

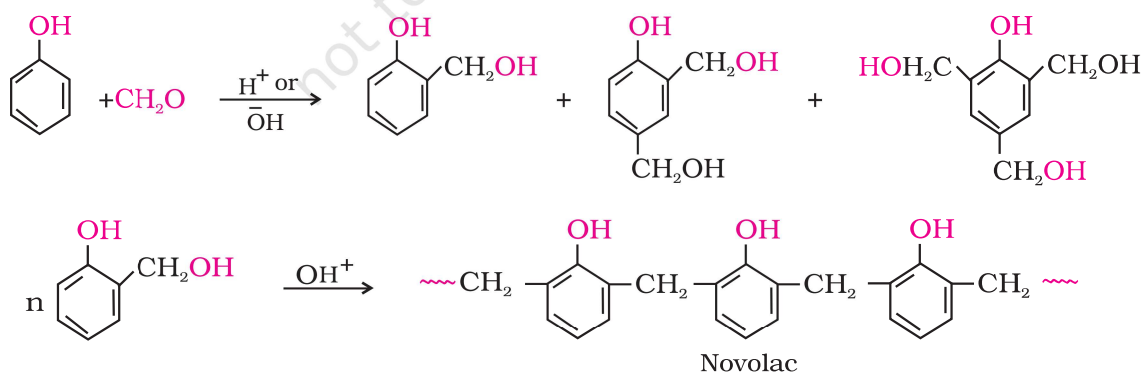
Nylon 6 is used for the manufacture of tyre cords, fabrics and ropes.

### (b) Polyesters

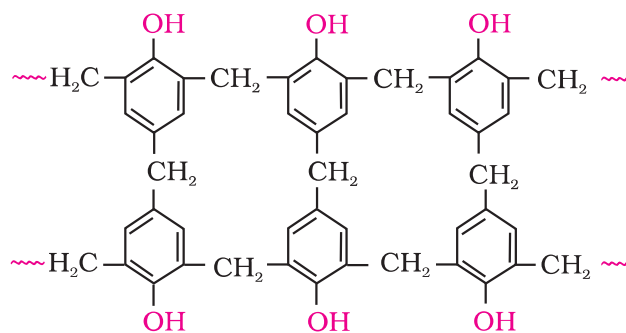
These are the polycondensation products of dicarboxylic acids and diols. Dacron or terylene is the best known example of polyesters. It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetate-antimony trioxide catalyst as per the reaction given earlier. 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.

### (c) 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  $-\text{CH}_2-$  groups. The initial product could be a linear product - **Novolac** used in paints.



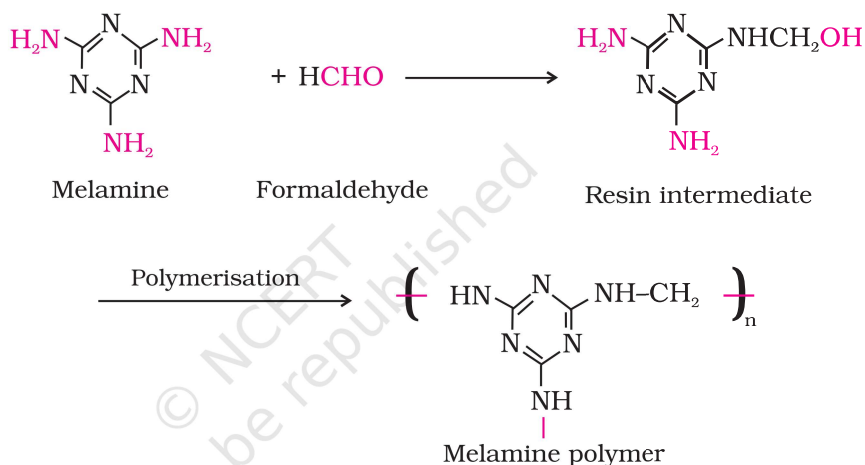
Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called **bakelite**. It is thermosetting polymer which cannot be reused or remoulded. Thus, bakelite is formed by cross linking of linear chains of the polymer novolac. Bakelite is used for making combs, phonograph records, electrical switches and handles of various utensils.



Bakelite

**(d) Melamine — formaldehyde polymer**

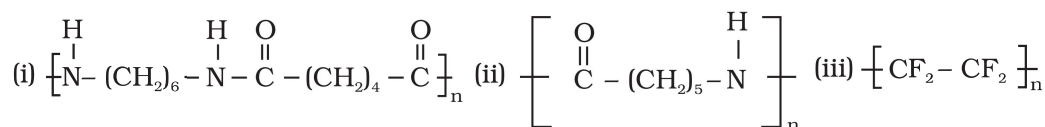
Melamine formaldehyde polymer is formed by the condensation polymerisation of melamine and formaldehyde.



It is used in the manufacture of unbreakable crockery.

Intext Questions

**15.2** Write the names of monomers of the following polymers:

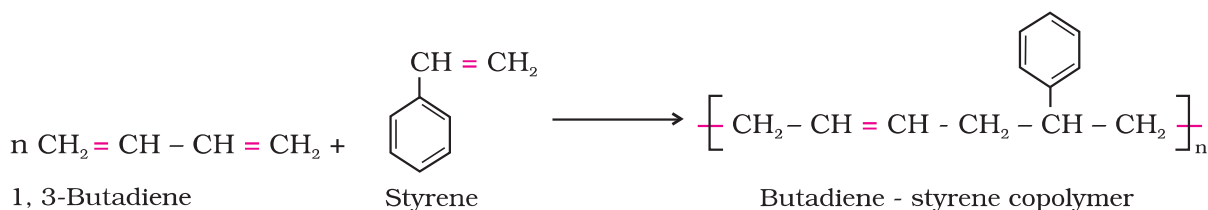


**15.3** Classify the following as addition and condensation polymers: Terylene, Bakelite, Polythene, Teflon.

**15.2.3 Copolymerisation**

Copolymerisation is a polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise and form a copolymer. The copolymer can be made not only by chain growth polymerisation but by step growth polymerisation also. It contains multiple units of each monomer used in the same polymeric chain.

For example, a mixture of buta-1, 3-diene 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 autotyres, floortiles, footwear components, cable insulation, etc.

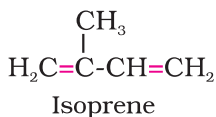
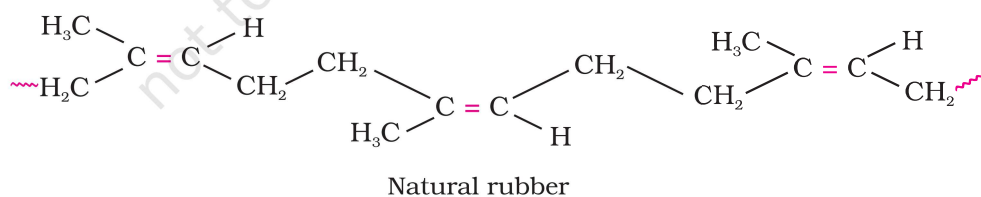
#### 15.2.4 Rubber

##### 1. Natural rubber

Rubber is a natural polymer and possesses elastic properties. It is also termed as elastomeric polymer. In elastomeric polymers, the polymer chains are held together by the weak intermolecular forces. These weak binding forces permit the polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released.

Rubber 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 rubber tree which is found in India, Srilanka, Indonesia, Malaysia and South America.

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.

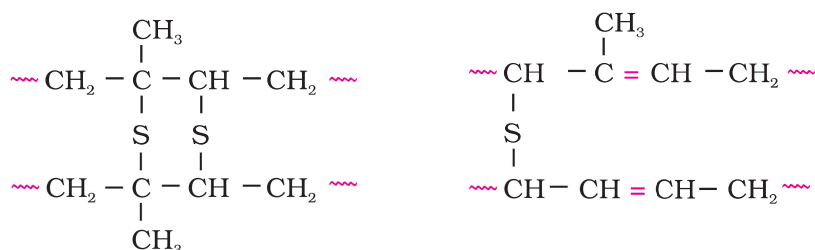


The *cis*-polyisoprene molecule consists of various chains held together by weak van der Waals interactions and has a coiled structure. Thus, it can be stretched like a spring and exhibits elastic properties.

**Vulcanisation 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 oxidising agents. To improve upon these physical properties, a process of vulcanisation is carried out. This process consists of heating a mixture of raw rubber with sulphur and an appropriate additive

at a temperature range between 373 K to 415 K. On vulcanisation, 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 vulcanised rubber molecules are depicted below:



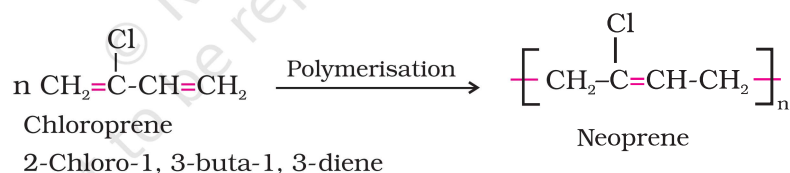
## 2. Synthetic rubbers

Synthetic rubber is any vulcanisable 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.

### Preparation of Synthetic Rubbers

#### 1. Neoprene

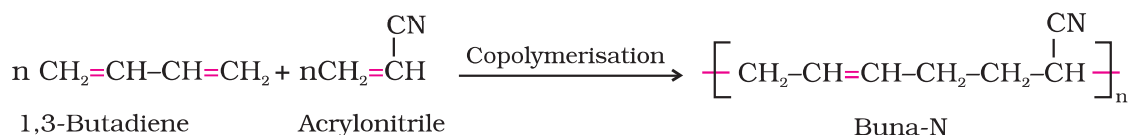
Neoprene or polychloroprene is formed by the free radical polymerisation of chloroprene.



It has superior resistance to vegetable and mineral oils. It is used for manufacturing conveyor belts, gaskets and hoses.

#### 2. Buna - N

You have already studied about Buna-S, in Section 15.1.3. Buna-N is obtained by the copolymerisation 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.

### Intext Questions

- 15.4 Explain the difference between Buna-N and Buna-S.
- 15.5 Arrange the following polymers in increasing order of their intermolecular forces.  
Nylon 6,6, Buna-S, Polythene.

### 15.3 Molecular Mass of Polymers

Polymer properties are closely related to their molecular mass, size and structure. The growth of the polymer chain during their synthesis is dependent upon the availability of the monomers in the reaction mixture. Thus, the polymer sample contains chains of varying lengths and hence its molecular mass is always expressed as an average. The molecular mass of polymers can be determined by chemical and physical methods.

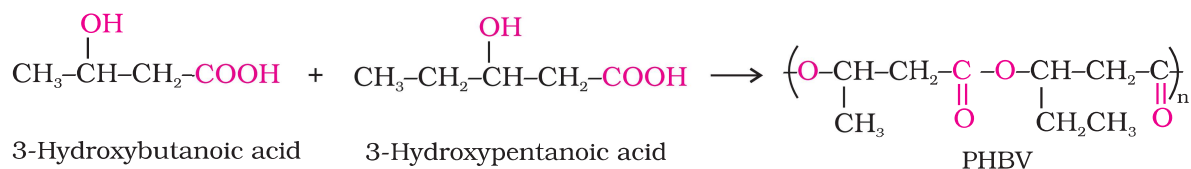
### 15.4 Biodegradable Polymers

A large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric solid waste materials. These solid wastes cause acute environmental problems and remain undegraded for quite a long time. In view of the general awareness and concern for the problems created by the polymeric solid wastes, certain new biodegradable synthetic polymers have been designed and developed. These polymers contain functional groups similar to the functional groups present in biopolymers.

Aliphatic polyesters are one of the important classes of biodegradable polymers. Some important examples are given below:

#### 1. Poly $\beta$ -hydroxybutyrate - co- $\beta$ -hydroxy valerate (PHBV)

It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.



#### 2. Nylon 2-nylon 6

It is an alternating polyamide copolymer of glycine ( $\text{H}_2\text{N-CH}_2\text{-COOH}$ ) and amino caproic acid [ $\text{H}_2\text{N}(\text{CH}_2)_5\text{COOH}$ ] and is biodegradable. Can you write the structure of this copolymer?

## 15.5 Polymers of Commercial Importance

Besides, the polymers already discussed, some other commercially important polymers along with their structures and uses are given below in Table 15.1.

**Table 15.1: Some Other Commercially Important Polymers**

Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$\left( \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} \right)_n$	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene	$\left( \text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right)_n$	As insulator, wrapping material, manufacture of toys, radio and television cabinets.
Polyvinyl chloride (PVC)	Vinyl chloride	$\left( \text{CH}_2 - \underset{\text{Cl}}{\text{CH}} \right)_n$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyde Resin	(a) Urea (b) Formaldehyde	$\left( \text{NH} - \text{CO} - \text{NH} - \text{CH}_2 \right)_n$	For making unbreakable cups and laminated sheets.
Glyptal	(a) Ethylene glycol (b) Phthalic acid	$\left( \text{OCH}_2 - \text{CH}_2 - \text{OOC} \begin{array}{c} \diagup \\ \text{C}_6\text{H}_4 \\ \diagdown \end{array} \text{CO} \right)_n$	Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde	$\left( \begin{array}{c} \text{O-H} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{CH}_2 \end{array} - \begin{array}{c} \text{O-H} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{CH}_2 \end{array} \right)_n$	For making combs, electrical switches, handles of utensils and computer discs.

### Summary

**Polymers** are defined as high molecular mass **macromolecules**, which consist of repeating structural units derived from the corresponding **monomers**. These polymers may be of natural or synthetic origin and are classified in a number of ways.

In the presence of an organic peroxide initiator, the alkenes and their derivatives undergo **addition polymerisation** or **chain growth polymerisation** through a **free radical mechanism**. Polythene, teflon, orlon, etc. are formed by addition polymerisation of an appropriate alkene or its derivative. **Condensation polymerisation** reactions are shown by the interaction of bi- or poly functional monomers containing  $-\text{NH}_2$ ,  $-\text{OH}$  and  $-\text{COOH}$  groups. This type of polymerisation proceeds through the elimination of certain simple molecules as  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , etc. Formaldehyde reacts with phenol and melamine to form the corresponding condensation polymer products. The condensation

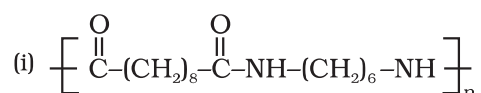


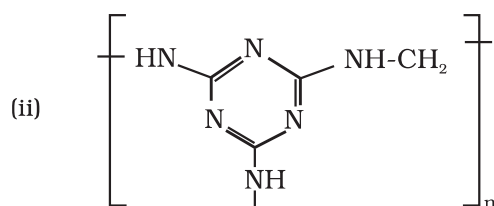
polymerisation progresses through step by step and is also called as **step growth polymerisation**. Nylon, bakelite and dacron are some of the important examples of condensation polymers. However, a mixture of two unsaturated monomers exhibits **copolymerisation** and forms a **co-polymer** containing multiple units of each monomer. Natural rubber is a *cis* 1, 4-polyisoprene and can be made more tough by the process of **vulcanisation** with sulphur. Synthetic rubbers are usually obtained by copolymerisation of alkene and 1, 3 butadiene derivatives.

In view of the potential environmental hazards of synthetic polymeric wastes, certain **biodegradable polymers** such as PHBV and Nylon-2- Nylon-6 are developed as alternatives.

## Exercises

- 15.1 Explain the terms polymer and monomer.
- 15.2 What are natural and synthetic polymers? Give two examples of each type.
- 15.3 Distinguish between the terms homopolymer and copolymer and give an example of each.
- 15.4 How do you explain the functionality of a monomer?
- 15.5 Define the term polymerisation.
- 15.6 Is  $(\text{NH-CHR-CO})_n$ , a homopolymer or copolymer?
- 15.7 Why do elastomers possess elastic properties?
- 15.8 How can you differentiate between addition and condensation polymerisation?
- 15.9 Explain the term copolymerisation and give two examples.
- 15.10 Write the free radical mechanism for the polymerisation of ethene.
- 15.11 Define thermoplastics and thermosetting polymers with two examples of each.
- 15.12 Write the monomers used for getting the following polymers.  
(i) Polyvinyl chloride (ii) Teflon (iii) Bakelite
- 15.13 Write the name and structure of one of the common initiators used in free radical addition polymerisation.
- 15.14 How does the presence of double bonds in rubber molecules influence their structure and reactivity?
- 15.15 Discuss the main purpose of vulcanisation of rubber.
- 15.16 What are the monomeric repeating units of Nylon-6 and Nylon-6,6?
- 15.17 Write the names and structures of the monomers of the following polymers:  
(i) Buna-S (ii) Buna-N (iii) Dacron (iv) Neoprene
- 15.18 Identify the monomer in the following polymeric structures.





**15.19** How is dacron obtained from ethylene glycol and terephthalic acid ?

**15.20** What is a biodegradable polymer ? Give an example of a biodegradable aliphatic polyester.

### Answers of Some Intext Questions

**15.1** Polymers are high molecular mass substances consisting of large numbers of repeating structural units. They are also called as macromolecules. Some examples of polymers are polythene, bakelite, rubber, nylon 6, 6, etc.

**15.2** (i) Hexamethylene diamine and adipic acid.

(ii) Caprolactam.

(iii) Tetrafluoroethene.

**15.3** Addition polymers: Polyvinyl chloride, Polythene.

Condensation polymers: Terylene, Bakelite.

**15.4** Buna-N is a copolymer of 1,3-butadiene and acrylonitrile and Buna-S is a copolymer of 1,3-butadiene and styrene.

**15.5** In order of increasing intermolecular forces.

Buna-S, Polythene, Nylon 6,6.