FUNDAMENTALS OF POLYMER CHEMISTRY

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7.01 INTRODUCTION

Today plastics, rubbers, paints and surface coatings, resins, adhesives, and synthetic fibers are household words. Most of these are not natural materials, and all of them belong to a class known as **polymers** or **high polymers**. Molecules of all these materials are very long, chain-like and of high molecular weights. Thus these are very big or giant compared to ordinary simple molecules. The molecular weight of water, for example, is 18, that of sugar is 342, but the lowest molecular weight of a polymer is usually 10,000 and the highest molecular weight is above a few million. The two most characteristic features of polymers are their large size and shape. Most of their important and useful properties are mainly due to these two factors.

Whatever may be the size and shape of polymers, the chemistry of bonding and nature of reactions governing these materials are the same as those in simple organic compounds. Almost all the synthetic polymers are organic compounds and are derived from petroleum fractions or natural gas or coal. That is why polymers are called **petro-chemicals** and, in fact, they are the second largest petrochemicals after fertilizers.

7.1.1 Definition

The generic name polymer is self-explanatory. 'Poly' means many and 'meros' means parts. Therefore, a polymer is a large molecule consisting of many small units or parts. In other words, when a large number of small molecules, called **monomers**, are united to form a big molecule, a polymer is formed. And the process of formation from monomers to a polymer is known as polymer forming reaction or **polymerization** :

$$\underset{\text{Monomer}}{n\,M} \xrightarrow{\text{Polymerization}} \underset{\text{Polymer}}{(M)_n \text{ or } P} \qquad \ldots 7.1$$

The monomer units are the **repeat unit** or **mer** of the polymer, and the number of repeat unit, ***n***, in the above eqn. (7.1) is called the **degree of polymerization**, *DP*. The molecular weight of a polymer is given by

$$M = m \times DP \qquad \ldots 7.2$$

where M and m are the molecular weight of the polymer and its repeat unit, respectively. In **chain polymerization** the entire monomer molecule is the repeat unit of its polymer, and therefore, molecular weight of a chain polymer is the degree of polymerization times its monomer molecular weight. However, in **step polymerization** some small molecules such as water, ammonia, hydrogen chloride, etc. are eliminated from the reacting molecules, and therefore, the mer weight is less than that of the reactants. Table 7.1 presents a list of some common polymers and their monomers and/or reactants.

Problem 1

P 7.01 A Sample of polystyrene has an average molecular weight of 1,04,000. What is the degree of polymerization of this sample of polystyrene?

Solution

Molecular weight of polymer $= m \times \overline{DP}$

where m = 'mer' weight

= monomer molecular weight

and $\overline{DP}$ = avarage degree of polymerization

$$\therefore \overline{DP} = \frac{1{,}04{,}000}{104} = 1{,}000;\ \overline{DP} = \frac{\text{Molecular weight of polymer}}{\text{Molecular weight of monomer}}$$

molecular weight of styrene monomer

$$\underset{\displaystyle C_6H_5}{CH_2 = \underset{|}{CH}} = (8 \times 12 + 8 \times 1) = 104\,.$$

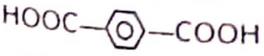
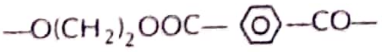
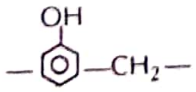
Problem 2

P 7.02 Calculate the molecular weight of a sample of polyvinyl chloride with a degree of polymerization of 750.

7.1.2 Classification of Polymers

Polymers may be classified into different classes on the basis of their chemistry of formation, thermal behaviour, composition of the chain, or application, etc. For example, on the basis of polymerization reaction, polymers may be classified as **chain polymers** and **step polymers.** The former are formed by chain reactions while the latter are obtained by step reactions.

Table 7.1 : Some Common Polymers and Their Monomers or Reactants*

Sl. No.	Monomer/ Reactant	Polymer	Repeat unit (mer) structure	Molecular weight of repeat (mer) unit	Molecular weight of mono-mer/ reactant
1.	Ethylene $CH_2 = CH_2$	Polyethylene (PE)	$-CH_2-CH_2-$	28	28
2.	Propylene $CH_2{=}\underset{\displaystyle CH_3}{\underset{\mid}{CH}}$	Polypropylene (PP)	$CH_2-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-$	42	42
3.	Acrylonitride $CH_2 = \underset{\displaystyle CN}{\underset{\mid}{CH}}$	Polyacrylonitrile (PAN)	$-CH_2-\underset{\displaystyle CN}{\underset{\mid}{CH}}-$	53	53
4.	Vinyl chloride $CH_2{=}\underset{\displaystyle Cl}{\underset{\mid}{CH}}$	Polyvinyl chloride (PVC)	$-CH_2-\underset{\displaystyle Cl}{\underset{\mid}{CH}}-$	62·5	62·5
5.	Styrene $CH_2 = \underset{\displaystyle C_6N_5}{\underset{\mid}{CH}}$	Polystyrene (PS)	$-CH_2-\underset{\displaystyle C_6H_5}{\underset{\mid}{CH}}-$	104	104
6.	Hexamethylene diamine $H_2N(CH_2)_6NH_2$ and Adipic acid $HOOC(CH_2)_4COOH$	Nylon—6, 6	$-HN(CH_2)_6NHOC(CH_2)_4CO-$	226	262
7.	Ethylene glycol $HO(CH_2)_2OH$ and Terephthalic acid 	Polyester (PET)		192	228
8.	Phenol  and Formalde-hyde HCHO	Phenol-formal-dehyde resin (PF – resin)		106	124

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* Polymers (Sl. Nos. 1-5) are **chain polymers** where molecular weight of the repeat or mer unit is equal to the molecular weight of the monomer. Polymers (Sl. Nos. 6-8) are **step polymers** where molecular weight of the repeat unit is usually less than the molecular weight of their reactants.

Similarly, on the basis of their thermal behavior, polymers are classified as **thermoplastics** and **thermosets** or **thermosetting polymers**. Thermoplastics, on heating, melt and on cooling solidify again, and this process of heating and cooling may be repeated almost indefinitely to make them molten and solid. Thermosets, on the other hand, melt on heating and solidify on cooling, but once hardened they cannot be melted again by heat. However, under high and prolonged heat the solidified thermoset may be degraded and decomposed.

Polymers may be conveniently classified, on the basis of the composition, or rather arrangement of the monomer units in their chain molecule, into **homopolymers** and **copolymers**. Homopolymers consist of *only* one type of monomer units in the chain. Polyethylene, for example, contains only ethylene monomer units in its chain, hence polyethylene is a homopolymer. In fact, all the polymers shown in Table 7.1 are homopolymers. Copolymers, on the other hand, contain more than one type of monomer units in their chain. These can, therefore, be prepared by simultaneous polymerization of more than one monomer present in a mixture (eqn. 7.3) :

$$\underset{\text{Monomer mixture}}{n\,M_1 + m\,M_2} \xrightarrow{\text{Copolymerization}} \underset{\text{Copolymer}}{(M_1)_n\,(M_2)_m} \qquad \ldots 7.3$$

It should be noted that both monomers M_1 and M_2 must be polymerizing with each other so that the polymer chains contain both monomer units as the mer unit in the same chain. If these monomers, M_1 and M_2, do not mutually react, such polymerization will result in a mixture of two homopolymers of M_1 and M_2 (eqn. 7.4) :

$$\underset{\text{Monomer mixture}}{n\,M_1 + m\,M_2} \xrightarrow{\text{Polymerization}} \underset{\text{Homopolymer mixture}}{(M_1)_n + (M_2)_m} \qquad \ldots 7.4$$

Copolymers again may be further classified into **(a) random copolymer, (b) alternating copolymer, (c) block copolymer**, and **(d) graft copolymer** according to the mode of arrangement of the different mer units in the chain. In random copolymers the comonomer units are distributed randomly

$$-M_1-M_2-M_2-M_1-M_2-$$

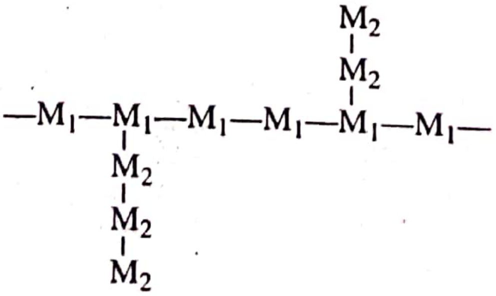
Random copolymer

$$-M_1-M_2-M_1-M_2-M_1-$$

Alternating copolymer

$$-M_1-M_2-M_1-M_2-M_2-M_2-$$

Block copolymer



$$-M_1-\underset{\substack{|\\M_2\\|\\M_2\\|\\M_2}}{M_1}-M_1-M_1-\overset{\substack{M_2\\|\\M_2\\|}}{M_1}-M_1-$$

Graft copolymer

Fig. 7.1 : Types of copolymers

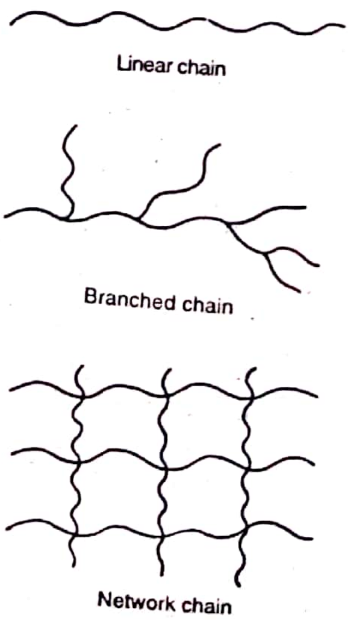
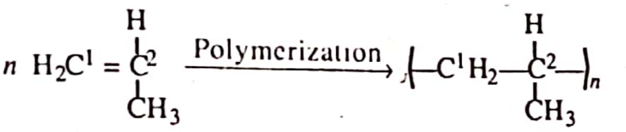


Fig. 7.2 : Various chain structures

in the chain, and in alternating copolymers these are strictly arranged alternately. But in the block and graft copolymers long sequences of one type of monomer units are linked with that of the other type. In a sense, these two types of copolymers may be regarded as a special case of one hompolymer linked to another homopolymer. In block copolymers the linking of two or more types of homopolymers is sequentitial, i.e., along the length axis of the copolymer chain. In graft copolymers, one type of homopolymer chain is linked to perpendicular to the other homopolymer as branches (Fig. 7.1). According to the chain structure polymers may be classified as (a) linear chain, (b) branched chain, and (c) network or crosslinked chain (Fig. 7.2).

Stereopolymers

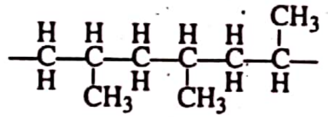
Two carbon atoms of an ethylene monomer are identical because both contain two hydrogen atoms. But in a propylene monomer the two carbon atoms are not identical, and therefore, on polymerization every second carbon becomes an asymmetric or a chiral center having either *d* or *l* configuration :



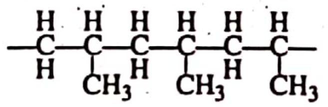
$$n\ H_2C^1=\overset{H}{\underset{CH_3}{C^2}} \xrightarrow{\text{Polymerization}} \left(C^1H_2-\overset{H}{\underset{CH_3}{C^2}}\right)_n$$

Propylene Polypropylene

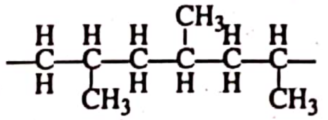
The steric arrangement of atoms in polypropylene, therefore, may be three types where the chiral carbons have **random** configuration (i.e., *dlldddld*), or strictly **alternating** configuration (i.e., *dldldldl*), or **identical** configuration (i.e., *dddddd*, or *llll*). These three configurations of chiral centres of polypropylene are known as **atactic** (i.e., random, GK. a = not, tactic = regular arrangement in space) **syndio-tactic** (i.e., alternating), and **isotactic** (i.e., same) polypropylene (Fig. 7.3).



Atactic polypropylene



Isotactic polypropylene



Syndiotactic prolypropylene

Fig. 7.3 : Stereopolymers of propylene

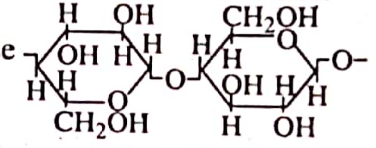
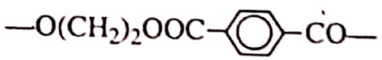
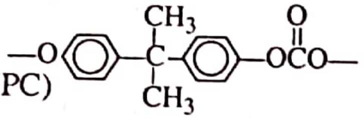
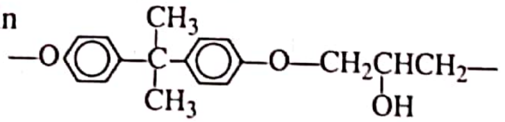
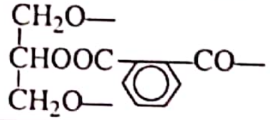
Thermoplastics vs Thermosets

It has been said earlier that on the basis of thermal behavior polymers are classified into thermoplastics and thermosets. The softening and hardening in thermoplastics on heating or cooling is reversible, but it is not in case of thermoset polymers. The explanation for this difference in behaviour of these two groups of polymers is due to the difference in their chain structure. Thermoplastics are composed of linear chain molecules, while thermosets are branched chain molecules having pendant reactive groups which on first heating are converted into a rigid network chain which cannot be further softened by heating (Fig. 7.4)

7.1.3 Rubbers, Plastics and Fibres

Polymers may be classified into three groups of materials known commonly as (a) rubbers, (b) plastics, and (c) fibres (Table 7.2). These three types of materials may either be natural or synthetic. For example, rubber may be obtained as a latex from rubber tree (**Haevea Brasiliensis**), or manufactured by synthetic processes. Natural rubber is the product from

Table 7.2 : Some Common Rubbers, Plastics and Fibres and their Repeat Unit

Rubbers	Repeat unit structure	Plastics	Repeat unit structure	Fibres	Repeat unit structure
Natural rubber (NR)	$-CH_2-\overset{CH_3}{C}=CH-CH_2-$	Polyethylene (PE)	$-CH_2-CH_2-$	Cellulose	
Styrene-butadiene rubber (SBR)	$-(CH_2-\overset{H}{\underset{C_6H_5}{C}})-(CH_2-CH=CH-CH_2)-$	Polypropylene (PP)	$-CH_2-\underset{CH_3}{CH}-$	Wool[a]	$-\underset{R}{CH}-NH-CO-$
Nitrile rubber (NR)	$-(CH_2-\overset{H}{\underset{CN}{C}})-(CH_2CH=CHCH_2)-$	Polystyrene (PS)	$-CH_2-\underset{C_6H_5}{CH}-$	Silk[a]	$-\underset{R'}{CH}-NH-CO-$
Polybutadiene rubber (BR)	$-CH_2-CH=CH-CH_2-$	Polymethyl methacrylate (PMMA)	$-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-$	Nylon-6, 6	$-HN(CH_2)_6-NHOC(CH_2)_4CO-$
Neoprene rubber (CR)	$-CH_2-\overset{Cl}{C}=CH-CH_2-$	Polyvinylchloride (PVC)	$-CH_2-\underset{Cl}{CH}-$	Polyester (PET)	
Butyl rubber	$-(CH_2-\overset{CH_3}{\underset{CH_3}{C}})-(CH_2-\overset{CH_3}{C}=CH-CH_2)$	Polycarbonate (PC)		Orlon[b] (PAN)	$-CH_2-\underset{CN}{CH}-$
		Polyacetal	$-CH_2O-$		
Ethylene-propylene-diene rubber (EPDM)	$-(CH_2-CH_2)-(CH_2-\underset{CH_3}{CH})-(D)-$	Epoxy resin			
	D = diene such as hexadiene etc.	Alkyd resin			

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[a] The nature of R and R′ varies with the aminoacid and about 18 and 16 different aminoacid residues are present in wool and silk fibres respectively.

[b] A small amount of polymethyl acrylate is used in orlon fibre.

nature, and neoprene, nitrile rubber, styrene-butadiene rubber are synthetic rubbers. Whether natural or synthetic all rubbers are soft, resilient with high elongation. These could be deformed easily by applied pressure.

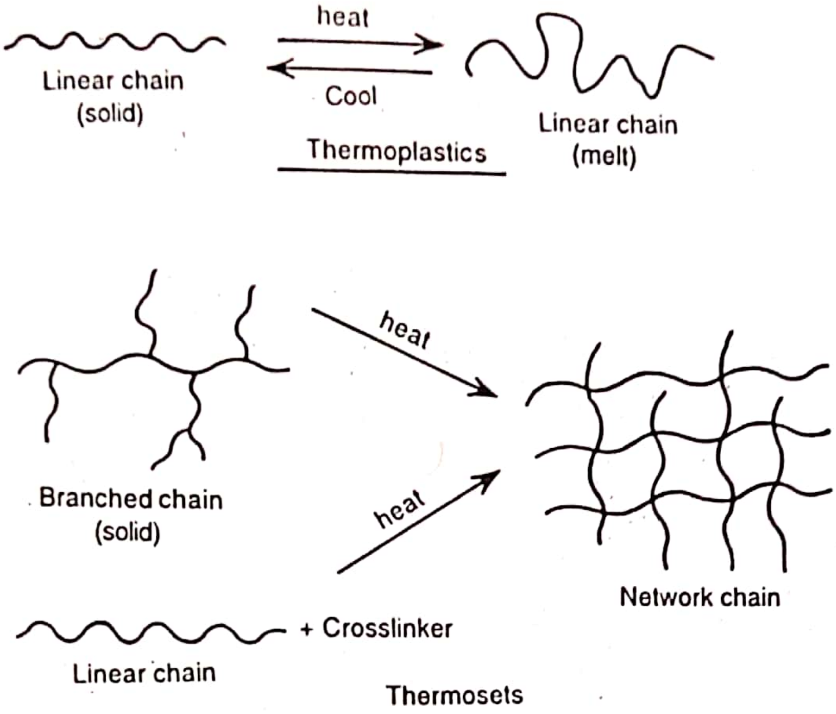


Fig. 7.4 : Response to heat by thermoplastics and thermosets

Plastics are also either natural or man-made. Shellac, wax, plant resins, etc. are natural plastics. Polyethylene, polystyrene, etc. are synthetic plastics. Irrespective of their origin plastics are hard and rigid and become rubbery in the softened or melted state, and on cooling they become hard again. Thus these are easily mouldable.

Similarly fibres may be natural like silk. cotton, wool, jute, etc. or man-made like polyester (terylene), nylon, orlon, etc. All fibres, both natural and synthetic, are stiff, mechanically strong and crystalline.

However, these differences in their behaviour and physical state are not one of fundamental difference of kind but one of degree. The apparent differences are due only to the degree of molecular order and intermolecular bonding forces present in these three classes of polymers. From rubbers to fibres the chain molecular order increases and so also the inter chain attractive forces. Thus the flexibility of polymer chain molecules decreases from rubbers to plastics to fibres. With this the rigidity, strength and associated mechanical properties increase from rubbers to fibres.

Thus rubbers, plastics and fibres are the same material with different degrees of chain order. By controlling the chain order the same polymer may behave as a rubber or a plastic or even a fibre. Polyethylene, for example, can be converted into a rubber called **Hypalon** by reducing its chain order by means of substitution of a few hydrogens by bulky groups such as chlorosulfonic group. It can be converted into a fibre by increasing its chain order by mechanical spinning and drawing.

7.02 CHAIN (ADDITION) POLYMERIZATION

Chain polymerizations involve a chain reaction which is carried out by an active chain carrier species. This chain carrier may be a free-radical, an anion, a cation, or a species which has both the characteristics of a free-radical and an ion. Accordingly, chain polymerization may be classified into : (a) Radical polymerization, (b) Anionic polymerization, (c) Cationic polymerization, and (d) Co-ordination polymerization.

Whatever may be the type of the chain carrier species involved, chain polymerizations have got three distinct steps, viz., (a) **Initiation**, (b) **Propagation**, and (c) **Termination**. In the first stage, i.e., initiation, the birth of a chain occurs by the activation of a monomer molecule by means of a free-radical (or by other chain carrier species) which is formed in the reaction site by the homolytic decomposition of a heat- or light-sensitive molecule, called an **initiator**, I, deliberately added to the polymerization reactor (eqns. 7.5 and 7.6) :

$$\underset{\text{Initiator}}{I} \xrightarrow[\text{heat/light}]{k_d} \underset{\text{Free radicals}}{2R^\bullet} \qquad \ldots 7.5$$

$$R^\bullet + M \xrightarrow{k_i} RM^\bullet \text{ or } M_1^\bullet \qquad \ldots 7.6$$

Eqn. (7.5) represents the decomposition of the initiator molecule for generation of **initiating** or **primary radical**, R•. Eqn. (7.6) represents the birth of a chain (M_1°) by the attack of the primary radical to the monomer molecule, *M*, and the chain formed contains the primary radical, i.e., the initiator fragment or the "birth mark". Since among these two reactions, the first one (i.e., eqn. 7.5) is slower than the second, and therefore, it is the rate determining step.

Since the radicals are formed in pairs, some of these may recombine to form the original initiator molecule in the solvent cage, which is known as cage recombination or **cage effect** (eqn. 7.7)

$$\underset{\substack{\text{Radicals in}\\ \text{solvent cage}}}{(2R^\bullet)} \longrightarrow R\text{–}R \text{ or } I \qquad \ldots 7.7$$

Particularly when high initiator concentrations are used for polymerization, a significant fraction of the radicals generated may be wasted so far as the chain initiation (eqn. 7.6) is concerned. Besides, primary radicals, R°, may react with the impurities or oxygen (which is a well-known radical killer due to its diradical character) present in the reaction system. Under some conditions, the primary radical may react with the growing chain radical and terminate the chain process. This is known as **termination by primary radical** (eqn. 7.8) :

$$\underset{\substack{\text{Growing}\\ \text{chain}}}{M^\bullet} + \underset{\substack{\text{Primary}\\ \text{radical}}}{R^\bullet} \xrightarrow{\text{termination}} \underset{\text{Dead polymer}}{M\text{–}R} \qquad \ldots 7.8$$

Thus it is now evident that only a fraction of the primary radicals is available for initiation; and the ratio of the number of initiating radicals to the total number of primary radicals theoretically possible by the decomposition of the initiator is called the **initiator efficiency** (f).

Propagation is the growth process of the chain. In this process monomer molecules are very rapidly added to the growing chain making the chain very long within a very short time. It is assumed that the rate of monomer addition to the growing chain is independent of its chain length (eqn. 7.9).

$$\begin{aligned} M_1^{\bullet} + M &\xrightarrow{k_p} M_2^{\bullet} \\ M_2^{\bullet} + M &\xrightarrow{k_p} M_3^{\bullet} \\ M_n^{\bullet} + M &\xrightarrow{k_p} M_{n+1}^{\bullet} \end{aligned} \qquad \ldots 7.9$$

Since almost all the monomer molecules are consumed by this process, the rate of chain propagation is equal to the rate of polymerization.

Termination is the last act of the three-stage drama of polymerization when the large growing chains lose their activity and cease to grow further. Termination is usually possible by two routes, viz., (a) **coupling**, and (b) **disproportionation**. Coupling or combination process is the mutual destruction of the *two* growing radical centres resulting in a *single* polymer molecule :

$$\underset{\text{Growing chains}}{M_n^{\bullet} + M_m^{\bullet}} \xrightarrow[\text{by coupling}]{\text{termination}} \underset{\text{Dead polymer}}{M_{n+m}} \qquad \ldots 7.10$$

The molecular weight of the 'dead' polymer formed by the coupling process is the sum of the molecular weight of the two reacting growing chains. Also the resultant polymer contains *two* "birth-marks", i.e., two primary radical species as endgroups. Thus by determining the number of endgroups per chain it is possible to determine the nature of the termination process. By analyzing the nature of the endgroups present in the polymer molecules it is also possible to identify the initiator used for the polymerization.

Termination by disproportionation is also a bimolecular process involving two growing chains, but *two* dead polymer molecules are formed by such process (eqn. 7.11) :

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow[\text{disproportionation}]{\text{termination by}} M_n' + M_m' \qquad \ldots 7.11$$

One hydrogen or other atom from one of the growing chains, M_n° or M_m°, is being transferred to the other so that one dead polymer molecule attains unsaturation at one end of the molecule (eqn. 7.12) :

$$\sim\!CH_2\!-\!\underset{X}{\underset{|}{\dot{C}H}} + \sim\!CH_2\!-\!\underset{X}{\underset{|}{\dot{C}H}} \longrightarrow \sim\!CH_2\!-\!\underset{X}{\underset{|}{CH_2}} + \sim\!CH\!=\!\underset{X}{\underset{|}{CH}} \qquad \ldots 7.12$$

The other end of both the dead polymer molecules contains the primary radical as endgroup. Thus termination by disproportionation results in polymers having *one* initiating fragments as endgroups per chain and the molecular weight will be half of that obtained by termination by coupling.

7.2.1 Kinetics of Chain Polymerization

From eqn. (7.5) rate of decomposition of the initiator, R_d, for chain polymerization may be expressed as

$$R_d = \frac{-d[I]}{dt} = k_d[I] \qquad \ldots 7.13$$

And the rate of initiation of the free radical chain polymerization, R_i, can be written from eqn. (7.6)

$$R_i = \frac{d[RM^{\bullet}]}{dt} = k_i[R^{\bullet}][M] \qquad \ldots 7.14$$

Since determination of $[R^\bullet]$ is difficult, the rate of initiation may be obtained from eqn. (7.13) as

$$R_i = 2fk_d[I], \qquad \text{... 7.15}$$

where f is the initiator efficiency, which is a measure of the fraction of the total radicals produced by decomposition of initiator molecules actually involved in chain initiation.

The rate of chain propagation of a radical polymerization, R_p, may be written as from eqn. (7.9)

$$R_p = \frac{-d[M]}{dt} = k_p[M][M^\bullet]. \qquad \text{... 7.16}$$

The rate of chain termination, R_t, may be written as from equns. (7.10) and (7.11).

$$R_t = 2k_t[M^\bullet][M^\bullet] = 2K_t[M^\bullet]^2 \qquad \text{... 7.17}$$

In actual chain polymerization, the number of growing chains is practically constant almost throughout the reaction. In other words, the number of chains initiated is equal to the number of chains terminated, i.e., $R_i = R_t$. This is known as a "steady state" where

$$\frac{d[M^\bullet]}{dt} = 0.$$

Therefore, from eqns. (7.14) and (7.17)

$$k_i[R^\bullet][M] = 2k_t[M^\bullet]^2. \qquad \text{... 7.18}$$

From eqns. (7.15) and (7.18)

$$[M^\bullet] = \left(\frac{k_i[R^\bullet][M]}{2k_t}\right)^{\frac{1}{2}} \qquad \text{... 7.19}$$

and

$$[R^\bullet] = \frac{2fk_d[I]}{k_i[M]}. \qquad \text{... 7.20}$$

From eqns. (7.19) and (7.20)

$$[M^\bullet] = \left(\frac{fk_d[I]}{k_t}\right)^{\frac{1}{2}} \qquad \text{... 7.21}$$

Substituting the value of $[M^\bullet]$ from eqn. (7.21) into eqn. (7.16)

$$\begin{aligned} R_p &= k_p[M]\left(\frac{fk_d[I]}{k_4}\right)^{\frac{1}{2}} \\ &= k_p\left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}}[M][I]^{\frac{1}{2}} \\ &= k'[M][I]^{\frac{1}{2}}, \end{aligned} \qquad \text{... 7.22}$$

where $k' = k_p\left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}}$.

Similarly substituting the value of $[M^\bullet]$ from eqn. (7.21) into eqn. (7.17)

$$R_t = 2k_t\left(\frac{fk_d[I]}{k_t}\right)$$

$$= 2fk_d[I]. \qquad \text{... 7.23}$$

Thus both the rate of propagation and rate of termination can be easily determined by the initial concentration of the monomer and initiator used for the chain polymerization.

The average degree of polymerization, $\overline{DP}$, may be defined as

$$\overline{DP} = \frac{\text{Rate of propagation}}{\text{Rate of termination}} = \frac{R_p}{R_t}. \qquad \text{... 7.24}$$

Solvng eqn. (7.24) with the help of eqns. (7.22) and (7.23)

$$\overline{DP} = k''\frac{[M]}{[I]^{\frac{1}{2}}}, \qquad \text{... 7.25}$$

where $k'' = \dfrac{k_p}{\left(2fk_d k_t\right)^{\frac{1}{2}}}$.

Problem 3

P 7.03 Acrylonitrile is polymerized by H_2O_2 in presence of UV-light. What will be the molecular weight of polyacrylonitrile when 0·2 wt% H_2O_2 is added to acrylonitrile ?

Solution

Molecular weight of polyacrylonitrile

$$= \overline{DP} \times \text{mole. wt. of acrylonitrile}$$

$$\overline{DP} = \frac{\text{Total no. of acrylonitrile molecules}}{\text{Total no. of } H_2O_2 \text{ molecules}}$$

$$H_2O_2 \xrightarrow{\text{UV-light}} 2OH$$

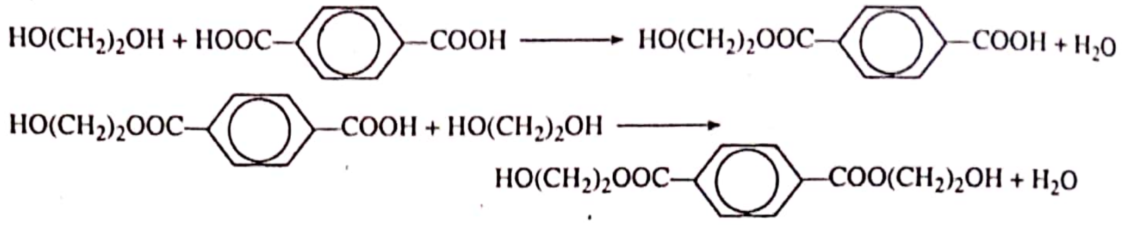
Assuming both the OH radicals are reused for initiation and termination of polymerization,

$$\overline{DP} = \frac{100/53}{0\cdot 2/34} = 321.$$

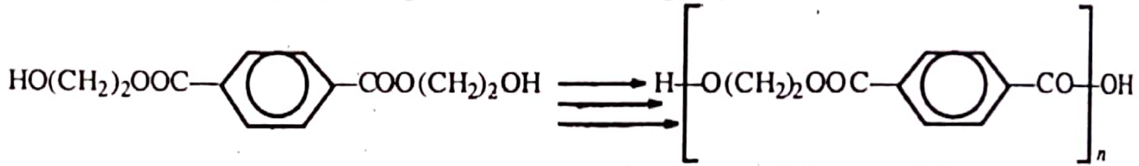
∴ mol. wt. of polyacrylonitrile $= 321 \times 53 = 17{,}013$.

7.03 STEP (CONDENSATION) POLYMERIZATION

Polymers are also formed by step polymerization reactions which proceed through successive steps of ordinary condensation where a small molecule (such as water, ammonia, carbon-dioxide, salt, etc.) is eliminated in each step. Although some condensation catalysts such as *p*-toluenesulfonic acid, sodium acetate, antimony oxide are used to speed up the reaction, the most important driving force for the reaction to go theoretical (i.e., 100%) conversion is the removal of the by-product small molecules from the reaction mixture by heat and/or vacuum. The condensation between ethylene glycol and terephthalic acid, for example, results in formation of the step polymer, polyethylene terephthalate (PET), by elimination of water of condensation by heat (up to 200°C or even more) and reduced pressure (up to 5–10 mm-Hg). The reaction may be represented as



And these steps of condensation are exactly similar to those of any ester forming reaction, and are repeated until one or both of the reactants are consumed to produce a high molecular weight polyester :



Polyester (PET)

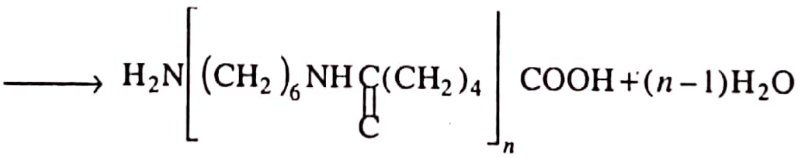
Problem 4

P 7.04 Calculate the average degree of polymerization of nylon-6, 6 having a number average molecular weight of 30,000.

Solution

The polymerization of nylon – 6, 6 may be written as

$n\ H_2N\,(CH_2)_6NH_2 + n\ HOOC\,(CH_2)_4\,COOH$



$$\longrightarrow H_2N\left[(CH_2)_6NH\underset{\Vert}{C}(CH_2)_4\right]_n COOH + (n-1)H_2O$$

∴ 'mer' weight of nylon– 6, 6 = 226.

∴ mol. wt. of nylon– 6, 6 = (n × 226) + 18

$30{,}000 = 226n + 18$

or, $29{,}982 = 226n$

$$\therefore\ n \text{ (i.e, } \overline{DP}) = \frac{29{,}982}{226} \cong 136.$$

7.3.1 Kinetics of Step Polymerization

Kinetics of step polymerization may be considered by the example of polyester formation between a dicarboxylic acid and ethylene glycol. This polycondensation reaction, like simple esterification, may proceed with or without the presence of an acid catalyst. The acid-catalyzed rate of polyesterification may be written as

$$-\frac{d\,[\text{COOH}]}{dt} = K\,[\text{COOH}]\,[\text{OH}]\,[\text{H}^+]$$

$$= K'\,[\text{COOH}]\,[\text{OH}], \qquad \ldots 7.19$$

where $K' = K\,[H^+]$ = constant, since the catalyst acid concentration $[H^+]$ remains constant throughout the polymerization.

Since equimolar or stoichiometric amount of acid and glycol is generally used, $[\text{COOH}] = [\text{OH}] = c$, eqn. (7.19) becomes the expression for a *second-order* reaction :

$$-\frac{dc}{dt} = K'c^2$$

$$\text{or,} \quad -\frac{dc}{c^2} = K'dt. \qquad \ldots 7.20$$

For uncatalyzed polycondensation of the above reaction, one molecule of the dicarboxylic acid is found to act as catalyst, and the rate of the polyesterification may be expressed as

$$-\frac{d\left[\mathrm{COOH}\right]}{dt} = K\,[\mathrm{COOH}]^2\,[\mathrm{OH}] \qquad \ldots 7.21$$

And considering [COOH] = [OH] = c, eqn. (7.21) becomes the expression for a *third-order* reaction :

$$-\frac{dc}{dt} = Kc^3$$

$$\text{or,} \quad -\frac{dc}{c^3} = Kdt. \qquad \ldots 7.22$$

Integrating eqn. (7.20)

$$\frac{1}{c} - \frac{1}{c_o} = K't \qquad \ldots 7.23$$

and eqn. (7.22)

$$\frac{1}{c^2} - \frac{1}{c_o} = 2\,Kt, \qquad \ldots 7.24$$

where c_0 is the initial concentration of the reactants. It is convenient to express the rate equation in terms of the extent of reaction, p, rather than in terms of the concentration of reactants. The extent of reaction, p, may be defined as the fraction of reactants or their functional groups that have reacted at time t.

Then $c = c_0\,(1 - p)$. $\qquad \ldots 7.25$

Replacing c from eqn. (7.23) by eqn. (7.25)

$$\frac{1}{1-p} = c_0\,K't + 1 \qquad \ldots 7.26$$

and similarly eqn. (7.24) becomes

$$\frac{1}{(1-p)^2} = 2c_0^2 K_t + 1. \qquad \ldots 7.27$$

Thus for *acid-catalyzed* polyesterification a plot of $\frac{1}{1-p}$ vs time of polymerization (eqn. 7.26) should result a straight line. Similarly for *uncatalyzed* polyesterification a plot of $\frac{1}{(1-p)^2}$ against time (eqn. 7.27) should be linear.

Molecular Weight in Step Polymerization

The number average molecular weight of a polymer, $\overline{M}_n$, is related to its number average degree of polymerization, $\overline{DP}_n$, by the relation (see eqn. 7.2),

$$\overline{M}_n = m \times \overline{DP}_n\,,$$

where m is the molecular weight of the polymer repeat unit.

Again

$$\overline{DP}_n = \frac{N_0}{N}, \qquad \ldots 7.28$$

where N_0 and N are the total number of molecules present initially and at time t in the polymerization reactor. Again, N_0/N is equal to $\frac{1}{1-p}$, therefore,

$$\overline{DP}_n = \frac{1}{(1-p)}. \qquad \ldots 7.29$$

Eqn. (7.29) is known as *Carothers equation*.

From eqns. (7.26) and (7.29) it is evident that $\overline{M}_n$ is approximately proportional to t for catalyzed polycondensation, and from eqns. (7.27) and (7.29) $\overline{M}_n$ is almost proportional to $t^{1/2}$ for uncatalyzed polycondensation. Thus the attainment of high molecular weight polymers is faster by the catalyzed polycondensation process. The Carothers equation (eqn. 7.29) shows that only at a very high degree of conversion, i.e., $p \rightarrow 1$, very high molecular weight step polymers may be obtained. For example, at 99·99% conversion where $p = 0{\cdot}9999$, the $\overline{DP}_n$ of the polymer obtained becomes 10,000. It means that for the polyethylene terephthalate (PET) synthesis the number average molecular weight of PET at this high conversion will be 1·92 million. However, this high molecular weight polyester would be very difficult for processing as a fibre or other application.

In step polymerization, the formation of linear, branched or network polymer structure depends on the average functionality, f_{av}, of the reactants. The average functionality, f_{av}, may be calculated by dividing the total number of functional (i.e., polymer forming reactive) groups by the total number of reactant molecules.

Problem 5

P 7.05 Calculate the f_{av} of a polymerizing reaction mixture consisting of 0·8 mole of ethylene glycol, 0·15 mole of glycerol and 0·05 mole of pentaerythritol.

Solution

Functionality of ethylene glycol = 2
Functionality of glycerol = 3
Functionality of pentaerythritol = 4
∴ average functionality of the mixture,

$$f_{av} = \frac{(0{\cdot}8\times 2)+(0{\cdot}15\times 3)+(0{\cdot}05\times 4)}{0{\cdot}8+0{\cdot}15+0{\cdot}05}$$

$$= \frac{1{\cdot}6+0{\cdot}45+0{\cdot}20}{1} = 2{\cdot}25.$$

Since $\overline{DP}_n$ is the ratio of the number of molecules (i.e., total number of functionality) initially present and the number of mlecules (or the total number of functionality) present after a certain time of reaction (i.e., at the specific extent of reaction, p), hence a relation can be obtained among f_{av}, $\overline{DP}$ and p.

$$p = \frac{\text{Number of functionalities lost}}{\text{Total number of functionality present initially}}$$

$$= \frac{2(N_0 - N)}{N_0 f} \quad \text{... 7.30}$$

since two functional groups react, and thereby lost, to form one bond.

From eqns. (7.28) and (7.30) the following two relations may be obtained :

$$p = \frac{2}{f_{av}} - \frac{2}{\left(\overline{DP}\right) f_{av}} \quad \text{... 7.31}$$

and $$\overline{DP} = \frac{2}{2 - p f_{av}} \quad \text{... 7.32}$$

If f_{av} of a reaction mixture is less than two, polymer formation does not occur. For formation of a linear polymer, f_{av} of the reactant mixture must be equal to two. But when the f_{av} is greater than two, branched polymer will be obtained, which at higher conversion, i.e., $p \rightarrow 1$, will form network structures through gelation. When gelation will just occur, $\overline{DP}$ becomes infinity, because the molecular weight of the crosslinked polymer is infinite. Hence, eqn. (7.31) can be written as

$$p = \frac{2}{f_{av}} \text{ (when } \overline{DP} \rightarrow \infty) \quad \text{... 7.33}$$

And for equimolar mixture of bifunctional reactants where $f_{av} = 2$, eqn. (7.33) becomes

$$p = 1 \text{ (when } \overline{DP} \rightarrow \infty) \quad \text{... 7.34}$$

Since 100% conversion in any step polymerization reaction is almost not possible to achieve, $\overline{DP}$ cannot be infinite, i.e., gelation or crosslinking will never occur in only bifunctional reactants.

Problem 6

P 7.06 In a polymerization reaction hexamethylene diamine reacts with adipic acid in equimolar concentration to form nylon-6, 6. Calculate the molecular weight of nylon-6, 6 when the convension is 90%.

Solution

Since conversion is 90%,

$p = 0{\cdot}9$.

From eqn. (7.29)

$$\overline{DP} = \frac{1}{(1 - 0{\cdot}9)} = 10.$$

Mer weight of nylon-6, 6 = 226 (from Table 7.1)

∴ molecular weight of nylon, according to eqn. (7.2),

= 226 × 10 = 2,260.

However, the weight of two endgroups of nylon-6, 6, viz. H and OH, i.e., 18, should also be added. Therefore, the molecular weight of nylon-6, 6 at 90% conversion = 2,260 + 18 = 2,278.

As the average functionality, f_{av}, of a polymerizing reaction mixture increases, the percent conversion, or the value of p decreases for just gelation to occur. For example, when $f_{av} = 2{\cdot}2$, the incipient gelation (or crosslinking) will occur at about 91% conversion.

7.04 MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

Unlike ordinary small molecular weight organic compounds, polymers are not characterized by fixed molecular weights. In fact, all polymers—natural or synthetic— are composed of molecules having different molecular weights. This is due to the statistical probability of growth of different chains during polymerization. Thus polymers are characterized by average molecular weights and molecular weight distributions.

The simple arithmatic average of molecular weight is the **number-average molecular weight**, $\overline{M}_n$, which is calculated by dividing the sum of the individual molecular weights by the total number of molecules present in the polymer sample :

$$\overline{M}_n = \frac{\sum_{i=1}^{n} n_i M_i}{\sum_{i=1}^{n} n_i} \qquad \ldots 7.35$$

where n_i and M_i are the mole fraction and the molecular weight of ith species of the molecules.

In the number-average molecular weight the contribution of each molecule of the polymer sample is *same* irrespective of the size of the molecule because $\overline{M}_n$ is a colligative property. $\overline{M}_n$ is sensitive to small molecules in the polymer, and in presence of small molecular weight fractions or impurities the $\overline{M}_n$ fails to recognize the contribution of larger molecules present. But the behavior and properties of polymers are very much dependent on the size of the molecules. In fact, polymer properties are contributed mostly by the larger molecules present. In order to represent the greater contribution of the larger molecules the molecular weight average should be weighted by the molecular weight of each species so that the contribution to the average molecular weight becomes greater as the greater is the molecular weight of the particular species. The generalized expression for such molecular weight averages may be written as

$$\overline{M} = \frac{\sum_{i=1}^{n} n_i M_i^{x}}{\sum_{i=1}^{n} n_i M_i^{x-1}} \qquad \ldots 7.36$$

where x is the index of the weightage of the molecules or chains. When $x = 1$, eqn. (7.36) becomes the expression for the number-average molecular wt., i.e., $\overline{M} = \overline{M}_n$. When $x = 2$, $\overline{M} = \overline{M}_w$, the weight-average molecular weight. When $x = 3$, $\overline{M} = \overline{M}_z$ the z-average molecular weight. When $2 < x > 1$, $\overline{M} = \overline{M}_v$, the viscosity-average molecular weight. Thus the order of increasing values of average-molecular weights are $\overline{M}_n$, $\overline{M}_v$, $\overline{M}_w$ and $\overline{M}_z$.

In a monodisperse system, i.e., $d = 1$ (where d is the dispersity index), $\overline{M}_n = \overline{M}_v = \overline{M}_w = \overline{M}_z$. As the dispersity increases, i.e., as the molecular weight distribution becomes wide in a polymer sample ($d > 1$), the various molecular weight averages are no longer equal. The measure of polydispersity is the dispersity index and is given by the relationship :

$$d = \frac{\overline{M}_w}{\overline{M}_n} \qquad \ldots 7.37$$

Problem 7

P 7.07 Calculate the number average ($\overline{M}_n$) and weight average ($\overline{M}_w$) mole-cular weights of a sample of polystyrene having the following analysis :

Fraction No.	Mol. wt. range	mole function
1	5,000 - 10,000	0·1
2	10,000 - 15,000	0·2
3	15,000 - 20,000	0·5
4	20,000 - 25,000	0·1
5	25,000 - 30,000	0·1

Solution

Fr. No.	Average mol. wt.
1	7,500
2	12,500
3	17,500
4	22,500
5	27,500

$$\overline{M}_n = \frac{\Sigma x_i M_i}{\Sigma x_i}$$

$$\text{Now } \Sigma x_i M_i = (0\cdot1\times7{,}500)+(0\cdot2\times12{,}500)+(0\cdot5\times17{,}500) +(0\cdot1\times22{,}500)+(1\times27{,}500)$$

$$= 17{,}000$$

$$\therefore \overline{M}_n = \frac{17{,}000}{\Sigma x_i} = \frac{17{,}000}{1} = 17{,}000$$

$$\overline{M}_w = \frac{\Sigma x_i M_i^2}{\Sigma x_i M_i}$$

$$\therefore \Sigma x_i M_i^2 = 0\cdot1 \times (7{,}500)^2 + 0\cdot2 \times (12{,}500)^2 + 0.5 \times (17{,}500)^2 + 0\cdot1 \times (22{,}500)^2 + 0\cdot1 \times (27{,}500)^2$$

$$= 316\cdot25 \times 10^6$$

$$\Sigma x_i M_i = 17{,}000$$

$$\therefore \overline{M}_w = \frac{316\cdot25 \times 10^6}{17{,}000} = 18{,}602.$$

Molecular weight distributions (MWD) represent the complete picture of the molecules present in polymers, while the molecular weight averages only indicate the average situation. Thus to have a complete and clear idea of the number and size of the chain molecules in a polymer sample, MWD is the most important parameter. For most polymers prepared by normal techniques the MWD curve is Gaussian, i.e., monomodal. For the most probable distribution, called the **Flory distribution**, for step polymers, the dispersity index $d = 2$, i.e., $\overline{M}_w = 2\ \overline{M}_n$. Polymers prepared by special techniques, e.g., anionic polymerization of styrene under a very controlled condition, have relatively narrow MWD having $d \rightarrow 1$. In fact, carefully prepared polystyrene standards have been synthesized anionically with $d = 1{\cdot}001$ or slightly higher.

Sometimes MWD is bimodal or even polymodal (Fig. 7.5). A polymer sample having bimodal distribution represents either a mixture of two samples of polymer (same or different types), or two distinct polymerization processes.

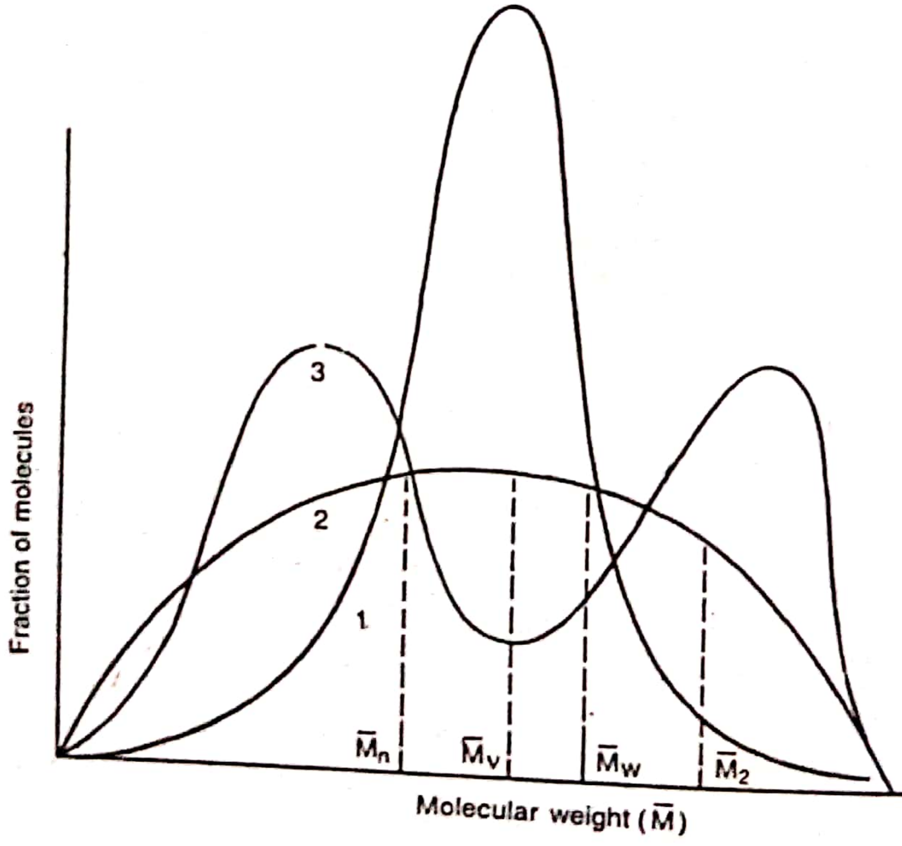


Fig. 7.5 : Different molecular weight distribution (MWD) curves : 1. narrow; 2. wide; and 3. bimodal MWD.

7.4.1 Control of Molecular Weight in Polymerization

Molecular weight control is very important for control of major properties of polymers. Since the rate of initiator decomposition depends on the polymerization temperature, the molecular weight decreases with increasing temperature. The rate of propagation (R_p), from eqn. (7.9), increases with increasing the monomer concentration, [M], and consequently the molecular weight of polymer increases. But the rate of initiation (R_i), from eqns. (7.5 and 7.6), is very much dependent on the initiator concentration, [I]. Thus the relation of molecular weight of polymers with the monomer and initiator concentrations in the polymerization reaction can be expressed by

$$\overline{M} = K\,\frac{[M]}{[I]^{1/2}}, \qquad \dots 7.38$$

where K is a constant which depends on the rate of polymerization, reaction temperature, rate of termination, etc.

From the above eqn. (7.38) it is evident that the control of polymer molecular weight can be conveniently done by controlling the initiator concentration.

Chain Transfer. Another convenient and widely practised route to control molecular weight in polymers is the use of **chain transfer agents.** These chemicals offer easy transfer of a hydrogen atom or other atoms to the growing chain and terminate it by a mechanism similar to normal disproportionation process :

$$\underset{\text{growing chain}}{\sim\!\sim CH_2{-}\dot{C}H_2} + \underset{\text{Chain transfer agent}}{CX} \longrightarrow \underset{\text{Dead polymer}}{\sim\!\sim CH_2{-}CH_2X} + \underset{\text{Chain transfer free-radical}}{\dot{C}} \qquad \dots 7.39$$

The chain transfer free-radical formed by this special termination process is able to initiate monomer molecules to form a growing chain. Thus the chain propagation or polymerization does not stop by this chain transfer termination, and in fact, R_p remains unaffected. The growing activity is merely shifted from one chain to other species. The control of polymer molecular weights by the chain transfer process is governed by the Mayo eqn. :

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_o} + C_s\,\frac{[CX]}{[M]} \qquad \dots 7.40$$

where C_s is the chain transfer constant (Table 7.3), $\overline{DP}$ and $\overline{DP}_o$ are the average degrees of polymerization in presence and absence of the chain transfer agent, CX, and $[CX]$ and $[M]$ are the concentrations of chain transfer

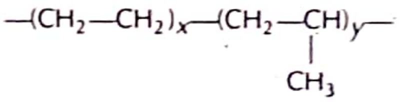
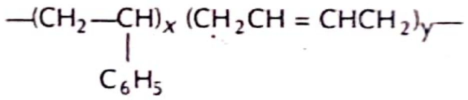
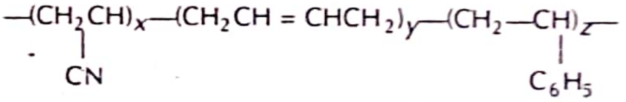
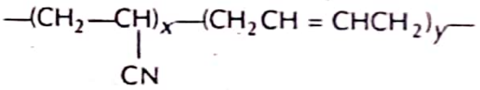
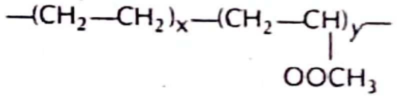
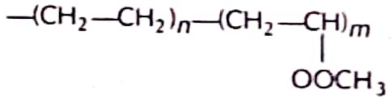
Table 7.3 : Some Common Chain Transfer Agents used in Radical Chain Polymerization of Styrene at 60°C.

Chain transfer agent	Chain transfer constant, $C_s \times 10^4$
Benzene	0·01
Toluene	0·10
Ethyl benzene	0·40
Triethylamine	1·40
o-Chlorophenol	6·0
Phenol	8·1
N, N-Dimethyl aniline	12·0
2, 6-*Ditert*-butyl phenol	49·0
Carbon tetrachloride	84·0
p-Methoxy phenol	260·0
1-Naphthalenethiol	1,500·0
Carbon tetrabromide	18,000·0
1-Dodecanethiol	1,48,000·0
1-Octanethiol	1,90,000·0

agent and monomer, respectively. Thus using a particular concentration of a chain transfer agent with a specific value of C_s, the molecular weight of the polymer to be obtained in a polymerization can be calculated. Thus chain transfer agents are termed as **chain modifier.** It may be noted here that the value of C_s depends also on the nature of the monomer and the temperature of polymerization.

If the rate of polymerization, R_p, does not remain unaltered in presence of a chain transfer agent, it is not then a case of the chain transfer process. If $R'_p < R_p$ where R'_p is the rate of polymerization in presence of the chain transfer agent, the latter is called a *retarder*. And if $R'_p \approx 0$, it is called an **inhibitor.** When, particularly during storage of monomers, polymerization is totally undesirable, an inhibitor is deliberately added to the monomer to arrest premature polymerization. This phenomenon is known as stabilization of monomers and the inhibitor is called a **monomer stabilizer.**

Table 7.4 : Some Typical Copolymers and their Comonomers

Copolymers	Structures	Comonomers
Chain Copolymers		
Ethylene-propylene rubber (EPR)	 $-(CH_2-CH_2)_x-(CH_2-\underset{\underset{CH_3}{\vert}}{CH})_y-$	Ethylene, Propylene
Styrene-butadiene rubber (SBR)	 $-(CH_2-\underset{\underset{C_6H_5}{\vert}}{CH})_x\ (CH_2CH=CHCH_2)_y-$	Styrene, Butadiene
Acrylonitrile-butadiene-styrene copolymer (ABS)	 $-(CH_2\underset{\underset{CN}{\vert}}{CH})_x-(CH_2CH=CHCH_2)_y-(CH_2-\underset{\underset{C_6H_5}{\vert}}{CH})_z-$	Acrylonitrile, Butadiene, Styrene
Nitrile rubber (NR)	 $-(CH_2-\underset{\underset{CN}{\vert}}{CH})_x-(CH_2CH=CHCH_2)_y-$	Acrylonitrile, Butadiene
Ethylene-vinyl acetate copolymer (EVA)	 $-(CH_2-CH_2)_x-(CH_2-\underset{\underset{OOCH_3}{\vert}}{CH})_y-$	Ethylene, Vinyl acetate
Vinyl chloride-vinyl acetate copolymer	 $-(CH_2-CH_2)_n-(CH_2-\underset{\underset{OOCH_3}{\vert}}{CH})_m$	Vinyl chloride, Vinyl acetate
Step Copolymers		
Polyester copolymer	$-OCRCOO(CH_2)_2OOCR'CO-$ R, R' are dicarboxylic acid residues	Ethylene glycol, Isophthalic acid, Terephthalic acid
Nylon copolymer	$-HNRNHOC(CH_2)_4COHNR'NH-$ R, R' are diamine residues	Adipic acid, Hexamethylene diamine, Tetramethylene diamine

Although these are shown as monomer blocks, in fact, the monomer units may be arranged randomly or otherwise.

7.05 COPOLYMERIZATION

It has been said that when a mixture of two or more monomers capable of mutually polymerizing is allowed to polymerize $R'_p = 0$, the polymer obtained contains all the monomer repeat units in its chain molecules. This polymer is called a **copolymer** of the monomers, which are now termed as **comonomers**, and the process of polymerization is known as **copolymerization.** The reaction mechanism of copolymerization is similar to that of **homopolymerization** (i.e., polymerization of a single monomer). Copolymerizations may be chain-reactions or step-reactions. Table 7.4 lists some typical copolymers with their comonomers.

Unlike homopolymerization, copolymerization involves more than one monomer with different reactivity depending on the polarity. This difference in reactivity observed in a pair of comonomers is termed as **reactivity ratio** (*r*), and is responsible for the difference between the composition of the copolymer and that of the monomer feed, i.e., the initial comonomer composition. The situation would be clear from the following discussion on the radical copolymerization of two monomers M_1 and M_2.

When the first monomer, M_1, is initiated by the primary radical, $R^\bullet$, the first monomer radical, $M_1^\bullet$, is formed :

$$R^\bullet + M_1 \longrightarrow M_1^\bullet$$

$M_1^\bullet$ radical finds two types of monomer molecules, M_1 and M_2, in its vicinity and may undergo the following two reactions :

1. $M_1^\bullet + M_1 \xrightarrow{k_{11}} M_1M_1^\bullet$ (which may be noted by $M_1^\bullet$) ... 7.41

2. $M_1^\bullet + M_2 \xrightarrow{k_{12}} M_1M_2^\bullet$ or $M_2^\bullet$ ... 7.42

Similarly, for the radical $M_2^\bullet$ the following two possibilities for reaction exist :

3. $M_2^\bullet + M_2 \xrightarrow{k_{22}} M_2M_2^\bullet$ or $M_2^\bullet$ ... 7.43

4. $M_2^\bullet + M_1 \xrightarrow{k_{21}} M_2M_1^\bullet$ or $M_1^\bullet$ ... 7.44

Among the above four probable reactions, reactions 1 and 3 are nothing but homopolymerization, and reactions 2 and 4 represent cross-propagation resulting in copolymerization. In other words, if in the monomer mixture of M_1 and M_2 polymerization proceeds only by routes 1 and 3, the resulting product would be a mixture of two homopolymers $(M_1)_n$ and $(M_2)_m$, and the process could not be considered as a case of copolymerization. If the polymerization proceeds by routes 2 and 4, the resulting product would be a copolymer of M_1 and M_2 and free from any homopolymer. But if all the above four reactions occur simultaneously but to different extent the resulting product is a mixture of two homopolymers and the copolymer.

In actual case the situation is not that clear-cut as described above. The fate of these four reactions are governed by the statistical probability depending on the relative reactivity of one radical species, say $M_1^\bullet$, with respect to the other species $M_2^\bullet$. This may be expressed as the ratio of the propagating rate constants and is known as the reactivity ratio of the monomer, r_1 or r_2. From reactions 1 and 2

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{... 7.45}$$

and from reactions 3 and 4

$$r_2 = \frac{k_{22}}{k_{21}}. \quad \text{... 7.46}$$

The copolymer composition (n) then can be calculated from the monomer feed composition, and monomer reactivity ratios as

$$n = \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad \ldots 7.47$$

$$\text{or, } n = \frac{r_1[M_1]/[M_2] + 1}{r_2[M_2]/[M_1] + 1} = \frac{r_1X + 1}{r_2/X + 1} \qquad \ldots 7.48$$

where $X = \frac{[M_1]}{[M_2]}$ = monomer feed composition .

When $X = n$, i.e., the copolymer composition is exactly equal to the monomer feed composition irrespective of the extent of copolymerization (i.e., % conversion), the copolymerization is called **azeotropic copolymerization.** This is similar to the azeotropic distillation when the composition of the liquid and the vapour phase is identical.

The type of copolymer obtained in a copolymerization reaction depends on the values of r_1 and r_2, although the copolymer composition may vary with the variation of the monomer feed composition.

When $r_1 > 1$, block copolymer or homopolymer results (see Fig. 7.1 for structure of different types of copolymers)

When $r_1 \approx r_2 \approx 1$ and $r_1r_2 \approx 1$, random copolymer is produced.

When $r_1 \approx r_2 \approx 0$ and $r_1r_2 \approx 0$, alternating copolymer is obtained.

For most copolymerizations r_1r_2 values lie in the range of 0 – 1.

Reactivity ratio of a monomer is not a constant quantity, and depends on (a) nature of the comonomer, (b) mechanism of copolymerization (i.e., free-radical, anionic or cationic, etc.), and (c) temperature of copolymerization.

7.06 SPECIAL FEATURES OF POLYMERIZATION

Polymerization, though a chemical reaction, has got many unique features not encounter in other chemical reactions. These are listed below :

1. Polymerization is highly exothermic. For example, the heat of polymerization of ethylene to polyethylene is 930 cals/gm.

2. Since long chain molecules show very high solution and melt viscosity, much higher than any other ordinary low molecular weight compound, the polymerization reaction medium becomes highly viscous even at low conversion. For example, the viscosity rises to about 10,000 times when styrene dissolved in toluene is polymerized only to the extent of 10%.

3. Monomers and other raw materials used for polymerization must be of very high purity. For example, **monomer grade** ethylene has a purity of 99·99% while that of **chemical grade** ethylene for manufacture of ethylene glycol is only 97% or even less.

4. The control of reaction parameters such as reaction temperature, catalyst concentration, pressure, time of reaction, etc. in polymerization must be very critically executed. Otherwise, the polymer obtained by such uncontrolled or improperly controlled polymerizations fails to meet the product specifications and therefore, may be rejected. In all other chemical reactions, only the yield and purity of the product would suffer by such uncontrolled reactions.

5. Removal of heat from a polymerization reactor is difficult due to the rise of the high solution (as well as melt) viscosity and deposition of a polymer coating on the reactor wall; unless the reaction temperature is controlled, the polymerization would become a 'run-away' reaction leading finally to explosion.

7.07 POLYMERIZATION TECHNIQUES

There are four general methods of laboratory or industrial polymerization, viz : (a) **bulk or mass**, (b) **solution**, (c) **suspension** or **bead**, and (d) **emulsion or latex**.

Bulk polymerization is the simplest form of polymerization resulting in the purest polymer product. It involves the initiation of a monomer— usually liquid — by heat or by light and high energy or by a chemical initiator. If heat and energy (UV or γ-ray, etc.) are used for initiation, the polymer may contain only the unconverted monomer which may either be removed by washing with a solvent or by the application of vacuum, or may be completely converted into polymer by continuing the polymerization process. But if a chemical initiator is used for polymerization, the initiator residues are present as impurities in the polymer. The major disadvantages of this process are the difficulty of controlling the rate of polymerization and high viscosity of the reaction mass. As a result uniform agitation of the polymerizing mass becomes extremely difficult and, therefore, gelation occurs and the molecular weight becomes very high. This phenomenon in mass polymerization is known as **gel-effect** or **Trommsdorff effect**. Heat transfer from the gel mass becomes difficult leading to rise in temperature and lowering of the chain termination process. This triggers autoacceleration and rise of both the rate of polymerization and molecular weight of the polymer formed.

Solution polymerization involves a solution of the monomer in a solvent in which the polymer may be soluble or insoluble. If the polymer is soluble in the solvent the mass becomes highly viscous and homogeneous. But if the polymer is insoluble in the solvent the polymer precipitates out and the mass becomes a slurry. The viscosity rise then is marginal. The removal and later purification of the solvent for reuse from the polymerization reactor are the major limitations of this technique. But if the homogeneous solution containing the dissolved polymer and unconverted residual monomer finds a ready market as in the case of paints, solvent removal is not necessary.

Suspension polymerization is a special case of bulk polymerization. Here the monomer is dispersed as droplets (diameter 0·1 – 5 μm) by agitation in water and the polymerization occurs in these droplets by a monomer-soluble initiator added to the polymerization mass. A suspending agent is also added in order to prevent the dispersed monomer droplets from coalescing into larger aggregates and also to stabilize the beads of polymer formed. The problems of high viscosity, stirring difficulty, heat transfer, removal and recovery of solvent, control of reaction rate and molecular weight of polymer have been solved by this process. Hence this polymerization technique is widely used in industry.

Emulsion polymerization is very similar to suspension polymerization with two notable differences, viz., the monomer droplets are smaller in size (0·05 – 0·1 μm) and the initiator is water soluble, not monomer soluble. An emulsifying agent is used to stabilize the emulsion by preventing the tiny monomer droplets from agglomeration. The product polymer obtained is in the form of a latex. The molecular weight of the polymer formed by emulsion polymerization is the highest. It enjoys almost the same advantages of suspension polymerization though the nature of initiation and propagation of this polymerization is quite complex and different from the suspension polymerization. This polymerization technique is also widely followed commercially, particularly for manufacture of high molecular weight polymers in the form of latex to be used as synthetic rubbers.

7.08 CONTROL OF POLYMER STRUCTURE AND PROPERTIES

Properties and behaviour of any material including polymers are related to their structure. Since properties dictate the field of application of materials, control of material structure is the first step for use of the material. Fortunately, modification and control of polymer structure are relatively much easier and more versatile than those for other materials like metals, alloys, glass or ceramics. In this respect polymer scientists have achieved the mastery of molecular manipulation in polymers.

First, molecular weight is the prime factor for strength properties of polymers. The mechanical strength and load-bearing characteristics increase with the increase in $\overline{M}$ of polymers. To sharpen this relation further, the MWD of the polymer must be narrow so that the dispersity index, *d*, approaches unity.

Second, to make the polymer stronger and somewhat rigid the chain molecules should be aligned in a regular order, i.e., the **degree of crystallinity** of the polymer must be higher. Alternatively, the interchain forces should be augmented through the agency of polar-polar interaction, hydrogen bonding, or by **crosslinking**. Crosslinking is a process of linking up of chains usually crosswise to the length of the chain by covalent bonds. For example, thermoplastics are linear chain flexible molecules and on crosslinking are converted into thermosets having rigid network chains. The strength of nylons is due to interchain hydrogen bonding. The rigidity or elasticity can be easily controlled by altering the extent of hydrogen bonding.

Third, stiffness and rigidity of polymer chains may also be brought about by substitution of bulky groups at regular intervals in the chain. Thus polyethylene molecules are flexible but polystyrene molecules are rigid because every alternate carbon atoms in polystyrene contains a bulky phenyl group.

Fourth, the chain symmetry is an important factor for behaviour of polymers. The strength, rigidity and stiffness increase with increase in the chain symmetry. Chain symmetry in polymers may be controlled by any one of the followings : presence of pendant groups, branching, copolymerization, presence of symmetric linkage in the chain, etc. If the chain is not symmetric it does not fit into the crystal lattice of polymers thereby reducing the strength, stiffness and rigidity. The polymer density is also reduced by the loss of chain symmetry. For example, low density polyethylene (LDPE) having specific gravity 0·93–0·94 is a branched polymer, while high density polyethylene (HDPE) having specific gravity 0·96–0·97 is practically linear with a few short branches in the backbone. Thus LDPE chains cannot be tightly packed like those of the HDPE in the crystal lattice making the latter stronger.

Fifth, a single-strand polymer is more flexible and less stronger than double or multi-strand polymer. For example, all polymers of α-olefins, such as polyethylenes, polypropylene, etc. and of vinyl monomers such as polystyrene, PVC, polyacrylonitrile, etc. are single-strand chain polymers. On the other hand, polyparaphenylenes, polyimides, aromatic polyethers, etc. are double-strand polymers. The latter are, therefore, more thermally stable, solvent and chemical resistant, and exhibit better mechanical strength than the former classes of polymers.

7.09 GENERAL PROPERTIES OF POLYMERS

The properties of polymers, like all other materials, depend on their structure and elemental composition. However, some general characteristic properties are discussed here.

Most of the high polymers are light weight (density ~ 1 gm/cm^3), solids; some are flexible while others are hard and rigid. Generally polymers are colourless, although some polymers are coloured. These are soluble in polar or nonpolar solvents depending on their polarity. The thumb rule : like dissolves like, is also applicable in polymers.

The solution and melt viscosity of polymers are very high. Even 1% polymer solution is highly viscous. This is one of the simplest identification experiment for polymers. These are non-conductors of heat and electricity, do not have characteristic metallic sound when hit by a hammer, and are pleasant to touch. Some polymers are ductile, some are rubbery, and others are brittle like glass. Thermoplastic polymers can be softened by heat and solidified on cooling. But thermoset polymers once softened and then hardened on cooling fail to soften again by heat, but if heating continues they degrade and decompose. Most polymers do not have a sharp melting point but a softening range. But they show **glass transition temperature**, T_g, at which the glassy polymers become rubbery. Only crystalline polymers such as nylons and linear polyethylene show sharp crystalline melting point, T_m. However, most of the polymers show poor thermal resistance and degrade and/or decompose completely above 400°C; some even start degradation at about 250°C.

Most of the virgin polymers need various additives to make them stable to outdoor environments, or to make them more useful and functional, or even to enhance their existing properties. Thus a single polymer can easily accommodate a host of additives for consumer and commercial applications. Although polymers can accommodate a number of additives, but most polymers show poor miscibility with each other.

Polymers are in general viscoelastic materials. Crystalline polymers exhibit elastic behavior. Amorphous and rubbery polymers show large deformation by application of stress, are nonelastic in nature, and undergo permanent deformation. Polymers show both ductile and brittle failure, creep and fatigue.

7.10 FACTORS FOR POPULARITY OF POLYMERS

Today polymers are the most popular materials. Polymers are gradually and continuously replacing other materials for manufacture of household goods and industrial products. For new and frontier technologies polymers are the most desirable material. A few examples may be given. A few years ago our bathrooms have galvanized steel or aluminium buckets and mugs. Today these are completely replaced by beautiful, coloured, light weight polyethylene buckets and mugs. Previously suitcases are made of either galvanized steel or leather. Now these are manufactured from synthetic leather (plasticized PVC) or polymers. Even chairs, tables, stools are made of various polymers replacing teak and other wood. Even plywood is a product of semi-synthetic polymer (in fact, it is a polymer-composite). Today even the entire automobile body and engine are manufactured from various plastics. A major part of space-ships or metro-rail or ocean-going ships are made up of various plastics and polymer composites. The list is a long one.

The reasons for this phenomenal growth of and demand for polymers are listed below :

(a) Polymers have the lowest density of all the existing materials—natural or man-made. Polymer's specific gravity ranges from 0·90 to 1·45 compared to that of 2·5 to 4·0 for most glass and ceramics, and 3 to 8 for most metals and alloys. Thus per unit weight polymers have the maximum volume so that larger number of parts and components, etc. can be fabricated compared to any other material. The transportation cost is also the lowest for polymer products.

(b) Polymers are usually cheap, readily available and can be prepared from a variety of raw materials such as crude oil, natural gas, coal, biomass, or agricultural renewable resources. Most of the other materials are raw material specific, i.e., copper or copper alloys can be manufactured from copper ores only and not from bauxite or magnesite. On the contrary, polymers enjoy the unique flexibility of feedstock. Any polymer can be prepared from any of the resources mentioned higher.

(c) Manufacture, modification and fabrication of polymers demand the lowest energy since the melting or softening temperatures of polymers are the lowest of all other materials. Polyethylene, for example, can be moulded at a temperature of 130° to 140°C while moulding of steel and glass article needs about 1000°C or higher.

(d) Control of properties of polymers enjoys ease and versatility not possible to that degree in any other material. In fact, the scope for modification of polymers is almost limited to the human imagination and innovativeness. Despite polymer molecules' complexity in shape, size and structure, polymer scientists have almost perfected the art of manipulation of polymer structure in the molecular scale.

(e) Intrinsic to the covalent bonded carbon compounds polymers are resistant to electrochemical corrosion, and to some extent resistant to microbial attack, i.e., polymers do not rust or rot in the environment.

(f) Other minor advantages of polymers include easy colourability, easy mouldability, better hand, non-conduction of heat and electricity, design flexibility, parts consolidation and ready customers appeal.

7.11 POLYMER APPLICATIONS

Due to their versatile properties polymers have found ready market in a large number of areas. From morning to night polymers are always with man. From bathroom to bedroom, dining hall to kitchen, living room to office or laboratory, polymers invade the every sphere of life. In public life or private life, in angry mood or loving mood, in the hard battlefield or in the sensuous moment, we need polymers. While we are driving an automobile, or moving in a train, or circling the mother earth in a space-vehicle, in fact, we ride on polymers. Can we imagine a day without polymers?

Our agriculture and forestry have been changed significantly by the application of polymers in the form of drip irrigation, water management by canal lining and water sprinkler systems, slow release devices for agrochemicals, mulching, plastic nursery bags, plasticulture methods, etc.

The strength is no longer a monopoly of metallic materials. Polymer science and technology have already developed and marketed a novel polymer, known as **Kevlar**, whose specific strength (i.e., strength to weight ratio) is much higher than steel. Kevlar woven fabrics can even resist the bullet from automatic rifles, and are, therefore, used in making bullet-proof vests and jackets. The new polymer glass is not only transparent like best quality glass but also non-brittle and tough. Therefore, these polyglasses are being used in the windshield of fighter jets and supersonic planes.

For dress materials and apparals natural fibres no longer remain the most coveted materials. New synthetic polymeric fibres such as polyester, nylons, orlon, etc. have captured the market for textile and clothing industry. These synthetic fibres are crease-resistant and more durable, possess superior soil-release and non-staining properties, good hand, versatile colourability and easy care properties. These may be crimped, textured, permanently set and blended with other synthetic or natural fibres. Synthetic polymers also offer fibres for better foundation garments, such as vests, brassiers, panties, sportswear, swimsuits, etc.

The field of medicine and surgery has been revolutionized through polymers. Polymers help spare-part surgery, cosmetic surgery, and new drug design and delivery. Prosthetics and othotics are now made from various polymers. Artificial limbs become more comfortable and near-natural in both appearance and function. Novel family planning devices become possible due to the development of polymers. Artificial skin for burn patients, artificial blood for seriously injured victims, heart valves for cardiac patients are a few examples to mention the versatile applications of polymers in medicine and surgery.

One of the recent frontiers of polymers' marvel is the development of conducting polymers. Until two decades ago polymers are used as insulating materials in electrical industry. Today polymers are no longer only insulators, they are semiconducting and even conducting materials. Thus plastics transistors, plastics battery, electronic junction devices, molecular electronic gadgets, etc. are being designed and fabricated from polymers. Computer science and information storage and retrieval systems would expect to undergo sea-change by the development of new conducting/semi-conducting polymers.

EXERCISE PROBLEMS

1. The molecular weight of a sample of polymethyl methacrylate is 1,50,000. Calculate the degree of polymerization of the polymer.
2. Calculate the number of polymer chains in 1·0 gm of polystyrene having a $\overline{DP} = 5000$.
3. Calculate the amount of hydrogen peroxide required to initiate 0·5 kg styrene to produce polystyrene having $\overline{DP} = 4{,}000$,
4. Sulphur is required to crosslink natural rubber. How much sulphur is required to fully crosslink 1 kg natural rubber?