# Unit 15 Polymers

### <u>Objectives</u>

After studying this Unit, you will be able to

- explain the terms monomer, polymer and polymerisation and appreciate their importance;
- distinguish between various classes of polymers and different types of polymerisation processes;
- appreciate the formation of polymers from mono- and bifunctional monomer molecules;
- describe the preparation of some important synthetic polymers and their properties;
- appreciate the importance of polymers in daily life.

diamine

"Copolymerisation has been used by nature in polypeptides which may contain as many as 20 different amino acids. Chemists are still far behind".

Do you think that daily life would have been easier and colourful without the discovery and varied applications of polymers? The use of polymers in the manufacture of plastic buckets, cups and saucers, children's toys, packaging bags, synthetic clothing materials, automobile tyres, gears and seals, electrical insulating materials and machine parts has completely revolutionised the daily life as well as the industrial scenario. Indeed, the polymers are the backbone of four major industries viz. plastics, elastomers, fibres and paints and varnishes.

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 (10³-10⁵u). These are also referred to as **macromolecules**, which are formed by joining of repeating structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as monomers and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called **polymerisation**. The transformation of ethene to polythene and interaction of hexamethylene diamine and adipic acid leading to the formation of Nylon 6, 6 are examples of two different types of polymerisation reactions.

(i) 
$$nCH_2 = CH_2$$
 Polymerisation  $n \left\{ CH_2 - CH_2 \right\}$   $\longrightarrow$   $\left\{ CH_2 - CH_2 \right\}_n$  Ethene Repeating unit Polythene polymer

(ii)  $nNH_2$   $(CH_2)_6$   $NH_2$  +  $nHOOC$   $(CH_2)_4$   $COOH$  Polymerisation  $\left\{ \begin{matrix} H & H & O & O \\ N-(CH_2)_6 - N - C - (CH_2)_4 - C \end{matrix} \right\}_n$  Hexamethylene Adipic acid Nylon 6.6

## 15.1 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:

#### 15.1.1 Classification Based on 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.

#### 15.1.2 Classification Based on Structure of Polymers

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

#### 1. Linear polymers

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



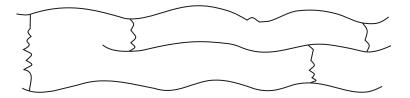
#### 2. Branched chain polymers

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



#### 3. 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:



#### 15.1.3 Classification Based on Mode of Polymerisation

Polymers can also be classified on the basis of mode of polymerisation into two sub groups.

#### 1. Addition polymers

The addition polymers are formed by the repeated addition of 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.

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

$$n \text{ CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 + n \text{ C}_6 \text{H}_5 \text{CH} = \text{CH}_2$$
  $\longrightarrow$   $-(\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_1) = \text{CH}_2 - \text{CH}_2$ 

#### 2. 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.

n H<sub>2</sub>N (CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub> + n HOOC (CH<sub>2</sub>)<sub>4</sub> COOH

$$\longrightarrow \frac{1}{2} \text{NH (CH2)}_6 \text{NHCO(CH2)}_4 \text{CO} = \frac{1}{2} + n \text{ H}_2 \text{O}$$
Nylon 6, 6

Is 
$$+CH_2-CH(C_6H_5)+_n$$
 a homopolymer or a copolymer?

Example 15.1

It is a homopolymer and the monomer from which it is obtained is styrene  $C_6H_5CH = CH_2$ .

Solution

#### Based on Molecular **Forces**

15.1.4 Classification A large number of polymer applications in different fields depend on their unique mechanical properties like tensile strength, elasticity, toughness, etc. These mechanical properties are governed by intermolecular forces, e.g., van der Waals forces and hydrogen bonds, present in the polymer. These forces also bind the polymer chains. Under this category, the polymers are classified into the following four sub groups on the basis of magnitude of intermolecular forces present in them.

#### 1. Elastomers

These are rubber - like solids with elastic properties. In these

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$$\left(\begin{array}{c} CH_2-C=CH-CH_2 \\ CI \\ Cl \\ Neoprene \end{array}\right)$$

elastomeric polymers, the polymer chains are held together by the weakest 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 as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc.

#### 2. Fibres

Fibres are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

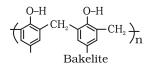
#### 3. Thermoplastic polymers

These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.



#### 4 Thermosetting polymers

These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.



The addition and condensation polymers are nowadays also referred as chain growth polymers and step growth polymers depending on the type of polymerisation mechanism they undergo during their formation.

15.1.5 Classification Based on Growth Polymerisation

Intext Questions

**15.1** What are polymers?

**15.2** How are polymers classified on the basis of structure?

15.2 Types of Polymerisation Reactions

There are two broad types of polymerisation reactions, i.e., the addition or chain growth polymerisation and condensation or step growth polymerisation.

15.2.1 Addition Polymerisation or Polymerisation

In this type of polymerisation, the molecules of the same monomer or diferent monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds, e.g., alkenes, alkadienes Chain Growth and their derivatives. This mode of polymerisation leading to an increase in chain length or chain growth can take place through the formation of either free radicals or ionic species. However, the free radical governed addition or chain growth polymerisation is the most common mode.

#### 1. Free radical mechanism

A variety of alkenes or dienes and their derivatives are polymerised in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. For example, the polymerisation of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide initiator. The process starts with the addition of phenyl free radical formed by the peroxide to the ethene double bond thus generating a new and larger free radical. This step is called chain initiating step. As this radical reacts with another molecule of ethene, another bigger sized radical is formed. The repetition of this sequence with new and bigger radicals carries the reaction forward and the step is termed as **chain propagating step**. Ultimately, at some stage the product radical thus formed reacts with another radical to form the polymerised product. This step is called the **chain terminating step**. The sequence of steps may be depicted as follows:

Chain initiation steps

Chain propagating step

Chain terminating step

For termination of the long chain, these free radicals can combine in different ways to form polythene. One mode of termination of chain is shown as under:

$$C_{6}H_{5} + CH_{2} - CH_{2} + \mathring{C}H_{2} - \mathring{C}H_{2}$$

$$C_{6}H_{5} + CH_{2} - \mathring{C}H_{2} + \mathring{C}H_{2} - \mathring{C}H_{2}$$

$$C_{6}H_{5} + CH_{2} - \mathring{C}H_{2} + \mathring{C}H_{2} - \mathring{C}H_{2}$$

$$C_{6}H_{5} + CH_{2} - \mathring{C}H_{2} + \mathring{C}H_{2} - \mathring{C}H_{2}$$

$$C_{6}H_{5} + CH_{2} - \mathring{C}H_{2} + \mathring{C}H_{2} - \mathring{C}H_{2} + \mathring{C}H_{2} - \mathring{C}H_{2}$$

$$Polythene$$

#### 2 Preparation of some important addition 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 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

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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.

(ii) 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 molecules and has a high density due to close packing. It is also chemically inert and more tougher and harder. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

(b) Polytetrafluoroethene (Teflon)

Teflon is manufactured by heating tetrafluoroethene with a free radical or persulphate 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.

$$\begin{array}{ccc} n & CF_2 = CF_2 & \xrightarrow{\quad \text{High pressure} \quad} & \xrightarrow{\quad \text{CF}_2 - CF_2 \quad} \xrightarrow{\quad \text{Teflon} \quad} \\ \end{array}$$

(c) Polyacrylonitrile

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

$$\begin{array}{c} \text{n CH}_2 = \text{CHCN} & \xrightarrow{\text{Polymerisation}} & \begin{array}{c} \text{CN} \\ \text{-} \text{CH}_2 - \text{CH} \end{array} \\ \text{Acrylonitrile} & \begin{array}{c} \text{CN} \\ \text{-} \text{CH}_2 - \text{CH} \end{array} \\ \end{array}$$

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

15.2.2 Condensation Polymerisation or Step merisation

G. Natta of Imperia and

Karl Ziegler of Germany

were awarded the Nobel

Prize for Chemistry in 1963 for the development

of Ziegler-Natta catalyst.

Teflon coatings undergo

Acrylic fibres have good

resistance to stains, chemicals, insects and

decomposition temperatures above

300 C.

fungi.

This type of polymerisation generally involves a repetitive condensation reaction between two bi-functional monomers. These polycondensation reactions may result in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass Growth poly- 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 functionalised species and is independent of each other, this process is also called as step growth polymerisation.

> The formation of terylene or dacron by the interaction of ethylene glycol and terephthalic acid is an example of this type of polymerisation.

Some important condensation polymerisation reactions characterised by their linking units are described below:

#### 1. 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 polymerisation of diamines with dicarboxylic acids and also of amino acids and their lactams.

#### (a) Preparation of nylons

**(i)** *Nylon 6,6:* It is prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.

$$n \operatorname{HOOC}(\operatorname{CH}_2)_4 \operatorname{COOH} + n \operatorname{H}_2\operatorname{N} (\operatorname{CH}_2)_6 \operatorname{NH}_2 \xrightarrow{553\operatorname{K}} \begin{array}{c} H & H & O & O \\ \hline H & H & O & O \\ \hline H & N - (\operatorname{CH}_2)_6 - \operatorname{N} - \operatorname{C}(\operatorname{CH}_2)_4 - \operatorname{C} \end{array} \right]_n$$

$$N \operatorname{NVlon} 6.6$$

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

(ii) *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.

#### 2. 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.

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#### 3. 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  $-\mathrm{CH}_2$  groups. The initial product could be a linear product - **Novolac** used in paints.

$$OH \longrightarrow OH \longrightarrow CH_2OH \longrightarrow$$

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

Bakelite

#### 4. 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.

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

**15.4** Classify the following as addition and condensation polymers: Terylene, Bakelite, Polyvinyl chloride, Polythene.

### 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 1, 3 – butadiene and styrene can form a copolymer.

$$CH = CH_{2}$$

$$n CH_{2} = CH - CH = CH_{2} + CH_{2} - CH - CH_{2} - CH - CH_{2}$$

$$1, 3-Butadiene Styrene Butadiene - styrene copolymer$$

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 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, 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.

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Natural rubber

$$CH_3$$
 $H_2C=C-CH=CH_2$ 
Isoprene

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.

$$\begin{array}{c} \text{Cl} & \text{Cl} \\ \text{n CH}_2\text{-C-CH=CH}_2 & \xrightarrow{\text{Polymerisation}} & \begin{array}{c} \text{Cl} \\ \text{l} \\ \text{CH}_2\text{-C=CH-CH}_2 \end{array} \end{array}$$

$$\begin{array}{c} \text{Cl} \\ \text{Neoprene} \\ \text{Neoprene} \end{array}$$

2-Chloro-1, 3-butadiene

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.

$$\begin{array}{c} \text{CN} \\ \text{n CH}_2\text{=CH-CH=CH}_2\text{+ nCH}_2\text{=CH} \end{array} \xrightarrow{\text{Copolymerisation}} \begin{array}{c} \text{CN} \\ \text{Copolymerisation} \end{array} \\ \begin{array}{c} \text{CH}_2\text{-CH=CH-CH}_2\text{-CH}_2\text{-CH} \end{array} \\ \begin{array}{c} \text{I} \\ \text{I} \\ \text{I} \\ \text{J} \end{array}$$

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

- **15.5** Explain the difference between Buna-N and Buna-S.
- **15.6** Arrange the following polymers in increasing order of their intermolecular forces.
  - (i) Nylon 6,6, Buna-S, Polythene.
  - (ii) Nylon 6, Neoprene, Polyvinyl chloride.

#### 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.

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15.4 Biodegradable 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.

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#### 2. Nylon 2-nylon 6

It is an alternating polyamide copolymer of glycine ( $H_2N-CH_2-COOH$ ) and amino caproic acid [ $H_2N$  ( $CH_2$ )<sub>5</sub> 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	$\left( - CH_2 - CH \right)_n$	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene	$ \begin{array}{c} C_6H_5\\ +CH_2-CH \end{array} $	As insulator, wrapping material, manufacture of toys, radio and television cabinets.
Polyvinyl chloride (PVC)	Vinyl chloride	CH <sub>2</sub> -CH	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyle Resin	(a) Urea (b) Formaldehyde	+ NH-CO-NH-CH <sub>2</sub>	For making unbreak- able cups and laminated sheets.
Glyptal	(a) Ethylene glycol (b) Phthalic acid	COH <sub>2</sub> -CH <sub>2</sub> OOC CO	Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	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 –  $\mathrm{NH}_2$ , –  $\mathrm{OH}$  and –  $\mathrm{COOH}$  groups. This type of polymerisation proceeds through the elimination of certain simple molecules as  $\mathrm{H}_2\mathrm{O}$ ,  $\mathrm{CH}_3\mathrm{OH}$ , 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 (NH-CHR-CO)<sub>n</sub>, a homopolymer or copolymer?
- 15.7 In which classes, the polymers are classified on the basis of molecular forces?
- 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.

(i) 
$$+ C - (CH_2)_8 - C - NH - (CH_2)_6 - NH = \frac{1}{n}$$

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- 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 On the basis of structure, the polymers are classified as below:
  - (i) Linear polymers such as polythene, polyvinyl chloride, etc.
  - (ii) Branched chain polymers such as low density polythene.
  - (iii) Cross linked polymers such as bakelite, melamine, etc.
- 15.3 (i) Hexamethylene diamine and adipic acid.
  - (ii) Caprolactam.
  - (iii) Tetrafluoroethene.
- **15.4** Addition polymers: Polyvinyl chloride, Polythene. Condensation polymers: Terylene, Bakelite.
- **15.5** Buna-N is a copolymer of 1,3-butadiene and acrylonitrile and Buna-S is a copolymer of 1,3-butadiene and styrene.
- 15.6 In order of increasing intermolecular forces.
  - (i) Buna-S, Polythene, Nylon 6,6.
  - (ii) Neoprene, Polyvinyl chloride, Nylon 6.

# Unit Chemistry Everyday

V.I. Lenin.

From living perception to abstract thought, and from this to practice.

### hiectives

After studying this Unit you will be able to

- visualise the importance Chemistry in daily life;
- explain the term 'chemotherapy';
- describe the basis of classification of drugs;
- explain drug-target interaction of enzymes and receptors;
- explain how various types of drugs function in the body;
- know about artificial sweetening agents and food preservatives;
- discuss the chemistry of cleansing agents.

By now, you have learnt the basic principles of chemistry and also realised that it influences every sphere of human life. The principles of chemistry have been used for the benefit of mankind. Think of cleanliness — the materials like soaps, detergents, household bleaches, tooth pastes, etc. will come to your mind. Look towards the beautiful clothes — immediately chemicals of the synthetic fibres used for making clothes and chemicals giving colours to them will come to your mind. Food materials — again a number of chemicals about which you have learnt in the previous Unit will appear in your mind. Of course, sickness and diseases remind us of medicines — again chemicals. Explosives, fuels, rocket propellents, building and electronic materials, etc., are all chemicals. Chemistry has influenced our life so much that we do not even realise that we come across chemicals at every moment; that we ourselves are beautiful chemical creations and all our activities are controlled by chemicals. In this Unit, we shall learn the application of Chemistry in three important and interesting areas, namely - medicines, food materials and cleansing agents.

16.1 Drugs and their Classification

**Drugs** are chemicals of low molecular masses (~100 - 500u). These interact with macromolecular targets and produce a biological response. When the biological response is therapeutic and useful, these chemicals are called medicines and are used in diagnosis, prevention and treatment of diseases. If taken in doses higher than those recommended, most of the drugs used as medicines are potential poisons. Use of chemicals for therapeutic effect is called chemotherapy,

#### 16.1.1

### Classification of Drugs

Drugs can be classified mainly on criteria outlined as follows:

#### (a) On the basis of pharmacological effect

This classification is based on pharmacological effect of the drugs. It is useful for doctors because it provides them the whole range of drugs available for the treatment of a particular type of problem. For example, analgesics have pain killing effect, antiseptics kill or arrest the growth of microorganisms.

#### (b) On the basis of drug action

It is based on the action of a drug on a particular biochemical process. For example, all antihistamines inhibit the action of the compound, histamine which causes inflammation in the body. There are various ways in which action of histamines can be blocked. You will learn about this in Section 16.3.2.

#### (c) On the basis of chemical structure

It is based on the chemical structure of the drug. Drugs classified in this way share common structural features and often have similar pharmacological activity. For example, sulphonamides have common structural feature, given below.

Structural features of sulphonamides

#### (d) On the basis of molecular targets

Drugs usually interact with biomolecules such as carbohydrates, lipids, proteins and nucleic acids. These are called target molecules or drug targets. Drugs possessing some common structural features may have the same mechanism of action on targets. The classification based on molecular targets is the most useful classification for medicinal chemists.

# 16.2 Drug-Target Interaction

Macromolecules of biological origin perform various functions in the body. For example, proteins which perform the role of biological catalysts in the body are called **enzymes**, those which are crucial to communication system in the body are called **receptors**. Carrier proteins carry polar molecules across the cell membrane. Nucleic acids have coded genetic information for the cell. Lipids and carbohydrates are structural parts of the cell membrane. We shall explain the drug-target interaction with the examples of enzymes and receptors.

#### 16.2.1 Enzymes as Drug Targets

#### (a) Catalytic action of enzymes

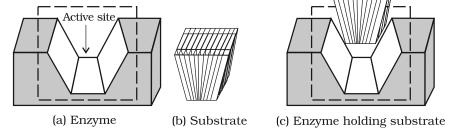
For understanding the interaction between a drug and an enzyme, it is important to know how enzymes catalyse the reaction (Section 5.2.4). In their catalytic activity, enzymes perform two major functions:

(i) The first function of an enzyme is to hold the substrate for a chemical reaction. Active sites of enzymes hold the substrate molecule in a suitable position, so that it can be attacked by the reagent effectively.

Substrates bind to the active site of the enzyme through a variety of interactions such as ionic bonding, hydrogen bonding, van der Waals interaction or dipole-dipole

interaction (Fig. 16.1).

Fig. 16.1 (a) Active site of an enzyme (b) Substrate (c) Substrate held in active site of the enzyme



(ii) The second function of an enzyme is to provide functional groups that will attack the substrate and carry out chemical reaction.

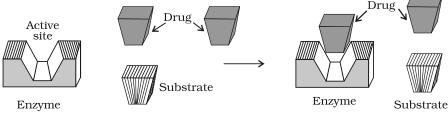
#### (b) Drug-enzyme interaction

Drugs inhibit any of the above mentioned activities of enzymes. These can block the binding site of the enzyme and prevent the binding of substrate, or can inhibit the catalytic activity of the enzyme. Such drugs are called enzyme inhibitors.

Drugs inhibit the attachment of substrate on active site of enzymes in two different ways;

(i) Drugs compete with the natural substrate for their attachment on the active sites of enzymes. Such drugs are called competitive inhibitors (Fig. 16.2).

Fig. 16.2 Drug and substrate competing for active site



Drug and substrate competing for active site of enzyme

Drug blocks the active site of enzyme

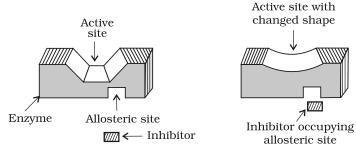


Fig. 16.3: Non-competitive inhibitor changes the active site of enzyme after binding at allosteric site.

(ii) Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is called allosteric site. This binding of inhibitor at allosteric site (Fig. 16.3) changes the shape of the active site in such a way that substrate cannot recognise it.

If the bond formed between an enzyme and an inhibitor is a strong covalent bond and

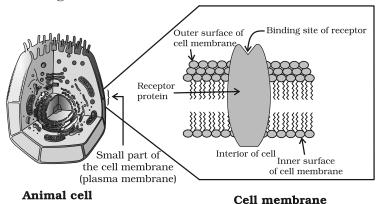
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cannot be broken easily, then the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesises the new enzyme.

#### 16.2.2 Receptors as Drug Targets

Receptors are proteins that are crucial to body's communication process. Majority of these are embedded in cell membranes (Fig. 16.4). Receptor proteins are embedded in the cell membrane in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane (Fig. 16.4).

Fig. 16.4
Receptor protein embedded in the cell membrane, the active site of the receptor opens on the outside region of the cell.



In the body, message between two neurons and that between neurons to muscles is communicated through certain chemicals. These chemicals, known as **chemical messengers** are received at the binding sites of receptor proteins. To accommodate a messenger, shape of the receptor site changes. This brings about the transfer of message into the cell. Thus, chemical messenger gives message to the cell without entering the cell (Fig. 16.5).

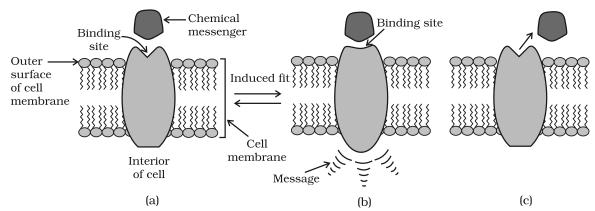


Fig. 16.5: (a) Receptor receiving chemical messenger

- (b) Shape of the receptor changed after attachment of messenger
- (c) Receptor regains structure after removal of chemical messenger.

There are a large number of different receptors in the body that interact with different chemical messengers. These receptors show selectivity for one chemical messenger over the other because their binding sites have different shape, structure and amino acid composition.

Drugs that bind to the receptor site and inhibit its natural function are called **antagonists**. These are useful when blocking of message is required. There are other types of drugs that mimic the natural messenger by switching on the receptor, these are called **agonists**. These are useful when there is lack of natural chemical messenger.

# 16.3 Therapeutic Action of Different Classes of Drugs

In this Section, we shall discuss the therapeutic action of a few important classes of drugs.

#### 16.3.1 Antacids

Over production of acid in the stomach causes irritation and pain. In severe cases, ulcers are developed in the stomach. Until 1970, only treatment for acidity was administration of antacids, such as sodium hydrogenearbonate or a mixture of aluminium and magnesium hydroxide. However, excessive hydrogenearbonate can make the stomach alkaline and trigger the production of even more acid. Metal hydroxides are better alternatives because of being insoluble, these do not increase the pH above neutrality. These treatments control only symptoms, and not the cause. Therefore, with these metal salts, the patients cannot be treated easily. In advanced stages, ulcers become life threatening and its only treatment is removal of the affected part of the stomach.

### 16.3.2 Antihistamines

A major breakthrough in the treatment of hyperacidity came through the discovery according to which a chemical, histamine, stimulates the secretion of pepsin and hydrochloric acid in the stomach. The drug cimetidine (Tegamet), was designed to prevent the interaction of histamine with the receptors present in the stomach wall. This resulted in release of lesser amount of acid. The importance of the drug was so much that it remained the largest selling drug in the world until another drug, ranitidine (Zantac), was discovered.

Histamine is a potent vasodilator. It has various functions. It contracts the smooth muscles in the bronchi and gut and relaxes other muscles, such as those in the walls of fine blood vessels. Histamine is also responsible for the nasal congestion associated with common cold and allergic response to pollen.

Synthetic drugs, **brompheniramine** (**Dimetapp**) and **terfenadine** (**Seldane**), act as antihistamines. They interfere with the natural action

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#### 16.3.3 Neurologically Active Drugs

#### (a) Tranquilizers

**Tranquilizers** and **analgesics** are neurologically active drugs. These affect the message transfer mechanism from nerve to receptor.

Tranquilizers are a class of chemical compounds used for the treatment of stress, and mild or even severe mental diseases. These relieve anxiety, stress, irritability or excitement by inducing a sense of well-being. They form an essential component of sleeping pills. There are various types of tranquilizers. They function by different mechanisms. For example, noradrenaline is one of the neurotransmitters that plays a role in mood changes. If the level of noradrenaline is low for some reason, then the signal-sending activity

O NHNHCH(
$$\mathrm{CH_3}$$
)<sub>2</sub>

$$\mathrm{NHNH_2}$$
Iproniazid Phenelzine (Nardil)

becomes low, and the person suffers from depression. In such situations, antidepressant drugs are required. These drugs inhibit the enzymes which catalyse the degradation of noradrenaline. If the enzyme is inhibited, this important neurotransmitter is slowly metabolised and can activate its receptor for longer periods of time, thus counteracting the effect of depression. Iproniazid and phenelzine are two such drugs.

of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.

Now the question that

arises is, "Why do above mentioned antihistamines not affect the secretion of acid in

stomach?" The reason is that

antiallergic and antacid drugs work on different receptors.

Some tranquilizers namely, chlordiazepoxide and meprobamate, are relatively mild tranquilizers suitable for relieving tension. Equanil is used in controlling depression and hypertension.

Derivatives of barbituric acid viz., veronal, amytal, nembutal, luminal and seconal constitute an important class of tranquilizers. These derivatives are called **barbiturates**. Barbiturates are hypnotic, *i.e.*, sleep producing agents. Some other substances used as tranquilizers are valium and serotonin.

#### (b) Analgesics

**Analgesics** reduce or abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system. These are classified as follows:

- (i) Non-narcotic (non-addictive) analgesics
- (ii) Narcotic drugs
- (i) Non-narcotic (non-addictive) analgesics: Aspirin and paracetamol belong to the class of non-narcotic analgesics. Aspirin is the most familiar example. Aspirin inhibits the synthesis of chemicals known as prostaglandins which stimulate inflammation in the tissue and cause pain. These drugs are effective in relieving skeletal pain such as that due to arthritis. These drugs have many other effects such as reducing fever (antipyretic) and preventing platelet coagulation. Because of its anti blood clotting action, aspirin finds use in prevention of heart attacks.
- (ii) *Narcotic analgesics:* Morphine and many of its homologues, when administered in medicinal doses, relieve pain and produce sleep. In poisonous doses, these produce stupor, coma, convulsions and ultimately death. Morphine narcotics are sometimes referred to as opiates, since they are obtained from the opium poppy.

These analgesics are chiefly used for the relief of postoperative pain, cardiac pain and pains of terminal cancer, and in child birth.

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#### 16.3.4 Antimicrobials

Diseases in human beings and animals may be caused by a variety of microorganisms such as bacteria, virus, fungi and other pathogens. An antimicrobial tends to destroy/prevent development or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (antifungal agents), virus (antiviral agents), or other parasites (antiparasitic drugs) selectively. Antibiotics, antiseptics and disinfectants are antimicrobial drugs.

#### (a) Antibiotics

Antibiotics are used as drugs to treat infections because of their low toxicity for humans and animals. Initially antibiotics were classified as chemical substances produced by microorganisms (bacteria, fungi and molds) that inhibit the growth or even destroy microorganisms. The development of synthetic methods has helped in synthesising some of the compounds that were originally discovered as products of microorganisms. Also, some purely synthetic compounds have antibacterial activity, and therefore, definition of antibiotic has been modified. An antibiotic now refers to a substance produced wholly or partly by chemical synthesis, which in low concentrations inhibits the growth or destroys microorganisms by intervening in their metabolic processes.

The search for chemicals that would adversely affect invading bacteria but not the host began in the nineteenth century. Paul Ehrlich, a German bacteriologist, conceived this idea. He investigated arsenic based structures in order to produce less toxic substances for the treatment of syphilis. He developed the medicine, **arsphenamine**, known as **salvarsan**. Paul Ehrlich got Nobel prize for Medicine in 1908 for this discovery. It was the first effective treatment discovered for syphilis. Although salvarsan is toxic to human beings, its effect on the bacteria, spirochete, which causes syphilis is much greater than on human beings. At the same time, Ehrlich was working on azodyes also. He noted that there is similarity in structures of salvarsan and

The structures of salvarsan, prontosil azodye and sulphapyridine showing structural

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similarity.

H.W. Florey and Alexander Fleming shared the Nobel prize for Medicine in 1945 for their independent contributions to the development of penicillin.

azodyes. The -As = As – linkage present in arsphenamine resembles the -N = N – linkage present in azodyes in the sense that arsenic atom is present in place of nitrogen. He also noted tissues getting coloured by dyes selectively. Therefore, Ehrlich began to search for the compounds which resemble in structure to azodyes and selectively bind to bacteria. In 1932, he succeeded in preparing the first effective antibacterial agent, **prontosil**, which resembles in structure to the compound, salvarsan. Soon it was discovered that in the body prontosil is converted to a compound called **sulphanilamide**, which is the real active compound. Thus the sulpha drugs were discovered. A large range of sulphonamide analogues was synthesised. One of the most effective is sulphapyridine.

Despite the success of sulfonamides, the real revolution in antibacterial therapy began with the discovery of Alexander Fleming in 1929, of the antibacterial properties of a *Penicillium* fungus. Isolation and purification of active compound to accumulate sufficient material for clinical trials took thirteen years.

Antibiotics have either cidal (killing) effect or a static (inhibitory) effect on microbes. A few examples of the two types of antibiotics are as follows:

BactericidalBacteriostaticPenicillinErythromycinAminoglycosidesTetracyclineOfloxacinChloramphenicol

The range of bacteria or other microorganisms that are affected by a certain antibiotic is expressed as its spectrum of action. Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be **broad spectrum antibiotics**. Those effective mainly against Gram-positive or Gram-negative bacteria are **narrow spectrum antibiotics**. If effective against a single organism or disease, they are referred to as **limited spectrum** antibiotics. Penicillin G has a narrow spectrum. Ampicillin and Amoxycillin are synthetic modifications of penicillins. These have broad spectrum. It is absolutely essential to test the patients for sensitivity (allergy) to penicillin before it is administered. In India, penicillin is manufactured at the Hindustan Antibiotics in Pimpri and in private sector industry.

Chloramphenicol, isolated in 1947, is a broad spectrum antibiotic. It is rapidly absorbed from the gastrointestinal tract and hence can be given orally in case of typhoid, dysentery, acute fever, certain form of urinary infections, meningitis and pneumonia. Vancomycin and ofloxacin are the other important broad spectrum antibiotics. The antibiotic dysidazirine is supposed to be toxic towards certain strains of cancer cells.

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#### (b) Antiseptics and disinfectants

Bithionol

Antiseptics and disinfectants are also the chemicals which either kill or prevent the growth of microorganisms.

**Antiseptics** are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces. Examples are **furacine**, **soframicine**, etc. These are not ingested like antibiotics. Commonly used antiseptic, dettol is a mixture of **chloroxylenol** and **terpineol**. Bithionol (the compound is also called bithional) is added to soaps to

Terpineol

Iodine is a powerful antiseptic. Its 2-3 per cent solution in alcoholwater mixture is known as **tincture of iodine**. It is applied on wounds. **Iodoform** is also used as an antiseptic for wounds. Boric acid in dilute aqueous solution is weak antiseptic for eyes.

impart antiseptic properties.

**Disinfectants** are applied to inanimate objects such as floors, drainage system, instruments, etc. Same substances can act as an antiseptic as well as disinfectant by varying the concentration. For example, 0.2 per cent solution of phenol is an antiseptic while its one percent solution is disinfectant.

Chlorine in the concentration of 0.2 to 0.4 ppm in aqueous solution and sulphur dioxide in very low concentrations, are disinfectants.

#### 16.3.5 Antifertility Drugs

Chloroxylenol

Antibiotic revolution has provided long and healthy life to people. The life expectancy has almost doubled. The increased population has caused many social problems in terms of food resources, environmental issues, employment, etc. To control these problems, population is required to be controlled. This has lead to the concept of family planning. Antifertility drugs are of use in this direction. Birth control pills essentially contain a mixture of synthetic estrogen and progesterone derivatives. Both of these compounds are hormones. It is known that progesterone suppresses ovulation. Synthetic progesterone derivatives are more potent than

progesterone. **Norethindrone** is an example of synthetic progesterone derivative most widely used as antifertility drug. The estrogen derivative which is used in combination with progesterone derivative is **ethynylestradiol (novestrol)**.

#### Intext Questions

- **16.1** Sleeping pills are recommended by doctors to the patients suffering from sleeplessness but it is not advisable to take its doses without consultation with the doctor. Why?
- **16.2** With reference to which classification has the statement, "ranitidine is an antacid" been given?

## 16.4 Chemicals in Food

Chemicals are added to food for (i) their preservation, (ii) enhancing their appeal, and (iii) adding nutritive value in them. Main categories of food additives are as follows:

- (i) Food colours
- (ii) Flavours and sweeteners
- (iii) Fat emulsifiers and stabilising agents
- (iv) Flour improvers antistaling agents and bleaches
- (v) Antioxidants
- (vi) Preservatives
- (vii) Nutritional supplements such as minerals, vitamins and amino acids.

Except for chemicals of category (vii), none of the above additives have nutritive value. These are added either to increase the shelf life of stored food or for cosmetic purposes. In this Section we will discuss only sweeteners and food preservatives.

#### 16.4.1 Artificial Sweetening Agents

Natural sweeteners, e.g., sucrose add to calorie intake and therefore many people prefer to use artificial sweeteners. Ortho-sulphobenzimide, also called saccharin, is the first popular artificial sweetening agent. It has been used as a sweetening agent ever since it was discovered in 1879. It is about 550 times as sweet as cane sugar. It is excreted from the body in urine unchanged. It appears to be entirely inert and harmless when taken. Its use is of great value to diabetic persons and people who need to control intake of calories. Some other commonly marketed artificial sweeteners are given in Table 16.1.

Table 16.1: Artificial Sweeteners

Artificial sweetener	Structural formula	Sweetness value in comparison to cane sugar
Aspartame	O O O HO-C-CH <sub>2</sub> -CH-C-NH-CH-C-OCH <sub>3</sub> NH <sub>2</sub> CH <sub>2</sub> Aspartic acid part	100
	Phenylalanine methyl ester part	
Saccharin	CO NH SO <sub>2</sub>	550
Sucrolose	H CH <sub>2</sub> OH O H OH H HO CH <sub>2</sub> Cl ClH <sub>2</sub> C O H	600

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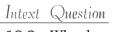
**Aspartame** is the most successful and widely used artificial sweetener. It is roughly 100 times as sweet as cane sugar. It is methyl ester of dipeptide formed from aspartic acid and phenylalanine. Use of aspartame is limited to cold foods and soft drinks because it is unstable at cooking temperature.

**Alitame** is high potency sweetener, although it is more stable than aspartame, the control of sweetness of food is difficult while using it.

**Sucrolose** is trichloro derivative of sucrose. Its appearance and taste are like sugar. It is stable at cooking temperature. It does not provide calories.

### 16.4.2 Food Preservatives

Food preservatives prevent spoilage of food due to microbial growth. The most commonly used preservatives include table salt, sugar, vegetable oils and sodium benzoate,  $C_6H_5COONa$ . Sodium benzoate is used in limited quantities and is metabolised in the body. Salts of sorbic acid and propanoic acid are also used as preservatives.



**16.3** Why do we require artificial sweetening agents?

# 16.5 Cleansing Agents

In this Section, we will learn about **detergents**. Two types of detergents are used as cleansing agents. These are soaps and synthetic detergents. These improve cleansing properties of water. These help in removal of fats which bind other materials to the fabric or skin.

#### 16.5.1 Soaps

Soaps are the detergents used since long. Soaps used for cleaning purpose are sodium or potassium salts of long chain fatty acids, e.g., stearic, oleic and palmitic acids. Soaps containing sodium salts are formed by heating fat (*i.e.*, glyceryl ester of fatty acid) with aqueous sodium hydroxide solution. This reaction is known as **saponification**.

In this reaction, esters of fatty acids are hydrolysed and the soap obtained remains in colloidal form. It is precipitated from the solution by adding sodium chloride. The solution left after removing the soap contains glycerol, which can be recovered by fractional distillation. Only sodium and potassium soaps are soluble in water and are used for cleaning purposes. Generally potassium soaps are soft to the skin than sodium soaps. These can be prepared by using potassium hydroxide solution in place of sodium hydroxide.

#### Types of soaps

Basically all soaps are made by boiling fats or oils with suitable soluble hydroxide. Variations are made by using different raw materials.

*Toilet soaps* are prepared by using better grades of fats and oils and care is taken to remove excess alkali. Colour and perfumes are added to make these more attractive.

Soaps that float in water are made by beating tiny air bubbles before their hardening. *Transparent soaps* are made by dissolving the soap in ethanol and then evaporating the excess solvent.

In *medicated soaps*, substances of medicinal value are added. In some soaps, deodorants are added. *Shaving soaps* contain glycerol to prevent rapid drying. A gum called, rosin is added while making them. It forms sodium rosinate which lathers well. *Laundry soaps* contain fillers like sodium rosinate, sodium silicate, borax and sodium carbonate.

Soap chips are made by running a thin sheet of melted soap onto a cool cylinder and scraping off the soaps in small broken pieces. *Soap granules* are dried miniature soap bubbles. *Soap powders* and *scouring soaps* contain some soap, a scouring agent (abrasive) such as powdered pumice or finely divided sand, and builders like sodium carbonate and trisodium phosphate. Builders make the soaps act more rapidly. The cleansing action of soap has been discussed in Unit 5.

#### Why do soaps not work in hard water?

Hard water contains calcium and magnesium ions. These ions form insoluble calcium and magnesium soaps respectively when sodium or potassium soaps are dissolved in hard water.

$$2C_{17}H_{35}COONa + CaCl_2 \longrightarrow 2NaCl + (C_{17}H_{35}COO)_2Ca$$
  
Soap Insoluble calcium stearate (Soap)

These insoluble soaps separate as scum in water and are useless as cleansing agent. In fact these are hinderance to good washing, because the precipitate adheres onto the fibre of the cloth as gummy mass. Hair washed with hard water looks dull because of this sticky precipitate. Dye does not absorb evenly on cloth washed with soap using hard water, because of this gummy mass.

### 16.5.2 Synthetic Detergents

Synthetic detergents are cleansing agents which have all the properties of soaps, but which actually do not contain any soap. These can be used both in soft and hard water as they give foam even in hard water. Some of the detergents give foam even in ice cold water.

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Synthetic detergents are mainly classified into three categories: (i) Anionic detergents (ii) Cationic detergents and (iii) Non-ionic detergents

(i) Anionic Detergents: Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons. Alkyl hydrogensulphates formed by treating long chain alcohols with concentrated sulphuric acid are neutralised with alkali to form anionic detergents. Similarly alkyl benzene sulphonates are obtained by neutralising alkyl benzene sulphonic acids with alkali.

$$CH_{3}(CH_{2})_{11} \longrightarrow CH_{3}(CH_{2})_{11} \longrightarrow SO_{3}H \xrightarrow{NaOH(aq)} CH_{3}(CH_{2})_{11} \longrightarrow SO_{3}Na$$

Dodecylbenzene

Dodecylbenzenesulphonic acid

Sodium dodecylbenzenesulphonate

In anionic detergents, the anionic part of the molecule is involved in the cleansing action. Sodium salts of alkylbenzenesulphonates are an important class of anionic detergents.

They are mostly used for household work. Anionic detergents are also used in toothpastes.

(ii) Cationic Detergents: Cationic detergents are quarternary ammonium salts of amines with acetates, chlorides or bromides

as anions. Cationic part possess a long hydrocarbon chain and a positive charge on nitrogen atom. Hence, these are called cationic detergents. Cetyltrimethylammonium bromide is a popular cationic detergent and is used in hair conditioners.

$$\begin{bmatrix} CH_3 \\ | \\ CH_3(CH_2)_{15} - N - CH_3 \\ | \\ CH_3 \end{bmatrix}^+ \mathbf{Br}$$

Cetyltrimethyl ammonium bromide

Cationic detergents have germicidal properties and are expensive, therefore, these are of limited use.

(iii) Non-ionic Detergents: Non-ionic detergents do not contain any ion in their constitution. One such detergent is formed when stearic acid reacts with polyethyleneglycol.

$$\begin{split} \mathrm{CH_3(CH_2)_{16}COOH} &+ \mathrm{HO(CH_2CH_2O)_nCH_2CH_2OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH} \\ \mathrm{Stearic\ acid} & \mathrm{Polyethyleneglycol} \end{split}$$

Liquid dishwashing detergents are non-ionic type. Mechanism of cleansing action of this type of detergents is the same as that of soaps. These also remove grease and oil by micelle formation.

Main problem that appears in the use of detergents is that if their hydrocarbon chain is highly branched, then bacteria cannot degrade

this easily. Slow degradation of detergents leads to their accumulation. Effluents containing such detergents reach the rivers, ponds, etc. These persist in water even after sewage treatment and cause foaming in rivers, ponds and streams and their water gets polluted.

These days the branching of the hydrocarbon chain is controlled and kept to the minimum. Unbranched chains can be biodegraded more easily and hence pollution is prevented.

#### Intext Questions

- **16.4** Write the chemical equation for preparing sodium soap from glyceryl oleate and glyceryl palmitate. Structural formulae of these compounds are given below.
  - (i)  $(C_{15}H_{31}COO)_3C_3H_5$  Glyceryl palmitate
  - (ii)  $(C_{17}H_{32}COO)_3C_3H_5$  Glyceryl oleate
- **16.5** Following type of non-ionic detergents are present in liquid detergents, emulsifying agents and wetting agents. Label the hydrophilic and hydrophobic parts in the molecule. Identify the functional group(s) present in the molecule.

$$C_9H_{19}$$
 O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>CH<sub>2</sub>CH<sub>2</sub>OH  
(x = 5 to 10)

#### Summary

Chemistry is essentially the study of materials and the development of new materials for the betterment of humanity. A **drug** is a chemical agent, which affects human metabolism and provides cure from ailment. If taken in doses higher than recommended, these may have poisonous effect. Use of chemicals for therapeutic effect is called **chemotherapy**. Drugs usually interact with biological macromolecules such as carbohydrates, proteins, lipids and nucleic acids. These are called **target molecules**. Drugs are designed to interact with specific targets so that these have the least chance of affecting other targets. This minimises the side effects and localises the action of the drug. Drug chemistry centres around arresting microbes/destroying microbes, preventing the body from various infectious diseases, releasing mental stress, etc. Thus, drugs like analgesics, antibiotics, antiseptics, disinfectants, antacids and tranquilizers are used for specific purpose. To check the population explosion, antifertility drugs have also become prominent in our life.

Food additives such as **preservatives**, **sweetening agents**, **flavours**, **antioxidants**, **edible colours** and **nutritional supplements** are added to the food to make it attractive, palatable and add nutritive value. Preservatives are added to the food to prevent spoilage due to microbial growth. Artificial sweeteners are used by those who need to check the calorie intake or are diabetic and want to avoid taking sucrose.

These days, detergents are much in vogue and get preference over soaps because they work even in hard water. Synthetic detergents are classified into

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three main categories, namely: **anionic, cationic** and **non-ionic,** and each category has its specific uses. Detergents with straight chain of hydrocarbons are preferred over branched chain as the latter are **non-biodegradable** and consequently cause **environmental pollution**.

### Exercises

- 16.1 Why do we need to classify drugs in different ways ?
- **16.2** Explain the term, target molecules or drug targets as used in medicinal chemistry.
- 16.3 Name the macromolecules that are chosen as drug targets.
- 16.4 Why should not medicines be taken without consulting doctors ?
- **16.5** Define the term chemotherapy.
- 16.6 Which forces are involved in holding the drugs to the active site of enzymes?
- **16.7** While antacids and antiallergic drugs interfere with the function of histamines, why do these not interfere with the function of each other?
- **16.8** Low level of noradrenaline is the cause of depression. What type of drugs are needed to cure this problem? Name two drugs.
- 16.9 What is meant by the term 'broad spectrum antibiotics'? Explain.
- 16.10 How do antiseptics differ from disinfectants? Give one example of each.
- **16.11** Why are cimetidine and ranitidine better antacids than sodium hydrogenearbonate or magnesium or aluminium hydroxide?
- **16.12** Name a substance which can be used as an antiseptic as well as disinfectant.
- 16.13 What are the main constituents of dettol?
- 16.14 What is tincture of iodine? What is its use?
- 16.15 What are food preservatives ?
- 16.16 Why is use of aspartame limited to cold foods and drinks?
- 16.17 What are artificial sweetening agents? Give two examples.
- **16.18** Name the sweetening agent used in the preparation of sweets for a diabetic patient.
- 16.19 What problem arises in using alitame as artificial sweetener?
- 16.20 How are synthetic detergents better than soaps ?
- 16.21 Explain the following terms with suitable examples
  - (i) cationic detergents
  - (ii) anionic detergents and
  - (iii) non-ionic detergents.
- **16.22** What are biodegradable and non-biodegradable detergents? Give one example of each.
- 16.23 Why do soaps not work in hard water?
- **16.24** Can you use soaps and synthetic detergents to check the hardness of water ?
- 16.25 Explain the cleansing action of soaps.

- **16.26** If water contains dissolved calcium hydrogencarbonate, out of soaps and synthetic detergents which one will you use for cleaning clothes ?
- 16.27 Label the hydrophilic and hydrophobic parts in the following compounds.
  - (i)  $CH_3(CH_2)_{10}CH_2OSO_3^{-}$ Na
  - (ii)  $CH_3(CH_2)_{15} N(CH_3)_3 Br$
  - (iii)  $CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$

#### Answers to Some Intext Questions

- **16.1** Most of the drugs taken in doses higher than recommended may cause harmful effect and act as poison. Therefore, a doctor should always be consulted before taking medicine.
- **16.2** This statement refers to the classification according to pharmacological effect of the drug because any drug which will be used to counteract the effect of excess acid in the stomach will be called antacid.

16.5

$$C_9H_{19}$$
 O( $CH_2CH_2O$ ) $_xCH_2CH_2OH$ 

Hydrophobic or Hydrophilic or polar part polar part

### Answers to Some Questions in Exercises

#### UNIT 11

11.1 (i) 2,2,4-Trimethylpentan -3-ol

(iii) Butane -2,3-diol

(v) 2- Methylphenol

(vii) 2,5 - Dimethylphenol

(ix) 1-Methoxy-2-methylpropane

(xi) 1-phenoxyheptane

$$\begin{array}{ccc} & & \text{CH}_3 \\ & & \text{I} \\ & \text{11.2} & \text{(i)} & \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3 \\ & & \text{OH} \end{array}$$

OH OH 
$$\mid$$
 (iii)  $HOCH_2 - CH_2 - C - CH_2 - C - CH_3 - CH_3 - CH_3$ 

(v) 
$$C_2H_5 - O - CH_2 - CH_3 - CH_3$$

(ii) 5-Ethylheptane -2, 4-diol

(iv) Propane -1,2,3,-triol

(vi) 4-Methylphenol

(viii) 2,6-Dimethylphenol

(x) Ethoxybenzene

(xii) 2 -Ethoxybutane

(ii) 
$$CH_2$$
- $CH$ - $CH_3$ 
OH

$$\begin{array}{c} \text{OH} \\ \text{C}_2 \text{H}_5 \\ \text{C}_2 \text{H}_5 \end{array}$$

(viii) 
$$CH_3-CH_2-C-CH_2-CH_3$$

11.3 (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, Pentan-1-ol;

(b)  $CH_3$ - $CH_2$ - $CH_2$ - $CH_2$ -OH, 2-Methylbutan-1-ol;

(c)  $CH_3$  (c)  $CH_3$ –C– $CH_2OH$ , 2,2-Dimethylpropan-1-ol  $CH_3$ 

(e)  $CH_3$ - $CH_2$ - $CH_2$ - $CH_-$ CH $_3$ , Pentan-2-ol OH

CH $_3$  (g) CH $_3$ -CH $_2$ -C-OH, 2-Methylbutan-2-ol CH

11.4 Hydrogen bonding in propanol.

- 11.5 Hydrogen bonding between alcohol and water molecules.
- 11.8 o-Nitrophenol is steam volatile because of intramolecular hydrogen bonding.
- 11.12 Hint: Carryout sulphonation followed by nucleophilic substitution.

11.13 (i) 
$$CH=CH_2$$
  $CH(OH)CH_3$   $H^*/H_2O$ 

(ii) 
$$CH_2CI$$
  $CH_2OH$  + NaOH  $CH_2OH$ 

- (iii) CH<sub>3</sub>(CH<sub>3</sub>)<sub>4</sub>Cl + NaOH ----> CH<sub>3</sub>(CH<sub>3</sub>)<sub>4</sub>OH + NaCl
- 11.14 Reaction with (i) sodium and (ii) sodium hydroxide
- 11.15 Due to electron withdrawing effect of nitro group and electron releasing effect of methoxy group.
- 11.20 (i) Hydration of Propene.
  - (ii) By nucleophilic substitution of -Cl in benzyl chloride using dilute NaOH.
  - (iii)  $C_2H_5MgBr + HCHO \rightarrow C_2H_5CH_2OMgBr \xrightarrow{H_2O} C_2H_5CH_2OH$

(iv) 
$$CH_3MgBr$$
 +  $CH_3COCH_3$   $\longrightarrow CH_3 - CH_3 - OMgBr$   $\xrightarrow{H_2O} CH_3 - CH_3 - OH$   $CH_3$   $CH_3$   $CH_3$ 

- 11.23 (i) 1-Ethoxy-2-methylpropane.
  - (ii) 2-Chloro-1-methoxyethane.
  - (iii) 4-Nitroanisole.
  - (iv) 1-Methoxypropane.
  - (v) 1-Ethoxy-4,4-dimethylcyclohexane.
  - (vi) Ethoxybenzene.

#### **UNIT 12**

- 12.2 (i) 4-Methylpentanal
  - (iii) But-2-enal
  - (v) 3,3,5-Trimethylhexan-2-one
  - (vii) Benzene -1,4-dicarbaldehyde

$$\begin{array}{ccc} & CH_3 & O \\ & \parallel & \parallel \\ \textbf{12.3} & \text{(i)} & H_3C-CH-CH_2-C-H \end{array}$$

(iii) 
$$H_3C$$
  $\longrightarrow$   $C-H$ 

- (ii) 6-Chloro-4-ethylhexan-3-one
- (iv) Pentane-2,4-dione
- (vi) 3,3-Dimethylbutanoic acid

(ii) 
$$O_2N$$
— $O$ 
 $C$ 
 $C$ 
 $C$ 
 $C$ 
 $C$ 

(iv) 
$$H_3C-C-CH=C-CH_1$$

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(vii) HO 
$$\stackrel{\circ}{\longrightarrow}$$
 OH (viii)  $_{\mathrm{H_3C-C}\equiv\mathrm{C-CH=CH-C-OH}}$ 

12.4 (i) Heptan-2-one (ii) 4-Bromo-2-methylhexanal (iii) Heptanal (iv) 3-Phenylpropenal (v)  $_{\mathrm{Y}}$ -Cyclopentanecarbaldehyde (vi) Diphenylmethanone (vi)  $_{\mathrm{Y}}$ -Cyclopentanecarbaldehyde (vi) Diphenylmethanone (vii) CH=N.NH  $\stackrel{\circ}{\longrightarrow}$  NO $_{\mathrm{Z}}$  (iv)  $\stackrel{\circ}{\longrightarrow}$  NNH-C-NH $_{\mathrm{Z}}$  (vi)  $\stackrel{\circ}{\longrightarrow}$  NNH-C-NH $_{\mathrm{Z}}$  (vii)  $\stackrel{\circ}{\longrightarrow}$  NNH-C-NH $_{\mathrm{Z}}$  (viii)  $\stackrel{\circ}{\longrightarrow}$  CH=NNH-C-NH $_{\mathrm{Z}}$  (viii)  $\stackrel{\circ}{\longrightarrow}$  CH=NNH-C-NH $_{\mathrm{Z}}$  (iv)  $\stackrel{\circ}{\longrightarrow}$  CH=NNH-C-NH $_{\mathrm{Z}}$  (ivi)  $\stackrel{\circ}{\longrightarrow}$  CH=NNH-C-NH $_{\mathrm{$ 

- 12.11 (A) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, butyl butanoate.
  - (B) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH (C) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH. Write equation yourself.
- (i) Di-tert-butyl ketone < Methyl tert-butyl ketone < Acetone < Acetaldehyde 12.12
  - (ii) (CH<sub>3</sub>)<sub>2</sub>CHCOOH < CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH < CH<sub>3</sub>CH(Br)CH<sub>2</sub>COOH < CH<sub>3</sub>CH<sub>2</sub>CH(Br)COOH
  - (iii) 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid.

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$$(ii) \qquad COCI$$

$$(iii) \qquad C_6H_5CH=NNHC-NH_2$$

$$(iv) \quad C_6H_5COCI-AlCl_3 \qquad (v) \qquad COO$$

$$(vii) \quad C_6H_5CH=C-CHO$$

$$CH_3 \qquad (viii) \quad CH_3CH(OH)CH_2COOC_2H_5 \qquad (ix) \qquad O$$

$$(x) \quad 1. \quad BH_3; \quad 2. \quad H_2O_2/OH; \quad 3. \quad PCC \qquad (xii) \qquad O$$

#### UNIT 13

13.1 (i) 1-methylethanamine

- (ii) Propan-1-amine
- (iii) N-methyl-2-methylethanamine
- (iv) 2-methylpropan-2-amine
- (v) N-methylbenzamine or N-methylaniline
- (vi) N-Ethyl-N-methylethanamine
- (vii) 3-Bromoaniline or 3-Bromobenzenamine
- **13.4** (i)  $C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$ 
  - (ii)  $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$
  - (iii) (a) p-nitroaniline < aniline < p-toluidine
    - (b)  $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$
  - (iv)  $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$  (v)  $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$
  - (vi)  $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

#### UNIT 15

- **15.1** Polymer is a high molecular mass macromolecule consisting of repeating structural units derived from monomers.
  - Monomer is a simple molecule capable of undergoing polymerisation and leading to the formation of the corresponding polymer.
- **15.2** Natural polymers are high molecular mass macromolecules and are found in plants and animals. The examples are proteins and nucleic acids.
  - Synthetic polymers are man-made high molecular mass macromolecules. These include synthetic plastics, fibres and rubbers. The two specific examples are polythene and dacron.
- 15.4 Functionality is the number of bonding sites in a monomer.
- **15.5** Polymerisation is a process of formation of a high molecular mass polymer from one or more monomers by linking together of repeating structural units with covalent bonds.
- 15.6 Since the unit + NH-CHR-CO+ is obtained from a single monomer unit, it is a homopolymer.
- 15.7 On the basis of molecular forces present between the chains of various polymers, the classification of polymers is given as follows.
  - (a) Elastomers (b) Fibres (c) Thermoplastics and (d) Thermosetting plastics.
- 15.8 In addition polymerisation, the molecules of the same or different monomers add together to form a large polymer molecule. Condensation polymerisation is a process in which two or more bi-functional molecules undergo a series of condensation reactions with the elimination of some simple molecules and leading to the formation of polymers.
- **15.9** Copolymerisation is a process in which a mixture of more than one monomeric species is allowed to polymerise. The copolymer contains multiple units of each monomer in the chain. The examples are copolymers of 1,3-butadiene and styrene and 1, 3-butadiene and acrylonitrile.
- 15.10

$$\begin{array}{c} C_6H_5-CH_2-\dot{C}H_2+CH_2=CH_2 & \longrightarrow & C_6H_5-CH_2-CH_2-CH_2-CH_2 \\ & & \downarrow chain \ termination \\ \\ C_6H_5+CH_2-CH_2+CH_2-CH_2-CH_2-CH_2-CH_2+CH_2+CH_2+CH_2+CH_2 \\ \\ & & Polythene \end{array}$$

- **15.11** A thermoplastic polymer can be repeatedly softened on heating and hardened on cooling, hence it can be used again and again. The examples are polythene, polypropylene, etc.
  - A thermosetting polymer is a permanent setting polymer as it gets hardened and sets during

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moulding process and cannot be softened again. The examples are bakelite and melamine-formaldehyde polymers.

- $\textbf{15.12} \quad \text{(i) The monomer of polyvinyl chloride is } \text{CH}_2 \text{=CHCl (vinyl chloride)}.$ 
  - (ii) The monomer of teflon is  $CF_2 = CF_2$  (tetrafluoroethylene).
  - (iii) The monomers involved in the formation of bakelite are HCHO (formaldehyde) and C<sub>6</sub>H<sub>5</sub>OH (phenol).
- 15.14 From the structural point of view, the natural rubber is a linear cis-1,4- polyisoprene. In this polymer the double bonds are located between  $C_2$  and  $C_3$  of isoprene units. This cis-configuration about double bonds do not allow the chains to come closer for effective attraction due to weak intermolecular attractions. Hence, the natural rubber has a coiled structure and shows elasticity.
- **15.16** The monomeric repeat unit of Nylon-6 polymer is:  $[NH-(CH_a)_c-CO]$

The monomeric repeat unit of Nylon-6,6 polymer is derived from the two monomers, hexamethylene diamine and adipic acid.

 $[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO]$ 

15.17 The names and structures of monomers are:

(i)	<b>Polymers</b> Buna-S	Monomer Names 1,3-Butadiene Styrene	$\begin{array}{c} \textbf{Monomer Structures} \\ \text{CH}_2\text{=CH-CH=CH}_2 \\ \text{C}_6\text{H}_5\text{CH=CH}_2 \end{array}$
(ii)	Buna-N	1,3- Butadiene Acrylonitrile	$\begin{array}{c} \mathrm{CH_2}\text{=}\mathrm{CH}\text{-}\mathrm{CH}\text{=}\mathrm{CH}_2 \\ \mathrm{CH_2}\text{=}\mathrm{CH} \ \ \mathrm{CN} \end{array}$
(iii)	Neoprene	Chloroprene	$\begin{array}{c} \text{Cl} \\ \text{I} \\ \text{CH}_2\text{=C-CH=CH}_2 \end{array}$
(iv)	Dacron	Ethylene glycol	$\mathrm{OHCH_2-CH_2OH}$
		Terephthalic acid	соон Соон

- **15.18** The monomers forming the polymer are:
  - (i) Decanoic acid  $HOOC (CH_2)_8 COOH$  and Hexamethylene diamine  $H_2N(CH_2)_6$   $NH_2$

(ii) 
$$\begin{matrix} H_2N & N & NH_2 \\ N & N & \text{and HCHO} \\ NH_2 & \end{matrix}$$

**15.19** The following are the equations for the formation of Dacron.

n HOCH<sub>2</sub>CH<sub>2</sub>OH + nHOOC 
$$\longrightarrow$$
 COOH  $\longrightarrow$   $\bigcirc$  O-CH<sub>2</sub>CH<sub>2</sub>O-CO  $\bigcirc$  CO  $\bigcirc$  Ethylene glycol Terephthalic acid Dacron