

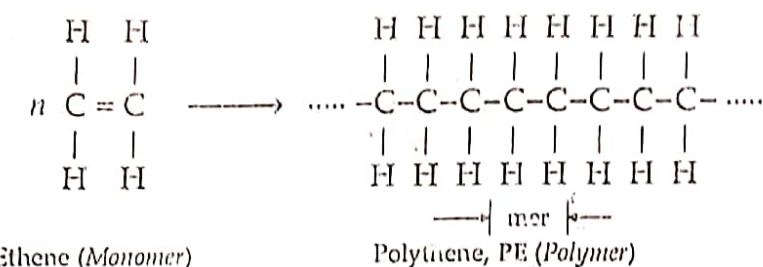
## CHAPTER 3

# HIGH POLYMERS

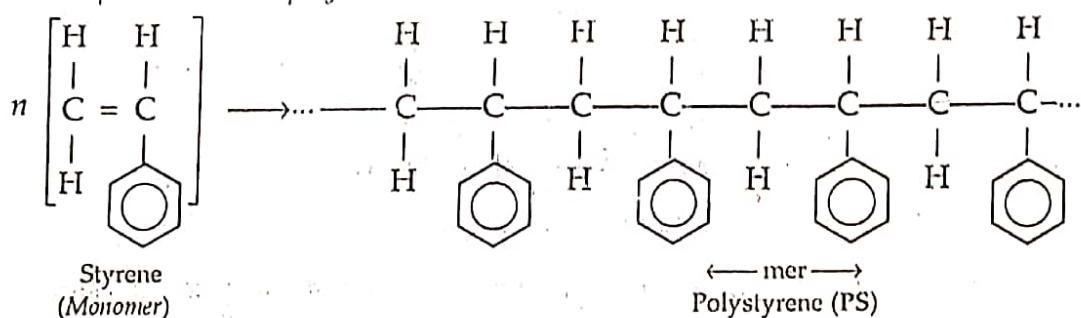
"Better things for better living - through polymers"

### 1 INTRODUCTION

Polymers' (Greek *poly* - many ; *mers* - units or parts) are 'macromolecules' (giant molecules of high molecular masses) built-up by the linking together of a large number of small molecules (called monomers). For example, polythene is a polymer formed by linking together of a large number of ethene ( $C_2H_4$ ) molecules. Thus :



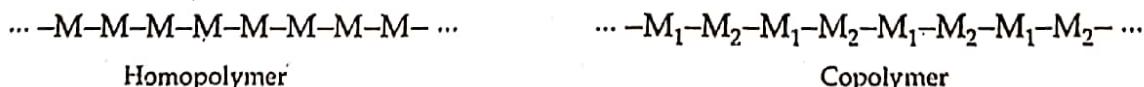
Thus, small molecules which combine with each other to form polymer molecules, are termed monomers ; and the "repeat unit" in a polymer is called mer. Thus :



The number of repeating units ( $n$ ) in chain formed in a polymer, is known as the "degree of polymerization" (DP). There may be hundreds or thousands or tens of thousands or more monomer molecules linked together in a polymer molecule. Most of the polymers, usually, fall into the 5,000–200,000 molecular mass range.

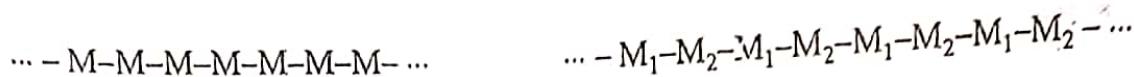
### 2 NOMENCLATURE OF POLYMERS

A polymer may consist of identical monomers or monomers of different chemical structure and accordingly they are, called homopolymers and copolymers respectively. Thus :

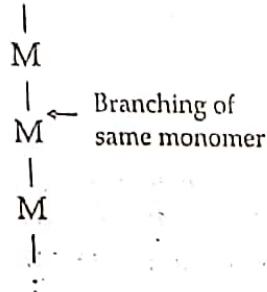
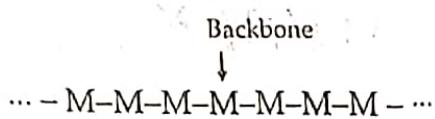


\* STAUDINGER, Hermann (1881-1963). German chemist. One of the pioneers in polymer chemistry, Staudinger was awarded the Nobel Prize in Chemistry in 1953.

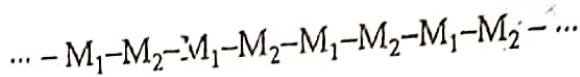
The monomeric unit in a polymer may be present in linear, branched or cross-linked (three-dimensional) structure. Thus :



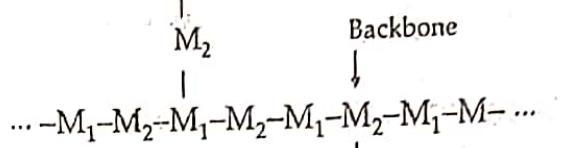
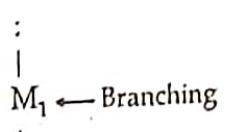
Linear homopolymer



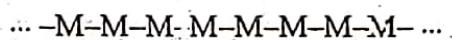
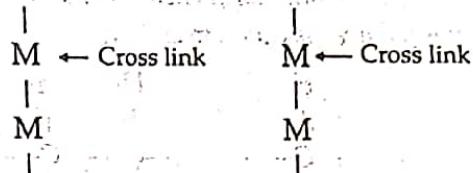
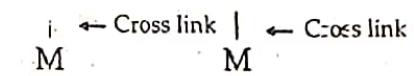
Branched chain homopolymer



Linear copolymer



Monomer unit

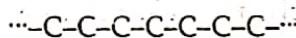


Cross-linked homopolymer

Branched copolymer

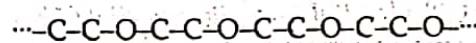
If the main chain is made up of same species of atoms, the polymer, is called "homochain polymer", and if the main chain is made up of different atoms, then it is called "heterochain polymer". Thus :

Homochain polymer :



Main chain

Heterochain polymer :

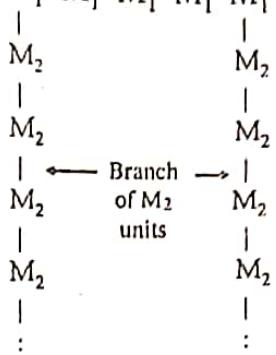


Main chain

Graft copolymers are branched structures in which the monomer segments on the branches and the backbone differ. Thus :

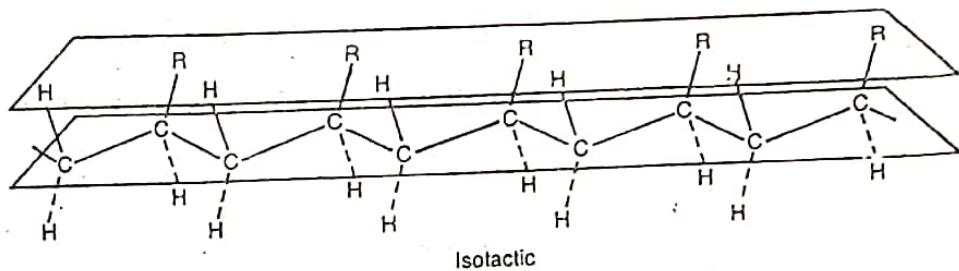
## HIGH POLYMERS

Graft copolymer : ... -M<sub>1</sub>-M<sub>1</sub>-M<sub>1</sub>-M<sub>1</sub>-M<sub>1</sub>-M<sub>1</sub>-M<sub>1</sub>- ...

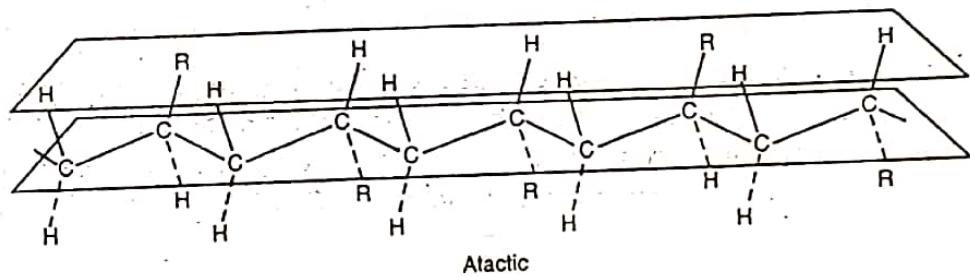


Tacticity : The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain. The difference in configuration (tacticity) do affect their physical properties.

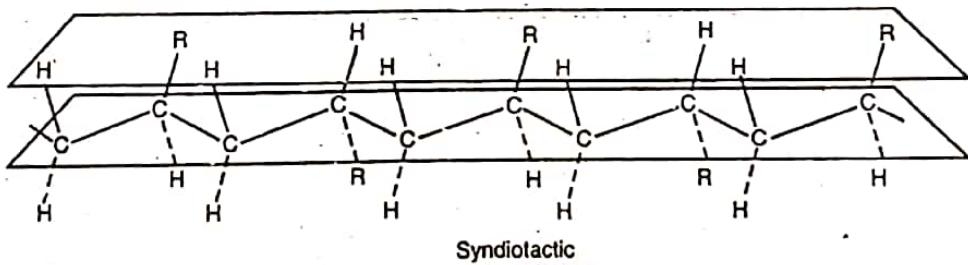
(i) The head-to-tail configuration, in which the functional groups are all on the same side of the chain, is called isotactic polymer, e.g.,



(ii) If the arrangement of functional groups are at random around the main chain, it is called atactic polymer, e.g., polypropylene.

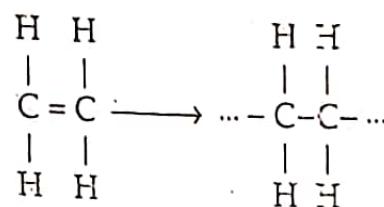


(iii) If the arrangement of side groups is in alternating fashion, it is called 'syndiotactic' polymer, e.g., gutta percha.



### 3 FUNCTIONALITY

For a substance to act as a monomer, it must have at least two reactive sites or bonding sites. The number of bonding sites in a monomer, is referred to as its functionality. In an olefin, the double bond can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination. Thus :



Thus, ethylene is considered to be bifunctional. Other reactive groups are hydroxyl, acid, amino-acid, di-ol, polyalcohols, di-amino acids, di-acids, etc.

(1) Depending upon the functionality of monomeric units, it is possible to obtain different types of structures. In case of a bifunctional monomer, two reactive groups attach side by side to each other forming a linear or straight-chain molecule. Linear molecules consist of monomer units linked by primary covalent bonds, but the different chains are held together by secondary van der Waals forces of molecular attraction. This gives the possibility of chain movement in one direction (see Fig 1).

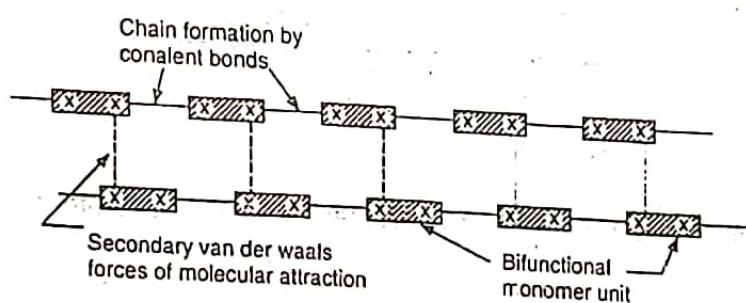


Fig. 1. Linear chain polymer from a bifunctional monomer.

(2) During the chain growth, side chains may also form, resulting in branched-chain molecules (see Fig. 2). Such a molecule is no doubt a linear, but the movement in branched-chain molecules is, generally, more restricted than that of simple straight-chain molecules. A branched-chain polymer also results, when a trifunctional monomer is mixed in small amounts with a bifunctional monomer and polymerized.

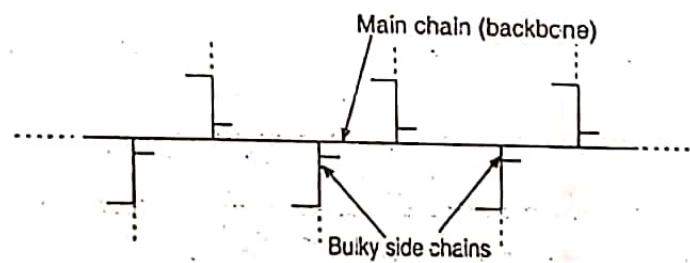


Fig. 2. Branched-chain polymer.

(3) In case of polyfunctional groups, monomer molecules are connected to each other by covalent bonds, resulting in the formation of a three-dimensional network. In such polymeric molecules, the movement of individual molecules is prevented by strong cross-links (see Fig. 3).

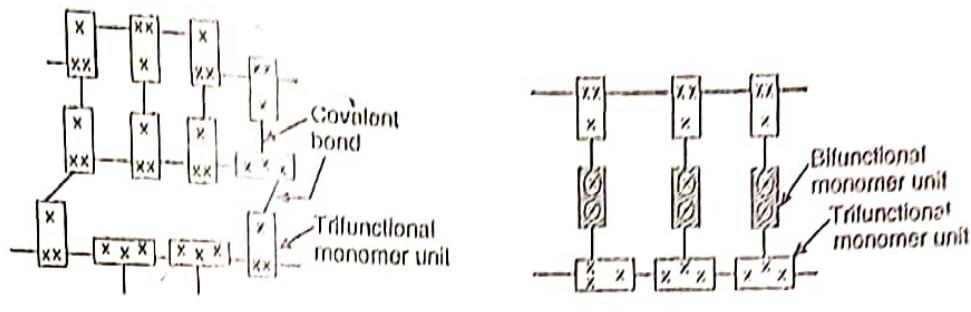


Fig. 3. Formation of a three-dimensional network polymer : (a) reaction of three-functional molecules, (b) reaction between two and three-functional molecules.

Note : A network polymer is formed only if one of its monomers is *trifunctional*.

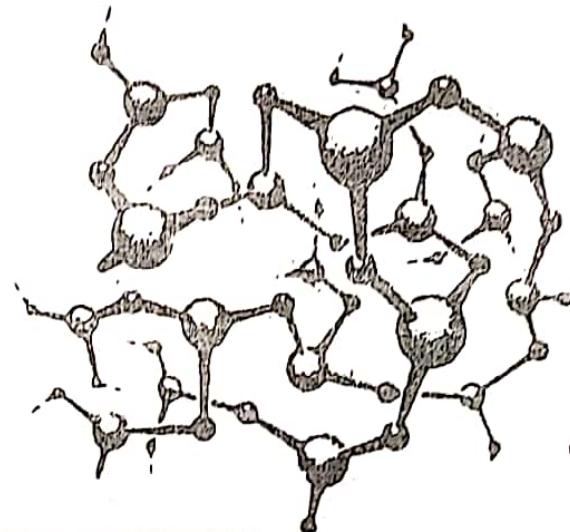
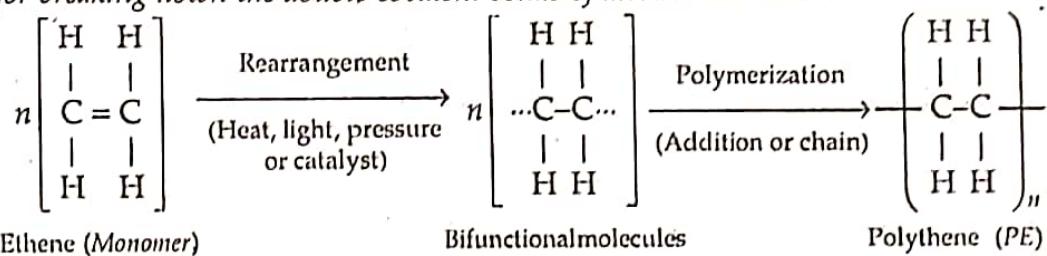


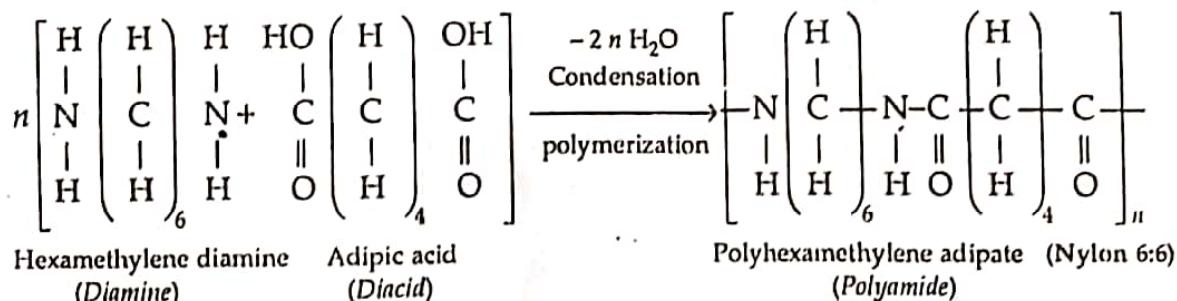
Fig. 4. Network polymer.

#### 4 TYPES OF POLYMERIZATION

(1) **Addition or chain polymerization** is a reaction that yields a product, which is an exact multiple of the original monomeric molecule. Such a monomeric molecule, usually, contains one or more double bonds, which by intermolecular rearrangement, may make the molecule *bifunctional*. The addition polymerization reaction must be instigated by the application of *heat, light, pressure or a catalyst for breaking down the double covalent bonds of monomers*. Thus :



(2) **Condensation or step-polymerization** may be defined as "a reaction occurring between simple polar-group-containing monomers with the formation of polymer and elimination of small molecules like water, HCl, etc." For example, hexamethylene diamine and adipic acid condense to form a polymer, nylon 6 : 6.



Thus, condensation polymerization is an intermolecular combination, and it takes place through the different functional groups (in the monomers) having affinity for each other. When monomers contain three functional groups, it may give rise to a cross-linked structure polymer. The types of functional groups, which are most important in the condensation reactions are :

1st group	2nd group	Product	Example
Hydroxyl -OH	Carboxyl -COOH	Polyester -OOC-	Polyethylene terephthalate (terylene)
Amino -NH <sub>2</sub>	Carboxyl -COOH	Polyamide -NH-CO-	Nylon-6 : 6
Hydroxyl -OH	Isocyanate OCN-	Polyurethane -OC-NH-	Spandex fibre

(3) Copolymerization is the joint polymerization of two or more monomer species. High molecular-weight compounds obtained by copolymerization, are called copolymers. For example, butadiene and styrene copolymerize to yield GR-S rubber:

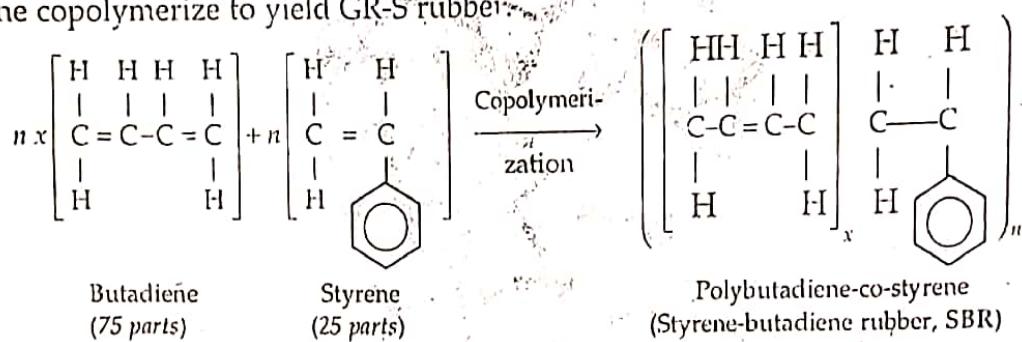


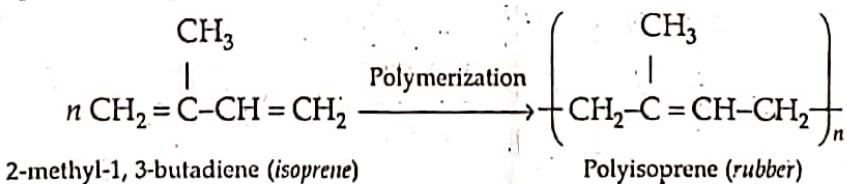
Table 1. Chain and condensation polymerizations.

Addition/chain polymerization	Condensation polymerization
1. Only growth reaction adds repeating units one at a time to the chain.	Any two molecular species present can react.
2. Number of units decreases steadily throughout the reaction.	Monomer disappears early in the reaction.
3. High molecular mass polymer is formed at once.	Polymer molecular mass (or DP) rises steadily throughout the reaction.
4. Longer reaction times have a little effect on molecular-weight, but gives higher yields.	To obtain high molecular-weight, longer reaction time is essential.
5. The reaction mixture contains only monomers, high polymers and about $10^{-8}$ part of growing chains.	All types of molecular species are present at any stage.

## 5 CLASSIFICATION OF POLYMERS

Polymers can be classified in a number of ways :

(1) Classification on the basis of source : (i) *Natural polymers* (which are found in nature in animals and plants). For example, *starch* (a polymer of  $\alpha$ -D-glucose), *cellulose* (a polymer of  $\beta$ -D-glucose), *proteins* (polypeptides and polyamides), *nucleic acids*, *natural rubber* (a polymer of *cis*-isoprene).



*Gutta percha* is polymer of isoprene having *trans* configuration.

(ii) *Synthetic polymers* (*man-made polymers*) like polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), nylon, terylene, bakelite, etc.

(2) Classification on the basis of structure : (i) *Linear polymers* in which monomeric units are joined in the form of long straight chains. For example, high density polythene (HDPE), nylons, polyester, etc. These polymers possess high m.p., density and tensile strength, due to close packing of polymer chains.

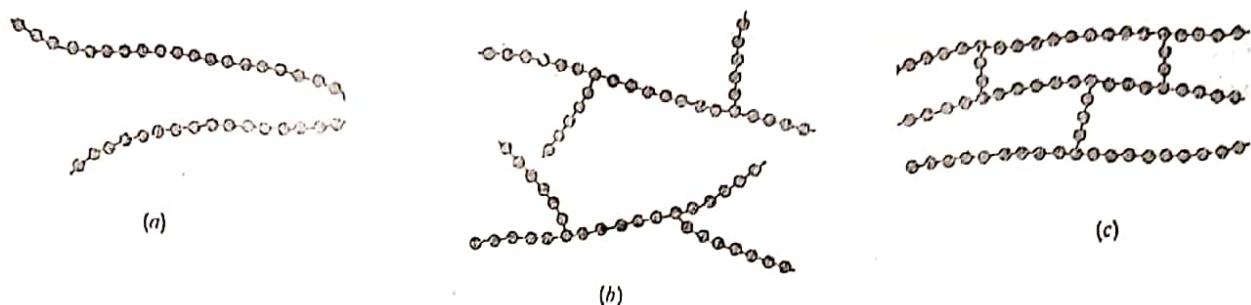


Fig. 5. (a) Linear, (b) branched, (c) cross-linked polymers.

(ii) Branched chain polymers are mainly linear in nature, but also possess some branches along the main chain. For example, low density polythene (LDPE), glycogen, amylopectin, etc. These polymers possess low m.p., density and tensile strength compared to linear polymers, due to poor packing of polymer chains in presence of branches.

(iii) Three-dimensional network polymers contains monomers molecules connected to each other by only covalent bonds. They are giant molecules in which movement of individual monomeric units is prevented by strong cross-links. Due to presence of strong cross-links, they are hard, rigid, brittle and do not melt, but burn on strong heating. Examples, are bakelite, urea-formaldehyde, melamine-formaldehyde, etc.

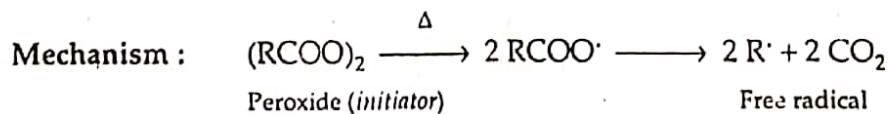
(3) Classification on the basis of their methods of synthesis : Based on the modes of synthesis, the polymers have been classified into two groups :

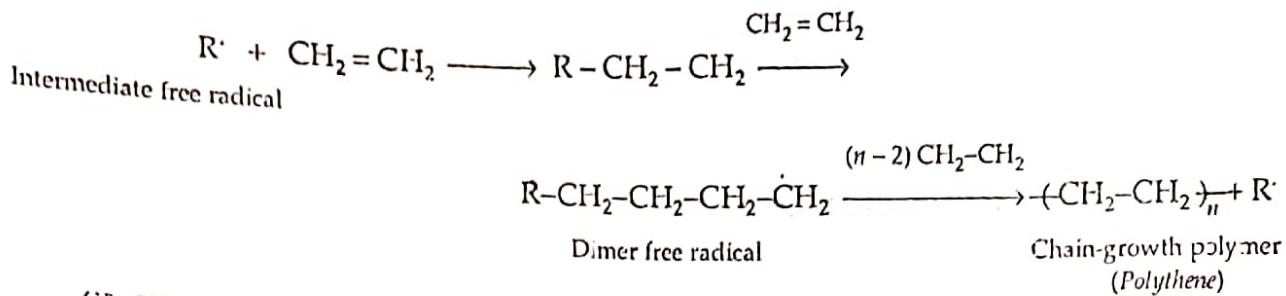
(i) Addition polymers are obtained by addition polymerization method, which involves the repeated addition of monomers (unsaturated derivatives of ethene) to yield long chains. Their empirical formula is same that of their monomers. For example, polyethylene, polypropylene, polystyrene, polyvinyl chloride, etc.

(ii) Condensation polymers are obtained by a series of condensation reaction, generally, involving two monomers. The condensation reactions, usually, result in the loss of small molecules (like  $\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{NH}_3$ , etc.). For example, nylon-6 (from adipic acid and hexamethylene diamine), bakelite (from phenol and formaldehyde), polyester (from terephthalic acid and ethylene glycol), etc.

(4) Classification on the basis of growth polymer chain :

(i) *Step growth polymers* are formed by the successive addition of monomer units to the growing chain carrying a reactive intermediate. Example are polyethene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), etc.





(ii) **Step-growth polymers** are formed through a series of independent reactions involving bond formation (condensation) between two different monomers with loss of small molecules like  $H_2O$ ,  $HCl$ ,  $NH_3$ , etc.

(5) Classification based on molecular forces : On the basis of the magnitude of intermolecular forces present in polymers, they are classified into four categories.

(i) *Thermoplastic polymers* are linear, long chain polymers, which can be softened on heating and hardened on cooling reversibly, i.e., their hardness is a temporary property, subject to change with rise or fall of temperature. Thus, they can be processed again and again.

**Examples :** Polythene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), nylons, polytetrafluoro ethylene (PTFE or teflon), etc.

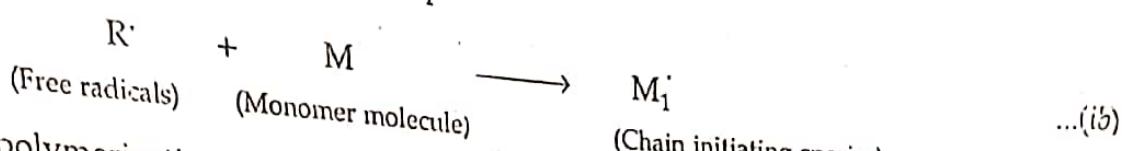
(ii) **Thermosetting polymers** (or *thermosets*) are those polymers, which during moulding (by heating, etc.) get hardened and once they have solidified, they cannot be softened, i.e., they are permanent setting polymers. Such polymers during moulding acquire three-dimensional cross-linked structure, with predominantly strong covalent bonds. Thus, a thermosetting polymer once moulded cannot be reprocessed.

*Examples : Polyester (terylene), bakelite, epoxy-resin (araldite), melamine urea form, etc.*

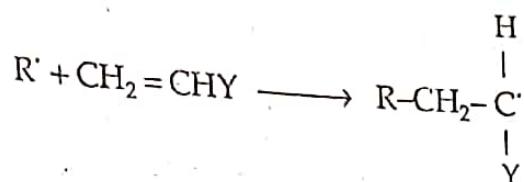
**Structural difference between thermoplastics and thermosetting polymers :** Thermoplastics possess comparatively weaker intermolecular forces and there is no cross-linking. Consequently, they are flexible and can easily be moulded on heating. On the other hand, there is excessive cross-linking in thermosetting plastics and different polymer chains are held through strong covalent bonds forming a three-dimensional network. Hence, these once set cannot be remoulded. On heating, they first fuse to form a hard mass and then burn.

(iii) **Elastomer (or synthetic rubber)** is any rubber-like elastic polymer, which can be stretched to at least thrice its length, but it returns to its original shape and dimensions as soon as stretching force is released. The elastic deformation in an elastomer arises from the fact that in an unstressed condition, an elastomer molecular chain is in the form of a coil and consequently, it can be stretched like a spring. The chains revert back to their original coiled state as the deforming stress is released. Thus, elasticity of an elastomer is caused by the lengthening and shortening of their polymeric chain springs.

The second part of initiation involves the addition of this radical to the first monomer molecule (M) to produce the chain initiating species,  $M_1^{\cdot}$

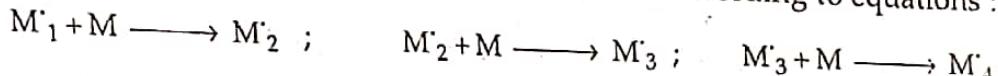


Thus, the polymerization of monomer,  $\text{CH}_2 = \text{CHY}$ , takes in the form :



(The radical  $R^{\cdot}$  is often referred as an *initiator radical* or a *primary radical*).

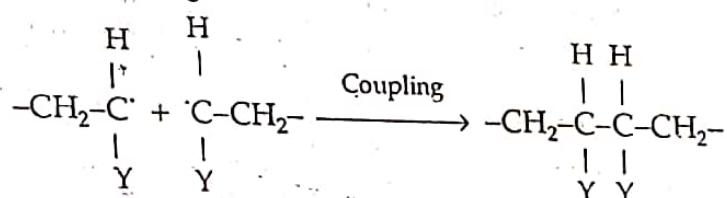
(ii) *Propagation step* consists of the growth of  $M_1^{\cdot}$  by successive additions of large numbers (hundreds, and perhaps, thousands) of monomer molecules according to equations :



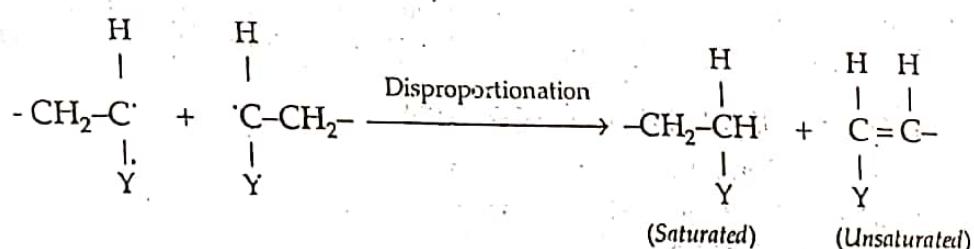
or in general terms :  $M_n^{\cdot} + M \longrightarrow M_{n+1}^{\cdot}$

(iii) *Termination step* : At some point, the propagating polymer chain stops growing and terminates.

(i) By coupling or combination, e.g.,



or (ii) more rarely, by disproportionation in which a hydrogen atom of one radical centre is transferred to another radical centre. This results in the formation of two polymer molecules, one saturated and one unsaturated, e.g.,



The two different modes of termination can be represented in general terms by :



The term '*dead polymer*' signifies the cessation of the growth of the propagating radical.

127

(iv) Fibres are those polymers whose chains are held by strong intermolecular forces like hydrogen bonding. They are crystalline in nature and of high tensile strength, due to strong intermolecular forces. For example, nylon, polyester, etc.

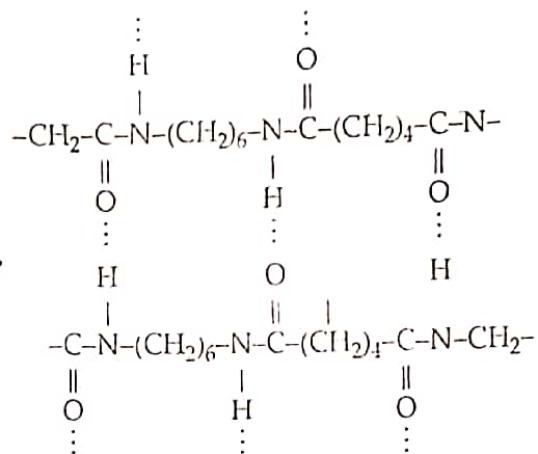


Fig. 6. Hydrogen bonding in nylon-66.

Table 2. Thermoplastic versus thermosetting polymers.

<i>Thermoplastic polymers</i>	<i>Thermosetting polymers</i>
1. They <i>soften</i> on heating readily.	They <i>do not soften</i> on heating. On prolong heating, however, they <i>burn</i> .
2. They consist of <i>long-chain linear</i> macromolecules.	Their set molecules have <i>three-dimensional</i> network structure, joined by strong covalent bonds.
3. They are formed mostly by <i>addition polymerization</i> .	They are formed by <i>condensation polymerization</i> .
4. By reheating to a suitable temperature, they <i>can be softened, reshaped</i> and thus <i>reused</i> .	They retain their shape and structure, even on heating. Hence, they <i>cannot be reshaped and reused</i> .
5. They are, usually <i>soft</i> , weak and less brittle.	They are, usually, <i>hard</i> , strong and more brittle.
6. These can be reclaimed from <i>wastes</i> .	They <i>cannot be reclaimed</i> from wastes.
7. They are, usually, <i>soluble</i> in some organic solvents.	Due to strong bonds and cross-linking, they are <i>insoluble</i> in almost all organic solvents.

## 6 MECHANISM OF ADDITION POLYMERIZATION

Polymerization reaction involve union of two or more small molecules to form a single large molecule, called *polymer*. Polymerization of ethylene and its substituted compound,  $CH_2 = CHX$  can be carried out by using any of the *four* mechanisms :

(1) **Free radical polymerization mechanism** involves the following steps :

(i) *Initiation step* is considered to involve two reactions. The first is the production of free radicals, usually, by the homolytic dissociation of an initiator (or catalyst) to yield a pair of radicals  $R^\cdot$



(ii) *Solution polymerization* technique involves in first dissolution of monomer a suitable solvent and then initiator is added to start the polymerization reaction. The heat of polymerization is mostly dissipated by evaporation (followed by condensation and recycling) of the solvent. After the required extent of polymerization, the polymer produced is precipitated by adding a suitable non-solvent to the mix. The solid polymer is then filtered off, washed free of any adhering monomer or solvent and dried before use. Polymerization of N-vinyl pyrrolidone, acrylonitrile, acrylic acid, etc. is also carried out by this method, wherein water is used as a cheap solvent for polymerization.

(iii) *Emulsion polymerization*: In this method, the monomers are dispersed as fine droplets (about  $10^{-5}$  to  $10^{-6}$  mm) in a large amount of water and then emulsified (or stabilized) by the addition of a soap or detergent or protective colloids (like casein, gum, gelatin or dextrose). Then initiator is added. Initiators are usually redox type, which may be either water-soluble or monomer soluble. Very often, persulphates are used, which give rise to sulphate-ion radical.  $\text{SO}_4^{\cdot-}$ . These ion radicals interact with the monomers in the emulsion or micelles form and polymerization occurs. Finally, the emulsion is used as such if used as adhesive, surface coating or textile finishing. Alternatively, polymer emulsion may be broken by adding an electrolyte (or a solvent), followed by washing, drying, etc. of the coagulated polymer. This method is widely used to prepare vinyl polymers like PVC, PVA, etc. This method combines the advantages of bulk and solution techniques, namely, rapid production of polymer, ease of temperature control, and high average molecular weights.

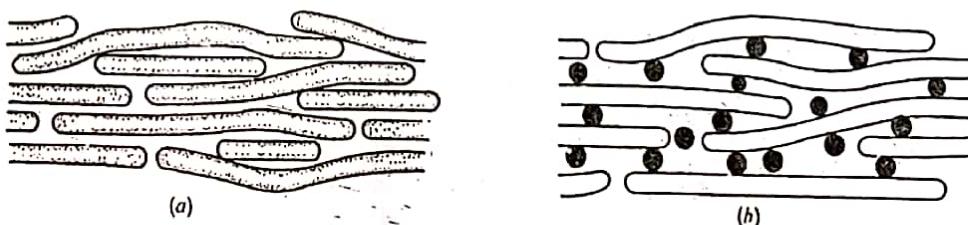
(iv) *Suspension polymerization* was developed with a view to improve and simplify the emulsion polymerization method. The monomer is dispersed as relatively large droplets (0.1 to 1 mm particle size) in water. It is kept in suspension by mechanical agitation. The catalyst is then added and initiation takes place. As the polymerization proceeds, the viscosity of dispersed drops increases and they become sticky. At this stage, suspension is stabilized by addition of a small amount of suspension stabilizer (e.g., kaolin, magnesium silicate, aluminium hydroxide, etc.) ; otherwise the droplets agglomerate together and drip away, thus breaking the suspension. When the reaction is complete, the reaction product (in the form of pearls) is washed (to remove stabilizer from the surface of the polymer), dried and used. This method is widely used to prepare PVC and polystyrene.

## 12 MOULDING CONSTITUENTS OF A PLASTIC

It is unusual for a finished high-polymer article to consist solely of high-polymeric material alone. Usually, the high-polymer material is mixed with 4 to 10 ingredients, each of which either discharges a useful function during moulding or imparts some useful property to the finished artifact. This is called a *mix*. The main types of compounding ingredients and their functions are described below :

1. *Resin is the binder, which holds the different constituents together. Thermosetting resins are, usually, supplied as linear-polymers of comparatively low molecular-weight, because at this stage they are fusible and hence, mouldable. The conversion of this fusible form into cross-linked infusible form takes place, during moulding itself, in presence of catalysts, etc.*

2. *Plasticizers are materials that are added to resins to increase their plasticity and flexibility. Their action is considered to be the result of the neutralization of part of the intermolecular forces of attraction between macromolecules of resins. Thus, they impart greater freedom of movement between the polymeric macromolecules of resins, thereby increasing the flexibility and plasticity of the compounded material, but at the same time reducing its strength and also decreasing its chemical-resistance [see Fig. 16]. Most commonly used plasticizers are vegetable oils (non-drying type), camphor, esters (of stearic or oleic or phthalic acids) and some phosphates (like tricresyl phosphate, tributyl phosphate, tetrabutyl phosphate and triphenyl phosphate).*



**Fig. 16. Action of plasticizer in plastics (schematic). The presence of small molecules of plasticizer reduces the attraction of the larger polymer molecules for each other, and so permits more flexibility and easier slip. (a) No plasticizer, and (b) plasticizer present.**

3. Fillers are added to give to the final plastic better hardness, tensile strength, opacity, finish and workability ; besides reducing the cost, shrinkage on setting and brittleness. Sometimes, fillers are added to impart special characters to the products. For example, (i) carborundum, quartz and mica are added to provide extra hardness ; (ii) barium salts are added to make the plastic impervious to X-rays ; (iii) addition of asbestos provides heat and corrosion-resistances.

Most commonly used fillers are wood-flour, asbestos, Chine clay, talc, gypsum, saw-dust, ground cork, marble flour, paper pulp, corn husk, mica, carbon black, pumic powder, cotton fibre, metallic oxides (like  $ZnO$ ,  $PbO$ ) and metal powders (like  $Al$ ,  $Cu$ ,  $Pb$ ). The percentage of filler varies and can be upto 50% of the total moulding mixture.

Note : Those fillers which enhance mechanical strength, are called reinforcing fillers. For example, addition of carbon black to natural rubber brings about a 40% increase in tensile strength and also greatly enhanced abrasion-resistance. Similarly, addition of 50% of cellulosic fillers (such as shredded rags, cotton floc, lamination of paper, fabric or wood) enhances the impact strength of moulded article from phenol-formaldehyde.

4. Lubricants like waxes, oils, stearates, oleates and soaps are employed to make the moulding of plastic easier and to impart a flawless, glossy finish to the products. Lubricants prevent the plastic material from sticking to the fabricating equipment.

5. Catalysts or accelerators are added only in the case of thermosetting plastics with the object of accelerating the polymerization of fusible resin, during moulding operation, into cross-linked infusible form. Catalysts used for compounding include hydroger peroxide ; benzoyl peroxide ; acetyl sulphuric acid ; metals like  $Ag$ ,  $Cu$  and  $Pb$  ; metallic oxides such as zinc oxide ( $ZnO$ ), ammonia and its salts.

6. Stabilizers : The purpose of adding stabilizers is to improve the thermal stability during processing. For example, vinyl chloride and vinylidene chloride polymers show a tendency to undergo decomposition and discoloration at moulding temperatures. So during their moulding, heat stabilizers are used. Stabilizers commonly used are : (a) opaque moulding compounds like salts of lead, e.g., white lead, lead chromate, litharge, red lead, lead silicate and lead naphthenate ; (b) transparent moulding compounds like stearates of lead, cadmium and barium.

7. Colouring materials : Colour appeal is often of prime importance in high-polymer artifacts. The main colouring materials are organic dyestuffs and opaque inorganic pigments.

### 13 MOULDING OF PLASTICS INTO ARTICLES

Many methods of fabricating plastics into desired-shaped articles are employed. The methods, usually, depend upon the type of resins used, i.e., whether thermosetting or thermoplastic. Commonly used plastic fabrication methods are described below :

1. Compression moulding is a method applied to both thermoplastic and thermosetting resins. The predetermined quantity of plastic ingredients in proper proportions get filled between the two half-pieces of mould (see Fig. 17), which are capable of being moved relative to each other. Heat and pressure are then applied according to specifications. The cavities get filled with fluidised plastic. Two halves are closed very slowly. Finally, curing is done either by heating (in case of thermosetting) or cooling (in case of thermoplastics). After curing, the moulded article is taken out by opening the mould parts.

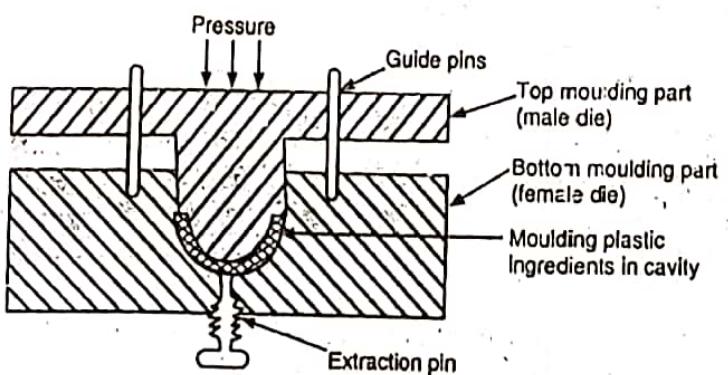


Fig. 17. Compressing moulding of plastics.

2. **Injection moulding** is applicable mainly to thermoplastic resins. In this, the moulding plastic powder is fed into a heated cylinder, from where it is injected at a controlled rate into the tightly-locked mould by means of a screw arrangement or by a piston plunger (see Fig. 18). The mould is kept cold to allow the hot plastic to cure and become rigid. When the material have been cured sufficiently, half of the mould is opened to allow the injection of the finished article without any deformation, etc. Heating is done by oil or electricity.

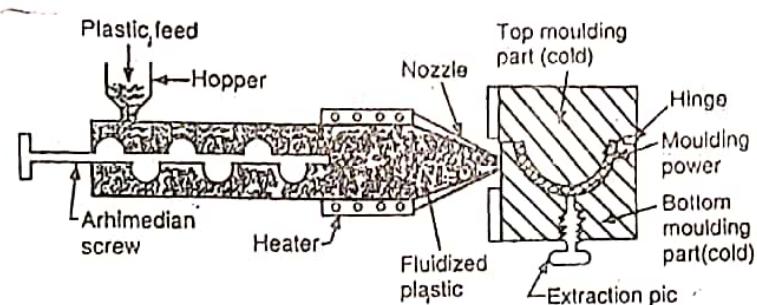


Fig. 18. Injection moulding of plastics.

**Advantages :** This method is the most widely used for moulding of thermoplastics, because of high speed production, low mould cost (since fewer cavities are needed), very low loss of material and low finishing cost. Because a large number of cavities cannot be filled simultaneously, so there is limitation of design of articles to be moulded.

3. **Transfer moulding** is a method, which uses the principle of *injection moulding for thermo-setting materials*. In this (see Fig. 19), the moulding powder is placed in a heated chamber, maintained at the minimum temperature at which the moulding powder just begins to become plastic. This plastic material is then injected through an orifice into the mould by a plunger, working at a high pressure. Due to the very great friction developed at the orifice, the temperature of the material, at the time of ejection from the orifice, rises to such an extent that the moulding powder becomes almost liquid, and consequently, it flows quickly into the mould, which is being heated up to the curing temperature required for setting. The moulded article is then ejected mechanically.

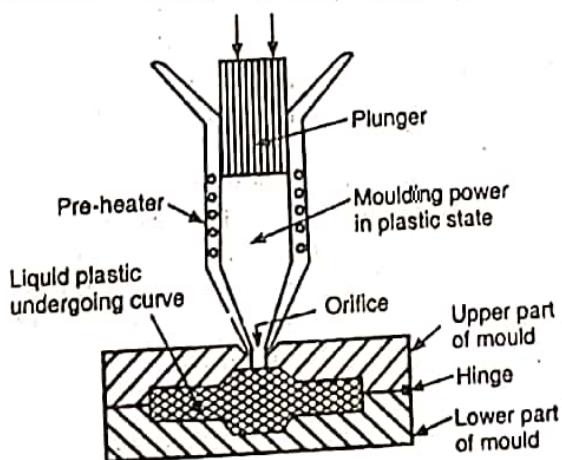


Fig. 19. Transfer moulding of plastics.

**Advantages :** (i) Since the mix flows into the mould cavity in a highly plasticized condition, so *very delicate* articles may be handled without distortion or displacement. Fine wires and glass fibres may be inserted into the mould. (ii) *Intricate shapes*, not attainable by compression moulding, can readily be produced. (iii) Article produced is free from flow marks. (iv) Even thick pieces cure almost completely and uniformly. (v) Owing to uniform and thorough cure, shrinkage and distortion are at a minimum and hence, the mechanical strength and density of fabricated piece is higher. (vi) Finishing cost of fabricated article is almost entirely eliminated. (vii) Blistering is almost eliminated and gases are expelled in the plasticizing chamber itself. (viii) Mould cost is less, since it involves very low abrasive action.

4. Extrusion moulding is used mainly for continuous moulding of thermoplastic materials into articles of uniform cross-section like tubes, rods, strips, insulated electric cables. The thermoplastic ingredients are heated to plastic condition and then pushed by means of a screw conveyor into a die, having the required outer shape of the article to the manufactured (see Fig. 20). Here the plastic mass gets cooled, due to the atmospheric exposure (or artificially by air jets). A long conveyor carries away continuously the cooled product.

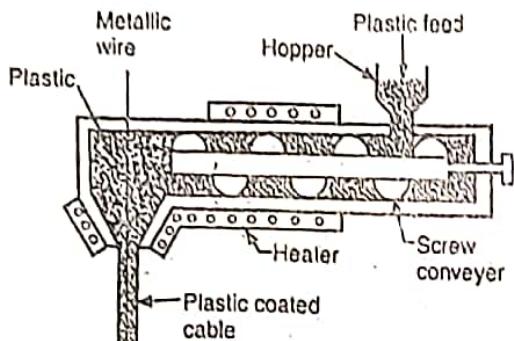
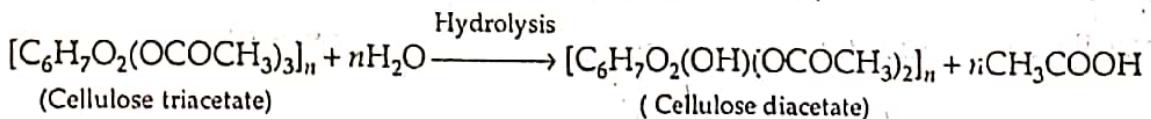
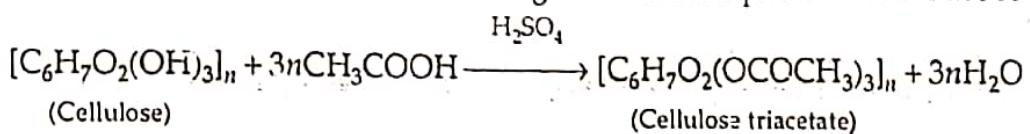


Fig. 20. Moulding of Insulated electric cable by vertical extrusion moulding.

## 14 IMPORTANT THERMOPLASTIC RESINS

### 1. Cellulose derivatives used as plastics are the following :

(i) Cellulose acetate is made by reacting natural cellulose (like cotton linters) with acetic anhydride or glacial acetic acid in the presence of a catalyst (such as sulphuric acid). The resultant cellulose triacetate ester is partially hydrolysed so that about 2 to 2.5 acetyl groups per  $C_6H_{10}O_5$  unit remains, and the product becomes soluble in organic solvent such as acetone, because the triacetate of cellulose is insoluble. Esterification reduces the molecular weight of cellulose product to about 300 to 400 units.

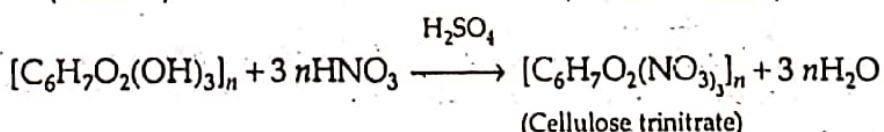
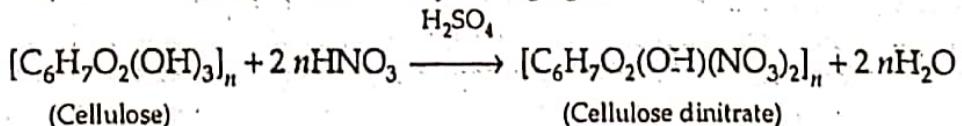


**Properties :** Cellulose acetates : (a) are quite tough ; (b) have high tensile strength ; (c) possess high dielectric strength ; (d) have some resistance to the mineral acids, and (e) can be spun into fibres or used in the form of plastics.

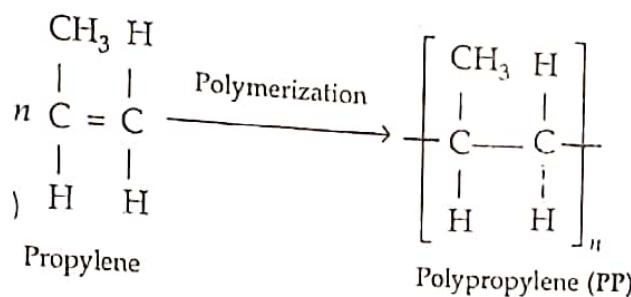
For making fibres, a solution of cellulose acetate is prepared ; while for making plastics, it is mixed with a plasticizer and solvent or only plasticizer and then moulded into stiff sheets on warm rollers. Suitable dyes and fillers can also be added at this stage. For making moulding powder, the sheets may be cut into granules of the desired size and dried to volatilize solvent content suitable for requisite moulding. The solvent process is used for making sheets, films, etc. ; whereas the non-solvent process is used for moulding other articles.

**Uses :** For the manufacture of radio appliances, automobile steering wheels, handles, windows, goggles, combs, musical instruments, etc.

(ii) Cellulose nitrate or nitrocellulose or celluloid is made by reacting cellulose with nitric acid in the presence of sulphuric acid, which acts as dehydrating agent.



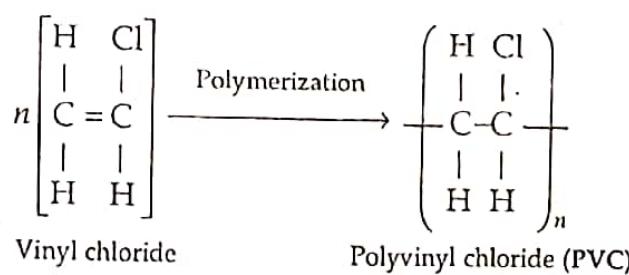
(ii) Polypropylene is obtained by polymerizing propylene in presence of Ziegler-Natta catalyst ( $\text{AlR}_3-\text{AlCl}_3$ ).



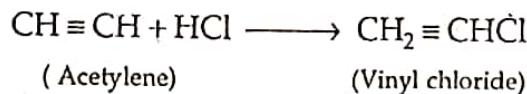
**Properties :** Polypropylene is *stereoregular (isotactic)* and highly crystalline polymer (m.p.  $160-170^\circ\text{C}$ ). It possesses better hardness, strength, stiffness than polyethylene. It is more resistant than PE.

**Uses :** In producing *moulded parts and fibres*. Its fibres are used in making ropes (extremely strong by weight), carpets (indoor as well as outdoor purposes), furniture upholstery, blankets, hand bags, apparels, etc. It is also used for making water-pipes, washing-machines parts, sterilizable hospital equipments, etc.

(iii) Polyvinyl chloride (PVC) is obtained by heating a water-emulsion of vinyl chloride in presence of a small amount of benzoyl peroxide or hydrogen peroxide in an autoclave under pressure.



Vinyl chloride, so-needed, is generally prepared by treating acetylene at 1 to 1.5 atmospheres with hydrogen chloride at  $60-80^\circ\text{C}$ , in presence of metal chloride as catalyst.



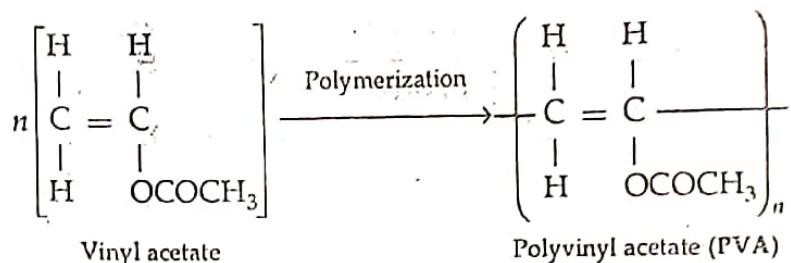
**Properties :** PVC is colourless odourless, non-inflammable and chemically inert powder (sp. gr. = 1.33), resistant to light, atmospheric oxygen, inorganic acids and alkalis, but soluble in hot chlorinated hydrocarbons such as ethyl chloride. Pure resin possesses a *high softening point* ( $148^\circ\text{C}$ ) and a greater stiffness and rigidity compared to polyethylene, but is brittle. PVC. It is the most widely used synthetic plastic.

**Uses :** (1) *Rigid PVC* or *unplasticized PVC* have superior chemical resistance and high rigidity, but is brittle. It is used for making sheets, which are employed for tank-linings, light-fittings, safety helmets, refrigerator components, tyres, cycle and motor cycle mudguards. It is also extruded in strip and tube form for use in place of non-ferrous metals.

(2) '*Plasticized PVC*' (i.e., obtained by adding plasticizers such as dibutyl phthalate, dioctyl phthalate, tricresyl phosphate, etc.) is used for making continuous sheets (of different thicknesses from 0.1 mm to 8 mm). Employed for packing rain-coats, table-cloths and curtains, electrical insulation like coverings of electric cables ; injection moulding of articles like toys, tool-handles, toiled-goods, radio-components, plastic-coated cloth, chemical containers, thermal insulating foam (used in buildings, cinemas and aircrafts), conveyor belts (used in coal mines), etc.

(iv) Polyvinyl acetate (PVA) is prepared by heating vinyl acetate (obtained by treating acetylene with acetic acid in presence of  $\text{HgSO}_4$  catalyst), in presence of benzoyl peroxide or acetyl chloride as catalyst.

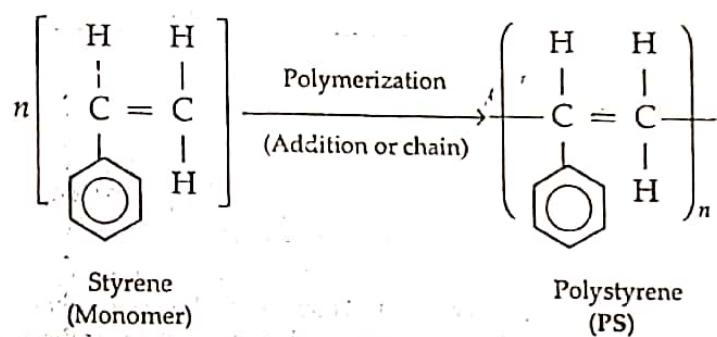
HIGH POLYMERS



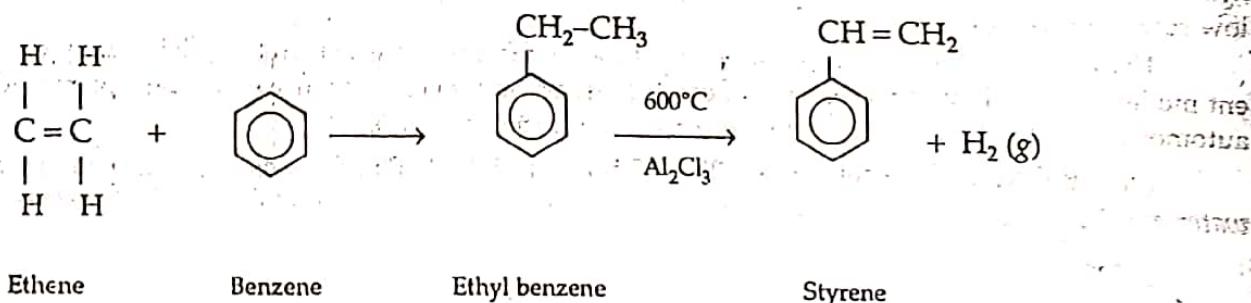
**Properties :** Polyvinyl acetate is a colourless, transparent material (of relatively low softening point), resistant to water, atmospheric oxygen and chemicals. It is fairly soluble in organic acids and organic solvents. It has got good heat resistance, but slight yellowing takes place after prolonged storage above 120°C. Polyvinyl acetate is *harmless*, if taken orally.

**Uses :** Under the influence of compressive or tensile forces, articles made from polyvinyl acetate are distorted, even at room temperature. So, it is *not* used for moulding purposes. However, it is used for making records, chewing-gums, surgical dressings, paints, lacquors, plastic emulsions, coatings, card-boards, wrapping paper, finishing textiles and other fabrics and bonding paper, leather, textiles, etc.

~~(d)~~ Polystyrene (PS) is prepared by polymerization of styrene (dissolved in ethyl benzene) in presence of benzoyl peroxide catalyst.



Styrene is, generally, produced from benzene and ethylene.

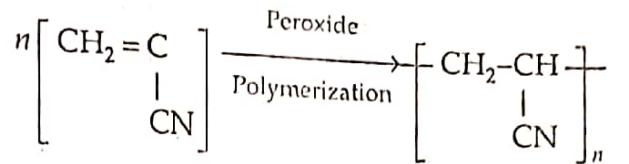


**Properties :** Polystyrene is a transparent, light (sp. gr. 1.05 to 1.07 g/cm<sup>3</sup>), good light-stable, excellent moisture-resistant. It can be nitrated by fuming nitric acid and sulphonated by conc. H<sub>2</sub>SO<sub>4</sub>. At about 100°C, it yields water-soluble emulsion. It is highly electric insulating, highly resistant to acids and good chemical-resistant. But it has relatively low softening range (90–100°C) and is brittle. However, it has the unique property of *transmitting light through curved sections*.

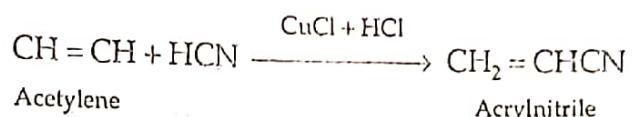
**Uses :** In moulding of articles like toys, combs; buttons, buckles, radio and television parts, refrigerator parts, battery cases, high frequency electric insulators, lenses, indoor lighting-panels, etc.

ENGINEERING CHEMISTRY

(vi) Polyacrylonitrile (PAN) is obtained by the polymerization of acrylonitrile in presence of a peroxide. It is an acrylic polymer.



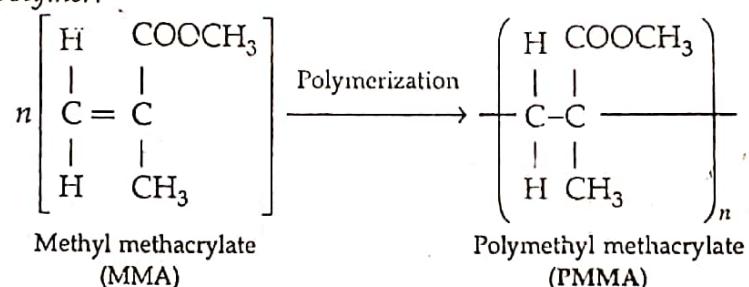
Acrylonitrile is prepared as follows : Polyacrylonitrile (PAN)



**Properties :** It is a high melting, hard and horny solid.

**Uses :** As a substitute for wool for making fibres like *acrilan*. Thus, it is used for making warm clothes, carpets, blankets, etc.

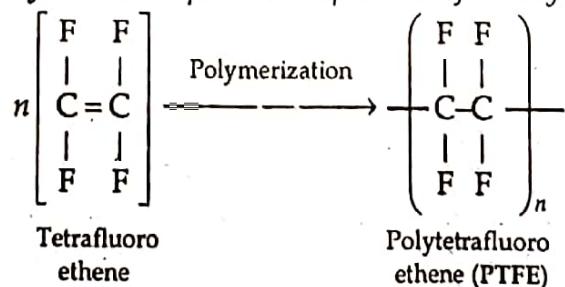
(vii) **Polymethyl methacrylate or Lucite or Plexiglass** is obtained by polymerization of methyl methacrylate (ester of methyl acrylic acid,  $\text{CH}_2 = \text{C}(\text{CH}_3)\text{COOH}$ ) in presence of acetyl peroxide or hydrogen peroxide. It is an acrylic polymer.



**Properties :** Polymethyl methacrylate (PMMA) is hard, fairly rigid material with a high softening point of about 130–140°C, but it becomes rubber-like at a temperature above 65°C. This relatively wide span of temperature from its rigid state to viscous consistency accounts for the outstanding shape-forming properties of polymethyl methacrylate. It has high optical-transparency, high resistance to sunlight and ability of transmitting light accurately, even in curved sections. However, it has low chemical-resistance to hot acids and alkalis and low scratch-resistance.

**Uses :** For making lenses, aircraft light fixtures, bomber noses, gun turrets, cockpit canopies, transparent models of complicated mechanisms, bone splints, artificial eyes, dentures, emulsions, paints, adhesives, automotive appliances, jewellery, wind screens, T.V. screens, guards, etc.

(viii) **Polytetrafluoroethylene (TEFLON) or FLUON (PTFE)** is obtained by polymerization of water-emulsion of tetrafluoro ethylene, under pressure in presence of benzoyl peroxide as catalyst.



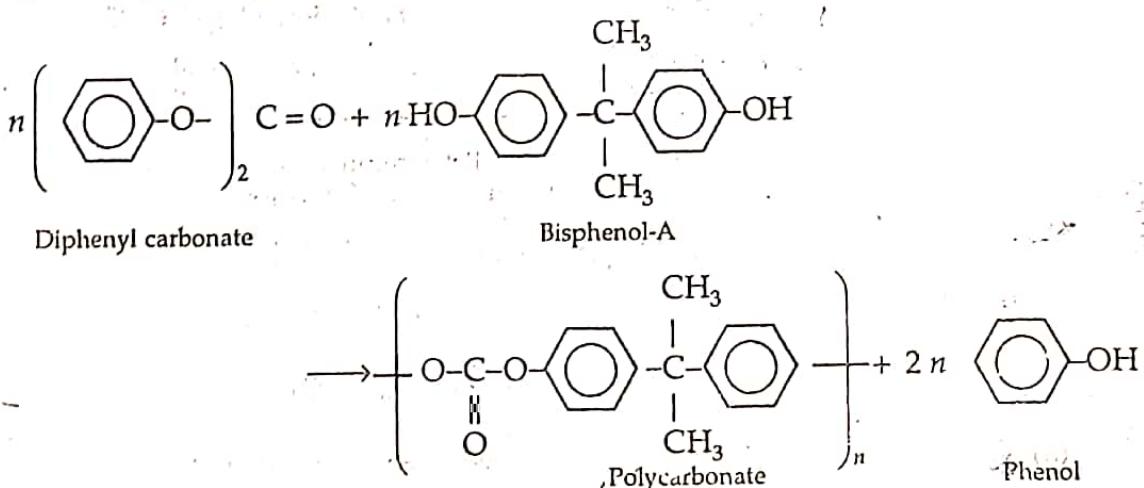
**Properties :** Due to the presence of highly electronegative fluorine atoms and the regular configuration of the polytetrafluoro ethylene molecule results in very strong attractive forces between the different chains. These strong attractive forces give the material extreme toughness, high softening point (about 350°C), exceptionally high chemical-resistance towards all chemicals (except hot alkali metal and hot fluorine), high density

## HIGH POLYMERS

(2.1 to 2.3 gcm<sup>-3</sup>), waxy touch, very low coefficient of friction, extremely good electrical and mechanical properties : It can be machined, punched and drilled. The material, however, has the disadvantage that it cannot be dissolved and cannot exist in a true molten state. Around 350°C, it sinters to form very viscous, opaque mass, which can be moulded into certain forms by applying high pressures.

Uses : As insulating material (for motors, transformers, cables, wires, fittings, etc.) and for making gaskets, packings, pump parts, tank linings, chemical-carrying pipes, tubings and tanks, etc ; for coating and impregnating glass fibres, asbestos fibres and cloths ; in non-lubricating bearings and non-sticking stop-cocks (for burettes), etc.

(ix) Polycarbonates (PC) (like Lexan, Merlon) are prepared by interaction of diphenyl carbonate with bisphenol-A [2, 2-bis (4-hydroxyphenyl) propane].

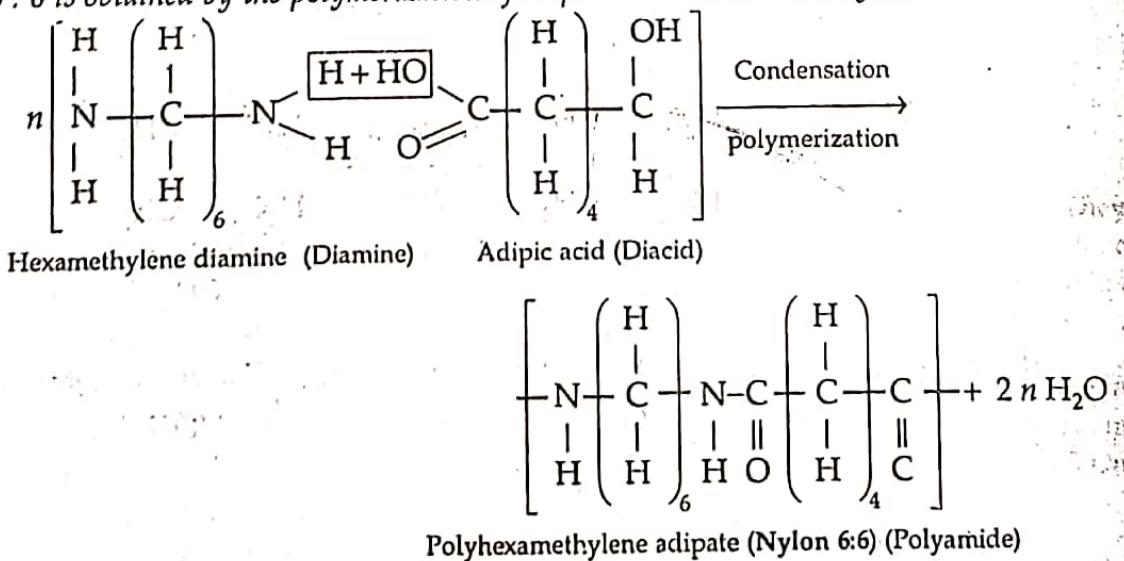


**Properties :** Polycarbonates are characterised by high impact and tensile strength over a wide range of temperature. However, they are soluble in organic solvents and alkalis.

Uses : For preparing moulded domestic ware, housing for apparatus, and electrical insulator in electronics and electrical industries.

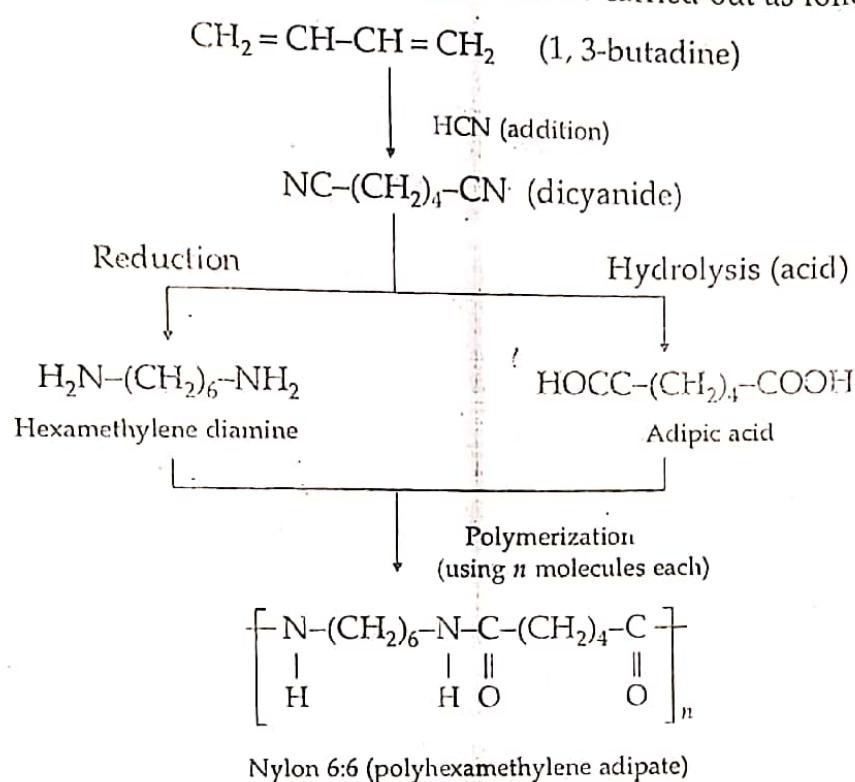
3. Polyamides are synthetic polymers, which have recurring amide groups. Nylons, used mostly for making fibres, belong to this class.

Nylon-6 : 6 is obtained by the polymerization of adipic acid with hexamethylene diamine.

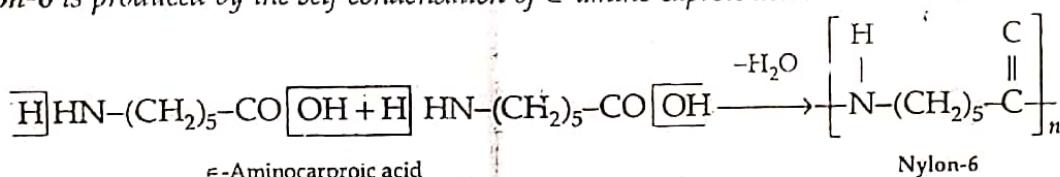


\* **CAROTHERS, Wallace H. (1896-1937).** American chemist. Besides its enormous commercial success, Carothers' work on nylon is ranked with that of Staudinger in clearly elucidating macromolecular structure and properties. Depressed by the death of his sister and convinced that his life's work was a failure, Carothers committed suicide at the age of 41.

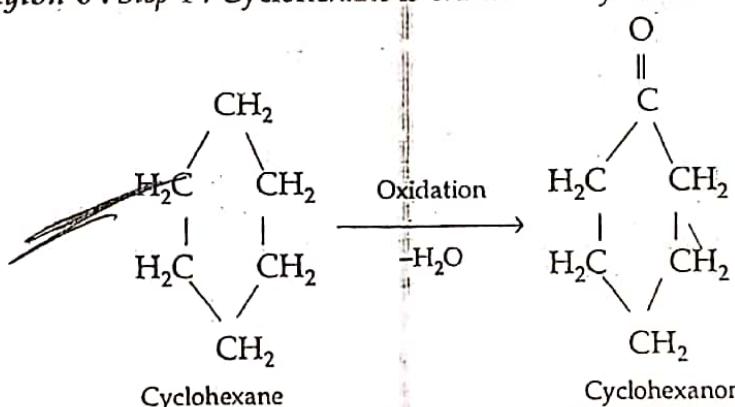
Preparation of nylon 6:6 from 1,3-butadiene can be carried out as follows:



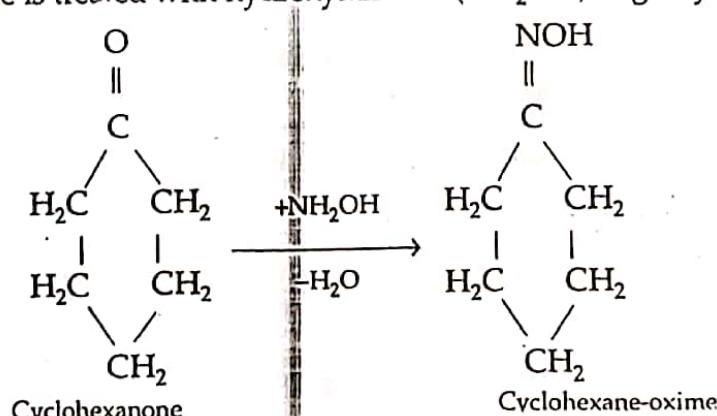
(ii) Nylon-6 is produced by the self-condensation of  $\epsilon$ -amino caproic acid.



Synthesis of nylon-6 : Step 1 : Cyclohexane is oxidised to cyclohexanone.

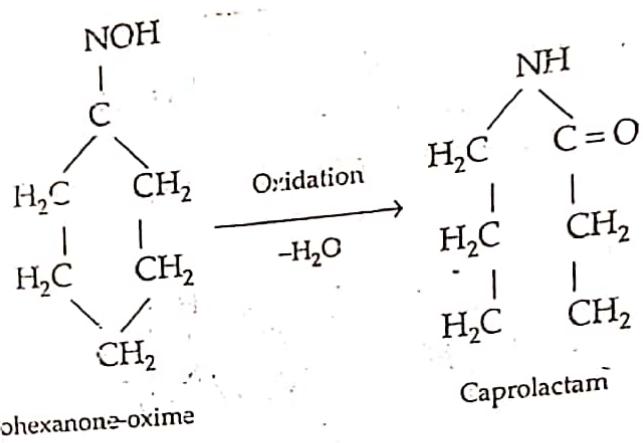


Step 2 : Cyclohexanone is treated with hydroxylamine ( $\text{NH}_2\text{OH}$ ) to get cyclohexanone-oxime.

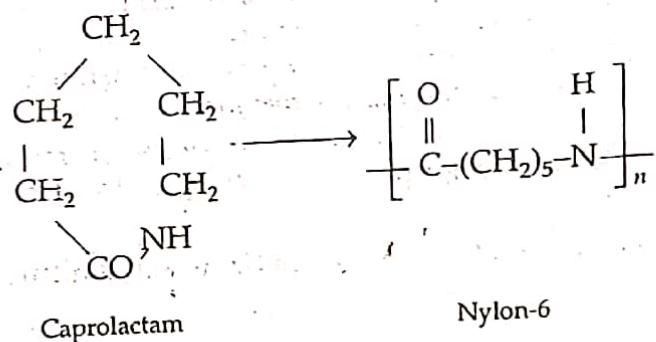


## HIGH POLYMERS

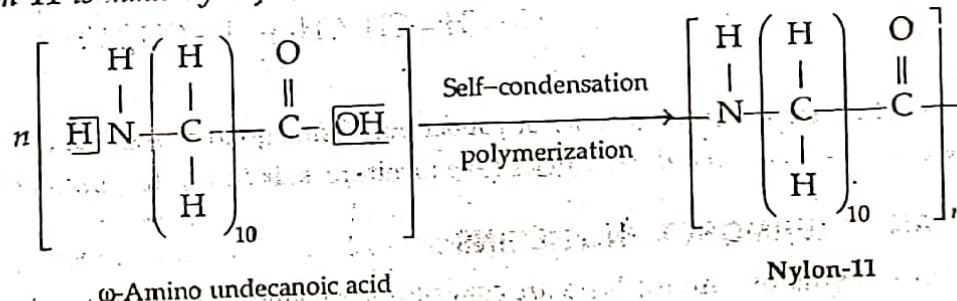
*Step 3 : Cyclohexanone-oxime in presence of ( $H_2SO_4$ ) undergoes Backmann rearrangement to yield caprolactam.*



*Step 4 : Caprolactam on self-polymerization yield nylon-6.*



(iii) Nyaon-11 is made by self-condensation of  $\omega$ -amino undecanoic acid.

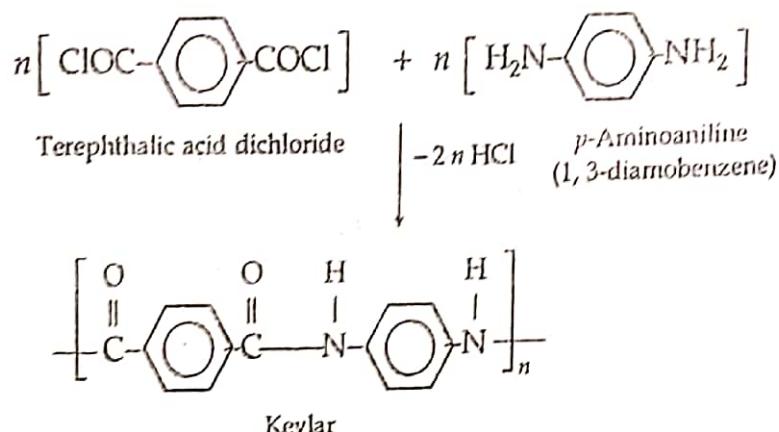


**Properties of nylons :** They are translucent, whitish, horny, high melting (160 to 264°C) polymers. They possess high temperature stability and good abrasion-resistance. They are insoluble in common organic solvents (like methylated spirit, benzene and acetone), and soluble in phenol and formic acid. Their mouldings and extrusions have good physical strengths (especially high impact strength) and self-lubricating properties.

**Characteristics of nylon fibres :** (i) They are light, horny and high melting. (ii) They are insoluble in common solvents. (iii) They have good strength. (iv) They absorb little moisture; and are thus 'drip-dry' in nature. (v) They are very flexible and retain original shape after use. (vi) They are resistant to abrasion. (vii) On blending with wool, the strength and abrasion resistance of the latter increases.

**Uses of nylons :** (1) Nylon-6:6 is primarily used for fibres, which find use in making socks, ladies' hose, under-garments, dresses, carpets, etc. (2) Nylon-6 and Nylon-11 are mainly used for moulding purposes for gears, bearings, electrical mountings, etc. Nylon bearings and gears work quietly without any lubrication. (3) They are also used for making filaments for ropes, bristles for tooth-brushes and films, tyre-cords, etc.

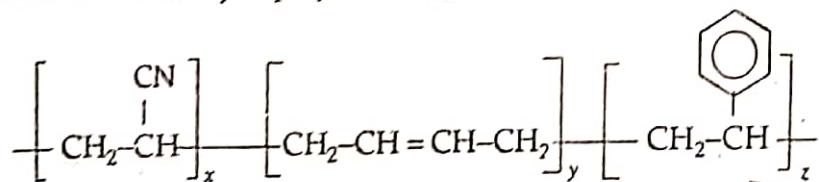
(iv) Kevlar is an aromatic polyamide similar to nylons, but with benzene rings rather than aliphatic chains linked to the amide groups  $\text{CONH}-$ . It is prepared by polycondensation between aromatic dichloride and aromatic diamines, e.g.,



**Properties :** Kevlar is exceptionally strong (5 times stronger than steel and 10 times stronger than Al on a weight-for-weight basis). It has high heat stability and flexibility. The unique properties of kevlar are due to the delocalized bonding which causes the benzene rings to be inflexible. Therefore, kevlar is far more rigid than nylons. The high electron-density in the chains of kevlar also results in relatively stronger van der Waals intermolecular forces between neighbouring polymer molecules.

**Uses :** Kevlar is used extensively in the aerospace and aircraft industries, car parts (such as tyres, brakes, clutch linings, etc.), ropes, cables, protective clothing, bullet-proof vests, motorcycle helmets and other high performance materials.

4. ABS polymers are made by copolymerizing acrylonitrile, butadiene and styrene.

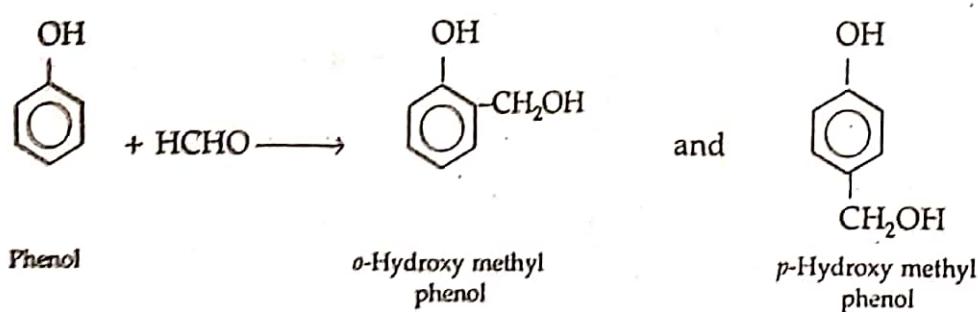


**Properties :** They are structural plastics or rubber possessing good strength and toughness.

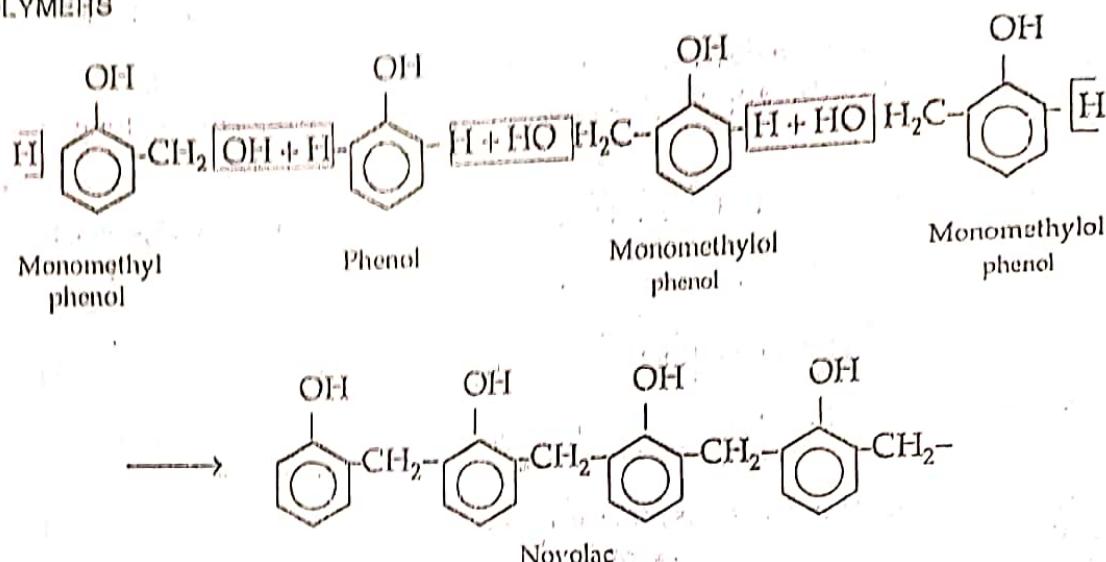
**Uses :** Telephones, pipes, moulded articles (like furniture, suit-cases, etc.), packing containers.

## 15 IMPORTANT THERMOSETTING RESINS

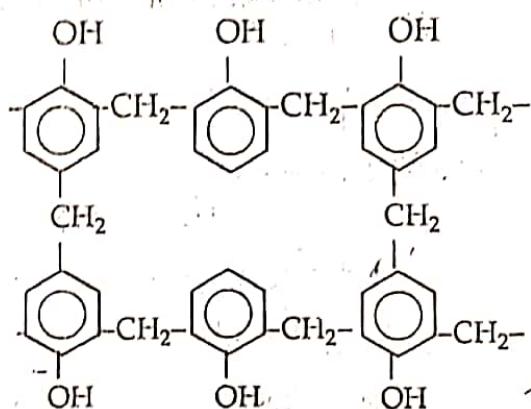
(1) Phenolic resins or phenoplasts are condensation polymerization products of phenolic derivatives (like phenol, resorcinol) with aldehydes (like formaldehyde, furfural). Most important member of this class is bakelite or phenol-formaldehyde resin. It is prepared by condensing phenol with formaldehyde in presence of acidic/alkaline catalyst. The initial reaction results in the formation of *o*- and *p*-hydroxy methyl phenol, which reacts to form linear polymer, novolac. Thus :



## HIGH POLYMERS



During moulding, hexamethylene tetramine  $[(\text{CH}_2)_6\text{N}_4]$  are added. The addition of hexamethylene tetramine provides formaldehyde, which converts the soluble and fusible novolac into a hard, infusible and insoluble solid of *cross-linked* structure.

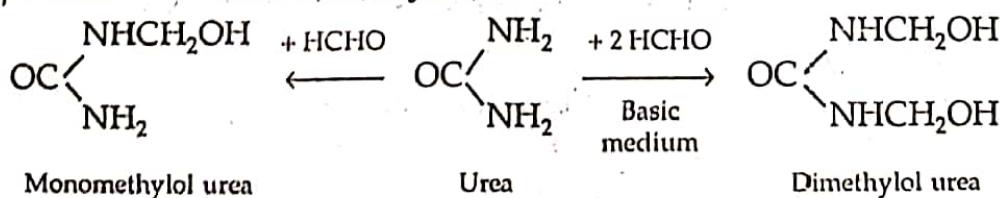


Cross-linked polymer bakelite

**Properties :** Phenolic resins (bakelite) set to rigid, hard, scratch-resistant, infusible, water-resistant, insoluble solids, which are resistant to non-oxidizing acids, salts and many organic solvents, but are attacked by alkalis, because of the presence of free hydroxyl group in their structures. They possess excellent electrical insulating character.

**Uses :** (1) For making electric insulator parts like switches, plugs, switch-boards, heater-handles, etc. (2) For making moulded articles like telephone parts, cabinets for radio and television. (3) For impregnating fabrics, wood and paper. (4) As adhesives (e.g., binder) for grinding wheels. (5) In paints and varnishes. (6) As hydrogen-exchanger resins in water softening. (7) For making bearings, used in propeller shafts for paper industry and rolling mills.

(2) **Amino resins** are condensation products, obtained by the reaction of urea or melamine with formaldehyde. Commercially important amino resin is urea-formaldehyde, which is prepared by the reaction between 2 parts of urea and 1 part of formaldehyde, in basic medium, in a stainless steel vessel at about  $50^\circ\text{C}$ . Primary products are mono and dimethylol ureas.



**Properties :** They possess exceptional resistance to prolonged exposure to sunlight, weathering, most common oils, boiling water, dilute acids and alkalis. They remain flexible in the temperature range of 90–250°C and hence, find use in making tyres of fighter aircrafts, since they prevent damage on landing. Ordinary rubber tyre becomes brittle and hence, disintegrates. Moreover, silicone rubber at very high temperatures (as in case of fibres) decomposes ; leaving behind the non-conducting silica ( $\text{SiO}_2$ ), instead of carbon tar.

**Uses :** (1) As a sealing material in search-lights and in aircraft engines. (2) For manufacture of tyres for fighter aircrafts. (3) For insulating the electrical wiring in ships. (4) In making lubricants, paints and protective coatings for fabric-finishing and water-proofing. (5) As adhesive in electronics industry. (6) For making insulation for washing machines and electric blankets for iron board covers. (7) For making artificial heart valves, transfusion tubings, and padding for plastic surgery. (8) For making boots for use at very low temperature, since they are less affected by temperature variation, e.g., Neil Armstrong used silicone rubber boots when he walked on the moon.

(iv) *Solid silicone resins* are highly cross-linked silicones, obtained by condensing bi-and tri-functional silicon halides such as  $(\text{CH}_3)_2\text{SiCl}_2$  and  $\text{CH}_3\text{SiCl}_3$ .

**Properties :** They are thermosetting, possess good electrical insulating properties and outstanding heat-resistance. Temperature up to 200°C can be safely operated on these resins. These resins are good water-repellent, chemically high thermal-stability.

**Uses :** For making high voltage insulators, high temperature insulating foams and in mouldings requiring high thermal stability.

## 20 MOLECULAR-MASS (WEIGHT) OF A POLYMER

When we speak of molecular-mass of a polymer, it is, however, quite different from that applied to small-sized compounds. Polymers are *polydisperse* and quite heterogenous in molecular-mass. *In other words, polymers are mixtures of molecules of different molecular-masses. Three main types of molecular-mass of polymers have been recognised :*

(1) **Number-average molecular-mass ( $\bar{M}_n$ )** is determined by measurement of *colligative properties* [such as freezing point depression (*cryoscopy*), boiling point elevation (*ebullimetry*), osmotic pressure and lowering of vapour pressure].  $\bar{M}_n$  is defined as the total mass ( $w$ ) of all the molecules in a polymer sample divided by the total number of molecules present. Thus, the number-average molecular mass is defined by :

$$\bar{M}_n = \frac{w}{\Sigma N} = \frac{\Sigma N_i M_i}{\Sigma N_i} \quad . . (1)$$

where,  $N_i$  is the number of molecules of mass  $M_i$ .

The number-average molecular-mass is a good index of physical properties such as *impact and tensile strength*, but is not a good index of other properties such as flow.

(2) **Weight-average molecular mass ( $\bar{M}_w$ )** is obtained from *light-scattering* and *ultra-centrifugation techniques*, which measure *molecular size*. It is defined as :

$$\bar{M}_w = \frac{\Sigma w_i M_i}{\Sigma w_i} \quad . . (2)$$

where  $w_i$  is the weight-fraction of molecules, whose mass is  $M_i$ .  $\bar{M}_w$  can also be defined as :

$$\overline{M}_w = \frac{\sum c_i M_i}{\sum c_i} = \frac{\sum c_i M_i}{c} = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad \dots(3)$$

where,  $c_i$  = weight-concentration of  $M_i$  molecules;  $c$  = total-weight concentration of all polymer molecules.

The weight-average molecular-mass is always greater than the number average molecular-mass. Moreover, since  $\overline{M}_w = \overline{M}_n$  in case of monodisperse system (i.e., in which all molecules have identical molecular mass), so the ratio  $\overline{M}_w/\overline{M}_n$  or  $(\overline{M}_w/\overline{M}_n) - 1$  may be used as a measure of the molecular-mass distribution or an "index of polydispersity".

Since the contribution of different fractions on their average value of the molecular weight depends on their weight proportions in case of  $\overline{M}_w$  and on their number proportions in case of  $\overline{M}_n$ , so the high-molecular weight fractions will have a greater effect on  $\overline{M}_w$ , and the low-molecular weight fractions will have a greater effect on  $\overline{M}_n$ . Hence,  $\overline{M}_w \geq \overline{M}_n$ .

(3) Viscosity-average molecular-mass ( $\overline{M}_v$ ) is obtained from viscosity measurement. It is defined by :

$$\overline{M}_v = \left[ \frac{\sum i v_i M_i^a}{\sum i v_i} \right] = \left[ \frac{\sum N_i M_i^{a+1}}{\sum N_i M_i} \right]^{1/a} \quad \dots(4)$$

where  $a$  = a constant. The viscosity and weight-average molecular-masses are equal, when  $a$  = unity. However,  $\overline{M}_v$  is almost always less than  $\overline{M}_w$ , since  $a$  is usually in the range of 0.5–0.9. Thus, for a polydisperse polymer :

$$\overline{M}_w > \overline{M}_v > \overline{M}_n \quad \dots(5)$$

Fig. 21 Illustrates the distribution of molecular-masses in a typical polymer sample.

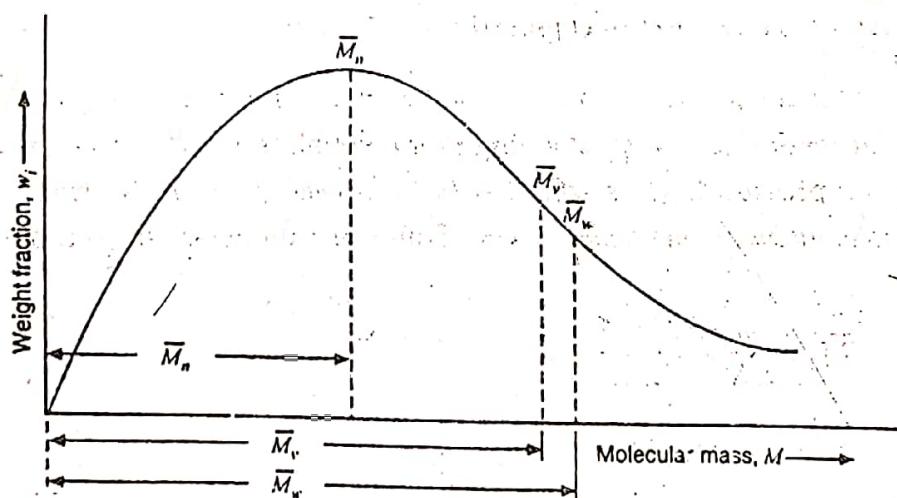


Fig. 21. Distribution of molecular-mass in polymer.

## 21 GLASS TRANSITION AND MELTING TEMPERATURES

**Glass transition :** The glass transition occurs in amorphous (or glassy) polymers, when, upon cooling from the liquid, crystallization does not take place, i.e., the polymer chains are unable to rearrange into a three-dimensional, long-range ordered structure. Upon cooling, the glass transition corresponds to an increase in viscosity, and the gradual transformation from a liquid, to a rubbery material, and, finally to a rigid solid. The temperature at which the polymer experiences the transition from rubbery to rigid states is termed the glass transition temperature ( $T_g$ ). These sequences of events occurs in the reverse order, when a rigid glass at a temperature below  $T_g$  is heated.

**2. RNA is ribonucleic acid, formed in the nucleus and is found in the cytoplasm of the cell.**

**Types of RNA :** (1) **Ribosomal-RNA (or r-RNA)** is found in the ribosomes ; and it is, usually, associated with proteins to form the ribosomes. It is synthesised in the nucleus by DNA. It is single-stranded, comprising about 80% of the total RNA. It is metabolically stable.

**Functions :** (i) This forms the site for protein synthesis. (ii) It is also supposed to help the binding of m-RNA to the ribosomes, during protein synthesis.

(2) **Messenger-RNA (or m-RNA)** carries the genetic message (code) from the DNA to ribosomes. It is produced by the DNA. m-RNA is also single-stranded ; and constitutes about 15% of total RNA.

**Functions :** It carries the genetic information from DNA to the ribosomes, where protein is synthesised.

(3) **Transfer-RNA (or t-RNA)** is synthesised in the nucleus by the DNA. It is also called soluble-RNA. It is single-stranded. There are 20 different kinds of t-RNA ; and each type has a specificity for a particular amino acid. It constitutes about 5% of total RNA. It has very short life.

**Functions :** It acts as 'carriers' of amino acids, i.e., it carries amino acids from different parts of cytoplasm to the ribosomes, during protein synthesis.

### Solved Examples

**Example 1.** If polymer sample has population as :

10 molecules of molecular mass each	= 5,000
20 " "	" = 7,500
20 " "	" = 10,000
25 " "	" = 15,000
20 " "	" = 20,000
5 " "	" = 25,000

Calculate its number-average and weight-average molecule mass of polymer.

**Solution.** Number-average molecular-mass of polymers

$$\begin{aligned}\overline{M}_n &= \frac{[10 \times 5,000 + 20 \times 7,500 + 20 \times 10,000 + 25 \times 15,000 + 20 \times 20,000 + 5 \times 25,000]}{10 + 20 + 20 + 25 + 20 + 5} \\ &= \frac{50,000 + 150,000 + 200,000 + 375,000 + 400,000 + 125,000}{100} \\ &= \frac{1.3 \times 10^6}{100} = 13,000.\end{aligned}$$

Weight-average molecular mass of polymer,

$$\begin{aligned}\overline{M}_w &= \frac{[10 \times (5,000)^2 + 20 \times (7,500)^2 + 20 \times (10,000)^2 + 25 \times (15,000)^2 + 20 \times (20,000)^2 + 5 \times (25,000)^2]}{1,300,000} \\ &\quad 250 \times 10^6 + 1,125 \times 10^6 + 2,000 \times 10^6 + 5,625 \times 10^6 + 8,000 \times 10^6 \\ &= \frac{+ 3,125 \times 10^6}{1.3 \times 10^6} \\ &= \frac{20,125 \times 10^6}{1.3 \times 10^6} = 15,480.\end{aligned}$$

## HIGH POLYMERS

**Example 2.** 28 g of ethene was polymerised by radical polymerization process and the average degree of polymerization of polythene was found to be 1,000. Calculate : (i) the number of molecules of ethene in original sample. (ii) the number of molecules of polythene produced.

**Solution.** (i) No. of molecules of ethene in 28 g

$$= 28 \text{ g} \times (6.02 \times 10^{23} \text{ molecules}/28 \text{ g}) = 6.02 \times 10^{23} \text{ molecules.}$$

(ii) No. of molecules of polythene formed

$$= \frac{\text{No. of ethene molecules}}{\text{Degree of polymerization}} = \frac{6.02 \times 10^{23}}{1,000} = 6.02 \times 10^{20} \text{ molecules.}$$

**Example 3.** Calculate the maximum percentage of sulphur that can be present in vulcanized rubber.

**Solution.** 2 monomer units of isoprene require = 2 S atoms for cross-links

$$\therefore 2 \times 68 \text{ g of isoprene requires} = 2 \times 32 \text{ g sulphur}$$

$$\text{or } 68 \text{ g of isoprene requires} = 32 \text{ g of sulphur}$$

$$\text{or } (68 + 32) \text{ g of vulcanized rubber contains} = 32 \text{ g of sulphur}$$

Hence, maximum percentage of S in vulcanized rubber

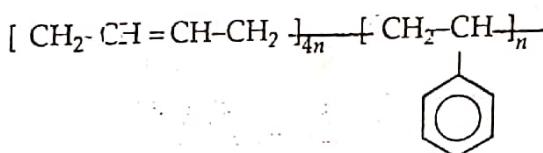
$$= \frac{32 \text{ g}}{100 \text{ g}} \times 100\% = 32\%$$

**Example 4.** 216 g butadiene is copolymerized with 104 g of styrene. What is the molecular formula of the copolymer?

**Solution.** 216 g of butadiene =  $216 \text{ g}/54 \text{ g mol}^{-1} = 4 \text{ mol}$

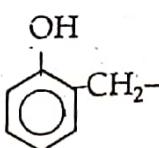
104 g of styrene =  $104 \text{ g}/104 \text{ g mol}^{-1} = 1 \text{ mol}$

∴ Molecular formula of copolymer is :



**Example 5.** 100 g of novolac is to cross-linked by one  $-\text{CH}_2-$  group of each benzene ring. What weight of formaldehyde is required for achieving this?

**Solution.** 2 molecules of



unit of novolac require

= 1 molecule of HCHO

∴ 2 × 96 g of novolac requires = 30 g HCHO

or 100 g of novolac requires =  $\frac{30 \text{ g} \times 100 \text{ g}}{2 \times 96 \text{ g}} \text{ HCHO} = 15.625 \text{ g HCHO.}$

**Example 6.** 28 g of ethylene was polymerized and average degree of polymerization of polyethylene (PE) so-produced was found to be 500. Calculate the number of PE molecules formed.

**Solution.**  $\overline{DP} = \frac{\text{No. of ethylene molecules}}{\text{No. of PE molecules formed}}$

∴ No. of PE molecules formed

$$= \frac{\text{No. of ethylene molecules}}{\overline{DP}} = \frac{28 \text{ g} \times (6.023 \times 10^{23} \text{ molecules}/28 \text{ g})}{500}$$

$$= 6.023 \times 10^{23} \text{ molecules}/500 = 1.2046 \times 10^{20} \text{ molecules.}$$

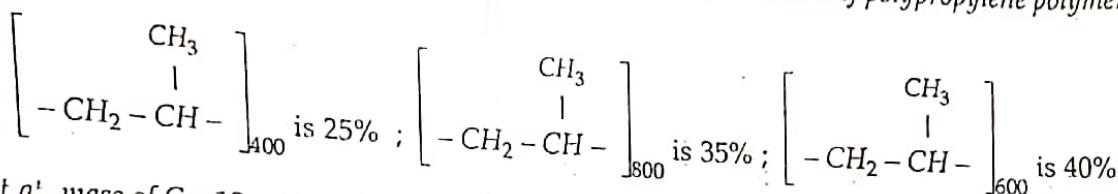
**Example 7.** A polymer sample contains :

Polymer of DP	400	500	600	800	1,000
Percentage	10	15	35	15	25

Calculate its average degree of polymerization.

Solution.  $\overline{DP} = \frac{10 \times 400 + 15 \times 500 + 35 \times 600 + 15 \times 800 + 25 \times 1000}{10 + 15 + 35 + 15 + 25} = 100$   
 $= 40 + 75 + 210 + 120 + 250 = 695$

**Example 8.** Calculate the number average and weight average molecular masses of polypropylene polymer with the following composition :



Given that at. mass of C = 12 and H = 1.

Solution. Mol. mass of repeat unit,  $-\text{CH}_2-\text{CH}(\text{CH}_3)-$  is 42.

[VT, Aug. 2K]

No. of repeat unit ( $n$ ) in polymer	400 in I	800 in II	600 in III
Mol. mass ( $M_i$ ) ( $= 42 n$ )	16,300	32,600	25,200
No. of molecules in 100	25	35	40

$$\therefore \overline{M_n} = \frac{\sum N_i M_i}{\sum N_i} = \frac{25 \times 16,300 + 35 \times 32,600 + 40 \times 25,200}{100} = 25,565$$

and 
$$\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{25(16,300)^2 + 35(32,600)^2 + 40(25,200)^2}{25 \times 16,300 + 35 \times 32,600 + 40(25,200)}$$

$$= \frac{69,24045 \times 10^4}{25,56,500} = 27,084$$

### Short Answer Question

1. Define a polymer.

(Amravati, June 94; Shivaji, Jan. 94)

Ans. A high molecular mass giant molecule formed by linking together of a large number of small molecules of monomer(s).

2. What is meant by degree of polymerization?

Ans. The number of repeating units [of monomer(s)] in a chain of a polymer.

3. Differentiate between homopolymer and copolymer.

(Mangalore, June 92)

Ans. A *homopolymer* consists of identical monomer units; while a *copolymer* consists of monomer units of different chemical structures.

4. What are resins?

(Vikram, June 96)

Ans. It is the basic polymeric material, which holds the different constituents together in a plastic.

5. What are homochain polymers?

(MK, April 94)

Ans. A polymer, which consists of same species of atoms, e.g., carbons in polythene chain.