Mass average molecular mass (Lecture – 23)

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Average molecular weights

- Number average molecular weight:

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

- Weight average molecular weight

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

- Viscocity average molecular weight

$$\overline{M}_v = \left[\frac{\sum n_i M_i^{a+1}}{\sum n_i M_i}\right]^{1/a}$$

Average molecular weights

- Z-average molecular weight
  (Z = zentrifuge/centrifuge)

$$\overline{M}_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2}$$

- Polydispersity

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

  - If PDI = 1, the polymer is **monodisperse**

n_i = Number of molecules with molecular weight M_i
w_i = weight fraction with molecular weight M_i
a = constant, depends on polymer/solvent combination

- ✓ A monodisperse, or uniform, polymer is composed of molecules of the same mass
- ✓ Nearly all natural polymers are monodisperse

Molecular weight and dispersion

Syntetic polymers always show a distribution in molecular weights.

number average : $M_n = \frac{\sum n_i M_i}{\sum n_i}$

weight average: $M_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i M_i}{\sum n_i M_i}$

(n_i and w_i are number and weight fractions, respectively, of molecules with molar mass M_i)

The polydispersity index is given by M_w / M_n

Molecular weight and dispersion an example:

Here are:
10 chains of 100 molecular weight
20 chains of 500 molecular weight
40 chains of 1000 molecular weight
5 chains of 10000 molecular weight

$$\overline{M}_n = \frac{(10\cdot 100)+(20\cdot 500)+(40\cdot 1000)+(5\cdot 10000)}{10+20+40+5} = 1347$$

$$\overline{M}_w = \frac{(10\cdot 100^2)+(20\cdot 500^2)+(40\cdot 1000^2)+(5\cdot 10000^2)}{(10\cdot 100)+(20\cdot 500)+(40\cdot 1000)+(5\cdot 10000)} = 5390$$

$$\text{Polydispersity} = \frac{\overline{M}_w}{\overline{M}_n} \approx 4$$

Number average molecular weight

- The number average molecular weight is not too difficult to understand.
- 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 ($n_1 + n_2 + n_3 + \text{----------} n_i$) i.e. weight (w)/molecular weight (M)

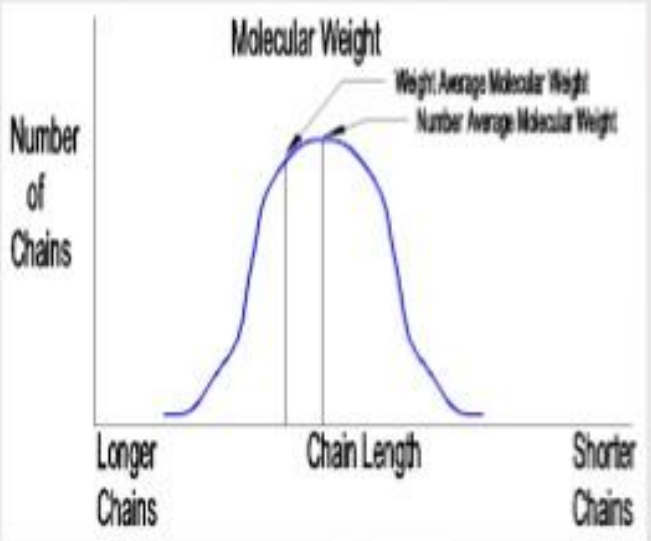
w = Weight of individual molecules ($w_1 + w_2 + w_3 + \text{---------} w_i$)

M = Molecular weight of each molecules

Weight average Molecular Weight

The Weight Average Molecular Weight ($\overline{M_w}$) 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 ($\overline{M_n}$).



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

Thank You