13

Polymers

IN THIS CHAPTER ....

Polymer are the giant molecules of chemistry. Chemists also called them macromolecules. Wool, silk and cotton are used for thousand of years but lately, synthetic fibres replaced them as protective material.

The word polymer is derived from two Greek words : '*poly*' means many and '*mer*' means units or parts. Polymers may be defined as the high molecular mass compounds which are prepared by the combination of a large number of one or more than one types of simple molecules or units.

Various Terms Related to Polymers

In order to understand the composition, structure and characteristics of polymers, it is necessary to become apprehensive with the following terms.

Monomers

The small molecules that combine together to give a polymer, are called **monomers**. e.g. When a large number of ethene molecules combine together (under suitable conditions) to form a high molecular weight substance are called **polymer**. It is named as polyethene as it contains several ethene units.

Repeating Units

The unit or part of a polymer, which is repeated at a regular interval is called **repeating unit**. Repeating unit may or may not be same as monomer. e.g.

(i) $\underset{\text{Ethene}}{n\text{CH}_2{=\!=}\text{CH}_2} \xrightarrow[\text{pressure}]{\text{O}_2,\ \text{heat}} \text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—}$ or $\underset{\text{Polyethene}}{\text{+}\!\!(\text{CH}_2\text{—CH}_2\text{+}\!\!)_n}$

Monomer → $\text{+}\!\!(\text{CH}_2\text{—CH}_2\text{+}\!\!)$; Repeating unit → $\text{+}\!\!(\text{CH}_2\text{—CH}_2\text{+}\!\!)_n$

(ii) $\underset{\text{Nylon-6,6}}{\text{—}\!\!\![\text{NH(CH}_2)_6\text{NHCO(CH}_2)_4\text{CO}]_n\!\!\!\text{—}}$

Monomer → $\underset{\text{Adipic acid}}{\text{HCOO(CH}_2)_4\text{COOH}}$ and $\underset{\text{Hexamethylene diamine}}{\text{NH}_2\text{+}\!\!(\text{CH}_2\text{+}\!\!)_6\text{NH}_2}$

Repeating unit → $\text{—}\!\!\![\text{NH(CH}_2)_6\text{NHCO(CH}_2)_4\text{CO}]_n\!\!\!\text{—}$

Macromolecules

High molecular weight compounds are called macromolecules. Polymers which have high molecular mass are also considered as macromolecules but all macromolecules are not polymers.

The main difference between macromolecules and polymers is that the later have a repeating unit, whereas the former may or may not. e.g. Polythene and chlorophyll both are macromolecules but only polythene due to the presence of $+\!\!\!\!-CH_2-CH_2-\!\!\!\!+_n$ is a polymer whereas chlorophyll due to the absence of repeating unit, is not a polymer.

Classification of Polymers

Polymers are classified into following categories are discussed below

On the Basis of Source of Origin

On this basis polymers are classified into following three categories

1. Natural Polymers

These are obtained from plants and animals. Some of these such as polysaccharides, proteins and nucleic acids are essential for the existence of life. So, these are also known as **biopolymers**. These are generally biodegradable in nature.

e.g. Nucleic acids, proteins, natural rubber, wool, silk, etc.

2. Semisynthetic Polymers

These are derived from natural polymers by chemical modifications. These are also called **man-made polymers**. e.g. Rubber is subjected to process of vulcanisation to get vulcanised rubber. Polymers derived from cellulose like cellulose acetate and cellulose nitrate also semisynthetic polymers.

3. Synthetic Polymers

These are man-made polymers. Such polymers have high tensile strength. Due to their extensive use in daily life as well as in industry, these are of great importance. e.g. Polythene $-[CH_2-CH_2-\!\!\!\!+_n$, polyvinyl chloride $+\!\!\!\!-CH_2-CHCl]_n$, polystyrene $-[CH_2-CHC_6H_5-\!\!\!\!+_n$, nylon-6, 6, bakelite, synthetic rubber etc.

On the Basis of Structure

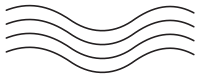
On this basis, polymers are classified into following categories

1. Linear Polymers

In linear polymers, monomers are combined together in the form of long and straight chains. These chains are closely packed, due to which, these polymers have high melting points, high densities and high tensile strength.

e.g. High density polythene, polyvinyl chloride (PVC), polystyrene, polypropylene etc.

It is represented as below

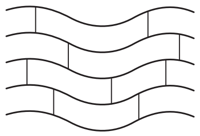


2. Branched Chain Polymers

They contain linear chains with some branches. Due to branching, the molecules of polymer do not pack perfectly. Consequently, these have low density, low melting point and low tensile strength.
e.g. Low density polythene. It is represented as below

3. Cross-linked or Network Polymers

These polymers are obtained from bi-or-tri functional monomers. In such polymers, the linear polymer chains are linked together through strong covalent bonds and results in a three dimensional network or cross-linked structure. Due to cross-linking, these polymers are hard, rigid and brittle.
e.g. Bakelite, melamine etc.



On the Basis of Mode of Polymerisation

On this basis polymers are divided into following two classes

1. Addition Polymers

These are formed by successive addition of repeated monomers without the elimination of small molecules. These are obtained from unsaturated monomer molecules, i.e. the molecules having double or triple bond.

The molecular mass of such polymers is whole number multiple of monomer. These are obtained by addition divided into chain growth polymerisation, so also known as **chain growth polymers**.

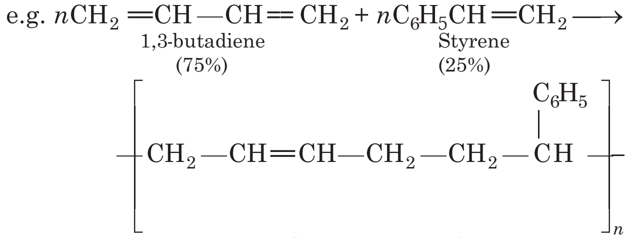
On the basis of monomers involved, these are further divided into two types

(i) **Homopolymers** which are obtained by the repeated addition of single monomer unit.

e.g. $$\underset{\text{Ethene}}{nCH_2=CH_2} \longrightarrow \underset{\text{Polyethene}}{+\!\!\!\!-CH_2-CH_2-\!\!\!\!+_n}$$

$$\underset{\text{Vinyl chloride}}{nCH_2=CHCl} \longrightarrow \underset{\text{Polyvinyl chloride}}{+\!\!\!\!-CH_2-CHCl-\!\!\!\!+_n}$$

(ii) **Copolymers** which are obtained by the repeated addition of more than one monomer units.



$$\text{e.g. } n\underset{\substack{\text{1,3-butadiene}\\(75\%)}}{CH_2=CH-CH=CH_2} + n\underset{\substack{\text{Styrene}\\(25\%)}}{C_6H_5CH=CH_2} \longrightarrow \left[CH_2-CH=CH-CH_2-CH_2-\overset{\overset{C_6H_5}{|}}{CH} \right]_n$$

Butadiene styrene copolymer (buna-S)

2. Condensation Polymers

These are obtained when monomer molecules combine together with the loss of small molecules such as ammonia, water, alcohol etc.

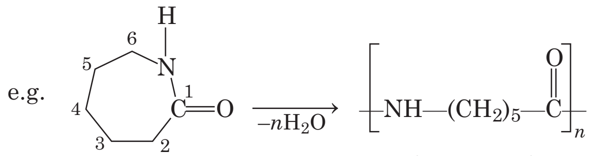
The molecular mass of such polymers is not a whole number multiple of monomer. These are the products of condensation polymerisation which generally occurs amongst the molecules possessing two or three functional groups, so are also called **step growth polymers**. These are usually copolymers but a few homopolymers are also consider.

(i) **Condensation copolymers** These are obtained form condensation of more than one monomer units.

$$\text{e.g. } \underset{\substack{\text{Hexamethylene}\\\text{diamine}}}{nH_2N(CH_2)_6NH_2} + \underset{\text{Adipic acid}}{nHOOC(CH_2)_4COOH} \longrightarrow \underset{\text{Nylon-6, 6}}{-\!\!\!\!\left(NH(CH_2)_6NHCO(CH_2)_4CO\right)\!\!\!\!-_n} + nH_2O$$

(ii) **Condensation homopolymers** These are prepared form condensation reaction between molecules of only one kind.

e.g.



Caprolactam

Nylon-6 or perlon (condensation homopolymer)

Classification on the Basis of Magnitude of Intermolecular Forces

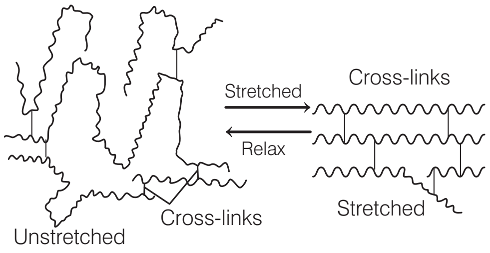
On the basis of intermolecular forces, polymers are classified into following classes

1. Elastomers

These are the polymers that have elastic character (i.e. have a property to regain their original shape after stretching).

In such polymers, the polymer chains are held together by weak intermolecular forces which are responsible for their elastic character.
e.g. Natural rubber, neoprene etc.

In order to increase their elastic character, a few cross-links are also introduced in between the chains.
e.g. Vulcanised rubber.



Unstretched and stretched forms of an elastomer

2. Fibres

These are long threads having high tensile strength, high modulus and less elasticity. These can be woven into fabric. These polymers have strong intermolecular forces such as hydrogen bonding, dipole-dipole interaction etc. Due to the presence of such strong forces of attraction, the polymer chains get closely packed and impart crystalline nature to polymers.

Thus, polymers show sharp melting points. As the crystalline nature increases, the polymers become denser, harder and more resistant to heat.
e.g. Polyamides (nylon-6, 6), polyesters (terylene) etc.
However, in the presence of substituents as in poly (methyl resulted methacrylates) or branches, no such close packing occurs, resulted density gets reduced.

3. Thermoplastic Polymers

These are the linear or slightly branched polymers in which the intermolecular forces of attraction are intermediate between elastomers and fibres. These polymers soften on heating and become rigid on cooling. This is due to absence of cross-linking between chains of such polymers.

The process of softening, moulding and cooling can be repeated as often as, desired. These polymers are soluble in many organic solvents.

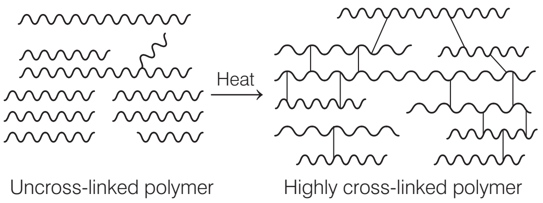
e.g. Nitrocellulose, vinyl polymers such as polythene, perspex, polystyrene etc.

4. Thermosetting Polymers

When heavily branched molecules or chains are heated, they result in hard infusible and insoluble three dimensional or extensively cross-linked products. These three dimensional or extensively cross-linked products are referred as **thermosetting polymers**.

Due to extensive cross-linking, these polymers have strongest intermolecular forces and are brittle as cross-linking reduces the mobility of polymer chains. On heating, these result in chemical decomposition, thus cannot be remelted or reused after hardening once.
e.g. Bakelite, urea-formaldehyde resin, melamine-formaldehyde etc.

Rigidity of polymers increases with increase cross-linking.

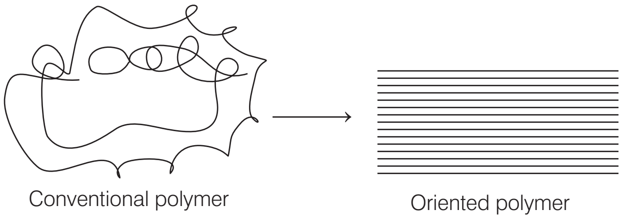


Uncross-linked polymer Highly cross-linked polymer

5. **Oriented Polymers**

These polymers are stronger than steel. These can be made to conduct electricity by stretching the polymer chains and putting them back together in a parallel fashion.

These are represented as follows



Conventional polymer Oriented polymer

Example 1. *Which of the following is a thermosetting polymer ?* ***(JEE Main 2019)***

(a) Bakelite (b) Buna-N

(c) Nylon-6 (d) PVC

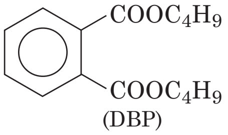
Sol. (a) Bakelite is a thermosetting polymer. These polymers are cross-linked or heavily branched molecules which on heating undergo extensive cross linking in moulds and become infusible. Once they get set, they cannot be reshaped and reused.

Plasticizers

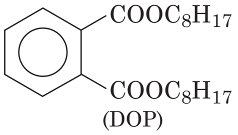
Those plastics, which do not soften very much on heating can be made soft by the addition of certain organic compounds called plasticizers. They do lower the melting point of a polymer but cannot convert a thermosetting polymer to thermoplastic polymer.

The plasticizers evaporate when exposed to air and light for a long time, leaving behind a hard and brittle plastic article.

e.g. Tricresyl phosphate (TCP), dioctylphthalate (DOP), dibutylphthalate (DBP) and chlorinated paraffin wax (CPW) etc.



(DBP)



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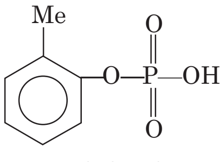


o-cresyl phosphate

Polymerisation

The process or technique through which monomer units combine to give a polymer is known as **polymerisation**. The polymerisation reaction can't be controlled easily. According to **Carothers** (1931) polymerisation is best defined as "intermolecular combinations that are functionally capable of proceeding indefinitely".

There are two principal methods through which monomers combine to give polymers.

- Addition polymerisation and condensation polymerisation.
- Copolymerisation and coordination polymerisation.

The methods of polymerisation are as follows

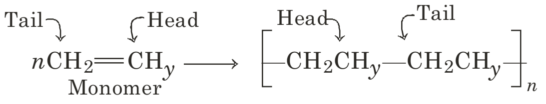
Addition Polymerisation

The process in which molecules of same or different monomers combine together to give a polymer without the elimination of small molecules. Since, there is an increase in the length of chain (i.e. chain grows) by this mode of polymerisation, it is also known as **chain growth polymerisation.**

This mode of polymerisation is observed in molecules having multiple bonds, mainly in $CH_2 = CHy$ type molecules (where, y may be —H, — X, —CO_2R, —CN etc.)

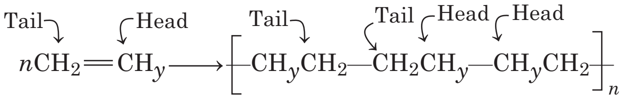
In chain growth polymerisation, there are three possible ways through which monomers can combine, *viz.*

- Head to tail manner



$$\underset{\text{Monomer}}{\overset{\text{Tail}\quad\text{Head}}{nCH_2{=}CH_y}} \longrightarrow \left[\overset{\text{Head}\quad\quad\text{Tail}}{-CH_2CH_y-CH_2CH_y-}\right]_n$$

- Head to head and tail to tail manner



$$\overset{\text{Tail}\quad\text{Head}}{nCH_2{=}CH_y} \longrightarrow \left[\overset{\text{Tail}\quad\text{Tail}\quad\text{Head}\quad\text{Head}}{-CH_yCH_2-CH_2CH_y-CH_yCH_2-}\right]_n$$

- In random manner which includes (i) and (ii) both.

Among these ways, 'Head to tail addition' is preferred for steric reason because propagating unit attacks the less sterically hindered carbon. Moreover, groups that stabilise adjacent radicals also favour "head to tail addition".

The addition or chain growth polymerisation can proceed by the following two mechanisms

(i) By the formation of free radicals. (Free radical polymerisation).

(ii) By the formation of ionic species. (Ionic polymerisation).

On the basis of structure of monomer and initiator used, each mechanism involve following three steps.

- Initiation step
- Propagation step
- Termination step

1. Free Radical Addition Polymerisation

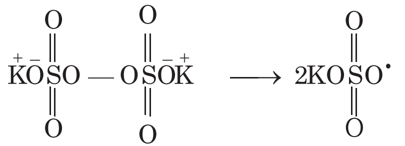
In this way of polymerisation, there is generation of free radicals by free radical generators, called **initiator**. Any compound which readily undergoes homolytic cleavage to give such radicals that are sufficiently energetic to convert an alkene into radical, can act as a radical generator (initiator) for free radical polymerisation.

e.g. Organic and inorganic peroxides and salts of per acids. Examples of some free radical generators are summarised below

$$\underset{\text{Benzoyl peroxide}}{(C_6H_5COO)_2} \longrightarrow 2C_6H_5COO^\bullet$$

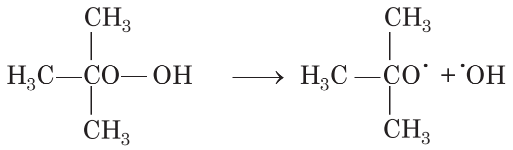
$$\underset{\text{Acetyl peroxide}}{(CH_3COO)_2} \longrightarrow 2CH_3COO^\bullet$$

$$\underset{\text{Hydrogen peroxide}}{H_2O_2} \longrightarrow 2\overset{\bullet}{O}H$$



$$\overset{+}{K}\overset{-}{O}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}O-O\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\overset{-}{O}\overset{+}{K} \longrightarrow 2KO\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}O^\bullet$$

Potassium perdisulphate



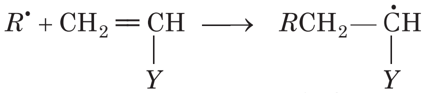
$$H_3C-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}O-OH \longrightarrow H_3C-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}O^\bullet + {}^\bullet OH$$

t-butyl hydrogen peroxide

This mode of polymerisation involves following three steps

***Step* I Initiation step** In this step, a monomer unit gets excited either by exposing to light or by small amount of free radical generator.

$$\text{e.g.}\quad \underset{\text{(Alkyl peroxide)}}{(RCOO)_2} \longrightarrow 2RCOO^\bullet \longrightarrow \underset{\substack{\text{(Free radical}\\ \text{generator)}}}{R^\bullet} + CO_2$$

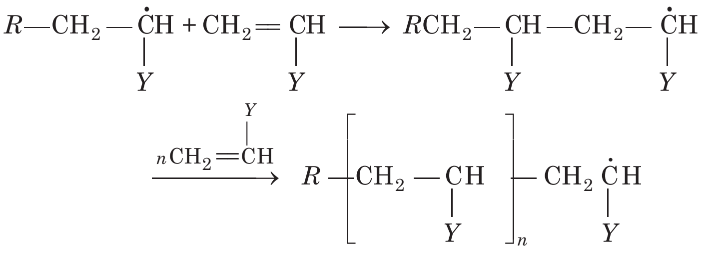


$$R^\bullet + CH_2=\underset{Y}{\underset{|}{CH}} \longrightarrow RCH_2-\underset{Y}{\underset{|}{\dot{C}H}}$$

Excited monomer unit (free radical)

(where, Y = H, Cl, CN, —R etc.)

***Step* II Propagation step** The excited monomer unit (or generated free radical) combines with another monomer unit, this step generates another free radical. This process of addition and generation continues and chain length increases. e.g.



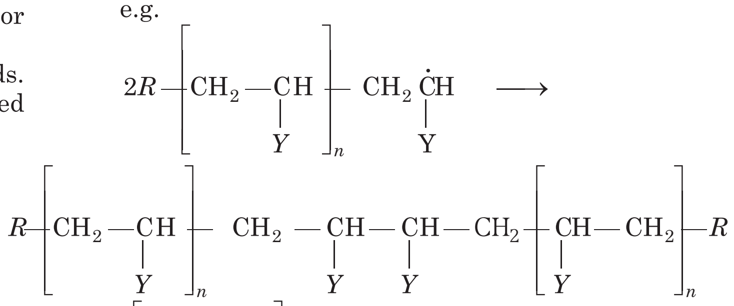
$$R-CH_2-\underset{Y}{\underset{|}{\dot{C}H}} + CH_2=\underset{Y}{\underset{|}{CH}} \longrightarrow RCH_2-\underset{Y}{\underset{|}{CH}}-CH_2-\underset{Y}{\underset{|}{\dot{C}H}}$$

$$\xrightarrow{n\,CH_2=\overset{Y}{\overset{|}{CH}}} R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n CH_2\underset{Y}{\underset{|}{\dot{C}H}}$$

***Step* III Termination step** In this step, the growing chain is terminated by one of the following methods.

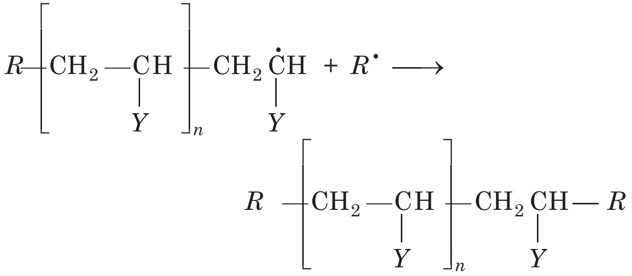
(i) When there is a coupling between the growing chains or between a growing chain and free radical generator, the chain gets terminated.

e.g.



$$2R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n CH_2\underset{Y}{\underset{|}{\dot{C}H}} \longrightarrow$$

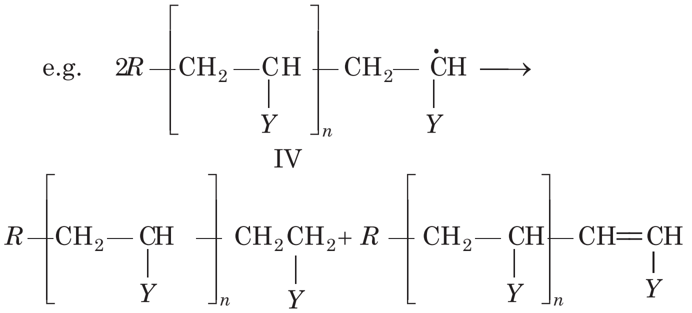
$$R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n CH_2-\underset{Y}{\underset{|}{CH}}-\underset{Y}{\underset{|}{CH}}-CH_2\left[\underset{Y}{\underset{|}{CH}}-CH_2\right]_n R$$



$$R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n CH_2\underset{Y}{\underset{|}{\dot{C}H}} + R^\bullet \longrightarrow$$

$$R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n CH_2\underset{Y}{\underset{|}{CH}}-R$$

(ii) When the growing chain undergoes disproportionation, the chain gets terminated

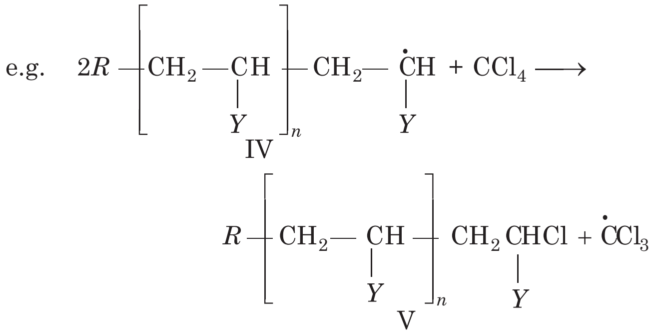


$$\text{e.g.}\quad 2R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n CH_2-\underset{Y}{\underset{|}{\dot{C}H}} \longrightarrow$$

IV

$$R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n \underset{Y}{\underset{|}{CH_2CH_2}} + R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n CH=\underset{Y}{\underset{|}{CH}}$$

(iii) When reagents such as CCl_4 or CBr_4 are added, the growing chain gets terminated. These reagents are called **chain transfer agents** and the process is called **chain transfer**. The molecular mass of a polymer can be controlled by this process. These reagents do not affect the rate of polymerisation but yield a polymer with lower average molecular mass and a small amount of chlorine.



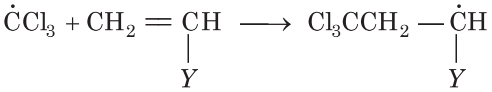
$$\text{e.g.}\quad 2R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n CH_2-\underset{Y}{\underset{|}{\dot{C}H}} + CCl_4 \longrightarrow$$

IV

$$R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n CH_2\underset{Y}{\underset{|}{CHCl}} + \dot{C}Cl_3$$

V

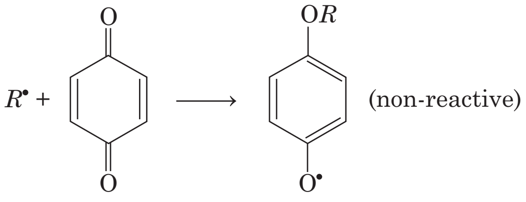
The obtained free radical again generates a excited monomer unit.



$$\dot{C}Cl_3 + CH_2{=}\underset{Y}{\underset{|}{CH}} \longrightarrow Cl_3CCH_2{-}\underset{Y}{\underset{|}{\dot{C}H}}$$

When the radical obtained from chain transfer agent, is highly stable and unreactive, the original chain gets terminated without the initiation of new one.

Consequently, the process of polymerisation is inhibited. Therefore, these reagents are termed as **chain inhibitors**. Several amines, phenols, quinones act as chain inhibitor. e.g. Free radical polymerisation of a vinyl derivative is inhibited in the presence of benzoquinone.



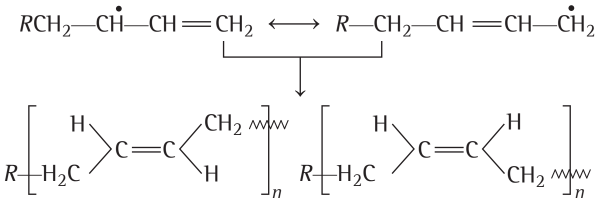
Free radical polymerisation

Conjugated Diene Polymerisation

Conjugated dienes such as 1, 3-butadiene can polymerise by one of the following two ways

(i) 1,4-addition When addition takes place at terminal carbon atoms (i.e. at C_1 and C_4 in case of butadiene), the result is an unbranched polymer with a repeating unit having double bond. Therefore, the polymers can exist as *cis* form or trans form or a mixture of both.

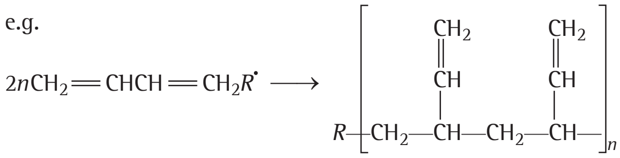
e.g. $R^{\bullet} + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow$



trans form *cis* form

(ii) 1,2-addition When addition takes place at successive carbon atoms (i.e. at C_1 and C_2 in case of butadiene), the result is a branched polymer.

e.g.



$$2nCH_2{=}CHCH{=}CH_2R^{\bullet} \longrightarrow R{-}\left[CH_2{-}\underset{}{\overset{\overset{CH_2}{\|}}{CH}}{-}CH_2{-}\overset{\overset{CH_2}{\|}}{CH}{-}\right]_n$$

2. Ionic Addition Polymerisation

In this mode of polymerisation, there is generation of ionic species (as intermediate) such as cations and anions, instead of free radicals.

Depending upon the nature of ionic species formed, ionic addition polymerisation may be classified into two types

(i) **Cationic addition polymerisation** It is the process, which involves formation of a carbocation as intermediate. The carbocation is generated by an initiator. Any compound which readily undergoes heterolytic cleavage to give a proton or cation that is able to convert an alkene into carbocation, can act as initiator for cationic polymerisation reaction.

Commonly used carbocation generators or initiators are Lewis acids such as BF_3, $AlCl_3$ or $SnCl_4$ etc., and protonic acids such as H_2SO_4, HF etc.

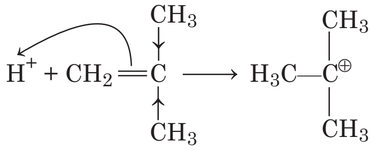
This polymerisation is facilitated in monomers having electron releasing groups such as CH_3, C_2H_5 etc. Higher the stability of carbocation intermediate, more is the reactivity of monomer towards cationic addition polymerisation.

Like free radical addition polymerisation, cationic addition polymerisation are also involves following three steps

***Step* I** **Initiation step** In this step, the proton generated from either Lewis acid or protonic acid, attacks on monomer unit and a carbocation is formed.

e.g. $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

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

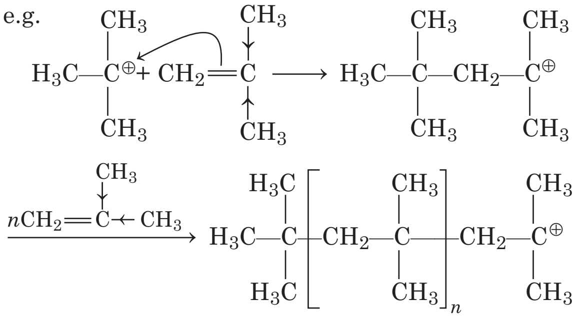


$$H^+ + CH_2{=}\underset{CH_3}{\overset{CH_3}{C}} \longrightarrow H_3C{-}\underset{CH_3}{\overset{CH_3}{C^{\oplus}}}$$

Carbocation (intermediate)

***Step* II** **Propagation step** A polymer spends most of its time in increasing its chain length or propagating. After the carbocation intermediate is formed, it attacks on monomer.

e.g.

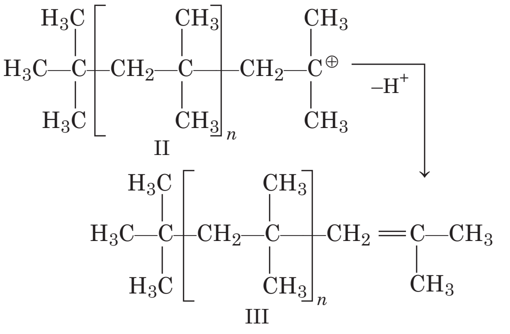


$$H_3C{-}\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} + CH_2{=}\underset{CH_3}{\overset{CH_3}{C}} \longrightarrow H_3C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C^{\oplus}}}$$

$$\xrightarrow{nCH_2{=}\overset{CH_3}{C}{-}CH_3} H_3C{-}\underset{H_3C}{\overset{H_3C}{C}}\left[{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\right]_n CH_2{-}\underset{CH_3}{\overset{CH_3}{C^{\oplus}}}$$

***Step* III** **Termination step** The growing chain is generally terminated by the loss of a hydrogen ion (i.e. proton).

e.g.



$$H_3C{-}\underset{H_3C}{\overset{H_3C}{C}}\left[{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\right]_n CH_2{-}\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} \quad \text{II}$$

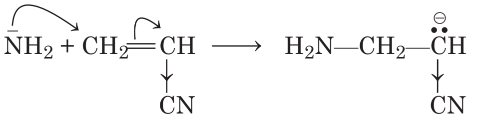
$$\xrightarrow{-H^+} H_3C{-}\underset{H_3C}{\overset{H_3C}{C}}\left[{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\right]_n CH_2{=}\underset{CH_3}{C}{-}CH_3 \quad \text{III}$$

(ii) **Anionic addition polymerisation** It is the process, in which intermediate formed is a carbanion. The initiator for this process are strong bases such as potassium amide (KNH_2), *n*-butyl lithium etc. Monomers (olefins) containing electron withdrawing groups (such as CN, C_6H_5 etc.) readily undergo anionic addition polymerisation. The monomers that give more stable carbanion intermediate, readily undergo in this type of polymerisation.

It involves following three steps

***Step* I Initiation step** In this step, the nucleophiles, generated from strong bases, attack on monomer and generate carbanion.

e.g. $KNH_2 \longrightarrow K^+ \bar{N}H_2$

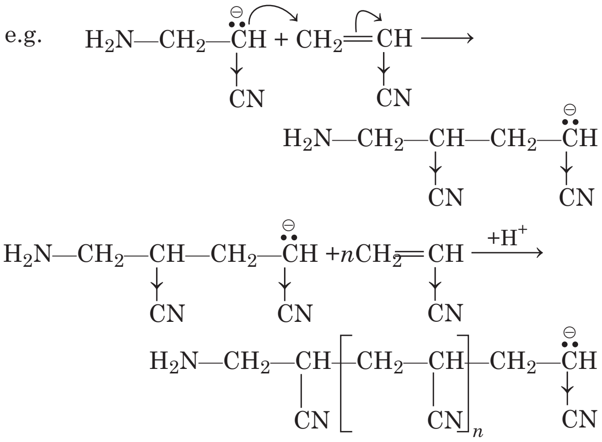


$$\bar{N}H_2 + CH_2{=}\underset{CN}{CH} \longrightarrow H_2N{-}CH_2{-}\underset{CN}{\overset{\ominus}{C}H}$$

Carbanion (intermediate)

***Step* II Propagation step** After the carbanion is formed in step I, it attacks on

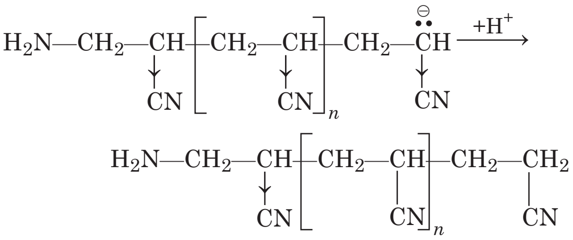
e.g.



$$H_2N{-}CH_2{-}\underset{CN}{\overset{\ominus}{C}H} + CH_2{=}\underset{CN}{CH} \longrightarrow H_2N{-}CH_2{-}\underset{CN}{CH}{-}CH_2{-}\underset{CN}{\overset{\ominus}{C}H}$$

$$H_2N{-}CH_2{-}\underset{CN}{CH}{-}CH_2{-}\underset{CN}{\overset{\ominus}{C}H} + nCH_2{=}\underset{CN}{CH} \xrightarrow{+H^+} H_2N{-}CH_2{-}\underset{CN}{CH}\left[CH_2{-}\underset{CN}{CH}\right]_n CH_2{-}\underset{CN}{\overset{\ominus}{C}H}$$

***Step* III Termination step** The growing chain is terminated by the addition of a proton or a Lewis acid, present in the reaction mixture. e.g.



$$H_2N{-}CH_2{-}\underset{CN}{CH}\left[CH_2{-}\underset{CN}{CH}\right]_n CH_2{-}\underset{CN}{\overset{\ominus}{C}H} \xrightarrow{+H^+} H_2N{-}CH_2{-}\underset{CN}{CH}\left[CH_2{-}\underset{CN}{CH}\right]_n CH_2{-}\underset{CN}{CH_2}$$

Example 2. *The species which can best serve as an initiator for the cationic polymerisation is* ***(AIEEE 2012)***

(a) $LiAlH_4$ (b) HNO_3 (c) $AlCl_3$ (d) BaLi

Sol. (c) Electron-deficient species (Lewis acid) is used as an initiator for cationic polymerisation.

Condensation Polymerisation

This type of polymerisation involves the combination of molecules having same or different monomers in a controlled stepwise manner with the elimination of small molecules such as water, ammonia, alcohol etc., as side product.

Monomers have functional groups such as alcohol, amine or carboxylic acid groups, instead of double bonds. The monomers having at least two functional groups, may be same or different, (i.e. bifunctional monomers), polymerise by this mode of polymerisation.

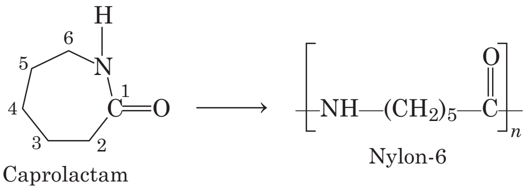
The product of each step is again a bifunctional molecule which can react with other monomer and dimer molecules until a long polymer chain is formed.

There is a repetitive condensation reaction between bifunctional monomers, the process is also known as **step growth polymerisation**.

On the basis of functional groups, there are two possible ways through which condensation polymerisation takes place. These are as follows

(i) When monomer has two kinds of functional groups, it undergoes self polymerisation.

e.g.



Caprolactam

Nylon-6

(ii) When both the functional groups of monomer are same, an another monomer bearing different functional groups is required for condensation polymerisation. e.g.

$$\underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH} + \underset{\text{Hexamethylene diamine}}{H_2N{+}CH_2{+}_6NH_2} \xrightarrow{-H_2O} \underset{\text{Nylon-6, 6}}{{+}NH(CH_2)_6NHCO(CH_2)_4CO{+}_n}$$

Copolymerisation

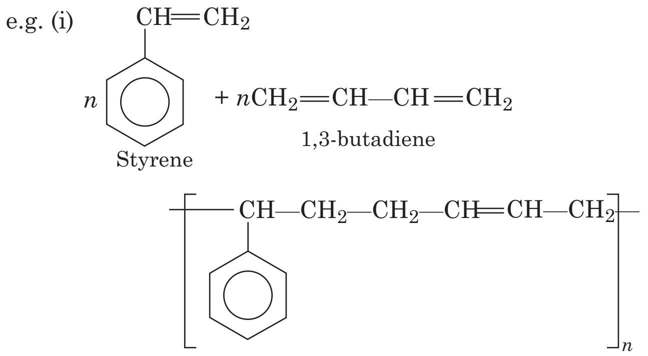
When two or more different monomer units are allowed to polymerise, a copolymer is formed which contains multiple units of each monomer used, in the same polymeric chain.

The process by which copolymers are formed is referred to as **copolymerisation**.

(i) $\text{Monomer 1} + \text{Monomer 2} \xrightarrow[\text{Copolymerisation}]{\text{Additional}} \text{Additional copolymer}$

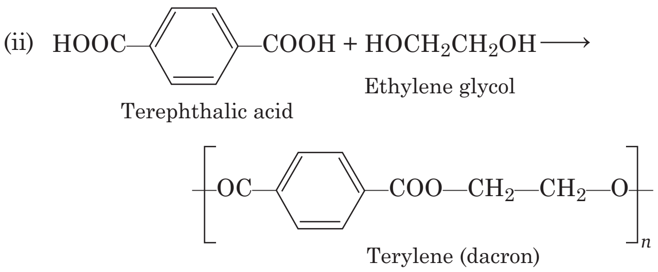
(ii) $\text{Monomer 1} + \text{Monomer 2} \xrightarrow[\text{Copolymerisation}]{\text{Condensation}} \text{Condensation copolymer}$

e.g. (i)



Butadiene-styrene (addition copolymer)

(ii)



Terylene (dacron)
(condensation copolymer)

On the basis of arrangement of monomer units in the polymer chain during copolymerisation, the copolymers can be of the following four types

(i) **Random copolymers** These are obtained, when the monomer units are arranged randomly in the polymer chain.

e.g. $nA + nB \longrightarrow -A-A-A-B-B-A-B-B-B-A-A-$

(ii) **Alternating copolymers** These are obtained, when monomer units are at the alternate positions, in the polymer chain.

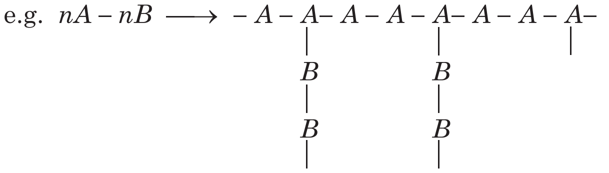
e.g. $nA + nB \longrightarrow -A-B-A-B-A-B-A-B-A-$

(iii) **Block copolymers** These are obtained, when different blocks of identical monomer units are at the alternate positions with each other.

e.g. $nA + nB \longrightarrow -(A-A-A)-(B-B-B)-(A-A-A)-$

(iv) **Graft copolymers** These are obtained, when homopolymer chains of one monomer units are grafted on the homopolymer chains of another monomer units.

e.g.



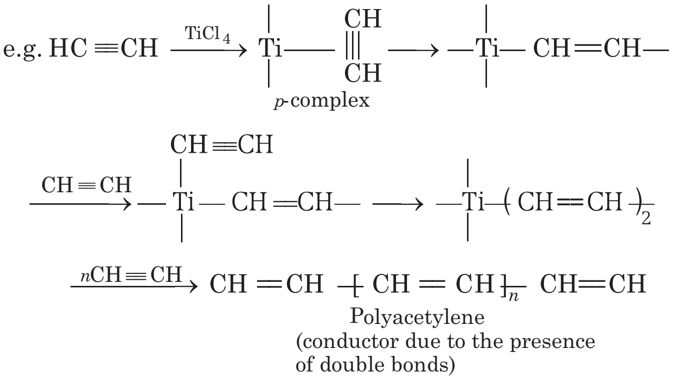
$$nA - nB \longrightarrow -A-\underset{\substack{| \\ B \\ | \\ B \\ |}}{A}-A-A-\underset{\substack{| \\ B \\ | \\ B \\ |}}{A}-A-A-\underset{|}{A}-$$

(Graft copolymers are prepared by radiating gamma rays on a completed homopolymer chain in the presence of an another monomer.)

Coordination Polymerisation

This type of polymerisation proceeds with the formation of coordination compound as intermediate. On treating with aluminium-titanium initiator $[(C_2H_5)_3Al + TiCl_4]$, monomer first forms a coordination complex with titanium by donating its π-electrons. The π-complex, thus, formed reacts with a large number of monomer units stepwise and leads to the formation of polymer.

e.g.



Polyacetylene
(conductor due to the presence of double bonds)

This process was found by two scientists, Ziegler and Natta, that's why it is known as Ziegler-Natta polymerisation and the catalyst used is called **Ziegler-Natta catalyst**.

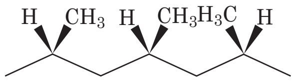
The major advantage of this polymerisation is that the polymer obtained has specific stereochemistry. Propene can polymerise to give any of the three possible stereochemical arrangements.

These are as follows

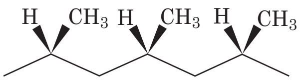
(i) **Atactic** (or random arrangement), in which methyl groups are arranged randomly.

(ii) **Isotactic** (or same arrangement), in which methyl groups are present on same side of *zig-zag* backbone.

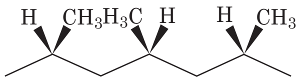
(iii) **Syndiotactic** (or alternate arrangement), in which methyl groups lie alternately on the opposite sides of *zig-zag* backbone. e.g.



(i) Atactic



(ii) Isotactic



(iii) Syndiotactic

Some Important Polymers

Some of the examples of important polymers are given below.

1. Rubber

Rubber is the polymer of buta-1, 3-diene. These have elastic properties due to which these are also included in class **'elastomers'**.

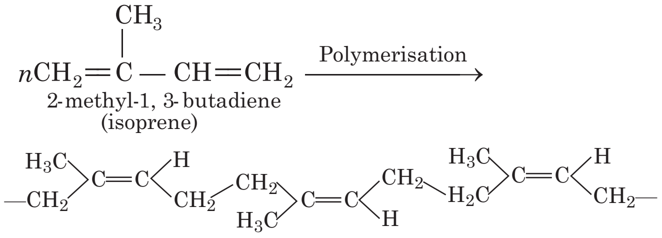
On the basis of origin, rubbers can be of two types.

(i) **Natural Rubber**

It is obtained as latex from rubber latex (*Hevea brasiliensis*) (contains 35% rubber), which is a colloidal dispersion of rubber in water. On treating latex with acids such as acetic acid, formic acid etc., crude rubber coagulates which either on masticating or on adding necessary agents gives natural rubber.

Natural rubber is linear 1, 4-polymer of isoprene (2-methyl-1, 3-butadiene). In other words, natural rubber is *cis*-polyisoprene or *cis*-1,4-polyisoprene.

e.g.



$$\underset{\substack{\text{2-methyl-1, 3-butadiene}\\ \text{(isoprene)}}}{n\mathrm{CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2}} \xrightarrow{\text{Polymerisation}}$$

cis-1,4-polyisoprene (natural rubber)

The weight average molar mass ($\overline{M}_w$) of rubber is in the range 1,30,000-3,40,000. Its *trans* form is known as ***gutta-percha***.

Vulcanisation of Rubber

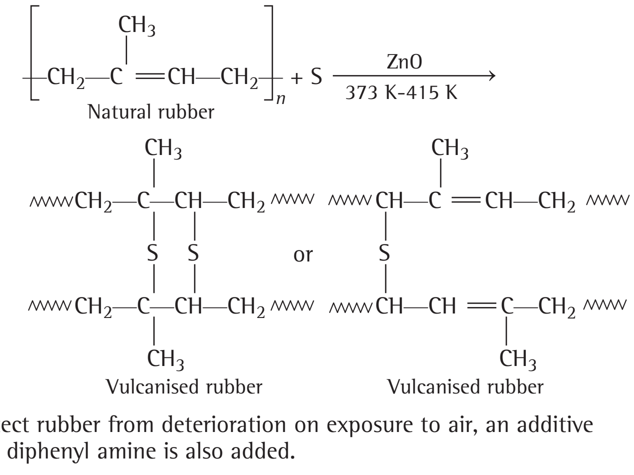
To improve the undesirable properties, natural rubber is heated with sulphur or sulphur compounds at 373 K to 415 K in the presence of ZnO. The process is called vulcanisation of rubber and was introduced by Charles Goodyear.

On vulcanisation, sulphur introduces at cross-links of double bonds and makes the rubber stiffened, more elastic and resistant to oxidation and organic solvents. The stiffness of rubber depends upon the amount of sulphur added.

e.g. when 5% sulphur is used as a cross-linking agent, the obtained vulcanised rubber is used for manufacturing tyres but if 30% sulphur is used, the obtained vulcanised rubber (ebonite) is used for making battery.

Zinc oxide used in the vulcanisation process, is an additive which accelerates the rate of vulcanisation because it is a slow process.

e.g.



$$\underset{\text{Natural rubber}}{\left[\mathrm{-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH-CH_2-}\right]_n} + \mathrm{S} \xrightarrow[\text{373 K-415 K}]{\text{ZnO}}$$

To protect rubber from deterioration on exposure to air, an additive such as diphenyl amine is also added.

Properties of Natural Rubber

- It is insoluble in water, dilute acids and alkalies but soluble in organic solvents such as benzene, chloroform, petrol etc.
- It absorbs a large amount of water and has low tensile strength and elasticity.

(ii) **Synthetic Rubbers**

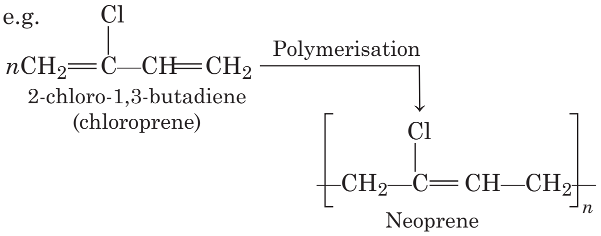
These are either homopolymer of **buta-1, 3-diene** derivatives or copolymer of **buta-1, 3-diene** or its derivatives with another unsaturated organic monomers, such as acrylonitrile, styrene etc. These are more resistant and have high tensile strength.

Some examples are as follows

I. **Neoprene**

It is a homopolymer of chloroprene (2-chloro-1, 3-butadiene). It is obtained by the free radical polymerisation or Ziegler-Natta polymerisation of chloroprene. It is also known as duprene.

e.g.



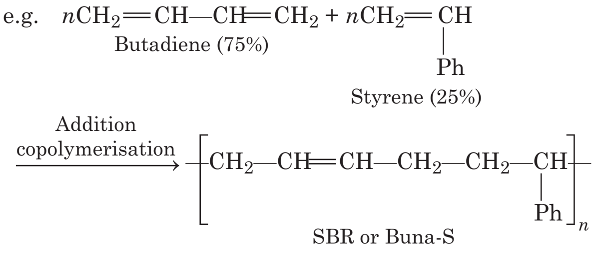
$$\underset{\substack{\text{2-chloro-1,3-butadiene}\\ \text{(chloroprene)}}}{n\mathrm{CH_2{=}\overset{\overset{\displaystyle Cl}{|}}{C}{-}CH{=}CH_2}} \xrightarrow{\text{Polymerisation}} \underset{\text{Neoprene}}{\left[\mathrm{-CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}{=}CH-CH_2-}\right]_n}$$

It is a thermoplastic and need not to be vulcanised. As it is resistant towards air, heat, light, chemicals, acids below 50% strength, it is superior to natural rubber. It is used in manufacture of gaskets, hoses and conveyor belts etc.

II. **Buna-S** (Styrene-Butadiene Rubber, SBR)

It is also called GRS (general purpose styrene rubber). It is obtained by the copolymerisation of 75% butadiene and 25% styrene in the presence of sodium metal.

e.g.



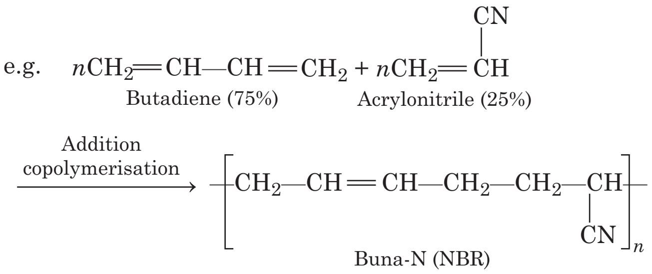
$$\underset{\text{Butadiene (75\%)}}{n\mathrm{CH_2{=}CH{-}CH{=}CH_2}} + \underset{\text{Styrene (25\%)}}{n\mathrm{CH_2{=}\underset{\underset{\displaystyle Ph}{|}}{CH}}} \xrightarrow{\substack{\text{Addition}\\ \text{copolymerisation}}} \underset{\text{SBR or Buna-S}}{\left[\mathrm{-CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle Ph}{|}}{CH}-}\right]_n}$$

It is an elastomer. It is generally mixed with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear. It is used in manufacture of tyres and other mechanical rubber goods.

III. **Buna-N** (NBR or GRA)

It is obtained by the copolymerisation of 75% butadiene and 25% acrylonitrile (vinyl cyanide) in the presence of peroxide catalyst or sodium metal.

e.g.



$$\underset{\text{Butadiene (75\%)}}{n\mathrm{CH_2{=}CH{-}CH{=}CH_2}} + \underset{\text{Acrylonitrile (25\%)}}{n\mathrm{CH_2{=}\overset{\overset{\displaystyle CN}{|}}{C}H}} \xrightarrow{\text{Addition copolymerisation}} \underset{\text{Buna-N (NBR)}}{\left[\mathrm{-CH_2-CH=CH-CH_2-CH_2-\underset{\underset{\displaystyle CN}{|}}{CH}-} \right]_n}$$

It is more rigid, responds less to heat and very much resistant to swelling action of petrol, oils and other organic solvents.

IV Thiokol or Polysulphide Rubber

It is obtained by the condensation copolymerisation of ethylene dichloride and sodium tetrasulphide (Na_2S_4).

V. Butyl Rubber

It is obtained by the copolymerisation of *iso*-butylene and isoprene.

2. Polythene or Polyethylene

It is a polymer of ethene ($CH_2{=}CH_2$). Depending upon the conditions of temperature, pressure and nature of catalyst.

Polythene are of the following two types

(i) Low Density Polythene

It is prepared by free radical addition polymerisation of ethene at 350 to 570 K, under 1000-2000 atm pressure and in the presence of traces of oxygen or a peroxide.

e.g. $$\underset{\text{Ethene}}{n\mathrm{CH_2{=}CH_2}} \xrightarrow[\text{350-570 K; 1000-2000 atm}]{\text{Traces of oxygen or peroxide}} \text{Low density polythene (highly branched)}$$

The branching does not allow the polymer to undergo close packing. Hence, the density of the polymer is low.

It is inert, tough but flexible and poor conductor of electricity. Therefore, it is used for insulating electric wires, for manufacturing squeeze bottles and toys.

(ii) High Density Polythene

It is prepared by the polymerisation of ethene in the presence of catalyst, such as triethyl aluminium and titanium tetrachloride, at 330-350 K and atmospheric pressure.

e.g. $$\underset{\text{Ethene}}{n\mathrm{CH_2{=}CH_2}} \xrightarrow[\text{Catalyst}]{\text{330-350 K, 1 atm}} \text{high density polythene (with linear chains)}$$

It is also inert but relatively tough and hard with high tensile strength, hence used for manufacturing containers, house wares etc.

The polymer, thus, obtained consists of practically linear molecules which get packed closely.

Hence, the density is high.

3. Polyamides

Polymers having amide linkages $\left(\mathrm{CONH}\right)$ are called nylons (or polyamides) (here, Ny=New York and Lon=London) as nylon-6, 6 was simultaneously prepared in New York and London.

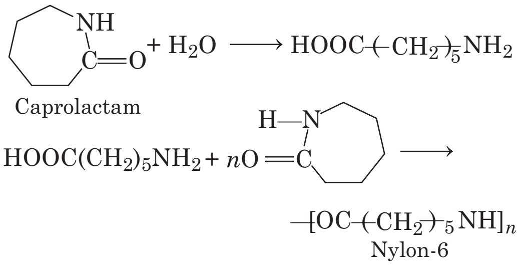
These are prepared by condensation copolymerisation of diamines with dicarboxylic acids or by condensation homopolymerisation of lactam.

Some examples are as follows

(i) Nylon-6 or Perlon

It is prepared by the polymerisation of amino caproic acid at high temperature and used for manufacturing fabrics, tyre cords etc. Since, caprolactam is more easily available, it is widely used for preparing nylon-6. For this, it is first hydrolysed with water to form amino acid.

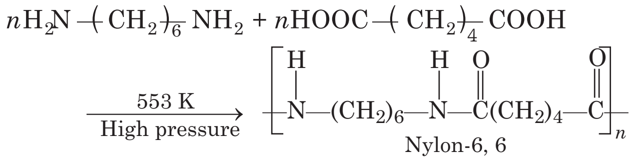
e.g.



(ii) Nylon-6, 6

It is prepared by the condensation polymerisation of hexamethylenediamine and adipic acid under high pressure and at high temperature.

e.g.



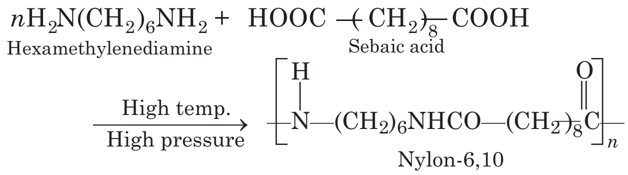
$$n\mathrm{H_2N}\left(\mathrm{CH_2}\right)_6\mathrm{NH_2} + n\mathrm{HOOC}\left(\mathrm{CH_2}\right)_4\mathrm{COOH} \xrightarrow[\text{High pressure}]{\text{553 K}} \underset{\text{Nylon-6, 6}}{\left[\mathrm{-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_6-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-}\right]_n}$$

It is used in making bristles for brushes and in textile industry.

(iii) Nylon-6, 10

It is prepared by the condensation polymerisation of hexamethylenediamine and sebaic acid under high pressure and at high temperature.

e.g.



$$\underset{\text{Hexamethylenediamine}}{n\mathrm{H_2N(CH_2)_6NH_2}} + \underset{\text{Sebaic acid}}{\mathrm{HOOC}\left(\mathrm{CH_2}\right)_8\mathrm{COOH}} \xrightarrow[\text{High pressure}]{\text{High temp.}} \underset{\text{Nylon-6,10}}{\left[\mathrm{-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_6NHCO-(CH_2)_8\overset{\overset{\displaystyle O}{\|}}{C}-}\right]_n}$$

It is used in mountaineering ropes, tyre cords and fabrics.

Naming the Nylons

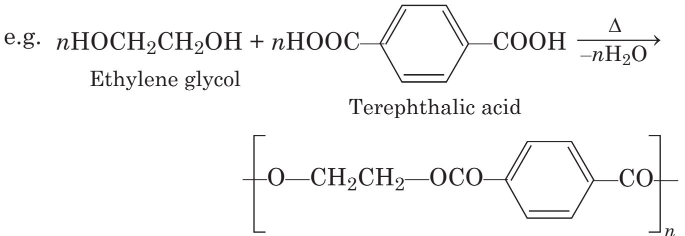
To write the name of nylon, first the number of carbon atoms of amines are written followed by the number of carbon atoms of acid. e.g. Nylon-6, 10 amine contains six carbon atoms and the acid contains ten carbon atoms.

4. Polyesters

Polymers having ester linkage (—COO—) are called polyesters. These are prepared by the condensation reaction between dialcohols and diacids.

(i) Terylene or Dacron

It is obtained by heating a mixture of ethylene glycol and terephthalic acid at 420-460 K and in the presence of catalyst such as mixture of zinc acetate and antimony trioxide.



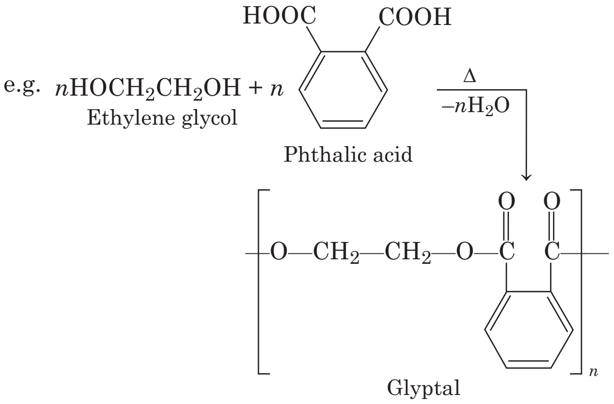
Terylene

It is a crease resistant fibre and used in blending with wool fibres, making wear fabrics, safety belts etc.

Note The film mode of terylene is called **mylar**.

(ii) Glyptal or Alkyl Resin

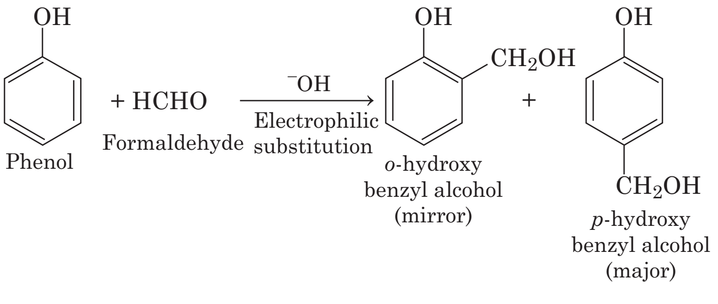
It is a polymer of ethylene glycol and phthalic acid and is used in making paints and lacquers.



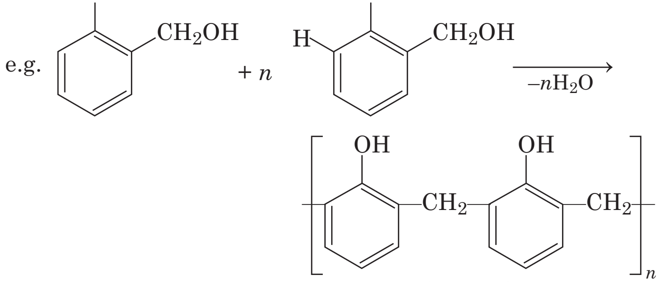
Glyptal

5. Bakelite

It is a condensation polymer of phenol and formaldehyde. When phenol is condensed with formaldehyde in the presence of a base, initially a mixture of *o*- and *p*-hydroxy benzyl alcohol is obtained. Out of which, *o*- forms again undergo self-condensation to give a linear polymer, called **novolac.** e.g.

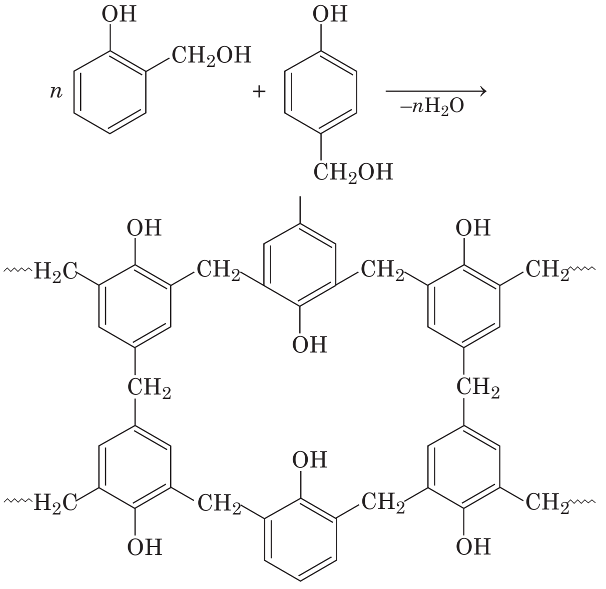


By using *o*-hydroxy beznyl alcohol we can prepare linear polymer.



Linear polymer

Here, both the isomers again undergo condensation polymerisation and a highly cross-linked polymer, called **'bakelite'** is obtained.



Bakelite

Bakelite with low degree of polymerisation is used in making glues, in varnishes and lacquers. Bakelite with high degree of polymerisation is widely used for making electrical goods, fountain pen barrels, combs etc.

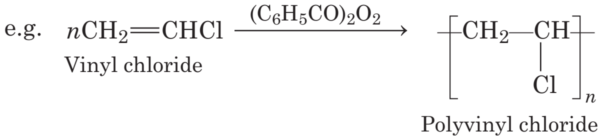
Example 3. *Preparation of bakelite proceeds via reactions* ***(JEE Main 2020)***

(a) electrophilic addition and dehydration
(b) condensation and elimination
(c) nucleophilic addition and dehydration
(d) Electrophilic substitution and dehydration

Sol. (*d*) Preparation of bakelite proceeds *via* electrophilic substituon and dehydration reactions.

6. Polyvinyl Chloride (PVC)

It is prepared by heating vinyl chloride in an inert solvent in the presence of benzoyl peroxide.



$$\text{e.g. } nCH_2{=}CHCl \xrightarrow{(C_6H_5CO)_2O_2} \left[-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}- \right]_n$$

Vinyl chloride

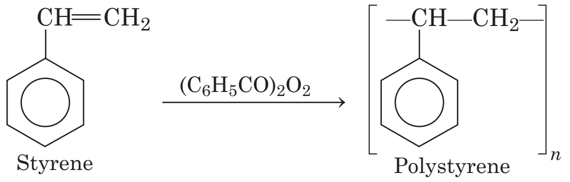
Polyvinyl chloride

It is a thermoplastic and its plasticity can be increased by addition of a plasticiser (ester of phthalic acid). It is an electrical insulator and is resistant to fire and chemicals. It is used for making sheets, pipes, waterproof outer clothing (rain coats), table clothes, plastic dolls, gramophone records, floor covering and electrical insulating coating on electrical cables.

7. **Polystyrene** (Styron)

It is manufactured by polymerisation of styrene in the presence of benzoyl peroxide.

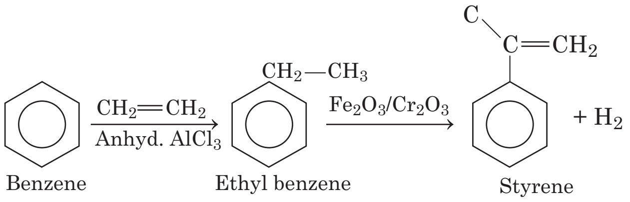
e.g.



Polystyrene is used in the manufacture of food containers, cosmetic bottles, television and radio cabinets, plastic cups, packaging and toys.

Note Styrene is obtained from benzene as follows

e.g.



8. **Teflon or Polytetrafluoroethylene** (PTFE)

It is manufactured by heating tetrafluoroethylene under pressure in the presence of ammonium peroxydisulphate.

e.g. $$n\mathrm{CF_2{=}CF_2} \xrightarrow[\text{High pressure}]{(\mathrm{NH_4})_2\mathrm{S_2O_8}} \underset{\text{Teflon (PTFE)}}{[\mathrm{-CF_2-CF_2-}]_n}$$

It is chemically inert and heat resistant polymer. It is very tough and electrical resistant. It is used for making seals and gaskets which have to withstand high temperature. It is also used for insulation of electrical items and for making non-stick surface coating and lubricant particularly for cooking utensils.

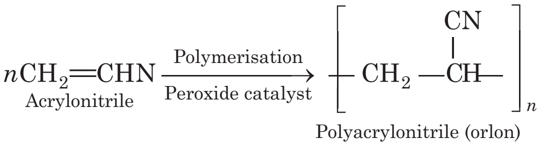
Note **Polymonochlorotrifluoroethylene** (PCTFE) can also be used at the place of teflon.

e.g. $$\underset{\text{Chlorotrifluoroethylene}}{n\mathrm{ClFC{=}CF_2}} \longrightarrow \underset{\text{PCTFE}}{[\mathrm{-ClFC-CF_2-}]_n}$$

9. **Polyacrylonitrile**

The addition polymerisation of acrylonitrile in presence of a peroxide catalyst leads to the formation of polyacrylanitrile.

e.g.



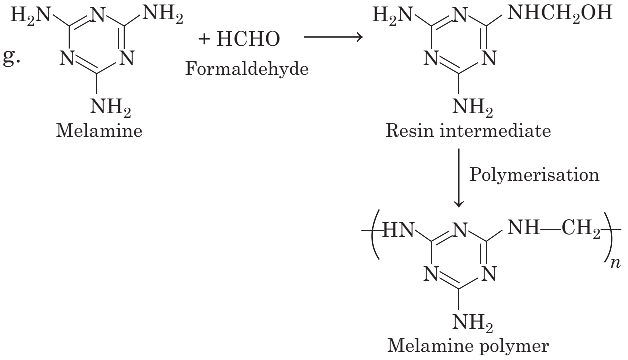
$$\underset{\text{Acrylonitrile}}{n\mathrm{CH_2{=}CHN}} \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerisation}} \underset{\text{Polyacrylonitrile (orlon)}}{\left[\mathrm{-CH_2-\overset{CN}{\overset{|}{C}H}-}\right]_n}$$

It is used as a substitute for wool in making commercial fibres.

10. **Melamine Formaldehyde Polymer**

It is formed by the condensation polymerisation of melamine and formaldehyde.

e.g.



Molecular Mass of Polymers

Polymerisation is quite complicated in nature. During the formation of polymers, the degree of polymerisation or the length of the polymer chain depends upon the availability of the monomer molecules near the growing polymer chain and also on the reaction conditions employed.

As a result in the synthetic polymers, the chains of different lengths may connect with one another. Hence, an average value of molecular mass is taken. But the same is not true for the natural polymers such as proteins, where the chains have identical lengths and hence, their molecular masses are singular and not average in nature.

There are two ways of expressing molecular mass of a polymer. These are as follows

1. **Number Average Molecular Mass**

When the total mass of all the molecules of a sample is divided by the total number of molecules, the result obtained is called the **number-average molecular mass**.

It is expressed as follows

$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

where, M_i = molecular

N_i = number of molecule

Osmotic pressure method is used to determine number average molecular mass.

2. **Weight Average Molecular Mass**

It is average of the molecular mass of the groups of the molecules having particular molecular masses multiplied by their respective molecular masses.

It is expressed as follows

$$\overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

where, N_i = number of molecules

M_i = molecular mass

It is determined by light scattering and ultracentrifugation methods.

Example 4. *Calculate the average molecular mass $\overline{M}_n$ and $\overline{M}_w$ of a polymer sample in which 30% molecules have a molecular mass of 20000, 40% have 30000 and the rest 30% have 60,000.*

(a) 36000, 43333 (b) 30000, 44000

(c) 48000, 55566 (d) 35000, 25001

Sol. (*a*) $\overline{M}_n$ and $\overline{M}_w$ of this sample will be

$$\overline{M}_n = \frac{(30 \times 20000) + (40 \times 30000) + (30 \times 60000)}{(30 + 40 + 30)}$$

$$= 36000$$

$$\overline{M}_w = \frac{30(20000)^2 + 40(30000)^2 + 30(60000)^2}{30 \times 20000 + 40 \times 30000 + 30 \times 60000}$$

$$= 43333$$

Polydispersity Index (PDI)

The ratio of weight average molecular mass and number average molecular mass is called poly dispersity index (PDI).

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

For natural polymers, PDI = 1,

$\therefore$ $\overline{M}_w = \overline{M}_n$ and polymer is monodispersed.

For synthetic polymers, PDI > 1,

$\therefore$ $\overline{M}_w > \overline{M}_n$ and polymer is polydispersed.

Note Polymers with narrrow range of molecular masses are called monodisperse and that with wide range are called polydisperse polymers.

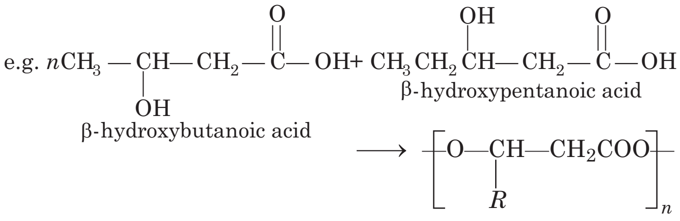
Biodegradable Polymers

The polymers that can be dissociated into small segments by enzymes, (produced by microorganisms) are called **biodegradable polymers**.

These are developed to reduce environmental problems caused by solid non-biodegradable polymer wastes. Chain growth polymers, because of the presence of inert C—C bond (towards enzyme catalysed reactions), usually are non-biodegradable but step growth polymers having functional groups may be biodegradable.

e.g.

(i) **PHBV** (poly-β-hydroxybutyrate-Co-β-hydroxy valerate). It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.

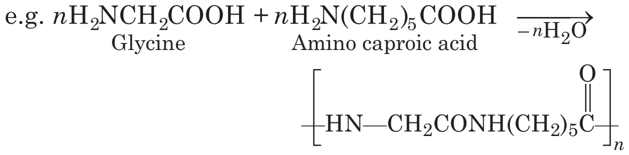


$$\text{e.g. } n\underset{\beta\text{-hydroxybutanoic acid}}{CH_3-\underset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-OH} + \underset{\beta\text{-hydroxypentanoic acid}}{CH_3CH_2\overset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-OH} \longrightarrow \underset{\text{PHBV}}{\left[O-\underset{R}{CH}-CH_2COO\right]_n}$$

(where, $R = CH_3$, C_2H_5 etc.)

β-hydroxybutanoic acid gives stiffness and β-hydroxy pentanoic acid imparts flexibility to PHBV. It is used in orthopaedic devices and in controlled drug release.

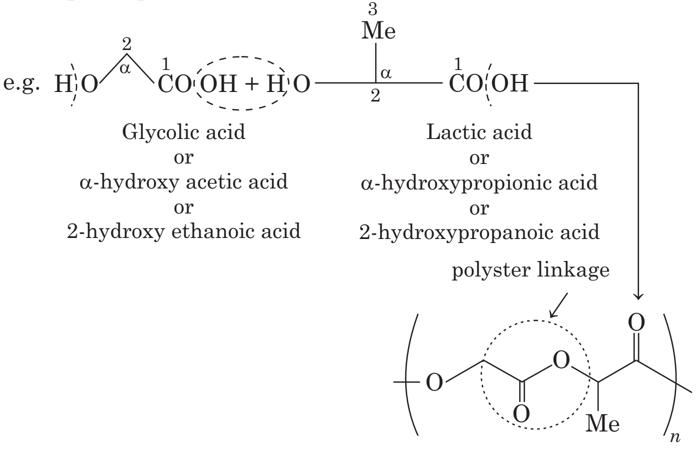
(ii) **Nylon-2-nylon-6** It is a polyamide copolymer of glycine H_2NCH_2 — COOH and amino caproic acid $[H_2N(CH_2)_5COOH]$.



$$\text{e.g. } \underset{\text{Glycine}}{nH_2NCH_2COOH} + \underset{\text{Amino caproic acid}}{nH_2N(CH_2)_5COOH} \xrightarrow[-nH_2O]{} \left[HN-CH_2CONH(CH_2)_5\overset{O}{\overset{\|}{C}}\right]_n$$

Nylon-2-nylon-6

(iii) **Polyglycolic acid and polyacetic acid** It is commercially successful biodegradable polymers such as sutures. Dextron was the first bioabsorbable or biodegradable suture prepared from the biodegradable polyesters. It is used for post-operative stitches.



Polyglycolic polyacetic acid

Example 5. *Poly-β-hydroxybutyrate-Co-β-hydroxyvalerate* (PHBV) *is a copolymer of ......*

(a) 3-hydroxybutanoic acid and 2-hydroxypentanoic acid

(b) 2-hydroxybutanoic acid and 3-hydroxypentanoic acid

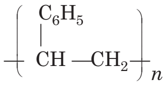
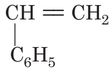
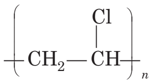
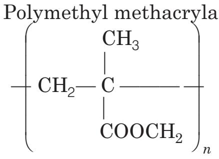
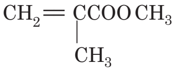
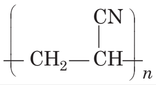
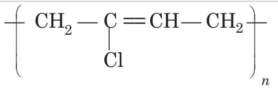
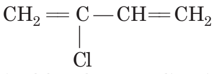
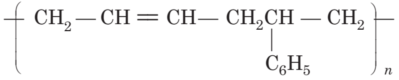
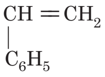
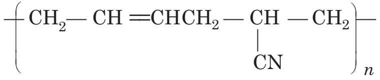
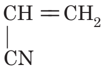
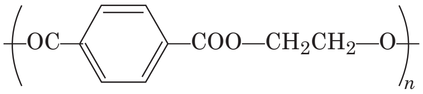
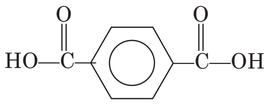
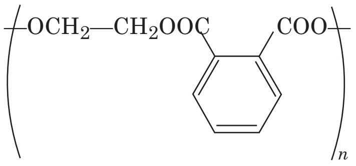
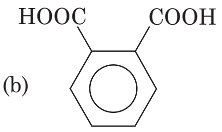
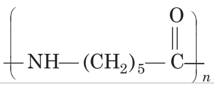
(c) 3-hydroxybutanoic acid and 4-hydroxypentanoic acid

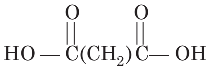
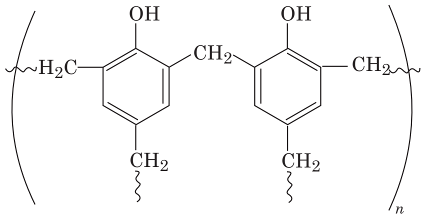
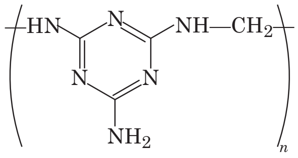
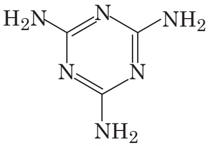
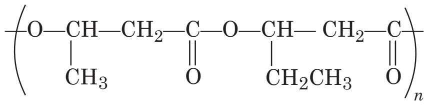
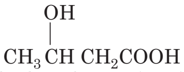
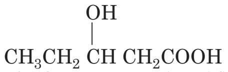
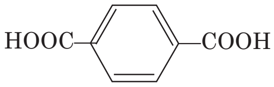
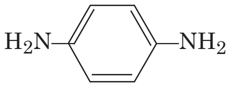
(d) 3-hydroxybutanoic acid and 3-hydroxypentanoic acid

(JEE Main 2019)

Sol. (*d*) Poly-β-hydroxybutyrate-Co-β-hydroxyvalerate (PHBV) is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. It is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.

Polymers (including their structure, monomers, nature of polymer and uses)

S.No.	Polymer name and structure	Monomer	Nature of polymer	Uses
1.	Polythene $+\!\left(CH_2-CH_2\right)\!+_n$	$CH_2=CH_2$ (Ethene)	Addition homopolymer	As insulator, anticorrosive, packing material, for household and laboratory wares.
2.	Polystyrene  $\left(\underset{}{\overset{C_6H_5}{\overset{\vert}{CH}}}-CH_2\right)_n$	 $\underset{\underset{C_6H_5}{\vert}}{CH}=CH_2$ (Styrene)	Addition homopolymer	As insulator, wrapping material, manufacture of toys and household articles.
3.	Polyvinyl chloride (PVC)  $\left(CH_2-\overset{Cl}{\overset{\vert}{CH}}\right)_n$	$CH_2=CHCl$ (Vinyl chloride)	Addition homopolymer	In manufacture of raincoats, hand bags, vinyl flooring and leather clothes.
4.	Polytetrafluoro ethylene (PTFE) or teflon $+\!\left(CF_2-CF_2\right)\!+_n$	$CF_2=CF_2$ (Tetra fluoroethene)	Addition homopolymer	As lubricant, insulator and in making cooking wares.
5.	Polymethyl methacrylate (PMMA or Plexi glass)  $\left(CH_2-\underset{\underset{COOCH_2}{\vert}}{\overset{CH_3}{\overset{\vert}{C}}}-\right)_n$	 $CH_2=\underset{\underset{CH_3}{\vert}}{C}COOCH_3$ (Methyl methacrylate)	Addition homopolymer	As substitute of glass and making decorative materials.
6.	Polyacrylonitrile (Orlon)  $\left(CH_2-\overset{CN}{\overset{\vert}{CH}}\right)_n$	$CH_2=CHCN$ (Vinyl cyanide)	Addition homopolymer	In making synthetic fibres and synthetic wool.
7.	Neoprene  $\left(CH_2-\underset{\underset{Cl}{\vert}}{C}=CH-CH_2\right)_n$	 $CH_2=\underset{\underset{Cl}{\vert}}{C}-CH=CH_2$ (2-chloro-but-1,3 -diene)	Addition homopolymer	As insulator, making conveyor belts and printing rollers.
8.	Buna-S (Styrene-butadiene rubber, SBR)  $\left(CH_2-CH=CH-CH_2\underset{\underset{C_6H_5}{\vert}}{CH}-CH_2\right)_n$	(a) $CH_2=CH-CH=CH_2$ (Buta-1,3-diene) (b)  $\underset{\underset{C_6H_5}{\vert}}{CH}=CH_2$ (Styrene)	Addition copolymer	In making automobile tyres, footwear and bubble gums.
9.	Buna-N (nitrile rubber, NBR)  $\left(CH_2-CH=CHCH_2-\underset{\underset{CN}{\vert}}{CH}-CH_2\right)_n$	(a) $CH_2=CH-CH=CH_2$ (Buta-1,3-diene) (b)  $\underset{\underset{CN}{\vert}}{CH}=CH_2$ (Styrene)	Addition copolymer	In making oil seals, manufacture of hoses and tank linings.
10.	Terylene or dacron 	(a) $HO-CH_2-CH_2-OH$ (Ethylene glycol or (ethane-1,2-diol) (b)  (Terephthalic acid) or (benzene-1,4-dicarboxylic acid)	Codensation or step growth copolymer, linear polymer	For making wash and wear fabrics, tyres cords, safety belts, tents, sea belts and sails.
11.	Glyptal or alkyl resin 	(a) $HO-CH_2-CH_2-OH$ Ethylene glycol (b)  (Phthalic acid)	Condensation copolymer, thermoplastic	As binding material in preparation of mixed plastics and paints.
12.	Nylon-6 or perlon  $\left(NH-(CH_2)_5-\overset{O}{\overset{\Vert}{C}}\right)_n$	Caprolactam	Condensation homopolymer, linear polymer	In making fibres, plastics, tyre cords and ropes.

S.No.	Polymer name and structure	Monomer	Nature of polymer	Uses
13.	Nylon-6, 6 $-\!\!\left(NH(CH_2)_6NHCO(CH_2)_4CO\right)\!\!-_n$	(a)  $HO-\overset{O}{\overset{\Vert}{C}}(CH_2)\overset{O}{\overset{\Vert}{C}}-OH$ (Adipic acid) (b) $H_2N-(CH_2)_6-NH_2$ (Hexamethylene diamine)	Condensation copolymer, linear polymer	In making bristles for brushes, synthetic fibres, parachutes, ropes and carpets, as a substitute for metal in bearings and gears. Crincked nylon is used for making elastic hosiery.
14.	Bakelite 	(a) HCHO (Formaldehyde) (b) C_6H_5OH (Phenol)	Condensation copolymer, cross-link or network polymer, thermosetting polymer	For making gears, protective coating and electrical fittings.
15.	Urea formaldehyde resin $-\!\!\left(NHCO-NH-CH_2\right)\!\!-_n$	(a) HCHO (Formaldehyde) (b) NH_2CONH_2 (Urea)	Condensation copolymer	For making unbreakable cups and laminated sheets.
16.	Melamine-formaldehyde resin or melmac 	(a)  (Melamine) (b) HCHO (Formaldehyde)	Condensation copolymer, highly branched thermosetting polymer	In making plastic crockery, unbreakable cups and plates.
17.	Poly-β-hydroxy butyrate-Co-β-hydroxy valerate (PHBV) 	(a)  $CH_3\overset{OH}{\overset{\vert}{C}H}CH_2COOH$ (β-hydroxybutanoic acid) (b)  $CH_3CH_2\overset{OH}{\overset{\vert}{C}H}CH_2COOH$ (β-hydroxypentanoic acid)	Condensation copolymer, biodegradable polymer	As packaging material in orthopaedic devices and for controlled drug release.
18.	Kevlar (nylon polymer)	(a)  (Terephthalic acid) (b)  (1,4-diaminobenzene)	Condensation copolymer	For making bullet proof vests.
19.	Lexan or polycarbonate (polyester)	(a) Diethyl carbonate (b) Bisphenol-*A*	Condensation copolymer	In making bullet proof windows and safety helmets.
20.	Polyurethanes	(a) Toluene di-isocyanate (b) Ethylene glycol	Condensation copolymer	For making washable and long lasting mattresses, cushions.
21.	VINYON	(a) $CH_2=CHCl$ (Vinyl chloride 90%) (b) $CH_2=CHCOOCH_3$ (Vinyl acetate (10%))	Addition copolymer	
22.	DYNEL	(a) Acrylonitrile (b) Vinyl chloride	Copolymer	For making synthetic hair wigs.
23.	SARAN	(a) Vinyl chloride (b) Vinylidine chloride ($CH_2=CCl_2$)	Copolymer	For wrapping food materials.
24.	ABS rubber	(a) Acrylonitrile (b) Buta-1,3-diene (c) Styrene	Copolymer	Bumpers, crash helmets, telephones, luggage.

Practice Exercise

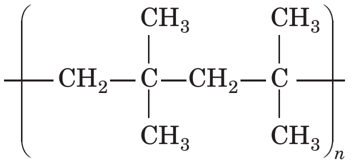
ROUND I Topically Divided Problems

General Items Related to Polymers and its Classification

1. A high molecular weight molecule, made up of a large number of smaller units, is known as
(a) monomer (b) macromolecule
(c) polymer (d) Both (b) and (c)

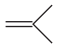
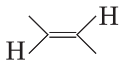
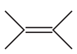
2. With increase in which of the following factors, tensile strength of a polymer increases?
(a) Crystallinity (b) Melting point
(c) Molecular weight (d) All of these

3. Which is not true about polymers?
(a) Polymers have high viscosity
(b) Polymers scatter light
(c) Polymers do not carry any charge
(d) Polymers have low molecular weight

4. 

$$\left(-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}- \right)_n$$

is a polymer having monomer units. *(NCERT Exemplar)*

(a) 
(b) 
(c) 
(d) 

5. Which factor imparts crystalline nature to a polymer like nylon? *(NCERT Exemplar)*
(a) Hydrogen bonding (b) Covalent bonding
(c) Ionic bonding (d) All of these

6. Which of the following polymers of glucose is stored by animals? *(NCERT Exemplar)*
(a) Cellulose (b) Amylose
(c) Amylopectin (d) Glycogen

7. Teflon is an example of polymer which is a/an
(a) polyamide (b) addition polymer
(c) polyester (d) formaldehyde resin

8. Which of the following are addition polymers?
(a) Nylon *(NCERT Exemplar)*
(b) Melamine formaldehyde resin
(c) Orlon
(d) All of the above

9. Which of the following polymers are condensation polymers? *(NCERT Exemplar)*
(a) Bakelite (b) Teflon
(c) Butyl rubber (d) None of these

10. Which among the following is step-growth polymer?
(a) PTFE (b) PVC
(c) Polyester (d) Polythene

11. Which of the following is an elastomer?
(a) Vulcanised rubber (b) Dacron
(c) Polystyrene (d) Malamine

12. Which of the following polymers are used as fibre?
1. Polytetrafluoroethane
2. Polychloroprene
3. Nylon
4. Terylene

The correct answer is *(NCERT Exemplar)*
(a) 1 and 2 (b) 2 and 3
(c) 3 and 4 (d) All of these

13. Nylon-6,6 is not a
(a) condensation polymer (b) polyamide
(c) homopolymer (d) copolymer

14. Thermosetting polymer, bakelite is formed by the reaction of phenol with *(AIEEE 2008, 2011)*
(a) CH_3CH_2CHO (b) CH_3CHO
(c) HCHO (d) HCOOH

15. Which of the following are characteristics of thermosetting polymers? *(NCERT Exemplar)*
(a) Heavily branched cross linked polymers
(b) Linear slightly branched long chain molecules
(c) Become infusible on moulding so cannot be reused
(d) Soften on heating and harden on cooling, can be reused

16. The polymer containing strong intermolecular forces, e.g. hydrogen bonding, is *(AIEEE 2010)*
(a) teflon (b) nylon-6, 6
(c) polystyrene (d) natural rubber

17. Given the polymers,
A = nylon-6, 6; B = buna-S; C = polythene.
Arrange these in increasing order of their intermolecular forces (lower to higher).
(a) $A < B < C$ (b) $B > C > A$
(c) $B < C < A$ (d) $A < C < B$

18. Which of the following polymers can have strong intermolecular forces?
I. Nylon II. Polystyrene
III. Rubber IV. Polyesters
The correct answer is ***(NCERT Exemplar)***
(a) I, IV (b) II, III
(c) I, III (d) All of these

19. The compound which cannot be used as a plasticizer, is
(a) di-*n*-butylphthalate (b) tricresyl phosphate
(c) di-*n*-octyphthalate (d) diethyl phthalate

20. The functionality of propene and adipic acid are respectively. ***(NCERT)***
(a) 1, 1 (b) 0, 1 (c) 0, 2 (d) 1, 2

Types of Polymerisation

21. Low density polythene is prepared by
(a) free radical polymerisation
(b) cationic polymerisation
(c) anionic polymerisation
(d) Ziegler-Natta polymerisation

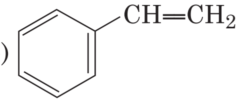
22. The compound that inhibits the growth of polymer chain during vinyl polymerisation, is
(a) carbon tetrachloride (b) *p*-benzoquinone
(c) benzophenone (d) carbon dioxide

23. Polystyrene, dacron and orlon are classified respectively as
(a) chain growth; step growth; step growth
(b) chain growth; chain growth; step growth
(c) chain growth; step growth; chain growth
(d) step growth; step growth; chain growth

24. The best way to prepare polyisobutylene is
(a) coordination polymerisation
(b) cationic polymerisation
(c) anionic polymerisation
(d) free radical polymerisation

25. Arrange the following monomers in order of decreasing ability to undergo cationic polymerisation
I. $NO_2C_6H_5—CH=CH_2$ II.
$CH_2=CH—C_6H_5CH_3$
III. $CH_2=CH—C_6H_5OCH_3$
(a) I > II > III (b) III > II > I
(c) II > I > III (d) I > III > II

26. Which of the following vinyl derivatives is most reactive towards anionic polymerisation?
(a) $CH_2=CHCH_3$ (b) $CH_2=CHC_2H_5$
(c) $CH_2=CHCl$ (d) $CH_2=CHC\equiv N$

27. Which one of the following cannot form addition polymers?
(a) $CH_2=CH_2$ (b) 
(c) $HOOC(CH_2)_4COOH$ (d) None of these

28. Bakelite is a condensation polymer of phenol and formaldehyde. The initial step between the two compounds is an example of
(a) free radical reaction
(b) aldol condensation
(c) aromatic nucleophilic substitution
(d) aromatic electrophilic substitution

29. Monomers are converted to polymer by ***(AIEEE 2002)***
(a) hydrolysis of monomers
(b) condensation reaction between monomers
(c) protonation of monomers
(d) None of the above

30. Condensation polymers are formed from monomers
(a) which have bifunctional groups
(b) which have multiple $(C=C)$ or $(C\equiv N)$ or $(C\equiv C)$ bonds
(c) in which elimination can take place
(d) in which addition can take place

31. Which of the following is a condensation polymer? ***(JEE Main 2019)***
(a) Nylon-6, 6 (b) Neoprene
(c) Teflon (d) Buna-S

32. When two or more chemically different monomers take part in polymerisation, it is called
(a) addition polymerisation
(b) copolymerisation
(c) chain polymerisation
(d) homopolymerisation

33. Number average molecular mass, $\overline{M}_n$ and weight average molecular mass $(\overline{M}_w)$ of synthetic polymers are related as
(a) $\overline{M}_n = (\overline{M}_w)^{1/2}$ (b) $\overline{M}_n = \overline{M}_w$
(c) $\overline{M}_w > \overline{M}_n$ (d) $\overline{M}_w < \overline{M}_n$

34. For natural polymers PDI is generally
(a) 0 (b) 1
(c) 100 (d) 1000

35. The chemical name of isoprene is
(a) 2-methyl-1,3-butadiene (b) 2-chloro-1,3-butadiene
(c) 2-methoxypropene (d) None of these

36. Synthetic polymer that resembles natural rubber is
(a) chloroprene (b) isoprene
(c) neoprene (d) glyptal

37. The correct statement about thiokol rubber is that
(a) it is a natural polysulphide rubber
(b) it is resistant to oils and abrasion
(c) it is prepared by addition polymerisation
(d) All of the above are correct

38. Heating of rubber with sulphur is called
(a) vulcanisation (b) galvanisation
(c) sulphonation (d) bessemerisation

39. Which of the following type of forces are present in vulcanised rubber?
(a) Weakest intermolecular forces
(b) Hydrogen bonding
(c) Three dimensional network of bonds
(d) Metallic bonding

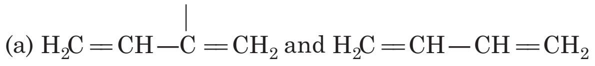
40. By the addition of 3% to 10% sulphur in rubber
(a) soft rubber is obtained
(b) hard rubber is obtained
(c) no change takes place
(d) soluble rubber is obtained

41. The main point of difference between buna-N and buna-S is *(NCERT)*
(a) the former is homopolymer whereas the later is copolymer
(b) former contains buta-1,3-diene but later does not
(c) former contains acrylonitrile but later contains styrene
(d) All of the above

42. Among the following, the wrong statement is
(a) PMMA is plexiglass
(b) SBR is natural rubber
(c) PTFE is teflon
(d) LDPE is low density polythene

43. Vulcanisation makes rubber
I. more elastic
II. soluble in inorganic solvent
III. crystalline
IV. more stiff
The correct options are *(NCERT Exemplar)*
(a) I and IV only (b) I and III only
(c) II and III only (d) II, III and IV only

44. Buna-N synthetic rubber is a copolymer of *(AIEEE 2009)*


(a) $H_2C=CH-\overset{\overset{\large Cl}{|}}{C}=CH_2$ and $H_2C=CH-CH=CH_2$

(b) $H_2C=CH-CH=CH_2$ and $H_5C_6-CH=CH_2$

(c) $H_2C=CH-CN$ and $H_2C=CH-CH=CH_2$


(d) $H_2C=CH-N$ and $H_2C-\underset{\underset{\large CH_3}{|}}{C}=CH_2$

Some Important Polymers

45. In vulcanisation of rubber,
(a) sulphur reacts of form new compound
(b) sulphur cross-links are introduced
(c) sulphur forms a very thin protective layer over rubber
(d) All of the above

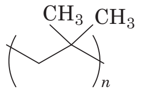
46. The tensile strength, elasticity and resistance to abrasion can be increased by a process called
(a) diazotisation (b) vulcanisation
(c) isomerisation (d) polymerisation

47. Amongst the following the branched chain polymer is
(a) polystyrene (b) low density polythene
(c) high density polythene (d) polyester

48. Which of the following statement is not true about low density polythene? *(NCERT Exemplar)*
(a) Tough
(b) Hard
(c) Poor conductor of electricity
(d) Highly branched structure

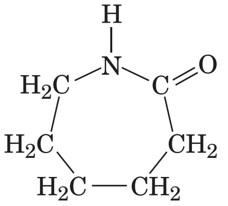
49. The catalyst used in the polymerisation of high density polythene is
(a) titanium oxide
(b) titanium isoperoxide
(c) lithium tetrachloride and triphenyl aluminium
(d) titanium tetrachloride and trimethyl aluminium

50. The correct name of the following polymer is



(JEE Main 2019)
(a) polyisobutane (b) polytert-butylene
(c) polyisoprene (d) polyisobutylene

51. Which of the following polymer can be formed by using the following monomer unit? *(NCERT Exemplar)*



(a) Nylon-6, 6 (b) Nylon 2-nylon-6
(c) Melamine polymer (d) Nylon-6

52. Which of the following polymer is used in the manufacture of wood laminates ? *(JEE Main 2021)*
(a) *cis*-poly isoprene
(b) Melamine formaldehyde resin
(c) Urea formaldehyde resin
(d) Phenol and formaldehyde resin

53. The two monomers for the synthesis of nylon-6, 6 are *(JEE Main 2019)*

(a) $HOOC(CH_2)_4COOH, H_2N(CH_2)_4NH_2$
(b) $HOOC(CH_2)_6COOH, H_2N(CH_2)_4NH_2$
(c) $HOOC(CH_2)_4COOH, H_2N(CH_2)_6NH_2$
(d) $HOOC(CH_2)_6COOH, H_2N(CH_2)_6NH_2$

54. Nylon threads are made up of *(AIEEE 2003)*

(a) polyvinyl polymer
(b) polyester polymer
(c) polyamide polymer
(d) polyethylene polymer

55. Esterification of terephthalic acid with glycol produces

(a) nylon (b) buna rubber
(c) polyurethane (d) terylene

56. Which of the following has an ester linkage?

(a) Nylon-6, 6 (b) Dacron
(c) PVC (d) Bakelite

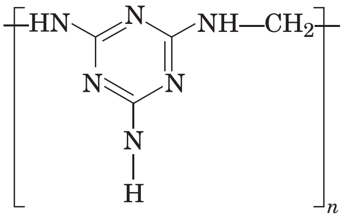
57. Which polymer is used in the manufacture of paints and lacquers? *(JEE Main 2015)*

(a) Bakelite (b) Glyptal
(c) Polypropene (d) Polyvinyl chloride

58. Which of the following polymers does not involve cross-linkages?

(a) Vulcanised rubber (b) Melamine
(c) Bakelite (d) Polystyrene

59. The monomers of the following polymer are



(a) hexamethylenediamine and decanedioic acid
(b) hexamethylenediamine and methanal
(c) melamine and methanal
(d) melamine and ethanal

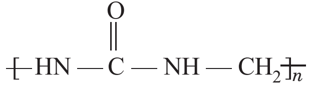
60. In which of the following polymers, empirical formula resembles with monomer?

(a) Bakelite (b) Teflon (c) Nylon-6, 6 (d) Dacron

61. Which of the following is fully fluorinated polymer? *(AIEEE 2005)*

(a) PVC (b) Thiokol
(c) Teflon (d) Neoprene

62. Which of the following compounds is a constituent of the polymer



$\left[HN-\overset{\overset{O}{\|}}{C}-NH-CH_2 \right]_n$? *(JEE Main 2019)*

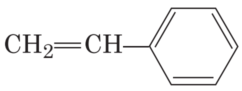
(a) N-methyl urea (b) Methylamine
(c) Ammonia (d) Formaldehyde

63. Monomer of buna-S and nylon-6, respectively are *(JEE Main 2021)*

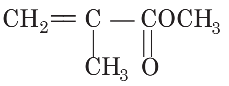
(a) Styrene and caprolactam
(b) Cyclohexane and caprolactam
(c) Ethylene glycol and styrene
(d) Styrene and amino acid

ROUND II Mixed Bag

1. Head-to-tail addition takes place in chain-growth polymerisation when monomer is

(a) 

(b) $CH_2{=}CH{-}CH{=}CH_2$

(c) 

$CH_2{=}\underset{CH_3}{\underset{|}{C}}-\underset{O}{\underset{\|}{C}}OCH_3$

(d) $CH_2{=}CH-C\equiv N$

2. Select the correct statement.

(a) Vinyon is a copolymer of vinyl chloride and vinyl acetate
(b) Saran is a copolymer of vinyl chloride and vinylidene chloride
(c) Butyl rubber is a copolymer of isobutylene and isoprene
(d) All of the above are correct

3. The polymer used in making synthetic hair wigs is made up of

(a) $CH_2{=}CHCl$ (b) $CH_2{=}CHCOOCH_3$
(c) $C_6H_5CH{=}CH_2$ (d) $CH_2{=}CH{-}CH{=}CH_2$

4. Which is a polymer of three different monomers?

(a) ABS (b) SBR
(c) NBR (d) Nylon-2-nylon-6

5. Which pair of polymers have similar properties?

(a) Nylon, PVC (b) PAN,PTFE
(c) PCTFE, PTFE (d) Bakelite, alkyl resin

6. The formation of which of the following polymers involves hydrolysis reaction? *(JEE Main 2017)*

(a) Nylon-6 (b) Bakelite
(c) Nylon-6, 6 (d) Terylene

7. Which of the following monomers form biodegradable polymers?

I. 3-hydroxybutanoic acid + 3-hydroxypentanoic acid
II. Glycine + amino caproic acid
III. Ethylene glycol + pthalic acid
IV. Caprolactum

The correct answer is *(NCERT Exemplar)*

(a) I, II only
(b) II, III only
(c) I, II and III
(d) II, III and IV

8. Which one of the following polymers is not obtained by condensation polymerisation? *(JEE Main 2020)*

(a) Nylon-6, 6
(b) Buna-N
(c) Bakelite
(d) Nylon-6

9. Which of the following polymers have vinylic monomer units? *(NCERT Exemplar)*

(a) Acrilan
(b) Nylon-6
(c) Nylon
(d) Teflon

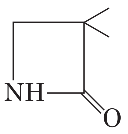
10. Which of the following polymers are thermoplastic? *(NCERT Exemplar)*

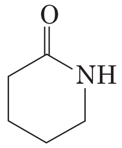
(a) Bakelite
(b) Natural rubber
(c) Neoprene
(d) Polystyrene

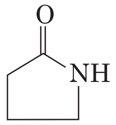
11. Which of the following has been used in the manufacture of non-inflammable photographic films?

(a) Cellulose nitrate
(b) Cellulose xanthate
(c) Cellulose perchlorate
(d) Cellulose acetate

12. Lactam from which nylon-4 is synthesised, is

(a)


(b)


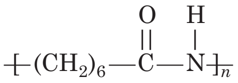
(c)


(d)

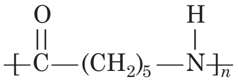

13. Which polymer has 'chiral' monomer(s)?

(a) PHBV
(b) Buna-N *(JEE Main 2020)*
(c) Nylon-6, 6
(d) Neoprene

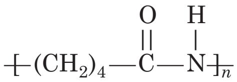
14. The structure of nylon-6 is *(JEE Main 2019)*

(a)


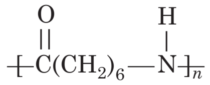
$-\!\left[(CH_2)_6-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}\right]_n$

(b)


$-\!\left[\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_5-\overset{\overset{\displaystyle H}{|}}{N}\right]_n$

(c)


$-\!\left[(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}\right]_n$

(d)


$-\!\left[\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_6-\overset{\overset{\displaystyle H}{|}}{N}\right]_n$

15. Give the decreasing order of reactivities of the following monomers towards cationic addition polymerisation.

I. $MeCH{=}CH_2$
II. $PhCH{=}CH_2$
III. $CH_2{=}CH{-}COOMe$
IV. $CH_2{=}CH{-}Cl$

(a) I > II > III > IV
(b) II > I > IV > III
(c) II > I > III > IV
(d) I > II > IV > III

16. Give the decreasing order of reactivities of the following monomers towards anionic addition polymerisation.

I. $Me{-}CH{=}CH_2$
II. $PhCH{=}CH_2$
III. $CH_2{=}CH{-}CN$
IV. $H_2C{=}CCl_2$
V. $H_2C{=}CF_2$
VI. $F_2C{=}CF_2$

The correct order is

(a) VI > III > V > IV > II > I
(b) VI > V > III > IV > II > I
(c) VI > IV > V > III > II > I
(d) VI > V > IV > II > I > III

17. The correct match between Item - I and Item-II is :

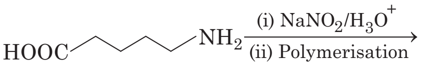
Item - I	Item - II
A. Natural rubber	I. 1,3- butadiene + styrene
B. Neoprene	II. 1,3- butadiene + acrylonitrile
C. Buna -N	III. Chloroprene
D. Buna -S	IV. Isoprene

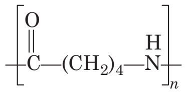
(JEE Main 2020)

Codes

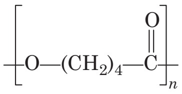
(a) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)
(b) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)
(c) (A)-(IV), (B)-(III), (C)-(II), (D)-(I)
(d) (A)-(IV), (B)-(III), (C)-(I), (D)-(II)

18. The polymer obtained from the following reaction is

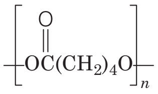


(a)


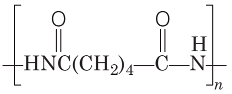
$\left[\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle H}{|}}{N}\right]_n$

(b)


$\left[O-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}\right]_n$

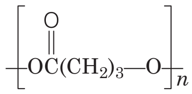
(c)


$\left[O\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_4O\right]_n$

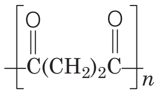
(d)


$\left[HN\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}\right]_n$

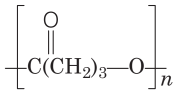
19. The homopolymer formed from 4-hydroxybutanoic acid is **(JEE Main 2019)**

(a) 

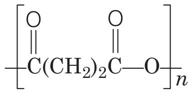
$\left[O\overset{\overset{O}{\|}}{C}(CH_2)_3-O \right]_n$

(b) 

$\left[\overset{\overset{O}{\|}}{C}(CH_2)_2\overset{\overset{O}{\|}}{C} \right]_n$

(c) 

$\left[\overset{\overset{O}{\|}}{C}(CH_2)_3-O \right]_n$

(d) 

$\left[\overset{\overset{O}{\|}}{C}(CH_2)_2\overset{\overset{O}{\|}}{C}-O \right]_n$

20. Which of the following statements about low density polythene is false? **(JEE Main 2016)**

(a) It is a poor conductor of electricity

(b) Its synthesis required dioxygen or a peroxide initiator as a catalyst

(c) It is used in the manufacture of buckets, dustbins etc.

(d) Its synthesis requires high pressure

21. The correct match between Item-I and Item-II is **(JEE Main 2019)**

Item-I	Item-II
A. High density polythene	I. Peroxide catalyst
B. Polyacrylonitrile	II. Condensation at high temperature and pressure
C. Novolac	III. Ziegler-Natta catalyst
D. Nylon-6	IV. Acid or base catalyst

Codes

	A	B	C	D		A	B	C	D
(a)	III	I	IV	II	(b)	IV	II	I	III
(c)	II	I	V	I	(d)	III	I	II	IV

Numeric Value Questions

22. A polydisperse mixture of a polymer can be described by the following composition of molar mass data

(Mass %)	25.0	50.0	25.0
M (kg mol^{-1})	1.00	1.20	1.40

The value of polydispersity index for the mixture is ....× 10^{-2}.

23. A copolymer of ethene and vinyl chloride contains alternate monomers of each type. The mass percentage of vinyl chloride in this polymer is ...... ? (in nearest integer)

24. The contour length (in nm) of a polymer chain modelled as a random coil. with $N = 1000$ and $l = 15$ pm, are closest to .... **(JEE Main 2021)**

25. A polymeric sample in which 10% molecules have a molecular mass 20,000, 30% have 30,000 and the rest 10% have 50,000. The number average molecular weight of this smaple is .... × 10^3.

Answers

Round I

1. (d)	**2.** (c)	**3.** (d)	**4.** (a)	**5.** (a)	**6.** (d)	**7.** (b)	**8.** (c)	**9.** (a)	**10.** (c)
11. (a)	**12.** (c)	**13.** (c)	**14.** (c)	**15.** (a)	**16.** (b)	**17.** (c)	**18.** (a)	**19.** (d)	**20.** (d)
21. (a)	**22.** (b)	**23.** (c)	**24.** (b)	**25.** (b)	**26.** (d)	**27.** (c)	**28.** (d)	**29.** (b)	**30.** (a)
31. (a)	**32.** (b)	**33.** (c)	**34.** (b)	**35.** (a)	**36.** (c)	**37.** (b)	**38.** (a)	**39.** (a)	**40.** (b)
41. (c)	**42.** (b)	**43.** (a)	**44.** (c)	**45.** (b)	**46.** (b)	**47.** (b)	**48.** (b)	**49.** (d)	**50.** (d)
51. (d)	**52.** (c)	**53.** (c)	**54.** (c)	**55.** (d)	**56.** (b)	**57.** (b)	**58.** (d)	**59.** (c)	**60.** (b)
61. (c)	**62.** (d)	**63.** (a)							

Round II

1. (a)	**2.** (d)	**3.** (a)	**4.** (a)	**5.** (c)	**6.** (a)	**7.** (a)	**8.** (b)	**9.** (d)	**10.** (d)
11. (d)	**12.** (c)	**13.** (a)	**14.** (b)	**15.** (b)	**16.** (a)	**17.** (c)	**18.** (b)	**19.** (c)	**20.** (c)
21. (a)	**22.** (1.02)	**23.** (69.02)	**24.** (150)	**25.** (32)					

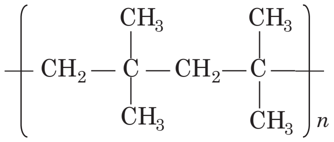
Solutions

Round I

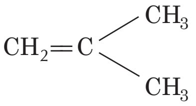
1. A high molecular weight molecule, made up of a large number of smaller units is called polymer and it is also known as macromolecule However, all macromolecules are not polymers.

2. With increase in molecular weight of a polymer, other properties such as tensile strength, crystallinity, melting point etc., also increases.

3. Polymers are large molecules with high molecular weight and a repeating unit. They do not carry any charge. They have high viscosity and can scatter light.

4. 

$$\left[CH_2 - C(CH_3)_2 - CH_2 - C(CH_3)_2 \right]_n$$

is a polymer having monomer units 

$$CH_2{=}C(CH_3)_2$$

5. Strong intermolecular forces like hydrogen bonding lead to close packing of chains that imparts crystalline character.

6. Glycogen is a polymers of glucose, which is stored by animals.

7. Teflon is prepared by the combination of a large number of tetrafluoroethylene molecules, without the elimination of any small molecule. Therefore, it is an example of addition homopolymer.

$$nCF_2{=}CF_2 \longrightarrow \underset{\text{Teflon}}{\left[CF_2 - CF_2 \right]_n}$$

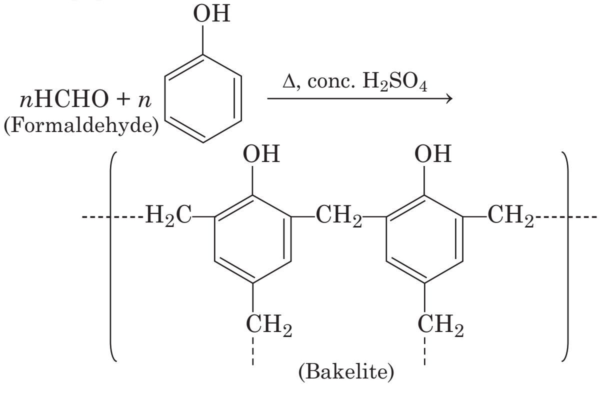
8. Orlon is an addition polymer as its molecular mass is integral multiple of molecular mass of its monomer.

11. Only vulcanised rubber has elastic character, so it is an elastomer.

12. Nylon and terylene are fibres whereas PTFE is a thermoplastic and polychloroprene is an elastomer.

14. Bakelite is a thermosetting plastic formed by reaction of phenol with HCHO in the presence of conc. H_2SO_4.

It is cross-linked polymer, condensation taking place at *o*-and *p*-positions.



(Bakelite)

15. The polymer which become infusible on moulding, i.e. can't be used further and are heavily branched (cross-linked) are called thermosetting ploymers.

17. Buna-S is an elastomer, it has weakest intermolecular forces. Nylon-6,6 is a fibre, it has strong intermolecular forces like H-bonding. Polythene is a thermoplastic polymers, thus the intermolecular forces present in polythene are in between elastomer and fibres.

Thus, the order of intermolecular forces of these polymers is

buna-S < polythene < nylon-6,6

18. Nylon and polyesters have strong intermolecular forces (i.e. hydrogen bonding).

19. Generally high boiling esters or haloalkanes act as plasticizer.

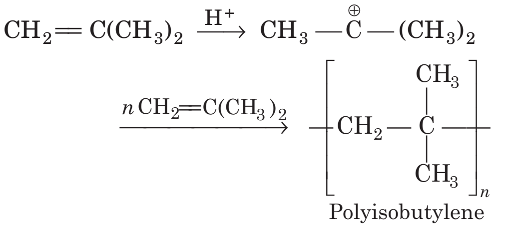
20. Functionality of a monomer means the number of bonding sites present in it. e.g. Functionality of ethene, propene, styrene, acrylonitrile is one and that of ethylene glycol, adipic acid, hexamethylenediamine is two.

21. Ethene on free radical polymerisation gives low density polythene.

22. Certain amines, phenols and quinones are used to inhibit the growth of polymer chain.

23. Polystyrene and orlon, being vinyl derivative, are chain growth polymers while dacron is a step growth polymer.

24. Since, 3° carbocations are most stable, the best way to obtain polyisobutylene is acid catalysed or cationic polymerisation in the presence of Lewis acid or protonic acid.



$$CH_2{=}C(CH_3)_2 \xrightarrow{H^+} CH_3 - \overset{\oplus}{C} - (CH_3)_2 \xrightarrow{n\,CH_2{=}C(CH_3)_2} \underset{\text{Polyisobutylene}}{\left[CH_2 - C(CH_3)_2 \right]_n}$$

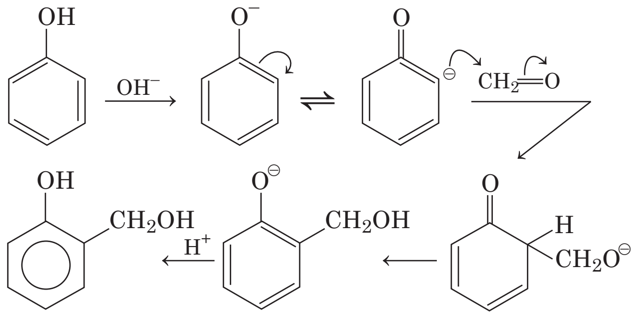
25. Electron releasing groups such as CH_3, $—OCH_3$ activate the monomer towards cationic polymerisation as these groups provide stability to the carbocation formed. Thus, the correct order is

$$CH_2{=}CHC_6H_5(OCH_3) > CH_2{=}CH - C_6H_5(CH_3) > (NO_2)C_6H_5 - CH{=}CH_2$$

26. Electron with drawing groups make the monomer more reactive towards anionic polymerisation.

27. $HOOC(CH_2)_2COOH$ form condensation polymers.

28. It is aromatic electrophilic substitution.



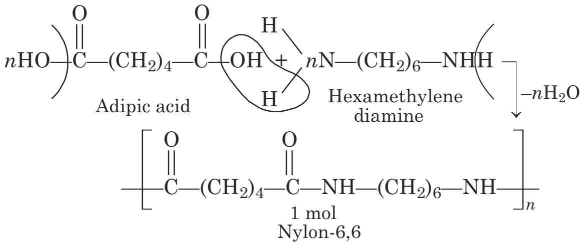
29. Condensation is the process of aggregation of more than one molecule without losing any atom or group (sometimes smaller group or atoms H_2O, R—OH etc., are released).

$$n\,\underset{\text{Monomer}}{CH_2{=}CH_2} \longrightarrow \underset{\text{Polymer}}{—CH_2—(CH_2—CH_2)—CH_2—}$$

30. Condensation polymers one formed from monomers adipic acid and hexamethylenediamine.

$$nNH_2(CH_2)_6NH_2 + _n(CH_2)_4(COOH)_2 \longrightarrow \underset{\text{Nylon-6, 6}}{\left[NH(CH_2)_6NHCO(CH_2)_4CO \right]_n} + nH_2O$$

31. Nylon-6, 6 (an amide) is a condensation copolymer because it is obtained by condensation between adipic acid and hexamethylenediamine.



32. When two or more chemically different monomers take part in polymerisation, it is called copolymerisation.

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

For synthetic polymer, PDI > 1

$\therefore \quad \overline{M}_w > \overline{M}_n$

34. Polydispersity index (PDI) = $\dfrac{\overline{M}_w}{\overline{M}_n}$

For natural polymers, PDI = 1

$\therefore \quad \overline{M}_w = \overline{M}_n$

35. Isoprene is $CH_2{=}C(CH_3)—CH{=}CH_2$ (2-methyl-1, 3-butadiene).

36. Neoprene (synthetic rubber) resembles with natural rubber.

$$\underset{\text{Neoprene}}{\left[CH_2 — CH = C(Cl) — CH_2 \right]_n}$$

$$\underset{\text{Natural rubber}}{\left[CH_2 — CH = C(CH_3) — CH_2 \right]_n}$$

37. Thiokol is a synthetic polysulphide rubber which is obtained by the condensation polymerisation of ethylene dichloride and sodium polysulphide. It is resistant to oils and abrasion.

38. Heating of rubber with sulphur or sulphur compounds at 373 K to 415 K in the presence of ZnO is called vulcanisation.

39. Vulcanised rubber is highly elastic, so intermolecular forces present in it, are weakest.

40. Additon of 3-10% sulphur to rubber, makes it hard.

41. Buna-N and buna-S both are synthetic rubber and copolymers. The difference lies in their compostiion.

Buna-N constituents are buta-1, 3-diene and acrylonitrile.

Buna-S constituents are buta-1, 3-diene and styrene.

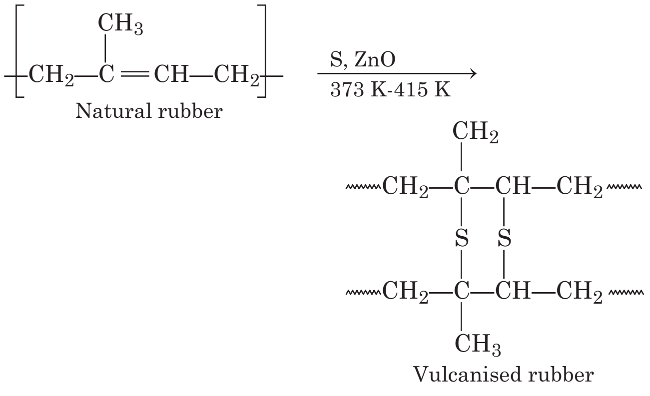
42. SBR (styrene-butadiene) is a synthetic rubber.

43. Vulcanisation makes rubber more elastic and more stiff.

44. Buna-N actually abbreviated from, where Bu represents
1, 3- butadiene, N represents nitrile (acrylonitrile).

Thus, buna-N is copolymer of 1,...3-butadiene and acrylonitrile usually polymerise in the presence of sodium.

45. During vulcanisation process, sulphur cross-links are introduced at the reactive sites of double bonds,



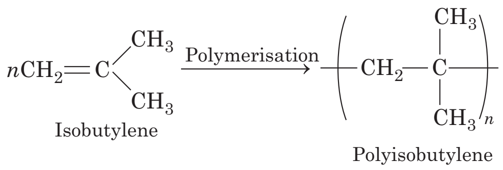
46. Vulcanisation is responsible for tensile strength, elasticity and resistance to abrasion of rubber.

47. Low density polythene is a branched chain polymer.

49. High density polythene is obtained, when ethene undergoes Ziegler-Natta polymerisation. In this process, Ziegler-Natta catalyst, a mixture of titanium tetrachloride ($TiCl_4$) and trimethyl aluminium [$(CH_3)_3Al$] is used to catalyse the polymerisation

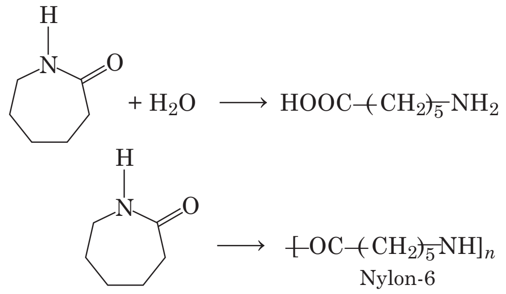
50. The correct name of the given polymer is polyisobutylene. It's monomer unit is isobutylene.

Reaction involved is as follows

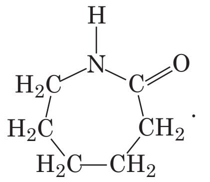


The above reaction proceed *via* addition polymerisation. Polymer is formed by the repeated addition of monomer molecules possessing double bond.

51. Caprolactam is widely used for preparing nylon-6. It is first hydrolysed with water to form amino acid.



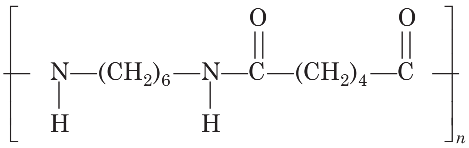
So, it is clear that nylon-6 (polymer) can be formed by the using of the caprolactam



Monomer unit

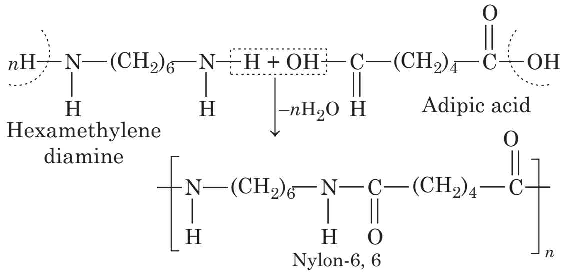
52. Urea -HCHO resin is used in manufacture of wood laminates.

53. Nylon-6, 6 has following structure



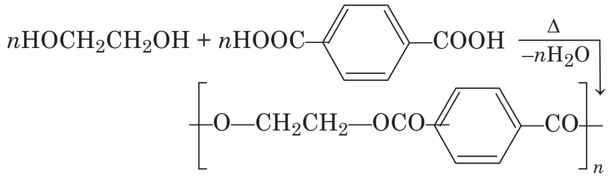
$$\left[-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}- \right]_n$$

As it is a condensation polymer hence, each of its monomeric unit must contain 6 carbon atoms in them. Hence, a combination of adipic acid and hexamethylene diamine is the correct answer. Both of these units react as follows to form nylon-6,6.



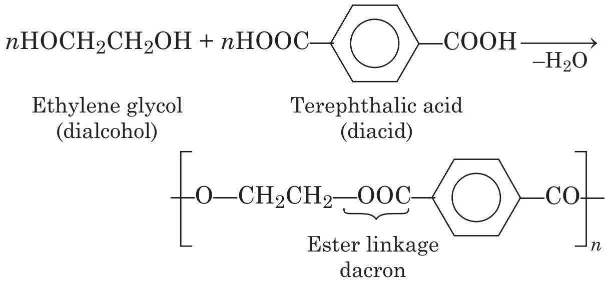
54. Nylon threads are made up of polyamide polymer.

55. Esterification of terephthalic acid with ethylene glycol produces terylene.



Terylene or Dacron

56. When a diacid is condensed with dialcohol, the polymer obtained contains ester linkage.



57. (a) Bakelite is used for making gears, protective coating and electrical fittings.

(b) Glyptal is used in the manufacture of paints and lacquers.

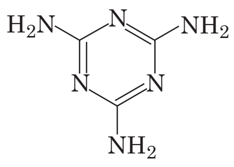
(c) Polypropene is used in the manufacture of textile, packaging materials etc.

(d) Polyvinyl chloride (PVC) is used in the manufacture of rain coats, hand bags, leather clothes etc.

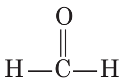
58. Polystyrene contains only linear chains.

59. Break—NH—CH_2 bond and add H_2O to get the structure of monomers.

(a) 2, 4, 6-triamino-1, 3, 5-triazine or melamine



(b) Formaldehyde or methanal (HCHO)



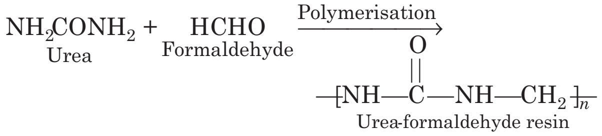
$$H-\overset{O}{\overset{\|}{C}}-H$$

60. In addition homopolymers such as teflon, empirical formula resembles with monomer.

61. Teflon is $-\!\!\left[CF_2-CF_2\right]\!\!-_n$

62. Monomer of $-\!\!\left[NH-\overset{\overset{O}{\|}}{C}-NH-CH_2\right]\!\!-_n$ is formaldehyde.

The polymer is also known as urea-formaldehyde resin. It is made from urea (NH_2CONH_2) and formaldehyde (HCHO).



$$\underset{\text{Urea}}{NH_2CONH_2} + \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{\text{Polymerisation}} \underset{\text{Urea-formaldehyde resin}}{-\!\!\left[NH-\overset{\overset{O}{\|}}{C}-NH-CH_2\right]\!\!-_n}$$

It is used for making unbreakable cups and laminated sheets.

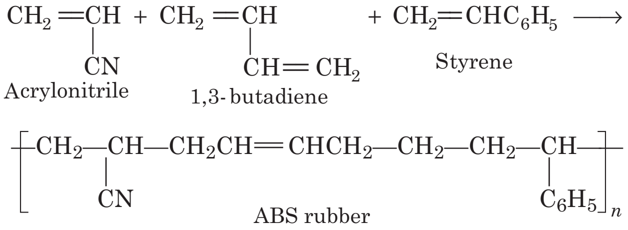
63. Monomer of buna-S is styrene and monomer of nylon-6 is caprolactam.

Round II

1. Vinyl derivatives containing electron donating group readily undergo head to tail addition polymerisation.

3. SARAN, a polymer of vinyl chloride ($CH_2 = CHCl$) and vinylidene chloride is used for making synthetic hair wigs.

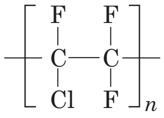
4. ABS is acrylonitrile-butadiene-styrene rubber which is obtained by copolymerisation of acrylonitrile, 1, 3-butadiene and styrene.



$$\underset{\text{Acrylonitrile}}{CH_2=\underset{\underset{CN}{|}}{CH}} + \underset{\text{1,3-butadiene}}{CH_2=\underset{\underset{CH=CH_2}{|}}{CH}} + \underset{\text{Styrene}}{CH_2=CHC_6H_5} \longrightarrow$$

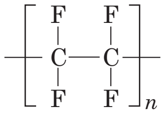
$$\underset{\text{ABS rubber}}{\left[-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2CH=CHCH_2-CH_2-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-\right]_n}$$

5. PCTFE and PTFE both have same carbon backbone.



$$\left[-\underset{\underset{Cl}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\right]_n$$

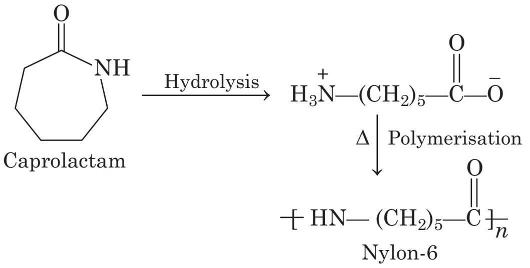
PCTFE (polymenochloro tetrafluoroethylene)



$$\left[-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\right]_n$$

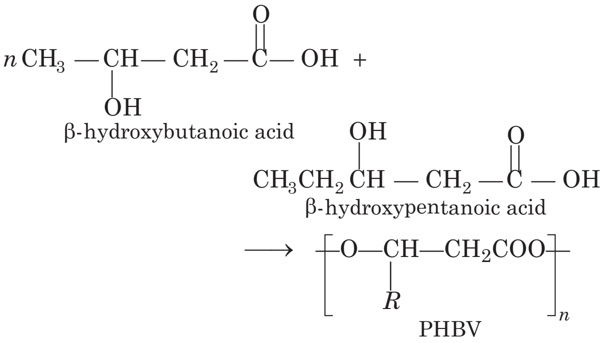
PTFE (polytetrafluoroethylene)

6. Nylon-6 or perlon is prepared by polymerisation of amino caproic acid at high temperature. Caprolactam is first hydrolysed with water to form amino acid which on heating undergoes polymerisation to give nylon-6.



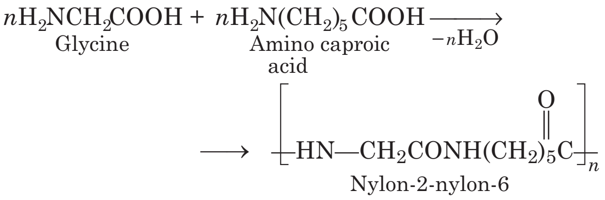
$$\xrightarrow{\text{Hydrolysis}} \overset{+}{H_3N}-(CH_2)_5-\overset{\overset{O}{\|}}{C}-\overset{-}{O} \xrightarrow[\text{Polymerisation}]{\Delta} \underset{\text{Nylon-6}}{-\!\!\left[HN-(CH_2)_5-\overset{\overset{O}{\|}}{C}\right]\!\!-_n}$$

7. Monomers 3-hydroxybutanoic acid and 3-hydroxypentanoic acid react each other and form biodegradable PHBV. Glycine and amino caproic acid also react to form biodegradable polymers nylon-2-nylon-6.



$$\underset{\beta\text{-hydroxybutanoic acid}}{n\,CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-OH} + \underset{\beta\text{-hydroxypentanoic acid}}{CH_3CH_2\overset{\overset{OH}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-OH}$$

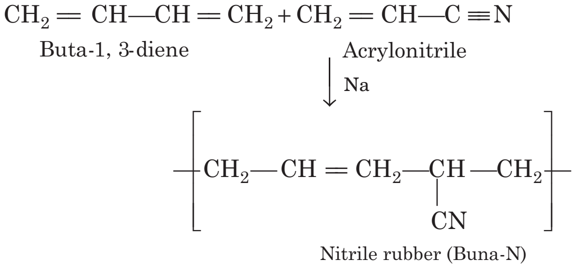
$$\longrightarrow \underset{\text{PHBV}}{\left[-O-\underset{\underset{R}{|}}{CH}-CH_2COO-\right]_n}$$



$$\underset{\text{Glycine}}{nH_2NCH_2COOH} + \underset{\text{Amino caproic acid}}{nH_2N(CH_2)_5COOH} \xrightarrow[-nH_2O]{}$$

$$\longrightarrow \underset{\text{Nylon-2-nylon-6}}{\left[-HN-CH_2CONH(CH_2)_5\overset{\overset{O}{\|}}{C}-\right]_n}$$

8. Buna-N is an addition polymer. It is obtained by copolymerisation of 1, 3-butadiene and acrylonitrile in the presence of a peroxide catalyst.



$$\underset{\text{Buta-1, 3-diene}}{CH_2=CH-CH=CH_2} + \underset{\text{Acrylonitrile}}{CH_2=CH-C\equiv N}$$

$$\Big\downarrow \text{Na}$$

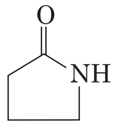
$$\underset{\text{Nitrile rubber (Buna-N)}}{\left[-CH_2-CH=CH_2-\underset{\underset{CN}{|}}{CH}-CH_2-\right]}$$

9. Polystyrene $\left[-\overset{\overset{C_6H_5}{|}}{CH}-CH_2-\right]_n$ and teflon $-\!\!\left[CF_2-CF_2\right]\!\!-_n$ have contains vinylic monomer units.

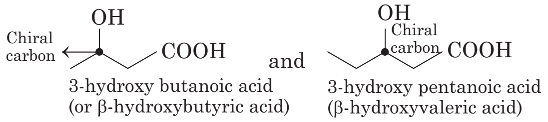
10. Teflon $-\!\left(CF_2-CF_2\right)\!-_n$ polystyrene $\left[-\overset{\overset{C_6H_5}{|}}{CH}-CH_2-\right]_n$ and polythene $-\!\left(CF_2-CF_2\right)\!-_n$ are thermoplastic polymers.

11. Cellulose acetate has been used in the manufacture of non-inflammable photographic films.

12. For the synthesis of nylon-4, lactam with four carbon atoms is required.



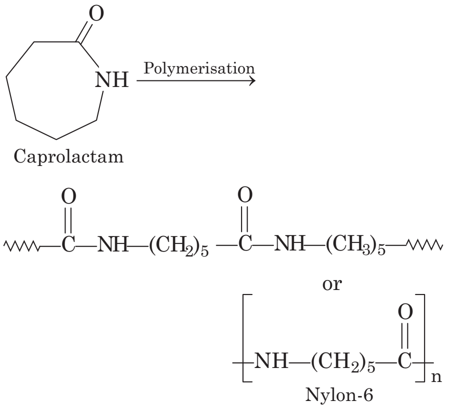
13. PHBV, (Poly 3- hydroxybutyrate -Co-3-hydroxyvalerate) is a copolymer of



In both monomers, there is one chiral centre (shown by dark spot).

∴ Polymer contains chiral monomers.

14.



Nylon-6 is prepared by ring opening polymerisation of caprolactam. It is heated about 533 K in an inert atmospheric nitrogen about 4-5 hrs. Nylon-6 fibres are tough, possessing high tensile strength, as well as elasticity and lustre.

They are wrinkle proof and highly resistant to abrasion and chemicals such as acids and alkalis.

15. Cationic polymerisation is favoured by the presence of electron donating group (e.g. Me group). More the electron donating group, the more stable is the intermediate carbocation formed and as a result more favoured is the cationic polymerisation.

Stability of ($-\!\!\!<\!C^{\oplus}$) is

II. $\mathrm{Ph} \rightarrow \mathrm{CH{=}CH_2} \xrightarrow{H^{\oplus}} \mathrm{Ph}-\overset{\oplus}{\mathrm{C}}\mathrm{H}-\mathrm{CH_3}$

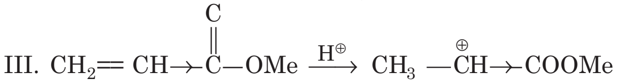
(+*R* and –*I* effects of Ph)

I. $\mathrm{Me} \rightarrow \mathrm{CH{=}CH_2} \xrightarrow{H^{\oplus}} \mathrm{Me}-\overset{\oplus}{\mathrm{C}}\mathrm{H}-\mathrm{CH_3}$

(+*I* effect of Me)

IV. $\mathrm{:\ddot{C}l} \leftarrow \mathrm{CH{=}CH_2} \xrightarrow{H^{\oplus}} \mathrm{Cl} \leftarrow \overset{\oplus}{\mathrm{C}}\mathrm{H}-\mathrm{CH_3}$

(–*I* and +*R* effects of Cl)



III. $\mathrm{CH_2{=}CH} \rightarrow \overset{\overset{\textstyle C}{\|}}{\mathrm{C}}-\mathrm{OMe} \xrightarrow{H^{\oplus}} \mathrm{CH_3}-\overset{\oplus}{\mathrm{C}}\mathrm{H} \rightarrow \mathrm{COOMe}$

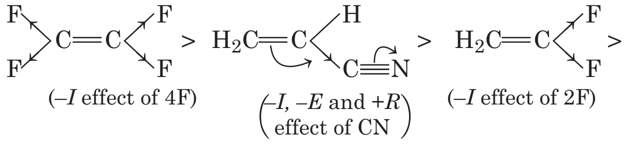
(–*I* effect of COOMe)

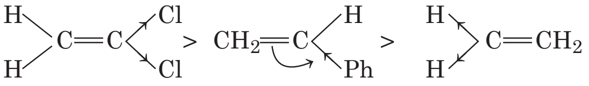
The decreasing reactivity order towards cation polymerisation is II > I > IV > III.

16. Anionic polymerisation is favoured by the presence of electron withdrawing group (e.g. —*X*, —COO*R*, —CN, etc.).

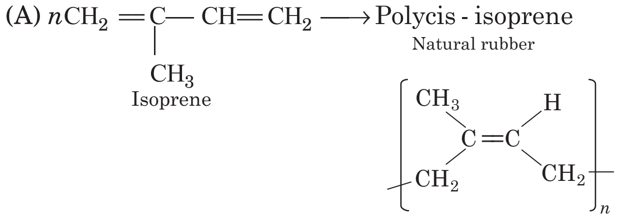
More the electron withdrawing group, more stable is the intermediate carbanion formed and consequently more favoured is the anionic polymerisation.

Stability of ($-\!\!\!<\!C^{\ominus}$) is





17. (A)

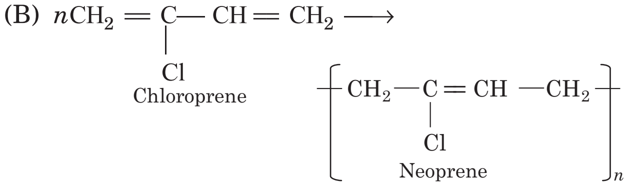


$n\mathrm{CH_2{=}\underset{\underset{\textstyle CH_3}{|}}{C}-CH{=}CH_2} \longrightarrow$ Polycis - isoprene

Isoprene

Natural rubber

(B)

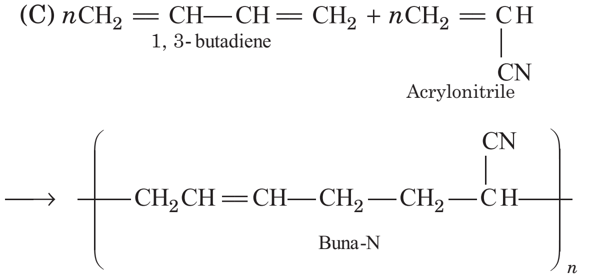


$n\mathrm{CH_2{=}\underset{\underset{\textstyle Cl}{|}}{C}-CH{=}CH_2} \longrightarrow \left[\mathrm{CH_2-\underset{\underset{\textstyle Cl}{|}}{C}{=}CH-CH_2}\right]_n$

Chloroprene

Neoprene

(C)



$n\mathrm{CH_2{=}CH-CH{=}CH_2} + n\mathrm{CH_2{=}\underset{\underset{\textstyle CN}{|}}{C}H}$

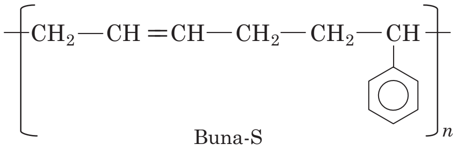
1, 3- butadiene

Acrylonitrile

$\longrightarrow \left(\mathrm{CH_2CH{=}CH-CH_2-CH_2-\overset{\overset{\textstyle CN}{|}}{C}H}\right)_n$

Buna-N

(D) 1, 3-butadiene + styrene reaction.

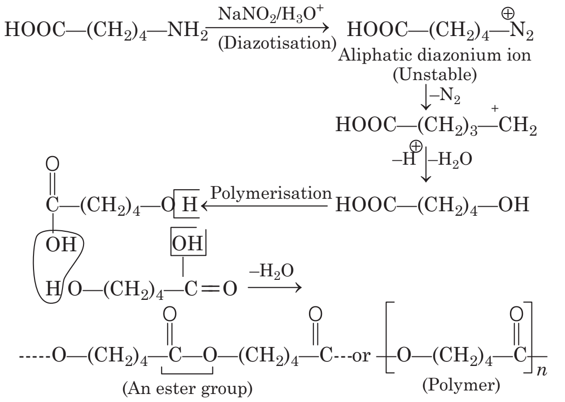


Correct match is
(A) – (IV), (B) – (III), (C) – (II), (D) – (I)

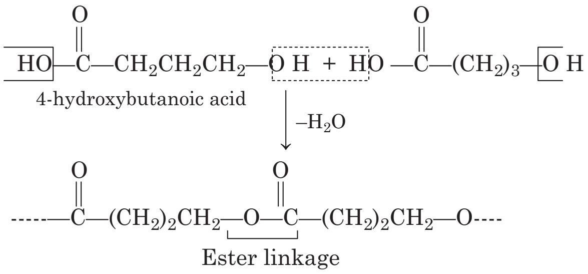
Hence, option (c) is correct match.

18. Given amino acid on reaction with $NaNO_2/H_3O^+$ gives diazotisation reaction which further evolves —N_2 gas along with formation of carbocation.

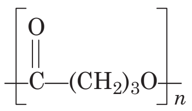
On further reaction with water, it form $HOOC—(CH_2)—OH$ that undergoes polymerisation to give polymer.



19. On polymerisation, 4-hydroxybutanoic acid will produce a condensation homopolymer by loss of H_2O molecules.



The homopolymer obtained can also be represented as



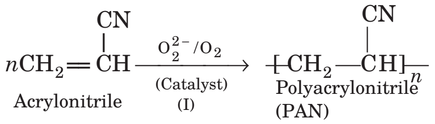
$$\left[\overset{\overset{\displaystyle O}{\|}}{C}—(CH_2)_3O\right]_n$$

20. High density polythene is used in the manufacture of buckets, dustbins etc.

21. (A)

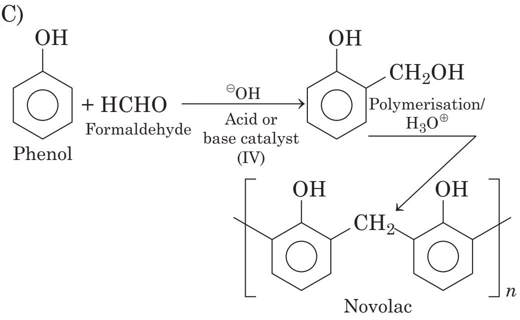
$$n\underset{\text{Ethylene}}{CH_2{=}CH_2} \xrightarrow[\text{Ziegler-Natta catalyst (III)}]{[TiCl_4+(C_2H_5)_3Al]} \underset{\text{High density polythene (HDPE)}}{+CH_2+_n}$$

(B)

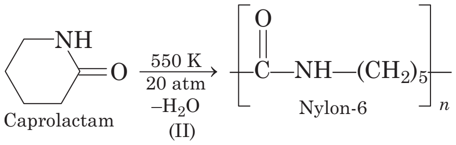


$$n\underset{\text{Acrylonitrile}}{CH_2{=}\overset{\overset{\displaystyle CN}{|}}{CH}} \xrightarrow[\text{(Catalyst) (I)}]{O_2^{2-}/O_2} \underset{\text{Polyacrylonitrile (PAN)}}{+CH_2—\overset{\overset{\displaystyle CN}{|}}{CH}+_n}$$

(C)



(D)



Thus, the correct match is as follows
(A) → (III), (B) → (I), (C) → (IV), (D) →(II)

22.

$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \qquad \text{...(i)}$$

and

$$\overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} \qquad \text{...(ii)}$$

Each of the mass% values must be converted to value of N_i. Assuming 100.0 g of the mixture, the amounts of each polymer are

$$\text{Moles} = \frac{\text{Weight } (w)}{\text{Molecular mass } (M)}$$

$$N_1 = \frac{25}{1000} = 2.50 \times 10^{-2} \text{ mol}$$

$$N_2 = \frac{50}{1200} = 4.17 \times 10^{-2} \text{ mol}$$

$$N_3 = \frac{25}{1400} = 1.79 \times 10^{-2} \text{ mol}$$

Substituting the values in Eq. (i) and (ii), we get

$$\overline{M}_n = \frac{\begin{bmatrix}(2.50 \times 10^{-2} \text{ mol})(1.00 \text{ kg mol}^{-1}) \\ + (4.17 \times 10^{-2} \text{ mol})(1.20 \text{ kg mol}^{-1}) \\ + (1.79 \times 10^{-2} \text{ mol})(1.40 \text{ kg mol}^{-1})\end{bmatrix}}{2.50 \times 10^{-2} \text{ mol} + 4.17 \times 10^{-2} \text{ mol} + 1.79 \times 10^{-2} \text{ mol}}$$

$$= 1.18 \text{ kg mol}^{-1}$$

$$\overline{M}_w = \frac{\begin{bmatrix}(2.50\times 10^{-2}\text{ mol})(1.00)^2 + (4.17\times 10^{-2})\ (1.20)^2\\ + (1.79\times 10^{-2})(1.40)^2\text{ kg}^2\text{ mol}^{-1}\end{bmatrix}}{\begin{bmatrix}(2.50\times 10^{-2})(1.00)\ + (4.17\times 10^{-2})(1.20)\\ + (1.79\times 10^{-2})(1.40)\end{bmatrix}\text{kg}}$$

$$= 1.20\text{ kg mol}^{-1}$$

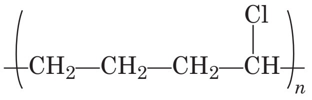
Polydispersity index = $\overline{M}_w/\overline{M}_n$.

Substituting the results gives

$$\text{Polydispersity index} = \frac{1.20\text{ kg mol}^{-1}}{1.18\text{ kg mol}^{-1}} = 1.02$$

23. The structure of copolymer is

$$n(CH_2{=}CH_2) + n(CH_2{=}CHCl) \longrightarrow$$



$$-\!\!\left(CH_2{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle Cl}{|}}{CH}\right)\!\!-_n$$

Molecular mass of ethene = 28.05 g/mol

Molecular mass of vinyl chloride = 62.5 g/mol

Empirical formula mass of copolymer

$$= 28.05 + 62.5$$
$$= 90.55$$

Mass percentage of vinyl chloride in the copolymer

$$= \frac{62.5\times 100}{90.55} = 69.02$$

24. Formula of contour length = $N.\ l$

$$= 1000\times 10^{-3}\times 150 = 150\text{ pm}$$

25. Number average molecular weight

$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

$= 10\,(20000) + 30\,(30000) + 10\,(50000)/10 + 10 + 30$

$= 32000$ or 32×10^3