Subject: **Applied Chemistry**

Faculty: **Dr. P Vinodkumar**

Topic: ENGINEERING MATERIALS

Unit No:
Lecture No:
Link to Session Planner (SP):S.No……of SP

Date Conducted:

Polymers

Polymers are high molecular weight organic compounds in which a large number of simple units repeat themselves in a regular fashion. The simple units are called as monomers. For any compound to be recognized as a true monomer, it should possess at least two functionalities (Not two functional groups necessarily---- as in some compounds, one functional group gives rise to only one functionality while in some compounds, one functional group gives rise to two functionalities), e.g.,

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

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

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

Therefore, it is clear that what is actually required for polymerization, is presence of at least two functionalities and not two functional groups, in the monomer.

Classification of Polymers

Polymers have been classified on different basis as follows:

(A).Classification on the basis of Origin/Source

On this basis, polymers have been broadly classified into **two types:**

1. Natural Polymers

They occur naturally and are found in plants and animals.

Examples: Proteins, Nucleic acids, Starch, Cellulose and Natural rubber.

2. Synthetic Polymers

These are man-made polymers. Plastic is the most common and widely used synthetic polymer.

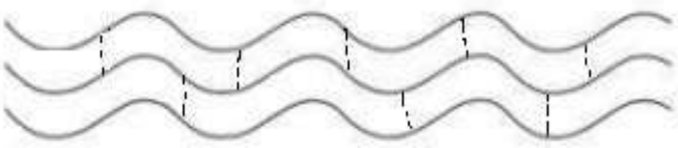
e.g., Nylons, Polythene, PVC, Synthetic rubbers, etc.

(B). Classification on the basis of Structure

On this basis, polymers have been broadly classified into **three types:**

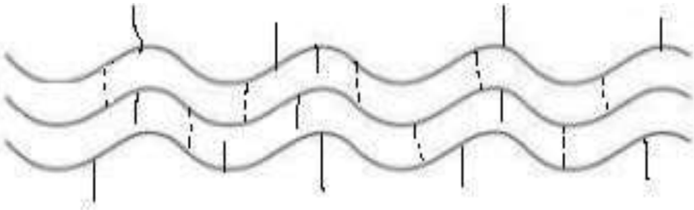
1. Linear Polymers

Polymers comprising of long and straight chains are called as linear or straight chain polymers. e.g., High density polyethene (HDPE)



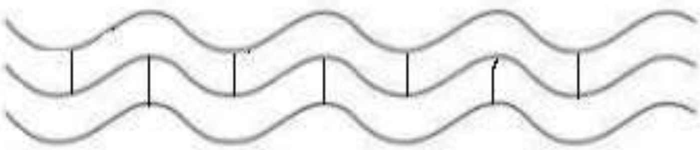
2. Branched-chain Polymers

Polymers comprising of linear chains with branches are called as branched chain polymers. e.g., Low-density polyethene (LDPE).



3. Cross-linked Polymers

Polymers in which various individual chains are connected together by covalent bonds (cross links) are called as cross linked polymers. These polymers are formed from bi-functional and tri-functional monomers and the additional functionality produces the cross links. e.g., Bakelite and Melamine.



(C). Classification on the basis of nature of Monomers

On this basis, polymers have been broadly classified into **two types:**

1. Homo-polymers

Polymers which comprise of only one type of monomers are called as homo-polymers. e.g., Polyethene, PVC, Nylon-6, etc. This can be represented as:

-A-A-A-A-A-A-A-A-A-A-A-A-A-A-, or -(A-)$_n$-

2. Co-polymers

Polymers which are comprising of more than one (generally two) types of monomers are called as homo-polymers. e.g., Nylon-6'6, Terylene, SBR, etc.

Co-polymers have further been classified into four types on the basis of relative arrangement of the monomer units with respect to each other. These are:

i). Alternate Co-polymers: Polymers comprising of alternating A and B units.

The order is regularly followed throughout the chain. This can be represented as:

-A-B-A-B-A-B-A-B-A-B-A-B-A-B-, or -(A-B)$_n$-

ii). Block Co-polymers: Polymers comprising of regular alternating blocks of A and B units. The order is regularly followed throughout the chain. This can be represented as:

-A-A-A-A-A-B-B-B-B-B-A-A-A-A-A-B-B-B-B-B-

iii). Graft Co-polymers: Polymers in which the main chain is comprising of one type of monomers and the other monomer forms the branches. Therefore, for being a graft co-polymer, the polymer must be branched.

This can be represented as:

iv). Random Co-polymers: Polymers in which no regular order of arrangement is followed by the monomer units. This can be represented as:

-A-A-A-A-A-B-B-A-B-B-B-B-B-B-B-A-A-A-

The most common type of co-polymers are alternate co-polymers.

(D). Classification on the basis of Inter-molecular Forces

On this basis, polymers have been broadly classified into **four types:**

1. Elastomers

Polymers in which intermolecular (inter-chain) forces are very weak (van der Waals forces) are called as elastomers. These are rubber-like solids weak interaction forces are present. e.g., Rubber.

2. Fibres

Polymers in which intermolecular (inter-chain) forces are very strong (Hydrogen bond or dipole-dipole interaction) are called as Fibres. These are strong, tough, with high tensile strength. e.g., Nylons, Terrylene, etc.

3. Thermo-plastics

Polymers in which intermolecular (inter-chain) forces are intermediate are called as thermo- plastics. These polymers on heating become soft and on cooling again become hard and retain their original shape. In this case, the intermolecular forces, on heating, get weaken and the polymer becomes soft and vise-versa. It is purely a physical change and physical changes are generally reversible. Therefore, these polymers are recyclable, i.e., they can be moulded and re-moulded again and again. e.g., Polyethene, Polyvinyl chloride, Polystyrene, etc.

4. Thermo-settings

Polymers in which there is extensive cross linking, are called as thermo-settings. These polymers on heating become soft and on cooling again become hard but do not retain their original shape. In this case, the cross links get broken and rearranged on heating. It is purely a chemical change and chemical changes are generally irreversible. Therefore, these polymers are not recyclable, i.e., once moulded, they cannot be moulded again. These polymers greatly improve the material's mechanical properties. e.g., Bakelite, Epoxy resins, etc.

(E). Classification Based on Synthesis

On this basis, polymers have been broadly classified into **two types:**

1. Addition Polymers

Polymers which are formed by addition reaction are called as addition polymers. e.g., Poly ethane, Teflon, Polyvinyl chloride, etc. For addition polymerization to take place, the monomer must be unsaturated. Taking the example of polyethene, the addition polymerization reaction can be shown as:

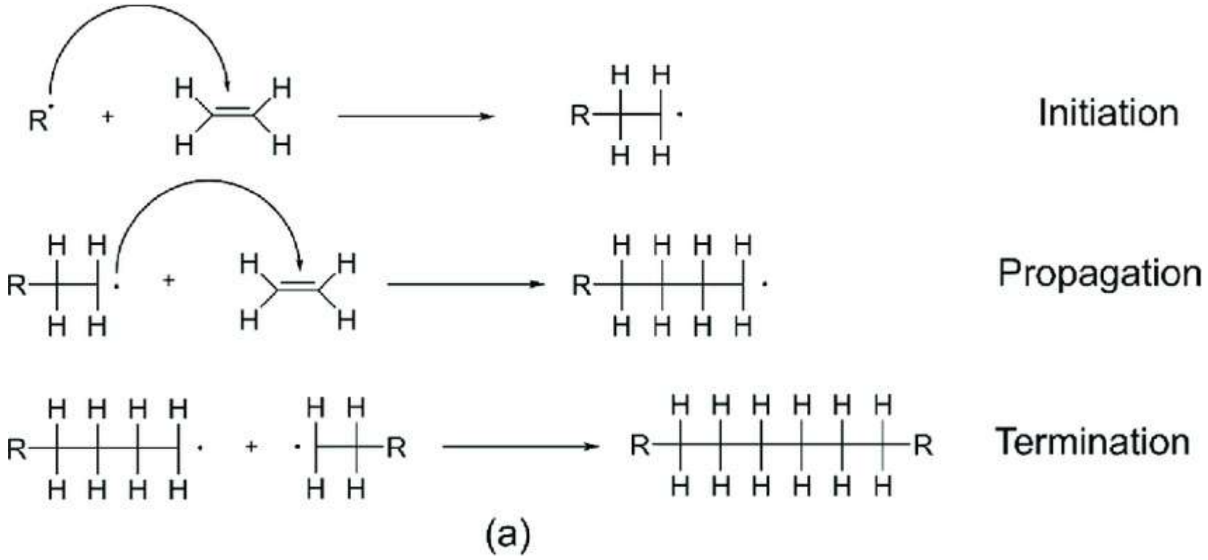
Addition polymerization is a chain reaction, which once initiated, propagates itself till the chain is not terminated. It involves three steps: Chain initiation, Chain propagation and Chain termination. Addition polymerization can take place via three different types of mechanisms:

(I). Cationic Mechanism (II). Anionic Mechanism (III). Free Radical Mechanism

Free Radical Mechanism:

In this mechanism, the reaction is initiated by a free radical resulting in the formation of a free radical as intermediate, thus known as free radical mechanism. The reaction can be terminated by an free radical. We can summarize that in this reaction, Initiator is Free radical, Intermediate is Free radical, Inhibitor (Terminator) is Free radical. The mechanism can be shown as:

a) Chain Initiation step b) Chain Propagation step c) Chain Termination step



In case of free radical mechanism, in addition to the normal chain termination by introducing a free radical, there are also other ways wherein the chains can terminate themselves. These are:

i). By Coupling: There is possibility that two propagating chains can collide with each other and couple. In this way, both the chains are terminated and the polymer chain obtained has molecular weight more than expected.

ii). By Dis-proportionation: There is possibility that a hydrogen radical from one propagating chain can be abstracted by another, thereby terminating both the chains, however, unsaturation is created in the chain from which H-radical is being abstracted.

2. Condensation Polymers

Polymers which are formed by condensation reaction are called as condensation polymers. e.g., Nylon-6'6, Nylon-6, Terylene, Bakelite, etc. This type of polymerization is called as condensation polymerization. Condensation polymers are mainly of three types:

I. Polyamides II. Polyesters III. Resins

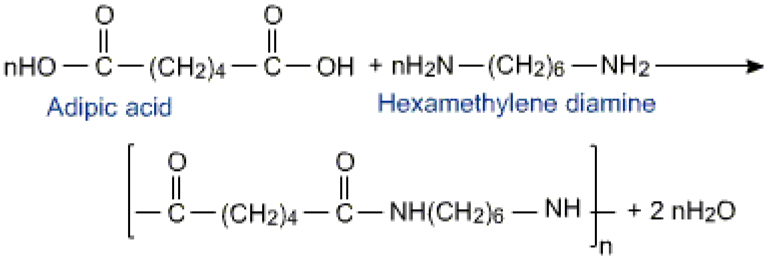
I. Polyamides

Polymers in which monomer units are linked together by amide bonds. For polyamide formation, the monomers should be polcarboxylic acids and polyamines. Generally, dicarboxylic acids and diamines are used. Polyamides belong to the fibres as per the classification on the basis of intermolecular forces.

Nylon (Poly amide resin):

Nylon is a polyamide resin containing recurring amide groups (-NHCO-) in its structure produced by copolymerization of di-amine with acid. Depending on the number of C atoms in di-amine & dioxide there are different types of nylons like nylon 6,6, nylon 6,10 etc., where the first number indicates number of carbon atoms in di-amine & the second number indicates the number of 'c' atoms in di-acid.

Nylon 6,6 is prepared by condensation polymerization of adipic acid and hexamethylene diamine in the absence of air.



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

Properties:

The structures of nylons are linear that permits side by side alignment. Moreover, the molecular chains are held together by hydrogen bonds. Thus, nylons have high crystalline which imparts high strength, high melting point, elasticity, toughness, abrasion resistance and retention of good mechanical properties up to 125^0C. They are polar polymers, they have good hydrocarbon resistance.

Applications:

(1) The major application is in textile industry.

(2) Because of its high thermal & abrasion resistance nylons are used in mechanical engineering applications like gears, bearings, machine parts where greater friction is there.

(3) Flexible tubing's for conveying petrol etc are made from nylons

(4) Nylons are used as electrical insulators.

(5) Nylon 6,6 is used for making tire cords.

(6) Nylons are used in automobile industry and telecommunication industry for making radiator parts and coil formers respectively.

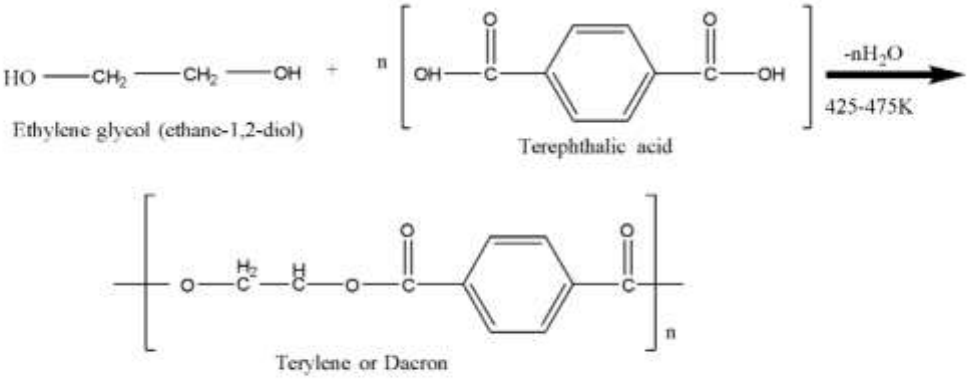
II. Polyesters

Polymers in which monomer units are linked together by ester bonds. For polyester formation, the monomers should be polcarboxylic acids and polyols. Generally, dicarboxylic acids and diols are used. Polyesters belong to the fibres as per the classification on the basis of intermolecular forces.

There are many synthetic polyesters like, Polyethylene Terephthalate (Terylene), Polyethylene Phthalate (Glyptal), Polybutylene Terephthalate, Polytrimethylene Terephthalate, etc.

Terylene (Polyethylene Terephthalate):

Polyethylene terphthalate is a copolymer and its monomer units are terephthalic acid (Benzene-1,4-dicarboxylic acid) and ethylene glycol (Ethane-1,2-diol). It is commercially known as **Terylene**. The reaction for preparation of Terylene can be shown as:



In Terylene various polymer chains are connected together by strong intermolecular forces, i.e., dipole-dipole interactions, next stronger to hydrogen bonding.

Properties of Terylene:

- Terylene has high mechanical strength and dimension stability.
- It is a very strong fibre and will suffer very little loss in strength when wet.
- It is elastic in nature and posses the property of high crease resistance.
- It is stable in the temperature range of -40 - 100oC.
- It shows creep and abrasion resistance and good insulating properties.
- It shows low water absorption and at room temperature, it is resistant to water, dilute acids, salts, aliphatic and aromatic hydrocarbons and alcohols.

Applications of Terylene:

- It is used for making video and audio tapes.
- It is used in textile industry for making hard wear clothes and other dress material.
- It is used for making clear bottles for food and beverages.
- The fibre may be blended with cotton and wool to form another fabrics like terycot and terywool, respectively.

PLASTICS:

The word plastic itself comes from the Greek word plastics, which means to be able to be shaped ormoulded by heat.

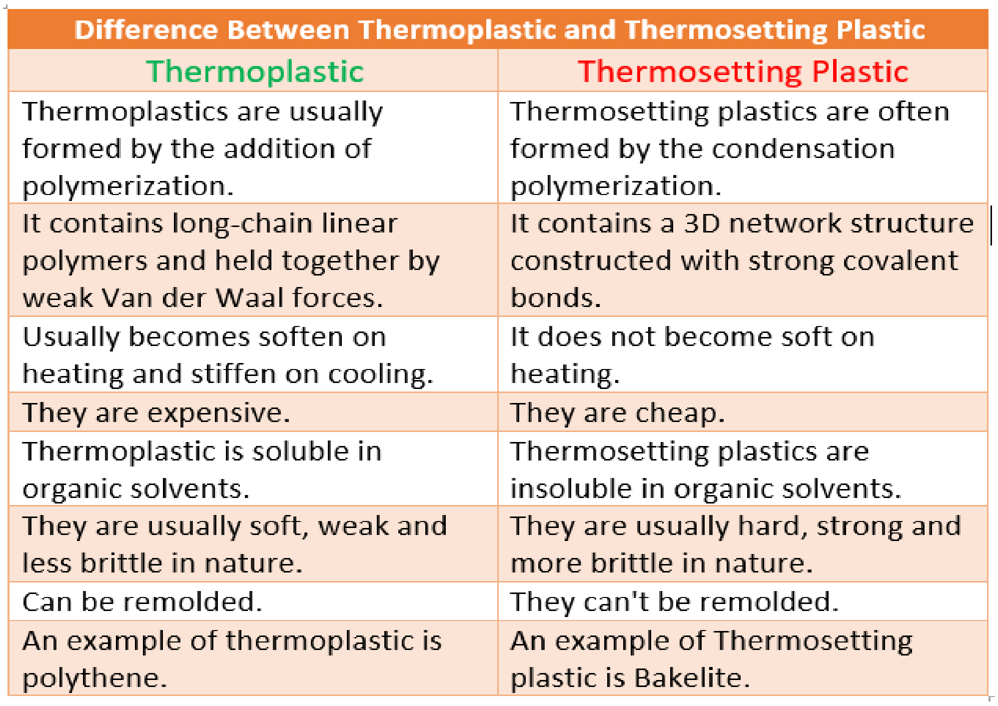
Advantages of plastics over other traditional materials (like wood, metals, glass etc):

1) Plastics are available in attractive colours.
2) They do not undergo corrosion.
3) They are not affected by insects.
4) They are light in weight
5) They are cheap.
6) They can be moulded into any shape easily.
7) They are chemically inert.
8) They have good abrasion resistance.
9) They are good insulators of heat and electricity.

Disadvantages:

1. Recycling of plastic is a costly process.
2. Plastic undergo biodegradation after long time.
3. Incineration of plastic causes pollution.
4. Plastics are derived from petrochemicals and their production causes environmental pollution.
5. Plastics are low heat resistance and brittle. They undergo deformation at low temperatures.

Differences between Thermo Plastics &Thermo Setting plastics :



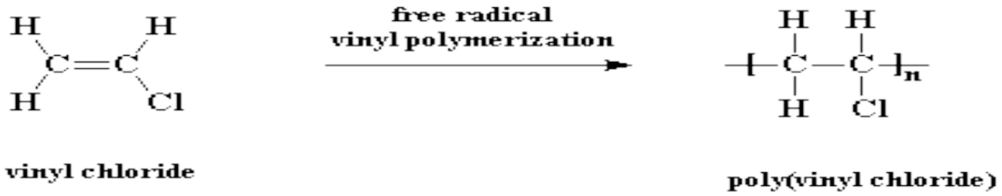
Difference Between Thermoplastic and Thermosetting Plastic

Thermoplastic	Thermosetting Plastic
Thermoplastics are usually formed by the addition of polymerization.	Thermosetting plastics are often formed by the condensation polymerization.
It contains long-chain linear polymers and held together by weak Van der Waal forces.	It contains a 3D network structure constructed with strong covalent bonds.
Usually becomes soften on heating and stiffen on cooling.	It does not become soft on heating.
They are expensive.	They are cheap.
Thermoplastic is soluble in organic solvents.	Thermosetting plastics are insoluble in organic solvents.
They are usually soft, weak and less brittle in nature.	They are usually hard, strong and more brittle in nature.
Can be remolded.	They can't be remolded.
An example of thermoplastic is polythene.	An example of Thermosetting plastic is Bakelite.

Write preparation, properties and applications of i) PVC.

i) **PVC (Poly vinyl chloride):**

Preparation: Poly vinyl chloride is produced by heating vinyl chloride in presence of benzyl peroxide or H_2O_2.



Properties: PVC is colourless, odourless, non-inflammable and chemically inert powder. Pure resin possesses greater stiffness and rigidity compared to poly ethylene. It is brittle in nature.

Applications: or Uses:

1. P.V. C is mainly used as an insulating material.
2. It is used for making table clothes, rain coats, toys, tool handles, radio components, etc.
3. It is used for making pipes, hoses, etc.
4. It is used for making helmets, refrigerator components, etc.
5. It is used in making cycle and automobile parts.

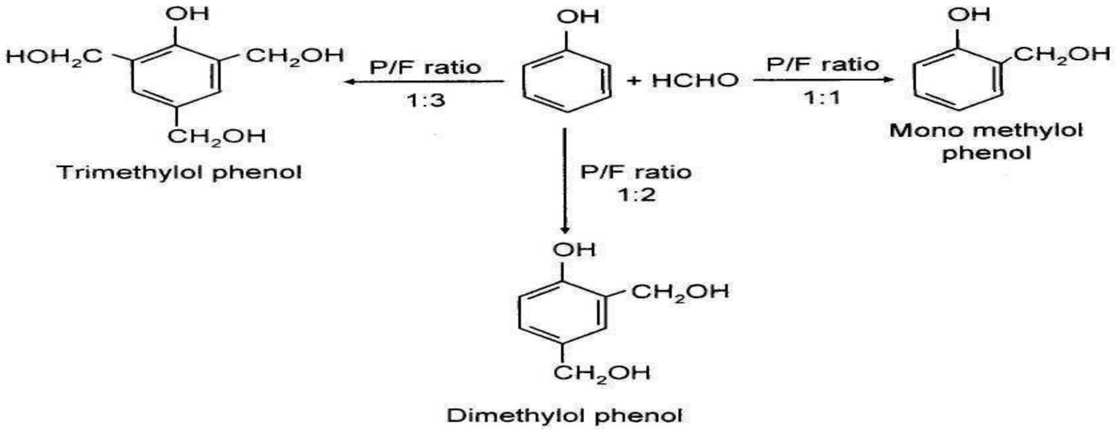
Phenol formaldehyde resins or Bakelite :

Bakelite is a condensation polymer of phenol and formaldehyde

Preparation :

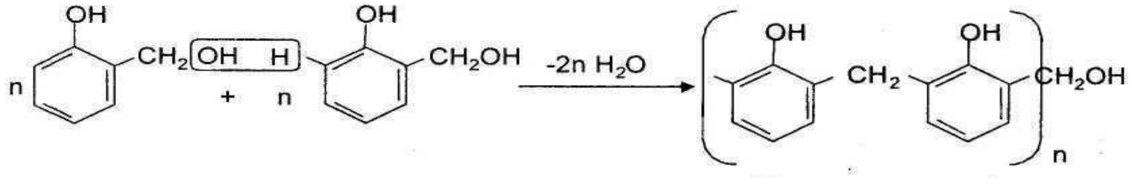
I) stage:

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

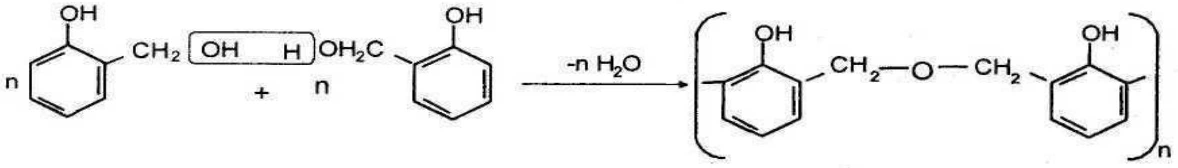


II) Stage:

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

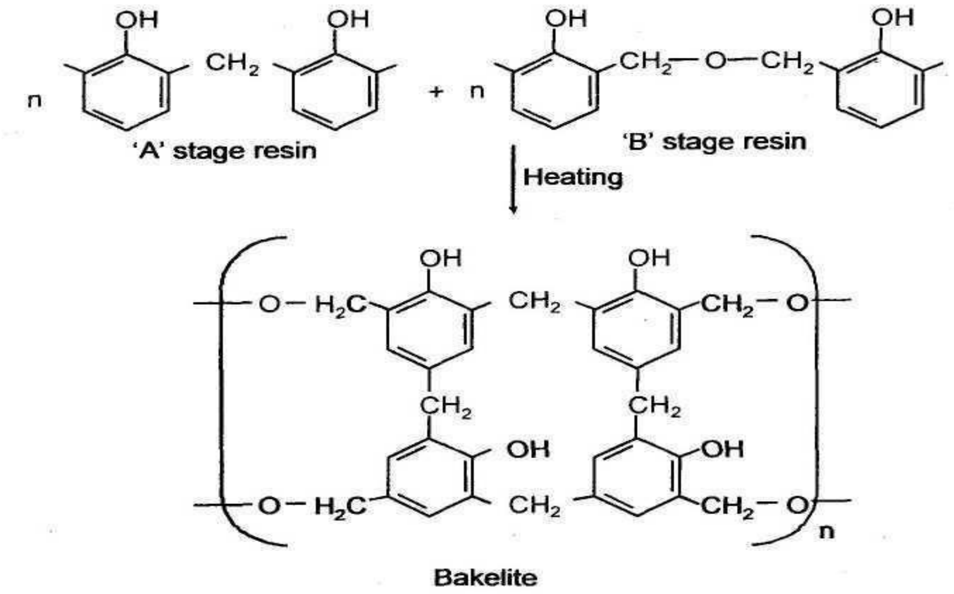


'A' stage resin/resol/Novolac



'B' stage resin/resol/Novolac

III) Stage: This stage of preparation includes heating of 'A' stage resin and 'B' stage resin together,which develops cross linking and bakelite plastic resin is produced.



Properties:

1. Bakelite plastic resin is hard, rigid, and strong.
2. It is a scratch resistant and water resistant polymer.
3. Bakelite has got good chemical resistance, resistant to acids, salts and any organic solvents, but it is attacked by alkalis due to the presence of- OH group.
4. It is a good anion exchanging resin, exchanges - OH group with any other anion.
5. Bakelite is an excellent electrical insulator.
6. It is a very good adhesive.
7. Bakelite has very good corrosion resistance, resistant to atmospheric conditions like O2, CO2, moisture, light, U.V.radiation etc.

Engineering applications: Bakelite is used widely.

1. For making electrical insulator parts like switches, switch 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.
7. For making bearings used in propeller shafts, paper industry and rolling mills.

ELASTOMERS:

- Elastomers are long chain of polymers which are highly elastic in nature.
- They can undergo very long elongation (500 – 1000%) under stress, yet regain original size fully on the release of the stress.
- The property of elastomers is known as elasticity.
- This arises due to the coiled structure of elastomers.
- The elastomers are held together by weak intermolecular forces.
- Eg: BuNa-S, Thiokol Rubber and Butyl Rubber

CHARACTERISTICS OF ELASTOMERS

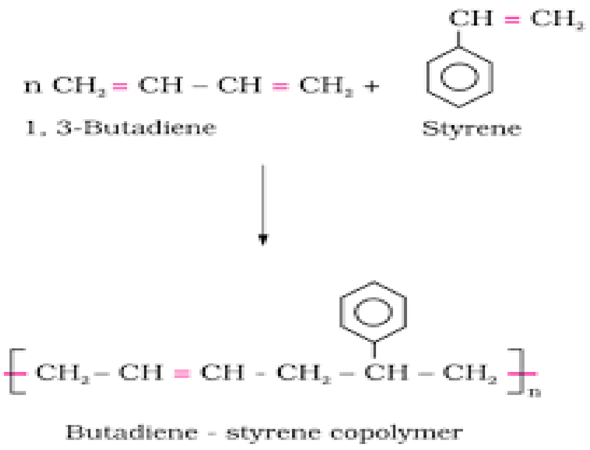
- Elastomers have linear but highly coiled structure,
- Inter chain cohesive forces are negligible because these are hydrocarbons.
- They have high degree of elasticity.
- They can retract to their original shape rapidly.

Write preparation, properties and applications of i) Buna-S ii) Thiokol

BUNA-S [or] SBR,[or] GRS) Styrene Butadiene Rubber) gov. regulated styrene rubber or Ameripol

BUNA - S is otherwise called styrene rubber or GRS (Government Rubber Styrene) or Ameripol. BUNA - S stands for the composition of the monomers and catalyst.
BU stands for Butadiene - monomer NA stands for Sodium - catalyst
S stands for Styrene - monomer

Buna-S is the most important synthetic rubber it is obtained by the co-polymerization of butadiene and styrene using sodium as a catalyst.
Preparation.



Properties:

1. Styrene rubber is a strong and tough polymer.
2. It is vulcanised by sulphur monochloride (S2CI2) 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 a good electrical insulator.
6. It is resistant to chemicals but swells in oils and attacked by even traces of ozone, present in the atmosphere.
7. Styrene rubber possess high load bearing capacity and resilience.

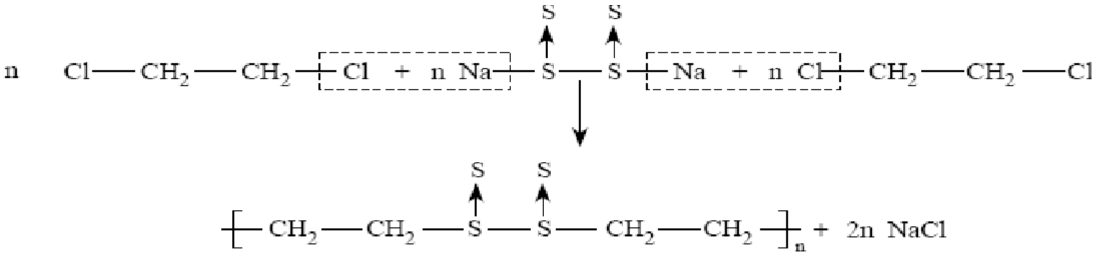
Applications:

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 components.
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 linings in chemical industries and as adhesives.

Thiokol (Polysulphide Rubber or GR-P):

Polysulphide rubbers are the condensation product of ethylene dichloride and sodium tetra sulphide.

Preparation :



Thiokol (yellow solid)

Properties:

Thiokol rubber possess strength and impermeability to gases.

This rubber cannot be vulcanized and it cannot form hard rubber.

Possess good resistance to mineral oils,fuels,oxygen,solvents,ozone and sunlight.

It is also resistant to the action of petrol lubricants and organic solvents

Applications:

1.Fabrics coated with thiokol are used for barrage balloons,life rafts and jackets. Thiokols are used for lining for canveying gasolin and oil.

2. Thiokols are used for lining for canveying gasolin and oil.

3.Used for making gaskets and seals for printing rolls.

4.Thiokol mixed with oxidizing agents in used as a fuel in rocket engine.

CONDUCTING POLYMERS:

A polymer which conducts electricity is called conducting polymer. Eg :- Polyaniline, polyacetylene, polypyrrole, etc

They are classified into two types : 1) Intrinsically conducting polymers.

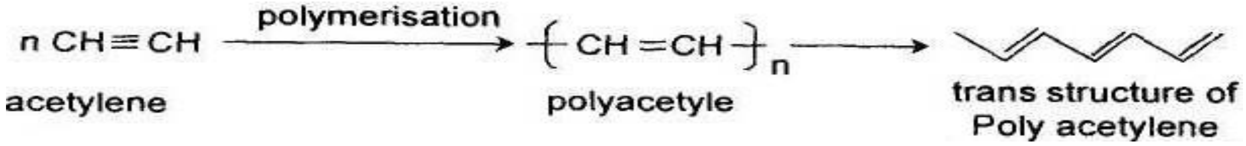
2) Extrinsically conducting polymers

1. Intrinsically conducting polymers:

These have extensive conjugation in the backbone which is responsible for conductance. These polymers can be divided into two:

a) Conducting polymers having conjugated π – electrons in the backbone: eg :- polyacetylene, polyaniline etc.

These types of polymers due to overlapping of conjugated π – electrons over the entire backbone results in the formation of valence bonds as well as conduction bands, which extends over the entire polymer molecule. But since the valence band and the conduction band are separated by a significant band gap, conductivity of these polymers is not very high.



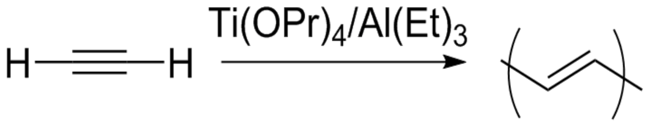
a) Doped conducting polymers:

Conductivities of polymers having conjugated π – electrons in the backbone can be increased by creating either +ve or –ve charges on the polymer backbone by oxidation or reduction. This process iscalled doping.
It can be done in two ways :

POLYACETYLENE:

- Polyacetylene is the simplest conjugated organic polymer.
- It consists of repetitive units of acetylene.

Preparation:



Polyacetylene is synthesized by the polymerization of the acetylene using Zeigler Natta catalyst, $\underline{Ti(O\textit{i}Pr)_4/Al(C_2H_5)_3}$

Properties:

- At high temperature polyacetylene gets converted to more stable trans form.
- This polymer is infusible, insoluble and becomes brittle on exposing to air.
- The conductivity is magnified by doping.

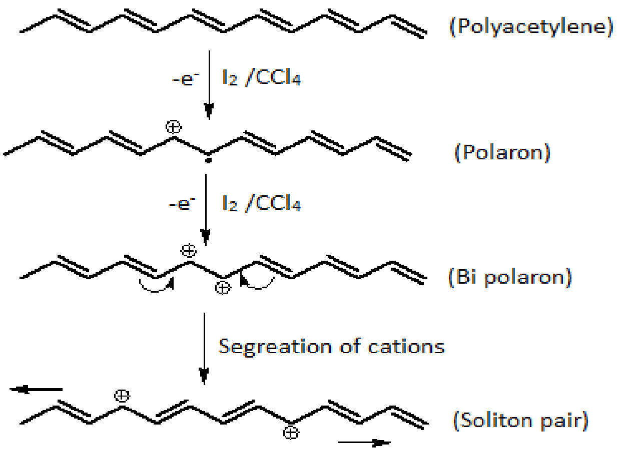
CONDUCTION MECHANISM OF POLYACETYLENE:

- The polyacetylene has a typical carbon-carbon backbone structure.
- The polyacetylene is a conjugate polymer i.e., it contains alternate single and double bonds.
- The sigma electrons dominate the mechanical properties, while the π-electrons are responsible for the electrical and optical properties of a conjugated polymer.
- The π -electrons are mobile and when doped they become anisotropic metallic conductors.
- There are two types of doping

1. P-Doping (oxidation)
2. N-Doping (Reduction)

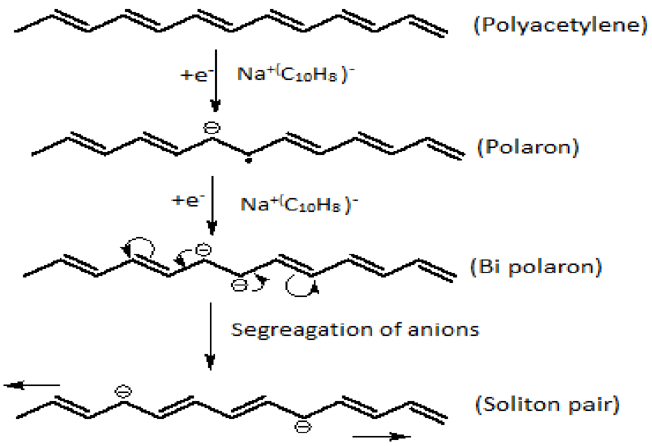
P DOPING OF POLYACETYLENE:

- In p-doping, conducting polymer having conjugation is partially oxidised using a suitable oxidising agent which leads to the formation of a delocalised radical ion called polaron.
- A second oxidation of this polaron, followed by radical recombination yields two positive charge carriers (bipolaron) on each chain which are mobile.
- Thus, these delocalised positive charges (soliton pair) are current carriers for conduction.



N DOPING OF POLYACETYLENE

- In n-doping, the reduction process leads to the formation of a polaron and bi polaron in two steps.
- This followed by recombination of radical ion yields two negative charge carriers on each chain of polyacetylene which are responsible for conduction.



APPLICATIONS OF POLYACETYLENE:

- It is used for corrosion protection, sensors, smart windows, printed circuit boards, conductive fabrics and conductive pipes for explosives
- Coating of films and semi-finished products
- Used as secondary electrode in rechargeable batteries
- Used in electro chromic display devices
- Used to produce dispersion paints

BIO-DEGRADABLE POLYMERS:

- Biodegradable polymers are defined as “the polymeric materials that undergo degradation by environmental factors like sunlight, temperature changes or by the action of micro organisms like algae, fungi and bacteria”.
- They are easily compostable and recyclable.
- Example: Polylactic acid, Poly Glycolic acid, Poly vinyl Alcohol etc.

TYPES OF BIO-DEGRADABLE POLYMERS:

Based on degradation they are of two types:
1. Naturally Biodegradable polymers: They are also called as biopolymers.
Eg: Silk, wool, cellulose and starch

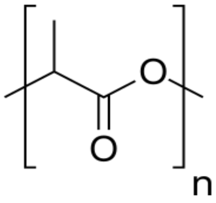
2. Synthetic Biodegradable polymers: They are of two sub-types.
a. Biosynthetic polymers:
They are produced by fermentation process by microorganisms. The rate of degradation depends and formation of metabolites depends on the structural complexity of material and the environment selected for degradation.
Eg: Lignin, Shellac, natural rubber, Albumin, Gelatin etc;
b. Synthetic biodegradable polymers:

These polymers are derived from petroleum or biological sources. These polymers undergo degradation by microorganisms and also by chemical and mechanical methods.
Eg: Poly vinyl Alcohol, PGA, PLA etc;

POLYLACTIC ACID (PLA):

- It is a biodegradable thermo plastic, aliphatic polyester derived from renewable resources such as corn starch (in USA), Tapioca products (roots, starch, mostly in Asia) and sugar cane in rest of the world.

Chemical Structure



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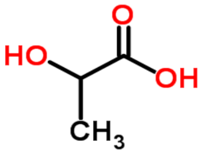
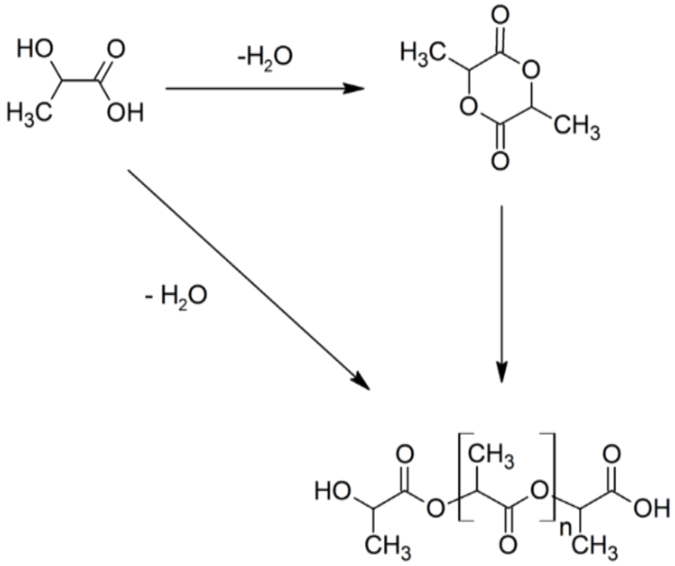


PREPARATION OF POLYLACTIC ACID:

- Oligomerisation and catalytic dimerization of lactic acid results in the formation of lactide monomer, which undergoes polymerization in the presence of stannous octate catalyst to give polylactic acid.



ADVANTAGES :

- It is ecofriendly.
- It has good mechanical and physical properties.
- It is biocompatible.

- It is nontoxic and can be metabolized by the organisms.
- It has high ductility and tensile strength.

APPLICATIONS:

- PLA is used in making disposable packing materials, bottles, cups and food containers
- It is widely used in orthopedic medical implants in the form of screws, plates, rods and tacks
- Biomedical applications include drug delivery systems, Sutures in surgery, Vascular grafts, skin tissue repair and scaffolds
- As a compostable packing material in the form of films
- Production of biodegradable synthetic garments, hygienic products and diapers