MOLECULAR MASS OF POLYMERS

The properties of polymers depend largely upon their mol. masses, size and structure. The degree of ~~of~~ polymerisation or length of the polymer chain during their synthesis, however, depends upon the availability of monomer molecules near the growing polymer chain. Since the no. of monomer molecules differs from one place to another in the reaction mixture, therefore, a particular sample of a synthetic polymer contains a no. of species of varying chain lengths.

Since each species has a different mol. mass and a given sample of a polymer contains a no. of such species, therefore, a polymer as a whole has an average mol. mass. In contrast, natural polymers such as proteins, contains chains of identical length and hence have definite mol. masses.

TYPES OF AVERAGE MOLECULAR MASS :- There are two types of average mol. masses of polymers -

→ Number Average Molecular Mass ($\bar{M}_n$) :- If N_1, N_2, N_3 --- are the no. of macromolecules with mol. masses M_1, M_2, M_3 --- resp. then the no. average mol. mass of ~~the~~ the polymer is given by -

$$\bar{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}{N_1 + N_2 + N_3 \cdots} = \frac{\Sigma N_iM_i}{\Sigma N_i}$$

Where N_i is the no. of macromolecules of ith type with mol. mass M_i. It is determined by using methods ~~and~~ which depend upon the no. of molecules present in the polymer sample viz - colligative properties e.g. osmotic pressure etc.

→ Wt Average Molecular Mass ($\bar{M}_w$) :- If m_1, m_2, m_3 .... are the masses of macromolecules with molecular masses M_1, M_2, M_3 --- resp. then the wt. average mol. mass of the polymer is given by - $\bar{M}_w = \frac{m_1M_1 + m_2M_2 + m_3M_3 + \cdots}{m_1 + m_2 + m_3} = \frac{\Sigma m_iM_i}{\Sigma m_i}$

but $m_i = N_iM_i$ where N_i is the no. of macromolecules of ith type with mol. mass M_i.

$$\therefore \bar{M}_w = \frac{\Sigma N_iM_i \times M_i}{\Sigma N_iM_i} = \frac{\Sigma N_iM_i^2}{\Sigma N_iM_i}$$

Wt average mol. mass ($\bar{M}_w$) is determined by using method which depend upon the masses of individual molecules. Viz - light scattering, sedimentation etc.

$\boxed{W = n \cdot M.Wt}$

$n = \frac{W}{M \cdot Wt}$

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Poly Dispersity Index (PDI) :- The ratio of wt average mol. mass and no. average mol. mass is called PDI.

$$\boxed{PDI = \bar{M}_w / \bar{M}_n}$$

PDI is used to determine the homogeneity of a polymer. On the basis of values of PDI, polymers have been classified into two categories :-

(i) MONODISPERSE Polymers :- Polymers whose molecules have same or narrow range of mol. masses. For these polymers, $\bar{M}_w = \bar{M}_n$ and hence their PDI = 1 (unity). Natural polymers usually have PDI equal to one and hence are more homogenous.

(ii) POLYDISPERSE Polymers :- Polymers whose molecules have a wide range of mol. masses. For these polymers $\bar{M}_w > \bar{M}_n$ hence their PDI > 1. Synthetic polymers usually have PDI > 1 and hence are less homogenous.

Thus, in general, monodisperse (natural) polymers are more homogenous than polydisperse (synthetic) polymers.

Q. If the no. average mol. wt. & wt average mol. wt of a polymer are 40,000 and 60,000 resp., then calculate the PDI of the polymer. Based on the value, predict the nature of polymer.

Soln $PDI = \frac{M_w}{M_n} = \frac{60,000}{40,000} = 1.5$ It is > 1 i.e. polymer with the value > 1 have monomer units arranged in chains of different length.

Q. ~~In a sample of polymer~~, 100 molecules have a mol. mass 10^3 each

Ex. 1. In a particular sample of a polymer, 100 molecules have Molar mass 10^3 each, 200 molecules have molar mass 10^4 each & 200 have 10^5 each. Calculate $\bar{M}_n$ & $\bar{M}_w$.

Sol^n $\bar{M}_n = \dfrac{\Sigma n_i M_i}{\Sigma n_i} = \dfrac{100 \times 10^3 + 200 \times 10^4 + 200 \times 10^5}{100 + 200 + 200} = 44200$

$\bar{M}_w = \dfrac{\Sigma n_i M_i^2}{\Sigma n_i M_i} = \dfrac{100 \times (10^3)^2 + 200 \times (10^4)^2 + 200 \times (10^5)^2}{100 \times 10^3 + 200 \times 10^4 + 200 \times 10^5} = 91,407$

Ex. 3 In a polymer sample, 30% molecules have mol. wt 20,000, 40% have mol. wt 30,000 and rest 30% have 60,000. Calculate $\bar{M}_w$ & $\bar{M}_n$.

Sol^n $\bar{M}_w = \dfrac{30 \times (20,000)^2 + 40 \times (30,000)^2 + 30 \times (60,000)^2}{30 \times 20,000 + 40 \times 30,000 + 30 \times 60000} = 43333$

$\bar{M}_n = \dfrac{30 \times 20,000 + 40 \times 30,000 + 30 \times 60,000}{30 + 40 + 30} = 36,000$

Ex. 4. You have a nylon-6,6 sample with an average mol. wt of 250,000 g/mol. What is the degree of polym^n for this polymer?

$n = \dfrac{M_w}{m} = \dfrac{250,000 \text{ g/mol}}{226.3 \text{ g/mol}}$

$n = 1104$

C = 12

O = 2

N = 2

H = 22

$12 \times 12 + 2 \times 16 + 2 \times 14 + 22 \times 1 = 226.3$ g/mol