Molecular Weight and Size of Macromolecules

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Simple chemical compounds are materials composed of molecules, all of which have the same chemical formula and the same configuration. In macromolecular science, this definition may apply only to some materials of biological origin. On the other hand, synthetic macromolecular materials are made up of a large variety of species differing mainly in the number of monomer units, nature of end groups, extent of branching etc. A typical polymer sample may contain thousands of macromolecules, each made up by linking hundreds of monomer units. Even if a single type monomer unit, say ethylene, is present, the sample is not molecularly homogeneous, as all the polyethylene chains are not of equal length, i.e., they possess a distribution of molecular weights. Hence molecular weights of polymers are described by their average values. The type of average one gets depends on the method of measurement and for a polydisperse polymer sample different methods yield different averages. In this article, different types of averages are discussed using very simple examples, and this concept has been further extended to describe the molecular weights of high polymers.

A Case of Mangoes and Oranges...

Consider a basket containing four different types of fruits: plums, oranges, mangoes and watermelon. Just for ease of

Table 1.

Fruit entity	Number of units in each entity n	Weight of each unit M(g)	Total weight of each entity W = nM(g)
Plums	5	10	50
Oranges	3	50	150
Mangoes	2	100	200
Watermelon	1	1000	1000
	$\Sigma n = 11$		$\Sigma nM = 1400$

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understanding, let each plum weigh the same and so also each of the other fruits. The number of each fruit and its weight may be described as in the *table 1*.

In order to find out the average weight of the fruits present in the basket one may assume that the individual fruit 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.

The total number of fruits contained in the basket is 11 and the number of plums present in the basket is 5, therefore, the number-fraction of plums is 5/11. Similarly, number-fractions of oranges, mangoes and watermelon are 3/11, 2/11 and 1/11, respectively.

Contribution made by 5 plums towards average weight of fruits in the basket = number–fraction of plums × weight of each plum = $(5/11) \times 10 = 4.54$g

Corresponding contributions made by 3 oranges, 2 mangoes and 1 watermelon to the average weight of fruits in the basket will be $(3/11) \times 50$, $(2/11) \times 100$ and $(1/11) \times 1000$ i.e., 13.64, 18.18 and 90.91, respectively. Summing up the contributions made by each fruit variety gives the number-average weight of the total fruits as

$$4.54 + 13.64 + 18.18 + 90.91 = 127.27\text{g} \qquad (1)$$

The other method of calculating the average weight is based on the assumption that the individual fruit 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:

The total weight of all fruits in the basket is 1400g and the weight of plums present in the basket is 50 g, therefore, weight-fraction of plums will be 50/1400. The weight-fractions of oranges, mangoes and watermelon then are 150/1400, 200/1400, and 1000/1400, respectively.

The contribution made by plums towards average weight of fruits in the basket = weight-fraction of plums × average weight of plums = (50/1400) × 10 = 0.36g.

Similarly, corresponding contributions by oranges, mangoes and watermelon will be (150/1400) × 50, (200/1400) × 100, (1000/1400) × 1000 i.e. 5.36, 14.29, 741.9, respectively.

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

$$0.36 + 5.36 + 14.29 + 741.9 = 734.30\text{g} \qquad (2)$$

The weight-average weight is highly dependent on the heavier species in contrast to the number-average weight, which is more sensitive to the number of lighter species. If all the species are of the same size in the sample , the two averages yield the same value; but if the species are of different sizes, comparing (1) and (2), we see that the weight-average yields a larger value.

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Generalization of the Averaging Concepts

In computing the molecular weight of a polymer, we can similarly use either the number-fraction or the weight-fraction of the molecules present in the polymer to get either the number-average molecular weight ($\overline{M}_n$) or the weight-average molecular weight ($\overline{M}_w$), respectively. Suppose that there are n molecules in a polymer sample and n_1 of them have will molecular weight M_1; n_2 have molecular weight M_2 and so on till we get n_i having molecular weight M_i.

We have a total number of molecules $n = n_1 + n_2 + n_3 + \ldots + n_i$.
Number of molecules in fraction 1 = n_1.
Number-fraction of fraction 1 = $n_1/n = n_1/\Sigma n_i$.
Molecular weight contribution by fraction 1= $(n_1 M_1 / \Sigma n_i)$.

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

Measurements based on colligative properties become less accurate when dealing with high molecular weight polymers.

$$\frac{n_2M_2}{\Sigma n_i}, \frac{n_3M_3}{\Sigma n_i}, \ldots \frac{n_iM_i}{\Sigma n_i}.$$

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

$$\frac{n_1M_1}{\Sigma n_i} + \frac{n_2M_2}{\Sigma n_i} + \ldots + \frac{n_iM_i}{\Sigma n_i} = \frac{\Sigma n_iM_i}{\Sigma n_i} = \overline{M}_n \qquad (3)$$

$\overline{M}_n$ can be considered as the first power-average (or the first moment) of molecular weight. Any measurement that leads to counting the number of molecules or particles present in the given sample allows the measurement of $\overline{M}_n$. Thus methods such as end-group analysis and measurements based on colligative properties like membrane osmometry, vapour phase osmometry and ebullimetry yield $\overline{M}_n$. For high molecular weight samples, as the number of molecules in a given mass becomes small, these measurements of $\overline{M}_n$ become less accurate.

For calculating weight-average molecular weight $\overline{M}_w$, we proceed as follows.

Total weight of the polymer = $W = \Sigma n_iM_i$
Weight of fraction 1 = $W_1 = n_1M_1$
Weight-fraction of fraction 1=(W_1/W)=$(n_1M_1 / \Sigma n_1M_1)$.

Molecular weight contribution by fraction 1 is given by

$$\frac{n_1M_1M_1}{\Sigma n_iM_i} = \frac{n_1M_1^2}{\Sigma n_iM_i}.$$

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

$$\frac{n_2M_2^2}{\Sigma n_iM_i}, \frac{n_3M_3^2}{\Sigma n_iM_i}, \ldots \frac{n_iM_i^2}{\Sigma n_iM_i}.$$

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

$$\frac{n_1 M_1^2}{\Sigma n_i M_i} + \frac{n_2 M_2^2}{\Sigma n_i M_i} + \ldots + \frac{n_i M_i^2}{\Sigma n_i M_i} = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i} = \overline{M}_w \qquad (4)$$

$\overline{M}_w$ would be the second power-average of molecular weight. Light scattering experiments, in which each polymer chain contributes according to its size, rather than the number, leads to the measurement of $\overline{M}_w$.

There can still be third power-average, usually called *z* average (from the German word zentrifuge) defined as:

$$\overline{M}_z = \frac{\Sigma n_i M_i^3}{\Sigma n_i M_i^2}. \qquad (5)$$

Sedimentation equilibrium measured in a centrifuge and melt viscosity measurements are dependent on the z-average. The third power-average molecular weight will have a value greater than the second power-average for polydisperse samples.

A number of other averages may also be defined and we mention one of them which is of relevance to macromolecular science, the viscosity-average molecular weight $\overline{M}_v$:

$$\overline{M}_v = \left[\frac{\Sigma n_i M_i^{1+a}}{\Sigma n_i M_i} \right]^{1/a} \qquad (6)$$

This type of average is useful when the molecular weight is calculated from intrinsic viscosity [1]. The parameter '*a*' in the above equation comes from the Mark-Houwink relation which describes the dependence of intrinsic viscosity on molecular weight. This parameter is a function of the shape of the polymer coil in a solvent and measures the interaction between the polymer and the solvent. The value of '*a*' is usually between 0.5

[1] Intrinsic viscosity is a solution property that describes the change in viscosity of the solvent as a result of dissolution of the polymer in it; it is normalized with respect to concentration (c) and extrapolated to the limit of c→0. It is, therefore, also often referred to as "limiting viscosity number".

Measurement of molecular weight using different methods thus can help us to find the dispersity or heterogeneity in a polymer sample.

and 0.8, and therefore $\overline{M}_v$ is less than $\overline{M}_w$; $\overline{M}_w$ is equal to $\overline{M}_v$ only when $a = 1$. The transport properties of polymer solutions are usually analyzed in term of a hydrodynamic model which is not yet fully developed, theoretically, as compared to the thermodynamic properties. Therefore, the viscosity method is semiempirical and the value of $\overline{M}_v$ is not the absolute value.

For a polydisperse polymer sample, $\overline{M}_z > \overline{M}_w > \overline{M}_v > \overline{M}_n$, but as the heterogeneity decreases various molecular weight values converge i.e., $\overline{M}_z = \overline{M}_w = \overline{M}_v = \overline{M}_n$. Values of the ratio $\overline{M}_z / \overline{M}_w$ or $\overline{M}_w / \overline{M}_n$ are often used as the polydispersity index which gives us an estimate of the width of the molecular weight distribution. The most probable value for this index for polymers synthesized by step-growth polymerization is 2.0. Measurement of molecular weight using different methods thus can help us to find the dispersity or heterogeneity in a polymer sample.

Suggested Reading

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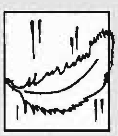

Everthing existing in the Universe is the fruit of chance and of necessity.

Democritus