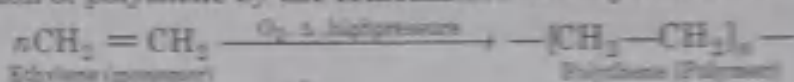


(A) Polymer

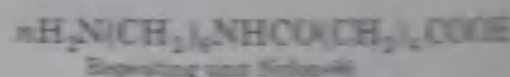
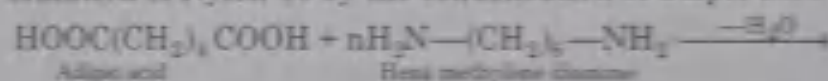
Polymers are the compounds of very high molecular mass. These are formed by the combination of a large number of simple molecules. The individual small and simple molecules which combine to give polymer are called monomers. The process by which the simple molecules (monomers) are converted into polymers is called polymerisation. Polymers occupy a very important place in our daily life. A number of articles of daily use like toys, bottles, T.V. Cabinet, cloth etc. are prepared from polymers. Polyethylene, polystyrene, nylon, teflon, terylene etc. are all synthetic polymers. In addition to synthetic polymers, they are found in nature also. Some of them are starch, cellulose, protein, rubber, DNA and RNA etc.

The main credit for the preparation of polymers goes to W.H. Carother. According to Carother polymerisation is the reaction in which molecules of one or more substance react with each other. For example,

- (i) Formation of polythene by the combination of ethylene molecules



- (ii) Formation of Nylon-66 by the condensation of adipic acid with 1, 6-diamino n-hexane

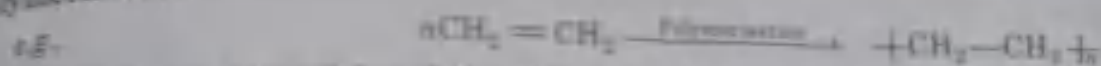


The polymerisation is possible with molecules of the same or of different monomer compounds. When molecules just add on to form the polymer, the process is called **addition polymerisation**. The monomer species in this case retains its structural identity when it is converted into a polymer. For example, the molecules of ethylene monomer can add on to form polythene, in which the structural identity of ethylene is retained.

However, when molecules do not just add on but also undergo some reaction in forming the polymer the process is called **condensation polymerisation**. Here, the two molecules of the same or different monomers condense to form a polymer. The condensation takes place between two reactive functional groups, like the carboxyl group of an acid and the hydroxy group of an alcohol. However, during the formation of polymer, water molecules also get eliminated.

Therefore, we can see that in addition polymerisation, the molecular weight of the polymer is roughly 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 by the weight of the simple molecules eliminated during the condensation process.

The number of times a repeat unit is contained in the polymer molecule is called degree of polymerisation.



In this case repeat unit is $\text{---CH}_2\text{---CH}_2\text{---}$. Which is repeated over and over again to produce the polymer, n denotes the degree of polymerisation. Usually, n is very large, of the order of a few thousands or tens of thousands.

It is essentially the 'giantness' of the size of the polymer molecule that makes its behaviour different from that of a commonly known chemical compound.

For example, solid benzene melts to become liquid benzene at 5.5°C and, on further heating boils into gaseous benzene. As against this well defined behaviour of a simple chemical compound, a polymer like polyethylene does not melt sharply at one particular temperature into a clean liquid. Instead, it becomes increasingly softer and ultimately, turns into a very viscous, tacky molten mass. Further heating of this hot, viscous, molten polymer does convert it into various gases but they are no longer polythene.

Another difference between the behaviour of a polymer and that of a low molecular weight compound concerns their solubility pattern. For example, when sodium chloride (low molecular weight compound) added in a fixed quantity of water, it dissolves in water up to a saturation point but thereafter, any further quantity added does not go into solution but settles at the bottom and just remains there as solid. The viscosity of the saturated salt solution is not very much different from that of water. But if the polymer say polyvinyl alcohol is added to a fixed quantity of water, the polymer does not go into solution immediately. The globules of polyvinyl alcohol first absorb water, swell and get distorted in shape and after a long time go into solution.

We can add a very large quantity of a polymer to the same quantity of water without the saturation point ever being reached. As more and more quantity of the polymer is added to water, the time taken for the dissolution of the polymer increases. One more difference is that, in water, polyvinyl alcohol never retains its original powdery nature as the excess sodium-chloride does in a saturated salt solution.

Classification of Polymers

Polymer is a generic name given to a vast number of materials of high molecular weight. Polymers can have different chemical structures, physical properties, mechanical behaviour, thermal characteristics, etc. and can be classified in different ways.

Depending upon the source from which they are obtained, polymer are broadly divided into two classes.

1. Natural polymers

2. Synthetic polymers.

1. Natural Polymers

Such polymers are obtained from animals and plants. Starch, cellulose, proteins, nucleic acids and natural rubber are some examples of natural polymers.

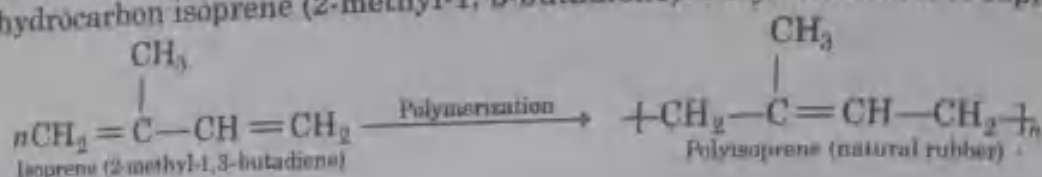
Starch : It is a polymer of α -glucose. It is the chief food reserve of the plants and is made up of two fractions amylose and amylopectin. Amylose is a linear polymer of α -glucose and amylopectin is a branched polymer of α -glucose.

Cellulose : It is a polymer of β -glucose. It is the chief structural material of the plants and is obtained from wood and cotton. About 50% of wood is cellulose. Cotton contains about 90-95% cellulose.

Both starch and cellulose are made by plants from glucose produced during photosynthesis.

Proteins : Proteins are polypeptides or polyamides. These polymers contain a large number of α -amino acids joined together through peptide bonds (NH—CO) in a particular sequence. These are either long chain or crossed linked polymers.

Natural rubber : Natural rubber is prepared from latex (obtained from rubber trees). It is a polymer of the hydrocarbon isoprene (2-methyl-1, 3-butadiene). Polymerization is represented as



2. Synthetic Polymers

Polymers which are made in the laboratory or in the industry are called synthetic polymers. Natural fibres such as cotton, wool, silk etc, can not meet the increasing demands. Natural rubber swells and loses elasticity after prolonged exposure to petrol and motor oil. All these needs led man to synthesize polymers in laboratory and industry. These man-made polymers are called synthetic polymers. Polyethylene, polystyrene, polyvinyl chloride, nylon, dacron and bakelite are some important synthetic polymers.

On the basis of structure, polymers are classified into three types :

1. Linear polymers
2. Branched chain polymers
3. Three-dimensional network polymers.

1. Linear Polymers : When the monomers are joined together to form long straight chains of polymer molecules, **linear polymers** are formed. The various polymeric chains are then stacked over one another to give a well packed structure as shown in Fig. (a). These polymers have high melting points, high densities and high tensile strength because of close packing of chains. Nylon and polyesters are the examples of linear polymers.



Fig. (a)

2. Branched Chain polymers : When the monomers units not only combine to form the linear chain but also form branches along the main chain, then **branched chain polymers** are formed as shown in fig. (b). These polymer molecules do not pack well because of branches. Due to this reason branched chain polymers have lower melting points, densities and tensile strength in comparison to linear polymers. For example low density polythene.



Fig. (b)

3. Three-dimensional Network Polymers : In such polymers, the linear chains formed initially are joined together to form a three dimensional network structure as shown in Fig. (c). Due to the presence of crosslinks, these polymers are also called **crosslinked polymers**.

These polymers are hard, rigid and brittle. Bakelite, urea-formaldehyde polymer and melamine formaldehyde polymer are the examples of three-dimensional network polymers.

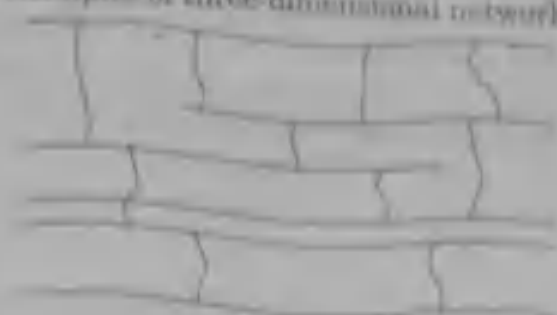


Fig. 10)

Different Types of Polymers

Polymers involving a wide variety of materials having different characteristics. Some of them are as follows:

(i) **Thermoplastics** : Such polymers are linear in shape and hard at room temperature, become soft and viscous on heating and again become hard and rigid on cooling. In these polymers, the intermolecular forces of attraction are the intermediate those of elastomers and fibres. The process of softening and cooling can be repeated as many times so that these plastics can be moulded into toys, buckets, telephone and television cases, etc.

Thermoplastics have some or no cross linking thus the individual polymer chains can slip on one another on heating. Polythene, polystyrene, polyvinyl chloride, teflon, polyvinyl acetate, acrylonitrile are some examples of thermoplastics.

These plastics which do not soften easily on heating can be made soft by the addition of certain specific compound called plasticizers. The commonly used plasticizers are Dialkylphthalates or organo phosphates.

(ii) **Elastomers** : The polymers, in which the intermolecular forces of attraction between the polymer chains are weakest are called elastomers. Elastomers are amorphous polymers having high degree of elasticity. These polymers consist of randomly coiled molecular chains of irregular shape having a few cross links. The coiled chains are opened when the force is applied and the polymer is stretched. Since the Vander Waal's forces of attraction between the polymer chains are very weak, these cannot maintain this stretched form. Therefore, as soon as the force is withdrawn, the polymer chains return to its original coiled state. They have the ability to stretch out many times their normal length and return to original position when the force is withdrawn. Thus, we observe that weak vander Waal's forces of attraction allow the polymer chains to be stretched on applying the force but the cross links bring the polymer back to the original position when the force is withdrawn. Natural rubber is an important example of natural polymer. Unstretched and stretched forms of elastomer are shown in the following figure.

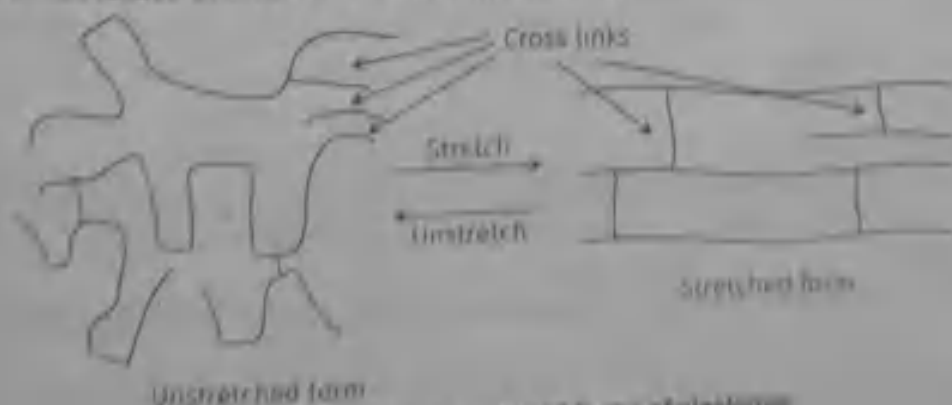
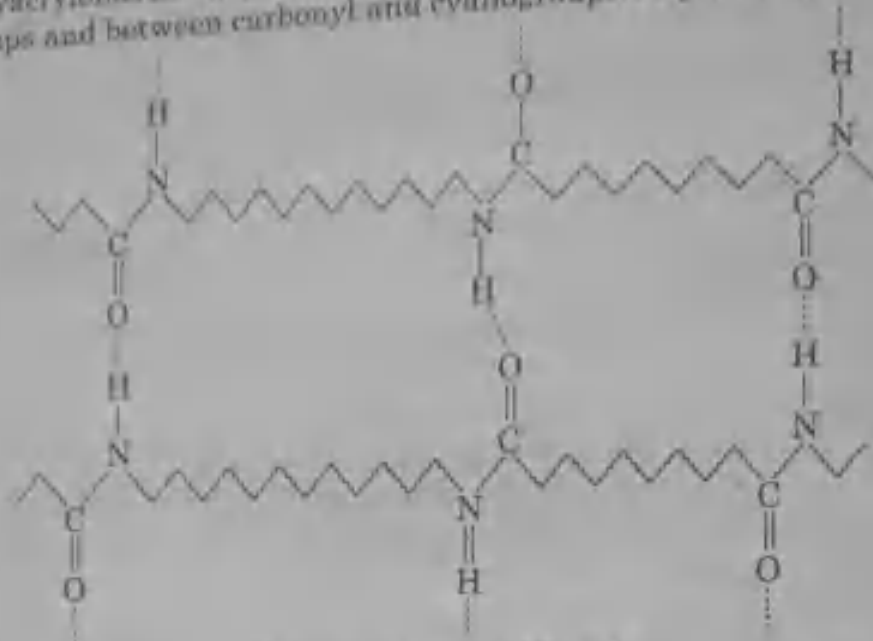


Fig. : Unstretched and stretched forms of elastomers

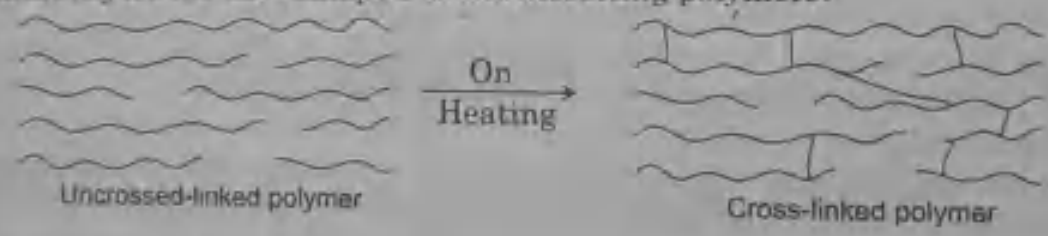
(iii) **Fibres** : Fibres are those polymers in which the polymer chains are strongest. These forces are due to hydrogen bonding or dipole-dipole interactions. In case of nylons, the intermolecular forces are due to hydrogen bonding while in polyesters and polyacrylonitrile they are due to powerful dipole-dipole interactions between the polar carbonyl groups and between carbonyl and cyanogroups respectively.



(Hydrogen bonding in nylon-6,6)

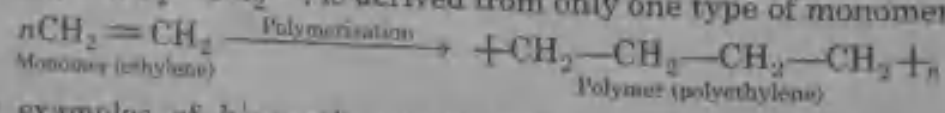
(iv) **Thermosetting polymers** : Such type of polymers are semi-fluid substances with low molecular weights which on heating, change to a hard, infusible and insoluble mass. This hardening on heating takes place due to extensive cross-linking between different polymer chains to give a three-dimensional network solid as shown in the following figure.

Thus, a thermosetting polymer can be heated only once when it permanently sets into a solid and cannot be remelted and reworked, while a thermoplastic polymer can be melted again and again without any change. Phenol-formaldehyde (bakelite), urea-formaldehyde and melamine-formaldehyde are the examples of thermosetting polymers.



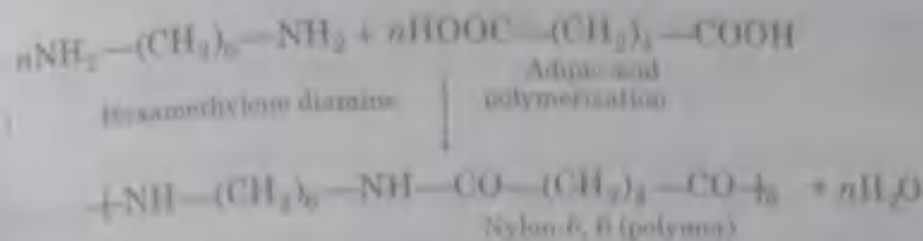
Homopolymers and Copolymers

Homopolymers : Homopolymers are the polymers in which repeat-unit is derived from only one type of monomer, for example, ethylene molecules on polymerisation give polyethylene polymer in which repeat unit, $-\text{CH}_2-\text{CH}_2-$, is derived from only one type of monomer, ethylene.



Some other examples of homopolymer are polypropylene, polyisoprene, polychloroprene (neoprene), polyacrylonitrile (PAN), polybutadiene, polytetra-fluoroethylene (teflon), polyvinyl chloride (PVC), nylon-6.

Copolymers : Copolymers are the polymers in which repeat units are derived from two or more types of monomers. e.g., nylon-66 has repeat unit $-\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO}-$ is derived from two monomers i.e., hexamethylene diamine and adipic acid.



Other examples of copolymer are polyesters, bakelite, Buna-S, melamine-formaldehyde

Molecular Mass of Polymers

A polymer is a giant or huge molecule obtained by the polymerisation of a large number of small, low molecular mass molecules of similar structure. The molecular mass of a polymer depends upon the number of simple molecules joined together during polymerisation reactions, i.e. upon the degree of polymerisation. But the polymerisation chains are broken at the different stages. Therefore, the final product will contain the polymers of different masses. For example all the molecules of styrene are similar and have the same mass. On the other hand the masses of various individual molecules are different. Hence it is necessary in their cases to take the average molecular mass. There are two types of average molecular masses.

(i) **Number-average Molecular mass (\bar{M}_n)**: The number-average molecular mass is defined as the total mass of the dispersed material divided by the total number of molecules present.

$$\bar{M}_n = \frac{n_1 m_1 + n_2 m_2 + n_3 m_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

Where, n_1, n_2, n_3, \dots are the number of molecules having masses m_1, m_2, m_3, \dots respectively. It may also be written as

$$\bar{M}_n = \frac{\sum n_i m_i}{\sum n_i} \quad \dots(1)$$

Where n_i is the number of molecules of molecular mass m_i .

The molecular weight of the polymer obtained from measurements of colligative properties like osmotic pressure is the number-average molecular mass. That is the reason, osmotic pressure depends upon the number of particles and not upon the masses of all the particles.

(ii) **Weight-average Molecular Mass (\bar{M}_w)**: Weight-average molecular mass gives contribution to various molecular species in proportion to their masses in the given substance. Thus, in weight average molecular mass, the molecular mass of each individual species is multiplied by the mass of that species and not by the number. If w_1, w_2, w_3, \dots represent the weight of the species of masses m_1, m_2, m_3, \dots , then the weight-average molecular mass (\bar{M}_w) is given by,

$$\bar{M}_w = \frac{w_1 m_1 + w_2 m_2 + w_3 m_3 + \dots}{w_1 + w_2 + w_3 + \dots}$$

If n_1, n_2, n_3, \dots represent the number of molecules of masses m_1, m_2, m_3, \dots etc., then $w_1 = m_1 n_1$;

$$w_2 = m_2 n_2 ; w_3 = m_3 n_3 \dots$$

$$\bar{M}_w = \frac{n_1 m_1^2 + n_2 m_2^2 + n_3 m_3^2 + \dots}{n_1 m_1 + n_2 m_2 + n_3 m_3 + \dots}$$

$$\bar{M}_w = \frac{\sum n_i m_i^2}{\sum n_i m_i} \quad \dots(2)$$

From equations (1) and (2) it follows that \bar{M}_w is always greater than \bar{M}_n .

To calculate the value of \bar{M}_n from \bar{M}_w , it is necessary to know the relative numbers of molecules present in the polymer.

The turbidity and refractive index at different concentrations are measured and the quantity $\frac{HC}{T}$ is plotted against concentration when a linear graph is obtained. This is extrapolated to zero concentration as shown in the figure. The intercept gives the value of $1/M$. Since the amount of light scattered by solutions is very small so every care should be taken to free them dust particles, which otherwise may also scatter light appreciably.

3. Gel permeation Chromatography : It is a type of size exclusion chromatography (SEC), that separates analytes on the basis of size, typically in organic solvents. The technique is often used for the analysis of polymers. As a technique, SEC was first developed in 1955 by Lathe and Rabinow.

When characterizing polymers, it is important to consider the dispersity (D) as well as the molecular mass. Polymers can be characterized by a variety of definitions for molecular mass including the number average molecular mass (M_n), the weight average molecular mass (M_w), the size average molecular mass (M_z) or the viscosity molecular mass (M_v). Gel permeation chromatography allows for the determination of D as well as M_n and based on other data, the M_w , M_z and M_v can be determined.

GPC separates based on the size or hydrodynamic volume of the analytes. This differs from other separation techniques which depend upon chemical or physical interactions to separate analytes. Separation occurs via the use of porous beads packed in a column. The smaller analytes can enter the pores more easily and therefore spend more time in these pores, increasing their retention time. These smaller molecules spend more time in the column and therefore will elute last. On the other hand larger analytes spend little time in the pores and are eluted quickly. All columns have a range of molecular masses that can be separated. If an analyte is too large, it will not be retained while, if the analyte is too small, it may be retained completely. Analytes that are not retained are eluted with the free volume outside of the particles (V_p), while analytes that are completely retained are eluted with volume of solvent held in the pores (v_i). The total volume can be considered by the following equation

$$V_t = V_p + V_i + V_o$$

Where, V_p is the volume of the polymer gel and V_t is the total volume.

There is a limited range of molecular masses that can be separated by each column, and therefore the size of the pores for the packing should be chosen according to the range of molecular mass of analytes to be separated. For polymer separations the pore sizes should be on the order of the polymers being analyzed.

Application : GPC is often used to determine the relative molecular mass of polymer samples as well as the distribution of molecular masses. If comparable standards are used, the relative data can be used to determine molecular masses within $\pm 5\%$ accuracy.

4. Osmometry and Ultracentrifuging :

(a) Osmometry : This method has been used in calculating the molecular mass of high polymers. This method gives accurate results than the other methods. The main advantage of osmotic pressure method is that the presence of a slight trace of an impurity of low molecular mass results in a serious error in other methods like freezing point or boiling point elevation method whereas it would pass through the cellophane membrane and therefore, would not alter the pressure measured. There are two relations for determining the molecular mass by this method.

