

15. INTRODUCTION TO POLYMER CHEMISTRY

Can you recall ?



- Classify the following materials as bio-degradable and non-bio-degradable : Thermocol, glass, wood, cotton clothes, paper bags, polythene bags, nylon ropes, fruit peels.
- Give examples of man made materials we use in our daily life.
- Which material is used in manufacture of toys, combs ?
- Write examples of thermosetting plastic articles.
- List various properties of plastic.

15.1 Introduction : Today the overall development in polymer science and technology has enriched human life. The world would be at totally different place without polymers such as artificial fibres, plastics and elastomers. From the throwaway candy wrapper to the artificial heart, polymers touch our lives as does no other class of material.

In short we are living in the world of polymers. Polymer chemistry emerged as a separate branch of chemistry during the last several decades due to the voluminous knowledge built up in this field and the ever increasing applications in everyday life.

Chemically polymers are complex, giant macromolecules made from the repeating units which are derived from small molecules called 'monomers'. The term 'polymer' originates from Greek word 'poly' meaning many and 'mer' meaning part or unit. Interlinking of many units constitutes polymers.

Polymers are high molecular mass macromolecules ($10^3 - 10^7$ u).

Both inorganic as well as organic polymers are known. In this chapter we will study some

aspects of organic polymers. You have learnt in Chapter 14 about carbohydrates, proteins and nucleic acids which are important organic biopolymers playing crucial role in living world.

In this chapter we will consider mainly man made organic polymers with reference to aspects such as types, preparation and applications.

Do you know ?



Nobel prizes for pioneering work in 'Polymers' :

- The polymeric substances, that we know today as macromolecules, were considered hundred years ago as associated molecules. Staudinger received Nobel prize (1953) for his work which established macromolecular nature of polymers.
- In 1963 Natta received Nobel prize for recognizing stereospecific regularity in vinyl polymers.
- In 1974 Flory received Nobel prize for elucidating the three step mechanism of chain-reaction in polymerization involving initiation, propagation and termination.

15.2 Classification of polymers : Polymers are classified in number of ways on the basis of their source, chemical structures, mode of polymerization, molecular forces, type of monomers and biodegradability.

15.2.1 Classification of polymers on the basis of source or origin : Polymers are divided into three categories : a. Natural b. Synthetic c. Semisynthetic

a. Natural polymers : The polymers obtained from natural source are said to be natural polymers. They are further subdivided into two types.

i. Plant polymers : These are obtained from plants. For example, cotton and linen are obtained from cotton plant and flax plant respectively. Natural rubber is another example of natural polymer which is manufactured from the latex obtained from bark of rubber trees.

ii. Animal polymers : These are derived from animal sources. For example, wool is obtained from hair of sheep. Silk is obtained from silkworm.

b. Synthetic Polymers : These are man-made polymers. These polymers are artificially prepared by polymerization of one monomer or copolymerization of two or more monomers. Nylon, terylene, neoprene are synthetic polymers. These are further divided into three subtypes, namely, fibres, synthetic rubbers and plastics.

c. Semisynthetic polymers : These are derived from natural polymers. These are also called regenerated fibres. Cellulose derivatives such as cellulose acetate rayon, cellulose nitrate, viscose rayon, cuprammonium rayon are a few examples of this category.

Semisynthetic polymers are used in preparation of non-inflammable photographic films, cinema films, varnishes, etc.

Use your brain power

- Differentiate between natural and synthetic polymers.



15.2.2 Classification of polymers on the basis of structure : Depending upon how the monomers are linked together, that is, the chain configuration, polymers are classified in three general types : a. linear b. branched and c. three dimensional cross - linked polymers (Fig. 15.1). The nature of linking the monomers depends upon the nature and number of functional groups in them.

a. Linear or straight chain polymers : When the monomer molecules are joined together in a linear arrangement the resulting polymer is straight chain polymer. It is obtained from

bifunctional monomers or alkenes. (Fig. 15.1(a)). For example : PVC, high density polythene.

b. Branched chain polymers : The second most common arrangement is that of branched chain. Monomer having 3 functional groups or already having side chains give rise to branched chain polymers. (Fig. 15.1 (b)). For example : low density polythene.

c. Cross-linked polymers : Third type of arrangement is said to be cross linked or network polymers where cross links are produced between linear chains as shown in Fig. 15.1 (c). Cross linking results from polyfunctional monomers. For example, bakelite, melamine.

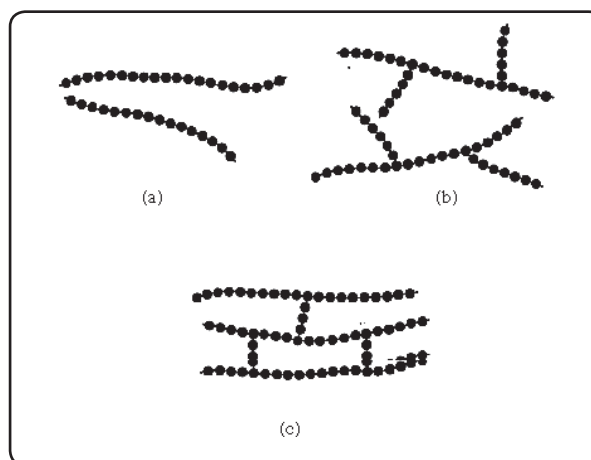
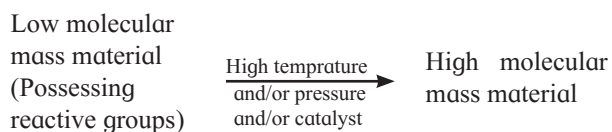


Fig. 15.1 : Different chain configurations of polymers

15.2.3 Classification of polymers on the basis of mode of polymerization : Polymerization is the fundamental process by which low molecular mass compounds are converted into high molecular weight compounds by linking together of repeating structural units with covalent bonds. This process is illustrated below.



There are three modes of polymerization according to the types of reactions taking place between the monomers.

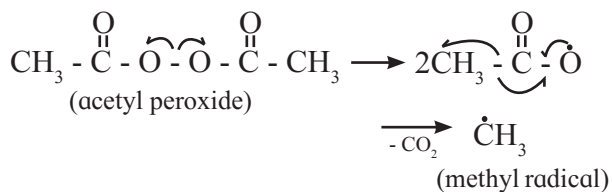
- Addition polymerization (or chain growth polymerization)
- Condensation polymerization (or step growth polymerization)
- Ring opening polymerization

a. Addition polymerization : Addition polymerization is a process of formation of polymers by addition of monomers without loss of any small molecules. The repeating unit of an addition polymer has the same elemental composition as that of original monomer.

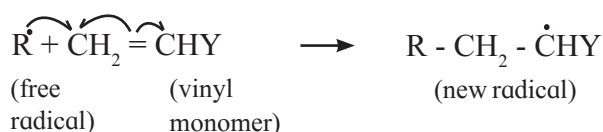
Compounds containing double bond undergo addition polymerization. It is also referred as vinyl polymerization, since majority of monomers are from vinyl category. For example : vinyl chloride ($\text{CH}_2=\text{CHCl}$), acrylonitrile ($\text{CH}_2=\text{CHCN}$). Formation of polyethylene from ethylene is well known example of addition polymerization. Addition polymerization produces high molecular mass polymeric materials without formation of any intermediate low molecular mass polymeric materials.

Free radical mechanism is most common in addition polymerisation. It is also called chain reaction which involves three distinct steps chain initiation, chain propagation and chain termination.

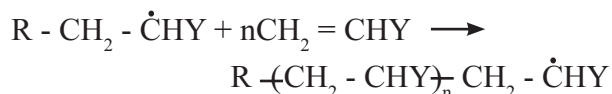
Step 1 : Chain initiation : The chain reaction is initiated by a free radical. An initiator (catalyst) such as benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. can be used to produce free radical. For example acetyl peroxide generates methyl radical as shown below :



The free radical (say R^\bullet) so formed attaches itself to the olefin (vinyl monomer) and produces a new radical, made up of two parts, namely, the attached radical and the monomer unit.

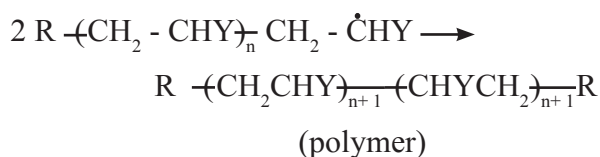


Step 2 : Chain propagation : The new radical formed in the initiation step reacts with another molecule of vinyl monomer, forming another still bigger sized radical, which in turn reacts with another monomer molecule. The repetition of this sequence takes place very rapidly. It is called chain propagation.



This step is very rapid and leads to high molecular mass radical.

Step 3 : Chain termination : Ultimately, at some stage, termination of the growing chain takes place. It may occur by several processes. One mode of termination is by combination of two growing chain radicals.



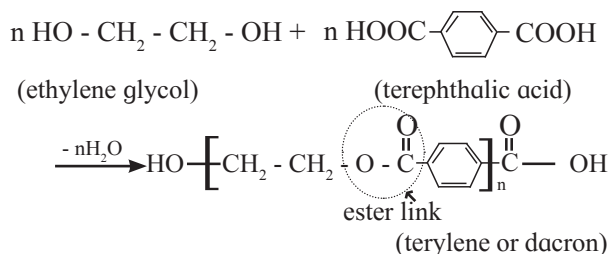
Internet my friend

Study audiovisual free radical mechanism of addition polymerization. (Refer/search for free radical polymerization.Animation (IQOG-CSIC) on youtube channel)



b. Condensation polymerization :

Consider the formation of terylene, a poly ester polymer, from ethylene glycol and terephthalic acid.



In this reaction an alcoholic OH group in ethylene glycol condenses with a carboxyl group in terephthalic acid by eliminating a water molecule to form an ester linkage.

The process of formation of polymers from polyfunctional monomers with the elimination of some small molecules such as water, hydrochloric acid, methanol, ammonia is called condensation polymerization.

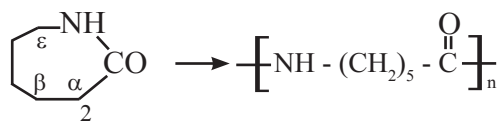
In this type of polymerization the chain growth occurs by a series of condensation steps. Therefore it is also referred to as **step growth polymerization**. This process is continued until a high molecular mass polymer is obtained.

Remember...

Repeating units of condensation polymer do not have the same elemental composition as that of monomer.



c. Ring opening polymerization : The third type of polymerization is ring opening polymerization. Cyclic compounds like lactams, cyclic ethers, lactones, etc. polymerize by ring opening polymerization. Strong acid or base catalyze this reaction. For example : polymerization of ϵ -caprolactam. (For more details see section 15.3.5 (b).

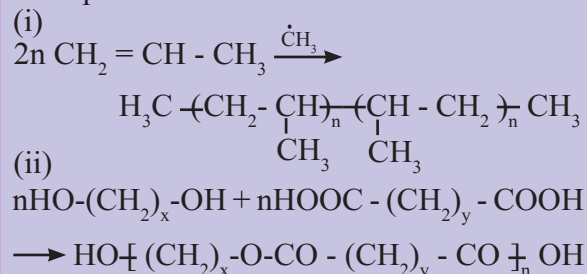


Elemental composition of the repeating unit in the polymer resulting from ring opening polymerization is same as that of the monomers, as in the case of addition polymerization. Addition polymerizations are often very rapid. But ring opening polymerization proceeds by addition of a single monomer unit (but never of larger units) to the growing chain molecules. In this sense, ring opening polymerization is a step growth polymerization similar to condensation polymerization.

Use your brain power



What is the type of polymerization in the following examples ?



15.2.4 Classification of polymers on the basis of intermolecular forces : Mechanical properties of polymers such as tensile strength, toughness, elasticity differ widely depending upon the intermolecular forces. Polymers are classified into various categories on the basis of intermolecular forces as follows.

a. Elastomers : Elasticity is a property by which a substance gets stretched by external force and restores its original shape on release of that force. Elastomers, the elastic polymers, have weak van der Waals type of intermolecular forces which permit the polymer to be stretched. A few crosslinks between the chains help the stretched polymer to retract to its original position on removal of applied force. For example : vulcanized rubber, buna-S, buna-N, neoprene, etc.



b. Fibres : Polymeric solids which form threads are called fibres. The fibres possess high tensile strength which is a property to have resistance to breaking under tension. This characteristic is due to the strong intermolecular forces like hydrogen bonding and strong dipole-dipole forces. Due to these strong intermolecular

forces the fibres are crystalline in nature. For example : polyamides (nylon 6, 6), polyesters (terylene), etc.



c. Thermoplastic polymers : Plasticity is a property of being easily shaped or moulded. Thermoplastic polymers are capable of repeated softening on heating and hardening on cooling. These polymers possess moderately strong intermolecular forces that are intermediate between elastomers and fibres. For example : polythene, polystyrene, polyvinyls, etc. :



d. Thermosetting polymers : Thermosetting polymers are rigid polymers. During their formation they have property of being shaped on heating; but they get hardened while hot. Once hardened these become infusible; cannot be softened by heating and therefore cannot be remoulded. This characteristic is the result of extensive cross linking by covalent bonds formed in the moulds during hardening/setting process while hot. For example : bakelite, urea formaldehyde resin, etc.



15.2.5 Classification of polymers on the basis of type of different monomers : Polymers are divided into two classes :

a. Homopolymers : The polymers which have only one type of repeating unit are called homopolymers. Usually they are formed from a single monomer. In some cases the repeating unit is formed by condensation of two distinct monomers. For example : polythene, polypropene, Nylon 6, polyacrylonitrile, Nylon 6, 6.

b. Copolymers : The polymers which have two or more types of repeating units are called copolymer. They are formed by polymerization of two or more different types of monomers in presence of each other. The different monomer units are randomly sequenced in the copolymer. For example : Buna-S, Buna-N.

Problem 15.1 : Refer to the following table listing for different polymers formed from respective monomer. Identify from the list whether it is copolymer or homopolymer.

Sr. No.	Monomer	Polymers
1.	Ethylene	Polyethylene
2.	Vinyl chloride	Polyvinyl chloride
3.	Isobutylene	Polyisobutylene
4.	Acrylonitrile	Polyacrylonitrile
5.	Caprolactum	Nylon 6
6.	Hexamethylene diammonium adipate	Nylon 6, 6
7.	Butdiene + styrene	Buna-S

Solution : In each of first five cases, there is only one monomer which gives corresponding homopolymer. In the sixth case hexamethylene diamine reacts with adipic acid to form the salt hexamethylene diammonium adipate which undergoes condensation to form Nylon 6, 6. Hence nylon 6, 6 is homopolymer. The polymer Buna-S is formed by polymerization of the monomers butadiene and styrene in presence of each other. The repeating units corresponding to the monomers butadiene and styrene are randomly arranged in the polymer. Hence Buna-S is copolymer.

Fig. 15.2 Shows all the classes of polymers in the form of a tree diagram.

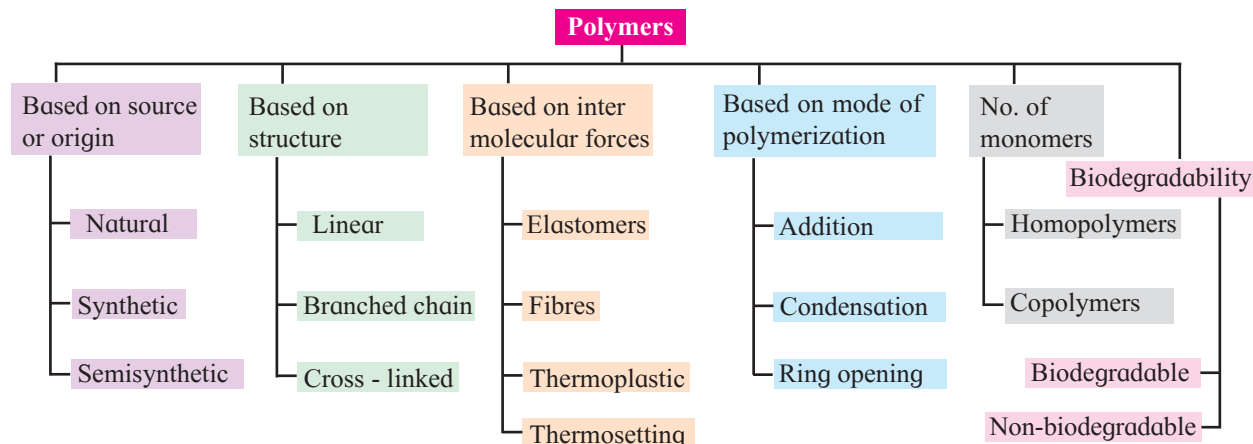


Fig. 15.2 : Classification of polymers

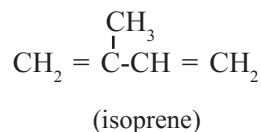
15.2.6 Classification of polymers on the basis of biodegradability :

Most of the synthetic polymers are not affected by microbes. These are called non-biodegradable polymers. These, in the form of waste material which stays in the environment for very long time and pose pollution hazards. Most natural fibres in contrast are biodegradable. In attempt to tackle the environmental problem, scientists have developed bio-degradable synthetic polymers. More details will be described in section 15.5.

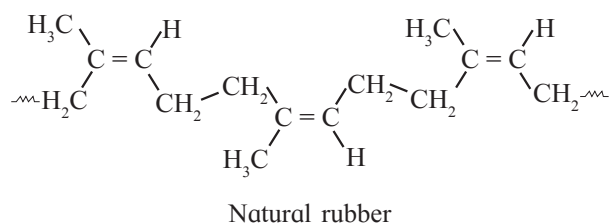
15.3 Some important polymers :

15.3.1 Rubber : Elastomers are popularly known as **rubbers**. For example, balloons, shoesoles, tyres, surgeon's gloves, garden hose, etc. are made from elastomeric material or rubber.

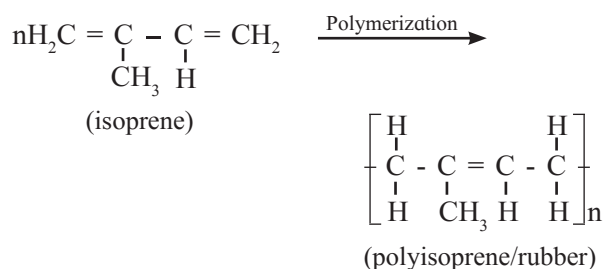
Natural rubber : Monomer of natural rubber is isoprene (2-methyl - 1, 3-butadiene).



Natural rubber is a high molecular mass linear polymer of isoprene. Its molecular mass varies from 130, 000u to 340, 000u (that is number of monomer units varies from 2000 to 5000).



Reaction involved in formation of natural rubber by the process of addition polymerization is as follows.



Properties of Natural rubber :

1. Polyisoprene molecule has cis configuration of the C = C double bond. It consists of various chains held together by weak van der Waals forces and has coiled structure.
2. It can be stretched like a spring and exhibits elastic property.

Vulcanization of rubber : To improve the physical properties of natural rubber, a process of vulcanization is carried out. In 1839 Charles Goodyear, an American inventor invented the process of vulcanization.

The process by which a network of cross links is introduced into an elastomers is called **vulcanization**. The profound effect of vulcanization enhances the properties like tensile strength, stiffness, elasticity, toughness; etc. of natural rubber. Sulfur vulcanization is the most frequently used process. Sulfur forms crosslinks between polyisoprene chains which results in improved properties of natural rubber.

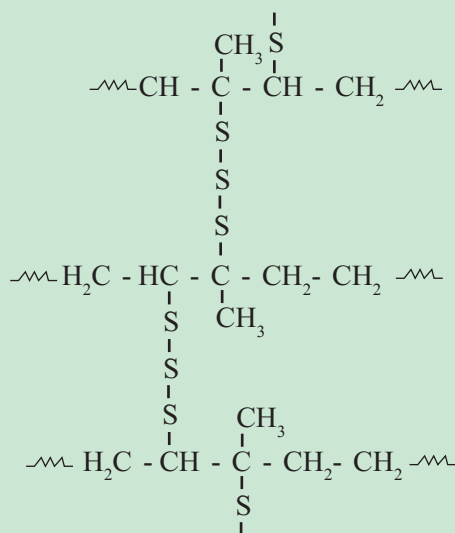
Do you know ?



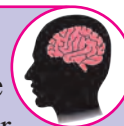
Vulcanizing is carried out by heating raw rubber with sulfur powder in presence of some organic compounds called accelerators at about 150 °C. (The most common accelerator is ZBX or zincbutyl xanthate). By increasing amount of sulfur the rubber can be hardened. For example when the amount of sulfur is raised to 40-45 % a non-elastic hard material known as **ebonite** is obtained.

One or more sulfur atoms cross-link two polyisoprene chains. Cross-linking takes place by opening of a double bond and produces three dimensional vulcanised rubber.

Probable 3-D structure of vulcanized rubber is



Use your brain power



- From the cis-polyisoprene structure of natural rubber explain the low strength of van der Waals forces in it.
- Explain how vulcanization of natural rubber improves its elasticity ? (Hint : consider the intermolecular links.)

Do you know ?



Natural Rubber first came into the market in early 19th century. It was entirely recovered from wild *Hevea brasiliensis* trees which usually grew on the banks of Amazon river and its tributaries in South America. The amount of hydrocarbon present in Hevea Tree is very high (35%). As per the demand the production of natural rubber increased by leaps and bounds and at present 1.5 million tons of natural rubber is sent to the market.

The latex is collected from a mature Hevea tree by making deep cuts on the bark and by allowing the latex stream in a pot attached below the cut. The latex is an emulsion like milk.

When a coagulant like acetic acid is added to the latex the rubber hydrocarbon gets coagulated in the amorphous solid form.

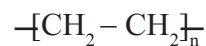
15.3.2 Polythene :

Can you recall ?



How is ethylene prepared ?

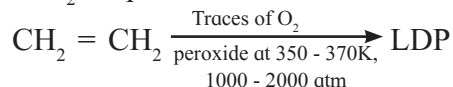
Polythene is the simplest and most commonly used hydrocarbon thermoplastic and has following structure.



The IUPAC name of polyethylene is polythene. Polythene is of two kinds, namely low density polythene (LDP) and high density polythene (HDP) .

a. Low density polyethylene (LDP) :

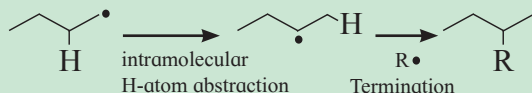
LDP is obtained by polymerization of ethylene under high pressure (1000 - 2000 atm) and temperature (350 - 570 K) in presence of traces of O_2 or peroxide as initiator.



The mechanism of this reaction involves free radical addition and H-atom abstraction. The latter results in branching. As a result the chains are loosely held and the polymer has low density.

Do you know ?

In the H-atom abstraction, process involved in formation of LDP; the terminal carbon radical abstracts H-atom from an internal carbon atom in the form of an internal carbon radical. Termination step in addition polymerization gives rise to branching of these internal carbons.

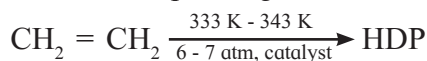


Properties of LDP : LDP films are extremely flexible, but tough, chemically inert and moisture resistant. It is poor conductor of electricity with melting point 110 °C.

Uses of LDP : LDP is mainly used in preparation of pipes for agriculture, irrigation, domestic water line connections as well as insulation to electric cables. It is also used in submarine cable insulation. It is used in producing extruded films, sheets, mainly for packaging and household uses like in preparation of squeeze bottles, attractive containers etc.



b. High density polyethylene (HDP) : It is essentially a linear polymer with high density due to close packing.



HDP is obtained by polymerization of ethene in presence of Ziegler-Natta catalyst which is a combination of triethyl aluminium with titanium tetrachloride at a temperature of 333K to 343K and a pressure of 6-7 atm.

Properties of HDP : HDP is crystalline, melting point in the range of 144 - 150 °C. It is much stiffer than LDP and has high tensile strength and hardness. It is more resistant to chemicals than LDP.

Uses of HDP : HDP is used in manufacture of toys and other household articles like buckets, dustbins, bottles, pipes etc. It is used to prepare laboratory wares and other objects where high tensile strength and stiffness is required.



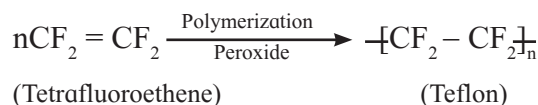
Internet my friend

Where is polythene manufactured in India ?



15.3.3 Teflon : Chemically teflon is polytetrafluoroethylene. The monomer used in preparation of teflon is tetrafluoroethylene, ($CF_2 = CF_2$) which is a gas at room temperature.

Tetrafluoroethylene is polymerized by using free radical initiators such as hydrogen peroxide or ammonium persulphate at high pressure.



Properties : Teflon is tough, chemically inert and resistant to heat and attack by corrosive reagents.

C - F bond is very difficult to break and remains unaffected by corrosive alkali, organic solvents.

Uses : Teflon is used in making non-stick cookware, oil seals, gaskets, etc.

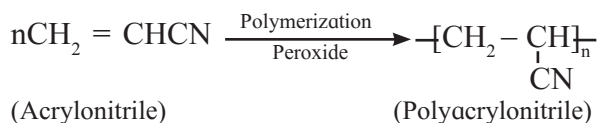


Internet my friend

Collect the information of Teflon coated products used in daily life and in industries.



15.3.4 Polyacrylonitrile : Polyacrylonitrile is prepared by addition polymerization of acrylonitrile by using peroxide initiator.



Polyacrylonitrile resembles wool and is used as wool substitute and for making orlon or acrilan.



Do you know ?

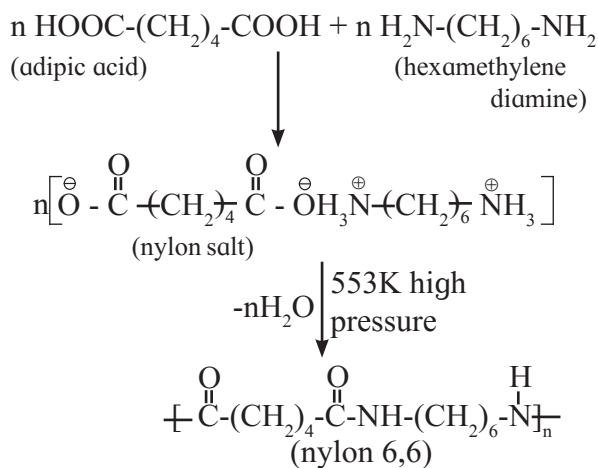
Orlon is used to make blankets, shawls, sweat shirts, sweaters.



15.3.5 Polyamide polymers : Polyamide polymers are generally known as nylons. Nylon is the generic name of the synthetic linear polyamides obtained by the condensation polymerization between dicarboxylic acids and diamines, the self condensation of an amino acid or by the ring opening polymerization of lactams.

Polyamides contain - CO - NH - groups as the inter unit linkages. Two important polyamide polymers are nylon 6, 6 and nylon 6.

a. Nylon 6,6 : The monomers adipic acid and hexamethylenediamine on mixing forms nylon salt, which upon condensation polymerization under conditions of high temperature and pressure give the polyamide fibre nylon 6,6.



The numerals 6,6 in the name of this polymer stand for the number of carbon atoms in the two bifunctional monomers, namely, adipic acid and hexamethylenediamine.

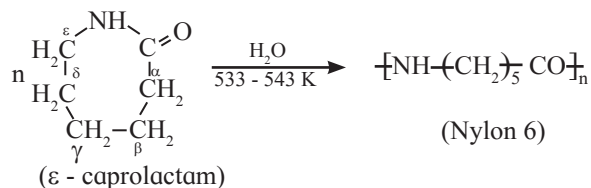
Nylon 6,6 is high molecular mass (12000-50000 u) linear condensation polymer. It possesses high tensile strength. It does not soak in water. It is used for making sheets, bristles for brushes, surgical sutures, textile fabrics, etc.

Do you know ?

- When an amino group and carboxyl group present in the same molecule react intramolecularly the resulting amide is cyclic and is called **lactam**.
- A cyclic ester formed by intramolecular reaction of hydroxyl and carboxyl groups is called **lactone**.

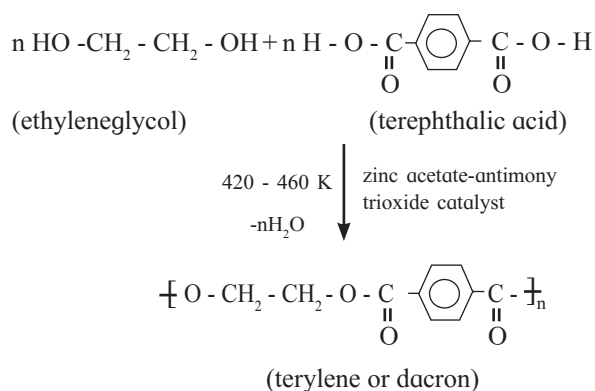


b. Nylon 6 : When epsilon (ϵ)-caprolactam is heated with water at high temperature it undergoes ring opening polymerization to give the polyamide polymer called nylon 6.



The name nylon 6 is given on the basis of six carbon atoms present in the monomer unit. Due to its high tensile strength and luster nylon 6 fibres are used for manufacture of tyre cords, fabrics and ropes.

15.3.6 Polyesters : The polyester polymers have ester linkage joining the repeating units. Commercially the most important polyester fibre is 'terylene' (also called dacron). It is obtained by condensation polymerization of ethylene glycol and terephthalic acid in presence of catalyst at high temperature.



Terylene has relatively high melting point (265°C) and is resistant to chemicals and water. It is used for making wrinkle free fabrics by blending with cotton (terycot) and wool (terywool), and also as glass reinforcing materials in safety helmets. PET is the most common thermoplastic which is another trade name of the polyester polyethyleneterephthalate. It is used for making many articles like bottles, jams, packaging containers.

Polycarbonates are also a kind of polyester polymers. These are high melting thermosetting resins.

15.3.7 Phenol - formaldehyde and related polymers :

a. Bakelite : Bakelite, the thermosetting polymer obtained from reaction of phenol and formaldehyde is the oldest synthetic polymer. Phenol and formaldehyde react in presence of acid or base catalyst to form thermosetting/ moulding powder (novolac) in two stages. In the third stage, various articles are shaped from novolac by putting it in appropriate moulds and heating at high temperature (138°C to 176°C) and at high pressure. The reactions involved are represented in the Fig. 15.3.

During the third stage of thermosetting in the moulds, many crosslinks are formed which results in formation of rigid polymeric material, called bakelite which is insoluble and infusible and has high tensile strength. It can also serve as substitute for glass. Bakelite is used for making articles like telephone instrument, kitchenware, electric insulators.

b. Melamine-formaldehyde polymer : Decorative table tops like formica and plastic dinner-ware are made from heat and moisture resistant thermosetting plastic called melamine - formaldehyde resin. The reactions are shown in Fig. 15.4. Melamine and formaldehyde undergo condensation polymerisation to give cross linked melamine formaldehyde.

Internet my friend

Find applications of bakelite in day to day life.



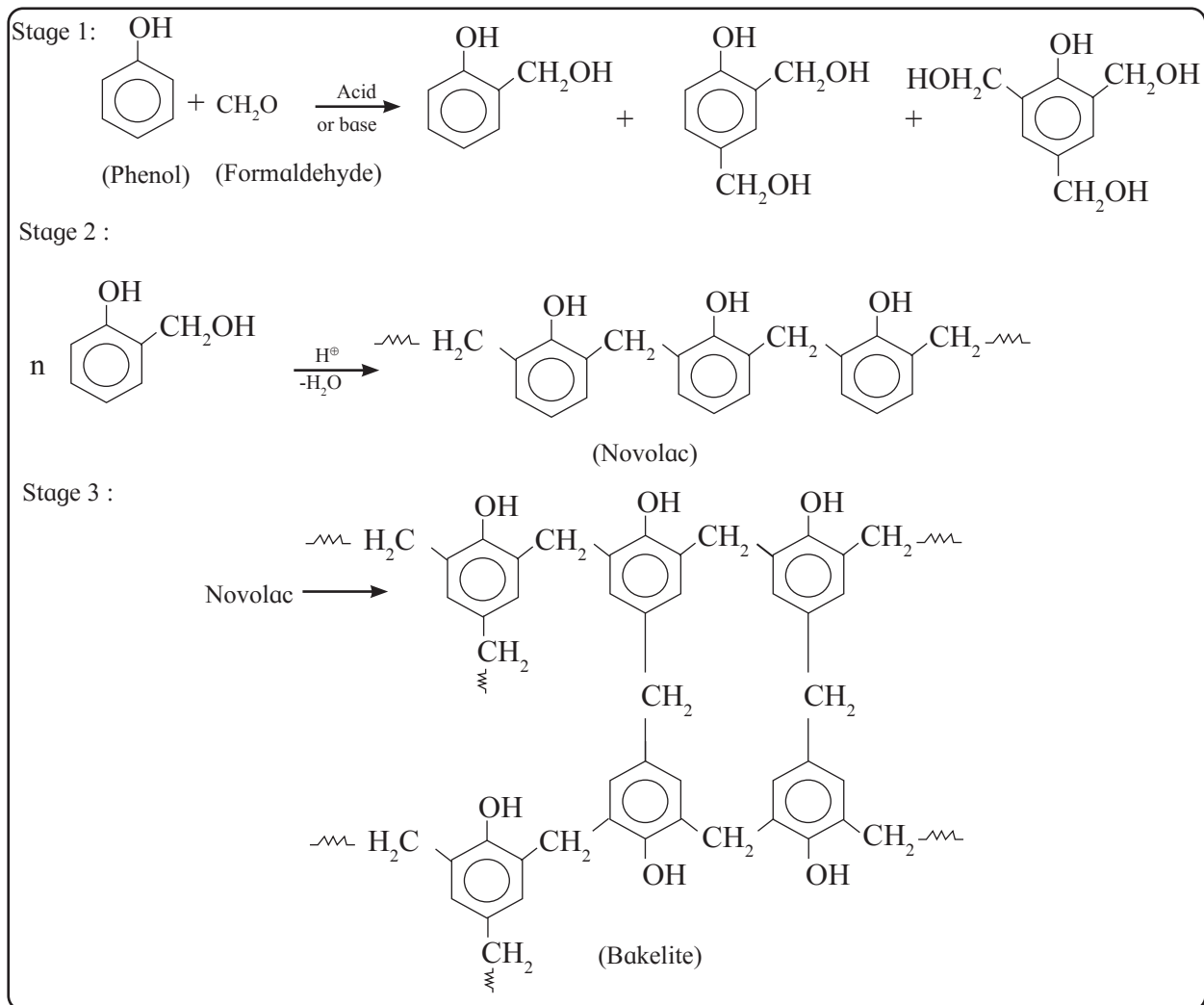


Fig. 15.3 Preparation of Bakelite

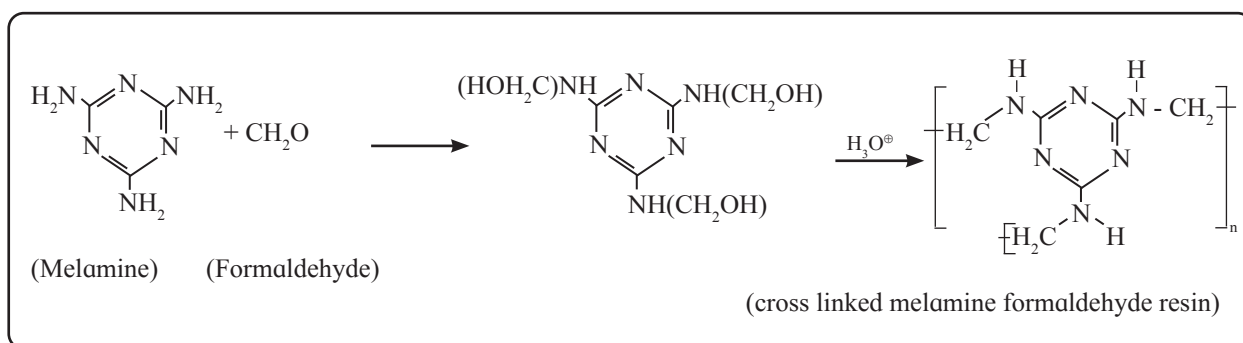


Fig. 15.4 Formation of cross linked melamine formaldehyde resin

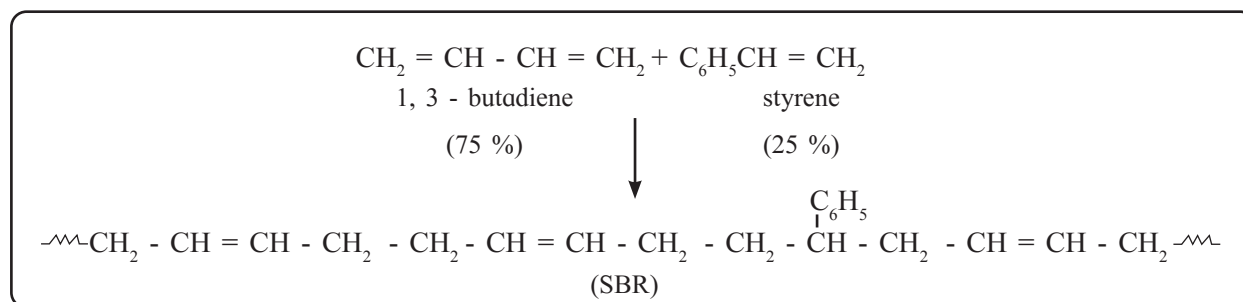


Fig. 15.5 Formation of SBR (Buna - S)

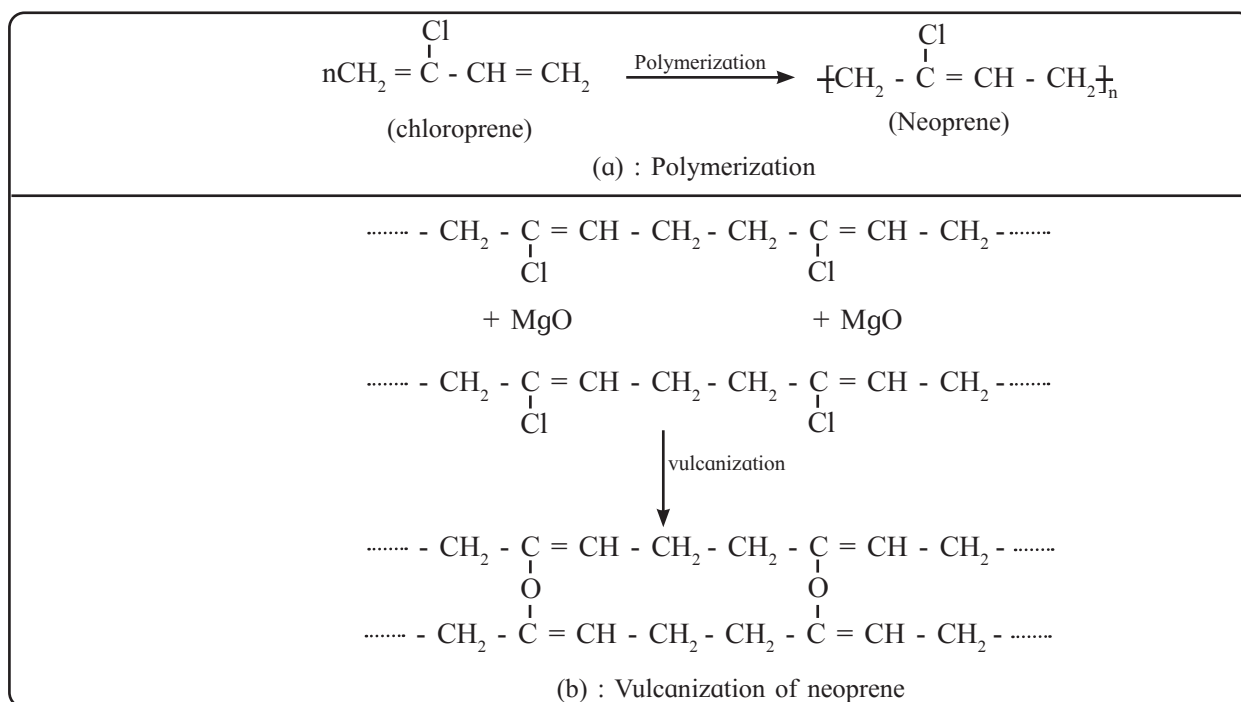


Fig. 15.6 Neoprene and vulcanization

15.3.8 Buna-S rubber : Buna-S is an elastomer which is a copolymer of styrene with butadiene (Fig.15.5). Its trade name is SBR (styrene-butadiene rubber). The copolymer is usually obtained from 75 parts of butadiene and 25 parts of styrene subjected to addition polymerization by the action of sodium. It is vulcanized with sulfur.

Buna-S is superior to natural rubber with regard to mechanical strength and has abrasion resistance. Hence it is used in tyre industry.



15.3.9 Neoprene : Neoprene, a synthetic rubber, is a addition polymer of chloroprene (2-chloro-1,3-butadiene). Chloroprenepolymerizes rapidly in presence of oxygen. Vulcanization of neoprene takes place in presence of magnesium oxide. The reactions involved can be represented in Fig. 15.6.

Neoprene is particularly resistant to petroleum, vegetable oils, light as well as heat. Neoprene is used in making hose pipes for transport of gasoline and making gaskets. It is used for manufacturing insulator cable, jackets, belts for power transmission and conveying.



15.3.10 Viscose rayon : Viscose rayon is a semisynthetic fibre which is regenerated cellulose. Cellulose in the form of wood pulp is transformed into viscose rayon. Cellulose is a linear polymer of glucose units and has molecular formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. A modified representation of the molecular formula of cellulose Cell-OH, is used in the reactions involved in viscose formation, as shown in Fig. 15.7. Cellulose in the form of wood pulp is treated with concentrated NaOH solution to get fluffy alkali cellulose. It is then converted to xanthate by treating with carbon disulphide. On mixing with dilute NaOH it gives viscose solution which is extruded through spinnerates

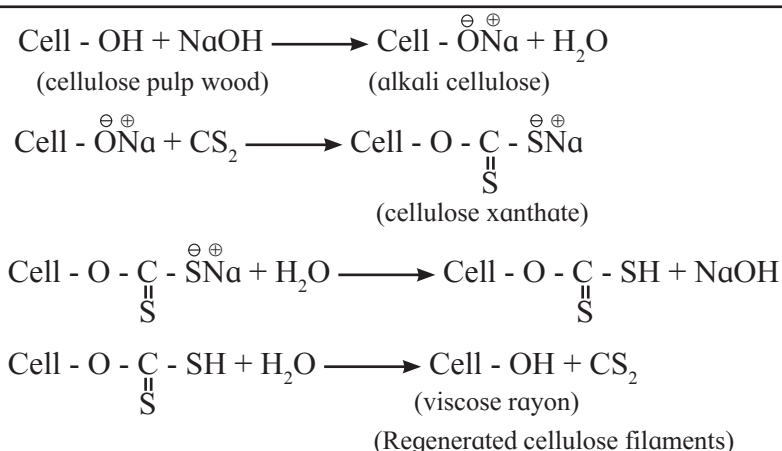


Fig. 15.7 : Formation of viscose rayon

of spinning machine into acid bath when regenerated cellulose fibres precipitate.

Use your brain power

- Write structural formulae of styrene and polybutadiene.



15.4 Molecular mass and degree of polymerization of polymers :

A polymer is usually a complex mixture of molecules of different molecular masses. Hence, molecular mass of a polymer is an average of the molecular masses of constituent molecules. Molecular mass of polymer depends upon the degree of polymerization (DP). DP is the number of monomer units in a polymer molecule.

Most of the mechanical properties of polymers depend upon their molecular mass. Low molecular mass polymers are liable to be brittle and have low mechanical strength. If a polymer is allowed to attain very high molecular mass it becomes tough and unmanageable. Both these ends are undesirable. A polymer must possess a molecular mass more than certain minimum value in order to exhibit the properties needed for a particular application. This minimum molecular mass corresponds to the critical degree of polymerization. But the polymerization process has to be controlled after certain stage. For polymers containing hydrogen bonding the critical degree of polymerization is lower than those containing weak intermolecular forces.

Can you tell ?

- Classify the following polymers as addition or condensation.
 - PVC
 - Polyamides
 - Polystyrene
 - Polycarbonates
 - Novolac
- Complete the following table :

Condensation polymers	Repeating unit	Name of monomer	Formula of monomer	Uses
1. Nylon 6				
2. Nylon 6, 6				
3. Terylene				
4. Melamine				



Problem 15.2 : The critical degree of polymerization is low for nylon 6 while high for polythene. Explain.

Solution : Nylon 6 is a polyamide polymer, and has strong intermolecular hydrogen bonding as inter molecular forces. On the other hand polythene chains have only weak van der Waals forces as intermolecular interaction. Because of the stronger intermolecular forces the critical DP is lower for nylon 6 than polythene.

15.5 Biodegradable polymers :

Can you recall ?

- Name some materials which undergo degradation after use.
- List the materials which do not decay even after a long time.
- How is the environment affected by non decaying substances ?
- Which bonds are broken during digestion of proteins and carbohydrates ?
- What happens to disposed natural wastes such as stale food, fruit peels, torn cotton cloth ?

In spite of large number of useful applications, polymers are blamed for creating environmental pollution. To strike the golden mean, certain new biodegradable synthetic polymers have been developed.

Aliphatic polyesters and polyamides with large proportion of polar linkages are one of the important classes of biodegradable polymers. Some important examples are discussed below.

Disposed natural wastes are usually attacked by soil microbes and get degraded to humus. But most synthetic polymers and plastics cannot be degraded by microbes and stay in the environment for very long period of time posing pollution problems. To overcome

Can you recall ?

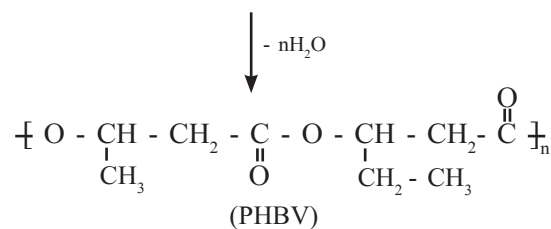
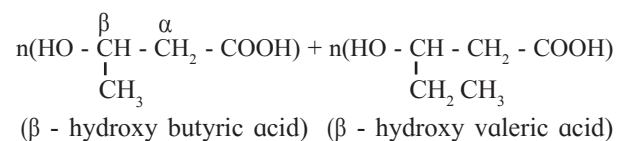
- What are the structural formulae of glycine and ϵ - amino caproic acid ?

this problem biodegradable polymers are being developed. These polymers contain functional groups similar to those in biopolymers such as proteins. Aliphatic polyesters are also an important class of biodegradable polymers.

Use your brain power

- Represent the copolymerization reaction between glycine and ϵ - amino caproic acid to form the copolymer nylon 2- nylon 6.
- What is the origin of the numbers 2 and 6 in the name of this polymer ?


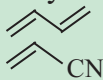


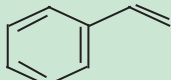
15.5.1 PHBV : PHBV is a copolymer of two bifunctional β - hydroxy carboxylic acids, namely, β - hydroxybutyric acid (3 - hydroxybutanoic acid) and β - hydroxyvaleric acid (3 - hydroxypentanoic acid). Hydroxyl group of one monomer forms ester link by reacting with carboxyl group of the other. Thus PHBV is an aliphatic polyester with name poly β - hydroxy butyrate - co - β - hydroxy valerate (PHBV). PHBV is degraded by microbes in the environment.



15.5.2 Nylon 2 - nylon 6 : Nylon 2 - nylon 6 is a polyamide copolymer of two amino acids, namely, glycine and ϵ - amino caproic acid. It is a biodegradable polymer.

15.6 Commercially important polymers : Apart from the polymers already discussed in this chapter, many more polymers are used extensively. Structures and applications of some of them are given in the Table 15.1.

Table 15.1 : Commercially important polymers

Trade name	Monomer	Polymer structure	Applications
Perspex/acrylic glass	methyl methacrylate 	$\text{[CH}_2\text{-C(CH}_3\text{)(COOMe)]}_n$	lenses, paint, security barrier, LCD screen, shatter resistant glass
Buna N	Butadiene and acrylonitrile 	$\text{[H}_2\text{C-CH=CH-CH}_2\text{-CH}_2\text{-CH(CN)]}_n$	adhesives, rubber belts, shoe soles, O-rings, gaskets
PVC (polyvinyl chloride)	vinyl chloride 	$\text{[CH}_2\text{-CH(Cl)]}_n$	water pipes, rain coats, flooring
Polyacrylamide	acrylamide 	$\text{[CH}_2\text{-CH(CONH}_2\text{)]}_n$	Polyacrylamide gel used in electrophoresis
Urea-formaldehyde resin	a. urea b. formaldehyde	$\text{[NH-CO-NH-CH}_2\text{]}_n$	unbreakable dinner ware, decorative laminates
Glyptal	a. ethyleneglycol b. phthalic acid	$\text{[O-CH}_2\text{-CH}_2\text{-OOC-C}_6\text{H}_4\text{-CO]}_n$	paints and lacquers
Polycarbonate	a. bisphenol b. phosgene	$\text{[O-C}_6\text{H}_4\text{-C(CH}_3\text{)}_2\text{-C}_6\text{H}_4\text{-O-CO]}_n$	electrical and telecommunication hardware, food grade plastic containers
Thermocol (made from airfilled thin walled beads of polystyrene)	Styrene 	$\text{[CH}_2\text{-CH(C}_6\text{H}_5\text{)]}_n$	non-biodegradable styrene can leach when heated. Therefore it is banned.

Exercises

1. Choose the correct option from the given alternatives.

- i. Nylon fibres are ----
A. Semisynthetic fibres
B. Polyamide fibres
C. Polyester fibres
D. Cellulose fibres
- ii. Which of the following is naturally occurring polymer ?
A. Telfon B. Polyethylene
C. PVC D. Protein
- iii. Silk is a kind of ---- fibre
A. Semisynthetic
B. Synthetic
C. Animal
D. Vegetable
- iv. Dacron is another name of ----
A. Nylon 6 B. Orlon
C. Novolac D. Terylene
- v. Which of the following is made up of polyamides ?
A. Dacron B. Rayon
C. Nylon D. Jute
- vi. The number of carbon atoms present in the ring of ϵ - caprolactam is
A. Five B. Two
C. Seven D. Six
- vii. Terylene is ----
A. Polyamide fibre
B. Polyester fibre
C. Vegetable fibre
D. Protein fibre

- viii. PET is formed by ----
A. Addition B. Condensation
C. Alkylation D. Hydration
- ix. Chemically pure cotton is ----
A. Acetate rayon
B. Viscose rayon
C. Cellulose nitrate
D. Cellulose
- x. Teflon is chemically inert, due to presence of
A. C-H bond B. C-F bond
C. H- bond D. C=C bond

2. Answer the following in one sentence each.

- i. Identify 'A' and 'B' in the following reaction ----
 a.
$$\begin{array}{ccc} \text{HO}-\text{CH}_2-\text{CH}_2-\text{OH} & & \\ + & & \\ \text{H}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H} & \xrightarrow[\Delta]{533\text{K}} & \text{'A'} \end{array}$$
- b.
$$\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2 + \text{HOOC}-(\text{CH}_2)_4\text{COOH} \xrightarrow[533\text{K}]{\text{N}_2} \text{'B'}$$
- ii. Complete the following statements
 - a. Caprolactam is used to prepare-----
 - b. Novolak is a copolymer of -----
-- and -----
 - c. Terylene is -----polymer of terephthalic acid and ethylene glycol.
 - d. Benzoyl peroxide used in addition polymerisation acts as -----
 - e. Polyethene consists of polymerised -----

- iii. Draw the flow chart diagram to show classification of polymers based on type of polymerisation.
- iv. Write examples of Addition polymers and condensation polymers.
- v. Name some chain growth polymers.
- vi. Define the terms :
 - 1) Monomer
 - 2) Vulcanisation
 - 3) Synthetic fibres
- vii. What type of intermolecular force leads to high density polymer ?
- viii. Give one example each of copolymer and homopolymer.
- ix. Identify Thermoplastic and Thermosetting Plastics from the following -----
 1. PET
 2. Urea formaldehyde resin
 3. Polythene
 4. Phenol formaldehyde

3. Answer the following.

- i. Write the names of classes of polymers formed according to intermolecular forces and describe briefly their structural characteristics.
- ii. Write reactions of formation of :
 - a. Nylon 6 b. Terylene
- iii. Write structure of natural rubber and neoprene rubber along with the name and structure of their monomers.
- iv. Name the polymer type in which following linkage is present.

$$\begin{array}{c} \text{-C-O-} \\ || \\ \text{O} \end{array}$$
- v. Write structural formula of the following synthetic rubbers :
 - a. SBR rubber
 - b. Buna-N rubber
 - c. Neoprene rubber

- vi. Match the following pairs :

Name of polymer	Monomer
1. Teflon	a. $\text{CH}_2=\text{CH}_2$
2. PVC	b. $\text{CF}_2=\text{CF}_2$
3. Polyester	c. $\text{CH}_2=\text{CHCl}$
4. Polythene	d. $\text{C}_6\text{H}_5\text{OH}$ and HCHO
5. Bakelite	e) Dicarboxylic acid and polyhydroxyglycol

- vii. Draw the structures of polymers formed from the following monomers

1. Adipic acid + Hexamethylenediamine

2. ϵ - Aminocaproic acid + Glycine

- viii. Name and draw structure of the repeating unit in natural rubber.

- ix. Classify the following polymers as natural and synthetic polymers

a. Cellulose b. Polystyrene

c. Terylene d. Starch

e. Protein f. Silicones

g. Orlon (Polyacrylonitrile)

h. Phenol-formaldehyde resins

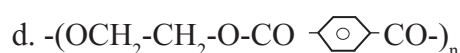
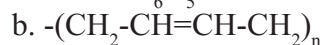
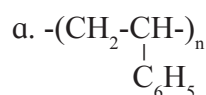
- x. What are synthetic resins? Name some natural and synthetic resins.

- xi. Distinguish between thermosetting and thermoplastic resins. Write example of both the classes.

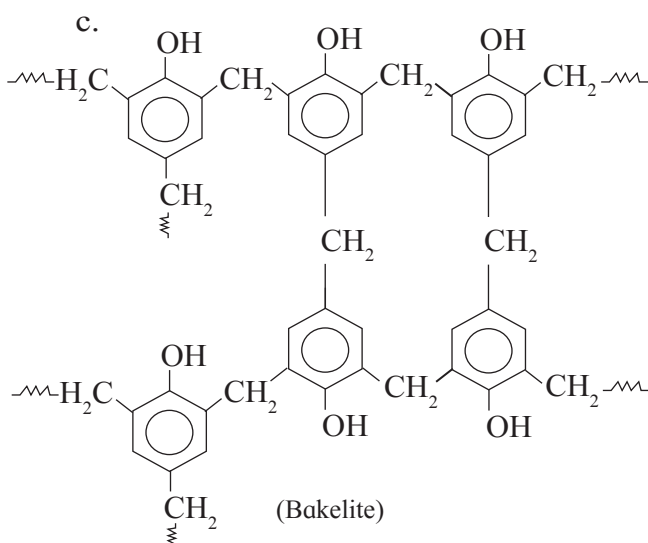
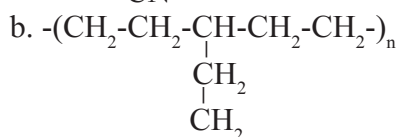
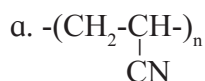
- xii. Write name and formula of raw material from which bakelite is made.

4. Attempt the following :

- i. Identify condensation polymers and addition polymers from the following.



- ii. Write the chemical reactions involved in manufacture of Nylon 6,6
- iii. Explain vulcanisation of rubber. Which vulcanizing agents are used for the following synthetic rubber.
 - a. Neoprene b. Buna-N
- iv. Write reactions involved in the formation of ---
 - 1) Teflon
 - 2) Bakelite
- v. What is meant by LDP and HDP? Mention the basic difference between the same with suitable examples.
- vi. Write preparation, properties and uses of Teflon.
- vii. Classify the following polymers as straight chain, branched chain and cross linked polymers.



5. Answer the following.

- i. How is polythene manufactured ? Give their properties and uses.
- ii. Is synthetic rubber better than natural rubber ? If so, in what respect?
- iii. Write main specialities of Buna-S, Neoprene rubber?
- iv. Write the structure of isoprene and the polymer obtained from it.
- v. Explain in detail free radical mechanism involved during preparation of addition polymer.

Activity :



- i. Collect the information of the process like extrusion and moulding in Textile Industries.
- ii. Make a list of polymers used to make the following articles
 - a. Photographic film
 - b. Frames of spectacles
 - c. Fountain pens
 - d. Moulded plastic chains
 - e. Terywool or Terycot fabric
- iii. Prepare a report on factors responsible for degradation of polymers giving suitable example.
- iv. Search and make a chart/note on silicones with reference to monomers, structure, properties and uses.
- v. Collect the information and data about Rubber industry, plastic industry and synthetic fibre (rayon) industries running in India.