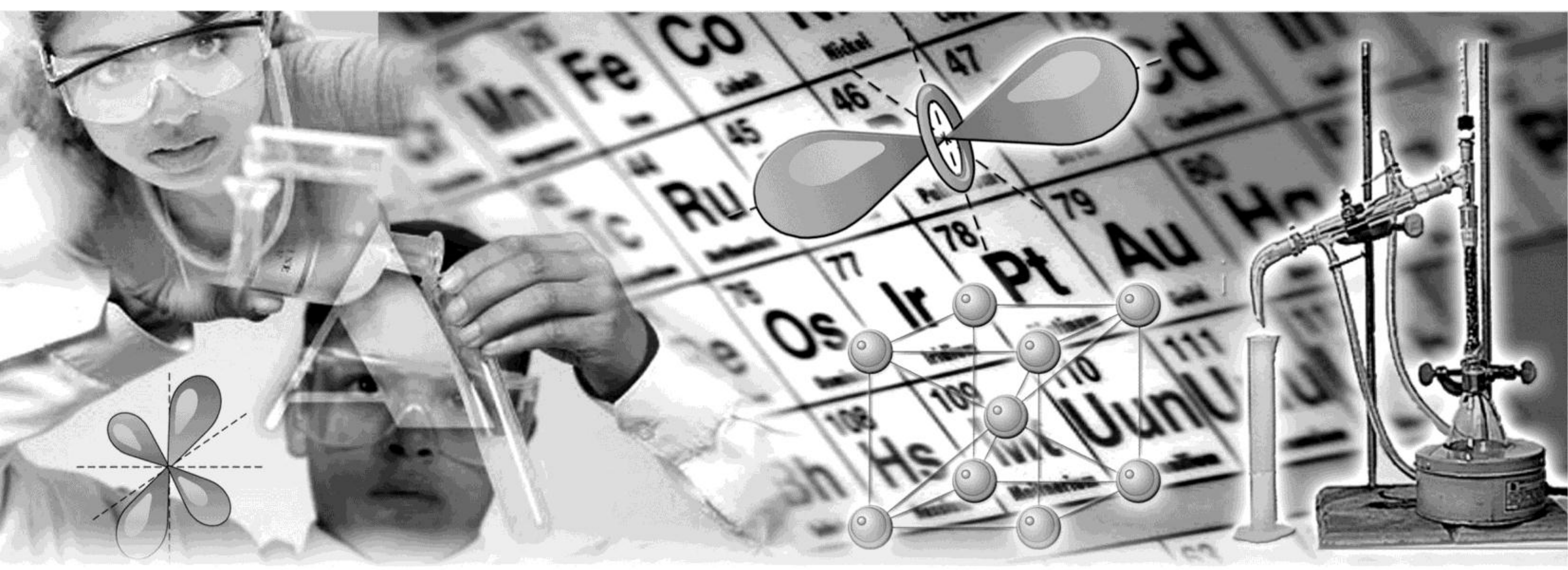


Chapter
30
Polymer

Polymers are compound of very high molecular masses formed by the combination of a large number of simple molecules.

The simple molecules which combine to give polymers are called monomers. The process by which the simple molecule (i.e. monomers) are converted into polymers is called polymerisation.

Example : Polyethylene

❑ All polymers are macromolecule but all macromolecules are not polymers because polymer consist repeating unit of monomer e.g., chlorophyll is a macromolecule but not a polymer.

Classification of polymers

(1) **Classification based on source of availability :** They are classified as

(i) Natural polymers (ii) Synthetic polymers
(iii) Semi-synthetic polymers

(i) ***Natural polymers*** **:** The polymers obtained from nature (plants and animals) are called natural polymers. These polymers are very essential for life. They are as under.

(a) *Starch* **:** It is polymer of glucose and it is food reserve of plant.

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

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

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

❑ It may be noted that polymers such as polysaccharides (starch, cellulose), proteins and nucleic acids etc. which control various life processes in plants and animals are also called ***biopolymers***.

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

(iii) ***Semisynthetic polymers*** **:** These polymers are mostly derived from naturally occurring polymers by chemical modifications. For example cellulose is naturally occurring polymers, cellulose on acetylation with acetic anhydride in the presence of sulphuric acid forms cellulose diacetate polymers. It is used in making thread and materials like films glasses etc. Vulcanized rubber is also an example of semisynthetic polymers used in making tyres etc. gun cotton which is cellulose nitrate used in making explosive.

❑ ***Semi-synthetic polymers :*** Rayon and other cellulose derivatives like cellulose nitrate, cellulose acetate etc., are semi-synthetic polymers. These are thermoplastic polymers. Viscose rayon in the form of a thin transparent film is known as cellophane. Cellophane is softened with glycerol. Unlike plastic sheets it absorbs water.

❑ ***Rayon :*** Rayon is a man made material which consists of purified cellulose in the form of long fibres. Cellulose is treated with cold $NaOH$ solution to purify it and then treated with CS_2 to form a viscose solution. This is why rayon is sometimes called viscose rayon. This solution is allowed to pass through fine pores in metal cylinder, into a dilute solution of H_2SO_4. This results in the formation of long fibres. Rayon fibre is chemically identical to cotton but has a shine like silk. As such rayon is also known as ***artificial silk***. Rayon is used on a large scale for making textiles, tyre-chord, carpets and surgical dressings. Unlike fully synthetic polymers, it absorbs moisture and is bio-degradable.

(2) **Classification based upon structure :** On the basis of structure of polymers these can be classified as

(i) Linear polymers (ii) Branched chain polymers
(iii) Cross linked polymers

(i) ***Linear polymers*** **:** These are polymers in which monomeric units are linked together to form linear chain. These linear polymers are well packed and have high magnitude of intermolecular forces of attraction and therefore have high densities, high tensil (pulling) strength and high melting points. Some common example of linear polymers are high density polyethylene nylon, polyester, PVC, PAN etc.

(ii) ***Branched chain polymers*** **:** These are polymers in which the monomers are joined to form long chains with side chains or branches of different lengths. These branched chain polymers are irregularly packed and therefore, they have low tensile strength, low density, boiling point and melting points than linear polymers. Some common examples are low density polythene, glycogen, starch etc. (Amylopectin).

(iii) ***Cross linked polymers*** **:** These are polymers in which monomers unit are crosslinked together to form a three dimensional network polymers.

These polymers are hard, rigid and brittle because of network structure *e.g.*, Bakelite, malamine formaldehyde resin etc.

(3) **Classification based upon molecular forces :** Depending upon the intermolecular forces, the polymers have been classified into four type.

(i) Elastomers (ii) Fibres

(iii) Thermoplastics (iv) Thermosetting polymers

(i) ***Elastomers*** **:** The polymers that have elastic character like rubber (a material that can return to its original shape after stretching is said to be elastic) are called elastomers. In elastomers the polymers 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 elastomers is natural rubber.

(ii) ***Fibres*** **:** These are the polymers which have strong intermolecular forces between the chain. These forces are either hydrogen bonds or dipole-dipole interaction. Because of strong forces, the chains are closely packed giving them high tensil strength and less elasticity. Therefore, these polymers have sharp melting points. These polymers are long, thin and thread like and can be woven in fabric. Therefore, these are used for making fibres.

Example : Nylon 66, dacron, silk etc.

(iii) ***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 chain. The softening occurs as the polymer chain move more and more freely because of absence of cross link. When heated, they melt and form a fluid which can be moulded into any desired shapes and then cooled to get the desired product.

Example : Polythene, polystyrene, PVC, teflon etc.

(iv) ***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 molecule in place so that heating does not allow them to move freely. Therefore a thermosetting plastic is cross linked and is permanently rigid.

Example : Bakelite, melamine formaldehyde resin etc.

☐ Plasticizers do lower the softening point (so called melting point) of a polymer. A plasticizer cannot convert a thermosetting polymer into thermoplastic one. In fact plasticizers can convert a hard and brittle plastic into soft and easily pliable. Plasticizers reduce the interparticle forces between polymer molecules. ***Plasticizers*** are generally high-boiling esters or high-boiling haloalkanes. They are added to plastics to make them soft and rubber-like. For example, polyvinyl chloride as such is hard, stiff and glass-like, but the addition of plasticizers like dioctylphthalate (DOP) or dibutylphthalate (DBP) can make it soft and rubber like. Similarly, chlorinated paraffin wax (CPW) is used as a plasticizer in polythene. On long exposure to air and sunlight, these plasticizers evaporate and the plastic articles become hard and brittle.

Table : 30.1 Difference between thermoplastic and thermosetting polymers

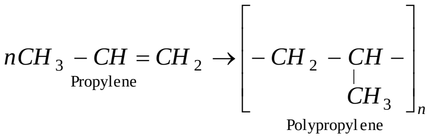
Thermoplastic polymers	Thermosetting polymers
(1) These soften and melt on heating.	These do not soften on heating but rather become hard in case prolonged heating is done these start burning.
(2) These can be remoulded recast and reshaped.	These can not be remoulded or reshaped.
(3) These are less brittle and soluble in some organic solvents.	These are more brittle and insoluble in organic solvents.
(4) These are formed by addition polymerisation.	These are formed by condensation polymerisation.
(5) These have usually linear structures. Ex. Polyethylene, PVC, teflon.	These have three dimensional cross linked structures. Ex. Bakelite, urea, formaldehyde, resin.

(4) **Classification based upon mode of synthesis :** They are of two types on the basis of their synthesis.

(i) Addition polymers (ii) Condensation polymers

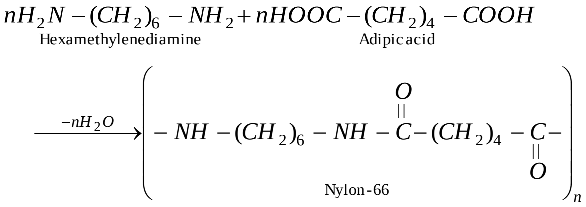
(i) ***Addition polymers*** **:** A polymer formed by direct addition of repeated monomers without the elimination of by product molecule is called addition polymers. For example,

$$\underset{\text{Ethene}}{nCH_2 = CH_2} \rightarrow \underset{\text{Polyethene}}{(-CH_2 - CH_2-)_n}$$



$$\underset{\text{Propylene}}{nCH_3 - CH = CH_2} \rightarrow \underset{\text{Polypropylene}}{\left[-CH_2 - \underset{\underset{CH_3}{|}}{CH} - \right]_n}$$

(ii) ***Condensation polymers*** **:** A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecule like water, ammonia, *HCl*, alcohol etc. is called condensation polymers. For example,



$$\underset{\text{Hexamethylenediamine}}{nH_2N - (CH_2)_6 - NH_2} + \underset{\text{Adipic acid}}{nHOOC - (CH_2)_4 - COOH}$$

$$\xrightarrow{-nH_2O} \underset{\text{Nylon-66}}{\left(- NH - (CH_2)_6 - NH - \overset{\overset{O}{||}}{C} - (CH_2)_4 - \underset{\underset{O}{||}}{C} - \right)_n}$$

Table : 30.2 Difference between addition and condensation polymers

Addition polymers	Condensation polymers
Formed by addition reaction.	Formed by condensation process with elimination of small molecules like H_2O.
Molecular mass is a whole number multiple of the monomer.	Molecular mass is not whole number multiple of the monomer units.
Generally involve one monomer unit.	Generally involve more than one monomer unit.
Monomers are unsaturated molecules.	Monomer units must have two active functional groups.
They are generally chain growth polymers.	They are generally step growth polymers.

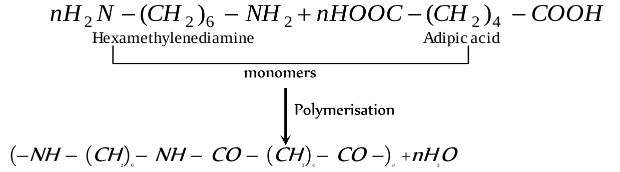
(5) **Classification based upon the nature of monomer :** On the basis of nature of monomer. Polymer are of two types

(i) Homopolymers (ii) Copolymers

(i) ***Homopolymers*** **:** A polymer formed from one type of monomers is called **homopolymer**. For example, polythene is a homopolymer of monomer ethene.

$$\underset{\text{Ethene}}{nH_2C = CH_2} \xrightarrow{\text{Polymerisation}} \underset{\text{Polythene}}{(-CH_2 - CH_2 -)_n} \text{ Homopolymer}$$

(ii) ***Copolymers*** **:** A polymer formed from two or more different monomers is called **copolymer** or **mixed polymer**. For example, nylon-66 is a polymer of two types of monomers : hexamethylenediamine and adipic acid.



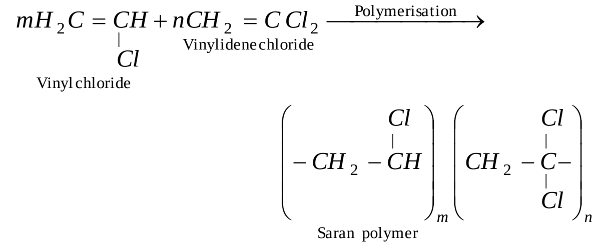
$$\underbrace{\underset{\text{Hexamethylenediamine}}{nH_2N - (CH_2)_6 - NH_2} + \underset{\text{Adipic acid}}{nHOOC - (CH_2)_4 - COOH}}_{\text{monomers}}$$

$$\downarrow \text{Polymerisation}$$

$$\underset{\text{Nylon-66 (Copolymer)}}{(-NH - (CH_2)_6 - NH - CO - (CH_2)_4 - CO -)_n} + nH_2O$$

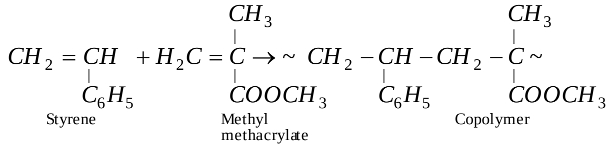
Copolymer are commercially more important.

For example copolymerisation of vinyl chloride with vinylidene chloride (1, 1 dichloroethane) in a 1 : 4 ratio forms a copolymer known as saran.



$$\underset{\text{Vinyl chloride}}{mH_2C=\underset{Cl}{\underset{|}{CH}}}+\underset{\text{Vinylidene chloride}}{nCH_2=CCl_2}\xrightarrow{\text{Polymerisation}}\underset{\text{Saran polymer}}{\left(-CH_2-\overset{Cl}{\overset{|}{CH}}\right)_m\left(CH_2-\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-\right)_n}$$

Copolymerisation of monomer mixtures often leads to the formation of polymers which have quite different properties than those of either corresponding homopolymer. For example, a mixture of styrene and methyl methacrylate can form a copolymer.



$$\underset{\text{Styrene}}{CH_2=\underset{C_6H_5}{\underset{|}{CH}}}+\underset{\text{Methyl methacrylate}}{H_2C=\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}}}\rightarrow\underset{\text{Copolymer}}{\sim CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}}\sim}$$

The composition of the copolymer depends on the proportion of the monomers and their reactivity. It may be noted that some monomers do not polymerise at all but copolymerize. For example, maleic anhydride does not polymerise as such. However, it copolymerises with styrene in a highly symmetrical manner to form styrene maleic anhydride copolymer.

It may be noted that many types of copolymers can be obtained depending upon the distribution of monomer units in the chain. Two monomers can combine in either regular fashion (although this is rare) or random fashion. For example, if monomer *A* is copolymerised with monomer *B*, the resultant product may have a random distribution of the two units throughout the chain or it might have alternating distribution.

$(-A-B-A-B-A-B-A-B-)$ Alternating copolymer

$(-A-A-A-B-A-B-B-A-B-)$ Random copolymer

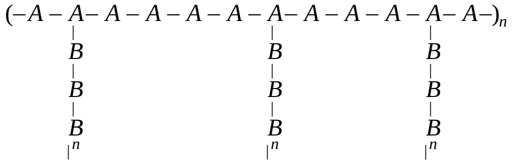
The exact distribution of monomer units depends on the initial proportion of the two-reactant monomers and their reactivities. Most copolymers have varying distributions. Two other types of copolymers that can be prepared under certain conditions are called block copolymers and graft copolymers.

(a) *Block copolymers* are those in which different blocks of identical monomer units alternate with each other as

$(-A-A-A-A-B-B-B-B-A-A-A-A-B-B-B-B-)$

These are prepared by initiating the polymerisation of one monomer as if growing a homopolymer and then adding an excess of second monomer to the active reaction mixture.

(b) *Graft polymers* are those in which homopolymer branches of one monomer units are grafted on the homopolymer chains of another monomer units as :



$$(-A-\underset{\underset{|^n}{B}}{\underset{|}{\underset{B}{\underset{|}{\underset{B}{\underset{|}{A}}}}}}-A-A-A-A-\underset{\underset{|^n}{B}}{\underset{|}{\underset{B}{\underset{|}{\underset{B}{\underset{|}{A}}}}}}-A-A-A-\underset{\underset{|^n}{B}}{\underset{|}{\underset{B}{\underset{|}{\underset{B}{\underset{|}{A}}}}}}-A-)_n$$

These are prepared by radiation of γ-rays on a completed homopolymer chain in the presence of the second monomer. The high energy radiation knocks hydrogen atoms of the homopolymer chain at random points resulting radical sites for initiation of the added monomer. By careful control of the polymerisation reaction, we can produce copolymers of desired properties by combination of different monomers in various ratios and geometric arrangements.

General methods and mechanism of polymerisation

(1) **Chain growth or addition polymerisation :** It involve a series of reaction each of which consumes a reactive particle and produces another similar one. The reactive particle may be free radicals or ion (cation or anion) 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 compounds that contain carbon-carbon double bond polythene, polypropylene, polybutadiene, teflon PVC, polystyrene are some of chain growth polymers. It is based on three mechanism

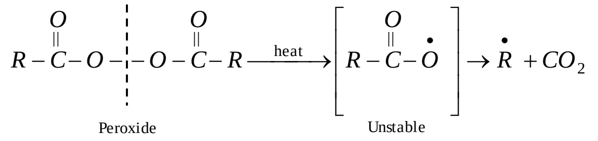
(i) Free radical mechanism (ii) Cation mechanism

(iii) Anion mechanism

Each mechanism of polymerisation reaction involves an initiator of their corresponding nature. The addition polymerisation reaction is very rapid and is also characterized by three steps *i.e.* chain initiation, chain propogation and chain termination step.

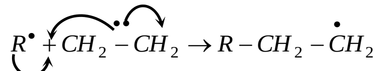
(i) ***Free-radical mechanism*** : Free-radical polymerisation is initiated by organic peroxide or other reagents which decompose to give free radicals. Following steps are involved.

(a) *Chain initiation* : Organic peroxides undergo homolytic fission to form free radicals.



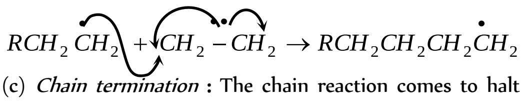
$$\underset{\text{Peroxide}}{R-\overset{O}{\overset{||}{C}}-O-\vdots-O-\overset{O}{\overset{||}{C}}-R}\xrightarrow{\text{heat}}\underset{\text{Unstable}}{\left[R-\overset{O}{\overset{||}{C}}-\dot{O}\right]}\rightarrow\dot{R}+CO_2$$

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



$$R^{\bullet}+CH_2-CH_2\rightarrow R-CH_2-\dot{C}H_2$$

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



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

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

$$2R(CH_2CH_2)_nCH_2\dot{C}H_2\rightarrow R(CH_2CH_2)_nCH_2CH_2$$

$$:CH_2CH_2(CH_2CH_2)_nR$$

❑ *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 $(FeSO_4+H_2O_2)$.

(ii) ***Cationic mechanism*** : Cationic polymerisation is initiated by use of acids such as H_2SO_4, *HF* or BF_3 in H_2O. The following steps are involved :

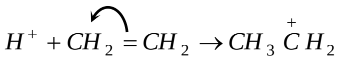
(a) *Chain initiation* : The acid furnishes proton.

$$H_2SO_4\rightleftharpoons H^++HSO_4^-$$

$$HF\rightleftharpoons H^++F^-$$

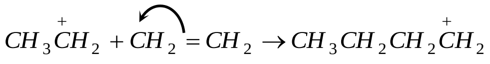
$$BF_3+H_2O\rightleftharpoons H^++BF_3(OH)^-$$

The proton adds to the carbon of the double bond of the alkene to form a carbonium ion.



$$H^++CH_2=CH_2\rightarrow CH_3\overset{+}{C}H_2$$

(b) *Chain propagation* : The carbonium ion combines with another molecule of alkene to form a new carbonium ion and the process continues to form a long chain.

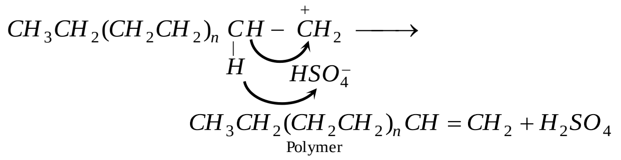


$$CH_3\overset{+}{C}H_2+CH_2=CH_2\rightarrow CH_3CH_2CH_2\overset{+}{C}H_2$$

$$CH_3CH_2CH_2\overset{+}{C}H_2+nCH_2=CH$$

$$\rightarrow CH_3CH_2(CH_2CH_2)_nCH_2\overset{+}{C}H_2$$

(c) *Chain termination* : The chain may be halted by combination with negative ion or loss of a proton.

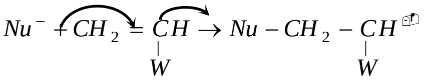


$$CH_3CH_2(CH_2CH_2)_n\underset{\underset{H}{|}}{C}H-\overset{+}{C}H_2 \xrightarrow{\quad HSO_4^- \quad} \underset{\text{Polymer}}{CH_3CH_2(CH_2CH_2)_nCH=CH_2}+H_2SO_4$$

(iii) ***Anionic polymerisation*** : This type of polymerisation is initiated by anion (Bases nucleophiles) it proceeds through the formation of carbanion. The initiation may be brought about by $K^+\overline{N}H_2$ of $L^+N\overline{H}_2$.

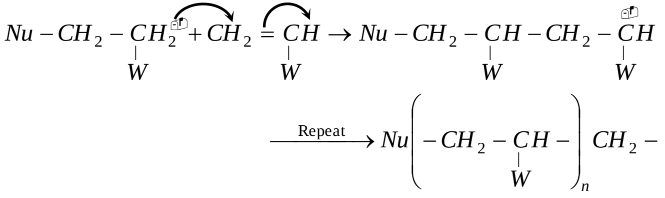
The following steps are involved

(a) *Chain initiation* :



$$Nu^- + CH_2=\underset{\underset{W}{|}}{C}H \rightarrow Nu-CH_2-\underset{\underset{W}{|}}{C}H^{\ominus}$$

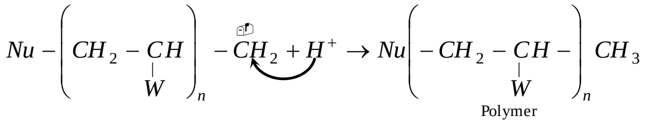
(b) *Chain propagation* :



$$Nu-CH_2-\underset{\underset{W}{|}}{C}H_2^{\ominus}+CH_2=\underset{\underset{W}{|}}{C}H \rightarrow Nu-CH_2-\underset{\underset{W}{|}}{C}H-CH_2-\underset{\underset{W}{|}}{\overset{\ominus}{C}}H$$

$$\xrightarrow{\text{Repeat}} Nu\left(-CH_2-\underset{\underset{W}{|}}{C}H-\right)_n CH_2-$$

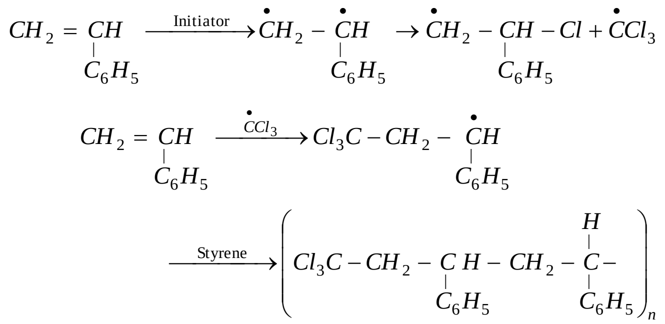
(c) *Termination* :



$$Nu-\left(CH_2-\underset{\underset{W}{|}}{C}H\right)_n-\overset{\ominus}{C}H_2+H^+ \rightarrow \underset{\text{Polymer}}{Nu\left(-CH_2-\underset{\underset{W}{|}}{C}H-\right)_n CH_3}$$

Chain transfer agents : In Vinylic polymerisation various other molecules react with main growing chain to interrupt the further growth of the original chain. This leads to lowering of average molecular mass of the polymer such reagents are called chain transfer agents. The common example CCl_4, CBr_4 etc.

For example in the presence of CCl_4 styrene polymerizes to form a polymer of lower average molecular mass which also contains some chlorine.



$$CH_2=\underset{\underset{C_6H_5}{|}}{C}H \xrightarrow{\text{Initiator}} \dot{C}H_2-\underset{\underset{C_6H_5}{|}}{\dot{C}}H \rightarrow \dot{C}H_2-\underset{\underset{C_6H_5}{|}}{C}H-Cl+\dot{C}Cl_3$$

$$CH_2=\underset{\underset{C_6H_5}{|}}{C}H \xrightarrow{\dot{C}Cl_3} Cl_3C-CH_2-\underset{\underset{C_6H_5}{|}}{\dot{C}}H$$

$$\xrightarrow{\text{Styrene}} \left(Cl_3C-CH_2-\underset{\underset{C_6H_5}{|}}{C}H-CH_2-\underset{\underset{C_6H_5}{|}}{\overset{\overset{H}{|}}{C}}-\right)_n$$

Chain transfer agents determinate chain reaction and inhibit further polymerisation and are also called inhibitors.

(2) **Step growth or condensation polymerisation** : In this type of polymerisation monomers generally contain two functional groups, *i.e.*, difunctional monomers. In this process no initiator is needed and each step is the same type of chemical reaction. Since in this polymerisation reaction the polymer is formed in a stepwise manner. It is called step growth polymer and the process is called step growth polymerisation. The process for two monomer *A* and *B* may be expressed as.

$$\underset{\text{Monomers}}{A+B} \xrightarrow{\text{Condense}} \underset{\text{Dimer}}{A-B}$$

$$A-B+A \xrightarrow{\text{Condense}} \underset{\text{Trimer}}{A-B-A}$$

$$A-B-A+B \longrightarrow A-B-A-B$$

Alternatively, step growth can proceed as

$$A+B \rightarrow A-B$$

$$A-B+A-B \rightarrow A-B-A-B \text{ or } (A-B)_2$$

$$A-B-A-B+A-B-A-B \xrightarrow[\text{Polymer}]{} (A-B)_n$$

Some common examples of step growth polymers are

Polymers	Monomers
Nylon-66	Hexamethylenediamine and adipic acid
Bakelite	Phenol and formaldehyde
Dacron (polyester)	Terephthalic acid and ethylene glycol

Rubber

It is a polymer which is capable of returning to its original length, shape or size after being stretched or deformed. It is the example of elastomer. Rubber are of two types.

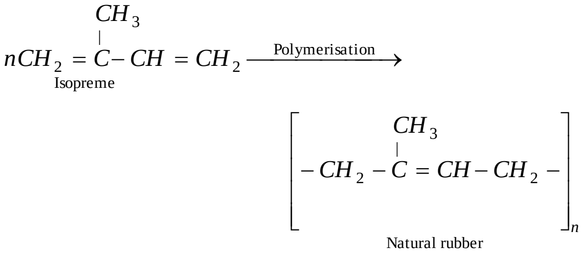
(1) Natural rubber (2) Synthetic rubber

(1) **Natural rubber** : It is obtained as latex from rubber trees. 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, dil. Acids and alkalies but soluble in benzene, chloroform, ether, petrol and carbon disulphide. It absorb a large amount of water. It has low elasticity and tensile strength.

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

Thus isoprene is a monomer of natural rubber the no. of isoprene unit are 11,000 to 20,000 which linked together in a chain.

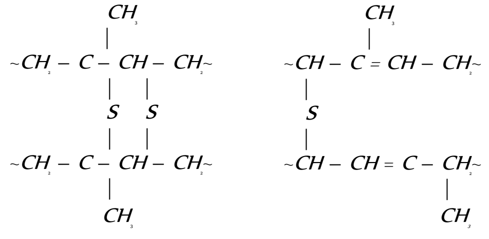


$$\underset{\text{Isopreme}}{nCH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH_2} \xrightarrow{\text{Polymerisation}} \underset{\text{Natural rubber}}{\left[-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-\right]_n}$$

(2) **Synthetic rubber** : The synthetic rubber is obtained by polymerising certain organic compounds which may have properties similar to rubber and some desirable properties. Most of these are derived from butadiene derivatives and contain carbon-carbon double bonds. The synthetic rubbers are either homopolymers of 1, 3 butadiene or copolymer in which one of the monomers is 1, 3 butadiene or its derivative so that the polymer has the availability of double bonds for its vulcanization. Some important examples are Neoprene, styrene, butadiene rubber (SBR) thiokol, silicones, polyurethane, rubber etc.

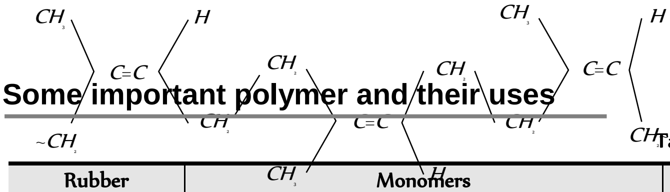
Vulcanization of rubber : The process of heating natural rubber with sulphur to improve its properties is called vulcanization. Vulcanization was introduced by Charles Goodyear.

Although natural rubber is thermoplastic substance in which there are no cross link between the polymer chain and it on vulcanization set into a given shape which is retained.



The vulcanization process performed originally was slow. Now a days, some additives such as zinc oxide etc. are used to accelerate the rate of vulcanization. During vulcanization, sulphur cross links are formed (figure) the double bonds in the rubber molecule acts as reactive sites. The allylic $-CH_2$, alpha to double bond is also very reactive. During vulcanization, sulphur forms cross links at these reactive sites. As a result, rubber gets stiffened and intermolecular movement of rubber springs is prevented resulting in physical character of rubber. The extent of stiffness of vulcanized rubber depend upon the amount of sulphur added. For example about 5% sulphur is used for making tyre rubber while 30% of the sulphur is used for making battery case rubber.

In a polymer, the chains are normally tangled up with each other. When the rubber is stretched, the chains straighten out to some extent. The chains cannot slip past each other because of the polysulphide bridges. Thus, rubber can be stretched only to a limited extent. When the tension is removed, the chains try to coil up again and the rubber resumes its original shape.



Natural rubber
All *cis* configuration

The comparison of the main properties of natural rubber and vulcanized rubber are given below in the table,

Table : 30.3

Natural rubber	Vulcanized rubber
(1) Natural rubber is soft and sticky	Vulcanized rubber is hard and non-sticky.
(2) It has low tensile strength.	It has high tensile strength.
(3) It has low elasticity.	It has high elasticity.
(4) It can be used over a narrow range of temperature (from 10° to 60°*C*).	It can be used over a wide range of temperature (–40° to 100°*C*).
(5) It has low wear and tear resistance.	It has high wear and tear resistance.
(6) It is soluble in solvents like ether, carbon, tetrachloride, petrol, etc.	It is insoluble in all the common solvents.

Some important polymer and their uses

Table : 30.4 Rubber

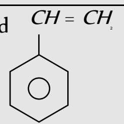
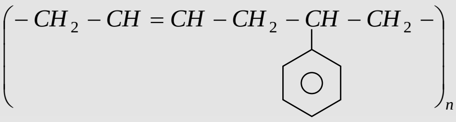
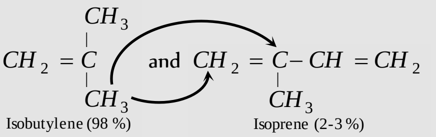
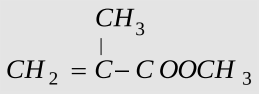
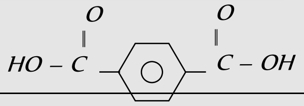
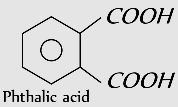
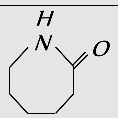
Rubber	Monomers	Formula	Applications
(i) Neoprene rubber	$CH_2 = \underset{\underset{Cl}{\vert}}{C} - CH = CH_2$ Chloroprene	$\left(-CH_2 - \underset{\underset{Cl}{\vert}}{C} = CH - CH_2 - \right)_n$	Making automobile, refrigerator parts and electric wire.
(ii) Styrene Butadiene Rubber (SBR) or Buna-*S*	$CH_2 = CH - CH = CH_2$ and Butadiene (75%)  $CH = CH_2$ Styrene (25%)	 $\left(-CH_2 - CH = CH - CH_2 - CH - CH_2 - \right)_n$	Making of tyre and other mechanical rubber goods.
(iii) Butyl rubber	 $CH_2 = \overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}$ and $CH_2 = \underset{\underset{CH_3}{\vert}}{C} - CH = CH_2$ Isobutylene (98 %) Isoprene (2-3 %)	$\left(-CH_2 - \overset{\overset{CH_3}{\vert}}{C} = CH - CH_2 - \overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}} - CH_2 - \right)_n$	Making of toys, tyre, tube etc.
(iv) Nitrile rubber or Buna *N* or GRA	$CH_2 = CH - CH = CH_2$ and Butadiene (75%) $CH_2 = CH - CN$ Acrylonitrile (25%)	$\left(-CH_2 - \underset{\underset{CN}{\vert}}{CH} - CH_2 - CH = CH - CH_2 - \right)_n$	Used for make of fuel tank.
(v) Polysulphide rubber (Thiokol)	$Cl - CH_2 - CH_2 - Cl$ Ethylene dichloride and Na_2S_4 Sodium tetrasulphide	$(-CH_2 - CH_2 - S - S - S - S-)_n$	Used in the manufacture of hoses and tank lining, engine gasket and rocket fuel.
(vi) Silicone rubber	$Cl - \overset{\overset{CH_3}{\vert}}{\underset{\underset{Cl}{\vert}}{Si}} - CH_3$ Chlorosilanes	$\left(-O - \overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{Si}} - \right)_n$	Silicon rubber
(vii) Polyurethane rubber	$HOCH_2 - CH_2OH$ Ethylene glycol and $\overset{\overset{O}{\Vert}}{C} = N - CH = CH - N = C = O$ Ethylene di-isocyanate		In the manufacture of fibre. Paints and heat insulator.

Table : 30.5 Plastics and resin

Name of polymer	Abbreviat-ion	Starting materials (monomers)	Nature of polymer	Properties	Applications
(i) Polyolefines (a) Polyethylene or polyethene	LDPE (Low density polyethene)	$CH_2 = CH_2$	*Low density* homopolymer (branched) chain growth.	Transparent, moderate tensile strength, high toughness.	Packing material carry bags, insulation for electrical wires and cables.
	HDPE (high density polyethene)	$CH_2 = CH_2$	*High density* homopolymer (linear) chain growth.	Transluscent, chemically inert, greater tensile strength, toughness.	Manufacture of buckets, tubs, house ware, pipes, bottles and toys.
(b) Polypropylene or polypropene	PP	$CH_3CH = CH_2$	Homopolymer, linear, chain growth.	Harder and stronger than polyethene.	Packing of textiles and foods, liners for bags, heat shrinkage wraps, carpet fibres, ropes, automobile mouldings, stronger pipes and bottles.
(c) Polystyrene or Styron or styrofoam		$C_6H_5CH = CH_2$	Homopolymer, linear, chain growth	Transparent	Plastic toys, house hold wares, radio and television bodies, refrigerator linings.
(ii) Polyhaloolefines (a) Polyvinyl chloride	PVC	$\underset{\text{Vinylchloride}}{CH_2 = CH - Cl}$	Homopolymer chains growth	Thermoplastic	(i) Plasticised with high boiling esters PVC used in rain coats, hand bags, shower curtains, fabrics, shoe soles, vinyl flooring (ii) Good electrical insulator (iii) Hose pipes.
(b) Polytetrafluoroethylene or Teflon	PTFE	$F_2C = CF_2$	Homopolymer, high melting point	Flexible and inert to solvents boiling acids even aqua regia. Stable upto 598 *K*.	(i) For nonstick utensiles coating (ii) Making gaskets, pump packings valves, seals, non lubricated bearings.
(c) Polymonochlorotri-fluroroethylene	PCTFE	$ClFC = CF_2$	Homopolymer	Less resistant to heat and chemicals due to presence of chlorine atoms.	Similar to those of teflon.
(iii) Formaldehyde resins (a) Phenol formaldehyde resin or Bakelite		Phenol and formaldehyde	Copolymer, step growth	Thermosetting polymer, hard and brittle	(i) With low degree polymerisation as bindings glue for wood varnishes, lacquers. (ii) With high degree polymerisation for combs, for mica table tops, fountain pen barrels electrical goods (switches and plugs).
(b) Melamine formaldehyde resin		Melamine and formaldehyde	Copolymer, step growth	Thermosetting polymer, hard but not so breakable.	Non-breakable crockery.
(iv) Polyacrylates (a) Polymethacrylate (lucite, acrylite and plexiglass and perspex)	PMMA	 $CH_2 = \overset{\overset{CH_3}{\vert}}{C} - COOCH_3$	Copolymer	Hard transparent, excellent light transmission, optical clarity better than glass takes up colours.	Lenses light covers lights, shades signboards transparent domes skylight aircraft window, dentures and plastic jewellery.

(b) Polyethylacrylate		$CH_2 = CH - COOC_2H_5$	Copolymer	Tough, rubber like product	

Table : 30.6 Fibre

Name of polymer	Abbreviation	Starting materials	Nature of polymer	Properties	Applications
(i) Polysters (a) Terylene or Dacron or mylar	PET (Polyethylene terephthalate)	$HO - CH_2 - CH_2 - OH$ and Ethylene glycolor Ethane -1, 2-diol  Terephthalic acid	Copolymer, step growth linear condensation polymer	Fibre crease resistant, low moisture absorption, not damaged by pests like moths etc.	For wash and wear fabrics, tyre cords seat belts and sails.
(b) Glyptal or alkyd resin		$HO - CH_2 - CH_2 - OH$ Ethylene glycol and  Phthalic acid	Copolymer, linear step growth condensation polymer	Thermoplastic, dissolves in suitable solvents and solutions on evaporation leaves a tough but not flexible film.	Paints and lacquers.
(ii) Polyamides (a) Nylon-66		 $HO - \overset{O}{\overset{\Vert}{C}}[CH_2]_4\overset{O}{\overset{\Vert}{C}} - OH$ Adipic acid and $H_2N - [CH_2]_6 - NH_2$ Hexamethyl lenediamin e	Copolymer, linear, step growth condensation polymer	Thermoplastic high tensile strength abrasion resistant.	Textile fabrics, bristles for brushes etc.
(b) Nylon-610		$H_2N - [CH_2]_6 - NH_2$ Hexamethyl lene diamine and $HOOC\,[CH_2]_8\,COOH$ Sebacic acid	Copolymer, linear, step growth	Thermoplastic, high tensile strength, abrasion resistant	(i) Textile fabrics, carpets, bristles for brushes etc. (ii) Substitute of metals in bearings. (iii) Gears elastic hosiery.
(c) Nylon-6 or Perlon		 Caprolactum or $H_2N - [CH_2]_5 - COOH$ ∈-Aminocaproic acid	Homopolymer, linear	Thermoplastic high tensile strength abrasion resistant.	Mountaineering ropes, tyre cords, fabrics.
(iii) Polyacryloni-trile or orlon or acrilon	PAN	$CH_2 = CH - CN$	Copolymer	Hard, horney and high melting materials.	Orlon, arcrilon used for making clothes, carpets blankets and preparation of other polymers.

❑ *Copolymer of acrylonitrile (40%) and vinyl chloride (60%) is called dynel it is used in hair wigs.*

❑ *Artificial silk is the term given to fibres derived from cellulose. The most important process for the production of artificial silk is viscose process. The difference between natural and artificial silk is natural silk contain nitrogen while artificial silk may not have nitrogen. Natural silk on burning gives a smell of burning hair and shrinks into a ball of cinder while artificial silk gives a thread of ash.*

Biodegradable polymers

These are the polymers which are degraded by micro-organisms within a suitable period so that biodegradable polymers and their degraded products do not cause any serious affects on the environment.

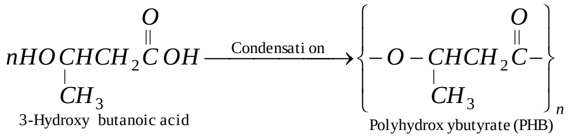
In biological systems, biopolymers degrade mainly by enzymatic hydrolysis and to some extent by oxidation. Therefore, in view of the disposal problems of polymer waste and for developing polymers for other safe uses in human systems, attempts have been made to develop biodegradable synthetic polymers. These synthetic polymers mostly have functional groups which are normally present in biopolymers and lipids.

Among these aliphatic polyesters are one important class of biodegradable polymers which are commercially potential biomaterials. The common examples of biodegradable polymers are polyhydroxy butyrate (PHB), polyhydroxy butyrate $-co-\beta$-hydroxy valerate (PHBV), polyglycolic acid (PGA), polylactic acid (PLA), poly (∈-caprolactone) (PCL), etc.

Uses : Biodegradable polymers are used mainly for medical goods such as surgical sutures, tissue in growth materials or for controlled drug release devices, plasma substitutes etc. The decomposition reactions usually involve hydrolysis (either enzymatically induced or by non-enzymatic mechanisms) to non-toxic small molecules which can be metabolized by or excreted from the body. These are also finding use in agriculture materials (such as films, seed coatings), fast food wrappers, personal hygiene products, etc.

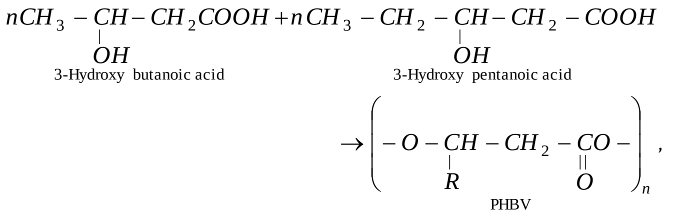
(i) ***Polyhydroxy butyrate (PHB)***

Polyhydroxy butyrate (PHB) is obtained from hydroxy butyric acid (3-hydroxy butanoic acid)



$$\underset{\text{3-Hydroxy butanoic acid}}{nHO\underset{CH_3}{\underset{|}{C}}HCH_2\overset{O}{\overset{||}{C}}OH} \xrightarrow{\text{Condensation}} \underset{\text{Polyhydroxybutyrate (PHB)}}{\left\{-O-\underset{CH_3}{\underset{|}{C}}HCH_2\overset{O}{\overset{||}{C}}-\right\}_n}$$

(ii) ***Poly-Hydroxybutyrate-co-β-Hydroxy valerate (PHBV)*** : It is copolymer of 3-hydroxy butanoic acid and 3-hydroxy pentanoic acid, in which the monomer units are joined by ester linkages.



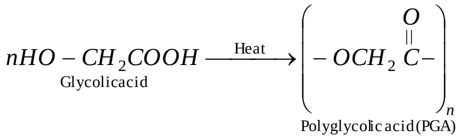
$$\underset{\text{3-Hydroxy butanoic acid}}{nCH_3-\underset{OH}{\underset{|}{C}}H-CH_2COOH}+\underset{\text{3-Hydroxy pentanoic acid}}{nCH_3-CH_2-\underset{OH}{\underset{|}{C}}H-CH_2-COOH}$$

$$\rightarrow \underset{\text{PHBV}}{\left(-O-\underset{R}{\underset{|}{C}}H-CH_2-\underset{O}{\underset{||}{C}}O-\right)_n},$$

$$R = CH_3,\ C_2H_5$$

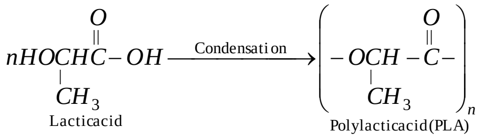
The properties of PHBV vary according to the ratio of both the acids. 3-Hydroxy butanoic acid provides stiffness while 3-Hydroxypentanoic acid gives flexibility to the copolymer.

(iii) ***Polyglycolic acid* (PGA)** : Polyglycolic acid (PGA) is obtained by the chain polymerisation of cyclic dimer of glycolic acid, $HO-CH_2-COOH$.



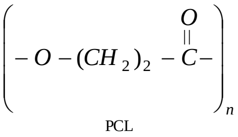
$$\underset{\text{Glycolic acid}}{nHO-CH_2COOH} \xrightarrow{\text{Heat}} \underset{\text{Polyglycolic acid (PGA)}}{\left(-OCH_2\overset{O}{\overset{||}{C}}-\right)_n}$$

(iv) ***Polylactic acid* (*PLA*)** : Polylactic acid (PLA) is obtained by polymerisation of the cyclic dimer of lactic acid $(HO-CH(CH_3)COOH)$ or by microbiological synthesis of lactic acid followed by the polycondensation and removal of water by evaporation.



$$\underset{\text{Lactic acid}}{nHO\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{||}{C}}-OH} \xrightarrow{\text{Condensation}} \underset{\text{Polylactic acid (PLA)}}{\left(-O\underset{CH_3}{\underset{|}{C}}H-\overset{O}{\overset{||}{C}}-\right)_n}$$

(v) ***Poly (∈-caprolactone) (PCL)*** : It is obtained by chain polymerisation of the lactone of 6-hydroxy hexanoic acid.



$$\underset{\text{PCL}}{\left(-O-(CH_2)_2-\overset{O}{\overset{||}{C}}-\right)_n}$$

Uses : PGA and PLA (90 : 10) is used to make absorbable structure to close an internal of external wound and has replaced cat gut these are completely degraded and absorbed by the body within 15 days to one month of the surgery.

Polyhydroxybutyrate (PHB) and (PHBV) have been used for making films for packaging and into moulded items.

Molecular masses of polymers

A polymer sample contains chain of varying lengths and therefore its molecular mass is always expressed as an average on the other hand natural polymer such as proteins contain chain of identical length and therefore they have definite molecular mass.

The molecular mass of a polymer can be expressed in two ways.

(1) Number average molecular mass $(\overline{M}_N)$

(2) Weight average molecular mass $(\overline{M}_W)$.

(1) **Number average molecular mass $(\overline{M}_N)$** : If N_1, N_2, N_3 ..... are the number of molecules with molecular masses M_1, M_2, M_3 ...... respectively, then the number average molecular mass is

$$\overline{M}_N = \frac{N_1M_1 + N_2M_2 + N_3M_3 + ...}{N_1 + N_2 + N_3 ...}$$

This may be expressed as : $\overline{M}_N = \dfrac{\Sigma N_iM_i}{\Sigma N_i}$

Where N_i is the number of molecules of the *i*th type with molecular mass M_i.

(2) **Weight average molecular mass $(\overline{M}_W)$** : If m_1, m_2, m_3 .... are the masses of species with molecular masses M_1, M_2, M_3 ..... respectively, then the weight average molecular mass is

$$\overline{M}_W = \frac{m_1M_1 + m_2M_2 + m_3M_3 ....}{m_1 + m_2 + m_3 + ...} \text{ or } = \frac{\Sigma m_iM_i}{\Sigma m_i}$$

But $m_i = N_iM_i$, so that $\overline{M}_W = \dfrac{\Sigma N_iM_i^2}{\Sigma N_iM_i}$

where N_i is the number of molecules of mass M_i.

❑ ***Polydispersity index*** : *The ratio of weight average molecular mass to the number average molecular mass is called* ***polydispersity index, PDI.***

$$PDI = \frac{\overline{M}_W}{\overline{M}_n}$$

This gives an idea about the homogeneity of a polymer.

(i) The polymers whose molecules have nearly same molecular masses are called ***monodisperse polymers****. For these molecules,* $\overline{M}_W = \overline{M}_N$ *and therefore, PDI is one.*

(ii) The polymers whose molecules have wide range of molecular masses are called ***polydisperse polymers.*** *For these polymers,* $\overline{M}_W > \overline{M}_N$ *and therefore, their PDI is greater than one.*

Thus, it may be concluded that in general, ***natural polymers are more homogeneous than synthetic polymers.***

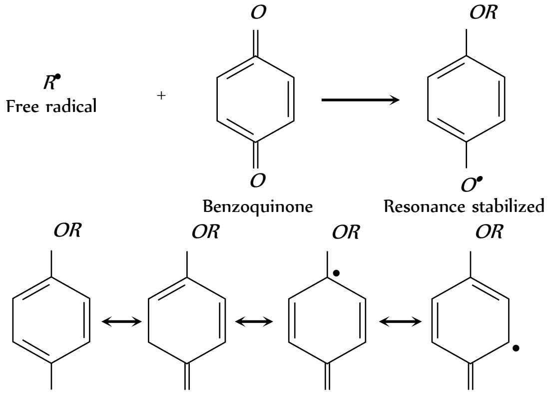
For natural polymers, PDI is usually unity and therefore, natural polymers are monodisperse.

For synthetic polymers, the PDI is greater than one and therefore $\overline{M}_W$ *is always greater than* $\overline{M}_N$. $\overline{M}_N$ *is always determined by employing methods which depend upon the number of molecules present in the polymer sample. For example, colligative property such as osmotic pressure is used. On the other hand, weight average molecular mass is measured by using the methods such as light scattering and ultracentrifugation, sedimentation, etc. which depend upon the mass of individual molecules.*

(3) Polymer in increasing order of their intermolecular forces are polythene < Buna S < Nylon-66.

(4) We always use purest monomer in free radical polymerisation reaction because the impurities can act as chain transfer agent and may combine with the free radical to slow down the reaction or even stop the reaction.

(5) Benzoquinone inhibit the free radical polymerisation of vinyl derivative because it combine with free radical intermediate to form a non reactive radical which is highly stabilized by resonance because of the lack of reactivity of the new radical formed, it inhibit the further progress of the chain reaction. Therefore the reaction stops.



(6) A thin film of polyester is known as Mylar film.

(7) PET plastic commonly used for soft drink bottles, transparent jars and bottles for use in kitchen are made up of polyethylene terephthalate.

(8) Glyptal resins or Alkyd resins obtained from ethylene glycol and phthalic acid are thermoplastic. However, resins obtained from glycerol and phthalic acid are thermosetting polymers, due to the formation of cross-links by the third $-OH$ group present in glycerol.

(9) Thermosetting plastics are also called heat setting plastics whereas thermoplastics are called cold setting plastics.

(10) Latex is a colloidal dispersion of rubber in water. It is not a colloidal solution of isoprene in water or any other solvent.

(11) Polymerisation of isoprene by free radical mechanism (in the presence of Na and heat) gives a product which is different from natural rubber (Natural rubber is a polymer of isoprene). The synthetic product so obtained is a mixture of *cis* and *trans* configurations **and resembled** *Gutta percha*. Gutta percha is a naturally occurring polymer in plants. It is all *trans*-stereoisomer and is non-elastic.

(12) Terylene is a British name of *Dacron*.

(13) Co-polymer of vinyl chloride 90% and vinyl acetate 10% is called *VINYON*.

(14) Co-polymer of acrylonitrile 40% and vinyl chloride 60% is called *DYNEL*.

(15) Co-polymer of vinyl chloride and vinyledene chloride is called *SARAN*.

(16) Plasticizers cannot convert a thermosetting polymer into thermoplastic one. It converts a hard and brittle plastic into soft and easily pliable one at room temperature.

(17) Free radical polymerisation of isoprene do not give Gutta percha (Gutta percha is a natural polymer). The synthetic product so obtained resembles Gutta percha.

(18) Co-ordination polymerisation of isoprene gives a product similar to natural rubber.

(19) Latex is not a colloidal dispersion of isoprene in water.

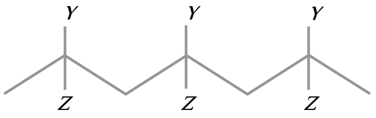
Advance level information

(1) Thermocol is polystyrene foamed with vapour of pentane.

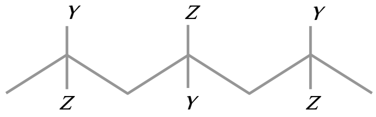
(2) Cups used for hot drinks are made up of polystyrene. It does not become soft like other plastics at temperatures near boiling point of water.

(3) A major development of co-ordination polymerisation is *stereochemical control*. For example Propene could polymerise to any of the three different arrangements.

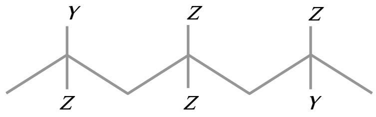
(i) ***Isotactic (Same order)*** **:** When groups are arranged on one side of the chain. All y group *i.e.* on one side and all Z groups on the opposite side of the chain.



(ii) ***Syndiotactic (Alternating order)*** **:** The Y and Z groups lie alternately on each side of the chain.



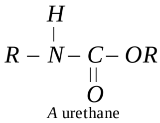
(iii) ***Atactic (Random order)*** **:** The Y and Z groups are arranged in a random fashion.



(4) Addition polymers, generally, have only carbon atoms in their main chain. On the other hand, condensation polymers, generally, have atoms other than carbon atoms, in their main chain.

(5) **Polyurethanes :** Polyurethanes are polymers obtained by the polymerisation of a urethane.

It is used for heat and sound insulation in the form of polyurethane foam. Mattresses, cushions and pillows made out of polyurethane foam are washable and long lasting.



$$R-\overset{\overset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle O}{||}}{C}-OR'$$

A urethane

(6) **Epoxy resins :** These are obtained by copolymerisation of epichlorohydrin and bisphenol-A. These resins have good adhesive strength. These are used for making adhesives (Araldite, M-seal etc.) for making glass reinforced plastic (fibre glass), for lamination, to impart crease resistance and shrinkage control to cotton, rayon and for making anti-skid surface for highways.

(7) **Polycarbonates :** These are obtained by copolymerisation of diphenyl carbonate and bisphenol-A. It has very high optical transparency, high impact strength over wide range of temperature. It is used for making bullet-proof glass, baby-feed bottles, fridge containers, mixi jars etc.

(8) Thermoplastics are also called cold setting polymers. They are moulded when hot but set into the required shape only on cooling. Thermosetting polymers are also called heat setting polymers. Such polymers are supplied in the partially polymerised form.

(9) On long exposure to air and sun-light thermo-plastics becomes brittle. It is due to the evaporation of plasticizer with time. The faint smell associated with various thermoplastics is due to slow evaporation of this plasticizer.

(10) High density polyethene is a linear polymer. Carry bags made out of it are not so soft and make a crackling sound when crushed in hands. You can easily tear them in one direction, but not at right angle to it. Plastic twine is made out of such a polymer. They have very high tensile strength in one direction (along the polymer chain) and a low tensile strength at

right angle to it. Such carry bags are used to carry clothes, note-books etc. Carry bags made of low density polyethene are soft, make no noise when crushed with hands, have same tensile strength in all directions. Such carry bags are used to carry heavy objects (vegetables, fruits etc.)

(11) **Kevlar** is a nylon-polymer and is obtained by condensation copolymerization of terephthalic acid with 1, 4-diaminobenzene (*p*-phenylenediamine). The fibres of this polymer are so strong that they are used to make bullet-proof vests.

(12) **Lexan** is a polycarbonate(polyester) and is prepared by condensation copolymerization of diethyl carbonate and bisphenol A. It has unusually high impact strength and hence is used in making bullet-proof windows and safety or crash helmits.

(13) **Nomex** is a polyamide made from *m*-phthalic acid and *m*-diaminobenzene. It is known for its fire-resistant properties and is used in protective clothing for firefighters, astronauts and race car drivers.

(14) **Ebonite** is high sulphur (20-30 %S) rubber and is obtained by vulcanization of natural rubber.

(15) **Rayon** was originally called artificial silk but now the name rayon is given to all fibres obtained by chemical treatment of cellulose. Thus, artificial silk is polysaccharide, *i.e.*, cellulose derivative.

Tips & Tricks

- Nucleic acids and proteins though macromolecules are also regarded as polymers
- Diphenylamine is added as an antioxidant to rubber to protect it from degradation on exposure to air.
- Plasticizers are non volatile liquid such as di-*n*-butylphthalate, tricresyl phosphates which are added to a polymer such as PVC to make it soft and readily workable on heating.
- Low density polythene is a branched polymer and is prepared by free radical polymerization while high density polythene is a linear polymer and is prepared by coordination polymerization.
- Coordination polymerization was developed by Zeigler and natta.
- Neoprene is a synthetic rubber. It is superior to natural rubber in its stability to aerial oxidation and resistance to oils, gasoline and solvents.
- Super glue is a polymer of methyl α-cyanoacrylate.
- Polyurethanes are obtained by condensation of toluene diisocyanate with ethylene glycol. During polymerization, low boiling liquid such as Freon-11 are added to the reaction mixture. The heat of polymerization vaporizes the volatile liquid producing bubble which convert the viscous polymer to a frothy mass of polyurethane foam.
- Ebonite is high sulphur (20-30%S) rubber and is obtained by vulcanization of natural rubber.