



## 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, some 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 man-made 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:



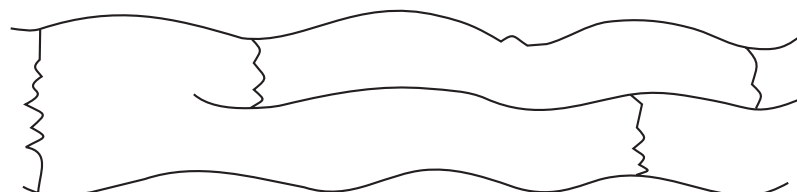
#### 2. Branched chain polymers

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

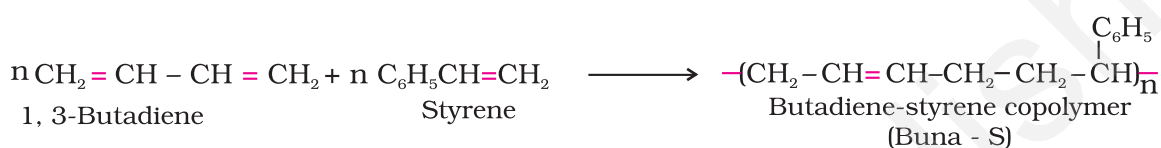
Polymers can also be classified on the basis of mode of polymerisation into two sub groups.

#### 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.

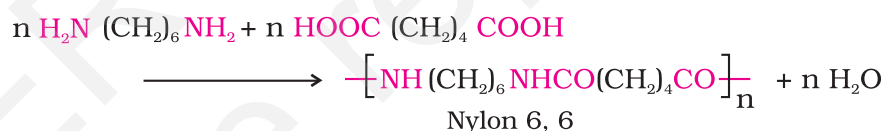


The polymers made by addition polymerisation from two different monomers are termed as **copolymers**, *e.g.*, Buna-S, Buna-N, etc.



#### 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.



Is  $\text{-(CH}_2\text{-CH(C}_6\text{H}_5\text{))}_n$  a homopolymer or a copolymer?

It is a homopolymer and the monomer from which it is obtained is styrene  $\text{C}_6\text{H}_5\text{CH} = \text{CH}_2$ .

**Example 15.1**

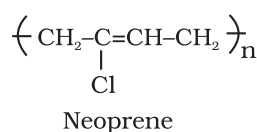
**Solution**

### 15.1.4 Classification Based on Molecular Forces

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.

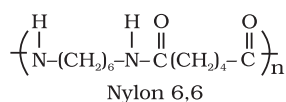
#### 1. Elastomers

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



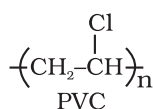
elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc.

## 2. Fibres



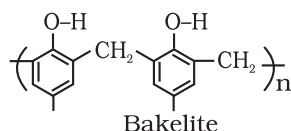
Fibres are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides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

### 15.1.5 Classification Based on Growth Polymerisation

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.

### 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.

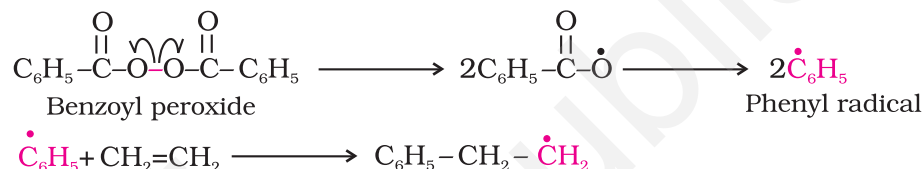
### 15.2.1 Addition Polymerisation or Chain Growth Polymerisation

In this type of polymerisation, the molecules of the same monomer or different monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds, *e.g.*, alkenes, alkadienes 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.

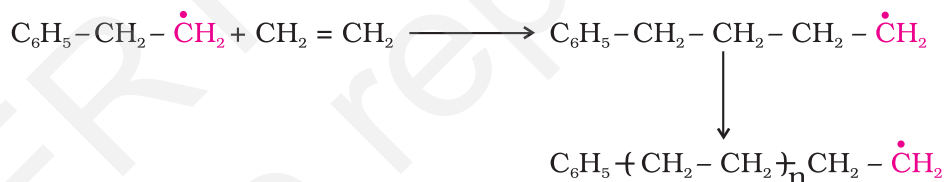
## 1. Free radical mechanism

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*

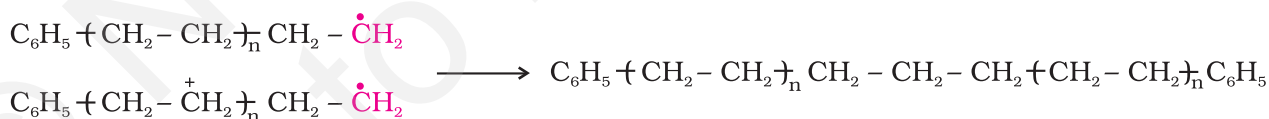


*Chain propagating step*



*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:



## 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

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 decomposition at temperatures above 300°C.

Acrylic fibres have good resistance to stains, chemicals, insects and fungi.

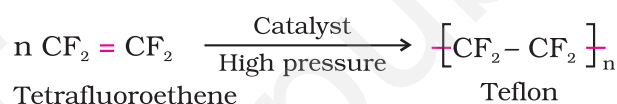
polythene (LDP) obtained through the free radical addition and H-atom abstraction has highly branched structure.

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 tough and hard. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

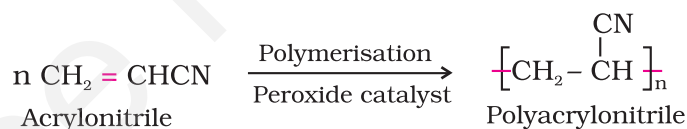
### (b) Polytetrafluoroethene (Teflon)

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.



### (c) Polyacrylonitrile

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



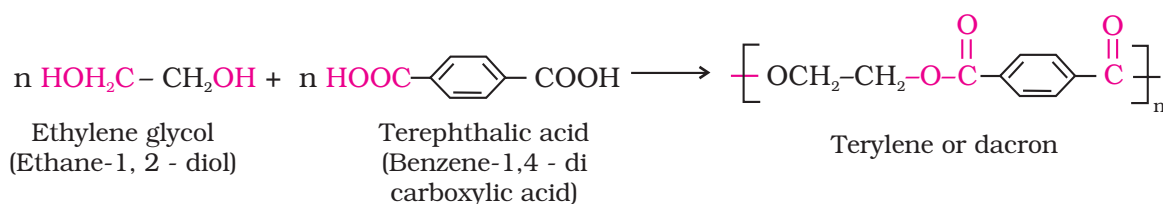
Polyacrylonitrile is used as a substitute for wool in making commercial fibres as orlon or acrilan.

## 15.2.2 Condensation Polymerisation or Step Growth polymerisation

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 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.



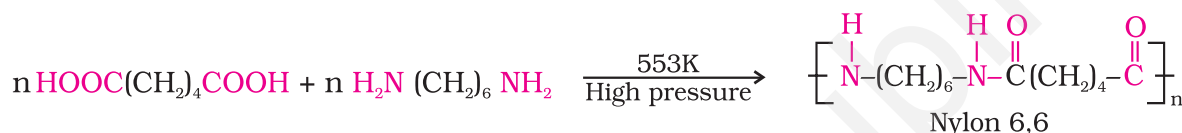
Some important condensation polymerisation reactions characterised by their linking units are described below:

### 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.

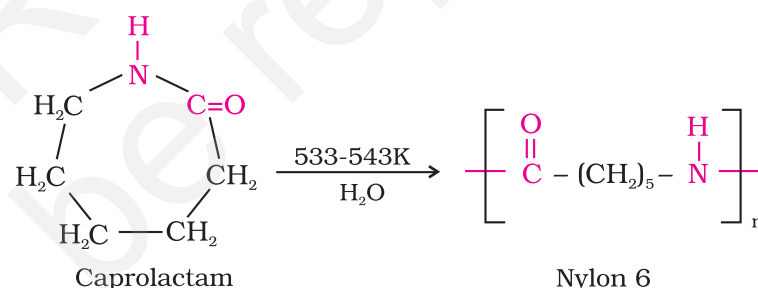
#### Preparation of nylons

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



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

- (ii) **Nylon 6:** It is obtained by heating caprolactam with water at a high temperature.



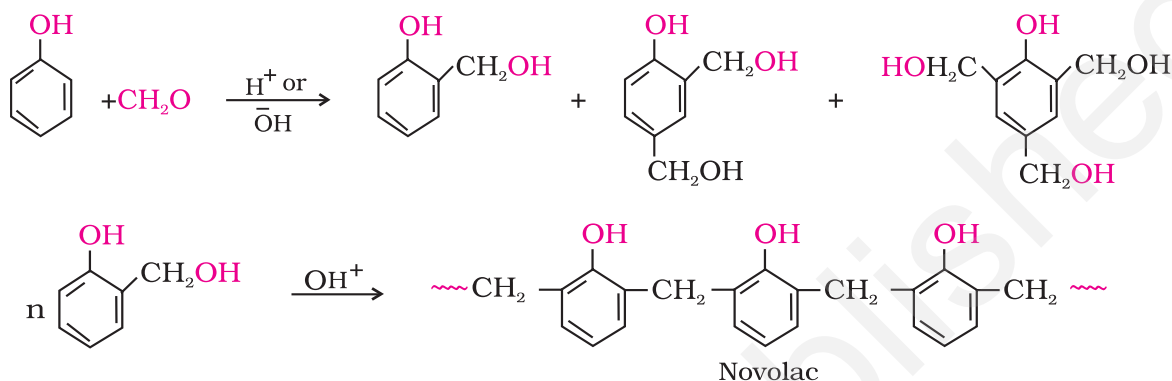
Nylon 6 is used for the manufacture of tyre cords, fabrics and ropes.

### 2. Polyesters

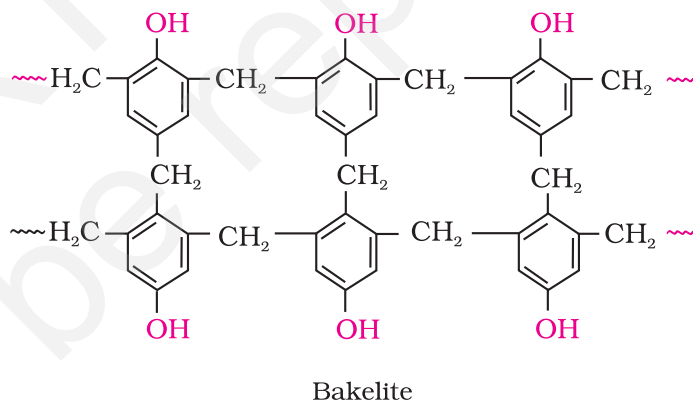
These are the polycondensation products of dicarboxylic acids and diols. Dacron or terylene is the best known example of polyesters. It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetate-antimony trioxide catalyst as per the reaction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

### 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  $-\text{CH}_2$  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 used for making combs, phonograph records, electrical switches and handles of various utensils.



### 4. Melamine - formaldehyde polymer

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

