Molecular weight and its determination

Number average molecular weight (M_n)

Total weight of polymer divided by number of molecules

$$\text{Total weight of the polymer} = \sum_{i=1}^{\infty} N_i M_i$$

$$\text{Total number of molecules} = \sum_{i=1}^{\infty} N_i$$

$$M_n = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} = \frac{\text{Total weight}}{\text{Number of polymers}} = \sum_{i=1}^{\infty} X_i M_i \quad (1)$$

$$\text{where, } X_i = \frac{N_i}{\sum N_i}$$

is number fraction or mole fraction of polymers

$$c_i = \frac{N_i M_i}{V}$$

where c_i = conc. of polymer species i in weight per unit volume

inserting c_i for $N_i M_i$ and expressing N_i in terms of c_i in equ (1)

$$M_n = \frac{\sum_{i=1}^{\infty} c_i}{\sum_{i=1}^{\infty} \frac{c_i}{M_i}}$$

Dividing numerator and denominator by $\sum c$

$$M_n = \frac{1}{\sum_{i=1}^{\infty} \frac{w_i}{M_i}}$$

where w_i is the weight fraction of polymer divided by total polymer weight

$$w_i = \frac{N_i M_i}{\sum_{i=1}^{\infty} N_i M_i} = \frac{c_i}{\sum_{i=1}^{\infty} c_i}$$

Number average molecular weight (M_n)

- Vapour pressure lowering (vapour pressure osmometry)
- Freezing point depression (cryoscopy)
- Boiling point elevation (ebulliometry)
- Osmotic pressure (membrane osmometry)

The colligative properties are same for small and large molecules for given conc. solution

Weight average molecular weight (M_w)

$$M_w = \frac{\sum N_i M_i^{\,2}}{\sum N_i M_i} = \sum w_i M_i \qquad \text{where, } w_i = \frac{N_i M_i}{\sum_{i=1}^{\infty} N_i M_i}$$

- Light scattering is used to measure larger molecules in a polymer solution.
- Molecular weight below 5,000-10,000 can not be measured accurately due of weak light scattering

Polydispersity index = M_w/M_n

Viscosity average molecular weight (M_v)

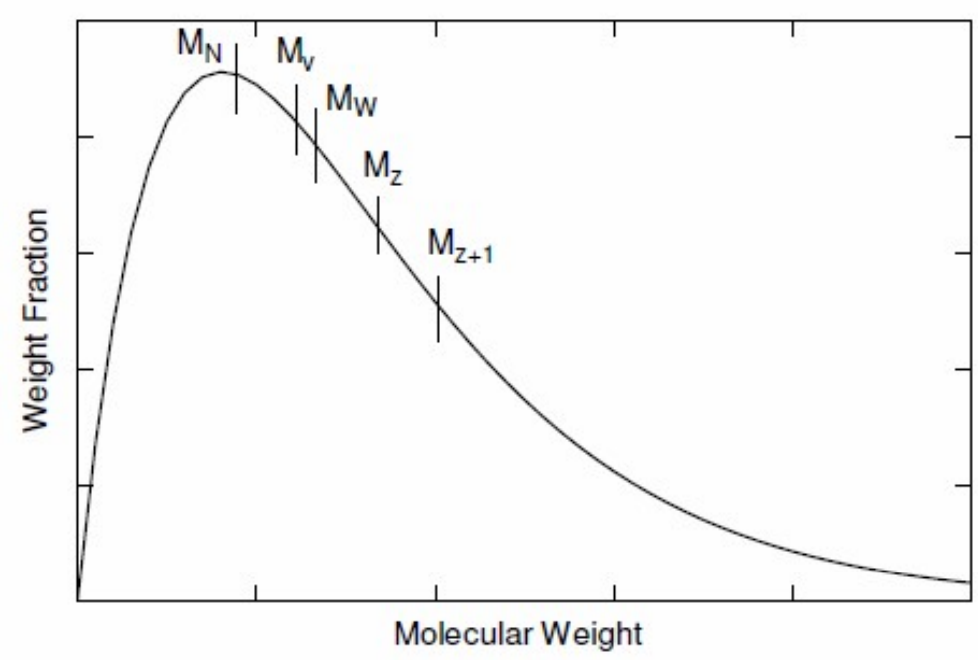
$$M_v = \left[\sum_{i=1}^{\infty} w_i M_i^a \right]^{1/a} = \left[\frac{\sum_{i=1}^{\infty} N_i M_i^{a+1}}{\sum_{i=1}^{\infty} N_i M_i} \right]^{1/a}$$

where a is a constant

M_v is less than M_w for most polymers, since a is in the range of $0.5 - 0.9$

M_v is much closer to M_w than M_n

a is dependant on hydrodynamic volume of the polymer



$$M_n < M_v < M_w < M_z .....$$

Size exclusion chromatography (SEC) or gel permeation chromatography (GPC) is Modern technique to measure the average mol wt.

- **Number average molecular weight (directly from osmometry)**
- **Weight average molecular weight (directly from light scattering)**
- **Viscosity average molecular weight (directly from solution viscometry)**
- **z-average molecular weight (directly from ultracentrifugation)**

However by using Size exclusion chromatography (SEC) or gel permeation Chromatography (GPC) one can determine M_n, M_w and M_v (if a is known) automatically