POLYMER

SESSION –1

AIM

✓ To introduce and classify polymers.

I] POLYMERS

Polymers are one of the most important substances which have a great impact on our modern life. The man-made fibres which are polymerized products have brought a revolution in the textile industry. Nylon and terylene have almost completely replaced cotton and silk. Similarly, resins, plastics, natural and synthetic rubber are a gift from the scientists to our society. In the present topic describes the study of the different classes of polymers, the nature of forces present and their mode of synthesis. We shall also briefly discuss a few important polymers which are of great significance in our daily life.

Polymers are compounds of very high molecular masses formed by the combination of a large number of simple molecules. In Greek, poly means many and meros means units or parts. The simple molecules which combine to give polymers are called monomers. The process by which the simple molecules (i.e., monomers) are converted into polymers is called **polymerization**. For example, polyethylene or commonly known as polythene is a polymer which is obtained from its monomers ethylene by the process of polymerization.

$$nCH_2 = CH_2 \xrightarrow{\text{polymerization}} (-CH_2 - CH_2)n$$

1) Homopolymer and Copolymer

A polymer formed from one type of monomers is called homopolymer. For example, polythene is a homopolymer of monomer ethylene.

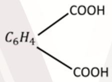
A polymer formed from two or more different monomers is called copolymer or mixed polymer, For example, terylene is a polymer of two types of monomers: ethylene glycol and terephthalic acid.

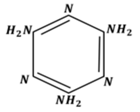
Polymers and macromolecules. The polymers are also called macromolecules because of their big size. The terms polymers and macromolecules are often used without any distinction. But, a polymer always consists of thousands of repeating monomer units. However, a macromolecule is a giant molecule which may or may not contain monomer units. For example, chlorophyll is a macromolecule but it is not regarded as a polymer because it does not contain monomers. However, polythene may be regarded as a polymer as well as a macromolecule because it contains a large number of repeating monomers. Thus, all polymers are macromolecules but all macromolecules are not polymers.

TABLE 1-HOMOPOLYMERS

	Common Name of the homopolymer	**Monomer**	**Uses**
1	Polyethylene	$CH_2 = CH_2$ Ethylene	In the manufacture of pipes, toys, bags, wire insulators, bottles, etc.
2	Polyvinyl chloride(PVC)	$CH_2 = CHCl$ Vinyl chloride	In the manufacture of sheets, water pipes, hoses, hand bags, etc.
3	Polystyrene	$C_6H_5CH = CH_2$ styrene	In the manufacture of combs, toys, radio and television cabinets, etc.
4	Polyacrylonitrile (PAN)	$CH_2 = CH - CN$ Acrylonitrile	In the manufacture of orlon (fibre) and acrilon films
5	Teflon (Polytetrafluoro ethene)	$CF_2 = CF_2$ Tetrafluoro ethylene	In the manufacture of insulators, gaskets, etc.
6	Buna rubber	$CH_2 = CH - CH = CH_2$ 1,3-Butadiene	In the manufacture of tyres, hoses, etc.
7	Polyvinyl acetate	$CH_2 = CHOOCCH_3$ Vinyl acetate	In the manufacture of latex paint.

TABLE 2-COPOLYMERS

	Common name of copolymer	**Monomers**	**Uses**
1	Synthetic rubber or styrene butadiene rubber(SBR) or (Buna-S)	(i) $C_6H_5CH = CH_2$ Styrene (ii)$CH_2 = CH - CH = CH_2$ 1,3-Butadiene	In the manufacture of light duty tyres, belting, hoses and rubber soles.
2	Dacron or Terylene	(i) $HOCH_2 - CH_2OH$ Ethylene glycol (ii) $H_3COOC(C_6H_4)COOCH_3$ Dimethyl terephthalate	In the manufacture of fabrics and magnetic recording tapes.
3	Glyptal	(i) $HOCH_2 - CH_2OH$ ethylene glycol  (ii) Phthalic acid	In the manufacture of points and lacquers.
4	Nylon-66	(i) $H_2N(CH_2)_6NH_2$ Hexamethylene diamine (ii) $HCOOC(CH_2)_4COOH$ Adipic acid	In the manufacture of fabrics, tyre cords, ropes, carpets, etc.
5	Bakelite	(i)$HCHO$ Formaldehyde (ii) C_6H_5OH Phenol	In the manufacture of electric goods, phonograph records, fountain pen barrels, comb, etc.
6	Melamine-formaldehyde resin or Melamine	(i)$HCHO$ Formaldehyde	In the manufacture of plastic crockery.

		(ii)  Melamine	
7	Polyurethane	(i) $HO - CH_2 - CH_2 - OH$ Ethylene glycol (ii) $O = C = N - CH = CH - N = C = O$ Ethylene di-isocyanate	In the manufacture of fibres, paints and heat insulators.

II] CLASSIFICATION OF POLYMERS:

Polymers are classified in a number of ways as described ahead:

(A) Classification of Polymers on the Basis of source

The polymers can be broadly classified as

1. Natural Polymers
2. Synthetic Polymers.
3. Semi synthetic polymers.

(1) Natural Polymers : The polymers obtained from nature (plants and animals) are called natural polymers. For example, starch, cellulose, natural rubber, proteins etc.

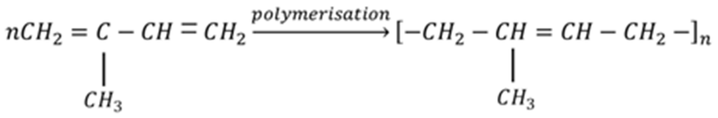
(i) ***Starch***. It is a polymer of glucose. It is a chief food reserve of plants

(ii) ***Cellulose***. It is also a polymer of glucose. It is a chief structural material of the plants. Both starch and cellulose are made by plants from glucose produced during photosynthesis.

(iii) ***Proteins***. These are polymers of **α-amino acids.** They have generally 20 to 1000 α-amino acids joined together in a highly organized arrangement. These are building blocks of animal body and constitute an essential part of our food.

(iv) ***Nucleic acids***. These are polymers of various **nucleotides.** For example. RNA and DNA are common nucleotides.

(v) ***Natural rubber.*** It is a polymer of unsaturated hydocarbon. 2 methyl-1, 3-butadiene also called isoprene. It is obtained from latex of rubber trees.



$$nCH_2 = \underset{CH_3}{\underset{|}{C}} - CH = CH_2 \xrightarrow{polymerisation} [-CH_2 - \underset{CH_3}{\underset{|}{CH}} = CH - CH_2 -]_n$$

2-methyl - 1, 3 - butadiene

polyisoprene (natural rubber)

In natural rubber 10,000 to 20,000 isoprene units are linked together,

polymers such as polysaccharides (starch, cellulose), proteins and nucleic acids etc. which control various life processes in plants and animals are also called biopolymers.

(2) ***Synthetic polymers:*** The polymers which are prepared in the laboratories are called **synthetic polymers.** These are also called **man-made polymers.** For example, polyethylene, PVC nylon, Teflon, bakelite, terylene, synthetic rubber, etc.

(3) ***Semi-synthetic polymers :*** These are the substances which are obtained by using natural polymers i.e., some modifications are made in natural polymers by artificial means, Nitrocellulose, Cellulose acetate, cellulose xanthate, etc., belong to this class of polymers.

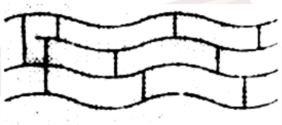
B) CLASSIFICATION BASED UPON STRUCTURE:

Based upon the mode of linkage in the monomer units, the polymers may be either linear, branched chain or cross-linked in nature. These are briefly discussed as follows:

1. ***Linear chain polymers.*** In this case, the monomer units are linked to one another to form long linear chains. These linear chains are placed one above the other and are closely packed in space. The close packing results in high densities, tensile strength and also high melting and boiling points. High density polythene is a very common example of this type. Nylon and polyesters are also linear chain polymers.

2. ***Branched chain polymers.*** In this type of polymers, the monomer units are linked to form long chains which have also side chains or branched chains of different lengths attached to them. As a result of branching, these polymers are not closely packed in space. They have low densities, low tensile strength as well as low melting and boiling points. Some common examples of such polymers are low density polythene, amylopectin, starch, glycogen etc.

3. ***Cross-linked polymers.*** In these polymers also called network polymers, the monomer units are linked together to form three dimensional net—work. These are expected to be quite hard, rigid and brittle. Example of cross linked polymers are bakelite, glyptal, melamine formaldehyde polymer etc.

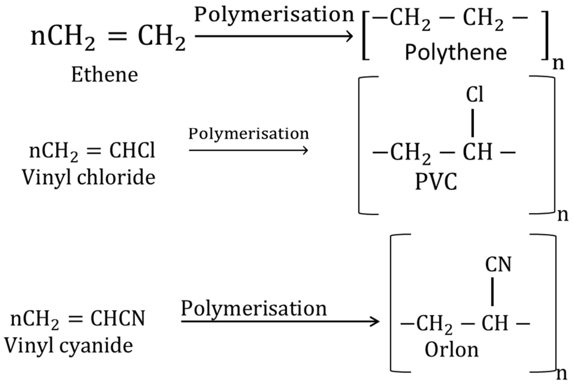


Cross Linked Polymer

C) CLASSIFICATION BASED UPON SYNTHESIS :

On the basis of mode of synthesis, polymers are classified into two categories.

(1) Addition polymers : These are polymers formed by the addition together of the molecules of the monomer or monomers to form a large molecule without elimination of any thing. The process of the formation of addition polymers is termed **addition polymerisation** . The addition polymers are formed by monomers which are unsaturated compounds e.g., ethane and derivatives of ethane. An addition polymer has the same empirical formula as the monomer. Ethene, vinyl chloride and vinyl cyanide are some of the compounds which undergo addition polymerization.



$$\underset{\text{Ethene}}{nCH_2 = CH_2} \xrightarrow{\text{Polymerisation}} \left[\underset{\text{Polythene}}{-CH_2 - CH_2 -}\right]_n$$

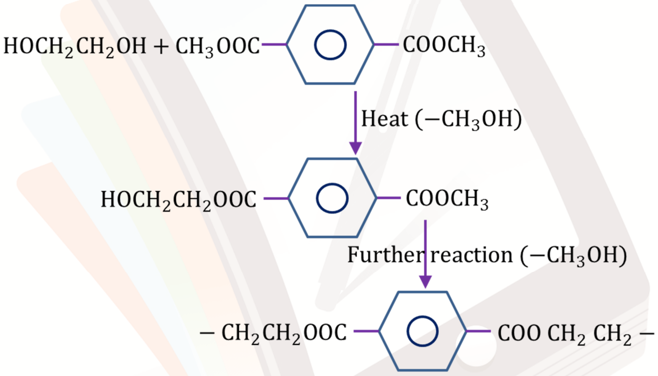
$$\underset{\text{Vinyl chloride}}{nCH_2 = CHCl} \xrightarrow{\text{Polymerisation}} \left[\underset{\text{PVC}}{-CH_2 - \overset{\overset{\displaystyle Cl}{|}}{CH} -}\right]_n$$

$$\underset{\text{Vinyl cyanide}}{nCH_2 = CHCN} \xrightarrow{\text{Polymerisation}} \left[\underset{\text{Orlon}}{-CH_2 - \overset{\overset{\displaystyle CN}{|}}{CH} -}\right]_n$$

(2) Condensation polymers : Condensation polymers are formed by the combination of monomers with the elimination of simple molecules such as water or alcohol. This process of formation of polymers is called condensation polymerization. Condensation polymers are generally formed by reaction between poly functional monomers, Proteins, starch, cellulose, etc., are the examples of natural condensation polymers. Among the synthetic polymers, two main types of condensation polymers are : Polyesters and polyamides.

i) Polyester – (Terylene or Dacron): The long chain of condensation polymers consists of ester linkages formed by condensation of an hydroxy group and carboxylic group with elimination of water molecules.

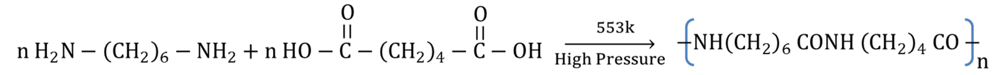
Terylene is the most important example of this group. It is made by heating ethylele glycol with dimethyl terephthalate.



Terylene

ii) Polyamides: These have linkages −CONH − in the chain. These polymers are popularly known as nylons.

For Example, nylon –6, 6: The monomer units of nylon – 6, 6 are hexamethylenediamine and adipic acid, with the elimination of water molecule under high pressure and temperature.



$$n\,H_2N-(CH_2)_6-NH_2 + n\,HO-\overset{O}{\overset{||}{C}}-(CH_2)_4-\overset{O}{\overset{||}{C}}-OH \xrightarrow[\text{High Pressure}]{553k} \left[NH(CH_2)_6\,CONH\,(CH_2)_4\,CO \right]_n$$

Hexamethylene diamine   Adipic Acid   Nylon − 6, 6

D) CLASSIFICATION OF POLYMERS ON THE BASIS OF MOLECULAR FORCES.

A large number of applications of polymers depend upon their mechanical properties such as tensile strength, elasticity, toughness etc. These mechanical properties depend upon intermolecular forces like Van der Waals forces, hydrogen bonds and dipole-dipole interactions existing in the macromolecules. Although these intermolecular forces are also present in simple molecules, their effect is less significant in them as compared to macromolecules. This is because in the polymers, these forces extend all along the chain resulting significant combined effect. Thus, longer the length of the polymer chain. stronger is the effect of intermolecular forces.

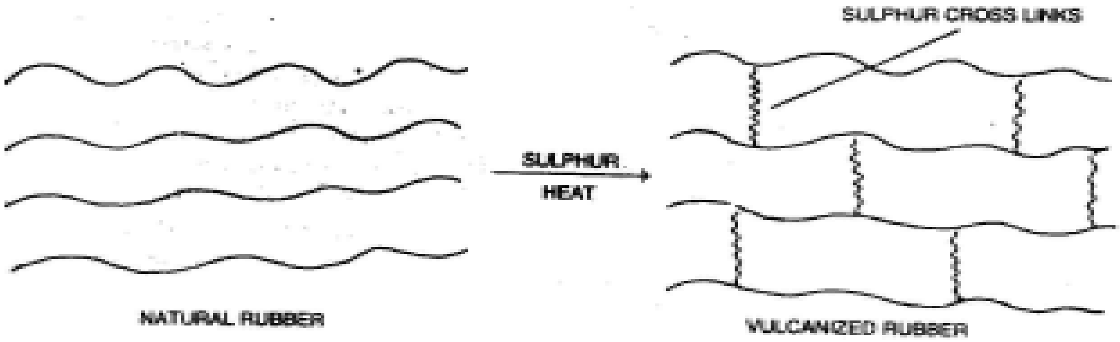
Depending upon the intermolecular forces, the polymers have been classified into four types:

1) Elastomers	2) Fibres
3) Thermoplastics	4) Thermosetting polymers

1. Elastomers: The polymers that have elastic character like rubber are called elastomers. In elastomers the polymer chains are held together by weak intermolecular forces. Because of the presence of weak forces, the polymers can be easily stretched by applying small stress and regains their original shape when the stress is removed. The most important example of elastomer is natural rubber. However, a few cross linked are also introduced in the chains. For example, natural rubber is a gummy material which has poor elasticity. It becomes soft and sticky when heated and becomes permanently deformed when stretched. However, when natural rubber is heated with 3-5% sulphur, it becomes non-sticky and more elastic. This process is called **vulcanization** and it was discovered by Charles Good Year in 1839. The product formed is called **vulcanized rubber** which has better tensile strength, elasticity and resistance to abrasion than natural rubber. This is due to sulphur cross links between polymer chains. Thus, cross links are introduced in natural rubber to

(i) Impart the property of regaining the original positions after stretching force is released.

(ii) Prevent the chains from slipping past each other when force is applied.



2. ***Fibres :*** These are the polymers which have strong intermolecular forces between the chains. These forces are either hydrogen bonds or dipole-dipole interactions. Because of strong forces, the chains are closely packed giving them high tensile strength and less elasticity. Therefore, these polymers have sharp melting points. These polymers are long, thin and thread like and can be woven in fabrics. Therefore, these are used for making fibres. The common examples are **nylon-66, Dacron, silk** etc.

3. ***Thermoplastics :*** These are the polymers which can be easily softened repeatedly when heated and hardened when cooled with little change in their properties. The intermolecular forces in these polymers are intermediate between those of elastomers and fibres. There is no cross linking between the chains. The softening occurs as the polymer chains move more and more freely because of absence of cross links. When heated, they melt and form a fluid which can be moulded into any desired shapes and then cooled to get the desired product. Common examples of thermoplastics are **polythene, polystyrene, polyvinyl chloride, Teflon etc.**

Plasticizers.

Certain plastics do not soften very much on heating. These can be easily softened by the addition of some organic compounds which are called plasticizers. For example, polyvinyl chloride (PVC) is very stiff and hard but it is made soft by adding di-n-butyl. Phthalate(a plasticizer). Some other common plasticizers are dialkyl phthalates, cresyl phthalate.

4. **Thermosetting polymers :** These are the polymers which undergo permanent change on heating. They become hard and infusible on heating. They are generally prepared from low molecular mass semifluid substances. When heated, they get highly cross linked to form hard, infusible and insoluble products. The cross links hold the molecules in place so that heating does not allow them to move freely. Therefore, a thermosetting plastic is cross linked and is permanently rigid. The common examples are bakelite, melamine formaldehyde etc.

Difference between Thermoplastic and Thermosetting Polymers

Thermoplastic Polymers. Thermosetting polymers

1. These soften and melt on heating

   These do not soften on heating but rather become hard. In case prolonged heating is done, these start burning

2. These can be remoulded , recast and reshaped

   These cannot be remoulded or reshaped

3. These are less brittle and soluble in some organic solvents.

   These are more brittle and insoluble in organic solvents

4. These are formed by addition polymerization

   These are formed by condensation polymerization.

5. These have usually linear structures

   These have three dimensional cross-linked structures

6. Examples: Polyethylene, PVC, Teflon, Nylon etc.

   Examples: Bakelite Urea- ormaldehyde Resin, Terylene etc.

CLASS EXCERCISE:

1] State which of the following is not true ?

a) Nylon fibres are elastic

b) Nylon fibres are not grease resistant

c) Nylon fibres have high tensile strength

d) Nylon fibres are wrinkle proof

2] Polyester and polyamide fibres get dried up fast because they:

a) Do no contain water
b) Do not absorb water
c) Lose water-easily
d) Gain water molecule with difficulty

3] Polymer formation from monomers starts by

a) Condensation reaction between monomers

b) Co ordination reaction between monomers

c) Conversion of monomers to monomer ion by protons

d) Hydrolysis of monomers

4] Given the polymers

A = Nylon – 6, 6, B = Buna – S, C = polyethene. Arrange these indecreasing order of their intermolecular forces

a) A > B > C
b) B > C > A
c) B < C < A
d) C < A < B

5] Bakelite is a polymer of

a) phenol and formic acid
b) urea and formaldehyde
c) phenol and formaldehyde
d) methanol and ethelen

SESSION – 2

AIM

✓ To discuss different methods of polymerization with important polymers.

I] *General Methods of Polymerisation :*

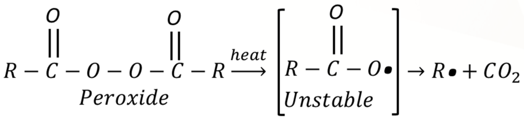
The polymersiation reactions occur in the following two principal types:

1. **Addition polymerization or chain growth polymerisation**
2. **Condensation polymerization or step growth polymerisation**

(1) Chain growth polymerization: It involves a series of reactions each of which consumers a reactive particles may be free radicals or ions (cations or anions) to which monomers get added by a chain reaction. The polymers thus formed are known as chain growth polymers. Chain growth polymerisation is an important reaction of alkenes and conjugated dienes or indeed of all kinds of compound that contain carbon-carbon double bonds. Polythene, polypropylene, polybutadiene, teflon (PTFE), polyvinyl choloride (PVC) polystyrene are some examples of chain growth polymers.

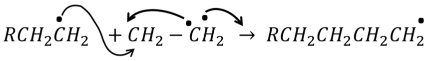
(a) Free-radical mechanism: Free-radical polymerisation is initiated by organic peroxide or other reagents which decompose to give free radicals. Following steps are involved.

(i) Chain initiation: Organic peroxides undergo homolytic fission to form free radicals



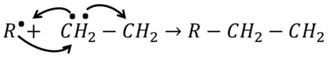
$$\underset{Peroxide}{R-\overset{\overset{O}{||}}{C}-O-O-\overset{\overset{O}{||}}{C}-R} \xrightarrow{heat} \left[\underset{Unstable}{R-\overset{\overset{O}{||}}{C}-O\bullet}\right] \to R\bullet + CO_2$$

(ii) Chain propagation: Free radical adds to an alkene molecule to form a new free radical



$$RCH_2\dot{C}H_2 + CH_2-CH_2 \to RCH_2CH_2CH_2\dot{C}H_2$$

The free radical formed attacks another alkene molecule and the process continues in building a long chain



$$R^{\bullet} + CH_2-CH_2 \to R-CH_2-CH_2$$

(iii) ***Chain termination:*** The chain reaction comes to halt when two free radical chains combine.

$$2R(CH_2CH_2)_nCH_2CH_2 \rightarrow R(CH_2CH_2)_nCH_2CH_2 : CH_2CH_2\ (CH_2CH_2)_nR$$

Benzoyl or t-Butyl peroxide are common initiators, used.

Free radical polymerisation can also be initiated by a mixture of ferrous sulphate and hydrogen peroxide ($FeSO_4 + H_2O_2$).

COPOLYMERISATION:

If a mixture of more than one monomeric species is allowed to polymerise, a copolymer is formed and it contains multiple units of each monomer used in the same polymeric chain. For example, mixture of styrene and methyl methacrylate can form a copolymer.

A] RUBBER

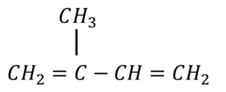
It is a polymer which is capable of returning to its original length, shape or size after being stretched or deformed. Rubber is a common example of an elastomer. The rubber obtained from natural sources is called **natural rubber** and polymers prepared in laboratory which are similar to natural rubber are known as synthetic rubbers.

(i) ***Natural Rubber:*** Natural rubber is a polymer which is obtained from rubber trees in the form of milky sap known as **latex.** The latex is coagulated with acetic acid or formic acid. The coagulated mass is then squeezed.

The raw natural rubber is a soft, gummy and sticky mass. It is insoluble in water, dilute acids and alkalies but soluble in benzene, chloroform, ether, petrol and carbon disulphide. It absorbs a large amount of water. It has low elasticity and low tensile strength. It breaks when too much stretched.

Natural rubber is a hydocarbon polymer. It has the composition (C_5H_8).

Destructive distillation of natural rubber gives mainly isoprene (2-methyl butadiene).

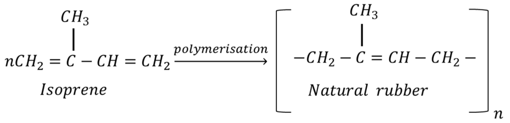


$$CH_2 = \overset{\overset{CH_3}{|}}{C} - CH = CH_2$$

Isoprene

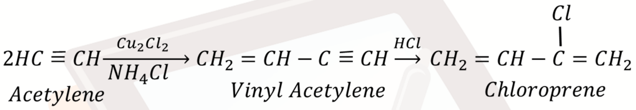
(2 – *methyl butadiene*)

Thus isoprene is a monomer of Natural Rubber.



$$\underset{Isoprene}{nCH_2 = \overset{CH_3}{\overset{|}{C}} - CH = CH_2} \xrightarrow{polymerisation} \left[\underset{Natural\ rubber}{-CH_2 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 -} \right]_n$$

In order to give strength and elasticity natural rubber is **vulcanised.** Vulcanisation is a process of treating natural rubber with sulphur or some compound of sulphur under heat as to modify its properties, i.e., to render it non-plastic and togive greater elasticity and ductility. The sulphur reacts with the polymer molecules forming a cross-linked network. This cross-linking give mechanical strength to the rubber. In addition, fillers such as carbon black and zinc oxide are usually added to the crude rubber before vulcanisation in order to improve its wearing characteristics.



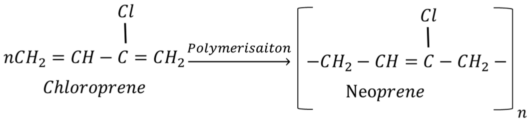
$$\underset{Acetylene}{2HC \equiv CH} \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{Vinyl\ Acetylene}{CH_2 = CH - C \equiv CH} \xrightarrow{HCl} \underset{Chloroprene}{CH_2 = CH - \overset{Cl}{\overset{|}{C}} = CH_2}$$

Natural rubber is used for making shoes, water proof coats and golf balls. vulcanised rubber is used for manufacturing rubber bands, gloves, tubing, conveyor belts and car tyres.

B] ***Synthetic Rubber :*** Neoprene, thiokol and buna-S are some examples of synthetic rubber.

(i) ***Neoprene :*** It was the first synthetic rubber manufactured on large scale, It is also called **dieprene.** Its monomer, chloroprene (2-chlorobutadiene) is prepared from acetylene.

Chloroprene undergoes free radical polymerisation to form neoprene (polychloroprene)



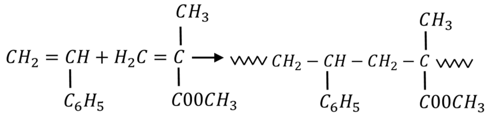
$$\underset{Chloroprene}{nCH_2 = CH - \overset{Cl}{\overset{|}{C}} = CH_2} \xrightarrow{Polymerisaiton} \left[\underset{\text{Neoprene}}{-CH_2 - CH = \overset{Cl}{\overset{|}{C}} - CH_2 -} \right]_n$$

Many of the properties of neoprene are similar to natural rubber, but neoprene is more resistant to action of oils, gasoline and other hydocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non-inflammable.

It is used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

COPOLYMERISATION:

If a mixture of more than one monomeric species is allowed to polymerise, a copolymer is formed and it contains multiple units of each monomer used in the same polymeric chain. For example mixture of styrene and methyl methacrylate can form a copolymer.

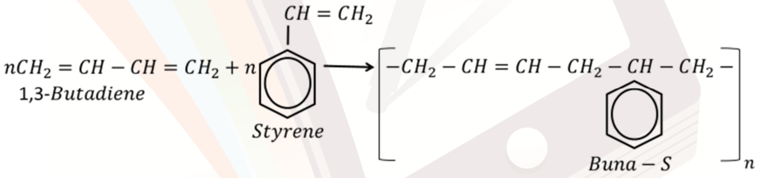


$$CH_2 = \underset{C_6H_5}{\underset{|}{CH}} + H_2C = \overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}} \longrightarrow \sim\sim CH_2 - \underset{C_6H_5}{\underset{|}{CH}} - CH_2 - \overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}} \sim\sim$$

Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

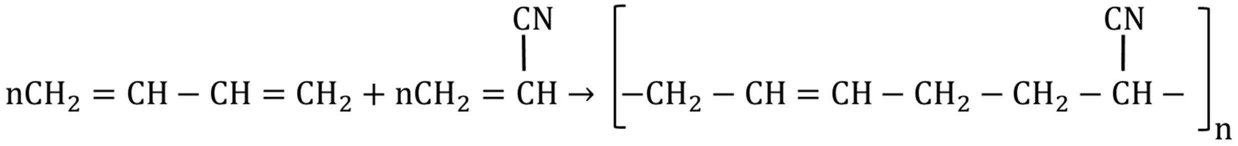
(ii) Buna-S(SBR-Styrene-butadiene rubber):

Buna-S-rubber is a copolymer of three moles of butadiene and one mole of styrene. In Buna-S, 'Bu' stands for butadiene, 'na' for symbol of sodium (Na) which is polymerising agent and s stands for styrene. It is an elastomer, (General purpose styrene Rubber or GRS).



Buna-S is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and therefore used in the manufacture of tyres and other mechanical rubber goods. It is obtained as a result of free radical copolymerisation of its monomers.

(iii) ***Buna-N:*** It is obtained by copolymerisation of butadiene and acrylonitrile, (General purpose Rubber Acrylonitrile or GRA).



$$nCH_2 = CH - CH = CH_2 + nCH_2 = \overset{CN}{\overset{|}{CH}} \rightarrow \left[-CH_2 - CH = CH - CH_2 - CH_2 - \overset{CN}{\overset{|}{CH}} - \right]_n$$

It is very rigid and is very resistant to action of petrol, lubricating oil and many organic solvents.

It is mainly used for making fuel tanks.

Summary

	General name of polymer group	Examples	Type
1	Polyolefins	(i)Polyethylene (ii) Polypropylene (iii) Polystyrene	Addition Addition Addition
2	Polydienes	(i)Neoprene (ii) Buna-S	Addition Addition
3	Poly acrylates	(i) Polyacrylonitrile(Orlon) (ii) Polymethyl methylacrylate(PMMA) (iii) Polyethylacrylate	Addition Addition Addition
4	Polyhalo olefins	(i)Polytetrafluoroethylene-(Teflon) (ii) Polyvinyl chloride(PVC) (iii) Polymonochloro-trifluoro-ethylene	Addition Addition Addition
5	Polyesters	(i)Terylene (ii) Glyptal or alkyd resin	Condensation Condensation
6	Polyamides	(i)Nylon-66 (ii) Nylon-6 (iii) Nylon-610	Condensation Condensation Condensation
7	Formaldehyde resins	(i)Phenol-formaldehyde resins(Bakelite) (ii) Melamine formaldehyde resin (Melamine) (iii) Urea-formaldehyde	Condensation Condensation Condensation

2] CONDENSATION POLYMERS:

These polymers are formed as a result of the condensation of the monomer units which are different and have also some specific functional groups. Thus they are co-polymers in nature.

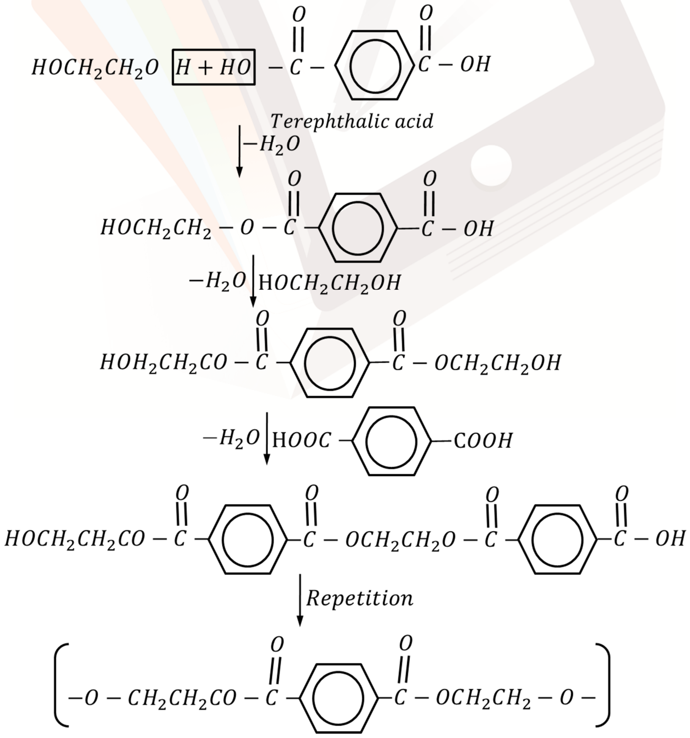
The main polymers belonging to this class are polyesters, polyamides and resins. These are briefly discussed as follows:

A] POLYESTERS

As the name suggests, these are the polyesters of dicarboxylic acids and glycols.Terylene and glyptal are the important polymers of this class.

1. ***Terylene.*** It is also known as dacron and is the condensation product of ethylene glycol and terephthalic acid.

   Polymerisation is carried out at 420 to 460 K in the presence of catalyst mixture of zinc acetate and antimony trioxide.



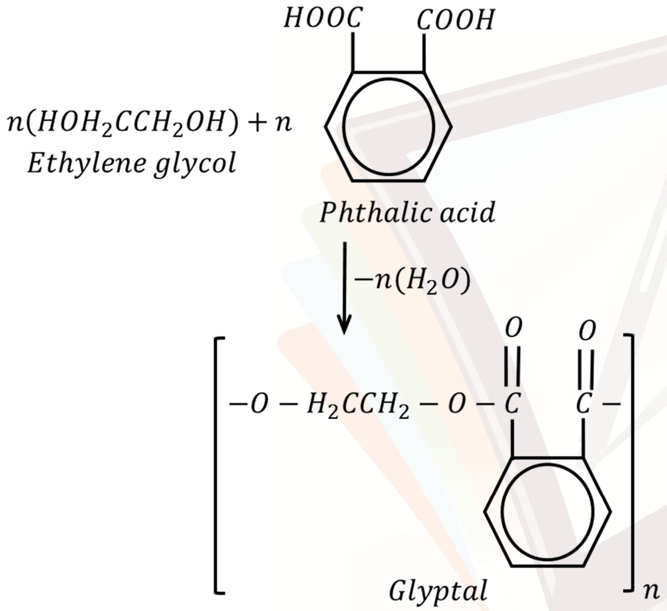
Properties and uses.

Terylene is highly resistant to the action of chemical and biological agents. Its fibres are quite strong and durable. It can also be blended with wool or cotton to obtain fabrics of desired composition. Terylene is used

(i) In the manufacture of a variety of cloth such as terycot, terywool and terysilk as a result of blending with other yarns.

(ii) For preparing magnetic recording tapes, conveyer belts, aprons for industrial workers etc.

2. Glyptal. It is a polymer of ethylene glycol and phthalic acid.



Properties and uses, Glyptal is a net-work cross-linked polymer. When dissolved in a suitable organic solvent, the solution formed upon evaporation leaves a tough and non-flexible film. Glyptal is chiefly used

(i) In the manufacture of paints and lacquers

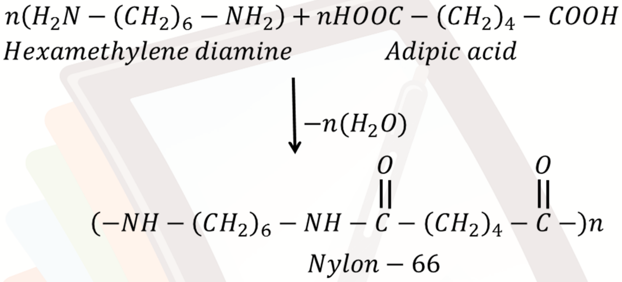
(ii) For making building materials such as asbestos and cement

B] POLYAMIDES :

These condensation polymers have an amide linkage (—CO – NH—) present in the monomer units. Two very popular polymers containing such linkages are Nylon –66 and Nylon-6.

1. Nylon-66. It is the polymerised product of the adipic acid (hexanedioc acid and hexamethylenediamine (hexane 1, 6-diamine). As both the acid and the amine have six carbon atoms each, it is given suffix 66.

Polymerisation is generally carried by heating the reaction mixture under pressure. The molecular mass of the polymer is quite high and ranges between 12000 to 20000 mu.



$$\underset{Hexamethylene\ diamine}{n(H_2N-(CH_2)_6-NH_2)} + \underset{Adipic\ acid}{nHOOC-(CH_2)_4-COOH} \xrightarrow{-n(H_2O)} \underset{Nylon-66}{(-NH-(CH_2)_6-NH-\overset{\overset{O}{||}}{C}-(CH_2)_4-\overset{\overset{O}{||}}{C}-)n}$$

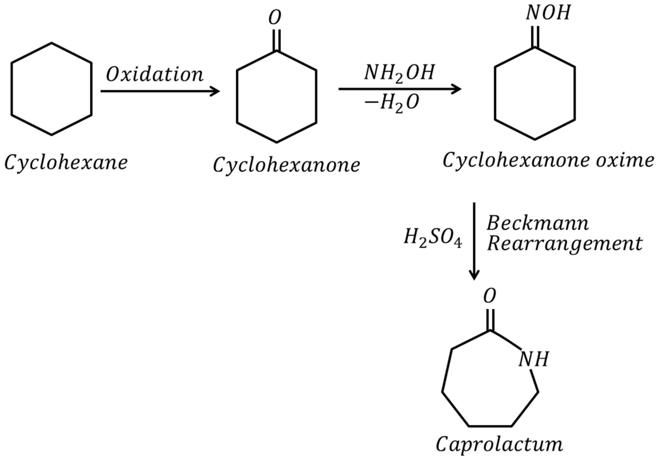
Properties and uses. Nylon-66 can be cast into sheet or fibres by suitable spinning devices. The fibres have very high tensile strength. They are quite tough and resistant to abrasion. Nylon-66 is used.

(i) In making bristles of tooth brushes

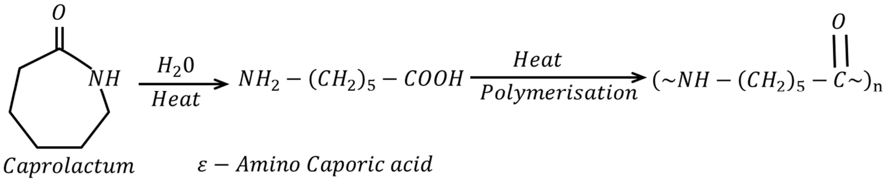
(ii) In the manufacture of cords and climbing ropes

(iii) For preparing socks and sweaters when blended with wool.

2. Nylon-6 : It is a polymerised product of caprolactum which is obtained from cyclothexane as a result of series of reactions as given below:



Upon heating in the presence of moisture, caprolactum ring cleaves to give e-amino caporic acid which is a monocarboxylic amino acid with six carbon atoms. This polymerises to give nylon-6.



Properties and uses. It is called nylon-6 since the monomer unit has six carbon atoms. It finds applications in the manufacture of fabrics, ropes tyre-cords etc.

Remember :

In Nylon-66, both the monomer units hexamethylene diamine and adipic acid have six carbon atoms each while in Nylon-6, the only monomer caprolactum has six carbon. Both of them are **polamides** in nature.

Nylon-11 and Nylon-12 have been synthesised. the product of self condensation of w-amino undecanoic acid.

$$\begin{array}{c} n(H_2N(CH_2)_{10}COOH) \\ W-Amin\,oundeconoic\ acid \end{array} \xrightarrow{polymerisation} \left[\begin{array}{c} -NH-(CH_2)_{10}-CO- \\ Nylon-11 \end{array}\right]_n$$

Nylon-12 is obtained by carrying the hydrolytic polymerisation of dodecanelactum.

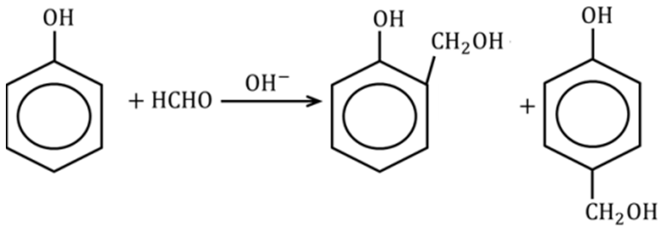
$$\begin{array}{c} [-NH-(CH_2)_{11}-CO]_n \\ Nylon-12 \end{array}$$

Nylon-2 Nylon-6 is a synthetic biopolymer (biodegradable in nature) in which the monomer units are of glycine and aminocaporic acid

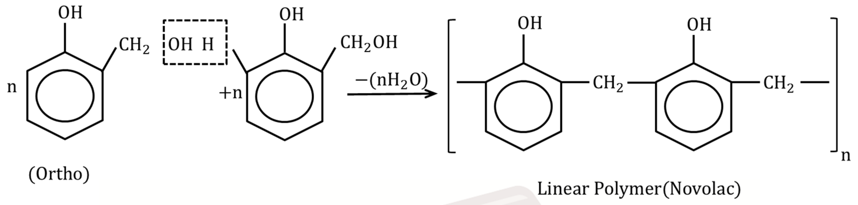
C] FORMALDENYDE RESINS :

Resins are the non-volatile solids which are obtained directly from certain plants and can also be prepared as a result of polymerisation . We are discussing two important formaldehyde resins.

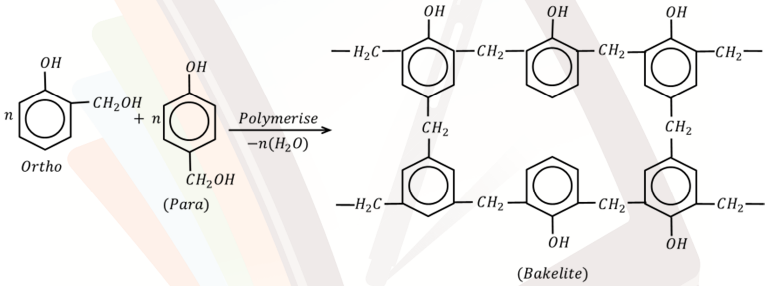
1. ***Phenol-formaldehyde resin (Bakelite).*** It is a condensation polymer and is formed by the combination of phenol and formaldehyde in the presence of acid or base acting as catalyst. It is called phenol formaldehyde resin. A mixture of ortho and para benzyyl alcohol is initially formed.



The condensation in the molecules of 0-hydroxybenzyl alcohol gives a linear polymer also called Novolac.



Cross linking can also take place in two isomeri benzyl alcohols giving rise to a cross linked polymer.

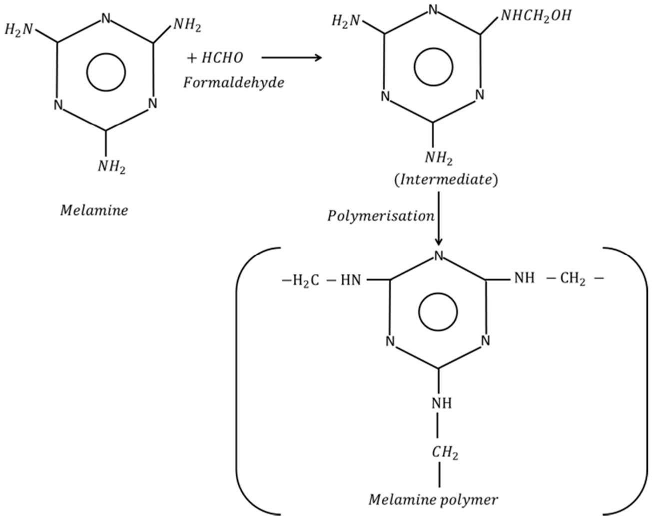


Properties and uses. Bakelite is a cross – linked thermosetting polymer. Low degree of polymerisation gives soft **bakelites** while high degree polymerisation yields **hard bakelites.**

(i) Soft bakelites are used for making glue for binding laminated wooden planks, in varnishes and in lacquers.

(ii) Hard bakelites are used in the manufacture of combs, fountain pens, formica table tops electrical goods etc.

2. Melamine-formaldehyde resin. It is a co-polymer formed by the polymerisation of melamine which is a heterocyclic triamine with formaldehyde as follows:



Properties and uses. Melamine-formaldehyde polymer is very hard and tough. It has assumed great importance these days particularly in making crockery. The cups and plates made from this polymer, available in the form of beautiful sheets, are quite hard and durable. They do not break even when dropped from a heights

3] There are several types of average molecular weights in polymers. They are

A. Number – average molecular weight, $\overline{M_n}$

B. Weight - average molecular weight, $\overline{M_w}$

A) **Number - average molecular weight ($\overline{M_n}$) :** Consider a polymer sample. It can be thought of as a mixture of molecules of same chemical type but of different molecular weights. The particles constituting it may be monomers, dimers, or .... Polymers. Let there be N_1 monomers each of mass M_1N_2 dimers of mass M_2 each; ...... N_1 polymers of mass M_1 each.

Then the mass of the sample is equal to $(N_1M_1 + N_2M_2 + N_3M_3 + \cdots + N_iM_i) = \sum_{n_i=1}^{\infty} N_iM_i$

and the total number of particles in the system = (N1 + N2 + ...Ni) = $\sum_{n_i=1}^{\infty} N_i$

Then the number - average mo.wt ($\overline{M_n}$) of the polymer =

$$\frac{(N_1M_1+N_2M_2+N_3M_3+\cdots+N_iM_i)}{N_1 + N_2 + N_3 \text{......Ni}} = \left[\frac{\sum_{n_i=1}^{\infty} N_iM_i}{\sum_{n_i=1}^{\infty} N_i}\right]$$

B) **Weight - average molecular weight, $\overline{M_w}$:** Consider again the sample of the polymer used to calculate the number-average Molecular weight. Then the total weight of all the particles in the system = $\sum_{n_i=1}^{\alpha} N_i M_i$ Wt. of the N_1 particles of mass M_1 = N1M1. The fraction of the total mass contributed by or corresponding to each particles of this type = $\frac{N_i M_i}{\sum_{n_i=1}^{\alpha} N_i M_i}$

Multipyling the mol wt of the species with the contribution of the respective species to the total wt we get for the particle of mass M_1 as

M1 $\left[\frac{N_1 M_1}{\sum_{n_i=1}^{\alpha} N_i M_i}\right]$ Similarly for other species it can be worked out.

Sum of the products of mol wt and fraction of the total wt of the respective species.

$$\sum_{N_i=1}^{\alpha} \frac{(N_i M_i) M_i}{\sum_{N_i=1}^{M} N_i M_i} = \left[\frac{\sum_{N_i=0}^{\alpha} N_i M_i^2}{\sum_{Ni=1}^{\alpha} N_i M_i}\right]$$

The wt - average mol wt of the polymer

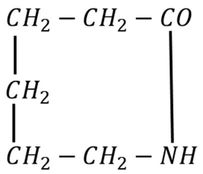
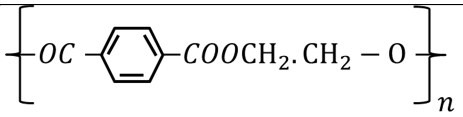
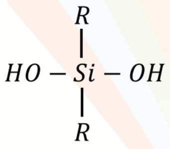
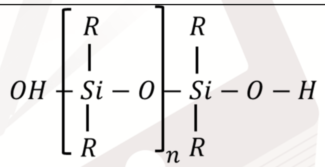
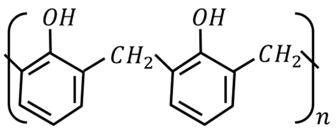
$$= \overline{M_n} = \left[\frac{\sum_{N_i=1}^{\alpha} N_i M_i^2}{\sum_{N_i=1}^{\alpha} N_i M_i}\right]$$

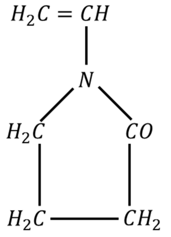
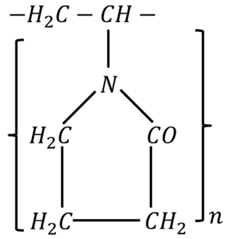
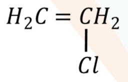
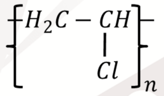
Polydispersity Index (PDI) :

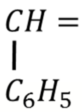
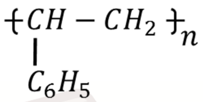
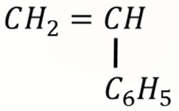
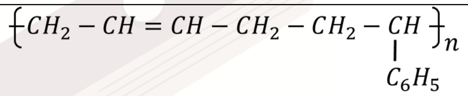
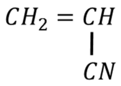
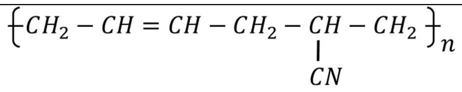
The ratio of the weight average ($\overline{M_w}$) and the number average ($\overline{M_n}$) molecular weights of a polymer is called “Polydispersity index” (PDI). Some natural polymers are usually consisting of monomers only. Then $\overline{M_n}$ = $\overline{M_w}$ for them. Hence PDI, for such samples, is equal to unity.

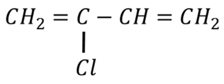
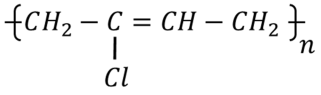
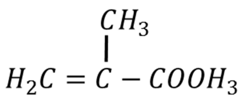
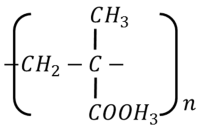
In the case of synthetic polymers, polymeric species is always dominant over monomeric species and so the PDI for such polymers is greater than unity because, then, $\overline{M_w}$ is always higher than $\overline{M_n}$.

S.NO	Name of the polymer	Constituent monomer unit	Polymer structure & some important properties	Applications in common life

1	Nylon 6(or) Perlon L	Caprolactam 	$\{-NH-(CH_2)_5-CO-\}_n$ High electrical resistivity (extreme resistance to abrasion)	In making textiles, plastics, tyre cords and ropes
2	Polyethylene Terephthalate (PET) Terylene or Dacron	a. $HOOC.C_6H_4.COOH$ b. $HO.CH_2.CH_2.OH$	 good resistance of water, attacked by bases like NaoH	Production of fibers, safety belts, tyre cords, tents
3	Artificial silk or Rayon	Cellulose	Four diffrerent types of rayon or artificial silks. (a) pyroxylin (b)viscose rayon (c)acetate rayon (d)cuprammonium rayon	Used in packages and wrapping industries; photofilms
4	Silicone polymers	 $HO-\underset{R}{\overset{R}{Si}}-OH$	 $OH\left[\underset{R}{\overset{R}{Si}}-O\right]_n\underset{R}{\overset{R}{Si}}-O-H$ Thermally very stable, available in liq., solid or gas phases as waxes or as rubbers	Surface coatings, as elastomers; in aeroplanes and missiles
5	Bakelite	a. CH_2O b. C_6H_5OH	 The resin cures under pressure and bonds the various layers firmly	For making laminates; in electrical circuits for protective coatings; making gears

6	Polyvinyl pyrrolidone	N-vinyl pyrrolidone 	 Resistant to attack by strong chemicals	Lifesaving substance as blood plasma. As an additive to many basic dye compositions to deepen the colour of the dye
7	Polytetrafluoroethylene(PTFE) (or) Teflon	$F_2C = CF_2$	$(-F_2C - CF_2 -)_n$ Mechanical strength remains unchanged over a wide range of temp. Resistant to any strong acid, alkalies and organic solvents.	As lubricant; insulator and for making cooking ware
8	Polyvinyl chloride (PVC)	 $H_2C = \underset{Cl}{\underset{\mid}{CH_2}}$	 $\left[H_2C - \underset{Cl}{\underset{\mid}{CH}}\right]_n$ resistant to acids and alkalies. Insoluble in H_2O, alcohol and hydrocarbons. Dissolves in acetone and CS_2 mixture	Cheap plastic for cable insulations. Manufacture of adhesives, coating and fibres
9	Polyethene	$H_2C = CH_2$	$(-CH_2 - CH_2 -)_n$ low density polyethene (LDPE) and high density polyethene (HDPE) are known	LDPE: Pipes in agriculture irrigation, domestic water lines, insulation in electric cables. HDPE:

				Manufacture of toys and household articles anticorrosives and laboratory apparatus.
10	Polysytrene	 $CH = CH_2$ (with C_6H_5 below CH)	 $\left[CH - CH_2 \right]_n$ (with C_6H_5 below CH) exposure to atmosphere causes yellowing depolymerization on heating, poor resistance to weather	Moulded containers; lids, jars, radio and TV cabinets, toys and foamed plastics. As an insulator and wrapping material
11	Styrene butadiene rubber BuNa-S or (SBR) or GRA	a.$CH_2 = CH - CH = CH_2$ b.  $CH_2 = CH$ (with C_6H_5 below CH)	 $\left[CH_2 - CH = CH - CH_2 - CH_2 - CH \right]_n$ (with C_6H_5 below the last CH)	In making automobile tyres and footwear
12	Nitrile rubber ($BuNa - N$) or GRN	a.$CH_2 = CH - CH = CH_2$ b.  $CH_2 = CH$ (with CN below CH)	 $\left[CH_2 - CH = CH - CH_2 - CH - CH_2 \right]_n$ (with CN below CH)	In making of oil seals; manufacture of hosepipes and tank linig

13	Neoprene	 $CH_2=\underset{Cl}{\underset{\mid}{C}}-CH=CH_2$	 $\left[CH_2-\underset{Cl}{\underset{\mid}{C}}=CH-CH_2\right]_n$	As an insulator; making conveyor belts and printing rollers
14	Polymethyl methacrylate (PMMA) or Plexi glass	 $H_2C=\overset{CH_3}{\overset{\mid}{C}}-COOH_3$	 $\left(CH_2-\overset{CH_3}{\underset{COOH_3}{\overset{\mid}{\underset{\mid}{C}}}}-\right)_n$	As a substitute of glass and for making decorative articles.
15	Urea formaldehyde	a. $HCHO$ b. $H_2N.CO\,NH_2$	$\left[NH-CO.NH-CH_2\right]_n$	For making unbreakable cups

CLASS EXCERCISE:

1] The material in the form of their filaments forming fabrics is known as :

a) Glyceride b) Carbohydrate c) Fibre d) Protein

2] Which one of the following is a cellulose fibre ?

a) Hair b) Wool c) Cotton d) Silk

3] Regenerated fibres have superior physical properties because :

a) They are fresh fibres

b) They are obtained naturally

c) They are chemically treated fibres

d) None of the above

4] Adipic acid and hexamethylene diamine polymerise to form:

a) Terlylene b) Nylon-6 c) Nylon-6, 6 d) Glyptal

5] Caprolactum is a monomer of Nylon-6. It can be obtained from:

a) Cyclohexane b) Benzene c) Formaldehdye d) Adipic acid

6] Epsilon caprolactum has.... carbon atoms in its ring:

a) 6 b) 7 c) 5 d) 8

KEY

SESSION - 1

CLASS EXERCISE

1) b 2) b 3) a 4) a 5) c

SESSION – 2

CLASS EXERCISE

1) c 2) c 3) c 4) c 5) a 6) a