Polymer Chemistry

Notes by

Dr. Indranil Chakraborty

Department of Chemistry

Part-II

(Molecular forces & chemical bonding in polymers)

Paper-DSE 4T (6th Sem)

Lecture Note-2

You all know from your elementary organic chemistry knowledge that the physical properties of members of a homologous series are functions of their molecular size (wt.). On moving from low molecular weight to high molecular weight along a homologous series there occurs a progressive change from the gaseous state through liquids of increasing viscosity (decreasing volatility) to low melting solids and ultimately leading to high-strength solids. Polymers are of high-molecular weight. The reason behind their unusual properties will be discussed here.

No. of Carbon Atoms	Molecular State
1	Methane — boiling point −162°C
2–4	Natural gas — liquefiable
5–10	Gasoline, diesel fuel — highly volatile, low viscosity liquid
10–10^2	Oil, grease — nonvolatile, high viscosity liquid
10_2–10^3	Wax — low melting solid
10^3–10^6	Solid — high strength

Equation 1: Change of state with Mol wt.

Structure of polymers

1. The chemical structure (atomic composition) of the monomer **(primary structure)**
2. The single polymer chain **(secondary structure)**
3. Aggregation of polymer chains **(tertiary structure)**

Bonding in polymers

Chemical bonds may be classified as primary or secondary, depending on the extent of electron involvement. Valence electrons are involved in the formation of primary bonds. This results in a substantial lowering of the potential energies. Consequently, primary bonds are quite strong. On the other hand, valence electrons are not involved in the formation of secondary bonds - leading to weak bonds.

Primary bonds can be further subdivided as **Ionic, Covalent & Metallic.** Secondary bonds on the other hand can be further subdivided as **Dipole, Hydrogen bond, Induction & Van der waals (dispersion).**

A. THE IONIC BOND

Every element has a desire to achieve the filled up electronic configuration (stable) of nearest inert gasses either by losing, gaining, or sharing electrons.

In doing so, elements that lose electrons (electropositive elements) form cations, and those that gain electrons (electronegative elements) form anions, leading to formation of ionic bonds.
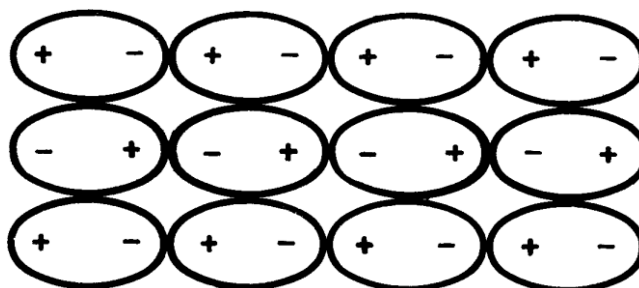
During the formation of sodium chloride, sodium easily loses the outermost 3s electron and forms Na^+ to achieve the stable inert gas configuration of He. Chlorine, on the other hand (with high electron affinity), can achieve a stable electronic configuration of Ne by gaining an extra electron forming Cl^-. Ionic bonds are not quite common in polymeric materials. However, divalent ions are known to act as cross-links between carboxyl groups in natural resins. **The polymers that contain ionic bonds are known as *ionomers*.**

B. THE COVALENT BOND

For certain elements, especially those residing at the central portions of the periodic table it is easier to attain stable electronic configuration by sharing of valence electrons, and the bonds formed by electron sharing are called *covalent* bonds. Consider the formation of methane. Carbon atom has four unpaired electrons in its outer electron shell, while hydrogen has one electron. By sharing electrons, one from each atom per bond, a stable octet is obtained for the carbon atom and a stable pair (duplet) for each hydrogen atom. This is the predominant bond in polymers. Covalent bonds can be single, double, or triple depending on the number of electron pairs. Bond dissociation energy has a direct relationship with the thermal stability of polymers.

C. DIPOLE FORCES

Molecules are electrically neutral, but might have a permanent dipole if the centres of the positive and negative charges do not coincide; this arises if the electrons shared by two atoms spend more time on one of the atoms due to differences in electronegativity. This can be illustrated by considering a diatomic molecule such as hydrogen chloride, HCl. Because chlorine is more electronegative than hydrogen, the shared pair of electrons between the chlorine atom and the hydrogen atom is drawn closer to the chlorine atom. Consequently, the chlorine atom has net partial negative charge while the hydrogen atom has a net partial positive charge. Any diatomic molecule in which there is a separation of positive and negative charge is said to be polar. In molecules containing more than two atoms the polarity of the molecule is determined by the bond angles. Polar molecules therefore have a small separation of charge, and this sets up a permanent dipole. Dipoles interact through coulombic forces, which can become quite significant at molecular distances. Polar molecules are held together in the solid state by the interaction between oppositely charged ends of the molecules. The forces of interaction between these molecules are called dipole-dipole interaction.
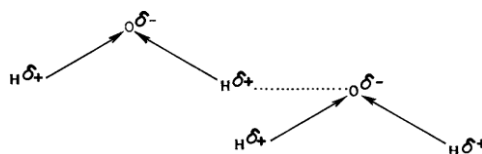

Dipole–dipole interaction between polar molecules.

This type of molecular orientation is generally opposed by thermal agitation. Consequently, the dipole-dipole interaction is temperature dependent. Dipole forces play a significant role in determining the tertiary structure and, hence, properties of some polymers.

D. HYDROGEN BOND

A particularly important kind of dipole interaction is the hydrogen bond. This is the special force of attraction between a positively (partially) charged hydrogen atom and a small electronegative atom like F, O, or N. The anomalous properties (e.g density) of water, for example, are associated with the hydrogen bonding between water molecules The difference in electronegativities between hydrogen and oxygen causes the bonding electrons in H_2O to shift markedly to the oxygen atom so that the hydrogens behave essentially as bare protons. Hydrogen bonding is limited primarily to compounds containing F, N, and O because the small size of hydrogen permits these atoms to approach the hydrogen atom in another molecule very closely. For example, in spite of the similarity in electronegativity between Cl and N (3.0 for both), HCl with the larger chlorine atoms shows hardly any tendency to form hydrogen bonds.

Hydrogen bonding between two water molecules

Hydrogen bonds are relatively stronger than dipole bonds due to the small size of the hydrogen ion. In polymers, hydrogen bonding usually occurs between functional groups in the same or different molecules. The hydrogen is generally part of such groups as carboxyl, hydroxyl, amine, or amide, while the other atom in the hydrogen bond is frequently oxygen (in carbonyl, ethers, or hydroxyls) or nitrogen (in amines, amides, urethanes, urea). The hydrogen bond plays a vital role in the structure and properties of polymers, particularly proteins.

Nature of Interaction	Interaction Energy (kJ/mol)
Dipole–induced dipole	≤2
van der Waals	0.08−4.0
Dipole–dipole	≤20
Hydrogen bond	≤50
Covalent bond	60−600
Ionic bond	560−1000

E. INDUCTION FORCES

Every dipole has an electric field associated with it. This electric field is capable of inducing relative displacements of the electrons and nuclei in neighbouring molecules. The result is that, the surrounding molecules

become polarized, i.e., the neighbouring molecules possess induced dipoles. Intermolecular forces, called induction forces, exist between the permanent and induced dipole. Induction forces are weak and temperature independent. Polarizability is the ease with which molecules can be polarized

F. VAN DER WAALS (DISPERSION) FORCES

Inert gases like He, Ne, Ar, and Kr are supposed to be incapable of forming any type of bonds (ionic, covalent, or metallic). Although these inert gases have usual stability (considerable reluctance to undergo reactions), however, at sufficiently low temperature these gases are known to condense to form solids. It is therefore apparent that some form of intermolecular force exists in these materials. Electrons are usually in constant motion about their nuclei. At any particular point of time, the centres of negative charge of the electron cloud may not coincide with those of the nuclei. Consequently, instantaneous (fluctuating) dipoles exist even in nonpolar materials. If the orientations of fluctuating dipoles in neighbouring molecules are in proper alignment, intermolecular attractions occur. These attractive forces are referred to as van der Waals (dispersion) forces. Van der Waals forces are present in all molecules and, as we shall see later, they contribute significantly to the bonding in polymers.

PRIMARY STRUCTURE

Primary structure refers to the atomic composition and chemical structure of the monomer. The chemical and electrical properties of a polymer are directly related to the chemistry of the constituent monomers. The physical and mechanical properties of polymers, on the other hand, are largely dependent on the macromolecular size of the polymer, which in itself is related to the nature of the monomer. Therefore, to understand the structure and properties of the resulting polymer is related to

• The nature of bonds in monomers (chemical bonding)
• The type of monomers capable of forming polymers (functionality of monomers)
• The mode of linkage of monomers (polymerization mechanisms)
• The chemical composition of monomers

We have already discussed chemical bonding, monomer functionality, and polymerization mechanisms. we shall now discuss on chemical composition of monomers.

CHEMICAL COMPOSITION OF MONOMERS (POLARITY OF MONOMERS)

The chemical composition and atomic arrangement of an organic molecule confer certain properties on the molecule. One such property is the polarity of the molecule. Sodium chloride, like all ionic substances where complete charge transfer has occurred, is highly polar. This polarity is responsible for the electrostatic attraction between adjacent ions in solid sodium chloride. Covalent molecules, on the other hand, are formed by the sharing of electrons between the constituent atoms. In a diatomic molecule formed from two *like* atoms (e.g., H_2), the

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electron pair linking the two atoms is equally shared and the molecule is said to be *nonpolar.* But when molecules are formed from two unlike atoms (e.g., HF), the distribution of the electron cloud is concentrated on the more electronegative atoms (fluorine, in this case). Here again, as in ionic compounds, there is a separation of positive and negative charge and the molecule is said to be polar. However, since no complete charge transfer has taken place in this case, the polarity (of covalent molecules) is less than that of ionic compounds. Even among covalent molecules, the degree of polarity varies depending on the electronegativities of the constituent atoms. Groups like C–Cl, C–F, –CO–, –CN, and –OH are polar. In a polyatomic molecule, the polarity is a vector sum of all the dipole moments of the groups within the molecule. This depends on the three-dimensional distribution (symmetry) of the groups within the molecule. To illustrate this, let us consider two triatomic molecules: water [H_2O] and carbon dioxide [CO_2]. Both the OH and CO groups are polar. But while the H_2O molecule is polar, CO_2 is a nonpolar molecule. The structure of CO_2 is linear, resulting in a cancellation of the dipole moments. However, H_2O has a triangular structure and, consequently, possesses an overall dipole moment. In fact the resultant of the dipole moments of the bonds is the actual dipole moment of the molecules. The characteristic interunit linkages in condensation polymers, for example, –CO.O– (ester), –CO.NH– (amide), –HN–CO–NH– (urea), and –O.CO–NH– (urethane) are polar. Polarity affects the intermolecular attraction between chain molecules, and thus the regularity and symmetry of polymer structure. Naturally, properties such as the solubility and electrical nature of polymers, which depend on polymer structure, are intimately related to polarity.

SECONDARY STRUCTURE

In order to understand the polymer properties, it is important to development of a physical picture of what these long molecules are really like. This is known as the secondary structure, i.e., the size and shape of an isolated single molecule. The size of the polymer is best discussed in terms of molecular weight. The shape of the polymer molecule (molecular architecture) will be influenced naturally by the nature of the repeating unit and the manner in which these units are linked together. Two terminologies namely, configuration and conformation, are therefore very important to consider in this regard.
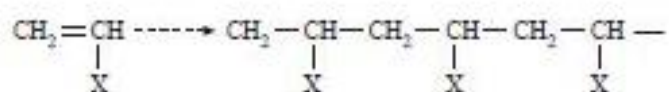
I) Configuration - Arrangement fixed by primary valence bonds; can be altered only through the breaking or reforming of chemical bonds

II) Conformation - Arrangement established by rotation about primary valence bonds
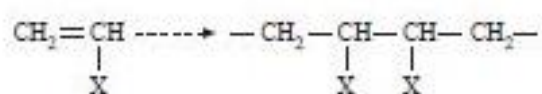
I) CONFIGURATION

As we saw earlier, a polymer molecule may be linear, branched, or cross-linked depending on the functionality of the monomers used. But if repeating units along the chain are chemically and satirically regular, then the polymer is said to possess structural regularity. To consider structural regularity, we need to define two terms: *recurrence regularity* and *stereoregularity*.

Recurrence regularity refers to the regularity with which the repeating unit occurs along the polymer chain. This may be illustrated by examining the polymers resulting from mono substituted vinyl monomers. Here there are three possible arrangements:
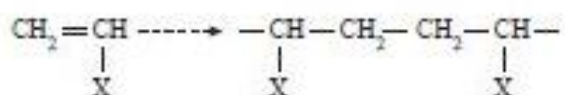
- Head-to-tail configuration

$$CH_2 = CH \ \cdots \cdots \rightarrow \ CH_2 - CH - CH_2 - CH - CH_2 - CH - $$
$$\quad\quad | \quad\quad\quad\quad | \quad\quad\quad | \quad\quad\quad | $$
$$\quad\quad X \quad\quad\quad\quad X \quad\quad\quad X \quad\quad\quad X$$

- Head-to-head configuration

$$CH_2 = CH \ \cdots \cdots \rightarrow \ - CH_2 - CH - CH - CH_2 - $$
$$\quad\quad | \quad\quad\quad\quad\quad\quad | \quad\quad | $$
$$\quad\quad X \quad\quad\quad\quad\quad\quad X \quad X$$

- Tail-to-tail configuration

$$CH_2 = CH \ \cdots \cdots \rightarrow \ - CH - CH_2 - CH_2 - CH - $$
$$\quad\quad | \quad\quad\quad\quad\quad | \quad\quad\quad\quad | $$
$$\quad\quad X \quad\quad\quad\quad\quad X \quad\quad\quad\quad X$$

The last two configurations do not appear in any measurable extent in known polymers.

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Table 3.6 *Polarity of Monomers and Their Associated Polymers*

Monomer	Polarity	Polymer	Polarity
$CH_2{=}CH_2$ Ethylene	Nonpolar	$[\!-CH_2-CH_2-]$ Polypropylene	Nonpolar
$CH_2{=}CH_2$ | CH_3 Propylene	Nonpolar	$[\!-CH_2-CH_2-]$ | CH_3 Polypropylene	Nonpolar
$CH_2{=}CH$ | Cl Vinyl chloride	Polar	$[-CH_2-CH-]$ | Cl Poly(vinyl chloride)	Polar
$CH_2{=}CCl_2$ Vinylidene chloride	Nonpolar	Cl | $[\!-CH_2-C-]$ | Cl Poly(vinylidene chloride)	Nonpolar
$CH_2{=}CH$ | CN Acroylonitrile	Polar	$[\!-CH_2-CN-]$ | CN Polyacrylonitrile	Polar
$CF_2{=}CF_2$ Tetrafluoroethylene (symmetrical)	Nonpolar	$[\!-CF_2-CF_2-]$ Polytetrafluorethylene (Teflon)	Nonpolar

Stereoregularity refers to the spatial properties of a polymer molecule. To discuss this, let us consider two examples.
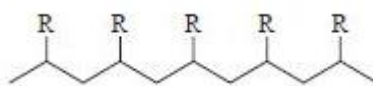
Diene Polymerization

Propagation step in the polymerization of diene monomers can proceed by either of two mechanisms: 1,2, and 1,4 additions. In 1,2 addition in the resulting polymer, unsaturation is part of the pendant group, while in 1,4 addition the unsaturation is part of the backbone. In the latter case, the backbone has a rigid structure and rotation is not free around it. Therefore, two different configurations, known as *cis* and *trans,* are possible. For example, 1,4-polyisoprene:

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cis-1,4-polyisoprene (natural rubber)
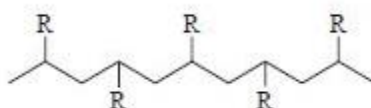

trans-1,4-polyisoprene (gutta-percha)

Tacticity

Polymers of monosubstituted olefins [CH$_2$› CHX] contain a series of asymmetric carbon atoms along the chain. For this type of polymers, in a planar zigzag form, three arrangements are possible, namely:
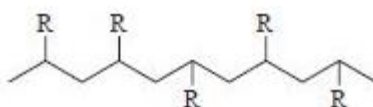
• **Isotactic** - All the substituent groups, R, on the vinyl polymer lie above (or below) the plane of the main chain.

• **Syndiotactic** -Substituent groups lie alternately above and below the plane.

• **Atactic** - Random sequence of position of substituent occurs along the chain.

II. CONFORMATION

In addition to the molecular shape fixed by chemical bonding, variations in the overall shape and size of the polymer chain may occur due to free rotation about primary valence bonds (conformation). A polymer molecule may assume a large or limited number of conformations depending on:

• **Steric factors**

• **Whether the polymer is amorphous or crystalline**

• **Whether the polymer is in a solution state, molten state, or solid state**

Let us consider the possible arrangements of a single isolated polymer chain in dilute solution. We start with a short segment of the chain consisting of four carbon atoms (Figure 1).
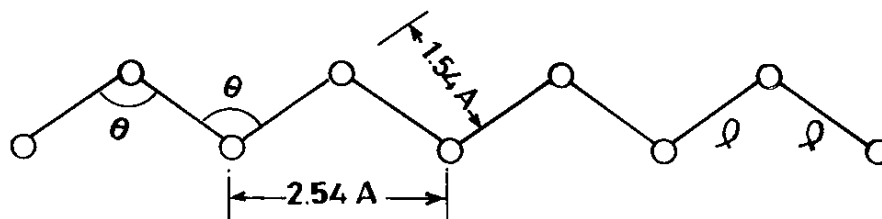
Figure 1. The fully extended all-trans conformation of a carbon–carbon chain.

For a chain consisting of thousands of carbon atoms, it can thus be seen that the number of conformations is literally infinite. One of these conformations of particular interest is that in which each successive carbon atoms lies in the same plane in the trans location with respect to earlier carbon atoms in the chain - thus forming *a fully extended plane of zigzag arrangement of carbon atoms* (Figure 1).

This represents one of the two extreme shapes of a polymer chain, the other being the completely random coil. The planar zigzag conformation exists in some crystalline polymers or in highly oriented amorphous polymers. In case of simple molecules like PE, PVC the small size of the pendant group does not complicate alignment and packing, but the polymers with large and bulky side groups like PP and PS (in general, isotactic and syndiotactic polyolefins), it is impossible (due to steric crowding) to accommodate the pendant groups in the planar zigzag. Consequently, the entire main chain is rotated in the same direction to form either a right or left-handed helix. This occurs exclusively in the crystalline form of stereoregular polymers with bulky side groups (Figure 2).
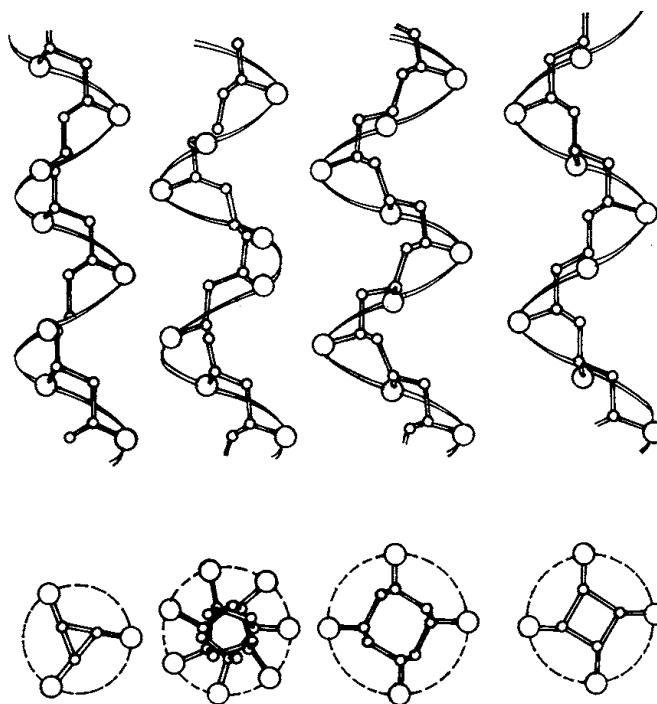

Figure 2. Helical conformations of isotactic vinyl polymers.

Polymers that are in solution, in melt, or amorphous in the solid state may assume random coil conformation. The free rotation about single bonds can give rise to a number of conformations in between zig-zag and random coil. In practice, however, there is no such thing as completely free rotation. All bonds have to overcome certain rotational energy barriers whose magnitude depends on such factors as steric hindrance, dipole forces, etc. (Figure 3). The thermal energy of the molecular environment provides the energy required to overcome the rotational energy barrier. Consequently, the shape (flexibility) of a polymer molecule is temperature dependent. At sufficiently high temperatures, the polymer chain constantly twists, assuming a numerous random coil conformation. The flexibility of polymer molecules, which is a function of substituents on the backbone, has a strong influence on polymer properties.
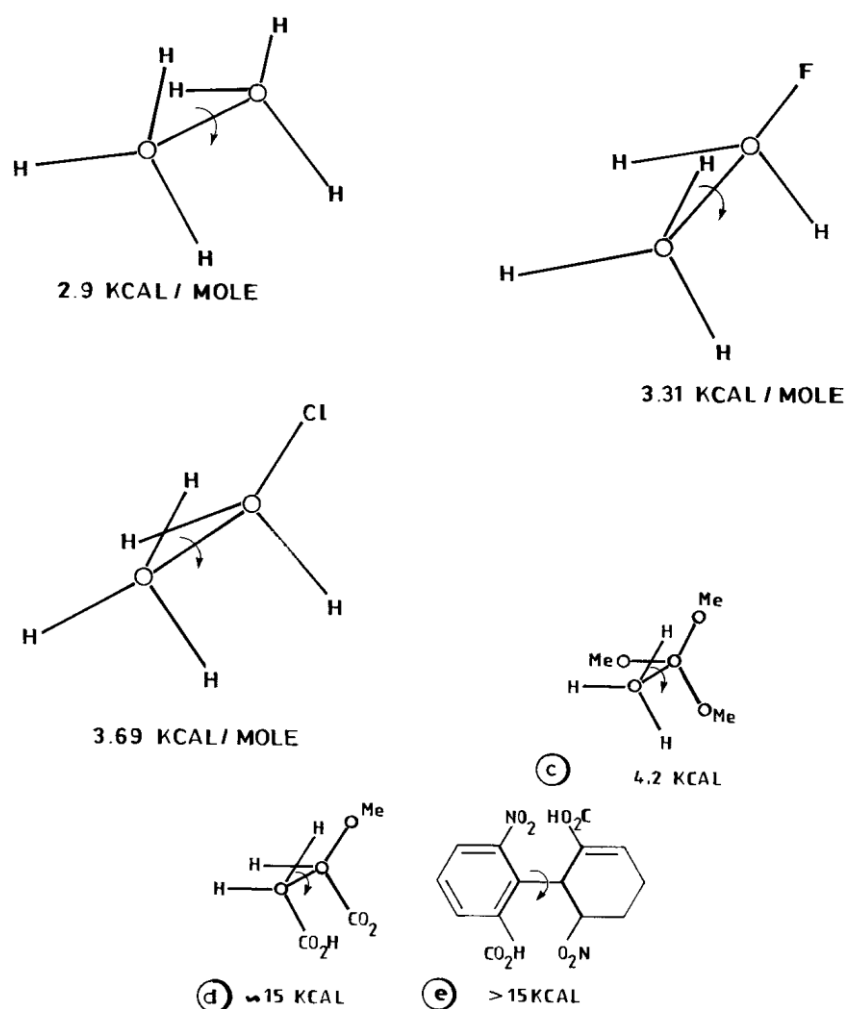

Figure 3 *Rotational energy as a function of substitution and interaction of substituent groups.*

C. MOLECULAR WEIGHT

The terms *giant molecule, macromolecule,* and *high polymer* are used to describe a polymer molecule to emphasize its large size. The unique properties exhibited by polymers and the difference in behaviour between polymers and their low-molecular-weight analogues are due to their large size and flexible nature. Important mechanical properties (tensile and compressive strengths, elongation at break, modulus, impact strength) and other properties (softening point, solution and melt viscosities, solubility) depend on molecular weight in a definite way. At very low molecular weights, almost no polymeric properties are developed. Beyond this MW or DP, there is a steep rise in the performance until a certain level. Beyond that certain level the properties change very little with increase in molecular weight. Finally, an asymptotic value is reached (Figure 4). The curve is general for all polymers. Optical and electrical properties, colour, and density show a less marked dependence on molecular weight.
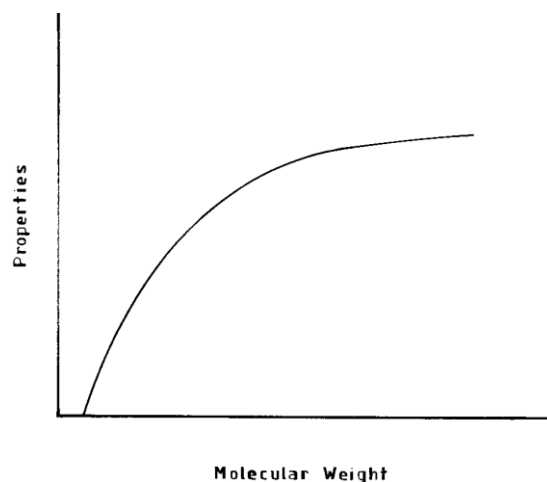

Figure 4. Change of physical properties with molecular weight.

It has already been discussed that irrespective of the polymerization mechanism, the formation of polymer is purely random. Consequently, unlike biological systems, synthetic polymers do not consist of identical molecules, but represent a mixture of many systems each of which has a different molecular weight. In order to characterize polymers, therefore, we use the molecular weight distribution (MWD) curve, which represents a plot of the percentage (frequency) of a particular species against its molecular weight (Figure 5)

As a result of the existence of different sizes of molecular species in a polymeric material, we cannot strictly speak of the molecular weight of a polymer. Instead, we use molecular weight averages to express the size of synthetic polymers. Different average molecular weights exist. The most common ones in use are number-average molecular weight, Mn, and weight-average molecular weight, Mw. Others are the z-average molecular weight, Mz, and viscosity-average molecular weight, Mv.

$$\overline{M}_n - \frac{W}{\sum\limits_{i=1}^{\infty} N_i} = \frac{\sum\limits_{i=1}^{\infty} N_i M_i}{\sum\limits_{i=1}^{\infty} N_i} = \frac{\sum\limits_{i=1}^{\infty} W_i}{\sum\limits_{i=1}^{\infty} W_i/M_i} = \frac{1}{\sum w_i/M_i}$$

Equation 2

$$\overline{M}_w = \sum\limits_{i=1}^{\infty} w_i M_i = \frac{\sum\limits_{i=1}^{\infty} w_i M_i}{W} = \frac{\sum\limits_{i=1}^{\infty} N_i M_i^2}{\sum\limits_{i=1}^{\infty} N_i M_i}$$

Equation 3

Ni = number of molecules having molecular weight Mi

W = total weight

N = total number of molecules

wi = weight fraction of molecules having molecular weight Mi

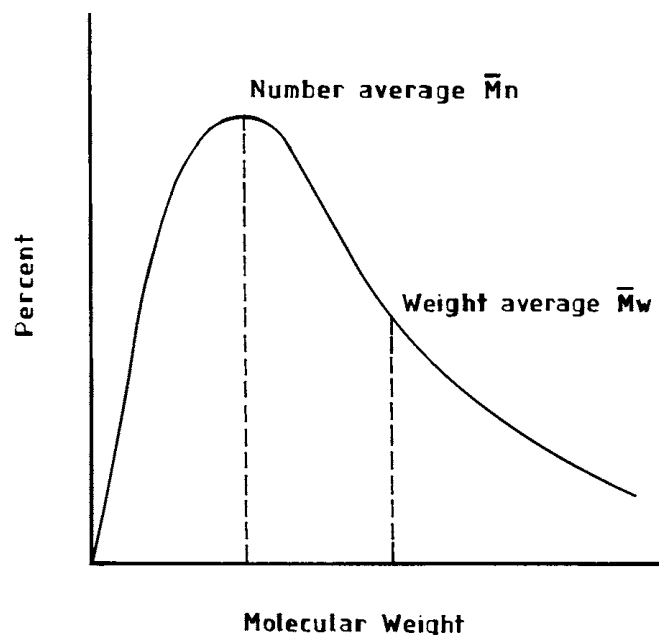Wi = weight of molecule having molecular weight Mi

Figure 5. Molecular weight distribution curve.

The molecular weight of polymers can be determined by a number of physical and chemical methods.

Such as end group analysis, measurement of colligative properties, light scattering, ultracentrifugation, dilute solution viscosity, and gel permeation chromatography. The first four methods permit a direct calculation of molecular weight without the need to resort to calibration by another method; that is, the methods are, in principle, absolute. The last two methods require proper calibration to obtain the value of molecular weight. Colligative properties are determined by the following measurements on dilute polymer solutions such as; Vapour pressure lowering, Boiling point elevation, Freezing point depression and Osmotic pressure.

The number-average weight, M_n, is observed from end-group analysis, colligative property measurements, and gel permeation chromatography.

The weight-average molecular weight, M_w, is determined from light scattering, ultracentrifugation and gel permeation chromatography.

z-average molecular weight, M_z, is determined from GPC, while viscosity-average molecular weight, M_v, can be determined from measurements of polymer solution viscosity.