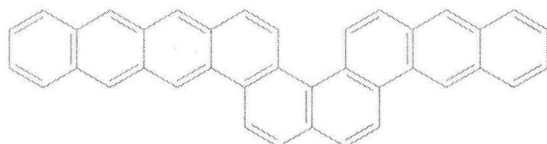


## PROLOGUE

- Importance of Polymers
- Monomers and Repeat Units
- Degree of Polymerisation
- Classification of Polymers
- Polymerisation
- Co-polymerisation
- Types of Co-polymers
- Polymer Reactions
- Polymerisation in Homogeneous and Heterogeneous systems
- Miscellaneous Polymerisation



## ▶ IMPORTANCE OF POLYMERS

The polymers are complex, giant, high molecular weight macromolecules formed by the combination of a large number of one or more type of small molecules of low molecular weight. The word **polymer** implies 'many part' (Greek : poly means 'many' and mer means 'part'). All the substances referred to as polymers, are big molecules with molar masses ranging from several thousands to several millions.

The term polymer is not new for human beings, infact it is 4 billion years ago since the formation of the earth was over. The origin of life was occurred by a polymer 'protein'. Protein is a complex molecule formed by the combination of elements like carbon, hydrogen, oxygen and nitrogen which were present on the earth. Almost the whole human body was built around the same polymer.

Polymers had also appeared in their other natural forms like wood, cellulose, starch, cotton, glue, rubber etc. The term rubber was coined by **Joseph Priestley** who discovered that this material would rub out or erase pencil marks. Although rubber was probably used as early as the eleventh century and the rapid growth of rubber industry led to the development of plantation rubber in 1876.

A Swiss scientist *Christian Schonbein* discovered a nitro derivative of a naturally occurring polymer 'cellulose' while working with a mixture of nitric acid and sulphuric acid.

During the experiment the glass beaker broken down, he mop up the mixture with a cotton cloth and left it for drying near a fire-place. The cotton cloth soon caught fire because of formation of 'gun cotton', a nitro derivative of cellulose.

In nineteenth century, elephant tusk, *i.e.*, ivory was used for making billiard balls. An American scientist *John Wesley Hyatt* invented a new polymer 'celluloid', resembled with ivory. This discovery has become a major invention contributing to our present 'plastic age'.

In 1909, *Leo Baekeland* developed a resin from phenol and formaldehyde which was named as 'Bakelite'.

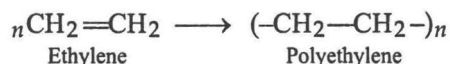
In 1912, *Jacques Brandenburger* discovered a transparent polymer 'cellophane'. Within a decade, several polymers were started appearing in newer forms with increasingly advanced properties. Most of the synthetic polymers are of a relatively recent origin.

Polymers are the chief products of modern chemical industry which form the backbone of present society. They have become so much a part of our daily life that it appears almost impossible that we could ever do without them. The materials made of polymers find multifarious uses and applications in all walks of our society. Common examples of these include plastic dishes, cups, non-stick pans, kitchen utensils, plastic pipes and fittings, plastic bags, rain coats, automobile tyres, seat covers, TV, radio, computer, transistor, cabinets, synthetic fibres, flooring materials, materials for biomedical and surgical operations, synthetic glues, telephone, mobile and other electrical components, light elegant plastic luggage, colourful plastic chairs and tables, etc.

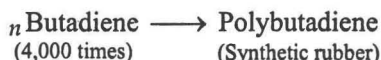
Polymers are the compounds of light weight, high strength, flexible, chemical resistant with special electrical properties. Polymers can be converted into an attractive choice of wide variety of colours, strong solid articles, transparent glass like sheets, flexible rubber-like materials, soft foams, smooth and fine fibres, jelly-like food materials etc. Polymers can be used to seal joints, bear loads, fill cavities, jerk resistant in between glasswares, and bond objects. Today the polymers are enriching the quality of human life.

## ♦ MONOMERS AND REPEAT UNITS

A polymer is made up of many small molecules which have combined to form a single large molecule. The individual small molecules which constitute the repeating units in a polymer are known as *monomers* (means, 'single parts'). The process by which the monomer molecules are linked to form a big polymer molecule is called '*polymerisation*'. For example, polyethylene is a polymer which is obtained by the polymerisation of ethylene. The ethylene molecules are referred to as monomer units.



Similarly, Butadiene is a gaseous compound, with a molecular weight of 54. It combines about 4000 times and forms a polymer known as polybutadiene, with about 2,00,000 molecular weight.

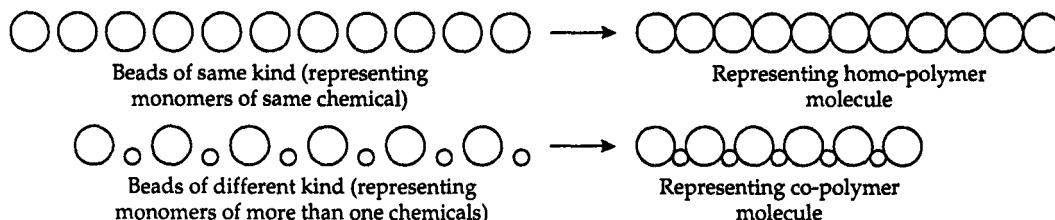


Polymers are divided into two broad categories depending upon the nature of the repeating units. These are :

- (1) Homopolymers
- (2) Copolymers (mixed polymers)

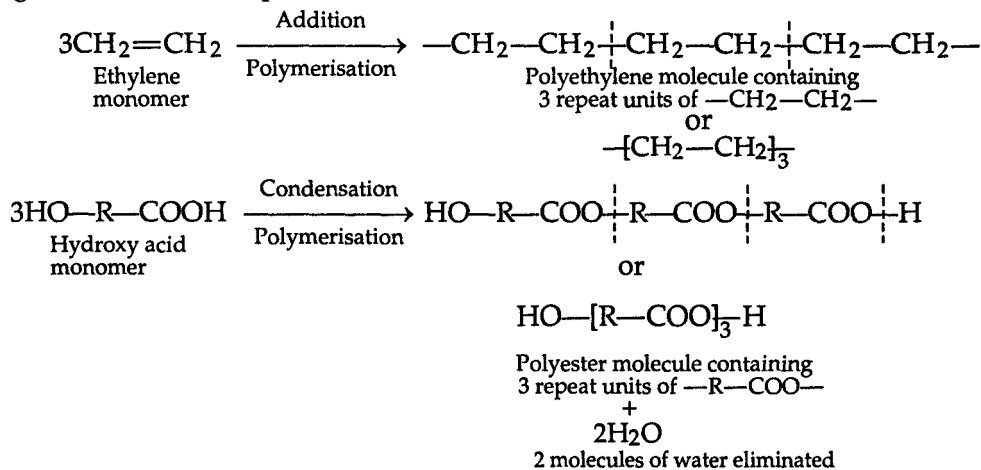
The polymer formed from one kind of monomers is called *homopolymers*. For example, *polyethylene* is an example of *homopolymer*.

The polymer formed from more than one kind of monomer units is called *co-polymer* or *mixed polymer*. For example, Buna-S rubber which is formed from 1, 3-butadiene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ ) and styrene ( $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ ) is an example of co-polymer.



As it is stated earlier that polymerisation is possible with molecules of same or of different monomeric compounds. When molecules just add and form the polymer, the process is called *addition polymerisation*. In this case the monomer units retain their structural identity when it gets transformed into a polymer. For example, the molecule of ethylene monomer can undergo addition polymerisation and form polyethylene, in which the structural identity of ethylene is retained.

When the two monomers (of the same or different molecules) link with each other by the elimination of a small molecule, such as water or methyl alcohol, as a by-product to form a polymer, the process is called *condensation polymerisation*. The condensation takes place between two reactive functional groups, like the carboxyl group ( $-\text{COOH}$ ) of an acid and the hydroxy group ( $-\text{OH}$ ) of an alcohol. It is, therefore, observed that in '**addition polymerisation**' the molecular weight of the polymer is almost equal to that of all the molecules which combine to form the polymer, while in '**condensation polymerisation**' the molecular weight of the polymer is lesser than the weight of the simple molecules eliminated during the condensation process.



## ▶ DEGREE OF POLYMERISATION

In polymerisation reactions, the polymer molecule formed contains a structural identity, repeating itself several times. These repeating entities are called the repeat units of the polymer molecule. The size of the polymer molecule is decided by the number of repeat units present in it. This number is called the '*degree of polymerisation*'. For example, in above case (last page), 3 monomers of ethylene molecule can add onto each other to form a single molecule of polyethylene. Here the polyethylene molecule contains  $3\text{—CH}_2\text{—CH}_2\text{—}$  repeat units, hence, the degree of polymerisation is 3.

Similarly, in other case, 3 molecules of a hydroxy acid ( $\text{HO—R—COOH}$ ) undergo condensation polymerisation reaction and form a polyester molecule. Here, the 3-repeat units will be  $\text{—R—COO—}$ . Hence, the degree of polymerisation is 3.

## ▶ CLASSIFICATION OF POLYMERS

Polymers are classified in a number of ways :

- (1) On the basis of source or origin
- (2) On the basis of structure
- (3) On the basis of mode of synthesis
- (4) On the basis of interparticle forces.

### (1) Classification of Polymers Based upon Origin or Source

On the basis of origin or source, the polymers are classified into two types :

- (a) Natural Polymers                      (b) Synthetic Polymers

(a) **Natural Polymers** : The polymers, which are isolated from natural materials, mostly plants and animal sources, are called natural polymers. A few examples are :

- (i) **Polysaccharides** : Starch and cellulose are very common examples of polysaccharides. They are the polymers of glucose. Starch is a chief food reserve of plants while cellulose is chief structural material of plants.
- (ii) **Proteins** : These are polymers of  $\alpha$ -amino acids. They are building blocks of animal cells. They constitute indispensable part of our food. Natural protein, wool, leather, etc., are proteins.
- (iii) **Nucleic Acids** : These are the polymers of various nucleotides. RNA and DNA are common examples.
- (iv) **Natural Rubber** : Substance obtained from latex is known as natural rubber. It is a polymer of 2-methyl-1, 3-butadiene (isoprene).

**Biopolymers** : It may be noted that polymers like polysaccharides, proteins nucleic acids, etc., which control different life processes in plants and animals are also called biopolymers.

(b) **Synthetic Polymers** : The polymers which are prepared in the laboratory are referred to as synthetic polymers or man-made polymers. Some examples of synthetic polymers are polyethylene, polystyrene, teflon, PVC, synthetic rubber, nylon, bakelite, orlon, polyester, terylene etc.

## (2) Classification of Polymers Based on Structure

This classification of polymers is based upon how the monomeric units are linked together. Based on their structure, the polymers are classified as :

- (a) Linear Polymers
- (b) Branched Chain Polymers
- (c) Cross-linked Polymers or Network Polymers

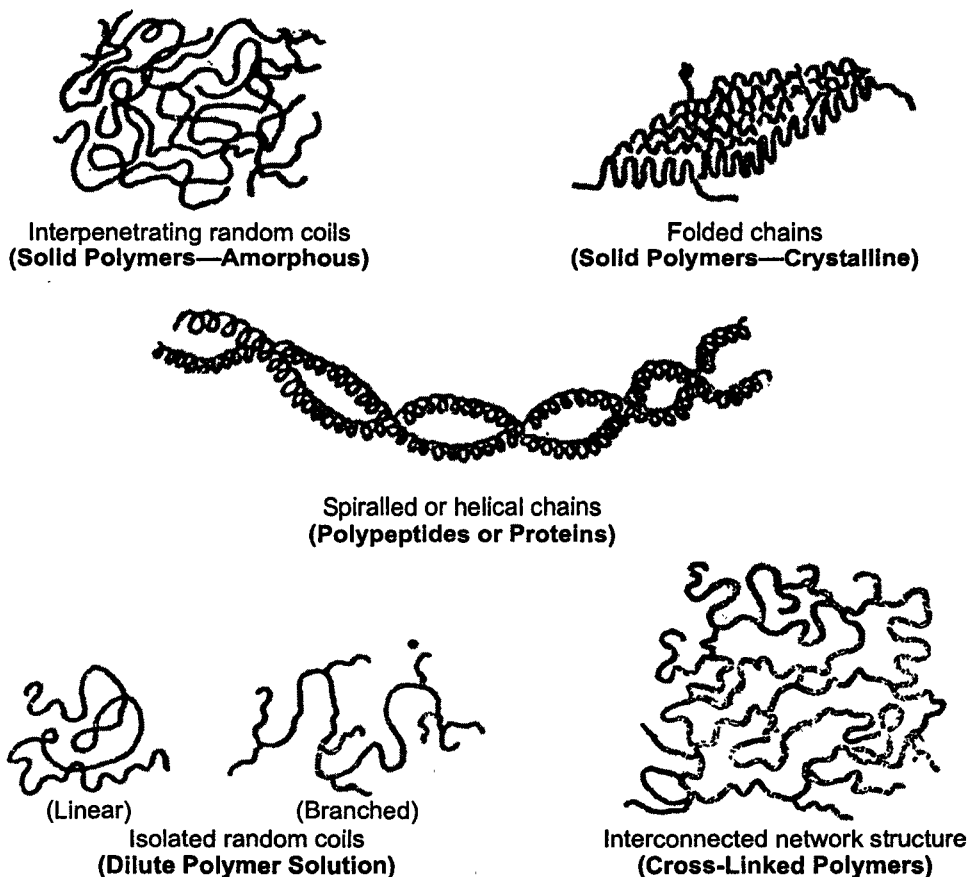


Fig. 1. Representative conformations of polymer molecules under different situations.

(a) **Linear Polymers** : These are the polymers where monomeric units are linked together to form long straight chains. The polymeric chains are stacked over one another to give a well packed structure. As a result of close packing, such polymers have high densities, high tensile strength and high melting points. Common examples of these type of polymers are polyethylene, polyester and nylon etc.

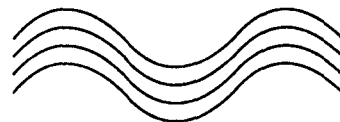


Fig. 2. Linear chain.

(b) **Branched Chain Polymers** : In this type of polymers, the monomeric units are linked to constitute long chains, which are also called main-chain. There are side chains of different lengths which constitute branches. Branched chain polymers are



Fig. 3. Branched chain.

irregularly packed and thus, they have low density, lower tensile strength and lower melting points as compared to linear polymers. Amylopectin and glycogen are common examples of such type.

(c) **Cross-Linked Polymers or Network Polymers** : In this type of polymers, the monomeric units are linked together to constitute a three dimensional network. The links involved are called cross links. Cross-linked polymers are hard, rigid and brittle because of their network structure. Common examples of this type of polymers are bakelite, formaldehyde resin, melamine, etc.

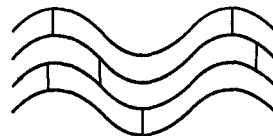


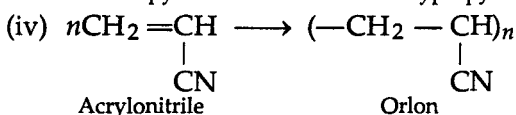
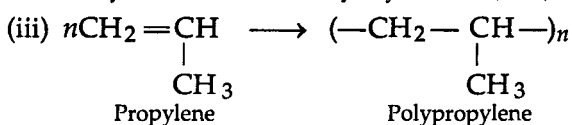
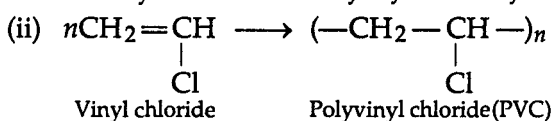
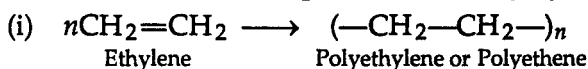
Fig. 4. Cross-linked chain.

### (3) Classification of Polymers Based on Synthesis

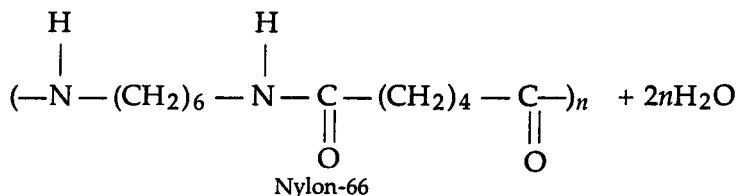
On the basis of the mode of synthesis, the polymers are classified as :

(a) Addition Polymers                      (b) Condensation Polymers

(a) **Addition Polymers** : When the monomer units are repeatedly added to form long chains without the elimination of any by-product molecules, the product formed is called addition polymer and the process involved is called addition polymerisation. The monomer units are unsaturated compounds and are usually of alkenes. The molecular formula and hence the molecular mass of the addition polymer is an integral multiple of that of the monomer units. A few examples of addition polymerisation are :

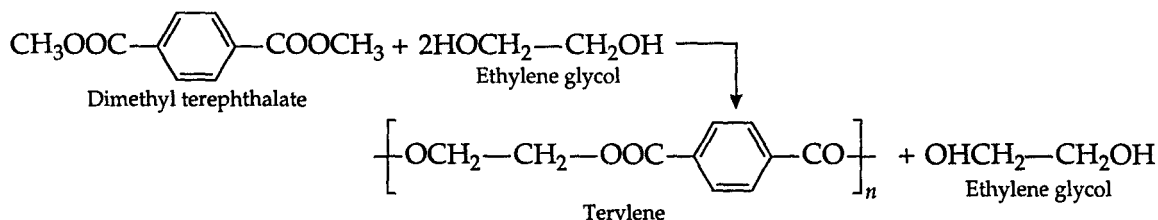


(b) **Condensation Polymers** : In this type of polymers, the monomers react together with the elimination of a simple molecule like H<sub>2</sub>O, NH<sub>3</sub> or ROH, etc. The reaction is called condensation and the product formed is called condensation polymer. As the process involves the elimination of by-product molecules, the molecular mass of the polymer is not the integral multiple of the monomer units. For example, nylon-66 is a condensation polymer of hexamethylene diamine and adipic acid.

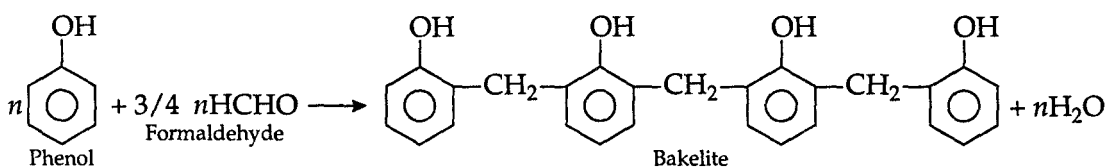


Some other examples of condensation polymers are :

**Dacron or Terylene (Polyester) :** It is a polyester fibre, made by the esterification of terephthalic acid with ethylene glycol. In England, it is known as terylene, whereas in U.S.A. it is called decron.



**Bakelite :** It is a polymer of phenol and formaldehyde.

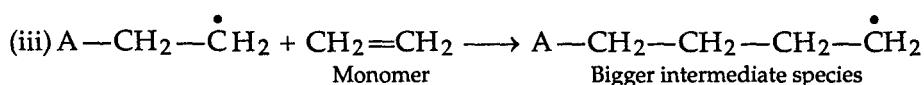
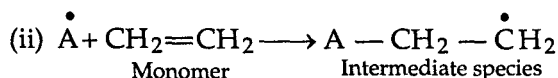
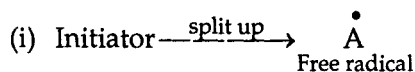


## ◆ CHAIN GROWTH AND STEP GROWTH POLYMERS

Many times, it becomes difficult to find out whether the polymerisation has occurred through condensation or through addition. Therefore, a more rational classification has recently been proposed according to the mechanism of combination of monomer units. According to this system, there are two types of polymers observed which are :

(a) Chain Growth Polymers      (b) Step Growth Polymers

**(a) Chain Growth Polymers :** Chain growth polymerisation is a process of successive addition of monomer units to the growing chain by a chain mechanism. The monomer unit gets converted to some active intermediate species by a small amount of initiator such as organic peroxide or an acid or a base. Depending upon the conditions, the intermediate species may be free radical or an ion, and it reacts with other monomer unit to form still bigger intermediate species. The monomer units are, thus, successively added to intermediate species by a chain process. The chain growth polymerisation of ethene involving free radical initiation is given below :

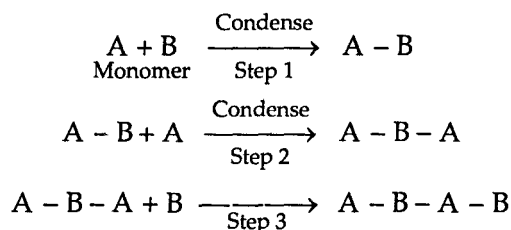


A chain propagation is, thus, set up which results in the growth of the chain by repeated addition of monomer units. The polymers formed by chain growth polymerisation are called chain growth polymers. Addition polymers are generally formed by this process.

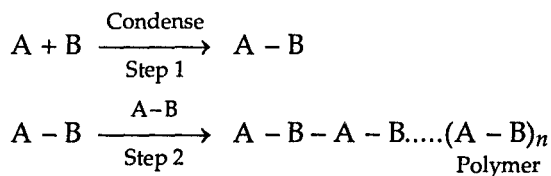
Some examples of chain growth polymers are :

Polyethylene, polyisoprene, polypropylene, teflon, etc.

**(b) Step-Growth Polymers :** As the name suggests, the step growth polymerisation involves stepwise intermolecular condensation, taking place through a series of independent reactions. Each reaction involves a condensation process involving the loss of a simple molecule like  $H_2O$ ,  $NH_3$ ,  $HCl$ ,  $ROH$  etc. This type of polymerisation occurs if the monomer molecules have more than one similar or dissimilar functional groups. The step growth polymerisation starting with two monomers A and B as :



The stepwise process of chain growth thus goes on. This process can also occur in another way :



The polymers formed by step growth polymerisation are called step growth polymers. The condensation polymers like nylon, bakelite, dacron are formed by this type of polymerisation.

## (1) Classification of Polymers Based on Inter Particle Forces

The mechanical properties of polymers such as elasticity, tensile strength, toughness, etc., depend upon intermolecular forces like Vanderwaal's force and hydrogen bonds existing in the macromolecules. Although these intermolecular forces are found in simple molecules also, but their effect is less significant in them as compared to that in macromolecules. It is because of the fact, that in polymers there is combined effect of these forces all along the long chains. Obviously, longer the chain, more intense is the effect of intermolecular forces.

On the basis of the magnitude of intermolecular forces, the polymers have been classified into the following four categories :

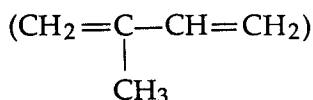
- (a) Elastomers
- (b) Fibers
- (c) Thermoplastics
- (d) Thermosetting Polymers

**(a) Elastomers :** These are the polymers in which the polymer chains are held up by weakest attractive forces. They are amorphous polymers having high degree of elasticity.



The weak forces permit the polymer to be stretched out about ten times their normal length but they return to their original position when the stretching forces is withdrawn. In fact, these polymers consist of randomly coiled molecular chains having few cross links. When the stress is applied, these randomly cross chains straighten out and the polymer gets stretched. As soon as the stretching force is released, the polymer regain the original shape because weak forces do not allow the polymer to remain in the stretched form.

The best known elastomer is rubber, whether synthetic or natural. The elasticity of such polymers can be further modified by introducing few cross-links between the chains. For example, natural rubber, a gummy material, has a poor elasticity. It is a polymer of isoprene



In 1839, *Charles Goodyear* discovered that heating gummy rubber with sulphur produced a material which was no longer sticky but had modified elasticity. Such a material was called **vulcanized rubber**. Vulcanization of natural rubber introduces sulphur cross-links which help to align the polymer chains in such a way so that the material does not undergo a permanent change when stretched, but springs back to original shape and size after the stress is removed.

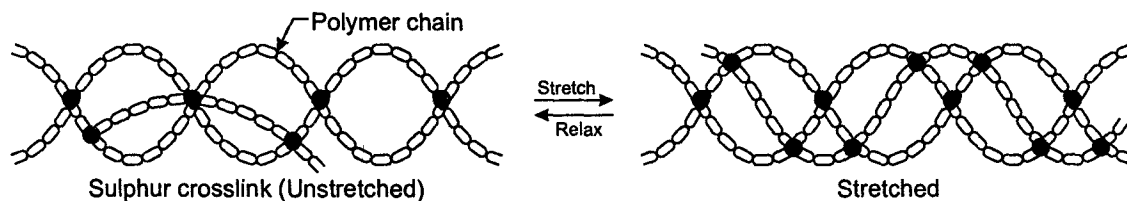
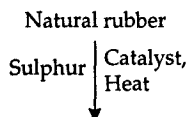
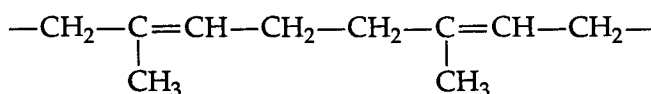
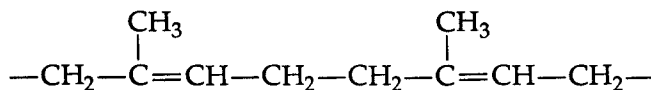
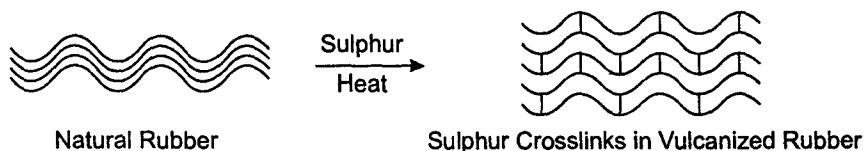


Fig. 5.

The cross-links of sulphur in isoprene units in vulcanised rubber have been shown below :



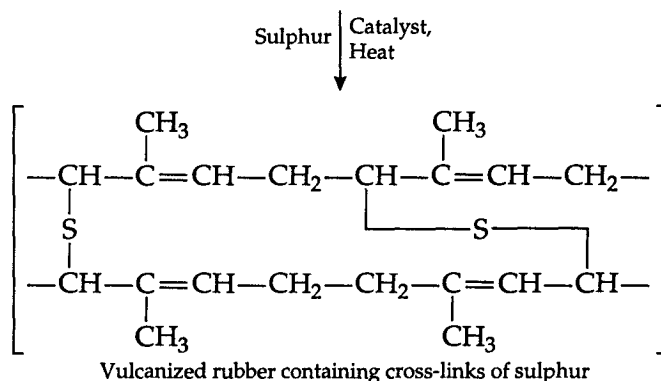
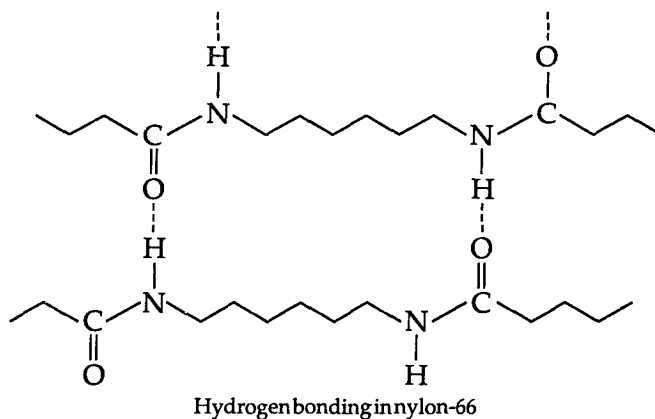


Fig. 6.

(b) **Fibers** : These are the polymers which have quite strong interparticle forces such as Hydrogen-bonds. They have high modulus and high tensile strength. These are thread-like polymers and can be woven into fabrics. Silk, terylene, nylon, etc., are some common examples of such types of polymers. The H-bonds in nylon-66 are shown below :



(c) **Thermoplastics** : These are the polymers in which the interparticle forces of attraction are in between those of elastomers and fibers. The polymers can be easily moulded into desired shapes by heating and subsequent cooling to room temperature. There is no cross-linking between the polymer chains. In fact, thermoplastic polymers soften on heating and becomes fluids, but on cooling they become hard. They are capable of undergoing such reversible changes on heating and cooling repeatedly. A few examples of thermoplastics are polyethylene, polystyrene, PVC, etc.

**Plasticizers** : Some plastics do not soften to workable extent on heating. Such plastics easily softened by the addition of some organic compounds which are known as plasticizers. For example PVC, *i.e.*, poly vinyl chloride is extremely stiff even while hot. However, addition of di-*n*-butylphthalate, a plasticizer, makes it soft and workable.

(d) **Thermosetting Polymers** : These are the polymers which become hard and infusible on heating. They are normally made from semi-fluid substances with low molecular masses, by heating in mould. Heating results in excessive cross-linking between the chains forming three dimensional network of bonds as a consequence of which a

non-fusible and insoluble hard material is produced. Bakelite is a common example of thermosetting polymer.

A thermoplastic material can be remelted without any change, while a thermosetting material undergoes a permanent change upon melting and thereafter sets to a solid which can not be remelted.

## ♦ NOMENCLATURE OF POLYMERS

### Standardized Polymer Nomenclature

There are multiple conventions for naming polymer substances. Many commonly used polymers, such as those found in consumer products, are referred to by a *common* or *trivial* name. The trivial name is assigned based on historical precedent or popular usage rather than a standardized naming convention. Both the **American Chemical Society** and **IUPAC** have proposed standardized naming conventions; the **ACS** and **IUPAC** conventions are similar but not identical. Examples of the difference between the various naming conventions are given in the table below :

Common Name	ACS Name	IUPAC Name
Poly (ethylene oxide) or (PEO)	poly(oxyethylene)	poly(oxyethylene)
Poly (ethylene terephthalate) or (PET)	poly (oxy-1, 2-ethanediyloxycarbonyl-1, 4-phenylenecarbonyl)	poly (oxyethyleneoxyterephth=aloyl)
Nylon	poly[imino(1-oxo-1, 6-hexanediy)]	poly[imino(1-oxohexane-1, 6-diy)]

For naming a polymer, a wide variety of trade names are commonly used which are based on its source. In addition (polymers, the prefix poly is attached to the name of the monomer, and so polyethylene, polystyrene, polyacrylonitrile denote polymers prepared from these single monomers.

When the monomer has a substituted parent name or has a multi-worded name then this is enclosed in parentheses and prefixed with poly, *e.g.*, poly (methylmethacrylate), poly(ethylene oxide), poly (vinyl chloride), etc.

If the polymer is prepared by self-condensation of a single monomer such as  $\omega$ -amino lauric acid, are named in a similar way, but this polymer, poly ( $\omega$ -amino lauric acid), can also be prepared by a ring-opening reaction using lauryl lactum and then be called poly (lauryl lactam). Both the names are correct.

IUPAC has suggested the nomenclature of single-stranded, regular, organic polymers and has proposed the procedures as follows :

- (1) In first step, select a constitutional repeat unit, CRU, which may consist of one or more subunits. The name of the polymer is then the name of the CRU, in parentheses prefixed by poly.
- (2) Before naming CRU, it must be orientated correctly. This involves placing the constituent parts in order of seniority with the highest to the left. In descending order this would be heterocyclic rings, chains with hetero atoms, carbocyclic rings and chains with only carbon atoms, if such an order is possible chemically. Thus