It is produced by the copolymerization of hexamethylene diamine with adipic acid.



PROPERTIES:

1. Nylons possess high strength, hardness and high melting point. The high melting point of the nylons is due to the hydrogen bonding between the hydrogen atom of the amide group (-NH) and oxygen of the C=O group.
2. They possess high crystallinity, abrasion resistance and good mechanical properties.
3. They possess good chemical resistance.
4. They are good electrical insulators.
5. They possess good resistance to environmental conditions.

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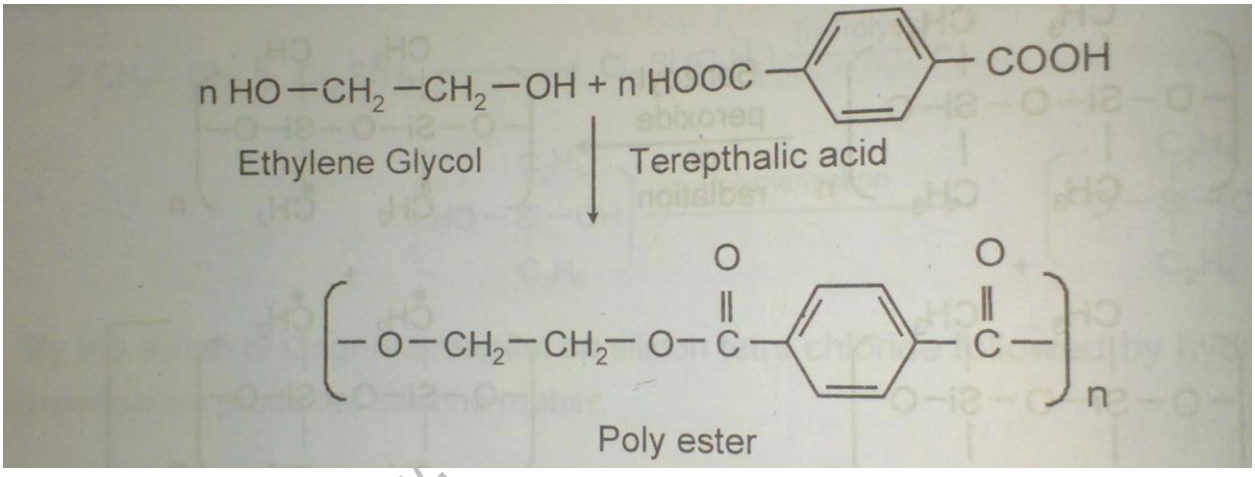
ENGINEERING APPLICATIONS:

1. The major application is in the textile industry.
2. Because of its high thermal and abrasion resistance nylons are used in mechanical engineering applications like gears, bearings, machine parts where greater friction is there.
3. Flexible tubings for convaying petrol etc are made from nylons.
4. Nylons are used as electrical insulators.
5. Nylons are used in auto mobile industry and telecommunication industry for making radiator parts and coil formers respectively.

2.DACRON:

Dacron is a saturated polyester otherwise known as terene or terylene.

The step polymerization of a diacid and dialcohol produces Dacron. The saturated polyeter is formed by the condensation polymerization of ethylene glycol with terepthalic acid.



PROPERTIES:

1. The fibers have high strtch resistance, high crease and wrinkle resistance.
2. Highly resistant to mineral acid.
3. It does not hold water.
4. It is very easy to dye.
5. It can be blended with wool, silk etc.
6. These are strong with good abrasion resistance.

APPLICATIONS:

1. It is used both as domestic fiber and industrial fiber.
2. Industrial application is to make nylon tyres.
3. It is used in the textile industry for making synthetic fibers.
4. It is blended with wool and cotton to provide better finish, wrinkle resistance enhanced life and resistance to acids and bases.

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FIBER REINFORCED PLASTICS (FRP):

Fiber reinforced plastics are produced by reinforcing a plastic matrix with a high strength fiber materials such as glass, graphite, alumina, carbon, boron, berylium and aromatic polyamide.

Natural fibers such as sisal, asbestos are also used for reinforcement.

Glass fiber is the most extensively used reinforced fiber because of durability, acid proof, water proof and fire proof nature of glass.

APPLICATIONS OF FRP:

Fibre reinforced plastics find extensive use in space crafts, aeroplance, boat hulls, acid storage tanks, motor cars, and building materials. Malamine FRP is used for insulation and making baskets.

Advantages of FRP : The fibre reinforced plastics have the following advantages.

1. Low efficient of thermal expansion.
2. High demensional stability.
3. Low cost of production.
4. Good tensile strength.
5. Low dielectric constant.
6. Non inflammaaility and corrosion and chemical resistance.

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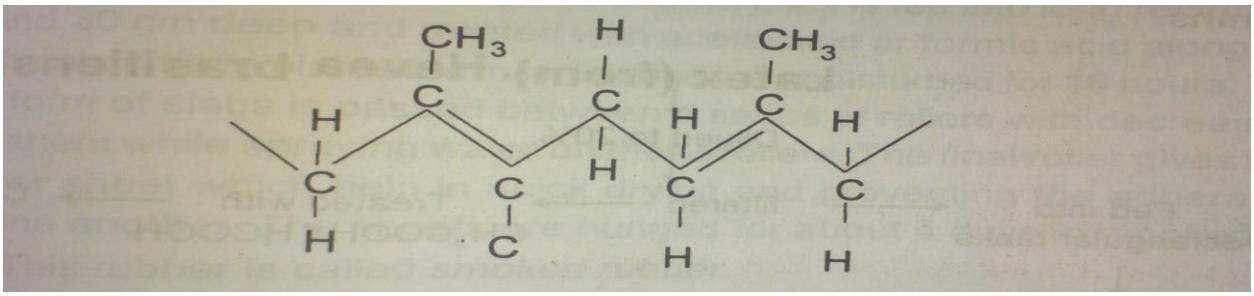
RUBBER- NATURAL RUBBER & ITS VULCANIZATION:

Those polymers which possess the property of elasticity is called rubber.

Natural rubber is processed from the cell sap (latex) of trees/ plants. The main composition of natural rubber is poly isoprene, which is in the form of long coiled chains, responsible for the elasticity of natural rubber.



VULCANIZATION OF RUBBER:

The natural rubber extracted from the trees or plants has got some disadvantages as listed below.

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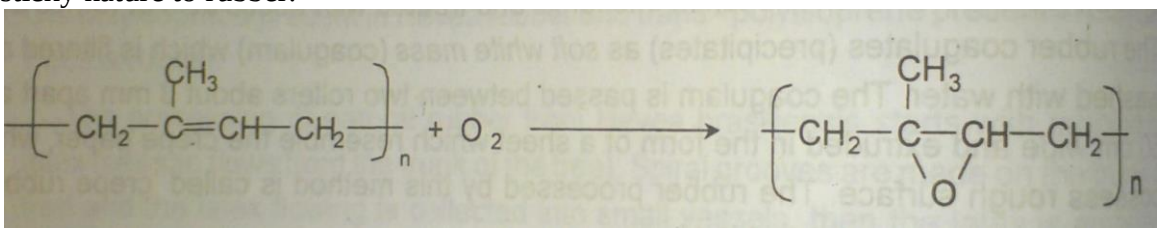
1. It is soft & plastic in nature.
2. It swells in water and easily attacked by organic solvents, acids, bases and non polar solvents like mineral oils, benzene and gasoline.
3. It posseses poor tensile strength.
4. Atmospheric oxygen attacks the rubber and produces epoxides which gives bad smell, sticky nature to rubber.



5. The rubber possess tackiness i.e., when two fresh raw rubber sheets were pressed together, they coalese to form a single sheet.
6. When stretched to a great extent, it suffers permanent deformation due to sliding or slippage of some molecular chains over each other.
7. It is attacked by atmospheric oxygen, CO_2, moisture, light, U.V radiation etc. and gets less durability.

To improve the properties of rubber, Charles Good in 1839 compounded the raw rubber with some chemicals and heated to 100^0C to 140^0C. Finally the compounded and vulcanized rubber is drawn in the form of sheet by calendering process.

Compounding & vulcanization:

The following are the materials adde to natural rubber.

1.vulcanizers:

Some chemicals like elemental sulphur, H_2S, SCl_2, benzoyl chloride and ZnO are added to both natural & synthetic rubbers.the most important vulcanizer is sulphur which combines chemically at the double bonds of the different chains producing sulphur cross linkings.

The percentage of sulphur added is in the range of 0.5 to 35%. For example the rubber used for making tyres contains 3-5% of sulphur and for making battery case the rubber contains 30% of sulphur. If the percentage of sulphur is more than 32, that rubber is called ebonite or vulcanite or hard rubber for some special purposes.

2.Plasticizers:

Plasticizers are also called as softners, which impart greater plasticity and adhesion to the rubber. The most commonly used plasticizers are vegetable oils, waxes, rosin etc.

3.Accelerators:

They catalyse the vulcanization process by reducing the time required for vulcanization. Most commonly used accelerators are litharge, magnesia and white lead. Generally 0.5 to 1% of acceleratirs are added. ZnO is also added which acts as an activator to accelerators.

4.Anti oxides:

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They retard the deterioration of rubber by light and air. Complex organic amines like phenylnaphthylamine, phenolic substances and phosphites are added as antioxides.

5.Reinforcing agents:

They give strength, rigidity, and toughness to the rubber and may form as much as 35% of rubber compound. Commonly used reinforcing agents are ZnO, $MgCO_3$, $BaSO_4$ and $CaCO_3$.

6.Colouring agents:

They impart desired color to the rubber as follows.

Lithophane, TiO_2 - white,

Lead chromate – yellow,

Carbon black – black,

Ferric oxide – red,

Chromium trioxide – green.

ADVANTAGES OF VULCANIZATION:

1. Vulcanised rubber has good tensile strength and load bearing capacity.
2. It has good elasticity depending on the extent of vulcanization.
3. It possesses low water absorption tendency.
4. Vulcanized rubber has higher resistance to oxidation and atmospheric gases like O_2, CO_2, moisture, light and UV radiation.
5. Vulcanized rubber is a good electrical insulator and ebonite is a best electrical insulator.
6. The abrasion resistance of natural rubber increases tremendously.
7. The resistance towards organic solvents and chemicals increased.
8. Vulcanized rubber possesses good impact resistance.
9. Vulcanized rubber possesses very good resilience i.e., the article made from it returns to original shape, when the deforming load is removed.

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APPLICATIONS OF NATURAL RUBBER:

1. The major application of natural rubber is in the manufacturing of tires.
2. It is used for preparing belts for power transmission and several types of materials like non-slipping, clean and shock absorbing.
3. The tank linings in chemical plants where corrosive chemicals are stored are prepared from rubber.
4. To reduce machine vibrations, rubber is used for sandwiching between two metal surfaces.
5. Foamed rubber is used for making cushions, mattresses etc.
6. Toys and sports items are manufactured from natural rubber.

ELASTOMERS:

1.BUNA-S:

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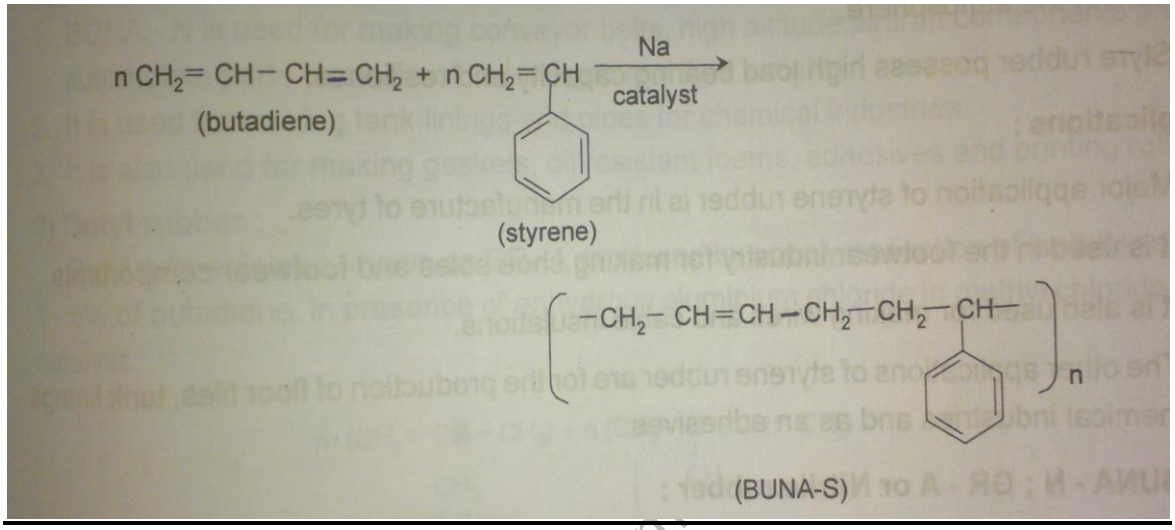
BUNA-S is otherwise called *styrene rubber* or *GRS* (Government Rubber Styrene) or *Ameripol*. BUNA-S stands for the composion of the monomers and catalyst.

BU stands for Butadiene – monomer
NA stands for Sodium – catalyst
S stands for styrene – monomer

BUNA-S is produced by the copolymerisation of butadience with styrene using sodium as a catalyst.



PROPERTIES:

1. *Styrene rubber* is a strong and tough polymer.
2. it is vulcanised by sulphur monochloride ($S_2 CI_2$) or sulphur.
3. It resembles natural rubber in processing characteristics and quality of finished products.
4. BUNA – S possess excellent abrasion resistance.
5. It is resistant to chemicalls but swell in oils and attacked by even traces of ozone, present in the atmosphere.

APPLICATIONS:

1. Major application of styrene rubber is in the manufacture of tyres.
2. It is used in the footwear industry for making shoe soles and footwear componets.
3. It is also used for making wires and cable insulations.
4. The other applications of styrene rubber are for the production of floor files, tank lininings in chemical industries and as an adhesives.

2. BUTYL RUBBER:

Butyl rubber is also known as GR-I, produced by copolymerization of iso butene with isoprene in presence of anhydrous aluminium chloride in methyl chloride as a catalyst.

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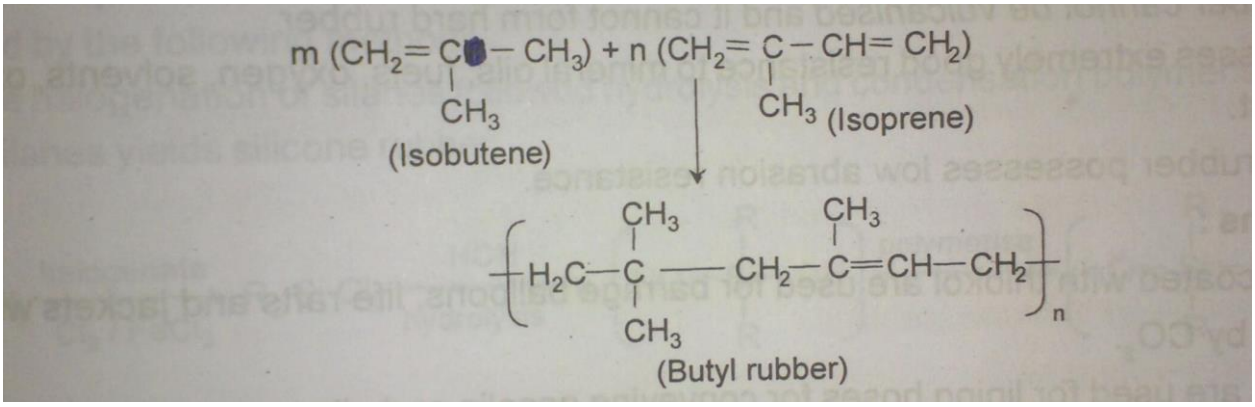

PROPERTIES:

1. It is a strong and tough synthetic rubber with low permeability to air and other gases.
2. It has excellent resistance to heat, abrasion, ageing and chemicals such as inorganic acids, polar solvents, but soluble in hydrocarbon solvents like benzene.
3. It possesses high abrasion resistance.
4. High resistance is to atmospheric gases and especially to ozone is possessed by butyl rubber.
5. It is a good electrical insulator.
6. It can be vulcanized with sulphur, but it possesses low hardness due to less number of double bonds.

APPLICATIONS:

1. It is used for making cycle tyres and auto mobile tubes.
2. It is used for making automobile parts, and conveyer belts in food processing industry.
3. It is used as an insulator for high voltage wires and cables.
4. In chemical industries butyl rubber is used for making the linings of the tanks where chemicals are stored.

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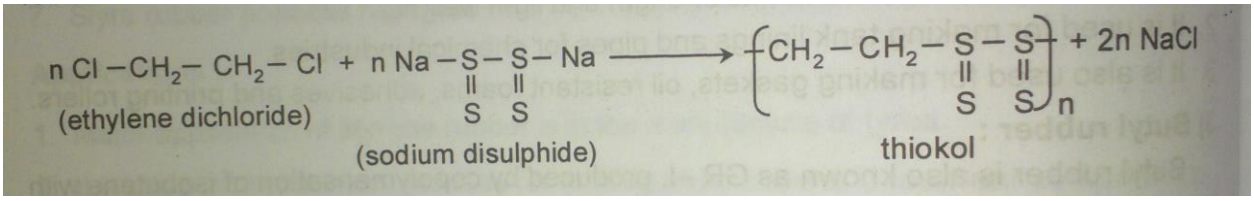
3. THIOKOL RUBBER (OR) POLYSULPHIDE RUBBER (OR) GRP:

Thiokol rubber can be prepared by the copolymerization of sodium poly sulphide and ethylene dichloride.



PROPERTIES:

1. It possess strength and impermeability to gases.
2. It cannot be vulcanized and it cannot form hard rubber.
3. It possesses extremely good resistance to mineral oils, fuels, oxygen, solvents, ozone and sun light.

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4. Thiokol rubber possesses low abrasion resistance.

APPLICATIONS:

1. Fabrics coated with Thiokol are used for barrage balloons and jackets which are inflated by CO_2.
2. Thiokols are used for lining hoses for conveying gasoline and oil.
3. It is used for making gaskets and seals for printing rolls.

CONDUCTING POLYMERS:

Those polymers which conduct electricity are called conducting polymers.

The conduction of polymer may be due to unsaturation or due to the presence of externally added ingrediants in them.

CLASSIFICATION OF CONDUCTING POLYMERS:

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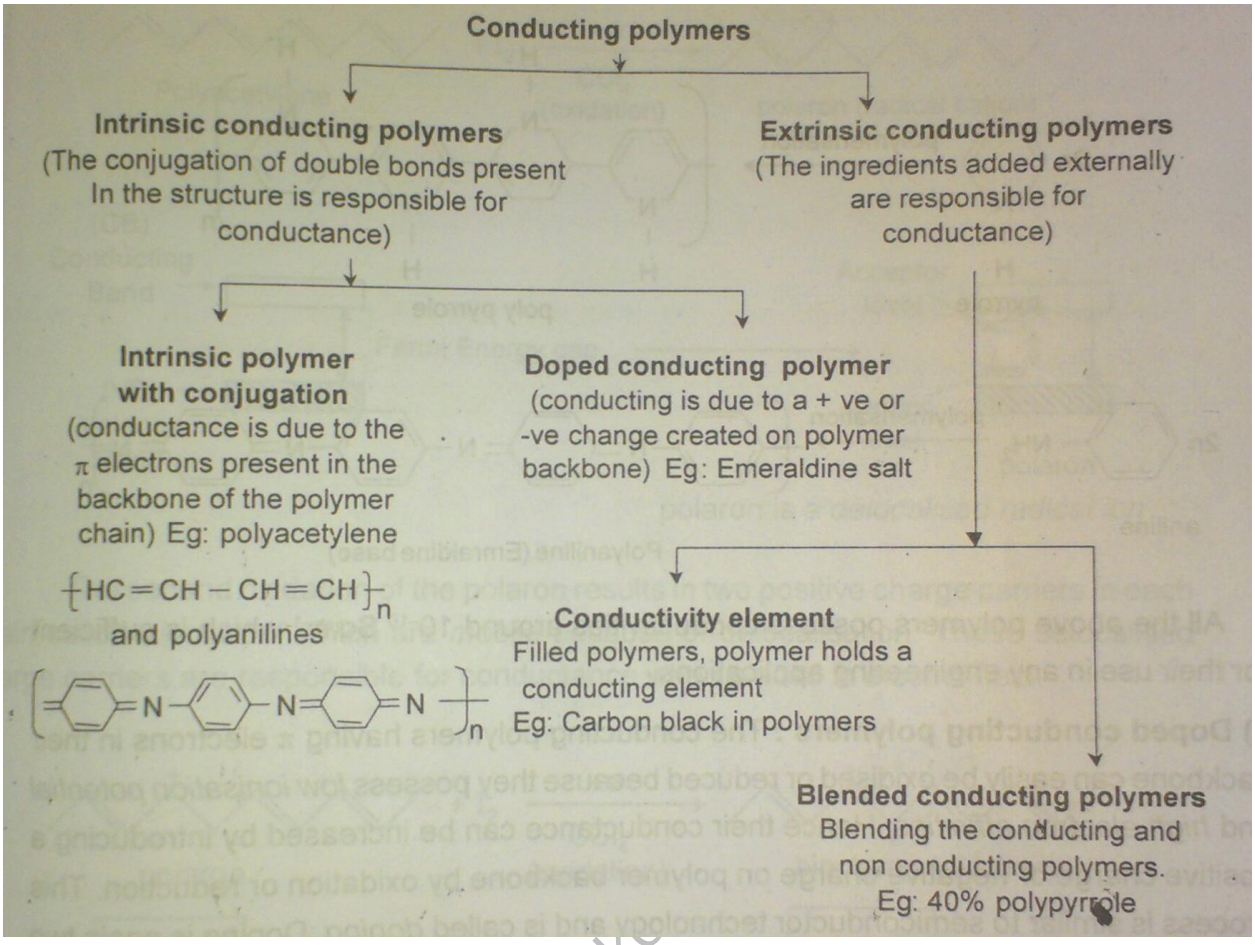

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Intrinsic conducting polymers:-

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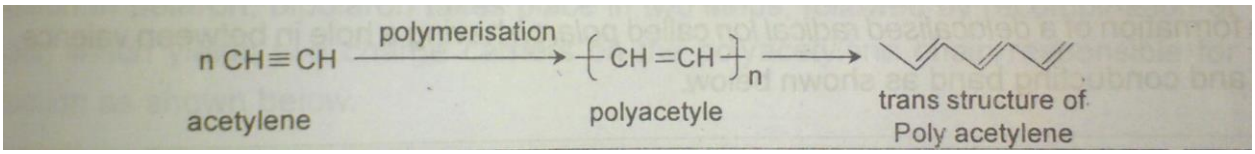
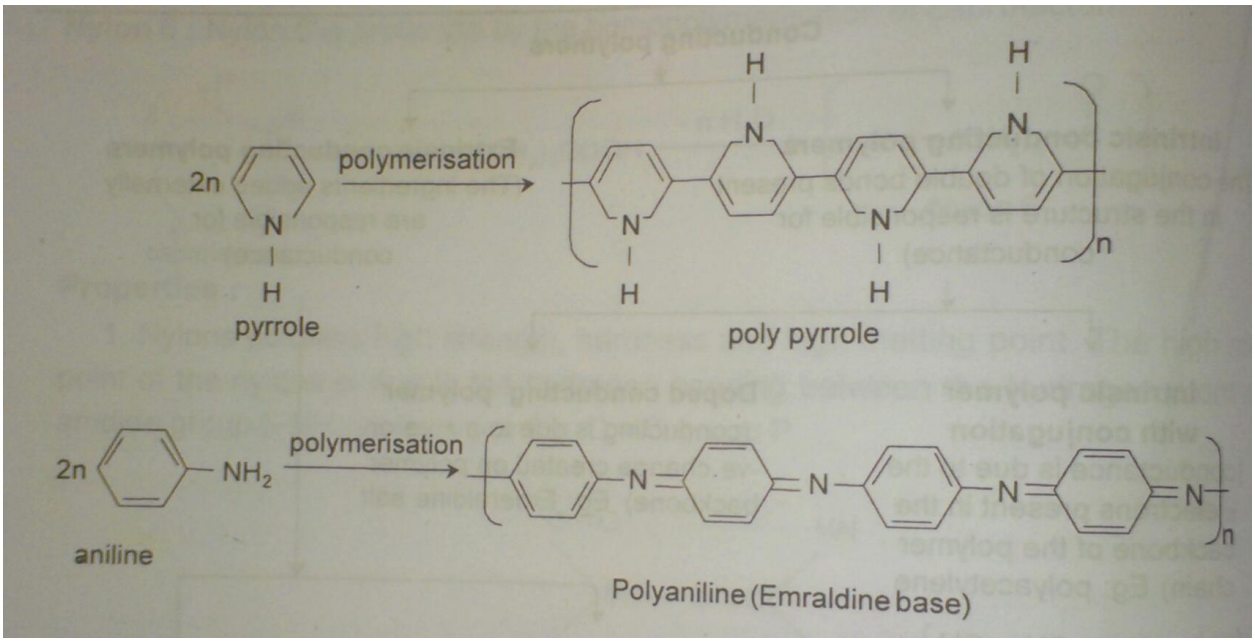
Polymers are characterized by intensive conjugation of double bonds in their structure. Its are 2 types.

1)Conducting polymers having conjugation: Such polymers having conjugation double bonds in the backbone possess their conductivity due to π electrons. In the formation of valence bands and conducting bands which were separated by significant Fermi energy gap. The electrical conductivity takes place only after thermal or photolytic activation of the electrons, which give them sufficient energy to jump the gap and into conduction band.





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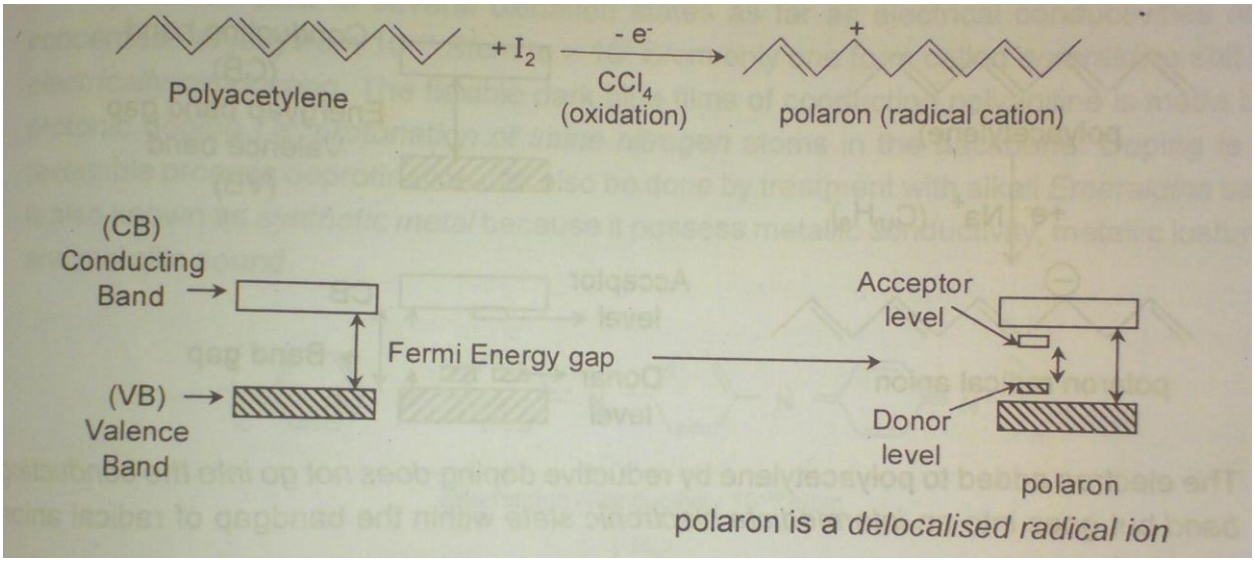
2)Doped conducting polymers : The conducting polymers having π electrons oxidized or reduced because they possess low ionization potential and high electron affinities and introducing + ve charge or –ve charge on polymer by oxidation or reduction.This processis similar to semiconductor technology and is called ***doping*** and 2 types

1. Creating a positive site on polymer backbone called p-doping .

2. Creating a negative site on polymer backbone called n-doping .

p-doping: p-doping is done by oxidation og a conducing polymer like polyacetylene with a Lewice acid or iodine vapour . This is also called oxidation doping.

During oxidation process the removal of π electron from polymer back bone lead to the formation a delocalised radical ion called polaron having a hole in between valence band and conducting band as shown below.



The second oxidation of the polaron results in two positive charge carriers in each chain called bipolaron, which are mobile because of delocalisation.

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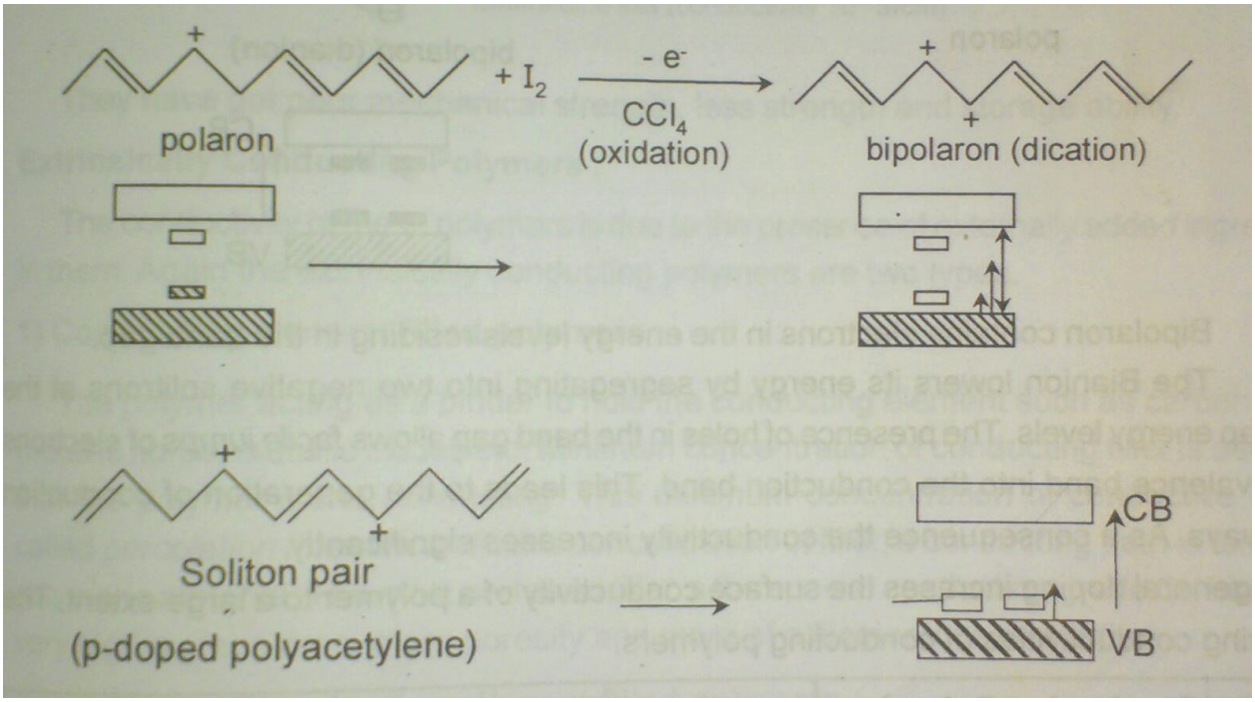
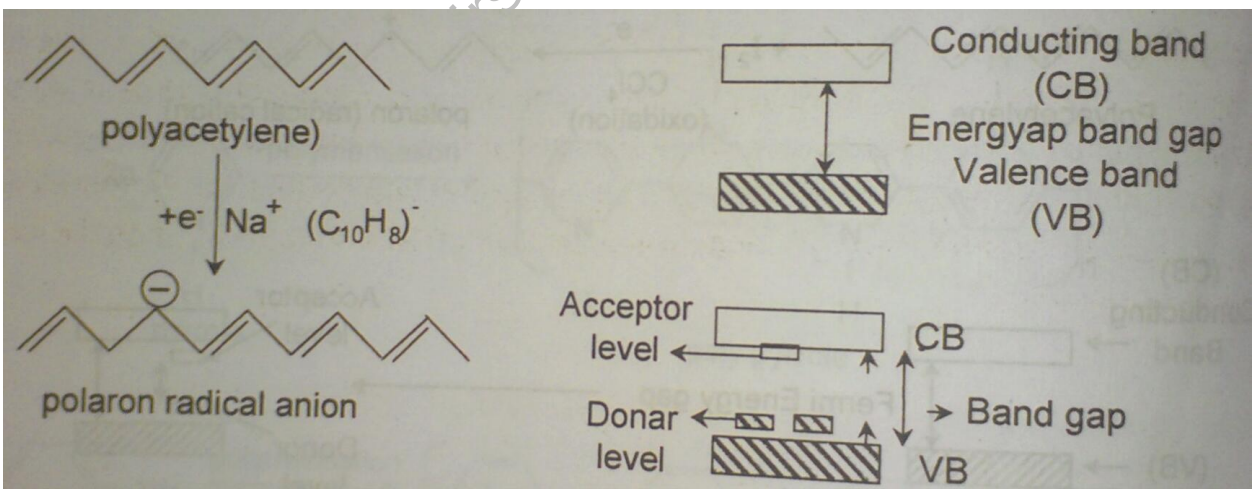


n-Doping: n-Doping is carried out by reduction process by addition of an electron to polymerbackbone by using reducing agents agents like sodium naphthalide. Formation of polaron, bipolaron takes place in two steps, followed by recombination of radicals, which yields 2 charge carriers on the polyacetylene chain responsible for conduction as shown.



The electron added to poluacetylene by reductive doping does not go into the conducting band but goes into an intermediate electronic state within the band gap of radical anion (polaron).

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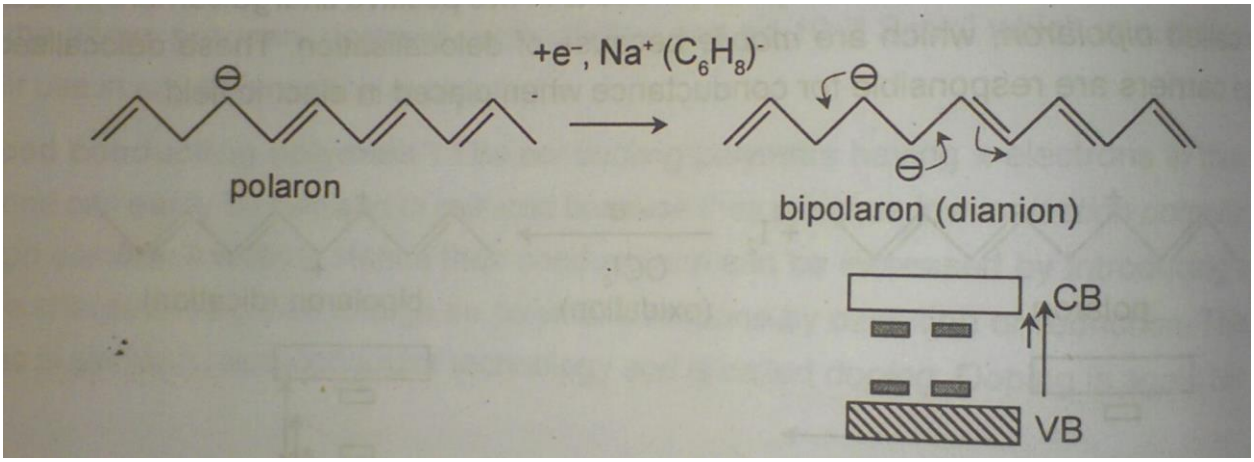

The presence of holes in gap allows facile jumps of elections from valence band into conduction band . consequence the conductivity increases significantly.

In general doping increases the surface conductivity of a polymer to a large extent. The following are the conductivities of conducting polymers.

s.No	Conducting polymer	Dopants	Conductance(Scm^{-1})
1.	Trans polyacetylene	I_2, Na ,Br_2 ,Li, ASF_5	10,000
2.	Polyaniline	HCL	1000
3.	Poly pyrrole	BF_4^+ ClO_4^+	500-7500

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Polyanilines exist in several oxidation states as far as electrical conductivities are concerned varying from 10^{-11} S cm^{-1} to . 10^5 S cm^{-1} only one form called emeraldine salt is electically conducting.

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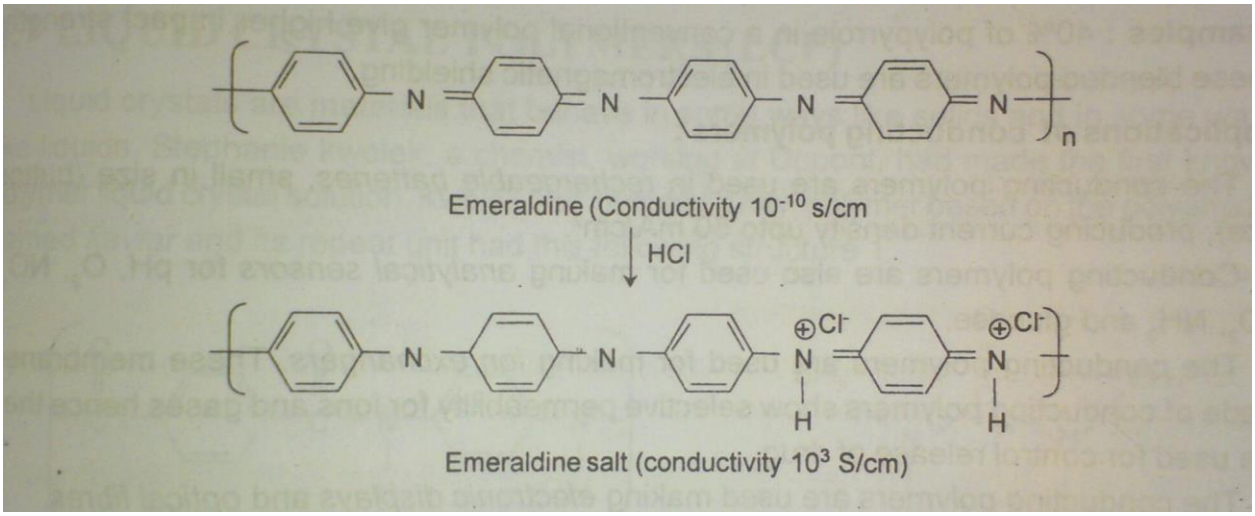

Extrinsically Conducting polymers:

The conductivity polymers presence of externally added ingredients. It is 2 types

1)Conducting element filled polymers:

The polymer acting as a binder to hold conducting element such as carbon black,metallic fibres, metallic oxidesetc .Minimum concertration of conducting filler is added Preferred filler is the special conducting grade C-black has very hidh surface area,more porosity and more of a filamentous properties

Advantages of conducting element filled polymers:

1)These polymers are low cost polymers

2)They are lidth in weight and mechanically durable.

3)These polymers are strong with good bulk conductivity .

4)They are fabricated very easily to any design.

Application of conducting elements filled polymers are used in hospitals and operation theatres.

Disavantage of conducting elements filled polymer addition 10% carbon black will drastically decrease the tensile strength, elongation strength and impact strength of polymer.

2)Blendded conducting polymers:

The conventional poluymer is blended with conducting polymer to improve physical, chemical,electrical mechanical properties along wih the processing properties.

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Application of conducting polymers:

1) conducting polymers are used in rechargeable batteries small in size producing current density upto 50 mA/cm^2

2)Conducting polymer are also used for making analytical sensors for pH, O^2, NO_x So_2 NH_3 and glucose.

3)The conducting polymer are used for making ion exchangers. These membrance made of conducting polymers show selective permeability for ions and gases hence they are for control release of drug.

4) The conducting polymer are used making electronic displays and optical fibres.

5)They are used for electron beam lithography.

6)The conducting polymers are application in photovoltaic devices.

Factors influencing the conductivity of organic polymers:

The conductivity of organic polymers is influenced by various factors, listed below.

1. Conjugation length of polymer chain: the conductivity of a polymer increase with increase in chain length or conjugation

2. Doping level: The conductivity increase with increase in doping level ,but after some time, it becomes saturated .

3. Temperature: The conductivity of conducting polymers increase with increase in temperature .At some high temperature, conductivity becomes constant.

4. Frequency of current: The conducting of these material also depend on the frequency of current, because doping is the transport mechanism of these materials.

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Advantages of intrinsic conducting polymers:

The following are the advantages of intrinsic conducting polymers

1. These polymers posses good conductivity.

2.They can store a charge.

3.Ion-exchange is possible with these polymers.

4.They absord visible light togive coloured products.

5.They are transparent to x-rays.

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6.They can be easily processed with product stability and efficient recycling.

Disadvantages of intrinsic conducting polymers:

Their conductivities are inferior to metal conductivities.

For example: The conductivity of poly acetylene is 4,00,000 S cm^{-1}.

Where as the conductivity of Cu is 6,00,000 S cm^{-1}.

BIODEGRADABLE POLYMERS:

Biodegradability is chemical transformation by enzymatic action of bacteria which are capable of further degradation.

Polymer are popular material as they attacked by environmental conditi0ons including biological attack .Biodegradation of polymers not only aimed at eliminating landfills but also compostable bags for the collection of leaf and yard waste. Those polymers which degradeby the enzymatic action of naturally occurring microorganisms and bacteria are called biodegradable polymers.

The basic requirements of the biodegradable polymer should be

(a) Production of non-toxic products
(b) Capable of maintaining good mechanical integrity until degradation
(c) Controlled rates of degradation

The factors controlling the rate of degradation include
(a) Percentage of crystallinity of polymer
(b) Molecular weight of polymer,
(c) Hydrophobicity of polymer and
(d) The environment surrounding

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The biodegradable polymers are classified as naturally occurring and synthesized polymers.

(a)Naturally occurring biodegradable polymers

There is a belief that anything that comes from nature goes back to nature. Hence it is assumed that these natural polymers are “beautiful for environment degradation”. The rate of degradation and the formation of metabolites depend very much on the structural complexity of material and the environment conditions selected for degradation. There are 4 groups of naturally occurring biodegradable polymers.

1. **Polysaccherides –Eg :Starch and Cellulose**
2. **Proteins- Eg :Gelatin ,Casein, Silk, Wool**

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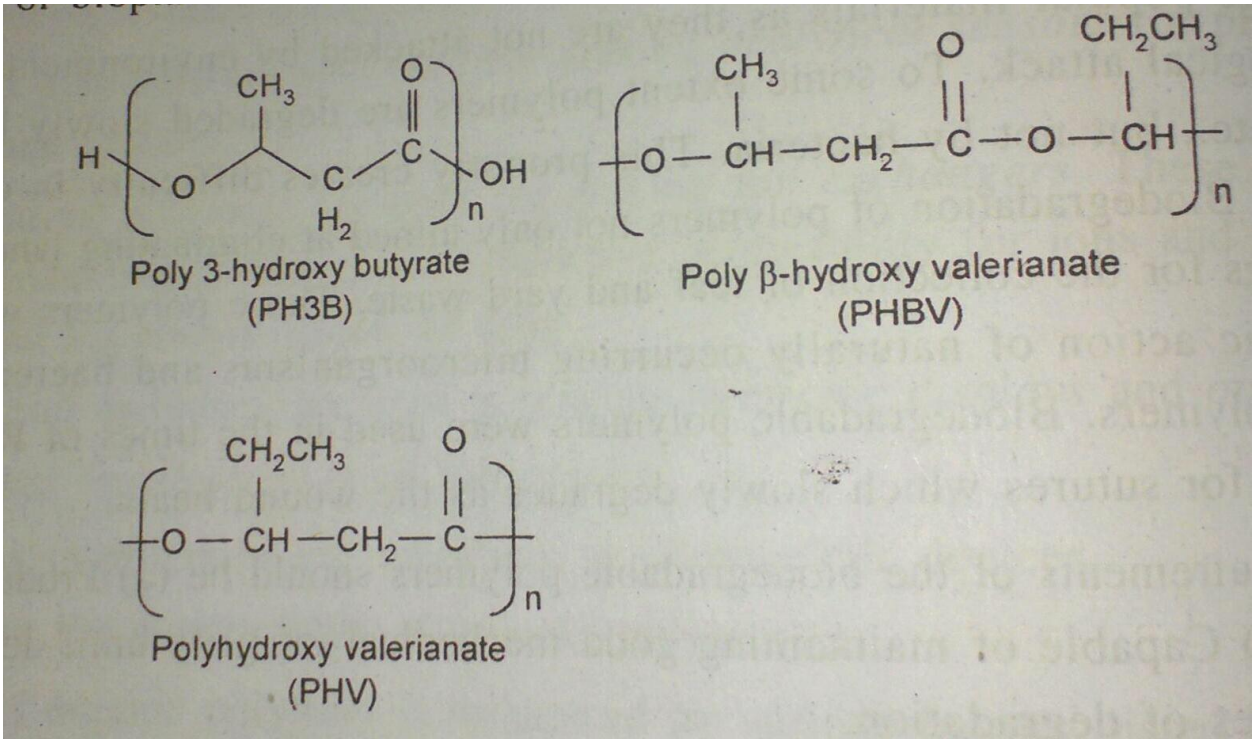
3. **Polyesters- Eg : Polyhydroxy alkanotes**
4. **Others- Eg : Lignin, Shellac, Natural rubber etc.**

(b)Synthetic biodegradable polymers

These polymers are produced from chemicals or biologogical sources that biodegradable. The following are some types of synthetic biodegradable polymers.

Polyhydroxy alkanoates (PHA) BOPAL: These are linear polyesters produced by bacterial fermentation of sugars or lipids and sold under the trade name biopal. These are produced by the bacteria to store carbon and energy. More than 150 monomers can be polymerized to give material with extremely different properties. These biopols are used in the production of bioplastics .The following are some biopols produced.



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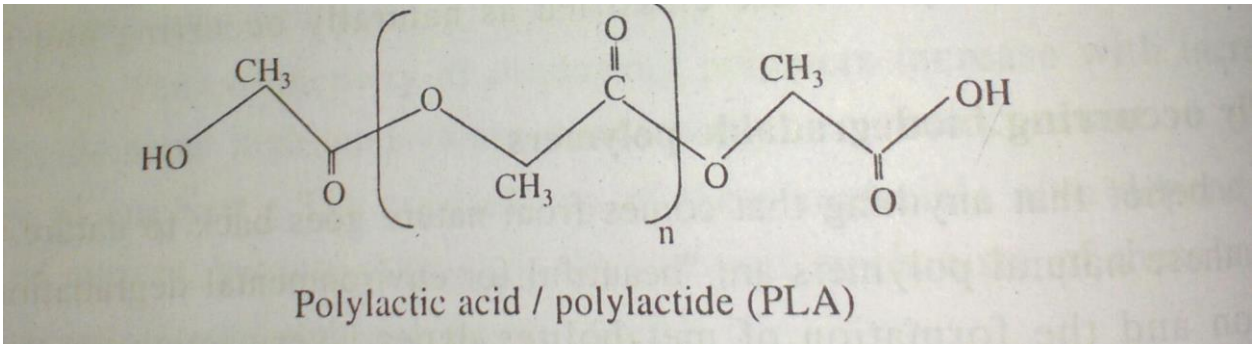
1.Polylactic acid/ polylactide (PLA): This is a biodegradable thermoplastic polyester belonging to class of polyhydroxy alkanoates, derived from renewable sources such as starch, topica or sugarcane possess the following structure.



Polylactic acid / polylactide (PLA)

Biosynthesis: PHA a culture of microorganisms such as alkaligenes entrophys is placed in a suitable medium along with appropriate nutrients and changed to synthesise PHA. The yield of PHA obtained from intracellular inclusions can be as high as 80% of the organism's dry weight.

Industrially PHA is produced by microbial fermentation of sugar or glucose. PHA granules is processed mainly by injection moulding and extrusion moulding into films and hollow bodies.

Properties:

i. PHA polymers are thermoplastic.
ii. Stable to u.v.radiation.
iii. The crystallinity lie in the range of 70%.
iv. Good resistance to moisture ,aroma barrier properties are possessed by the PHA.
v. PHBV possesses good elasticity.
vi. The glass transition temperature of PLA is 60-65^{o}C.
vii. PLA possess melting point 173-178^{o}C
viii. PLA is a chiral compound existing as poly *l*-lactic acid (PLLA)
ix. PLA possess good biocompatibility, process ability as well as high strength and modulus.

Application:

The potential application of PHA is in the medical and pharmaceutical industries, like fixation and orthopedic application including sutures ,suture fasteners, meniscus repair devices, rivets ,tacks,staples,bone plating and lemostats are produced from PHA.

Polyvinyl acetate(PVA): Polyvinyl acetate is a water soluble and biodegradable polymer, possessing excellent mechanical properties and compatibility with starch. The structure of PVA is

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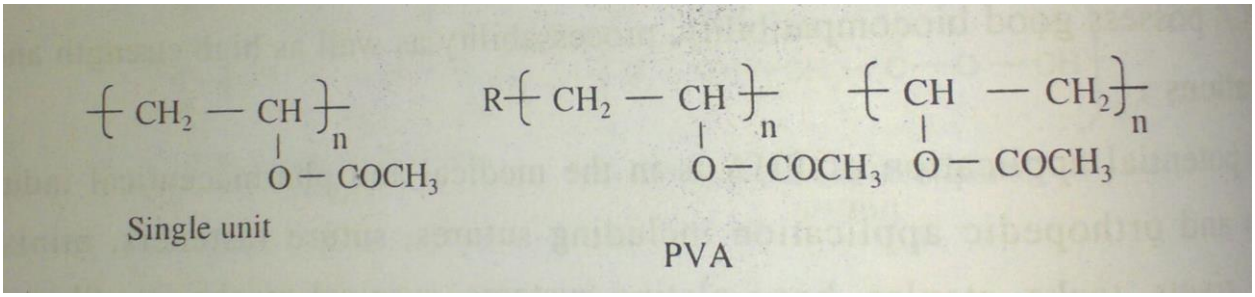

PVA is another class of innovative biodegradable polymer produced from starch when is totally biodegradable in a environment as it can be hydrolysed to glucose by microorganisms or enzymes and then metabolized to CO2 and H2O. Biodegradable PVA is produced from acetic acid and acetaldehyde produced from molasses by fermentation.

Properties:

1. It belongs to the class of vinyl polymers.
2. It is water soluble
3. Posses excellent mechanical properties
4. It is compatible with starch. i.e starch mole can be introduced into the backbone for quick biodegradability.

Application:

1. Polyvinyl acetate is used in food industry as a packing material, food storage and catering, mailing compost bags.

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QUESTIONS

(1) (a) How are synthetic high polymers classified?

(b) Discuss the preparation, properties and uses of various grades of polythenes.

(2) (a) What is the difference between free-radical and ionic chain polymerization?

(b) Write a note on preparation, properties and uses of

i. bakelite

ii. PVC.

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(3) Explain the synthetic methods, properties and applications of the following elastomers:-

(a) Buna-S rubber

(b) Butyl rubber

(c) Thiokol rubber.

(4) Differentiate the following with suitable examples:-

(a) Polymer from monomer

(b) Homo polymer from co-polymer

(c) Step growth polymerization from chain polymersation.

(5) (a) Explain the terms chain and step-growth polymerizations with appropriate examples.

(b) Describe the preparation, properties and uses of

i. polythene

ii. nylon (6,6)

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(6) (a) Explain the di_erences between thermoplastics and thermoset plastics.

(b) Outline the preparation, properties and uses of polyester.

(7) (a) What is natural rubber? How is it processed?

(b) How is crude rubber obtained from latex?

(c) Write a note on preparation, properties and uses of buna-s-rubber?

OBJECTIVE QUESTIONS

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- High polymers are (c)
  a) liquids b) gasesc) solids d) colloids

- The structural units of polymers are called (b)
  a) fibres b) monomers c) fabrics d) thermo units

- Phenol formaldehyde resin is commercially known as (b)
  a) PVC b) Bakelite c) Nylon d) teflon

- Polymer commonly used in textile industry is (b)
  a) Rubber b) Nylon c) PVC d) bakelite

- Which of the following is an elastomer (d)
  a) PVC b) Nylon c) Polystyrene d) Butyle rubber

- Which one of the following is not a macromolecule (d)
  a) cellulose b) rubber c) protein d)wood

- The following polymer has ester links in its structure (d)
  a) Nylon b) Bakelite c) PVC d) Terylene

- Functionality of phenol is (c)
  a) 1 b) 2 c) 3 d) 6

- The only rubber which cannot be vulcanized is (b)
  a) butyl rubber b)Thiokol rubber c) neoprene d) nitrile

- Polyurethane rubber is also known as (d)
  a) hypanol b) Thiokol c) neoprene d) isocyanate rubber

- The common reinforcing agent to give strength and rigidity to rubber is (a)
  a) carbon b) mercaptol c) phenylnapthylamine d) wax

- Plasticizers are materials which are added to resins to increase their (d)
  a) strength b) corrosion resistance c) stability d) plasticity and flexibility

- Thermosetting resin fabricated by transfer moulding which uses the principle of (c)
  a) blowing b) extrusion moulding c) injection moulding d) compression moulding

- The least functionality of a monomer is convert to polymer is (c)
  a) 1 b) 3 c) 2 d) 6

- If the arrangement of functional groups on carbonchain is alternating,it is called (b)
  a) isotactic b) syndiotatic c) atactic d) tacticity

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