Example 1. *A polymer sample consists of 10% by weight of macromolecules of molecular weight 10,000 and 90% by weight of macromolecules with molecular weight 100,000. Calculate* $\overline{M}_n$ *and* $\overline{M}_w$.

Solution. As $\overline{M}_n = \dfrac{\Sigma N_i M_i}{\Sigma N_i} = \dfrac{\Sigma W_i}{\Sigma N_i}$

where W_i = weight of i^{th} constituent,

N_i = number of moles of i^{th} constituent,

and M_i = molecular weight of i^{th} constituent

Given $W_1 = 10$ gms. and $W_2 = 90$ gm.

$\therefore \quad \Sigma W_i = W_1 + W_2 = 10 + 90 = 100$ gm.

Since $N_i = \dfrac{W_i}{M_i}$

Hence $N_1 = \dfrac{10}{10{,}000}$ and $N_2 = \dfrac{90}{100{,}000}$

Now $\overline{M}_n = \dfrac{\Sigma W_i}{\Sigma N_i} = \dfrac{W_1 + W_2}{N_1 + N_2} = \dfrac{10 + 90}{\dfrac{10}{10{,}000} + \dfrac{90}{100{,}000}} = 5.26 \times 10^4$

Similarly, $\overline{M}_w = \dfrac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \dfrac{N_1 M_1^2 + N_2 M_2^2}{N_1 M_1 + N_2 M_2} = \dfrac{N_1 M_1^2 + N_2 M_2^2}{W_1 + W_2}$

$$= \frac{\dfrac{10}{10{,}000} \times (10{,}000)^2 + \dfrac{90}{100{,}000}(100{,}000)^2}{10 + 90}$$

$$= 9.1 \times 10^4$$

Example 2. *A polymeric mixture is prepared by mixing three polymers : A, B and C having $\overline{M}_n$, $\overline{M}_w$ and weights in mixture as given below :*

Polymer	$\overline{M}_n$	$\overline{M}_w$	*Wt. in Mixture (gms.)*
A	1.2×10^5	4.5×10^5	200
B	5.6×10^5	8.9×10^5	200
C	10×10^5	10×10^5	100

Find $\overline{M}_n$ and $\overline{M}_w$ of mixture.

Solution. Since $(\overline{M}_n)_A = \dfrac{\Sigma W_A}{\Sigma N_A}$

Hence $\Sigma N_A = \dfrac{\Sigma W_A}{(\overline{M}_n)_A}$

Thus, $(\overline{M}_n)_{Mixture} = \dfrac{(\Sigma W)_{Mixture}}{(\Sigma N_i)_{Mixture}} = \dfrac{W_A + W_B + W_C}{N_A + N_B + N_C}$

$$= \frac{W_A + W_B + W_C}{\dfrac{W_A}{(\overline{M}_n)_A} + \dfrac{W_B}{(\overline{M}_n)_B} + \dfrac{W_C}{(\overline{M}_n)_C}}$$

$$= \frac{200 + 200 + 100}{\dfrac{200}{1.2 \times 10^5} + \dfrac{200}{5.6 \times 10^5} + \dfrac{100}{10 \times 10^5}} = 2.35 \times 10^5$$

As $\overline{M}_w = \dfrac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \dfrac{\Sigma W_i N_i}{\Sigma W_i}$

Hence $(\overline{M}_w)_A = \frac{\Sigma(W_A N_A)}{\Sigma W_A} \Rightarrow \Sigma(W_A N_A) = (\overline{M}_w)_A \Sigma W_A$

$$(\overline{M}_w)_{Mixture} = \frac{\Sigma(W_A N_A) + \Sigma(W_B N_B) + \Sigma(W_C N_C)}{\Sigma W_A + \Sigma W_B + \Sigma W_C}$$

$$= \frac{(\overline{M}_w)_A \Sigma W_A + (\overline{M}_w)_B \Sigma W_B + (\overline{M}_w)_C \Sigma W_C}{\Sigma(W_A + W_B + W_C)}$$

$$= \frac{(4.5 \times 10^5 \times 200) + (8.9 \times 10^5 \times 200) + (10 \times 10^5 \times 100)}{200 + 200 + 100}$$

$$= 7.36 \times 10^5$$

Example 3. *In a polymer, there are 100 molecules of molecular weight 100, 200 molecules of molecular weight 1000 and 300 molecules of molecular weight 10,000. Find* $\overline{M}_n$, $\overline{M}_w$ *and* PDI.

Solution. $\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3}$

$$= \frac{100 \times 100 + 200 \times 1000 + 300 \times 10{,}000}{100 + 200 + 300}$$

$$= \frac{3.21 \times 10^6}{600} = 5.35 \times 10^3$$

$$\overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \frac{100 \times (100)^2 + 200 \times (1000)^2 + 300 \times (10{,}000)^2}{100 \times 100 + 200 \times 1000 + 300 \times 10{,}000}$$

$$= 9.4 \times 10^3$$

$$\text{PDI} = \frac{\overline{M}_w}{\overline{M}_n} = 1.757$$

Example 4. *42 gm of propene was polymerized by radical polymerization process and* $\overline{DP}$ *was found to be 1000. Calculate the number of molecules of PP produced.*

Solution. As $\overline{DP}$ of PP $= \frac{\text{Numbers of Propene molecules}}{\text{Number of PP molecules formed}}$

Hence, number of PP molecules formed

$$= \frac{\text{Number of propene molecules}}{\overline{DP} \text{ of PP}}$$

$$= \frac{42 \text{ gm} \times (6.023 \times 10^{23} \text{ molecules}/42 \text{ gm})}{1000}$$

$$= 6.023 \times 10^{20} \text{ molecules}$$

Example 5. *The* $\overline{M}_n$ *of a polystyrene is* 10^5 gm/mol. *Find its* $\overline{DP}_n$.

Solution. Since $\overline{DP}_n = \frac{\overline{M}_n}{M_0}$

(M_0) is $\quad 12 \times 8 + 1 \times 8 = 104$

Hence $\overline{DP}_n = \dfrac{\overline{M}_n}{M_0} = \dfrac{10^6}{104} = 9615.4$

Example 6. *Find $\overline{M}_w$ for PP given its degree of polymerization as 10,000.*

Solution. Since $\overline{DP}_w = \dfrac{\overline{M}_w}{M_0}$

$\therefore \quad \overline{M}_w = \overline{DP}_w \times M_0$

where $\quad \overline{DP}_w$ = Degree of Polymerization = 10,000 (given)

And $\quad M_0$ = Molecular weight of repeat unit of PP

$$= \left(\begin{array}{c} -CH_2-CH- \\ | \\ CH_3 \end{array}\right) = 12 \times 3 + 6 \times 1 = 42$$

Hence, $\overline{M}_w = 10{,}000 \times 42$

$\Rightarrow \quad \overline{M}_w = 42 \times 10^4$ gm/mol

Example 7. *Calculate the numb... average and weight average molecular masses of polypropylene polymer with the following composition :*

(a) $\left[-CH_2-\underset{\displaystyle CH_3}{\overset{|}{CH}}-\right]_{400}$ *is 25 % ;*

(b) $\left[-CH_2-\underset{\displaystyle CH_3}{\overset{|}{CH}}-\right]_{800}$ *is 35 % and*

(c) $\left[-CH_2-\underset{\displaystyle CH_3}{\overset{|}{CH}}-\right]_{600}$ *is 40 %. Given that Atomic mass of C = 12 and H = 1.*

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Solution. Molecular mass of (*a*) = $[(12 \times 3) + (6 \times 1)] \times 400 \Rightarrow M_1 = 16800$

Molecular mass of (*b*) = $[(12 \times 3) + (6 \times 1)] \times 800 \Rightarrow M_2 = 33600$

Molecular mass of (*c*) = $[(12 \times 3) + (6 \times 1)] \times 600 \Rightarrow M_3 = 25200$

As $n_1 = 25$, $n_2 = 35$ and $n_3 = 40$

Thus $\quad \overline{M}_n = \dfrac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3}$