Unit

8

Polymers

8.1 Introduction

Polymer is part of our daily life. Daily requirement is incomplete without its usage. Thinking about universe without polymer is impossible. Polymer is a compulsory need for the physical comfort and for making our life easier. Any material of plastic, like toys for children, polythene shopping bags for purchase or synthetic clothes, tyres of vehicles or the spare parts of machines, insulated (nonconductor) wires of electric cable, or electric shock proof, devices interiors of vehicles or houses, medical field or pharmacy; in each of these polymer has established its dominance. There is a possibillity that polymer will replace the metal in futures.

For daily requirement or industrial growth polymer has been used all over. In industries polymer is used in manufacturing of plastic, elastomer fiber, paint and varnish. Polymer word is formed by combination of two Greek words "poly" and "mer" in which 'poly' means many and 'mer' means unit, part or section. Polymer means huge molecule (10^3–10^7 u) containing higher molecular masses and many simple molecules combined. In general, polymer is represented by the name of macromolecules. The simple unit or molecule which is repeated many times in the polymer is known as **monomer.** Such simple units or active molecules are joined together with each other in large amount by covalent bond and form a huge molecule (polymer). This process is called **polymerisation.** The unit which is repeated several times in a huge molecule is called **repeating unit. This number of repeating unit 'n' in polymer molecule is called "degree of polymerization".** e.g., innumerable molecules of ethene monomer combined with each other by polymerisation reaction which forms a huge molecule is called polythene. Polymer molecule containing huge volume is formed by intereaction between innumerable molecules of hexamethylene diamine and adipic acid, which is called nylon-6,6.

(i) $$nCH_2{=}CH_2 \xrightarrow{\text{Polymerisation}} n\left[CH_2-CH_2\right] \longrightarrow \left[CH_2-CH_2\right]_n$$

Ethene — Repeating unit — Polythene

(ii) $$nNH_2(CH_2)_6NH_2 + nHOOC-(CH_2)_4-COOH \xrightarrow{\text{Polymerisation}} \left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n + nH_2O$$

Hexamethylene diamine — Adipic acid — Nylon-6,6

If the value of repeating unit 'n' is less than 25 (n < 25) then that polymer is called **oligomer.** Generally oligomer is in liquid state. Liquid polymers used in fevicol like adhesives paints are oligomers. If the value of repeating unit 'n' is more than 25 then that polymer is called **heavy polymer.** Generally heavy polymers are in solid state.

8.2 Classification of Polymers

Classification of polymers is possible on some acceptable bases which are shown as under :

8.2.1 Classification based on source :

Polymers are classified in three types on the basis of their availability (source) :

(1) Natural Polymers : Polymers present in nature are obtained from plants or animals, e.g., protein, cellulose, starch, nucleic acids, resins, rubber, etc., are examples of natural polymers.

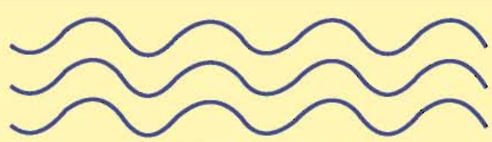
(2) Semisynthetic polymers : Polymers which are formed by chemical reaction with the polymers present in nature are called semisynthetic polymers. By changing the properties of natural polymers according to their requirement, polymers like explosive cellulose nitrate are formed by nitration of cellulose; Cellulose diacetate (rayon) is obtained by acetylation reaction of cellulose with acetic anhydride in acidic medium. Vulcanised rubber obtained by vulcanisation of natural rubber can be included in these type of polymers.

(3) Synthetic polymers : It is totally man-made polymer because synthetic polymer possesses large series of man-made polymers. In this type of polymers plastic (polythene, PVC, teflon) synthetic fibers (terylene, nylon, polyester orlon), synthetic rubber (Buna-S, Buna-N) etc are included.

8.2.2 Classification based on structures :

Polymers are classified into three types according to their structures.

(1) Linear polymers : This type of polymers contain long straight chain in their constitution. There is no branch in their straight chain. Monomer units combine with each other, forming a long straight chain and linear polymer is obtained. Fibers are included in linear polymers. Linear polymers are obtained from natural cources like cotton, silk, wool, linen whereas synthetic linear polymers are terylene, nylon, polyesters, orlon etc. Linear polymers are arranged in a long chain as shown in fig. 8.1.



Linear polymer

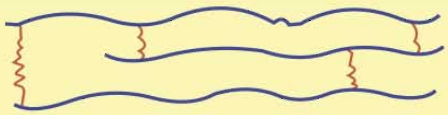
Fig. 8.1

(2) Branched chain polymers : This type of polymers contain branch inbetween the long straight chain in their constitution. Monomer units combine with each other, make a long straight chain and if this chain contains brachning inbetween, then it is called branched polymer. This type of thermoplastic polymer contains low density polymer (LDP). For example, polystyrene, PVC, teflon, etc are branched polymers. Branched polymers in long chain possess branches as shown in fig 8.2.

Branched polymer

Fig. 8.2

(3) Cross linked polymers : In this type of polymers, bifunctional or trifunctional monomer combines with covalent bond inbetween the long polymer chain. Long polymer chain is joined by strong covalent bond and forms a net like structure. This type of thermosetting polymer contains high density polymer. For instance, Bakelite, Melamine are crossed linked polymers. Long chain at certain distances joined by strong binding which is shown in fig 8.3.



Crossed linked polymers

Fig. 8.3

8.2.3 Classification based on reaction mode of polymerisation :

On the basis of polymerisation reaction, polymers are classified into two categories

(1) Addition Polymers : Due to addition reaction, when double bond or triple bond containing innumerable monomer molecules combine with each other by chemical bond, then they form addition polymer, like polythene formed from ethene. Polypropene formed from propene and polystyrene formed from styrene are addition polymers. e.g., innumerable molecules of propene monomers are joined with each other by addition polymerisation reaction and form polypropylene polymer.

$$\underset{\text{Propene monomer}}{nCH_2{=}CH{-}CH_3} \xrightarrow[\text{polymerisation}]{\text{Addition}} \underset{\text{Polypropene (polymers)}}{\left[CH_2{-}\underset{|}{\overset{CH_3}{CH}} \right]_n}$$

(a) Homopolymers : When same type of innumerable monomers combine with each other in addition polymerisation reaction, and form a polymer, it is known as Homopolymer. Polythene, polystyrene, polyvinyl chloride, teflon, orlon, butyl rubber, neoprene etc are hompopolymers. For example,

(i) When same kind of innumerable molecules of ethene monomers are joined by addition polymerisation reaction, then they form homopolymer polythene.

$$\underset{\text{Ethene}}{nCH_2{=}CH_2} \xrightarrow[\text{polymerisation}]{\text{Addition}} \underset{\text{Polythene (homopolymer)}}{\left[CH_2{-}CH_2 \right]_n}$$

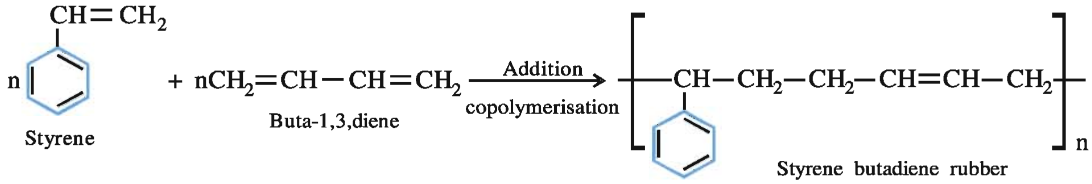
(ii) Innumerable molecules of propene monomer are joined by addition reaction to form polypropene.

$$\underset{\text{Propene}}{nCH_2{=}CH{-}CH_3} \xrightarrow[\text{polymerisation}]{\text{Addition}} \underset{\text{Polypropene (Homopolymer)}}{\left[CH_2{-}\underset{|}{\overset{CH_3}{CH}} \right]_n}$$

Here same kind of innumerable molecules (ethene or propene) combine with one another by addition reaction to form polymer, so it is called Homopolymer. In homopolymer, which is formed by the addition reaction, the repeating unit is totally based on the monomer. Naming of these homopolymers is based on the name of monomer unit.

(b) Copolymer : In addition polymerisation reaction when two or more than two different types of innumerable monomers combine with each other to form polymer then it is known as copolymer. Nylon-6,6, Terylene, Bakelite, Melamine, PHBV, etc are copolymers. For example,

Innumerable molecules of two different types of buta-1,3-diene and styrene combine by addition polymerisation reaction to form a copolymer type of rubber, Butadiene, styrene.



Styrene butadiene rubber (Buna-S) (copolymer)

Here two different types of innumerable monomers of 1,3-butadiene and styrene combine with each other by addition reaction to form polymers. Hence, it is called copolymer. Repeating unit of this copolymer formed by addition reaction is dependent on the functional group of two different monomers. Names of these copolymers are represented on the basis of two different monomer units.

(2) Condensation polymer : In polymerisation reaction, two different types of innumerable monomer units containing equally bi or tri functional groups combine with each other in equal proportion by condensation reaction to form polymer. Hence, it is called condensation polymer. This type of polymerisation reaction is known as condensation polymerisation. During this condensation polymerisation reaction; water, ammonia, alcohol or hydrogen chloride molecule is released. Certain types of repeating units in condensation polymerisation depend on functional group present in two diffirent types of monomer. Its name is given by the functional group present in repeating unit. **Polyamide** condensation polymer contains –CONH– functional group and condensation polymer containing –COO– functional group is called **polyester.** For example terylene (dacron) nylon-6, nylon-6,6 are condensation polymer substances. e.g.,

Polymerisation reaction between adipic acid and hexamethylene diamine forms a condensation polymer nylon-6,6.

$$\underset{\text{Hexamethylene-diamine}}{nNH_2-(CH_2)_6-NH_2} + \underset{\text{adipic acid}}{nHOOC-(CH_2)_4-COOH} \xrightarrow[\text{polymerisation}]{\text{condensation}}$$

$$\underset{\text{Nylon-6,6}}{\left[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO \right]_n}$$

In above reaction hexamethylenediamine monomer, contains two similar functional groups $-NH_2$. Another monomer adipic acid possesses two similar functional group –COOH. When equal proportion (n : n) of inumerable units of two monomers are combined by chemical reaction, then nH_2O

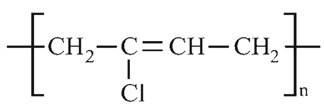
molecules are released. Due to the presence of amide (–CONH–) functional group, the obtained condensation polymer nylon-6,6 is called polyamide series polymer.

8.2.4 Classification based on molecular forces :

Polymers are used in different fields according to its charactaristrics. Polymers are classified by its mechanical properties, such as tensile strength, elasticity and toughness. These properties are shown with the help of intermolecular attraction forces and hydrogen bonding in polymers. Due to this attraction forces, variation is observed in long chain and branches in polymers.

It is classified on the basis of intermolecular attraction forces present in the polymer in four subcategories as under :

(1) Elastomers : This rubber is a solid substance, possessing elastic property. In elastomeric polymers, long chain of polymers are held together by weak intermolecular attraction forces. Due to weak intermolecular binding forces elastomer can be streched. A few cross linked molecules are observed in this long chain of polymers which help the polymer to retract to its original position when the force is removed. Natural rubber, Neoprene, Isoprene, Buna-S, Buna-N etc can be included in the examples of elastomers.

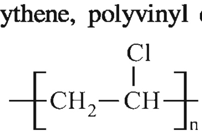


Neoprene

(2) Fibers : Those polymeric compounds which possess high tensile strength and high modulus are known as **fibers.** Because of strong intermolecular forces and hydrogen bonding, this property is seen in fibers. These strong intermolecular forces lead to close packing of long chains. As a result, crystallising property is added to it. Nylon, Terylene (polyesters) are examples of fibers.

$$\left[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO \right]_n$$ Nylon-6,6

(3) Thermoplastic polymers : In this type of polymers slightly branched configuration is seen in long chain of huge molecule. This polymer becomes soft on heating at higher temperature than normal temperature and again becomes infusible on cooling. Its structure changes at higher temperature. In these type of polymers, intermolecular forces are more than elastomers and less than fibers. Thermoplastic polymer is soft (fusible) and less strong than thermosetting polymer. Some examples of thermoplastics are polythene, polyvinyl chloride (PVC), polystyrene etc.



Polyvinyl chloride (PVC)

(4) Thermosetting polymers : The constitution of this polymer is a large molecular structure of cross linked type of polymers, or the structure is seen like long chain containing many branches. These polymers are heated at higher temperature than normal temperature and their cross linked binding is increased, yet they do not become soft. In these polymers, even at higher temperature, there are no changes in its structure. Thermosetting polymers are hard and strong. They are resistant toward scratch. They are good insulator of electricity and heat. Bakelite and melamine are this type of polymers.

8.2.5 Classification based on growth of polymerisation reaction :

Nowadays structure of polymer molecules can be changed by changing the reaction mechanism of polymerisation. The method of polymerisation reaction can be developed by chain growth or step growth.

Types of polymerisation reactions : Mainly there are two types of polymerisation reactions : (A) Addition polymerisation or chain growth polymerisation (B) Condensation polymerisation or step growth polymerisation

(A) Addition polymerisation or chain growth polymerisation : In this type of polymerisation reaction polymer is formed by addition reaction of unsaturated monomers containing double bond combined with each other by chemical bond. Innumerable monomers containing same type of double bond or innumerable monomers containing two different types of monomers, combined with each other form a polymer. So it is called **addition polymerisation** reaction. This addition polymerisation reaction is represented in various forms based on their mechanism.

Addition homopolymerisation : Where same type of monomer, containing one or more than one double bond, are combined with each other by chemical bonding; then addition polymerisation takes place. Polythene from ethene, polypropene from propene, polystryrene from styrene, butyl rubber from isobutylene, polyvinyl chloride from vinyl chloride, polyacrylonitrile (orlon) from vinyl nitrile, polytetrafluoro ethene (Teflon) from tetrafluoro ethene etc. are the examples of polymers obtained by homopolymerisation addition reaction.

This reaction takes place by free radical or carbocation, or carbanion reactive intermediate which is produced by monomer.

Free radical addition polymerisation : Addition polymerisation reaction takes place by free radical reactive intermediate in unsaturated compounds and its derivatives, like alkene or diene.

Free radical reactive intermediate is produced by the use of initiators like benzoyl peroxide, acetyl peroxide, 3^0 butyl peroxide in the first step of this reaction with the help of proper temperature and pressure.

For example in polymerisation reaction of ethene, ethene is heated with trace amount of benzoyl peroxide as initiator at high temperature and phenyl free radical is obtained in initial stage of reaction. This phenyl free radical monomer combines with double bond of ethene molecule and forms a bigger size free radical.

First step of chain reaction :

$$\underset{\text{Benzoyl peroxide initiator}}{C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5} \longrightarrow 2C_6H_5-\overset{\overset{O}{\|}}{C}-\dot{O} \xrightarrow[-2CO_2]{} \underset{\text{Phenyl free radical}}{2\,\dot{C}_6H_5}$$

$$\underset{\text{Phenyl free radical}}{{}^{\bullet}C_6H_5} + \underset{\text{Monomer}}{CH_2{=}CH_2} \longrightarrow \underset{\text{Free radical (Bigger size)}}{C_6H_5-CH_2-\dot{C}H_2}$$

This new bigger size free radical combine alternatively with many ethene molecules and at every step longer chain of new free radicals is formed.

Second step of chain reaction :

At the end, on the basis of reaction condition, long chain of free radicals combine with each other in different ways to form polythene; out of which one of the combinations is represented as below :

$$C_6H_5-CH_2-\dot{C}H_2 + CH_2=CH_2 \longrightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2$$

$$\downarrow n\,CH_2=CH_2$$

$$C_6H_5-(CH_2-CH_2)_n-CH_2-\dot{C}H_2$$

Last step of chain reaction :

$$C_6H_5-(CH_2-CH_2)_n-CH_2-\dot{C}H_2 + C_6H_5-(CH_2-CH_2)_n-CH_2-\dot{C}H_2$$

$$\downarrow$$

$$C_6H_5-(CH_2-CH_2)_n-CH_2-CH_2-CH_2-CH_2-(CH_2-CH_2)_n-C_6H_5$$

Industrial manufacturing, properties and uses of some important homo addition polymers :

(a) Polythene : According to the reaction conditions, two types of polythene can be prepared which are as under.

(i) Low Density Polythene (LDP) : Preparation : Low Density Polythene (LDP) is obtained by free radical homo addition polymerisation reaction of ethene monomer in presence of dioxygen or tertiary (3^0) butyl peroxide initiator, at 350-570 K and 1000 to 2000 bar pressure.

$$\underset{\text{Ethene}}{nCH_2=CH_2} \xrightarrow[350\ \text{K to } 570\ \text{K}/1000\ \text{to } 2000\ \text{bar}]{[\text{Dioxygen / tertiary butyl peroxide}]} \underset{\text{Homopolymer polythene}}{-\!\!\left[CH_2-CH_2\right]_n\!\!-}$$

Properties :

- Low density polythene possesses branching structure.
- It is a kind of thermoplastic polymer.
- It is chemically inert.
- It is water resistant.
- It has more number of polymer molecules containing less molecular mass.
- Its boiling point and melting point are lower due to its low density.
- It is insulator towards electricity and is flexible.

Uses :

- Low density polythene is used in insulation of wires carrying electricity.
- It is useful in manufacturing of toys and packing of instruments, flexible pipes and squeeze bottles.

(ii) High Density Polythene (HDP) :

Preparation : For the preparation of high density polymer, free radical homo addition polymerisation reaction of ethene monomer in organic solvent in presence of triethyl aluminium ($(C_2H_5)_3Al$) and titanium trichloride ($TiCl_3$) or titanium tetrachloride ($TiCl_4$) (Ziegler-Natta catalyst) at 333 to 343 K temperature and under 6 to 7 bar pressure is carried out. German scientist G. Natta and Karl Ziegler were awarded the Nobel prize in 1963 for the invention of Ziegler-Natta catalyst.

$$\underset{\text{Ethane}}{nCH_2{=}CH_2} \xrightarrow[\text{333 K to 343 K, 6 to 7 bar}]{\substack{\text{Free radical homo-addition} \\ \text{polymerisation [Ziegler-Natta]}}} \underset{\text{Polythene (Homopolymer)}}{\left[CH_2 - CH_2 \right]_n}$$

Properties :

- In high density polythene, the density is higher as the molecules are arranged closely packed with each other in a branch.
- It is a kind of thermoplastic polymer.
- It is chemically inert.
- It is quite hard and stronger than low density polymer.
- It has more number of molecules having higher molecular mass of polymers.
- It has higher boiling point and melting point as it has higher number of polymerisation.
- They are non-conductors of electricity.

Uses :

- High density polythene is used in preparation of unbreakable instruments.
- Buckets, dustbins, bottles and pipes are manufactured from it.

(b) Polytetrafluoroethene (Teflon) PTFE :

Preparation : On heating tetrafluoro ethene, teflon is obtained by the homo addition polymerisation reaction at high pressure and in presence of free radical or persulphate catalyst.

$$\underset{\substack{\text{Tetrafluoro} \\ \text{ethane}}}{nCF_2{=}CF_2} \xrightarrow[\Delta\text{, and High temperature}]{\substack{\text{Free radical addition polymerisation} \\ \text{[Free radical or persulphate catalyst]}}} \underset{\text{Teflon}}{\left[CF_2 - CF_2 \right]_n}$$

Properties :

- Teflon is chemically inert.
- It is resistant towards corrosion.
- Teflon can bear high temperature so it is a type of thermoplastic and in some cases it is thermosetting.
- Teflon coating gets decomposed at temperature higher than 573 K.

Uses :

- It is used as lubricant in machines to resist scratching.
- It is used in making instruments for insulation of electricity.
- Teflon is used in munufacturing of seat and gasket.
- Teflon is used in manufacturing of non-stick kitchen vessels and tensile surface.

(c) Polyacrylonitrile (Orlon) PAN :

Preparation : Polyacrylonitrile polymer is obtained by addition polymerisation reaction of acrylonitrile monomer in presence of peroxide catalyst.

$$\underset{\text{Acrylonitrile}}{nCH_2{=}CHCN} \xrightarrow[\text{[Peroxide]}]{\text{Addition polymerisation}} \underset{\text{Ployacrylonitrile}}{\left[CH_2 - \underset{|}{\overset{CN}{C}}H \right]_n}$$

Properties :

- Orlon is a branched polymer.
- It behaves like linear polymer such as natural rubber.
- It is a type of thermoplastic polymer.
- It is chemically inert.
- Acrylic fibers made out of it have good tensile strength. There is no effect of fungi and micro insects on it.

Uses :

- It is useful in making synthetic wool as a substitute of natural wool.
- Used in preparation of synthetic fibers.
- Used in making of acrylic fibers.

(d) Polyvinyl chloride (PVC)

Preparation : Polyvinyl chloride is formed by free radical addition polymerisation reaction of vinyl chloride monomer in presence of triethyl aluminium and titanium trichloride or titanium tetrachloride (Ziegler-Natta) catalyst. If reaction condition changes then ionic reactive intermediate is formed from vinyl chloride monomer. As a result polyvinyl chloride is obtained by addition polymerisation reaction.

$$\underset{\text{Vinyl chloride}}{nCH_2{=}\overset{Cl}{\overset{|}{C}}H} \xrightarrow[\text{[Ziegler-Natta]}]{\text{Free radical or anionic addition polymerisation}} \underset{\text{Polyvinylchloride (PVC)}}{\left[CH_2 - \overset{Cl}{\overset{|}{C}}H \right]_n}$$

Properties :

- PVC is a branched polymer.
- It is a kind of thermoplastic polymer.
- It is water resistant.

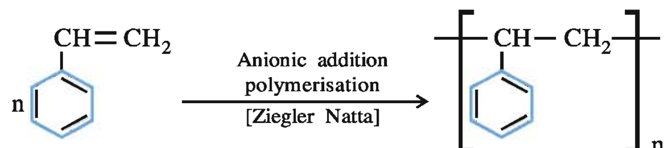
- It is resistant towards electricity.
- It is chemically inert.
- It is stronger than polythene.

Uses :

- As it is water resistant, it is useful in making rain coats, carpets, purses, etc.
- PVC is useful in making pipes, bottles, ragzin footware.

(e) Polystryrene :

Preparation : Polystyrene polymer is obtained by anionic addition polymerisation reaction of stryrene monomer in presence of triethyl aluminium and titanium trichloride titanium or tetrachloride (Ziegler-Natta) catalyst.



Styrene   Polystyrene

Properties :

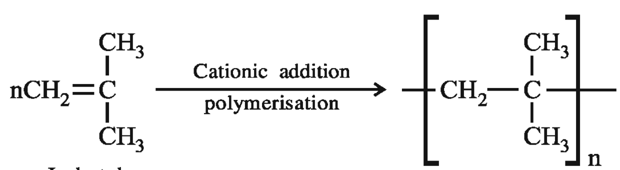
- Polystyrene is a branched polymer.
- It is a kind of thermoplastic polymer.
- It is chemically inert.
- It is lighter in weight than polythene.
- It is heat resistant and non-conductor of electricity.

Uses :

- Polystyrene is used in making cabinets of radio, friedge and T.V.
- Polystyrene is useful in making utensils as non-conductor of heat such as hot water conducting pipes, buckets, bottles etc.

(f) Butyl Rubber :

Preparation : Butyl rubber is obtained by cationic addition polymerisation reaction of iso-butylene monomer.



Isobutylene   Butyl rubber

Properties :

- Butyl rubber is a branched polymer.
- It is a kind of thermoplastic polymer.

- It has a characteristic of more elasticity than natural rubber.
- It is inert towards water.

Uses :

- It is used in place of natural rubber.

Addition Copolymerisation : When polymer substance is formed by addition reaction, when two different types of monmers combine alternatively with each other, by chemical bond, then copolymer substance is formed. This reaction is called addition copolymerisation reaction. Copolymer styrene butadiene rubber is obtained from styrene and butadiene monomer whereas nitrile rubber is obtained from acrylonitrile and butadiene are polymers.

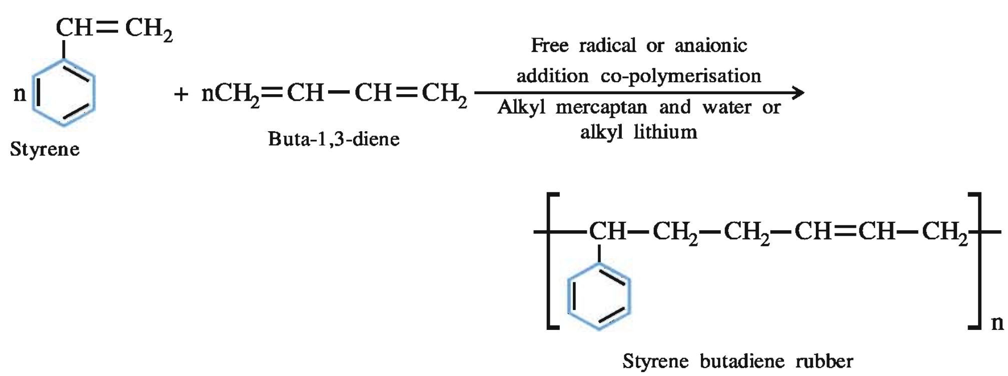
Industrial manufacturing, properties and uses of some important additon copolymer substances :

(a) Styrene Butadiene Rubber (Buna-S), SBR

Preparation : By addition reaction of two monomers-styrene and butadiene combined one by one with each other by chemical bond, styrene butadiene rubber forms a series of copolymers. Two types of products are obtained by this reaction.

(1) If addition reaction takes place between styrene and butadiene with free radical reactive intermediate alkyl mercaptan and water, then mercaptan controls the molecular mass of polymer and forms a small size and high viscosity molecules of polymer. As a result emulsion type of styrene butadiene rubber is obtained.

(2) If addition reaction takes place between styrene and butadiene at higher pressure in presence of ionic intermediate alkyl lithium and in absence of water, then ionic addition polymerisation reaction takes place where more styrene molecules combine and higher molecular mass containing hard and less flexible solution type of styrene butadiene rubber is obtained.



Properties :

- It is a synthetic rubber.
- Buna-S is reactive towards oil, waste water and ozone.
- It possesses higher viscosity than natural rubber.
- It possess high tensile strength and strong extensive property.

- Strong intermolecular H-bonding exists between their molecules.
- At higher temperature, it maintains its elastic character.
- It has higher electric capacity.

Uses :

- Its elastomer form is used in chewinggum, rubber coating and paints.
- Its solution form is used in tyres, shoes sole, gaskets etc.

(B) Condensation polymerisation or step growth polymerisation : In this type of polymerisation condensation reaction repeatedly takes place between two different types of monomers possessing two similar functional groups. As a result of this condensation polymerisation reaction, simple molecules such as water, ammonia or alcohol are removed and condensation polymer containing high molecular mass is obtained.

In condensation polymerisation reaction, repeating unit obtained in first step again reacts with bifunctional species in the second step and forms a new repeating unit. These repeating units formed possess different functional groups; then the functional group in both monomers in each step, and these repeating unit are independent from each other. Hence, this polymerisation is also called as step growth polymerisation as there is addition of repeating units.

Polymers obtained from the condensation polymerisation reaction are classified on the basis of their functional groups in repeating unit. If there is –CONH– group in repeating unit then it is called polyamide and if there is –COO– group in repeating unit, then it is called polyester. Some examples of condensation polymers are as under :

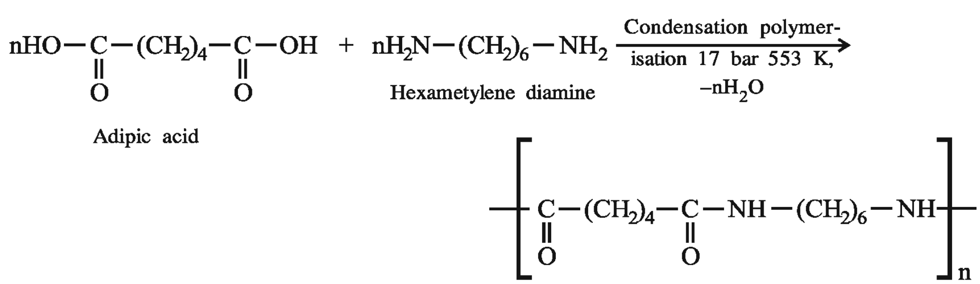
Industrial preparation, properties and uses of some important condensation polymers :

(a) Nylon 6,6 :

Preparation : Two monomers used in preparation of nylon 6,6 are (i) adipic acid containing two –COOH– functional groups and (ii) hexamethylene diamine containing two $-NH_2$ functional groups.

By condensation polymerisation reaction of mixture of two different monomers. adipic acid and hexamethylene diamine at 17 bar pressure and 553 K temperature by heating in closed vessels and on release of water molecule, Nylon-6,6 is obtained.

It is a series of polyamide polymer due to –CONH– amide group in repeating unit of nylon-6,6, and repeating units of nylon-6,6 contain 6 carbon of adipic acid and 6 carbon of hexamethylene diamine, therefore it is called nylon-6,6.



Nylon-6,6

Properties :

- Nylon-6,6 is the chief polymer of polyamide class.
- Nylon-6,6 is a linear polymer.
- –CONH– amide group is a repeating unit of nylon-6,6.
- Nylon-6,6 is a kind of thermoplasitc polymer.
- Fibers of Nylon-6,6 are hard, strong elastic and water resistant.

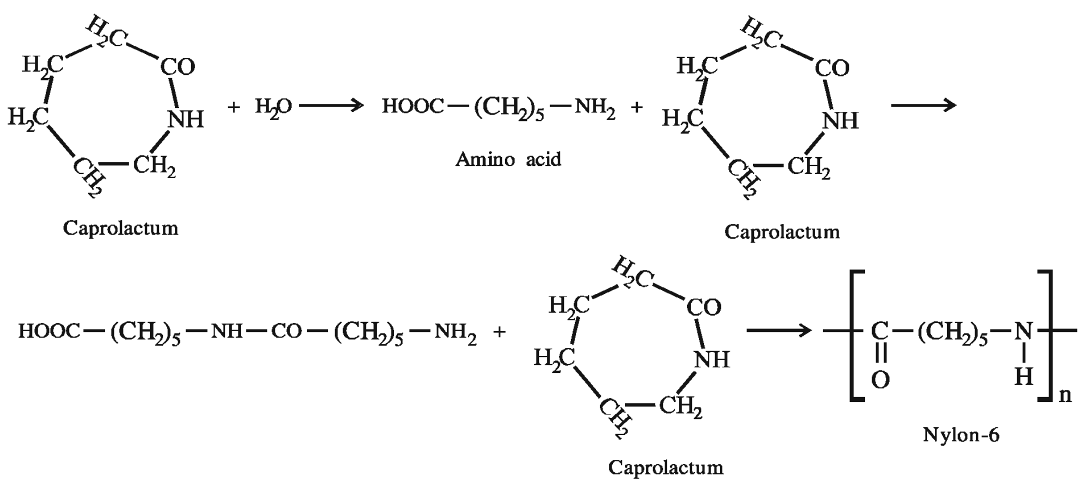
Uses :

- It is used in textile industry, preparation of fishing net, ropes and tyre industries.

(b) Nylon-6 :

Industrial preparation : On hydrolysis of one molecule of caprolactum in presence of water gives an amino acid, which reacts one by one with other caprolactum molecules by self condensation polymerisation reaction giving nylon-6.

The repeating unit of polymer nylon 6 is monomer caprolactum which contains 6 carbon atoms, therefore it is called nylon 6.



Properties :

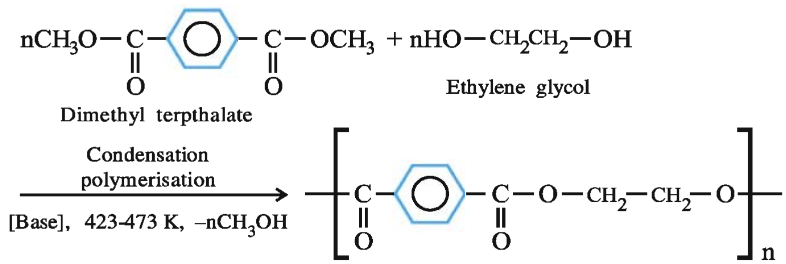
- It is the chief polymer of polyamide class.
- $-\!\!\!\!+$CONH$+\!\!\!\!-$ amide is repeating unit in Nylon-6
- The fibers of Nylon-6 are insoluble in common solvents and are very strong.
- It is a linear polymer.
- It is a kind of thermoplastic polymer.

Uses :

- It is useful in carpet, ropes and tyre industries.

(c) Terylene (Decron) :

Industrial Preparation : The mixture of two different monomers dimethyl terpthalate and ethylene glycol on heating in presence of basic catalyst at 423 to 473 K temperature, by condensation polymerisation reaction gives terylene or decron.



Terylene or dacron

Properties :

- It is the chief polymer of polyester group.
- Terylene is a linear polymer.
- (–COO–) ester is a repeating unit in terylene
- Terylene is a kind of thermoplastic polymer.
- Fibers of terylene are less elastic than nylon fibers.

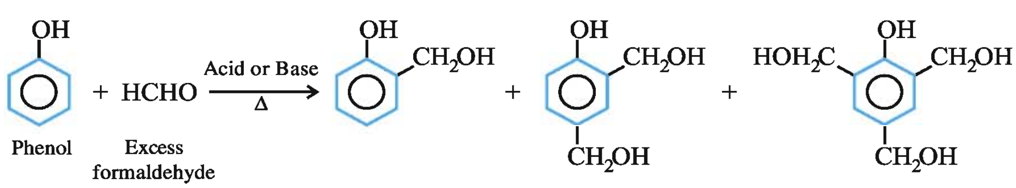
Uses :

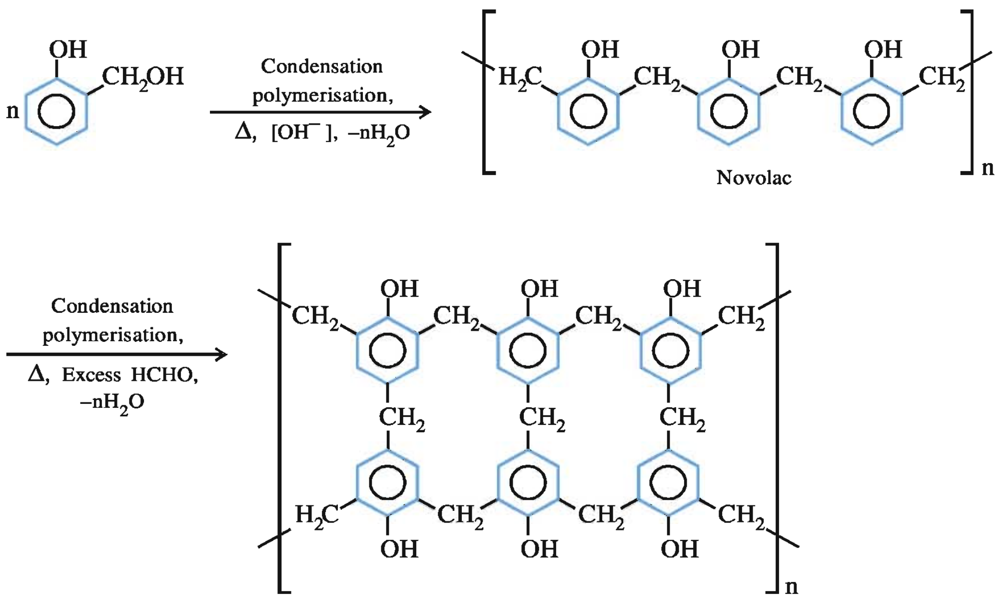
- In textile industries.
- In preparation of rope.

(d) Bakelite :

Industrial preparation :

- The mixture of phenol and formaldehyde on heating in presence of acid or base catalyst, the condensation polymerisation reaction takes place in ortho and para positions and Bakelite is obtained.
- In the begining reaction of phenol with excess formaldehyde takes place and ortho and para hydroxy methyl derivatives are obtained.
- In the begining Novolac linear polymer obtained by polymerisation reaction of hydroxy methyl phenol which on heating at higher temperature with excess of formaldehyde, the condensation takes place in p-position of Novolac and gives Bakelite.





Bakelite (cross linked polymer)

Properties :

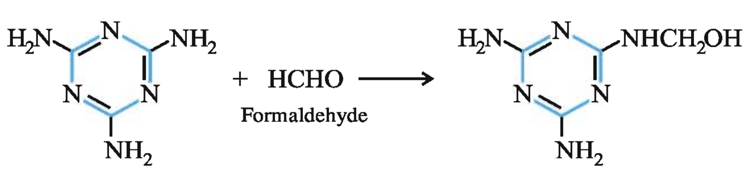
- Bakelite is a synthetic polymer of phenol formaldehyde class.
- It is a cross-linked polymer.
- It is a kind of thermosetting polymer.
- Bakelite does not fuse even on heating.
- It is water resistant, hard, brittle and scratch resistant.
- As it is brittle it cracks or breaks on striking or dropping.
- It possesses very good property as non-conductor of electricity.

Uses :

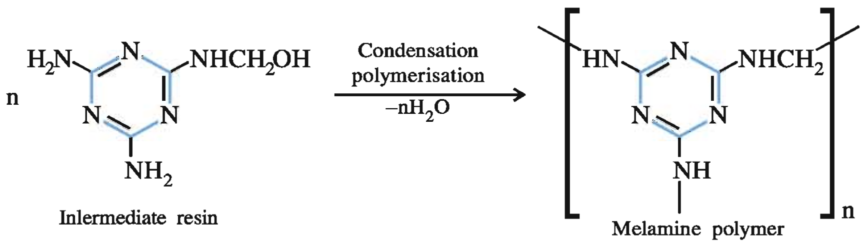
- It is used in making combs, gramophone records, handles of kitchenware and electrical appliances like plug, pin, switches.

(e) Melamine :

Preparation : Melamine polymer is formed by condensation polymerisation reaction of melamine and formaldehyde on heating.



Melamine   Intermediate resin



Properties :

- Melamine is synthetic polymer of formaldehyde class.
- It is a kind of thermosetting polymer.
- It is a cross linked polymer.
- It is hard and strong.
- It does not fuse or its structure does not change at higher temperature.
- It is resistant towards scratching.
- The melamine appliances do not crack or break on striking or dropping.

Uses :

- Melamine is useful in preparation of unbreakable crokery.

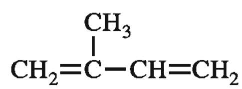
8.3 Rubber

Rubber is available in three forms : (1) Natural rubber (2) Vulcanised rubber and (3) Synthetic rubber.

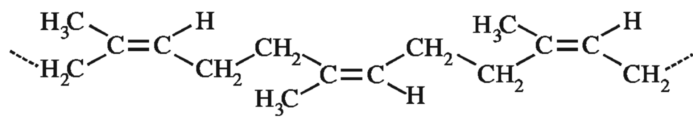
8.3.1 Natural rubber :

Structure :

- Rubber trees are found in forests of India, Sri-Lanka, Indonesia, Malaysia and South Africa.
- By making incision in the trunk of rubber trees, the colloidal suspension of milky rubber in water, called latex is obtained. The natural rubber is obtained by physical and chemical processes.
- Natural rubber is linear polymer of isoprene monomer.
- Isoprene (2-methyl buta-1,3-diene) is also called a 1,4-polyisoprene.
- Its geometrical isomerism is cis due to which it is called cis-1,4-polyisoprene.
- During polymerisation reaction of innumerable molecules of isoprene monomers C1 = C2 and C3 = C4 breaks and bond between C2 = C3 is formed. Hence there is double bond between C2 = C3 in its repeating unit.
- Linear molecules of cis-1,4-polyisoprene are held together by weak van der Waals interaction forces and has a coiled structure. As a result, in natural polymer, elastic property is observed.



Isoprene
(2methyl buta-1,3-diene)



Natural rubber
cis-1,4-polyisoprene

Properties :

- This rubber is a natural polymer.
- Natural rubber can be streched like spring and possesses elastic property.
- In it, if force is applied, even for longer time, then retension force is maintained.
- In natural rubber, this property of elasticity is maintained at 273 to 335 K temperature.
- It becomes brittle at temperature less than 273 K.
- At temperature, higher than 335 K, it becomes fusible.
- Its water absorbing capacity is higher.
- It is soluble in non-polar solvents.
- It is non-resistant against the attack of oxidising agents

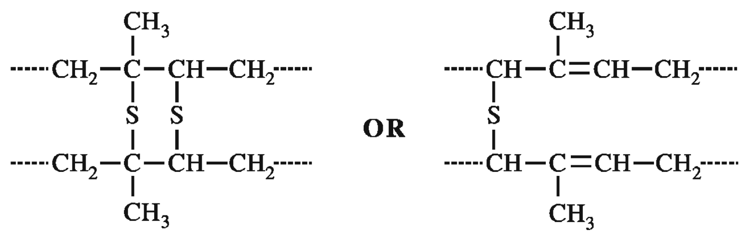
Uses :

- Natural rubber is used in many fields because of its elastic character. like in preparation of eraser, rubber band and hand gloves etc.

8.3.2 Vulcanised rubber :

Preparation :

- In 1893, Charles Goodyear discovered that mixture of natural rubber and sulphur when heated at temperature 373 to 415 K, its physical properties can be necessarily improved to a spectacular manner. This process is called vulcanisation.
- This process is slow but by adding zinc oxide as additive substance, the rate of reaction becomes fast.
- During vulcanisation process, repeating unit cis-1, 4-polyisoprene in natural rubber C2–C3 double bond of unit and adjacent $-CH_2$ groups become reactive. Therefore, bonding of these two reactive positions take place in cross through sulphur, between the two molecules of rubber and becomes hard.



Linear polymer of rubber molecules (cis-1, 4-isoprene)

Properties :

- Vulcanised rubber possesses very good elasticity.
- It does not melt (fuse) at higher temperatures and does not break at lower temperatures.
- It has very low water absorbing capacity.
- It is insoluble in organic solvents.
- It resists oxidation reaction.

Uses :

- During vulcanisation process, 5 % sulphur is used in making rubber for tyres.
- During vulcanisation process 30 % sulphur is used in making rubber for battery-cases.

8.3.3 Synthetic rubbers :

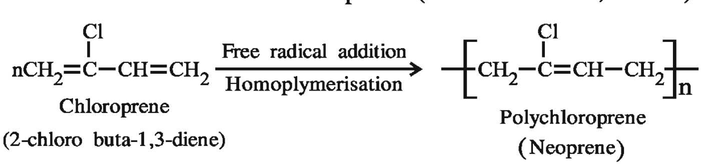
Synthetic rubber is vulcanisable rubber like polymer. On giving external streching force, to the synthetic polymer or stretching it to twice its length, it regains its original shape and size.

Generally synthetic rubber is copolymer of buta-1,3-diene or hompolymer of buta-1,3-diene derivatives or it is a polymer of buta-1,3-diene derivatives with its unsaturated monomers.

Preparation, properties and uses of synthetic rubber :

(1) Neoprene :

Preparation : Polychloroprene (neoprene) homopolymer is obtained by addition polymerisation reaction of innumerable molecules of chloroprene (2-chloro buta-1,3-diene)



Properties :

- Neoprene is a synthetic rubber of homopolymer class.
- It has superior resistance to vegetable and mineral oils.

Uses :

- Neoprene is used in conveyor belts, hose pipes, gaskets, printing rollers and as an insulator.

(2) Nitrile rubber (Buna-N)

Preparation : Nitrile rubber is obtained by addition copolymerisation reaction of mixture of two different monomers buta-1,3-diene and acrylonitrile in presence of peroxide catalyst.

$$\underset{\text{Buta-1, 3-diene}}{nCH_2{=}CH{-}CH{=}CH_2} + \underset{\substack{\text{Acrylonitrile}\\ \text{(vinyl cynide)}}}{nCH_2{=}\overset{\overset{CN}{|}}{C}H} \xrightarrow[\text{Copolymerisation}]{\text{Addition}} \underset{\text{Nitrile rubber (Buna-N)}}{\left[CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{CN}{|}}{C}H \right]_n}$$

Properties :

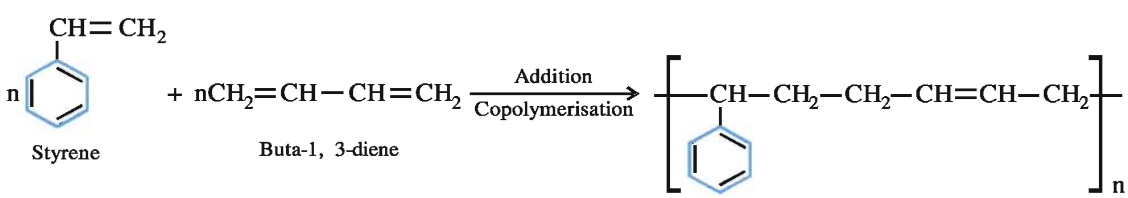
- Nitrile rubber is a copolymer obtained by addition reaction.
- Nitrile rubber has superior resistance towards lubricant oil and organic solvents.
- It does not react with petrol.

Uses :

- Nitrile rubber is used in oil seals, hose pipes and petrol tank linings.

(3) Styrene Butadiene Rubber (Buna-S, SBR)

Preparation : Two different types of innumerable molecules of styrene and buta-1,3-diene monomer joined with each other by addition copolymerisation reaction and forms copolymer named styrene butadiene rubber.



Styrene butadiene rubber
(Buna-S) (copolymer)

Properties :

- Styrene butadiene rubber is a copolymer obtained by addition reaction.
- It possesses good elasticity.
- At higher temperature, its shape does not change.

Uses :

- Styrene butadiene rubber is used in making tyres and footwears.

8.4 Molecular Mass of Polymers

Polymer being an amorphous solid substance; there is no regular arrangement of atoms and molecules. Number of monomers present in different molecules of same polymer means number of repeating unit is different. Thus its molecular mass is always taken as average molecular mass because of different branch lengths in any sample of polymer.

- The highly modern techniques used to determine the molecular mass of polymer are classical light scattering, Quasi-Elastic Light Scattering (QELS) and Dynamic Light Scattering (DLS).
- In determining the molecular mass of polymer substances, some chromatographic mode methods are used such as High Performance Liquid Chromatography (HPLC), Size Exclusion Chromatography (SEC), Gel-Permeation Chromatography (GPC). In addition to these Ultra-centrifuge technique is also used. To find out the molecular mass of polymer by calculation, the following symbols are used.
- Number average molecular mass = $\overline{M}_n$
- Weight average molecular mass = $\overline{M}_w$
- Number average molecular mass $\overline{M}_n = \dfrac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} = \dfrac{\text{Total mass of polymer}}{\text{Total number of polymer molecules}}$
- Weight average molecular mass $\overline{M}_w = \dfrac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}$

  where N_i = Number of species molecules of each polymer,

  M_i = Molecular mass of each polymer species.
- **Calculation of $\overline{M}_n$:** $\overline{M}_n$ is determined by the method which depends upon the number of molecules present in the polymer sample.
- **Calculation of $\overline{M}_w$:** Molar mass of single molecule present is polymer substance and is calculated on the basis of light scattering, chromatographic and ultracentrifuge methods as indicated above.
- **PDI :** The ratio of mass and number moleular mass $\left(\overline{M}_w / \overline{M}_n\right)$ is called polydispersity Index (PDI)
- Natural polymers are generally monodispersed, therefore PDI = 1. This means is $\overline{M}_w = \overline{M}_n$.
- PDI > 1 means that $\overline{M}_w > \overline{M}_n$. Because synthetic polymer is always polydispersed.

8.5 Biopolymer

- The polymer substances present in the nature such as polysaccharide, protein and nucleic acid, which are very useful for the human life are called **Biopolymer.**

8.5.1 Biodegradable polymers :

- **The degradation of those polymers which takes place mainly by enzymes, bacteria like microorganisms, hydrolysis and to some extent by oxidation are called Biodegradable polymers.**
- Biodegradable polymers are active towards environmental processes.
- Due to the easy degradation of these polymers, after there usage, there is no issue of its disposal. As a result, there is no environmental pollution.
- After the degradation of these polymers, they can be converted into the life essential products.
- During the usage, the degradation of this polymer takes place and can be used in various fields like medical and industries.
- Synthetic biodegradable polymers can be synthesized which are convenient to living system and helpful to enviornmental cycles.
- Using some aliphatic substances as monomer, many polymers are industrially prepared such as PolyHydroxy Butyrate-co-β-hydroxy Valerate (PHBV), PolyGlycolic Acid (PGA), PolyLactic Acid (PLA), Dextran, Nylon 2 Nylon 6, etc.
- The polymers present in nature are called biopolymer. They are biodegradable polymers.

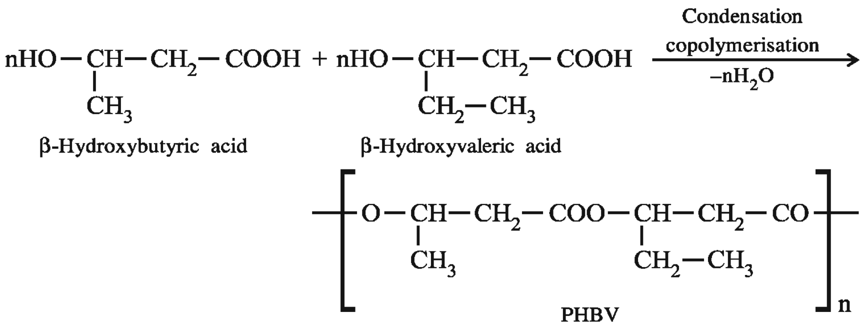
8.5.2 Non-biodegradable polymers :

- **Those synthetic polymers which do not get degraded by enzymes, bacteria like microorganism or by hydrolysis and oxidation reaction; are called non-biodegradable polymers.**
- Non-biodegradable polymer shows inertness towards the environmental process.
- As these polymers cannot be easily degraded, in everyday usage therefore disposal of polymeric waste is an acute problem. As a result environmental problems such as global warming, green house effect have been created.
- The degradation reaction does not take place; it is not converted into life essential products.
- Nowadays mostly synthesised polymer substances prepeared are nonbiodegradable polymers.
- Largely used non biodegradable polymers incude polythene, polystyrene, PVC, Teflon, Orlon, Butyl rubber, Neoprene, Stryrene Butadiene Rubber, Nitrile rubber, Nylon-6, Nylon-6,6, Terylene, Bakelite, Melamine etc.

Information of some important synthetic biodegradable polymers is given below :

Poly-HydroxyButyrate-Co-β-Hydroxyvalerate (PHBV)

Preparation : PHBV is the polymer of polyester class prepared from β-hydroxy butyric acid monomer and β-hydroxy valeric acid monomer by copolymerisation condensation reaction and on release of H_2O molecule.



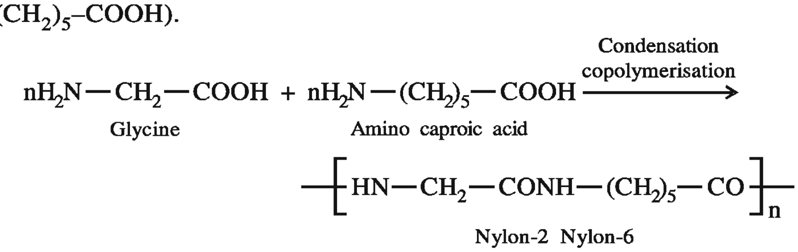
Properties :

- This polymer is of polyester class.
- It possesses biodegradable character.
- There is stiffness property of β-hydroxy butyric acid and has flexibility property of β-hydroxy valeric acid.
- PHBV also undergoes bacterial degradation in enviornmental conditions.

Uses :

- PHBV is used in special types of packaging
- In orthopaedic devices
- In capsules for filling controlled release of drugs.

Nylon-2 Nylon-6 : Nylon-2 Nylon-6 copolymer of polyamide series is obtained by condensation polymerisation reaction of two different types of monomer glycine ($H_2N–CH_2–COOH$) and amino caproic acid ($H_2N–(CH_2)_5–COOH$).



- Nylon-2 Nylon-6 is a biodegradable polymer.
- Nylon-2 Nylon-6 is of polyamide class.

PGA and PLA :

- They are prepared industrially.
- They are biodegradable polymers used for post operation stiches.

Dextran :

- Dextran is the first biodegradable polyester polymer used for post operative stitches.
- It is biodegradable polymer of polyeseter class.

SUMMARY

- Our modern life style is incomplete without polymers.
- The biological requirements of human body are fulfilled by biopolymers, while physical requirements are fulfilled by natural and synthetic polymers.
- Polymer is a group of molecules having giant (macro) size and high molecular mass.
- Innumerable molecules of one type or two or more than two types simple organic molecules combine with one another and form a giant molecule (macro), is called polymer.
- The molecules of only one type which combine through chemical bond is called monomer. In polymerisation reaction, first of all two monomers combine and dimer is formed. On combining third molecule, trimer is formed. Thus by combination of one by one molecule, polymer is formed.
- In each polymer series, the definite part which is repeated and this repeating part is called "Repeating unit"
- The number of this repeating unit is called 'Degree of polymerisation' (n).
- If the value of degree of polymerisation 'n' is less than 25 ($n < 25$), then that polymer is called oligomer.
- Generally oligomer is in liquid state. Fevicol like adhesives and liquid polymers used in paint are oligomers.
- If the value of degree of polymerisation 'n' is more than 25 ($n > 25$) then that polymer is called heavy polymer. Generally heavy polymer is in solid state.
- The classification of polymers is as follows :

Polymers

On the basis of source	On the basis of structure	On the basis of polymerisation reaction	On the basis of molecular forces	On the basis of growth of polymerisation reaction
(1) Natural polymers	(1) Linear	(1) Addition polymer	(1) Elastomer	
(2) Semisynthetic polymer	(2) Branched	(2) Homopolymer	(2) Fibers	
(3) Synthetic polymers	(3) Cross linked	(3) Copolymer	(3) Thermoplastic	
		(4) Condensation polymer	(4) Thermosetting	

- Polymerisation reaction is mainly classified in to two classes (1) Addition polymerisation and (2) Condensation polymerisation.
- The addition polymerisation reaction occurs from the monomer through free radical or carbocation or carbonium ion mechanism. In both these methods, if polymer is obtained from only one type of monomer, it is called homopolymer and if polymer is obtained from two different types of monomers, it is called co-polymer.
- In the addition hompolymers obtained by addition reaction of only one monomer are included as polythene, teflon, orlon PVC, polystyrene, butyl rubber etc.
- In the addition copolymer obtained by addition reaction of two or more different monomers, styrene butadiene rubber can be included.
- The polymerisation reaction during which water, ammonia, alcohol, or hydrochloric acid is liberated and polymer is formed, then that reaction is called condensation polymerisation reaction.
- Nylon 66, nylon 6, terylene, bakelite, melamine etc can be included in the polymers obtained by condensation polymerisation.
- In the polymer obtained by polymerisation reaction, if the functional group ester (–COO–) is present, then it is called polymer of polyester class and if the functional group is amide (–CONH–), then it is called polymer of polyamide class
- Terylene is polymer of polyester class, where as nylon 6 and nylon 6,6 is polymer of polyamide class.
- Natural rubber possesses unique property of elasticity, which cannot be destroyed at high or low temperatures, sulphur can be added to it and vulcanised rubber can be prepared.
- Vulcanised rubber maintains its property of elasticity at high or low temperatures. In addition, synthetic rubber containing more strength viz. neoprene, nitrile rubber, styrene butadiene rubber could be prepared which are inert towards the organic solvents.
- To determine molecular mass of polymer, different methods have been developed, and yet, its correct molecular mass cannot be determined because in the same polymer, the value of degree of polymerisation of its any two molecules is not same.
- To find molecular mass of polymer, in addition to colligative methods, light scattering and chromatographic methods have been proved more effective.
- To determine molecular mass of polymer, number average molecular mass $\overline{M}_n$ and mass average molecular mass $\overline{M}_w$ formulas can be used.
- The ratio of mass average molecular mass $\overline{M}_w$ and number average molecular mass $\overline{M}_n$ is called polydispersity index (PDI).

- The polydispersity index of natural polymer or biopolymers is PDI = 1, while for synthetic polymers it is PDI > 1.
- Polymers found in living beings are biopolymers. The decomposition of biopolymer by microorganisms like bacteria is possible. While using them, its transformation occurs in simple components and so they are called biodegradable polymers. Biodegradable polymers are friends of environment.
- The polymers which are not decomposed by microorganisms like bacteria, and the simple components are not obtained during their use, are called non-biodegradable polymers. Many problems are created in the environment by use of non-degradable polymers.
- To cure of environmental problems, it is necessary to increase the use of biodegradable polymers. In some synthetic biodegradable polymer substances, PHBV, PGA, PLA, dextran, nylon-2 nylon-6 are included.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Those simple organic molecules which chemically combine with one another and form a polymer, is called ....

(A) Monomer (B) Tetramer (C) Dimer (D) Trimer

(2) The number 'n' of repeating unit in polymer molecule is called ....

(A) Degree of polymerisation (B) Oligomer

(C) Heavy polymer (D) Repeating unit

(3) Which functional group is present in polyester ?

(A) –COO– (B) $-CH_2-CH_2-$ (C) –CONH– (D) $-CH_2-CN$

(4) What type of polymer can be considered novolac ?

(A) Linear (B) Branched (C) Cross linked (d) (A) and (B)

(5) Which of the following substances is an elastomer ?

(A) Nylon 6 (B) Nylon 6,6

(C) Vulcanised rubber (D) Melamine

(6) Which of the following polymers is obtained by condensation polymerisation ?

(A) PVC (B) Polythene (C) Polystyrene (D) Nylon 6,6

(7) Light Scattering method is used ....

(A) to find concentration (B) to find molecular mass of polymer

(C) to test elements (D) to find number of molecules

(8) HDP is used in preparation of ....

(A) Light and soft devices (B) Hard and durable devices

(C) Cotton and wool (D) Light and cheap devices

(9) Which monomer is used for preparation of orlon ?

(A) $CF_2=CF_2$ (B) $CH_2=CH-CN$ (C) $CH_2=CHCl$ (D) $CH_2=CH-OH$

(10) From the following .... is the example of biopolymer ?

(A) Teflon (B) Neoprene (C) Nylon-6,6 (D) DNA

(11) Which of the following two monomers are used in preparation of nylon-6,6 ?

(A) Hexamethylene diamine and ethylene glycol

(B) Adipic acid and hexamethylene diamine

(C) Dimethyl terphthalate and ethylene glycol

(D) Adipic acid and ethylene glycol

(12) .... possesses biodegradable property

(A) PTFE (B) PAN (C) SBR (D) PHBV

(13) Which choice is correct for synthetic polymer substance ?

(A) $\overline{M}_n = \overline{M}_w$ (B) $\overline{M}_n \geqslant \overline{M}_w$ (C) $\overline{M}_w > \overline{M}_n$ (D) $\overline{M}_w < \overline{M}_n$

(14) Which is the formula to find mass average molecular mass ?

(A) $\overline{M}_w = \dfrac{\sum_{i=1}^{\infty} N_i^2 \cdot M_i}{\sum_{i=1}^{\infty} N_i \cdot M_i}$ (B) $\overline{M}_w = \dfrac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i}$

(C) $\overline{M}_w = \dfrac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i^2}$ (D) $\overline{M}_w = \dfrac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}$

(15) What can be obtained by ultracentrifuge method in polymer chemistry ?

(A) Concentration (B) Molecular mass (C) Precipitation (D) Solution

2. Write answers of the following questions in brief :

(1) Give definitions :

(i) Degree of polymerisation

(ii) Repeating unit.

(2) Give examples of natural polymer.

(3) When is called that the condensation polymer has occurred ?

(4) What is meant by addition polymerisation reaction ?

(5) Mention the types of addition reaction on the basis of their methods.

(6) Mention the uses of high density polythene (HDP).

(7) Upto which temperature the layer of teflon does not decompose ?

(8) What type of polymer is polystyrene ?

(9) Which rubber is used in place of natural rubber ?

(10) Give equation of chemical reaction for preparation of nylon 6.

(11) Mention repeating unit of bakelite.

(12) What is PDI ?

(13) What is meant by biopolymer ?

(14) Give example of natural elastomer.

(15) The capsules used for filling controlled drugs is prepared from which polymer ?

(16) Mention the repeating unit in PTFE.

3. Answer the following questions :

(1) Give information about semisynthetic polymer substances.

(2) What are oligomers and heavy polymers ?

(3) Explain elastomers.

(4) Mention characteristics of thermoplastic polymers.

(5) Explain the preparation of any one polymer obtained by addition co-polymerisation reaction.

(6) Give properties and uses of nylon-6,6.

(7) How is melamine prepared ?

(8) Give difference between natural rubber and vulcanised rubber.

(9) Mention methods to find molecular mass of polymer.

(10) Mention the formulas of weight average molecular mass and number average molecular mass.

(11) Give differences between biodegradable and non-biodegradable polymers.

(12) Mention characteristics of PGA, PLA, dextran.

4. Answer the following questions in detail :

(1) Give classification of polymers and give one example of each.

(2) What is meant by monomer, polymer and degree of polymerisation? Explain with example.

(3) Explain condensation polymerisation reaction.

(4) Explain steps of free radical addition polymerisation reaction.

(5) Mention preparation, properties and uses of high density polythene (HDP).

(6) Explain stepwise polymerisation reaction.

(7) Mention properties and uses of bakellite.

(8) Write a note on vulcanised rubber.

(9) Write a note on 'PHBV'

(10) Explain oligomer and heavy polymer.

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