POLYMERS

1.1 Polymers

The word 'polymer' is coined from two Greek words : poly means many and mer means unit or part. The term polymer is defined as very large molecules having high molecular mass. These are also referred to as **macromolecules**

1.2 Monomers

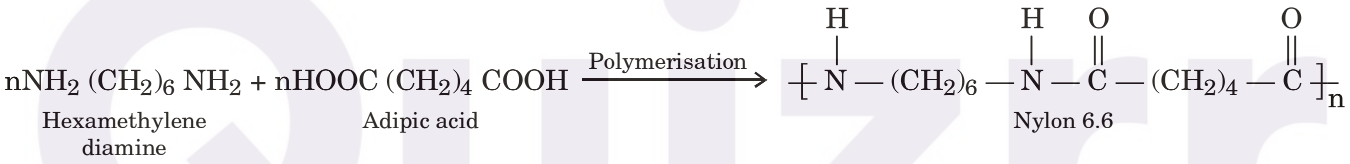
The repeating structural units are derived from some simple and reactive molecules known as monomers. They are linked to each other by covalent bonds.

1.3 Polymerisation

This process of formation of polymers from respective monomers is called **polymerisation.**

Examples :

$$\underset{\text{Ethene}}{nCH_2 = CH_2} \xrightarrow{\text{Polymerisation}} \underset{\text{Repeating unit}}{n\left[CH_2 - CH_2\right]} \longrightarrow \underset{\text{Polythene polymer}}{\left[CH_2 - CH_2\right]_n}$$



$$\underset{\text{Hexamethylene diamine}}{nNH_2(CH_2)_6NH_2} + \underset{\text{Adipic acid}}{nHOOC(CH_2)_4COOH} \xrightarrow{\text{Polymerisation}} \underset{\text{Nylon 6.6}}{\left[\overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}}\right]_n}$$

Classification Of Polymers

There are several ways of classification of polymers based on some special considerations. The following are some of the common classifications of polymers:

(I) Classification based upon source

Under this type of classification, there are three sub categories.

1. Natural polymers

These polymers are found in plants and animals. Examples are proteins, cellulose, starch, resins and rubber.

2. Semi-synthetic polymers

Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are the usual examples of this sub category.

3. Synthetic polymers

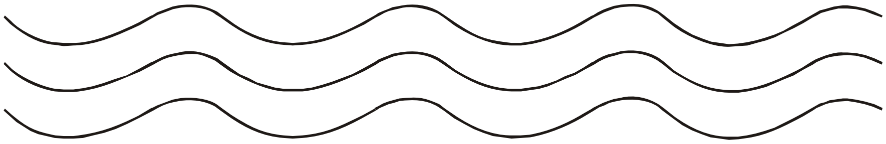
A variety of synthetic polymers as plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna - S) are examples of manmade polymers extensively used in daily life as well as in industry.

(II) Classification based upon structure

There are three different types based on the structure of the polymers.

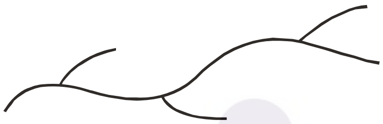
(i) Linear polymers

These polymers consist of long and straight chains. The examples are high density polythene, polyvinyl chloride, etc. These are represented as :



(ii) Branched chain polymers

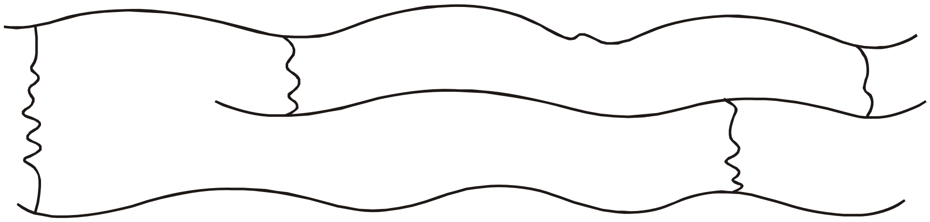
These polymers contain linear chains having some branches, e.g., low density polythene. These are depicted as follows :



Examples are glycogen, low density polyethylene, etc.

(iii) Cross linked or Network polymers

These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains, e.g. bakelite, melamine, etc. These polymers are depicted as follows :



(III) Classification based upon synthesis

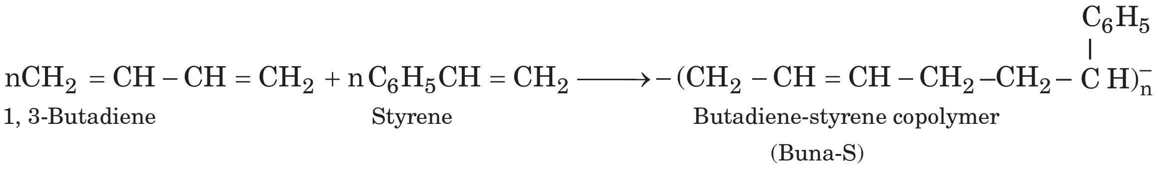
(i) **Addition polymers :**

monomer molecules possessing double or triple bonds, e.g., the formation of polythene from ethene and polypropene from propene. However, the addition polymers formed by the polymerisation of a single monomeric species are known as homopolymers, e.g., polythene.

$$nCH_2 = CH_2 \longrightarrow -(CH_2 - CH_2)_n - \text{Homopolymer}$$

Ethene Polythene

The polymers made by addition polymerisation from two different monomers are termed as copolymers, e.g., Buna-S, Buna-N, etc.

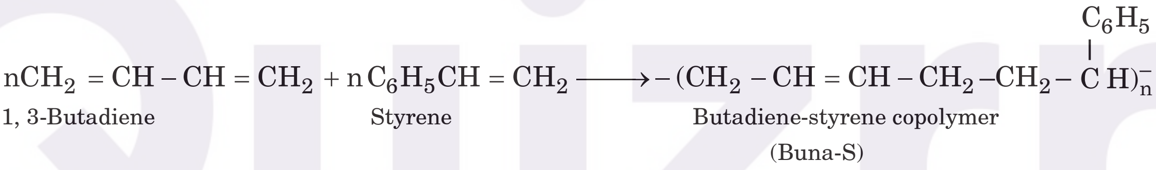


$$nCH_2 = CH - CH = CH_2 + nC_6H_5CH = CH_2 \longrightarrow -(CH_2 - CH = CH - CH_2 - CH_2 - \overset{C_6H_5}{\overset{|}{C}}H)_n^-$$

1, 3-Butadiene Styrene Butadiene-styrene copolymer (Buna-S)

(ii) Condensation polymers

The condensation polymers are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units. In these polymerisation reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place. The examples are terylene (dacron), nylon 6,6, nylon 6, etc. For example, nylon 6,6 is formed by the condensation of hexamethylene diamine with adipic acid.



$$nCH_2 = CH - CH = CH_2 + nC_6H_5CH = CH_2 \longrightarrow -(CH_2 - CH = CH - CH_2 - CH_2 - \overset{C_6H_5}{\overset{|}{C}}H)_n^-$$

1, 3-Butadiene Styrene Butadiene-styrene copolymer (Buna-S)

(IV) Classification based on inter-molecular forces (secondary forces)

1. Elastomers

Elastomers are polymers in which the polymer chains are held by weakest intermolecular forces. These forces permit the polymers to be stretched. A few cross links are introduced between the chains to help the polymer retract to its original position after the force is released.

Example : Vulcanized rubber

2. Fibers

These polymers possess high tensile strength and high modulus, because of strong intermolecular forces like hydrogen bonding which operate in polyamides. These strong forces also lead to close packing of chains and thus impart crystalline nature. As a result these polymers show sharp melting points. These polymers are used for making fibers.

Examples : Nylon and terylene

3. **Thermoplastics**

   In thermoplastics, the intermolecular forces are intermediate between elastomers and fibers and the polymer chain has no cross-links.

   Thus thermoplastics can be moulded on heating. These polymers have no cross-linking between chains.

   Examples : Polyethylene, polystyrene etc.

4. **Thermosetting polymers**

   Polymers which become hard on heating are called thermo setting polymers. Thermo setting polymers can be heated only once when it permanently sets into a solid, which cannot be remelted by heating.

   Thermosetting polymers made from relatively low molecular mass semi-fluid polymers which when heated in a mould forms an insoluble hard mass which is infusible. This is due to extensive crosslinks between the different polymer chains forming three dimensional network of bonds.

   Example : Bakelite and melamine

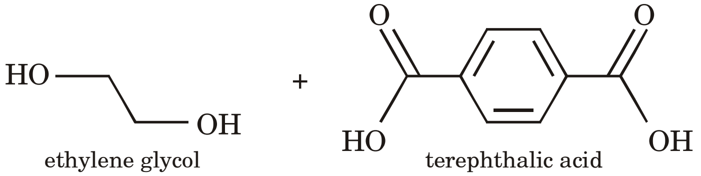
Polymerization, the joining together of many small molecules to form very large molecules. The simple compounds from which polymers are made are called monomers.

Polymers are formed in two general ways.

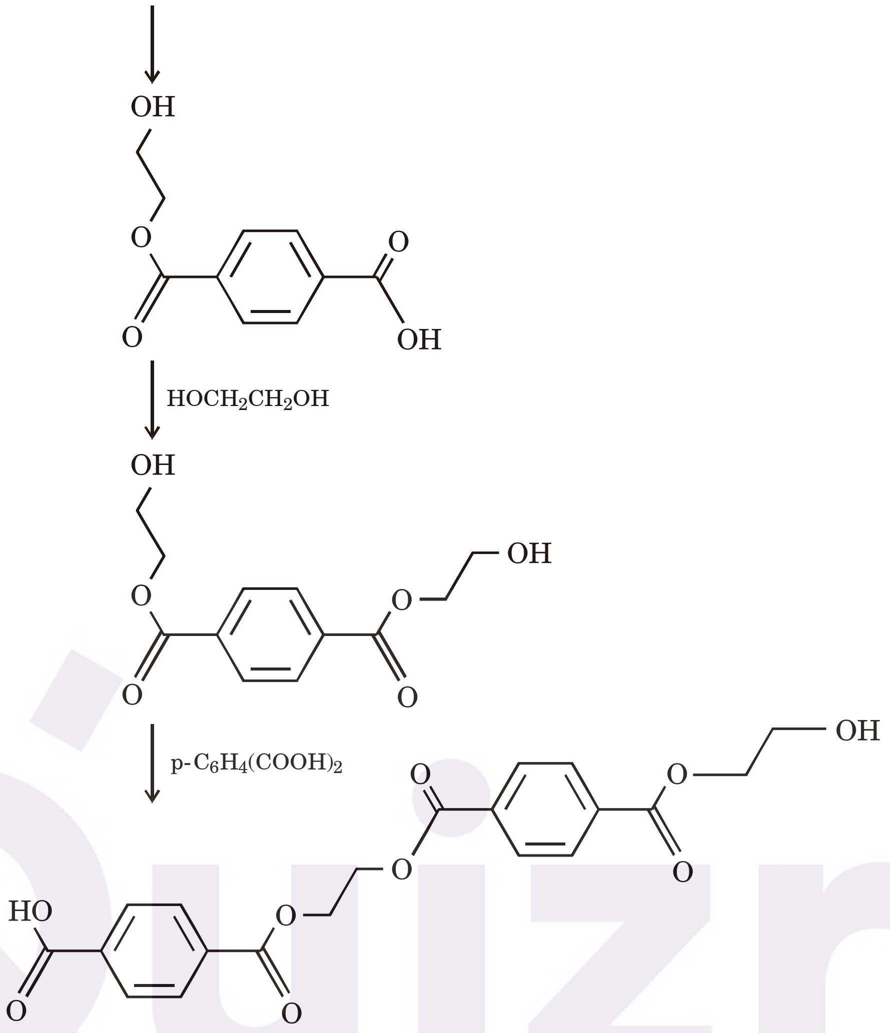
(a) In **chain-reaction polymerization,** there is a series of reactions each of which consumes a reactive particle and produces another, similar particle; each individual reaction thus depends upon the previous one. The reactive particles can be free radicals, cations, or anions. A typical example is the polymerization of ethylene. Here the chain-carrying particles are free radicals, each of which adds to a monomer molecule to form a new, bigger free radical.

$$\text{Rad.} + CH_2=CH_2 \longrightarrow \text{Rad } CH_2CH_2. \xrightarrow{CH_2=CH_2} \text{Rad}CH_2CH_2CH_2CH_2. \longrightarrow \text{etc.}$$

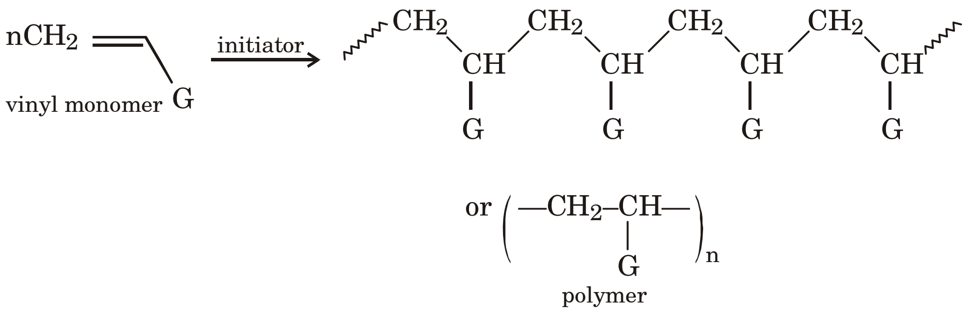
(b) In **step reaction polymerization,** there is a series of reactions each of which is essentially independent of the preceding one; a plymer is formed simply because the monomer happens to undergo reaction at more than one functional group. A diol, for example, reacts with a dicarboxylic acid to form an ester; but each moiety of the simple ester still contains a group that can react to generate another ester linkage and hence a larger molecule, which itself can react further, and so on.



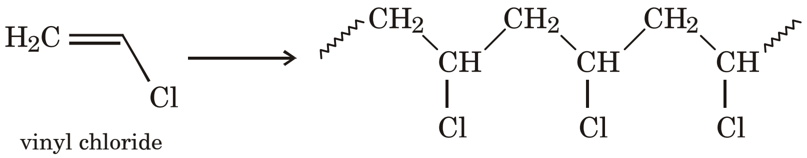
ethylene glycol terephthalic acid



FREE RADICAL VINYL POLYMERIZATION

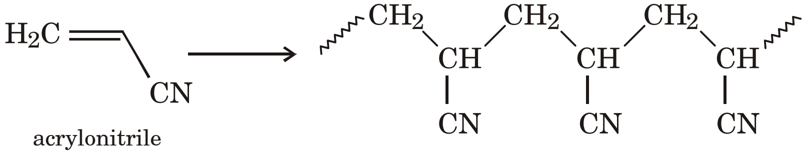


at the doubly bonded carbons — the vinyl groups — and is called vinyl polymerization. A wide variety of unsaturated monomers may be used, to yield polymers with different pendant groups (G) attached to the polymer backbone. For example :



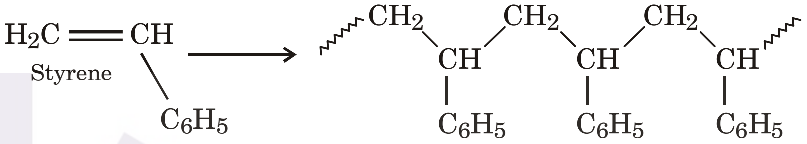
vinyl chloride

Poly (vinyl chloride) (PVC)



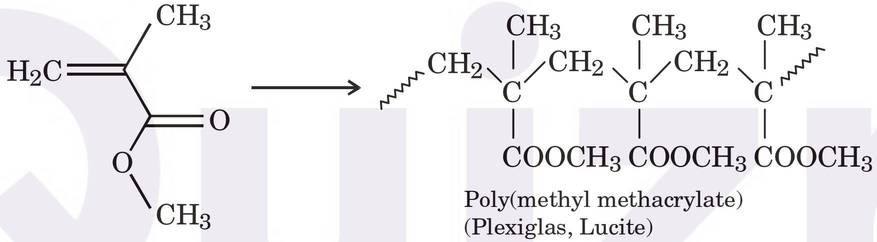
acrylonitrile

Polyacrylonitrile (Orion)



Styrene

Polystyrene

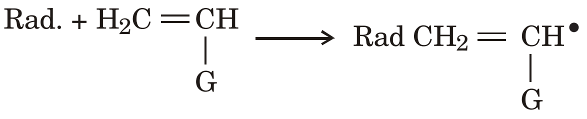


Methyl methacrylate

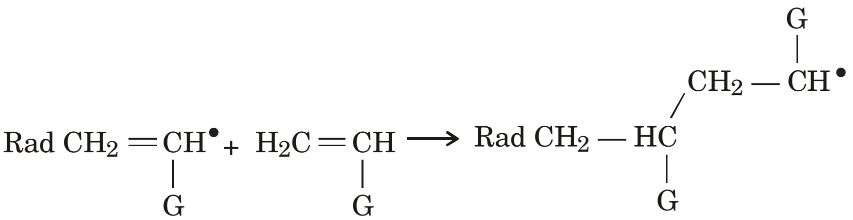
Poly(methyl methacrylate)
(Plexiglas, Lucite)

Polymerzation involves addition of free radicals to the double bond of the monomer: addition, first, of the free radicals generated from the initiator, and then of the growing polymer molecule. This is, of course, an example of chain-reaction polymerization.

1. Peroxide $\longrightarrow$ Rad



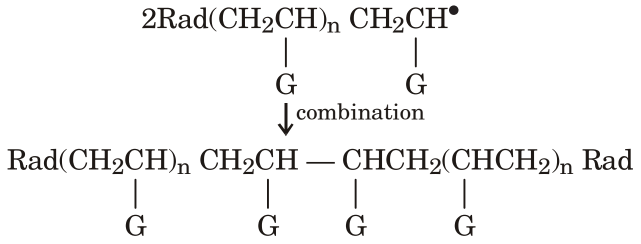
2. $\text{Rad.} + H_2C{=}\underset{|\atop G}{CH} \longrightarrow \text{Rad } CH_2{=}\underset{|\atop G}{CH^\bullet}$ Chain — initiating steps



3. $\text{Rad } CH_2{=}\underset{|\atop G}{CH^\bullet} + H_2C{=}\underset{|\atop G}{CH} \longrightarrow \text{Rad } CH_2-\underset{|\atop G}{HC}-CH_2-\overset{G\atop |}{CH^\bullet}$ Chain propagating steps

then steps like (3) repeated, until finally :

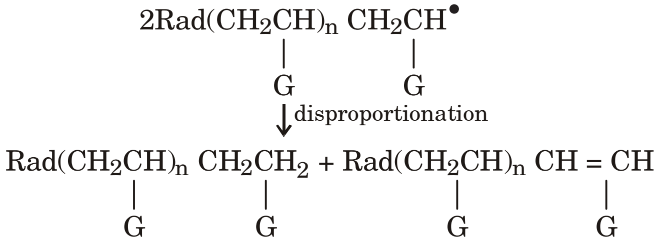
4.



$$2\mathrm{Rad}(\underset{\displaystyle G}{\underset{|}{CH_2CH}})_n\ \underset{\displaystyle G}{\underset{|}{CH_2CH^{\bullet}}}$$
$$\Big\downarrow \text{combination}$$
$$\mathrm{Rad}(\underset{\displaystyle G}{\underset{|}{CH_2CH}})_n\ \underset{\displaystyle G}{\underset{|}{CH_2CH}}-\underset{\displaystyle G}{\underset{|}{CHCH_2}}(\underset{\displaystyle G}{\underset{|}{CHCH_2}})_n\ \mathrm{Rad}$$

or Chain terminating steps

5.

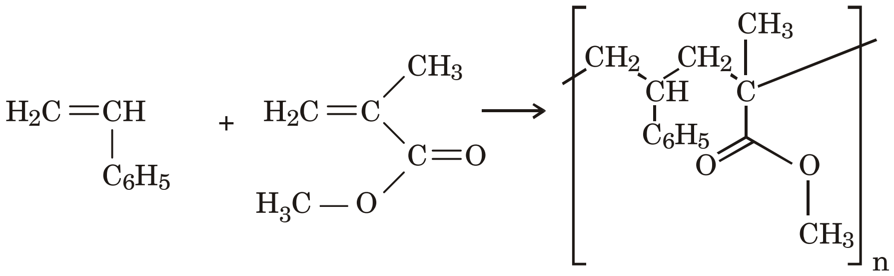


$$2\mathrm{Rad}(\underset{\displaystyle G}{\underset{|}{CH_2CH}})_n\ \underset{\displaystyle G}{\underset{|}{CH_2CH^{\bullet}}}$$
$$\Big\downarrow \text{disproportionation}$$
$$\mathrm{Rad}(\underset{\displaystyle G}{\underset{|}{CH_2CH}})_n\ \underset{\displaystyle G}{\underset{|}{CH_2CH_2}} + \mathrm{Rad}(\underset{\displaystyle G}{\underset{|}{CH_2CH}})_n\ CH=\underset{\displaystyle G}{\underset{|}{CH}}$$

In each step the consumption of a free radical is accompanied by the formation of a new, bigger free radical. Eventually, the reaction chain is terminated by steps that consume but do not form free radicals; combination or disproportionation of two free radicals.

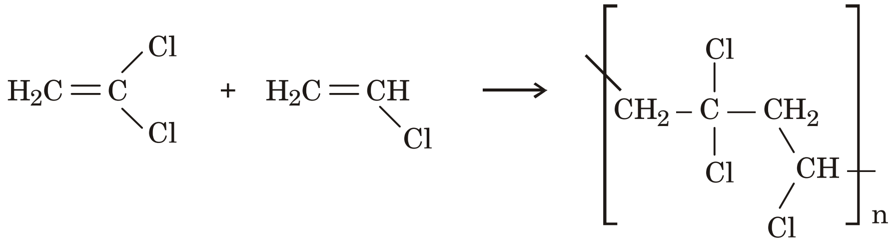
Copolymerization: Polymerization of a single monomeric compound to form a homopolymer is known as homopolymerization. Evidently such a polymer is made up of identical units. In contrast, a copolymer results when two different kinds of monomers are polymerized together to give a product containing both the monomers. Such as process, known as copolymerization, is of great industrial importance as it enables us to get a polymer possessing desired properties. To a certain extent we can control the composition of a copolymer by varying the proportions of the monomer in the polymerizing mixture. However, the composition of the polymer depends not only on the relative concentrations of the two monomers, but also on the relative reactivities of the monomers toward free radical addition. In other words, a more reactive monomer has greater chance of being incorporated into a copolymer. As the reactivity of a carbon-carbon double bond toward free radical addition is affected by the stability of the new free radical being formed, the more stable free radicals will preferentially be produced.

Copolymerization of styrene with methyl methacrylate to produce polystyrene (co-methyl methacrylate) (A) is an industrially important process.



(A)

Saran Wrap (B) is another copolymer formed by the copolymerization of vinylidene and chlorides.

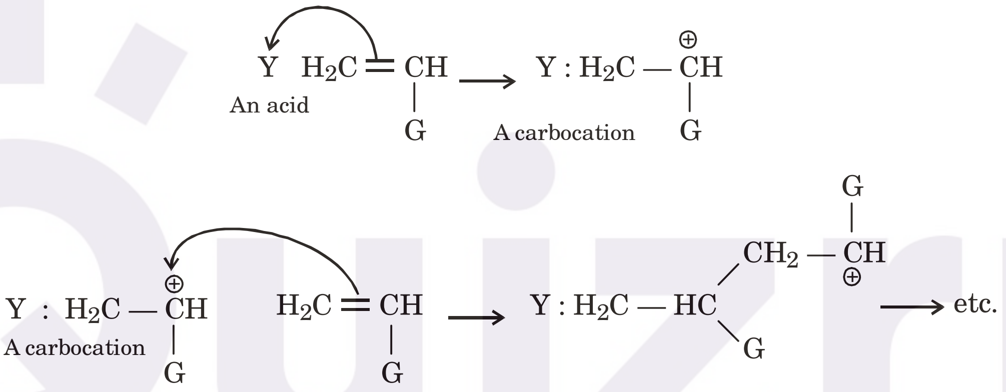


(B)

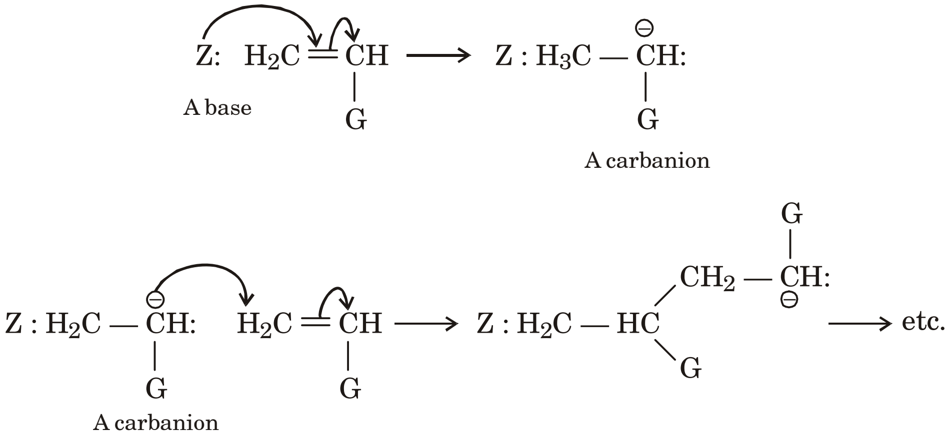
IONIC POLYMERIZATION: LIVING POLYMERS

Chain-reaction polymerization can proceed with ions instead of free radicals as the chain-carrying particles : either cations or anions, depending on the kind of initiator that is used.

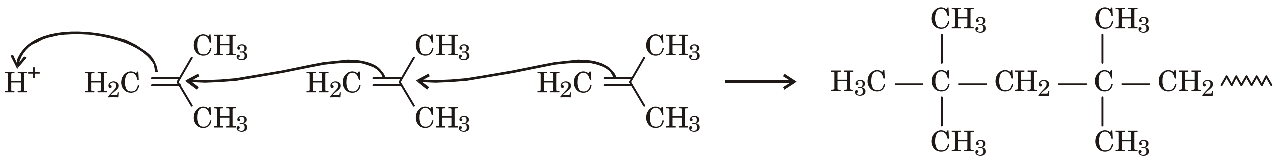
Cationic Polymerization



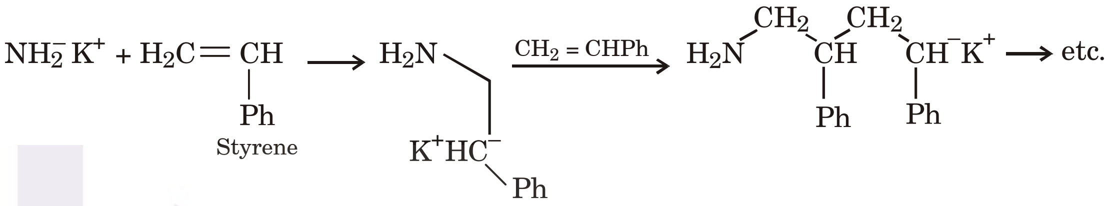
Anionic polymerization

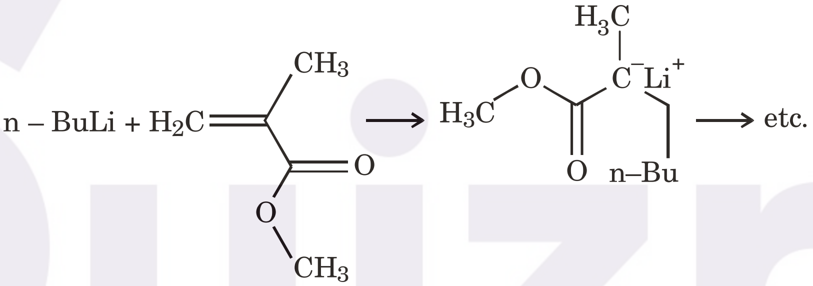


Cationic Polymerization is initiated by acids. Isobutylene, for example, undergoes cationic polymerization to a tacky material used in adhesives. Copolymerization with a little isoprene gives butyl rubber, used to make automobile inner tubes and tire liners. A variety of acids can be used: sulfuric acid; $AlCl_3$ or BF_3 plus a trace of water.



Anionic polymerization, as we might expect, is initiated by bases: Li^+, NH_2^-, for example, or organometallic compounds like n-butyllithium. For example :



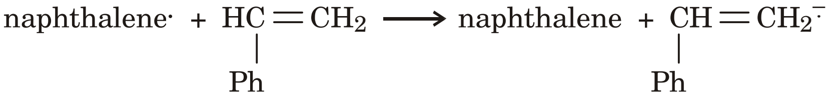


methyl methacrylate

Active metals like Na or Li can be used: here the initiation becomes a little more complicated, as in the polymerization of styrene by the action of sodium metal and naphthalene. A sodium atom transfers an electron (1) to naphthalene to form a radical-anion:

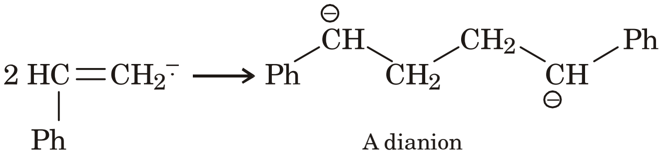
1. $\text{Na} + \text{naphthalene} \rightleftharpoons \text{Na}^+\text{naphthalene}^{\overset{\cdot}{-}}$

Naphthalene radical–anion

2. 

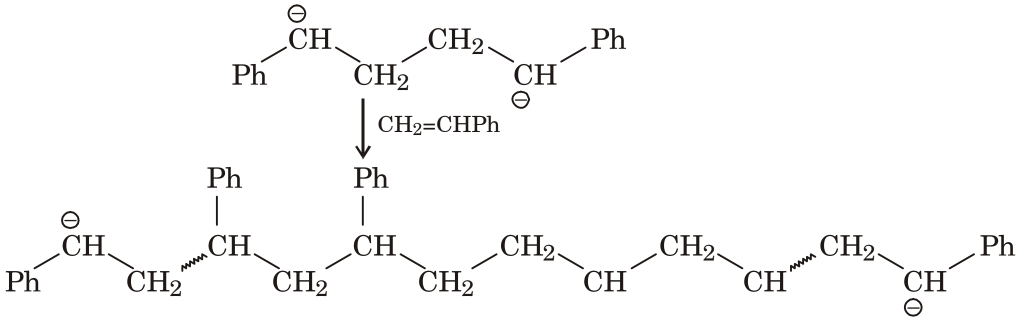
$$\text{naphthalene}^{\cdot} + \underset{\text{Ph}}{\text{HC}}{=}\text{CH}_2 \longrightarrow \text{naphthalene} + \underset{\text{Ph}}{\text{CH}}{=}\text{CH}_2^{\overset{\cdot}{-}}$$

styrene radical–anion Formed by one–electron transfer

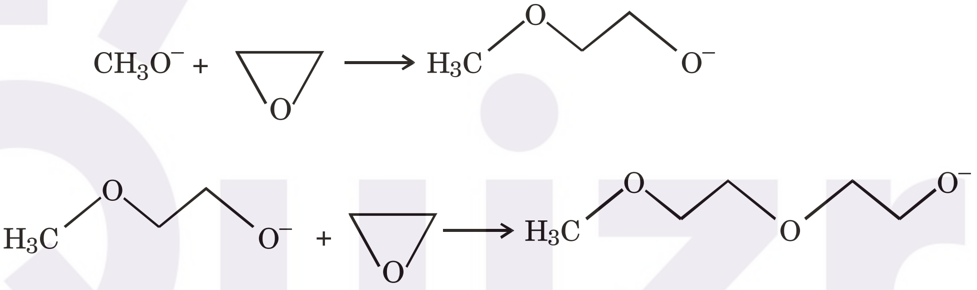
3. 

A dianion

The radical-anion then donates the electron to styrene (2) to form the styrene radical-anion. Like many other free radicals, these dimerize (3). The resulting dianion is the true initiator, and begins to grow at both ends :



Anionic polymerization is not limited to the vinyl kind, involving addition to carbon-carbon double bonds. Ethylene oxide, for example, is converted by a small amount of base into a high molecular weight polyether.



Some important polymers

(a) Polythene :

There are two types of polythene as given below:

(i) Low density polythene :

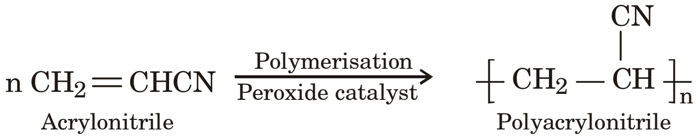
- It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmoshpheres at a temperature of 350 K to 570 K in the presence of traces of dioxygen or a peroxide initiator (catalyst).
- The low density polythene (LDP) obtained through the free radical addition and H-atom obstraction has highly branched structure.
- Low density polythene is chemically inert and tough but flexible and a poor conductor of electricity.

High density polythene : It is formed when addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres.

- High density polythene (HDP) thus produced, consists of linear of Ziegler-Natta catalyst. molecules and has a high density due to close packing.
- It is also chemically inert and more tougher and harder.

(b) Polyacrylonitrile :

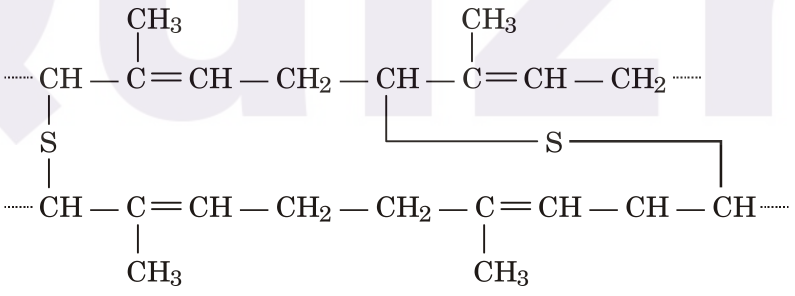
- The addition polymerisation of acrylonitrile in presence of a Acrylic fibres leads to the formation of polyacrylonitrile.
- It has resistance to stains, chemicals, insects and fungi.
- Polyacrylonitrile is used as a substitute for wool in making commercial fibres as orlon or acrilan



$$\underset{\text{Acrylonitrile}}{n\,CH_2=CHCN} \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerisation}} \underset{\text{Polyacrylonitrile}}{\left[CH_2-\overset{\overset{\displaystyle CN}{|}}{CH} \right]_n}$$

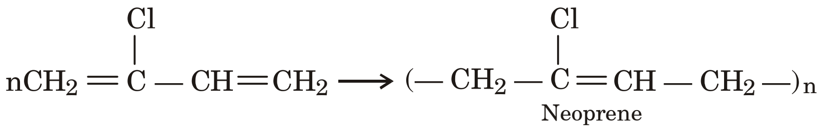
(c) Natural Rubber : Natural rubber is an addition polymer of isoprene (2-methyl-1,3-butadiene). Rubber has an average chain length of 5000 monomer units of isoprene.

The rubber in which the arrangement of carbon chain is trans with respect to the double bond is known as **Gutta Percha** and this is the natural rubber obtained from bark of various trees. Natural rubber is sticky material. This disadvantage is removed by 'VULCANISATION' which involves addition of sulphur to rubber and heating the mixture, sulphur forms short chains of sulphur atoms that link hydrocarbon (isoprene) units together.



When tension is applied the chains can strengthen out but they cannot slip over each other because of sulphur bridges. Thus rubber can be stretched only to a certain extent and hydrocarbon chains have the tendency to regain their shape when tension is removed. Vulcanised rubber is thus stronger and less sticky than the natural rubber.

(d) Synthetic rubber : (Polychloroprene or Neoprene) it is obtained by free radical polymerisation of chloroprene

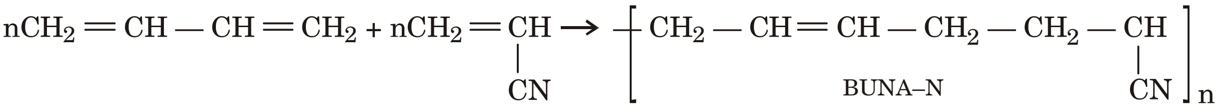


$$nCH_2=\overset{\overset{\displaystyle Cl}{|}}{C}-CH=CH_2 \longrightarrow \underset{\text{Neoprene}}{(-CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}=CH-CH_2-)_n}$$

it is a thermoplastic and need not to be vulcanised. It is a good general purpose rubber and superior to natural rubber as it is resistant to the reaction of air, heat, light chemicals, alkalis and acids below 50% strength. It is used for making transmission belts, printing rolls and flexible tubing employed for conveyence of oil and petrol.

(e) **Buna rubbers :** Butadiene polymerises in the presence of sodium to give a rubber substitute viz. Buna. It is of two types :

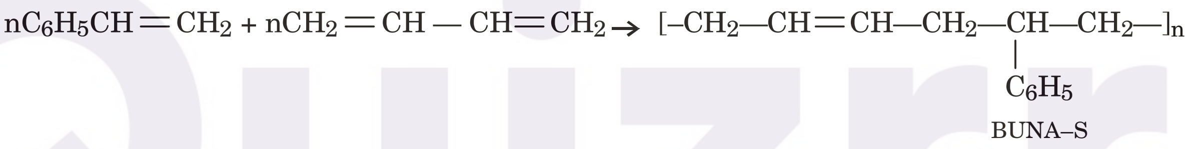
(i) Buna - N or GRA: it is synthetic rubber obtained by copolymerisation of one part of acryl nitrile and two parts of butadiene.



$$nCH_2{=}CH{-}CH{=}CH_2 + nCH_2{=}\underset{\displaystyle CN}{\underset{|}{CH}} \rightarrow \left[\underset{\text{BUNA–N}}{CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH}}} \right]_n$$

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

(ii) Buna -S or GRS (General purpose Styrene rubber): It is a copolymer of three moles of butadiene and one mole of styrene and is an elastomer. It is obtained as a result of free radical copolymerisation of its monomers.



$$nC_6H_5CH{=}CH_2 + nCH_2{=}CH{-}CH{=}CH_2 \rightarrow [-CH_2{-}CH{=}CH{-}CH_2{-}\underset{\underset{\text{BUNA–S}}{\displaystyle C_6H_5}}{\underset{|}{CH}}{-}CH_2{-}]_n$$

It is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and finds use in manufacture of tyres and other mechanical rubber goods.

(e) **Teflon :** It is polymer of tetrafluroethylene ($F_2C{=}CF_2$) which on polymerization gives telfon.

$$nCF_2{=}CF_2 \xrightarrow{(NH_4)_2S_2O_8\ \ 870 - 1020K} (-CF_2-CF_2-)_n$$

It is thermoplastic polymer with a high softening point (600K). It is very tough and difficult to work. It is ipert to most chemicals except fluorine and molten alkali metals. It withstands high temperatures. Its electrical properties make it an ideal insulating material for high frequency installation.

Example 1

Which of the following is an elastomer?

(1) Vulcanized rubber (2) Dacron (3) Polystyrene

Solution :

Vulcanized rubber is an elastomer.

NYLON

Nylon is used as a general name for all synthetic fibres forming polyamides, i.e., having a protein like structure. A number is usually suffixed with the name 'nylon' which refers to the number of carbon atoms present in the monomers.

NYLON–66

(read as nylon six, six)

It is obtained by the condensation polymerisation of hexamethylenediamine (a diamine with six carbon atoms) and adipic acid (a dibasic acid having 6 carbon atoms).

$$\underset{\text{Adipic acid}}{nHOOC(CH_2)_4COOH} + \underset{\text{Hexamethylene diamine}}{nH_2N(CH_2)_6NH_2} \xrightarrow[\substack{\text{High pressure} \\ -(n-1)H_2O}]{280\ C} \underset{\text{Nylon–66}}{\left[OC(CH_2)_4CONH(CH_2)_6NH \right]_n}$$

NYON–610

(read as nylon six, ten)

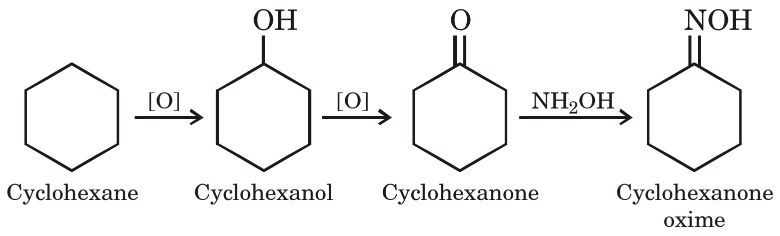
It is obtained by condensation polymerisation of hexamethylenediamine (six carbon atoms) and sebacic acid (a dibasic acid with 10 carbon atoms).

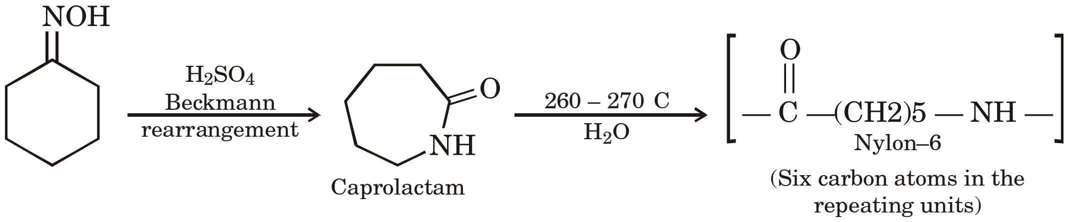
Nylon fibres are stronger than natural fibres and so are used in making cords and ropes. The fibres are elastic, light, very strong and flexible. They have drip dry property and retain creases. It is inert towards chemicals and biological agents. It can be blended with wool. Nylon fibres are used in making garments, carpets, fabrics, tyre cords, ropes, etc.

NYLON–6 (Perlon L)

A polyamide closely related to nylon is known as perlon L (Germany) or Nylon–6 (USA). It is prepared by prolonged heating of caprolactum at 260–270 C. It is formed by self condensation of a large number of molecules of amino caproic acid. Since, caprolactum is more easily available, it is used for polymerization, which is carried out in the presence of H_2O that first hydrolyses the lactam to amino acid. Subsequently, the amino group of the amino acid can react with the lactam and the process goes on and onto form the polyamide polymer.

Carpolactam is obtained by Beckmann rearrangement of cyclohexanone oxime.





NYLON–2–NYLON–6

It is an alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.

Example 2

Nylon–66 is obtained by condensation polymerization of

- **(a) Adipic acid and hexamethylene diamine**
- **(b) Phenol and formaldehyde**
- **(c) Terephthalic acid and ethylene glycol**
- **(d) Sebacic acid and hexamethylene diamine**

Solution :

(a) Adipic acid and hexamethylene diamine on condensation will generate Nylon–66

Example 3

Which of the following type of forces are present in Nylon–66?

- **(a) Van der Waal's forces of attraction**
- **(b) Hydrogen bonding**
- **(c) Three–dimensional network of bonds**
- **(d) None of these**

Solution :

(b) Hydrogen bonds are present in Nylon–66.

POLYETHYLENE

Polyethylene is of two types:

(a) **Low Density Poly Ethylene (LDPE) :** It is manufactured by heating ethylene at 200 C under a pressure of 1500 atmoshperes and in the presence of traces of oxygen. This polymerisation is a free radical polymerisation.

$$nCH_2 = CH_2 \xrightarrow[\text{1500 atmosphere}]{\text{200 C}} \left(CH_2 - CH_2 \right)_n$$

The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point (110 C).

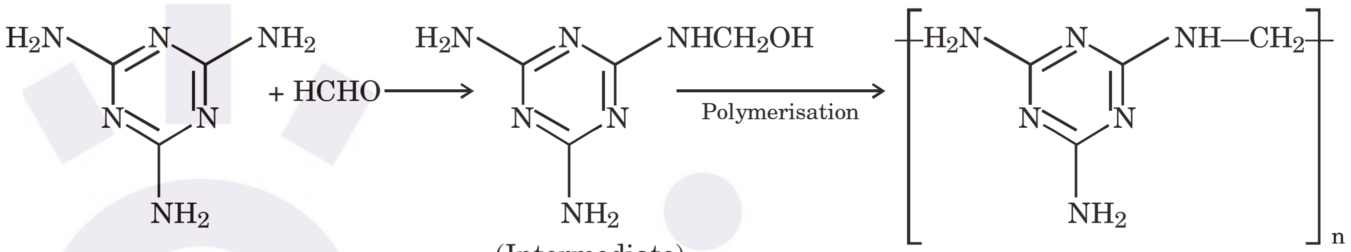
That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent polymer of moderate and as insulation for electrical wires and cables.

(b) **High Density Poly Ethylene (HDPE) :** It is prepared by the use of Zieglar–Natta catalyst at 160 under pressure of 6 to 7 atmoshphere.

The polymer is linear chain, hence it has high density (0.97) and has high melting point (130 C). That is why it is called high density polyethylene. It is a translucent polymer. It has greater tough ness, hardness and tensile strength than low density polyethylene. It is used in the manufacture of containers (buckets, tubes), house wares, bottles and toys.

MELAMINE–FORMALDEHYDE RESIN

This resin is formed by condensation polymerisation of melamine and formaldehyde.



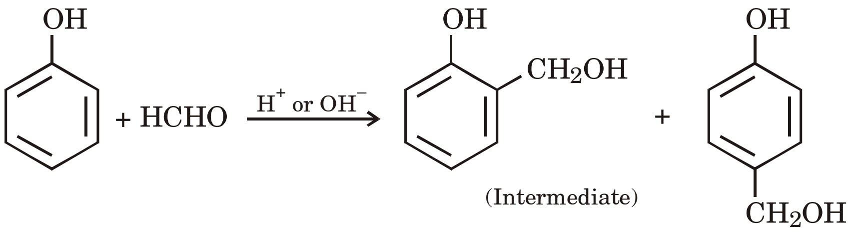
(Intermediate)

Melamine–formaldehyde polymer

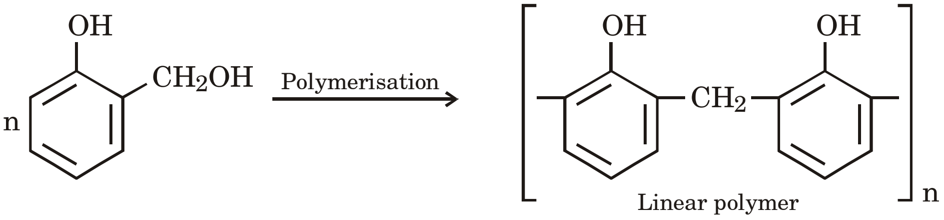
It is a quite hard polymer and is used widely for making plastic crockery under the name melamine. The articles made from this polymer do not break even when dropped from considerable height.

BAKELITE

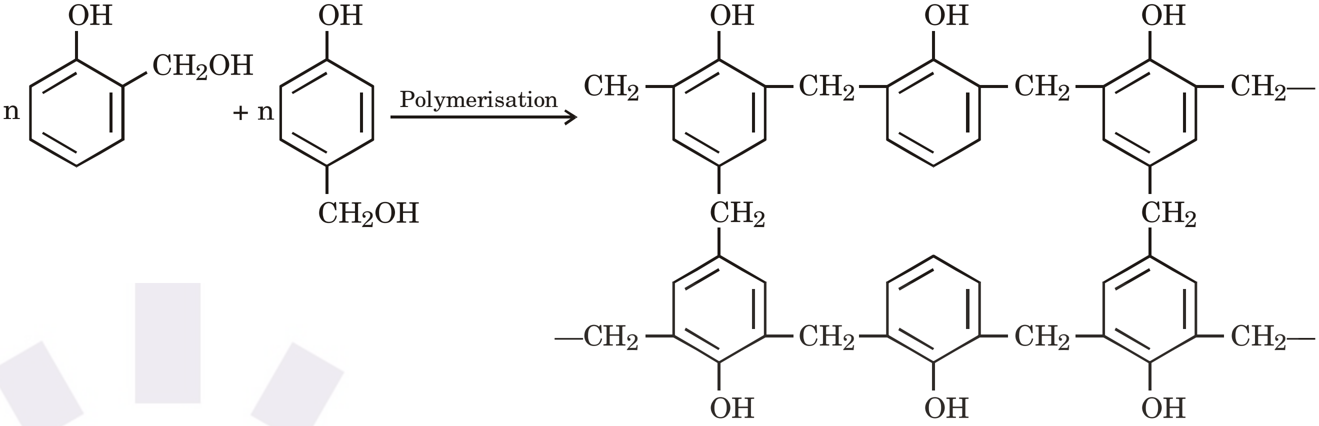
Phenol–formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of either an acid or a basic catalyst. The reaction starts with the initial formation of ortho and para–hydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with $-CH_2$ groups. The reaction involves the formation of methylene bridges in ortho, para or both ortho and para positions. Linear or cross–linked materials are obtained depending on the conditions of the reaction.



O–and p–hydroxymethyl phenol



Linear polymer
Novolac



Cross–linked polymer (Bakelite)

POLYESTERS

Dacron is a common polyester, prepared using ethylene glycol and terephthalic acid. The reaction is carried out at 140 to 180 C in the presence of zinc acetate and Sb_2O_3 as catalyst.

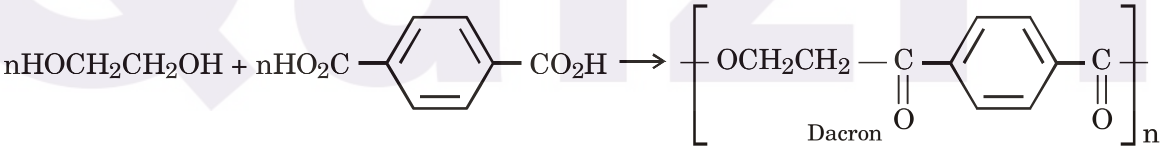
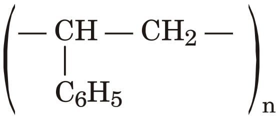
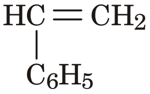
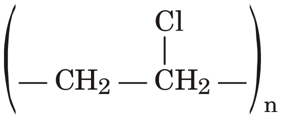
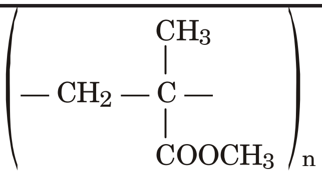
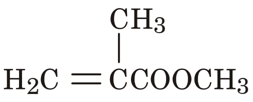
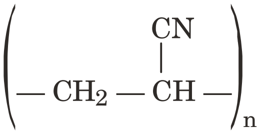
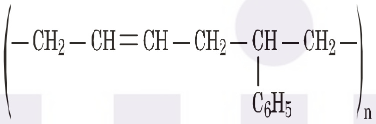
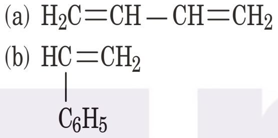
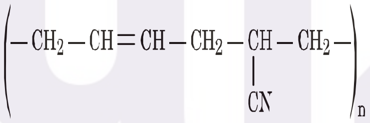
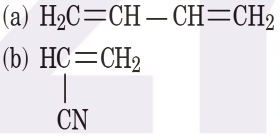
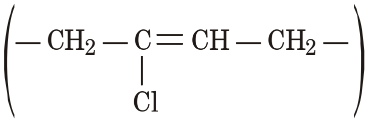
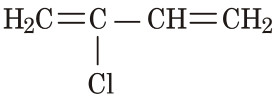
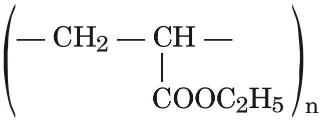
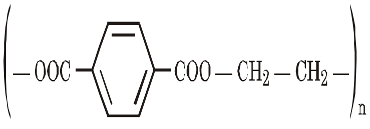
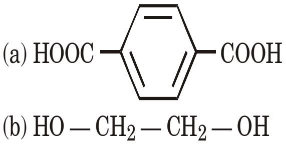
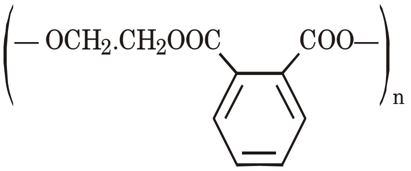
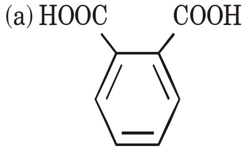
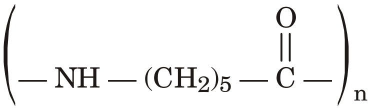
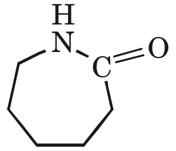
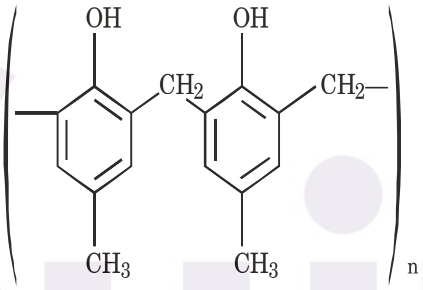
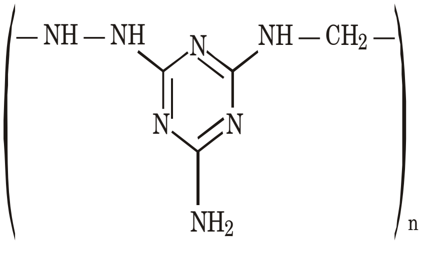
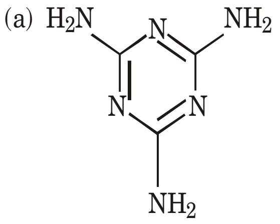
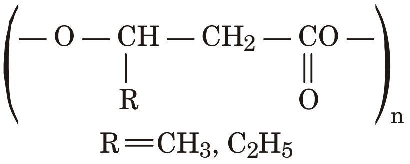
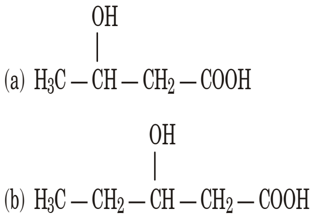


TABLE OF POLYMERS

S.N.	Name of Polymer	Structure	Monomer	Uses
1.	Polythene	$\left(-CH_2-CH_2-\right)_n$	$CH_2=CH_2$	An insulator, anticorrosive, packing material, household and laboratory wares.
2.	Polysyrene	 $\left(\underset{C_6H_5}{\underset{\vert}{-CH}}-CH_2-\right)_n$	 $\underset{C_6H_5}{\underset{\vert}{HC}}=CH_2$	An insulator, wrapping material, manufacture of toys and household articles.

3.	Polyvinylchloride (PVC)	 $\left(-CH_2-\underset{}{\overset{Cl}{\overset{\vert}{CH_2}}}-\right)_n$	$CH_2=CHCl$	In manufacture of raincoats, hand bags, vinyl flooring and leather clothes.
4.	Polytetrafluoro ethylene (PTFE) or Telflon	$(-CF_2-CF_2-)_n$	$CF_2=CF_2$	As lubricant, insulator and making cooking wares.
5.	Polymethyl metha acrylate (PMMA) or Plexi glass	 $\left(-CH_2-\underset{\underset{COOCH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-\right)_n$	 $H_2C=\overset{\overset{CH_3}{\vert}}{C}COOCH_3$	As subsitute of glass and making decorative materials.
6.	Polyacrylonitrile (Orlon)(PAN)	 $\left(-CH_2-\overset{\overset{CN}{\vert}}{CH}-\right)_n$	$CH_2=CHCN$	In making synthetic fibres and synthetic wool.
7.	Styrene butadiene rubber (SBR or BuNa-S)	 $\left(-CH_2-CH=CH-CH_2-\underset{\underset{C_6H_5}{\vert}}{CH}-CH_2-\right)_n$	 (a) $H_2C=CH-CH=CH_2$ (b) $\underset{\underset{C_6H_5}{\vert}}{HC}=CH_2$	In making automobile tyres and footwear.
8.	Nitrile rubber (Buna-N)	 $\left(-CH_2-CH=CH-CH_2-\underset{\underset{CN}{\vert}}{CH}-CH_2-\right)_n$	 (a) $H_2C=CH-CH=CH_2$ (b) $\underset{\underset{CN}{\vert}}{HC}=CH_2$	In making oil seals, manufacture of hoses and tank linings.
9.	Neoprene	 $\left(-CH_2-\underset{\underset{Cl}{\vert}}{C}=CH-CH_2-\right)$	 $H_2C=\underset{\underset{Cl}{\vert}}{C}-CH=CH_2$	As insulator, making conveyor belts and printing rollers.
10.	Polyethyl acrylate	 $\left(-CH_2-\underset{\underset{COOC_2H_5}{\vert}}{CH}-\right)_n$	$CH_2=CH-COOC_2H_5$	In making films, house pipes and finishing fabrics.
11.	Terylene (Dacron)			For making fibres, safety belts, tyre cords, tents etc.

12.	Glyptal		 (b) $HO-CH_2-CH_2-OH$	As binding material in preparation of mixed plastics and paints.
13.	Nylon 6	 $\left(-NH-(CH_2)_5-\overset{O}{\overset{\Vert}{C}}-\right)_n$		In making fibres, plastics, tyre cords and ropes.
14.	Nylon 66	$(-NH(CH_2)_6NHCO(CH_2)_4CO-)_n$	(a) $HOOC-(CH_2)_4-COOH$ (b) $H_2N-(CH_2)_6-NH_2$	In making brushes, synthetic fibres, parachutes, ropes and carpets.
15.	Bakelite		(a) HCHO (b) C_6H_5OH	For making gears, protective coating and electrical fittings.
16.	Urea formaldehyde resin	$(-NH-CO-NH-CH_3-)_n$	(a) HCHO (b) NH_2CONH_2	For making unbreakable cups and laminated sheets.
17.	Melamine formaldehyde resin		 (b) HCHO	In making plastic crockery, unbreakable cups and plates.
18.	Poly-β-hydroxy butyrate-co-β-hydroxy valerate (PHBV)	 $\left(-O-\underset{R}{CH}-CH_2-\underset{O}{\underset{\Vert}{CO}}-\right)_n$ $R=CH_3, C_2H_5$	 (a) $H_3C-\overset{OH}{CH}-CH_2-COOH$ (b) $H_3C-CH_2-\overset{OH}{CH}-CH_2-COOH$	As packaging orthopaedic devices and in controlled drug release.

Example 4

A polymeric substance, tetrafluoroethylene, can be represented by the formula (C_2F_4) where x is a large number. The material was prepared by polymerizing C_2F_4 in the presence of a sulphur bearing catalyst that served as a nucleus upon which the polymer grew. The final product was found to contain 0.012% S. What is the value of x if each polymeric molecule contains 2 sulphur atoms? Assume that the catalyst contributes a negligible amount to the total mass of polymer.

Solution :

Final product contain 0.012% S

If contains two S atoms

$$\therefore \quad \frac{\text{Molecular weight} \quad 0.012}{100} = 2 \times 32$$

Weight of monomer, i.e. C_2F_4 is 100

$\therefore$ 100 x = 5.33 10^5

$\therefore$ x = 5.33 10^3

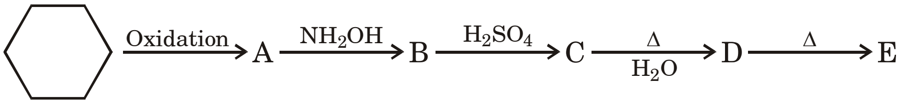
Example 5

$$n\mathbf{CF_2 = CF_2} \xrightarrow[\text{heat, high pressure}]{\text{A}} \mathbf{(–CF_2 – CF_2 –)_n} \text{ \textbf{Teflon}}$$

Solution :

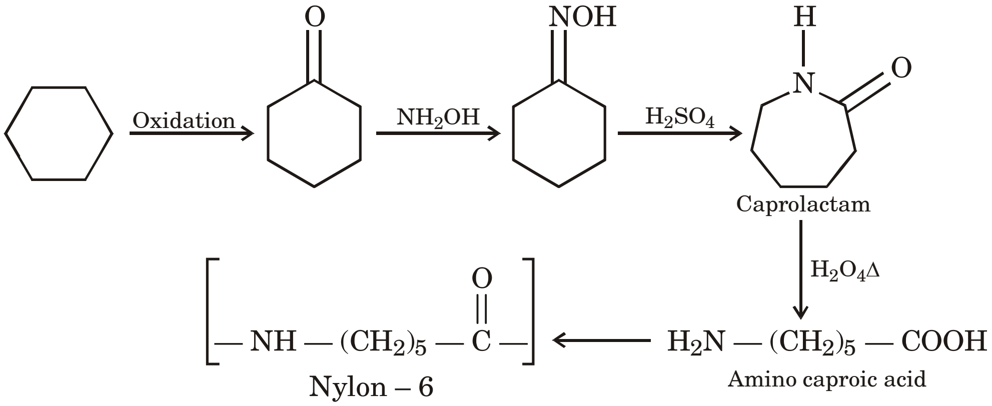
A = $(NH_4)_2S_2O_8$

Example 6

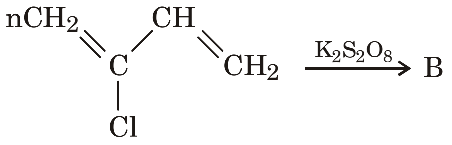


Identify A to E.

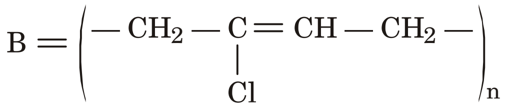
Solution :



Example 7



Solution :



$$B = \left(-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2- \right)_n$$

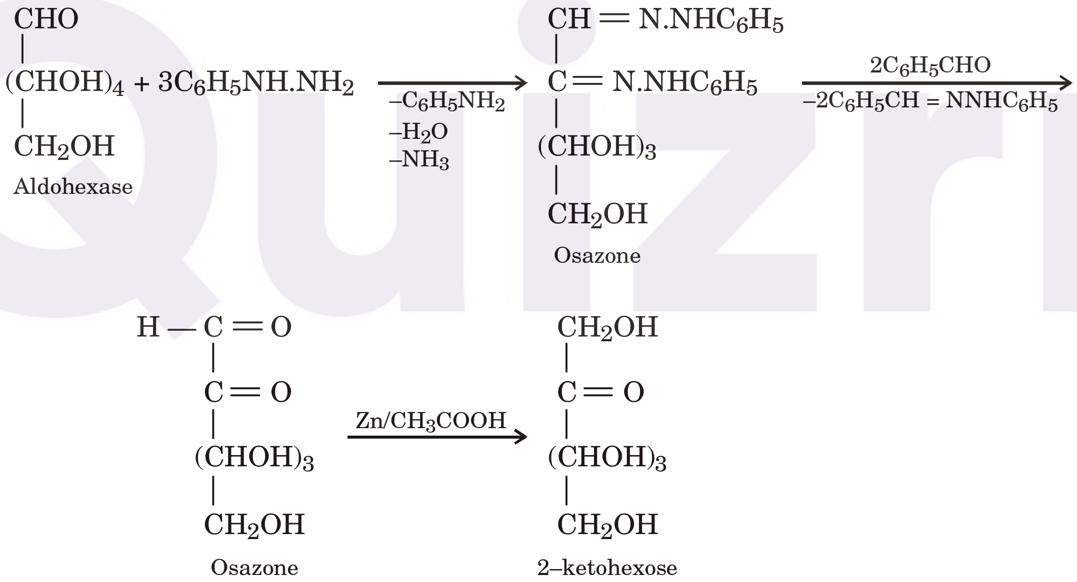
neoprene

Example 8

(a) Show how an aldohexose can be used to syntheisze 2-ketohexose. (b) Since glucose is converted to fructose by this method, what can you say about the configurations of C^3, C^4 and C^5 in the sugars.

Solution :

(a)



Here aldohexose reacts with one molecule of phenylhyrazine which condenses with the aldehyde group to give phenylhydrazone. When warmed with excess of phenyl hydrazine, the secondary alcoholic group adjacent to the aldehyde group is oxidized by another molecule of phenylhydrazine, to a ketonic group. With this ketonic group, the third molecule of phenylhydrazine condenses to give osazone. The phenylhydrazinyl group is transferred from osazone to C_6H_5CHO giving $C_6H_5CH = N.NHC_6H_5$ and a dicarbonyl compound called an osone. The more reactive aldehyde group of the osone is reduced, not the less reactive keto group and it gives the 2-ketohexose.

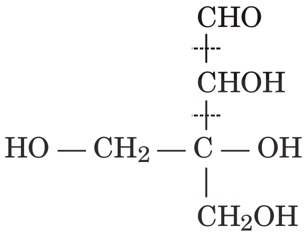
(b) The configurations of these carbons which are unchanged in the reactions, must be identical in order to get the same osazone.

Example 9

Compound (A) $C_5H_{10}O_5$, give a tetra-acetate with Ac_2O and oxidation of (A) with Br_2–H_2O gives an acid, $C_5H_{10}O_6$. Reduction of (A) with HI and red phosphorous gives 2-methylbutane. What is structure of (A)?

Solution :

The formation of tetraacetate indicates presence of 4 OH groups and oxidation with bromine water indicates presence of CHO group. Reduction with red phosphorous and HI indicates presence of one carbon in the side chain. Thus, the structure of (A) would be



$$\begin{array}{rcl} & \text{CHO} & \\ & | & \\ & \text{CHOH} & \\ & | & \\ \text{HO — CH}_2\text{ —} & \text{C} & \text{— OH} \\ & | & \\ & \text{CH}_2\text{OH} & \end{array}$$

Example 10

Compound (A) $C_5H_{10}O_4$, is oxidised by Br_2–H_2O to the acid, $C_5H_{10}O_5$, which readily forms a lactone. (A) forms a triacetate with Ac_2O and an osazone with $PhNHNH_2$. (A) is oxidised by HIO_4, only one molecule of which is consumed. What is the structure of (A) ?

Solution :

(A) contains three hydroxyl groups and an aldehyde group. Formation of a lactone shows that one hydroxyl group is in the γ – or δ-position with respect to the carboxyl group. Since (A) contains four oxygen atoms and these have been accounted for as three hydroxyl groups and an aldehyde group, the formation of an osazone shows the presence of the group –CH(OH)CHO. Since only one molecule of periodic acid is consumed, (A) contains only one set of adjacent oxidisable groups. This must therefore be the CH(OH)CHO group and so the other CHOH groups must be 'separated' from each other and from the CHOH of CH(OH)CHO. Also, the absence of four hydroxyl groups in a five-carbon chain suggests (A) is a deoxy-compound. this 'deoxy-carbon atom' is therefore the one that 'separates' all the three CHOH groups. (A) structure which fits all the facts is

Example 12

(a) Supply structures of H through K. Given :

$$\text{An aldohexose} \xrightarrow{\text{NH}_2\text{OH/base}} \text{H} \xrightarrow{\text{Ac}_2\text{O/NaOAc}} \text{I} \xrightarrow{\text{–HOAC}} \text{J} \xrightarrow{\text{NaOMe/MeOH}} \text{K}$$

(b) Explain the last step (c). What is net structural change (d) Name this overall method.

(e) Discuss the possibility of epimer formation.

Solution :

(a) H is an oxime $HOCH_2(CHOH)_4CH = NOH$; I is the completely acetylated oxime, $AcOCH_2\ (CHOAc)_4CH = NOAc$ that loses 1 mole of HOAc to form J, $AcOCH_2(CHOAc)_4C{\equiv}N$; K is an aldopentose, $HOCH_2(CHOH)_2CHO$.

(b) The acetates undergo transesterification to give methyl acetate freeing all the sugar OH's. This is followed by reversal of HCN addition.

(c) There is loss of one C from the carbon chain.

(d) Wohl degradation

(e) The α-CHOH becomes the –CH = O without any configurational changes of the other chiral carbons. Thus no epimers are formed.