

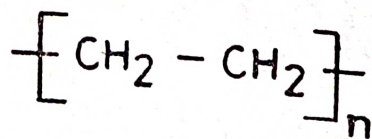
Molecular Weight and Size

3.1 'AVERAGE' MOLECULAR WEIGHT

The molecular weight can vary from a single-digit figure for a simple chemical entity to a number in millions for a complex polymer. For example, the molecular weight of hydrogen is just two, while that of circular DNA in *Escherichia coli* is around 2 billion! One then wonders, if the term molecular weight conveys the same meaning in the two cases. Well, let us examine the matter in detail.

A simple compound has a fixed molecular weight which, for acetone, for instance, is 58 regardless of how it is made. If this 58 becomes 60, the compound is no longer acetone but may be acetic acid. Moreover, in any given sample of acetone, for example, each molecule has the same molecular weight. This is true for all low molecular weight compounds. There is thus some definiteness about the molecular weight of simple chemical compounds. In contrast, a polymer comprises molecules of different molecular weights and, hence, its molecular weight is expressed in terms of an 'average' value. There are many 'averages' as we will presently see.

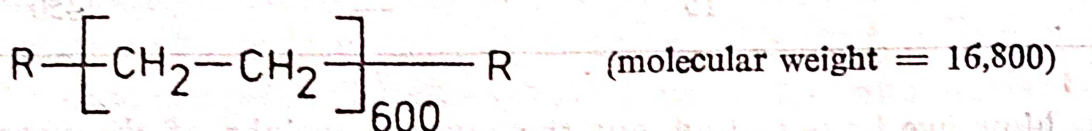
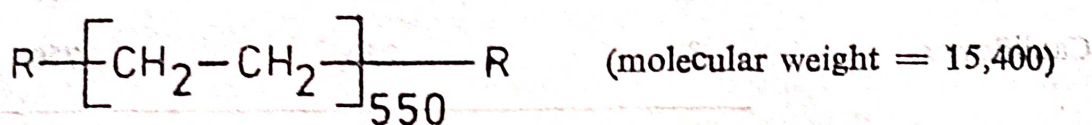
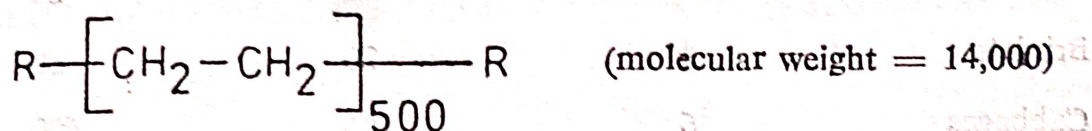
Ethylene gas, for instance, is a low molecular weight, simple chemical compound; each of its molecules has the same chemical structure (viz., $\text{CH}_2=\text{CH}_2$) and hence, a fixed molecular weight of 28. But we polymerise ethylene to make polyethylene and we encounter an indefinite chemical structure of



wherein n can change its value from one polyethylene molecule to another present in the same polymer sample. This is so because

when ethylene is polymerised to form polyethylene, a number of polymer chains start growing at any instant, but all of them do not get terminated after growing to the same size. The chain termination is a random process and, hence, each polymer molecule formed can have a different number of monomer units and thus different molecular weights.

The following three structures, for example represent polyethylene molecules, but each has a different molecular weight:



We can see that the three molecules have different sizes, their molecular weights are different, but yet, they are all very much 'polyethylenes'. A polymer sample can, therefore, be thought of as a mixture of molecules of the same chemical type, but of different molecular weights. In this situation, the molecular weight of the polymer sample can only be viewed statistically and expressed as some average of the molecular weights contributed by the individual molecules that make the sample. By contrast, the molecular weight of a simple compound such as ethylene or acetone is constant.

3.2 NUMBER-AVERAGE AND WEIGHT-AVERAGE MOLECULAR WEIGHTS

We have to now consider ways and means of averaging out the molecular weight of the polymer. The two most common and experimentally verifiable methods of averaging are called 'number'-average and 'weight'-average methods. The following sections will clarify the concept.

3.2.1 Number-average Concept

Consider a basket containing four vegetables: onions, brinjals, cabbages and cauliflowers. Just for ease of understanding, let each

onion of the onion lot weigh the same and so also each of the other vegetables. Assume that the number of each vegetable and its weight are as tabulated.

Vegetable entity	Number of units in each entity, n	Weight of each unit, $M(g)$	Total weight of each entity $W = nM(g)$
Onions	2	10	20
Brinjals	4	20	80
Cabbages	6	100	600
Cauliflowers	3	250	750
	15	—	1450

Now, we have to find out the average weight of the vegetables present in the basket. To work this out, one might assume that the individual vegetable entity contributes to the average weight in the proportion of its numbers. What we then get is the number-average weight, arrived at as follows:

total number of vegetables contained in the basket = 15

number of onions present in the basket = 2

Therefore,

number fraction of onions

$$\text{(to the total number of vegetables)} = 2/15$$

Similarly,

$$\text{number fraction of brinjals} = 4/15$$

$$\text{number fraction of cabbages} = 6/15$$

$$\text{number fraction of cauliflowers} = 3/15$$

Contribution made by 2 onions towards average weight of vegetables in the basket:

$$\begin{aligned} \text{number fraction of onions} \times \text{weight of each onion} &= (2/15) \times 10 \\ &= 1.33 \text{ g} \end{aligned}$$

Similarly,

$$\begin{aligned} \text{contribution made by 4 brinjals to the average weight of vegetables} \\ \text{in the basket} &= (4/15) \times 20 \\ &= 5.33 \text{ g} \end{aligned}$$

Similarly,

contribution made by 6 cabbages to the average weight of vegetables in the basket $= (6/15) \times 100 = 40.00$ g

Similarly,

contribution made by 3 cauliflowers to the average weight of vegetables in the basket $= (3/15) \times 250 = 50.00$ g

Summing up the contributions made by each vegetable variety, we get the 'number-average' weight of the total vegetables as

$$1.33 + 5.33 + 40 + 50 = 96.66 \text{ g}$$

3.2.2 Weight-average Concept

The other method of calculating the average weight is based on the assumption that the individual vegetable variety contributes to the total weight in the proportion not of its number but its weight. What we then get is the 'weight-average', arrived at as follows:

total weight of all vegetables in the basket $= 1450$ g

weight of onions present in the basket $= 20$ g

Therefore,

weight fraction of onions $= 20/1450$

Similarly, weight fractions of brinjals, cabbages and cauliflowers are $80/1450$, $600/1450$, and $750/1450$, respectively.

Next, contribution made by onions towards average weight of vegetables in the basket $=$ weight fraction of onions \times average weight of onions $= (20/1450) \times 100 = 0.14$ g

Similarly,

corresponding contribution by brinjals $= (80/1450) \times 20 = 1.10$ g

corresponding contribution by cabbages $= (600/1450) \times 100$

$$= 41.38 \text{ g}$$

corresponding contribution by cauliflowers $= (750/1450) \times 250$

$$= 129.31 \text{ g}$$

Summing up the contributions made by each vegetable variety, we get the weight-average weight of the total vegetables as

$$0.14 + 1.10 + 41.38 + 129.31 = 171.93 \text{ g}$$

3.2.3 Generalisation of the Foregoing Concepts

In computing the molecular weight of a polymer we can also use either the number fraction or the weight fraction of the molecules present in the polymer to get either the number-average molecular weight (designated as \bar{M}_n) or the weight-average molecular weight (designated as \bar{M}_w), respectively.

The method of working out \bar{M}_n and \bar{M}_w can now be easily generalised, using *simple* mathematics. Assume that there are n number of molecules in a polymer sample and n_1 of them have M_1 molecular weight; n_2 have M_2 molecular weight and so on till we get n_i having M_i molecular weight (see Fig. 3.1).

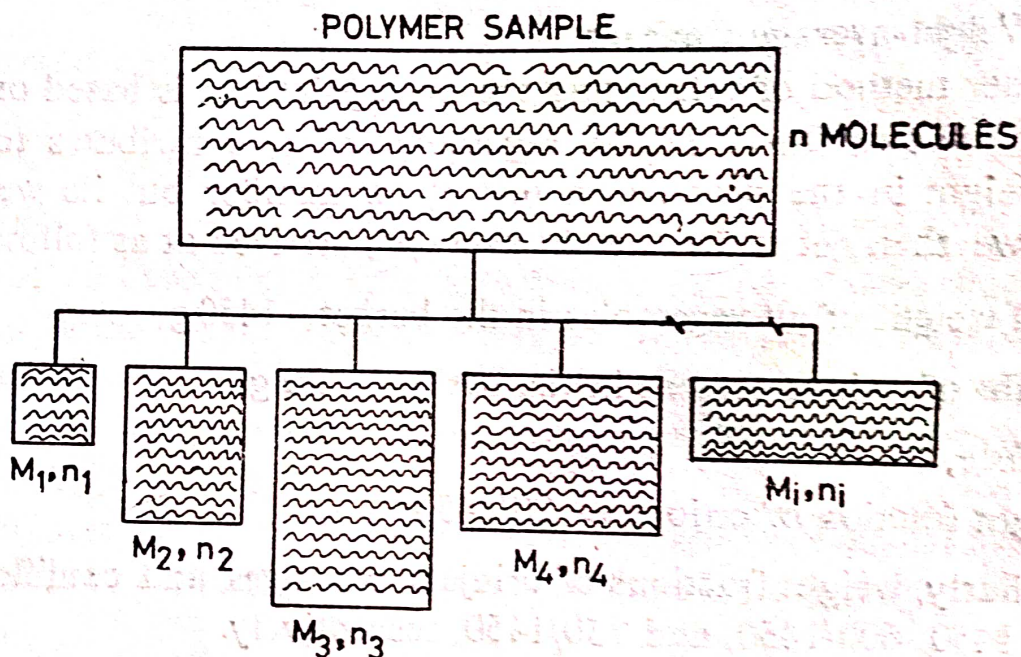


Fig. 3.1. Conceptual representation of a polymer sample containing n number of molecules of different molecular weights, of which n_1 have a molecular weight of M_1 , n_2 have M_2 and so on.

Now, we have a total number of molecules (n) given by

$$n = n_1 + n_2 + n_3 + \dots + n_i = \sum n_i$$

Number of molecules in fraction 1 = n_1 .

Number fraction of fraction 1 = $\frac{n_1}{n} = \frac{n_1}{\sum n_i}$.

Molecular weight contribution by fraction 1 = $\frac{n_1 M_1}{\sum n_i}$.

Similarly, molecular weight contribution by other fractions will be as follows:

$$\frac{n_2 M_2}{\Sigma n_i}, \frac{n_3 M_3}{\Sigma n_i}, \dots, \frac{n_i M_i}{\Sigma n_i}$$

Number-average molecular weight of the whole polymer will then be given by

$$\frac{n_1 M_1}{\Sigma n_i} + \frac{n_2 M_2}{\Sigma n_i} + \dots + \frac{n_i M_i}{\Sigma n_i} = \frac{\Sigma n_i M_i}{\Sigma n_i} = \bar{M}_n \quad (3.1)$$

Similarly, total weight of the polymer = $W = \Sigma n_i M_i$.

Weight of fraction 1 = $W_1 = n_1 M_1$.

Weight fraction of fraction 1 = $\frac{n_1 M_1}{W} = \frac{n_1 M_1}{\Sigma n_i M_i}$.

Molecular weight contribution by fraction 1 is given by

$$\frac{n_1 M_1 M_1}{\Sigma n_i M_i} = \frac{n_1 M_1^2}{\Sigma n_i M_i}$$

Similarly, the molecular weight contribution by the other fractions will be

$$\frac{n_2 M_2^2}{\Sigma n_i M_i}, \frac{n_3 M_3^2}{\Sigma n_i M_i}, \dots, \frac{n_i M_i^2}{\Sigma n_i M_i}$$

The weight-average molecular weight of the whole polymer will then be

$$\frac{n_1 M_1^2}{\Sigma n_i M_i} + \frac{n_2 M_2^2}{\Sigma n_i M_i} + \dots + \frac{n_i M_i^2}{\Sigma n_i M_i} = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i} = \bar{M}_w \quad (3.2)$$

For all synthetic polymers, \bar{M}_w is greater than \bar{M}_n . If they were to be equal, the polymer sample may be considered as perfectly homogeneous (i.e., each molecule has the same molecular weight); but this does not happen.

3.3 SEDIMENTATION AND VISCOSITY-AVERAGE MOLECULAR WEIGHTS

Apart from \bar{M}_n and \bar{M}_w , there are two other ways of expressing the molecular weight based on the sedimentation and flow behaviour of the polymer in solution. They are: z-average molecular weight (\bar{M}_z) and viscosity-average molecular weight (\bar{M}_v), expressed as

$$\bar{M}_z = \frac{\Sigma n_i M_i^3}{\Sigma n_i M_i^2} \quad (3.3)$$

and

$$\bar{M}_v = \left(\frac{\Sigma n_i M_i^{1+a}}{\Sigma n_i M_i} \right)^{1/a} \quad (3.4)$$

In these two equations n_i is, as before, the number of molecules having the molecular weight of M_i present in the sample and a is a variable (its value ranging from 0.5 to 1) in the Mark-Houwink equation which relates intrinsic viscosity $[\eta]$ with the viscosity average molecular weight (\bar{M}_v). (see Section 12.6.)

We will deal with experimental techniques used for determining molecular weights in Chapter 13. It will suffice here to know that light scattering, osmotic pressure, viscosity and ultracentrifugation methods are used to get \bar{M}_w , \bar{M}_n , \bar{M}_v and \bar{M}_z , respectively.

3.4 MOLECULAR WEIGHT AND DEGREE OF POLYMERISATION

We have briefly remarked in Section 1.3 that the size of a polymer molecule depends on the number of repeat units it contains and that this number represents the "degree of polymerisation". For instance, if there are 1000 repeat units in a polymer molecule, the degree of polymerisation (DP) is 1000. DP provides another way of expressing the molecular weight as follows:

$$M = D_p \cdot m \quad (3.5)$$

where M is the molecular weight of the polymer, D_p its degree of polymerisation and m the molecular weight of the monomer or the repeat unit.

Both DP and molecular weight are related to the molecular size. Hence, like the molecular weight, DP can also be averaged over the size of the sample. The "number-average" and "weight-average" degree of polymerisation can then be defined in a manner similar to that in which \bar{M}_n , \bar{M}_w , are defined earlier, viz.,

$$(\bar{D}_p)_n = \frac{\sum n_i (D_p)_i}{\sum n_i} \quad (3.6)$$

and

$$(\bar{D}_p)_w = \frac{\sum n_i (D_p)_i^2}{\sum n_i (D_p)_i} \quad (3.7)$$

Each of these averages can be related to the corresponding molecular weight averages by the following two equations:

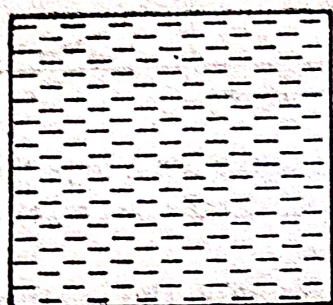
$$\bar{M}_n = (\bar{D}_p)_n \cdot m \quad (3.8)$$

$$\bar{M}_w = (\bar{D}_p)_w \cdot m \quad (3.9)$$

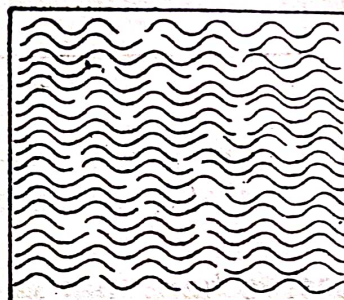
3.5 POLYDISPERSITY AND MOLECULAR WEIGHT DISTRIBUTION IN POLYMERS

It may be recalled that a simple chemical compound contains molecules, each of which has the same molecular weight (a 'monodispersed' system), whereas a polymer contains molecules, each of which can have different molecular weights (a 'polydispersed' system). Monodispersity and polydispersity can be represented as shown in Fig. 3.2.

Monodispersed system



Polydispersed system



All molecules are of same size (simple chemical compounds like H_2O , alcohol are monodispersed systems)

Molecules are of different sizes (polymers are polydispersed systems)

Fig. 3.2 Conceptual representation of monodispersed and polydispersed systems (dispersity is with respect to molecular weight).

While the polydisperse nature of the polymer is the basis of the concept of 'average' molecular weight, this 'average' by itself conveys nothing on the dispersity pattern in a given polymer sample. Take a polymer sample of, say, 40,000 average molecular weight. Now, this may mean that the molecules have molecular weights ranging from 20,000 to 80,000 or from 500 to 100,000—the figure is uncertain. This is the reason why two polymer samples of the same 40,000 \bar{M}_n can display similar properties in some respects but not in some others. To know a polymer properly, we must have a knowledge of both the average molecular weight as well as its dispersion pattern. This dispersity with respect to the lowest to the highest molecular weight homologues is expressed by a simple molecular weight distribution curve. Such a curve for a polymer sample is computed by plotting the number fraction (n_i) of molecules having a particular molecular weight (M_i) against the corresponding molecular weight (Fig. 3.3). While the details of computing a molecular weight distribution curve are given in Chapter 13,

Table 3.1 \bar{M}_w/\bar{M}_n values for synthetic polymers obtained by different polymerisation techniques

Polymerisation type	\bar{M}_w/\bar{M}_n
Free-radical chain polymerisation:	
(i) with precise temperature control (solution, suspension and emulsion systems):	1.5-2
(ii) with moderate temperature control (bulk system):	2-5
(iii) without temperature control (with autoacceleration):	8-10
Cationic/anionic chain polymerisation:	
(i) using homogeneous catalyst system:	< 1.5
(ii) using heterogeneous catalyst system:	> 10
Polycondensation, polyaddition and ring-opening polymerisation	2-3
Coordination polymerisation	> 10
Polymerisation systems leading to chain-branching	> 20

3.6 THE PRACTICAL SIGNIFICANCE OF POLYMER MOLECULAR WEIGHT

One might ask as to what is the practical use of the knowledge of molecular weights. Let us look at this aspect.

Many commercially useful polymers are selected on the basis of their properties such as melt viscosity, impact strength or tensile strength. These properties are directly dependent on the molecular weight of the polymer or its degree of polymerisation. For example, tensile and impact strengths increase with molecular weight. The increase is up to a point and then it levels off (Fig. 3.6). The melt

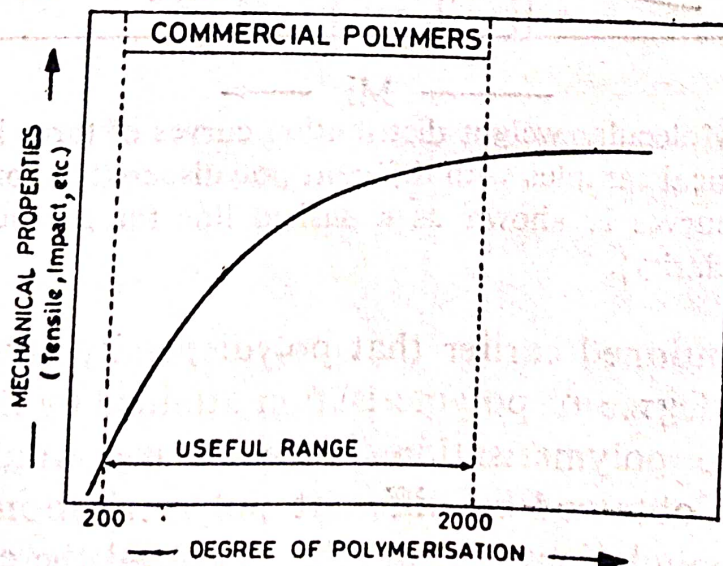


Fig. 3.6. Trend showing dependence of tensile or impact strength of a polymer on degree of polymerisation.

viscosity of the polymer, however, shows a different trend. At very high molecular weights, the melt viscosity rises more steeply than at low molecular weights (Fig. 3.7). A commercially useful polymer should have a low melt viscosity to permit ease of processing, but, at the same time, should exhibit good strength. The patterns shown in Figs. 3.6 and 3.7 help to select the useful range of molecular weights for polymers.

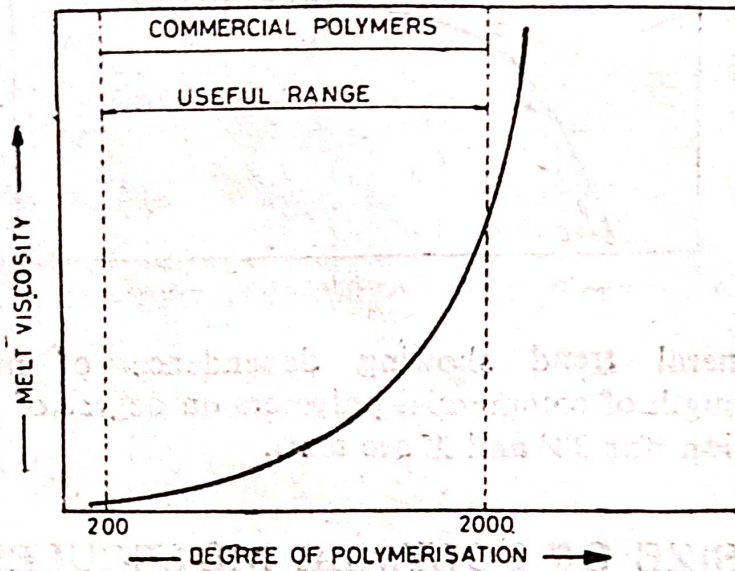


Fig. 3.7. Trend showing the dependence of melt viscosity of a polymer on degree of polymerisation.

To bring into sharper focus the effect of molecular weight on physical properties, a more generalised form of representation is shown in Fig. 3.8. Here, mechanical strength is plotted against DP. Qualitatively, the nature of the curve is valid for all polymers, differing from one polymer to another only with respect to the numerical value. Every polymer has a threshold value (TV) for its DP below which the polymer does not possess any strength and exists as friable powder or as liquid resin. The threshold DP value varies from one polymer to another. For instance, cellulose has a threshold DP value of 60, and a good number of vinyl polymers are found to have a value of around 100. Similarly, the knee portion of the curve (indicated as X in Fig. 3.8), at which DP value, the polymer attains more or less full strength, also varies from one polymer to another. For instance, this value is 400 for vinyl type polymers, 250 for cellulose and roughly 150 for polyamides. Based on a wide range of data collected, it has been established that polymers do not exhibit strength for DP values of lower than 30 and that the optimum strength of most of the polymers is obtained at a DP value of around 600. The useful range of DP is from 200 to

2,000 which corresponds to molecular weights of roughly 20,000 to 200,000.

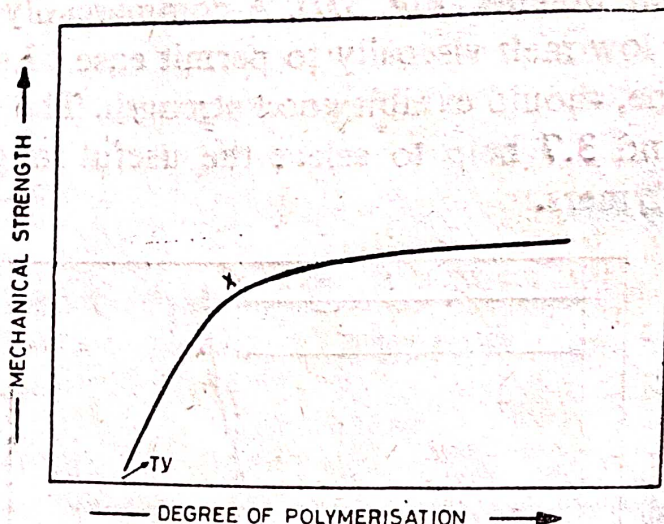


Fig. 3.8. General trend showing dependence of mechanical strength of commercial polymers on degree of polymerisation (for *TV* and *X* see text).

3.7 SIZE OF POLYMER MOLECULES

3.7.1 Freely Jointed Chain Model

For the sake of simplicity, let us imagine that a polymer molecule is made up of n segments, each having a length of l joined together freely end to end. Also, let us assume the joints at each segment are such that (say, as in the case of the ball-and-socket joint) the segments can freely rotate at these joints and that there is no restriction on the angle formed between any two segments. This simplified version of an imaginary polymer chain is called a 'freely jointed chain'. Figure 3.9(A) shows a simple representation of a freely jointed chain.

Now, how are we to express the size of this chain? One way of expressing it would be by its total length which is equal to $n \times l$. This length is known as the 'contour length'. Another way of expressing the size of the chain would be by the distance between the two chain ends. Let us call this distance as chain end-to-end distance, and denote it by r . But how do we comprehend this distance r ? Let us first assume that in a particular model of a freely jointed chain, the joints are not of the ball-and-socket type but of the hinge type. The result would be that the segment cannot undergo free rotation at each joint but can only have free movement in one plane without any restriction on the angle formed between them. All the

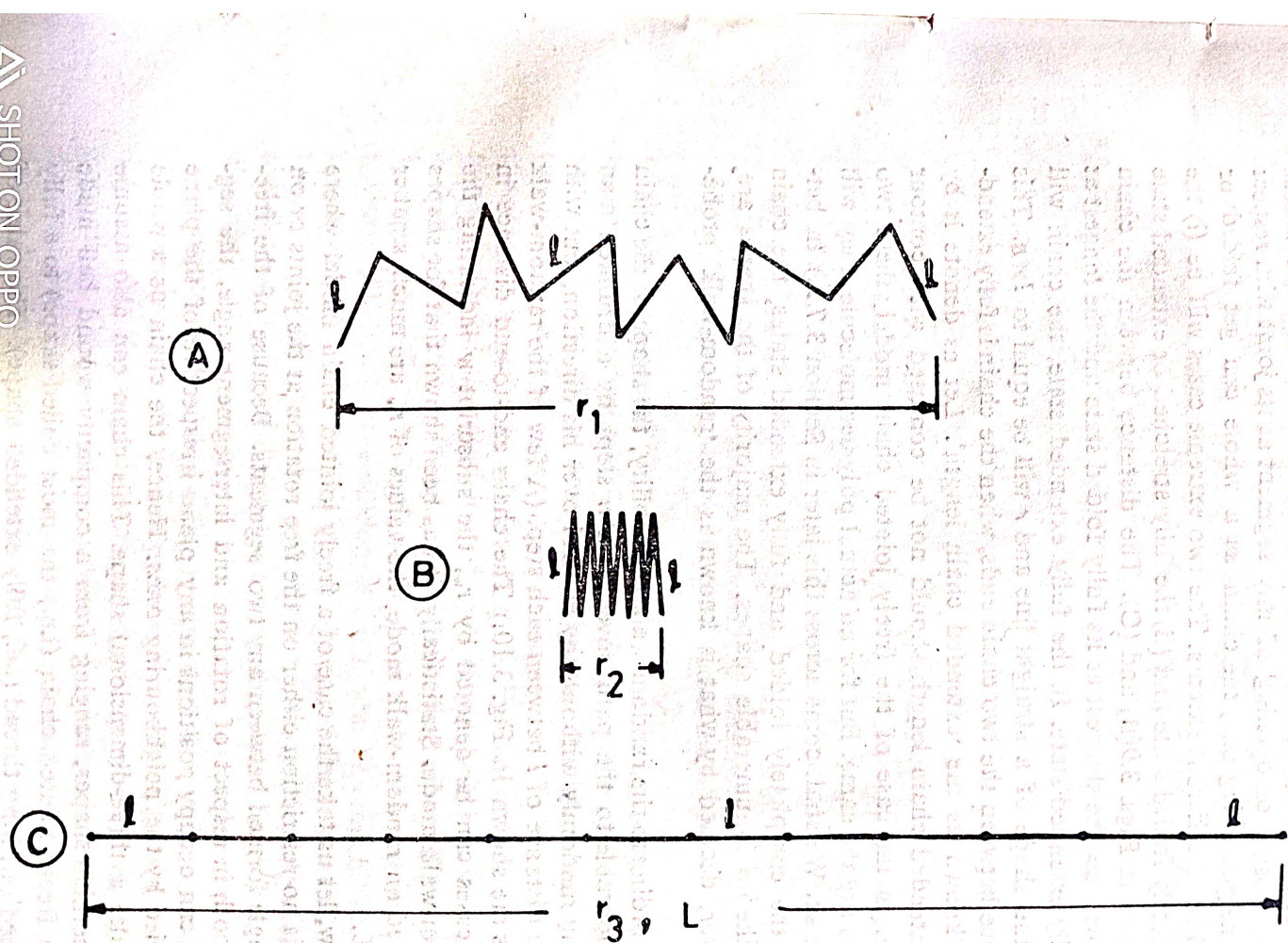


Fig. 3.9. Illustration of a freely jointed chain model: (A) simple representation, (B) completely folded form, and (C) fully extended form (l =length of each segment, L =extended chain length, r_1 , r_2 and r_3 are chain end-to-end distances and $r_3=L$).

segments of this chain will, therefore, be on the same plane and the shape of the whole chain will be coplanar. Because of the unrestricted closing or opening of any segment at its joint with respect to its neighbouring one, the chain as a whole can get folded or stretched to different extents. The two extreme cases will be (i) the completely folded state and (ii) the fully stretched or extended state as shown in Figs. 3.9(B) and (C). The distance between the chain ends will be the shortest at its fully folded state and the longest at its fully extended state. In the fully extended state, the chain will take the shape of a straight line and r will be equal to $l \times n$. This distance between the two chain ends, when the chain is fully extended, is known as the 'extended chain length'. Let us denote it by L . (Extended chain length should not be confused with contour length. In the case of the freely jointed chain model, these two lengths are the same. But for an actual polymer molecule, they will not be so. We shall come across this later in Section 3.7.2.) In between the completely folded and fully extended states, the chain can take up innumerable shapes. The majority of the shapes are, however, decided by what is known as the 'random-walk' probability.

According to the random-walk probability, the shape of the chain is comparable to the path covered in n steps by a drunken man walking randomly without any control over his direction, but with a fixed distance of l between each step. (A few of the random-walk shapes are shown in Fig. 3.10.) The chain end-to-end distance in these cases can be denoted by r_w , the subscript w indicating the random-walk mode. Statistically, it has been shown that for shapes assumed on random-walk mode, the values of r_w are much smaller than L .

Now, let us take the case of a freely jointed chain model where there is no restriction either on the free rotation at the joints or on the angle formed between any two segments. Because of the freedom both in respect of rotation and intersegment angle, the segments can occupy positions in any plane irrespective of the plane occupied by the neighbouring ones. Hence, the chain as a whole can take a three-dimensional shape. This chain can also assume innumerable shapes, ranging from a compactly wound ball made of the freely jointed chain (i.e., the most coiled shape) to a fully stretched out long thread (i.e., fully extended shape). The value of r in the fully stretched mode will again be equal to L . The majority

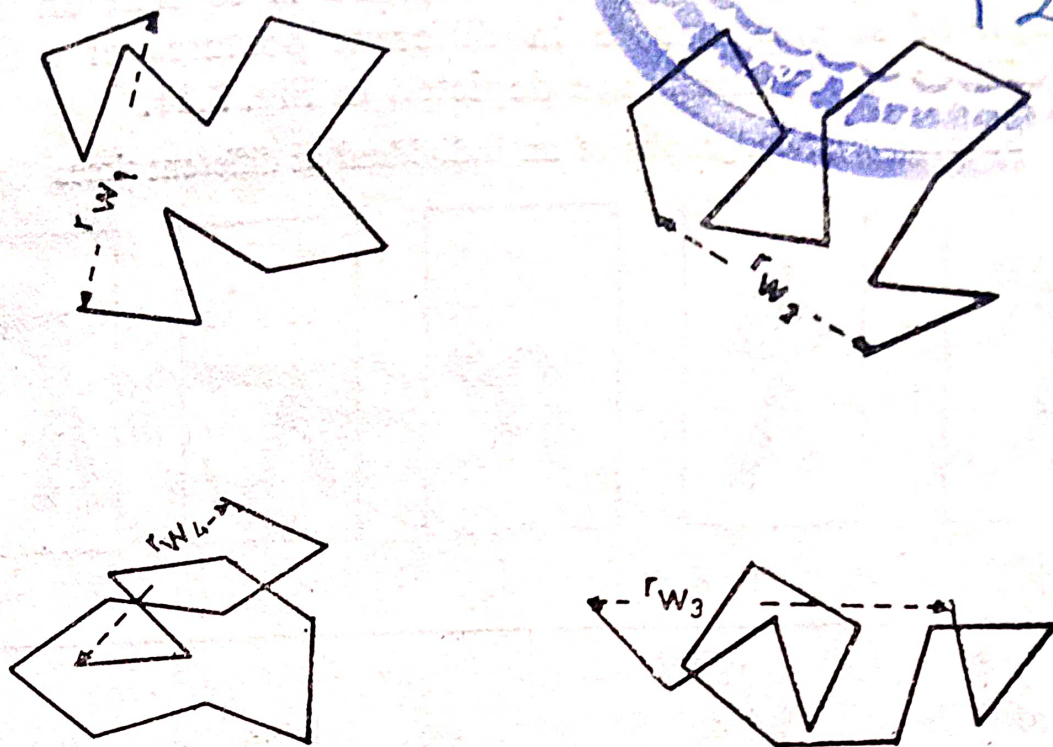


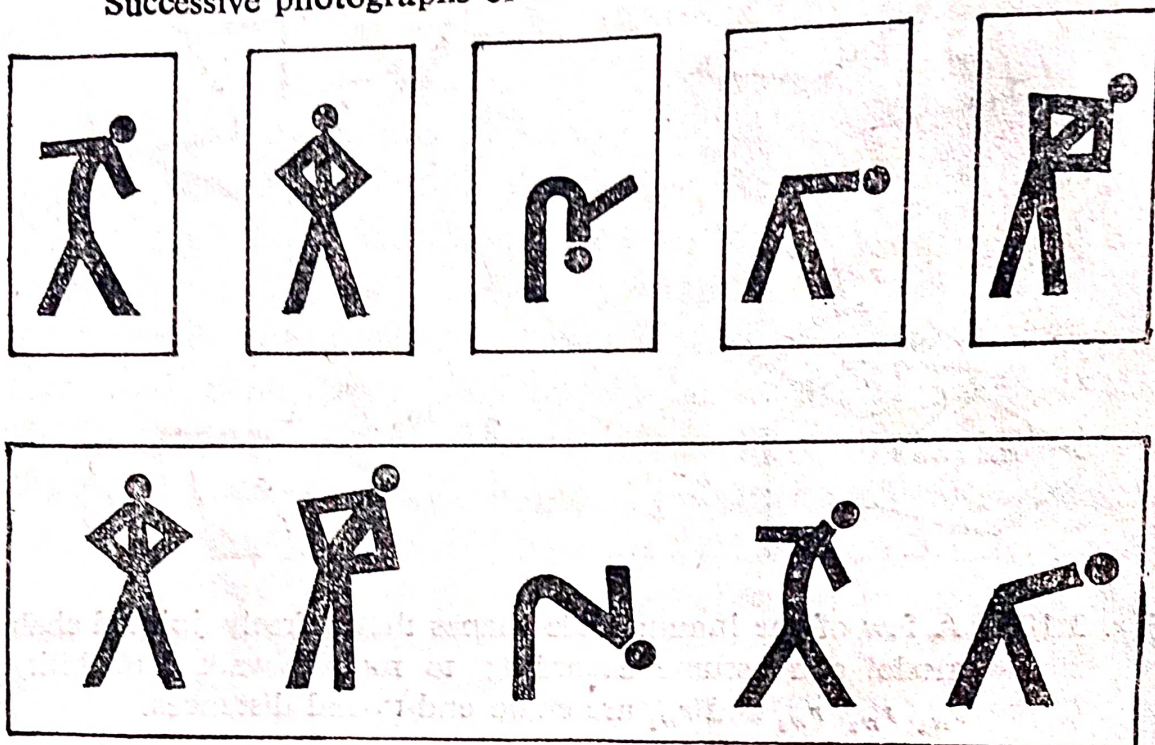
Fig. 3.10. A few of the innumerable shapes that a freely jointed chain model can assume according to random-walk probability. r_{w1} , r_{w2} , r_{w3} and r_{w4} are chain end-to-end distances.

of the shapes assumed by such a chain is given by what is known as 'random-flight' probability. According to this probability, the shape of the chain is comparable to the path traced in space by a free particle undergoing n number of successive displacements with the conditions that the distance of each displacement is the same (equal to l) and the direction of each displacement is at random and is independent of that of all the preceding ones. The distance between the chain ends for these shapes can be denoted by r_f , the subscript f indicating the random-flight mode. The magnitude of r_f is much smaller than L . The overall shapes of the chain attained in the random-flight mode are loosely wound spheres or ellipsoids and the distance r_f is usually used to indicate the end-to-end chain distance.

Let us now assume that a freely jointed chain changes its shape continuously. How do we comprehend its shape over a period of time? At this stage, we draw an analogy with men exercising in a gymnasium. Our objective is to study the various postures of an exercise. But this is difficult, as the movements are fast and rhythmic. As all the men are performing the same exercise, to identify the various poses, we have two options. One is that we take a series of photographs of one man, till he completes the cycle and comes

back to the original pose. Another method is to take an instant photograph of several people in different postures of the same exercise. The two situations are depicted in Fig. 3.11.

Successive photographs of an individual at different times



Instant photograph of several individuals

Fig. 3.11. The two ways of arriving at the various postures adopted by an individual doing an exercise.

We have made the above mentioned analogy because of the similarity of situations when it comes to describing the shapes assumed by polymer chains at different instants of time. If we could take an instant photograph of several freely jointed chains, we get an idea of the various coiling patterns assumed by these chains. This imaginary photograph could reveal, say, n_1 chains with end-to-end distance r_{f1} , n_2 chains with end-to-end distance r_{f2} , and so on. We can then write an equation for an average end-to-end distance as

$$\bar{r}_f = \frac{n_1 r_{f1} + n_2 r_{f2} + \dots + n_i r_{fi}}{n_1 + n_2 + \dots + n_i} \quad (3.10)$$

To get a better representation of the average, however, a term $\langle \bar{r}_f^2 \rangle^{1/2}$, called the root-mean-square end-to-end distance, is used as given by the following expression:

$$\langle \bar{r}_f^2 \rangle^{1/2} = \left[\frac{n_1 r_{f1}^2 + n_2 r_{f2}^2 + \dots + n_i r_{fi}^2}{n_1 + n_2 + \dots + n_i} \right]^{1/2}$$

$$\langle \bar{r}_f^2 \rangle^{1/2} = \left[\frac{\sum n_i r_{fi}^2}{\sum n_i} \right]^{1/2} \quad (3.11)$$

According to the random-flight calculations, the root-mean-square end-to-end distance is related to the chain segments by the equation

$$\langle \bar{r}_f^2 \rangle^{1/2} = l(n)^{1/2} \quad (3.12)$$

where n is the number of segments in the polymer chain and l is the segment length.

3.7.2 Actual Polymer Molecules

Actual polymer molecules are often made of many segments linked together in a linear fashion. The difference between the freely jointed chain model and the actual polymer chains is that, in the latter case, the bond angles between the adjacent links are fixed and individual segments do not rotate that freely, owing to steric and other factors.

Assume a linear polymer molecule made of n number of segments of length l each and that the segments are made up completely of the C—C bonds. The fully extended form of such a chain is represented in Fig. 3.12. The segment length, l , for such a —C—C— chain is 1.54 Å and the bond angle is $109^\circ 28'$. Assuming a value of

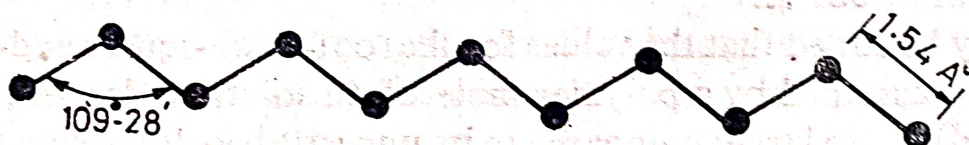


Fig. 3.12 Fully extended form of a polymer chain made of C—C backbone comprising ten C—C bonds.

500 for n , we can show by calculation that the fully extended length of the chain is 629 Å and the contour length (i.e., actual length of the chain following all the zigzags) is $1.54 \times 500 = 770$ Å.

A real polymer molecule can, and, in fact, does, assume different shapes over a period of time, governed again by the random-flight probability. Since the bond angle of the actual polymer molecule is fixed and there is hindrance to free rotation, the end-to-end distance of the polymer molecule will always be higher than that obtained for the random-flight model of the freely jointed chain of the same contour length. The dimension of a polymer molecule and that of the freely jointed chain (both containing the same number of segments of equal segment lengths) are related by the equation

$$\langle \bar{r}_0^2 \rangle^{1/2} = N \langle \bar{r}_f^2 \rangle^{1/2} \quad (3.13)$$

where $\langle \bar{r}_0^2 \rangle^{1/2}$ is the root-mean-square end-to-end distance of the polymer molecule and N is a number whose value is always more

than unity. The value of N for polyethylene, for instance, is 2.6. Here, $\langle \bar{r}_0^2 \rangle^{1/2}$ is called the unperturbed dimension of the polymer molecule. The word 'unperturbed' is used to denote the fact that apart from the fixed bond angle and hindrance to rotation, there are no other attractive or repulsive forces acting upon the segments of the chain that can alter its shape.

Polymer molecules keep on changing their shape continuously and, as a consequence, the end-to-end distance of the molecule also keeps on varying. The change in shape can be from the fully extended form at one end of the spectrum to a compactly coiled up form at the other. The fully extended form will have the highest value for $(\bar{r}_0^2)^{1/2}$, whereas the compactly coiled up form will have the least. According to the random-flight probability, neither the fully extended form nor the compactly coiled up form is the favoured shape, but randomly coiled forms are more common. Calculations have shown that the value of $(\bar{r}_0^2)^{1/2}$ for a polymer chain is quite small as compared to its extended length. The value for a chain of 500 —C—C— segments would be as low as 45 Å against its extended length of 629 Å.

It may be added that the values for the root-mean-square end-to-end distances assumed by a polymer molecule in solution, denoted by the term $(\bar{r}_f^2)^{1/2}$, are larger compared to its unperturbed dimension $(\bar{r}_0^2)^{1/2}$. This is due to the effect of solvent molecules exerting certain attractive or repulsive forces upon the segments of the polymer chain (i.e., solvent-solute interaction), the details of which are given in Chapter 12 (Section 12.5).

Books for Further Reading

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- Petites, L.H., *Molecular Weight Distribution in Polymers*, Wiley-Interscience, New York, 1971.