

Polymers

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15. POLYMERS

15.1 Introduction:-

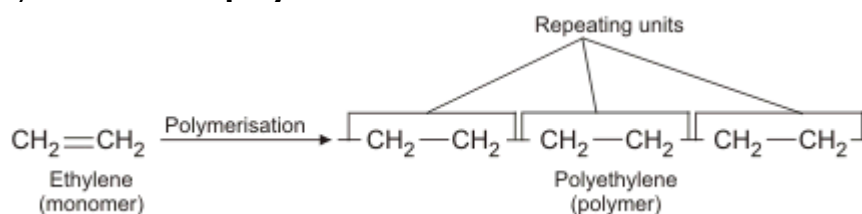
Polymers are the backbone of modern civilization. In almost all walks of life polymers are extensively used. The use of polymers in the manufacture of plastic buckets, cups and saucers, children's toys, packaging bags, synthetic clothing materials (nylon, terylene, etc.), furniture, automobile parts, tires, gears and seals, electrical insulating materials, machine parts, biochemical and surgical equipment, have completely revolutionized our daily life and industrial scenario. In fact, polymers are the backbone of four major chemical industries, viz., plastics, elastomers, fibers and, paints and varnishes.

15.2 Definition of polymers:-

The term polymer is derived from two Greek words: **poly** means many and **mer** means unit or part. These are very large molecules having high molecular mass ($10^3 - 10^7 u$) and hence are also called macromolecules. Thus,

Polymers or macromolecules are very high molecular mass ($10^3 - 10^7 u$) substances each molecule of which consists of a very large number of simple repeating structural units joined together through covalent bonds in a regular fashion.

The simple and reactive molecules from which the repeating structural units are derived are called monomers and the process by which these simple molecules, i.e., monomers are converted into polymers is called **polymerization**.



15.3 Polymers and macromolecules:-

The terms polymers and macromolecules are often used without any distinction. But strictly speaking, a polymer always consists of hundreds to thousands of repeating structural units but a macromolecule may or may not contain repeating structural units. For example, proteins and nucleic acids should be regarded as macromolecules but not polymers since their molecules do not contain repeating structural units. In contrast, polythene may be regarded both as a macromolecule as well as a polymer since it contains a large number of repeating structural units. Thus all polymers are macromolecules but all macromolecules are not polymers.

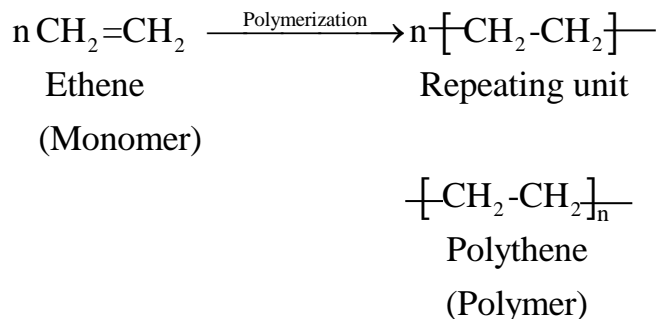
Although proteins and nucleic acids are macromolecules they are usually called polymers. This is due to the reason that proteins are made up of a large number of α -amino acids which if not structurally are chemically similar. Similarly, nucleic acids (polynucleotides) are made up of a large number of nucleotides which are also chemically similar.

15.4 Homopolymers and copolymers:-

Depending upon the nature of the repeating structural unit, polymers are divided into two categories:

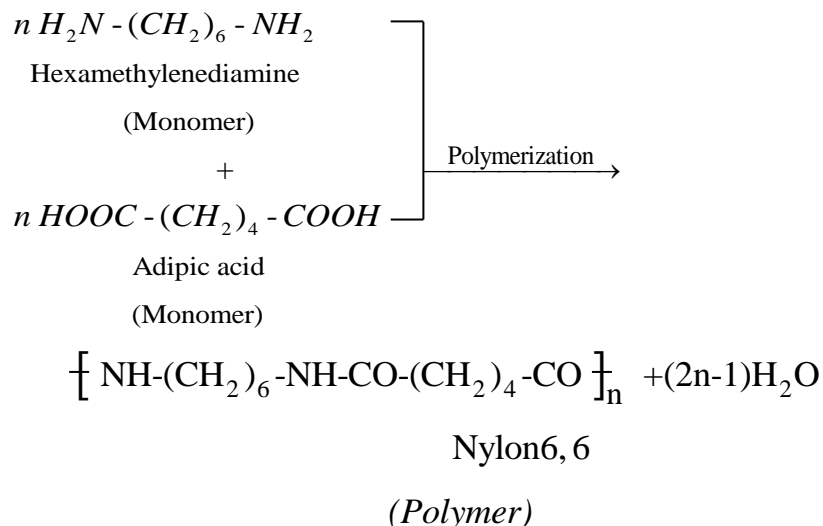
(i) Homopolymers and (ii) Copolymers.

(i) **Homopolymers.** Polymers whose repeating structural units are derived from only one type of monomer units are called **homopolymers**. For example, in case of polythene (polyethylene) polymer which is obtained by polymerization of ethene (ethylene) molecules, the repeating structural unit, i.e., $-CH_2 - CH_2 -$ is derived from only one type of monomer, i.e., ethene.



Other examples of homopolymers are polypropene, polyvinyl chloride (PVC), polyisoprene, neoprene (polychloroprene), polyacrylonitrile (PAN), nylon-6, polybutadiene, teflon (polytetrafluoroethylene), cellulose, starch, etc.

(ii) Copolymers. *Polymers whose repeating structural units are derived from two or more types of monomer units are called **copolymers**.* For example, in case of nylon-6, 6, the repeating structural unit, i.e., $-\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO}-$ is derived from two monomer units, i.e., hexamethylenediamine and adipic acid.



Other examples of copolymers are : Buna-S, polyesters, alkyd resins, bakelite, melamine-formaldehyde polymer, etc.

15.5 Classification of polymers :-

Polymers are classified in a number of ways:

- (i) Classification based upon source of availability.
- (ii) Classification based upon structure.
- (iii) Classification based upon mode of polymerization and
- (iv) Classification based upon molecular forces.

15.5.1 Classification based upon Source :-

Depending upon the source from which they are obtained, polymers are broadly divided into the following three classes:

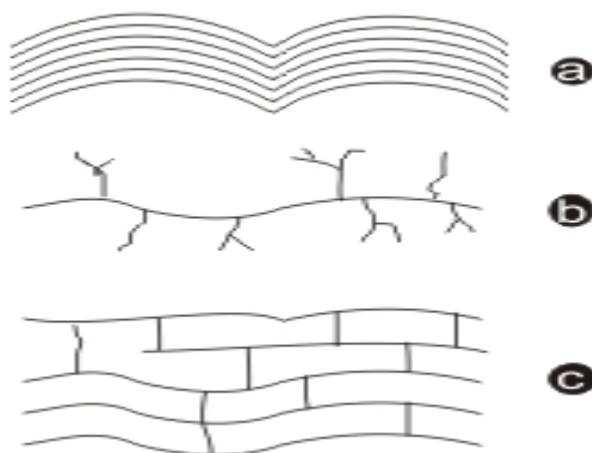
1. Natural polymers and
2. Semi-synthetic polymers
3. Synthetic polymers.

- 1. Natural polymers.** Polymers which are found in nature, i.e., in animals and plants are called **natural polymers**. Proteins which make much of our body, nucleic acids which control heredity at molecular level, cellulose which provides food, clothing and shelter and rubber which is used for making various articles of daily use are all natural polymers.
- 2. Semi-synthetic polymers.** These are mostly derived from naturally occurring polymers by chemical modifications. For example, cellulose on acetylation with acetic anhydride in presence of conc. H_2SO_4 gives cellulose diacetate which is used for making threads of acetate rayon and other materials like films, glasses, etc.
- 3. Synthetic polymers.** A large number of manmade polymers are extensively used in daily life as well as in industry. These include fibers (nylon, polyester) plastics (polythene, polypropene), rubbers (neoprene, polystyrene), etc.

15.5.2 Classification based on Structure:-

On the basis of structures, polymers are divided into three types:

- (i) Linear polymers.** In these polymers, the monomers are joined together to form long straight chains of polymer molecules. The various polymeric chains are then stacked over one another to give a well packed structure (Fig.). Because of the close packing of polymer chains, linear polymers have high melting points, high densities and high tensile (pulling) strength. Some important examples of linear polymers are high density polythene, polyvinyl chloride (PVC) nylons, polyesters, etc.
- (ii) Branched chain polymers.** In these polymers, the monomer units not only combine to produce the linear chain (called the main chain) but also form branches of different lengths along the main chain (Fig.). These polymer molecules because of branches do not pack well. As a result, branched chain polymers have lower melting points, densities and tensile strength as compared to linear polymers. An important example of a branched chain polymer is low density polythene. Others are amylopectin, glycogen, etc.



Different structures of polymers (a) linear structure (b) branched chain structure and (c) three-dimensional network structure.

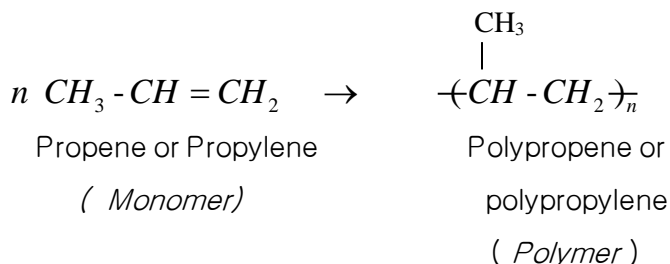
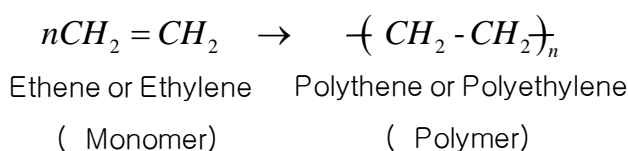
(iii) Cross-linked or Three-dimensional network polymers. In these polymers, the initially formed linear polymer chains are joined together to form a three-dimensional network structure (Fig.). Only two cross-links per polymer chain are required to join together all the long chain polymer molecules to form a giant molecule. Because of the presence of cross-links, these polymers are also called **cross-linked polymer**.

15.5.3 Classification based on Mode of Polymerization.

On the basis of mode of polymerization, polymers have been classified into the following two sub groups:

1. Addition polymers and
2. Condensation polymers

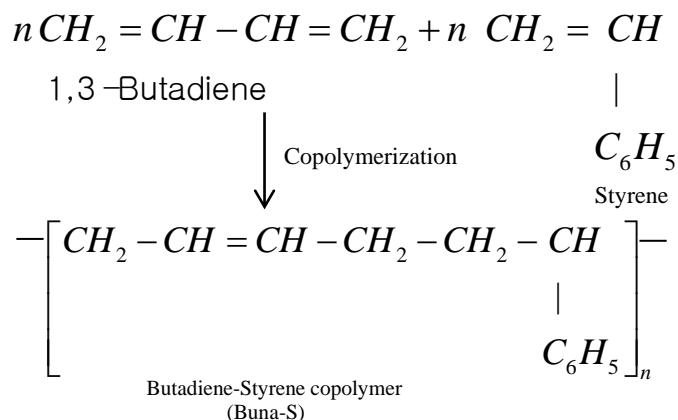
1. **Addition Polymers.** Addition polymers are formed by the repeated addition of a large number of same or different monomers possessing double and triple bonds. For Example,



The addition polymers can be either addition homopolymers or addition copolymers. Both polythene and polypropene are addition homopolymers because they are formed by the addition polymerization of only one type of monomer units. Other examples of addition homopolymers are:

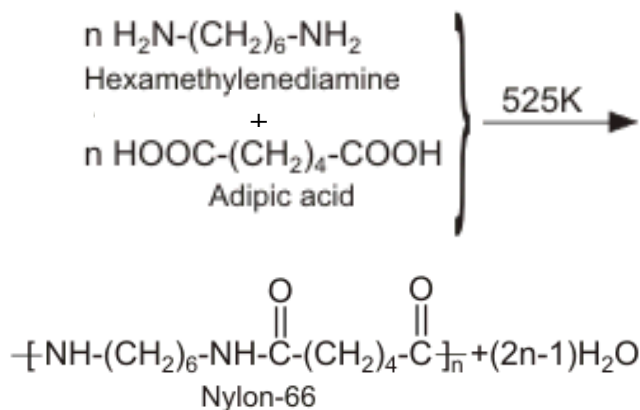
Monomer	Polymer
I. Butadiene	Polybutadiene
II. Tetrafluoroethylene	Polytetrafluoroethylene (PTFE) or Teflon
III. Vinyl chloride	Polyvinyl chloride (PVC)
IV. Isoprene	Cist - Polyisoprene (natural rubber)

On the other hand, addition polymers formed by repeated addition of two or more types of monomer units, are called **addition copolymers**. For example, Buna-S is an addition polymer of 1, 3-butadiene and styrene.



Other examples of addition copolymers, are Buna-N (1, 3-butadiene and acrylonitrile), butyl rubber (isobutylene and isobutylene and isoprene), saran (vinyl chloride and vinylidene chloride), etc.

2. Condensation polymers and condensation polymerization. *Condensation polymers are formed by repeated condensation reaction between two bifunctional or trifunctional monomer units usually with the elimination of small molecules like water, alcohol, ammonia, carbon dioxide, hydrogen chloride, etc. and the process by which condensation polymers are formed is called **condensation polymerization**.* For example, nylon6,6 is obtained by condensation polymerization, of two monomers, i.e., hexamethylenediamine and adipic acid, each containing two functional groups, with the loss of water molecules. Thus,



Like addition polymers, condensation polymers can be either condensation copolymers or condensation homopolymers. The polymer nylon 6, 6 discussed above is an example of condensation copolymer.

Some other examples of condensation copolymers are:

Polymer	Monomers
(i) Terylene or Dacron	Ethylene glycol and terephthalic acid or its methyl ester
(ii) Alkyd resin	Ethylene glycol and phthalic acid
(iii) Bakelite	Phenol and formaldehyde
(iv) Melamine-formaldehyde resin	Melamine and formaldehyde
(v) Polyurethane	Ethylene glycol and toluene m-diisocyanate

Some examples of condensation homopolymers are :

	Polymer	Monomer
(i)	Nylon-6	Caprolactam
(ii)	Starch (amylose, and amylopectin) and glycogen	α -D-Glucose
(iii)	Cellulose	β -D-Glucose

15.5.4 Classification based on molecular Forces:-

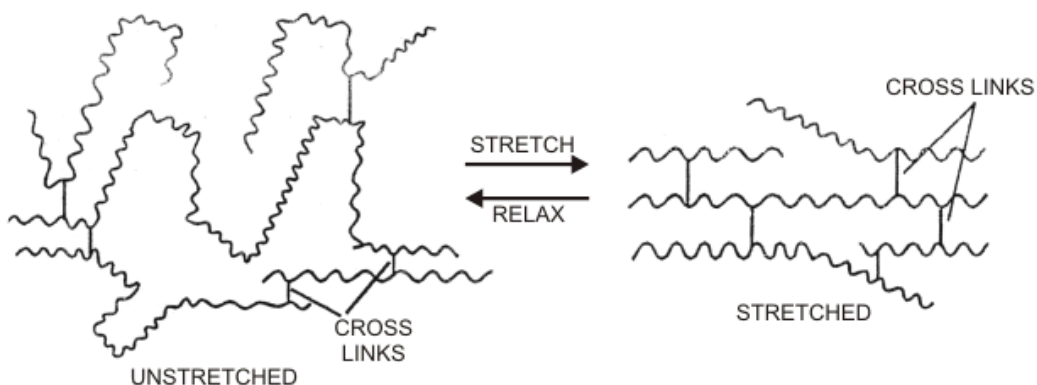
The application to which a polymer is put depends largely upon its mechanical properties such as tensile strength, elasticity, toughness, etc. These mechanical properties, in turn, depend upon the intermolecular forces of attraction such as van der Waals forces, hydrogen bonds and dipole-dipole interactions between the adjacent polymer chains.

The magnitude of these intermolecular forces depends upon the size of the molecule and the number of functional groups along the polymer chain. Obviously, greater the lengths of the polymer chain, stronger are the intermolecular forces.

Depending upon the magnitude of these intermolecular forces, polymers have been divided into the following four categories:

(i) Elastomers. *Polymers in which the intermolecular forces of attraction between the polymer chains are the weakest are called **elastomers**.*

These polymers consist of randomly coiled molecular chains of irregular shape having a few cross links. When the force is applied, these randomly coiled chains straighten out and the polymer is stretched. Since the van der Waals forces of attraction between the polymer chains are too few and too weak, these cannot maintain this stretched form. Therefore, as soon as the force is withdrawn, the polymer returns to its original randomly coiled state. Thus, *whereas weak van der Waals forces of attraction permit the polymer chains to be stretched, the cross links help the polymer to come back to the original position when the force is withdrawn.* The most important example of an elastomer is natural rubber. Other examples are vulcanized rubber, Buna-S or SBR-a copolymer of butadiene (75%) and styrene (25%). Buna-N, neoprene, etc.



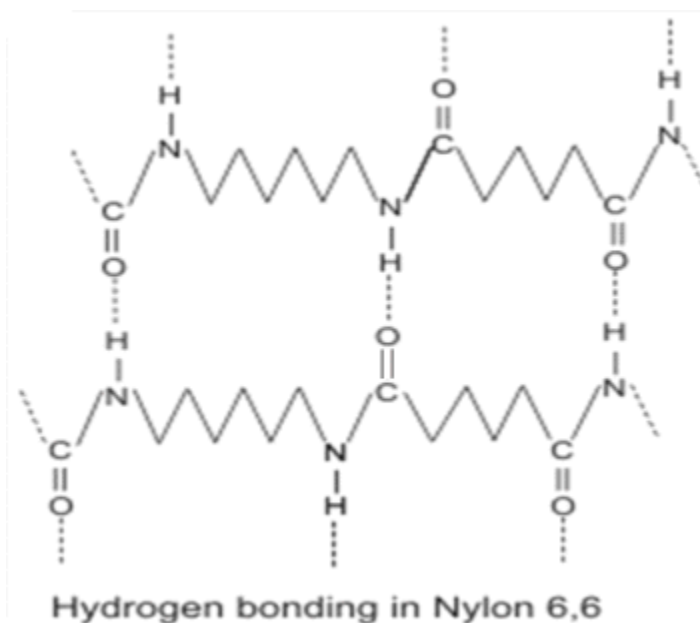
Unstretched and stretched forms of an elastomer.

Highly vulcanized rubber containing 20-25% S is called **ebonite**.

(ii) Fibers. Polymers in which the intermolecular forces of attraction are the strongest are called fibers. These forces are either due to **H** – bonding or dipole-dipole interactions. In case of nylons (polyamides), the intermolecular forces are due to **H**-bonding (Fig.) while in polyesters (Terylene, Dacron, etc.) and polyacrylonitrile (orlon, acrilan, etc.) they are due to powerful dipole-dipole interactions between carbonyl and cyano ($-C=N$) groups respectively.

(iii) Thermoplastics. Polymers in which the intermolecular forces of attraction are in between those of elastomers and fibers are called **thermoplastics**.

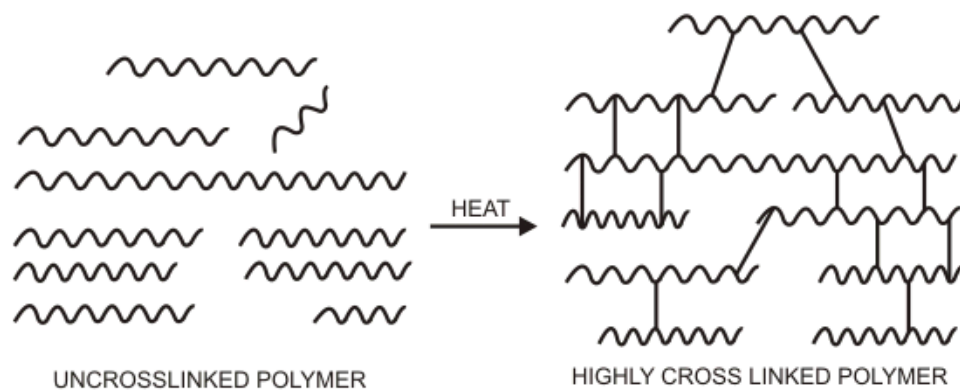
These are linear or slightly branched chain polymers which are hard at room temperature, become soft and viscous on heating and again rigid on cooling. The process of heat softening and hardening on cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic. As a result, these plastics can be molded into toys, beads, buckets, and telephone and television cases links and hence the individual polymer chains can slip past one another on heating.



Some common examples of thermoplastics are polythene, polypropene, polystyrene, polyvinyl chloride, Teflon, polyvinyl acetate, polyacrylonitrile poly (methacrylate) nylon 6 nylon 6, 6 etc.

Plasticizers. Those plastics which do not soften very much on heating can be made soft and readily workable by the addition of certain organic compounds called Plasticizers. Dialkyl phthalates (such as di-*n*-butyl phthalate, di-*n*-octylphthalate) or cresyl triphosphates ($(\text{CH}_3 - \text{C}_6\text{H}_4 - \text{O})_3\text{PO}_2$) are the most commonly used plasticizers. For example, Polyvinyl chloride is extremely stiff and hard even when hot but the addition of di-*n*-butyl phthalate makes it soft and rubber-like.

(iv) Thermosetting polymers. These are semi-fluid substances with low molecular masses which when heated in a mould; undergo a permanent change in chemical composition to give a hard, infusible and insoluble mass. This hardening on heating is due to extensive cross-linking between different polymer chains to give a three-dimensional network solid (Fig.)



Conversion of uncrosslinked polymer into highly crosslinked thermosetting polymer

In nut shell, a **thermoplastic polymer** can be melted time and again without any change, while a **thermosetting polymer** can be heated only once when it undergoes a permanent change and sets into a solid which cannot be remolded and reworked. Some examples of thermosetting polymers are: phenol-formaldehyde (Bakelite), urea-formaldehyde, melamine-formaldehyde, etc.

15.5.5 Classification based on the type of mechanism involved during growth of polymerization chain.

Now a day, polymers are also classified on the basis of type of mechanism involved during the growth of polymerization chain. On this basis, addition polymers are also called **chain growth polymers** since they are formed by repeated addition of monomer molecules to the growing chain carrying a reactive intermediate such as a free radical, carbocation or a carbanion. On the other hand, condensation polymers are also called **step growth polymers** since they are formed as a result of stepwise condensation reactions.

15.6 Types of Polymerization:-

Depending upon the mode of polymerization, polymerization mainly occurs by the following two methods:

1. Addition polymerization of chain growth polymerization.
2. Condensation polymerization or step growth polymerization.

15.6.1 Addition Polymerization or Chain Growth Polymerization:-

Addition polymerization involves successive addition of monomer units to the growing chain carrying a reactive intermediate such as a free radical, carbocation or a carbanion. This type of polymerization is also called **chain growth polymerization** because it takes place in stages leading to increase in chain length and each stage produces a reactive intermediate for

use in the next stage of growth of the chain. Depending upon the nature of the reactive species involved, addition polymerization occurs by the following three mechanisms:

- (i) Free radical addition polymerization.
- (ii) Cationic polymerization.
- (iii) Anionic polymerization.

However, here we shall discuss only free radical addition polymerization.

Free radical addition polymerization. A variety of unsaturated compounds such as alkenes, alkadienes and their derivatives readily undergo polymerization in presence of a radical initiator (radical generating catalyst) such as dioxygen, benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. For example, polymerization of ethane is carried out at high temperatures (350-570 K) and at high pressures (1000-2000atm) in presence of dioxygen or a small amount of benzyl peroxide as radical initiator.

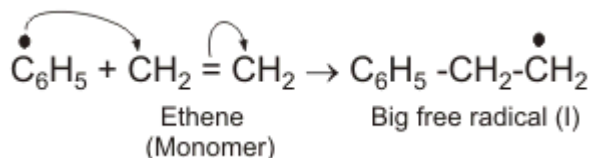
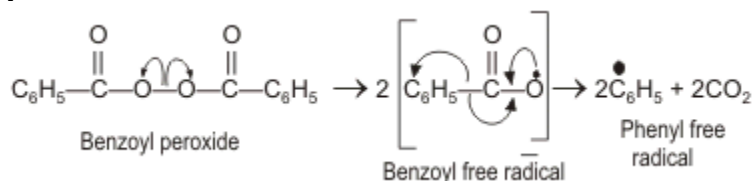
These initiator molecules readily decompose on mild heating to form initiator free radicals. For example, benzoyl peroxide on heating produces phenyl initiator free radicals.

The phenyl free radical thus formed ads to the double bond of ethene molecule (monomer) to form a new and larger free radical. This is called chain initiating step.

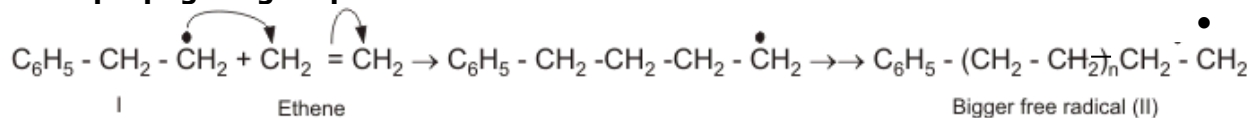
The new and large free radical (I) produced in the chain initiating step reacts with another molecule of ethene to form another bigger sized radical. Repetition of this sequence with new and bigger radicals carries the reaction forward. This step is called chain propagating step.

Ultimately, the growing free radical chain gets terminated by reactions which consume these free radicals either by combination (**Step 1**) or by disproportion (**Step 2**). These are called chain terminating steps. The entire sequence of steps governing the free radical polymerization of ethane to form polythene is depicted below:

Chain initiating steps :



Chain propagating steps:



Chain terminating steps :

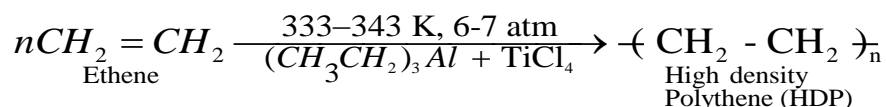
Step 1. By combination of free radicals (II) :

These branched polythene molecules do not pack well and hence this type of polythene has a low density (0.92 g/cm^3) and a low melting point (384 K). That is why polythene prepared by free radical polymerization is called low density polythene (LDP).

Properties and Uses. Low density polythene is a transparent polymer of moderate tensile strength and high toughness. It is chemically inert, slightly flexible and is a poor conductor of electricity.

It is widely used as a packaging material (in the form of thin plastic films, bags, etc.) as insulation for electrical wires and cables, in manufacturing of squeeze bottles, toys and flexible pipes.

(b) High density polyethene (HDP) or High density polyethylene (HDPE). It is prepared by co-ordination polymerization of ethene. In this process, ethene (in a hydrocarbon solvent) is heated to 333-343 K under a pressure of 6-7 atmospheres in presence of a catalyst consisting of triethylaluminium and titanium trichloride or tetrachloride (Ziegler – Natta catalyst).

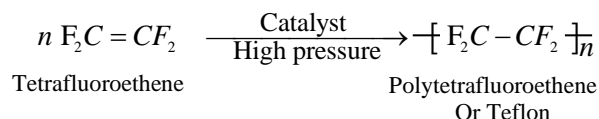


The polythene thus produced practically consists of linear chains of polymer molecules. These polymer molecules pack well and hence this type of polythene has higher density (0.97 g/cm^3) and higher melting point (403 K) than the polymer produced by free-radical polymerization. That is why polythene prepared by coordination polymerization is called high density polythene.

Properties and Uses. High density polythene is a translucent polymer. It is also chemically inert but has greater toughness, hardness and tensile strength than low density polythene.

It is used in the manufacture of containers (buckets, tubs, etc.), house wares pipes, bottles and toys.

2. Polytetrafluoroethene (PTFE) or Teflon. Teflon is manufactured by heating tetrafluoroethene in presence of a free radical or persulphate catalyst at high pressures.



Uses. Teflon is flexible and inert to solvents and to boiling acids even to aqua regia and is stable upto 598 K.

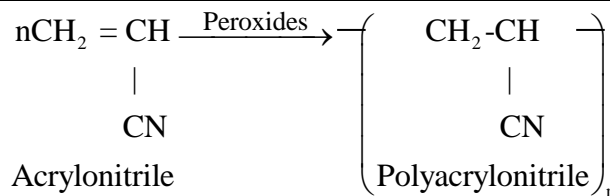
(i) Because of its great chemical inertness and high thermal stability, Teflon is used for making non-stick utensils. For this purpose, a thin layer of Teflon is coated on the inner side of the vessel.

(ii) It is also used for making gaskets, pump packing's, valves, seals, non-Lubricated bearings, filter cloth, etc.

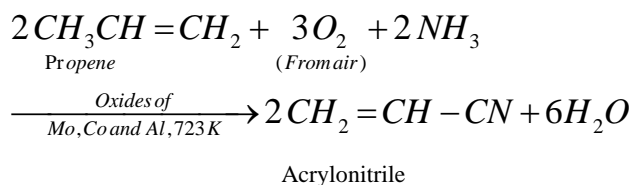
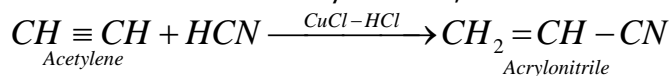
3. Polyacrylonitrile (PAN)

Starting material. Acrylonitrile
($\text{CH}_2 = \text{CH} - \text{CN}$).

Reaction. Addition polymerization of acrylonitrile in presence of a peroxide catalyst gives polyacrylonitrile.



The monomer acrylonitrile is itself manufactured either by addition of HCN to acetylene in presence of CuCl – HCl as catalyst or by passing a mixture of propene, ammonia and air over a catalyst consisting of a mixture of oxides of molybdenum, cobalt and aluminium at 723 K.

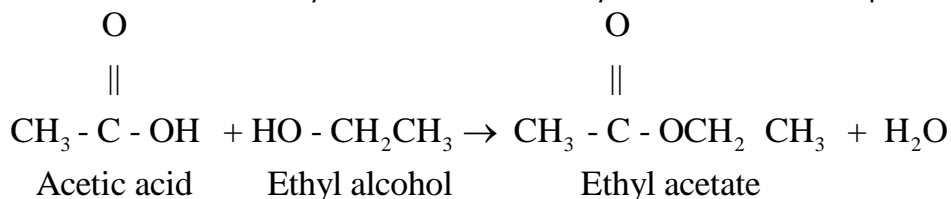


Uses. Polyacrylonitrile is hard, horny and high melting material.

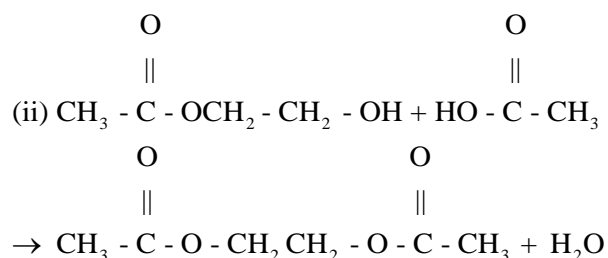
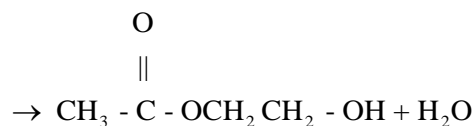
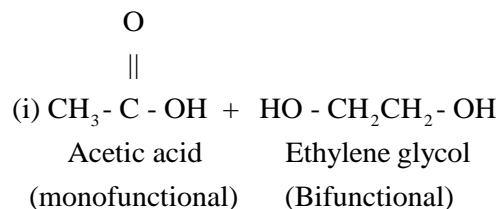
- (i) It is used as a substitute for wool in the manufacture of Orlon and Acrilan Fibers which are used for making clothes, carpets and blankets.
- (ii) It is also used in the preparation of other polymers to improve their qualities.

15.6.3 Condensation polymerization or Step Growth Polymerization.

If two reacting molecules have one functional group each, the reaction stops after one step. For example, acetic acid reacts with ethyl alcohol to form ethyl acetate in one step:



If, however, one of reacting molecules has two functional groups and the other has one functional group, i.e. acetic acid and ethylene glycol, the reaction stops after two steps:



However, when both the reactants are bifunctional, i.e., have two functional groups each, they undergo a series of condensations in a stepwise manner with the loss of simple molecules like water alcohol, etc. At each step leading ultimately to the formation of a high molecular mass condensation polymer.

Initially, the two bifunctional monomer molecules undergo condensation (bond formation) with the loss of simple molecule of water, alcohol, etc. to form a dimer which is again a bifunctional compound. This dimer may react with another molecule of one of the monomers (say first) and the resulting product may react with another molecule of the second monomer to form a tetramer which is again a bifunctional compound. Since the product of each reaction is a bifunctional compound, therefore, the sequence of condensation reaction goes on and the polymer chain keeps on growing step by step.

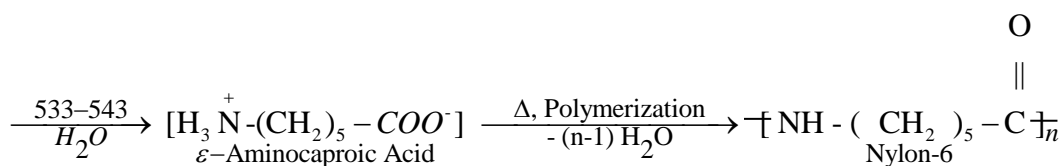
Since in this process, the polymer is formed in a stepwise manner, it is called step-growth polymer and the process is called step-growth polymerization.

It may be pointed out here that in contrast to chain growth polymers, the formation of step growth polymers does not occur through chain reactions involving free radicals, carboanions or carbocations as reactive chemical species.

Some important condensation polymers are discussed below:

1. Polyamides. Polymers which have amide linkages are called polyamides. These are prepared by the condensation polymerization of dibasic acids with diamines or their equivalents. These polymers are commonly called nylons.

(a) Nylon 6, 6. It manufactured by the condensation polymerization of adipic acid and hexamethylenediamine. The acid and the amine first react to form a salt which when heated to 525 K under pressure undergoes polymerization with elimination of water as steam and the nylon is produce in the molten state. It can then be cast into a sheet or fibers by passing through a spinneret*.

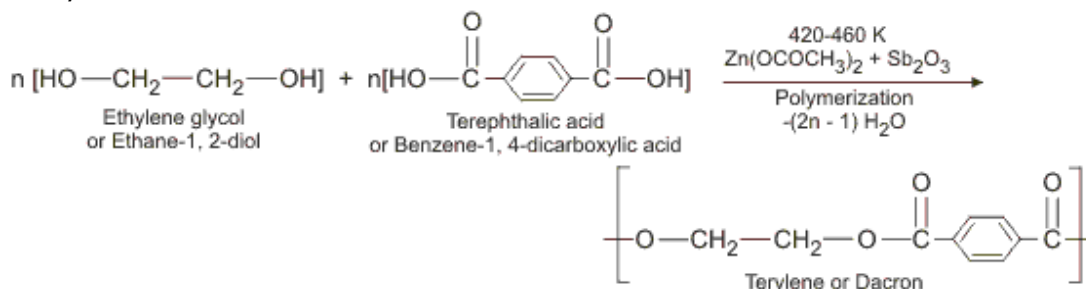


The filaments (fibers) of nylon-6 are obtained when molten polymer is forced through a spinneret and the fibers formed are cooled by a stream of air.

Uses. It is used for the manufacture of tire cords, fabric and mountaineering ropes.

2. Polyesters. Polymers which have ester linkages are called polyesters and are prepared by the condensation polymerization of diacids with diols.

Terylene or Dacron is the best known example of polyesters. It is prepared by condensation polymerization of ethylene glycol and terephthalic acid with elimination of water. The reaction is carried out at about 420-460 K in presence of a catalyst consisting of a mixture of zinc acetate and antimony trioxide.



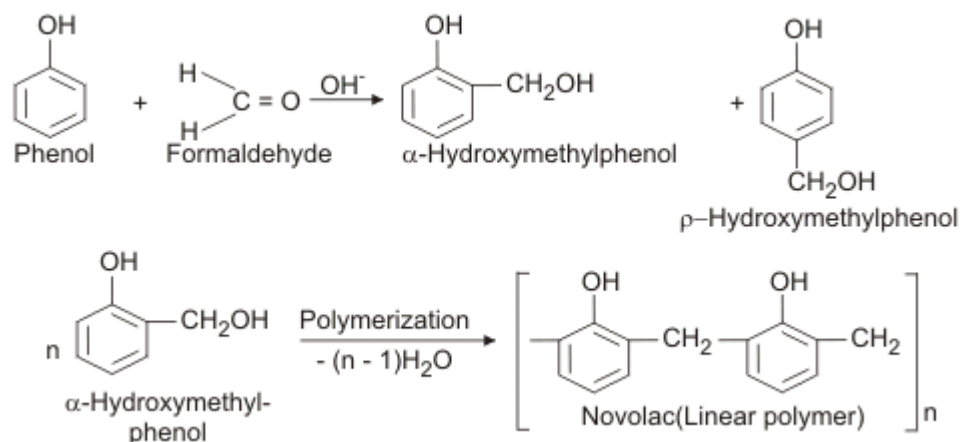
In practice, a better product is obtained by using a trans- esterification process. The dimethyl ester of terephthalic acid heated to about 475b with ethylene glycol. Methanol is evolved as a gas, driving the reaction to completion. The molten product thus obtained is spun into Dacron or cast into a film called Mylar.

Uses.

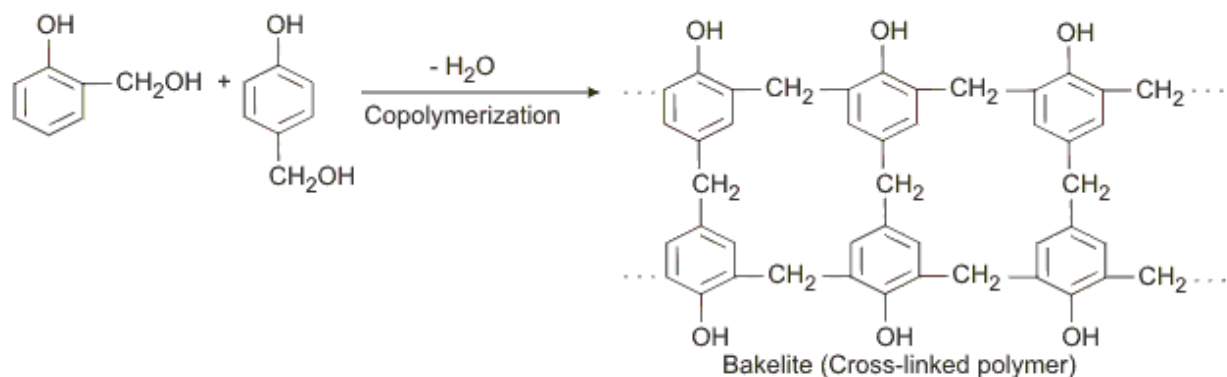
(i) the fibers of terylene is highly crease-resistant, durable and has low moisture content. It is also not damaged by pests like moths and mildew. It is, therefore, used for the manufacture of wash and wear fabrics, tyre cords, seat belts and sails. It is also blended with cotton and wool to increase their resistance to wear and tear.

(ii) The Mylar film is extremely flexible, tear-resistant and resistant to ultraviolet degradation. It is, therefore, used for making magnetic recording tapes.

3. Phenol-formaldehyde Polymers (Bakelite and related polymers). Phenol formaldehyde Polymers are the oldest synthetic polymers. These are obtained by condensation of phenol with formaldehyde in the presence of either an acid or a base catalyst. The reaction begins with the formation of o- and/or phydroxymethylphenol derivatives which further react with phenol to form compounds containing rings joined to each other through methylene (- CH₂ -) bridges. The initial product is a linear polymer called novalac which is used in paints.



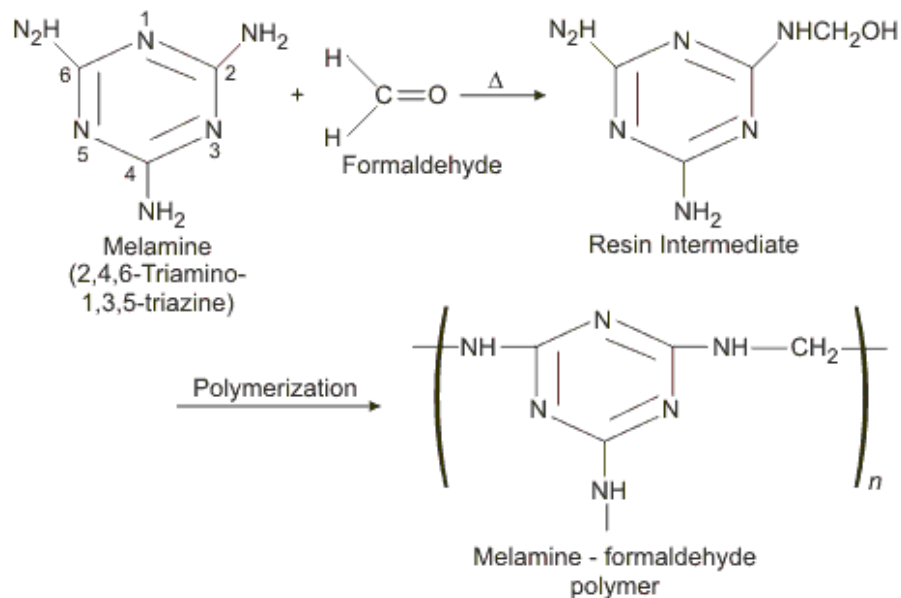
Novolac on heating with formaldehyde undergoes cross-linkage to form an infusible solid called Bakelite.



Uses. Soft Bakelite with low degree of polymerization are used as binding glue for laminated wooden planks, and in varnishes and lacquers. High degree polymerization leads to the formation of a hard Bakelite which is highly cross-linked and is a thermosetting polymer. It is

scratch and water resistant polymer and hence is used for the manufacture of combs, Formica table-tops, fountain pen barrels, phonograph records, computer discs, etc. It also possesses excellent electrical insulating properties and hence is widely used in making electrical goods (switches, plugs, handles of various utensils, etc.). Sulphonated Bakelite's are used as ion exchange resins.

4. Melamine-formaldehyde polymer. Melamine and formaldehyde undergo condensation copolymerization to form melamine-formaldehyde polymer also called **melmac**.

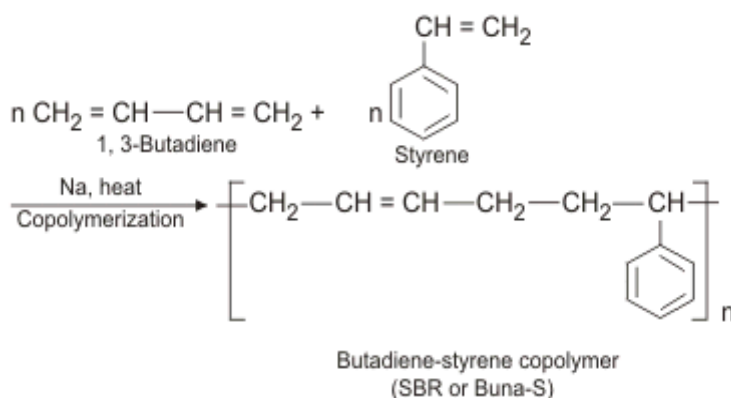


Uses. Melamine-formaldehyde copolymer is widely used for making non-breakable plastic crockery i.e. cups and plates made from melamine polymer are hard and do not break on being dropped.

15.7 Copolymerization :-

When two or more different monomers are allowed to polymerize together, the product formed is called a **copolymer** and the process is called **copolymerization**.

A copolymer can be made not only by chain growth polymerization but also by step growth polymerization. It contains a large number of units of each monomer used in the same polymeric chain. For example, copolymerization of a mixture of 1, 3-butadiene and styrene in the ratio 3:1 in presence of sodium gives styrene-butadiene copolymer commonly called as styrene-butadiene rubber (SBR) or Buna-S. In Buna-S, Bu stands for butadiene, Na for sodium which is the polymerizing agent and S stands for styrene.



Composition of copolymers: In general, the composition of the copolymer depends not only upon the proportion of the monomers but also upon their relative reactivity. *Some monomers as such do not polymerize at all but undergo copolymerization.* For example, maleic anhydride does not polymerize as such but undergoes copolymerization with styrene in a highly symmetrical manner to form styrene-maleic anhydride copolymer.

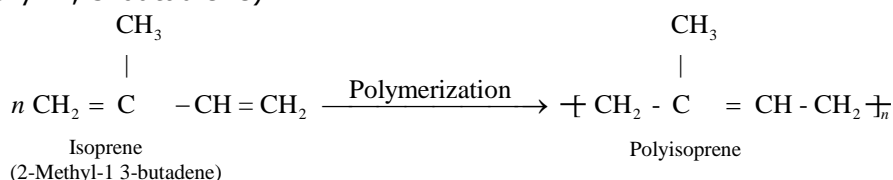
Properties and uses of copolymers: The properties of copolymers are usually quite different from those of homopolymers derived from each of the combining monomers. Actually, copolymers have better physical and mechanical properties. Copolymerization is similar to alloying in metallurgy. Just like alloys, various copolymers can be synthesized having desired properties. For example, polystyrene is an homopolymer of styrene. It is a good electrical insulator and can be moulded into toys, combs, radio and television parts. In contrast, SBR or Buna-S is a copolymer of styrene and butadiene. It is very tough and is a good substitute for natural rubber. It possesses high abrasion resistance, high load bearing capacity and is used for the manufacture of automobile tyres. It is also used for making floor tiles, footwear components, cable insulation, etc.

15.8 Rubber

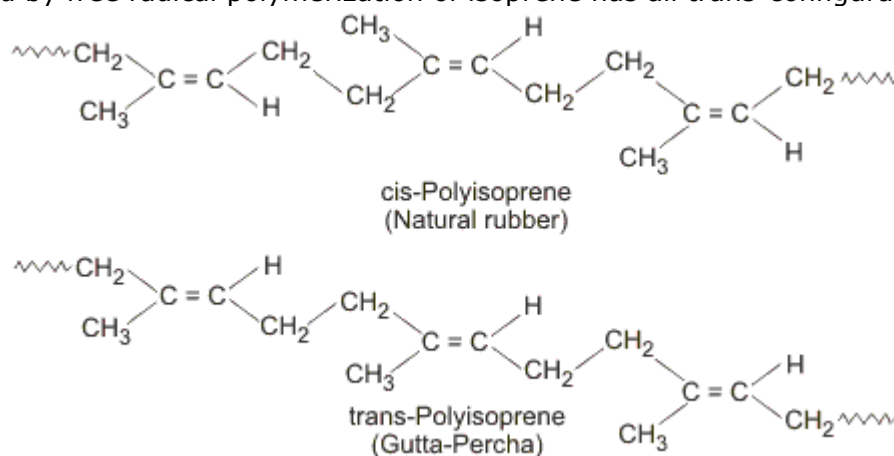
Natural Rubber :-

It is a natural polymer. It has remarkable elasticity and undergoes long range reversible extension even under relatively small applied force. That is why it is also called an elastomer. It is manufactured from latex which is a colloidal solution of rubber particles in water. Latex is obtained by making incisions in the bark of rubber trees found in tropical and semitropical countries such as Southern India (Kerala, Tamilnadu, Karnatka, etc.) Indonesia, Malaysia, Srilanka, South America, etc.

Structure. Chemically, natural rubber is a linear 1, 4-addition polymer of isoprene (i.e. 2-methyl-1, 3-butadiene)



Since each repeating unit in polyisoprene contains a double bond, it may have either a cis or a trans-orientation. Actually, in natural rubber, all the double bonds have cis-stereochemistry. In other words, natural rubber is cis-polyisoprene. In contrast, synthetic rubber (gutta percha) obtained by free radical polymerization of isoprene has all trans-configuration.



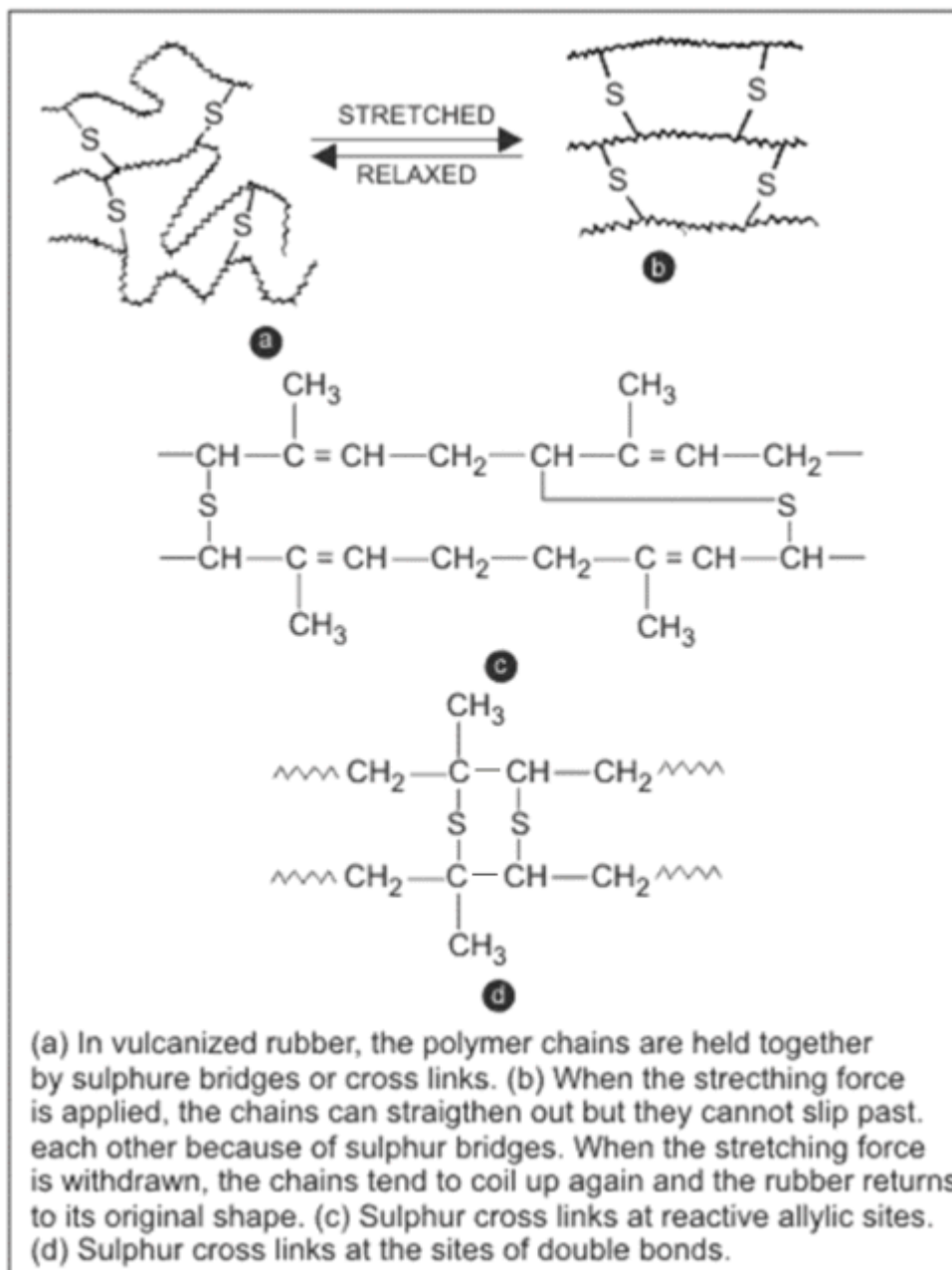
Inspection of the structure of natural rubber reveals that there are no polar groups/substituents and hence intermolecular forces of attraction are only weak van der Waals interactions. These forces are further weakened because of the cis-configuration of all the double bonds which does not allow the polymer chains to come close enough for effective interactions. Thus, cis-polyisoprene does not have a straight chain but has a coiled structure. As a result, it can be stretched like a spring. On stretching, the molecules become partially aligned w.r.t. each other and on withdrawing the force, the chains come back to their original coiled state. Thus, natural rubber is elastic. In contrast, due to trans-orientation of double bonds, gutta percha has highly

regular zig-zag chains which cannot be stretched much. Therefore, gutta percha is considered to be non-elastic.

Further, due to coiled structure, natural rubber does not fit closely in the crystal lattice and hence is considered to be non-crystalline. In contrast, due to highly regular zig-zag structure, gutta percha fits closely in the crystal lattice and hence is considered to be crystalline.

15.8.1 Vulcanized Rubber :-

Natural rubber is soft and tacky (sticky) and becomes even more so at high temperatures and brittle at low temperatures. Therefore, rubber is generally used in the temperature range 283-335 K where its elasticity is maintained. It has a large water, absorption capacity, has low tensile strength



and low resistance to abrasion. It is also not-resistant to the action of organic solvents and is also easily attacked by oxidizing agents. These properties can be improved markedly by a

process called **Vulcanization**. It consists of heating raw rubber with sulphur at 373-415 K. Since this process is slow, therefore, additives like zinc oxide, etc. are used to accelerate the rate of vulcanization. The vulcanized rubber thus obtained has excellent elasticity, low water absorption tendency and is resistant to the action of organic solvents and oxidizing agents. During vulcanization, sulphur bridges or crosslink between polymer chains are introduced either at their reactive allylic positions or at the sites of the double bonds . These cross links make rubber hard and stronger and remove the tackiness of natural rubber since the individual chains can no longer slip over the other but are instead locked together in a giant size molecule. The extent of hardness or toughness, however, depends upon the amount of sulphur added. Thus, about 5% sulphur is used for making tyre rubber, 20-25% S for making **ebonite** and 30% S for making battery case rubber. The process of vulcanization was discovered by Charles Goodyear in 1839.

15.8.2 Synthetic Rubbers:-

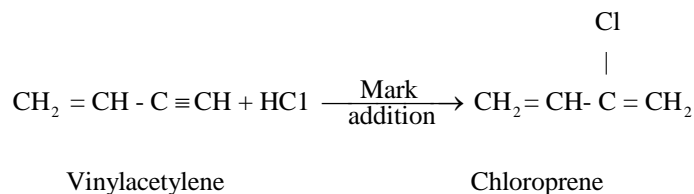
Synthetic rubber may be defined as any vulcanisable rubber like polymer which is capable of getting stretched to twice its length. However, it returns to its original size and shape when the stretching force is withdrawn.

Majority of these rubbers are derived from butadiene derivatives and contain carbon-carbon double bonds so that they can also be vulcanized. Thus synthetic rubbers are either homopolymers of 1, 3-butadiene or its derivatives or are copolymers of 1, 3-butadiene or its derivatives with another unsaturated monomer.

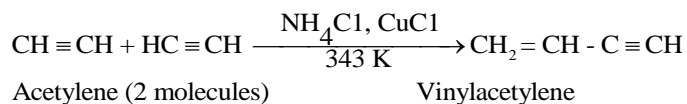
Some important synthetic rubbers are:

Neoprene, Buta-S, Buna-N and Thiokol:

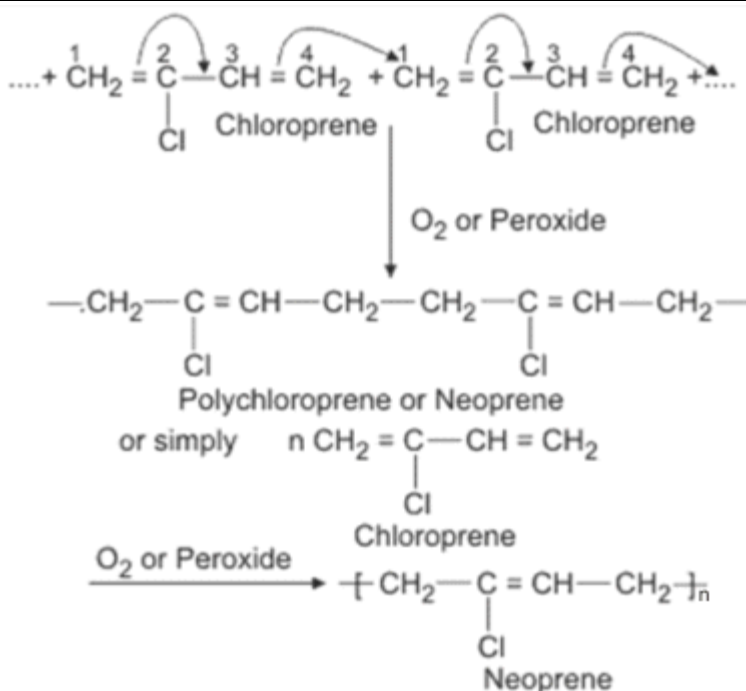
- 1. Neoprene.** It is a polymer of chloroprene (2-chloro-1, 3-butadiene) and is also called polychloroprene. Chloroprene needed for the purpose is prepared by the addition of HCl to vinyl acetylene. The addition takes place on the triple bond in accordance with the Markownikov's rule,



Vinylacetylene needed for the purpose is prepared by dimerization of acetylene by passing it through an aqueous solution of ammonium chloride and cuprous chloride at 343 K.



Reaction. Chloroprene polymerizes very readily (700times faster than isoprene). No specific catalysts are needed but the polymerization is slower in absence of oxygen. The reaction occurs by 1, 4-addition of one chloroprene molecule to the other as shown below:

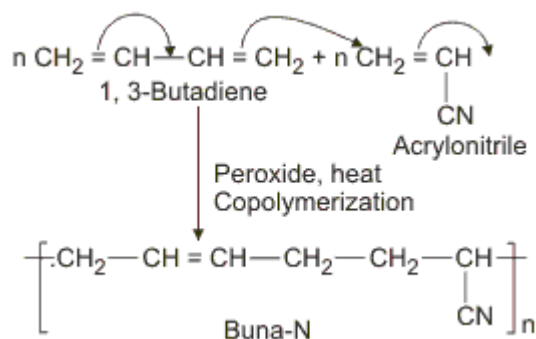


It is an excellent rubber like material.

Uses. Neoprene is inferior to natural rubber in some properties but superior in its stability to aerial oxidation and in its resistance to vegetable or mineral oils. It is, therefore, used in the manufacture of hoses, gaskets, shoe heels, stoppers, etc. It is also used as an insulator and for making conveyor belts and printing rollers.

2. Buna-S. It has already been discussed under copolymerization.

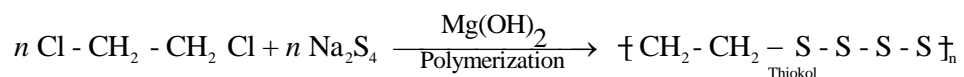
3. Buna-N or Nitrile rubber. Buta-N is obtained by copolymerization of 1, 3-butadiene and acrylonitrile in presence of a peroxide catalyst.



The letter 'N' in Buna-N stands for acrylonitrile.

Uses. It is resistant to the action of petrol, lubricating oils and organic solvents. It is, therefore, used in making oil seals, hoses and tank linings, etc.

4. Thiokol. It is prepared by copolymerization of 1, 2-dichloroethane (ethylene dichloride) with sodium tetrasulphide (Na_2S_4) in presence of magnesium hydroxide



Properties and uses. It is also called polysulphide rubber. It has slightly less tensile strength than natural rubber but is exceptionally resistant to the action of mineral oils, solvents, oxygen and ozone.

15.9 Molecular Mass of Polymers:-

The properties of polymers depend largely upon their molecular mass, size and structure. The degree of polymerization or the length of the polymer chain during their synthesis, however, depends upon the availability of monomer molecules near the growing polymer chain. Since the number of monomer molecules differs from one place to another in the reaction mixture, therefore, a particular sample of a synthetic polymer contains a number of species of varying chain lengths. Since each species has a different molecular mass and a given sample of a polymer contains a number of such species, therefore, the polymer as a whole has an average molecular mass. In contrast, natural polymers such as proteins contain chains of identical length and hence have definite molecular masses.

15.10 Biodegradable Polymers:-

Polymers such as polysaccharides (starch, cellulose etc.) proteins and nucleic acids which control the various life processes are called **biopolymers**.

All these biopolymers disintegrate by themselves in biological systems during a certain period of time by enzymatic hydrolysis and to some extent by oxidation and hence are biodegradable. As a result, they do not cause any pollution.

In contrast, synthetic polymers – a major portion of which are being used as throw away containers and packing materials do not disintegrate by themselves (i.e., are non-biodegradable) over a period of time. This durability is not altogether an advantage. Rather it

has presented mankind with a serious waste disposal problem. With the ever increasing use of plastics, soon entire civilization will be buried under a pile of plastic debris.

In view of the disposable problem of the polymer waste and for preparing polymers for other safe uses in human system, biodegradable synthetic polymers have been developed. These synthetic polymers mostly have functional groups present in biopolymers and lipids.

By far the most important class of biodegradable polymers is aliphatic polyesters and polyamides. Some of these are discussed below.

(i) Poly-β-hydroxybutyrate-co- β-hydroxy-valerate (PHBV). It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid in which the two monomer units are connected by ester linkages.

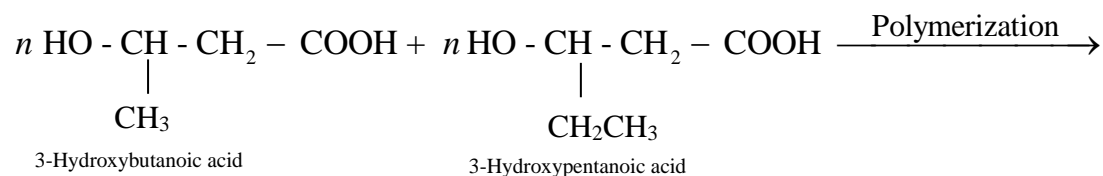


Table: Some Other Commercially Important Polymers.

Sr. No.	Name of Polymer	Monomer unit/s	Structure	Uses
1.	Polypropene	Propene ($\text{CH}_3\text{CH} = \text{CH}_2$)	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 - \text{CH} \end{array} \right]_n$ Addition polymer	In manufacture of carpet fibres, ropes, stronger pipes, toys and bottles.
2.	Polystyrene	Styrene ($\text{C}_6\text{H}_5\text{CH} = \text{CH}_2$)	$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{CH}_2 - \text{CH} \end{array} \right]_n$ Addition polymer	As insulator, wrapping material, used for making soft drink and baby feeding bottles, plastic toys, telephone, radio and television bodies, refrigerator linings, etc.
3.	Polyvinyl chloride (PVC)	Vinyl chloride ($\text{CH}_2 = \text{CH} - \text{Cl}$)	$\left[\begin{array}{c} \text{Cl} \\ \\ \text{CH}_2 - \text{CH} \end{array} \right]_n$ Addition polymer	When plasticized with high boiling esters such as di-n-butyl phthalate, it is used for making rain coats, hand bags, shower curtains, vinyl flooring, water pipes, etc.
4.	Poly (methyl methacrylate) (PMMA)	Methyl methacrylate $\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 = \text{C} - \text{COOCH}_3 \end{array} \right)$	$\left[\begin{array}{c} \text{COOCH}_3 \\ \\ \text{CH}_2 - \text{C} \\ \\ \text{CH}_3 \end{array} \right]_n$ Addition polymer	It has excellent light transmission properties even better than glass. It can also take up beautiful colours and tints. Therefore, it is widely used in the manufacture of lenses, light covers, light shades, sign boards, transparent domes and sky domes, aircraft windows, protective coatings, dentures, plastic jewellery, etc.
5.	Urea formaldehyde resin	(i) Urea (NH_2CONH_2) (ii) Formaldehyde	$\left[\text{NH} - \text{CO} - \text{NH} - \text{CH}_2 \right]_n$ Condensation polymer	For making unbreakable cups and laminated sheets.
6.	Glyptal	(i) Ethylene glycol (ii) Phthalic acid	$\left[\text{OCH}_2\text{CH}_2 - \text{OOC} \begin{array}{c} \diagup \text{CO} \\ \diagdown \end{array} \right]_n$ Condensation polymer	In manufacture of paints and lacquers.

Competition window

1. **Linear polymers** have high magnitude of intermolecular forces of attraction. They have high density, high melting points, boiling points and high tensile strength. For example, high density polythene, cellulose, nylon, polyester etc.
2. **Branched chain polymers** have low density, low melting points, boiling points and tensile strength. For example, low density polythene, amylopectin, glycogen etc.
3. **Nucleic acids and proteins** though macromolecules are also regarded as polymers.
4. **Rayon** was originally called **artificial silk** but now the name rayon is given to all fibres obtained by chemical treatment of cellulose. Thus, artificial silk is a polysaccharide, i.e., cellulose derivative.
5. **Natural silk** is a protein or polypeptide. On burning it gives a smell of burning hair and shrinks into a ball of cedar while artificial silk on burning gives a thread of ash.
6. **Natural rubber** is poly cis-isoprene. It is prepared from **latex** (obtained from rubber tree by coagulation with acetic acid). It is a soft and tacky material. **Gutta-percha**, on the other hand, is poly trans-isoprene. It is a hard and horny material.
7. **Vulcanization** is a process in which natural rubber is treated with 3 – 5% sulphur. It introduces sulphur bridges between polymer chains thereby increasing its tensile strength, elasticity and resistance to abrasion. The rigidity of any vulcanized rubber depends upon the extent of sulphur cross-linking.
The process of vulcanization was developed by Charles Goodyear in 1839.
8. **Chain transfer agents.** Substances such as CCl₄ (or CBr₄) which bring about the termination of the original polymer chain with simultaneous initiation of another polymer chain are called chain transfer agents. Although the addition of such substances does not affect the rate of polymerization yet the polymer formed has a lower average molecular mass and also contains small amounts of chlorine (or bromine).
9. **Chain inhibitors.** If the chain transfer agent forms a radical which is highly stable and hence highly unreactive; the original reaction chain gets terminated without the new being initiated. As a result, the process of polymerization is inhibited. Such chain transfer agents which inhibit the process of polymerization are called chain inhibitors. Many amines, phenols and quinines act as inhibitors. For example, addition of p-benzoquinone inhibits the radical polymerization of vinyl derivatives.
10. **Plasticizers** are non-volatile liquids such as di-n-butylphthalate, tricresylphosphates which are added to a polymer such as PVC to make it soft and readily workable on heating.
11. **Thiokol** is a polysulphide rubber and is obtained by condensation polymerization of ethylene chloride and sodium tetrasulphide.
12. **Low density polythene** is a branched polymer and is prepared by free radical polymerization while high density polythene is a linear polymer and is prepared by coordination polymerization.
13. **Coordination polymerization** was developed by Ziegler and Natta who awarded Nobel Prize in 1963.
14. **Ziegler Natta catalyst** consists of (C₂H₅)₃Al + TiCl₄ (or TiCl₃).
15. If N₁, N₂, N₃, ... N_i are the number of molecules with molecular masses M₁, M₂, M₃, ... M_i respectively, then the weight average (\overline{M}_w) and number average molecular weight (\overline{M}_n) are given by the equations :

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad \text{and} \quad \overline{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

16. PDI or Poly dispersity index $\frac{\overline{M}_w}{\overline{M}_n}$ where (\overline{M}_w) and (\overline{M}_n) are weight average and number-average molecular weights respectively.

For natural or monodisperse polymers, $PDI = 1$, i.e., $\overline{M}_w = \overline{M}_n$

For synthetic or polydisperse polymers, $PDI > 1$, i.e., $\overline{M}_w > \overline{M}_n$.

17. Thermosetting polymers (Bakelite, urea-formaldehyde, melmac etc.) cannot be remoulded while **thermoplastic polymers** (polythene, polystyrene, polypropylene, PVC, PMMA, teflon etc.) can be remoulded.

18. Poly(methyl methacrylate) or PMMA is obtained by free-radical polymerization of methyl methacrylate. It has better light transmission properties than even glass.

19. Neoprene is a synthetic rubber. It is superior to natural rubber in its stability to aerial oxidation and resistance to oils, gasoline and solvents.

20. Terylene or Dacron is a polymer containing ester linkages.

21. Nylons are polyamides. Nylon-6 is a condensation homopolymer while Nylon-66 and Nylon-610 are condensation copolymers.

22. Super glue is a polymer of methyl α -cyanoacrylate.

23. Polyurethanes are obtained by condensation of toluene diisocyanate with ethylene glycol. During polymerization, low boiling liquids such as Freon-11 are added to the reaction mixture. The heat of polymerization vaporizes the volatile liquid producing bubbles which convert the viscous polymer to a frothy mass of polyurethane foam.

24. Saran is a copolymer of vinyl chloride and vinylidene chloride and is used for wrapping food materials.

25. Vinyon is a copolymer of vinyl chloride and vinyl acetate.

26. Butyl rubber is a copolymer of isobutylene and isoprene.

27. Buna-N or Nitrile rubber is a copolymer of acrylonitrile and butadiene while Buna-S is a copolymer of styrene and butadiene.

28. ABS rubber is a copolymer of acrylonitrile, 1,3-butadiene and styrene.

29. Novolac is a linear condensation polymer of phenol and formaldehyde.

Do you know?

- 1. Kevlar** is nylon-polymer and is obtained by condensation copolymerization of terephthalic acid with 1, 4-diamobenzene (p-phenylenediamine). The fibres of this polymer are so strong that they are used to make bullet-proof vests.
 - 2. Lexan** is a polycarbonate (polyester) and is prepared by condensation copolymerization of diethyl carbonate and bisphenol A. It has unusually high impact strength and hence is used in making bullet proof windows and safety or crash helmets.
 - 3. Nomex** is a polyamide made from m-phthalic acid and m-diaminobenzene. It is known for its fire-resistant properties and is used in protective clothing for fire fighters, astronauts, and race-car drivers.
 - 4. Ebonite** is high sulphur (20-30%S) rubber and is obtained by vulcanization of natural rubber.
 - 5. Dynel** is a copolymer of vinyl chloride and acrylonitrile and is used for making human hair wigs.
 - 6. Bubble gum** contains styrene butadiene rubber.
 - 7. Dextron** was the first biodegradable suture made from biodegradable polyesters used for stitching of wounds after operations.
 - 8. PHBV** stands for polyhydroxybutyrate-co- β -Hydroxyvalerate and is used for making capsules for drugs.
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