POLYMER SCIENCE

FUNDAMENTALS OF POLYMER SCIENCE

Basic Concepts

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CONTENTS

Key Words

Polymer, Polymerization, Copolymer, Copolymerization, Step-growth polymerization, Chain-growth polymerization, Macromolecular concept, Structure-property relationship, Rubber, Plastics, Fibre, Deformation behaviour, Glass transition, Melting, Cross linking, Stress-induced orientation; Gelation, Gel point.

Introduction and Historical Perspective

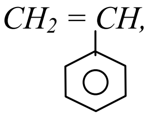
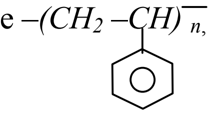
Man's quest for new and improved materials has been expanding with time and it can be said to be unending. The materials that have grown into familiarity and acceptance with the ages since the dawn of man's existence on the mother planet, the Earth are: pieces of rocks and stones, sand, soil and various ceramic items; nails, horns, hydes, skins and bones of animals; wood, leaves and plant fibres, covering grass and straw, cotton, coir, jute, hemp, hair, wool and many other fibres of plant and animal origin; silk fibre of insect origin; natural adhesive / film – forming gums and resins (e.g. agar, algies, rosin, shellac etc.); fossil fuels, viz., coal, lignite, natural gas and petroleum; glass and quartz, and metals and alloys extracted from minerals and ores. Polymers, as a class of materials with potential for use as rubbers, resins, plastics and composites, and as adhesives, laminates and coatings came nearly in the end of the chain of discoveries and developments of materials. Unfolding of the science of polymers and polymer – based materials really had its beginning and headway in the second and third decade of the twentieth century.

Though introduced very late in the chain of materials, polymers occupy a major place and pivotal position in our materials map today. In application prospects and performance characteristics and in property range and diversity, they offer novelty and versatility that can hardly be matched by any other kind of materials. Polymers have gone deep, and far and wide in moulding the present – day human civilization and culture.

Even though scientists, particularly the chemists used to talk about polymers earlier to the early twentieth century, there remained a lot of confusion over the basic understanding of the structures of polymer molecules. It was a common experience for chemists working with polymers that most such materials were very viscous and tacky under melt or solution conditions. One could readily spread the melt or solution into thin films or draw them into fine filaments. In solution, they were recognized more as colloids or associated molecules. Attempts to find their molecular weights from dilute solutions in suitable solvents by cryoscopy often produced irreproducible, doubtful and uncertain and sometimes very high values. For natural rubber, rayon and cellulose derivatives, molecular weights ranging 45,000 – 50,000 or even higher were measured. Such high molecular weight values implied that the relevant polymer molecules were really very large; but this view – point was not favoured or accepted in view of a total lack of structural concept about such large or big molecules. The chemists continued to favour the concept of large associations of much smaller molecules of short – chain or cyclic structures. A state of growing dilemma and confusion imparted fresh impetus to the thinking about the size, shape, complexity, and behavioral patterns of the molecular systems called polymers.

Long Chain Structure and Macromolecular Concept

The realization of the long – chain molecular or the macromolecular concept of polymer molecular systems in the 1920s proved to be a vital turning point. Accumulated confused ideas and uncertainties of the earlier decades became meaningful and they were soon translated into practice through production of a large variety of hitherto unknown structures by polymerization and copolymerization of a host of olefinic, diolefinic and vinylic compounds and combinations thereof and by polycondensation reactions between a large variety of bifunctional or polyfunctional compounds bearing well characterizable chemical functional groups.

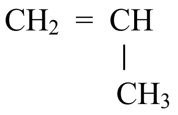
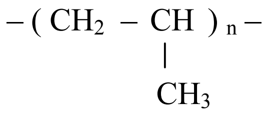
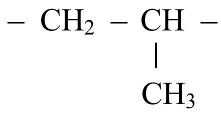
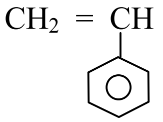
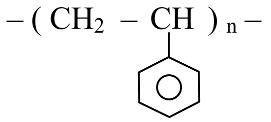
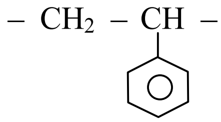
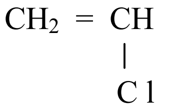
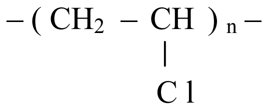
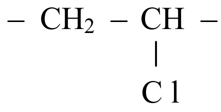
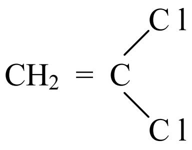
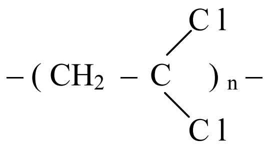
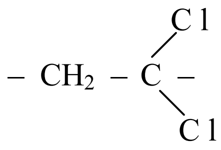
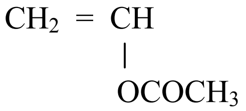
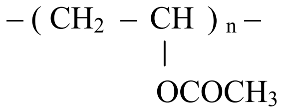
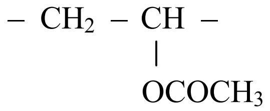
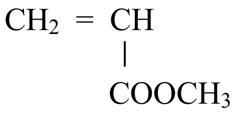
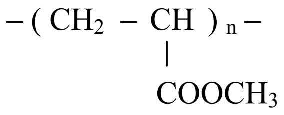
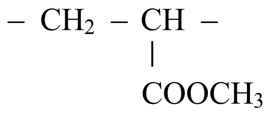
The macromolecular or chain molecular concept found wide acceptance and appreciation soon after it was propounded by Staudinger in 1920. He advanced long – chain structural formulas for natural rubber, cellulosics such as cellulose nitrate, and polystyrene. Long sequences of simple chemical units interlinked with covalent bonds came into recognition as the basic structural feature for all polymer molecules. The polystyrene molecule produced by polymerization of styrene,  $CH_2 = CH$, came to be recognized to have the structure  $-(CH_2 - CH)_{n}$, where, n had a large value. Staudinger was not initially certain about the nature or identity of the terminal points or end groups of the long chain polymer molecules. He was initially of the view that there was no need to saturate the terminal valences and suggested that no end groups were needed or necessary. Development and elucidation of the chain reaction theory of vinyl and related polymerization by Flory and others, however, clearly established that polymer materials consisted of long – chain molecules with well characterizable end groups. One more distinctive feature of the same or the following decade is the pioneering work of Carothers in the area of polycondensation and towards the first rational synthesis of linear macromolecules, viz., polyesters and polyamides.

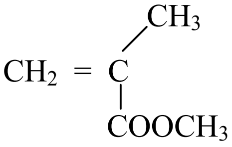
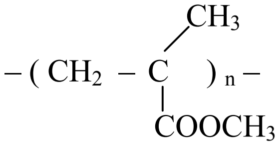
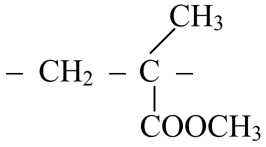
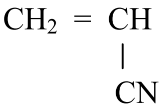
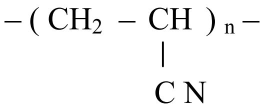
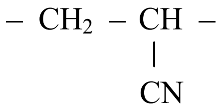
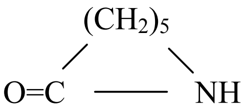
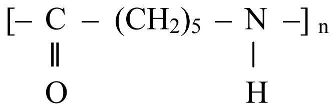
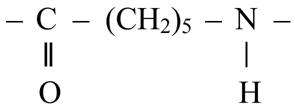
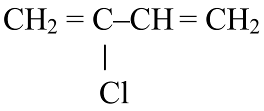
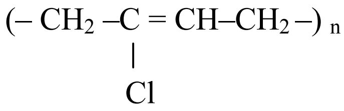
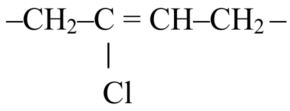
A stage was soon reached by the mid – 20th century, when the prospect of attaining any conceivable material property of structural importance through polymerization, copolymerization or polycondensation and through physical and chemical modifications covering changes in (or incorporation of new) functional groups, compounding and reinforcements, making polymer blends and alloys, irradiation, and thermo – mechanical treatments looked very bright and within our competence. By then, we had actually reached the era of tailor–made polymers in a comprehensive sense. Material prospect widened and brightened through what may be termed as "Molecular Engineering".

Structural Features of a Polymer or Macromolecule

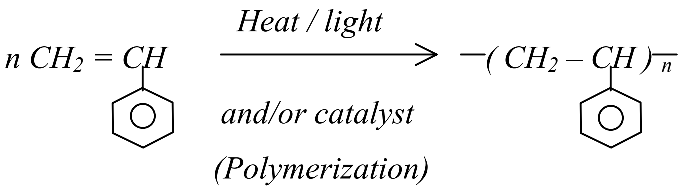
The word polymer literally means many (poly) units (mer). A small, simple chemical unit appears to repeat itself a (very) large number of times in the structure of a polymer molecule or macromolecule. The so called repeat unit may consist of a single atom, say, sulfur atom, S, exemplified by the well known plastic sulfur $(- S - S - S - S - S - S - S - S -)_n$, or more commonly a small group of atoms, such as in polystyrene, mentioned in the preceding section, with the distinctive feature that the repeat units are successively linked to one another on each side by covalent bonds. The polymeric form of sulfur, favourably formed on heating the elemental sulfur powder is, however, unstable and it reverts to the powdery (monomeric S_8 ring) form on keeping at room temperature. The simple molecular species from which a chain polymer molecule may be obtained or to which a polymer molecular system may be degraded is called the monomer. Some common polymers and structural representation of the respective monomers and repeat units are listed in Table 1.

Table 1:Some Monomers and Corresponding Polymers and Repeat Units

S.No.	Monomer	Polymer	Repeat Unit
1.	Ethylene $CH_2 = CH_2$	Polyethylene $-(CH_2 - CH_2)_n-$	$- CH_2 - CH_2 -$
2.	Propylene  $CH_2 = \underset{\substack{\vert \\ CH_3}}{CH}$	Polypropylene  $-(CH_2 - \underset{\substack{\vert \\ CH_3}}{CH})_n-$	 $- CH_2 - \underset{\substack{\vert \\ CH_3}}{CH} -$
3.	Styrene 	Polystyrene 	
4.	Vinyl chloride  $CH_2 = \underset{\substack{\vert \\ Cl}}{CH}$	Poly (vinyl chloride)  $-(CH_2 - \underset{\substack{\vert \\ Cl}}{CH})_n-$	 $- CH_2 - \underset{\substack{\vert \\ Cl}}{CH} -$
5.	Vinylidene chloride  $CH_2 = \overset{Cl}{\underset{Cl}{C}}$	Poly (vinylidene chloride)  $-(CH_2 - \overset{Cl}{\underset{Cl}{C}})_n-$	 $- CH_2 - \overset{Cl}{\underset{Cl}{C}} -$
6.	Vinyl acetate  $CH_2 = \underset{\substack{\vert \\ OCOCH_3}}{CH}$	Poly (vinyl acetate)  $-(CH_2 - \underset{\substack{\vert \\ OCOCH_3}}{CH})_n-$	 $- CH_2 - \underset{\substack{\vert \\ OCOCH_3}}{CH} -$
7.	Tetrafluoroethylene $CF_2 = CF_2$	Poly (tetrafluoroethylene) $-(CF_2 - CF_2)_n-$	$- CF_2 - CF_2 -$
8.	Methyl acrylate  $CH_2 = \underset{\substack{\vert \\ COOCH_3}}{CH}$	Poly (methyl acrylate)  $-(CH_2 - \underset{\substack{\vert \\ COOCH_3}}{CH})_n-$	 $- CH_2 - \underset{\substack{\vert \\ COOCH_3}}{CH} -$

S.No.	Monomer	Polymer	Repeat Unit
9	Methyl methacrylate	Poly (methyl methacrylate)	
	 $CH_2 = \underset{COOCH_3}{\overset{CH_3}{C}}$	 $-(CH_2 - \underset{COOCH_3}{\overset{CH_3}{C}})_n-$	 $-\ CH_2 - \underset{COOCH_3}{\overset{CH_3}{C}} -$
10.	Acrylonitrile	Polyacrylonitrile	
	 $CH_2 = \underset{CN}{CH}$	 $-(CH_2 - \underset{C\,N}{CH})_n-$	 $-\ CH_2 - \underset{CN}{CH} -$
11.	Formaldehyde	Polyformaldehyde or Poly (oxymethylene)	
	$CH_2 = O$	$-(CH_2 - O)_n-$	$-\ CH_2 - O -$
12.	Caprolactam	Polycaprolactam (Nylon 6 polyamide)	
		 $[-\underset{O}{\overset{\parallel}{C}} - (CH_2)_5 - \underset{H}{\overset{\mid}{N}} -]_n$	 $-\ \underset{O}{\overset{\parallel}{C}} - (CH_2)_5 - \underset{H}{\overset{\mid}{N}} -$
13.	Butadiene	Polybutadiene	
	$CH_2 = CH–CH = CH_2$	$(- CH_2 –CH = CH–CH_2 –)_n$	$–CH_2–CH=CH–CH_2 –$
14.	Chloroprene	Polychloroprene	
	 $CH_2 = \underset{Cl}{C}–CH = CH_2$	 $(- CH_2 –\underset{Cl}{C} = CH–CH_2 –)_n$	 $–CH_2–\underset{Cl}{C} = CH–CH_2 –$

Polymerization of monomer styrene to polystyrene may be represented by



$$n\ CH_2 = \underset{C_6H_5}{CH} \xrightarrow[\text{and/or catalyst (Polymerization)}]{\text{Heat / light}} -(CH_2 - \underset{C_6H_5}{CH})_n- \qquad (1)$$

Styrene
(monomer)

Polystyrene
(polymer)

Here, *n* – number of styrene monomer molecules are shown to polymerize under the influence of heat, light or a selected catalyst (initiator) system to produce a polystyrene macromolecule, having a degree of polymerization (DP) of n, where n may have a value ranging between several tens and hundreds or even higher. The molecular weight of the polymer molecule formed is given by the product of the molecular weight of the repeat unit (or the monomer, here) and DP.

In case a polymer would have more than one kind of repeat units in its chain molecular structure, it is called a copolymer. Polymers of the molecular weight range 1,000 – 20,000 are commonly called low polymers and those having molecular > 20,000 are commonly referred to as high polymers.

Length to Diameter (L/D) Ratio

Length to Diameter (L/D) ratio of polymer molecules in general is very high compared to that of a simple, small molecule (such as the monomer molecule). If a small molecule such as the styrene molecule is represented by a dot (•), then the molecule of a polymer, say, polystyrene of DP of 1000 will be represented by a line (——) formed by firmly jointing or sticking together of 1000 dots in a linear fashion. This unique difference in the L/D ratio between a monomer (small) molecule and a polymer or a high polymer molecule makes all the difference in their physical and mechanical properties. A long pearl necklace could be viewed as a model for a polymer molecule, fig. 1

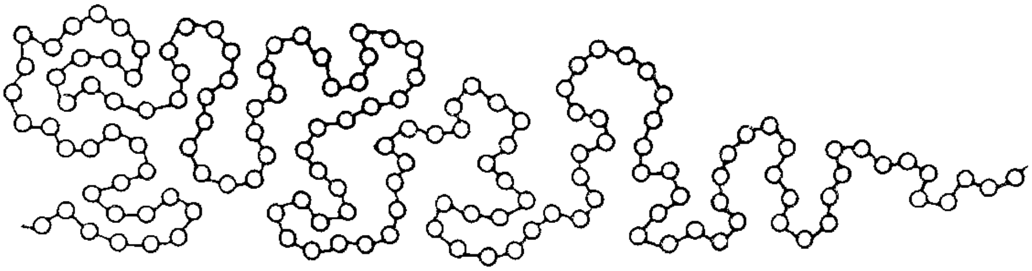


Fig. 1: Model of a polymer molecule

In view of their long lengths, molecules in a given sample of a polymeric material exist in a state of different degrees of entanglement, both intermolecular and intramolecular, depending on the prevalent thermomechanical conditions. High melting or softening temperatures and high melt or solution viscosities exhibited by polymeric materials are direct consequences of the big size and long lengths of their molecules and the complex entanglements of the molecular chains.

Polymer Classifications

Classification of polymers giving the basis of classification and examples in each case is shown in Table 2.

(a) Origin : There are on one side the natural polymers including proteins, nucleuo proteins and enzymes, the polysaccharides, natural rubber, natural gums, natural silk and other natural fibres, cellulosic and lingo-cellulosic, viz, cotton (cellulosic), and jute, ramie, flax, hemp, sisal, coir etc. (all lingo-cellulosic) containing different percentages (10 – 24%) of hemicellulose as well; lignin content is the least in flax (3 – 4%) and the highest in coir (30 – 34%). Lignin and hemicellulose contents of jute, a major bast fibre produced in India, are 11 – 14% and 20 – 23% respectively. Semi-synthetic (modified natural) polymers and synthetic polymers are also called man – made polymers. Synthetic polymers are man – made from the very outset.

Table 2: Classification of Polymers

Basis of Classification	**Polymer Types**	**Examples**
1. Origin	(a) *Natural* (as available in nature)	Natural rubber, natural silk, cellulose, proteins, starch etc.
	(b) *Semisynthetic* (Man – made)	Hydrogenated, halogenated and cyclo (natural) rubber; cellulosics (cellulose esters/ethers), etc.
	(c) *Synthetic* (Man – made)	Polyethylene, polypropylene, polystyrene, polybutadiene, nylon polyamides, polycarbonates, phenolics, amino resins, epoxy resins etc.
2. Thermal response	(a) *Thermoplastics* (they soften or melt on heating and harden on cooling over many cycles of heating and cooling and retain solubility and fusibility).	Polyethylene, polypropylene, polystyrene, nylon polyamides, linear polyester [poly (ethylene terephthalate)] , etc.
	(b) *Thermosetting* (they usually soften or melt initially on heating, but fast undergo chemical changes to finally turn insoluble and infusible).	Phenolic resin, amino resins, epoxy resins, diene rubbers (vulcanized), unsaturated polyesters.
3. Mode of formation	(a) *Chain – growth or addition*	Polyethylene and other polyolefins, Polystyrene and related vinyl polymers etc.
	(b) *Step – growth or condensation*	Polyesters and polyamides, polycarbonates, phenol (urea, melamine) – formaldehyde resins, epoxy resins etc.
4. Line Structure	(a) *Linear* (having no branches)	High density polyethylene (HDPE), polyvinyls, bifunctional (polyesters and polyamides) etc.
	(b) *Branched* (having branches)	Low density polyethylene (LDPE), higher poly (α-olefins), phenolic resoles and resitols, poly (3-hydroxy alkanoates) etc.
	(c) *Cross linked or network* (having a complex network structure)	Phenolic C-stage (resite) resin, C-stage amino (urea / melamine-formaldehyde) resins, cured epoxy resin and unsaturated polyester resin etc.

Basis of Classification	**Polymer Types**	**Examples**
5. Application and Physical properties	(a) *Rubbers* (showing long – range elasticity)	Natural rubber, (1, 4 cis poly isoprene) synthetic rubbers (polybutadiene, SBR, nitrile rubber, polychloroprene rubber, polylacrylate rubber, polyurethane rubbers, silicone rubbers etc.)
	(b) *Plastics* (shapable under pressure, aided by heat)	Polyethylenes, polypropylene (isotactic), polystyrene, poly (vinyl chloride), nylon polyamides linear aromatic polyesters and polyamides, polycarbonates, acetal resins etc.
	(c) *Fibres* (available in fibrillar or filamentous form)	Cotton (cellulose), natural silk, artificial silk (rayons), poly (ethylene terephthalate) fibre, nylon polyamide fibres etc.
6. Tacticity	(a) *Isotactic* (stereoregular)	Poly (α-olefins) and all vinyl and related polymers.
	(b) *Syndiotactic* (do)	
	(c) *Atactic* (stereo irregular)	
7. Crystallinity	(a) *Crystalline* (crystallinity, $\geq$ 50%)	Polyethylene (HDPE and LDPE), polypropylene (isotactic), stretched nylon polyamides, polyoxymethylene etc. cellulose (cotton) fibre.
	(b) *Semi – crystalline* (crystallinity, 30 – 50%)	Polybutene, cellulosics (cellulose esters (rayons) particularly if stretched), Gutta percha (1, 4 trans polyisoprene) etc.
	(c) *Amorphous or non-crystalline* (crystallinity < 25%)	Natural rubber and most synthetic rubbers,N-alkylated(>15% alkylation) nylon polyamides, poly (methacrylates and acrylates) poly (vinyl acetate), polystyrene etc.

(b)Thermal response: A molecule of a linear polymer may be schematically represented by a simple line of finite length (straight or zig – zag, but usually wavy)(fig. 2 (a)). A molecule of a branched polymer may, however, be represented by a line of finite length with short or long finite – length branches attached to some of the repeat units in the chain molecule, fig.2 (b). A cross linked polymer can be represented by a network structure that may be a planar network as in graphite or space network, as in diamond, Fig. 2 (c and d). A linear polymer is best exemplified by high-density polyethylene (HDPE), while a branched polymer is exemplified by low-density polyethylene (LDPE) or poly (α – olefins). Linear and branched polymers are commonly thermoplastics, that are soluble and fusible, while the network resins or polymers are examples of thermosetting resins or polymers that turn ultimately insoluble and infusible.

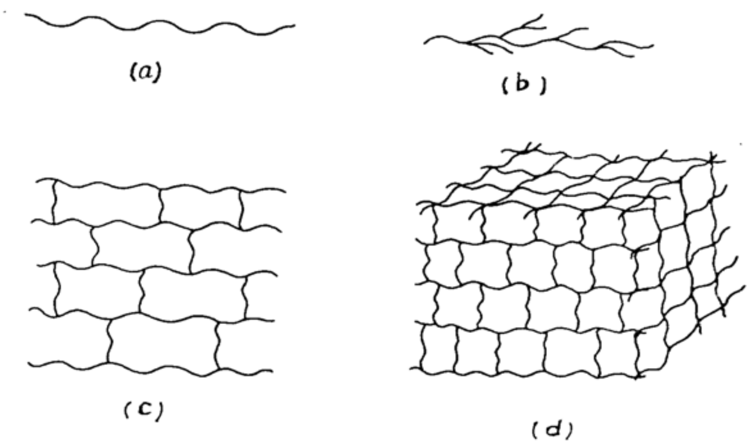
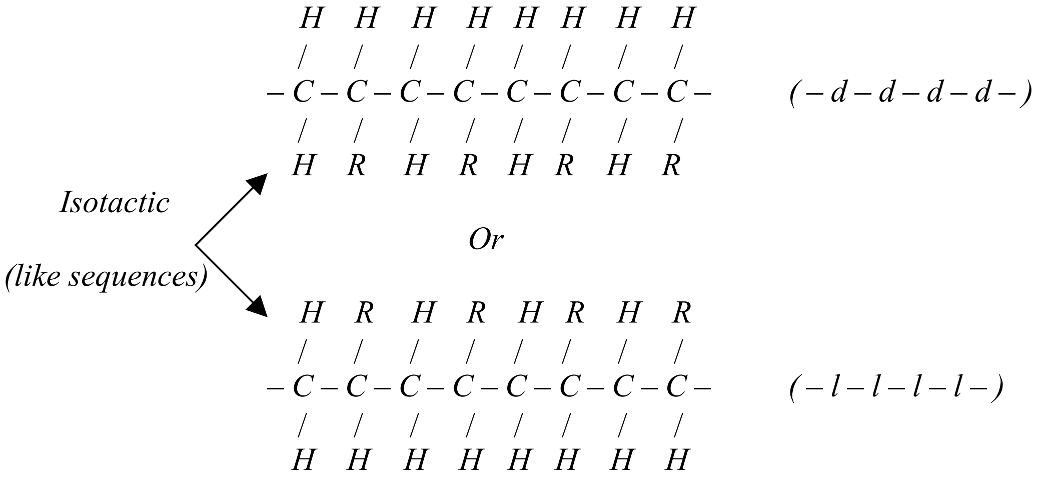


Fig. 2: Line Structures for different types of molecules

(c) **Tacticity :** A vinyl and related polymer $(-CH_2 - \overset{*}{C}HR -)$ is characterized by an asymmetric carbon atom (marked with a little asterisk on it) in each of the repeat units of its chain molecules and a type of stereochemical difference that may arise in the segments of the chain is *d –*, *l –* isomerism. Considering head to tail linkage of the repeat units, the stereo sequences may be all *– d –* or all *– l –* sequences, identified in terms of tacticity or spatial disposition of the substituent group, *R* as isotactic ;



$$\begin{array}{cccccccccc} H & H & H & H & H & H & H & H & & \\ / & / & / & / & / & / & / & / & & \\ -C- & C- & C- & C- & C- & C- & C- & C- & & (-d-d-d-d-) \\ / & / & / & / & / & / & / & / & & \\ H & R & H & R & H & R & H & R & & \end{array}$$

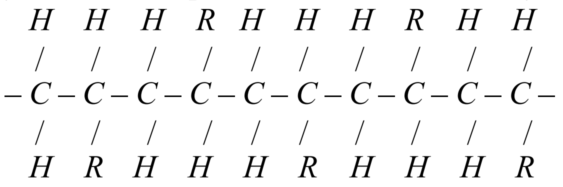
Isotactic

(like sequences)

Or

$$\begin{array}{cccccccccc} H & R & H & R & H & R & H & R & & \\ / & / & / & / & / & / & / & / & & \\ -C- & C- & C- & C- & C- & C- & C- & C- & & (-l-l-l-l-) \\ / & / & / & / & / & / & / & / & & \\ H & H & H & H & H & H & H & H & & \end{array}$$

For alternate appearance of *d –* and *l –* sequences, the relevant polymer is called syndiotactic. The syndiotactic sequence or stereoisomer may be represented as



$$\begin{array}{cccccccccc} H & H & H & R & H & H & H & R & H & H \\ / & / & / & / & / & / & / & / & / & / \\ -C- & C- & C- & C- & C- & C- & C- & C- & C- & C- \\ / & / & / & / & / & / & / & / & / & / \\ H & R & H & H & H & R & H & H & H & R \end{array}$$

Syndiotactic

(Alternate sequences; $(-d-l-d-l-d-)$)

A third distinguishable long chain sequence called atactic sequence would be given by a random spatial disposition of the substituent – R groups, also exemplified by a random mix of isotactic and syndiotactic sequences, viz.

$$\begin{array}{cccccccccccc}
H & H & H & H & H & R & H & H & H & R & H & R \\
/ & / & / & / & / & / & / & / & / & / & / & / \\
-C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- \\
/ & / & / & / & / & / & / & / & / & / & / & / \\
H & R & H & R & H & H & H & R & H & H & H & H
\end{array}$$

Atactic

(Random sequence, $(-d-d-l-d-l-l-)$ *)*

Isotactic sequence is distinctive as being very regular, while atactic sequence is one that is highly irregular. Syndiotactic sequence may be viewed as regularly irregular or vice versa. Isotactic and syndiotactic polymers are considered as stereospecific or stereoregular while atactic polymers are viewed as random or stereo–irregular. The overall molecular symmetry and crystallinity are in the order isotactic $\geq$ syndiotactic >> atactic. Isotactic polymers are generally characterized by high melting temperature (T_m) and high mechanical properties with relatively high resistance to solvents and chemicals.

Structure – Property Relationship

The wide variety and diversity of natural, semi-synthetic and synthetic polymers known currently exhibit wide diversity of properties or property ranges. Some appear rigid, hard, strong and dimensionally stable, while others appear soft, flexible or largely extensible under the influence of stress. Some show ready solubility and fusibility, while others appear more resistant to heat and solvents and may appear even insoluble and infusible. All such properties may vary from a polymer of one type to a polymer of a different type. They may even vary between samples of the same type of polymer depending on molecular weight and molecular weight distribution (MWD) or on how they were synthesized or thermomechanically treated before being tested.

(a) Linearity, Branching and Networking: Depending on the property ranges they exhibit, the polymers are classified as rubbers, plastics and fibres. Factors that influence the polymer properties are: molar cohesion, polarity, molecular weight, crystallinity, overall molecular symmetry (both recurrence symmetry and architectural symmetry), linearity and non – linearity of chain molecules, thermomechanical history of the polymer and temperature of observation. Higher molecular weight permits greater degree of chain entanglements, thus resulting in higher melting temperature (T_m) and tensile strength ($T.S.$).

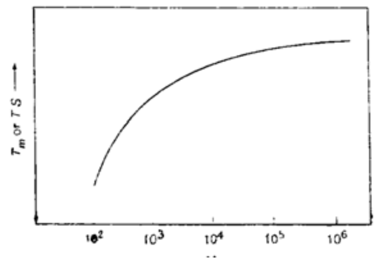


Fig. 3: Trend of change in T_m and $T.S.$ with change in molecular weight of polymers (Courtesy: Tata McGraw –Hill, New Delhi)

Small extents of branching make the otherwise equivalent polymer less resistant to solvents, chemicals and heat owing to increased molecular mobility manifested through the branch units or pendent groups. High degrees of branching with enhanced branch lengths and ultimate cross linking render the polymer relatively stiff arising from greater degrees of chain entanglements and ultimately forming giant molecules of a network structure, thereby restraining or eliminating scope for large scale molecular mobility or chain slippage and improving resistances to thermal and mechanical loading and hence dimensional stability. Polymers thereby turn less soluble or difficultly fusible or ultimately insoluble and infusible. Cured phenolic and amino resins, epoxy resin systems and vulcanized rubbers are good examples of cross-linked, network polymers or resins.

On cross-linking, basic structural changes in the polymers are introduced and consequently, basic changes or improvements in properties are invariably achieved. By proper process – design and in tune with the set objectives, different degrees of cross linking or cross link density, high or low may be duly achieved, fig. 4.

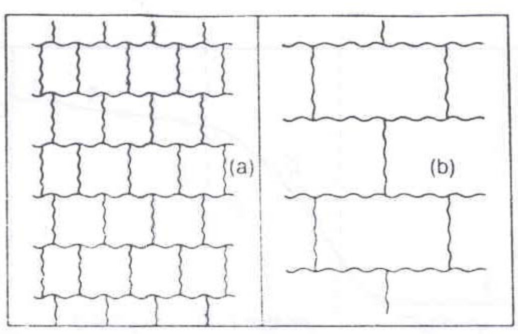
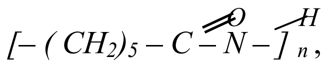


Fig. 4: Schematic representation of network or cross-linked structures
(a) High cross-link density, and (b) Low cross-link density
(Courtesy: Tata McGraw –Hill, New Delhi)

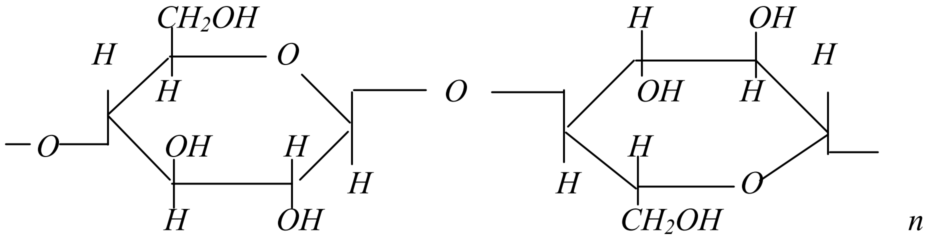
(b) Molar Cohesion, Polarity and Crystallinity : These parameters are interrelated and interdependent. A chain molecule having a strong polar structure for its repeat units exerts strong attractive forces on molecules around it. In non–polar polymer systems, the molar cohesion would be substantially weak. Between non–polar polyethylene $(-CH_2-CH_2-)_n$ and polar nylon 6 polyamide  $[-(CH_2)_5-\overset{O}{C}-\overset{H}{N}-]_n$, the methylene links are common, but in the polyamide, the strongly polar $-CONH-$ inter-unit linkage gets repeated in the chain molecular structure and finds place between every two successive $-(CH_2)_5-$ chain units. Assuming degrees of polymerization such that the polyethylene and the polyamide chains are of equal length, the forces of attraction between the polyamide chains will be very much stronger than those between the polyethylene chains. This is actually reflected in much higher rigidity, stiffness, tensile strength, melting temperature and crystallizing tendencies of the polyamide. On top of this, extensive intermolecular hydrogen bond formation takes place in the nylon 6 polyamide, more so, on stretching it from the melt condition as it is cooled, thereby resulting in the ready formation of the polyamide fibre. However, melt – cooled nylon 6 polyamide behaves much as a very good engineering plastic.

The polyamide fibre – formation during melt – drawing is associated with stress – induced molecular orientation in the axial direction and in the direction of stress – application, thereby leading to measurable enhancement in density and manifold enhancements in tensile strength. The chain orientation leading to densification and strength enhancements are cones-quences of establishment of more of intermolecular hydrogen bonds (between $C = O$ groups and N – hydrogens of segments of neighbouring chains) at the expense of a large proportion of the initially existing intramolecular H – bonds ; enhancements in the degree of crystallinity of the drawn–out product (i.e. the polyamide fibre) also result simultaneously.

(c) Role of Molecular Symmetry: On the other hand, even though polyethylene has a weak molar cohesion that is of the same order as for various rubbers, natural or synthetic, it does not really behave as a rubber; instead, it is recognized as one of the most useful plastics known. Its improved mechanical properties are basically due to the very simple and symmetrical chemical structure of the monomer and hence of the repeat units of the polymer, polyethylene, facilitating close packing of its chain molecules into a lattice structure, thereby inducing crystallinity and strength.

Besides architectural symmetry, recurrence symmetry too is important in determining the total forces of attraction between chain molecules, particularly when oriented. Polyethylene, prepared by the high – pressure method (free radical mechanism) and the one by the low pressure method (anionic coordination mechanism) widely differ in their properties; the low – pressure polyethylene being higher melting and its density, rigidity, tensile strength and crystallinity degree also being higher. The reason is that the low – pressure polyethylene is predominantly linear and it is endowed with a high degree of molecular symmetry, while the high – pressure polyethylene is fairly branched and thus poorer in molecular symmetry.

(d) Role of Chemical Modification in Effecting Internal Plasticization : The role and influence of molecular symmetry and of H – bonding in determining polymer properties are further exemplified by the chemical modification of cellulose.



Cellulose

Cellulose, originally an infusible *fibre* of good strength, resistant to solvents and having a good degree of crystallinity due to extensive intermolecular H – bonds established through the *OH* groups, is easily modified to useful *plastic* products with ready solubility in selected solvents and more or less well defined softening or melting points on progressive substitution of the *OH* groups by esterification or etherification. As a result of such chemical modifications, the high architectural and recurrence symmetry of cellulose chain molecular segments are progressively lost and H–bonds are destroyed considerably due to progressive transformation of the – *OH* groups to ester or ether groups ($-ONO_2$ in cellulose nitrate, $-OCOCH_3$ in cellulose acetate, $-OCH_3$ in methyl cellulose, $-OCH_2COOH$ in carboxymethyl cellulose etc.). The completely modified cellulose, giving a degree of substitution (DS) for each glucose unit in the chain molecules equal to three, would be expected to show better strength characteristics than the incompletely modified derivatives, because on complete modification, the overall molecular symmetry is regained.

(e) Copolymerization and Internal Plasticization : Further, it is interesting to note that the homopolymers of monomer M_1 and of monomer M_2 prepared separately would be characterized by a high order of recurrence symmetry each, but when the two monomers will be copolymerized or polymerized together, the resultant copolymer will bear both M_1 and M_2 repeat units in its chain molecular structure thereby infusing a loss of recurrence symmetry; a copolymer of monomers M_1 and M_2 is commonly viewed as a polymer that is internally plasticized, consequent to having duel repeat units and hence loss of molecular symmetry; a 1 : 1 copolymer will generally have melting point (T_m) and tensile strength (*T.S*) that are significantly lower than those of the two respective homopolymers as schematically shown in fig. 5, the curve indicating the trend of change of each property parameter with change in mole ratio of M_1 and M_2 monomers used in copolymerization.

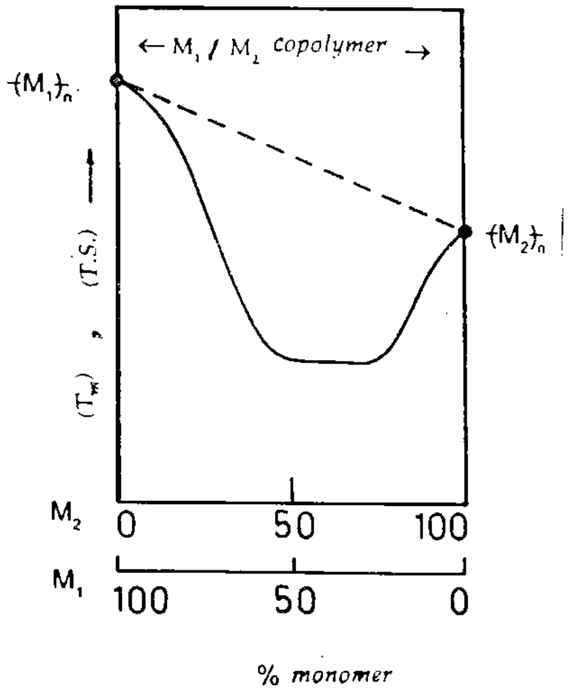
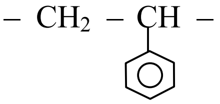
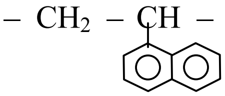
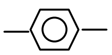
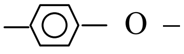
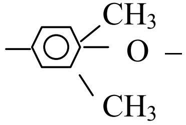
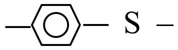
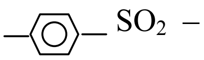
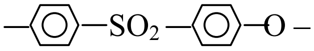
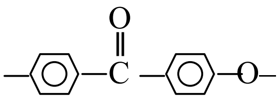
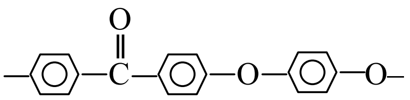


Fig. 5: Trend of change in T_m and T.S. with variation of copolymer composition

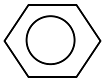
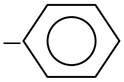
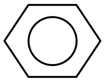
(f) Effect of inclusion of flexible inter-unit linkages and rigid bulky groups: It is apparently surprising that the melting points of most linear aliphatic polyesters $[-(CH_2)_x-\overset{O}{\overset{\|}{C}}-O-]_n$ lie well below that of polyethylene. This can be partly explained considering that the contributions of the polar $(-\overset{O}{\overset{\|}{C}}-O-)$ groups in enhancing molar cohesion are far outweighed by the flexibility effects imparted to the chains through the *–O–* linkages in the chain backbone. The increase in chain flexibility and hence lowering in melting point by oxygen linkages in the main chain is further illustrated by a much lower melting point (~ 150^0C) for the polyurethane $[-(CH_2)_5-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-]_n$ than that for the analogous polyamide $[-(CH_2)_5-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-]_n$ that shows a melting point of 215^0C. Table 3 shows that *– S –* and *– SO₂ –* interunit linkages respectively infuse flexibility with softness, and rigidity with higher thermostability to the polymer chains.

Table 3: Effect of Variation of Polymer Structure on Properties and Application Prospects

Polymer	Repeat Unit	T_g, ^{0}C	T_m, ^{0}C	Remarks
Polyethylene (linear), PE	$-CH_2-CH_2-$	–115, –60	137	General purpose, low modulus polymer with good degree of toughness; excellent electrical insulator.
Polystyrene, PS		80 to 100	240	Rigid, brittle transparent polymer; excellent insulator.
Poly(vinyl naph-thalene) PVN		150	360	Highly, rigid, brittle polymer; excellent insulator.
Poly(para-phenylene), PPP		---	530	Tough, thermostable, intractable polymer with semi-conducting or even good conducting (when doped) properties with electrical conductivity in the range 10^{-18} to 10^2 $(\Omega\ cm)^{-1}$
Poly(tetramethylene Oxide), PTMO	$-(CH_2)_4-O-$	– 80	60	Weak, flexible polymer.
Poly (phenylene Ether), PPE		80	300	A good engineering thermoplastic having high strength & toughness.

Polymer	**Repeat Unit**	**T_g, ^0C**	**T_m, ^0C**	**Remarks**
Poly (phenylene Oxide), PPO		209	---	Very low water absorption, more resistant (chemically, mechanically and thermally) than PPE.
Poly (tetramethylene sulphide), PTMS	$–(CH_2)_4 – S –$	---	70	Weak, flexible polymer.
Poly (phenylene Sulphide), PPS		90	295	Strong, tough, thermally resistant polymer. Normally a good insulator But when properly doped, say with 2-5% AsF_5, it assumes a semiconducting character.
Poly(tetramethylene Sulphone), PTMSO	$–(CH_2)_4 – SO_2 –$	---	270	Presence of strongly polar sulphone ($– SO_2 –$) links makes the polymer mechanically strong and thermally more stable, as can be realized by comparing PTMSO with PTMS or PTMO.
Poly (phenylene sulphone), PPSO		350	525	Mechanically very strong and thermally stable upto 500^{0}C; high-performance plastic.
Poly (ether sul-Phone), PES		230	---	Thermostable, high performance transparent thermoplastic with improved processability in comparison with PPSO.
Poly(ether ketone), PEK		155	365	High performance thermoplastic with excellent environmental stress cracking resistance; continuous use temperature nearly 275^{0}C.
Poly(ether ether ketone) PEEK		140	343	High performance, chemical resistant thermoplastic, showing a high continuous use temperature(250^{0}C)

Rigid, bulky aromatic ring substituents make a vinyl polymer more rigid and brittle. When aromatic rings constitute the chain backbone, the polymer becomes rigid, stiff, strong and tough, -S- and –O- inter unit linkages make the polymer weak, relatively soft and flexible, while highly polar $–SO_2-$ linkages along the chain backbone make the polymer more rigid, strong and thermostable.

Incorporation of rigid, bulky groups, such as aromatic rings as side groups in the polymer chain renders it more stiff and higher melting, Table 3. Comparison of relevant features of polyethylene, polystyrene and poly (vinyl naphthalene) would bring home the point. Incorporation of an aromatic ring in each repeat unit of a linear polyester, e.g. poly (ethylene terephthalate), $[-OOC-$  $-COO-(CH_2)_2-]_n$ turns the polymer relatively rigid and very much higher melting (>250^{0}C) and it can be readily melt – drawn into a very useful fibre, the most common polyester fibre. The aromatic hydrocarbon polymer, poly (para phenylene), $[-$  $-]_n$ is a difficultly processable, tough, thermostable engineering polymer of much high performance ($T_m = 530^0$C), while poly (phenylene ether), $[-$  $-O-]_n$ is a more readily processable, tough, high performance polymer having a much lower melting point (300^{0}C); presence of the ether $-O-$ linkage renders the aromatic polymer somewhat more flexible and easily processable at a lower temperature.

In polymer material systems, intermolecular forces are opposed by thermal agitation. The influence of chain length is mainly extensive, i.e. total (cumulative) force of intermolecular attraction increases with molecular weight owing to availability of greater molecular surface, while the force per unit length or area remains by and large constant. By contrast, polarity is intensive and the more polar the structure of the repeat unit, greater is the attractive force per unit length or area.

It is logically appreciable that, lengthening of the substituent group of the isotactic poly (α – olefin) homologues causes progressive decrease in the melting point from polypropylene (having one carbon side chain or substituent group) to polyheptene (having five-carbon side chain or substituent group); for still higher isotactic α – olefin polymers, the side chains on the alternate carbon atoms become even longer so as to be able to infuse a developing trend of side chain crystallization; as a consequence, the melting point curve reverses its falling trend and then follows an upward trend, as shown in fig. 6.

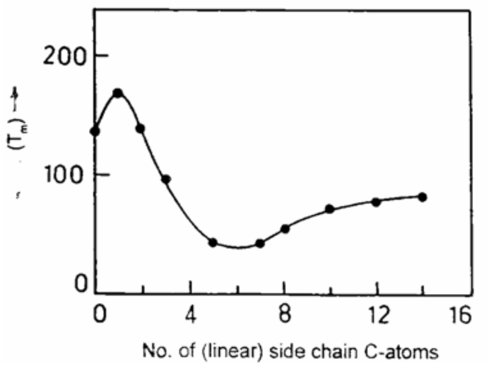


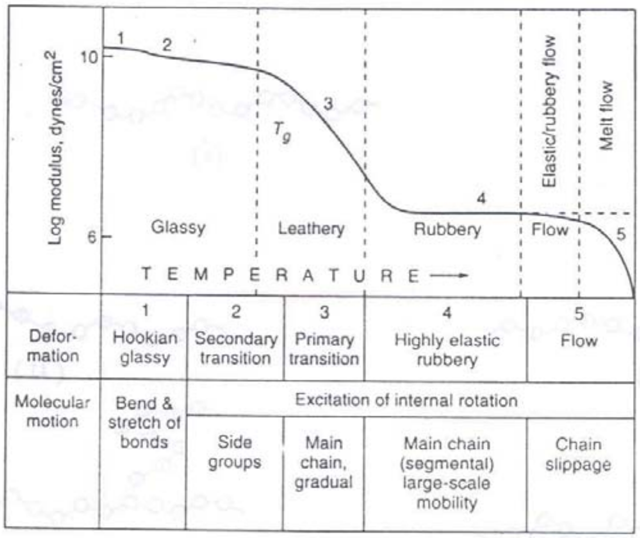
Fig. 6: Trend of change of T_m of isotactic poly(α – olefin) $(-CH_2-CH-)_n$ with increase in branch (substituent) unit length.

Further, dependence of physical properties on structural (geometrical) isomerism is distinctively exemplified by the well known examples of 1, 4–cis polyisoprene (*natural rubber*) and 1, 4 – turns poly isoprene (*gutta percha*); the former, being devoid of or much poorer in symmetry and hence in crystallinity, is more flexible and behaves as a rubber, while the latter, having a good degree of symmetry and balanced structure, is dimensionally stable under normal conditions and useful as a good plastic.

(g) Effect of Temperature: Generally speaking, all linear amorphous polymers can behave as Hookian elastic (*glassy*) materials, highly elastic (*rubbery*) substances or *viscous melts*, according to the prevailing temperature of observation and time – scale of experiments. Different property ranges for the same polymer at different temperatures are related to variation in the physical structures or arrangements of the chain molecules, much as a consequence of different types and degrees of deformation.

Survey of Deformation Patterns in the Amorphous State

An idealized plot of log (shear) modulus vs. temperature, as in fig. 7, may now be examined and analyzed. The modulus curve commonly shows a number of transitions each of which is connected with the gradual development of an additional molecular movement.



	1	2	3	4	5
Defor-mation	Hookian glassy	Secondary transition	Primary transition	Highly elastic rubbery	Flow
Molecular motion	Bend & stretch of bonds	Excitation of internal rotation			
		Side groups	Main chain, gradual	Main chain (segmental) large-scale mobility	Chain slippage

Fig. 7: Temperature dependence of log (shear modulus) in a polymer system showing molecular mechanism of the deformations taking place at different points and notable transition phenomena (Courtesy: Tata McGraw –Hill, New Delhi)

At a temperature below a specified transition temperature, the molecular processes in question are frozen in. With rise in temperature, as the transition point is approached, an additional molecular movement begins to contribute to the deformation mechanism and hence lowers the resistance to deformation, i.e. the modulus.

At very low temperatures, the only deformation occurring is Hookian elastic deformation, which is time-independent and mechanically reversible. The deformation takes place instantaneously on a specified stress application, and it reverts giving complete dimensional recovery on removal of the applied force or stress. The Hookian deformation is also thermodynamically reversible, as no energy is dissipated during the stress – strain cycle. The Hookian deformation is attributed to the small changes in valence angles and valence distances (bend and stretch of bonds) that occur against the strong binding forces of the homopolar bonds (dissociation energy, 30 – 200 kcal/mol), and hence it is associated with a high modulus of the order of $\geq 10^{10}$ dynes/cm^2. At sufficiently high temperatures, flow that is totally irreversible, both mechanically and thermodynamically, takes place. The energy of deformation is dissipated in the viscous melt as heat and little configurational free energy is left after the deformation and as a result, there is no recovery. A polymer melt is viewed as a slipping cluster of randomly coiled entangled chain molecules with limited or little restriction on rotation of molecular segments due to the presence of closeby neighbouring molecules.

The deformation mechanism prevalent at this stage is slippage of the molecular chains relative to each other, but at the same instance, large-scale displacement of chain segments normal to their chain axes is restricted due to chain entanglement, thereby giving rise to high melt viscosity. Cross linked or network polymers are not expected to exhibit the flow phenomenon.

Transitions and Rubbery and Flow Regions

The mid regions in the temperature scale present some significant and interesting behaviours. The different transitions, shown schematically in fig. 7, are manifestations of viscoelastic deformations, which are time-dependent in nature. The deformation in this region may often show mechanical reversibility, but owing to time-dependency, it is thermodynamically irreversible. A part of the deformation energy is stored as free energy, which accounts for mechanical reversibility and the remaining part of the deformation energy is dissipated or lost as heat.

The transitions schematically indicated, as *primary* and *secondary* transitions may be close or somewhat separated, depending on the nature, molecular weight and associated factors of the polymer. The secondary transition arises as a consequence of inception or inducement of thermal excitations involving rotation of side groups or branch units of the chain molecules. This usually leads to a very small, if not insignificant decrease in modulus.

The primary transition is commonly referred to as glass transition and the corresponding temperature is known as the glass transition temperature (T_g). Glass transition results from inducement of excitation of rotation of segments of the main chains. Almost all polymers exhibit a primary transition or a characteristic glass transition, but many of them may not show a distinct secondary transition. Through the glass transition, the polymers suffer a large and sharp change in modulus. Transition from the glassy region to the long rubbery plateau zone commonly passes though an intermediate zone, recognized as the leathery zone.

Property Demand and Polymer Applications

A rough or approximate and schematic phase diagram shown in fig. 8 shows (i) how the melting temperature (T_m) and the glass transition temperature (T_g) vary and tend to level off with increase in molecular weight, (ii) how viscosity of melts varies with change in molecular weight or chain length; it also shows (iii) the different regions or zones over which properties typical of plastics, rubbers, viscous fluids etc. may be found.

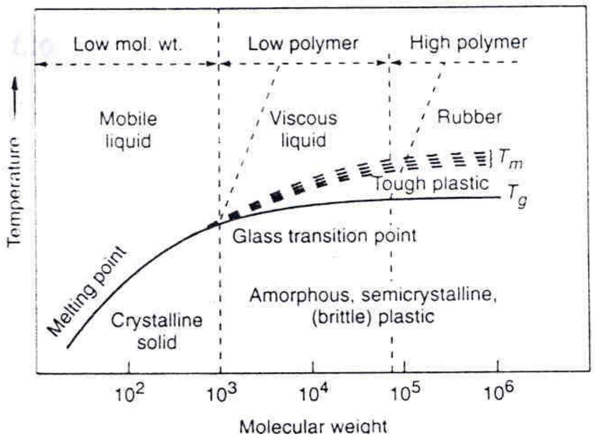


Fig. 8: Temperature-molecular weight plot (Courtesy: Tata McGraw –Hill, New Delhi)

(a) Rubbers or Elastomers : The diagram (fig. 8) further reveals that while useful plastic properties may be exhibited by polymers of wide molecular weight range (≥ 1000, low polymer or high polymer), good useful rubbery properties are exhibited by polymers which are essentially high polymeric in nature (molecular weight ≥ 100,000). To reveal rubberiness, the polymers must be far above their T_g, and for practical advantage and rightful use, T_g for elastomers or rubbers should be in the range of – 40 to – 80^{0}C. This is commonly attained in systems of low cohesive energy density, Table 4, and poor molecular symmetry, resulting in amorphousness, at least in the unstrained state and permitting adequate freedom of molecular motion, so that deformation of high magnitudes take place rapidly. Even though these requirements and features for rubbers imply high local or segmental mobility, the gross or full – scale mobility as in the flow region must be low. Restricted chain slippage must be assured in view of property demand in the form of prompt dimensional regain or recovery on stress release. This restriction is technically achieved by introduction of widely spaced primary valance cross links in the chain molecular system such that on application of forces of extension, large deformations may take place without rupture of primary bonds of the backbone chains. The molar cohesion for rubbers is in the range of 1.9 – 2.1 kcal/g.mol over segmental length of 5 Å.

Table 4: Cohesive Energy Densities of Some (Linear) Polymers

Polymer	**Cohesive energy density, cal/cm**
Polyethylene	56 – 64
Polystyrene	75 – 88
Polyisobutylene	56 – 64
Polyisoprene (natural rubber)	60 – 67
Poly (vinyl acetate)	82 – 94
Poly (vinyl chloride)	85 – 95
Poly (methyl methacrylate)	78 – 85
Poly (ethylene terephthalate)	90 – 115
Poly (hexamethylene adipamide), nylon 66	180 – 220
Polyacrylonitrile	150 – 230

(b) Fibres : For a typical fibre characterized by high tensile strength and modulus, the polymer must normally possess a combination of high molecular symmetry and high cohesive energy density manifested through polar structures in the repeat units, fostering high order of permanent crystallinity (in the useful temperature zone) on cold drawing. The crystalline melting point, T_m (without decomposition) must preferably be in the range of 200 – 300^{0}C so as to make fabrics made from them suitable for hot – pressing or ironing and for trouble-free spinning into a fibre. Resistance to solvents is an advantage, keeping dry – cleaning in view. Again, the molecular weight should be moderate (25,000 – 30,000) and not too high for synthetic fibre – forming polymers so as to ensure speedy, trouble – free spinning from melts and solutions and at the same time, it should be high enough to ensure full development of tensile strength and related properties. Presence of aromatic rings in chain backbones is sometimes helpful as in poly (ethylene terephthalate) or the PET fibre. Extensive intermolecular hydrogen bond formation is often a key factor in synthetic fibre technology; viscose and acetate rayons and polyacrylonitrile – based acrylic fibres as well as polyamide and poly (vinyl alcohol) based fibres stand in testimony to this. Molar cohesion for 5 Å chain length segment of fibres is quite high and it ranges 4 – 10 kcal/g.mol in general. Fig. 9 shows the feature of orientation of chain molecules on stretch application.

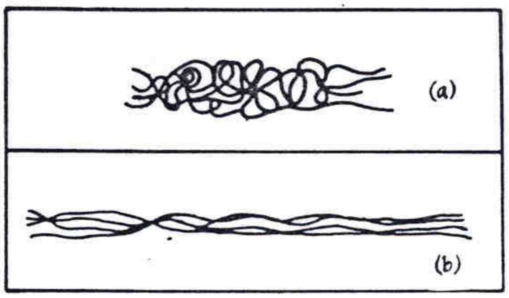


Fig. 9: Orientation of disorganized chain molecules in axial direction on stretching
(a) Unstretched (b) Stretched

(c) Plastics: Generally, the properties of plastics are more or less intermediate between those of fibres and elastomers or rubbers, with possible good degree of overlap on either side. Plastics are put to use in a vast range of application areas and hence, a wide range of property combinations is associated with them. It is no wonder then that a wide variety of chemical structures may adequately represent and describe them.

Some polymers having high cohesive energy density, such as the nylon polyamides behave as plastics when simply melt – cooled and used without orientation of the molecules by stretching. Orientation of such polymer molecular systems by stretching or cold – drawing infuses major changes in the structure of their physical agglomerates. Axial orientation of the chain molecules find permanence due to (i) establishment of extensive intermolecular H – bonding (as in the polyamides, the acrylic fibre systems etc.) or (ii) physical interlocking of the oriented chain segments (as in PET polyester) of neighbouring chains. Consequently a high order of crystallization sets in and the relevant polymers then behave as excellent fibres. Molar cohesion for 5 Å chain segment of plastics generally fall between 2.2 and 4.0 kcal/g.mol. T_g for plastics and fibres should be far above the room temperature.

The difference between rubbers, plastics and fibres is not really basic or intrinsic; it is rather a matter of degree. Small or minor variations in chemical structure or physical conditio-ning of the polymers bring about significant property variations and may result in transformation of a rubber to a resin or vice versa and of a plastic to a fibre and vice versa. Thus, (i) moderate to high degrees of cyclization, hydro-halogenation, halogenation and hydrogenation of natural rubber turn it into different types of resinous products; (ii) limited chlorosulfonation of poly ethylene, introducing – Cl atoms and – SO_2Cl groups in the chain molecules through simultane-ous treatment with chlorine and sulfur dioxide gases under pressure, breaks its molecular symmetry and thereby transforms the general – purpose polymer, polyethylene into a synthetic rubber, known in the trade as Hypalon, despite enhancement of polarity; (iii) blending or mixing with a liquid plasticizer, such as dioctyl phthalate, tricresyl phosphate etc., readily transforms the hard, rigid plastic, poly (vinyl chloride), (PVC), into a leathery or rubbery product; (iv) limited N – alkylation of the nylon polyamides makes them stretchable even when made into a fibre (the stretchable, elastomeric nylons or what is also known as stretchlons), and highly N – alkylated polyamides of comparable chain length become very soft and may even turn into viscous liquids at room temperature. Cellulose, an insoluble and infusible fibre is readily transformed into attractive plastics on esterification (nitration, acetylation etc.). N – alkylation of nylon polyamides and substitution of – OH groups in cellulose (by – ONO_2, – $OCOCH_3$ etc.) contribute to lowering in the scope for intermolecular H – bond formation, thereby resulting in weakening of the polymer systems. Natural rubber, when cooled well below its T_g (-73^0C), readily turns into the so called glassy state and gets transformed into a rock–hard, brittle material.

Step – Growth (Condensation) Polymerization

Polymerization is generally defined as intermolecular reaction between bifunctional or polyfunctional compounds (covering olefins, diolefins and related compounds) in a manner that makes the process functionally capable of proceeding indefinitely, avoiding formation of ring or cyclic structures. Functional groups or atoms through reactions of which polymerization of different kinds take place are: reactive hydrogen ($-H$), hydroxyl group ($-OH$), halogen atom ($-Cl$, $-Br$), carboxyl group ($-COOH$), amino group ($-NH_2$), isocyanate group ($-NCO$), aldehyde group ($-CHO$), double bond ($C = C$) etc.

(a) Functionality Principle: According to the functionality principle and concept, each of the reacting molecules taking part in polymerization must at least be bifunctional, giving the minimum average functionality for the system as 2. For reaction between molecules containing different kinds of functional groups, the average functionality is calculated on the basis of stoichiometric equivalence of the two kinds of mutually reacting functional groups. Thus, for reaction between a dicarboxylic acid and a trihydric alcohol, to strike stoichiometric equivalence of – $COOH$ and – OH groups, the diacid and the triol should be used in a molar ratio of 3 : 2 which would then give the average functionality for the system as 12/5, i.e., 2.4, which is less than the arithmetic average (5/2 = 2.5) for the said functional system. Thus, on the above basis of stoichiometric equivalence of reactive functional groups, a system having a polyfunctional compound (functionality of 3 or more) bearing a given kind of functional group (say, – OH) and a related monofunctional compound bearing a different kind of functional group (say, – $COOH$), would give an average functionality less than 2. So, for any system, if one type of reacting molecules are monofunctional then the system would fail to yield polymer molecules. On consideration of functionality, a double bond ($C = C$), bearing two π electrons, would be viewed as bifunctional and in fact, on thermal or photo activation, the π bond may open up to yield a biradical intermediate.

(b) Basic Features of Step–Growth or Condensation Polymerization: Condensation polymerization of a selected, suitable functional system (also viewed as the monomeric system) allows the monomeric bifunctional or polyfunctional molecules to duly condense intermolecularly in a manner that permits molecular growth or chain extension reactions to proceed in controlled, distinguishable, steps. The sequence of reactions is normally associated with the formation of a condensed interunit chemical link and liberation of a small byproduct such as H_2O, HCl, etc. at each step; a sequence of step reactions for bifunctional polyesterification involving a diol and a diacid is shown below:

Step – 1:

$$HO-R-OH + HOOC-R'-COOH \xrightarrow{-H_2O} HO-R-OOC-R'-COOH \qquad (2)$$

(Monomers) *(I)*

Step – 2:

$$(I) + HOOC-R'-COOH \xrightarrow{-H_2O} HOOC-R'-COO-R-OOC-R'-COOH \qquad (3)$$

(II)

$$\text{Or,}\ (I) + HO-R-OH \xrightarrow{-H_2O} HO-R-OOC-R'-COO-R-OH \qquad (4)$$

(III)

$$\text{Or,}\ (I) + (I) \xrightarrow{-H_2O} HO-R-OOC-R'-COO-R-OOC-R'-COOH \qquad (5)$$

(IV)

The condensation process beyond the 1st step need not necessarily involve reaction with one more molecule of the either monomeric species. Condensation products of all the successive steps retain the bifunctional character, and each bifunctional species, formed and remaining in the system at any point of time or extent of reaction, is in a position to react with any other bi-functional species, including another of its own kind and size if, however, the functional group of one kind is present at one end and of the other kind is present at the other end. Reaction of a grown – up intermediate with an unreacted monomer molecule is always a distinct possibility. Use of mixed diols or mixed diacids will produce what may be called as copolymers having more than one kind of repeat units.

One more step of condensation results in the loss of one more bifunctional species and as a consequence, two more functional groups, one of each kind are lost in each step. Production of a polymer molecule of chain length n involves completion of (2n – 1) successive steps of condensation and one may write:

$$n\ .\ HO-R\ .\ OH + n\ HOOC-R'-COOH$$

$$\longrightarrow HO\ [-R-OOC-R'-COO-]_n\ H + (2n-1)\ H_2O \qquad (6)$$

The chain – growth process at any point of time may be generally expressed by a general equation

$$\sum M_n + \sum M_m \xrightarrow{-H_2O} \sum M_{(n+m)} \qquad (7)$$

where, n and m may have any integral value between 1 and ∞. For the monomer, the value of n or m is 1. For a hydroxy acid, $HO - R - COOH$, equation (6) would assume the form :

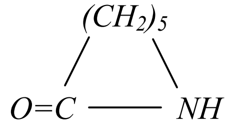
$$n \,.\, HO - R - COOH \longrightarrow H[- O - R - CO -]_n OH + (n-1)\, H_2O \qquad (8)$$

Polycondensation between a diacid chloride $(ClCO - R - COCl)$ and a diamine $(H_2N - R' - NH_2)$ may be similarly written as :

$$n\ ClCO - R - COCl + n\ H_2N - R' - NH_2 \longrightarrow$$

$$Cl\ [- OC - R - CONH - R - NH -]_n H + (2n - 1)\, HCl \qquad (9)$$

Ring opening polymerization of caprolactam to yield nylon 6 polyamide may be shown as:

n 

$$\xrightarrow{H_2O} HO\ [- OC - (CH_2)_5 - NH -]_n H \qquad (10)$$

(Caprolactam) (Catalyst) (nylon 6 polyamide)

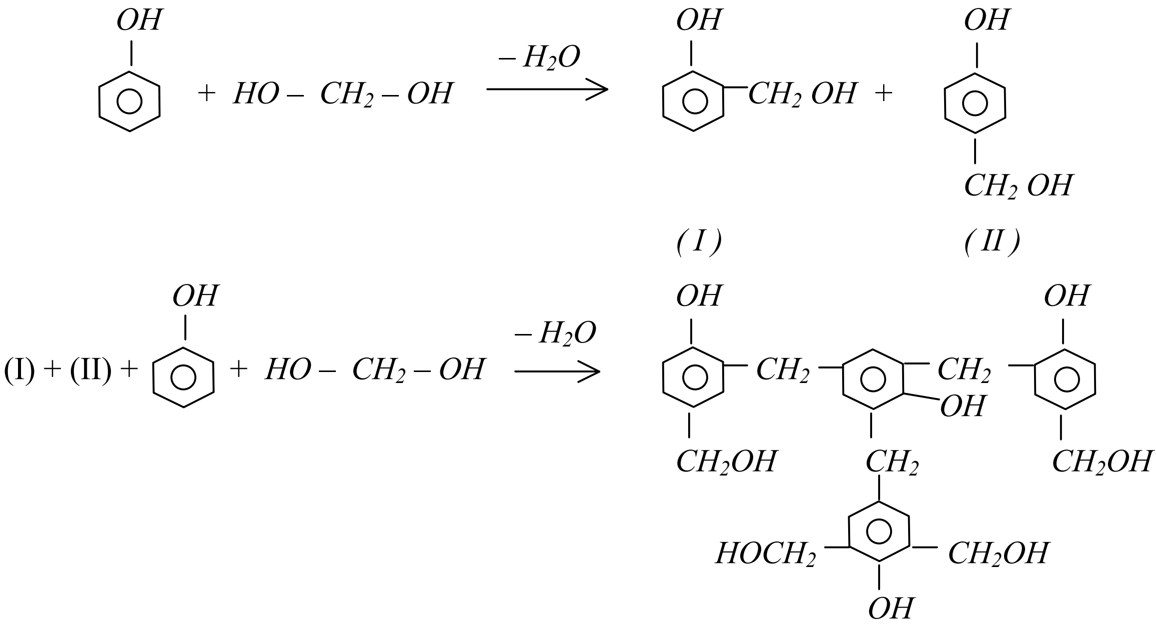
Nylon 66, poly(hexamethylene adipamide) is formed by reaction between hexamethylene diamine and adipic acid. :

$$n\ H_2N - (CH_2)_6 - NH_2 + n\, HOOC - (CH_2)_4 - COOH \longrightarrow$$

$$H\ [- HN - (CH_2)_6 - NHCO - (CH_2)_4 - CO -]_n OH + (2n - 1)\, H_2O \qquad (11)$$

(c) Phenolic (p – f) Resins: Reaction between phenol (trifunctional with three active hydrogens, one each at the two ortho positions and one at the para position) and aqueous formaldehyde (bifunctional, appearing as methylene glycol in the aqueous medium, $(CH_2O + H_2O \longrightarrow HO - CH_2 - OH)$ has the potentiality of ultimately forming a complex, crosslinked, polymer network (insoluble and insoluble and commonly known as the C–stage phenolic resin) that also goes by the name Resite. In the intermediate stage of growth, the base catalyzed phenolic resin, called Resitol is believed to be a heavily branched resinoid that is soluble in acetone but insoluble in alcohol and water. Resitol is also called the B – stage phenolic resin. The initial base catalyzed phenolic resin, called the A – stage resin or Resole is soluble in alcohol or alcohol – water mixture. Acid catalyzed phenolic resin is a linear polymer called novolac, and it is usually free from methylol groups, while the base–catalyzed phenolic resinoids bear some methylol $(-CH_2OH)$ groups in their structures. The base catalyzed phenolic resinoids are potentially thermosetting while the acid–catalyzed resin, novolac as such retains the thermoplastic character even though it can potentially turn thermosetting when heated with formaldehyde liberators such as hexamethylene tetramine or paraformaldehyde, which are used as curing or cross linking agents in novolac – based phenolic resin processing technology. Formation of phenol – formaldehyde (p – f) resinoids are shown below :

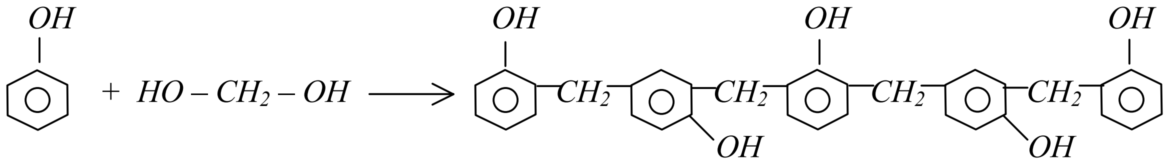
(i) Based Catalyzed Reaction :



(12)

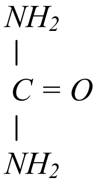
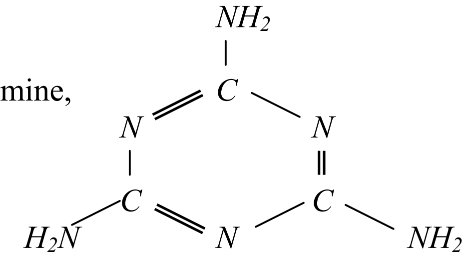
(Resole, A-stage phenolic resin)

(ii) Acid Catalyzed Reaction :



(Novolac) (13)

(d) Amino Resins (Urea – Formaldehyde and Melamine – Formaldehyde Resins) :

Urea,  $\begin{array}{c}NH_2\\ | \\ C=O\\ | \\ NH_2\end{array}$ and Melamine,  are potentially tetrafunctional and hexafunctional respectively and a reaction step with formaldehyde ($HO - CH_2 - OH$) with a base catalyst may yield methylol ureas or methylol melamines according to the following general reaction :

$$R - NH_2 + HO - CH_2 - OH \xrightarrow{-H_2O} R - NHCH_2\,OH \qquad (14)$$

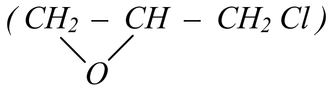
Phenolic and urea – based resins are used as binders for making moulding powders to produce thermosetting moulded objects, as industrial adhesives and in making structural and decorative laminates. Several (alkylated) grades of the amino resins are also used in making paints and enamels, as appropriate degree of alkylation (butylation) makes the respective amino resins organosoluble. Para substituted phenol is used to make linear organosoluble phenolic resins for use in paint and other surface coating applications.

(e) Polyurethanes (PU) : Polyurethanes are also produced by step – processes which can however, be described as rearrangement polymerization involving diols / polyols and di – or poly – isocyanates, e.g.

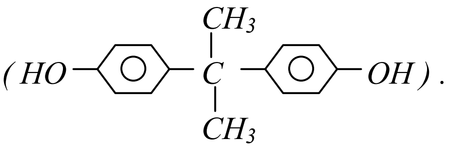
$$n\,OCN - R - NCO + n\,HO - R' - OH \longrightarrow$$
$$OCN - R - [- NHCOOR' - OOCNHR -]_{n-1} - NHCOOR'OH \qquad (15)$$

Use of hydroxy – terminated polyesters / polyethers are commonly used in making flexible elastomeric polyurethanes which can be vulcanized or cross linked on heating with excess diisocyanate.

(f) Epoxy Resins : Most common epoxy resin oligomers are polycondensation products of epichlorohydrin



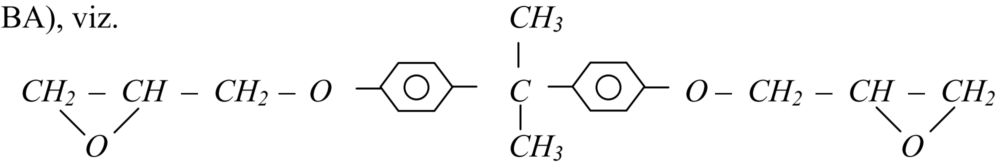
$(CH_2 - CH - CH_2\,Cl)$ and biophenol A



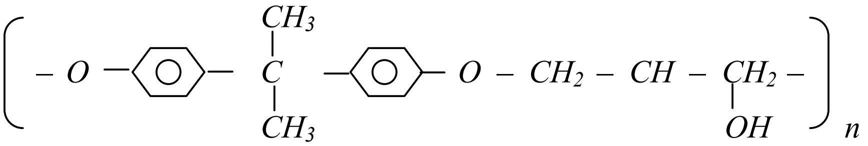
.

The commercially produced liquid epoxy resins are essentially diglycidyl ether of bisphenol A

(DGEBA), viz.



mixed with small proportions of some high molecular weight polymers. The epoxy resins are effectively cured by use of diamines/polyamines or diacids and di-isocyanates. *OH* groups in the polymer repeat units are utilized by diisocyanates (such as toluene diisocyanate, hexamethylene



diisocyanate etc.) in establishing urethane cross linkages.

Degree of Polymerization as related to Average Functionality and Extent of Reaction
W. H. Carothers deduced a general equation relating average functionality (*f*), extent of reaction (*p*) and average degree of polymerization (X_n) for polycondensation reactions carried out for a time period *t*. The equation is well known as Carothers' equation.

Let N_0 be the total number of reacting molecules initially present, giving an average functionality for the system as (*f*). The related functional groups (say – *OH* and – *COOH*) are also considered to exist in the system in stoichiometric equivalence. Let *N* be the number of molecules existing in the system at time (*t*), when the extent of reaction is (*p*).

Now, the number of molecules lost during the reaction over the time period *t* is $(N_0 - N)$. For each molecule lost, the number of functional groups lost is 2 (one of each kind) and therefore, the total number of functional groups lost is 2 $(N_0 - N)$ against the initial total number of functional groups of N0f.

So, the extent of reaction $p = \dfrac{2\,(N_0 - N)}{N_0 f}$

$$i.e.,\quad p = \frac{2}{f}\left(1 - \frac{N}{N_0}\right) \qquad (16)$$

The average degree of polymerization, $\overline{X}_n$ is defined as the average number of structural units per polymer molecule, which can be simply expressed as :

$$\overline{X}_n = \frac{N_0}{N} \qquad (17)$$

Combining equations (16) and (17), one obtains

$$p = \frac{2}{f}\left(1 - \frac{1}{\overline{X}_n}\right) \qquad (18)$$

Equation (18) is well known as Carothers' equation. At gel point, $\overline{X}_n \rightarrow \infty$ and under this condition, the critical extent of reaction p_c is given by

$$p_c = \frac{2}{f}$$

For a bifunctional system, $f = 2$, so that equation (18) reduces to

$$p = \left(1 - \frac{1}{\overline{X}_n}\right) \qquad (19)$$

such that, for $p = 1$, i.e. for the limiting condition of the reaction going to completion, $\overline{X}_n = \infty$. This means that, short of complete reaction, the degree of polymerization, $\overline{X}_n$ is always a finite quantity. So, a polymer obtained in a bifunctional system is, under all practical situations, linear and hence soluble and fusible. The upper theoretical limit in the degree of polymerization is infinity and this can be attained only in the hypothetical condition of completion of the reaction, i.e., p becoming equal to 1. For bifunctional system Equation (19) may be rearranged and one gets,

$$\overline{X}_n = \frac{1}{(1 - p)} \qquad (20)$$

If the mean molecular weight of the repeat unit of the polymer molecules formed is M_0, then the average molecular weight $\overline{M}_n$ of the polymer system is given by

$$\overline{M}_n = \overline{X}_n \, . \, M_0 = \frac{M_0}{(1 - p)} \qquad (21)$$

For a polyfunctional polycondensation system, exemplified by the reaction between glycerol and phthalic anhydride, equation (18) will assume the form

$$p = \frac{2}{2.4} \left(1 - \frac{1}{\overline{X}_n} \right) \qquad (22)$$

It is now easy to find out the critical extent of reaction, p_c , at which geletion or cross linking would commence, i.e. when $\overline{X}_n$ would first assume the value of infinity, and the calculated value of p_c will then be 2 / 2.4 = 0.83. Theoretically, it means that, when the reaction is 83% complete, the polymer being formed starts getting cross linked and the system turns into a gel, i.e. to an insoluble, infusible mass. In practice, however, due to some uncertainties, gelation may start at an earlier extent of reaction and it is advisable to arrest the reaction by cooling the reaction mass at an extent of reaction that is about 10% less than the theoretical p_c value.

Carothers' equation is very simple and useful as it relates p, f and $\overline{X}_n$ in one expression and it can be used to predict gelation in polyfunctional systems. Its limitation is that practically gelation starts at earlier stages than the theoretical prediction due to uncontrolled local conditions in the hot, viscous reaction mass in many cases. Moreover, Carothers' equation is applicable to polycondensation reactions only, and it loses relevance in cases of addition or chain growth polymerization.

Chain – Growth (Addition) Polymerization

Chain – growth or addition polymerization is a process by which unsaturated (olefinic, diolefinic, vinylic) monomers are converted to polymers of high molecular weight exhibiting the characteristics of typical chain reactions that takes place very fast. Such very fast, or the so called explosive reactions are typified by three successive, distinguishable stages, viz., (i) triggering off or initiation of the chain process, (ii) propagation of the chain or the chain – growth process, and (iii) cessation of the chain – growth process, commonly referred to as chain termination.

The chain polymerization may be initiated or induced by heat, light or other radiations and by a host of catalysts, called initiators. If induced by light, the process is referred to as photo polymerization. The chain propagation may take place by free radical or ionic (cationic or anionic) mechanisms, depending on the initiator system used and the prevailing polymerization environment.

Free radical polymerization is in wide practice and has been studied extensively. The initiation of chain polymerization is normally a direct consequence of generation or introduction of a highly reactive species (R*) through degradation or dissociation of some monomer molecules (M) under the influence of physical agencies such as heat, light or high – energy radiation (high – speed electron, X-ray, γ-ray etc.) or as a result of decomposition or dissociation of the catalyst or initiator molecules (I) present, viz.

$$I \xrightarrow{k_d} R^* \qquad (23)$$

Or, simply, $$M \xrightarrow{k_d} R^* \qquad (24)$$

The reactive species, R* (free radical, cation or anion) then readily attacks the unsaturated monomer (M) molecule (e.g. $CH_2 = CHX$, where, X may be H, Cl, Br, CN, $COOH$, $COOR$, CH_3, C_2H_5, C_6H_5, OCH_3, $CH = CH_2$ etc.). If conditions are favourable, R^* adds itself to the monomer molecule by opening the π bond in the monomer to form a fresh bigger reactive center (free radical, cation (carbonium ion) or anion (carbanion), as the case may be). The fresh or new reactive center likewise adds to another monomer molecule M, and the process is repeated fast in quick succession. Thus, many more monomer molecules are successively added to the same growing or propagating species at its remote reactive or growth center, thus carrying forward the chain propagation process, yielding a big, long growing chain of chain length, say n. The chain growth process is terminated at some point by annihilation of the reactive or propagating center by one or more permissible or appropriate mechanism, largely dependent on the type of the reactive center (radical, cation or anion), monomer nature and overall environment or condition of the reaction system.

(a) **Free Radical Polymerization :** For free radical polymerization, the initiator decomposition, often taking place by homolytic cleavage of specific weak bond or bonds in the (lone) initiator molecule (I), results in generation of a pair of free radicals, viz.,

(i) Initiator decomposition and radical generation

$$I \xrightarrow{k_d} 2\,R^{\bullet} \qquad (25)$$

Good examples of free radical initiators are peroxides such as benzoyl peroxide

$(C_6H_5 - \overset{\diagup\!\!\diagup O}{C} - O - O - \overset{\diagup\!\!\diagup O}{C} - C_6H_5)$, hydroperoxides such as t–butyl hydroperoxide [$(CH_3)_3 - C - O - OH$] or azo compounds such as azobisisobutyronitrile [$(CH_3)_2 - \overset{\diagup CN}{C} - N = N - \overset{\diagup CN}{C} - (CH_3)_2$].

The decomposition to a pair of radicals may be generally represented as

$$R - O - O - R \xrightarrow{k_d} 2\,RO^{\bullet} \qquad (26)$$

$$H - O - O - R \xrightarrow{k_d} 2\,\overset{\bullet}{O}H \qquad (27)$$

$$R - N = N - R \xrightarrow{k_d} 2\,R^{\bullet} + N_2 \qquad (28)$$

One also extensively uses selected redox pairs for free radical generation in chain polymerization systems :

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \underset{\bullet}{O}H + OH^{-} \qquad (29)$$

$$S_2O_8^{=} + HSO_3^{-} \longrightarrow SO_4^{=} + \overset{\bullet}{H}SO_3^{=} + SO^{\bullet}{}_4^{-} \qquad (30)$$

$$R - O - O - R + R'NH_2 \longrightarrow ROH + RO + R'\overset{\bullet}{N}H \qquad (31)$$

The radicals or ion – radicals, so generated, equations (25) to (31), induce free radical polymerization. The radical ($R^{\bullet}$) derived from the initiator system, equation (25), first brings about chain initiation by adding itself to a monomer molecule (M), and then a long sequence of chain propagation reaction follows :

(ii) Chain initiation

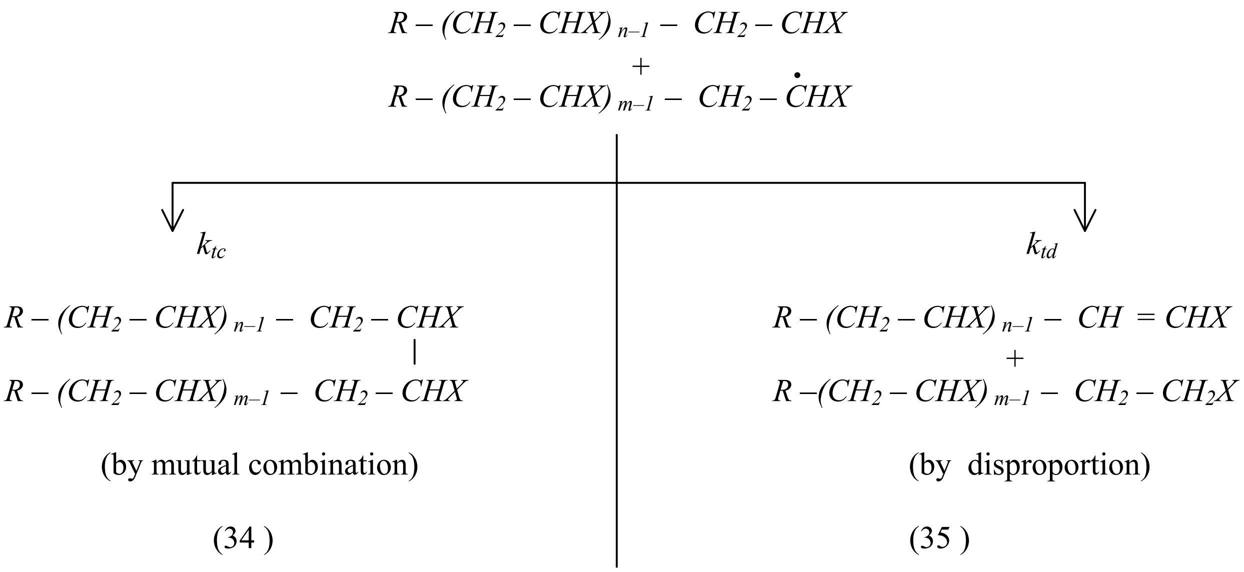
$$R^{\bullet} + M \xrightarrow{k_i} R - M^{\bullet}{}_1 \qquad (32)$$

(iii) Followed by chain propagation

$$R - M^{\bullet}{}_1 + M \xrightarrow{k_p} R - M_1 - M^{\bullet} \xrightarrow[k_p]{(n-2)\,M} R - (M)_{n-1} - M^{\bullet} \qquad (33)$$

(iv) Chain termination

In homogeneous free radical polymerization, the chain termination is commonly bimolecular in nature and the termination reactions involve a pair of (growing) chain radicals and may alternatively or simultaneously occur by (a) mutual combination (rate constant, k_{tc}) or by (b) disproportion (rate constant, k_{td}).



$$R-(CH_2-CHX)_{n-1}-CH_2-CHX + R-(CH_2-CHX)_{m-1}-CH_2-\dot{C}HX$$

k_{tc}:

$$\begin{array}{l} R-(CH_2-CHX)_{n-1}-CH_2-CHX \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ R-(CH_2-CHX)_{m-1}-CH_2-CHX \end{array}$$

(by mutual combination)

(34)

k_{td}:

$$R-(CH_2-CHX)_{n-1}-CH=CHX + R-(CH_2-CHX)_{m-1}-CH_2-CH_2X$$

(by disproportion)

(35)

Further, it may be understood that the initiator fragment (*R*) appears in the polymer structure as terminal functions or end groups, sealing both the ends of the linear polymer molecule formed by termination by (mutual) combination, equation (34) or sealing only one end of the linear polymer molecules formed by termination by disproportion, equation (35). The end groups remain as potential centers of chemical reactivity or as tell – tale birthmarks for the polymer molecules, indicating the identity of the radical or the initiator fragment responsible for chain initiation during polymerization.

Other reactive centers, in addition to the chain – end unsaturation arising from termination by disproportion, may be the substituent X groups attached to each alternate carbon atom in the chain molecules of the vinyl and related polymers.

When one makes a copolymer taking two different kinds of monomers, $CH_2 = CHX$ and $CH_2 = CHY$ together for polymerization, substituent groups X and Y of the two different kinds of repeat units appearing in the chain copolymer molecules may act differently. In fibre forming copolymers, one of the comonomers used is specially and particularly selected to infuse or improve processibility, resilience and dyeability. Use of acidic comonomers (acrylic / methacrylic acid, maleic anhydride etc.) contributes to improve dyeability using basic dyes, while incorporation of basic comonomers (vinyl pyridine, amino acrylates / methacrylates etc.) improve dyeability using acid dyes.

Variations in molecular weight and molecular weight distribution (MWD), degree of stretching (to vary degree of molecular orientation and hence of crystallization) and in the case of preparing a copolymer, variations of monomer feed ratio (giving rise to variations in copolymer composition) largely influence physical, chemical, mechanical, thermal, optical and almost all textile related properties of the polymers/copolymers or the fibres and textiles made from them.

(b) Molecular Weight Control and Importance of Chain Transfer: Molecular weight can be controlled by variation of initiator or monomer concentrations and temperature of polymerization but more importantly, by judicious and selective use of a solvent or other additive commonly known as a chain transfer agent. The chain transfer allows termination of a specified chain –

growth process by transfer of the growth center (free radical or other kind) to the new species, called the chain transfer agent. The chain transfer process appears much like a relay race taking place through transfer of a flag or torch to a new / subsequent racer as opposed to a single racer taking part to run through the whole specified distance without sharing the racing with any one else and transfer of flag or torch.

The chain transfer reaction actually intercepts an on-going chain propagation reaction without actually causing chain termination and instant disappearance of the active center (equivalent of flag or torch in a relay race, for an example) from the scene. The transfer process, however, limits or restricts further growth or progress of the initial, on-growing chain and literally terminates it and simultaniously creates a new chain–growth center on the intercepting species (better known as chain transfer agent) and the chain propagation is subsequently carried on by the activated intercepting species without materially disturbing the polymerization rate. The sequence of reactions referred to here involving a growing chain $M^\bullet_n$ and a chain transfer agent, SH may be shown as follows:

(i) Chain transfer $M^\bullet_n + SH \xrightarrow{k_{tr}} M_nH + S^\bullet$ (36)

(ii) Reinitiation $S^\bullet + M \xrightarrow{ki} S - M^\bullet_1$ (37)

(iii) Propagation of $SM^\bullet_1 + M \xrightarrow{k_p} SM^\bullet_2$

a new chain $----\xrightarrow{(n-2)\,M} SM^\bullet_n$ (38)

Due to chain transfer, more number of polymer molecules is obtained and they are characterized by lower than normal degree of polymerization (otherwise expected in the absence of the transferring solvent / additive, SH) for a given mass of polymer obtained over a given period of polymerization. Some monomers and relevant polymers are also known to be effective as chain transfer agents. They may cause increase in the number of polymer molecules and moderate to severe (and calculable) lowering in molecular weight; polymer – transfer may lead to moderate to extensive chain branching (as prevalent in high pressure radical polymerization of ethylene, yielding the well known low density polyethylene, LDPE), and sometimes to an increase in molecular weight as well.

Chain transfer reactions are taken advantage of not only for controlling molecular weight of useful polymers, but also to modify specified preformed polymers (natural, semi-synthetic and synthetic) leading to production of graft copolymer. Such modifications are done by allowing graft copolymerization of a monomer of a different kind in the presence of a preformed polymer so as to get the polymer being formed chemically linked to or grafted on it by chain transfer.

(c) Copolymers and their Importance: Two different homopolymers are obtainable from separate polymerizations of the two different monomers pictorially represented by symbols of an open circle and a divided circle respectively and different types of copolymers (random, alternate, block and graft) that they may produce, are shown schematically in fig.10. Copolymers of different properties or property ranges are readily produced by copolymerization of selected monomer pairs or even of more than two kinds of monomers together; by variation of their molar proportions, it is possible to obtain copolymers of varied comonomer sequences and molecular compositions, thereby making it possible to derive a wide diversity of application prospects for them depending on the infused property variations. It is no wonder that, there are more copolymers in the market than homopolymers in view of this type of variations and literally unending possibilities. Some important copolymers of wide use and applications are: (i) Styrene–butadiene (copolymer) rubber (SBR), (ii) ethylene – vinyl acetate (EVA) copolymers used as wax–additives, hot–melt adhesives and rubbers, (iii) ethylene – propylene copolymer (rubbers), [EPR and EPDM (containing also low content of a diene)] (iv) nitrile rubber (a copolymer of 75 parts butadiene and 25 parts acrylonitrile) etc.

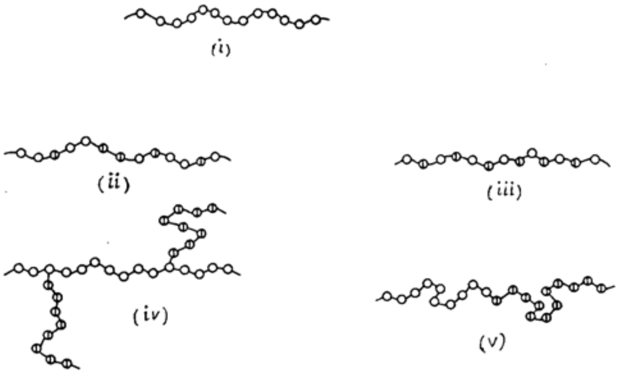
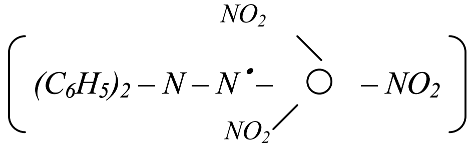


Fig.10: Models of (i) homopolymer (ii) random copolymer (iii) alternate copolymer (iv) graft copolymer and (v) block copolymer

(d) Ionic Polymerizations: Unlike free radical polymerization, ionic polymerizations are associated with what may be termed as monomer selectivity. Generally, monomers having electron-releasing substituents (alkoxy, 1, 1 di-alkyl or aryl – alkyl, phenyl and vinyl groups) exemplified by isobutyl vinyl ether, isobutylene, α – methyl styrene and butadiene are readily susceptible to cationic polymerization and not as readily or really to anionic polymerization. Monomers having electron withdrawing substituents such as nitrile ($-CN$), carboxyl ($-COOH$) and ester ($-COOR$) groups exemplified by acrylonitrile, acrylic / methacrylic acid and methyl acrylate etc. are readily susceptible to anionic polymerization. Phenyl and vinyl substituents also make the monomer (styrene, butadiene etc.) capable of polymerizing anionically.

Protonic acids viz., H_2SO_4 and $HClO_4$ or Lewis acids such as BF_3, $SnCl_4$, $AlCl_3$, $TiCl_4$ etc. which are strong electron acceptors, readily induce cationic polymerization. On the other hand, basic compounds such as amides, alkoxides, alkyls and aryls of alkali metals and different Grignard reagents are known to act as catalysts for polymerization of appropriate monomers by anionic mechanism. Bases or basic solvents inhibit cationic polymerization while acids or acidic solvents inhibit anionic polymerization, but they do not inhibit free radical polymerizations as such.

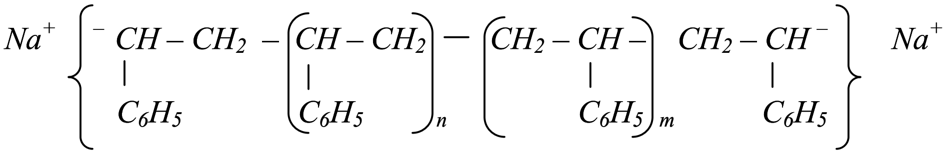
Free radical polymerizations are inhibited by stable or living free radicals such as triphenyl methyl [$(C_6H_5)_3 - C^\bullet$] and diphenyl picryl hydrazyl



and by oxygen, quinones and some phenols or polyphenols. Such compounds are also known as inhibitors. Bimolecular termination as prevalent in free radical polymerization is totally prohibitive in ionic polymerizations, as like charges repel each other and can not come close enough for mutual interaction and annihilation.

Solvents of such polarity as to favour formation of ion – pairs and as not to permit large scale ion dissociation, offer different degrees of stability and reactivity for the propagating ion centers; for cationic polymerizations, often very low temperatures (-40^0 to -100^0C), as for polymerization of isobutylene with BF_3 as the catalyst and only traces of H_2O as co-catalyst, are needed. Highly polar media or additives, such as water, alcohol, etc. react with and destroy most ionic catalysts or reduces their catalytic activity to insignificance. Methyl chloride, ethylene dichloride, pentane, hexane, heptane etc. act as good media for ionic polymerization. Liquid ammonia is a good medium for anionic polymerization using KNH_2 as anionic initiator.

Polymerization of styrene by sodium naphthalene in tetrahydrofuran (THF) turns into a living polymer system where long chain orange coloured polystyryl anions remain in THF solution in close association with Na^+ counter ions, without suffering termination.



$$Na^+\left\{ {}^-\underset{C_6H_5}{\underset{|}{CH}} - CH_2 - \left(\underset{C_6H_5}{\underset{|}{CH}} - CH_2\right)_n - \left(CH_2 - \underset{C_6H_5}{\underset{|}{CH}} -\right)_m CH_2 - \underset{C_6H_5}{\underset{|}{CH^-}} \right\} Na^+$$

(Living polymer showing orange coloured polystyryl anions)

Transition metal chlorides such as $TiCl_4$ and aluminium trialkyl ($AlEt_3$, aluminium triethyl) form complexes of the kind [$(TiCl_3)^+$ $(AlEt_3Cl)^-$]; such complexes, known as Ziegler – Natta complexes, catalyze stereoregular, low – pressure polymerization of olefins, diolefins and some vinyl monomers by what is understood to be cationic initiation and anionic propagation following a propagation mechanism called anionic coordination mechanism. Such polymerizations are commonly characterized by (i) cationic initiation, (ii) anionic propagation, (iii) hair – like growth, (iv) prominent stereoregularity in appropriate systems and (v) head – to – tail linkage between the repeat units.

Metallocene catalysts based on *Zr/Ti* complexes with organic ligands such as cyclopentadienes (Cp), in conjunction with an oxyaluminium complex, such as methyl aluminoxane ($\underset{CH_3}{>}Al - O -$) , (*MAO*), have grown in popularity and advantageous use as single site catalysts (*SSC*); they provide nearly 100% active sites as against 1 – 3% active sites for the conventional Ziegler – Natta or some metal oxide catalyst systems.

Gas phase, slurry (suspension) and solution processes have been in practice for industrial polymerization of olefins and related monomers using coordination catalysts such as supported metal oxide (CrO_3, MoO_2) catalysts and Ziegler – Natta complex and metallocene complex catalysts. Free radical polymerizations are also accomplished traditionally following bulk, suspension, solution and emulsion techniques. Suspension and emulsion polymerizations are commonly carried out using aqueous media. Emulsion polymerization is commonly accomplished at low (0 – 50^0C) temperatures. Paint – grade acrylate / methacrylate polymers are prepared by solution and emulsion polymerization techniques. Diene – based copolymer rubbers as well as some grade of poly (vinyl chloride), PVC are widely produced by emulsion technique. Transparent acrylate / methacrylate polymers, polystyrene and some grades of PVC also are polymerized by bulk polymerization. Condensation polymers are more commonly produced employing bulk polymerization technique.

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