15
Polymer

15.1 Introduction

Polymers, generally known as 'Plastics', are backbone of modern era. It would be difficult to imagine today's life without polymers. They are not only used in household utilities, cloths, etc. but also in vehicles, space-crafts and medical field. Now a days polymers are used in making of aritificial organs.

Generally, carbon compounds contain 30-40 or less carbon atoms but in polymers, there are thousands of carbon atoms. This large or giant size is responsible for special properties of polymers.

Polymers are made up of both inorganic and organic molecules.

The word 'polymer' is coined from two Greek words 'Poly' means 'many' and 'mer' means 'unit' or 'part'.

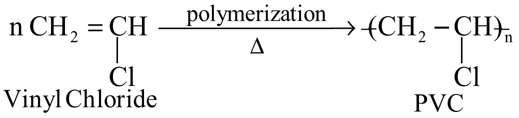
Polymers are formed by joining of repeating structural units on a large scale. These units are linked to each other by covalent bond. These structural units are known as "monomer' and are linked to each other to form 'polymers', this process of formation of polymers is called 'polymerization'.

For example :

1. Formation of polythene by polymerization of ethene. Here, ethene is 'Monomer' and Pdythene is 'Polymer'.

$$\underset{\text{Ethene}}{n(CH_2 = CH_2)} \xrightarrow[\Delta]{O_2,\text{High Pressure}} \underset{\text{Polyethene}}{\left(CH_2 - CH_2\right)_n}$$

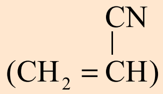
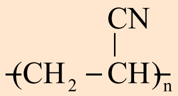
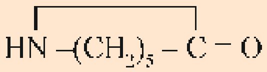
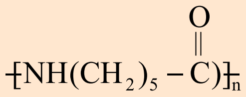
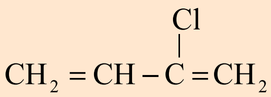
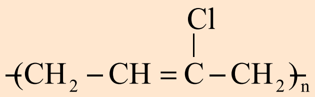
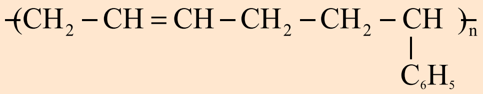
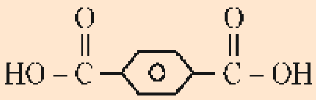
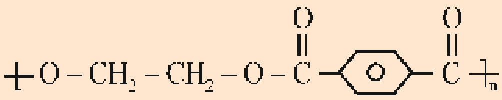
2. Formation of polyvinyl chloride (General name is PVC) by polymerization of vinyl chloride



$$\underset{\text{Vinyl Chloride}}{n\,CH_2 = \underset{\substack{|\\ Cl}}{CH}} \xrightarrow[\Delta]{\text{polymerization}} \underset{\text{PVC}}{\left(CH_2 - \underset{\substack{|\\ Cl}}{CH}\right)_n}$$

Table 15.1 : Some polymers and their monomers

S. No.	Polymer	Monomer	Structural Units (Repeat Unit)
1.	Polythene (PE)	Ethylene ($CH_2 = CH_2$)	$\left(CH_2 - CH_2\right)_n$
2.	Polypropylene (PP)	Propylene ($CH_2 = \overset{\overset{CH_3}{\mid}}{CH}$)	$\left(CH_2 - \overset{\overset{CH_3}{\mid}}{CH}\right)_n$
3.	Polystyrene (PS)	Styrene ($CH_2 = \overset{\overset{C_6H_5}{\mid}}{CH}$)	$\left(CH_2 - \overset{\overset{C_6H_5}{\mid}}{CH}\right)_n$
4.	Polyvinyl Chloride (PVC)	Vinyl Chloride ($CH_2 = \overset{\overset{Cl}{\mid}}{CH}$)	Largely used for making pipes in electric cables $\left(CH_2 - \overset{\overset{Cl}{\mid}}{CH}\right)_n$

S. No.	Polymer	Monomer	Structural Units (Repeat Unit)
5.	Polyacrylonitrile	Acrylonitrile  $(CH_2=\overset{\overset{CN}{\vert}}{C}H)$	 $-\!\!(CH_2-\overset{\overset{CN}{\vert}}{C}H)\!\!-_n$
6.	Nylon-6	Caprolactam  $HN-(CH_2)_5-C=O$	 $-[NH(CH_2)_5-\overset{\overset{O}{\Vert}}{C}]-_n$
7.	Polybutadiene	1,3 butadiene $CH_2=CH-CH=CH_2$	$-\!\!(CH_2-CH=CH-CH_2)\!\!-_n$
8.	Nylon 6,6	Hexamethylenediamine and Adipic acid $H_2N-(CH_2)_6-NH_2$ and $HOOC-(CH_2)_4-COOH$	$-\!\!(CO-(CH_2)_6-CONH-(CH_2)_4-NH)\!\!-_n$
9.	Neoprene or Chloroprene	2-chloro-1, 3-butadiene  $CH_2=CH-\overset{\overset{Cl}{\vert}}{C}=CH_2$	 $-\!\!(CH_2-CH=\overset{\overset{Cl}{\vert}}{C}-CH_2)\!\!-_n$
10.	Styrene-butadiene rubber	Styrene and 1, 3-butadiene $C_6H_5-CH=CH_2$ and $CH_2=CH-CH=CH_2$	 $-\!\!(CH_2-CH=CH-CH_2-CH_2-\underset{\underset{C_6H_5}{\vert}}{CH})\!\!-_n$
11.	Teflon	Tetrafluoroethylene $(F_2C=CF_2)$	$-\!\!(F_2C-CF_2)\!\!-_n$
12.	Terylene or Dacron	Ethylene glycol and terephthalic acid $HO-CH_2-CH_2-OH$ and 	

15.1.1 Polymer and Macromolecule

Generally, Polymers and Macromolecules cannot be distinguished but 'polymers' are formed by repeating of structural units whereas in 'Macromolecules' there may or may not be repetition of structural units. It can be understood by taking an example of protein.

'Protein' is a macromolecule, made up of amino acids, where, amino acids are chemically same but unite in a structurally different manner.

"All polymers are macromolecules but all macromolecules are not polymers".

15.2 Classification of Polymers

Polymers are classified on the basis of different criteria.

15.2.1 Classification based on Source/origin

Polymers are classified into three categories on the basis of source/origin.

1. **Natural Polymers :** The polymers obtained from natural or made by nature, are called natural polymer. These are found in plants and animals.

Examples : Cotton, Silk, Wool, Rubber, Cellulose, etc.

2. **Synthetic polymers :** The polymers which are prepared in laboratories by low molecular weight molecules (monomers) are called synthetic polymers. This man-made polymers have great importance in our daily life.

Examples : Polyethene, Nylons, Polyesters, PVC, etc.

3. **Semi synthetic polymers :** Natural polymers which are modified by chemical reactions are called semi synthetic polymers.

Examples : Gun-cotton (Nitro derivative of cellulose), Vulcanized rubber, cellulose diacetate cellophane, leather, etc.

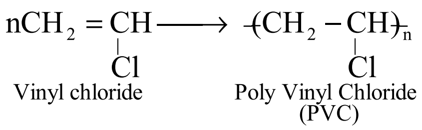
15.2.2 Classification on the basis of types of Monomers

Polymers are divided in two parts :–

1. **Homopolymers :** Polymers containing a single type of repeating units i.e. monomers, are called homopolymers.

Example : Polyethene (Poly ethylene), PVC etc. are homopolymers made by single type of monomer units.

$$n\,\underset{\text{Ethene}}{CH_2=CH_2} \longrightarrow \underset{\text{Polyethene}}{(CH_2=CH_2)_n}$$



$$n\underset{\text{Vinyl chloride}}{CH_2=\underset{|\atop Cl}{CH}} \longrightarrow \underset{\text{Poly Vinyl Chloride (PVC)}}{(CH_2-\underset{|\atop Cl}{CH})_n}$$

2. **Co-polymers :-** Polymers containing more than one type of repeating units i.e. monomers, are called co-polymers.

Example : Nylon 6, 6 is made by two type of monomers.

$$n\underset{\text{Hexamethylene diamine}}{NH_2-(CH_2)_6-NH_2} + n\underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH}$$

$$\Big\downarrow -H_2O$$

$$\underset{\text{Nylon 6,6}}{[NH_2-(CH_2)_6-NHCO-(CH_2)_4-CO]_n}$$

15.2.3 Classification on the basis of Polymerization process

In 1928, Carothers classified polymers into two types on the basis of polymerization process.

1. Addition polymer
2. Condensation polymer

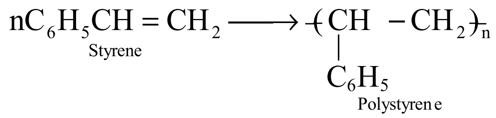
But when some polymers can not be classified in these two groups then in 1950, H.F. Mark classified polymers into two types on the basis of kinetics of polymerization, namely, Chain growth polymers and Step growth polymers.

(1) **Addition Polymers :** Addition polymers formed by the polymerization of monomer molecules possessing double or triple bond i.e. repeating addition polymerization of unsaturated monomer molecules. As by-product is not formed here so molecular weight of polymers is multiple of molecular weight of monomers.

Examples :

(i) All vinyl monomers form addition polymers

(ii)



$$n\underset{\text{Styrene}}{C_6H_5CH=CH_2} \longrightarrow \underset{\text{Polystyrene}}{(\underset{|\atop C_6H_5}{CH}-CH_2)_n}$$

(iii) $$n\underset{\text{Tetrafluoroethene}}{F_2C=CF_2} \longrightarrow \underset{\text{Polytetrafluoroethene *(Teflon)}}{(F_2C-CF_2)_n}$$

[* Teflon coating is used in non-stick cookware.]

(2) **Condensation Polymers :** Condensation

polymers are formed by the condensation polymerization of two different bi or tri functional monomer molecules.

As these are formed by condensation reaction so small molecules like, H_2O, alcohols, Cl etc. are eliminated in condensation polymerization reaction.

Their molecular weight in not multiple of monomer molecular weight.

For example :

Nylon 6, 6, Polyesters etc. are examples of condensation polymers.

15.2.4 Classification on the basis of line Structure

In polymers, monomer units produce three types of structure and on this basis polymers are classified into three groups.

(1) Linear polymer :

In these polymers, monomer units are linked together to form straight chain. These monomer units are arranged on each other and due to this reason, these polymers have high densities. Their tensile strength and melting point is also high.

For example : high density polyethylene (HDPE) PVC, Nylon, polyester, etc.

(2) Branched chain polymers :

These are polymers in which the monomers are joined to form long straight chain, which is called main chain. Many side chain or branches of different lengths are attached with main chain, whcih are called brached chains. These branched chain can be made by same or different type of molecules. These polymers have low density. Their tensile strength and melting point is also low. (Fig. 15.1)

For example : Low density polyethylene (LDPE), glycogen, amylopectin, etc.

3. Crosslinked or Network Polymers :

These are the polymers in which many polymer chains are cross linked together to form a three dimensional network. These polymers are formed by difunctional or trifunctional monomers and here two linear chains are joined by strong covalent bond. These polymers are hard, brittle and rigid. Normally, these polymers are not soluble in any solvent but they absorb solvents.

Example : Vulcanized Rubber, Bakelite Melamine-Formaldehyde Resin, etc.

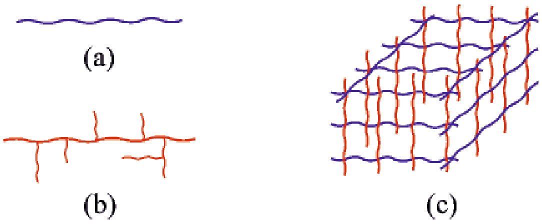


Fig. 15.1 : (a) Linear Polymer (b) Branched chain Polymer (c) Cross linked or Network Polymer

15.2.5 Classification on the basis of behaviour of polymers towards temperature

(1) Thermoplastic polymers :

These polymers become soft on heating and become hard on cooling and this process can be performed repeatedly. The chains of these polymers possess intermolecular forces of attraction which are intermediate to those of elastomers and fibers but there is no cross linkage between chains. There is no chemical changes in molecules of these polymers on heating again and again so they can be recycled many times. They can be easily moulded. They have a linear structure.

For example : All linear polymers, polystyrene, polythene, PVC, etc.

(2) Thermosetting polymers :

When these polymers are heated, the chains develop crosslinking and form three dimensional network so these polymers become hard, infusible and insoluble. They cannot be reused i.e. cannot remelted on again heating. They are formed by condensation reaction and do not get soft on heating.

For example : All cross-linked polymers, Bakelite, Melamine-Formaldehyde Resin, etc.

15.2.6 Classification based on molecular forces:

The use of polymers in different fields depends upon their mechanical properties like tensile strength, elasticity, rigidity, hardness, softness, etc. and these mechanical properties depend upon their intermolecular forces like van der Waals force, hydrogen bonding or dipole-dipole interaction, etc. These forces held the polymer chains and on the basis of these forces, polymers are classified into two types-

1. **Elastomers :** Generally these polymers are also known as 'Rubber'. In these, polymer chains are held together by weakest intermolecular forces. Due to this weak binding forces, they can be stretched upto a limit and these chains also have few 'crosslinks', which helps the polymers to retract to its original position after the force is released. With this, the chains of these polymers have few coil like structure, which opens to form long chain on stretching.

The elasticity of elastomers can be increased by introducing some 'crosslinks'.

For example – The elasticity of natural rubber increases, after vulcanisation with sulphur and due to this the elasticity of vulcanised rubber is higher.

Other examples are– Buna-S, Buna-N Neoprene, etc.

2. **Fibres :** Generally, these polymers are known as 'thread' and they are used in textile industries. In this polymers the chains are linked with strong intermolecular forces. These strong forces lead to close packing of chains and thus impart crystalline character. These polymers have high tensile strength and melting point.

For example – Polyesters (terylene), polyamides (Nylon-6,6), Natural fibres (Silk, woolen, cotton), Rayon, etc.

Table 15.2 : Classification of Polymers

S. No.	Basis of Classification	Types of Polymer
1.	Sources	1. Natural Polymer 2. Synthetic Polymer 3. Semi-synthetic Polymer
2.	Monomers	1. Homopolymer 2. Copolymer
3.	Polymerization	1. Addition polymer 2. Condensation polymer
4.	Structure	1. Linear polymer 2. Branched chain polymer 3. Cross linked or network polymer
5.	Behaviour of polymer with temperature	1. Thermoplastic polymer 2. Thermosetting polymer
6.	Molecular forces	1. Elastomers 2. Resin

15.3 Method of Polymerization

Two important methods of polymerization are -

(1) Addition Polymerization

(2) Condensation Polymerization

(1) Addition Polymerization

When unsaturated monomer molecules form polymers by addition reaction, then this process is called addition polymerization. Monomer units may be same or different types.

Unsaturated monomer molecules or units-Alkenes, alkadienes and their derivatives. As this process involves the addition of monomer units to themselves to form a growing chain, so this process is also known as chain growth polymerization.

In addition polymerization monomer units are unsaturated molecules and are neutral. For process of polymerization these should be active. Thus initiator is required to initiate polymerization process. Any active particle of this initiator react with neutral monomer molecule or unit to make it active. This initiators may be free radicals or any ionic species. However, free radical addition polymerization process is most common. On the basis of nature of initiator the addition polymerization can be of two types-

(i) Free radical addition polymerization

(ii) Ionic addition polymerization

The above both kinds of polymerization have three steps-

(A) Chain initiation step

(B) Chain propagation step

(C) Chain termination step

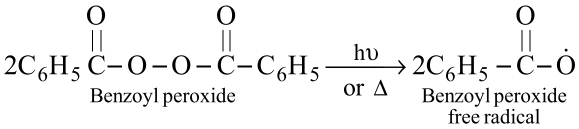
(i) Free Radical Addition Polymerization

Step 1 : In free radical addition polymerization intiators are peroxides or peroxy acids. They dissociate in the presence of heat or light to form free radical. This free radical react/add with monomer molecule to generate a new and large free radical. This step is called chain initiation step.

Step 2 : Second step is chain propagation step. In this, the free radical of first step, reacts with another monomer molecule and like this addition of monomer molecules takes place one by one.

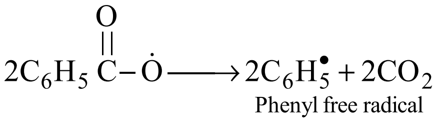
Step 3 : Last step is chain termination step. Above two steps continue till the monomer molecules are present in reacton mixture and when these monomer molecules are consumed, then these radicals react with each other to form neutral polymer molecules. Thus, this step is known as chain termination step. Some times, chain termination can be carried out by external elements.

Step 1 :

(i) 

$$2C_6H_5\overset{\overset{\displaystyle O}{||}}{C}-O-O-\overset{\overset{\displaystyle O}{||}}{C}-C_6H_5 \xrightarrow[\text{or } \Delta]{h\upsilon} 2C_6H_5-\overset{\overset{\displaystyle O}{||}}{C}-\dot{O}$$

Benzoyl peroxide; Benzoyl peroxide free radical



$$2C_6H_5\overset{\overset{\displaystyle O}{||}}{C}-\dot{O} \longrightarrow 2C_6H_5^{\bullet} + 2CO_2$$

Phenyl free radical

or

$$\underset{\text{Peroxide}}{R-O-O-R} \longrightarrow \underset{\text{Free radical}}{2R-O^{\bullet}}$$

$$\text{(ii)}\quad R-O^{\bullet} + \underset{\text{Ethene}}{CH_2=CH_2} \longrightarrow \underset{\text{Monomer free radical}}{R-O-CH_2-\dot{C}H_2}$$

Step 2 :

$$R-O-CH_2-\overset{\bullet}{C}H_2 + CH_2=CH_2 \longrightarrow R-O-CH_2-CH_2-CH_2-\overset{\bullet}{C}H_2$$

$$R-O-CH_2-CH_2-CH_2-\overset{\bullet}{C}H_2 + nCH_2=CH_2 \quad R-O-(CH_2-CH_2)_n-CH_2-\overset{\bullet}{C}H_2$$

Step 3 :

Chain termination can take place by four methods.

(i) **Coupling-** Two propagating chains containing free radicals combine to form neutral polymer molecule.

$$R-O\!-\!(CH_2-CH_2)\!\!-_{n_1}CH_2-\dot{C}H_2 + \dot{C}H_2-CH_2\!-\!(CH_2-CH_2)\!\!-_{n_2}-O-R$$
$$\downarrow$$
$$R-O\!-\!(CH_2-CH_2)_{n_1}-CH_2-CH_2-CH_2-CH_2\!-\!(CH_2-CH_2)\!\!-_{n_2}-O-R$$

(ii) **Disproportionation-** Neutral molecule is formed by the transfer of hydrogen.

$$R-O\!-\!(CH_2-CH_2)\!\!-_{n_1}CH_2-\dot{C}H_2 + \dot{C}H_2-CH_2\!-\!(CH_2-CH_2)\!\!-_{n_2}-O-R$$
$$\downarrow$$
$$R-O\!-\!(CH_2-CH_2)_{n_1}-CH=CH_2 + CH_3-CH_2\!-\!(CH_2-CH_2)\!\!-_{n_2}-O-R$$

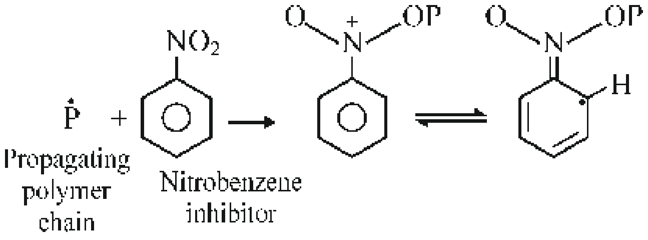
(iii) **Chain Transfer-** This takes place as follows :

$$R-O\!-\!(CH_2-CH_2)\!\!-_{n}CH_2-\dot{C}H_2 + RH$$
$$\downarrow$$
$$R-O\!-\!(CH_2-CH_2)\!\!-_{n}CH_2-CH_3 + \dot{R}$$

Here, RH is chain transfer agent. In polymerization process, monomer, initiator or solvent may be as chain transfer agents but as the polymerization process starts the concentration of monomer decreases and initiator is already taken in small proportions. Hence, when chain termination takes place by chain transfer, it should be done by solvent only.

(iv) **Inhibitors-** The propagating chains can be terminated by the use of inhibitors also. Inhibitors are chemical substances which are attached with active free radicals. Hydroquinone, Nitrobenzene, dinitrobenzene are generally used as inhibitors.

If P is propagating polymer chain and nitrobenzene is inhibitor, then chain termination can takes place as follows :



(ii) **Ionic addition Polymerization-** These Polymers can be prepared by polymerization of almost all the unsaturated monomer moleculs by free radical addition reaction but in some conditions polymerization is done by ions. For example, polymerizaiton of vinyl derivatives can be done by ionic mechanism.

Polymerization of monomers of vinyl derivatives containing electron donating group is done by electrophiles and polymerization of monomers of vinyl derivatives containing electron attracting group is done by nucleophilies. On the above basis, ionic addition polymerization can be of two types :

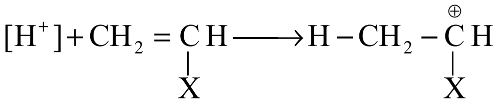
1. Cationic Polymerization
2. Anionic Polymerization

1. Cationic Polymerization-

These reactions are catalysed by protons or Lewis acids, hence these reactions are also known as acid catalysed polymerization. This process also takes place in three steps.

Step 1 : This is chain initiation step. Lewis acids ($AlCl_3$, BF_3 etc) react with co-catalyst to form proton (H^+). Then this proton reacts with monomer molecule to form carbocation and process of polymerization starts.

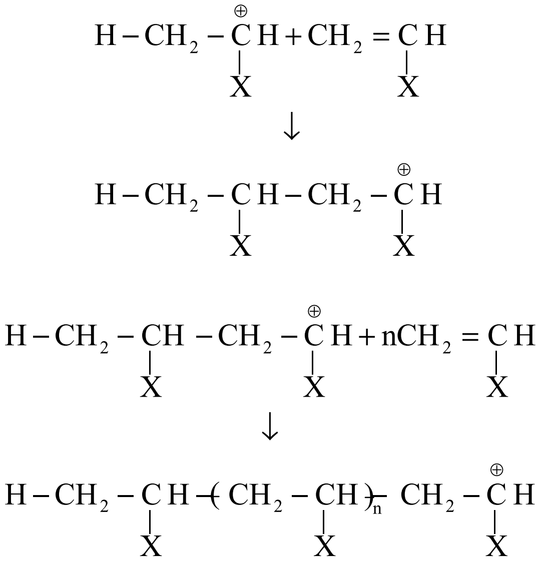
$$\underset{\text{Catalyst}}{AlCl_3} + \underset{\text{Co-catalyst}}{H_2O} \longrightarrow [AlCl_3OH]^- + [H]^+$$



$$[H^+] + CH_2 = \underset{\underset{X}{|}}{C}H \longrightarrow H-CH_2-\underset{\underset{X}{|}}{\overset{\oplus}{C}}H$$

X = electron donating group

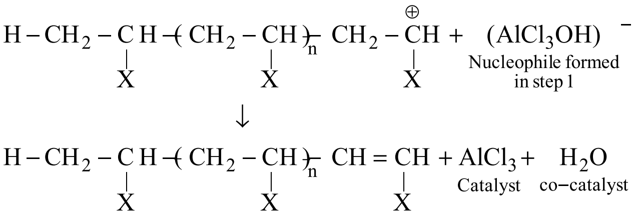
Step 2 : This is chain propagation step. In this step, carbocation formed in step-1 reacts with another monomer molecule to form a new carbocation and thus, this process goes on continuously.



$$H-CH_2-\underset{\underset{X}{|}}{\overset{\oplus}{C}}H + CH_2 = \underset{\underset{X}{|}}{C}H$$
$$\downarrow$$
$$H-CH_2-\underset{\underset{X}{|}}{C}H-CH_2-\underset{\underset{X}{|}}{\overset{\oplus}{C}}H$$

$$H-CH_2-\underset{\underset{X}{|}}{CH}-CH_2-\underset{\underset{X}{|}}{\overset{\oplus}{C}}H + nCH_2 = \underset{\underset{X}{|}}{C}H$$
$$\downarrow$$
$$H-CH_2-\underset{\underset{X}{|}}{C}H \left(CH_2-\underset{\underset{X}{|}}{CH} \right)_n CH_2-\underset{\underset{X}{|}}{\overset{\oplus}{C}}H$$

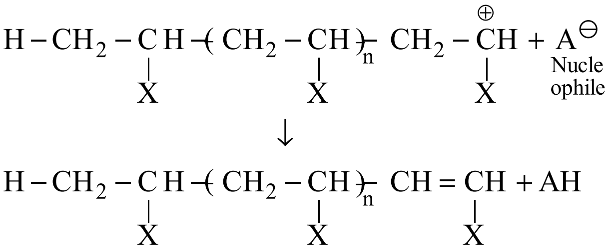
Step-3 : This is chain termination step. In cationic polymerization, chain termination is done either spontaneously or in the presence of any nucleophile.



$$H-CH_2-\underset{\underset{X}{|}}{C}H \left(CH_2-\underset{\underset{X}{|}}{CH} \right)_n CH_2-\underset{\underset{X}{|}}{\overset{\oplus}{C}H} + \underset{\text{Nucleophile formed in step 1}}{(AlCl_3OH)^-}$$
$$\downarrow$$
$$H-CH_2-\underset{\underset{X}{|}}{C}H \left(CH_2-\underset{\underset{X}{|}}{CH} \right)_n CH = \underset{\underset{X}{|}}{C}H + \underset{\text{Catalyst}}{AlCl_3} + \underset{\text{co-catalyst}}{H_2O}$$

Here, catalyst and co-catalyst are again formed

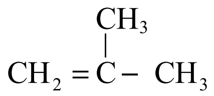
OR



$$H-CH_2-\underset{\underset{X}{|}}{C}H \left(CH_2-\underset{\underset{X}{|}}{CH} \right)_n CH_2-\underset{\underset{X}{|}}{\overset{\oplus}{C}H} + \underset{\text{Nucleophile}}{A^{\ominus}}$$
$$\downarrow$$
$$H-CH_2-\underset{\underset{X}{|}}{C}H \left(CH_2-\underset{\underset{X}{|}}{CH} \right)_n CH = \underset{\underset{X}{|}}{C}H + AH$$

Important : All vinyl monomers containing electron donating group can be polymerised by cationic polymerization.

For example : isobutylene

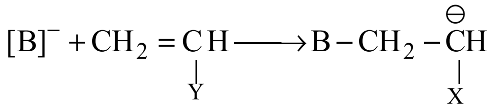


$$CH_2=\overset{\overset{CH_3}{|}}{C}-CH_3$$

2. Anionic Polymerization-

These reactions are catalysed by strong base like alkyl sodium, sodamide, alkyl and aryl derivatives of alkyl metals, sodium and lithium metals and different Grignard reagents. This takes place in three steps :

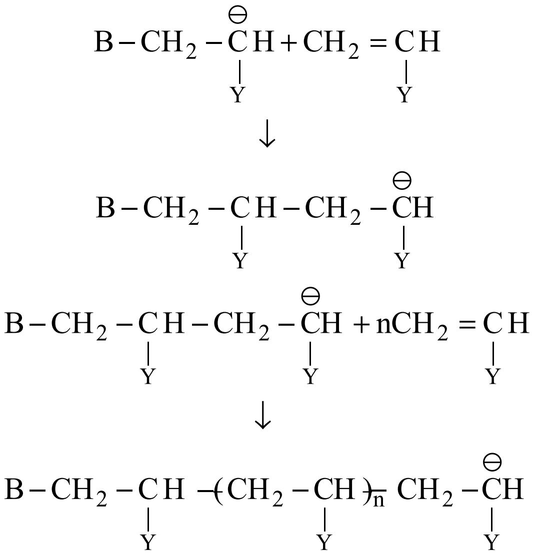
Step 1 : This is chain initiation step, in this step, base acts as nucleophile and reacts with monomer molecule to form carbanion and process of polymerization starts.



$$[B]^- + CH_2=\underset{\underset{Y}{|}}{CH} \longrightarrow B-CH_2-\underset{\underset{X}{|}}{\overset{\ominus}{CH}}$$

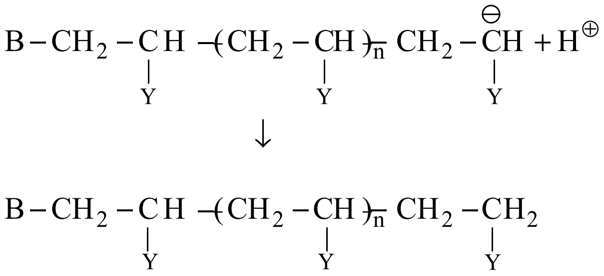
Y = electron attracting group

Step 2 : This is chain propagating step. In this step, carbanion formed in step 1 reacts with another monomer molecule to form a new carbanion and thus this process goes on continuously.



$$B-CH_2-\underset{\underset{Y}{|}}{\overset{\ominus}{CH}}+CH_2=\underset{\underset{Y}{|}}{CH}$$
$$\downarrow$$
$$B-CH_2-\underset{\underset{Y}{|}}{CH}-CH_2-\underset{\underset{Y}{|}}{\overset{\ominus}{CH}}$$
$$B-CH_2-\underset{\underset{Y}{|}}{CH}-CH_2-\underset{\underset{Y}{|}}{\overset{\ominus}{CH}}+nCH_2=\underset{\underset{Y}{|}}{CH}$$
$$\downarrow$$
$$B-CH_2-\underset{\underset{Y}{|}}{CH}-(CH_2-\underset{\underset{Y}{|}}{CH})_n-CH_2-\underset{\underset{Y}{|}}{\overset{\ominus}{CH}}$$

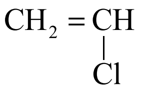
Step 3 : This is chain termination step. In anionic polymerization, chain termination is not spontaneous but chain termination occurs in presence of any electrophile.



$$B-CH_2-\underset{\underset{Y}{|}}{CH}-(CH_2-\underset{\underset{Y}{|}}{CH})_n-CH_2-\underset{\underset{Y}{|}}{\overset{\ominus}{CH}}+H^{\oplus}$$
$$\downarrow$$
$$B-CH_2-\underset{\underset{Y}{|}}{CH}-(CH_2-\underset{\underset{Y}{|}}{CH})_n-CH_2-\underset{\underset{Y}{|}}{CH_2}$$

Important : All vinyl monomers containing electron attracting group ($-CN$, $-COOR$, $-Cl$, $-C_6H_5$ etc.) are easily polymerized to form polymers by anionic polymerization.

For example - vinyl chloride



$$CH_2=\underset{\underset{Cl}{|}}{CH}$$

15.3.2 Condensation Polymerization

Monomers, containing two or more functional groups form polymers by condensation polymerization.

Bifunctional monomers form condensation polymers by repeating condensation reactions. In this polycondensation reactions, elimination of small molecules like water (H_2O), alcohol (ROH), ammonia (NH_3), etc. take place.

These reactions are completed in one by one step, so this polymerization is also called as **step growth polymerization.** In each step, one small molecule is released and product is also a bifunctional species.

For example :

(1) Formation of polyesters by dialcohols and diacids.

$$nHOOC-R-COOH+nOH-R_1OH$$
$$\downarrow$$
$$H-[OOC-R-\boxed{COO}-R_1]_n OH+(2n-1)H_2O$$

(2) Formation of polyomides (Nylon) by diamines and diacids.

$$nH_2N-R-NH_2+nHOOC-R_1-COOH$$
$$\downarrow$$
$$H-[NH-R-NHCO-R_1-CO]_n OH+(n-1)H_2O$$

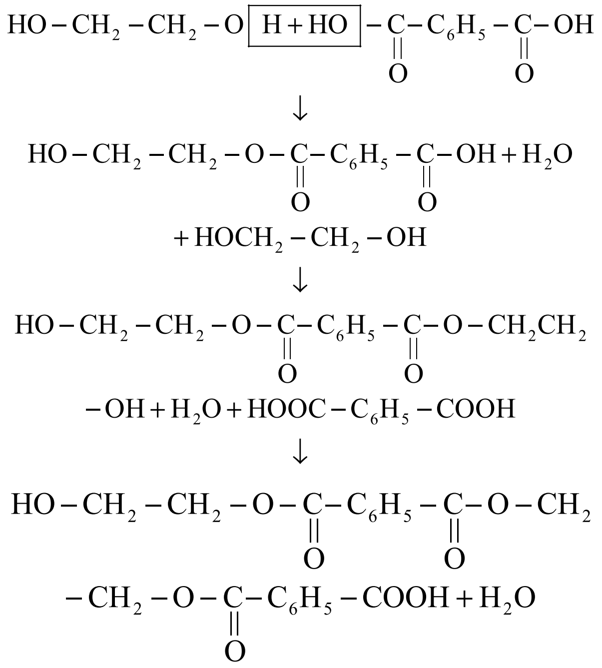
(3) Formation of polyethers by dialcohols

$$nHO-R-OH \rightarrow HO\text{+}[RO]_n H + (n-1)H_2O$$

(4) Formation of polyamides by amino acids.

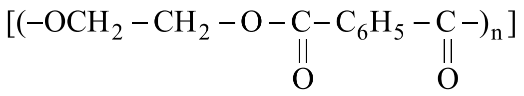
$$nH_2N-R-COOH \rightarrow$$
$$H\text{+}[HN-R-CONH-R-CO]_n OH + (n-1)H_2O$$

(5) Dacron is a polyester, which is formed by the condensation polymerization of ethylene glycol and terephthalic acid. Mechanism of formation of Dacron is as follow -



$$HO-CH_2-CH_2-O\boxed{H+HO}-\underset{\substack{\| \\ O}}{C}-C_6H_5-\underset{\substack{\| \\ O}}{C}-OH$$
$$\downarrow$$
$$HO-CH_2-CH_2-O-\underset{\substack{\| \\ O}}{C}-C_6H_5-\underset{\substack{\| \\ O}}{C}-OH+H_2O$$
$$+HOCH_2-CH_2-OH$$
$$\downarrow$$
$$HO-CH_2-CH_2-O-\underset{\substack{\| \\ O}}{C}-C_6H_5-\underset{\substack{\| \\ O}}{C}-O-CH_2CH_2$$
$$-OH+H_2O+HOOC-C_6H_5-COOH$$
$$\downarrow$$
$$HO-CH_2-CH_2-O-\underset{\substack{\| \\ O}}{C}-C_6H_5-\underset{\substack{\| \\ O}}{C}-O-CH_2$$
$$-CH_2-O-\underset{\substack{\| \\ O}}{C}-C_6H_5-COOH+H_2O$$

In this way, this reaction is completed in many steps and product of each step is a bifunctional species.



$$[(-OCH_2-CH_2-O-\underset{\substack{\| \\ O}}{C}-C_6H_5-\underset{\substack{\| \\ O}}{C}-)_n]$$

Dacron (Terylene) is a polyester

15.4 Copolymerization or Heteropolymerization

Two or more than two monomer molecules or units combine with each other to form polymer, which is called copolymer and this process of polymerization is known as copolymerization or heteropolymerization. It can be completed through both types of processes, addition or condensation. It is generally represented as-

$$nA + nB \rightarrow \text{+}[A-A-B-B-B-A-B]_n$$

For example -

1. Styrene - butadiene rubber is formed by addition-copolymerization.
2. Nylon-6,6 is formed by condensation polymerization because it contains two types of monomers, adipic acid and hexamethylene diamine, thus polymers formed by this condensation polymerization are called copolymers.

$$\underset{\text{adipic acid}}{nHOOC-(CH_2)_4-COOH} + \underset{\text{hexamethylene diamine}}{nH_2N-(CH_2)_6-NH_2}$$

$$\underset{\text{Nylon-6,6}}{HO\text{+}[CO-(CH_2)_4-CONH-(CH_2)_6-NH]_n H}$$

15.4.1 Types of copolymers

In copolymers, different monomer units are joined in different ways. On the basis of arrangement of monomer units, copolymers are of four types-

1. **Random copolymer :** In these polymers, there is no regular arrangement of monomer units. These can be represented as :

$$-A-B-A-A-A-B-B-B-A-A-B-$$

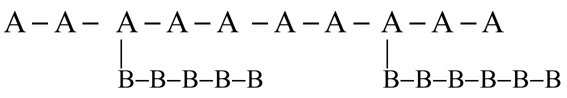
2. **Alternating Copolymer :** In these polymers, monomer units are joined in alternating manner. These can be represented as :

$$-A-B-A-B-A-B-A-B-A-B-$$

3. **Block Copolymer :** In these polymers, first, one type of monomer units joined to form a one block, then another monomer units joined to form second block and this process continue. This can be represented as :

$$A-A-A-A-A-B-B-B-B-B-B$$
$$-A-A-A-A-A$$

4. **Graft Copolymer :** In this polymer, one monomer unit combine to form a chain then another monomer unit adds as branches. It can be represented as-



$$A-A-\underset{\substack{| \\ B-B-B-B-B}}{A}-A-A-A-A-\underset{\substack{| \\ B-B-B-B-B-B}}{A}-A-A$$

15.4.2 Applications of Copolymerization

Copolymers can be used commercially by modifying their properties.

1. Nylon-6,6 is formed by condensation polymerization of hexamethylene diamine and adipic acid but it has low melting point, a hard crystalline material but if terephthalic acid is added to it and copolymerization of all three monomers is carried out, then its crystalline property and melting point both will increase.
2. The copolymer formed by adding 20-30% acrylonitrile to styrene is resistant to impact and hydrocarbons.
3. Copolymer of styrene and butadiene is a synthetic rubber.
4. Homopolymers are formed by polymerization of same monomer units and copolymer shows properties of two homopolymers. Thus copolymerization is a useful method for increasing commerical applications of polymers. In this, properties of more than one homopolymers can be mixed.

5.5 Molecular Mass of Polymers

The properties of polymers are strongly related to their molecular weight, shape and structure. The number of monomer units/molecules present in a polymer molecule is called degree of polymerization and this number of monomer molecules determine the size of polymer molecule.

The molecular mass of organic compound (it can also be a monomer) is fixed whether it is formed by any method.

For example : Molecular weight of ethylene molecule is 28 but when it is polymerized it can be represented as -

$$-\!\!\left[CH_2 - CH_2 \right]\!\!-_n$$

Here, value of n is different for different polymer molecules, therefore, molecular weight of all the polymer molecules present in polymer sample will be different. The reason for this is that degree of polymerization of different polymer (macro) molecule is different i.e. their chain length is different. Thus the molecular weight of polymer (macro) molecules in polymer is different or not fixed. So it is expressed as average molecular mass in two forms-

1. Number average molecular weight $(\overline{M}_n)$
2. Weight average molecular wieght $(\overline{M}_w)$

1. Number average molecular weight

It is represented as $\overline{M}_n$. The sum of molecular weight of all the polymer molecules present in a polymer sample, is divided by total number of polymer molecules, the obtained result gives number average molecular weight of polymer.

If in any polymer sample, total number of molecules are n and molecular weight of n_1 is m_1, molecular weight of n_2 is m_2 and similarly molecular weight of n_i is m_i then

Total molecular mass of all molecules = $n_1m_1 + n_2m_2 + ... + n_im_i$

and total number of molecules = $n_1 + n_2 + ... + n_i$

$$\text{Therefore, } \overline{M}_n = \frac{n_1m_1 + n_2m_2 + ... + n_im_i}{n_1 + n_2 + ... + n_i}$$

$$\text{or} \quad \overline{M}_n = \frac{\sum n_im_i}{\sum n_i}$$

$$\text{Number average molecular weight } (\overline{M}_n) = \frac{\sum n_im_i}{\sum n_i}$$

Number average molecular weight $(\overline{M}_n)$ is determined by osmotic pressure method or other colligative properties related methods.

2. **Weight average Molecular weight :** It is represented as $\overline{M}_w$. In a polymer sample, total number of molecules of different weight are multiplied by their molecular weight and the product obtained is divided by total molecular weight of molecules. This gives the weight average molecular weight $(\overline{M}_w)$. If in any polymer sample, total number of molecules are n and

molecular weight of n_1 is m_1, molecular weight of n_2 is m_2 and similarly molecular weight of n_i is m_i, then

Total mass of n_1 molecules = n_1m_1

Total mass of n_2 molecules = n_2m_2

Similarly, total mass of n_i molecules = n_im_i and the value of multiplication with their molecular mass will be as follows :

$$(n_1 \times m_1 \times m_1),\ (n_2 \times m_2 \times m_2) \text{ and } (n_i m_i \times m_i)$$

or $$(n_1\, m_1^2),\ (n_2\, m_2^2) \text{ and } (n_i\, m_i^2)$$

sum of above multiplication = $n_1\, m_1^2 +\ n_2\, m_2^2 + ... + n_i\, m_i^2$

or $\sum n_i m_i^2$

Total mass of all molecules = $n_1m_1 +\ n_2m_2 ... + n_i\, m_i$

or $\sum n_i m_i$

Therefore weight average molecular weight

$$(\overline{M}_w) = \frac{\sum n_i m_i^2}{\sum n_i m_i}$$

Weight average molecular weight ($\overline{M}_w$) can be determined by light scattering method, ultracentrifugation method, etc.

15.5.1 Polydispersity Index

In a simple organic compound the molecular weight of all the molecules is same so they are monodisperse but in polymers, molecular weight of all molecules is different, therefore, polymers are polydisperse. Some naturally occurring polymers like proteins are monodisperse.

Polydispersity Index (PDI) is the ratio of weight average molecular weight ($\overline{M}_w$)and number average molecular weight ($\overline{M}_n$) of any polymer.

$$\text{PDI} = \frac{\overline{M}_w}{\overline{M}_n}$$

For natural polymer, like protein, PDI value is usually equal to unity and for synthetic polymers, which are polydisperse, the value of PDI is more than 1 because here value of $\overline{M}_w$ is always higher than $\overline{M}_n$.

15.5.2 Numerical

In a polymer sample, the molecular weight of 20 molecules is 20,000, molecular weight of 40 molecules is 30,000 and molecular weight of another 20 molecules is 40,000 then calculate $\overline{M}_n$ and $\overline{M}_w$ of polymer.

For number average molecular weight we know that,

$$\overline{M}_n = \frac{\sum n_i m_i}{\sum n_i}$$

$$= \frac{(20\times20{,}000) + (40\times30{,}000) + (20\times40{,}000)}{(20+40+20)}$$

$$= \frac{400000 + 1200000 + 800000}{80}$$

$$= \frac{24{,}00{,}000}{80}$$

$$(\overline{M}_n) = 30{,}000$$

(2) For weight average molecular weight, we have,

$$\overline{M}_w = \frac{\sum n_i m_i^2}{\sum n_i m_i}$$

$$= \frac{20\times(20{,}000)^2 + 40\times(30{,}000)^2 + 20\times(40{,}000)^2}{(20\times20{,}000) + (40\times30{,}000) + (20\times40{,}000)}$$

$$= \frac{(20\times40{,}00{,}000) + (40\times90{,}00{,}00{,}000) + (20\times1{,}60{,}00{,}00{,}000)}{4{,}00{,}000 + 12{,}00{,}000 + 8{,}00{,}000}$$

$$= \frac{76\times10^9}{24\times10^5} = \frac{76}{24}\times10^4$$

$$= \frac{7{,}60{,}000}{24} = 31667$$

15.6 Rubber

It is of both types, natural and synthetic.

15.6.1 Natural Rubber

Rubber is a natural polymer and it possesses elastic properties so it is also termed as elastomer. It is very soft. It is manufactured from milk like material known as latex, which is obtained form Rubber trees like Hevea brasiliensis, Gutta percha. Latex is a colloidal dispersion of rubber in water. Rubber trees are mostly found in India, Srilanka, Indonesia, Malaysia and South america.

(1) Method to obtain natural rubber :

To obtain natural rubber, first of all latex is collected from the special cut in the bank of rubber tree. Then this latex is diluted with water to a solid content of up to 10-12%. Then acetic acid is mixed due to which rubber coagulates and precipitates out. It is separated by filtration, this rubber is known as crepe rubber but it is not very useful due to following reasons:

(i) It has low elasticity.

(ii) It is very soft at high temperature (<335K) and brittle at low temperature (<283K).

(iii) Its water absorption capacity is very high.

(iv) It is soluble in non-polar solvents (ether, benzene, petrol)

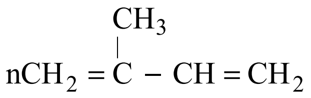
(v) It is not resistant to oxidising agents.

To improve the physical properties of rubber, Vulcanization is done.

Uses : Natural rubber is mainly used for shoes, rain coat, golf ball, etc.

(2) Composition and structure :

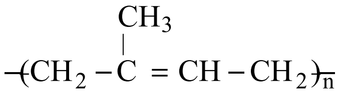
Natural rubber is a linear polymer of isoprene (2-methyl-1, 3-butadiene). Its composition is $(C_5H_8)n$



$$nCH_2 = \overset{\overset{\large CH_3}{|}}{C} - CH = CH_2$$

Isoprene
(2-methyl-1, 3-butadiene)

$\downarrow$ polymerization

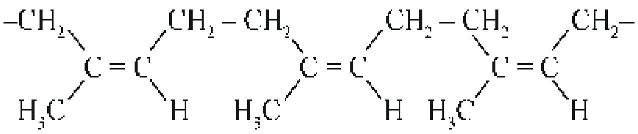


$$-\!\!\left(CH_2 - \overset{\overset{\large CH_3}{|}}{C} = CH - CH_2\right)\!\!-_n$$

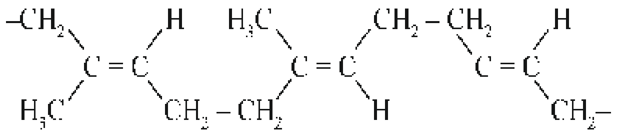
polyisopre ne
(natural rubber)

Two isomers, **cis** and **trans** are obtained by combination of 1,4-isoprene. Natural rubber is **cis**-isomer, in which monomer units are joined by weak van der waal's force and form spring like structure. Due to this structure, rubber shows the property of elasticity, i.e. they can be stretched like spring.

The arrangement of isoprene units in natural rubber obtained from rubber tree, Gutta Percha, is **trans.**



Cis-polyisoprene (natural rubber)

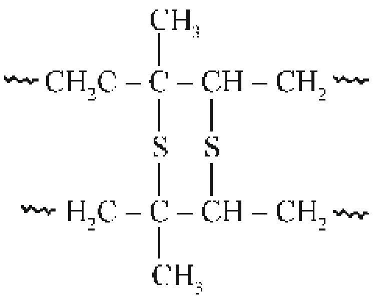


Trans-polyisoprene (Gutta Percha)

(3) Vulcanization of Rubber :

Vulcanization is done to improve the physical properties of rubber. In the year 1839, Charles Goodyear Vulcanized rubber by sulphur in USA. At the same time, Thomas Hancock also Vulcanized rubber in London and obtained patent in 1843.

On vulcanization, sulphur forms cross links at the reactive sites of double bonds, thus the rubber gets stiffened.



and

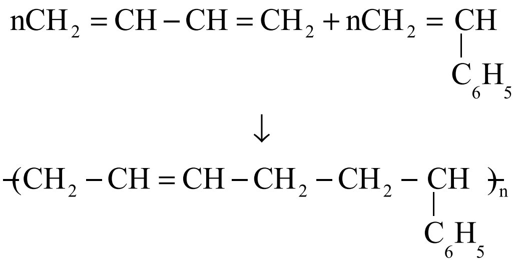
15.6.2 Synthetic Rubber

Synthetic rubbers are man made rubber and possesses similar physical properties as that of natural rubber. They also contain carbon-carbon double bonds therefore, synthetic rubbers are also vulcanized. Most of the synthetic rubbers are synthesized by derivatives of 1,3-butadiene.

Some examples are as follows :

(i) SBR or Buna-S :

Styrene-butadiene Rubber or Buna-S (SBR)



$$nCH_2=CH-CH=CH_2+nCH_2=\underset{\underset{C_6H_5}{|}}{CH}$$

$$\downarrow$$

$$-\!\!\left(CH_2-CH=CH-CH_2-CH_2-\underset{\underset{C_6H_5}{|}}{CH}\right)_n$$

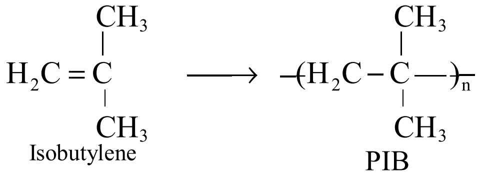
SBR or Buna-S

It is obtained by copolymerization of styrene and 1,3-butadiene monomers.

Uses : Mostly styrene butadiene rubber is used in automobile industries for making tyres. Other than this it is also used in making shoes.

(ii) Polyisobutylene or PIB :

It is obtained by polymerization of isobutylene monomer.



$$\underset{\text{Isobutylene}}{H_2C=\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}} \longrightarrow \underset{\text{PIB}}{-\!\!\left(H_2C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\right)_n}$$

Uses : It is the only polymer which can hold air for long time i.e. impermeable to gas, so it is used in making inner liners of tyres and basketball. Apart from this, it is also used as adhesive.

Important : Balloons made of simple rubber (polyisoprene) contracts after some time because they are permeable to air.

(iii) Polybutadiene :

It is obtained by addition polymerization of butadiene monomer.

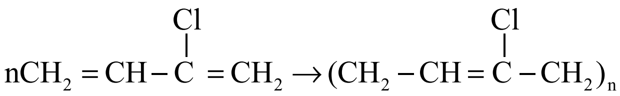
$$\underset{\text{Butadiene}}{nCH_2=CH-CH=CH_2} \rightarrow$$

$$\underset{\text{Polybutadiene}}{-\!\!\left(CH_2-CH=CH-CH_2\right)_n}$$

Uses : It is a first synthetic rubber and shows similarity with natural rubber. Wherever rubber is required to use at low temperature, polybutadiene is used there. Other than this it is also used for making Gascoat and some parts of vehicles.

(iv) Polychloroprene or Neoprene :

This synthetic rubber is formed by addition polymerization of chloroprene monomer units.

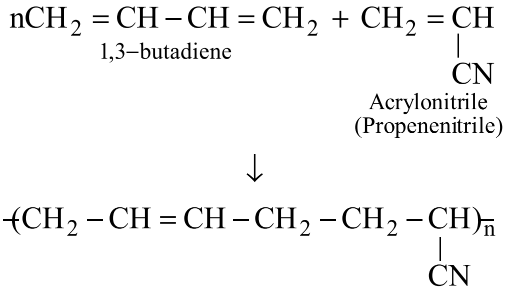


$$nCH_2=CH-\overset{\overset{Cl}{|}}{C}=CH_2 \rightarrow (CH_2-CH=\overset{\overset{Cl}{|}}{C}-CH_2)_n$$

Uses : It is a hard rubber and has superior resistance to oil. It is used for manufacturing Gaskets, Conveyor belts, hoses, etc.

(v) Nitrile Rubber (NBR) or Buna-N :

This synthetic rubber is formed by copolymerization of butadiene and acrylonitrile (Propenenitrile)



$$\underset{\text{1,3-butadiene}}{nCH_2=CH-CH=CH_2} + \underset{\substack{\text{Acrylonitrile}\\\text{(Propenenitrile)}}}{CH_2=\underset{\underset{CN}{|}}{CH}}$$

$$\downarrow$$

$$-\!\!\left(CH_2-CH=CH-CH_2-CH_2-\underset{\underset{CN}{|}}{CH}\right)_n$$

Buna-N (NBR)

Uses : This rubber has superior resistant to ozone weathering and oil. Its abrasion is also less. It is also flame resistant. Therefore it is used in tanks used for storage of fuel, oil seals, gaskets and sometimes in cables.

(vi) Acrylonitrile–Butadiene–Styrene Rubber (ABS rubber)

It is formed by copolymerization of acrylonitrile (30%), 1,3-butadiene (20%) and styrene (50%).

15.7 Some Commercially Important Polymers

(1) Polyethylene (PE)

Monomer-Ethene ($CH_2 = CH_2$)

Method of Polymerization : This polymer was first prepared in England in 1933. It is a homopolymer of ethene. Polyethene is formed by the addition polymerization of ethene. It is mainly of two types-

$$CH_2 = CH_2 \xrightarrow[\text{Peroxide}]{R-O-O-R} \underset{\text{Polythene (LDPE)}}{\left(CH_2 - CH_2 \right)_n}$$

(i) low density polyethylene (LDPE)

(ii) high density polyethylene (HDPE)

LDPE is formed by free radical addition polymerization and HDPE is formed by using Ziegler-Natta catalyst.

Uses :

(i) Low density polyethylene is mostly used in packing, LDPE is chemically inert hence it is used for making attractive containers and bottles. Pipes made by it are used in agriculture.

(ii) Hight density polyethylene is used for making toys and other household articles.

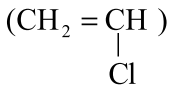
Properties :

(i) Melting point of LDPE is 110°-125°C. At room temperature it is not soluble in any solvent but at high temperature it is soluble in carbon tetra chloride (CCl_4), Toluene, Xylene, etc.

(ii) Melting point of HDPE is 144°-150°C. It is more crystalline than LDPE. Its tensile strength, rigidity and resistance to solvent is higher than LDPE.

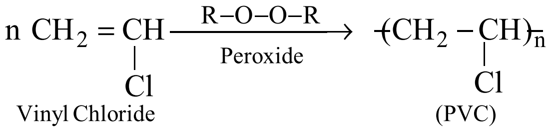
(2) Polyvinyl Chloride (PVC) :

Monomer – Vinyl Chloride



$$(CH_2 = \underset{\displaystyle Cl}{\underset{|}{CH}})$$

Method of polymerization : Polyvinyl chloridcor PVC is formed by addition polymerization of vinyl chloride. It is a homopolymer of vinyl chloride. This polymerization is completed in the presence of peroxide.



$$n\ \underset{\text{Vinyl Chloride}}{CH_2 = \underset{\displaystyle Cl}{\underset{|}{CH}}} \xrightarrow[\text{Peroxide}]{R-O-O-R} \underset{\text{(PVC)}}{\left(CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} \right)_n}$$

Properties :

1. PVC is a bright, rigid and hard polymer.
2. It is insoluble in vinylchloride, alcohols, water and organic solvents. Upto 20°C temperature, there is no effect of acids and bases on it.
3. But it is soluble in solvent made by mixing ketone and carbon disulphide (CS_2).

Uses :

1. PVC is a cheap and mostly used plastic (polymer). Mainly it is used for making pipes, doors, cables, rods, sheets, etc.
2. When PVC is dissolved in suitable solvent like chlorobenzene, chlorination occurs. It is known as chlorinated PVC. Chlorinated PVC is used in making adhesives, laminates and fibers.
3. It is mixed in ester as plastisizer to make ester soft and it is used as vinyl leather. This vinyl leather is used in manufacturing raincoat, floor polishing, handbags, curtain cloths, etc.
4. Above 200°C, PVC degrades and release HCl. To prevent this, suitable stabilizers are used.

(3) Polyester :

Monomers :

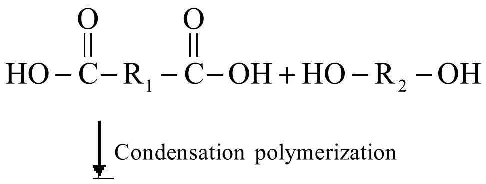
(i) Dicarboxylic acids and diols

(ii) Diesters and diols

(iii) Dihydroxy acids (HO-R-COOH)

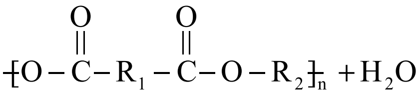
Method of polymerization : Polyesters are formed by condensation polymerization

(i) Condensation polymerization of dicarboxylic acids and diols



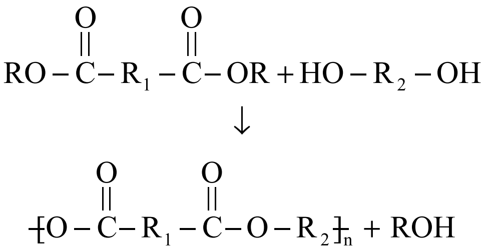
$$HO - \overset{\displaystyle O}{\overset{||}{C}} - R_1 - \overset{\displaystyle O}{\overset{||}{C}} - OH + HO - R_2 - OH$$

$$\Big\downarrow \text{Condensation polymerization}$$



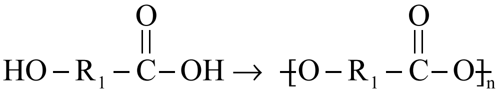
$$\left[O-\overset{\overset{O}{\|}}{C}-R_1-\overset{\overset{O}{\|}}{C}-O-R_2\right]_n+H_2O$$

(ii) Condensation polymerization of diesters and diols.



$$RO-\overset{\overset{O}{\|}}{C}-R_1-\overset{\overset{O}{\|}}{C}-OR+HO-R_2-OH \downarrow \left[O-\overset{\overset{O}{\|}}{C}-R_1-\overset{\overset{O}{\|}}{C}-O-R_2\right]_n+ROH$$

(iii) Self-condensation of dihydroxy acids.



$$HO-R_1-\overset{\overset{O}{\|}}{C}-OH \rightarrow \left[O-R_1-\overset{\overset{O}{\|}}{C}-O\right]_n$$

Uses : The well known example of polyester is terylene (Dacron). It is mainly used in making fibres and also used in making helmets. If polyesters are made up of aliphatic monomers then it is known as aliphatic polyesters and their melting point is very low (50-80°C) but presene of aromatic group increases the melting point. For example, Terylene.

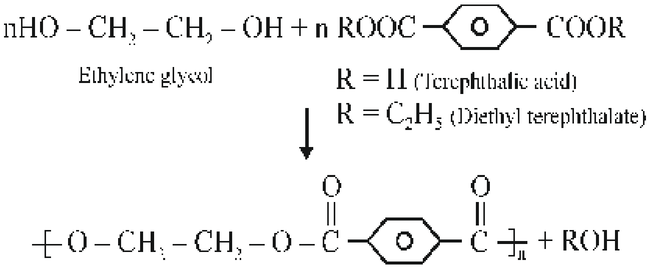
Commercial uses of aliphatic polyesters are very less as compared to aromatic polyesters.

(4) Terylene or polyethylene terephthalate (PET)

It is a saturated polyester. It is also known as Dacron.

Monomer : Terephthalic acid or its esters and ethylene glycol

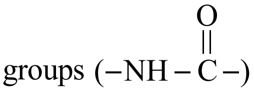
Method of Polymerization : Polyethylene terephthalate polymer is formed by condensation polymerization of terephthalic acid or its ester and ethylene glycol. Its commercial name is Terelene or Dacron.



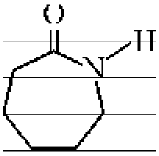
Uses : These polymers are mainly used in textile industries because these are strong fibres. These are also used for making belts, ropes, boat sail, etc.

(5) Nylon-6 :

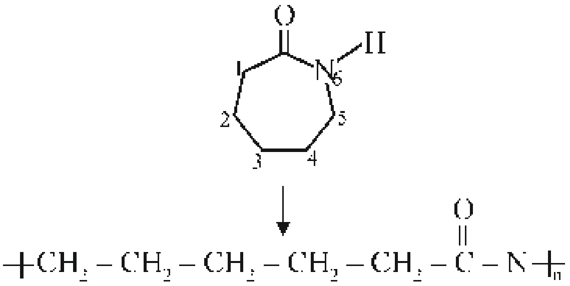
It is a polyamide. Its polymer chain contains amide groups $(-NH-\overset{\overset{O}{\|}}{C}-)$



Monomer : ε- Caprolactam



Method of polymerization : ε-caprolactam is a monomer with ring structure. Nylon-6 is formed by anionic addition polymerization of ε-caprolactam. The monomer contains six carbon atoms therefore, it is known as Nylon-6



$$\left[CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-N\right]_n$$

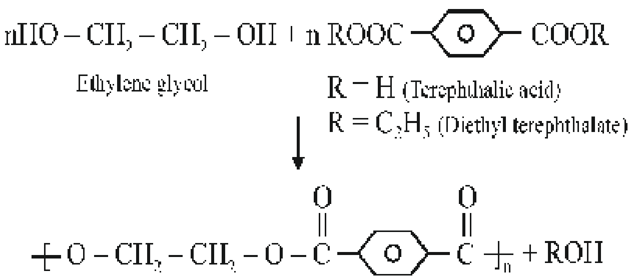
Uses : Nylon 6 is a synthetic fibres having high tensile strength. It is generally white in colour and resistant to acids and bases. Mainly, it is used in glass of vehicles. Apart from this, it is also used in toothbrushes, musical instruments such as guitar, sitar, violin, etc. It is also used in making threads, ropes, filaments, nets, etc.

(6) Nylon-6,6 :

It is also a polyamide.

Monomer : Hexamethylene diamine and adipic acid

Method of polymerization : Nylon-6,6 is prepared by the condensation polymerization of hexamethylenediamine and adipic acid.



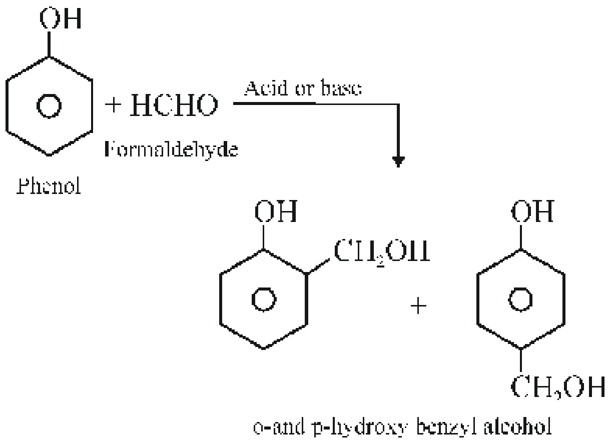
Here, diamine and dicarboxylic acid both have six carbon atom therefore it is called Nylon 6,6. First six indicates carbon atoms of diamine and second six, indicates carbon atoms of dicarboxylic acid.

Uses : It is a polymer of high tensile strength and abrasion resistance. It is used both as plastic and fibre. Nylon 6,6 is mostly used in making tyre cord. Apart from this, it is also used in making cloths, parashot, ropes, etc.

7. Bakelite :

It is a thermosetting resin made by condensation of phenol and formaldehyde.

Monomer : Phenol and formaldehyde react in presence of acid or base to form intermediate ortho and p- hydroxy benzyl alcohol which further reacts as monomer to form the polymer Bakelite.

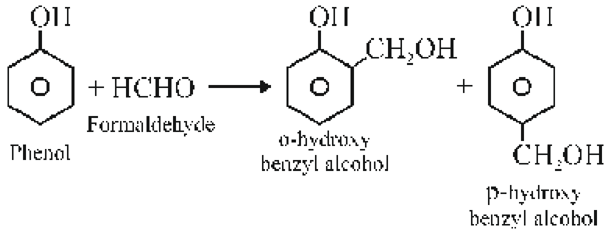


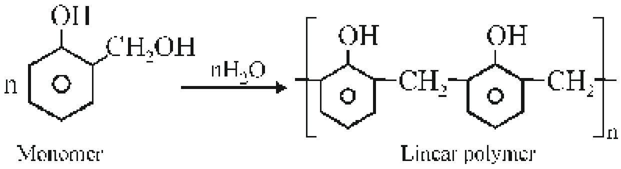
Method of Polymerization : Condensation reaction of phenol and formaldehyde is possible by two ways.

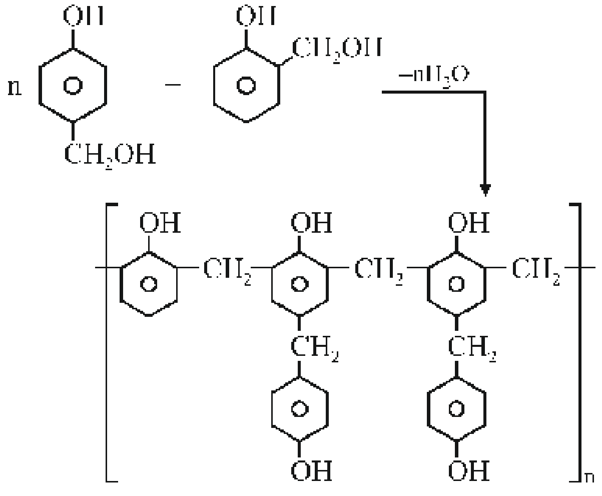
(i) Reaction in presence of dilute acid form linear polymer. It is thermoplastic material. It is known as Novolac. The ratio of phenol and formaldehyde is less than one during the formation of novolac.

Novolac contains many free –CH$_2$OH groups. Taking ratio of formaldehyde more than one, and when heated at appropriate temperature and pressure, then cross links are introduced and form three dimensional network, which is known as 'Bakelite'. This means that the product obtained by heating phenol and formaldehyde at high temperature and pressure is 'Bakelite'.

(ii) When the ratio of phenol and formaldehye is taken more than one and reaction is carried out in presence of base, thermosetting product is obtained. It is known as Resol.







Cross linked polymer (Bakelite)

Uses : Bakelite is a thermosetting resin made by phenol and formaldehyde. It is resistant to temperature and heat. Therefore it is used in making switches, handle of utensiles, electric resistance articles, cashes of radio, television and computer, etc. Apart from this, Bakelite is also used in kitchen cookware, toys, etc.

8. Teflon (polytetrafluoroethylene, PTFE) :

Monomer : Tetrafluoroethylene($CF_2 = CF_2$)

Method of Polymerization : Teflon is a homopolymer of tetrafluoroethylene.

$$n\,CF_2 = CF_2 \longrightarrow (CF_2 \quad CF_2)_n$$

Uses : It is linear and highly crystalline polymer. It is not soluble in strong acids (nitric acid) and highly thermally stable. Apart form this, it does not react with corrosive alkali and organic solvents. Therefore it is used in electric resistance, non-stick cookware and lubricants.

15.8 Biodegradable and non-biodegradable Polymers

Definitions :

(i) Biopolymers : These are natural polymers present in animals and plants. These polymers are useful for growth and development. Example- Protein, Polysaccharides. Nucleic acids, lipids, etc.

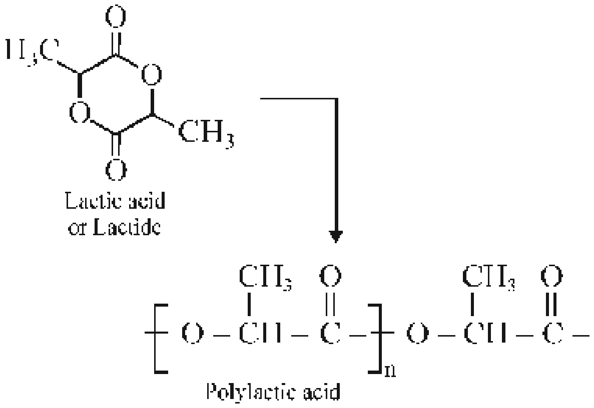
(ii) Biodegradable Polymers : These can be natural or synthetic, both. These are degraded to small molecules by bacteria. Example- Poly 3-hydroxy-butyrate -CO-β-3-hydroxyvalerate (PHBV), Nylon-2-Nylon-6, etc.

(iii) Non-biodegradable polymers : These are synthetic polymers and cannot be biodegraded. Example-Polyethylene, Bakelite, Teflon, PVC, Terelene, etc.

Non-biodegradable polymers are very useful in daily life but as these are non-biodengradable therefore management of polymer waste is a very serious problem. Therefore, such polymers are synthesized which can be degraded by bacteria. Some important bio-degradable polymers are -

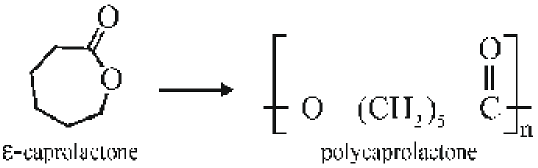
(i) Polylactic acid (PLA) : It is a thermoplastic alphatic polyester. It is formed by polymerization of lactic acid (lactide).

Uses : It is mainly used in medical field for making stitches, dialysis, etc. It is also used in preparation of bioplastic.



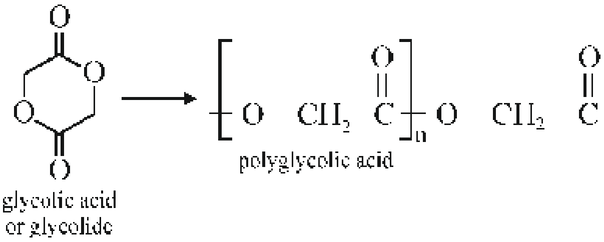
(ii) Polycaprolactone (PCL) : It is a polyester of low melting point. It is formed by polymerization of ε-caprolactam.

Uses : It is mainly used in making controlled drug release capsules. These capsules when enter in human body then ester chain of PCL is degraded and drugs is released slowly in the body.

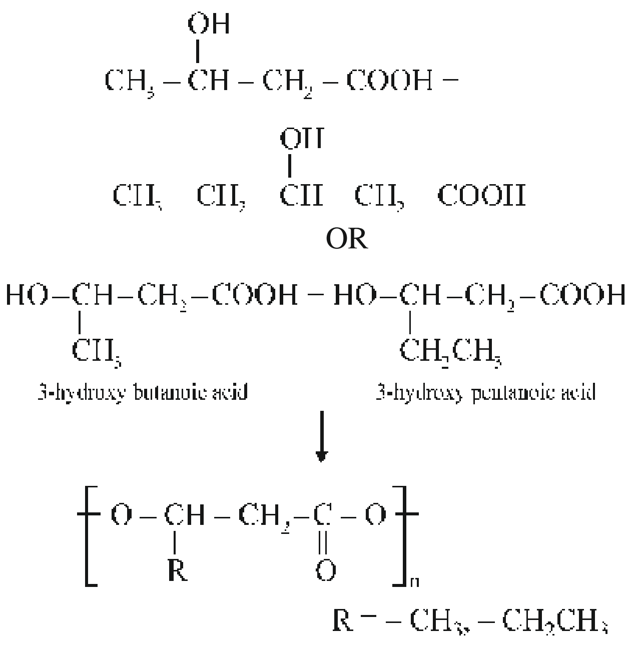


(iii) Polyglycolic acid (PGA) : It is a linear aliphatic polyester which is formed by polymerization of glycolic acid (glycolide)

Uses : PGA is very strong fibres and is soluble in water. Mainly these are used in stitching. These stiches dissolve automatically



(iv) Poly Hydroxy butyrate-CO- β-hyroxyval-erate (PHBV) : It is biodegradable polyester. It is a copolymer of 3-hydroxy butanoic acid and 3-hydroxy pentanoic acid.



(v) **Nylon-2-Nylon-6 :** It is an alternating copolymer of glycine and aminocaproic acid. It is a polyamide and biodegradable.

Important Points

- Polymers are macromolecules made up of small molecules.
- Monomers are those structural units from which polymers are made.
- The process of formation of polymers from monomer is known as polymerisation.
- Homopolymers are those polymers which have same monomer units.
- Copolymers are those polymers in which monomer units are different.
- Addition polymerisation is also known as chain growth polymerisation. In this, monomer units are unsaturated.
- Addition polymerisation takes place by free radicals, carbocations and carbanions.
- Condensation polymerisation is also known as step growth polymerisation. In this, monomer units contain functional groups.
- Molecular mass i.e. molecular weight of polymers is not fixed. Therefore, their molecular mass is taken as average molecular mass.
- Average molecular weight can be represented as number average molecular weight $(\overline{M}_n)$ and mass average molecular weight $(\overline{M}_w)$.
- Rubber can be natural or synthetic.
- Natural rubber is obtained by latex of rubber trees. The monomer units of natural rubber is isoprene.
- SBR, PIB, Polybutadiene, Neoprene, etc, are synthetic rubber.
- HDPE is prepared by Ziegler Natta Catalyst and LDPE is prepared by free radical mechanism.
- PVC is cheap and very useful polymer.
- Bakelite is a thermosetting polymer.
- PHBV, Nylon-2-Nylon-6, etc, are synthetic biodegradable polymers, which can be degraded naturally by bacteria.

EXERCISE QUESTIONS

Multiple Choice Questions

Which of the following is not true about Polymers?
(a) Polymers have low molecular weight
(b) Polymers have no charge.
(c) Polymers have high viscosity
(d) Polymers scatter light.

2. On the basis of method of Polymerisation, polymers are classified as :
(a) Only addition polymers
(b) Only condensation polymers
(c) Both addition and condensation Polymers.
(d) Copolymers

3. Teflon, styrene and neoprene are :
(a) Copolymer
(b) Homopolymer
(c) Monomer
(d) Condensation Polymer

4. Which of the following is condensation polymer?
(a) Dacron (b) Teflon
(c) PVC (d) Polythene

5. Monomer of Natural rubber is -
(a) Ethene (b) Styrene
(c) Isoprene (d) Butadiene

6. Which of the following has ester bond?
(a) Nylon (b) Bakelite
(c) Terelene (d) Rubber

7. Terelene is condensation polymer of ethylene glycol and ?
(a) Terephthalic acid (b) Phthalic acid
(c) Benzoic acid (d) Acetic acid

8. The monomer of Nylon-6 is :
(a) Adipic acid (b) Caprolactam
(c) 1, 3-butadiene (d) Chloroprene

9. Teflon is a polymer of :
(a) Tetrafluoroethylene
(b) Tetraiodoethylene
(c) Tetrachloroethylene
(d) Tetrabromoethylene

10. Which of the following is a bio-degradable polymer?
(a) PVC (b) Cellulose
(c) Polythene (d) Nylon-6

Very Short Answer Questions

11. Define Polymers.

12. Give one example each of natural and synthetic polymers.

13. Give one difference between homopolymer and Copolymer.

14. How many methods of chain termination are there in free radical mechanism?

15. Which monomers are polymerised by cationic polymerisation?

16. Write formula for number average molecular weight $(\overline{M}_n)$.

17. Give the name of substance used in vulcanisation of rubber.

18. Write the name of monomer of neoprene.

19. Write the chemical formula of Nylon-6,6.

20. Give two examples of synthetic biopolymers.

Short Answer Type Questions

21. On the basis of source, how polymers are classified? Give one example of each.

22. Write difference between thermosetting and thermoplastic polymers.

23. In free radical polymerisation, what is the role of hydroquinone. Explain.

24. Give the monomer of dacron and process of polymerisation of dacron.

25. What is polydispersity index? Explain.

26. Why rubber is vulcanised ? Explain.

27. What does LDPE and HDPE indicates ? How are they formed?

28. Write the names of monomers and structures of following polymers :
(i) Teflon (ii) Terelene
(iii) Nylon-6,6 (iv) Bakelite

29. What is PHBV?

30. Why PDI of proteins is one?

Long Answer Questions

31. Classify polymers on the following basis :
(i) On the basis of monomer units
(ii) Type of Polymerisation
(iii) Molecular forces

32. What is addition polymerisation? Explain free radical addition polymerisation mechanism by taking an example.

33. How natural rubber is obtained? Write its composition and structure.

34. Why molecular weiht of polymers is taken as average molecular weight. How many types average molecular weight can be represented? Explain each type.

35. Write short notes on biopolymers and biodegradable polymers.

36. Write method of polymerisation and uses of following polymers:
(i) Bakelite (ii) PVC
(iii) Polyester (iv) Nylon-6,6

Answers (Multiple Choice Questions)

1. (a), 2. (c), 3. (b), 4. (a), 5. (c),
6. (c), 7. (a), 8. (b), 9. (a), 10. (b).