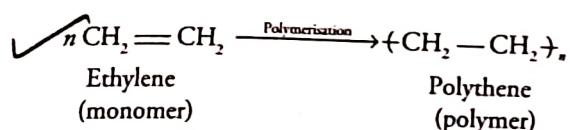


Chapter 6

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

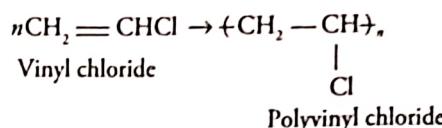
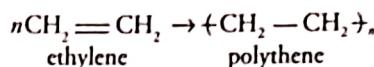
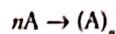
- 1. On the basis of origin** On the basis of origin, polymers are of two types:
(a) Natural polymers (b) Synthetic polymers

- (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.

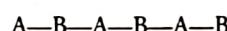


Depending on the arrangement of the monomeric units, the copolymers may be further classified as

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



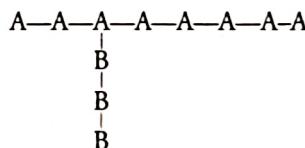
- (ii) **Alternating copolymers** The monomeric units are arranged in an alternating manner.



- (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

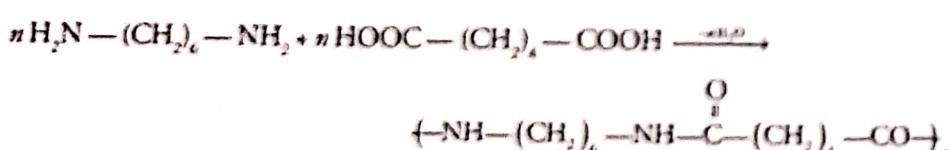
- Linear polymer** It has no branching other than the pendant groups associated with the monomer. Linear polymers are well packed and therefore have high densities. For example, polythene, nylons and polyesters.
- Branched polymers** These are polymers in which the monomers are joined to form long chains 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 polyethylene, glycogen, etc.
- 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

- Homochain polymer** Polymers having all carbon atoms along their backbone are called homochain polymers. For example, polyethylene, PVC, rubber, etc.
- 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

- 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.
 $n \text{ (monomer)} \longrightarrow \text{polymer}$
Molecular weight of polymer = $n \times$ molecular weight of monomer.
For example, polyethylene, PVC, etc.
- 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.

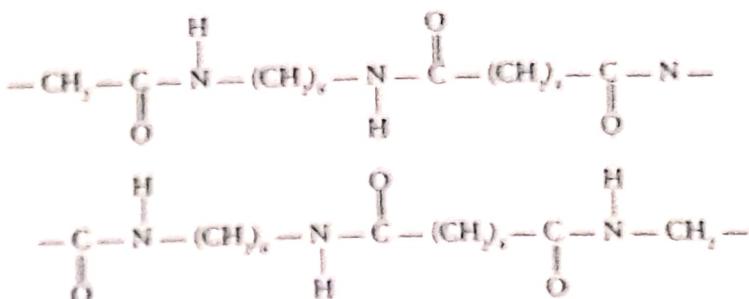


6. Based on molecular forces

- Elastomers** They are polymers held by weakest intermolecular forces and have elastic behavior. For example, natural rubber. These can be stretched to at least three times their original length.

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.

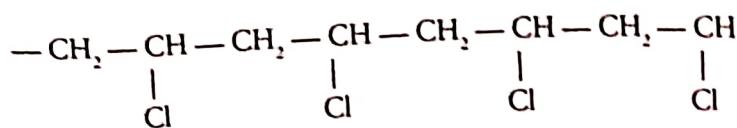
- (iv) **Thermosetting plastics** They are polymers that can change irreversibly into hard and rigid materials on heating and cannot be reshaped once they set. They form hard, infusible, insoluble products because of cross-linkages. For example, bakelite, melamine, etc.

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

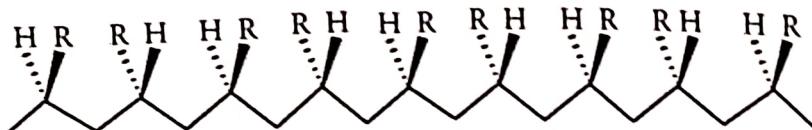
- (i) **Isotactic polymers** When the orientation of side groups (R) on all asymmetric carbon atoms is the same, the polymer is termed as an isotactic polymer



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.

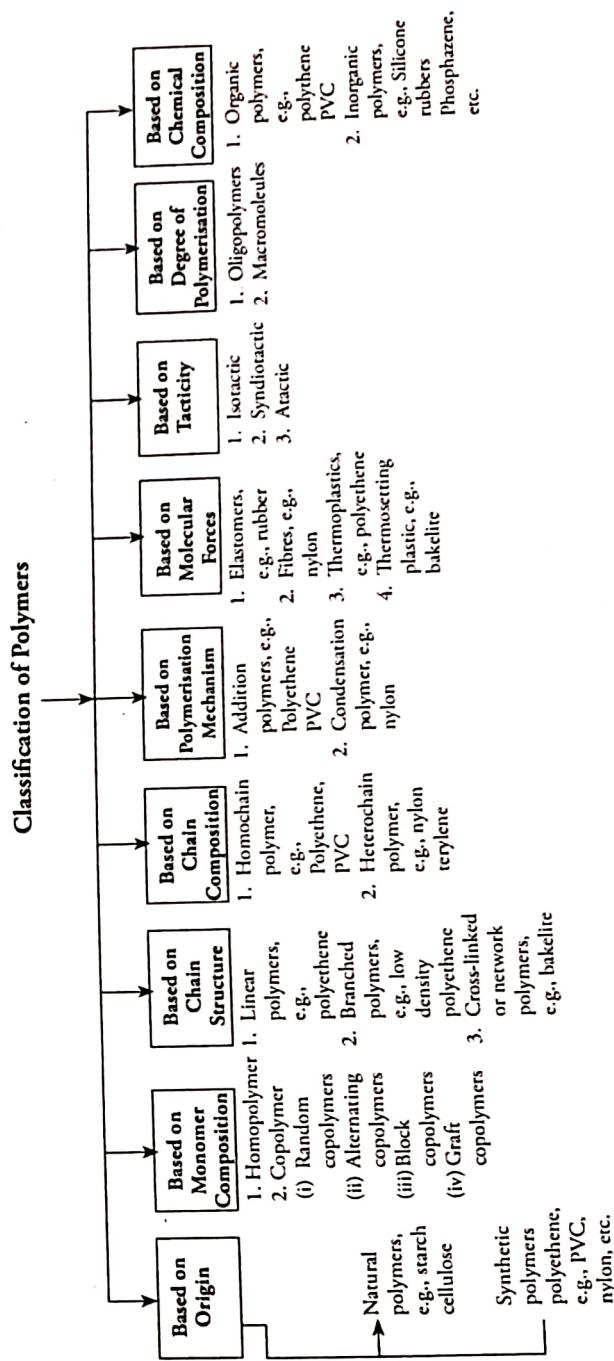
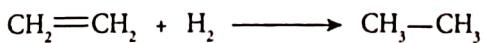


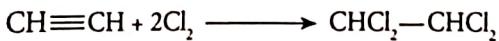
Figure 6.1 Classification of polymers

6.3 Functionality

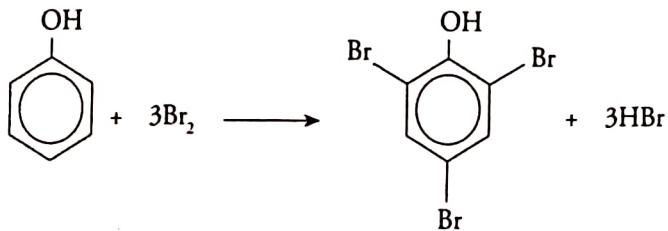
The number of reactive sites in a molecule is termed as its functionality. For a molecule to act as a monomer it must have at least two reactive sites, that is, its functionality should be two. For example, ethylene can add two molecules of hydrogen or halogen. Hence, it is bifunctional (functionality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



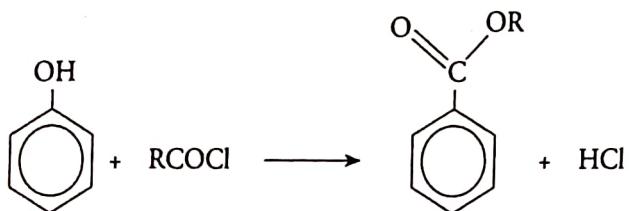
Similarly, acetylene has a functionality of four (tetrafunctional), as it can react with four atoms of hydrogen or halogen.



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

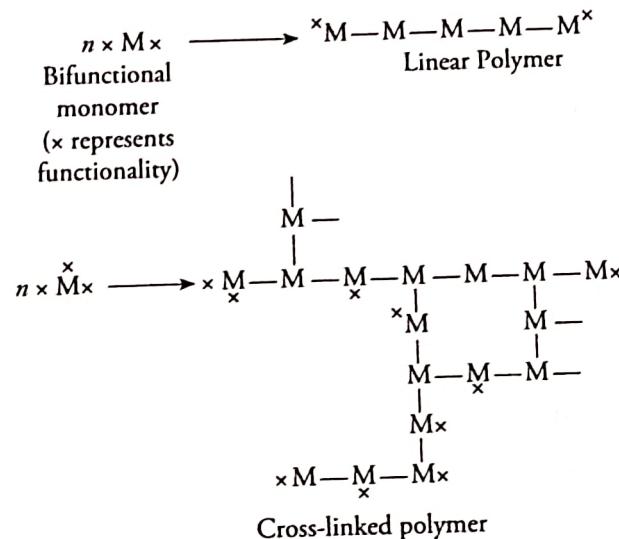


Phenol also exhibits a functionality of one as shown below.



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

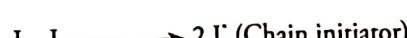
1. **Addition polymerisation or chain polymerisation** In this type of polymerisation, the monomer molecules are added to each other without the formation of any byproduct. The elemental composition of polymer is similar to that of the monomer and its molecular weight is an exact multiple of the molecular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

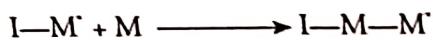
- (i) **Chain initiation** This step involves the formation of active molecules called chain initiators.

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





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.

Free radical mechanism

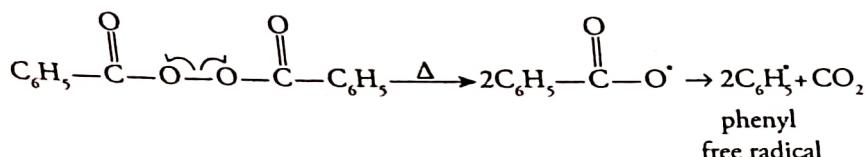
Ionic mechanism (anionic and cationic)

Coordination mechanism

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 ($\text{—N}=\text{N}\text{—}$), disulphides (—S—S—), peroxides (—O—O—), hydroperoxides, peracids and peresters. An important example of a free radical initiator is benzoyl peroxide that dissociates as follows:

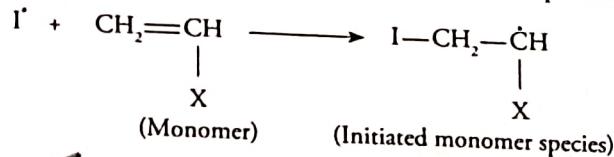


Here, half arrow (\curvearrowleft) represents single electron shift. In $\text{C}_6\text{H}_5^\cdot$, the dot (•) represents single electron.

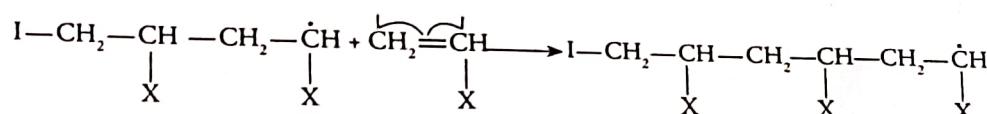
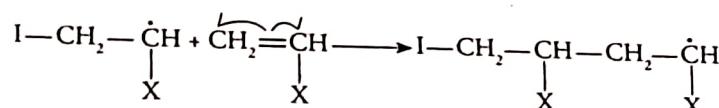
In general, the dissociation of the initiator (I—I) to form free radical species can be represented as



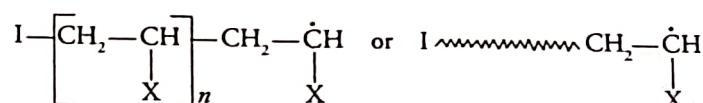
In the second step of initiation, a monomer molecule (M) is attached to the initiator radical. Considering vinyl as the monomer, this step can be represented as



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

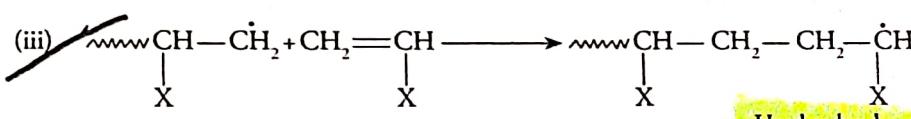
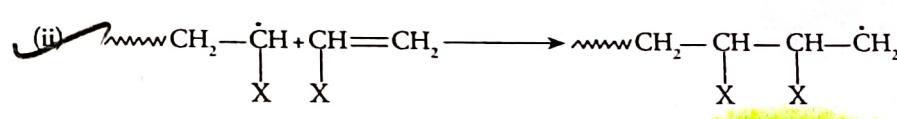
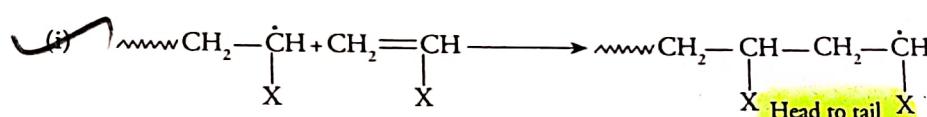


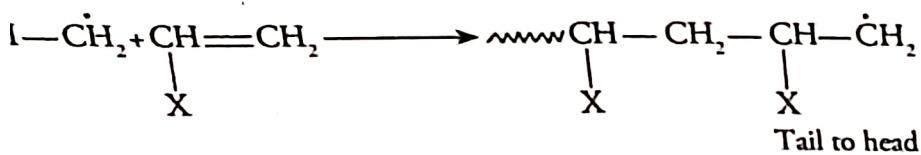
The propagation continues until the chain growth is stopped by some impurities or by termination process or till there is no further monomer left for attack. The structure of the growing chain can be represented as



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.

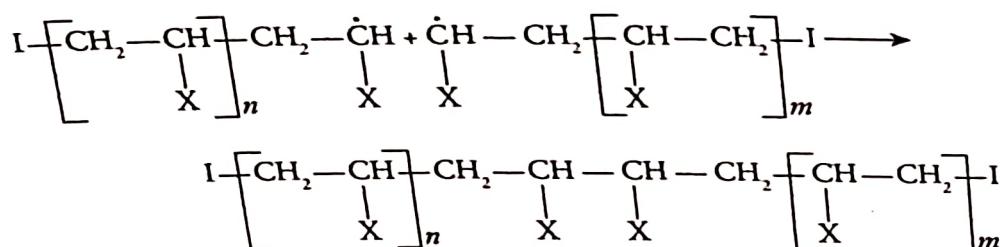
If the CH_2 part of monomeric chain is called head and CH_2X part is termed as tail, then four modes of addition can take place.





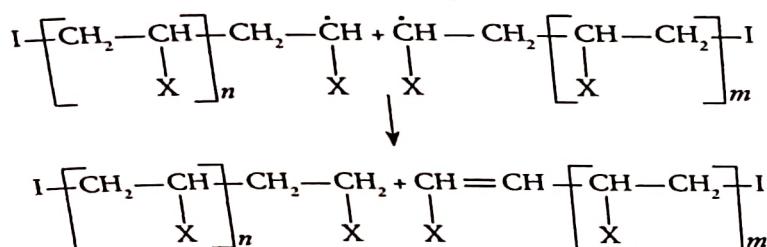
Termination This is the last step of polymerisation process where the growth of chain is arrested. It can occur as follows.

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 activated.



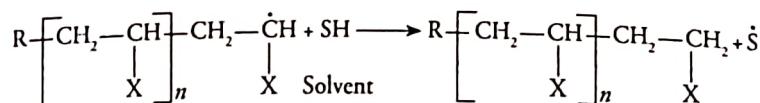
As this process involves the coupling of two lone pairs of electrons, this kind of termination is known as *termination by coupling*.

(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.

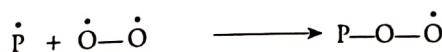
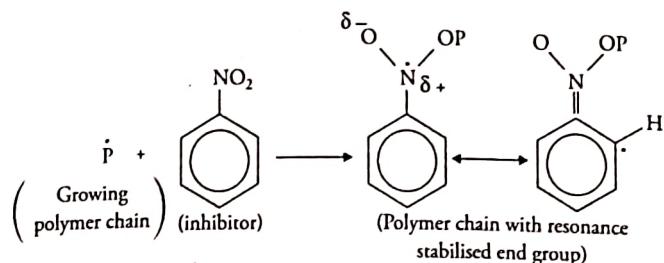


The products formed do not contain any reactive sites and may be termed as 'dead' polymer chain.

(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.



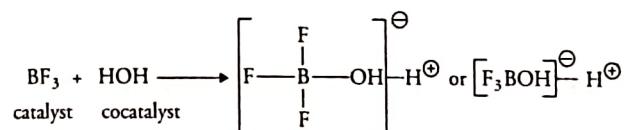
The chain can also be terminated by the addition of certain compounds, which are called inhibitors. Hydroquinone, nitrobenzene and dinitrobenzene are some of the commonly used inhibitors. Atmospheric oxygen is also a good inhibitor.



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.

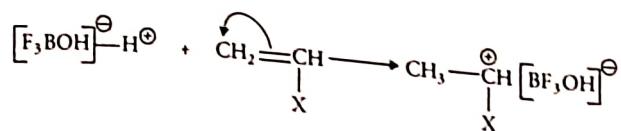
(i) Cationic polymerisation

(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.

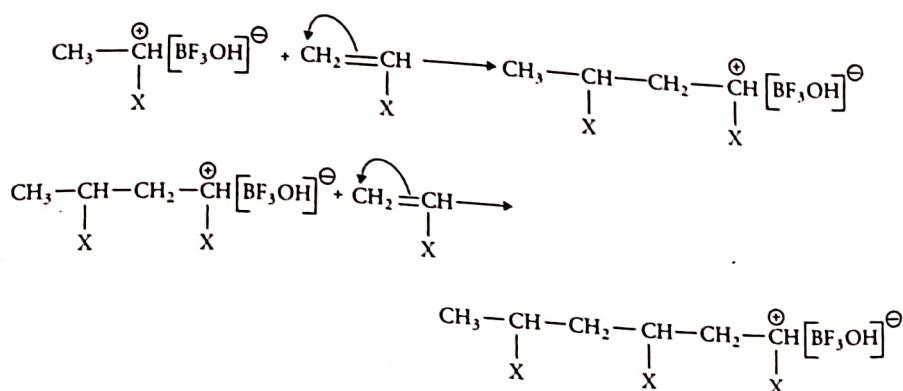
The H^\oplus ion now attacks the π -electron cloud of the monomer and a carbocation is formed.



where X = electron-donating group.

~~Chain propagation~~

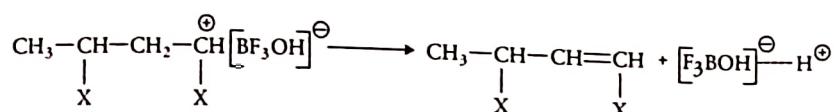
The chain initiator formed in the initiation step attacks new monomer units.



~~Chain termination~~

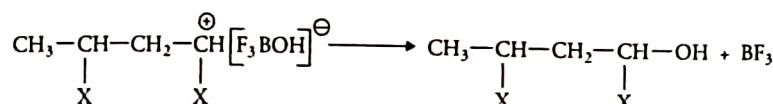
Chain termination can occur in two ways

- (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.

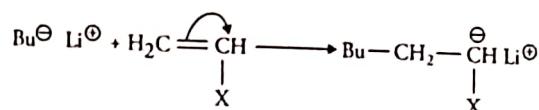
- (b) Formation of covalent bond between the carbocation and counter ion (coupling).



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

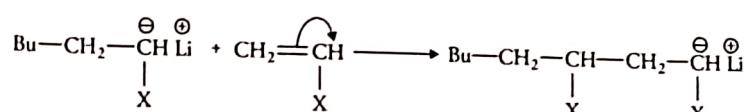
(ii) Anionic polymerisation

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



where X = electron-withdrawing group.

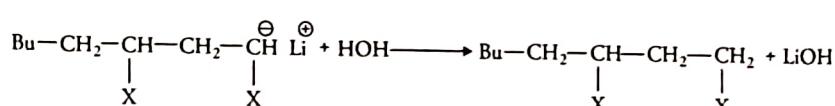
Chain propagation



Chain termination

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

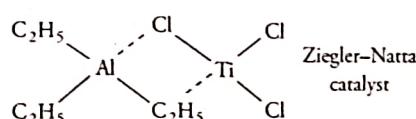
However, termination can be accomplished by transfer of negative charge to a species that is not directly involved in the reaction like CO_2 , methanol, water, etc.



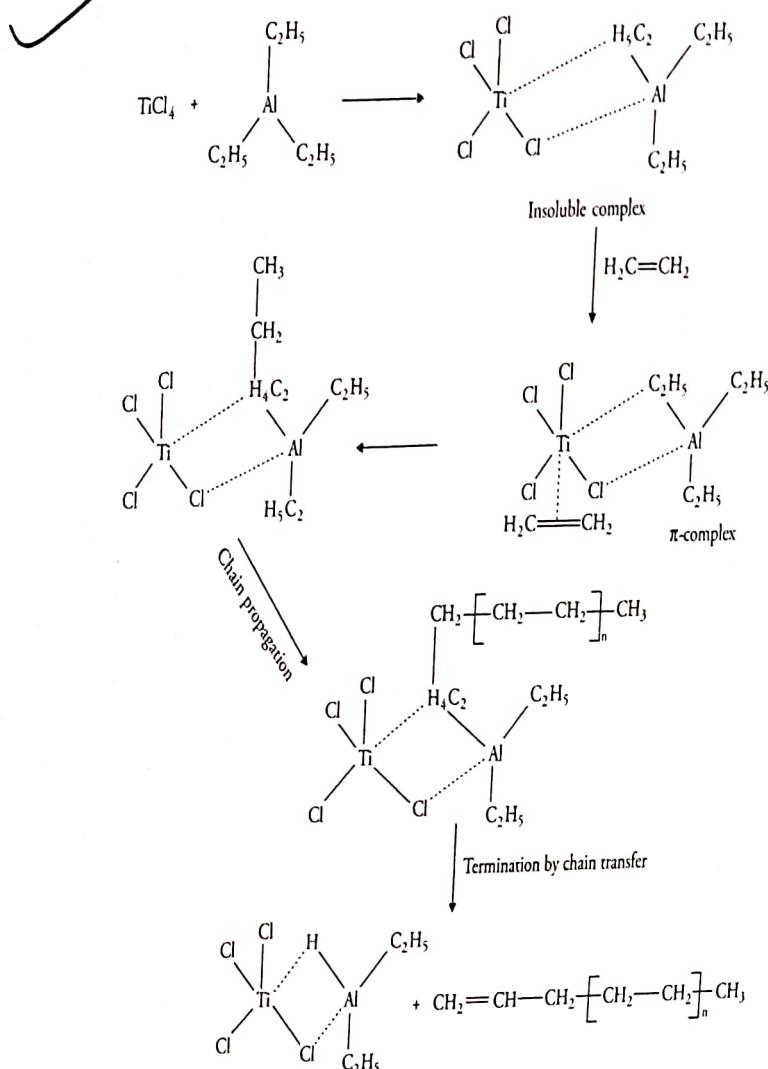
Monomers capable of undergoing anionic polymerisation are butadiene, isoprene, styrene and acrylonitrile.

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.

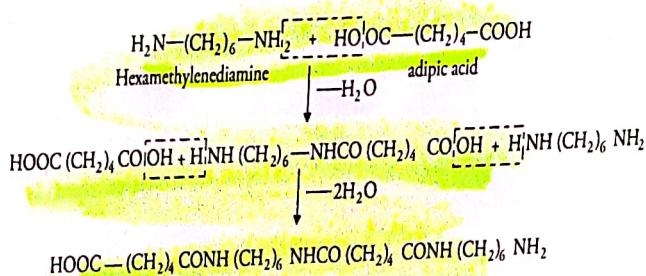


Mechanism of coordination polymerisation



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.

~~(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).

$$\left(\overline{DP}_n \right) = \frac{\overline{M}_n}{\overline{M}_0} \quad \overline{DP}_w = \frac{\overline{M}_w}{\overline{M}_0}$$

\overline{M}_n = number average molecular weight

\overline{M}_w = weight average molecular weight

\overline{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.

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

20 molecules of molecular mass each = 10,000

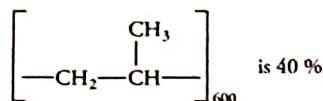
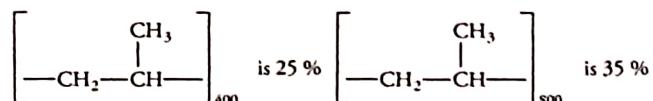
25 molecules of molecular mass each = 15,000

20 molecules of molecular mass each = 20,000.

5 molecules of molecular mass each = 25000

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

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



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

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:

- (i) Thermoplastics
- (ii) 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.



Polymeric chains held by attractive forces



Presence of plasticizer makes the chain flexible

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.

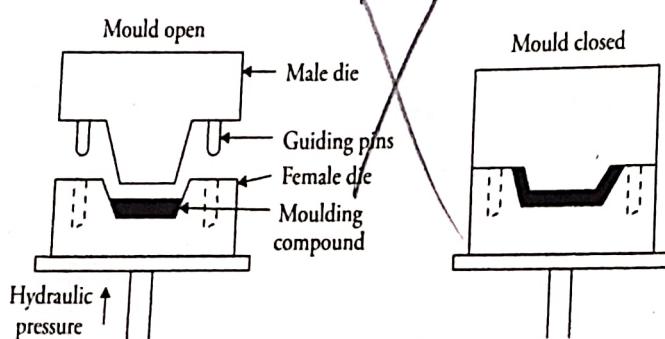


Figure 6.3 Compression moulding

20 molecules of molecular mass each = 10,000

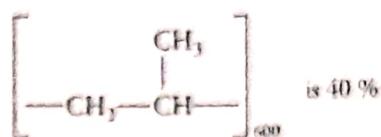
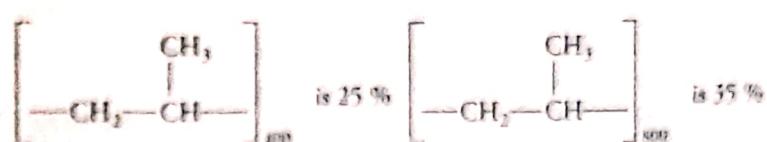
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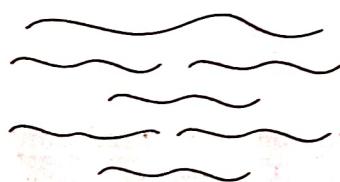
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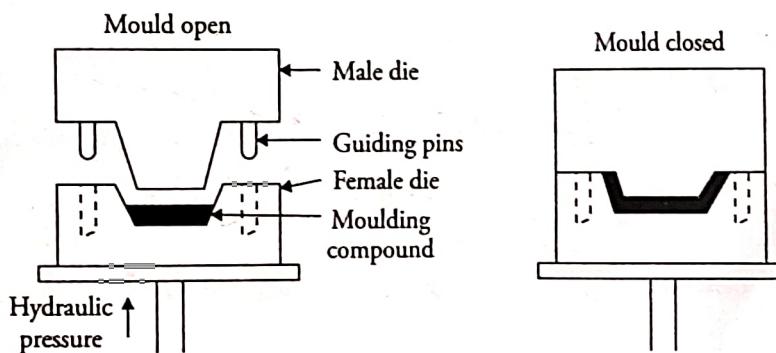
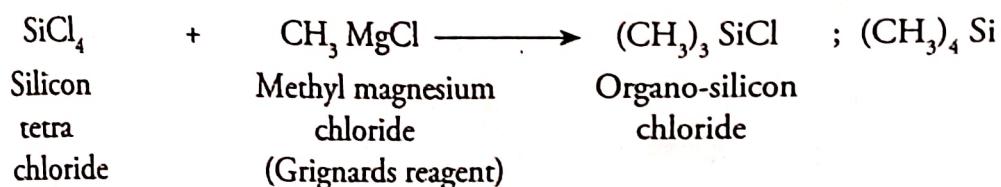


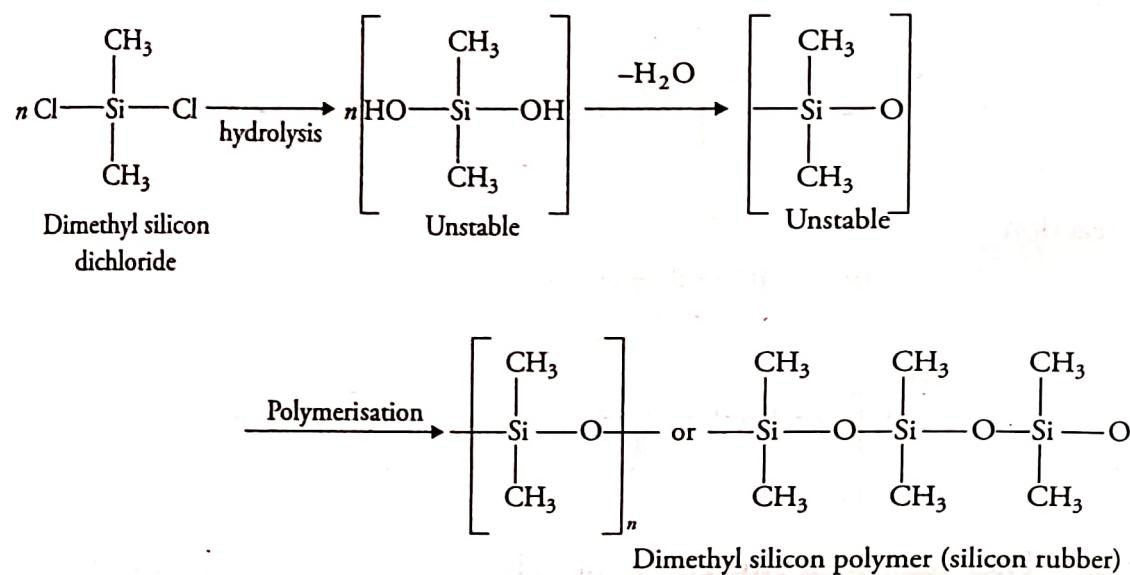
Figure 6.3 Compression moulding

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

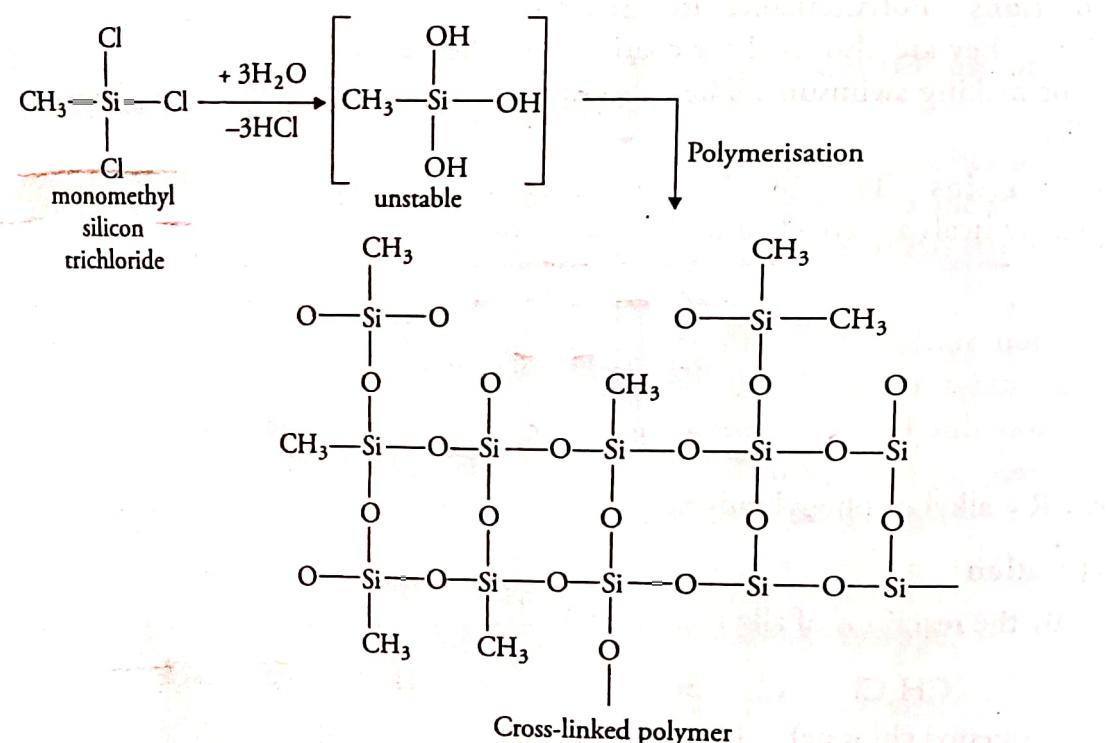


Mixture of organosilicon chlorides is obtained, which is separated by fractional distillation and polymerised by controlled hydrolysis.

- 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.

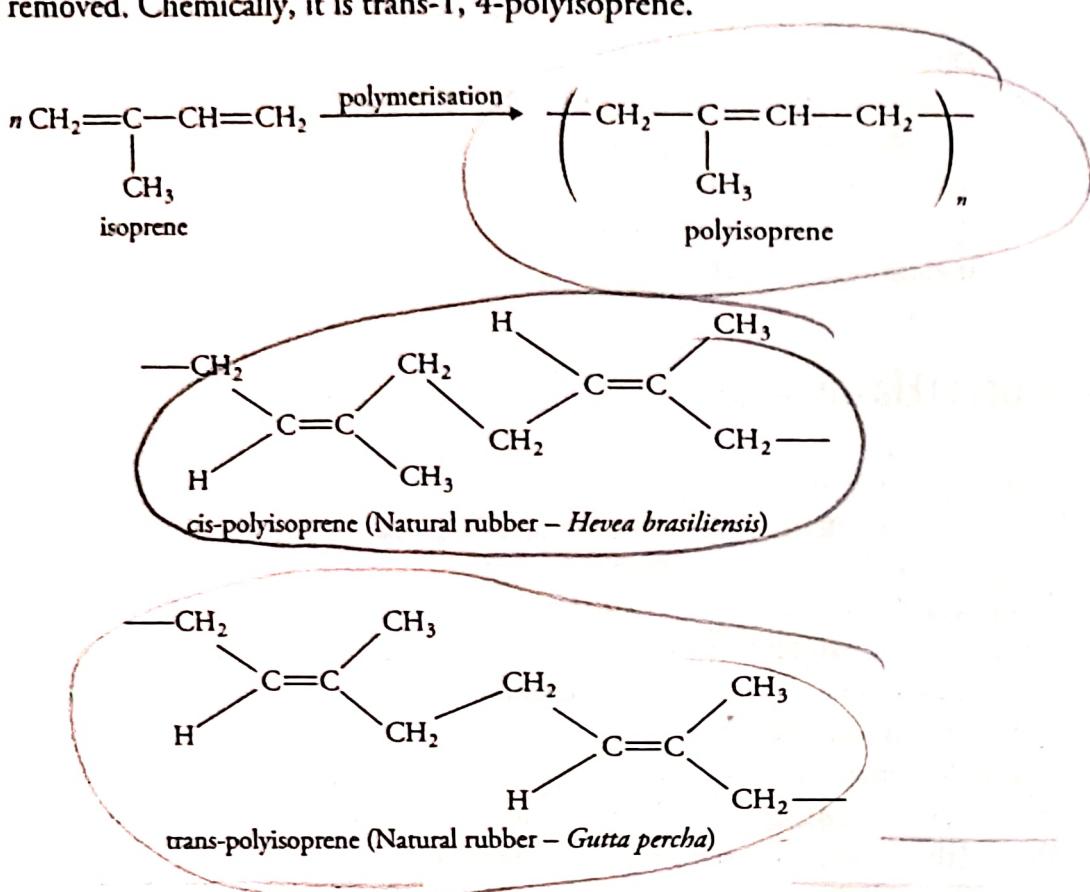
Natural rubber

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 wildly 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.

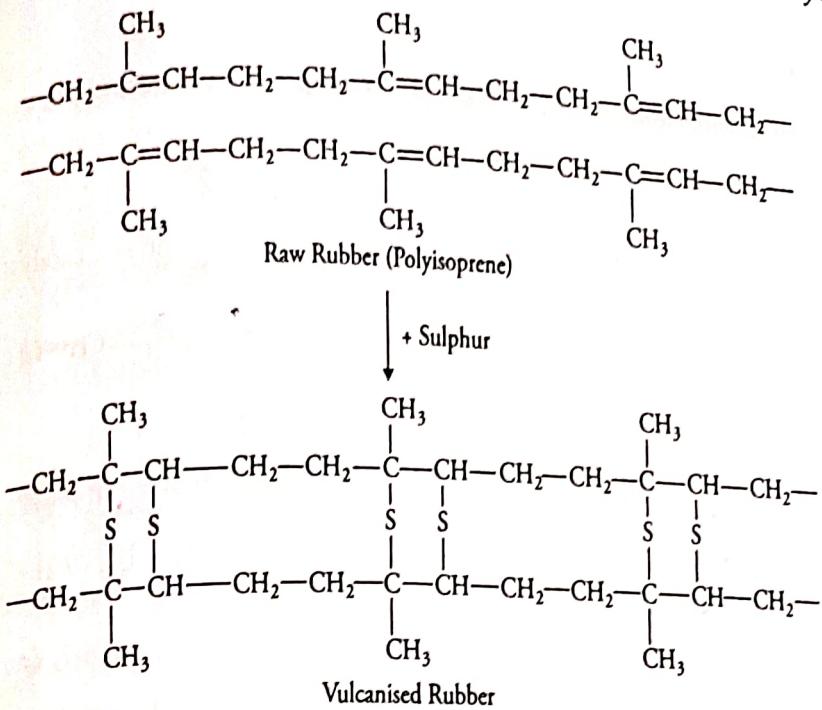


Properties of natural rubber

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 → heated with S (or cork lining)

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

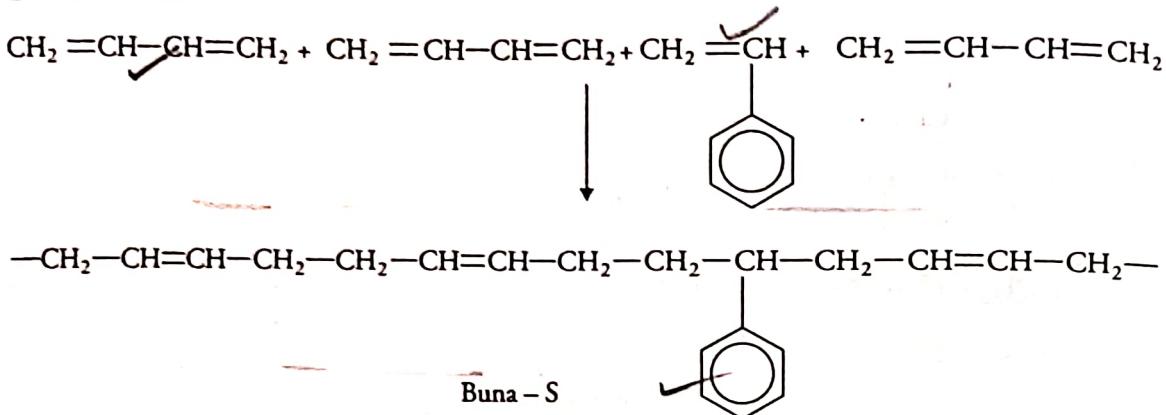
Property	Non-vulcanised rubber	Vulcanised rubber
Tensile strength	70	700
Elongation at break %	1200	800
Permanent set	Large	Small
Rapidity of retraction (snap)	Good	Very good
Water absorption	Large	Small
Swelling in hydrocarbon solvents	Infinite (soluble)	Large, but limited
Tackiness	Marked	Slight
Useful 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.

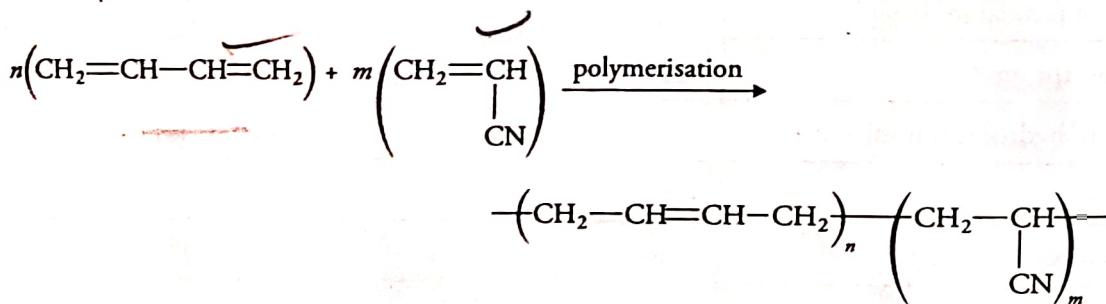
Like natural rubber, they are non-oil-resistant and are generally poor in chemical resistance. However, they have excellent impact and abrasion resistance. Carbon black is generally added as a filler to improve its abrasion resistance. They are oxidised easily and are below natural rubber in tensile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

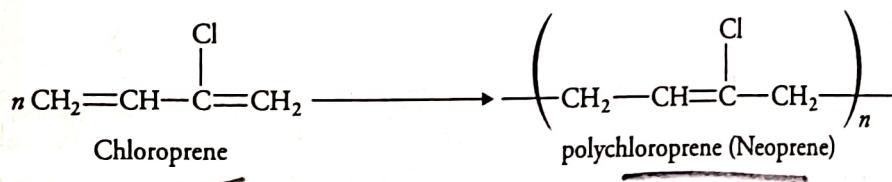
Nitrile rubbers are known for their outstanding resistance to oil and fuels both at normal and elevated temperatures. Nitrile rubbers are low in most mechanical properties. Their tensile strength is low and resilience is roughly one-third to half that of natural rubber. Their properties can be altered 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.

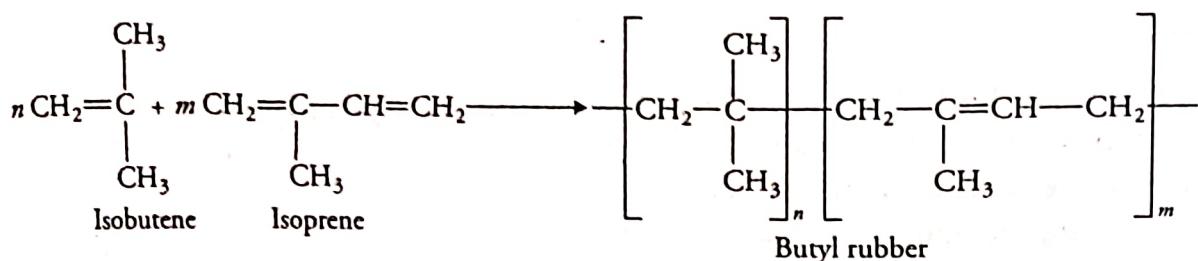
Its permeability is one-fourth to one-tenth the permeability of natural rubber depending on the gas. Being a polar polymer, its solubility in polar solvents is also higher. Although it is slightly inferior to natural rubber in most mechanical properties, neoprene has superior resistance to compression 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 , HNO_3 , H_2SO_4 , etc.

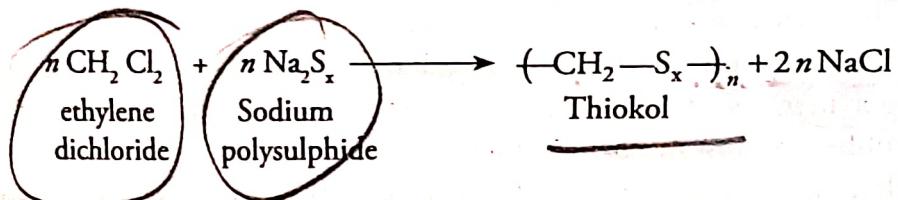
They also have good low-temperature flexibility (remains flexible upto -50°C) and high heat resistance; however, they are not flame-resistant. They generally have lower mechanical properties such as tensile strength, resilience and compression set than the other elastomers. They can be vulcanised; however, 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 (Na_2S_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.

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.

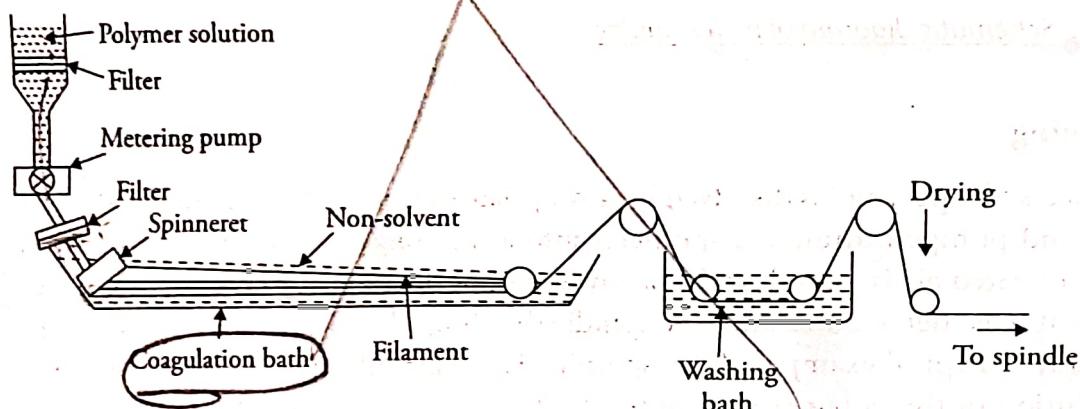


Figure 6.11 Schematic diagram of wet spinning process

Preparation, properties and uses of some important fibres

Cellulose acetate

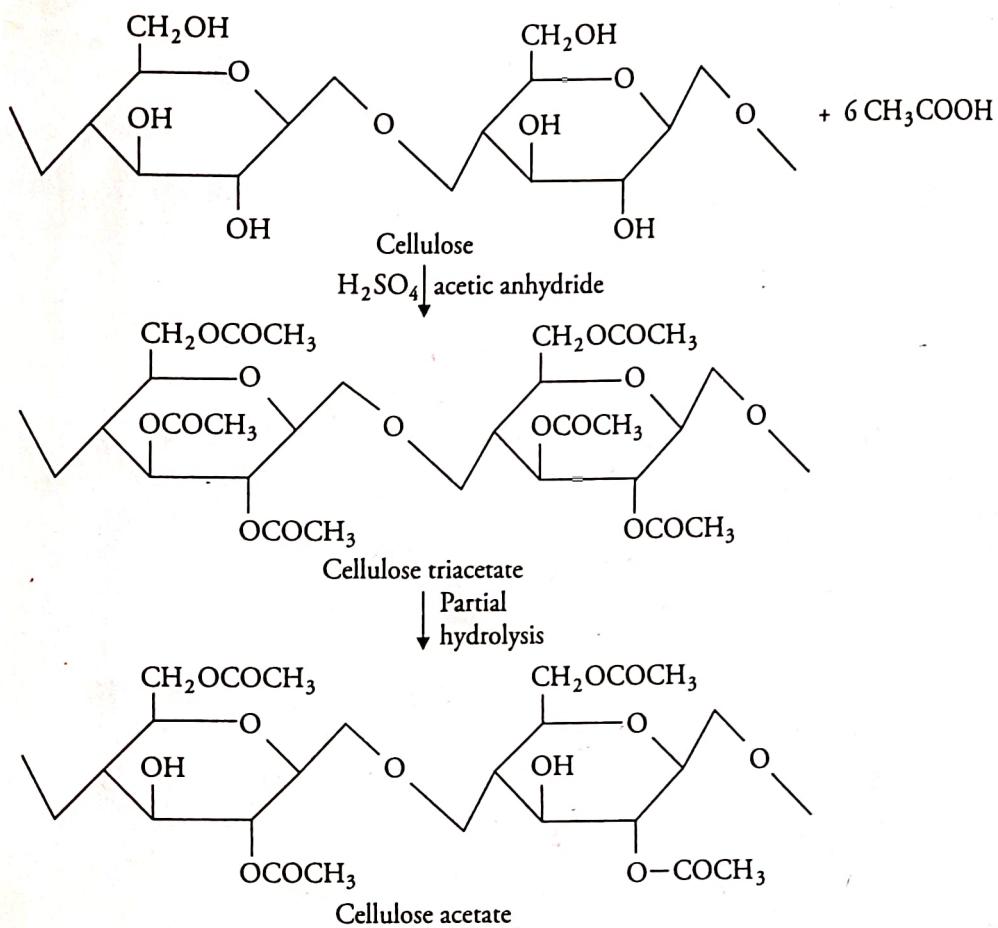
Preparation It was first prepared by Paul Schutzenberger of Germany in 1865. It is obtained by reacting cellulose obtained from processed wood pulp with acetic acid in the presence of acetic anhydride and traces of sulphuric acid in refluxing methylene chloride.

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.

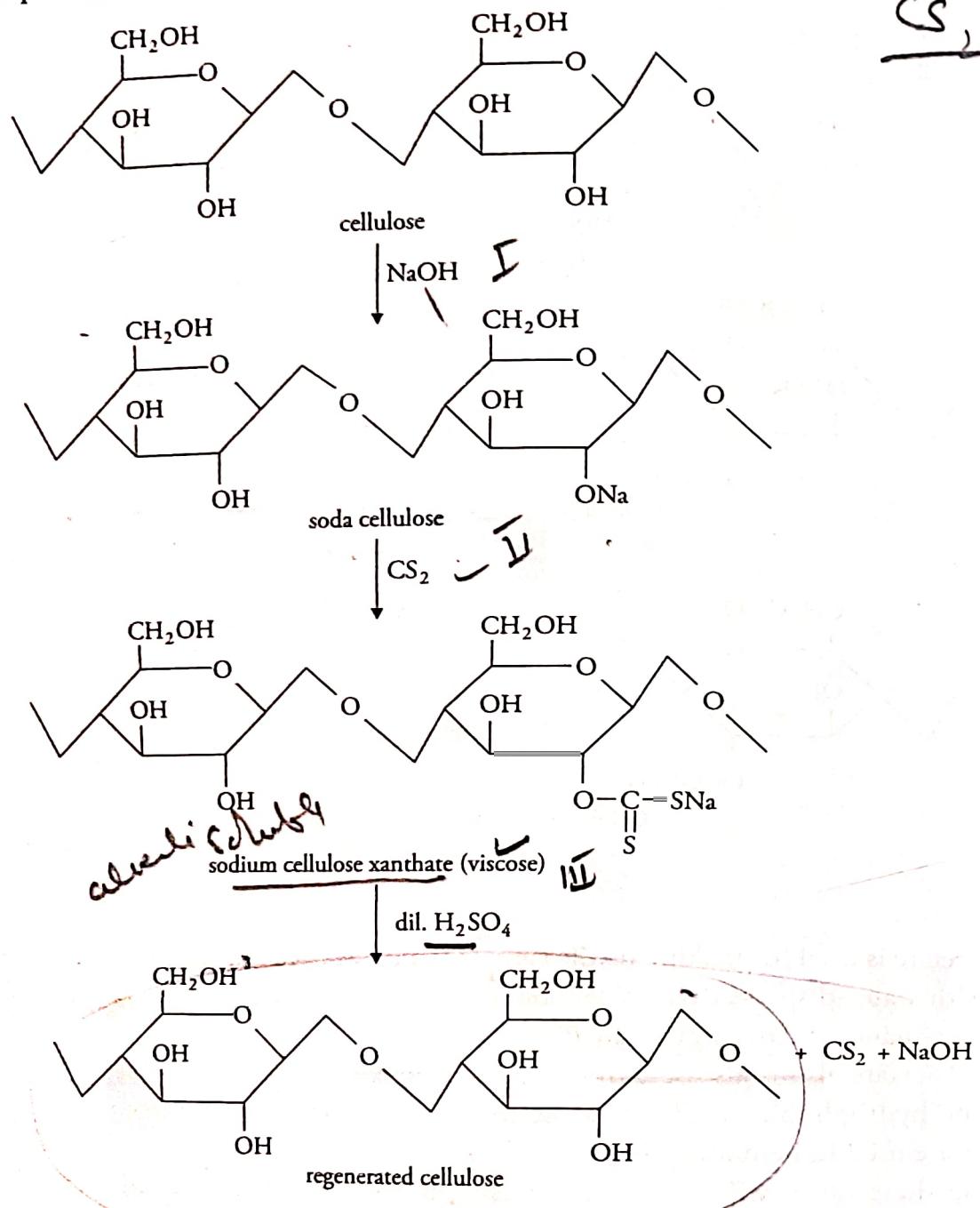
Cellulose acetate also finds use in filter media including cigarette filters called 'tow'. Owing to their unique hydrophobic and hydrophilic properties, semipermeable membranes made out of these fibres are used in hemodialysis and desalination by reverse osmosis.

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 use in medical field. It is used for wound dressings and in the preparation of sustained release system for pills.

Cellulose I → Sodium hydroxide

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 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.

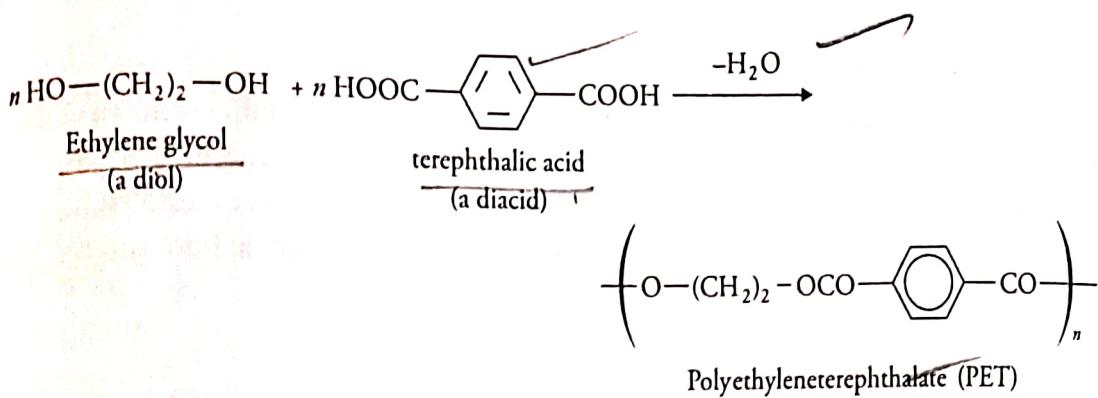
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Polyesters

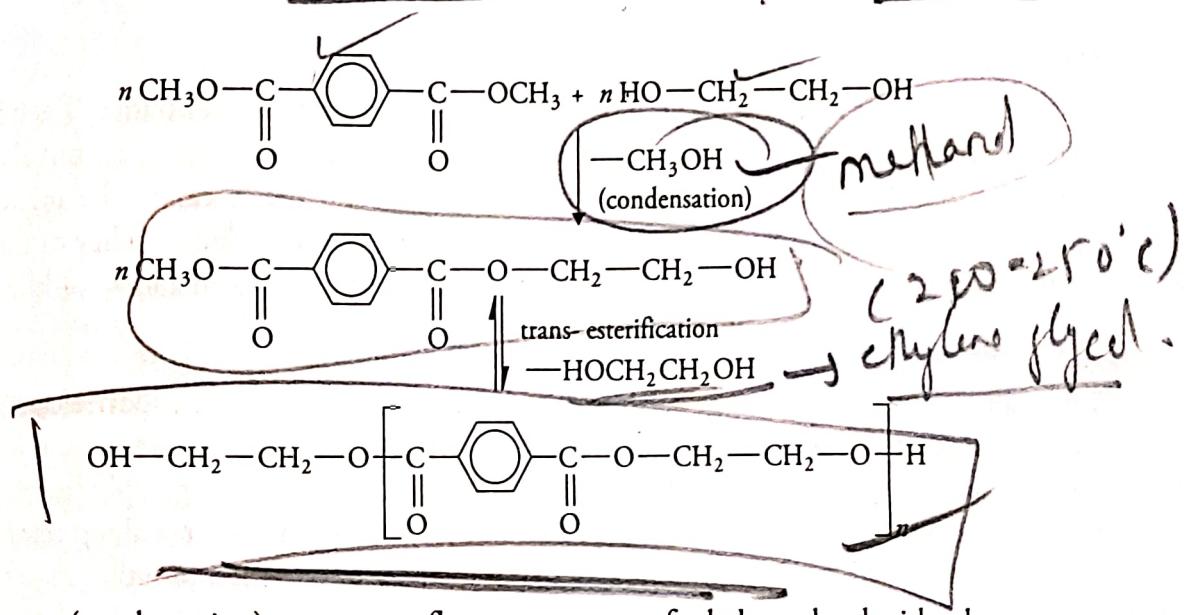
They are formed by the condensation of dicarboxylic acid with dihydroxyalcohol.

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.

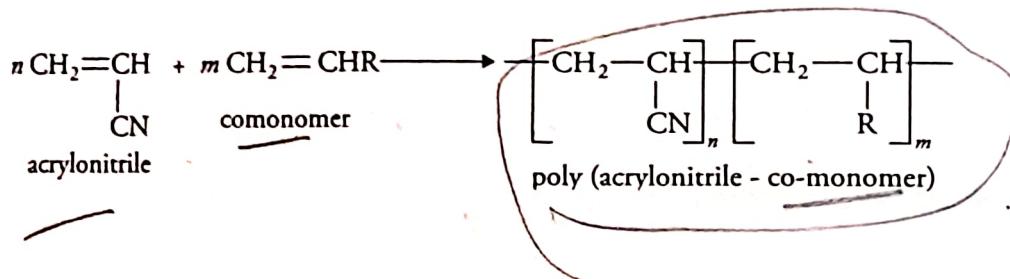
Uses

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

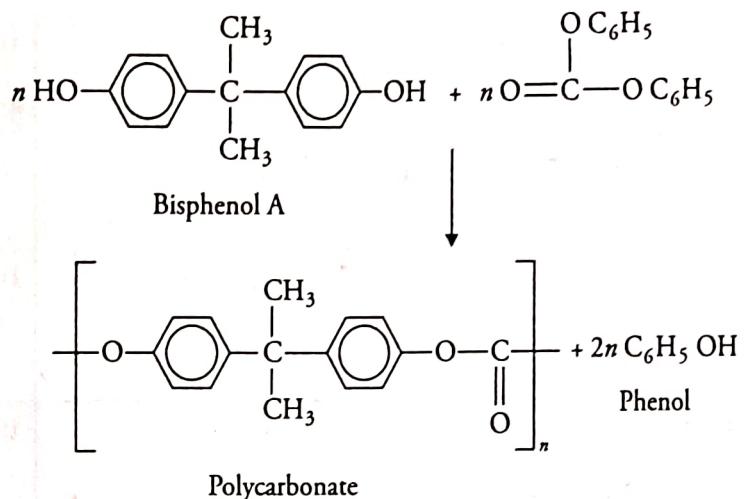
Polycarbonates are polyesters of phenols and carbonic acid. They can be prepared by the condensation of diphenoxymethylene derivatives with diphenyl carbonate.

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 Alam. 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.

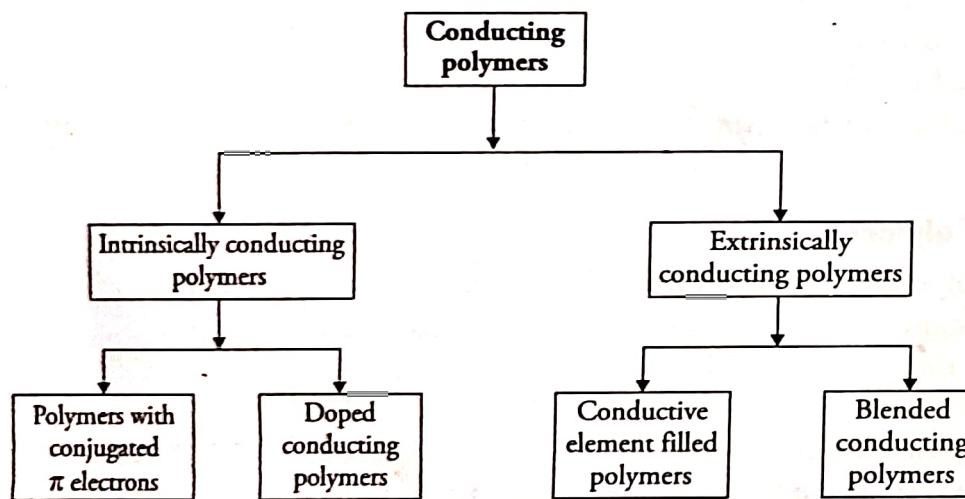
After the above discovery, research continued in this field and a large number of electrically conducting polymers were discovered gradually. Some common conducting polymers are as follows.

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.

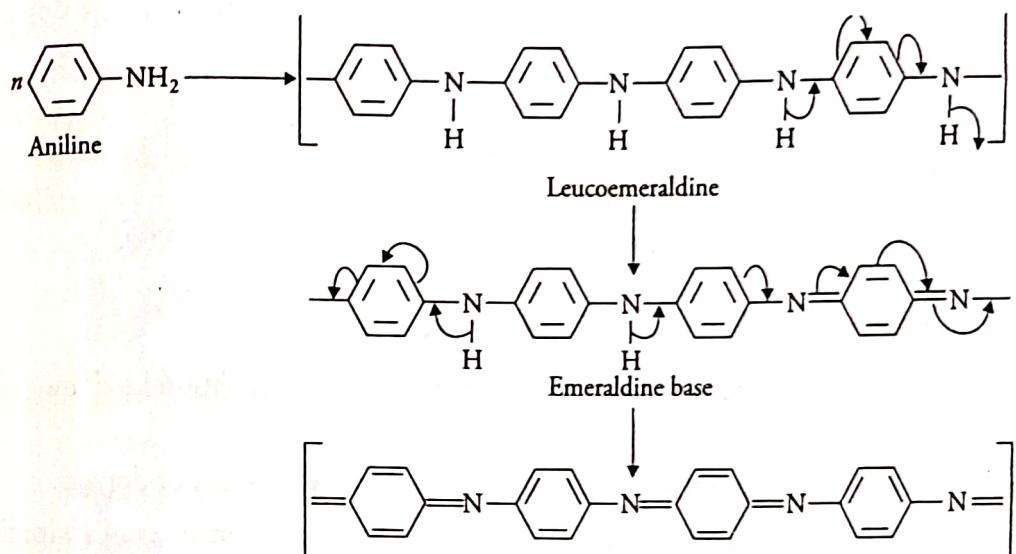
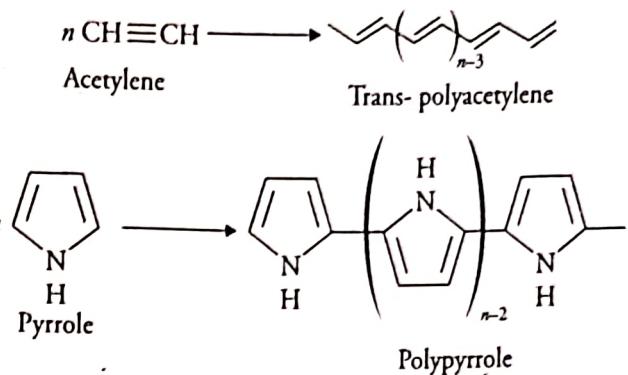
**Figure 6.12** Classification of conducting polymers

Intrinsically conducting polymers

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

(a) **Conjugated π -electron conducting polymers** The conductivity of these polymers is due to the presence of conjugated π -electrons. The conjugated π electrons are delocalised. In an electric field, the π electrons get excited and are transported through the solid polymeric material. However, the conductivity of these polymers is not sufficient for their use in various industrial applications.

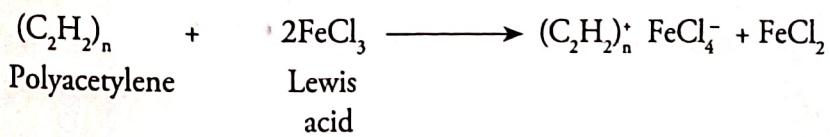
Example

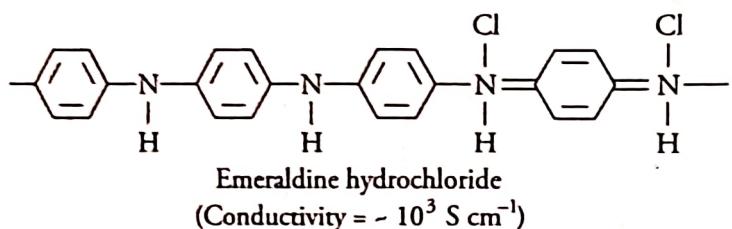
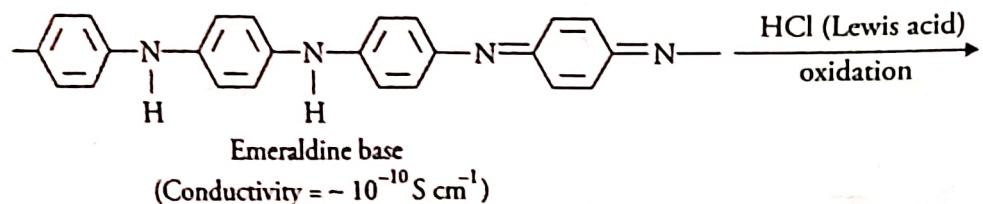


All the three forms of aniline conduct electricity. The conductivity of polyacetylene is $1.7 \times 10^{-9} \text{ S cm}^{-1}$ and that of polyaniline is $10^{-10} \text{ S cm}^{-1}$. The conductivity is greatly enhanced by doping.

(b) **Doped conducting polymers** The polymers are doped by adding either electron donors or electron acceptors on the polymeric backbone. Doping can be of two types.

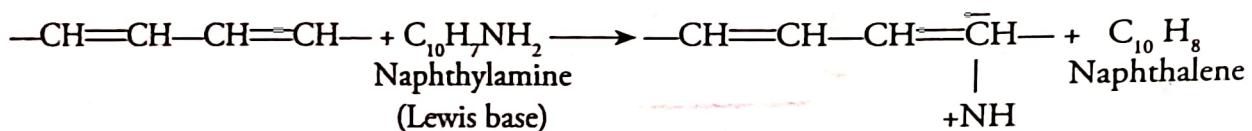
(i) **p-type doping** When the polymer is treated with a lewis acid, its oxidation takes place and holes (positive charges) are created on the polymer backbone. Commonly used p dopants are I_2 , $FeCl_3$, Br_2 , AsF_5 , etc. For example,





Because of its conductivity it is also known as *synthetic metal*.

- (ii) **n-type doping** When the polymer is treated with Lewis base, reduction takes place and negative charges are added on the polymeric chain. Some common n-type dopants are Li, Na, naphthylamine, etc. For example,



The conductivity of the above polymers depends on various factors.

- (i) **Length of conjugation of the polymeric chain** Greater the conjugation level, more will be the delocalised electrons and greater will be the conductivity.
 - (ii) **Doping level** Conductivity increases with the increase in the amount of dopant.
 - (iii) **Temperature** Contrary to metals, the conductivity of these polymers increases with the rise in temperature.

Extrinsically conducting polymers

The conductivity of these polymers is due to presence of externally added ingredients. They are of two types.

Conductive element-filled polymers When the polymer is filled with conducting elements like carbon black, metallic fibres, metal oxides, their conductivity rises. Here the polymer acts as the binder of the conducting elements. However, addition of these elements affects tensile strength and impact strength of the polymer. This problem is overcome by blending a conventional polymer with a conducting polymer.

Blended conducting polymer Conducting polymers are added to conventional polymers. The blended polymers have better physical, chemical and mechanical properties.

Applications of conducting polymers

Conducting polymers find use in electronics, solar cells, displays, illumination sources and microchips. Some of the major application areas are

- In rechargeable light weight batteries. These have perchlorate-doped polyacetylene-lithium system. These batteries are light in weight, leak-proof and small in size.
- Used in photovoltaic devices like in Al/polymer/Au photovoltaic cells.
- In telecommunication systems.
- Electrically conducting polyaniline is used for antistatic coatings, and also for producing 'smart windows'. Polyaniline shows different colors in different oxidation states. Hence, its color changes in response to sunlight or temperature changes.
- They are also used in organic light-emitting diodes (OLEDs).
- In electronic devices such as transistors and diodes.

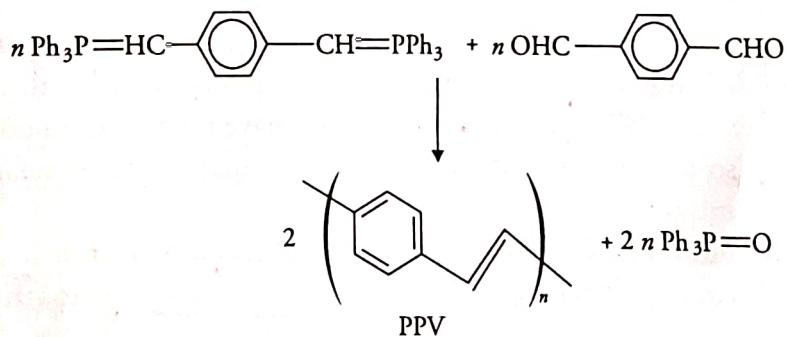
Electroluminescent Polymers

Electroluminescence is light emission stimulated by electric current. Electroluminescence in organic polymers has been known since early 1950s. Research continued and many organic polymers showing electroluminescence have been discovered. The phenomenon is particularly useful as enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs, solar panels and optical amplifiers. A light-emitting diode (LED) is a crystalline semiconductor chip that glows. The first LEDs introduced in 1960s had only red and green colors. An OLED is made of sheets of polymer semiconductor material resembling plastic. Polymer LEDs were first discovered in 1989 by Richard Friend and co-workers at Cambridge University using polyphenylene vinylene (PPV) as the emissive layer.

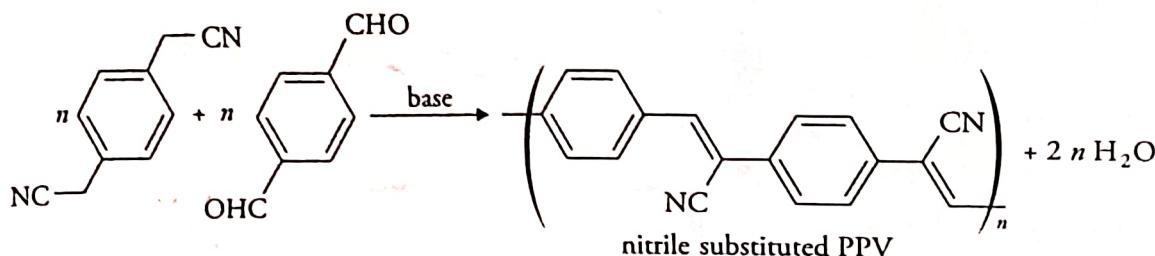
Polyphenylene vinylene It is the simplest and cheapest poly (arylenevinylene). It is the only polymer of this type that has so far been successfully processed into a highly ordered crystalline thin film.

Preparation

PPV can be synthesised by Wittig-type coupling between bis (ylide) derived from an aromatic bisphosphonium salt and dialdehyde, especially 1, 4-benzenedialdehyde.



Knoevenagel condensation between a benzylic nitrile and an aromatic dialdehyde leads to the formation of PPV derivatives. Many side reactions occur in this method such as hydrolysis of nitrile group; hence, careful optimisation of the reaction conditions is needed.



Properties

- PPV is a bright yellow, fluorescent-polymer. Its emission maxima is at 551 nm (2.25 eV) and 520 nm (2.4 eV). It lies in the yellow green region of the visible spectrum.
- It is insoluble, intractable and infusible. Incorporation of side groups like alkyl, alkoxy or phenyl increases the solubility of the polymer.
- It is a diamagnetic material with low intrinsic electrical conductivity (of the order of 10^{-13} S cm⁻¹). The electrical conductivity increases upon doping with iodine, ferric chloride, alkali metals or acids. However, the stability of these doped materials is low. Alkoxy-substituted PPVs are easier to oxidise than the parent PPV and hence have much higher conductivities.

Applications

Owing to its stability, processability, electrical and optical properties, PPV has been considered for a variety of uses. As PPV is capable of electroluminescence, it is used in polymer-based OLEDs. Devices based on PPV emit yellow green light. Derivatives obtained by substitution of PPV are used when light of a different color is desired. PPV is also used as an electron-donating material in organic solar cells.

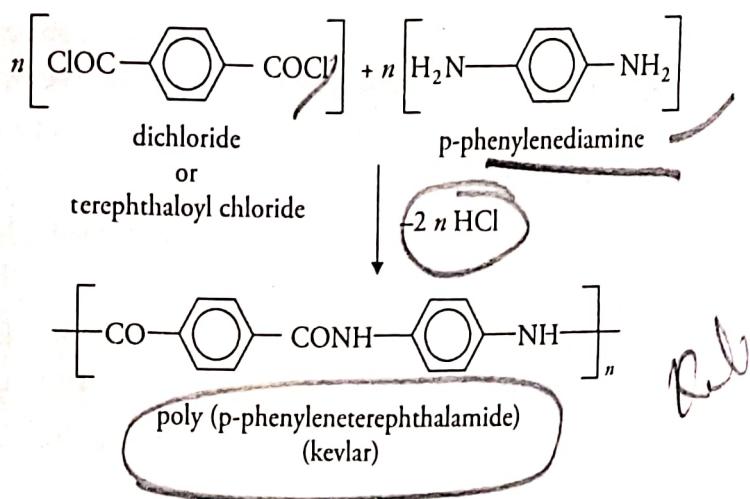
Limitations of PPV

It is susceptible to photodegradation and oxidative degradation in the presence of oxygen. Hence, precautions are to be taken to prevent oxygen contamination during manufacturing.

Liquid crystalline polymers

Liquid crystalline polymers are those polymers that are capable of forming regions of highly ordered structure while in liquid phase. The degree of order is somewhat less than that of a regular solid crystal. LCPs are very useful polymers because they have high mechanical strength at high temperatures. They also have extreme chemical resistance, inherent flame retardancy and good weatherability and are exceptionally inert.

A very commonly known liquid crystalline polymer is kevlar. It is an aromatic polyamide, poly(p-phenyleneterephthalamide). It is prepared by the polycondensation of aromatic dichloride and aromatic diamines.



Properties

Kevlar has extraordinary mechanical properties, high elastic modulus and high tensile strength. Kevlar is known for its ability to be spun into fibres that have five times the tensile strength of steel and 10 times that of Al on a weight to weight basis. The high tensile strength is due to extensive hydrogen bonding between the adjacent polymeric chains. It has extreme chemical inertness, high heat stability and flexibility. It is also extremely resistant to fire.

Uses

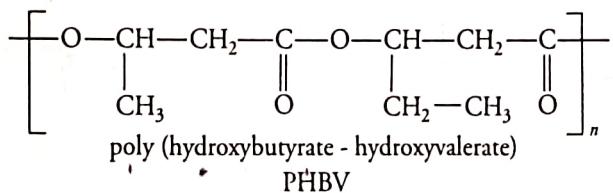
It is used in the fabrication of protective wear including bullet-proof vests. It is extensively used in aerospace and aircraft industries, boat hulls, drum heads, sports equipments, car parts (such as tyres, brakes, clutch linings), helmets, brake pads, ropes, cables, etc. LCPs are generally used as reinforced (composite) materials with carbon or glass fibres.

Presently, the high cost of liquid crystalline polymers limits its use to speciality applications like electronic components (e.g., computer memory modules), housings for light wave conductors and various aerospace applications.

Biodegradable polymers

Biodegradation is the degradation of a material by environmental factors such as sunlight, temperature changes or by the action of microbes (bacteria, fungi, etc.).

The use of biodegradable polymers is increasing day by day. Many natural polymers like rubber and cellulose are biodegradable. They degrade gradually by bacterial action. Biodegradable synthetic polymers are polyvinyl alcohol, hydroxyethylcellulose polymer, polycaprolactone, polylactic acid, hydroxybutyrate polymer, hydroxyvalerate polymer and poly(hydroxybutyrate hydroxyvalerate) (PHBV) a copolymer of hydroxybutyrate and hydroxyvalerate. PHBV is a biodegradable aliphatic polyester.



Applications

Biodegradable polymers find extensive use in the medical field. They are used commercially in tissue engineering and drug delivery field of biomedicine. Typical medical applications include the following.

- Use in orthopaedic fixation devices. Biodegradable polymers are used to join fractured bones. They provide the required strength to the bone and after the bone heals and can take the load, they harmlessly degrade over time. This prevents the patient from an additional operation for removal, as would be required if a metallic device was used.
- In controlled drug delivery, the polymer slowly degrades into smaller fragments releasing the drug gradually and in a controlled manner.
- It is used in dental devices, biodegradable vascular stents, biodegradable soft tissue anchors, etc. Biodegradable polymers are also being increasingly used in the manufacture of plastic bags, toys and other plastic products. These polymers gradually degrade in the environment (or in landfills) and leave the environment 'greener'.

6.12 Properties of Polymers

The properties of a polymer largely depend on their structural characteristics. Properties like tensile strength, elasticity, crystallinity, chemical reactivity and electrical properties depend upon various structural characteristics like chemical composition, sequence of monomer units, spatial arrangement of side groups, nature of packing, molecular weight, etc.

The various properties of polymers in light of their structural variations are discussed below

1. **Mechanical properties** Properties like strength, elasticity and hardness depend on the crystallinity of the polymer, whereas tensile strength and impact resistance are related to the molecular weight of the polymer.

(i) **Strength** Strength of a polymer depends upon the magnitude and distribution of intermolecular forces of attraction between the polymeric chains. Branched and straight chain polymers are held together by weak intermolecular forces of attraction. The magnitude of these forces increases with increase in length of the polymeric chain or the degree of polymerisation. Higher the degree of polymerisation greater is the strength of the polymer. Polymers with nearly 150–200 monomeric units show appreciable strength. Polymers with low molecular weights are soft and gummy. High molecular weight and long chain polymers are hard, tough and more heat-resistant.

Strength of a polymer can be controlled by making necessary changes in its structure. Polymers with polar groups like carboxyl, hydroxyl, chlorine, fluorine and nitrile are strong

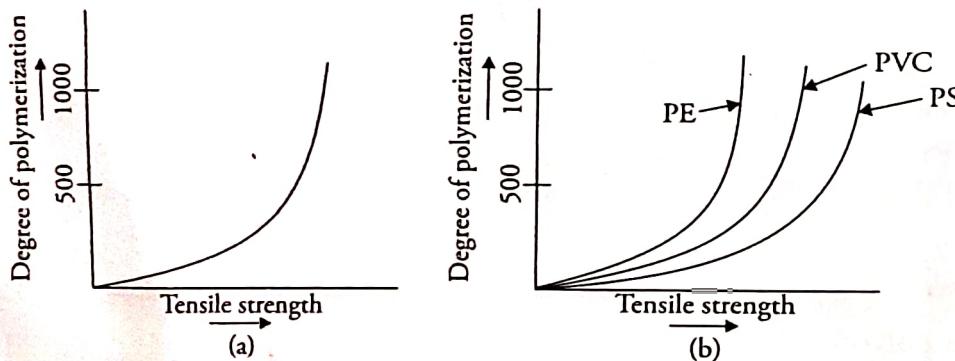


Figure 6.13 Dependence of strength of a polymer on degree of polymerisation

for example, nylon, polyester, etc. Nylon and terylene are strong due to the presence of hydrogen bonding between the polymeric chains. Similarly, teflon is the toughest known polymer because the fluorine atom is highly polar. Cross-linking also enhances the strength of the polymer. For example, natural rubber is soft. Introduction of sulphur cross-linkages (vulcanisation) greatly improves the strength of natural rubber.

Shape of a polymer also affects its strength. On comparing PE and PVC it is found that PVC is tougher. This is because the presence of chloride groups restricts the chain movement and increases van der Waals forces of attraction. Consequently, the chains cannot slip over each other and the strength of the polymer increases. Bakelite is a cross-linked polymer. All structural units are connected by strong covalent forces resulting in a giant solid three-dimensional molecule. Hence, they are strong and tough as the movement of chains is totally restricted.

Elastic deformation (elongation)

- Elastic deformation or elasticity is the property by virtue of which a polymer changes shape under stress but recovers its original shape when the stress is released. The term 'elastomer' is generally used for such types of polymeric materials.

$$\text{Percentage elongation} = \frac{L}{L_0} \times 100$$

where

L_0 = original length of the polymer.

L = length of polymer after being stretched.

Elastomers can stretch from 500 to 1000 percent elongation and return to their original length without any difficulty. This is because unstretched polymer is randomly arranged (disordered with high entropy). On being stretched, the chains straighten resulting in crystallisation, entropy decreases; and so does the stability, and hence stiffening of the material takes place (Fig. 6.14). Hence, when the stretching force is released the chain returns to its original shape. A polymer behaves as an elastomer if it contains long chain of molecules having free rotating groups.

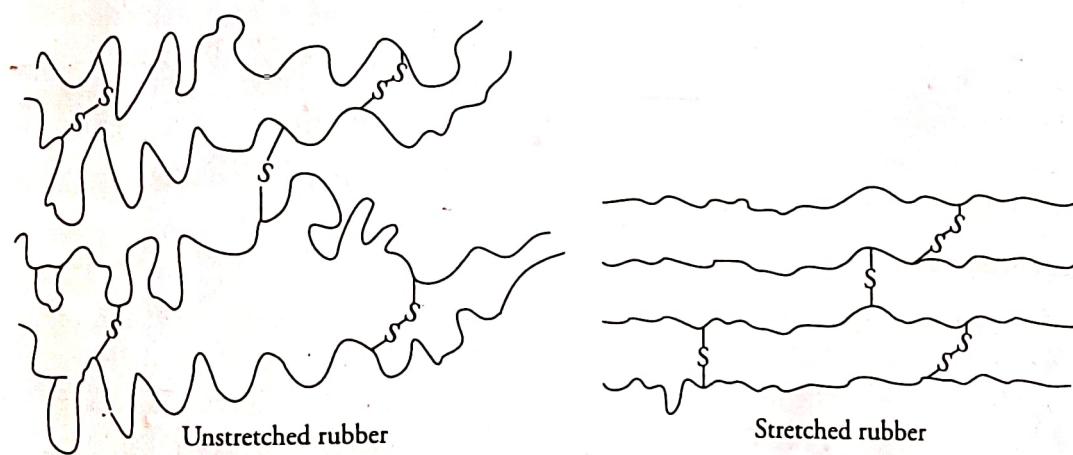


Figure 6.14 Effect of stretching on crystallinity of rubber

Rigid plastics such as polystyrene cannot be elongated. They break on applying excess stress. Flexible plastics like PE and polypropylene resist deformation to a large extent. Elastomers like rubber have high reversible elongation.

(iii) **Plastic deformation** A substance is said to be in a plastic state if it is capable of flowing at some stage of its formation. Plastics are moulded into different shapes under flow condition. They retain their shape on cooling. Such materials that undergo plastic deformation on the application of heat and pressure are called thermoplastics. Generally, linear polymers whose polymeric chains are held together by weak van der Waals forces of attraction undergo plastic deformation very easily.

On the other hand, cross-linked polymers do not undergo plastic deformation. These polymers become hard and rigid due to the presence of primary covalent bonds throughout their structure. Owing to the presence of strong covalent bonds, the molecules cannot slip past each other; hence, plastic deformation cannot take place. These cross-linked polymers are called thermosets. If, however, their covalent bonds are broken by the application of heat and pressure, it results in total destruction of the molecule.

Solubility

The process of dissolution of polymers is very slow compared with simple molecules. First, the solvent diffuses into the polymer molecule producing a swollen gel. After that the solvent disintegrates the polymer leading to dissolution of the polymer.

The principle of 'like dissolves like' prevails for the polymeric molecules also. Non-polar polymers dissolve in non-polar solvents. Polymers with polar groups like -OH and -COOH are usually swollen or even dissolve in polar solvents like water, alcohol and ketones, but are resistant to chemicals like benzene, toluene, petrol and carbon tetrachloride. Polymers with aliphatic character are soluble in aliphatic solvents whereas those with aromatic character show greater solubility in aromatic solvents. Linear polymers dissolve because the solvent gets in between the chains. Cross-linked polymers only swell, they do not dissolve. Greater the cross-linking in the polymer, lesser is its solubility. Amorphous polymers containing bulky polar groups swell readily in polar solvents but do not form solutions at room temperatures. Crystalline polymers dissolve at high temperatures.

Chemical reactivity

The polymers like PE having all single bonds are mostly inert and undergo only substitution reactions. However, if the polymer is branched then oxidation may take place at tertiary carbon atoms. Polymers with double bonds are susceptible to oxidation. Polymers having ester, amide and carbonate groups are susceptible to hydrolysis. Polymers with free functional groups undergo reactions of those functional groups. For example, cellulose polymers with free hydroxyl groups react with nitric acid to produce nitrocellulose.

Electrical properties

Polymers are generally insulators, that is, poor conductors of heat and electricity. Electrical properties of a material are expressed as dielectric strength and dielectric constant. The dielectric strength of a material is defined as the maximum voltage which the material withstands and beyond which its dielectric nature is lost. The voltage is increased until the material breaks down; there is an arc across the electrodes and substantial current flows. It is expressed as voltage per unit thickness.

$$\text{Dielectric strength} = \text{V/mm or V/cm}$$

Dielectric strength helps us to evaluate the insulating properties of the material. Higher the resistance of a material for electric flow, larger is its dielectric strength or insulating capacity. Most plastics have good dielectric strength (in the order of 100–300 kV/cm). The other term which is used to determine the insulating or dielectric capacity of a material is the dielectric constant. Dielectric constant or permittivity ϵ is a dimensionless quantity and describes the ability of a dielectric to store electrically separated charges (electrostatic energy). It is defined as the ratio of the capacitance of a set of electrodes with the dielectric material between them to the capacitance of the same electrodes with vacuum between them. The dielectric constant for a vacuum is one and for all other materials is greater than one.

Electrical properties and polymeric structures

Dielectric properties of a polymer largely depend upon their chemical structure. The chemical structure determines whether a polymer is polar or non-polar and this in turn decides the electrical properties of the polymer.

In polar polymers like PMMA, PVC and nylon dipoles are created due to imbalance in the distribution of electrons. In the presence of electric field these dipoles tend to align with the field. This will create dipole polarisation of the material. Hence, these materials tend to be only moderately good as insulators. Their dielectric constant is high and generally lies between 3 and 7. Symmetrical molecular and non-polar polymers are truly covalent. No dipoles are present in these materials and the application of electric field does not align the dipoles. However, slight electron polarisation occurs due to movement of electrons in the direction of the electric field. This electron movement is instantaneous. Non-polar polymers like PTFE, PE, PP and PS have high resistivities and low dielectric constant. Their dielectric constant is always less than 3.

Table 6.4 Dielectric constant of some polymers

Polymer	Dielectric constant (1000 cycles)
Nylon 66	3.9 – 4.5
Cellulose acetate	3.4 – 7.0
PMMA	3.0 – 3.6
Polyvinylidene fluoride	7.46
Polybutene	2.25

Effect of environment on electric properties of polar polymers

Moisture and temperature of the environment have a considerable effect on the electrical properties of polymers. Polar plastics have a tendency to absorb moisture from the atmosphere. Presence of moisture raises the dielectric constant and lowers the resistivity.

If the temperature is raised, there is faster movement of the polymer chains and fast alignment of the dipoles. This holds good particularly if the temperature is raised above T_g , because above T_g , much more molecular movement is possible. Raising the temperature invariably raises the dielectric constant of polar plastics (i.e., lowers resistivity).

Non-polar plastics are not affected by water because they do not absorb water. Temperature does not affect electronic polarisation in non-polar plastics and hence does not have a marked effect on their electrical properties.

Crystallinity of polymers

The degree to which the molecules of a polymer are arranged in an ordered pattern with respect to each other is a measure of its crystallinity. Crystallinity has a vital role in determining the hardness, permeability, density, tensile strength, impact resistance, heat capacity and solubility of a polymer. In fact no polymer is 100% crystalline. Higher the crystallinity of the polymer, stronger is the secondary bonding and the polymer will be stronger and more brittle. Crystallinity of the polymer increases as the molecular weight increases. An isotactic polymer has higher crystallinity. Intramolecular bonding (e.g., hydrogen bonding in nylon and terylene) increases crystallinity.

Effect of polymer crystallinity on optical properties of the polymers

Amorphous polymers are generally transparent. They have a constant refractive index throughout the material. In crystalline polymers, the refractive index arising out of difference in densities of crystalline regions is different. There will be light scattering and the polymer will be translucent. Sometimes crystalline polymers are also transparent. If crystalline structures such as spherulites are smaller than the wavelength of light, they will not interfere with the passage of light. As a result, the polymer will appear transparent.

Effect of polymer crystallinity on permeability

Permeability is defined as the rate of penetration of liquid or gases through the polymer matrix. It depends on polymer crystallinity. Crystalline polymers have close packing and hence permeability is quite low. Amorphous polymers above glass transition temperature have enough free volume between the molecules. Hence, liquids and gases pass through them making them permeable.

Thermal behavior of polymers

Glass transition temperature (T_g) is defined as the temperature below which an amorphous polymer (sometimes crystalline polymer) becomes hard, brittle and breaks like glass. Above this temperature it is soft, flexible and rubbery. The hard and the brittle state is called the glassy state because random arrangement of polymeric chains is similar to the random molecular arrangement found in glass. The soft, flexible state is the rubbery or viscoelastic state. On heating beyond T_g the polymer first changes into soft, flexible rubbery state and then converts into the highly viscous liquid and starts flowing. This is called as viscofluid state and the temperature at which this occurs is called the flow temperature T_f , as explained in Figure 6.15.

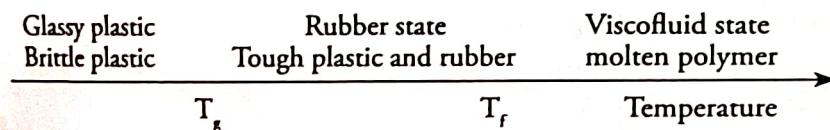


Figure 6.15 Thermal behavior of Polymers

Some polymers are used to above T_g and some below. Hard plastics like polystyrene and poly methylmethacrylate are used below T_g , that is, in their glassy state. Rubbers, elastomers like polyisoprene and polyisobutylene are used above their T_g , that is, in their rubbery state when

they are flexible. Some polymers like polycarbonate, although amorphous, are considered tough at temperatures well below their T_g . This behavior is because of the chemical bonds in polycarbonates rather than the arrangement of the polymeric chains.

The above phenomenon can be explained considering the three states of matter solid, liquid and gas. Polymers however exist only in two phases solid and liquid because they decompose before reaching their boiling points. In a long chain of polymer molecule, some segments have freedom of movement while others do not. When such a polymer molecule is heated first there is internal mobility of the polymeric segments (called segmental mobility), and then the whole molecule starts moving (molecular mobility; segmental mobility can be compared with the audience standing in their position or stretching their arms while watching a movie, whereas molecular mobility is the moving out of the audience during intermission or after the movie). When segmental mobility comes into play the solid polymer acquires a soft and rubbery state. With the onset of molecular mobility the polymer changes into the liquid state.

Behavior of amorphous polymer In an amorphous polymer, there is absence of long range order in the solid state. When such a solid is heated the energy increases. The segmental mobility increases followed by increase in molecular mobility; hence, it changes into liquid form. During the transition of an amorphous solid into liquid there is no change in the internal order of the molecular arrangement (molecules are randomly arranged both in solid and liquid states), there is change only in the energy of motion. If such a liquid is cooled the absence of long-range order, which is a characteristic of liquid phase, is retained. However, because of decrease in thermal energy the molecule loses its ability to move and becomes immobile or becomes solid physically. Hence, a glassy solid is considered as a super-cooled liquid. At low temperature, an amorphous polymer does not possess segmental or molecular mobility and exists as glassy solid. On heating gradually, it acquires segmental mobility and becomes rubbery. The temperature at which the amorphous polymer passes from glassy state to rubbery state is called the glass transition temperature T_g . On further heating, molecular mobility sets in and the polymer passes into liquid state and starts flowing; this is the flow point temperature T_f .

Behavior of crystalline polymer

A crystalline polymer has long range order. All the atoms or molecules of the polymer occupy fixed position in the crystal. The segments in crystalline polymer are held by strong intermolecular forces; hence they do not possess segmental mobility. The energy required to overcome these intermolecular forces is almost equal to the energy required to induce molecular mobility. Hence, when a crystalline polymer is heated segmental mobility alone cannot set in and hence the polymer does not pass into rubbery state and does not possess a glass transition temperature. It changes directly into liquid state. The temperature at which a crystalline polymer changes into liquid state is called the melting temperature T_m .

Behavior of semicrystalline polymer

Polymers are mostly partially crystalline and consist of both amorphous as well as crystalline regions. Such polymers have both glass transition temperature T_g as well as melting temperature T_m . Below T_g the amorphous region exists in glassy state and the crystalline region is in crystalline state. At T_g the amorphous region passes into rubbery state, whereas the crystalline region remains crystalline. At T_m crystalline region melts into a liquid state. Beyond T_m the amorphous and crystalline regions become one and the polymer as a whole is in liquid state.

Factors effecting T_g

1. **Molecular weight** As the molecular weight increases, bulkiness increases and hence T_g increases.
2. **Molecular structure**
 - (a) Insertion of bulky inflexible side group increases T_g because of decrease in mobility.
 - (b) Increase in the length of the side chain, presence of double bond in the backbone of polymeric chain decreases T_g .
 - (c) Increase in cross-linking decreases mobility and increases T_g .
3. **Plasticiser** Addition of plasticiser to the polymer helps the polymeric chains to slide past each other even at low temperature resulting in decrease in T_g .
4. **Water or moisture content** Increase in moisture leads to increase in the formation of hydrogen bond with polymeric chain. This increases the distance between the polymeric chains. The increase in free volume between polymeric chains results in the decrease in T_g .
5. **Cooling rate** If the cooling rate of molten solid is higher, the T_g is higher. Moreover, if the rate of cooling is slower, then T_g obtained is low.
6. **Flexibility of polymer chain** Polymers in which the polymeric chains are flexible have low T_g , whereas those in which the chains do not move have high T_g .
7. **Branching** Increased branching results in decreased mobility of the polymer chain and increased chain rigidity results in high T_g .

Importance of T_g

The T_g value gives information whether the polymer could be used as rubber or plastic. The materials having low T_g are usually sticky in nature. Hence if the T_g of the material is increased by addition of substance having high T_g values then the product would not be sticky. It becomes hard and easy to process for industrial use. In glassy state, the substance is tough and has good strength. Glass transition temperature can be used to modify physical properties of solids. By altering T_g of the polymer or drug they can be maintained in an amorphous solid form at ambient or body temperature. Improvement in handling characteristics, solubility and reproducibility in dissolution of solids can be achieved by increasing the T_g of solids.

Anelasticity

Elastic deformation is **time-independent**, that is, an applied stress produces instantaneous elastic strain that remains constant over a period of time till the stress is maintained. Upon release of the stress, the strain is totally recovered and the material returns to its original undisturbed position.

In most engineering materials, there exists a **time-dependent** elastic strain component. In this, the elastic deformation continues after the application of stress and the material takes a finite time for the recovery after the release of stress. This time-dependent elastic behavior is called **anelasticity**. This effect is also termed as **elastic after effect**.

In some materials, when they are loaded, the material undergoes a certain instantaneous elastic deformation E_d , followed by a delayed or retarded elastic deformation E_{an} (anelastic effect) during a time t , which approaches a final value asymptotically. If the load is removed, the instantaneous elastic recovery, equal to E_d is followed by a delayed recovery in time t .

For metals, the anelastic component is generally small and often neglected. However, for polymeric materials its magnitude is significant. In this case, it is termed as **viscoelastic behavior**.

Viscoelasticity

There are two types of deformations (or strains): (i) elastic deformation and (ii) plastic deformation.

- (i) **Elastic deformation** is reversible. When stress is applied, the atoms in a material move and come back to their original position on the removal of stress. A rubber band is a typical example of this type. It stretches on applying force and returns to normal condition when the stretching force is removed.
- (ii) **Plastic deformation** is a permanent deformation. When the stresses are released, the atoms do not return to their original states and consequently the material remains deformed. The deformation or load remaining after load release is referred to as the **permanent set**.

A third kind of deformation called **viscoelasticity** is found in some polymers, such as plastics. Here, when the applied stress, which is within the materials' elastic range, is removed the material will not completely recover its original size. If a force is applied on a polymer and withdrawn quickly, the polymer tends to return to its original undisturbed configuration, a process called relaxation (elastic behavior). If the force is applied gradually and consistently, the molecules begin to flow irreversibly. The flowing liquid will be viscous because of chain entanglement and frictional effects. This combination of properties **elasticity and viscous flow** is referred to as **viscoelastic behavior**. This behavior is ideally illustrated by Silly Putty, a siloxane polymer. If rolled into a ball and dropped to the floor, it will bounce back demonstrating its elastic behavior. However, if strain is applied gradually the ball will elongate with high extension (viscoelastic behavior). If left on a desk for several days, the ball will flatten and flow like a viscous liquid over long time.

Viscoelastic behavior is dependent both on time and temperature. This behavior has been quantified experimentally. In these tests, a specimen is initially strained rapidly in tension to a predetermined and relatively low strain level. Keeping temperature constant, the stress necessary to maintain this strain is measured as a function of time. Stress is found to decrease with time because of molecular relaxation process taking place within the polymer.

Relaxation modulus $E_r(t)$, a time-dependent elastic modulus for viscoelastic polymers, may be defined as

$$E_r(t) = \frac{\sigma(t)}{\epsilon_0}$$

where $\sigma(t)$ is the measured time-dependent stress and ϵ_0 is the strain level that is maintained constant. Moreover, relaxation modulus is a function of temperature, and to fully characterise the viscoelastic behavior of a polymer isothermal stress relaxation measurements must be conducted over different temperature ranges.

As most polymers exhibit both anelastic and viscous responses to external forces, models for such viscoelastic behavior consist of viscous and elastic elements. The spring illustrates purely elastic behavior and the dashpot purely viscous behavior.

(d) **Mechanical degradation** Some polymers degrade under mechanical stress. Polystyrene dissolved in a solvent when stirred vigorously undergoes molecular degradation or fragmentation. Similarly, rubber on being subjected to mechanical stress called mastication undergoes chain scission, leading to the formation of low-molecular-weight fragments.

Polymers also undergo degradation by ultrasonic waves, X-rays, gamma rays, alpha rays, beta rays and other high-energy radiations.

6.14 Polymer Composites

A composite material is a hybrid material formed by the combination of two or more dissimilar materials to produce a new material, having the advantageous properties of the different components. A composite material is better suited for a particular application than either of the original materials alone.

Modern technologies require materials of unusual combination of properties that cannot be met by the conventional polymeric materials, alloys, ceramics and cements. These materials can be combined in composite material to produce unique characteristics such as stiffness, toughness, high temperature strength. These types of materials find use particularly in aerospace, underwater and transportation applications. The composite materials comprise of two phases 'matrix', which is the continuous phase and the 'dispersed phase' or the reinforcing material.

The most common example of a composite material is the fibre-glass reinforced plastic. The plastic acts as the matrix and fibre glass is the dispersed phase. Plastic alone is relatively weak and has a low elastic modulus, that is, it bends and stretches easily. The glass fibres provide it strength and stiffness, and their modulus of elasticity may be 50 times greater than that of plastic alone. Glass fibres take most of the load when the composite is stressed.

Fibre-reinforced plastic (FRP) They are composites that contain fibre in the dispersed phase. The design goals of fibre reinforced composites often include high-strength and stiffness on a weight basis.

Glass-reinforced plastics (GRP) Glass-reinforced plastic is popularly known as 'fibreglass'. It is a composite material made of plastic material reinforced by fine glass fibres in the dispersed phase.

Properties

Dimensional stability Glass fibre exhibits dimensional stability. It does not stretch or shrink on exposure to extremely high or low temperatures.

Moisture resistance Glass fibres do not absorb moisture.

High strength They have high strength-to-weight ratio. This property makes them useful for applications in areas where high strength and minimum weight is required.

Fire resistance Being inorganic in nature, glass fibre does not burn or support combustion.

Chemical resistance They are chemically inert. However, they are affected by hydrofluoric acid, hot phosphoric acids and strong alkaline substances.

Electrical properties They have low dielectric constant. Glass fibres are excellent materials for electrical insulation.

Uses

The combination of properties such as low moisture absorption, high strength, heat resistance, chemical inertness and low dielectric constant makes glass fibres ideal polymers for a variety of end uses. They are mainly used in the aerospace industry for making high-performance aircraft (gliders), boats, automobiles, hot tubs, water tanks, baths, pipes, etc. They are used for making mats and fabrics for thermal insulation, electrical insulation, sound insulation, high-strength fabrics, heat- and corrosion-resistant fabrics. They are also used to reinforce various materials like translucent roofing panels and automobile bodies. GRP pipe systems are used over and under the ground for firewater system, drinking water system, gas system, waste water or sewage system.

GRPs are also used in construction of buildings and for producing chimneys. GRPs can be used to construct panels with appropriate insulation, which reduces heat loss.

Owing to their light weight characteristics, they are used for making helmets, sports use articles like goal tender masks or catches masks. Fibre glass also finds use in the telecommunication industry.

Manufacture methods The various techniques employed for the manufacture of reinforced plastics are

- (a) Hand lay-up technique
- (b) Filament winding technique
- (c) Spray lay-up technique
- (d) Pultrusion

(a) Hand lay-up technique

In this process, the mould used is coated with a thin coating of polyvinyl alcohol, silicone oil or wax to prevent the polymer from sticking to the mould. The resin matrix or plastic matrix is then put in the mould followed by glass mat or cloth. Then another layer of resin is put. These layers are then pressed with the help of rollers. Alternate layers of glass, cloth and resin are laid until the required thickness is built. The whole set up is then cured at ambient or elevated temperature. The reinforced plastic is then removed from the mould. It is finally trimmed and finished. This technique is used to produce auto body parts, boat hulls, ducts and building components.

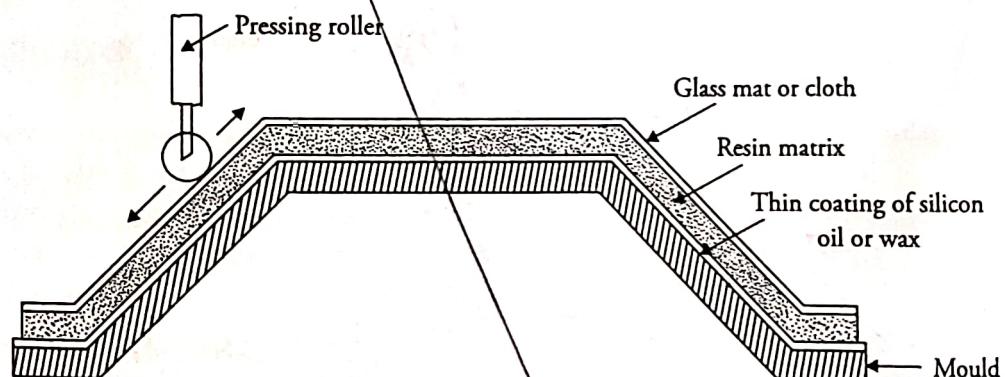


Figure 6.16 Schematic diagram of hand lay-up technique

(b) Filament winding technique

In this process, fibres are pulled from spindles and passed through a bath containing composite resin such as epoxy resin. The excess resin is squeezed out of the strand coming out of the resin

bath. The resin-dipped filament is wound onto a mandrel in some predetermined manner. Once the mandrel is uniformly covered to the desired thickness and fibre orientation, the composite is cured at an elevated temperature. The mandrel may be removed later or left as an integral part of the composite.

Filament winding is used for producing reinforced plastic articles such as corrosion-resistant (fibre glass) tanks, pipes and high-pressure cylinders. It is used to prepare composites for use in aerospace and automotive industry.



Figure 6.17 Schematic diagram of filament winding technique

(c) Spray lay up technique

In this technique, the resin, a curative, and the chopped fibres are sprayed simultaneously in a combined stream from a spray gun onto a mould. Once the desired thickness is achieved, it is compacted and then cured, cooled and removed from the reusable mould. Before application of fibre and resin, the mould is prepared with either polyvinylalcohol or non-silicon wax to facilitate the release of the product. This technique is used to produce reinforced plastic articles such as truck bodies, storage vessels, boat hulls, lorry, cabs, etc.

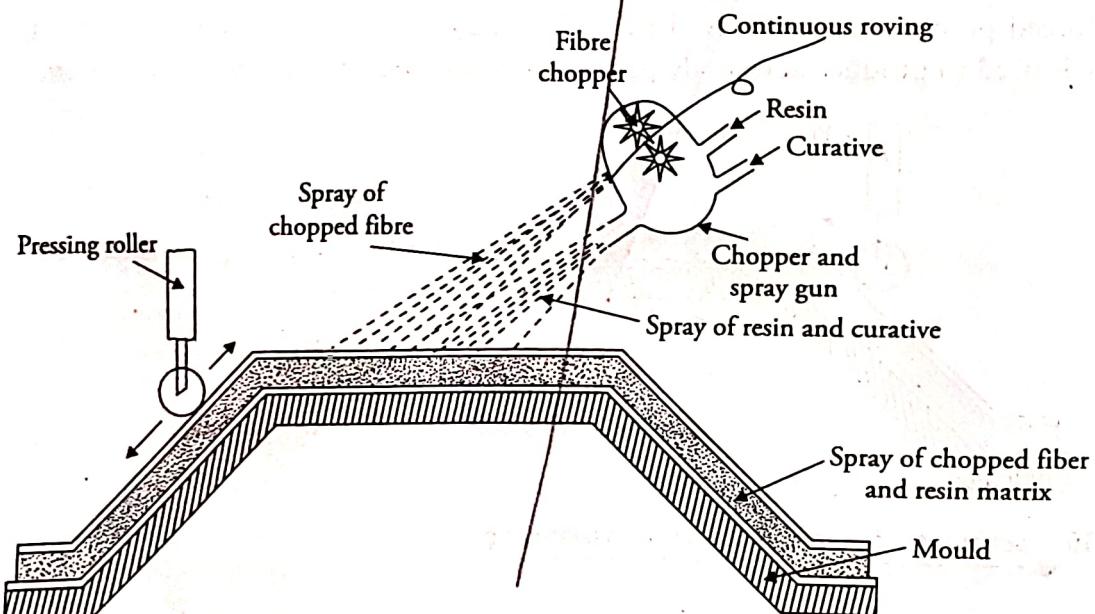


Figure 6.18 Schematic diagram of spray lay up technique

(d) Pultrusion

Pultrusion is the process for manufacture of composite materials with constant cross-section. It involves 'pulling' of raw material through a shaped die. The term pultrusion combines the words, 'pull' and 'extrusion'.

The pultrusion process starts with racks or creels holding rolls of fibre. This raw fibre is pulled off the racks and is guided through the resin bath. In some pultrusion systems, the resin is injected directly into the die.

The fibre becomes impregnated with the resin. The resin-impregnated fibre passes through the 'preformer' where the excess resin is squeezed out. The composite now passes through a heated steel die where the resin undergoes polymerisation. Initially, the die used was stationary but these days moving dies are also used. The cured pultruded fibre-reinforced polymer (FRP) composite then passes through the rollers. At the end of the pultruded machine is a cut off saw that cuts the fibres into specific length.

This technique is used for the manufacture of fibres used in agriculture, chemical industry, sports, etc.

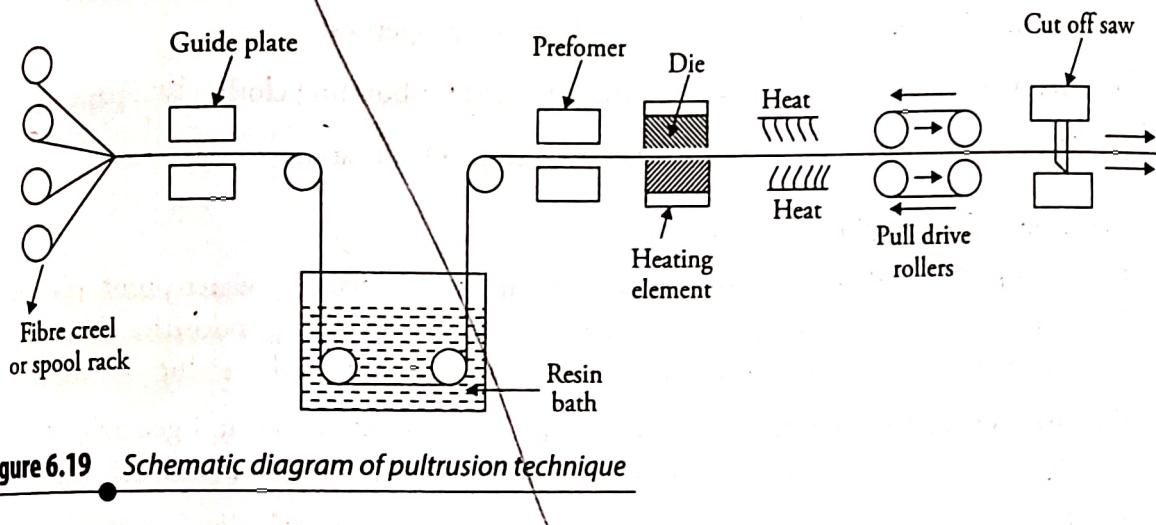


Figure 6.19 Schematic diagram of pultrusion technique

6.15 Adhesives

An adhesive is a substance, organic or inorganic, natural or synthetic, that is capable of bonding two or more substances together by surface attachment.

Adhesives are generally applied as a thin film between the surfaces to be joined, in either a plastic or liquid state and it gradually hardens due to the evaporation of the solvent, adhering the two surfaces together.

Adhesive is a general term and it includes cement, gum, glue, fevicol and paste.

Classification of Adhesives

Adhesives can be classified in various ways. A brief description of some important classes of adhesives based on their chemical nature is given as follows.

1. Natural resin adhesives

- (a) **Vegetable glues or protein glues** They are prepared from soyabean and corn. These include starch, gum, etc. They are used for common adhesive jobs like bonding paper.
- (b) **Animal glues** They are popular variety of protein glues that can be prepared from bones of dead animals, wastes of animals, fish, hide scrapes from leather industry, casein and blood albumin. These are used in furniture, radio cabinets, etc. Shellac resin obtained from an insect is one of the oldest adhesive. It possesses good strength and is to be applied when hot.
- (c) **Natural adhesive** Like asphalt, it is used for bonding paper, cloth and also for metal bonding.

2. Synthetic adhesives

(I) Thermoplastic resins

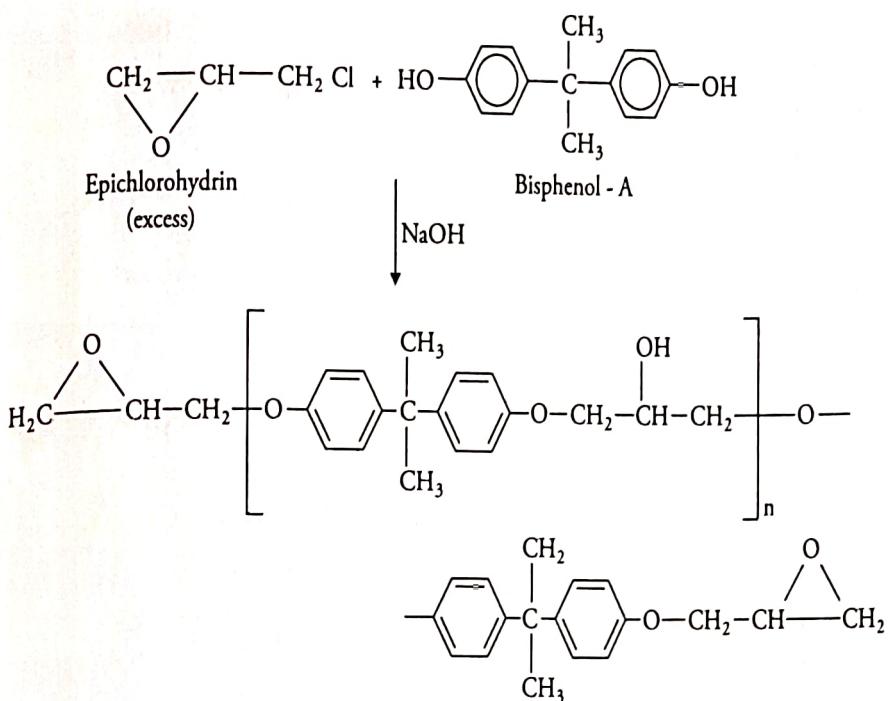
- (a) **Cellulose derivatives** Cellulose acetate and cellulose nitrate when mixed with benzene and alcohol, respectively, show excellent bonding properties.
- (b) **Acrylics** Like plexiglass (PMMA), they are used for bonding cloth, glass, paper, etc.
- (c) **Polyvinyls** Like PVA and PVC, they are also good adhesives.

(II) Thermosetting plastic resins

- (a) **Phenol formaldehyde resins** These are used for making water-proof plywood, laminates and for bonding articles in spacecraft and shipbuilding industries. The resin is applied between the two surfaces and then cured by heating and pressing.
- (b) **Urea formaldehyde resin** They are syrupy, transparent compound generally used as such or after mixing with water. End uses are similar to phenol formaldehyde resin.
- (c) **Polyesters** They work as good adhesives on being mixed with alkyd resins. They are employed for making laminated glass and cloth.
- (d) **Silicone resins** They are stable, water repellent used for bonding metals, ceramics, plastics, rubbers, etc.
- (e) **Epoxy resins** They have very good adhesion properties. They can be used in solid as well as liquid forms. The solvent evaporates leaving behind a very thin film that provides excellent adhesion. Araldite is a very good example of epoxy resin.

Preparation of epoxy resins

They are prepared from epichlorohydrin and bisphenol-A. The reaction is carried out with excess of epichlorohydrin.



Instead of Bisphenol-A, many other compounds with hydroxyl groups such as glycols, glycerols and resorcinols can also be used.

Uses

Epoxy resins have remarkable adhesion. When properly cured, they can yield very tough materials. They are used as adhesives for metals, glass and ceramics. They also find use in floor surfacing, wall panels, cements, mortars, rigid foams, matrix for stained glass windows, surface coatings on household appliances and gas storage vessels.

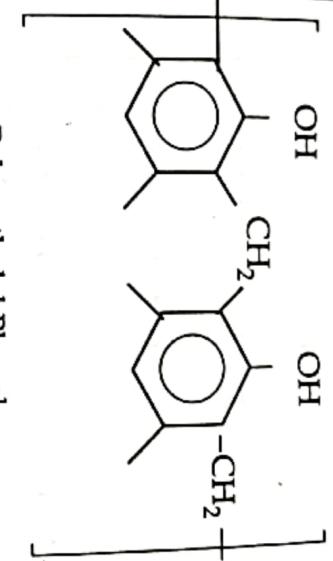
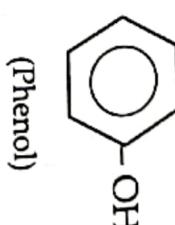
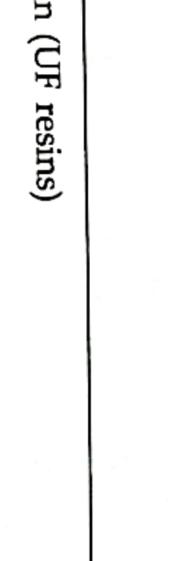
Summary

- Polymers are very-high-molecular-weight compounds formed by the combination of large number of small repeating units called monomers.
- Polymers are classified on the basis of their origin, monomer composition, chain structure, polymerisation mechanism, nature of molecular forces, tacticity and chemical composition.
- Polymerisation takes place by two mechanisms
 - (i) Addition polymerisation
 - (ii) Condensation polymerisation.
- Addition polymerisation consists of three steps: chain initiation, chain propagation and chain termination.
- Depending on the type of chain initiator, the addition polymerisation can be cationic (chain initiated by cation), anionic (chain initiator is an anion) or free radical polymerisation.

S.No.	Name of polymer	Structure of polymer	Important Applications	Monomer	Name of polymer	Structure of polymer	Important Applications
20.1 Structures and Industrial Applications of Important Thermoplastic Polymers							
1.	Polythene (PE)	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \\ \text{CH}_2=\text{CH}_2 \end{array}$	■ HDPE. As anti-corrosive packing material, insulator for wires and cables, household and laboratory wares [like toys, crates, closures, buckets, over head tanks, gas piping, milk bottles etc.]	$\begin{array}{c} \text{CH}_2-\text{C}(\text{Y})-\text{CH}_2 \\ \\ \text{X} \end{array}$	Vinyl Polymer	$\begin{array}{c} \text{CH}_2-\text{C}(\text{X})-\text{CH}_2 \\ \\ \text{X} \end{array}$	■ LDPE. As squeeze bottles for detergents, and wrapping material.
2.	Polypropylene (PP)	$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_3 \\ \\ \text{CH}_2=\text{CH} \end{array}$	As Disposabale syringes, Accelerator Pedals, boxes, car-bumpers, films for wrapping confectionery items, chairs etc.	$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_3 \\ \\ \text{CH}_2=\text{CH} \end{array}$	Polystyrene (PS)	$\begin{array}{c} \text{CH}_2-\text{CH}-\text{C}_6\text{H}_5 \\ \\ \text{CH}_2=\text{CH} \end{array}$	■ (In foamed form) as disposabale drinking cups, cushioned packaging and thermal insulation.
3.	Polystyrene (PS)	$\begin{array}{c} \text{CH}_2-\text{CH}-\text{C}_6\text{H}_5 \\ \\ \text{CH}_2=\text{CH} \end{array}$	■ In impact reinforced form as interliners of refriggerators and Radio/TV cabinets ; As raw material for preparation of synthetic ion exchange resins.	$\begin{array}{c} \text{CH}_2-\text{CH}-\text{C}_6\text{H}_5 \\ \\ \text{CH}_2=\text{CH} \end{array}$	Poly vinyl chloride (PVC)	$\begin{array}{c} \text{CH}_2-\text{CH}-\text{Cl} \\ \\ \text{CH}_2=\text{CH} \end{array}$	■ Rigid PVC. For making window frames, doors, bottles, safety helmets, pipes etc.
4.	Poly vinyl chloride (PVC)	$\begin{array}{c} \text{CH}_2-\text{CH}-\text{Cl} \\ \\ \text{CH}_2=\text{CH} \end{array}$	■ Plasticized PVC. For making kitchen upholstery, bathroon curtains, ladies hand bags and for insulation of domestic wires and cables.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}(\text{COOC}_2\text{H}_5)-\text{CH}_3 \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	Poly methyl methacrylate (PMMA)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}(\text{COOC}_2\text{H}_5)-\text{CH}_3 \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	■ Medical Applications. Dentures, hard contact lenses, artificial eyes.
5.	Poly methyl methacrylate (PMMA)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}(\text{COOC}_2\text{H}_5)-\text{CH}_3 \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	■ Automotive Applications. Housing for rear lamps, light fittings, etc.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}(\text{COOC}_2\text{H}_5)-\text{CH}_3 \\ \\ \text{COOC}_2\text{H}_5 \end{array}$			■ As substitute of glass. As plexiglass or Lucite for making TV screens, wind screens etc.

S.No.	Name of polymer	Structure of polymer	Monomer	Important Applications
6.	Polytetrafluoroethylene (PTFE) or Teflon	$\text{--}\text{CF}_2 - \text{CF}_2\text{--}_n$	$\text{CF}_2 = \text{CF}_2$ (Tetrafluoroethylene)	As insulating materials for transformers, cables, wires, fittings, etc., As non-stick coatings for frying pans, as gaskets and seals, for stop-cock of burettes.
7.	Nylon-6	$\left[\text{NH} - (\text{CH}_2)_5 - \text{C} \right]_n$	$\begin{array}{c} \text{H} \\ \\ \text{N} \\ \backslash \\ (\text{CH}_2)_5 \\ \text{C} = \text{O} \end{array}$ (Caprolactum)	In making tyre cords, ropes, fibres and plastics.
8.	Nylon-66	$\left[\begin{array}{c} \text{O} \\ \\ \text{C} - (\text{CH}_2)_4 - \text{C} \end{array} \right]_n$ $\text{NH} - (\text{CH}_2)_6 - \text{NH}$	$\text{HOOC} - (\text{CH}_2)_4 - \text{COOH}$ Adipic acid + $\text{H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2$ Hexamethylene diamine	As fibers : Automobile tyre cords, parachute ropes, threads and fibers for socks, under-garments, and carpets. As plastics : As metal substitute for gears and bearings, rollers, slides and door latches.
9.	Poly ethylene terephthalate (PET) or Terylene or Decron	$\left[\begin{array}{c} \text{O} \\ \\ \text{C} - \text{C}_6\text{H}_4 - \text{C} \end{array} \right]_n$ $\text{O} - \text{CH}_2 - \text{CH}_2 - \text{O}$	$\text{HOOC} - \text{C}_6\text{H}_4 - \text{COOH}$ Terephthalic acid + $\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH}$ Ethylene glycol	As plastics. For making bottles for cola drinks, magnetic recording tapes, Housings for coffee machines, toasters etc. As fibers : For polyester shirts and garments ; tyre cords, tents etc.
10.	Poly acrylonitrile (orlon)	$\left[\text{CH}_2 - \text{CH} \right]_n$ CN	$\text{CH}_2 = \text{CH}$ CN (Acrylonitrile)	For making synthetic fibers and synthetic wool.

20.2 Structures and Industrial Applications of Important Thermosetting Polymers

S.No.	Name of polymer	Structure of polymer	Monomer	Important applications
1.	Bakelite (PF resins)		HCHO (Formaldehyde) +  (Phenol)	<ul style="list-style-type: none"> ■ Electrical fittings : Switches, plugs, heater handles, switch boards. ■ As abrasive wheels, sand paper and brake linings. ■ As moulded objects : Cabinets for radio/TV, telephone and automobile parts. ■ As core binders in foundries (when mixed with sand). ■ For the manufacture of ion exchange resins for water softening.
2.	Urea formaldehyde resin (UF resins)		HCHO (Formaldehyde) + NH2CONH2 (Urea)	<ul style="list-style-type: none"> ■ As moulded articles : Vacuum flask cups ■ As adhesives : For plywood and laminating. ■ For the manufacture of cation exchange resins.

20.3 Structures and Industrial Applications of Important Elastomers

S.No.	Name of Polymer	Structure of Polymer	Monomer	Important Applications
1.	Styrene butadiene rubber (SBR or Buna-S)	$\left[-\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \overset{\text{C}_6\text{H}_5}{\underset{ }{\text{CH}}} - \text{CH}_2 \right]_n$	$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ (Butadiene) $+$ $\text{CH}_2 = \text{CH}$ $\overset{\text{C}_6\text{H}_5}{ }$ (Styrene)	In making footwear shoe soles and automobile tyres of lighter duty, for making hose, floor tiles, carpet backing.
2.	Nitrile rubber (Buna-N) (NBR or GR-A)	$\left[-\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \overset{\text{CN}}{\underset{ }{\text{CH}}} - \text{CH}_2 \right]_n$	$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ (Butadiene) $+$ $\text{CH}_2 = \text{CH}$ $\overset{\text{CN}}{ }$	For manufacture of hoses and tank linings. In making oil seals, gasoline hoses, gaskets, fuel tanks etc.
3.	Butyl rubber (GR-I)	$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2 - \overset{\text{CH}_3}{\underset{ }{\text{C}}} - \text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2 - \end{array} \right]_n$	$\text{CH}_2 = \text{C}(\text{CH}_3)_2$ (Isobutene) $+$ $\text{CH}_2 = \text{C} - \overset{\text{CH}_3}{\underset{ }{\text{CH}}} = \text{CH}_2$ (Isoprene)	For making inner tubes of tires, for wire and cable insulation, and for lining of tanks, hoses etc.