Molecular Mass. Number And Mass-average Molecular Mass

⇒ The molecular mass of a polymer increases continuously during the condensation reaction involved depending upon the degree of polymerisation. However, since the polymerisation chains might be broken at different stages, the final product generally contains macromolecules of different masses.

It is necessary, therefore, to take an average Molecular Mass in these substances. Two types of Molecular mass are reckoned with.

(a) Number average molecular mass $\overline{M}_N$

(b) Mass-average molecular mass $\overline{M}_M$

for a sample consisting of N polymer molecules containing n_1 monomer molecules of Molecular mass M_1 and n_2 monomer molecules of Molecular Mass M_2 and.....

The Number-average Molecular Mass is defined as

$$\overline{M}_N = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \cdots}{n_1 + n_2 + n_3}$$

or $\overline{M}_N = \sum_i n_i M_i / \sum n_i$

The mass-average Molecular Mass is defined as

$$\overline{M}_M = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + \cdots}{n_1 M_1 + n_2 M_2 + n_3 M_3 + \cdots}$$

or, $\overline{M}_M = \sum_i n_i M_i^2 / \sum n_i M_i$

If c denotes the concentration of the polymer solution in grams per unit volume, Then

$$c_i = \sum n_i M_i$$

So that

$$\overline{M}_M = \sum c_i M_i / \sum c_i$$

The number-average molecular Mass is the airthmetic mean of all the molar masses where as the mass-average molar mass is the sum of the fractional masses that each molecule in a given sample contributes to the average according to the ratio of its mass to that of the whole sample.

In the number-average each molecule counts equally but in the mass-average molecules contributes according to their masses.

The heterogeneity of the polymer sample is called its Polydispersity as opposed to a monodisperse sample in which all the chains are identical chemically as well as in size.

The mass-average Molecular mass $\overline{M}_M$ is always larger than the number-average molecular mass $\overline{M}_N$, unless the sample is monodisperse in which case

$$\overline{M}_M = \overline{M}_N .$$

The ratio $\frac{\overline{M}_M}{\overline{M}_N}$ is called the Polydispersity index (P.D.I.) of a Polymer Sample.

Problems

① ⇒ Equal no. of molecules with $M_1 = 10,000$ and $M_2 = 100,000$ are mixed. Calculate $\overline{M}_N$ and $\overline{M}_M$.

⇒ Let $n_1 = n_2 = 10$ (Say) Then

$$\overline{M}_N = \frac{n_1M_1 + n_2M_2}{n_1 + n_2} = \frac{10\times10,000 + 10\times100,000}{10+10}$$

$$= \frac{10^5 + 10^6}{20} = \frac{10^5(1+10)}{20} = \frac{11}{2}\times10^4 = 55000$$

$\therefore \overline{M}_N = 55000$

$$\overline{M}_M = \frac{n_1M_1^2 + n_2M_2^2}{n_1M_1 + n_2M_2} = \frac{10\times(10000)^2 + 10\times(100000)^2}{10\times10000 + 10\times100,000}$$

$$= \frac{10^9 + 10^{11}}{10^5 + 10^6} = \frac{10^9(1+100)}{10^5(1+10)} = \left(\frac{101}{11}\right)\times10^4$$

$\therefore \overline{M}_M = 91818$

② Equal Masses of Polymer molecules with $M_1 = 10000$ and $M_2 = 100\,000$ are mixed. Calculate $\overline{M}_N$ and $\overline{M}_M$.

$\Rightarrow$ Let $m_1 = m_2 = 200{,}000$ (say)

$$n_1 = \frac{\text{Mass } M_1}{\text{Molar Mass } M_1} = \frac{200000}{10000} = 20$$

$$n_2 = \frac{\text{Mass } M_2}{\text{Molar Mass } M_2} = \frac{200{,}000}{10000} = 2$$

$$\therefore \bar{M}_N = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} = \frac{20 \times 10000 + 2 \times 100{,}000}{20 + 2}$$

$$= \frac{10^5 + 10^5}{11} = \frac{2 \times 10^5}{11}$$

or, $\bar{M}_N = 18182$.

$$\therefore \bar{M}_M = \frac{n_1 M_1^2 + n_2 M_2^2}{n_1 M_1 + n_2 M_2} = \frac{20 \times (10000)^2 + 2 \times (100000)^2}{20 \times 10000 + 2 \times 10{,}0000}$$

$$= \frac{2 \times 10^9 + 2 \times 10^{10}}{2 \times 10^5 + 2 \times 10^5} = \frac{10^9 (1 + 10)}{2 \times 10^5}$$

$$= \frac{11}{2} \times 10^4$$

or, $\bar{M}_M = 55000$.