Molecular Weight of Polymers

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Introduction

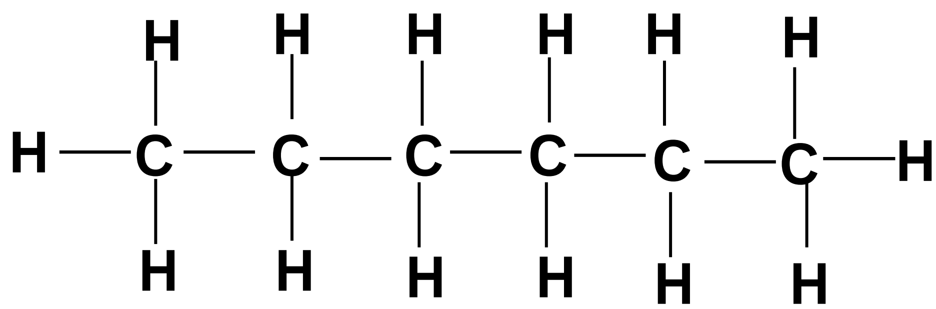
- ❖ Polymers are long chain molecules produced by linking small repeat units (monomers) together
- ❖ Polymers exhibit very different physical properties compared to the monomers, dependent on the length of the polymer chains
- ❖ The presence of small amounts of very long or very short chains can have drastic effects on properties of the material

Molecular Weight

- ❖Repetitive units make up a polymer.
- ❖These repetitive units were originally the monomer molecules.
- ❖When polymer chains form their lengths their weights differ.
- ❖It is important to be able to characterize the polymer structure.
- ❖Determining the weight-average molecular weight or the number-average molecular weight is a part of any polymer characterization

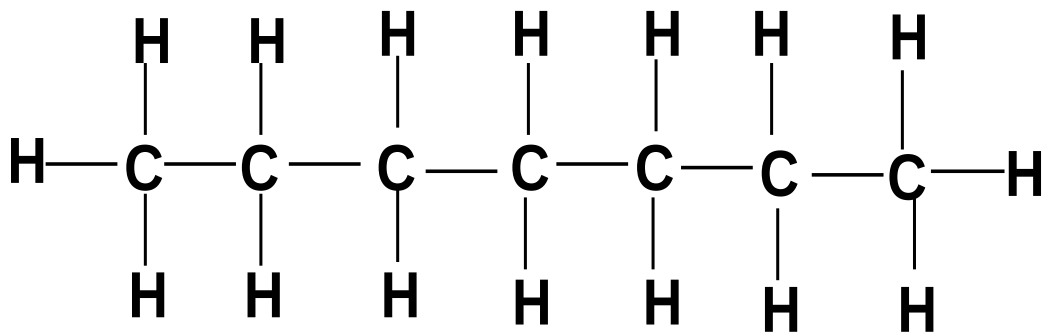
“Molecular weight of a polymer is defined as sum of the atomic weight of each of the atoms in the molecules, which is present in the polymer”

Let's think about a small molecule, say, hexane. Hexane has a molecular weight of 86. Every hexane molecule has a molecular weight of 86.



Hexane has one molecular weight, 86

Now if we add another carbon to our chain, and the appropriate amount of hydrogen atoms, we've increased our molecular weight to 100.



Lengthening the carbon chain by one carbon turns hexane into a completely different compound, Heptane, molecular weight = 100

A bell curve is used to understand the distribution of molecular weights.

Some of the polymer chains will be much larger than all the others, at the high end of the curve.

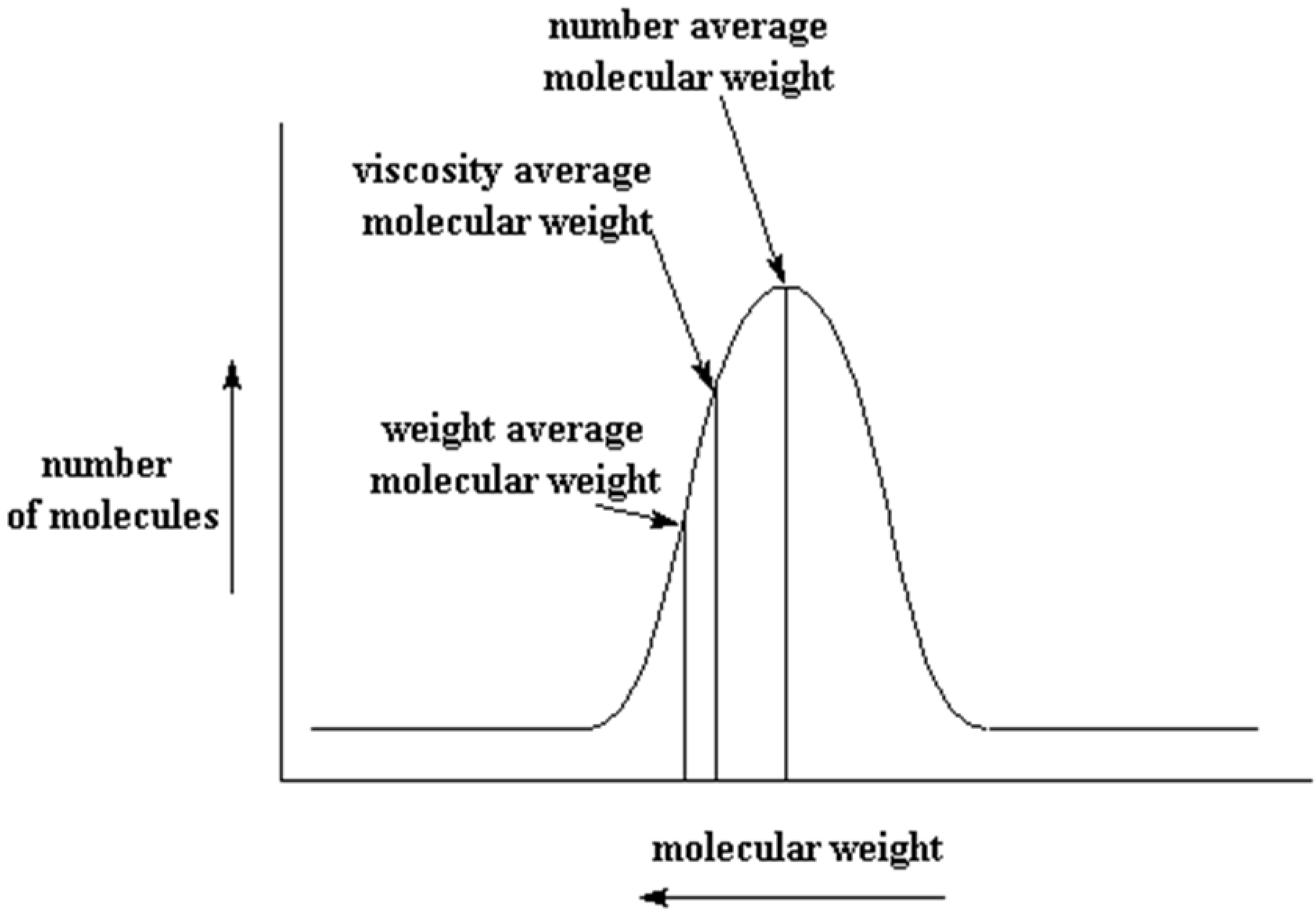
Some will be much smaller, and at the low end of the curve.

The largest number will usually be clumped around a central point, the highest point on the curve.

So it's usually best to try to know the molecular weight *distribution*.

It plots molecular weight on the *x*-axis, and plots the amount of polymer at a given molecular weight on the *y*-axis.

From this plot, we will come to know the number, viscosity, and weight averages.


number average
molecular weight
viscosity average
molecular weight
weight average
molecular weight
number
of molecules
molecular weight

Number-average molecular weight

- It is just the total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in a sample

$$Mn = \frac{\sum niMi}{\sum ni} = \frac{\sum wi}{\sum wi/Mi}$$

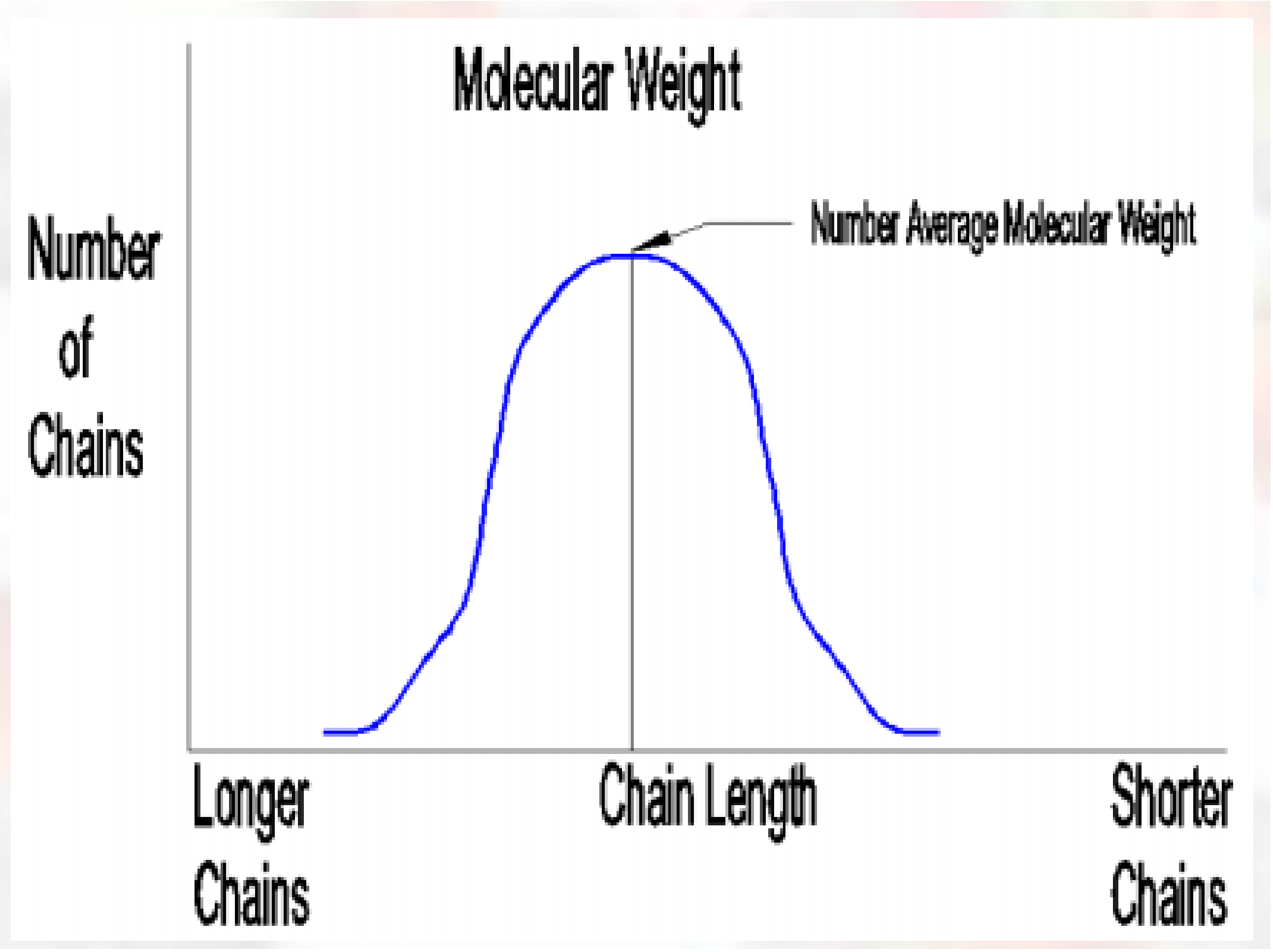
Where,

n = Moles of molecules (n1 + n2 + n3 + ----------ni)

w = Weight of individual molecules (w1 + w2 + w3 + ---------wi)

M = Molecular weight of each molecules

The Number Average Molecular Weight (Mn) is the total weight of the polymer molecules divided by the total number of polymer molecules.



Consider a polymer, which contains four molecular weight polymers in different numbers and weight

Polymer entity	Number of unit in each entity, n	Weight of each grams, M(g)	Total weight of each entity, W = nM(g)
Poly-1	2	10	20
Poly-2	4	20	80
Poly-3	6	100	600
Poly-4	3	250	750
Total	15	-	1450

Total number of polymer containing each entity of poly-1, poly-2, poly-3 and poly-4 is = 15

Number of Poly-1 present in the polymer = 2

Number of fraction of poly-1 = 2/15

Similarly, Number of fraction of poly-2 = 4/15,

Number of fraction of poly-3 = 6/15,

Number of fraction of poly-4 = 3/15

Contribution made by poly-1 towards the average weight of polymer = number of fraction of each polymer x weight of each poly entity

Therefore, each poly contribution is

(2/15) x 10 =1.33g, (4/15) x 20 = 5.33g, (6/15) x 100 =40g, (3/15) x 250 = 50g

Summing up the contribution to get Number Average Molecular Weight= 1.33 + 5.33 + 40 + 50 = 96.66

Generalization of concept

Total number of molecules (n) is given by

$$n = n_1 + n_2 + n_3 + n_4 + \dots\dots\dots = \sum n_i$$

Number fraction of each molecule is = $\frac{n_i}{\sum n_i}$

Number average weight contribution of each entity is = $\frac{n_i M_i}{\sum n_i}$

Number average weight molecular weight is

$$\frac{n_1 M_2}{\sum n_i} + \frac{n_2 M_2}{\sum n_i} + \frac{n_3 M_3}{\sum n_i} + \frac{n_4 M_4}{\sum n_i} \dots\dots = \frac{\sum n_i M_i}{\sum n_i} = M_n$$

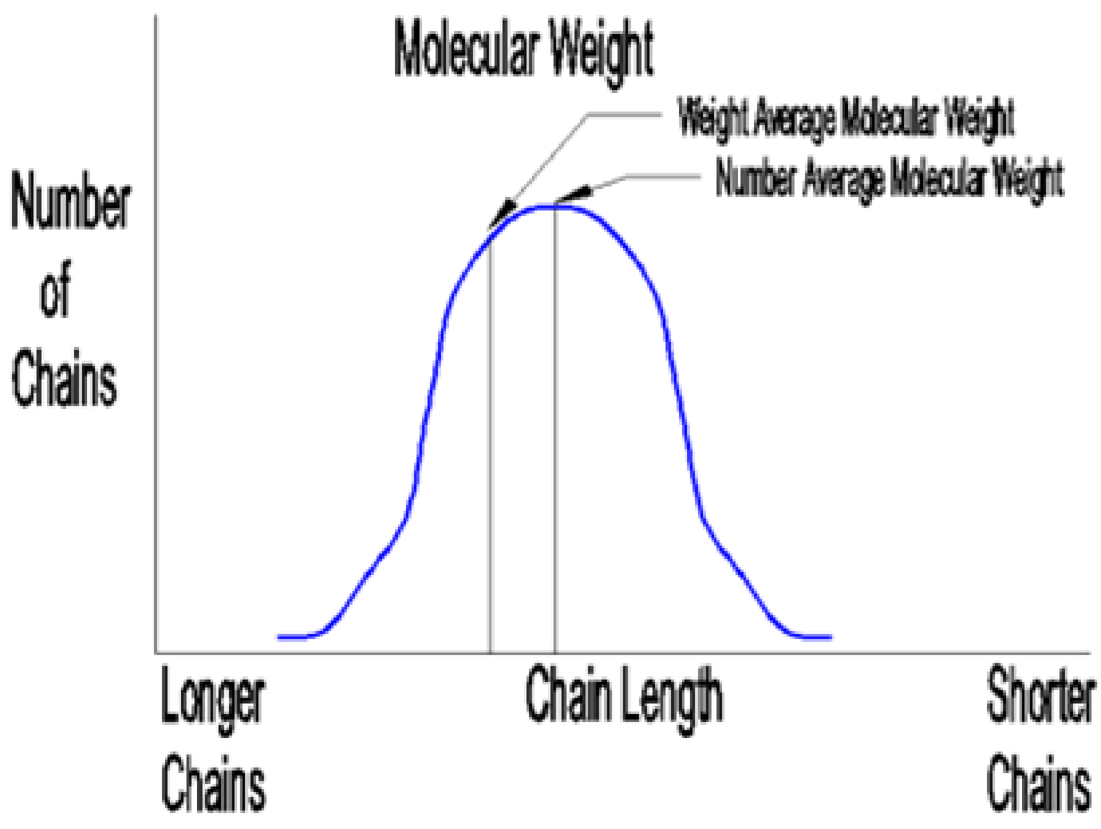
Weight-average molecular weight

The weight average molecular weight depends not only on the number of molecules present, but also on the weight of each molecule.

$$\frac{\sum n_i M_i^{\,2}}{\sum n_i M_i} = M_w$$

The Weight Average Molecular Weight takes into account that the larger molecules contain a much higher amount of the molecular mass of the polymer.

The Weight Average Molecular Weight is almost always higher than the Number Average Molecular Weight



Total weight of each poly present in the polymer =1450g

Weight of poly-1 present in polymer = 20g

Weight fraction of poly-1 = 20/1450, Weight fraction of poly-2 = 80/1450, Weight fraction of poly-3 = 600/1450, Weight fraction of poly-4 = 750/1450

Contribution made by each poly towards average weight of polymer = weight fraction of poly-1x weight of each unit

For poly-1 (20/1450) x 10 = 0.14g

For poly-2 (80/1450) x 20 = 1.10g

For poly-3 (600/1450) x 100 = 41.38g

For poly-4 (750/1450) x 250 = 129.31g

Summing up the contribution made by each poly to get weight average molecular weight is 0.14 + 1.10 + 41.38 + 129.31 = 171.93

Generalization of concept

Total number of molecules (n) is given by $n = n_1 + n_2 + n_3 + n_4 + ... = \sum n_i$

Total weight of the polymer is = $\sum N_i M_i$

Weight fraction of each molecule is = $\frac{n_1 M_1}{W} = \frac{n_1 M_1}{\sum n_1 M_1}$

Weight average weight contribution of each entity is = $\frac{n_1 M_1 M_1}{\sum n_i M_i} \frac{n_i M_i^2}{\sum n_i M_i}$

Number average weight molecular weight is

$$\frac{n_1 M_1^2}{\sum n_i M_i} + \frac{n_2 M_2^2}{\sum n_i M_i} + \frac{n_3 M_3^2}{\sum n_i M_i} + \frac{n_4 M_4^2}{\sum n_i M_i} ...... = \frac{\sum n_i M_i^2}{\sum n_i M_i} = M_w$$

For synthetic polymers *Mw* is greater than the *Mn*.

If they are equal than they will consider as perfectly homogeneous. (Each molecule has same molecular weight).

Degree of polymerisation (DP)

Number of repeating unit in a polymer is called as degree of polymerisation (DP). DP represents the average number of monomer units in the polymer chain and is an alternate way of expressing average chain size of the polymer.

DP provides the indirect method of expressing the molecular weight and the relation is as follows; M = DP x m

Where, M is the molecular weight of polymer, DP is the degree of polymerisation and m is the molecular weight of the monomer

Both number average (DPn) and weight average (DPw) degree of polymerization can be defined as-

$$(DP)_n = \frac{\sum n_i (DP)_i}{\sum n_i} \text{ and } (DP)_w = \frac{\sum n_i (DP)_i^2}{\sum n_i (DP)_i}$$

OR

$$DPn = \frac{Mn}{Mo}$$

$$DPw = \frac{Mw}{Mo}$$

Polydispersity index(PDI)

Index of polydispersity or PDI is used as a measure of molecular weight distribution and is defined as

$$PDI = \frac{Mw}{Mn}$$

In case of monodisperse system(natural polymers and synthetic polymers made by anionic polymerization), PDI= 1, Since, Mn= Mw; and for other cases, PDI>1 or Mw is used as a measure of molecular weight distribution and is defined as- Mw>Mn.

Viscosity average molecular weight

The average molecular weight is related to the viscosity of the polymer under specific conditions. In the case of solution viscosity, the weight dependence of the viscosity can be described by the well-known empirical Mark-Houwink relation:

$$[\eta] = K_\eta \, M_\eta^{\alpha}$$

where $[\eta]$ is the intrinsic viscosity, and α, K_η are the Mark-Houwink parameters

Measurements of the viscosity yields the viscosity average molar weight

$$\overline{M_\eta} = \left[\frac{\sum_{i=1}^{N} N_i M_i^{\alpha+1}}{\sum_{i=1}^{N} N_i M_i}\right]^{1/\alpha}$$

The viscosity average is usually larger than the mass average but smaller than the number average, $M_n < M_\eta < M_w$

Problems

1. A polymer has the following molar mass.

Number of molecules	Molar mass (g/mol)
50	5000
75	6000

Calculate the number average, weight average and PDI

(1) $n_1 = 50$, $m_1 = 5000$
$n_2 = 75$, $m_2 = 6000$

$$\overline{M}_n = \frac{\Sigma n_i M_i}{\Sigma n_i}$$

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$$

$$\overline{M}_n = \frac{(50 \times 5000) + (75 \times 6000)}{50 + 75}$$

$$= \frac{250000 + 450000}{125}$$

$$= \frac{700000}{125} = 5600 \text{ g mol}^{-1}$$

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

$$= \frac{50(5000)^2 + 75(6000)^2}{(50 \times 5000) + (75 \times 6000)}$$

$$= \frac{125 \times 10^7 + 270 \times 10^7}{7 \times 10^5}$$

$$= \frac{395 \times 10^7}{7 \times 10^5} = 5642 \ g\,mol^{-1}$$

$$PDI = \frac{\overline{M}_w}{\overline{M}_n} = \frac{5642}{5600} = 1.0075$$

2. An equal number of protein mixture containing Haemoglobin 15.5 Kg/mol, Ribonuclease 13.7 Kg/mol, Myoglobin 17.2 Kg/mol. Calculate the number average and mass average molecular weight of the protein solution

(2) Heamoglobin = 15.5 kg mol^{-1}
ribo = 13.7 kg mol^{-1}
Myoglo = 17.2 kg mol^{-1}

Molecules are in Equal number

$n_1 = n_2 = n_3 = n$

$\frac{1}{3} = 0.333$

$$\bar{M}_n = \frac{\Sigma n_i M_i}{\Sigma n_i}$$

$$= \frac{(n \times 15.5) + (n \times 13.7) + (n \times 17.2)}{n + n + n}$$

$$= \frac{n\,(46.4)}{3n}$$

$$= 15.49 \text{ Kg mol}^{-1}$$

$$\bar{M}_w = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i}$$

$$= \frac{n(15.5)^2 + n(13.7)^2 + n(17.2)^2}{(n \times 15.5) + (n \times 13.7) + (n \times 17.2)}$$

$$= \frac{n\,[240.25 + 187.69 + 295.84]}{n\,(46.4)}$$

$$= 15.59 \text{ Kg mol}^{-1}$$

3. Intrinsic viscosity of polyisobutene is 180 cm^3/gm and the Mark-Houwink constants K is 3.60 10^{-2}, α is 0.64.

(3) $\eta_i = K M^a$

$\log \eta_i = \log K + a \log M$

$\log 180 = \log (3.6 + 10^{-2}) + 0.64 \log M$

$2.255 = -1.44 + 0.64 \log M$

$0.64 \log M = 3.695$

$\log M = \frac{3.695}{0.64} = 5.773$

$M = \text{antilog} (5.773)$

$\overline{M}_{vis} = 5.9 \times 10^5$ gm/mol

Thank You