# Polymers

# 15

## Introduction :

[a] A polymer is a compound of high molecular mass formed by the combination of large number of small molecules and process is called polymerisation. The small molecules which constitute the repeating units in a polymer are called monomer units. These large molecule have relative molecular masses in the rarge $10^4 - 10^6$.

**e.g.**

$$nCH_2 = CH_2 \xrightarrow[\text{Catalysed polymerization}]{\text{Free radical or ion}} [-CH_2-CH_2-]_n.$$

ethene polythene

Where n is as high as $10^5$. The number of monomers units in a polymer is called the degree of polymerisation.

[b] **Homopolymer :** The polymer formed from one kind of monomer is called homopolymer.

**e.g.** Polyethylene

[c] **Copolymer or mixed polymer :** Polymer formed from more than one kind of monomer units is called copolymer.

**e.g.** Buna – S

## Classification of Polymers :

Polymers are classification on the following ways :

**1. Calssification based upon origin or source :**

These are of two types based on source

[a] Natural polymers whose source is animal and plants are called natural polymers eg. starch, cellulose, protein etc.

[b] Synthetic polymers : These are man made polymers synthesised in the laboratory from low molecular weight compounds.

**e.g.** Nylon, dacron, bakelite, synthetic rubber, polystyrene etc.

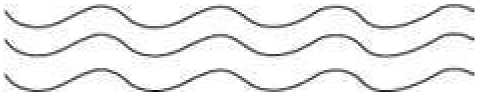
**2. Classification bassed on structure :**

These are of three types based on structure :

[a] Linear polymers
[b] Branched chain polymers
[c] Cross linked polymers

**[a] Linear polymers :** In which monomer units are linked together to form long straight chains. The polymeric chains are stacked over one another to give a well packed structure. Such polymers have high densities, high tensile strength and high melting point.

**eg.** Polythene, Nylon and polyesters

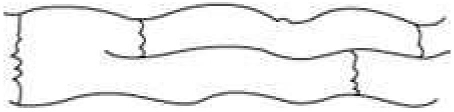


**[b] Branched chain polymers :** In this type of polymers, the monomeric units are linked to consitute long chains (called main chain). There are side chains of different lengths which constitute branches. Brnached chain polymers are irregularly packed and they have lower tensile strength and lower melting points as compared to linear polymers.

**eg.** Amylopectin

**[c] Cross linked polymers :** The monomeric units are linked together to constitute a three dimensional network, Cross linked polymers are hard, rigid and brittle because of their network structure.

**eg.** Bakelite, Formladehyde, resin etc.



**3. Classification based on synthesis :**

These are of two types based on synthesis :

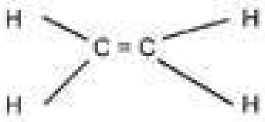
**[a]** Condensation polymerisation : In this the monomer (same or different) units linke with each other by the elimination of a small molecule (e.g. water, methyl alcohol) as a by product. The polymer formed in known as condensation polymer. Nylon and terylene are the most common examles.

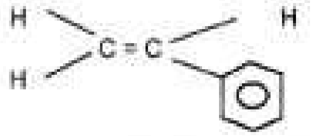
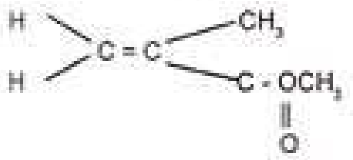
Since the condensation polymerisation proceeds by a stepwise intermolecular condensation, it is also known as step polymersation and the polymer formed is known as step growth polymer.

**[b]** Addition polymerisation : This involves the self addition of several unsaturated molecules to one or two monomers without loss of any small mulecule to form a single giant molecule. The polymer formed is known as addition polymer. Polythene is the most common example.

| Differences between Addition and Condensation Polymers | | |
|---|---|---|
| **S.N.** | **Addition Polymers** | **Condensation Polymers** |
| 1. | Formed by addition reaction | Fromed by condensation process with elimination of small molecules like $H_2O$. |
| 2. | Molecular mass is a whole number multiple of monomer. | Molecular mass is not whole number multiple of the monomer units. |
| 3. | Generally involve one monomer unit. | Generally involve more than one monomer unit. |
| 4. | Monomers are unsaturated molecules. | Monomer units must have two active functional groups. |
| 5. | They are generally chain growth polymers. | They are generally step growth polymers. |

## SOME COMMON ADDITION POLYMERS

| Monomer | Name | Polymer | Uses |
|---|---|---|---|
|  | Ethylene | Polythene | Bags , toys. etc |
|  | Propylene | Polypropylene | Beakers , mill cartons etc. |

| | | | |
|---|---|---|---|
|  | Vinyl chloride | Poly vinyl chloride (PVC) | Rain coats, pipes, tiles etc. |
|  | Acrylonitrile | Poly acrylonitrile (PAN), Orlon | Carpets etc. |
|  | Styrene | Polystyrene | Thermocole, Insulating material etc. |
|  | Methyl methacrylate | Perspere or plexiglass | Transparent objects lenses etc. |
|  | Tetra fluoro ethylene | Teflon (PTFE) | Chemical equipment (Non stick cookware) |

**2.4 Classification based on interparticle forces :** The mechanical properties of polymers such as tensile strength, toughness, elastically etc depend upon intermolcular forces like vander wall forces and hydrogen bonds existing in the macromolecules. In polymers there is a combined effect of these forces all along chains longer chain are more intense in the effect intermolcular forces. Polymers have been classified into four categories.

**[a] Elastomers :** These are the polymers having elastic character. The polymer chains in such type of polymers are held together by weakest intermolcular forces. These forces permit the polymer to be streched under stress but they regain their former shape when the stress is relieved. The elasticity of such polymers can be further modified by introducing few cross links between the chains.

**eg.** Natural rubber, a gummy material has poor elasticity, but heating gummy rubber with sulphur produced a material which was no longer sticky but had modified elasticity. Such a material was called vulcanised rubber.

## *Solved Examples*

**Ex. 1** Give an example of elastomer.

**Sol.** Natural rubber is an example of elastomer.

**[b] Fibers :** These are th polymers which have quite strong interparticle forces such as H–bonds.

**eg.** Nylon, dacron etc.

**[c] Thermoplastics :** These are the polymers which can be easily moulded into desired shapes by heating and subsequent cooling to room temperature. The intermolcular forces in thermoplastic polymers are intermediate to those of elastomers and fibers. Thermoplastic polymers soften on heating and becomes fluids but on cooling they become hard.

**eg.** Polyethene and polystyrene

**[d] Thermosetting polymers :** These are the polymers which become hard and infusible on heating. Heating reuslts in excessive cross linking between the chains forming three dimensional network of bonds.

**eg.** Bakelite, malamine

## Molecular weight of Polymers :

There are two types of average molecular weight in case of polymers.

[a] $\overline{M}_n$ = Number average molecular weight.

[b] $\overline{M}_w$ = Weight average molecular weight.

### [a] Number average molecular weight ($\overline{M}_n$)

$$(\overline{M}_n) = \xrightarrow{\text{Oxidation}}$$

**If :**

$n_1$ molecules are there of mol. wt. $M_1$.

$n_2$ molecules are there of mol. wt. $M_2$.

$n_3$ molecules are there of mol. wt. $M_3$. Then

$$\overline{M}_n = \xrightarrow[n_1 + n_2 + n_3 + ---]{n_1M_1 + n_2M_2 + n_3M_3 + -----}$$

$$\overline{M}_n = \xrightarrow[\Sigma n_i]{\Sigma n_i M_i}$$

### [b] Weight average molecular weight $\overline{M}_w$

$$\overline{M}_w = \xrightarrow[w_1 + w_2\ w_3 + ---]{w_1M_1 + w_2M_2 + w_3M_3 + ---}$$

[Weight = no. of molecules × molecular weight]

**Where :**

$w_1$ = weight of the molecules of mol. wt. $M_1$

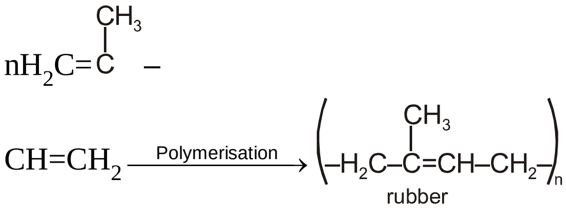
$w_2$ = weight of the molecules of mol. wt. $M_2$

$w_3$ = weight of the molecules of mo. wt. $M_3$

**Note :** It should be noted that $\overline{M}_w > \overline{M}_n$

## Natural Rubber :

**Preparation :** When isoprene is heated with concentrated HCl, a rubber like material is obtained.

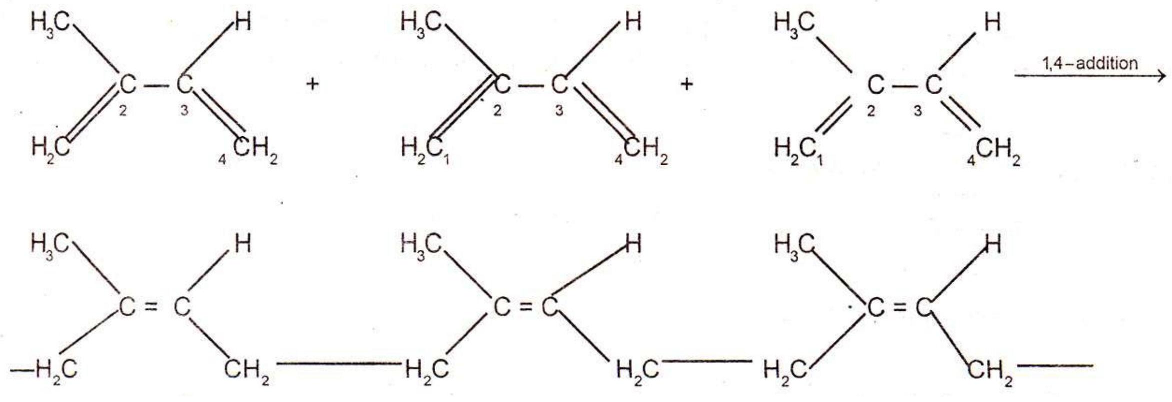


$$nH_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}} - CH{=}CH_2 \xrightarrow{\text{Polymerisation}} \underset{\text{rubber}}{\left(-H_2C-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH-CH_2-\right)_n}$$

There are two kinds of natural rubber

[a] Natural rubber [b] Gutta percha

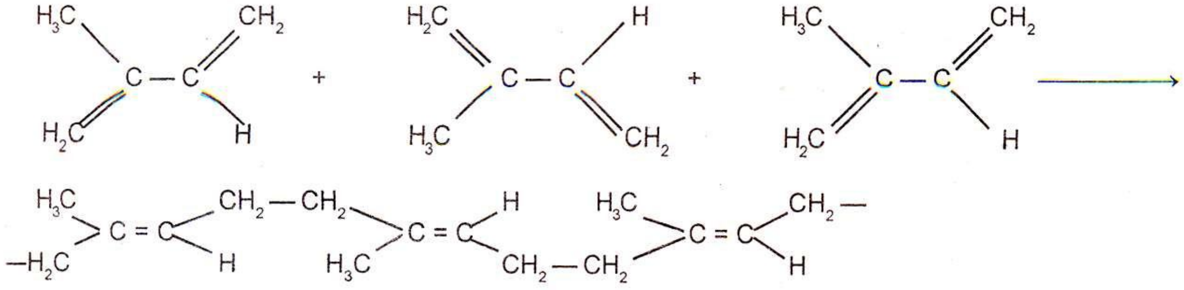
### [a] Natural rubber



cis–polyisoprene (natural rubber)

In the above structure all the $–CH_2–CH_2–$groups are on the one side (cis form)

### [b] Gutta percha



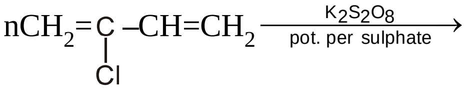
trans–polyisoprene (gutta percha)

## Some Important polymers :

1. Addition polymers

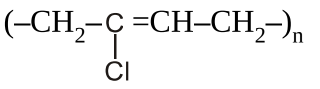
[a] Polydienes:

[i] Neoprene



$$nCH_2=\underset{\underset{Cl}{|}}{C}-CH=CH_2 \xrightarrow[\text{pot. per sulphate}]{K_2S_2O_8}$$

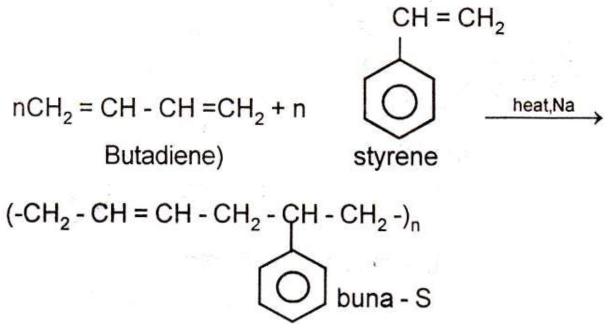
chloroprene



$$(-CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2-)_n$$

neoprene

**[ii] Buna S :** It is copolymer of 1, 3 butadiene and styrene, It is obtained by the polymerisation of butadiene and styrene in the ratio of 3 : 1 in the presence of sodium.



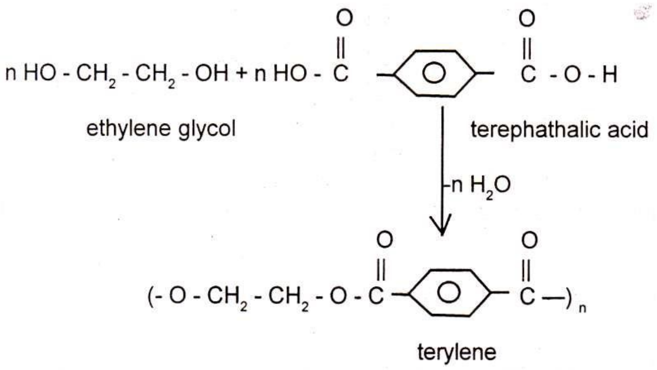
**Uses :** Buna – S is also vulcanised and used in making tyres for the vehicles. It is also used as rubber soles and in making water proof shoes.

2. **Condensation polymers :**

**[a] Polysters :** These are the polymers having ester linkage $(-\overset{\overset{O}{\|}}{C}-O-)$

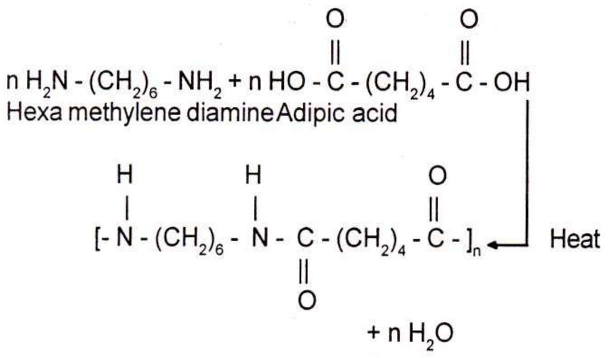
**Examples :**

[a] Terylene :



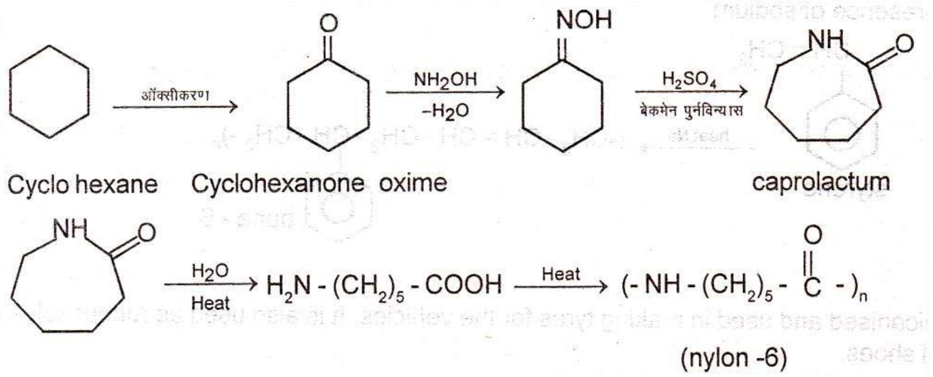
**[b] Polyamides :** Such polymers have amide linkage $(-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-)$ in the chain

[i] Nylon – 66

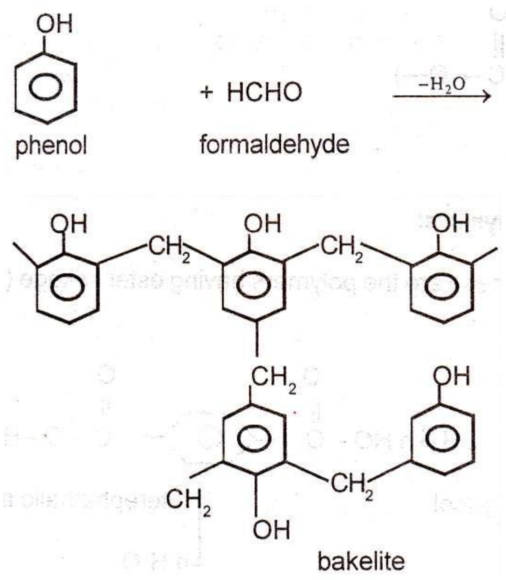


**Uses :** Nylone 66 have high tensile strength so it is used in the manufacture of carpets, testile fibres and bristles for brushes. It is used in making elastic hoisery.

[ii] Nylon – 6



**[c] Phenol – Formaldehyde resins (Bakelite)**



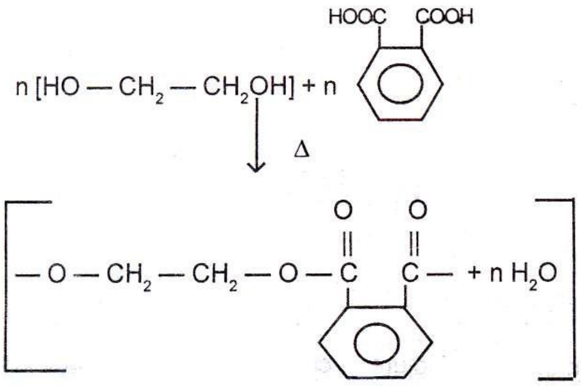
Because bakelite is hard and is a good electrical insulator, it is extensively used on making electrical switches, fuse holders, etc.

**[d] Thiokol –** It is prepared by the polymerisation of ethylene chloride with sodium polysulphide.

$$n(Cl–CH_2– CH_2–Cl) + Na_2S_2$$
$$\downarrow$$
$$\underset{\text{thiokol rubber}}{(H_2C–CH_2–S–S–)_n}$$

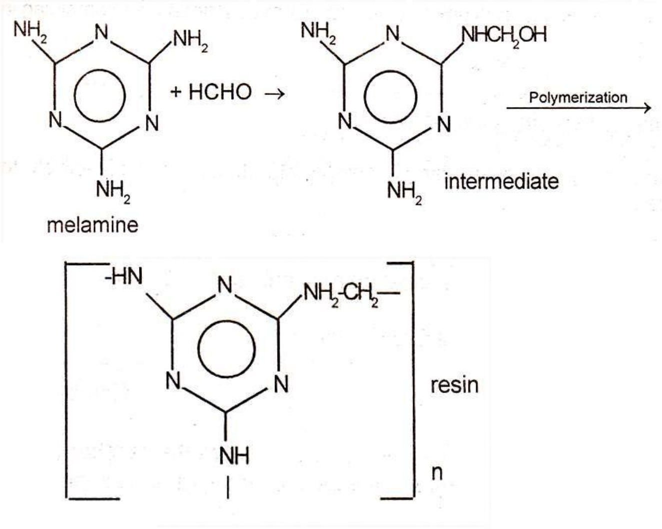
**Uses :** It is used for making gaskets, seals, pulleys etc.

**[e] Glyptal or (alkyl resin) :** The most simple glyptal (polyethylene phthalate) formed from the polycondensation of glycol and phthalic acid.



**Uses :** It is used in the manufacture of paints and lacquers.

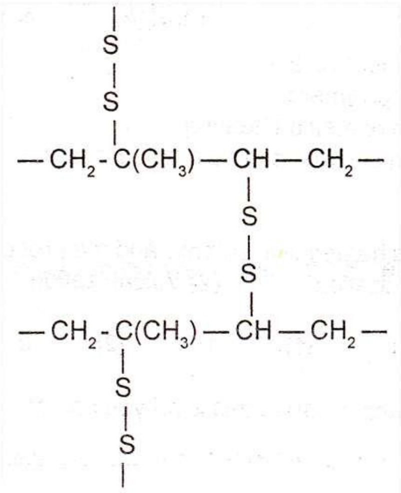
**[f] Melamine formaldehyde resin :** Melamine formaldehyde resin is formed by the co–polymerisation of melamine and formaldehyde.



**Uses :** It is used for making non breakable plastic crockery i.e. cup plates etc.

**[g]** In vucanisation rubber is cured by heating (3 hrs) it with sulphur (3–10%) at a temperature of 125–140ºC. Rubber hydrocarbon combines with the sulphur atoms to form the sulphur bridges. The resulting products is tough, non–elastic and resistance to heat. It becomes non abrasive and not affected by chemicals.

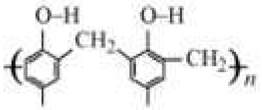
$$\begin{array}{l} —CH_2–C(CH_3)=CH–CH_2— \\ —CH_2–C(CH_3)=CH–CH_2— \end{array} \xrightarrow[\text{Vucanisation}]{+S}$$



## Polymers of Commercial Importance

Besides, the polymers already discussed, some other commerciall important polymers along with their structures and uses are given below in Table.

**Some Other Commercially Important Polymers with Their Use**

| Name of Polymer | Monomer | Structure | Uses |
|---|---|---|---|
| Polypropene | Propene |  $\left(CH_2-\overset{\overset{CH_3}{\vert}}{C}H\right)_n$ | Manufacture of ropes, toys, pipes, fibres, etc. |
| Polystyrene | Styrene |  $\left(CH_2-\overset{\overset{C_6H_5}{\vert}}{C}H\right)_n$ | As insulator, wrapping material, manufacture of toys, radio and television cabinets |
| Polyvinyl chloride(PVC) | Vinyl chloride |  $\left(CH_2-\overset{\overset{Cl}{\vert}}{C}H\right)_n$ | Manufacture of raincoats, hand bags, vinyl flooring, water pipes |
| Urea-formaldehyde resin | (a) Urea<br>(b) Formaldehyde | $\left(NH-CO-NH-CH_2\right)_n$ | For making un-breakable cups and laminated sheets |
| Glyptal | (a) Ethylene glycol<br>(b) Phthalic acid |  | Manufacture of paints and lacquers |
| Bakelite | (a) Phenol<br>(b) Formaldehyde |  | For making combs, electrical switches, handles of utensils and computer discs |

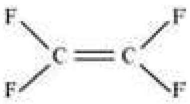
## *Solved Examples*

**Ex. 2** Draw the structures of monomers for the following polymers. Also draw the structures of the polymers and uses of:

(i) Teflon (ii) PMMA (iii) Buna-S

**Sol.**

(i) The monomer of teflon is



Tetrafluoroethene

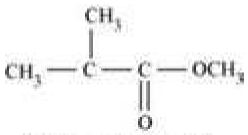
The structure of teflon is

$$\left[CF_2-CF_2\right]_n$$

Teflon (Polytetrafluoroethene)

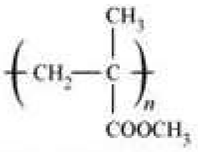
Teflon is used for making oil seals, gaskets and utensils having non-stick surface coating.

(ii) The monomer of PMMA is



Methyl metha acrylate

The structure of PMMA is



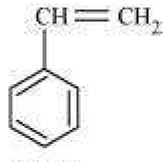
PMMA (Polymethyl metha acrylate) or Plexi glass

PMMA is used as a substitute for glass, and for making decorative materials.

(iii) The monomers of Buna-S are

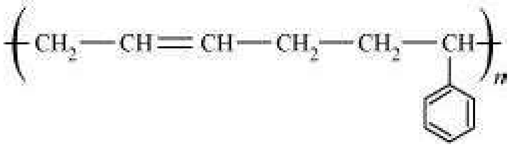
$CH_2=CH-CH=CH_2$ and

1, 3 – Butadiene



Styrene

The structure of Buna-S is

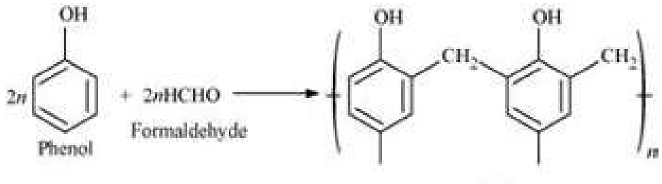


Buna-S is used for making automobile tyres and footwear.

## *Solved Examples*

**Ex.3** How is bakelite made and what is its major use? Why is bakelite a thermo-setting polymer?

**Sol.** Bakelite is made by the co-polymerisation of phenol and formaldehyde.



Bakelite

Bakelite is used for making combs, electrical switches, handles of utensils, computer discs, etc.

When moulded once, bakelite cannot be softened on heating. So, it is a thermosetting plastic.

**Ex. 4** (a) How does vulcanisation change the character of natural rubber?

(b) Why are the numbers 66 and 6 put in the names of nylon-66 and nylon-6?

**Sol.** (a) The rubber obtained by the vulcanisation of natural rubber has excellent elasticity over a long range of temperature. This is because heating rubber with sulphur causes cross-linking of polymer chains through disulphide bonds. This prevents the tearing of the polymers on stretching. Thus, vulcanised rubber has low water-absorption tendency, and is resistant to the action of organic solvents and oxidising agents.

(b) Nylon-66 is derived from two monomers, hexamethylenediamine and adipic acid. Each of these monomeric units contains six carbon atoms. Hence, the two '6's in nylon-66 represent the numbers of carbon atoms present in these monomers (adipic acid and hexamethylenediamine).

Nylon-6 is derived from the monomer, caprolactam. Caprolactam contains six carbon atoms. Thus, the number 6 in nylon-6 represents the number of carbon atoms present in this monomer.

**Ex. 5** Draw the structure of the monomer of each of the following polymers:

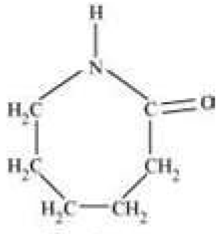
(i) Polyvinylchloride (PVC) (ii) Nylon-6

**Sol.**

(i) The monomer of polyvinylchloride (PVC) is

Vinyl chloride

(ii) The monomer of nylon-6 is



Caprolactam

**Ex. 6** Write the names and structures of the monomers of the following polymers:

(i) Buna-S (ii) Neoprene (iii) Nylon-6

**Sol.** (i) Buna-S : (See in example : 1)

(ii) Neoprene :

Monomer

$CH_2=C(Cl)-CH=CH_2$

Chloroprene

(iii) Nylon-6 (See in example : 4)

**Ex.7** Draw the structures of the monomers of the following polymers:

(i) Teflon (ii) Polythene

OR

What is the repeating unit in the condensation polymer obtained by combining $HO_2CCH_2CH_2CO_2H$ (succinic acid) and $H_2NCH_2CH_2NH_2$ (ethylene diamine)?

**Sol.** (i) The monomer present in Teflon is Tetrafloroethylene. The structure of the monomer of teflon is

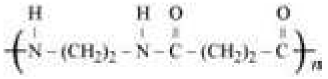
$nCF_2=CF_2$

(ii) The monomer present in polythene is ethene. The structure of the monomer of polythene is

$nCH_2=CH_2$

OR

The repeating unit of the condensation polymer obtained by combining succinic acid and ethylene diamine is



$-\!\!\left(\overset{H}{N}-(CH_2)_2-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}\right)\!\!-_n$