

## CLASS 12 CHEMISTRY Chapter 15 POLYMERS

- (a) **Polymer:** The word “Polymer” is derived from two Greek words, ‘Poly’ that means many (numerous) and ‘Mer’ which means units. In basic terms, a polymer is a long-chain molecule that is composed of a large number of repeating units of identical structure. These identical structures, we understand as a unit made up of two or more molecules, join together to form a long chain.
- (b) **Classification of Polymers:**
- (c) **Based on Source:**
- Natural:** Found in plants and animals, e.g., Proteins, cellulose, natural rubber, silk, wool.
  - Synthetic:** Man-made, e.g., Nylon, polyester, neoprene, bakelite, teflon, PVC, polystyrene.
  - Semisynthetic:** Natural but modified by man e.g. cellulose nitrate.
- (d) **Based on Structure:**
- Linear polymers:** This consist of long and straight chain repeating units, e.g., Polythene (HDPE), PVC, nylon, polyester.
  - Branched polymers:** This contains linear chains having some branches, e.g., amylopectin, glycogen etc.
  - Cross-linked polymers:** Strong covalent bonds are present between various linear polymer chains, e.g., Bakelite, urea-formaldehyde polymer, melamine, formaldehyde polymer etc.
- (e) **Based on mode of polymerization:**
- Addition polymers:** These are formed by the repeated addition of monomer molecules possessing multiple bonds, e.g., polythene, polypropene, polystyrene, PMMA (polymethyl methacrylate).
  - Condensation polymers:** These are formed by the repeated condensation reaction of different bifunctional or trifunctional monomers with the elimination of small molecules like water, HCl, NH<sub>3</sub>, alcohol, etc., e.g., Bakelite, nylon, polyester, urea-formaldehyde resin.

**(f) Based on molecular forces:**

- (i) Elastomers:** Forces of interaction between polymer chains is weakest, e.g., natural rubber, neoprene, vulcanized rubber.
- (ii) Fibers:** Strong hydrogen bonds are present between the polymer chains. They have high tensile strength, e.g., Nylon, polyester, silk, wool, orlon, rayon etc.
- (iii) Thermoplastics:** They are linear/slightly branched chains molecules capable of repeated softening on heating and hardening on cooling, e.g., Polythene, PVC, polystyrene, polypropene.
- (iv) Thermosetting plastics:** They are cross-linked or heavily branched molecules, which on heating undergo extensive cross-linkages and become infusible, e.g., Bakelite, urea-formaldehyde resin.

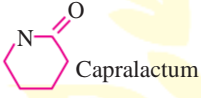
**(g) Based on growth of polymerization:** Depending upon the mechanism of polymerization, polymers are classified as:

- (i) Addition polymers or Chain growth polymers:** They follow mostly free radical mechanism.
- (ii) Condensation polymers or Step growth polymers:** Because they are formed in gradual steps.



## Polymers and Their Monomers

S. No.	Name of Polymer	Structure	Monomer	Uses
1.	Polythene	$(-\text{CH}_2-\text{CH}_2-)_n$	$\text{CH}_2=\text{CH}_2$	As insulator, anticorrosive, packing material, household and laboratory wares.
2.	Polystyrene	$\left( \begin{array}{c} \text{CH} - \text{CH}_2 \\   \\ \text{C}_6\text{H}_5 \end{array} \right)_n$ PolyStyrene	$\begin{array}{c} \text{CH} = \text{CH}_2 \\   \\ \text{C}_6\text{H}_5 \end{array}$ Styrene	As insulator, wrapping material, manufacture of toys and household articles.
3.	Polyvinylchloride (PVC)	$\begin{array}{c} \text{Cl} \\   \\ (-\text{CH}_2-\text{CH}-)_n \end{array}$	$\text{CH}_2 = \text{CHCl}$ Vinyl chloride	In manufacture of rain-coats, hand bags, vinyl flooring and leather clothes.
4.	Polytetrafluoroethylene (PTFE) or Teflon	$(-\text{CF}_2-\text{CF}_2-)_n$	$\text{CF}_2 = \text{CF}_2$ TFE	As lubricant, insulator and making cooking wares.
5.	NOVOLAC	$\left( \begin{array}{c} \text{OH} \quad \text{OH} \\   \quad   \\ \text{C}_6\text{H}_4 \quad \text{C}_6\text{H}_4 \\   \quad   \\ \text{CH}_2 \quad \text{CH}_2 \end{array} \right)_n$	(a) HCHO (b) $\text{C}_6\text{H}_5\text{OH}$	In making bonding give varnishes, lacquers etc.
6.	Polyacrylonitrile (Orion) (Acrilian)	$\begin{array}{c} \text{CN} \\   \\ (-\text{CH}_2-\text{CH}-)_n \end{array}$	$\text{CH}_2 = \text{CHCN}$ Acrylonitrile	In making synthetic fibres and synthetic wool.
7.	Styrene butadiene rubber (SBR or Buna-S)	$(-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-)_n$	(a) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ (b)	In making automobile tyres and footwear.

8.	Nitrile rubber (Buna-N)	$(-\text{CH}_2-\text{CH}(\text{CN})-\text{CH}_2-\text{CH}(\text{CN})-\text{CH}_2-)_n$	(a) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ (b) $\begin{array}{c} \text{CH} = \text{CH}_2 \\   \\ \text{CN} \end{array}$	In making oil seals, manufacture of hoses and tank linings.
9.	Neoprene	$(-\text{CH}_2-\text{C}(\text{Cl})=\text{CH}-\text{CH}_2-)_n$	$\text{CH}_2 = \underset{\text{Cl}}{\text{C}} - \text{CH} = \text{CH}_2$ Chloroprene	As insulator, making conveyor belts and printing rollers.
10.	Natural rubber (NR)	$\left( \begin{array}{c} \text{CH}_2 \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \\ \text{CH}_3 \end{array} \begin{array}{c} \text{CH}_2 \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \\ \text{H} \end{array} \right)_n$ is form	$\text{CH}_2 = \underset{\text{CH}_3}{\text{C}} - \text{CH} = \text{CH}_2$ Isoprene	In making erasers, tyres, tubes, vulcanised rubber etc.
11.	Terylene (Dacron)	$(-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-)_n$	(a) $\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$ (b) $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	For making fibres, safety belts, tyre cords, tents etc.
12.	Polypropene = P Propene	$(-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-)_n$	Propene $\text{CH}_3 - \text{CH} = \text{CH}_2$	Ropes, toys, pipes, fibre etc. strings.
13.	Glyptal	$(-\text{OCH}_2-\text{CH}_2\text{OOC}-\text{C}_6\text{H}_4-\text{COO}-)_n$	$\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$ $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	As binding material in preparation of mixed plastics and plants.
14.	Nylon 6	$(\text{NH}-[\text{CH}_2]_5-\overset{\text{O}}{\parallel}{\text{C}}-)_n$	 Caprolactum	In making fibres, plastics, tyre cords and ropes.
15.	Nylon 66	$(\text{NH}-\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-)_n$	(a) $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$ (b) $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$	In making brushes, synthetic fibres, parachutes, ropes and carpets.
16.	Bakelite	$\left( \begin{array}{c} \text{OH} \quad \text{OH} \\   \quad   \\ \text{C}_6\text{H}_3 \quad \text{C}_6\text{H}_3 \\   \quad   \\ \text{CH}_2 \quad \text{CH}_2 \end{array} \right)_n$	(a) HCHO (b) $\text{C}_6\text{H}_5\text{OH}$	For making gears, protective coating and electrical fittings.
17.	Urea formaldehyde resin	$(-\text{NH}-\text{CO}-\text{NH}-\text{CH}_2-)_n$	(a) HCHO (b) $\text{NH}_2\text{CONH}_2$	For making unbreakable cups and laminated sheets.
18.	Melamine formaldehyde resin	$\left( \begin{array}{c} \text{NH}_2 \quad \text{NH}_2 \\ \diagdown \quad \diagup \\ \text{N} \quad \text{N} \\ \diagup \quad \diagdown \\ \text{N} \quad \text{N} \\   \quad   \\ \text{NH}_2 \quad \text{NH}_2 \end{array} \right)_n$	(a) $\text{H}_2\text{N}-\text{N}(\text{NH}_2)-\text{N}(\text{NH}_2)-\text{NH}_2$ (b) HCHO	In making plastic crockery, unbreakable cups and plates.
19.	Poly-β-hydroxy butyrate-co-β-hydroxy valerate [PHBV]	$(-\text{O}-\underset{\text{R}}{\text{CH}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-)_n$ $\text{R} = \text{CH}_3\text{C}_2\text{H}_5$	$\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{COOH}$ $\text{CH}_3-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{COOH}$	As packaging, orthopaedic devices and in controlled drug release.

## Types of Polymerization:

You are perhaps already aware of various polymers such as PVC, nylon, Bakelite etc. As you will notice although all these are polymers, they have very distinctly different physical appearance and properties. This is due to the difference in their monomers and their polymerization. So let us study a bit more about condensation and addition polymerization. Polymerization By now you are familiar with the concept of polymers. They are huge chains or sometimes even 3D structures of repeating units known as monomers. The monomer is the basic unit of a polymer. These monomers can bond to each other on each side, potentially forever.

. Broadly polymerization can be classified into two categories,

- Step-Growth or Condensation Polymerization
- Chain-Growth or Addition Polymerization

## Addition Polymerization

As the name suggests addition polymers form when an addition reaction occurs. The repeating monomers form a linear or branch structure depending on the type of monomer. During addition polymerization, the monomers rearrange themselves to form a new structure. But there is no loss of an atom or a molecule. Again there are four types of addition polymerizations which are:

- **Free Radical Polymerization:** Here the addition polymer forms by addition of atoms with a free electron in its valence shells. These are known as free radicals. They join in a successive chain during free radical polymerization.

- **Cationic polymerization:** A polymerization where a cation is formed causing a chain reaction. It results in forming a long chain of repeating monomers
- **Anionic Vinyl Polymerization:** Involves the polymerization of particularly vinyl polymers with a strong electronegative group to form a chain reaction'
- **Coordination Polymerization:** This method was invented by two scientists Ziegler and Natta who won a Nobel Prize for their work. They developed a catalyst which let us control the free radical polymerization. It produces a polymer which has more density and strength

## Condensation Polymerization

Condensation polymers form from the step growth polymerization. Here when molecules of monomers react to form a bond they replace certain molecules. These molecules are the by-product of the reaction. In most cases, this by-product is a water molecule.

The type of polymers that result from a condensation polymerization depends on the monomers. If the monomer has only one reactive group, the polymers that form have low molecular weight. When monomers have two reactive end groups we get linear polymers. And monomers with higher than two reactive groups results in a polymer with a three-dimensional network.

Polyester and nylon are two common condensation polymers. Even Proteins and Carbohydrates are a result of condensation polymerization.

## Preparation of Important Addition Polymers

**Polythene:** - There are two types of polythene-

### Low density polythene:

It is obtained by the polymerization of Ethene under high pressure of 1000 to 2000 atmospheres 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 abstraction has highly branched structure.

Low density polythene is chemically inert and tough but flexible and a poor conductor of electricity.

Hence, it is used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes.

High density polythene:

It is formed when addition polymerization 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.

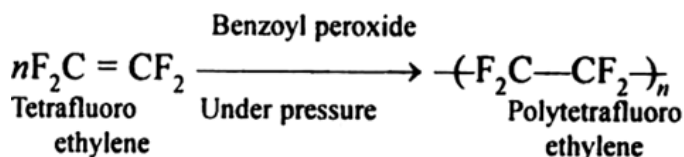
High density polythene (HDP) thus produced, consists of linear molecules and has a high density due to close packing.

It is also chemically inert and more tough and hard. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

### Polytetrafluoroethylene (Teflon)

Teflon is manufactured by heating tetrafluoroethene with a free radical or per sulphate catalyst at high pressures.

It is chemically inert and resistant to attack by corrosive reagents. It is used in making oil seals and gaskets and also used for non – stick surface coated utensils.

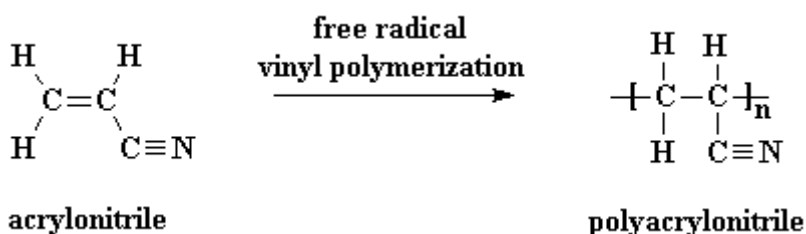




## Polyacrylonitrile

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

Polyacrylonitrile is used as a substitute for wool in making commercial fibres as Orlon or acrilan.



## Condensation Polymerization or step growth polymerization

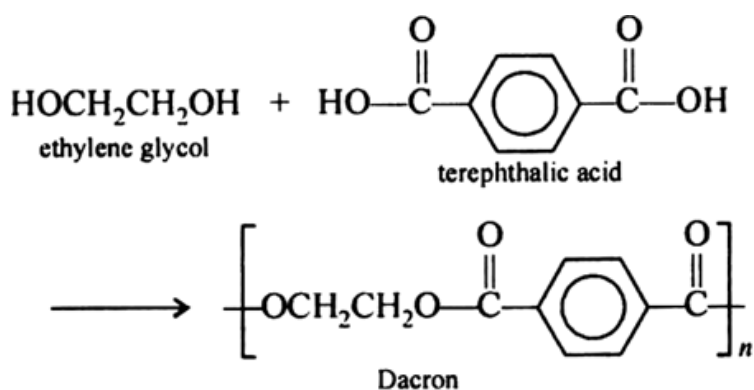
This type of polymerisation involves a repetitive condensation reaction between two bi-functional monomers.

These poly condensation reactions results in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers.

In these reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on.

Since, each step produces a distinct functionalized species and is independent of each other; this process is also called as step growth polymerization.

The formation of Terylene or Dacron by the interaction of ethylene glycol and terephthalic acid is an example of this type of polymerization.



### Polyamides:-

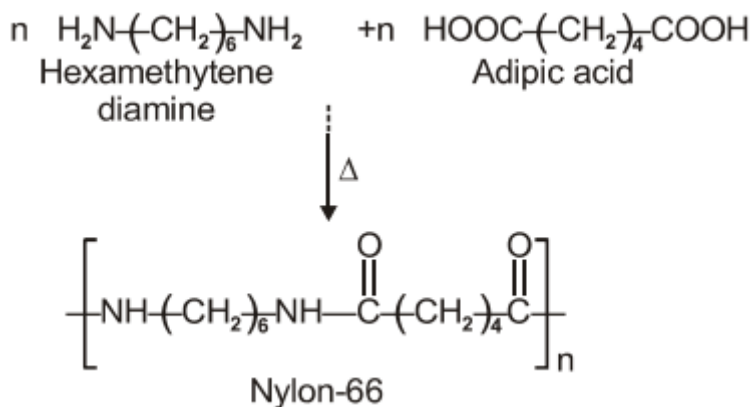
These polymers possessing amide linkages are important examples of synthetic fibres and are termed as nylons. The general method of preparation consists of the condensation polymerization of diamines with dicarboxylic acids and also of amino acids and their lactams.

### Preparation of Nylons

#### Nylon 6, 6:-

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

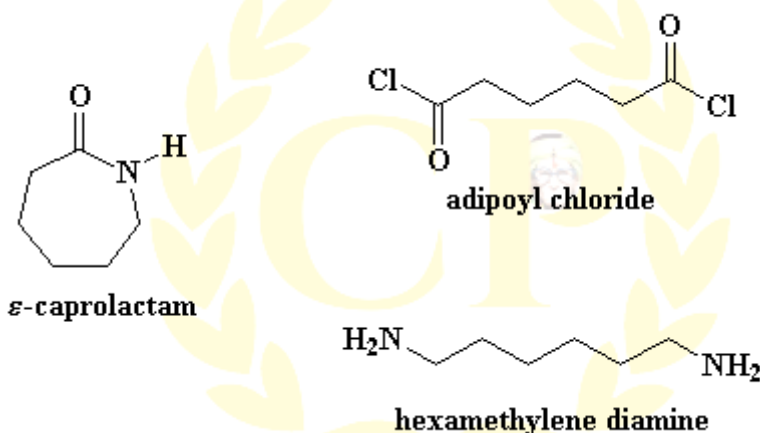
Nylon 6, 6 is used in making sheets, bristles for brushes and in textile industry.



### Nylon 6:-

It is obtained by heating Caprolactum with water at a high temperature.

Nylon 6 is used for the manufacture of tyre cords, fabrics and ropes.

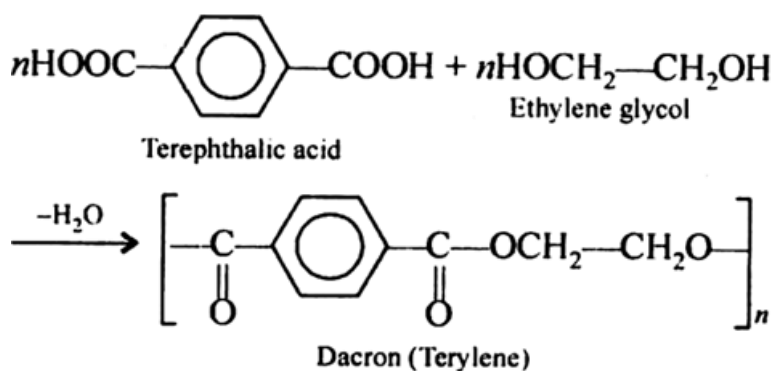


**Polyesters:** - These are the poly condensation products of dicarboxylic acids and diols.

### Dacron or Terylene

It is the best-known example of polyesters. It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of Zinc acetate antimony trioxide catalyst.

Dacron fibre (Terylene) is crease resistant and is used in blending with cotton and wool fibres and also as glass reinforcing materials in safety helmets, etc.



### Phenol – formaldehyde polymer (Bakelite and related polymers):-

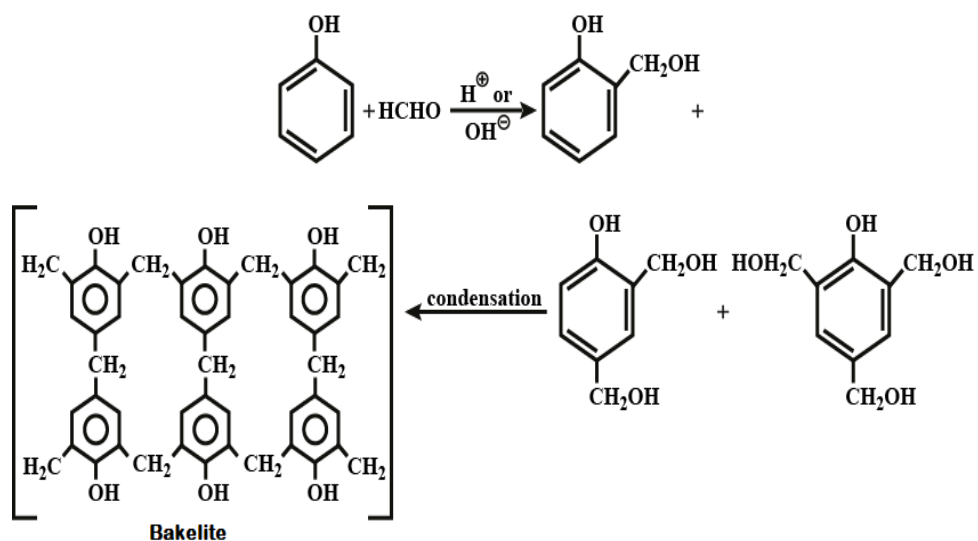
Phenol - formaldehyde polymers are the oldest synthetic polymers.

These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst.

The reaction starts with the initial formation of o-and/or p-hydroxymethylphenol derivatives, which further react with phenol to form compounds having rings joined to each other through  $-\text{CH}_2-$

The initial product could be a linear product – Novolac used in paints.

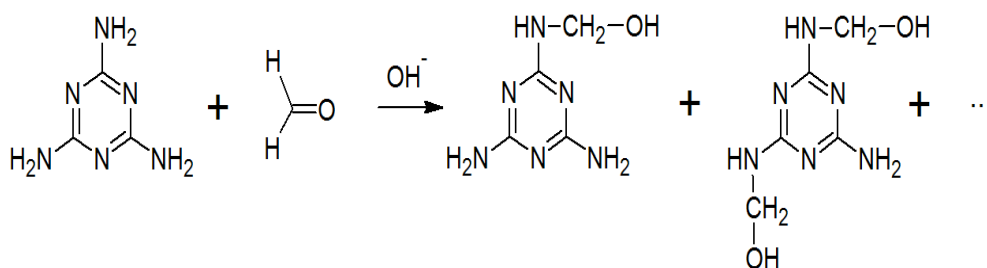
Novolac on heating with formaldehyde undergoes cross linking to form infusible solid mass called Bakelite. It is used for making combs, phonograph records, electrical switches and handles of various utensils.



## Melamine- formaldehyde Polymer:-

Melamine formaldehyde polymer is formed by the condensation polymerization of melamine and formaldehyde.

It is used in the manufacture of unbreakable crockery.



## Co- Polymerization

Co-polymerization is a polymerization reaction in which a mixture of more than one monomeric species is allowed to polymerize and form a copolymer.

The copolymer can be made not only by chain growth polymerization but by step growth polymerization also.

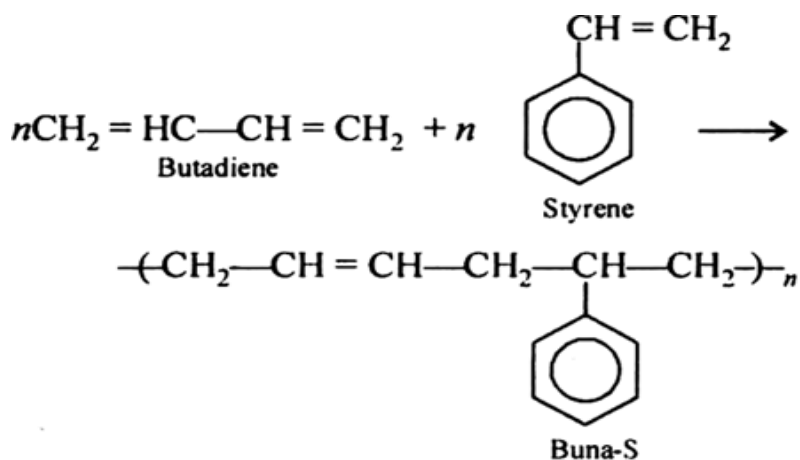
It contains multiple units of each monomer used in the same polymeric chain.

For example:-a mixture of 1, 3 – butadiene and styrene can form a copolymer.

Copolymers have properties quite different from homopolymers.

For example: - butadiene - styrene copolymer is quite tough and is a good substitute for natural rubber.

It is used for the manufacture of auto tyres, floor tiles, footwear components, cable insulation, etc.



## Rubber

Rubber is a natural polymer and possesses elastic properties.

It is also termed as elastomer and has a variety of uses.

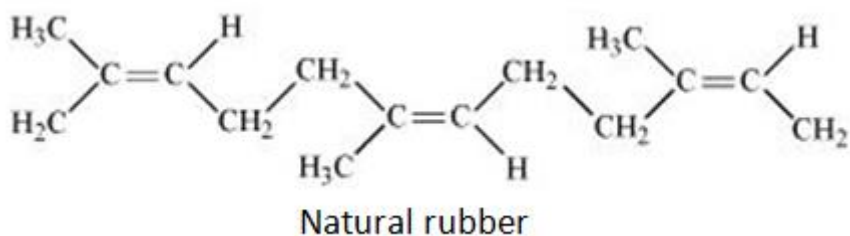
It is manufactured from rubber latex which is a colloidal dispersion of rubber in water. This latex is obtained from the bark of rubber tree and is found in India, Sri Lanka, Indonesia, Malaysia and South America.

## Natural Rubber

Natural rubber may be considered as a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as cis - 1, 4 -polyisoprene.

The cis-polyisoprene molecule consists of various chains held together by weak van der Waals interactions and has a coiled structure.

Thus, it can be stretched like a spring and exhibits elastic properties.



## Vulcanization of Rubber:-

Natural rubber becomes soft at high temperature (>335 K) and brittle at low temperatures (<283 K) and shows high water absorption capacity.

It is soluble in non-polar solvents and is non-resistant to attack by oxidizing agents.

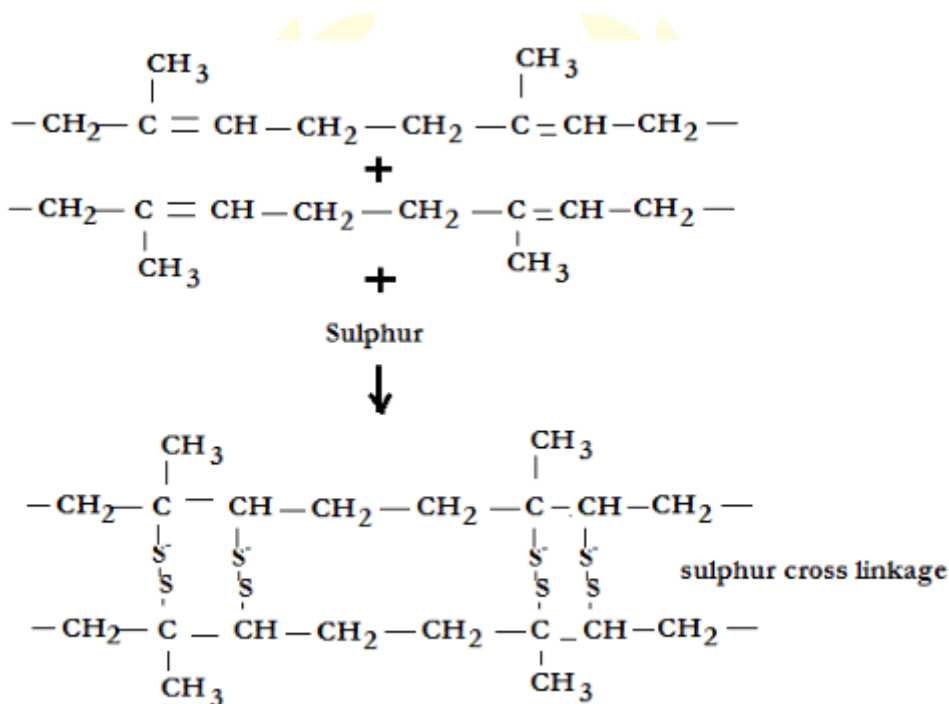
To improve upon these physical properties, a process of vulcanization is carried out.

This process consists of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range 373 K to 415K.

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

In the manufacture of tyre rubber, 5% of sulphur is used as a crosslinking agent.

The probable structures of vulcanized rubber molecules are depicted below:



## Synthetic Rubber

Synthetic rubber is any vulcanizable rubber like polymer, which is capable of getting stretched to twice its length.

However, it returns to its original shape and size as soon as the external stretching force is released.

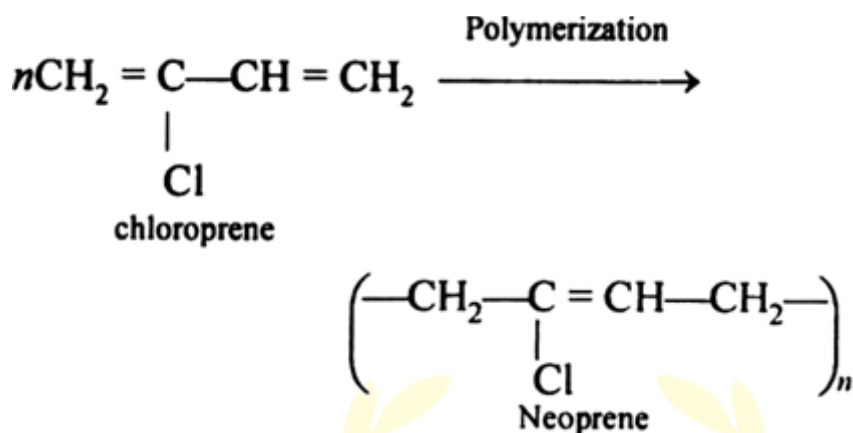
Thus, synthetic rubbers are either homopolymers of 1, 3 - butadiene derivatives or copolymers of 1, 3 - butadiene or its derivatives with another unsaturated monomer.

## Neoprene:-

Neoprene or poly chloroprene is formed by the free radical polymerization of chloroprene.

It has superior resistance to vegetable and mineral oils.

It is used for manufacturing conveyor belts, gaskets and hoses.



### Buna -N:-

Buna -N is obtained by the copolymerization of 1, 3 - butadiene and acrylonitrile in the presence of a peroxide catalyst.

It is resistant to the action of petrol, lubricating oil and organic solvents. It is used in making oil seals, tank lining, etc.

