UNIT-III POLYMERS FOR ENGINEERING APPLICATIONS

Polymers - Introduction, Molecular weight - number average and weight average molecular weight, Polydispersion index and its significance, numerical problems; Glass transition temperature (T_g); Structure and property relationship in polymers; Plastics - Definition of resins and plastics; Synthesis, properties and applications of PMMA and UF resin; Elastomers - Synthesis, properties and application of butyl rubber and nitrile rubber; Polymer composites - Composites as structural material; Synthesis and applications of Kevlar and Carbon fibers; Conducting polymers - Introduction, synthesis of polyaniline, mechanism of conduction and uses.

Biodegradable polymers - Introduction, Polyglycolic acid - synthesis, degradation and uses.

Self study: Polycarbonates - Synthesis and applications

INTRODUCTION

- Polymers are essential part of everyday household stuff and have profound applications in industry as well.
- Paints (polyacrylate), adhesives (epoxy resin), fibres (nylon, polyester), elastomer (rubbers) are used everywhere.
- Polyethylene and polypropylene are used in packing industry and electronic industry has also been greatly benefitted from polymers. Thus it is of high importance and interest to understand the chemistry behind such polymers so as to be better utilized by any community.

TERMINOLOGIES

Polymer: *"A polymer is defined as a macromolecule of high molecular weight formed by the repeated combination of several simple molecules called monomers of one or more type through covalent bonds"*

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

Monomer: Simple/small molecules which combine with each other to form polymer. Examples: Ethylene, vinyl chloride, butylene, chloroprene etc.

Polymerization: It is defined as "*the chemical reaction in which monomer is converted into polymer*"

Degree of polymerization: The number of repeating units in a polymer.

Functionality: The number of bonding sites in a monomer molecule. For example, ethylene can add two molecules of hydrogen or halogen. Hence, it is bifunctional (functionality two). Similarly, acetylene has a functionality of four (tetrafunctional), as it can react with four atoms of hydrogen or halogen.

Molecular Mass of polymer

- During the formation of polymers, different polymers have different degrees of polymerization.
- Thus, molecular masses of individual macromolecules in a particular sample of polymer are different. Hence, an average value of the molecular mass is taken.
- There are two ways through which average molecular masses can be calculated.

1. Number- average molecular mass (M_n)
2. Mass – average molecular mass (M_w)

1. Number Average Molecular weight (M_n):

- It is determined by measurement of colligative properties such as depression in freezing point, elevation of boiling point, osmotic pressure and lowering of vapour pressure.
- It is defined as the total mass of all the molecules in a polymer sample divided by total number of molecules present. Thus the number average molecular mass is given by:

$$\boxed{\overline{M_n} = \frac{\sum N_i\, M_i}{\sum N_i}}$$

where M_i is the molecular weight of a chain, N_i is the number of chains of that molecular weight, and i is the number of polymer molecules.

2. <u>Weight average molecular mass (M_w):</u>

- It is obtained by light scattering and ultra centrifugation techniques, which measures/property depends on the molecular size. It is given by

$$\boxed{\overline{M_n} = \frac{\sum N_i\, M_i^2}{\sum N_i\, M_i}}$$

- The weight average molecular mass is always greater than number average molecular mass.

Poly Dispersity Index (PDI): In order to obtain the idea of homogeneity of a polymer, the term poly dispersity index is used. It is the ratio of mass average molecular mass to the number average molecular mass.

$$\boxed{PDI = \frac{\overline{M_W}}{\overline{M_n}}}$$

Significance of PDI:

1. Polymers whose molecules have same or narrow range of molecular masses. Such polymers are said to be monodisperse. For natural polymers, PDI is usually equal to one and they are monodisperse.

2. Polymers which have wide range of molecular masses. Such polymers are called polydisperse. Synthetic polymers generally have PDI > 1.

Glass transition temperature (Tg):

"The glass temperature is the temperature at which a polymer abruptly transforms from the glassy (hard) to the rubbery state (soft)"

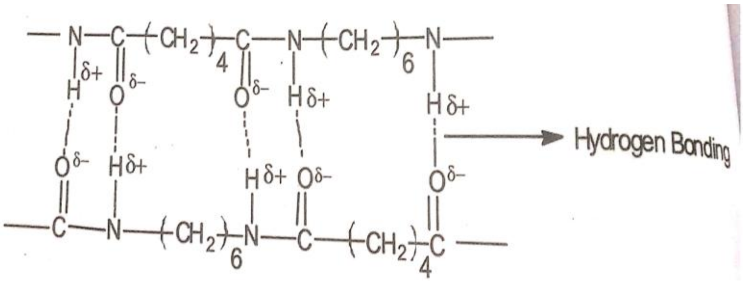
Factors affecting Tg value:

1) Flexibility: Higher flexibility of a polymeric chain, lower is the Tg value due to higher segmental mobility. Thus, flexibility of the chain and Tg are always inversely related.

Example: Polyethylene polymer has Tg value -110 °C (only single bonds), polybutadiene has -85 °C (presence of double bonds), polystyrene has 100 °C (bulky side group).

2) Intermolecular forces: Presence of polar groups in the molecular chain lead to strong inter molecular cohesive forces which restrict the molecular mobility. This leads to an increase in Tg value due to the restriction of segmental mobility.

For example Tg value of polypropylene is -18°C, whereas that of nylon 6,6 containing polar polyamide groups is 57°C due to the presence of hydrogen bonding.



3) Branching and cross linking: A small amount of branching will reduce the value of Tg, because the free volume increases with branching and thus decreases the Tg. Higher degree of branching put a restriction on segmental motion and hence Tg increases. When the chains are crosslinked through covalent bonds there is almost total immobility of chains and hence high Tg. Examples: Poly (α-methyl styrene) has higher Tg value (170^{o}C) whereas polystyrene has lower Tg value (100 ^{o}C).

4) Molecular weight: Tg increases with increase in the molecular mass up to 20,000. Molecular mass beyond 20,000 will have negligible effect on Tg.

Under high molecular mass, long polymeric chains coil and entangle with one another which restricts free mobility of the chain increasing Tg.

5) Addition of plasticizers: A plasticizer is a substance which when added to a plastic material makes it flexible, resilient (returning quickly to original shape) and easier to handle. The plasticizers dilute the intermolecular force of attraction.

Addition of plasticizers **reduces** the glass transition temperature.

Eg: Diisooctyl Phthalate is a used as a plasticizer for PVC. Tg decreases from ~85 ˚C to below room temperature on its addition

6) Stereoregularity: Isotactic is more symmetric than syndiotactic, which is more symmetric than atactic configuration. Thus, Tg of these polymers is in the order of isotactic > syndiotactic > atactic polymer.

For example, Tg of isotactic PVC > syndiotactic PVC > atactic PVC.

Significance of Tg:

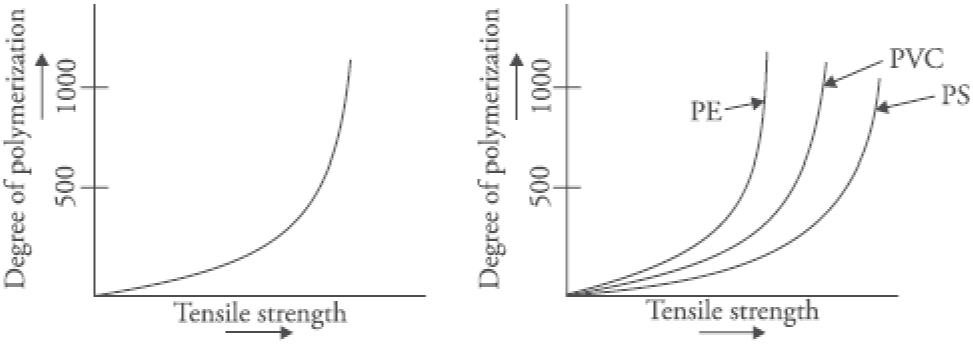
1. Tg value gives an idea about the thermal expansion, heat capacity, electrical and mechanical properties in addition to flexibility of polymer.
2. Tg value gives an idea for choosing right temperature for fabrication operations.

Structure-property relationship of polymers:

The structure of a polymer has profound influence on some of the properties of polymers. The properties such as crystallinity, tensile strength, elastic nature and chemical resistance are largely dependent on the structure of the polymer.

1. Tensile strength:

- Density, melt viscosity and tensile strength are a few important mechanical properties of a polymer.
- These are highly influenced by molecular weight of polymers.
- Tensile strength increases with *molecular mass* of the polymer up to 20000. Beyond that the increase is negligible.



2. Crystallinity:

- Polymers are generally amorphous in nature, but certain degree of crystallinity will be embedded in an amorphous matrix.
- The degree of crystallinity of polymer depends on its *structure* and *stereo regularity*.
- Linear polymers, homopolymer and the presence of polar groups increases the crystallinity whereas branched, copolymer and bulky side groups decreases the crystallinity.
- Higher crystallinity leads to sharp melting point, lower solubility, lower permeability to gases, higher chemical resistance.
- Example: Polyethene (linear) is more crystalline than polystyrene (bulky side groups) or polymethylacrylate (more branched). Nylons are more crystalline due to hydrogen bonding.

3. Chemical resistance:

- The chemical resistance of a polymer depends on the composition of the polymer and also on the nature of attacking reagents.
- The hydrocarbon polymers having *no polar groups* are generally swell or dissolved in *hydrocarbon solvents like gasoline, benzene etc.* But chemically resistant towards *polar solvents.*
- The polymer containing *polar groups* are attacked *by polar solvents*. But chemically resistant towards *non-polar solvents*.
- Polymers containing *residual unsaturation* undergo *oxidative degradation* when exposed to air and light. Natural and synthetic rubbers which contain residual unsaturation are susceptible for oxidative degradation in service.

"Higher the degree of *crystallinity,* greater will be chemical resistance".

"Higher the degree of *cross linking* in the polymer, higher its chemical resistance".

PLASTICS

Definition of plastics: These are organic materials of high molecular weight, which can be moulded into any desired form, when subjected to heat, pressure in presence of a catalyst.

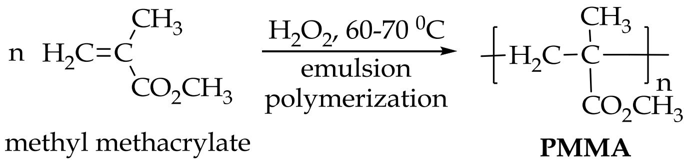
Properties: lightness in weight, corrosion resistance, thermal and electrical insulation, high resistance to abrasion, chemical attack & insect attack, high refractive index, water repellant, decorative finish etc. They are very important engineering materials used for making electrical goods, furniture, floor and wall linings, plugs, switches, holders, propeller shafts, rolling mills, refrigeration, storage, lenses, fibres etc.

Definition of resins: Resins are basic binding material which form a main part of the plastic and which actually has undergone polymerization reactions during the preparation or moulding of a plastic.

Resin is a solid or liquid or semisolid organic polymer used as basis for plastics, adhesives, varnishes.

Polymethyl Methacrylate (PMMA) or Plexi Glass or Lucite

Synthesis: PMMA is obtained by suspension polymerization of methyl methacrylate in presence of hydrogen peroxide as radical initiator.



$$n\ H_2C{=}C(CH_3)(CO_2CH_3) \xrightarrow[\text{emulsion polymerization}]{H_2O_2,\ 60\text{-}70\ ^0C} \left[H_2C{-}C(CH_3)(CO_2CH_3) \right]_n$$

Properties:

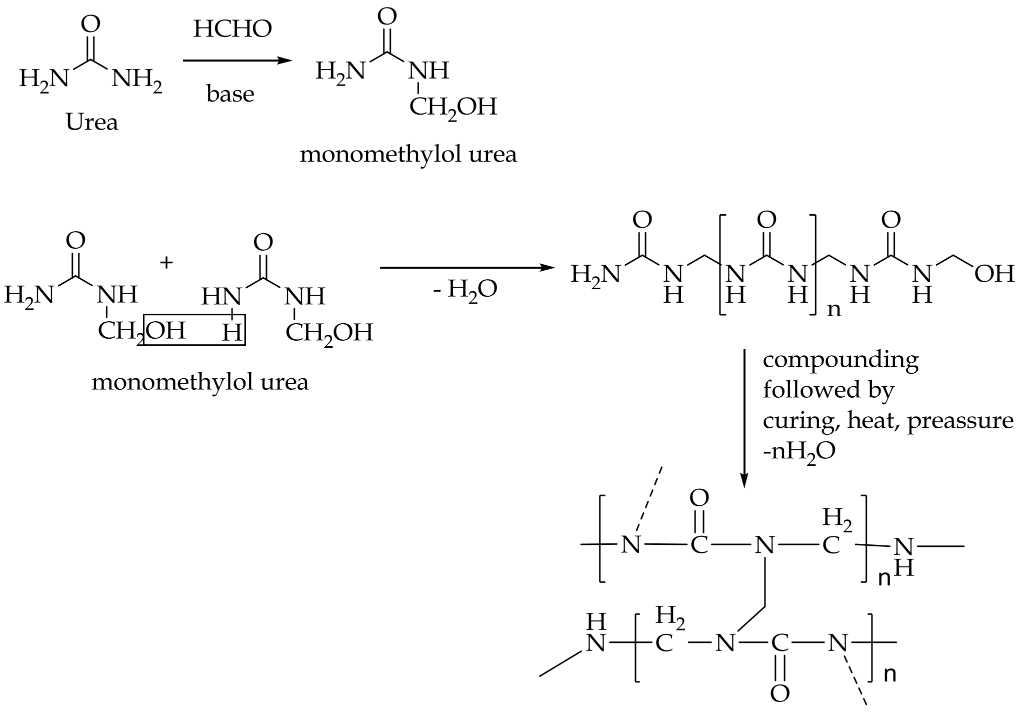
- PMMA is a hard, fairly rigid material with high softening point of about 130-140 °C , but it becomes rubber-like at ~65 °C.
- It has excellent optical clarity, good dimensional stability and has 'outstanding shape forming' property, but has poor scratch resistance.
- Low resistance to hot acids and alkalis.

Applications:

- Manufacturing of automotive lenses, aircraft windows and signal boards.
- Artificial teeth and contact lenses, laser disks, DVDs, transparent bath tubs and wash basins.
- As paint and adhesive.

Urea-Formaldehyde Resins (UF Resin)

Synthesis: It is prepared by condensation of urea with formaldehyde in presence of a base in stainless steel reactor at 50 °C. The intial products monomethylol urea are compounded by addition of filler, plasticizer, pigment or catalyst followed by curing by applying heat and pressure to provide long -C-N-C-N chain polymer. This is called urea-formaldehyde resin and is a cross-linked polymer.



Urea-Formaldehyde Resin

Properties:

- It gives clear, water-white products of good tensile strength, good electrical insulation.
- Good chemical resistance, greater hardness, good abrasion resistance.
- Amorphous and transparent plastic.
- Outstanding shape formation.
- Resistant to water, alkalis and inorganic salts but dissolves in organic solvents.

Applications:

- It is employed for bonding in grinding wheels, as cation-exchange resins.
- Binder for glass fibre, rock, wool, plywood, to provide electrical insulation etc.

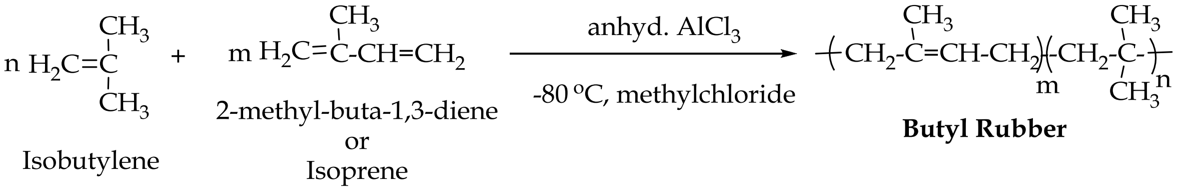
ELASTOMERS

<u>Definition:</u> They are high molecular weight polymers that possess elastic properties. i.e., they can undergo deformation under stress (to an extent 5-10 times original length) but regain their original shape when the stress is released. This property is called elasticity and it is due to coiled nature of chains in them.

Advantages of Synthetic Rubber - (a) resistance to heat, light (b) water repellent and solvent resistance (c) high chemical resistance - alkali/acid (d) high temperature stability (e) high abrasion resistant

Butyl Rubber

Synthesis: Butyl Rubber is synthesized by mixing isobutylene with up to 5% of isoprene monomer using methyl chloride as solvent using anhydrous aluminium chloride as catalyst at -80 °C. The product was vulcanized and dried by mixing with antioxidant.

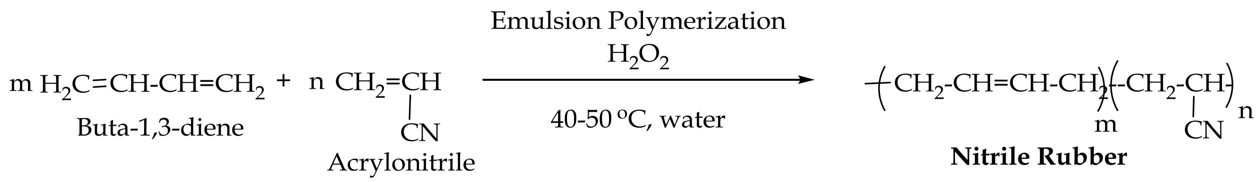


Properties: It is less sensitive to oxidative aging. It has very low gas permeability and shows good solvent resistance. It has excellent resistance to heat, abrasion, ageing, chemicals, polar solvents like alcohol and acetone. It has good electrical insulation properties.

Applications: (a) inner tube for tyres, automobile parts, hoses, tank-linings (b) insulating materials for high voltage transmission lines and cables.

Nitrile Rubber (Buna-N or Europrene)

Synthesis: Nitrile Rubber is synthesized by Emulsion Polymerization of butadiene and acrylonitrile monomers in a steel vessel at 30-40 °C using water as solvent in presence of H_2O_2 as free radical initiator. The resulting polymer latex was coagulated followed by vulcanization to provide Nitrile rubber.



$$m\,H_2C{=}CH{-}CH{=}CH_2 + n\,CH_2{=}\underset{CN}{\underset{|}{CH}} \xrightarrow[40\text{-}50\,^{o}C,\ water]{\text{Emulsion Polymerization}\ H_2O_2} \left(CH_2{-}CH{=}CH{-}CH_2\right)_m\left(CH_2{-}\underset{CN}{\underset{|}{CH}}\right)_n$$

Properties: Nitrile rubber co-polymer has high tensile strength, excellent resistance to heat, sunlight, oils, fats, organic solvents, dilute acids but is less resistant to alkalies due to presence of base labile -CN group. Lower acrylonitrile composition in the rubber lead to decrease in glass transition temperature and show greater resistance to solvents upon increasing nitrile composition. This rubber can withstand a temperature of -40 ^{o}C to 100 ^{o}C.

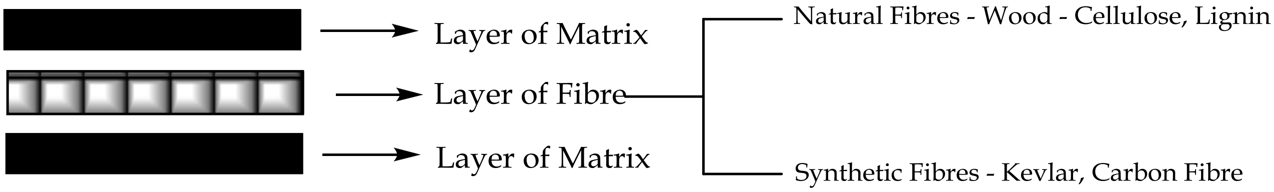
Applications: (a) Nuclear, medical and aeronautical industry applications since it can withstand low and high temperatures (b) Used as sealant, expanded foam, floor mats, non-latex gloves, automotive transmission belts, gaskets, oil seals (c) as pigment binder, fuel and oil handling hoses.

POLYMER COMPOSITES

An ideal structural material (air craft industry) should have properties such as: (a) Low density (b) High strength and stiffness (c) Corrosion resistance and (d) Abrasion and impact resistance. No single metal, alloy, ceramic or polymeric materials are known that can offer combination of aforesaid properties. This is because a strong material is relatively dense and an increase in stiffness generally results in a decrease in impact strength. The search for materials possessing above properties led to the development of composite materials. They are initially developed for military and aerospace applications in 1940's and are currently used for house decoration, bridge repair, mooring cables, structural strengthening and other applications.

"A combination of two or more distinct components to form a new class of material suitable for structural applications is referred as composite materials".

Polymer composites are generally made of two components, namely (i) matrix and (ii) fibre. The fibre is generally embedded in the matrix in order to make the matrix stronger. The matrix is usually a thermoset material such as epoxy resin and it holds the fibre together. Fibre is most often glass; other synthetic fibres include carbon fibre, Kevlar etc. Naturally occurring fibres such as wood - lignin, cellulose can also be employed.



Importance as structure material

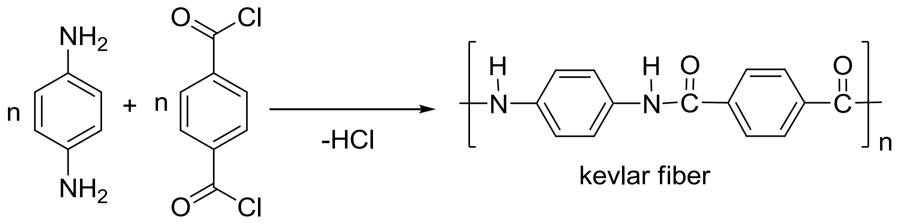
- Matrix binds the fibers together and can transmit and distribute any externally applied stress to the fibers.
- Matrix protects individual fiber from surface damage due to mechanical abrasion or any chemical reaction with the surroundings.
- The strength of the composite material is primarily due to the bonding forces between fibers and matrix.

Kevlar (Aromatic polyamide)

Kevlar is synthetic fibre, it as an organic in aromatic polyamide (aramide), Kevlar has a unique combination of high strength, modulus, toughness and thermal stability. A unique combination of properties makes Kevlar the first for ever growing applications in safety with high efficiency.

Preparation:

It is an aromatic polyamide with the name poly(para-phenylene terephthamide). It is prepared by poly condensation between 1,4- phenyl-diamine and 1,4-benzedicarbonyl chloride is resulting a kevlar and HCl is a byproduct.



Properties:

- Kevlar is five times stronger than steel
- It has high modulus and structural rigidity, not flex easily or bend under the high applied force.
- Its reasonably good at withstanding temperature and decomposed only at 450 ^{o}C.
- Kevlar maintains its strength and resilience down to cryogenic temperature nearly -196 ^{o}C.
- It will not easily rust or corrode and it absorbs vibrations readily.
- Kevlar can be ignited but burning usually stops when the heat sources removed.

Applications:

- Used as reinforcement for boat hulls, airplanes and bicycles and in automobile tires.
- Used in bridge structures and bullet proof vests.
- Used in puncture resistant bicycle tyres.

Carbon fibre:

Carbon fibres are a new breed of high strength materials. Carbon fibre containing at least 90% carbon obtained by the controlled pyrolysis of appropriate fibres. Generally, its formed as a composites with a light weight matrix. It has high strength, stiffness, light weight and outstanding properties.

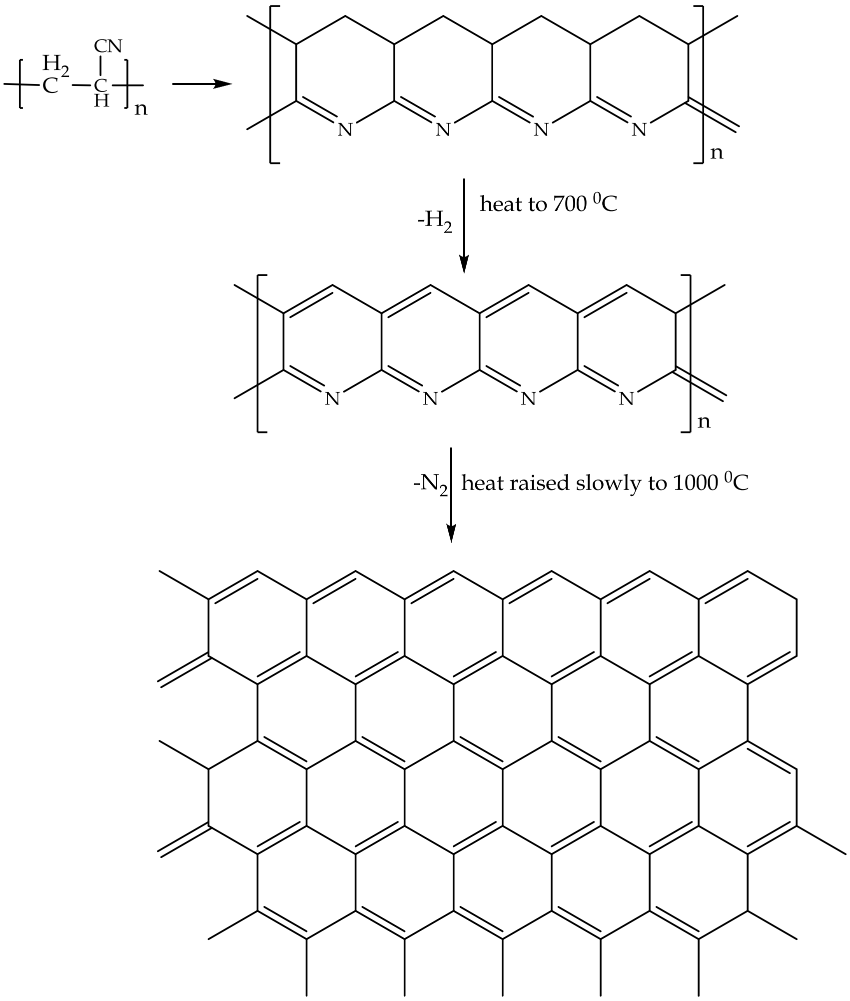
Various metal organic frame precursor materials are used to synthesis carbon fibre of different morphologies and various characteristics. The most prefer precursor is Polyacrylonitrile (PAN) cellulosic fibres, and phenolic fibres.

Synthesis of Carbon fibre from PAN :

Three stages are in the conversion of PAN in to high performance carbon fibre.

- Oxidative Stabilization: The polyacrylonitrile is first stretched and simultaneously oxidized in a temperature range of 200-300C. This treatment converts thermoplastic PAN to a non-plastic cyclic compound.
- Carbonization: After the oxidative, the fibres are carbonized at about 1000C with nitrogen atmosphere for 2 hours. While this process non-carbon elements are removed and yield of about 60% of the mass of original PAN.
- Graphitization: After the carbonization the fibres are treated at 1500-3000C, which improves the ordering and orientation of the crystallites in the direction of the fibre axis.

Preparation



ribbon-like carbon fibre

Applications:

- It is used in making parts of aeroplanes, space shuttles and modern motor bikes.
- It is used in tennis rackets, guitar strings and golf clubs.
- It is used in tripods, fishing rods and archery equipments,

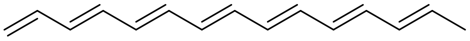
CONDUCTING POLYMERS

“An organic polymer with highly delocalized pi-electron system, having electrical conductance of the order of a conductor is called a conducting polymer”. The electrical conductivity of polyacetylene can be increased to 13 folds by doping with electron acceptors and donors. Tremendous applications would exist as they are flexible, ease of fabrication, stability, ease of processability, etc.

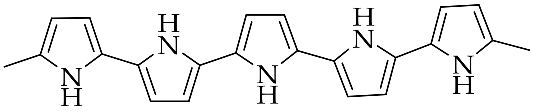
Key structural feature of conducting polymer - linear structure with alternate single and double bonds, i.e., extensive pi conjugation in the backbone.

The conducting polymers are synthesized by doping, in which charged species are introduced in organic polymers having pi-backbone. The important doping reactions are (a) oxidative doping (p-doping) (b) reductive doping (n-doping) & (c) protonic acid doping. The electrical conductivity of doped polyacetylene (10^5 sm^{-1}) is remarkable to Teflon (10^{-8} sm^{-1}) but is marginally lower than copper (10^8 sm^{-1}).

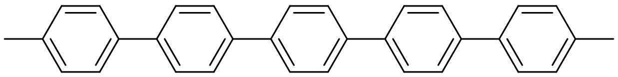
Examples are below are some of the conducting polymers



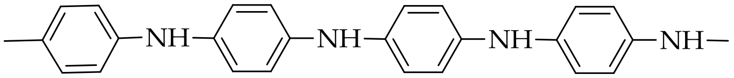
Polyacetylene



Polypyrrole



Polyphenylene

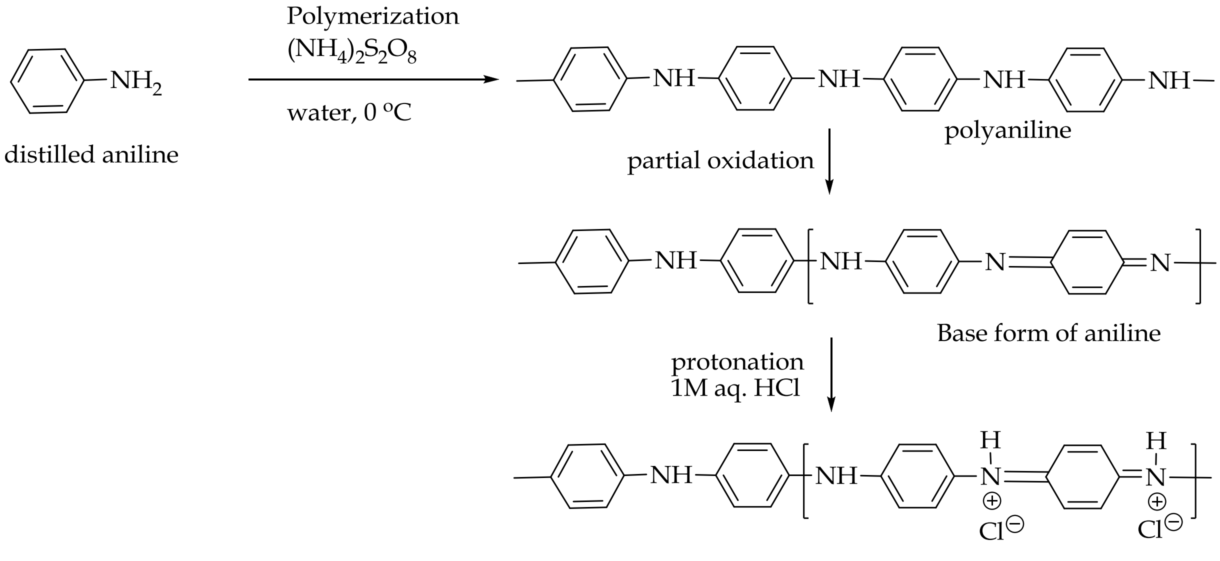


Polyaniline

Synthesis of conducting polyaniline:

Polyaniline is obtained by oxidation of freshly distilled aniline using Ammonium peroxy di-sulphate catalyst. The initially obtained base form of aniline is treated with aqueous hydrochloric acid (1M). This result in protonation of quinoid imines conjugated to benzenoid amines. Current carrying positive charges are created in the polymer backbone.

These charges are compensated by negative charged anions (Cl^-) that are held by electrostatic attraction to result the salt. These polymers show very low ionization potential and good electron affinities. According to band theory, when a pi-bond is formed, valence band and conduction bands are formed. The electrons remain in the valence bond and it will be full. There will be sufficient energy gap between valence band and conduction band. So, polyaniline is not a good conductor. But upon protonation (doping with proton), polaron like bands are formed which fill the energy gap. When sufficient number of polarons is formed, a band is formed that overlaps with the conduction and valence band. This provides continuity for charge flow accounting for conduction as in Emeraldine.

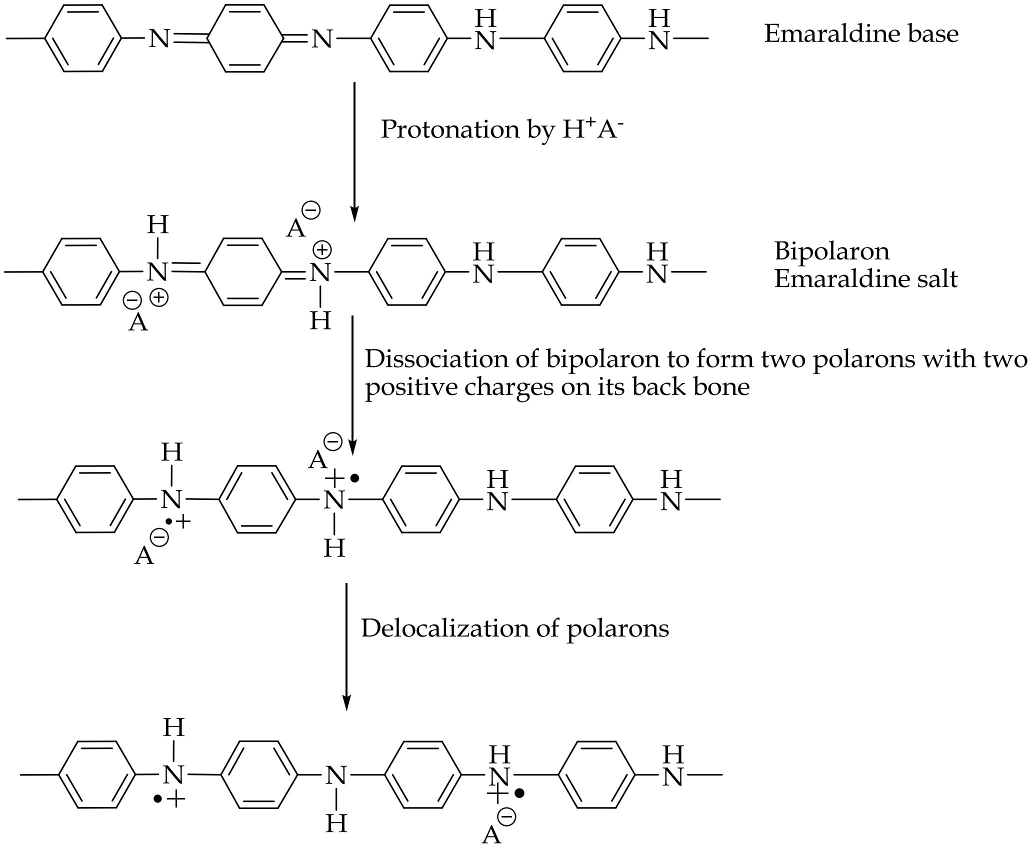


Emeraldine (conducting polyaniline)

Mechanism of conduction in polyaniline (protonic acid doping):

Conducting form of polyaniline is obtained from emeraldine base consisting of equal proportions of amines (-NH-) and imine (=N-) sites. Protonation of imine group introduces one positive charge into polymeric backbone. After protonation, there is formation of bipolaron (dication salt).

The bipolaron then undergoes rearrangement to form polarons and are delocalazied in the polymeric chain which is responsible for the electrical conductivity. The positive charges are compensated by anions of the acid. Thus polymer as a whole is electrically neutral. This type of protonic acid doping increases the conductivity of polyaniline by 9 to 10 times.



Mechanism of conduction in polyaniline (Emaraldine base)

<u>Application of conducting polymers</u>:

They are used as electrode material in capacitors, ion-exchange devices, light emitting diodes, electrochromic display windows, bio sensor, humidity sensor, radiation sensors, conductive tracks on PCBs etc.

BIODEGRADABLE POLYMERS

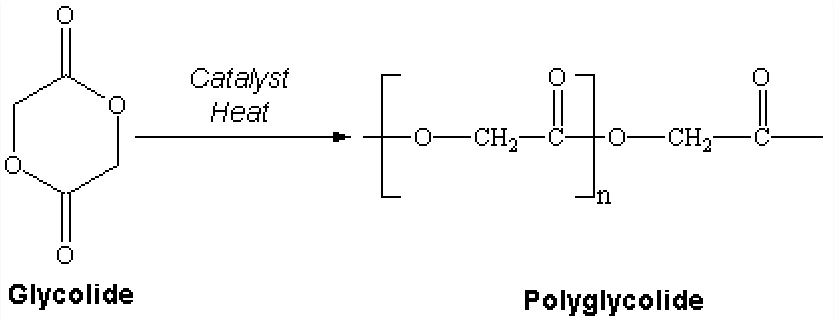
Biodegradable polymers contain polymer chains that are hydrolytically or enzymatically cleaved, resulting in soluble degradation products. Biodegradability is particularly desired in biomedical applications, in which degradation of the polymer ensures clearance from the body and eliminates the need for retrieval or explant. Biodegradable polymers have applications in controlled/sustained release drug delivery approaches

Tissue engineering scaffolds

Temporary prosthetic implants

Polgycolic acid

Polyglycolide can be obtained through ring-opening polymerization of glycolide, the cyclic diester of glycolic acid. Ring-opening polymerization of glycolide can be catalyzed using aluminium isopropoxide as catalyst. In the presence of a catalyst glycolide heated temperature of 195 °C to



Degradation

Polyglycolide is characterized by hydrolytic instability owing to the presence of the ester linkage in its backbone. The degradation process is erosive and appears to take place in two steps during which the polymer is converted back to its monomer glycolic acid: first water diffuses into the amorphous (non-crystalline) regions of the polymer matrix, cleaving the ester bonds; the second step starts after the amorphous regions have been eroded, leaving the crystalline portion of the polymer susceptible to hydrolytic attack. Upon collapse of the crystalline regions the polymer chain dissolves.

When exposed to physiological conditions, polyglycolide is degraded by random hydrolysis, and apparently it is also broken down by certain enzymes, especially those with esterase activity. The degradation product, glycolic acid, is nontoxic, and it can enter the tricarboxylic acid cycle, after which it is excreted as water and carbon dioxide. A part of the glycolic acid is also excreted by urine.

Applications:

Biodegradable polymers are used commercially in both the tissue engineering and drug delivery field of biomedicine.

Specific applications include:

- Sutures
- Dental devices (PLGA)
- Orthopaedic fixation devices
- Tissue engineering scaffolds
- Biodegradable vascular stents
- Biodegradable soft tissue anchors