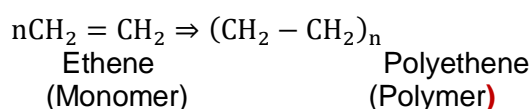


UNIT 4 POLYMERS

POLYMERS

The word 'polymer' is derived from the classical Greek words poly meaning 'many' and 'meres' meaning 'parts'. Simply stated, a polymer is a molecular compound with high molecular mass, ranging into thousands and millions of gram. It is composed of a large number of repeating units of identical structure called monomers. For example, polythene is a polymer formed by linking together of a large number of ethene molecules.



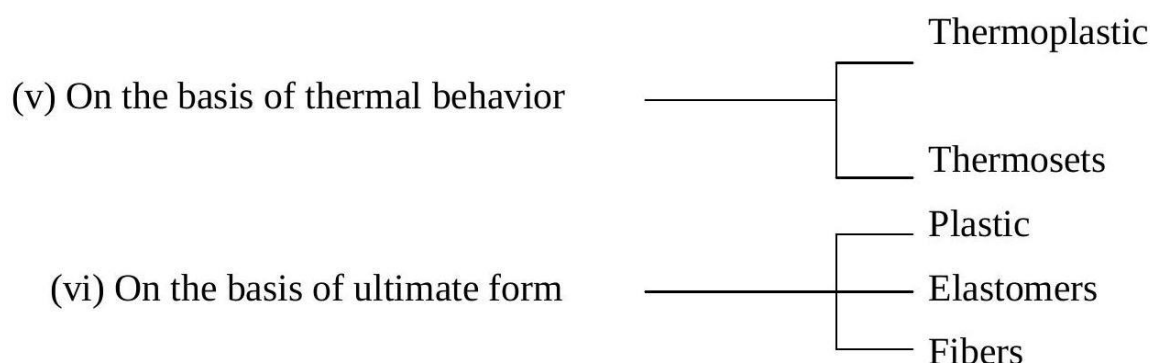
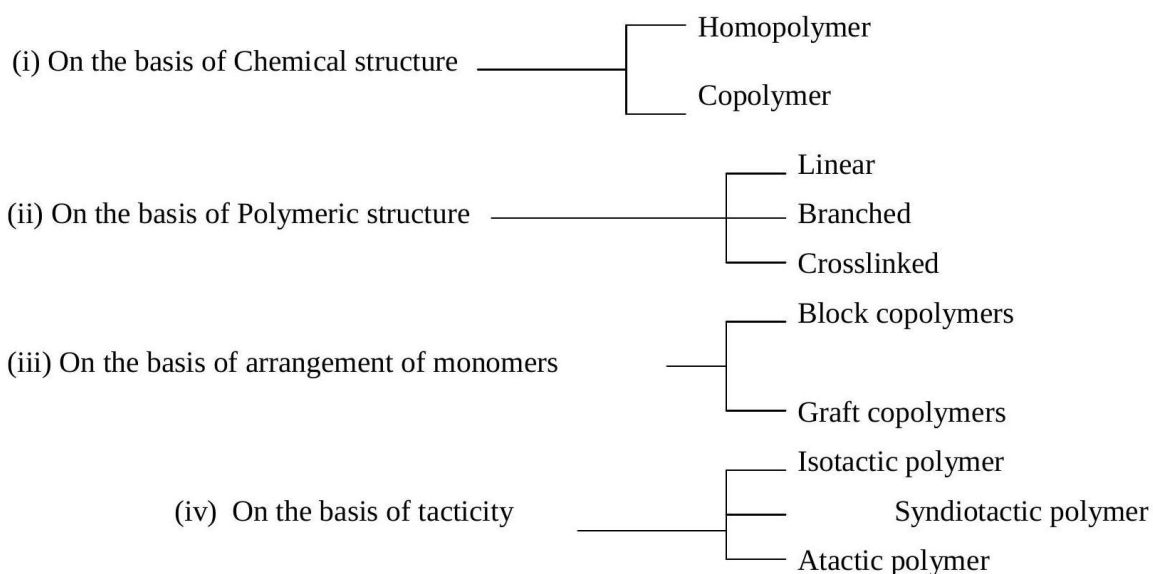
Certain polymers, such as proteins, cellulose, and silk are found in nature and hence are called natural polymers, whereas, a number of polymers are produced by synthetic routes and are called synthetic polymers. In some cases, naturally occurring polymers can also be prepared synthetically. For e.g. rubber, which is also known as polyisoprene?

Both natural and synthetic polymers impinge on every aspect of our existence. The idea is often expressed that we live in "a plastic age". The range of polymeric materials is so wide that they have found applications in practically every branch of industry. About 80% of today's chemists, including biochemists, work with polymers.

The number of repeating; units in a chain formed in a polymer, is known as the "degree of polymerization". Polymers with high degree of polymerization are termed as "high polymers" and those with low degree of polymerization are called oligopolymers.

CLASSIFICATION OF POLYMERS

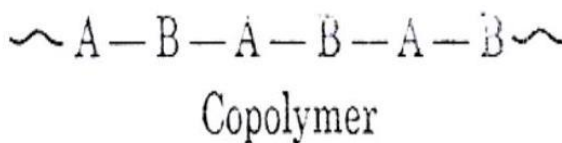
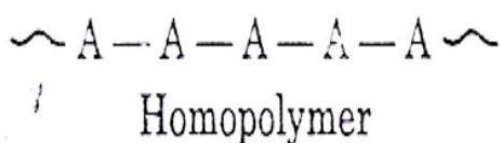
Synthetic polymers have been classified into various groups, in various manners.



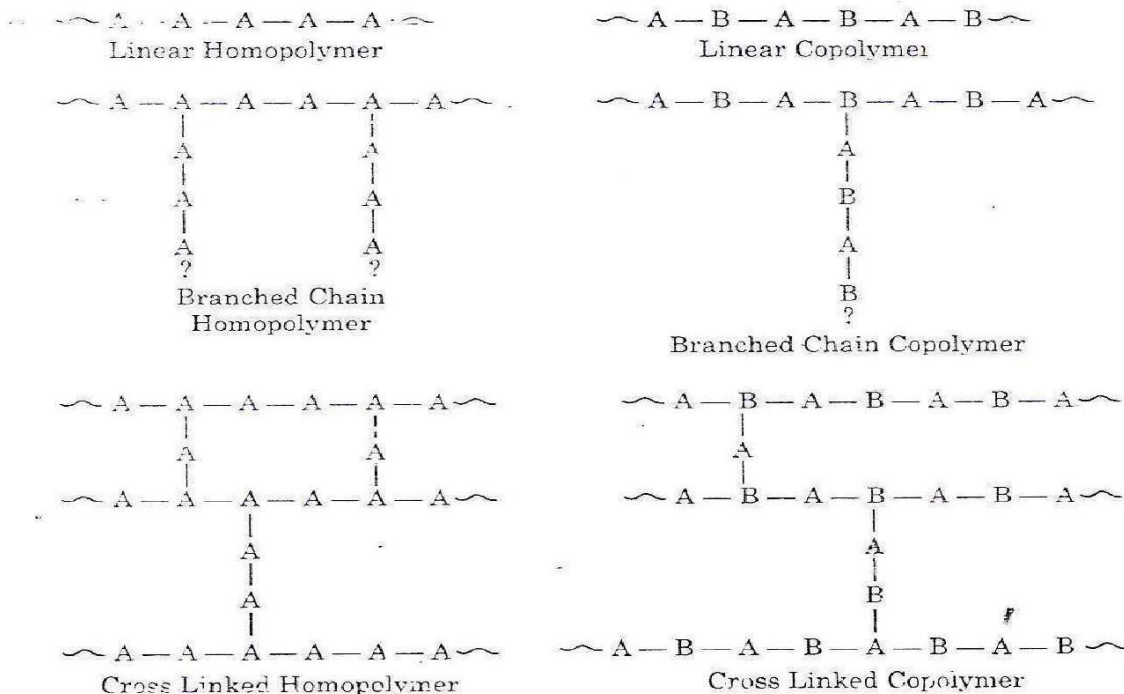
(i) On the basis of the chemical structure of their backbone, polymers are of two types:

Homopolymer: If a polymer consists of identical monomer, the polymer is termed as homopolymer.

Copolymer: If the polymer is a mixture of more than one type of monomer it is termed as copolymer.

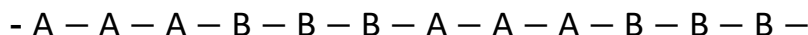


- (ii) On the basis of their polymeric structures, the polymers can be classified as linear, branched or Crosslinked.

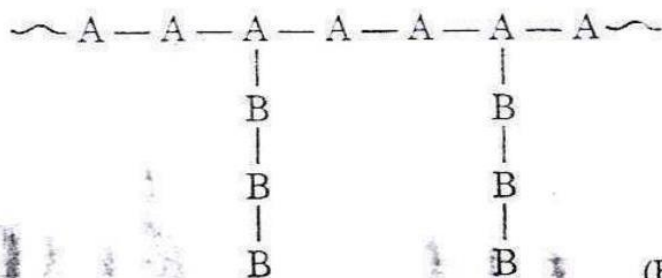


- (iii) Depending upon the arrangement of the monomers in the case of copolymers, the polymers are divided into block copolymers and graft copolymers.

Block Copolymers: Linear polymers in which the identical monomeric units occur in relatively long sequences are called block co-polymers.



Graft Copolymers: Graft copolymers are branched copolymers in which the backbone is formed from one type of monomer and branches are formed of the other, i.e., the monomer segments on the branches and backbone are not the same.



Graft Copolymer

(HOMOCHAIN POLYMER)

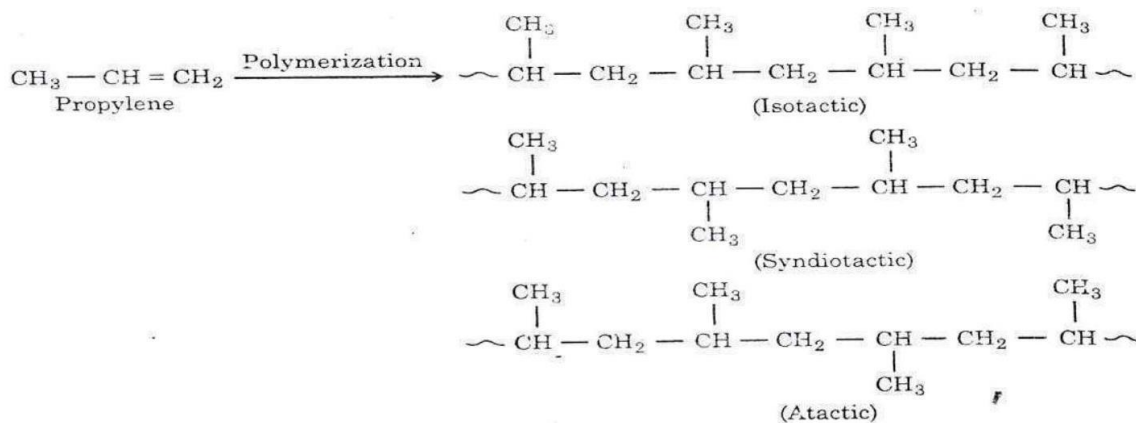
(HETROCHAIN POLYMER)

- (iv) Depending upon the orientation of monomer units in a polymer molecule: With respect to the main chain the polymers are classified as:

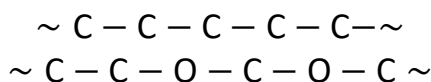
Isotactic polymer: If the side groups of the monomers lie on the same side of the chain, it is called an "isotactic" polymer.

Syndiotactic polymer: If the side groups are arranged in an alternate fashion, it is called syndiotactic polymer.

Atactic polymer: If the side groups are arranged in irregular fashion on randomly around the main chain, it is called atactic polymer.



- (v) If the main chain is composed of the atoms of the same specie, the polymer is called homochain and if the main chain is made up of different atoms then they are called heterochain polymers.



- (vi) According to their behavior on heating, the polymers are divided into two groups.

Thermoplastics: Those polymers, which soften on heating and become plastic so that they can be converted to any shape by moulding, are known as thermoplastics.

Thermosets: Those polymers which change irreversibly into hard and rigid materials on heating and cannot be reshaped, once they are set are called thermosets. They form infusible and insoluble mass on heating.

Plastics: All the synthetic polymers (other than elastomers) are usually referred to as plastics. The polymers, which are shaped into hard and tough utility articles by the application of heat and pressure, are called plastics. At some stage of manufacture, these are in plastic condition (Plasticity is the property by virtue of which a material undergoes permanent deformation under stress).

Elastomers: The polymers which are capable of being stretched rapidly at least 150 percent of their original length without breaking and return to their original shape on release of stress is known as elastomers. Synthetic rubbers constitute important of this group.

FUNCTIONALITY

The functionality of a molecule is the number of reactive sites it has. For a substance to act as a monomer, it must have two reactive sites. In other words, they should have functionality of at least two. A compound assumes functionality because of the presence of reactive functional groups present in a compound defines its functionality. For example -

Compound	Chemical Formula	Functionality
Acetic Acid	CH_3COOH	1
Molonic acid	$\text{HOOCCH}_2\text{COOH}$	2
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	1
Ethylene glycol	$\text{HOCH}_2\text{CH}_2\text{OH}$	2
Lactic acid	$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	2
Tartaric acid	$\text{HOOC}(\text{CHOH})_2\text{COOH}$	4

'vinyl' category, addition polymerization is also customarily termed as vinyl polymerization.

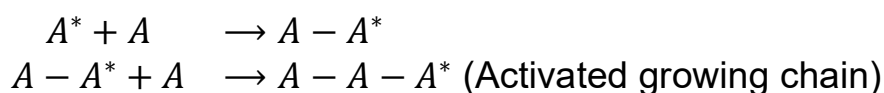
MECHANISM OF ADDITION POLYMERIZATION

Addition polymerization is a typical chain reaction and consists of three important steps:

(i) Initiation of the formation of active centers.

A A* (Excited monomer)

(ii) Chain propagation



(iii) Chain termination or removal of active centre.



(vii) The process of addition polymerization can be brought about by three methods:

1. Free radical mechanism
2. Ionic mechanism (Anionic and Cationic)
3. Coordination mechanism

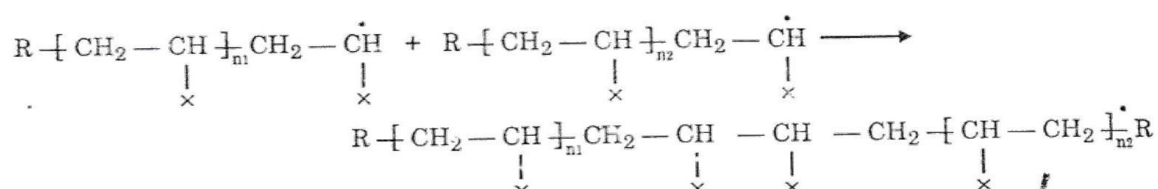
The three types of mechanisms for addition polymerization, depending upon the active centres formed, are discussed below.

1. Free **Radical Addition** Polymerization: The free radical addition polymerization involves the formation of free radicals in the initiation step, which can be produced by decomposition of compounds called initiators. The free radical polymerization has three principal steps:
 - (i) Initiation: Initiation in a free radical polymerization consists of two steps. The first is the 'generation of the free radical species, followed by the second step which involves the addition of a single monomer molecule to the free radical. The generation of free radical takes place as a result of homolytic dissociation of an initiator, which may take place in the presence of heat energy, light

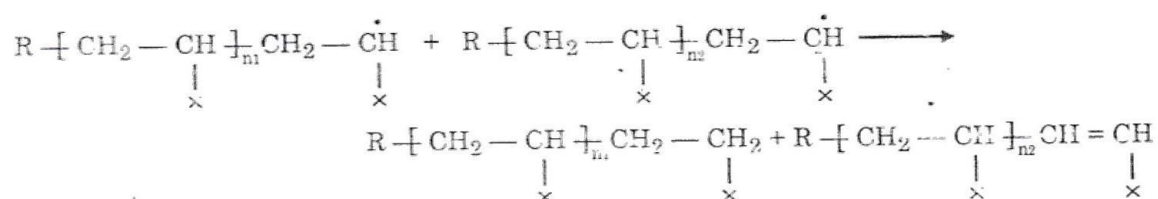
The propagation step involves a continuing attack on fresh monomer molecules which, in turn, keep successively adding to the growing chain one after another.

(iii) Termination: Propagation will continue until some termination process takes place. The propagating polymer chain is terminated by any of the following reactions.

(a) By combination: Since the decomposition of the initiator produces many free radicals at the same time, each one of them can initiate and propagate the growth of a number of chains simultaneously. The two growing chains may come close and collide with each other and get deactivated.

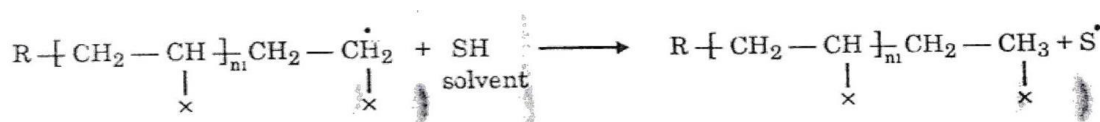


(b) By disproportionation: In some cases, one hydrogen atom from one growing chain is abstracted by the other growing chain and results in the formation of two polymer molecules, one saturated and other unsaturated. In this case the termination process results in the formation of two polymer molecules of shorter chain length as against a single molecule of a longer chain length obtained by first method.



Thus the products so formed do not contain any reactive sites and may be termed as dead polymers as these cannot grow further.

(c) In addition to the above two methods of chain termination, chain transfer by hydrogen abstraction from solvent molecule, may also terminate the growing chain.



In this reaction the original growing chain is terminated whereas the new chain gets initiated by the solvent free radical, hence this is called termination by chain transfer. Certain chemical compounds, which are capable of inhibiting or completely stopping the chain growth process, are called radical inhibitors. Phenolic compounds are widely used as inhibitors, because phenolic hydrogen can be easily abstracted by the polymer chain. The phenolic free radical so formed is highly stabilized and no further reaction is possible. Hydroquinone is often added as inhibitor.

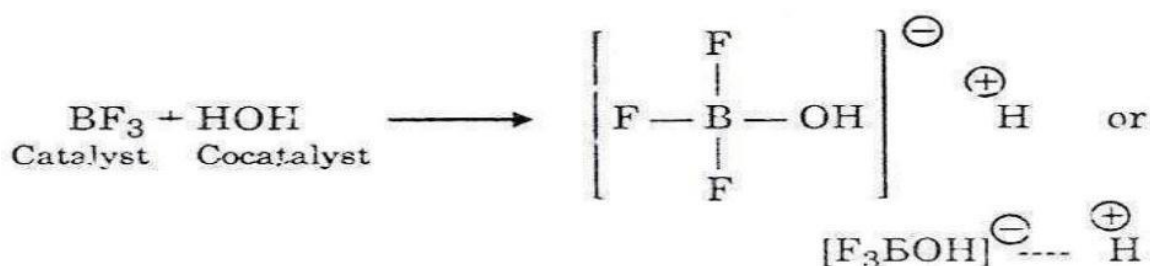
Polythene, polypropylene, styrene etc. are some of the polymers that can prepare by free radical polymerization. Branching and cross linking during the free-radical addition polymerization.

2. Ionic Addition Polymerization: Ionic polymerization follow the same basic steps as freeradical addition polymerization i.e. initiation, propagation and termination, in this process, the initiation step involves the formation of carbonium ion or the carbanion as the active site and hence the polymerization can be termed as cationic or anionic polymerization respectively.

(i) Cationic Polymerization

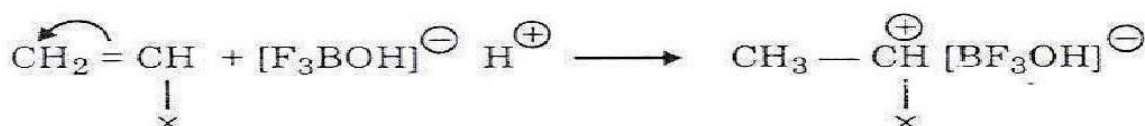
Cationic polymerization takes place in the presence of catalyst that is regenerated at the end of polymerization (in contrast to free radical and anionic polymerization where the catalyst added become incorporated into the terminated Polymer chain) Polymerization of vinyl monomers with an electron-donating group (such as - OC₂H₅ -OCH₃ - C₆H₅ etc.) may take place by a cationic mechanism which involves the following steps.

Initiation: This step involves the formation of a carbonium ion by the attack of a proton on the monomer. Any strong Lewis acid like BF₃, AlCl₃ etc can be used as a catalyst. In this case a cocatalyst like water is required to provide the proton source.

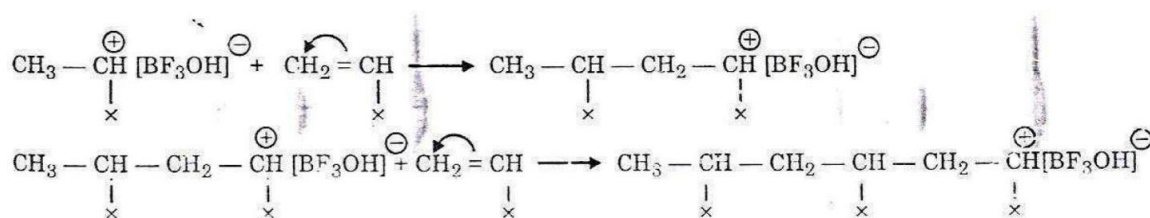


H^{+} is the initiator and $[\text{F}_3\text{BOH}]^{-}$ is the counter ion.

The H^{+} now attacks the π electron of the monomer and forms the carbonium ion. The counter ion $[\text{F}_3\text{BOH}]^{-}$ anion faces the growing chain end.



Propagation: The propagation reaction involves the addition of monomer units and simultaneous transfer of the charge to the newly added monomer unit.

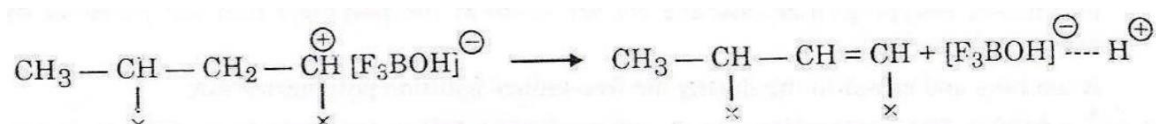


More and more units are added up and the chain keeps on growing. The electron pair of the adding monomer units are pulled in a direction opposite to the growth of the chain and the positive charge keeps on moving in the direction of the chain growth. The counter ion $[\text{BF}_3\text{OH}]^{-}$, moves along the positive charge all the time.

Termination: Termination takes place when the growing polymer chain having C^{+} collides with an anion, which may be added deliberately or with the counter ion.

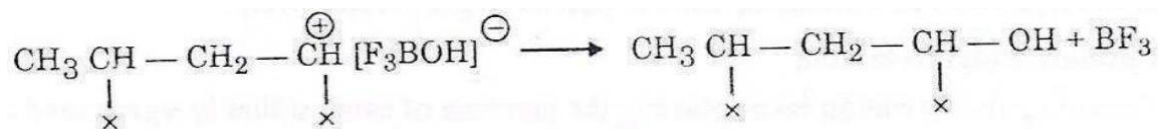
The possible reactions may be:

(a) Donation of a portion to the counter by the growing polymer chain. This results in the formation of a double bond at the end of growing polymer molecule.



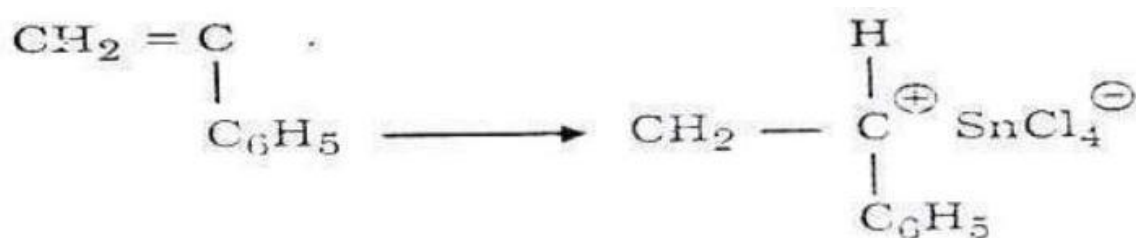
Thus the initiator or catalyst is regenerated.

(b) Formation of covalent bond between the carbonium ion and the counterion (coupling):

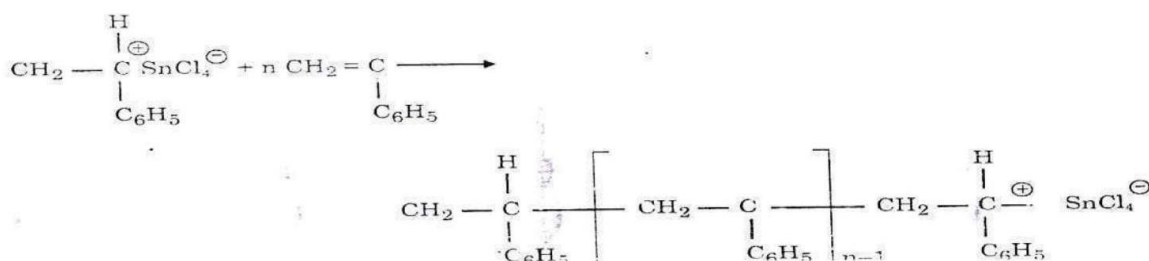


In this case also the regeneration of the initiator takes place.

Examples of the monomers that can undergo cationic polymerization are isobutylene, styrene methyl styrene and many vinyl others. Cationic

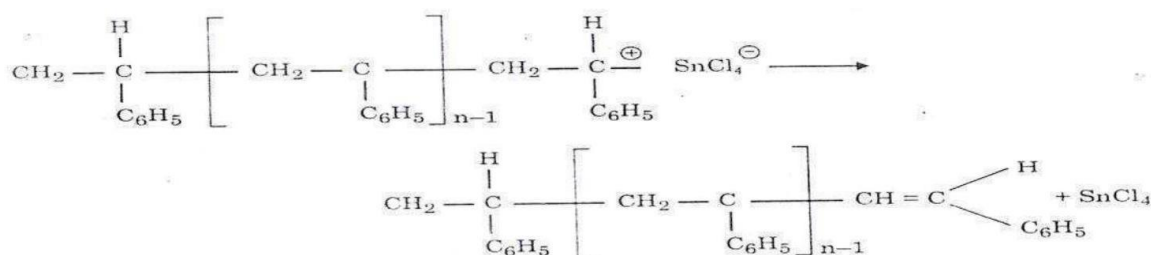


Propagation Carbonium ion attaches the another molecule of styrene.



More and more styrene molecules are added and the charge is simultaneously transferred to the newly added monomer unit.

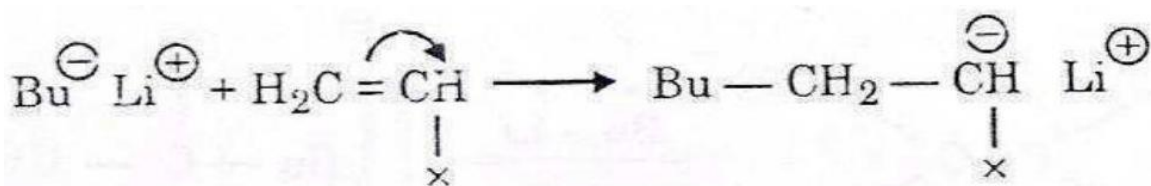
Termination: Termination takes places by donation of a proton to the counter ion by growing polymer chain forming a double bond



(ii) Anionic Polymerization

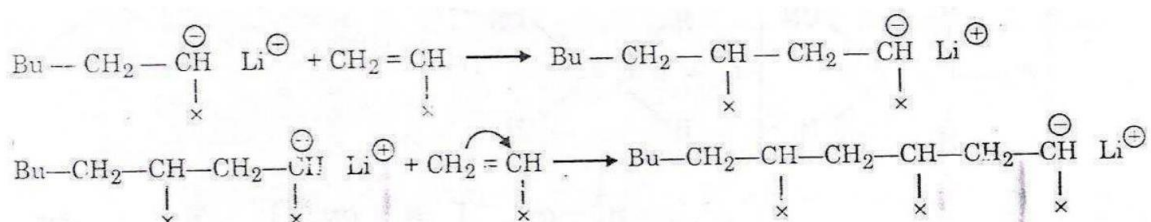
Anionic polymerization involves the formation of the carbanion in the initiation step. Polymerization of vinyl monomers with an electron withdrawing group can proceed by an anionic mechanism, involving the following steps:

Initiation: The initiators or the catalysts used in anionic addition polymerization are strong bases such as organo alkali compounds (alkyl or aryl derivatives of alkali metals) like n-butyl lithium, ethyl sodium etc. Alkali metal amides, hydroxides etc. can also be used.



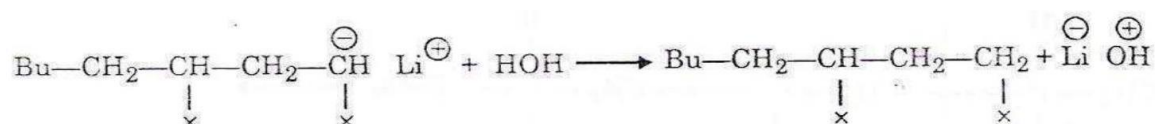
The electron pair in this case is pushed to the end of the molecule forming the carbanion. Li^{\oplus} is the counter ion.

Propagation: The carbanion formed, propagates the chain growth by attacking the second monomer **PAI** unit, pushing its electron pair further away to the end and forming a sigma bond with the new monomer unit.



In the case of anionic polymerization the movement of the PAI electrons is towards the direction of the chain growth (in cationic polymerization, the movement of the PAI electrons is opposite to the chain growth).

Termination: The termination in anionic polymerization is not a spontaneous process. If the starting reagents are pure and no impurities are present, propagation can proceed indefinitely or until all the monomer is consumed. Termination is generally accomplished by the transfer of negative charge to a species which is not directly involved in the reaction. For example CO_2 , methanol, water etc.

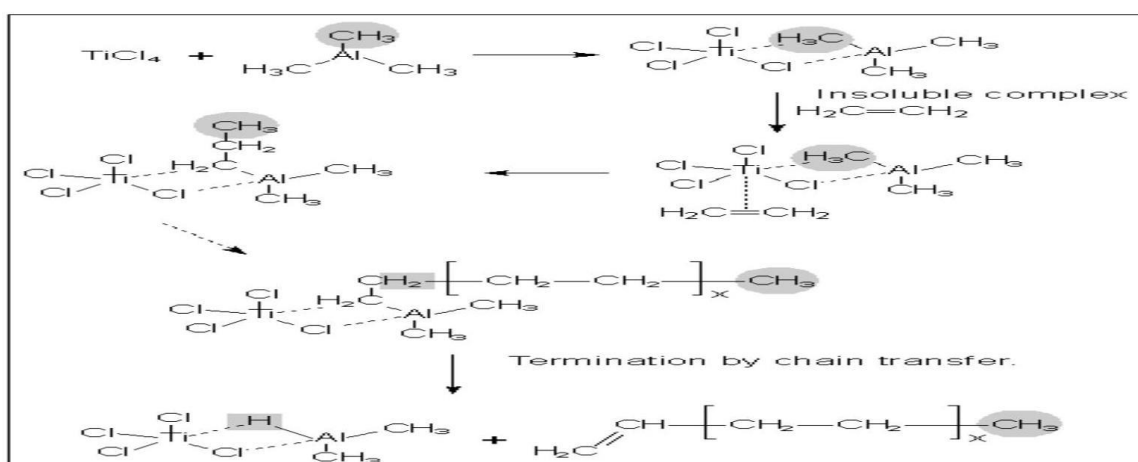


3. Coordination Polymerization: Polymerization reactions, taking place in the presence of organometallic compounds as catalysts, are termed as coordination polymerizations.

Zeigler (1953) and Natta (1955) discovered that in the presence of a catalyst which is a combination of a transition metal halide (like TiCl_4 or TiCl_3) with organo-metallic compounds (like triethyl aluminium), stereoregular polymers can be prepared. The combination is often referred to as, ZeiglerNatta catalyst. The commonly used Zeigler-Natta is trhethylaluminium in combination with titanium trichloride.

In the formation of the monomer catalyst complex, a co-ordinate bond is involved between a carbon atom of a monomer and metal atom of the catalyst that is why, this type of polymerization is known as coordination polymerization. The co-ordinate metal-carbon bond formed in the monomer-catalyst complex acts as an active center from where propagation starts.

Mechanism of coordination polymerization can be illustrated as follows:



Coordination polymerization is used to prepare stereospecific polypropylene; polydiene etc. polypropylene of nearly 90% isotacticity can be prepared. The exact mechanism of coordination polymerization is still unclear.

Condensation Polymerization

Condensation polymerization is brought about by monomers containing two or more reactive functional groups with the elimination of small molecules like O , HCl etc. For example, It is seen from the above reaction that the polymer formed still contains both the reactive functional groups at its chain ends and hence, is 'active' and not 'dead'. In the above example, the different type of reactive functional groups, viz. $-\text{NH}_2$ and $-\text{COOH}$ are present on two different monomers. In some cases, both the reactive groups may be present on the same monomer and hence lead to self-condensation reaction. For example, polycondensation of amino acids. Some polycondensation reactions leading to different types of polymers are:

- Polycondensation of dihydric alcohols and dicarboxylic acids leads to the formation of **polyesters**.
- Polycondensation of dicarboxylic acids and diamines to give **polyamides**.
- Polycondensation of dihydric alcohols and methyl esters of dicarboxylic acids to give **polyesters**.
- Self condensation of $-\text{hydrogen}$ acids yields **polyesters**.
- Self condensation of amides to form **polyamides**.
- Polycondensation of bisphenol A and phosgene to form **polycarbonate**.

COPOLYMERIZATION

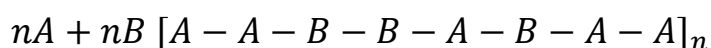
Commonly available nature and synthetic polymer suffer from many disadvantages and therefore cannot be used for special purposes. However, it is possible to modify a number of natural and commercially available synthetic polymers to give products which can be utilized for performing desired functions.

Copolymerization is the most general and powerful method of affecting modification in polymers and is widely used in the production of commercial polymers. It provides a technique to combine the properties of two or more different polymers into a single polymer. Copolymerization can be defined as any process whereby two or more monomers are copolymerized to form a single polymer. The resulting high molecular weight compound is known as copolymer. For example, butadiene and styrene, copolymerize to form butadienestyrene rubber.

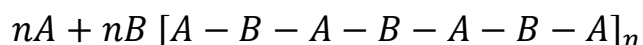
Depending upon the sequence in which different polymeric units are arranged, copolymers are of following types:

- (a) Random copolymers
- (b) Alternating copolymers
- (c) Block copolymers
- (d) Graft copolymers

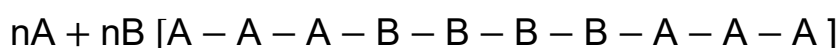
(a) Random copolymers: In random copolymers the two monomers A and B are distributed randomly along the polymer chain.



(b) Alternating copolymers: In block copolymers, a sequence or block of one monomer is followed by the block of the other monomer.



(c) Block copolymers: In block copolymers, a sequence or block of one monomer is followed by the block of the other monomer.

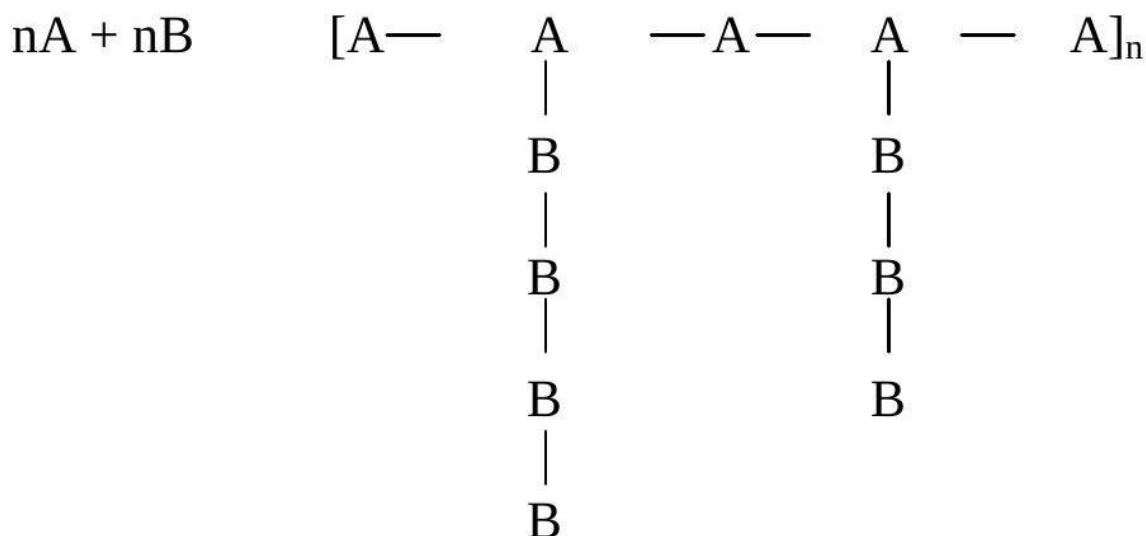


Block

(d) Graft copolymer: Graft copolymers are branched polymers and contain main chain

or backbone consisting of one monomer and branches formed from the other

monomer:



PLASTICS

As was discussed earlier, plastics are a group of artificially synthesized materials, which can be moulded into any desired form, when subjected to heat and pressure in the presence of a catalyst.

The resins are the basic binding materials, which form the major part of the plastics and determine the type of treatment needed in the moulding operations.

From an engineering point of view there are two types of resins -

- (i) Thermoplastic resins.
- (ii) Thermosetting resins.

(i) Thermoplastics: Thermoplastics or resins soften on heating and become plastic so that they can be converted to any desired shape by moulding. On cooling, they become hard and rigid but their hardness is a temporary property subject to change with increase or decrease in temperature. In thermoplastic resins, the chemical structure or the molecular weight are not changed during the heating or moulding operations, because the changes involved are of physical nature. Only the secondary bonds between the individual molecular chains are broken on heating which results in their softening. On cooling, these secondary bonds are again formed and hence they become hard again. Some common examples of thermoplastics are polyethene, polypropylene, polystyrene, polyvinyl chloride, teflon, polyacrylonitrile etc.

Plasticizer: Sometimes, the substances called plasticizers are added to improve plasticity and flexibility of the plastics. A variety of organic materials are used as plasticizers including non-drying vegetable oils, tributyl phosphate, triphenyl phosphate, triacetin camphor, esters of oleic or stearic acid.

(ii) Thermosetting resins: Thermosetting resins are those, which upon heating, change irreversibly into hard and rigid materials on heating. After cooling, if the set article is again heated, it will not soften again. The thermosetting resins during moulding acquire three-dimensional cross-linked structures with predominantly covalent bonds, which retain their strength even on heating. Thus, the three dimensional network structure joined by strong covalent bonds make the thermosetting resins harder, stronger and more brittle than thermoplastic resins, if heating of a thermoset resin is prolonged, these undergo change in chemical composition to give a hard, infusible and insoluble mass. Some common examples include phenol formaldehyde, malamine formaldehyde, alkyds, epoxy resins etc.

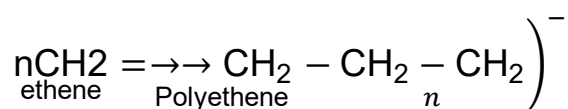
Difference between Thermoplastics and Thermosetting Resins

	Thermoplastic	Thermosetting Resin
1.	They are generally long chain linear polymers.	They have three dimensional crosslinked network structure joined by strong covalent bonds.
2.	On heating, they soften readily because secondary forces between the chain can be easily broken.	They do not soften on heating because cross links and strong covalent bonds retain their strength on heating. They can, however, be changed on strong heating.
3.	They can be softened, reshaped and even reused by reheating to a suitable temperature.	They can not be reshaped and reused because they do not soften on heating and retain their shape and structure.
4.	They are generally weak, soft and less brittle.	They are usually hard, strong and more brittle.
5.	They can be reclaimed from waste.	They can not be reclaimed from waste.

6.	They can dissolve in some organic solvents.	They are insoluble almost in all organic solvents because of the presence of cross linking and strong covalent bonds.
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COMMERCIALY IMPORTANT THERMOPLASTICS

1. **Polyethene:** Ethylene, one of the most important petrochemicals, may be polymerized by a number of methods to produce thermoplastic polymer, polyethene.



The starting material (monomer) is obtained either by dehydration of alcohol or by the cracking of petroleum. There are two varieties of polyethylenes, viz., low density polyethylene (LDPE) and high density polyethylene (HDPE).

(a) **LDPE** : Low density polyethylene is prepared by polymerizing ethylene at high pressures (1000-5000 atm) at a temperature of 250°C in the presence of oxygen as a free radical initiator. LDPE consists of highly branched structure, which does not allow the polymeric chains to pack close together and hence results in low density (0.91 to 0.925 g/cm³) of the polymer.

Properties:

- (i) Low-density polyethylene melts at 110 – 125°C and is only 40 – 50% crystalline.
- (ii) It has low density (0.91 g/cm³).
- (iii) It is a transparent polymer having moderate tensile strength and high toughness.
- (iv) It is chemically inert, slightly flexible and poor electrical conductor.
- (v) Its elasticity is preserved even at lower temperatures
- (vi) It is moisture resistant.

Uses:

- (i) LDPE films are mainly used for packing and wrapping frozen food, textile products etc because of their flexibility, chemical and moisture resistance.
- (ii) The non-polar nature of the polymer makes it suitable for insulation for electric wires and cables.
- (iii) Its inertness to chemicals and resistance to breakage makes it a useful material for the manufacture of 'squeeze bottles' and in many attractive containers.

(iv) It is also used for making pipes for agricultural, irrigation and cold water plumbing and chemical plants,

(b) HDPE: High-density polyethylene is prepared by polymerizing ethylene at low pressure (3200 – 2000 atm) and at a temperature of 180 – 200°C in the presence of metal oxide catalysts. HDPE can also be produced by using Ziegler Natta catalyst by coordination polymerization. In this second method ethylene is heated to 60 – 200°C under a pressure of 6-7 atmospheres in the presence of a catalyst consisting of triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst). The polyethene so produced consists of linear chains of polymer molecules which pack close together resulting in high density polyethene (0.97 g/cm³).

Properties:

- (i) High density polyethene has melting point in the range of 145 – 150°C and is 90% crystalline,
- (ii) It possesses density in the range of 0.941 to 0.965 g/cm³.
- (iii) It is much stiffer than LDPE and has higher tensile strength and hardness.
- (iv) It is chemical resistant and has significantly lower gas permeability.
- (v) Insulating and moisture resistant properties are similar to LDPE.
- (vi) Due to high crystallinity, it has low gas and water vapour permeability.

Uses:

- (i) HDPE is used in the manufacture of toys, crates closures, caps, buckets etc because it is more tough and stiffer than LDPE.
- (ii) Its greaseproof nature and chemical inertness makes it suitable for wrapping material for food products.
- (iii) Low gas permeability makes it suitable for domestic gas piping.
- (iv) It is also used for manufacturing bottles for milk, household chemicals and drug packaging.
- (v) It is used in the manufacture of overhead tanks for water storage.

Whenever high tensile strength and stiffness are required HDPE finds better use than LDPE.

2. Polypropylene: Polypropylene is probably the lightest known industrial polymer and can be prepared in isotactic, syndiotactic or atactic forms. The monomer propylene is obtained as a byproduct from gasoline refineries. Polypropylene

(isotactic) is produced by polymerizing propylene in the presence of Ziegler-Natta catalyst $[\text{Al}(\text{C}_2\text{H}_5)_3 - \text{TiCl}_4]$

Properties:

- (i) Polypropylene is stereoregular (isotactic) and highly crystalline polymer (slightly lower than HDPE).
- (ii) Isotactic polypropylene (IPP) melts at $160 - 170^\circ\text{C}$.
- (iii) It exhibits high stiffness, hardness and tensile strength,
- (iv) Its moisture resistance is comparable to that of polyethylene.
- (v) Polypropylene is resistant to many chemicals such as alkalis, acids and oils. But due to presence of methyl groups attached to alternate carbon atoms, it is susceptible to oxidation.
- (vi) Its electrical properties are similar to polyethylene.
- (vii) Films of polypropylene are impermeable to a number of vapours and gases.

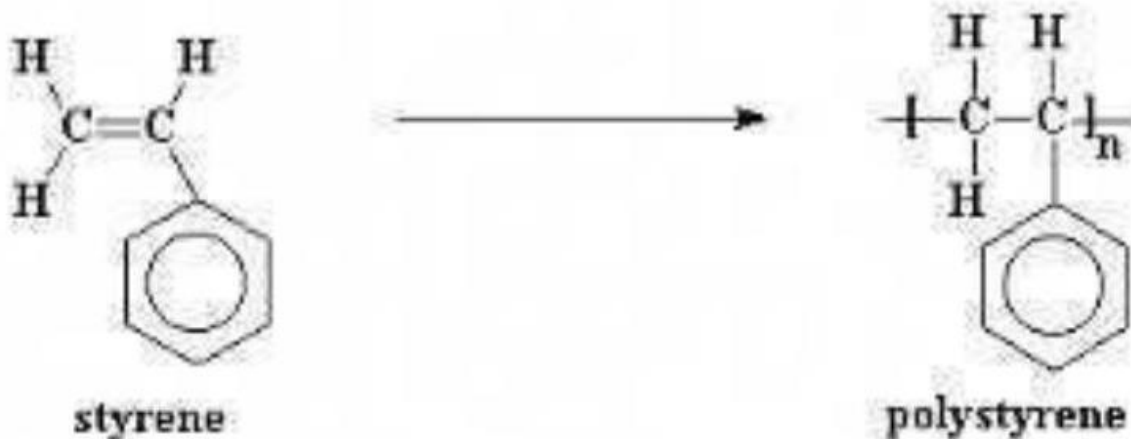
Uses:

- (i) The higher melting point of polypropylene allows it to be used in products that must be steam sterilized such as baby bottles, flasks etc.
- (ii) Its fibres are extremely strong by weight and hence are used in making ropes and filaments; it is also used for the manufacture of drinking glasses.
- (iii) Polypropylene films are used to: packaging due to high clarity and their impermeable nature to a number of vapours and gases. It is also used for wrapping confectionary items (bread, biscuits etc) and potato chips.
- (iv) Due to high strength, rigidity and temperature and chemical resistance it is used for the production of chemical process equipments such as pipes and tanks.
- (v) It is used for the preparation of textile machinery parts (bobbins, spools, spindles etc), when blended with suitable elastomer it is widely used for making bumpers, radiator grills etc.
- (vi) It is also used as an insulating material for electrical wires.

3. Polystyrene: Polystyrene is also known as polyvinyl benzene. The monomer styrene is produced from ethylene and benzene. When ethylene is passed into benzene in the presence of AlCl_3 catalyst, ethyl benzene is formed, which on passing over iron oxide catalyst at high temperatures is converted into styrene.

Properties:

(i) Polystyrene is refractive high brilliance.



monomer

transparent and has high index (1.6) which gives it

(ii) It has got low heat distortion temperature (85°C) and hence articles made of polystyrene cannot be sterilized with steam.

(iii) It consists generally of linear chains and is chemically inert and resistant to most alkalies, oxidising and reducing agents and acids.

(iv) It is susceptible to photooxidative degradation, which results in brittleness and yellowing.

(v) It has got excellent moisture resistance.

(vi) It has good electrical insulating properties.

(vii) It can be dyed to different colors.

(viii) It has the unique property of transmitting light of all wavelengths through curved sections.

(ix) Polystyrene is attacked by a number of solvents.

Uses:

(i) Polystyrene is widely used in the manufacture of articles such as lids, jars, bottles, combs, brush handles, radio and television cabinets.

(ii) It is used for preparing synthetic ion exchange resins in combination with p-divinyl benzene.

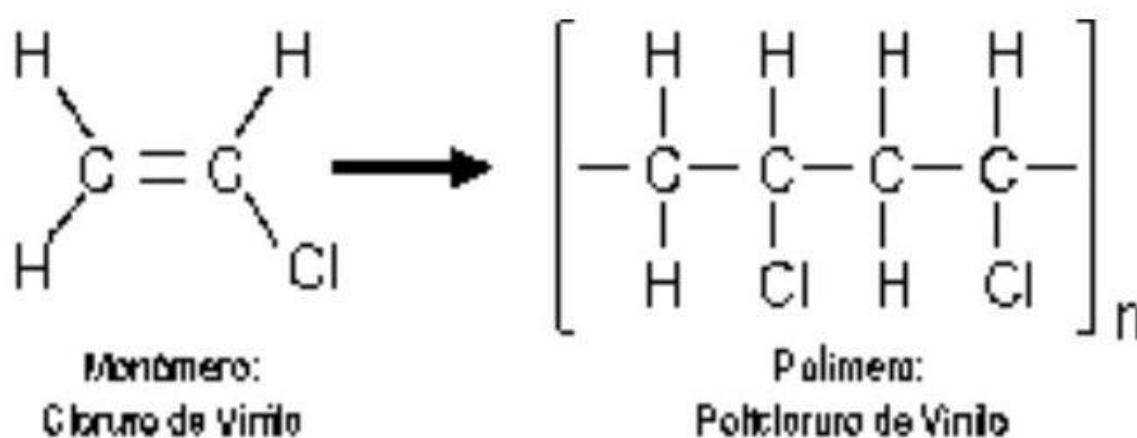
(iii) An important use of polystyrene is the manufacture of foam and bead for insulation and packaging material. The polymer is foamed by using blowing agents, usually pentane.

(iv) High-impact polystyrene (HIPS), produced by combination of polystyrene with rubbery material such as polybutadiene (SBR). Contributes to improved impact properties and is used for door liners, inner liners of refrigerators, etc.

(v) Polystyrene copolymerized with acrylonitrile and butadiene (ABS), due to its high impact resistance and high dimensional stability at elevated temperatures is used in the manufacture of door handles, radiator grills, loudspeaker housings etc.

(vi) Styreneacrylonitrile (SAN) copolymer is a transparent plastic with very good impact strength and is used for moulding crockery items and machine components.

4. Polyvinyl Chloride (PVC): Polyvinyl chloride is one of the cheapest and most widely used plastic globally. The monomer vinyl chloride is a gas, boiling at -14°C . Polyvinyl chloride is prepared by the polymerization of vinyl chloride by heating its water emulsion in presence of a small amount of benzoyl peroxide.



Properties:

- (i) It is colourless, odourless and non-inflammable.
- (ii) PVC is partially syndiotactic and has low crystallinity.
- (ii) PVC is thermally not very stable and degrades above 200°C , with the evolution of HCL.
- (iv) It is resistant to atmospheric oxygen, inorganic acids and alkalies.
- (v) It has greater abrasion and flex resistance compared to leather.

- (vi) It is water proof and washable
- (vii) It is less brittle and lighter when compared to glass.

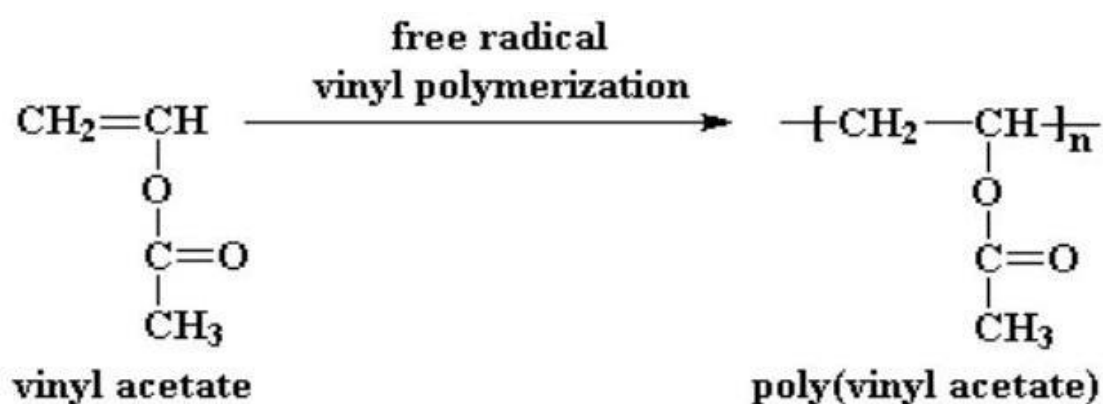
Uses: (Rigid PVC)

- (i) Rigid PVC or unplasticized PVC has superior chemical resistance and high rigidity but is brittle. It is used as sheets for tank linings, safety helmets, and mudguards.
- (ii) It is used for making window frames as a substitute for wood because the frames do not corrode.
- (iii) It is used for the manufacture of containers for detergents, cosmetics, mineral water.
- (iv) Because of its oil-resistant property, it is used for storing consumable liquids like edible oils, fruit squashes, table wine etc.

(Plasticized PVC)

- (i) Plasticized PVC is used as an insulating material.
- (ii) Because it is washable and has greater abrasion resistance therefore it is used for making ladies-handbags, bathroom curtains, kitchen upholstery.
- (iii) Used for upholstery for seats in public transport vehicles,
- (iv) In the film form it is used in membrane separation technology.

5. Polyvinylacetate (PVA): Polyvinyl acetate is produced by heating vinyl acetate in the presence of small amount of benzoyl peroxide.



Properties

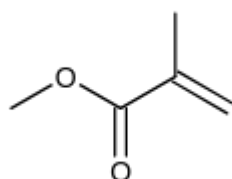
- (i) Polyvinyl acetate is a solid, clear resin, and has no taste or odour and is soft sticky material.
- (ii) It is insoluble in water and is saponified with great difficulty and hence is not absorbed by the digestive system. Moreover if at all saponification takes place, the products polyvinyl alcohol and acetic acid are not harmful. Due to the above-stated reasons, polyvinyl acetate is used as a basic material for chewing gums and surgical dressings.
- (iii) It is resistant to atmospheric oxygen, water and chemicals.

Uses

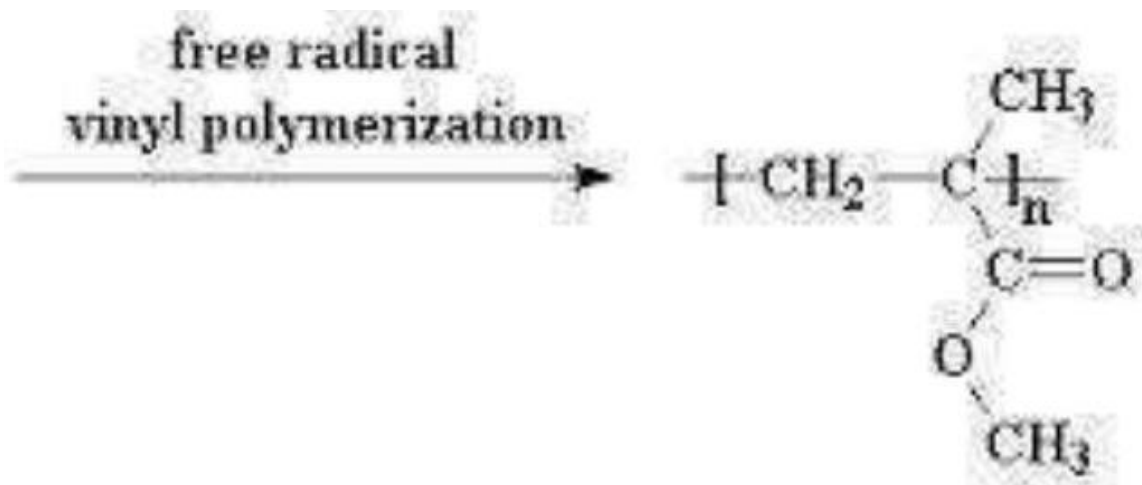
- (i) Polyvinyl acetate is used for the manufacture of lacquers, paints and adhesives. Polyvinyl acetate adhesives are used for bonding of textile to textile, leather to leather/paper to paper, paper to textile, leather to wood etc.
- (ii) It is used as a basic material for chewing gum and surgical dressings.
- (iii) It is also used for finishing of textile fabrics.
- (iv) On copolymerization with polyvinyl chloride, it is converted into a polymer having varying degree of softness. For example, vinylite, which is a copolymer of polyvinyl acetate and polyvinyl chloride, is especially useful as a surface coating material for metals.
- (v) It is mainly used for the manufacture of polyvinyl alcohol.

Polyvinyl butyral is tough and elastic and is used for laminating safety glass. It holds the broken pieces of glass in case of accident and thus minimizes the danger from flying glass fragments.

5. Polymethylmethacrylate (PMMA): Polymethyl methacrylate (PMMA) is one of the important thermoplastic from commercial point of view, because of its outstanding optical properties. It is prepared by the polymerization of methylmethacrylate in presence of free radical initiator such as peroxides.



methyl methacrylate



poly(methyl methacrylate)

Properties

- (i) It is a colorless transparent plastic with an excellent outdoor life period and good strength.
- (ii) Owing to the presence of bulky side groups, it is amorphous in nature.
- (iii) It can be depolymerized to yield back the monomer.
- (iv) It has high softening point of about 130 – 140°C but it becomes rubber-like at a temperature above 65°C.
- (v) The main feature of this plastic is its high optical transparency and capacity of transmitting light accurately, even in curved sections.
- (vi) It has good mechanical properties but has poor scratch resistance as compared to glass.
- (vii) It has low chemical resistance to hot acids and alkalies.
- (viii) It has excellent weathering properties.

Uses

- (i) PMMA is the nearest alternative to glass as it does not shatter and can be moulded into any shape. Infact, PMMA sheets known as plexiglass or lucite are used as an alternative to glass.
- (ii) PMMA finds major use in automotive industry (e.g. housing for rear lamps, profiles, light fittings, ceiling lighting signal-light etc).
- (iii) It is used for making hard contact lenses due to its high transparency.
- (iv) It is used as composite materials for kitchen sinks, basins and bathtubs because

it provides wide range of colour and are cheap and light.

(v) PMMA is also used for making windscreens T. V. screens etc. The fragments formed after cracking are less sharp and hence less harmful.

(vi) It is also used for decorative purposes such as in jewellery etc. (vii) It is also used in bone splints, artificial eyes, dentures etc.

6. Polytetrafluoro Ethylene (Teflon) (PTFE): Polytetra fluoroethylene is prepared by the polymerization of tetrafluoroethylene ($\text{CF}_2 = \text{CF}_2$), under high pressure in presence of benzoyl peroxide as catalyst.

The polymerization is associated with the release of large quantities of heat and if sufficient precautions are not taken, this can result in violent explosions.

n



Properties

(i) PTFE has a highly regular structure and is highly crystalline.

(ii) Due to the presence of highly electronegative fluorine atoms and regular configuration of PTFE molecule there are very strong attractive forces between different chains, which give the material extreme toughness.

(iii) PTFE has high softening point of about 327°C . above 400°C it decomposes without changing into vapour.

(iv) It is extremely resistant to attack by chemicals such as strong alkalis and acids. Only hot alkali metals and hot fluorine can attack PTFE.

(v) PTFE is highly dense polymer (2.1 to 2.3 g/cm³) having excellent mechanical properties.

(vi) It can be machined, punched and drilled.

(vii) It has a very low coefficient of friction

(viii) It has extremely good electrical insulating properties.

(ix) It is slippery and waxy to touch.

(x) It does not melt like other thermoplastics and hence behaves somewhat like a

thermosetting polymer.

(xi) It has non-adhesive characteristics.

Uses

(i) Due to its chemical inertness, it is used in chemical carrying pipes, tubing's, stop-cock for burettes,

(ii) Its extreme inertness and stability to temperature makes it a suitable material for making gaskets and seals.

(iii) It is used as an insulating material for transformers, cables, wires, fittings etc.

(iv) Because of its low coefficient of friction, it is used in non-lubricating bearings.

(v) Its most important application is, as non-stick coming for Dots and pan.,. PTFE is applied as a coating over the rollers and mixing equipments used for preparing sticky materials such as adhesives and jams.

(vi) Its fiber is used to form belts, filter cloth etc.

(a) Polyamides: Polyamides are a group of polymers which contain the amide (-CONH-) linkage in the main polymer chain.. Polymers of this type are the synthetic linear aliphatic polyamides, which are capable of fibre formation.

Nylon is the generic name for synthetic polyamides capable of forming fibres.

Polyamides (nylons) are prepared by the polycondensation between dicarboxylic acids and diamines. Nylons are designated by two numbers, the first representing the diamine. Polyamides of commercial importance are Nylon 6.6; Nylon 6, 10, Nylon 6 etc.

(i) Nylon 6.6: Nylon 6,6 is prepared by the polycondensation of hexamethylene diamine with adipic acid.

Properties of Nylons

(i) Nylons are characterized by a combination of high strength, elasticity, toughness and abrasion resistance.

(ii) They have very good moisture resistance.

(iii) They are insoluble in common solvents.

(iv) The molecular chains are held together to each other by hydrogen bonds having linear structure, permitting side-by-side alignment.

(v) They are very flexible and retain their original shape after use.

(vi) Nylons provide excellent resistance to wear and abrasion

(vii) Due to the presence of hydrogen bonding, all nylons are water sensitive. Water acts as plasticizer, which reduces tensile strength and dimensional stability.

Uses

- (i) Nylon 6.6 is used as a plastic as well as a fibre. Its most important fibre applications include automobile tire cords, ropes, threads, cords having high tenacity and good elasticity.
- (ii) Nylon 6.6 is also used to make textile fibres for use in dresses, undergarments, socks etc.
- (iii) Nylon 6.6 being a tough plastic is used/as a substitute for metals in gears and bearings etc. Nylon 6.6 can be moulded in one piece whereas similar item in metal require assembling of several parts. Moreover, nylon bearings and gears perform quietly and need little or no lubrication.
- (iv) It is also used in making rollers, slides and door latches.
- (v) Nylon 6.10 is not used much as synthetic fibre, but is used to manufacture articles like brushes and bristles.
- (vi) Nylon 11, is used as textile fibre.
- (vii) Due to its good barrier properties, nylon-6 film is used for packaging some oxygen sensitive food.
- (viii) Due to its high tenacity, nylon is suitably used for parachute fabric. (ix) Nylons are also used in making transmission belting, ribbons for electric typewriters, spindle bands on textile spinning machines etc because of its high durability, (x) Nylon is also used for making insect screens because of their biological resistance.
- Aromatic polyamides, often called aramids have been produced to improve the heat and flame-resistance of nylons. These polymers have very high melting points (greater than 500°C). One such nylon is Kevlar. It is prepared by polycondensation between aromatic dichloride and aromatic diamines.

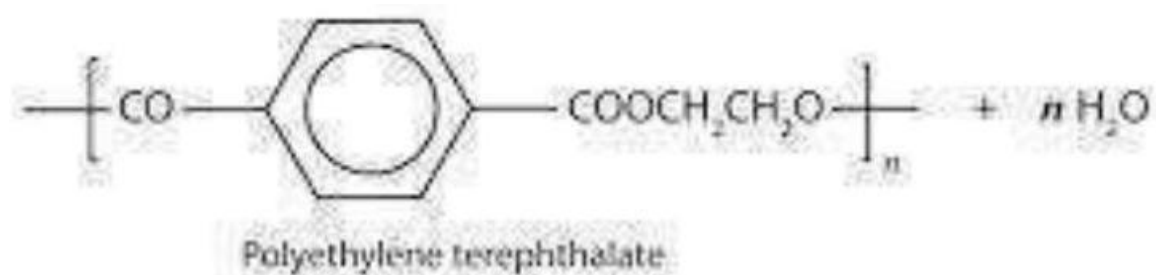
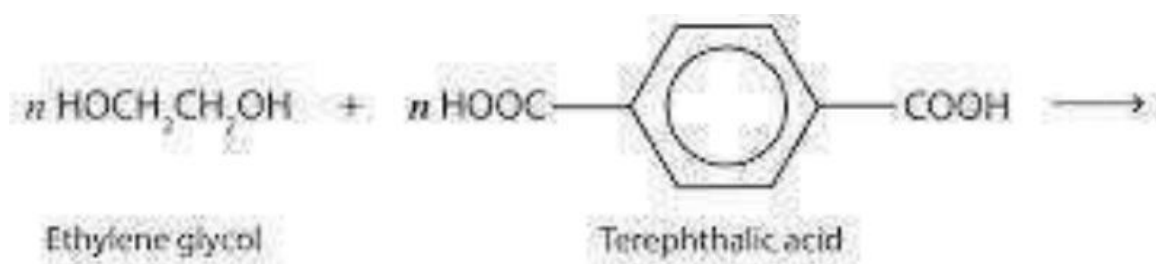
Kevlar is exceptionally strong and decomposes only above 500°C . It is 5 times stronger than steel and it is used as a substitute for steel in belted radial tires as well as in bullet resistant vests. It is also used in making car parts such as tyres, brackets, clutch linings etc.

COMMERCIALLY IMPORTANT THERMOSETTING RESINS

1. Polyesters: Polyester resins are the condensation products of dicarboxylic acid with dihydroxy alcohols. The industrially most important polyester is poly(ethylene terephthalate) (PET), with the trade name Terylene or Dacron. PET can be prepared from terephthalic acid and ethylene glycol, either by direct esterification or by catalyzed ester interchange. Nowadays, dimethyl terephthalate is used instead of terephthalic acid. This is because of the fact that terephthalic acid is nonvolatile and is very slightly soluble in most of the solvents. The reaction takes place in two successive

stages:

The ethylene glycol so formed is distilled off at such high temperature.



Properties

- (i) PET is resistant to heat and moisture.
- (ii) It is strongly resistant to both weak acids and bases at room temperature but readily attacked by strong acids and bases.
- (iii) Presence of numerous polar groups results in powerful dipole attractions in it.
- (iv) It has good mechanical strength up to 175°C.
- (v) It is resistant to almost all kinds of insect attacks.
- (i) It can be dyed at 100°C or in presence of a carrier.
- (ii) The fibre has good wrinkle resistance due to good elasticity,
- (iii) PET fibres are abrasion and oxidation resistant.

Uses:

- (i) PET is mostly used for making synthetic fibres like Terylene, Dacron etc. Garments made from its fibres resist the formation of wrinkles and have many desirable properties such as warmth to touch, low moisture absorption (and hence dry rapidly), crease resistance, shape retention, and mildew proof. Moreover, these may be blended with other fibres, such as wool and cotton.
- (ii) PET is also useful for making films because of its high strength, resistance to

tearing durability, transparency etc. PET is used in making the transparencies of overhead projector.

(iii) Due to its impermeability to a number of organic and inorganic gases it is used in the manufacture of plastic bottles for carbonated beverages (barrier to CO_2 and water)

(iv) It is also used to make magnetic recording tapes.

(v) Due to their high dielectric strength they are used for electrical insulation.

(vi) Glass reinforced PET is used for the manufacture of housings-for coffee machines, car heaters, toasters.

2. Phenolic Resins: Phenol formaldehyde resins are the most important and extensively used synthetic plastics and perhaps the oldest synthetic plastics. In these resins one of the monomers is always a phenol molecule. One of the most important member of this class is

Phenol formaldehyde resin.

The phenol formaldehyde reaction is catalyzed by alkalies and acids. The nature of the product depends on several factors, the major one being the nature of the catalyst and the proportion of the reactants (phenol formaldehyde ratio). The formation of phenol formaldehyde resin comprises of the following steps:

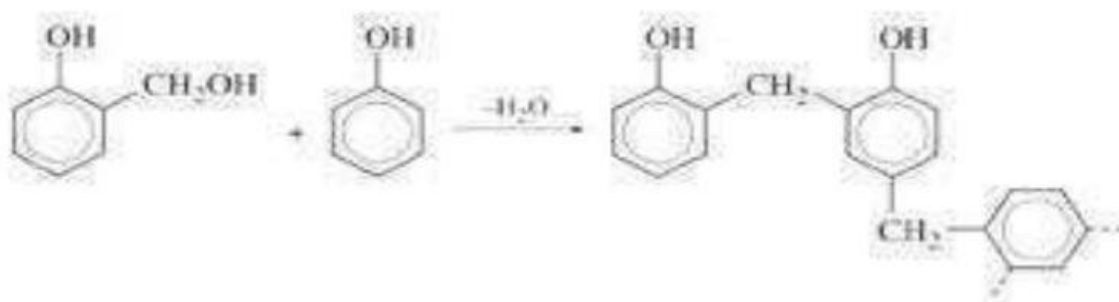
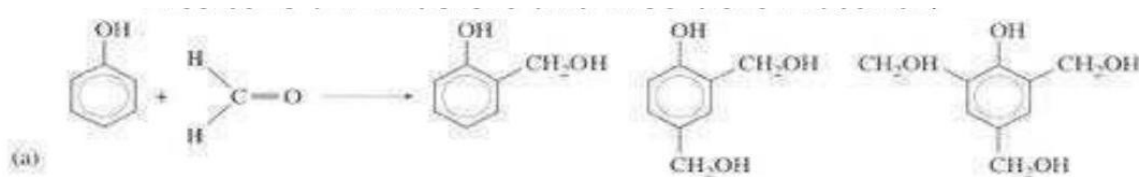
(i) Methylation: When phenol and formaldehyde react together, the first step is the entry of methylol (CH_2OH) groups in ortho and para positions to the hydroxy group. The reaction takes place in the presence of acid or alkali. Depending upon phenol formaldehyde ratio, various phenol-alcohols may be formed.

(ii) Novolac formation: Depending upon the ratio of phenol formaldehyde (P/F) different resins, namely novolac and resol resins are obtained. In the presence of acid catalyst, when the P/F ratio is greater than unity, the methylol derivatives condense with phenol to form a linear polymer with little methylol groups. The product is thermoplastic in nature and is known as novolac.

(iii) Resole formation: In the presence of alkaline catalysts with P/F ratio less than 3, the methylol phenols condense to form linear structure called resoles. The resoles are soluble in the reaction mixture and have excess of methylol groups capable of further reaction during continued heating. Resols, therefore have limited shelf-life. However, the reaction may be stopped at the desired step by cooling.

(iv) Resin formation: On further heating, resole is transformed into a three dimensional polymer, called resin, due to the presence of active groups and mobile

hydrogens Resite is an infusible and insoluble material.



(b)



Properties

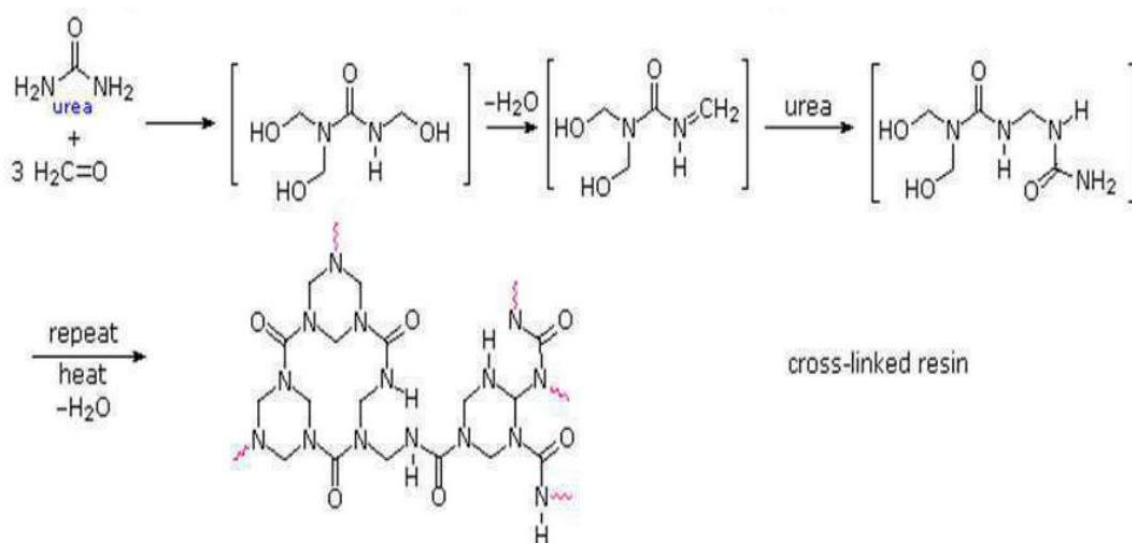
- (i) Phenol formaldehyde moulding resins have excellent heat resistance.
- (ii) These have high dimensional stability.
- (iii) To improve the properties further, fillers such as wood, flour, mica, asbestos etc are added to them.
- (iv) Phenolic resins have good dielectric properties.
- (v) These have remarkable adhesive properties and bonding strength.
- (vi) They are however attacked by alkalis, because of the presence of free hydroxy groups.
- (vii) They are hard, rigid and scratch-resistant.

Uses Phenolic resins have wide applications.

- (i) The main use of phenolic resin is in moulding applications. They are widely used in making telephone parts, cabinets for radio, television and automobile parts
- (ii) Due to their adhesive properties and bonding strength, they are used for producing brake linings, abrasive wheels and sand paper.
- (iii) They are used for making electric insulator parts like switches, plugs, switch boards, heater-handles etc,
- (iv) Phenolic resins are used for impregnating paper, wood and other fillers.
- (v) These are also used in varnishes, paints and protective coatings.
- (vi) These are used in the production of ion exchange resin for water softening.

4. Amine Resins: Amino resins or amino plasts are prepared by the reactions of formaldehyde with nitrogen compounds such as urea, melamine and other amino compounds. Because of their attractive light colours, these resins have great commercial importance.

- (a) Urea formaldehyde resins: This is prepared by the condensation reaction between urea and formaldehyde in neutral or alkaline conditions. The first products formed during the formation of resin are monomethylol and dimethylol ureas.
- (ii) Polymerization can take place from mono or dimethylol urea, or possibly through both, with the formation of long chains.
- (iii) Thermosetting of the resin takes place during the moulding process. For moulding, the methylol derivatives are compound with fillers, plasticizers, pigments etc. and then are subjected to heat and pressure, resulting into a hard, infusible product.



Properties

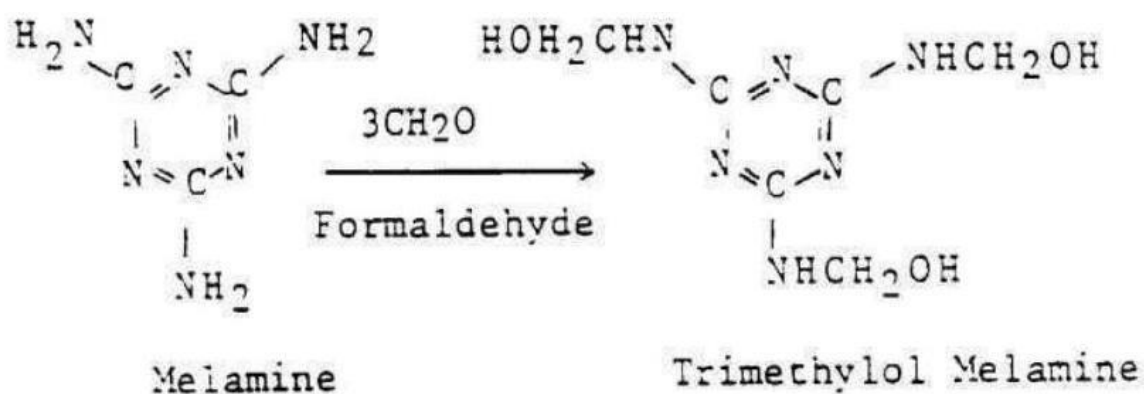
- (i) The urea formaldehyde resins are light in colour and enable the production of light or pastel coloured objects.
- (ii) Their heat and moisture resistance are lower than those of phenolic resins.
- (iii) They have good electrical insulating properties.
- (iv) They are resistant to oxidation to oil, grease and weak acids.
- (v) They are hard, resist abrasion and scratching.
- (vi) They have good adhesive properties.

Uses

- (i) Urea-formaldehyde resins are widely used to make moulded articles like vacuum flask cups jugs buttons, bottle caps etc where the darker colour of phenolics may be objectionable.
- (ii) They are also used for adhesive applications for the production of plywood and laminating.
- (ii) They are used for the manufacture of coated abrasive paper and binder for foundry

cores.

- (iv) They are used for the manufacture of cation exchange resins.
 - (v) These also find use in the manufacture of electrical switches, plugs and insulating foams,
 - (vi) Their applications also include the treatment of textile fibers for improving their shrink and crease resistance.
- (b) Melamine-formaldehyde resin: Melamine formaldehyde resins are another class of amino resins. They are produced by the condensation of melamine (2,4,6 triamino – 1,3,5 triazine), trimer of dicyandiamide with formaldehyde, exactly in the same manner as in the formation of urea formaldehyde resin. The reaction takes place under mild alkaline or neutral conditions.



Properties:

(i) The melamine resins have better hardness, heat resistance, and moisture resistance than the urea - formaldehyde resins. However these are expensive. Rest of the properties is similar to urea-formaldehyde resins.

Uses

- (i) Typical applications of urea formaldehyde resins include the production of decorative plastic ware, laminated worktops.
- (ii) They are used in electrical fittings.
- (iii) They are used for resin bonded grinding wheels.
- (iv) They are used for textile finishing providing crease resistance, stiffness, water repellency etc.
- (v) They are also used in automotive finishes.
- (vi) Melamine resins are also used as a tanning material for leather. The presence of small amount of this resin in the tanning material improves the strength of the leather.
- (vii) They are also used for the preparation of lacquer

RUBBERS (ELASTOMERS)

It was discussed in the beginning of the chapter that depending on the ultimate form and use a polymer can be classified into two broad categories: Plastics and Elastomers (rubbers).

Elastomers are the polymers which are capable of being stretched rapidly at least 150 percent of their original length without breaking and return to their original shape on release of stress. For example, rubber band is a typical elastomeric material. When stretched, it is elongated to many times its length. But when the force is released it gets back to its original length.

The properties of typical elastomers are defined by the following:

- They must stretch rapidly and considerably when stretched, reaching high elongations (500-1000%).
- They must exhibit high tensile strength and high stiffness when fully stretched.
- They must snap back to their original length once the stretching force is withdrawn or the stress is released.

These criteria are met with the materials which:

- Have high molecular mass (high polymers).
- Are above their glass transition temperature.
- Are amorphous.
- Contain a network of crosslinks to restrain gross mobility of its chains.

Columbus on this voyage to America found the native of West Indies were playing with the solid mass collected from the exudate of a tree. Years later, Joseph Priestly showed that this solid mass could rub off pencil marks from paper and hence the material was called rubber. The main source of natural rubber is the species of tree known as 'Hevea Basiliensis' even today, which account for multibillion-dollar rubber industry. Rubber or elastomers can be obtained naturally or synthetically. Consequently we have natural rubber and synthetic rubber.

NATURAL RUBBER

Natural rubber of nearly same characteristics occur in the inner bark and to a lesser extent in the leaves and roots of a number of tropical plants But the latex from the tree 'Hevea Basiliensis' is proved to be the main source of rubber. Latex is an emulsion of poly hydrocarbon droplets in an aqueous solution and looks like milk. The negatively charged particles of polyhydrocarbons, a colloidal dispersion, stabilize the emulsion.

Processing

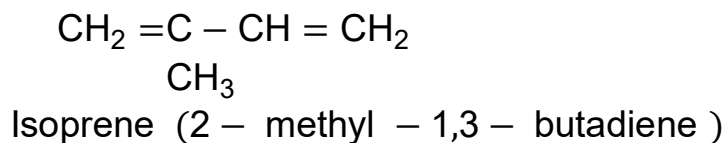
The latex is collected by making small incisions in the trees in such a manner so as to allow the latex to accumulate in small cups. The percentage of rubber in it is 25 – 35%. A fully grown tree gives about 5 gm of rubber in a day.

The average composition of the latex is:

Water = 60%; Rubber = 35%; Proteins, enzymes and nucleic acid = 3%; fatty acids

and esters = 1% and inorganic salts = 0.5%.

In these trees, the rubber is formed from polymerization of isoprene i.e. (2-methyl-1,3-butadiene) to produce poly-(cis)isoprene by a biochemical reaction in which a particular type of enzyme acts as a catalyst.



The latex is first sieved to remove the impurities such as leaves, bark etc. From 25 – 35% dry rubber content the latex is diluted to contain about 15 – 20% of rubber content. The rubber is then separated from the latex by the process of coagulation. The acetic acid or formic acid is added as coagulants and the rubber is coagulated to soft white mass. About 1 g of acetic acid/formic acid is added per 200 kg of rubber material. This coagulated mass is the crude rubber and consists of 90 – 95% rubber, 2 – 4% proteins and 1 – 2% resins. The crude rubber is washed and treated for producing the following types of rubber depending upon the process.

1. **Crepe Rubber:** Crepe rubber is prepared by adding a small amount of sodium bisulphite (NaHSO₃) to the coagulated mass to bleach the rubber. Then the rubber is passed through a creping machine. The creping machine is rolling machine which consists of two rollers having longitudinal grooves. Thus, after passing through it, the spongy rubber is converted into a sheet having a rough surface which resembles the crepe paper and hence the name.
2. **Smoked Rubber:** The smoked rubber is produced by carrying out the coagulation of latex in the tanks provided with vertical grooves on sides and fitted with metal plates which run across the width of the tank. First the diluted latex is poured into the tanks, with the metal plates removed. Then the coagulant is added (acetic or formic acid) and the plates are inserted. The tanks are kept undisturbed for 15-16 hours. The tough slabs are formed. These slabs are passed through a series of rolling machines and finally rubber sheets having ribbed pattern are obtained. The ribbed surface prevents the sticking of the rubber with each other. These sheets are then dried in smoke houses at about 50°C in the smoke obtained from burning wood or coconut shells. The smoked rubber so obtained is translucent and ambre coloured.

GUTTA PERCHA

Gutta percha is another variety of natural rubber; it is obtained from the mature leaves of *Dioscorea gupta* and *Palagum gutta* trees. The hevea rubber and gutta

percha, both are composed of isoprene units with structures shown in the figure? But natural rubber is cis-isomer where a bending back of successive isoprene units take place giving the molecule a coiled structure. The gutta percha. on the other hand is a trans-isomer which consist of straight chains, giving a rod like structure to the molecule. The rod-like structure results into close packing of adjacent chains. Thus gutta percha is more crystalline.

Processing of Gutta Percha

The mature leaves obtained from the trees *Dichopsis gutta* or *palagum gutta* are carefully ground in mills and are then treated with water maintained at 70°C for about half an hour when the gutta percha is extracted in water. The solution is dropped into cold water and gutta percha floats on the surface. Alternatively, gutta percha can be recovered by solvent extraction.

Properties of natural (Hevea)rubber and gutta percha: Natural Rubber (Hevea rubber)	Gutta Percha
1. Natural rubber is highly soft and elastic material 1000°C	Gutta percha is a hard thermoplastic material at room temperature but it softens and becomes tacky at about
2. It is soluble in carbon disuphid-: and petrol.	It is soluble in petrol,
3. It Is cis poiyisioprene	It is transpolyisoprene.

Drawbacks of Raw Rubber: Raw rubber has a number of drawbacks when put to use. Some of the drawbacks are:

- (i) Crude rubber is soft at high temperatures but becomes brittle at low temperatures. So it can be used in a limited temnerature range.
- (ii) It is too" weak with a tensile strength of 200 kg/cm²
- (iii) It is not resistant to mineral oils, organic solvents.
- (iv) It has large water absorption capacity.
- (v) Due to oxidation in air. it deteriorates and hence is durability its decreased.
- (vi) It is also attacked by the oxidizing agents like nitric acid, Conc. sulphuric acid, chromic acid etc.
- (v) It undergoes permanent deformation when stretched. This may be due to

stretching the individual chains slip past each other and get separated resulting in the breakage of the material.

(vi) However the above drawbacks can be overcome by improving the properties by the addition of suitable materials and further heat treatments.

Some of the processes for improving the properties of rubber are discussed below:

PROCESSES FOR IMPROVING THE PROPERTIES OF RUBBER

The desired properties in rubber can be obtained by compounding it with certain chemicals. The compounding of rubber is generally facilitated by a process called mastication.

Mastication: When rubber is subjected to mechanical stresses arising from say, high-speed stirring or milling, it undergoes considerable molecular degradation or fragmentation. The process is called mastication. The mastication converts hard and tough rubber into a soft, supple and semisolid mass. The $\text{CH}_2 - \text{CH}_2$ links between the isoprene units in the rubber are weak and hence break when subjected to mechanical stresses. The net effect is that the big molecule is broken into small fragments. After mastication is complete the compounding agents are added to the rubber.

Compounding: The process involving the incorporation of chemicals such as plasticizers, vulcanizing agents, stabilizers, fillers, fillers etc., into the rubber industry was discovered by Charles Goodyear in 1839. The process by which a network of crosslinks is introduced into an elastomers is called vulcanization. Charles Goodyear used sulphur to crosslink polyisoprene molecules in natural rubber. The added sulphur combines chemically at the double bonds bringing about changes in its properties profoundly. Vulcanization transforms elastomers which are a weak thermoplastic mass of no use into a strong, elastic and tough rubber. The tensile strength, stiffness, durability, resistance to changes in temperature, elasticity and chemical resistance of a vulcanized rubber are increased manifold as compared to unvulcanized rubber.

The introduction of sulphur links in between the polymer chains restrict the intermolecular movement which brings about stiffening of rubber.

The extent of stiffness of vulcanized rubber depends upon the amount of sulphur added. For example, a rubber may contain 3 to 5% sulphur whereas Vulcanite or ebonite (hard rubber) contains about 32% sulphur. The extensive Crosslinking in hard rubber makes it so stiffer that there is practically no elasticity in it. Fig. shows the effect of vulcanization on rubber. Ordinary rubber molecules are bent and

convoluted (a) When stretched the molecules can slip past one another. But vulcanization introduces crosslinks between these and hence on stretching the molecular chains cannot slip past each other.

(a) Unvulcanized Rubber

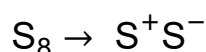
(b) Vulcanized Rubber (Unstretched)

(c) Vulcanized Rubber (Stretched)

Chemistry of Vulcanization

The addition of sulphur develops crosslinks, thereby improving the processibility and utility of rubber. But the mechanism of vulcanization is quite complex and is still not known in detail. Both free radical and ionic intermediates have been postulated. Sulphur exists as S_8 i.e. cyclo octasulphur. The probable mechanism can be:

- Sulphur (S_8) dissociates into S^+S^-



Where m and n are the numbers of sulphur atoms.

- The sulphur cation S_m^+ reacts with a diene molecule of rubber to give I .
- This cation adds to other polymer molecule to give II and carbonium ion iii
- The arlylic carbonium ion reacts with S_8 to form IV which adds to polydiene to form sulphur bridges (V). This can further react with S_8 and the cycle goes on It must be emphasized that neither heat nor sulphur is essential for the vulcanization process. Vulcanization can even be carried out by number of other substances. Hence vulcanization can be of two types:
(a) Sulphur Vulcanization: As stated earlier, in this process the rubber is heated with sulphur or CS_2 .
(b) Non-sulphur Vulcanization: Non-sulphur vulcanization is achieved through a free radical.
- Free radical can be generated from a curing agent such as benzoyl peroxide or as a step in the oxidative degradation of rubber.
- This free radical abstracts a hydrogen atom from one of the -methylene groups.
- The rubber free radical so formed attacks a double bond in an adjacent polymer chain resulting into crosslink (vulcanization) and regeneration of a free radical.
This cross linked free radical will further attacks more $C = C$ bonds to form a large number of cross linkages leading to vulcanization.

Further, the compounds such as Se, Te, ZnO, benzoyl, chloride, trinitrobenzene, etc., are also used as vulcanizing agents.

Advantages of Vulcanization

Vulcanized rubber has got ideal elastomeric properties which increase its utility manifolds. The main advantages of vulcanized rubber are:

1. **Tensile strength:** Tensile strength is the measure of the ability of a polymer to withstand pulling stresses. Vulcanized rubber has got good tensile strength and extensibility. The tensile of the raw rubber is 20 kg/cm^2 , which increases to 2000 kg/cm^2 on vulcanization.
2. **Resilience:** It is the property of a elastomers to return to its original shape on the release of stress. Resilience of vulcanized rubber improves manifolds as compared to raw rubber.
3. **Water Absorption Capacity:** The water absorption capacity of vulcanized rubber is greatly reduced.
4. **Vulcanized rubber is resistant to organic solvents** such as benzene CCl_4 , fats and oils. Though it swells in these solvents but to a lesser extent than raw rubber.
5. **Insulation Properties:** Vulcanized rubber has better insulation properties than raw rubber. Raw rubber vulcanized with 32% sulphur (ebonite) has extremely good insulating properties.
6. **Elasticity:** The elasticity of vulcanized rubber is greatly reduced. The elasticity of the vulcanized rubber depends upon the extent of vulcanization. If 30 – 50% of sulphur is present in vulcanized rubber then a rigid, non-elastomeric plastic (ebonite or hard rubber) is formed.
7. **The working temperature range for vulcanized rubber is -40°C to 100°C as compared to raw rubber, which has working temperature range of 10°C to 60°C .**
8. **It is resistant to abrasion, ageing and reactivity with oxygen and ozone.**

A comparison of raw rubber and vulcanized rubber is given in the following table:

Table: Comparison of properties of Raw, Vulcanized Rubber, Reinforced Vulcanized Rubber.

Property	Raw Rubber	Vercanized Rubber	Reinforced Valcanized Rubber
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1.	Tensile strength (psi)	300	3000	4500
2.	Elongation at break (%)	1200	800	600
3.	Elasticity	Very high	Low, depends upon extent of vulcanization	Very low, depends upon extent of vulcanization and reinforcement
4.	Water absorption	Large	Small	Small
5.	Solvent resistance (hydrocarbons)	Sluble	Swells only	Swells only
6.	Chemical resistance	Poor	Much better	Much better

Other Compounding Techniques

Though vulcanization improves the properties of natural rubber to a great extent but even vulcanized rubber do not exhibit satisfactory properties for various utility items. These properties can be enhanced by other compounding techniques discussed below:

(i) Reinforcing Fillers: To give strength and rigidity to the rubber, fillers are added. Fillers are of two types: (a) inert fillers, such as clay which make the rubber mixture easy to handle before vulcanization, but have no effect on the physical properties, and (b) reinforcing fillers which greatly improve the properties of rubber or vulcanized rubber.

Common fillers include carbon black, zinc oxide, magnesium carbonate, barium sulphate, calcium carbonate etc. Carbon black is remarkable reinforcing filler for both natural and synthetic rubbers. Table gives the comparison of raw rubber and non-reinforced vulcanized rubber and reinforced vulcanized rubber. In vulcanization, though the long range movement of the polymer molecules is restricted, still movement of local chains is high. Reinforcement of vulcanized rubber restricts this local freedom of movement, making the polymer stiffer and tougher.

(ii) Plasticizers or Softeners: Plasticizers are added to rubber to improve flow and therefore, processability-plasticizers also reduce the brittleness of the product. The common plasticizers used are hydrocarbon oils, resins, waxes, etc. The oil serves as a plasticizer and a softener by reducing the melt viscosity of the rubber to the

levels required Compounding.

(iii) Antioxidants: Rubbers that retain double bonds in their vulcanized structure are sensitive to heat, light and particularly oxygen. Thus rubber deteriorates in presence of light and air due to oxidation and as a result becomes soft and degrades.

Antioxidants" are substances that protect the polymer by preventing oxidation. In many cases these also prevent undesirable reactions promoted by oxygen.

Common antioxidant is complex organic amines like phenyl p-naphthylamine, phenolic substances and phosphates. The structures of two common antioxidants are given below:

Antioxidants

(iv) Accelerators: Vulcanization takes place by heat and in presence of sulphur, but the process is very slow. The process can be speeded up by addition of small amounts of organic or inorganic compounds known as accelerators. The inorganic accelerators include lime, magnesia and white lead whereas organic accelerators are complex organic compounds such as aldehydes, amines, thicarbonates and 2-mercaptol benzothiozole. Sometimes accelerators require the presence of still other chemicals known as activators or promoters. These activators are usually metallic oxides such as zinc oxide. The best combination for efficient vulcanization include sulphur, an organic accelerator, a metallic oxide and a soap.

(v) Colouring Agents: Several dyes and pigments are used to impart colours to elastomers. Common colourants for polymers include:

Appearance	Chemical used
White	TiO ₂ , BaSO ₄
Yellow	Lead Chromate
Red	Ferric oxide
Crimson	Antimony sulphides
Blue	Ultramarine
Green	Chromium trioxide
Silver metallic effect	Flake Aluminium
Pearlescence	Lead carbonate and mica.

The oil-soluble dyes or which have small particle size and refractive index near that of the plastic (organic pigments such as phthalocyanins) are added to get transparent coloured products from transparent plastics. The inorganic pigments impart opacity to the plastic.

SYNTHETIC RUBBERS

The polymers possessing similar physical properties as that of natural rubber are called synthetic rubbers. As natural rubber suffers from many disadvantages, attempts to find out a substitute for natural rubber began very early.

Greville William (1860) was first to isolate isoprene as a decomposition product by heating rubber to a high temperature. This gave a clue that rubber can be synthesized by the polymerization of monomers like isoprene. By the end of 19th century the fact was confirmed when polymerization of isoprene yielded rubber like product.

Since then attempts were on to prepare synthetic rubber by other monomers as well. Synthetic rubbers have been produced by the polymerization of a large number of conjugated dienes resembling isoprene. The foremost of all is, Buna Rubber (polymer of butadiene) which was prepared by the action of sodium on butadiene. That is why synthetic rubber is known as Buna rubber-'Bu' for Butadiene and 'Na' for sodium. However, the product prepared had poor tensile strength, and ageing characteristics. Improvements in properties were made by developing copolymers of butadiene. Several types of synthetic rubber are available today and some of them are described below:

1. SBR or Buna-s Rubber

Styrene-butadiene rubber (SBR) is the first commercially made synthetic rubber. It is a copolymer obtained by the free-radical polymerization of two monomers, styrene and butadiene. The two components are allowed to react in a mixing vessel containing an aqueous solution of an emulsifying agent in presence of free radical initiator such as. cumene hydroperoxide or p-menthane hydroperoxide.

According to the temperature used, two processes have been developed, the hot process (at 50°C) and the cold process. In the cold process the temperature is kept in the range –18°C to 5°C. The rubber is known as cold rubber. Cold process is

more efficient than the hot process because chain length can be controlled more efficiently. The SBR copolymer contains about 75% butadiene and 25% styrene and is a random copolymer. Both type of rubbers 'cold' as well as 'warm rubbers' can be vulcanized by conventional methods using sulphur. A reinforcing filler is added to achieve good physical properties.

Properties

- (i) SBR possesses high abrasion loses resistance and high load bearing capacity,
- (ii) At elevated temperatures SBR almost 2/3 of their tensile strength whereas natural rubber only loses 1/4th.
- (iii) Its resilience is poorer than that of natural rubber, which restricts its use in tire industry.
- (iv) The weather ability of SBR is better than that of natural rubber.
- (v) 'Cold' SBR is superior to the standard product because it contains less chain branching and crosslinking.
- (vi) SBR gets easily oxidized in presence of traces of ozone present in atmosphere.
- (vii) It swells in oils and solvents.

Uses

Of all the synthetic elastomers; SBR enjoys the major share of the market. SBR has the

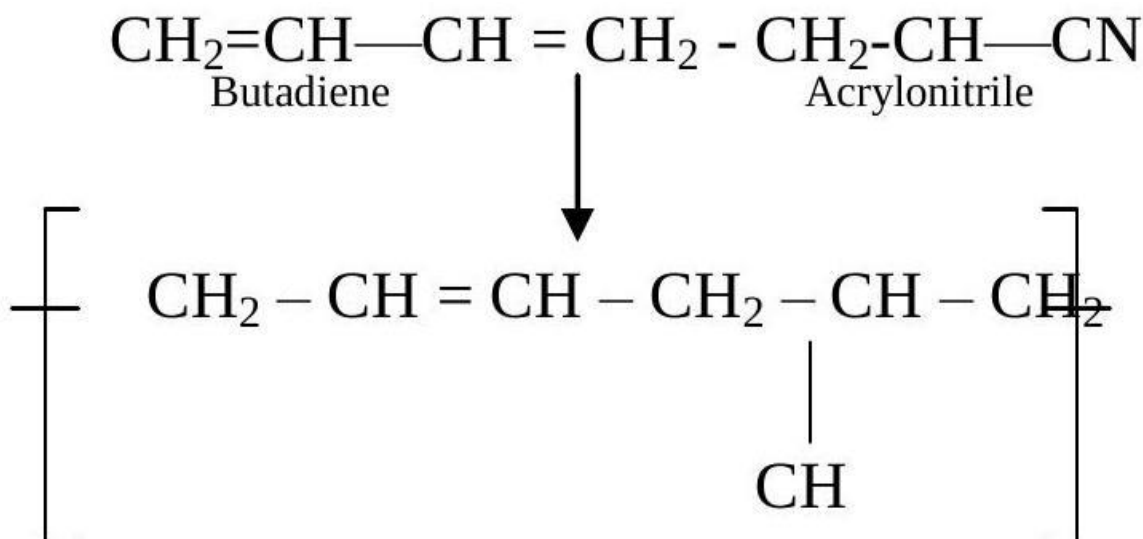
following applications:

- (i) The principal use of SBR is in the production of tires and tire, products which are typically blends of both natural and synthetic rubbers. SBR is used for lighter duty tyres but is inferior to the natural rubber in its use for truck tyres.
- (ii) For many mechanical goods, it is superior to natural rubber and is used because of its easier processing.
- (iii) It is used for making hose, shoe soles, gaskets, floor tiles, carpet backing, tank linings etc.
- (iv) It is widely used for electrical insulation, although its properties are not good as those of butyl rubber.

2. Buna-N or Nitrile Rubber (NBR) or GR-A

The nitrile rubbers are polymers of butadiene and acrylonitrile in the ratio of 75% and 25% respectively. It is prepared by emulsion polymerization using cumene

hydroperoxide as initiator. Hydrogen peroxide and ferros sulphate can also be used as initiators. Vulcaniza ion is done by conventional means by adding sulphur.



- (i) Nitrile rubbers are noted f or their oil resistance. However the oil resistance varies with composition. If the acrylonitrile content is between 18% then the rubber has fair oil resistance and if it is more than 40% then it is extremely oil resistant.
- (ii) It possesses excellent resistance to heat, sunlight, acids and salts.
- (iii) Because of the presence of cyano groups (-CN). it is less resistant to alkalies than natural rubber.
- (iv) it has good tensile strength and abrasion resistance.
- (v) The rubbers are less resilient than natural rubbers.
- (vi) It has good heat resistance and if properly protects by antioxidants, it snows resistance to oxidative degradation as well.

Uses

- (i) Nitrile rubber is used primarily for its oil resistance. These are extensively used for fuel tanks, gasoline hoses, gaskets, printing rollers and high attitude aircraft components.
- (ii) They can be used in contact with water and antifreeze solutions.
- (iii) They are also used in the form of latex for impregnating paper, textile and leather.
- (iv) It can also be used as blend component in tyre manufacture.

3. Neoprene or GR-M Rubber

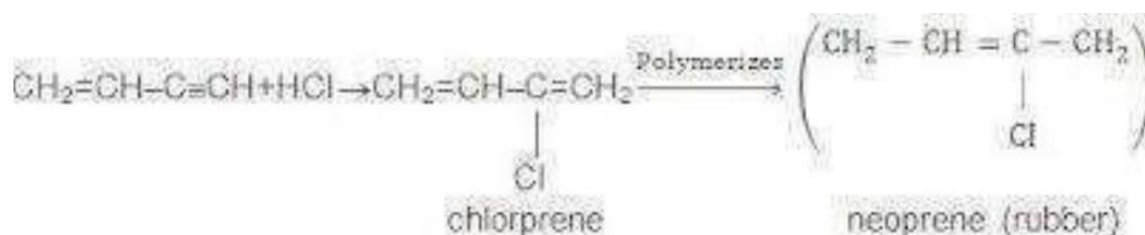
This is also known as polychloroprene or polychlorobutadiene or duprene. Neoprene was the first synthetic rubber developed in the United States.

Preparation: Neoprene or polychloroprene is prepared by polymerization of chloroprene, which is 2-chloro-1, 3 butadiene.

The preferred configuration produced during the polymerization is trans 1-4 polychloroprene. The polymerization of chloroprene takes place through emulsion polymerization.

The starting material, chloroprene is manufactured by the addition of hydrogen chloride to vinyl acetylene, which in turn is prepared by dimerization of acetylene.

The vulcanization of neoprene is different from that of other elastomers in that it can be vulcanized by heat alone. Although some types are polymerized in presence of sulphur which introduces crosslinks in the polymer. Neoprene can also be vulcanized using zinc oxide or magnesium oxide.



Properties: Neoprene is closely related to the natural rubber and can replace rubber because similarly in the properties of the two. Some of the properties of Neoprene are:

- (i) As H atom in the natural rubber is replaced by Cl atom in Neoprene, Neoprene has superior resistance to vegetable and mineral oils.
- (ii) It is superior to natural rubber as far as ageing and effects of high temperatures are concerned.
- (iii) Neoprene is soluble in polar solvents due to the presence of chloro-group.
- (iv) Vulcanized neoprenes have high tensile strength (3500 – 4000psi) in the absence of protection.
- (v) Vulcanized neoprene is extremely resistant to oxidative degradation if suitably protected.
- (vi) It has good weathering and ozone resistance.

(vii) It has got excellent oil resistance, though inferior to Nitrile rubber but better than natural rubber or SBR.

Uses

Neoprene is used for:

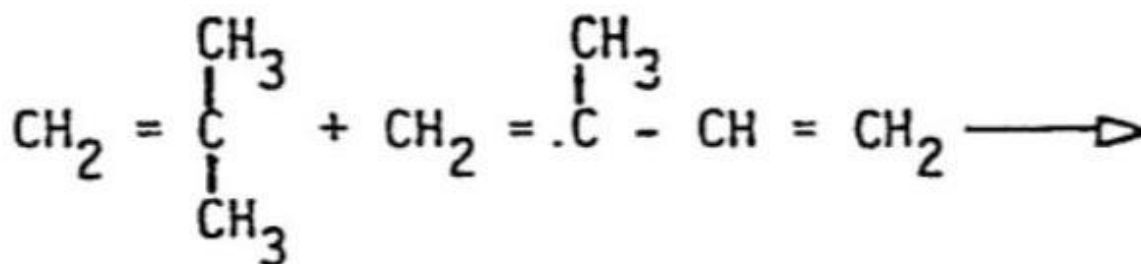
- (i) It is used in oil resistant wire and cable coatings, industrial hoses, shoe soles.
- (ii) Its latex is used for the manufacture of gloves and coated fabrics.
- (iii) It is used for making tubings for carrying corrosive gases and oils.
- (iv) It is used for the manufacture of sponges, conveyor belts, linings of reaction vessels etc.

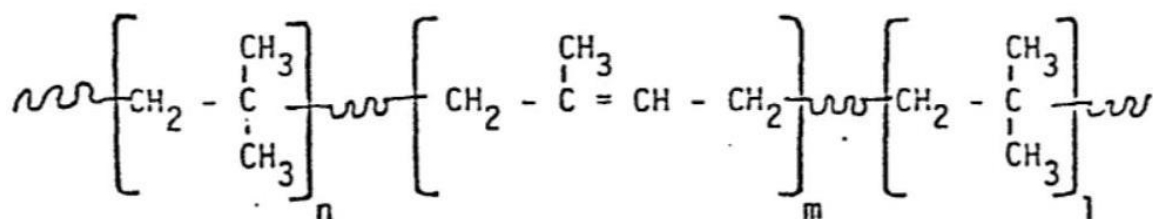
4. Butyl Rubber (GR-I)

Butyl rubber belongs to the class of elastomers which do not have unsaturated chain structure. However, a small amount of diene monomer that provides a site for vulcanization is included by means of copolymerization.

Preparation

Butyl rubber or polyisobutylene are prepared by the copolymerization of isobutylene with a small amount (1.5 to 4.5%) of isoprene. Isoprene is added to render them vulcanizable. It is prepared by low temperature cationic polymerization using Friedel-Crafts catalyst at -80°C .





Properties

The absence or low concentrations of double bonds in the main chain of butyl rubber results in high resistance to attack by a number of chemicals. It has the following properties.

- (i) Polyisobutylene or butyl rubber is amorphous under normal conditions but crystallize on stretching.
- (ii) It exhibits outstanding resistance to attack by oxygen and ozone due to low concentration of double bonds. It is less sensitive to oxidative ageing as compared to other elastomers except silicones.
- (iii) Butyl rubber becomes soft on oxidative degradation.
- (iv) It exhibits low gas permeability due to closepacked linear paraffinic chains.
- (v) It has high ozone and acid resistance.
- (vi) Due to very low unsaturation, it cannot be hardened much on vulcanization.
- (vii) Unstabilized polyisobutylenes are degraded by light or heat to sticky lowmolecular weight products. Therefore usual rubber antioxidants should be added to stabilize the polymer.
- (viii) It has excellent insulating properties as predicted from its non-polar, saturated nature.
- (ix) It is soluble in hydrocarbons such as benzene.
- (x) The tear resistance of butyl rubber is quite good and is retained well at high temperature and for long times, in contrast to natural rubber.

Uses

- (i) Butyl rubber is used for inner tubes for tires because of its impermeability to gases.
- (ii) It is used for wire and cable insulation.
- (iii) It is used for linings of tanks, hoses etc.

5. Polysulphide Rubber (Thicol or GR-P)

Polysulphide Rubbers are the condensation products of ethylene dihalides and alkali sulphides. These are linear condensation polymers.

Preparation

Polysulphide rubber is obtained by the reaction between sodium polysulphide and ethylene dichloride. Thus sulphur forms the part of the polymer chain. During the reaction NaCl gets eliminated. Vulcanization cannot be achieved by sulphur because polymer chain is not unsaturated. Hence it is not a hard rubber. However vulcanization can be achieved by reacting with ZnO which reacts with sulphur links forcing crosslinks.

Properties

The properties of the materials depend on the length of the aliphatic groups and the number of sulphur atoms present in it. With four sulphur per monomer, the product is rubbery, whereas if only two sulphur atoms are present per monomer, the polymer do not behave as elastomer. In that case at least four methylene groups are needed in the dihalide to induce elastomeric properties to the products. Some of the important properties are:

- (i) Thiokol is resistant to swelling.
- (ii) It is resistant to oils and solvents. Fuel oils, lubricating oils, gasoline and kerosene have no effect on Thiokol.
- (iii) Thiokol films are impermeable to gases to a large extent.
- (iv) It cannot be vulcanized and hence does not form hard rubber.

Thiokol rubbers from many disadvantages:

- (i) It has disagreeable odour (mercaptan odour).
- (ii) It has poor heat resistance, poor abrasion resistance and low tensile strength.
- (iii) It tends to lose its shape under continuous pressure.

However, recent developments of Thiokol have overcome these disadvantages.

Uses

- (i) Polysulphides or Thiokol is used to make sealants, gaskets, balloons, fabric coating.
- (ii) Due to low permeability it is used to make gasoline hoses.
- (iii) Liquid Thiokol can be cured at room temperature to tough solvent-resistant rubbers. These liquid compounds are used as gasoline tank sealants and liners for aircraft and in variety of other sealing applications.

(iv) The liquid polymers, when combined with oxidizers burn with great intensity and generate large volume of gas. Thus it can be used in solid-fuel rocket propellants.

6. Polyurethane (PU)

Polyurethanes are polymers containing the group (carbonate group) these are known as urethane linkages

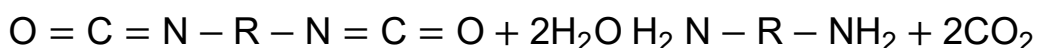
Preparation: The polyurethanes are formed through the reaction diisocyanate with the compound containing at least two active hydrogen atoms such as diols or diamines. The reaction of diisocyanate with glycol is represented as:

The properties of the final product depend upon the type of monomers and their chain length. A wide variety of polymers can be prepared ranging from rigid to elastic polymers. Crosslinking takes place through isocyanate groups which are capable of reacting with hydrogen atoms attached to the polymers leading to vulcanization. The polyurethanes can be produced in the form of fibers, elastomers or foams.

The foamed plastic can be obtained by blowing air/gas through molten polyurethane. This foamed plastic is also known as thermocol.

Note: Thermocol is also prepared by blowing air/gas through polystyrene.

Alternatively, for the production of foamed polyurethane little water is mixed with the reaction mixture, which reacts with isocyanate group to evolve CO₂. The CO₂ produced foams the polymer as it sets.



Properties

(i) Polyurethanes have high strength, good resistance to gas and aromatic hydrocarbons.

(ii) They have excellent resistance to ozone and oxygen but are susceptible to microbial attack.

(iii) The polyurethanes can be prepared in different forms varying from hard coatings to

flexible rubbers and rigid foams each having different properties.

Coatings: Coatings are hard, glassy and solvent resistant. They have good flexibility and impact resistance.

Elastomers: Elastomers have excellent abrasion resistance and are resistant to oils, greases and solvents.

Fibers: Fibers are obtained by reacting di-isocyanate with long chain glycols which

are usually polyesters or polyethers.

Foams: Foams can be flexible or tough depending upon the polymer and the type of Crosslinking produced. They are light, tough and resistant to heat.

Uses

(i) The polyurethane foams have found the widest use. The flexible foams are used as upholstery material for furniture, insulation and crash pads.

(ii) The rigid polyurethane foams are used as core material as insulation cover in refrigerated appliances and vehicles.

(iii) Flexible polyurethanes can also be used for coating rubber articles to give them additional resistance to abrasion, such as in gymnasium and dance floors.

(iv) Polyurethane resin is used to insulate the wires polyurethane coated wires can be soldered directly.

(v) Polyurethane fibers with unusually high elasticity are used in foundation garments and swim wear. They have replaced rubber latex thread in this use.

(vi) Flexible urethane foams are used as cushions for furniture and automobiles and have replaced rubber foams in these applications because of improved strength, lower density and easier fabrication.

(vii) Polyurethanes are also used in making mattresses and pillows.

(viii) As they are radiation resistant, they are also used in encapsulation for integrated-circuit devices.

(ix) Its applications in medical field include its use in dental materials, artificial heart and skin.

7. Chlorosulphonated Polyethylene Rubber (Hypalon)

Preparation: When polyethylene is treated with a mixture of chlorine and sulphur dioxide, chlorosulphonated polyethylene is formed. The chlorosulphonation can be carried out either on the solid material or in solutions.

Properties

The chlorosulphonylation of ethane provides two modifications:

(a) The chlorine atoms break the regularity of polyethene chain structure changing the crystalline polyethylene to an elastomer.



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