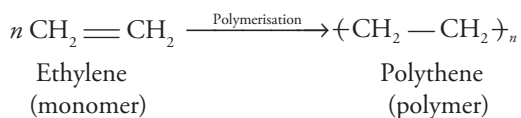


Chapter 6

POLYMERS

6.1 Introduction

Polymers are compounds of very high molecular weights formed by the combination of a large number of small repeating units. The word 'polymer' is derived from the Greek word *poly* meaning 'many' and *mer* meaning 'part'. The process by which the simple molecules (monomers) are converted into polymers is called polymerisation. For example, many ethylene molecules combine to form a giant molecule of polythene.



where n = number of monomers in the polymeric chain.

The number of repeating units in a polymeric chain is called 'degree of polymerisation'. In the above example, ' n ' is the degree of polymerisation.

Polymers are also called *macromolecules* because of their big size. In fact, the terms polymers and macromolecules are often used synonymously. However, strictly speaking, a polymer contains repeating units (monomers), whereas a macromolecule is a giant molecule that may or may not contain monomer units. For example, chlorophyll and haemoglobin are macromolecules but not polymers.

Polyethene may be regarded as a polymer as well as a macromolecule because it contains a large number of repeating units. Thus, all polymers are macromolecules and not *vice versa*.

6.2 Classification of Polymers

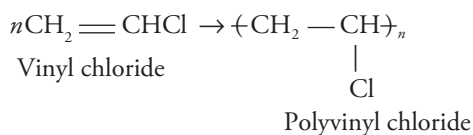
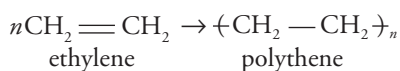
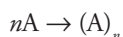
Polymers may be classified in various manners.

1. **On the basis of origin** On the basis of origin, polymers are of two types:
 - (a) Natural polymers
 - (b) Synthetic polymers

- (a) **Natural polymers** They are polymers that occur in nature. For example, starch (polymer of α -D-glucose), cellulose (a polymer of β -D-glucose), proteins (polymer of α -amino acids) and natural rubber (a polymer of poly-cis-isoprene).
- (b) **Synthetic polymer** It is a polymer that is prepared artificially in the laboratory. For example, polyethylene (PE), polyvinylchloride (PVC), nylon, terylene, bakelite, synthetic rubber, etc.

2. On the basis of monomer composition

- (a) **Homopolymer** If a polymer consists of identical monomers, it is termed as homopolymer.



- (b) **Copolymer** If a polymer is made up of more than one type of monomers it is called a copolymer.



Depending on the arrangement of the monomeric units, the copolymers may be further classified as

- (i) **Random copolymers** The monomeric units are randomly arranged.



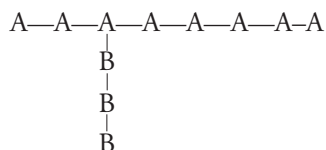
- (ii) **Alternating copolymers** The monomeric units are arranged in an alternating manner.



- (iii) **Block copolymers** The monomeric units are arranged in blocks.



- (iv) **Graft copolymers** They are branched copolymers in which the backbone is formed of one type of monomer and the branches are formed of the other types of monomers.



3. **On the basis of chain structure**

- (i) **Linear polymer** It has no branching other than the pendant groups associated with the monomer. Linear polymers are well packed and therefore have high densities. For example, polythene, nylons and polyesters.
- (ii) **Branched polymers** These are polymers in which the monomers are joined to form long chains with side chains or branches of different lengths. They are irregularly packed and have low densities. If the side chain is different from parent chain, they are called graft polymers. For example, low-density polyethene, glycogen, etc.
- (iii) **Cross-linked polymers** These are polymers in which the monomer units are linked together to form a three-dimensional network. These polymers are hard, rigid and brittle. They are also called network polymers. For example, bakelite, vulcanised rubber, etc.

4. **Based on chain composition**

- (i) **Homochain polymer** Polymers having all carbon atoms along their backbone are called homochain polymers. For example, polyethene, PVC, rubber, etc.
- (ii) **Heterochain polymer** If the polymeric chain contains a heteroatom, then they are called heterochain polymers. For example, nylon (polymeric chain contains nitrogen atom) and terylene (polymeric chain contains oxygen atom).

5. **Based on polymerisation mechanism**

- (i) **Addition polymers** Those polymers that are obtained by the addition of monomeric units are called addition polymers. The molecular weight of such a polymer is an exact multiple of the molecular weight of the monomer.

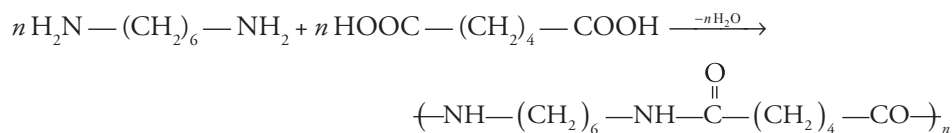


Molecular weight of polymer = $n \times$ molecular weight of monomer.

For example, polyethene, PVC, etc.

- (ii) **Condensation polymers** A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia and hydrochloric acid is termed as a condensation polymer. The molecular weight of such a polymer is not an exact multiple of the molecular weight of the monomer.

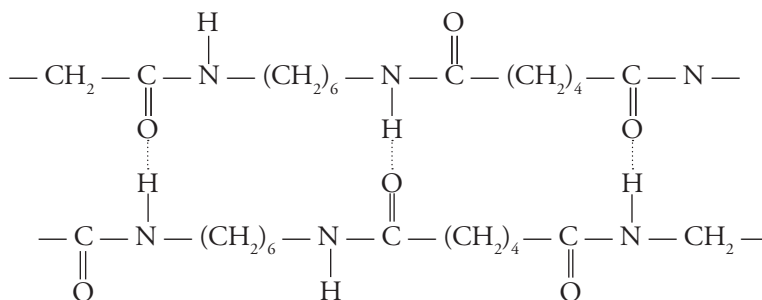
For example, Nylon 66 is obtained by the condensation of two monomers, hexamethylenediamine and adipic acid with the loss of water molecules.

6. **Based on molecular forces**

- (i) **Elastomers** They are polymers held by weakest intermolecular forces and have elastic behavior. For example, natural rubber. These can be stretched to at least thrice their

original length but return to their original shape and dimension as soon as the stretching force is removed.

- (ii) **Fibres** These are polymers whose polymeric chains are held together by strong intermolecular forces like hydrogen bonds or dipole–dipole interactions. They are crystalline in nature and have high tensile strength. For example, nylon 66, polyester, silk, etc.



Hydrogen bonding in Nylon 66

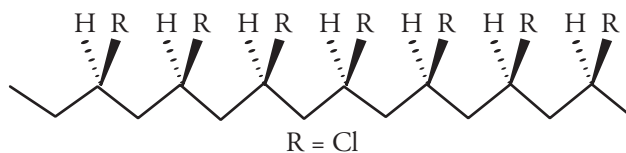
- (iii) **Thermoplastics** They are linear, long-chain polymers that soften on heating and harden when cooled. The intermolecular forces of these polymers are intermediate between those of elastomers and fibres. There is no cross-linking between the polymeric chains. They can be processed again and again.

For example, polyethene (PE), polystyrene, PVC, teflon, polypropylene, etc.

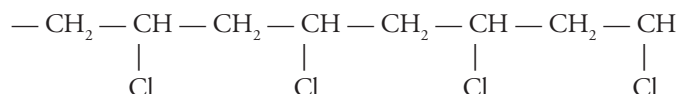
- (iv) **Thermosetting plastics** They are polymers that can change irreversibly into hard and rigid materials on heating and cannot be reshaped once they set. They form hard, infusible, insoluble products because of cross-linkages. For example, bakelite, melamine, etc.

7. **Based on tacticity** Tacticity is defined as the spatial arrangement of the substituent groups on the asymmetric carbon atom. Based on the orientation of side groups in space the polymers can be of three types

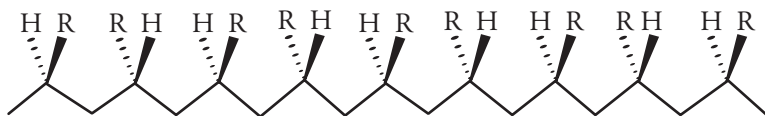
- (i) **Isotactic polymers** When the orientation of side groups (R) on all asymmetric carbon atoms is the same, the polymer is termed as an isotactic polymer



For example, PVC.



- (ii) **Syndiotactic polymer** When the orientation of the side groups on alternate asymmetric carbon atoms is the same, the polymer is termed as a syndiotactic polymer.



- (iii) **Atactic polymer** When the side groups have no preferential arrangement and are randomly arranged, the polymer is called an atactic polymer.



In general, isotactic and syndiotactic polymers are partially crystalline, whereas atactic polymers are amorphous, indicating the absence of crystalline order.

8. Based on degree of polymerisation

- (i) **Oligopolymers** Polymers with low degree of polymerisation are called 'oligopolymers'.
 (ii) **Macromolecules** Polymers with a high degree of polymerisation are called 'high polymers'. They have very high molecular weights (10^4 – 10^6) and hence are called macromolecules.

9. Based on chemical composition

- (i) **Organic polymers** A polymer whose backbone chain is made mainly of carbon atoms and the side chains consist of oxygen, nitrogen, sulphur, etc. Examples include polythene, PVC, nylon, etc.
 (ii) **Inorganic polymers** These polymers do not have a carbon backbone chain. Examples include silicone rubbers, phosphazene, etc.

The classification of polymers is summarised in Figure 6.1.

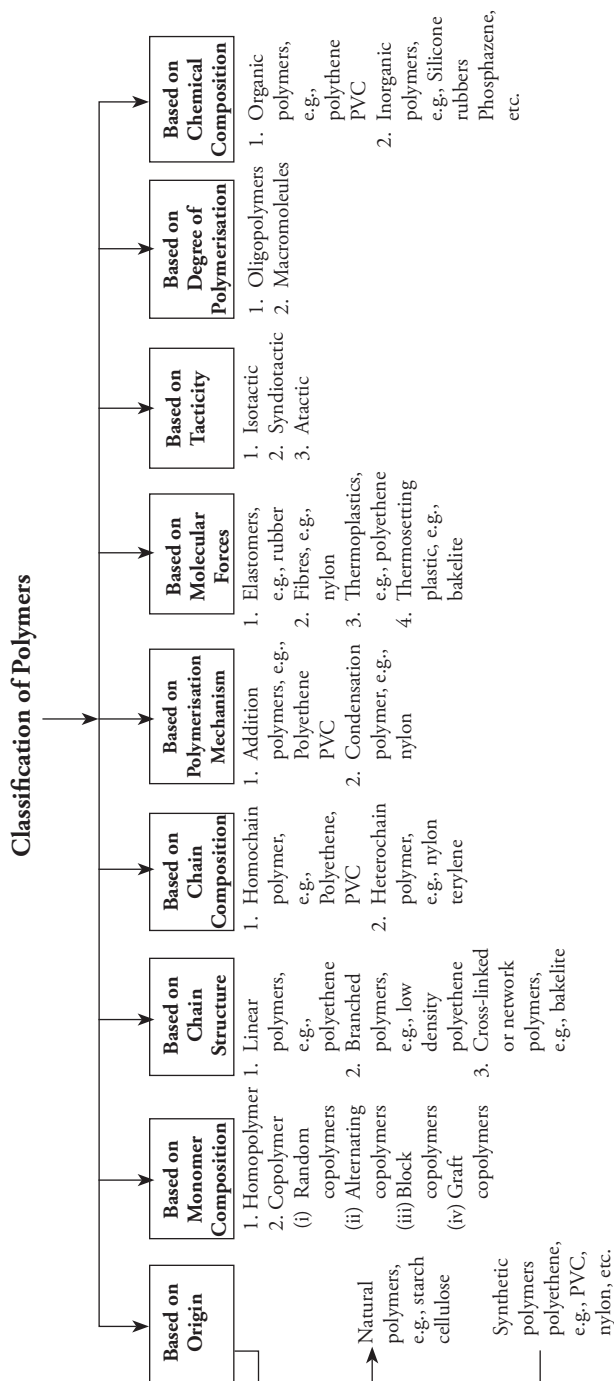


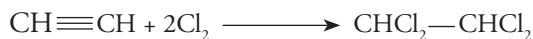
Figure 6.1 Classification of polymers

6.3 Functionality

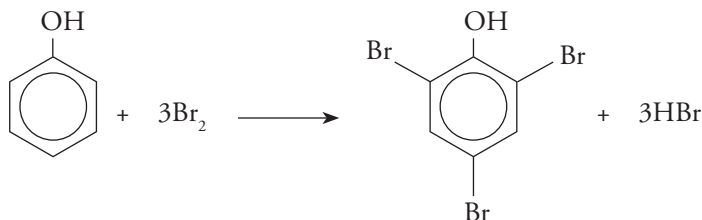
The number of reactive sites in a molecule is termed as its functionality. For a molecule to act as a monomer it must have at least two reactive sites, that is, its functionality should be two. For example, ethylene can add two molecules of hydrogen or halogen. Hence, it is bifunctional (functionality two).



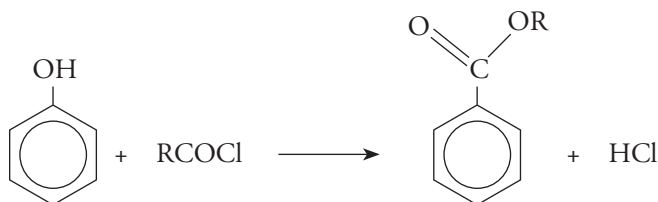
Similarly, acetylene has a functionality of four (tetrafunctional), as it can react with four atoms of hydrogen or halogen.



Similarly, phenol has three reaction sites (2-ortho and one para). It undergoes substitution reaction at these sites. Hence, it is trifunctional.

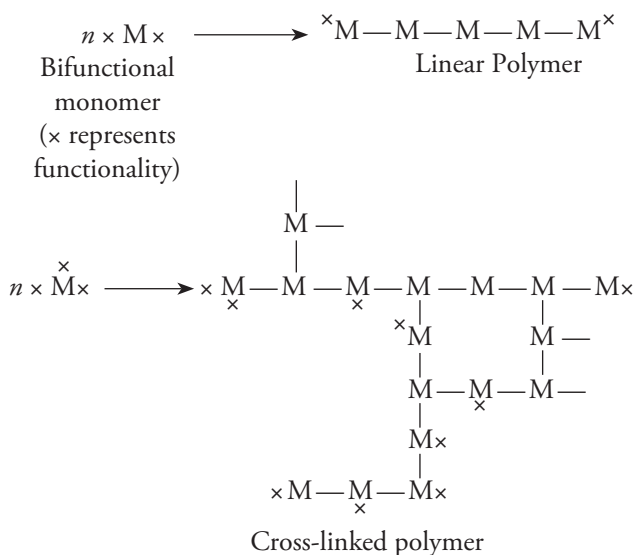


Phenol also exhibits a functionality of one as shown below.



Depending on functionality of the monomers used, we get linear, branched or three-dimensional cross-linked polymers.

If the monomer is bifunctional (ethylene, propylene, vinyl chloride, styrene, etc.), a linear polymer is formed. A trifunctional monomer leads to the formation of a cross-linked polymer, whereas a mixture of bifunctional and trifunctional monomer may form branched or cross-linked polymer.



6.4 Mechanism of Polymerisation

There are two types of polymerisation processes:

1. Addition polymerisation or chain polymerisation
2. Condensation polymerisation

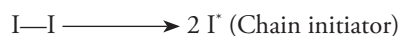
1. **Addition polymerisation or chain polymerisation** In this type of polymerisation, the monomer molecules are added to each other without the formation of any byproduct. The elemental composition of polymer is similar to that of the monomer and its molecular weight is an exact multiple of the molecular weight of the original monomeric molecule.

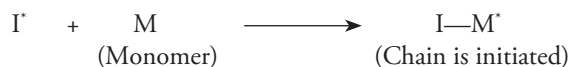
Bifunctional molecules like ethylene, propylene (olefins), vinyl compounds and allyl compounds generally undergo this type of polymerisation. As majority of these monomers fall under the 'vinyl' category; hence, chain polymerisation is also customarily termed as 'vinyl polymerisation'.

Addition polymerisation consists of three important steps

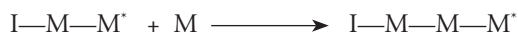
- (i) **Chain initiation** This step involves the formation of active molecules called chain initiators.

These chain initiators then attack the monomer to initiate the chain formation.





(ii) **Chain propagation** The initiated chain then attacks more monomeric molecules leading to the increase in the length of the chain.



Hence the polymeric chain propagates.

(iii) **Chain termination** The active centers are removed or they combine with each other and the chain propagation comes to an end.



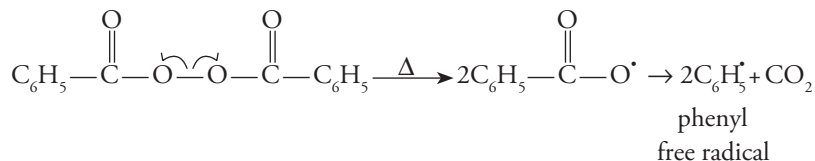
The addition polymerisation reaction can take place by three methods.

1. Free radical mechanism
2. Ionic mechanism (anionic and cationic)
3. Coordination mechanism

1. **Free radical addition polymerisation** It has three steps.

(i) **Chain initiation step** It involves the formation of free radicals in the initiation step.

The free radicals are formed as a result of homolytic dissociation of the initiator in the presence of heat, light or catalyst. Commonly used free radical initiators are azo compounds ($-\text{N}=\text{N}-$), disulphides ($-\text{S}-\text{S}-$), peroxides ($-\text{O}-\text{O}-$), hydroperoxides, peracids and peresters. An important example of a free radical initiator is benzoyl peroxide that dissociates as follows:

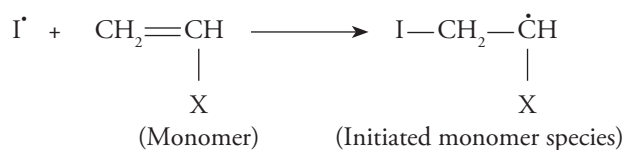


Here, half arrow (\curvearrowright) represents single electron shift. In $C_6H_5^\bullet$, the dot (\bullet) represents single electron.

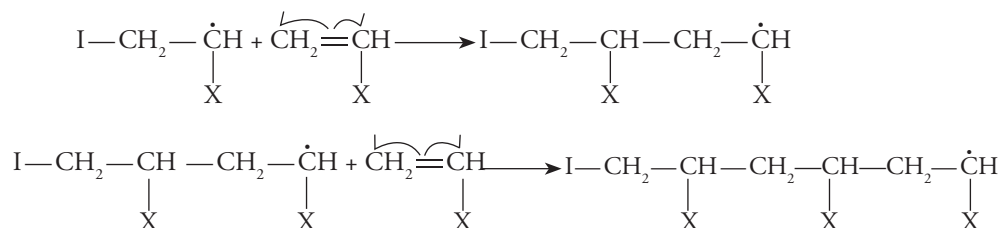
In general, the dissociation of the initiator (I—I) to form free radical species can be represented as



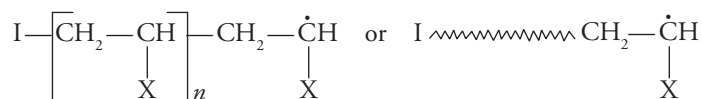
In the second step of initiation, a monomer molecule (M) is attached to the initiator radical. Considering vinyl as the monomer, this step can be represented as



- (ii) **Chain propagation step** In this step, the initiated monomer species adds additional monomer units as follows:

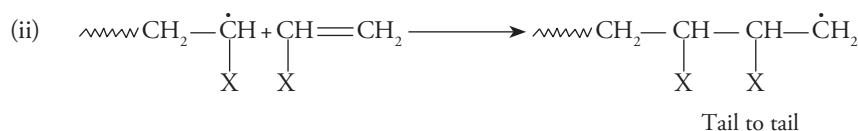
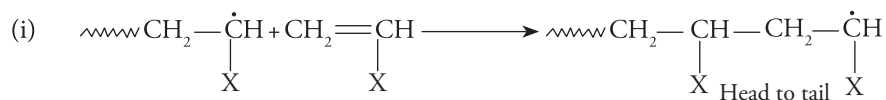


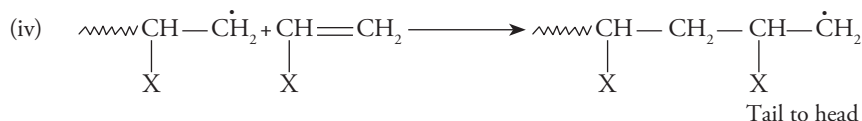
The propagation continues until the chain growth is stopped by some impurities or by termination process or till there is no further monomer left for attack. The structure of the growing chain can be represented as



n denotes the number of monomeric units added up in the chain growth and the wavy line also indicates the number of monomeric units added.

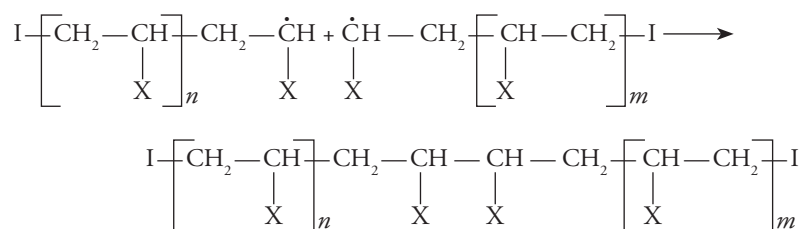
If the CH_2 part of monomeric chain is called head and CH_2X part is termed as tail, then four modes of addition can take place.





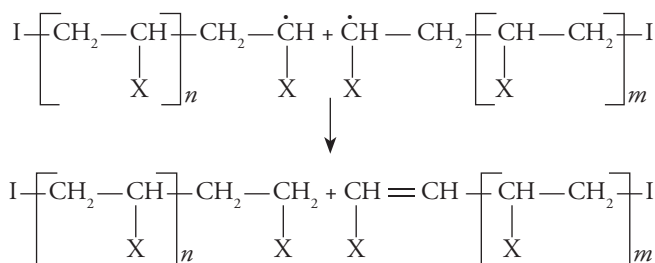
(iii) **Chain termination** This is the last step of polymerisation process where the growth of the chain is arrested. It can occur as follows.

- (a) **By combination of two growing chains (coupling)** As the decomposition of the initiator produces many free radicals at the same time, many chains are initiated and propagated simultaneously. The two growing chains can come close, collide and get deactivated.



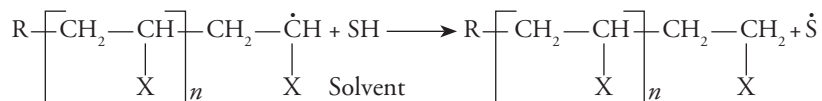
As this process involves the coupling of two lone pairs of electrons, this kind of termination is known as *termination by coupling*.

- (b) **By disproportionation** In this kind of chain termination, the hydrogen from one growing chain is abstracted by the other growing chain and results in the formation of two polymer molecules, one saturated and the other unsaturated. Contrary to the first type where a long-chain polymer is obtained, by this method we obtain two polymer molecules of shorter chain length.

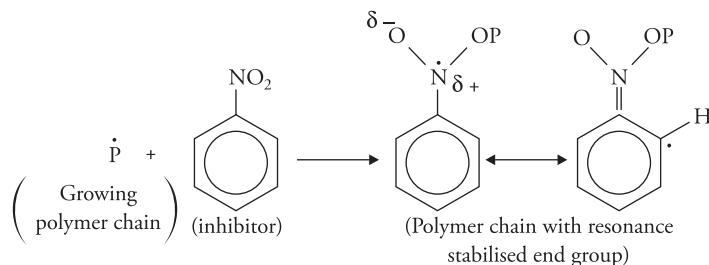


The products formed do not contain any reactive sites and may be termed as 'dead' polymer chain.

- (c) **Chain transfer** In this type of termination process, the growth of one polymer chain is stopped forming a dead polymer but there is simultaneous generation of a new free radical capable of initiating a fresh polymer chain growth. This reaction takes place by hydrogen abstraction from either solvent or some impurities present in the system.



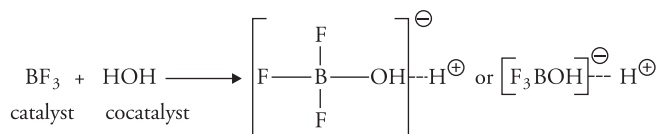
The chain can also be terminated by the addition of certain compounds, which are called inhibitors. Hydroquinone, nitrobenzene and dinitrobenzene are some of the commonly used inhibitors. Atmospheric oxygen is also a good inhibitor.



2. **Ionic addition polymerisation** Ionic polymerisations follow the same basic steps (initiation, propagation and termination). The chain is initiated either by a carbanion (C^\ominus) or carbocation (C^\oplus). Vinyl groups with electron-withdrawing groups polymerise by the anionic pathway, whereas vinyl groups with electron-donating groups can polymerise by a cationic mechanism.

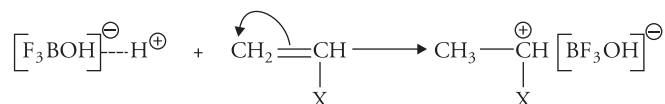
(i) **Cationic polymerisation**

- (a) **Chain initiation** Strong lewis acids like BF_3 and AlCl_3 are used as catalysts. Water exists as a co-catalyst to provide the proton.



where H^\oplus is the cationic initiator and $[\text{F}_3\text{BOH}]^\ominus$ is the counter ion.

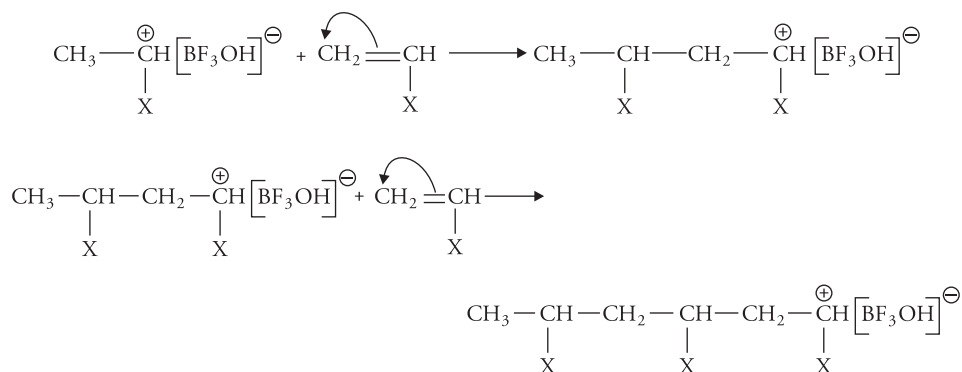
The H^\oplus ion now attacks the π -electron cloud of the monomer and a carbocation is formed.



where X = electron-donating group.

Chain propagation

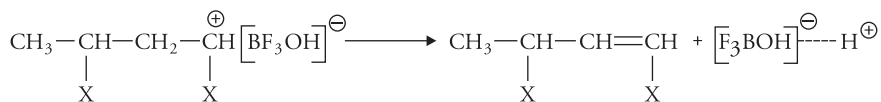
The chain initiator formed in the initiation step attacks new monomer units.



Chain termination

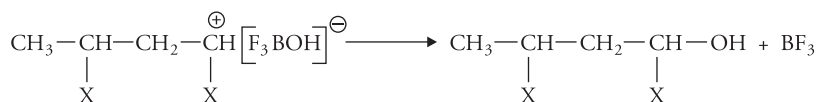
Chain termination can occur in two ways

- (a) Donation of proton to counterion by the growing chain resulting in the formation of a double bond at the end of the polymeric chain.



Thus, the initiator or catalyst is regenerated.

- (b) Formation of covalent bond between the carbocation and counter ion (coupling).



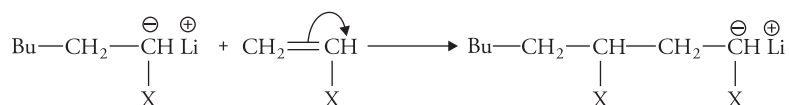
Again the catalyst BF_3 is regenerated. Monomers capable of undergoing cationic polymerisation are isobutylene, styrene, methyl styrene and many vinyl ethers.

(ii) **Anionic polymerisation**

Chain initiation Strong bases such as organoalkali compounds like n-butyllithium and ethylsodium initiate the anionic addition polymerisation.

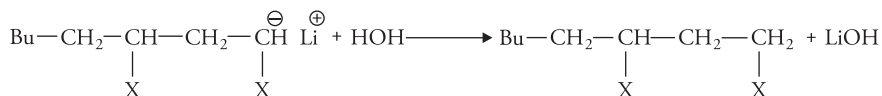


where X = electron-withdrawing group.

Chain propagation**Chain termination**

The termination in anionic polymerisation is not a spontaneous process. The polymerisation process continues till all the monomers are consumed.

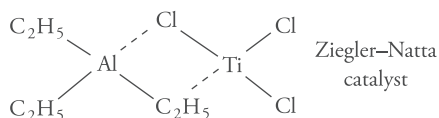
However, termination can be accomplished by transfer of negative charge to a species that is not directly involved in the reaction like CO_2 , methanol, water, etc.



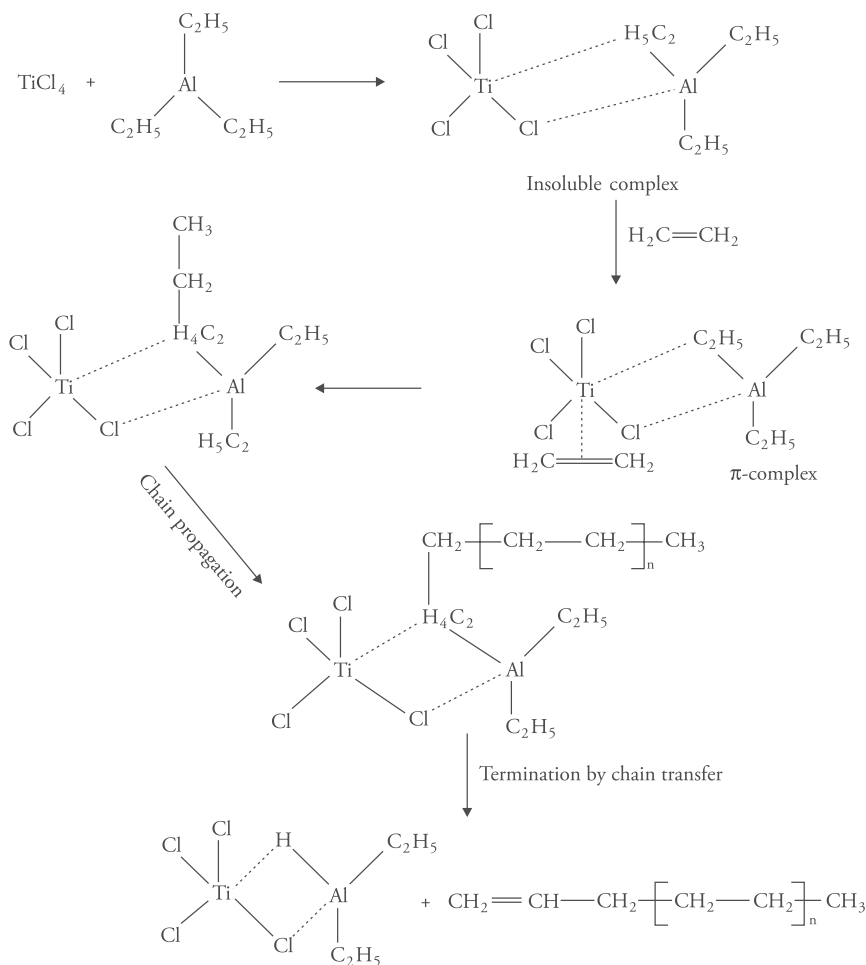
Monomers capable of undergoing anionic polymerisation are butadiene, isoprene, styrene and acrylonitrile.

3. **Coordination mechanism** These are polymerisation reactions taking place in the presence of organometallic compounds as catalysts.

Ziegler (1953) and Natta (1955) discovered that an organometallic compound in combination with transition metal halide (TiCl_4 and TiCl_3) can be used to prepare stereospecific polymers. The commonly used Ziegler–Natta catalyst is triethylaluminium in combination with titanium trichloride or titanium tetrachloride.

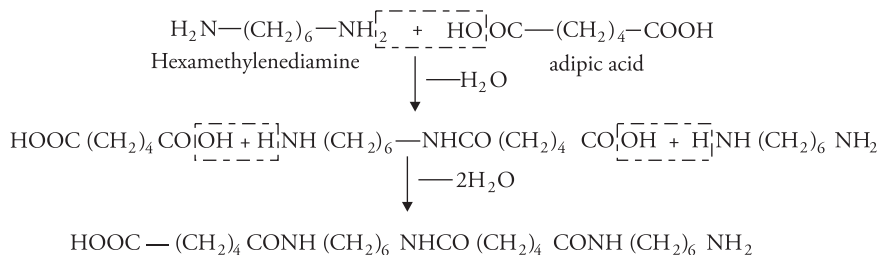


Mechanism of coordination polymerisation



Condensation polymerisation

Step polymerisation In condensation polymerisation, the polymerisation reaction proceeds step by step through reaction between the functional groups of the monomers with the removal of small molecules like water. For example, consider the formation of Nylon 6, 6:



The reaction proceeds step by step and the chain elongates.

6.5 Polymerisation Techniques

The various techniques of polymerisation are discussed below.

- (i) **Bulk polymerisation** Bulk polymerisation is simpler from the standpoint of formulation and equipment, but it is very difficult to control because the polymerisation is highly exothermic.

In this method, the monomer is taken in liquid state and the free radical initiator is dissolved in it. The chain transfer agent, used to control molecular weight, is also dissolved in the monomer. The homogenous reaction mixture is then heated or exposed to radiation for initiating the polymerisation. The mixture is stirred well because the reaction is highly exothermic. As the reaction proceeds, the viscosity of the medium increases and mixing becomes difficult. However, the polymer is insoluble in the monomer, polymer precipitates and the viscosity of the medium does not change appreciably.

Disadvantage The reaction mixture becomes viscous, the probability of chain collision becomes less and chain termination becomes difficult. Active radicals accumulate increasing the rate of polymerisation to such an extent that it may become uncontrolled and lead to explosion.

However, this method gives the polymer of highest purity because except chain initiator and chain transfer agents no other additive is used in the process.

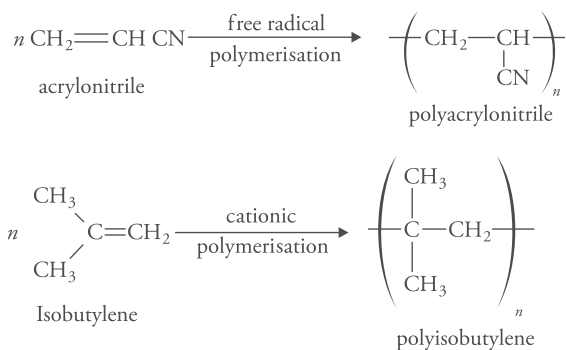
Bulk polymerisation technique is used in the polymerisation of methyl methacrylate or styrene and vinyl chloride.

- (ii) **Solution polymerisation** In this method, the monomer, free radical initiator and the chain transfer agent (whenever used) are dissolved in an inert solvent. The ionic or coordination catalysts are either dissolved or suspended. The polymer formed is in solution form. It is separated from solution either by evaporation of the solvent or by precipitation in a non-solvent. The inert solvent controls viscosity and promotes proper heat transfer.

Disadvantages

- (i) It is difficult to get high molecular weight polymers because no matter how inert the solvent is, chain transfer to the solvent cannot be completely ruled out.
- (ii) It is often difficult to remove the solvent completely from the finished polymer.

Solution polymerisation is used to manufacture polyacrylonitrile by free radical polymerisation and polyisobutylene by cationic polymerisation. Block co-polymers are also made exclusively by the technique.



(iii) Suspension polymerisation

This technique finds use in heterogeneous systems and is used only for water insoluble monomers. The monomer is first mechanically dispersed in a non-compatible liquid, usually water to form a suspension. The resultant monomer droplets are then polymerised using an initiator soluble in the monomer. The monomer is kept in suspension by continuous agitation and by the addition of stabilisers such as polyvinyl alcohol or methylcellulose. The polymer obtained is in the form of granular beads that are isolated by filtration or by spraying into a heated chamber (spray drying). As the polymer is granular in the form of beads or pearls, this method is also referred to as **beads or pearls polymerisation**.

Disadvantage This technique cannot be used for tacky polymers such as elastomers because of the tendency of agglomeration of polymer particles.

Suspension methods are used to prepare a number of granular polymers like polystyrene, styrene divinylbenzene beads (used for ion exchange resins), polymethylmethacrylate, polyvinylacetate, etc.

(iv) Emulsion polymerisation

This method was developed by Goodyear Tire and Rubber Company in the 1920s. Like suspension polymerisation, this technique also uses water as a dispersing medium. However, unlike suspension polymerisation, here the monomer is dispersed in the aqueous phase by an emulsifying agent such as soap or detergent. Redox type initiator radicals like hydrogen peroxide and persulphates are generated in the aqueous phase and they diffuse into soap micelles containing monomer molecules. As the polymerisation proceeds, more and more monomer migrates into micelles to continue the reaction. When new radical diffuses into the micelle, radical combination occurs and the polymerisation reaction is terminated. This method results in the formation of extremely high molecular weight polymers. Chain transfer agents are added to control the degree of polymerisation.

Emulsion polymerisation is widely used in industry for manufacturing water-based (latex) paints or adhesives in which the emulsified product is directly used. It is also used for preparing tacky polymers. Monomers such as vinyl chloride, butadiene, chloroprene and vinylacetate are polymerised by this technique.

6.6 Molecular Weight of Polymers

As the chain termination is a random process, all the polymeric chains formed are of different lengths. Under such a situation, it becomes difficult to express the molecular weight of the polymer. Hence, the molecular weight can be expressed as average of the molecular weights contributed by individual molecules present in the sample.

The molecular weight of a polymer is expressed in two ways.

(i) Number average molecular weight M_n

If n_1, n_2, n_3, \dots are the numbers of molecules with molecular masses M_1, M_2, M_3, \dots , respectively, then the number average molecular weight is

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}{n_1 + n_2 + n_3 + \dots} = \frac{\text{Total mass of the polymer sample}}{\text{Total number of molecules present in the sample}}$$

$$= \frac{\sum n_i M_i}{\sum n_i}$$

where n_i is the number of molecules or number of moles of molecules having molecular weight M_i .

Number average molecular weight can be measured on the basis of colligative property like osmotic pressure.

- (ii) **Weight average molecular weight** If m_1, m_2, m_3, \dots are the weights of species with molecular masses M_1, M_2, M_3, \dots , respectively, then the weight average molecular weight is

$$\overline{M}_w = \frac{m_1 M_1 + m_2 M_2 + m_3 M_3 + \dots}{m_1 + m_2 + m_3}$$

$$\overline{M}_w = \frac{\sum m_i M_i}{\sum m_i}$$

But $m_i = n_i M_i$

hence
$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

where n_i = number of molecules of mass M_i . \overline{M}_w is determined by methods like sedimentation, ultracentrifugation, etc.

Degree of polymerisation It represents the number of repeating units in a polymeric chain. For example, if a polymer has 5000 repeating units, then the degree of polymerisation is 5000.

Degree of polymerisation can be number average degree of polymerisation (\overline{DP}_n) or weight average degree of polymerisation (\overline{DP}_w).

$$(\overline{DP}_n) = \frac{\overline{M}_n}{M_0} \quad \overline{DP}_w = \frac{\overline{M}_w}{M_0}$$

\overline{M}_n = number average molecular weight

\overline{M}_w = weight average molecular weight

M_0 = molecular weight of monomer

Polydispersity index The ratio of mass average molecular mass to the number average molecular mass is called polydispersity index PDI.

$$\text{PDI} = \frac{\overline{M}_w}{\overline{M}_n}$$

This gives an idea about the homogeneity of the polymer.

Solved examples

1. In a polymer sample, 30% molecules have a molecular mass 20,000, 40% have molecular mass 30,000 and the rest have 60,000. Calculate mass average and number average molecular masses.

Solution

$$\begin{aligned}\overline{M}_n &= \frac{\sum n_i M_i}{\sum n_i} = \frac{(30 \times 20,000) + (40 \times 30,000) + (30 \times 60,000)}{30 + 40 + 30} \\ &= 36000\end{aligned}$$

$$\begin{aligned}\overline{M}_w &= \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{30(20,000)^2 + 40(30,000)^2 + 30(60,000)^2}{30 \times 20,000 + 40 \times 30,000 + 30 \times 60,000} \\ &= 43333.\end{aligned}$$

2. There are two fractions with molecular weights 10^4 and 10^5 . Let us consider 100 g of the polymer, 10 g fraction has molecular weight 10^4 and 90 g has 10^5 . Calculate \overline{M}_w and \overline{M}_n .

Solution

$$\overline{M}_w = \frac{m_1 M_1 + m_2 M_2}{m_1 + m_2} = \frac{10 \times 10^4 + 90 \times 10^5}{10 + 90} = 91000$$

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} = \frac{\frac{10}{10^4} \times 10^4 + \frac{90}{10^5} \times 10^5}{\frac{10}{10^4} + \frac{90}{10^5}}$$

$$n_1 = \frac{m_1}{M_1}$$

$$\frac{100}{\frac{100 + 90}{10^5}} = \frac{100 \times 10^5}{190} = 5.26 \times 10^4$$

Practice problems

1. Calculate the number average and weight average molecular mass of a polymer having
10 molecules of molecular mass each = 5000
20 molecules of molecular mass each = 7500

20 molecules of molecular mass each = 10,000

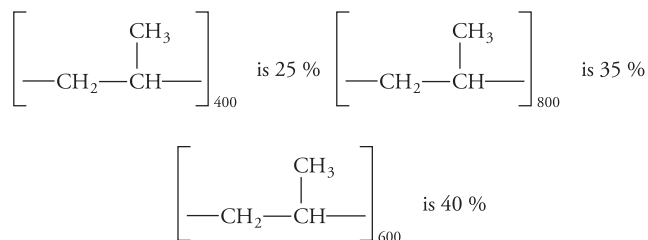
25 molecules of molecular mass each = 15,000

20 molecules of molecular mass each = 20,000.

5 molecules of molecular mass each = 25000

[Ans $\overline{M}_n = 13000$; $\overline{M}_w = 15,480$]

2. Calculate the number average and weight average molecular masses of polypropylene polymer with the following composition.



[Ans $\overline{M}_n = 25,565$; $\overline{M}_w = 27,084$]

6.7 Plastics

The term 'plastic' refers to the class of polymers that can be shaped into hard and tough utility articles by the application of heat and pressure.

They are strong, light, highly dielectric, durable and corrosion-resistant. Because of these properties, the use of plastics is increasing tremendously. Plastic materials are replacing metals in all walks of life. The reason for using plastics over metals is that

- They are light in weight and at the same time possess good strength, toughness and rigidity.
- They are corrosion-resistant and also resist the action of chemicals.
- They are less brittle than glass and can be made equally smooth and transparent.
- They do not absorb moisture.
- They can be easily moulded into desired shape.
- They can take a variety of colors, are heat-resistant and abrasion-resistant, and have good dimensional stability. Their maintenance cost is low.

Types of plastics Plastics are generally classified into two categories:

- Thermoplastics
- Thermosetting plastics

Thermoplastics They are plastic materials that soften on heating and can be moulded into desired shape. On cooling, they become hard. However, they can be resoftened and remoulded by the application of heat and pressure. The reason for resoftening of thermoplastic is that they are composed of linear or long-chain molecules. On heating the intermolecular bonds weaken, the material softens and thus can be moulded again without any damage.

Common examples of thermoplastics are polyethene, polypropylene, polystyrene, teflon, polyamides, etc.

Thermosetting plastics They are those plastic materials that, when subjected to heat and pressure, change into a hard and rigid substance. Once they set, they cannot be softened again by the application of heat. The reason is that during moulding they acquire three-dimensional cross-linked structure. Such three-dimensional polymers will not soften when heated but may decompose or disintegrate at high temperatures.

Common examples are bakelite, melamine formaldehyde, epoxy resins, etc.

Table 6.1 Difference between the thermoplastics and thermosetting plastics

Thermoplastics	Thermosetting plastics
1. Once moulded, they can be resoftened and reused	Once moulded, they set permanently. They do not soften again on heating
2. They are softer and less strong. The polymeric chains are held together by weak van der Waals forces	They are strong and hard. There are cross-linkages and covalent bond formation between the adjacent polymeric chains
3. They are generally formed by addition polymerisation reaction	These are formed by condensation polymerisation reaction
4. As they soften again and again, they can be recycled, reused and reclaimed from waste	They cannot be recycled, reused or reclaimed from waste
5. Examples include polythene, polypropylene, teflon, nylon, natural rubber	Examples include bakelite, melamine formaldehyde, epoxy resins, vulcanised rubber

Moulding constituents of a plastics During moulding, different constituents are added to impart the required property. These constituents that are added to plastics during its moulding process are termed as its *moulding constituents*. The main compounding ingredients and their functions are given below.

1. **Resin** These are substances that hold the different constituents together. Usually thermosetting resins are used.
2. **Plasticisers** These materials increase the plasticity and flexibility. They neutralise the intermolecular forces of attraction and impart greater freedom of movement between the polymeric macromolecules. Commonly used plasticisers are vegetable oils, camphor, esters (of stearic, oleic or phthalic acids) and phosphates like tricresyl phosphate.

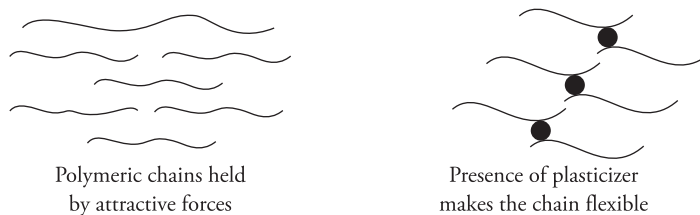


Figure 6.2 Effect of plasticiser on the polymer chain

3. **Fillers** These are added to improve the hardness, tensile strength, opacity and workability of the plastic. Fillers impart special characters to products. For example, addition of carbon black to natural rubber increases its tensile strength and makes it abrasion-resistant, addition of asbestos to a plastic material provides heat and corrosion resistance, addition of barium makes the plastic impervious to X-rays, whereas quartz, mica and carborundum are added to provide extra hardness.
4. **Lubricants** Lubricants like waxes, oils and soaps prevent the plastic material from sticking to the mould. They also impart flawless, glossy finish to the final products.
5. **Catalysts or accelerators** They are added to accelerate the polymerisation process. They are particularly used for thermosetting plastics. Commonly used catalysts are hydrogen peroxide, benzoylperoxides, metals like Ag, Cu and Pb and oxides like ZnO.
6. **Stabilisers** They improve the thermal stability during processing. Stabilisers are added to those polymers which have a tendency to decompose at moulding temperature. For example, vinyl polymers. Commonly used stabilisers are salts of lead and stearates of lead, cadmium and barium.
7. **Coloring materials** Organic dye stuffs and opaque inorganic pigments are commonly used to impart color to the plastic products.

Plastic moulding processes Plastic materials supplied in granular, powder or other forms are moulded into articles by various methods. The commonly used methods are as follows:

- (a) Compression moulding
 - (b) Transfer moulding
 - (c) Injection moulding
 - (d) Blow moulding
 - (e) Extrusion moulding
- (a) **Compression moulding** Compression moulding is widely used to produce articles from thermosetting plastics. It is used for manufacturing electrical parts such as switches, switch boards, cooker handles, etc. The mould used for the purpose is made up of two halves. The upper half has a projection and is called the male die, whereas the lower half called the female die has a cavity.

The material to be moulded is placed in the lower female cavity and is heated continuously by steam or electricity. The movable bolster is raised so that the female mould portion contacts the male die, which is also heated. As the mould closes down under pressure, the excess material flows out of the mould as *flash*. Under the influence of heat, the compacted material gets cured and hardened. The mould is opened while it is still hot to release the moulded product.

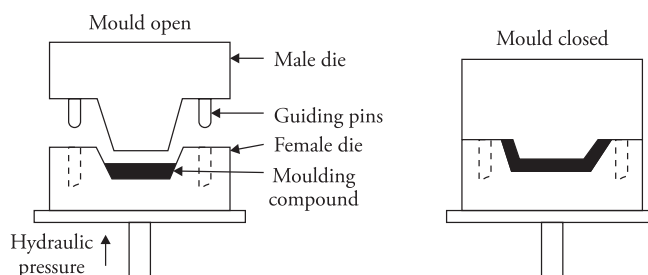


Figure 6.3 Compression moulding

- (b) **Transfer moulding** It is used for moulding thermosetting materials. Unlike compression moulding, the moulded material in transfer moulding is preheated and loaded into a chamber known as the pot. A plunger (piston) forces the molten material into the mould cavities through channels known as *sprue and runner system*. The mould remains closed as the material is inserted. The molten material sets, gets cured and is released by opening the mould. The moulds in both compression and transfer moulding remain closed till the curing reaction within the material is complete. Transfer moulding, unlike compression moulding, uses closed mould.

Transfer moulding differs from compression moulding as in transfer moulding heated, molten resin is inserted in the mould, whereas in compression moulding granular or powdered resin is placed in the mould, which is then heated and pressure is applied. No further pressure is needed in transfer moulding.

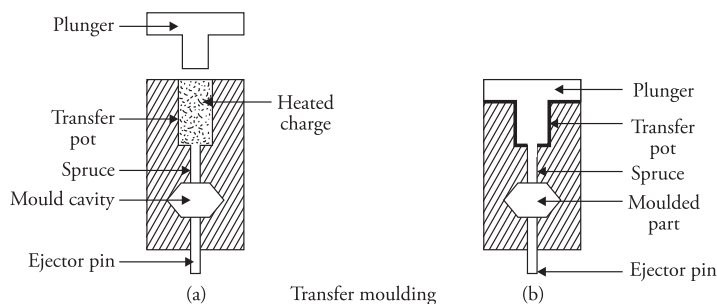


Figure 6.4 Transfer moulding

- (c) **Injection moulding** It is used for producing articles made of thermoplastic materials like mugs, buckets, dust bins, chairs, etc.

The mould consists of a two-part system; one part is movable and the other is stationary. The stationary part is fixed to the end of the cylinder, whereas the movable part can be opened or closed on to the stationary part.

In this process, a correct amount of plastic material as granules, pellets or powder is fed from the hopper into the cylinder. The piston pushes the plastic material into the heating chamber where it melts to form a viscous liquid. Again with the help of the piston the molten plastic material is injected through the nozzle into the mould cavity. Pressure is maintained in the mould cavity. The material is cooled by water circulation. It solidifies. Finally, the mould is opened, the piece is ejected, the mould is closed and the entire cycle is repeated. The most outstanding feature of this technique is the speed with which the pieces may be produced.

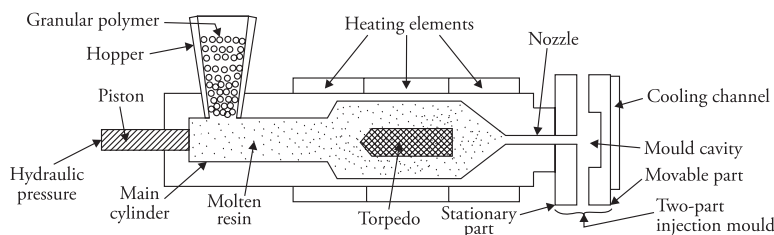


Figure 6.5 Schematic diagram of injection moulding machine

- (d) **Blow moulding** It is used for producing hollow articles like bottles and hollow toys. Thermoplastic articles such as PE, polycarbonate, PVC, nylon and styrene are blow-moulded.

In this process a hot, softened thermoplastic tube called 'parison' is properly placed inside the two-piece hollow mould. The split mould is then closed, sealing the bottom. This joint is usually seen at the bottom of the plastic bottles. Air is then blown in the hot parison. It is inflated and acquires the shape of the mould. The mould is allowed to cool and the rigid thermoplastic article formed is removed by opening the mould.

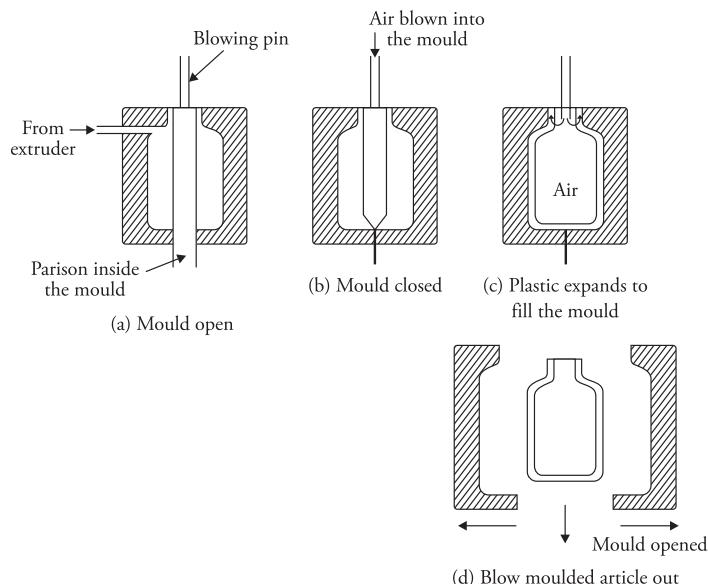


Figure 6.6 *Blow moulding*

- (e) **Extrusion moulding** This method is used for making elongated and continuous articles such as rods, pipes, tubes, hose pipes films, filaments and sheets. An extruder resembles the injection moulding apparatus, except that the mould cavity is replaced with a die.

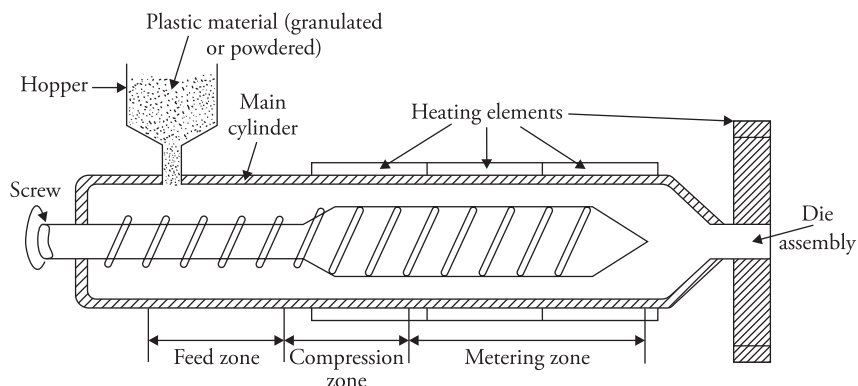


Figure 6.7 *Schematic diagram of extrusion moulding machine*

In this process, the compounded plastic material in the form of powder or granules is fed into the electrically heated cylinder using a hopper. A helically rotating screw inside the cylinder further works the plastic charge. During the journey from hopper to the die, the plastic material passes through three zones namely feed zone, compression zone and metering zone. The feed zone receives the charge from the hopper. No heating takes place in the feed zone. In the compression zone, the powdered charge melts because of heating and compression by the moving screw. The pasty molten mass enters the metering zone. The pressure in this region enables the molten polymer to enter the die and come out of it with the desired shaped. The material extruded out of the die is quite hot (usually 125–350 °C) and is carried over the conveyor belt through a tub containing cold water.

The process of extrusion is also used for coating wires and cables with PVC or rubber. This method gives products of good surface finish and dimensional stability.

This process is widely used to encapsulate or enclose items such as coils, plugs, integrated circuits, utensil handles, etc.

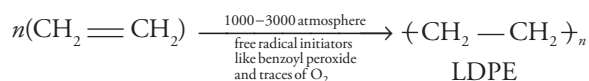
6.8 Individual Polymers

Addition polymers

1. **Polyethylene** Also known as polyethene, it is an important thermoplastic resin prepared by the addition polymerisation of ethylene. It is of several types

(a) Low-density polyethene

Preparation It is prepared by the polymerisation of ethylene at high pressure (1000–3000 atmospheres) at 250 °C in the presence of free radical initiators like benzoyl peroxide. Traces of oxygen catalyse the reaction.



Properties It is a waxy solid that floats on water and has a linear branched structure. The branches do not allow the chains to pack efficiently; hence, its density is low (0.91–0.925 g/cm³). It is not polar and has weak intermolecular forces. It is tough, flexible, chemically inert and has excellent electrical insulation properties.

Applications Low-density polyethene (LDPE) is used for storing a variety of foodstuffs. It is used for making carrier bags, films for general packing, moulded toys, mugs and ink tubes for pens.

(b) High-density polyethene

Preparation

- (i) Ethylene is polymerised under 6–8 atmospheric pressure at 60–70 °C in the presence of Ziegler–Natta catalyst (triethylaluminium and titanium tetrachloride).
- (ii) At 35 atmospheric pressure, 60–200 °C temperature and in the presence of metal oxide catalyst like CrO₃ supported on silica alumina, ethylene polymerises to give high-density polyethene (HDPE).

Properties The polymeric chains are linear and hence they pack easily. Hence, it has high density ($0.95\text{--}0.97\text{ g/cm}^3$). It is more stiff, hard and has greater tensile strength compared with LDPE. Its softening temperature is high ($135\text{ }^\circ\text{C}$). It has excellent electrical insulation properties, has low water and gas permeability, has excellent chemical resistance and is free from odor and toxicity.

Applications

It is used for making insulations, pipes, bottles for milk, household chemicals and drug packing. It is also used for the manufacture of crates, industrial containers and overhead tanks. HDPE sheets are used for packing materials and for making toys.

(c) LLDPE (linear low-density polyethylene) It is actually a copolymer of ethylene and 1-butene (with lesser amounts of 1-hexene and higher 1-alkenes to vary the density) manufactured with Ziegler-type catalysts. First marketed in the 1970s, LLDPE is attractive because it requires considerably less energy to produce than LDPE.

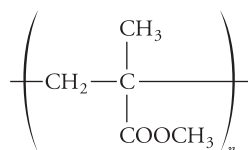
Uses It is used in making golf ball covers, orthopaedic devices, blending with LDPE, packing films and bottles.

(d) UHMWPE (ultrahigh molecular-weight polyethylene)

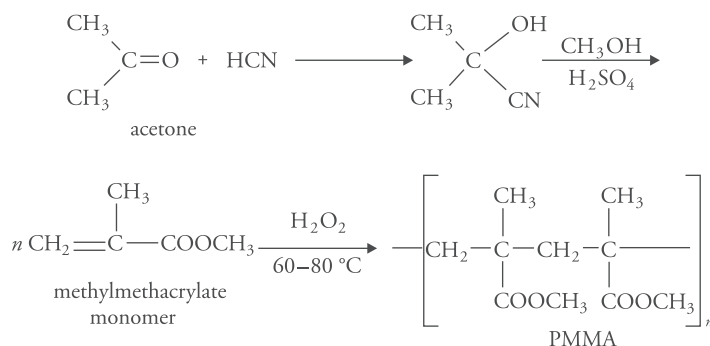
Uses It is used in making surgical prostheses, machine parts, heavy-duty liners.

Polymethylmethacrylate (PMMA)

The polymethylmethacrylate polymer has the following structure:



It is manufactured by the polymerisation of methylmethacrylate monomer in the presence of free radical catalyst hydrogen peroxide at $60\text{--}80\text{ }^\circ\text{C}$. The mechanism is as follows:



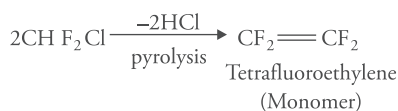
Properties It is also known as plexi glass. It is colorless, transparent, amorphous and has good strength.

Although chemically inert, it dissolves in organic solvents such as ketones, chlorinated hydrocarbons and esters.

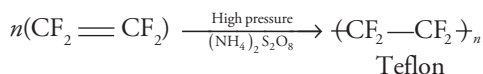
Applications

Its optical transparency is better than that of glass. Hence, it is an excellent substitute for glass. It is used for the manufacture of contact lens, spectacles and windscreens. Because of its good mechanical properties it is used for the manufacture of cockpit canopies, attractive signboards and for decorative purposes. It has high weather resistance. It does not turn yellow or crumble when exposed to sunlight. It is used for making transparent windows, aquariums, tail-lights of automobiles, bathtub liners, sinks, cell phone display screens and so on.

Teflon (polytetrafluoroethylene, PTFE) Its trade name is teflon. It is prepared by the polymerisation of tetrafluoroethylene at high pressure in the presence of ammonium persulphate as catalyst.



The monomer is polymerised using ammoniumpersulphate as initiator.



Properties

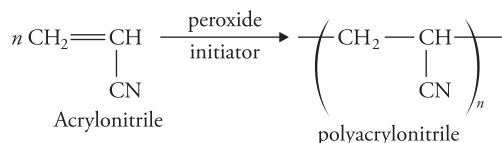
It is a linear polymer with practically no branching. It has high mechanical strength and is chemically inert. Its softening temperature is high (350 °C). It does not dissolve in acids, including fuming nitric acid, and is also resistant to the attack of corrosive alkali and organic solvents.

Applications

It is used for making articles like pump valves and pipes where chemical resistance is required. It is used for manufacturing insulations for motors, transformers, capacitors, electrical cables, etc. It is also used for making gaskets, gas seals, non-sticking stopcocks for burette and for making teflon-coated non-stick utensils.

Polyacrylonitrile (PAN)

Also known as orlon or acrilon, it is produced by the radical polymerisation of acrylonitrile (vinyl cyanide) using peroxide initiators. The chemical reactions involved are as follows:

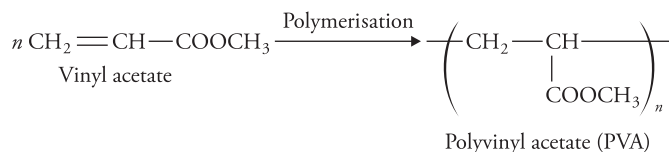


Properties It has high heat resistance (softening temperature 220 °C) and exhibits good mechanical properties. It is soluble in solvents like dimethyl formamide, dimethylsulphoxide, etc.

Applications It is used to produce PAN fibres that find use in making blankets, sweaters, bathing suits, synthetic carpets, etc. On copolymerisation with butadiene, it produces nitrile rubber (Buna-N), which is of great industrial importance.

Polyvinylacetate (PVA)

It is obtained by heating vinyl acetate in the presence of small amount of benzoylperoxide.



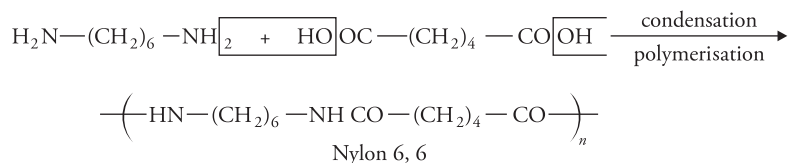
The polymer can be prepared by bulk, emulsion or solution polymerisation methods.

Properties PVA is a solid resin that is insoluble in water but is soluble in aromatic solvents and also in alcohols and esters. It is saponified with great difficulty and is not absorbed by the digestive system. It is resistant to atmospheric air, water and chemicals.

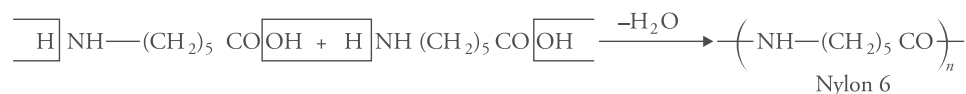
Uses It is used in adhesives, lacquers, paints and for large-scale manufacture of gramophone records. Polyvinyl acetate adhesives are used for bonding textile to textile, leather to leather, paper to textile, etc. Polyvinyl acetate is used as a basic material for chewing gums and surgical dressings. On copolymerisation with polyvinyl chloride, it is converted into a soft polymer, vinylite, which is used as a surface-coating material for metals. Polyvinyl acetate is mainly used for the manufacture of polyvinylalcohol.

Condensation polymers

Nylon They are polyamide polymers having recurring amide groups. Nylon 6, 6 is formed by the condensation of hexamethylenediamine and adipic acid.

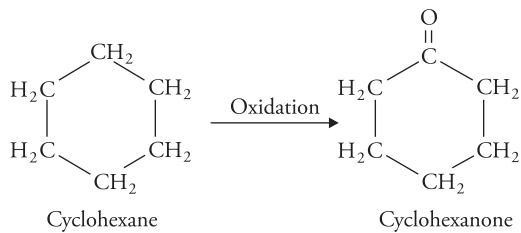


Nylon 6 It is produced by the self-condensation of ϵ -aminocaproic acid.

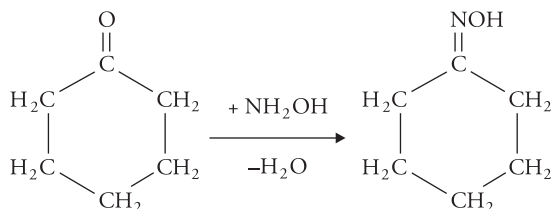


The various steps for the synthesis of nylon-6 starting from cyclohexane are as follows:

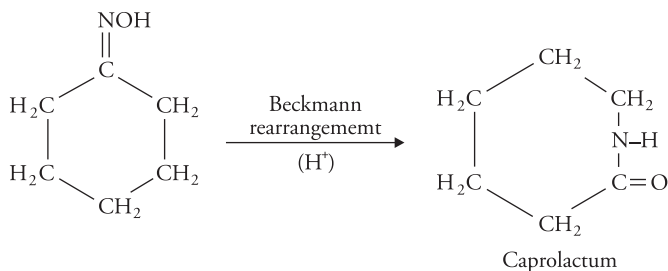
Step (i) Conversion of cyclohexane to cyclohexanone by oxidation.



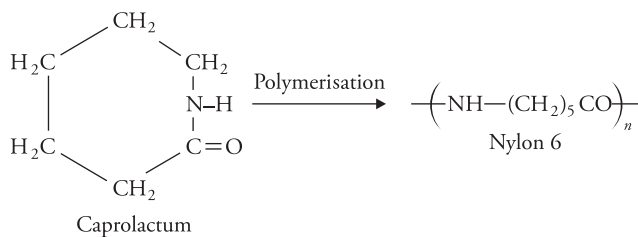
Step (ii) Cyclohexanone reacts with hydroxylamine NH_2OH to form cyclohexanone-oxime.



Step (iii) Conversion of cyclohexanone-oxime into caprolactum by Beckmann rearrangement in the presence of H_2SO_4 .

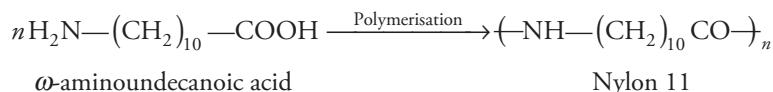


Step (iv) Ring opening and polymerisation of caprolactum to give nylon-6.



Nylon-11

It is prepared by the self-condensation of ω -aminoundecanoic acid.

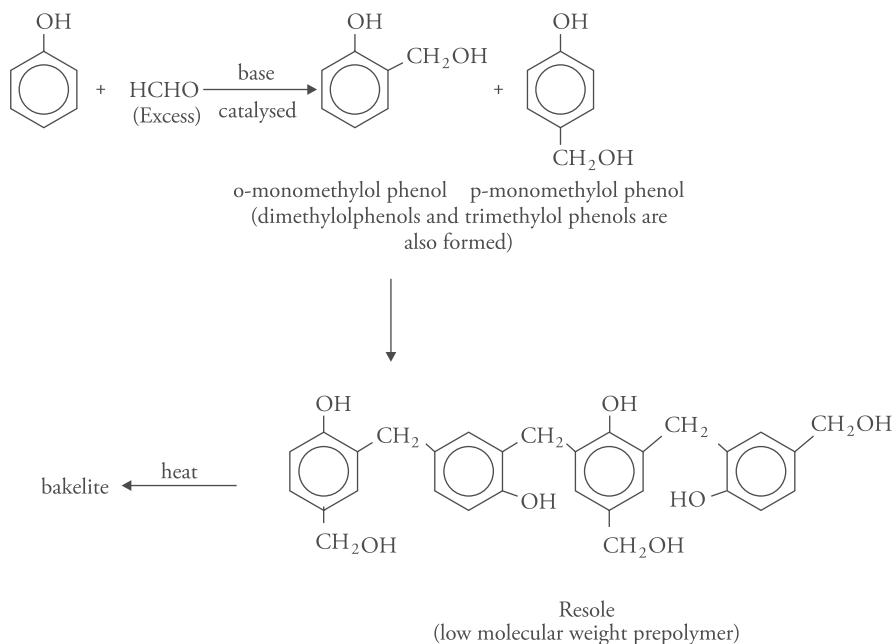


Properties It is a linear polymer. The polymeric chains are held together by hydrogen bonding. They are translucent, high-melting polymers known for their toughness, abrasion resistance, elasticity and high crystallinity.

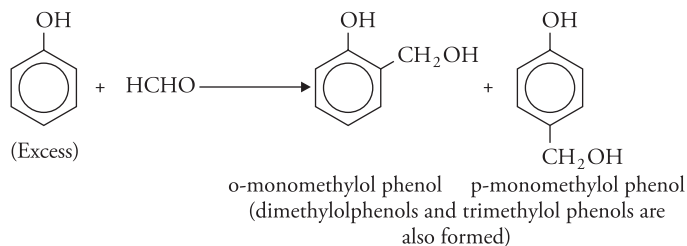
Applications Nylon 66 is used for making fibres that are used for making socks, undergarments, carpets, etc. It also finds use in mechanical engineering for the manufacture of gears, bearings, bushes, electrical mountings. Nylon moving parts work quietly without any lubrication. Nylon 6 is mainly used for making tyre cords. Bristles, brushes are generally made of Nylon 6, 10. Nylon 11 and Nylon 12 are used for making flexible tubings for conveying petrol. Glass-reinforced nylon plastics find use in domestic appliances, radiator parts of cars, etc.

Phenol formaldehyde resin (bakelite) Commercially known as bakelite, this polymer is formed by the condensation of phenol and formaldehyde in the presence of acidic/alkaline catalyst. They are also known as phenoplasts and PF resins. Phenol-formaldehyde resins are normally prepared by two different methods.

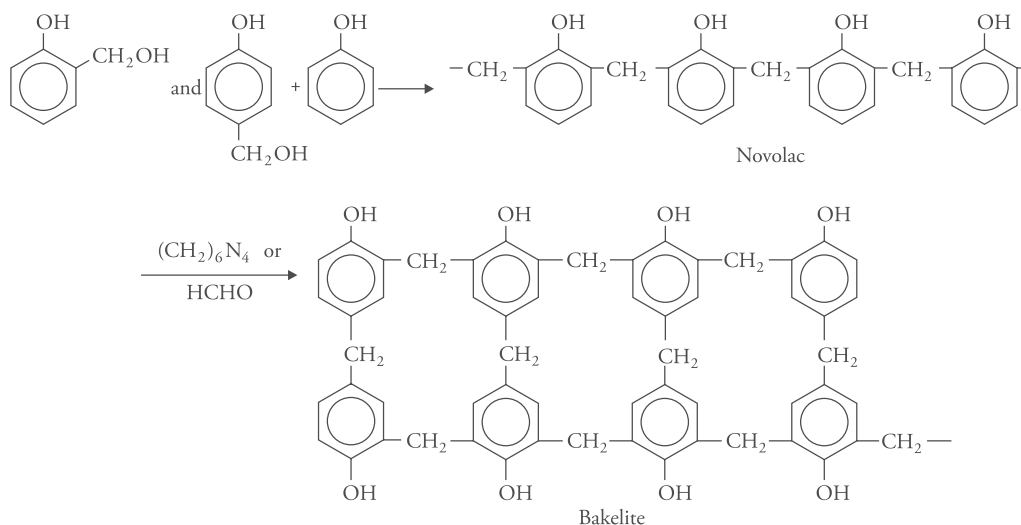
- (i) Base catalysed using excess of formaldehyde over phenol. The initially formed product called 'resole' changes into thermosetting polymer 'bakelite' simply by heating.



(ii) Acid catalysed method using excess of phenol.



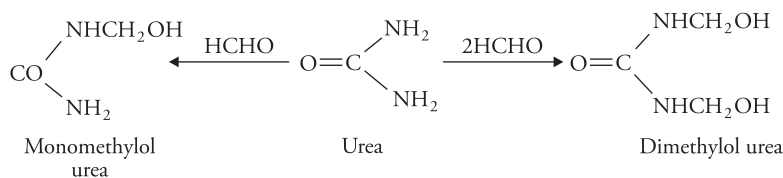
These undergo condensation to form a linear prepolymer novolac. Unlike resole, novolac contains no residual hydroxymethyl groups. Bakelite is obtained by heating novolac with formaldehyde, paraformaldehyde or hexamethylenetetramine (it produces HCHO).



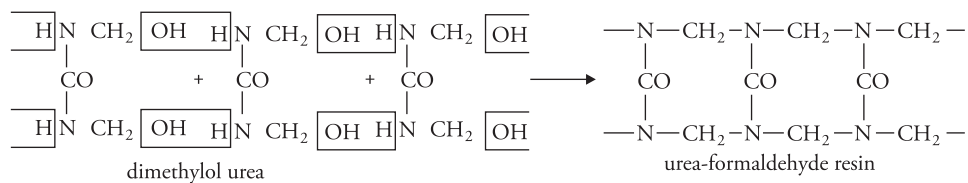
Properties Phenolic resins are hard, rigid, strong with excellent heat, moisture, chemical and abrasion-resistance. They are scratch-resistant and possess excellent electrical insulating properties.

Applications They are used for making domestic switches, plugs, handles for pressure cookers, saucepans and frypans. They are also used for making moulded articles like telephone parts, cabinets for radio and television. They find use as adhesives for grinding wheels and brake linings. They are used in paints and varnishes, in the production of ion-exchange resins for water-softening and for making bearings used in propeller shafts for paper industry and rolling mills.

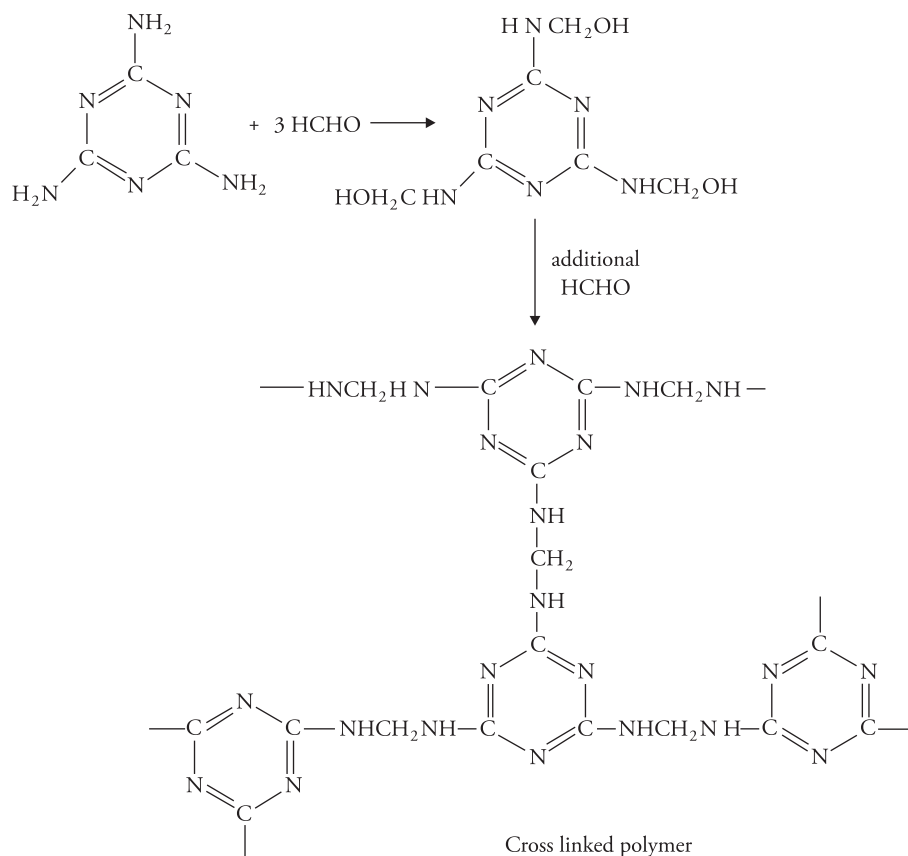
Urea-formaldehyde resin and melamine formaldehyde resin They are obtained by the reaction of urea or melamine with formaldehyde. Two parts of urea and one part of formaldehyde react in a stainless steel vessel in a basic medium at about 50 °C to give mono and dimethylol urea.



These methylol derivatives are compounded with fillers, plasticisers, pigments, etc., and then cured by applying heat and pressure. During curing, cross-linked urea-formaldehyde polymer is formed.



Melamine and formaldehyde also react to give methylol derivatives of melamine.

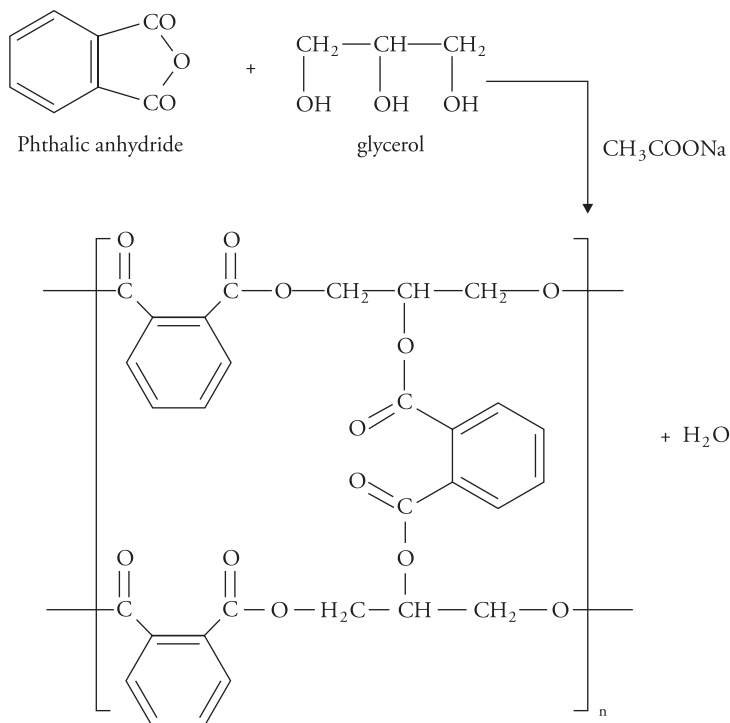


Properties Their tensile strength and hardness is better than phenolic resins. However, heat and moisture resistance are low.

Applications They are used for the preparation of lacquers and in the manufacture of decorative laminates.

Glyptal

Glyptal is a cross-linked, thermoset polyester. It is prepared by condensing glycerol (a triol with phthalic anhydride)



Glyptal

During polymerisation, the monomers join to form large molecules and because of increased attractive forces between the molecules the mixture becomes viscous.

Properties Glyptal is harder and more brittle than the linear polyesters. It does not soften when heated. The cross-linking keeps the polymer chains from moving with respect to one another when heated. It is a fast drying thermoplastic that can bond a variety of materials. It has strong, durable bonds that have excellent resistance to oil, gasoline and moisture.

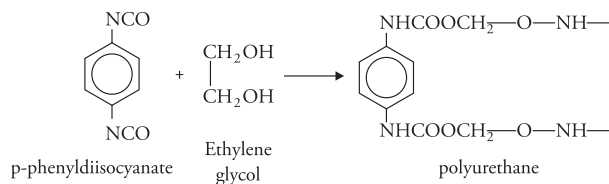
Uses Glyptal and other alkyd polyesters are useful as coating materials and are not used for making fibres and plastic products. Glyptal was first commercialised in 1902 for use in paints and varnish industry. Glyptal is added in paints to improve their washability and adhesion. Its fast drying time along with its good dielectric strength makes it an excellent general-purpose adhesive for many electrical and non-electrical applications. It is also used as a sealing wax.

Polyurethanes Polyurethanes were developed by Otto Bayer and co-workers in 1937.

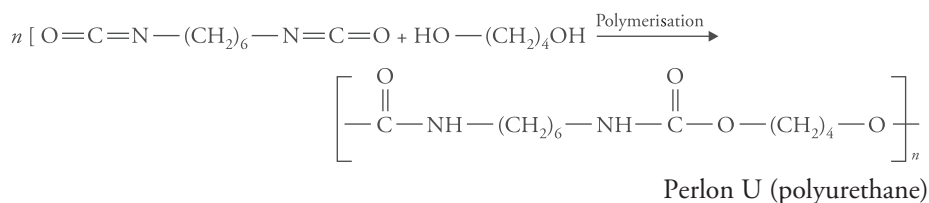
They are characterised by the presence of urethane group —N—C—O— linkage.



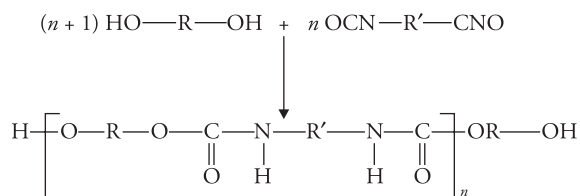
They are obtained by condensing di-isocyanate and diol. When ethylene glycol reacts with p-phenyldi-isocyanate polyurethane is formed.



1, 4-butanediol and 1,6-hexanediisocyanate react to yield Perlon- U (a crystalline polymer).



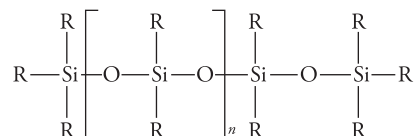
General reaction



Properties They have high strength; good resistance to gas, oil and aromatic hydrocarbons; high abrasion resistance; excellent resistance to oxygen and ozone, but are susceptible to microbial attack. They are also less stable at high temperatures.

Applications Polyurethanes are used to make foams used in cushions for automobiles and furniture, they are also used for coatings, as adhesives and as elastomers. Polyurethane fibres are used for making swimsuits. They also find use in the manufacture of shoe soles, solid tyres and impellers.

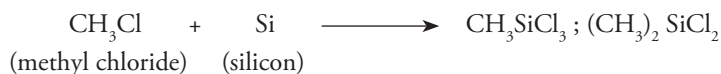
Silicone resins They are inorganic polymers containing alternate silicon–oxygen structure. Organic radicals are attached to the silicon atoms.



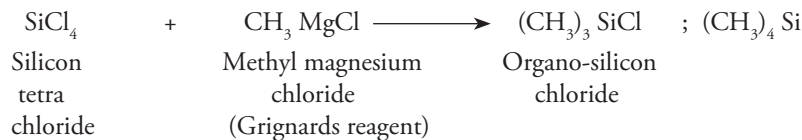
where R = alkyl or phenyl radical.

Preparation

(i) By the reactions of alkyl halide with silicon.

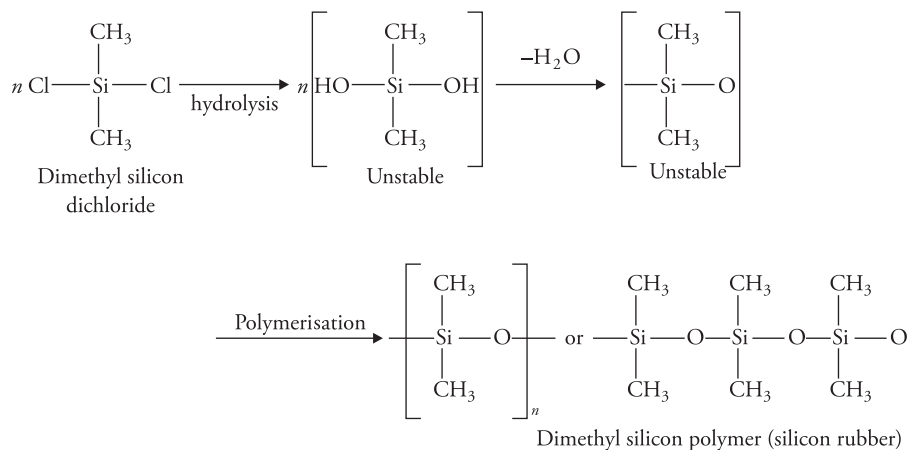


(ii) Reaction of silicon halide with Grignard's reagent

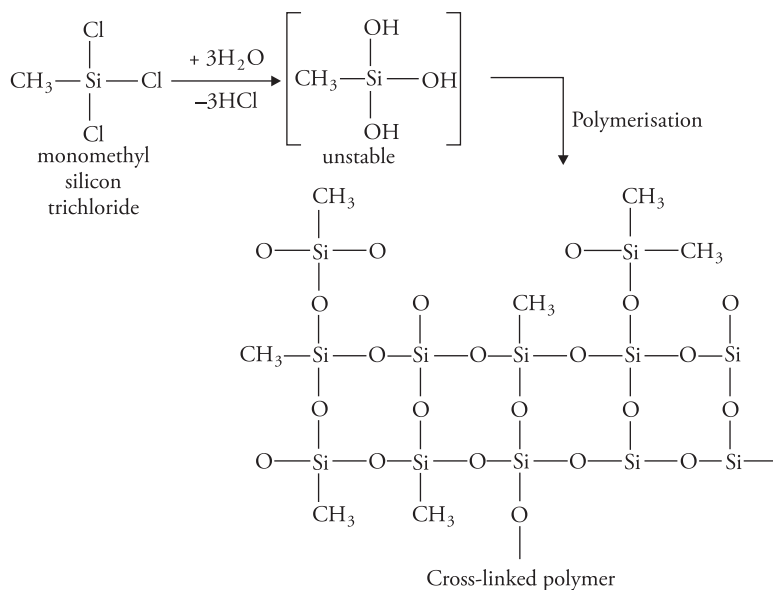


Mixture of organosilicon chlorides is obtained, which is separated by fractional distillation and polymerised by controlled hydrolysis.

1. Dimethyl-silicon dichloride yields long-chain polymer as it is 'bifunctional'.



2. Monomethylsilicontrichloride yields a cross-linked polymer as it is trifunctional.



Properties Silicones are water repellent and chemically inert. They are resistant to oxidation, thermal decomposition and attack by organic reagents. They are also good electrical insulators and antifoaming agents.

Uses Their viscosities do not change with temperature; hence, they are used for making all weather lubricants. They are used for coating papers, textiles and wools to make them water-proof. They are used as antifoaming agents in industries. Silicones are also added to paint for resisting dampness and for water-proofing. Owing to their water-repellant nature and high dielectric constant, they also find use in electrical condensers.

6.9 Rubbers (Elastomers)

The American Society for Testing and Materials (ASTM) defines an elastomer as ‘a polymeric material that at room temperature can be stretched to at least twice its original length and upon release of stress it will return immediately its original length.’

As rubbers can be stretched to 4–10 times of their original length and return to their original length as soon as the stretching force is removed, they are also termed as elastomers. The terms ‘rubber’ and ‘elastomers’ are used interchangeably and refer to polymers that exhibit resilience, or the ability to stretch and retract rapidly.

The elastic deformation in an elastomer arises from the fact that under unstressed condition an elastomer molecule is not straight-chained but is in the form of a coil. Hence, unstretched rubber is amorphous (the polymeric chain is randomly entangled). As soon as it is stretched, the polymer chain tends to straighten and becomes aligned. This increases its crystallinity and decreases the entropy (as it becomes ordered). Hence, as soon as the stretching force is removed, it again reverts back to its original coiled state so that the material becomes amorphous, its randomness or entropy increases and it acquires a stable state.

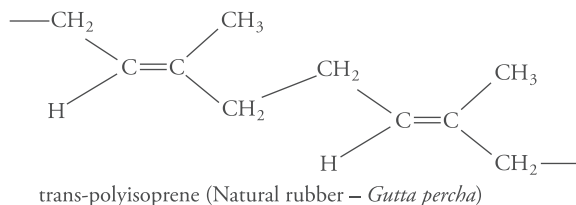
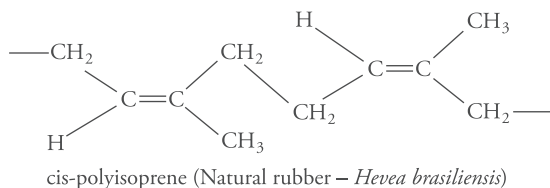
Natural rubber

The term *rubber* was coined by Joseph Priestley when he noted that it could be used to *rub* pencil marks. It is obtained from the bark of a tree (*Hevea brasiliensis*) that grows wildy in South America. Natural rubber consists of 97% cis-1, 4 polyisoprene. To obtain rubber from the Hevea tree, incisions are made in the bark of the rubber tree. The milky latex that flows out is collected in small vessels and then sent to the factories for treatment. The latex is an aqueous suspension of about 32–35% rubber and about 5% other compounds including fatty acids, sugars, proteins, sterols, esters and salts. It is coagulated with acetic acid or formic acid and filtered. It is then bleached with sodium bisulphite (NaHSO_3), washed and dried. The rubber is converted into a soft gummy mass, which is then passed through a creping machine with (having two rollers about 3 mm apart and 50 cm wide) longitudinal grooves. A sheet having rough surface is obtained. It is dried in air at 50 °C. This is called crepe rubber.

To obtain **smoked rubber**, thicker sheets are obtained by passing first through a series of smooth rollers and then finally through a roller to give it a ribbed pattern. The sheets are then hung in smoke houses and dried at 40–50 °C by burning wood or coconut shells.

Rubber can also be obtained from the mature leaves of *Gutta percha*. It is recovered by solvent extraction. It can also be obtained by grinding the mature leaves and treating them with water at

70 °C for half an hour and then pouring them into cold water. The rubber floats on the water surface and is removed. Chemically, it is trans-1, 4-polyisoprene.

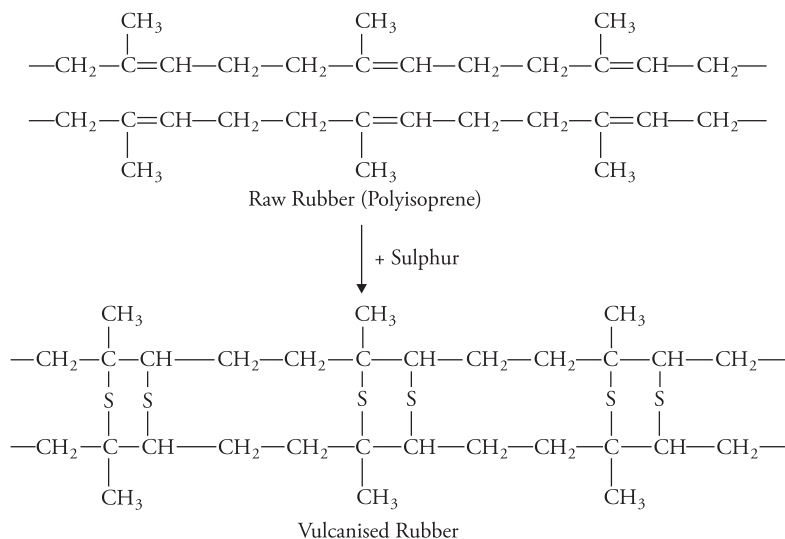


Properties of natural rubber

1. Natural rubber is a tough elastic material that softens on heating.
2. It hardens at 5 °C.
3. It becomes tacky at 30 °C (i.e., when two pieces of rubbers are pressed together, they coalesce to form a single piece).
4. It oxidises to a sticky mass on exposure to sunlight.
5. It is soluble in organic solvents.
6. It has large water absorption capacity.
7. It is plastic in nature and undergoes permanent deformation when stretched chains slip past each other and then get separated resulting in the breakage of the rubber.
8. It is weak and has low tensile strength (200 kg/cm²).
9. It is non-resistant to vegetable oils, minerals oils, gasoline, benzene and carbon tetrachloride.

Vulcanisation

It was developed by Charles Goodyear in the year 1839. When natural rubber is heated with sulphur or other suitable reagents, a non-reversible chemical reaction occurs. Cross-linkages are formed between the adjacent polymeric chains and natural rubber (a thermoplastic) changes into a cross-linked polymer (a thermoset). The following reaction occurs:



Advantages of vulcanisation

Vulcanisation transforms a weak elastomer into a strong, elastic and tough rubber. It improves the tensile strength, stiffness, durability, elasticity, chemical resistance, resistance to changes in temperature and tackiness remarkably. Its water absorption capacity reduces greatly. Vulcanised rubber has better insulation properties than raw rubber. Ebonite (32% sulphur) has extremely good insulating properties. Resilience (tendency of an elastomer to return to its original shape on the release of stress) of vulcanised rubber improves manifolds as compared with raw rubber.

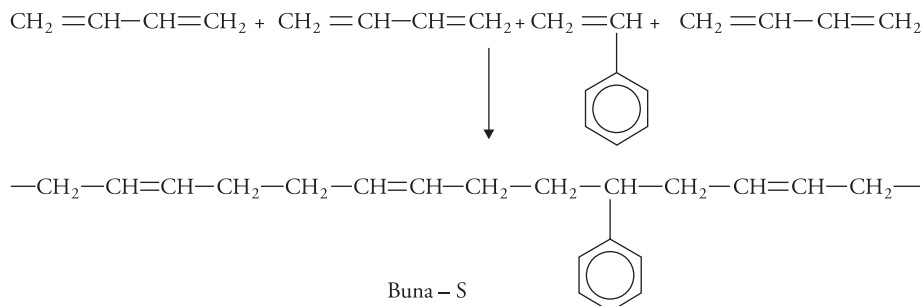
Table 6.2 Comparison of raw rubber and vulcanised rubber

Property	Non-vulcanised rubber	Vulcanised rubber
Tensile strength	70	700
Elongation at break %	1200	800
Permanent set	Large	Small
Rapidity of retraction (snap)	Good	Very good
Water absorption	Large	Small
Swelling in hydrocarbon solvents	Infinite (soluble)	Large, but limited
Tackiness	Marked	Slight
Useful temperature range	10 to 60 °C	−40 to + 100 °C
Chemical resistance	Poor	Much better

Synthetic rubbers**(i) Styrene butadiene rubber (SBR or Buna-S or GR-S)**

It is a random copolymer of butadiene and 10–25% styrene.

They are prepared by the copolymerisation of butadiene (75%) and styrene (25%) in an emulsion system at 50 °C in the presence of cumene hydroperoxide as a catalyst.



Vulcanisation of Buna-S is carried out by using either sulphur or sulphur monochloride (S_2Cl_2).

Properties

They are similar in many ways to natural rubbers and were the first widely used synthetics.

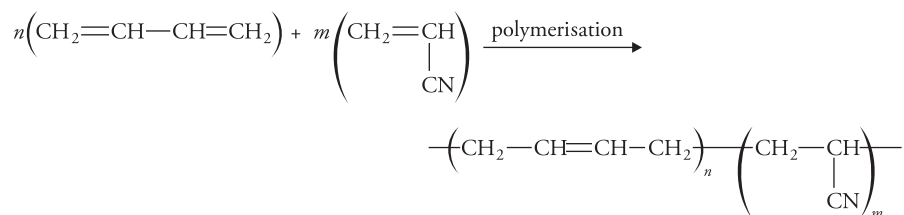
Like natural rubber, they are non-oil-resistant and are generally poor in chemical resistance. However, they have excellent impact and abrasion resistance. Carbon black is generally added as a filler to improve its abrasion resistance. They are oxidised easily and are below natural rubber in tensile strength and resilience.

Uses

Their single largest use is in the manufacture of motor tyres. They also find uses in the manufacture of footwear components, carpet backing, gaskets, adhesives, tank lining and insulation of wires and cable components.

Nitrile rubber (NBR or Buna-N or GR-A)

They are copolymers of butadiene and acrylonitrile.



Compounding and vulcanisation are similar to natural rubber.

Properties

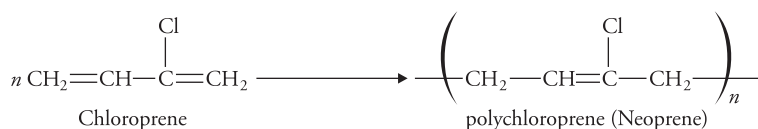
Nitrile rubbers are known for their outstanding resistance to oil and fuels both at normal and elevated temperatures. Nitrile rubbers are low in most mechanical properties. Their tensile strength is low and resilience is roughly one-third to half that of natural rubber. Their properties can be altered by varying the ratio of the two monomers. In general, as the acrylonitrile content increases oil resistance, tensile strength and processability improve, whereas resilience, low-temperature flexibility deteriorates. Elastomers with low acrylonitrile contents are used where good flexibility at low temperatures is required.

Uses

Nitrile rubber finds its use in the manufacture of flexible couplings, rubber rollers, printing blankets, washing machine parts, oil-resistant foams, hoses, adhesives, gaskets, lining of tanks, automobile parts and high-altitude aircraft components.

3. Neoprene (GR-M or polychloroprene) or polychlorobutadiene or duprene

It was developed in 1930s and has the distinction of being the first commercial synthetic rubber. It is prepared by the polymerisation of chloroprene, a chlorinated butadiene.



Properties

It is chemically and structurally similar to natural rubber. Its mechanical properties are also similar to natural rubber. Its resistance to oils, chemicals, sunlight, weathering, ageing and oxidation due to ozone are outstanding. It has excellent resistance to permeability by gases.

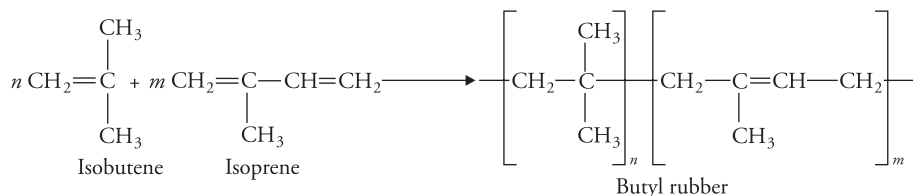
Its permeability is one-fourth to one-tenth the permeability of natural rubber depending on the gas. Being a polar polymer, its solubility in polar solvents is also higher. Although it is slightly inferior to natural rubber in most mechanical properties, neoprene has superior resistance to compression set, particularly at elevated temperatures. It retains its properties at temperatures upto 120 °C and is one of those few elastomers that does not support combustion, although it is consumed by fire.

Uses

It is used for making heavy duty conveyer belts, hose covers, footwears, brake diaphragms, motor mounts, tubing for carrying corrosive gases and oils, linings of reaction vessels and adhesives. Because of its low dielectric strength, it can be used for low-voltage insulation.

Butyl rubber (GR- I or Polyisobutylene-isoprene)

It is prepared by the aluminium chloride-initiated cationic copolymerisation of isobutylene and about 1–3% isoprene.



Properties

It is similar in many ways to natural rubber and is one of the lowest-priced synthetics. It possesses low gas and air permeability (about 10 times better than natural rubber).

Although they are non-resistant to oils, they have excellent resistance to sunlight, weathering, abrasion, tearing and generally have good chemical resistance. Because of its hydrocarbon nature, it is soluble in hydrocarbon solvents like benzene but is resistant to polar solvents like alcohol, acetone and ageing chemicals like HCl, HF, HNO₃, H₂SO₄, etc.

They also have good low-temperature flexibility (remains flexible upto -50 °C) and high heat resistance; however, they are not flame-resistant. They generally have lower mechanical properties such as tensile strength, resilience and compression set than the other elastomers. They can be vulcanised; however, due to low unsaturation they are not hardened much.

Uses

Because of its low permeability to gases it is used for making inner tubes of tyres, hoses, tubing and diaphragms. Because of their excellent dielectric strength, they are widely used for cable insulation and have a variety of electrical applications. They also find use in curtain wall gaskets, high-pressure steam hoses, machinery mounts, seals for food jars and medicine bottles, coated fabrics, etc.

Polysulfide rubber (Thiokol)

It is made by the reaction between sodium polysulphide (Na₂S_x) and ethylene dichloride:



Properties

Thiokol, a speciality polymer, is rated highest in having resistance to oil and gasoline. It also has excellent solvent resistance, extremely low gas permeability and is practically unaffected by ozone. Aging is very slow in this polymer. However, thiokol has poor mechanical properties like strength, compression set and resilience. It cannot be vulcanised and hence does not form hard rubber. Thiokol also has poor flame resistance and can be used only upto temperatures of 250 °F.

Uses

It is used in the manufacture of oil and gasoline hoses, gaskets, washers and diaphragms. It is widely used in liquid form in sealants for aircraft and marine industries. Moreover, in general, polysulphides form excellent fuel materials and become solid propellants for rockets when they are mixed with inorganic oxidizers such as ammonium perchlorate.

6.10 Fibres

Fibres are semicrystalline polymers that can be spun into long strands having length at least 100 times greater than their width or diameter. They have high strength-to-weight ratios and are used for textile as well as composite applications.

Classification

On the basis of their source, fibres can be (i) natural and (ii) synthetic.

Natural fibre It is a fibre made from a material originated from natural sources. Fibres can be derived from plants. For example, natural fibres can be cellulosic fibres (origin from plants like cotton, jute), protein fibres (origin from animals like wool, silk) or mineral fibres (from different rocks like asbestos fibre). Animal fibres are generally composed of keratin (fibrous protein found in skin, nails and hair), except silk filament, which is made up of fibroin.

Synthetic fibre The term synthetic fibre refers to materials that are developed by humans by using chemical and mechanical processes. Thus, synthetic fibres are commonly known as man-made fibres. Two types of synthetic fibres are commonly used in the textile industry: cellulosic and non-cellulosic.

Cellulosic fibres They are also known as regenerated fibres. They are derived from naturally occurring cellulosic sources such as wood pulp or cotton linters. The composition of these cellulosic fibres is altered by chemical reaction and polymerisation techniques to regenerate into a new form of fibre. For example, viscose rayon and cellulose acetate are regenerated from naturally occurring cellulose.

Non-cellulosics These are made totally by the man-made processes, by using chemical substances as the sources. Examples of these types are polyester, nylon, polyolefin and acrylics.

Fibres can also be classified from consumer's point of view into three types: (i) comfort fibres, (ii) safety fibres and (iii) industrial fibres.

Comfort fibres They are fibres that are used for making undergarments and garments, fibres used for making socks, underwears, ladies garments, shirting, suitings come in this category. These fibres should be soft and extensible and have adequate strength, flame retardancy and should be capable of being dyed. Examples of comfort fibres are cotton, silk, nylon, polyesters, acrylics, etc.

Safety fibres These fibres are used for making carpets, curtains, seat covers, etc. They should be tough, strong, durable and abrasion-resistant. These fibres should not burn easily, and should have minimum flame spread. If they catch fire they should liberate minimum heat, smoke and toxic gases. Examples are aromatic polyamides, polyimides, polybenzimidazoles and polyoxy diazoles are useful as safety fibres.

Industrial fibres These fibres have very high modulus, strength, thermal stability, toughness and durability. They are also called structural fibres and are used as reinforcing materials in composite structures. They are used to reinforce articles such as rigid and flexible tubes, pipes and tyres. Fibre-reinforced composites having high strength and stiffness on a weight basis are used in the construction of cars, planes, boats and even buildings. Uniaxially oriented fibres like aromatic polyamides, polyesters, carbon fibres and silica fibres belong to this category.

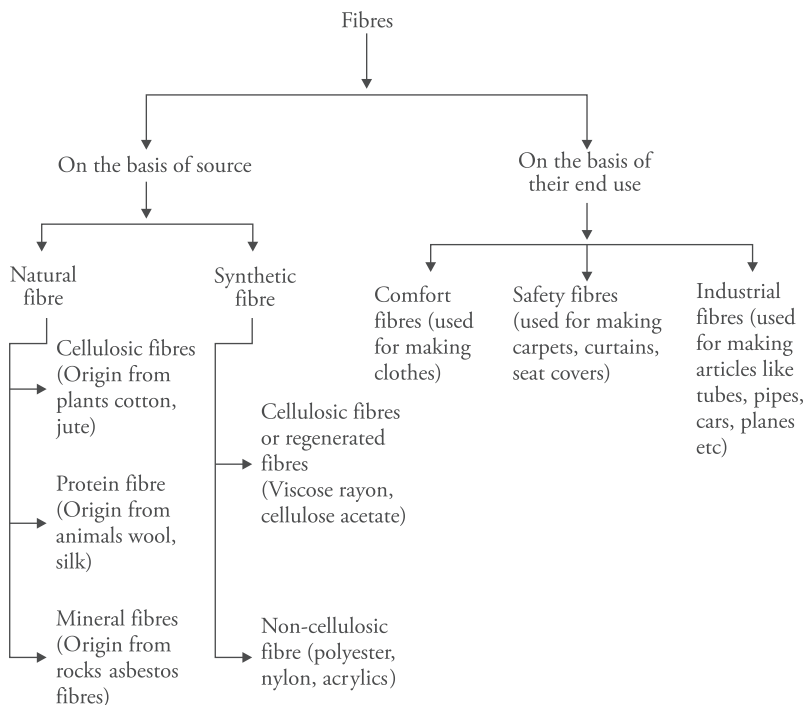


Figure 6.8 Classification of fibres

Fibre-spinning operations

The process of making fibres from polymers is called ‘spinning’. There are three principal spinning methods in use: (i) melt spinning, (ii) dry spinning and (iii) wet spinning.

Melt spinning includes spinning of a polymer in molten state. Polyamide, polyester and polyolefin fibres are generally obtained by the melt spinning process. In dry and wet spinning, the polymer is used as a solution in appropriate solvent. Solution spinning is used for cellulosic and acrylic fibres.

Melt Spinning

It was developed in the late 1930s. In this process the polymer is converted into a viscous mobile liquid by heating the polymer chips electrically and melting them in a heating grid. The molten polymer is surrounded by an inert atmosphere of N_2 , CO_2 or steam to prevent it from oxidative degradation due to environmental oxygen. The polymer is filtered using a filter pack (to remove lumps formed due to cross-linking or thermal degradation of the polymer during heating) and then it enters a metering pump, which pumps the polymer through a die having fine holes. This die is called the spinneret. Filaments emerging from the spinneret are cooled in a cold-air blast.

Cooled fibre is wound onto a spindle for subsequent treatment such as texturing and dyeing before being woven into fabric. The polymers that are generally melt-spun are polyolefins (for example, PE and polypropylene), polyamides (e.g., nylon 6 and nylon 6, 6) and polyesters.

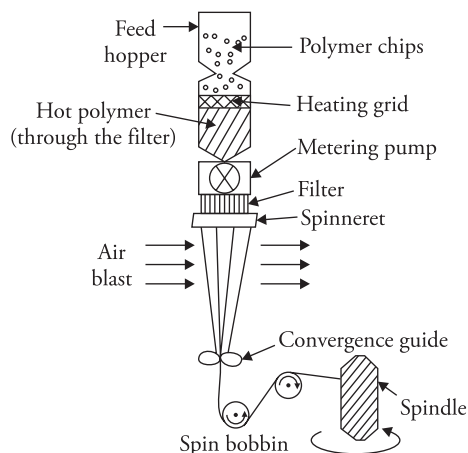


Figure 6.9 Schematic diagram of melt spinning

Dry Spinning

In this process, the polymer is dissolved in appropriate solvent in the range of 20–40%. The solution is filtered and pumped through a spinneret into a spinning cabinet (upto 25 feet in length). Dry nitrogen or heated air is passed from the lower end of the cabinet to enhance solvent evaporation. The dried fibre is then wound onto the spindle (bobbin). The fibres can be spun at a rate as high as 1000 m min^{-1} . Typical example of dry spinning is the manufacture of cellulose acetate fibres from a 35% solution of the polymer in acetone at 40°C . Other polymers that are converted into fibres using the above process are polyacrylonitrile and PVC.

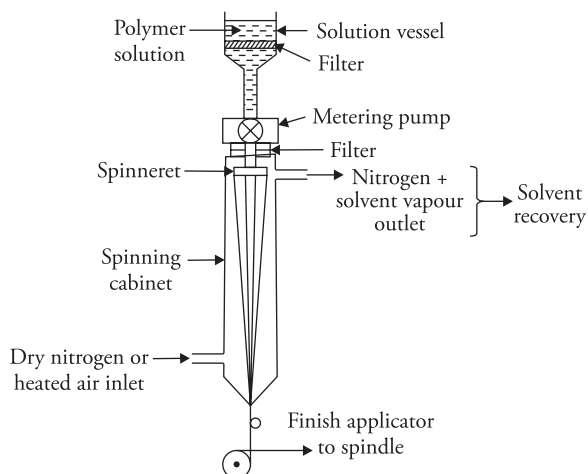


Figure 6.10 Schematic diagram of dry spinning

Wet spinning

It is one of the oldest fibre production methods. Wet spinning like dry spinning employs a fairly concentrated polymer solution. It differs from dry spinning in that the fibre is formed by the coagulation of the polymer solution by immersion in a non-solvent such as water. As shown in Figure 6.11, the spinneret is immersed into the non-solvent bath. The continuous jets of polymer coming out of the spinneret come in contact with a non-solvent and precipitate in the form of fine filaments. The filaments formed are washed, dried and gathered on a spindle.

The wet spinning process has been used to obtain fibres of polyvinylacetate (PVA), polyvinyl chloride (PVC), polyacrylonitrile (PAN), cellulose, viscose rayon, etc. PAN fibres can be wet-spun from dimethylformamide (DMF) solution into dimethylacetamide (DMAC) or from 50% sodium thiocyanate into aqueous 10% sodium thiocyanate. Similarly, polyurethane fibres such as spandex can be wet-spun from DMF solution into water.

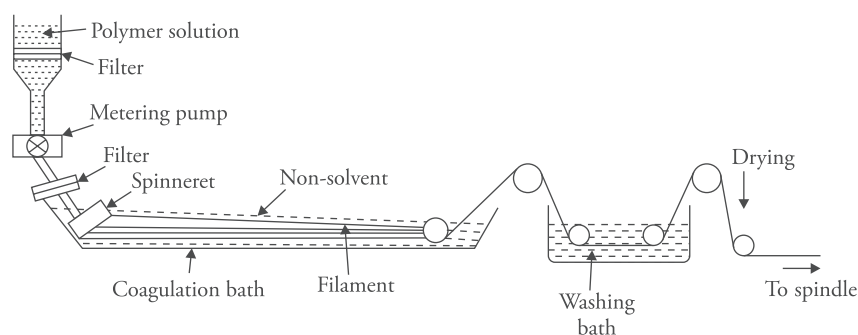


Figure 6.11 Schematic diagram of wet spinning process

Preparation, properties and uses of some important fibres

Cellulose acetate

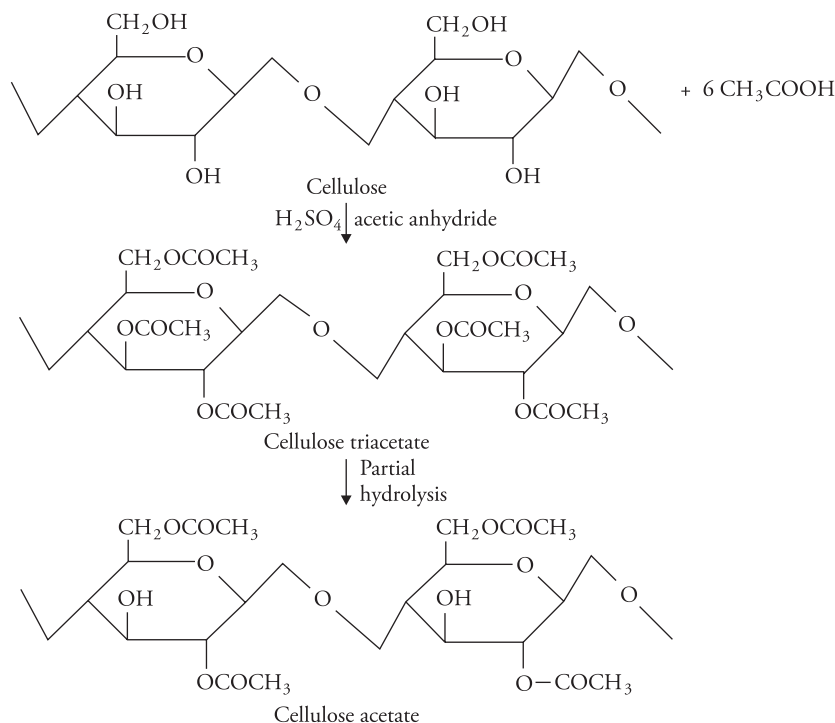
Preparation It was first prepared by Paul Schutzenberger of Germany in 1865. It is obtained by reacting cellulose obtained from processed wood pulp with acetic acid in the presence of acetic anhydride and traces of sulphuric acid in refluxing methylene chloride.

Cellulose triacetate is obtained. Commercial cellulose acetate is obtained by the partial hydrolysis of cellulose triacetate where the secondary acetate groups are hydrolysed.

Properties

Cellulose acetate is a white, amorphous product available commercially as powder or flakes. It is non-toxic, odorless, tasteless and a biodegradable polymer. It is lustrous, glossy, smooth, satiny with a silky finish, has high transparency, has good toughness and is skin-friendly. Its solubility, mechanical properties and compatibility with softeners, resins, varnish, etc depend on the degree

of esterification. It is hydrolysed by strong acids and alkalis, but resists the action of weak acids, animal and vegetable oils, gasoline, etc. It is sensitive to strong oxidising agents but is not affected by mild oxidising agents, peroxide solutions. The viscosity of the polymer depends upon the degree of polymerisation. Acetate fibres are stable against sunlight, relatively flame-resistant, have high melting point and have low conductivity, and hence serve as good insulating material.



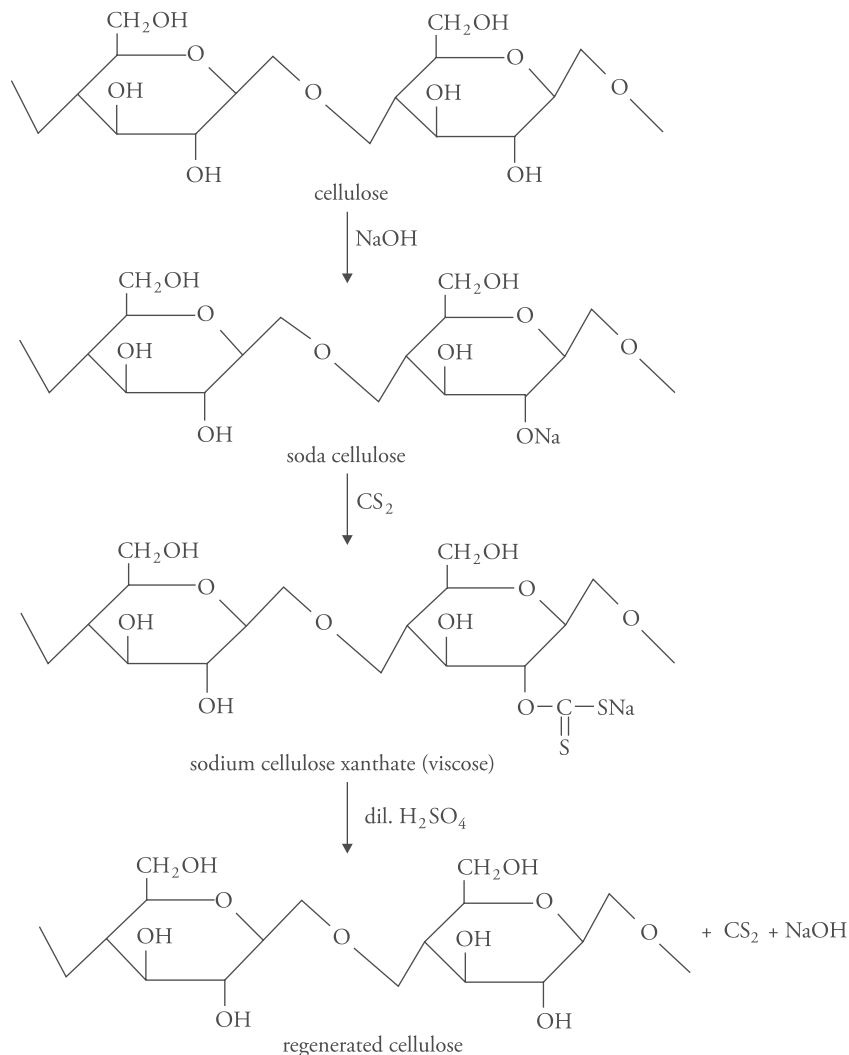
Uses

Cellulose acetate is used for making textile yarn. It cannot be dyed like viscose rayon. Acetate fibres are dyed with water-disperse dyes at the boiling point of the medium in the presence of carriers. The carriers enhance the dye uptake by the fibres.

Cellulose acetate also finds use in filter media including cigarette filters called 'tow'. Owing to their unique hydrophobic and hydrophilic properties, semipermeable membranes made out of these fibres are used in hemodialysis and desalination by reverse osmosis.

Blending these fibres with nylon or polyester makes them suitable for different end uses in linings, films, packing toys, playing cards, optical applications, frames of spectacles, eyeglasses, sporting goods, personal care products, etc. Being a biodegradable polymer, it also finds used in medical field. It is used for wound dressings and in the preparation of sustained release system for pills.

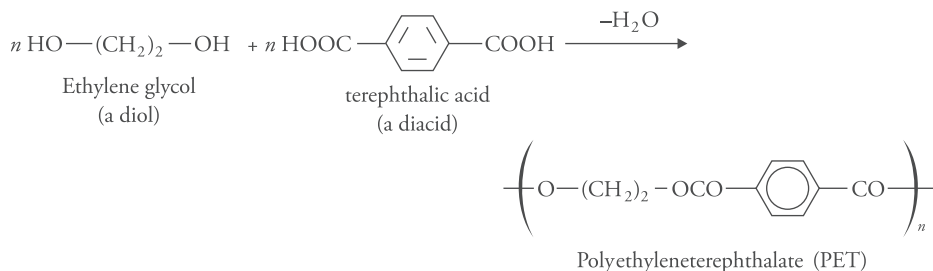
Viscose Rayon Viscose rayon is a fibre made from regenerated wood cellulose. Viscose rayon is prepared by treating either the pure cellulose or wood cellulose with 15–20% sodium hydroxide solution by which the cellulose is converted into soda or alkali cellulose. The alkali cellulose is then treated with carbon disulphide to form the alkali-soluble cellulose xanthate, which is allowed to stand for sometime. A viscous yellow liquid called *viscose* is formed, which is forced through the spinneret opening into dilute acid bath that regenerates the cellulose filament.



Polyesters

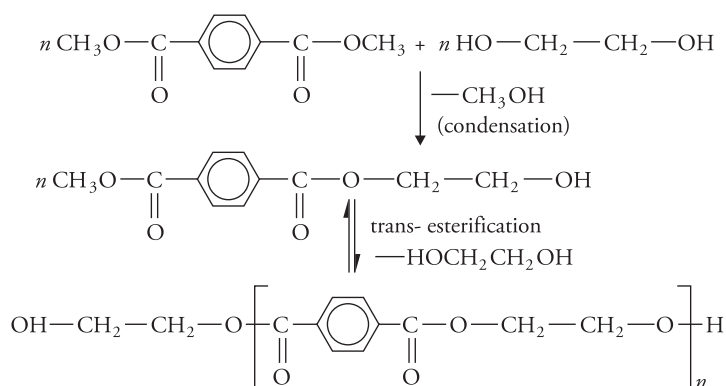
They are formed by the condensation of dicarboxylic acid with dihydroxyalcohol.

Polyethylene terephthalate (PET) a polyester is prepared by the condensation of terephthalic acid and ethylene glycol.



PET is commercially the most important polyester and is marketed under the trade name of *Terylene* or *Terene* or *Dacron*.

In commercial practice, dimethyl terephthalate (DMT) is used instead of terephthalic acid.



The first step (condensation) occurs at reflux temperature of ethylene glycol with a low vacuum. Methanol is recovered. The second step (trans-esterification) occurs at a high temperature of 200–250 °C under very high vacuum so that ethylene glycol is removed and the reaction proceeds in the forward direction.

Properties

PET (Terylene) is a very good fibre forming polymer. It is resistant to heat and moisture and melts at around 265 °C. It is inert to the attack of mineral and organic acids but is readily attacked by alkalis. PET fibres are oxidation-resistant, abrasion-resistant, have good mechanical strength upto 175 °C. They can also be dyed easily in the presence of a carrier.

Further, they are resistant to attacks by insects or moths.

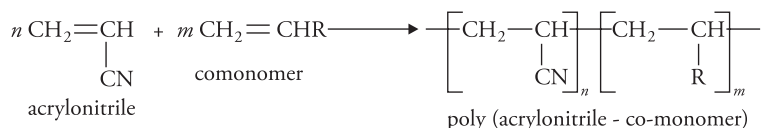
Uses

PET is used for making synthetic fibres like terylene, dacron. The garments made of these fibres are wrinkle resistant, have low moisture absorption and are not attacked by insects and moths. These fibres can be blended with wool and cotton to improve their properties. PET is also useful for making films that are used in the manufacture of magnetic recording tapes, transparencies for overhead projectors, etc.

They are used for electrical insulation due to their high dielectric strength. Glass-reinforced PET is used for the manufacture of toasters, car heaters, etc.

Acrylics

Acrylic fibre (or polyacrylonitrile fibre) is defined as a polymeric material that contains at least 85% by weight of acrylonitrile monomer. The comonomers are vinyl acetate and methyl acrylate. If the polymer contains large amounts of comonomers (from 15% to 50%) and at least 35 weight percent acrylonitrile monomer, then the polymer is considered as modified acrylic fibre and is referred to as modacrylic fibres.



Properties

Acrylic fibres have excellent chemical, biological, sunlight and weather resistance. They have high electrical resistance and good tenacity. They are resistant to moths, oils, chemicals but are attacked by strong bases. Acrylic fibres decompose before melting and hence cannot be made by melt spinning. Acrylic fibres are easy to wash and have good dimensional stability. They can be dyed in bright colors and the colors are very fast. They are lightweight, soft, warm and wool-like to touch.

Applications

Acrylic fibres are used for making apparels, sweaters, socks and tracksuits, sportswear, children's wear and as lining for boots and gloves. However, acrylics can cause irritation to people suffering from 'eczema'. They are used in furnishing fabrics, carpets, blankets, rugs upholstery, car tops, boat covers and outdoor furniture. Acrylics also find use in industries for making reinforcement materials in construction. Other industrial end uses include car batteries, filtration materials, etc.

Apart from acrylic fibres other acrylics in use are as follows:

Acrylic glass It is chemically polymethyl methacrylate PMMA or plexiglass.

Acrylic paints These are fast drying paints containing the pigment suspended in an acrylic polymer suspension. It is commonly used in modern fine arts. Acrylate polymers or resins are used to make hard plastics with various light-emitting properties.

6.11 Speciality Polymers

Engineering thermoplastics-Polycarbonate

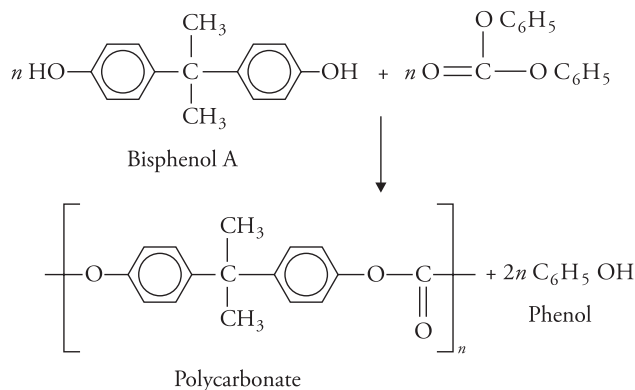
Polycarbonates are polyesters of phenols and carbonic acid. They can be prepared by the condensation of diphenoxymethylene derivatives with diphenyl carbonate.

2,2-bis(4-hydroxyphenyl) propane (bisphenol-A) on reaction with diphenyl carbonate gives polycarbonate.

Properties

Polycarbonate, a high-performance engineering thermoplastic, is a tough, strong, generally transparent, amorphous solid with outstanding impact resistance. It maintains its shape and size

even under great stress over a wide range of temperature. It is resistant to water, acids, detergents, oils and greases, but is attacked by bases, halogenated solvents (chloroform, carbon tetrachloride), ketones (acetones, acetonitrile), organic solvents like benzene, benzylalcohol, dimethyl ether, carbondisulphide, etc. It has excellent resistance to high temperatures upto 140 °C and maintains toughness at low temperatures upto -20 °C. It has good electrical insulation properties.



Uses

Owing to its electrical properties and dimensional stability, it is used for mouldings for computers, calculating machines, for making hair driers, electric razors, CDs and DVDs. Owing to its excellent impact resistance, it is used in automobile industry for making motorcycle windshields, police shields, headlight covers, car bumpers, front panels, safety helmets, etc.

As it is not stained by oils, greases and domestic beverages, it is used for making blenders, food processing bowls, coffee maker, food mixer housings.

Owing to its temperature resistance, stability and chemical inertness, it finds use in the manufacture of baby bottles, syringes.

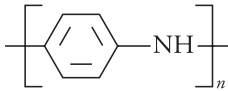

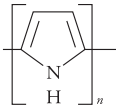

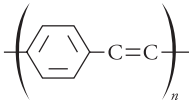
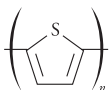
It is also used for making water dispensers, furniture (office and institutional), vacuum cleaner bases, cord hooks, impellers, spectacles, cameras and also for the manufacture of other unbreakable items.

Conducting Polymers

The use of polymers is increasing rapidly in our day to day life. Because of their light weight, corrosion resistance, easily workability, easy maintenance they are replacing metals in all walks of life. However, the drawback with polymers is that they do not conduct electricity. Research went on in this area and in 1977, three scientists Professor Alan-J. Heeger, Professor Alan. G Macdiarmid and Professor Hideki Shirakawa discovered that oxidation of polyacetylene with iodine results in 10^8 fold increase in its conductivity, that is, the conductivity of the doped polymer approaches the conductivity of one of the best conductors. The conductivity of doped 'polyacetylene' was found to be as high as 10^3 S cm^{-1} . This is comparable to the conductivity of copper on an equal weight basis. The three scientists received the Nobel prize in chemistry in the year 2000 for their discovery and the development of electrically conducting polymers.

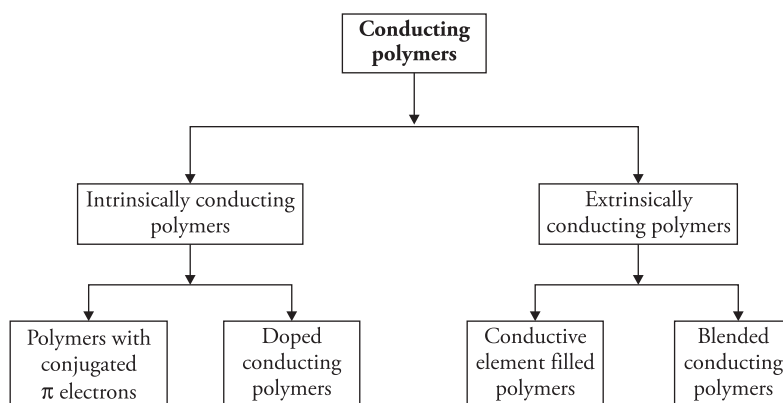
After the above discovery, research continued in this field and a large number of electrically conducting polymers were discovered gradually. Some common conducting polymers are as follows.

Table 6.3 Common conducting polymers and their conductivity

Conducting polymer	Repeating unit	Dopant	Conductivity (S cm ⁻¹)
Polyaniline		HCl	200
Trans polyacetylene		I ₂ , Br ₂ , Li, Na, AsF ₅	10 ⁴
Polypyrrole		BF ₄ ⁻ , ClO ₄ ⁻ , tosylate	500–7500
Poly(p-phenylene)		AsF ₅ , Li, K	10 ³
Poly(p-phenylene vinylene)		AsF ₅	10 ⁴
Polythiophene		BF ₄ ⁻ , ClO ₄ ⁻ , tosylate, FeCl ₄ ⁻	10 ³

Classification of conducting polymers

Polymers that conduct electricity are called conducting polymers. They can be classified as follows.

**Figure 6.12** Classification of conducting polymers

Intrinsically conducting polymers

The conductance of these polymers is due to the extensive conjugation in their backbone. They are further of two types.