

2. MOLECULAR MASS DISTRIBUTION (MMDs) FOR LINEAR CHAINS

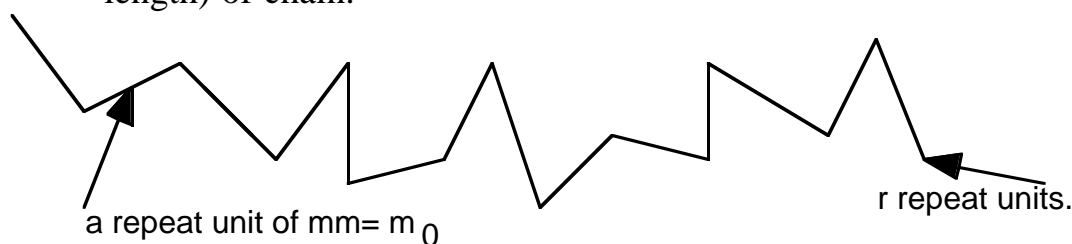
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2. Molecular Mass Distributions MMDs for linear chains

This section briefly describes why polymer MMDs are important. It then describes how MMDs can be measured and finally develops the mathematics used to describe both discrete and continuous MMDs.

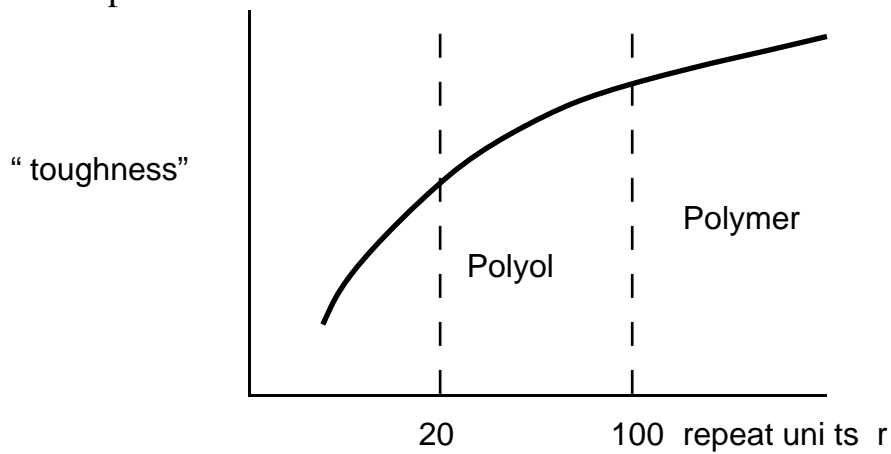
2.1 The importance of MMDs

Nearly all, but not recent Metallocene catalysed, commercial polymers have broad MMD and many physical properties are sensitive to the molecular mass (or equivalently molecular length) of chain.



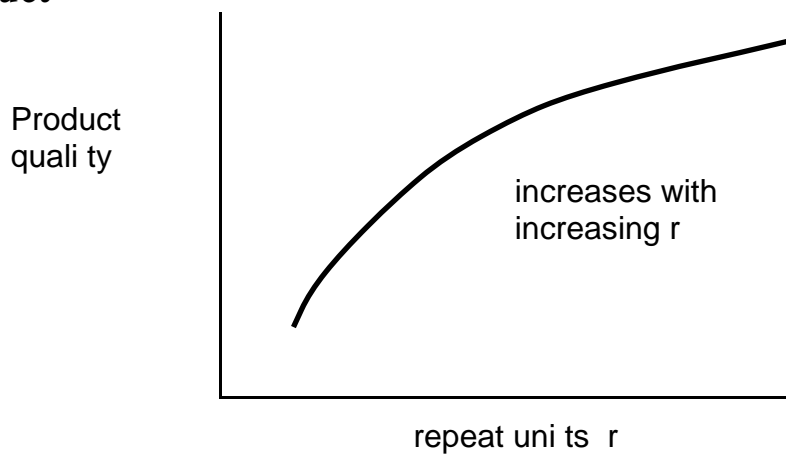
r repeat units each repeat unit with molecular mass m_0 .
Molecular mass of chain $m = m_0 r$.

Chain needs to have $r > \sim 100$ before you can safely call it a polymer. You often need to have $r > 100$ before useful different properties develop.

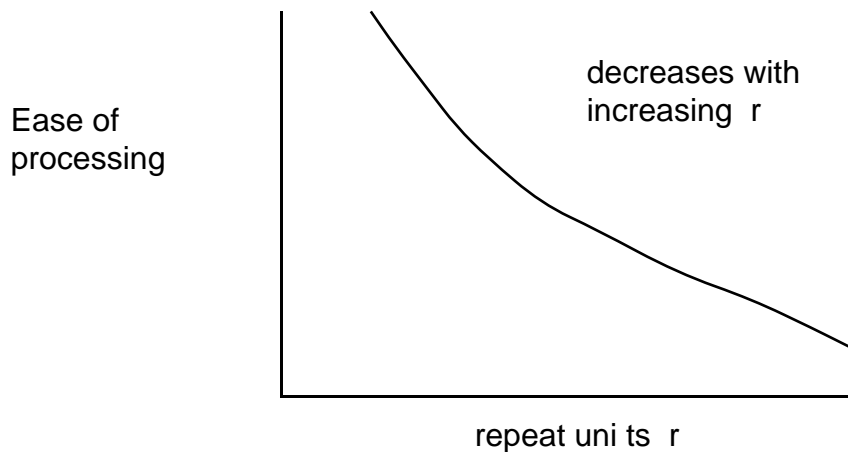


What r do you choose? A classic Chemical Engineering compromise.

Product



Process



So you usually end up with a compromise.

$M \sim 10^3 - 10^5$ fast processing. Fibres, injection moulding.

$M \sim 10^4 - 10^6$ slow processing. Extrusion.

The fact that you have a MMD means that you can often tailor a particular MMD for a particular process and product function.

A major manufacturer of bulk polymers such as BP Amoco might have ~ 100 different grades of polyethylene, each one having a different MMD.

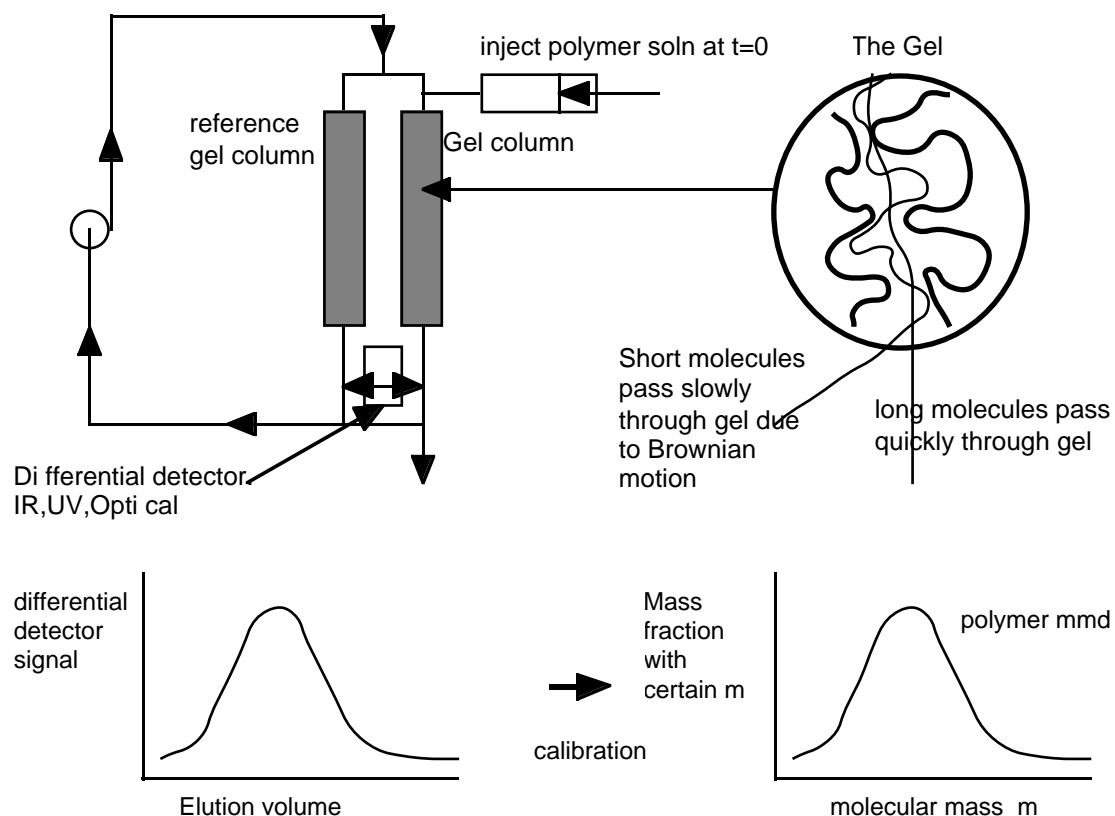
2.2 The experimental measurement of molecular mass and molecular mass distribution

There are a number of absolute methods of determining MMs (see Flory, Principles of Polymer Chemistry, if you are really interested). These methods include:-

- Osmotic Vapour Pressure Depression
- Light Scattering
- Intrinsic Viscosity
- Electrophoresis

The most common method used by the major commodity chemical manufacturers is Gel Permeation Chromatography (GPC).

The principle of operation of GPC



2.3 Mathematical description

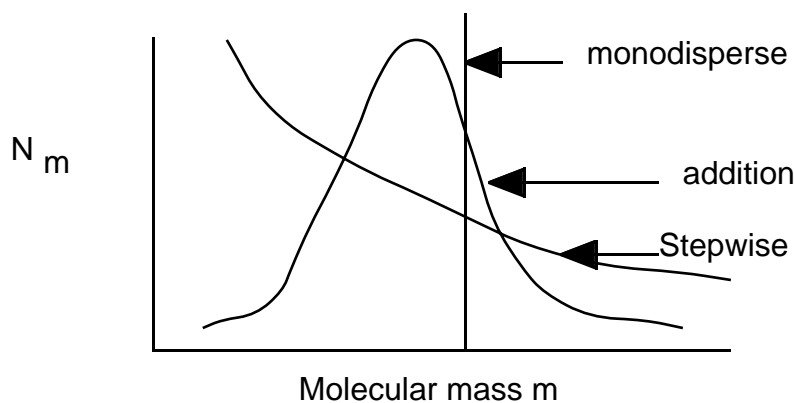
Molecular mass of r mer $m = m_0 r$, where $r =$ number of repeat units = degree of polymerisation of chain. Initially let us consider a discrete contribution of chain lengths.

Let $N_m =$ number of chains with a molecular mass of m (or equivalent Let $N_r =$ number of chain with r repeat units).

There are two (essentially) equivalent forms of presenting data.

2.3.1 Number distribution

Plot N_m as ftn of m (or equivalently Plot N_r as ftn of r)



Define number fraction

$$x_m = \frac{N_m}{\sum N_m} \quad \left(x_r = \frac{N_r}{\sum N_r} \right)$$

If distribution is continuous.

$N_m =$ Nos fraction between m and $m + dm$

$$x_m = \frac{N_m dm}{\int_0^{\infty} N_m dm}$$

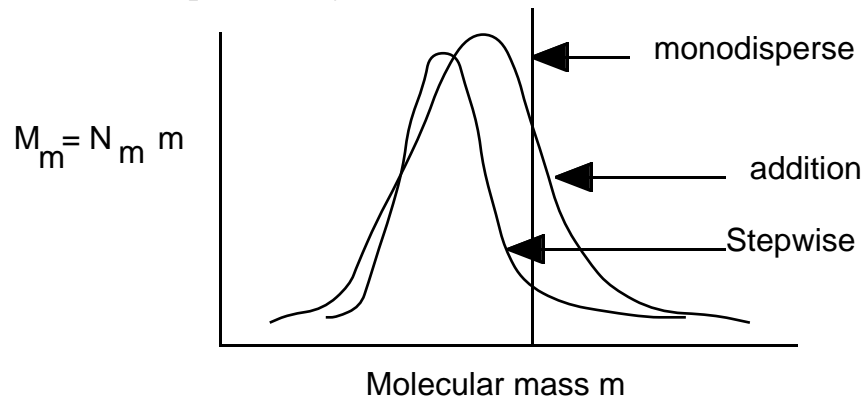
strictly this should be m_0 , but integration from 0 easier.

We can also define a cumulative number fraction.

$$X = \sum_{m_0}^m x_m \approx \int_0^m x_m dm$$

2.3.2 Weight (mass) distribution

Plot molecular mass, m N_m as a ftn of m
(or equivalently, r N_r as a ftn of m)



define weight (mass) fraction

$$w_m = \frac{N_m m}{\sum N_m m} \quad \left(w_r = \frac{N_r r}{\sum N_r r} \right)$$

Weight fraction curve will be same form as above.

Note Neither the number fraction or weight fraction curves are necessarily symmetric about a mean.

Second Note

We can present data in a number of ways.

Number fraction x_m as a function of mol mass m

" " x_r " " " of degree of polymerisation

Weight fraction w_m as a function of mol mass m

" " w_r as a " of degree of polymerisation

All are essentially equivalent!

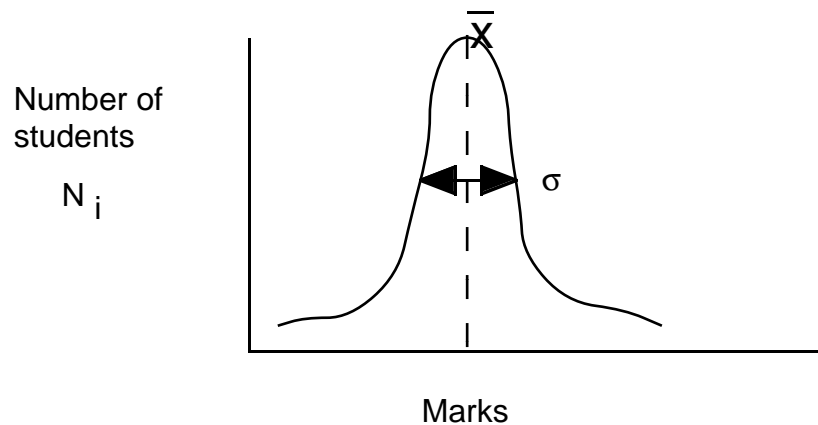
We can define a cumulative weight fraction W

$$W = \sum_{m_0}^m w_m \approx \int_0^m w_m dm$$

2.3.3 Distributions in Chemical Engineering.

A slight digression

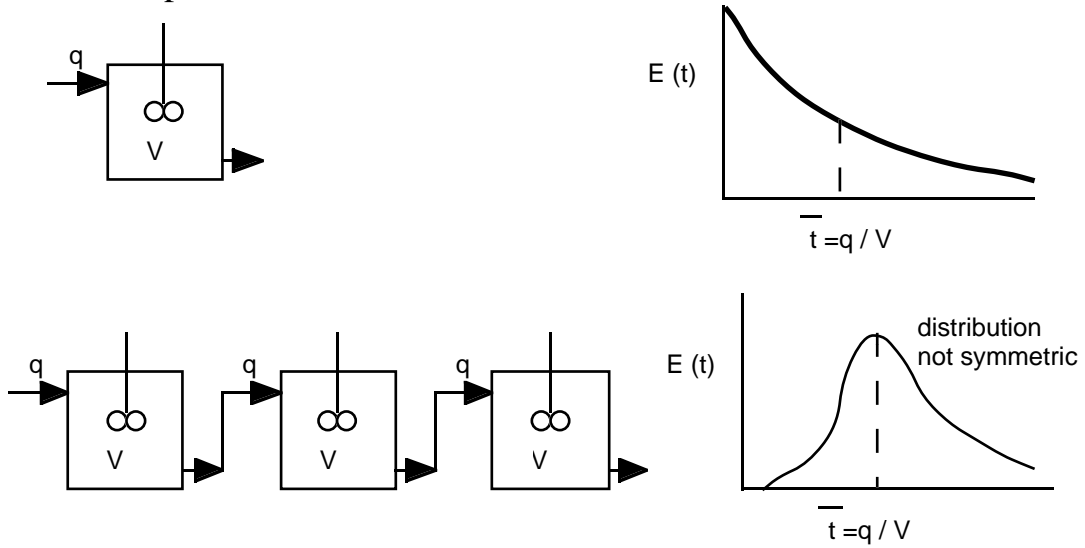
Example 1. Exam results



We usually characterise the distribution by the mean and standard deviation.

$$\bar{x} = \frac{\sum N_i x_i}{\sum N_i}, \quad \sigma = \left(\frac{\sum (x_i - \bar{x})^2}{\sum N_i} \right)^{1/2}$$

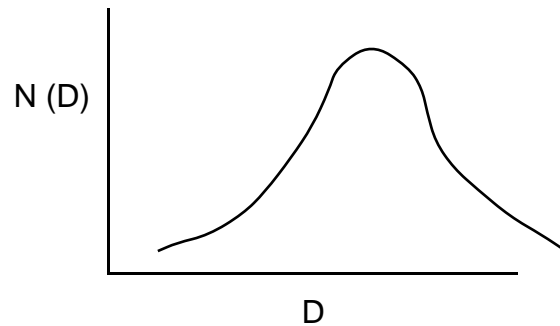
Example 2. Residence time distributions



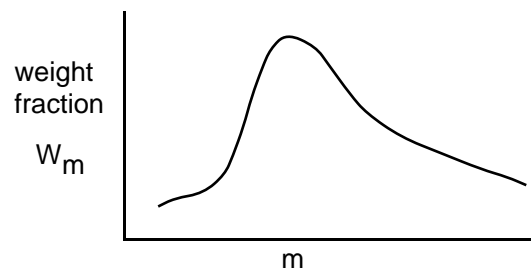
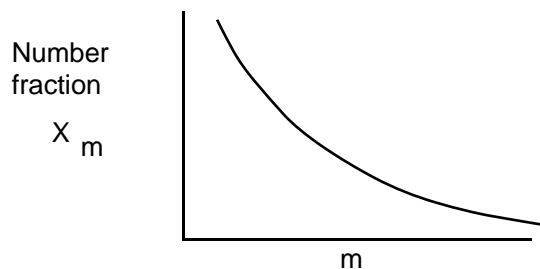
Example 3 Particle size distribution

(PSD)

Number of particles with size $D - D + dD$



Example 4 Polymers



Distribution not always symmetric; so define moments μ_i .

$$\mu_0 = \sum N_m$$

$$\mu_1 = \sum N_m m$$

$$\mu_2 = \sum N_m m^2$$

$$DP_0 = \sum N_r$$

$$DP_1 = \sum N_r r$$

$$DP_2 = \sum N_r r^2$$

each moment has a different dimension

2.3.3 so define normalised moments

Molecular mass averages

Degree of polymerisation averages

$$\bar{M}_j = \frac{\sum N_m m^j}{\sum N_m m^{j-1}} \text{ kg/kmol}$$

$$\overline{DP}_j = \frac{\sum N_r r^j}{\sum N_r r^{j-1}}$$

Note simple linking

$$\bar{M}_j = M_o \overline{DP}_j$$

The 1st moment $j = 1$.

$$\bar{M}_1 = \bar{M}_n = \frac{\sum N_m m}{\sum N_m}$$

$$\overline{DP}_1 = \overline{DP}_n = \frac{\sum N_r r}{\sum N_r}$$

\bar{M}_n = Number average molecular mass

\overline{DP}_n = Number average degree of polymerisation

The 2nd Moment $j = 2$

$$\bar{M}_2 = \bar{M}_w = \frac{\sum N_m m^2}{\sum N_m m}$$

$$\overline{DP}_2 = \overline{DP}_w = \frac{\sum N_r r^2}{\sum N_r r}$$

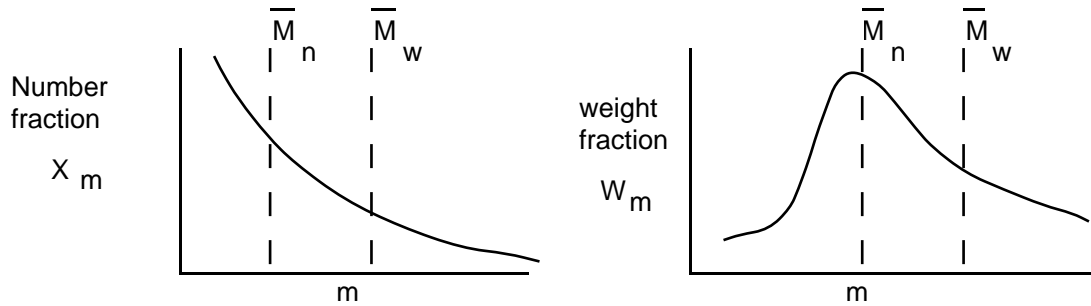
\bar{M}_w = Weight average molecular mass

\overline{DP}_w = Weight average degree of polymerisation

The z moment $z > 2$

$$\bar{M}_z = \frac{\sum N_m m^z}{\sum N_m m^{z-1}}$$

So instead of "talking", about the whole distribution we often "talk about" \bar{M}_n and \bar{M}_w as a two parameter description of the distribution.



For example a commercial Polyethylene

$$\begin{aligned}
 \bar{M}_n &= 150,000 \text{ kg/mol} \\
 \bar{M}_w &= 600,000 \\
 \bar{M}_3 &= 1,500,000
 \end{aligned}$$

2.3.5 Analytic descriptions of MMDs

Strictly MMD is discreet, but often assume continuous.

$$\text{Then ex } \bar{M}_n = \frac{\int_0^{\infty} N_m m \, dm}{\int_0^{\infty} N_m \, dm}$$

$$\bar{M}_w = \int_0^{\infty} w_m m \, dm$$

see Ex sheet.

where w_m is wt frac from $m \rightarrow m + dm$.

2.3.6 Two "popular" distributions

(a) "Most probable"

$$w(m) = \frac{m}{\bar{m}_n^2} \exp\left(-\frac{m}{\bar{m}_n}\right)$$

Many Stepwise Polymers model using this.

(b) "Log normal"

$$w(m) = \frac{1}{\beta \pi^{1/2} m'} \exp\left\{-\frac{(\ln(m/m'))^2}{\beta^2}\right\}$$

m' = location of maximum

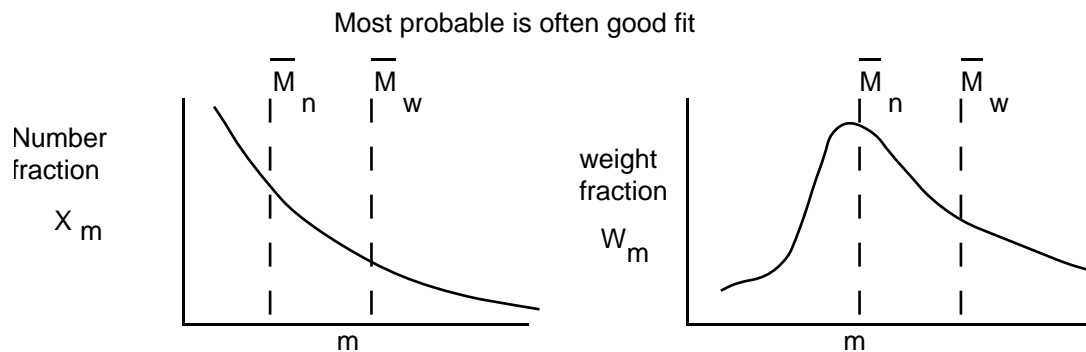
β = Breadth

$$\bar{M}_w = m' \exp\left(\frac{\beta^2}{4}\right)$$

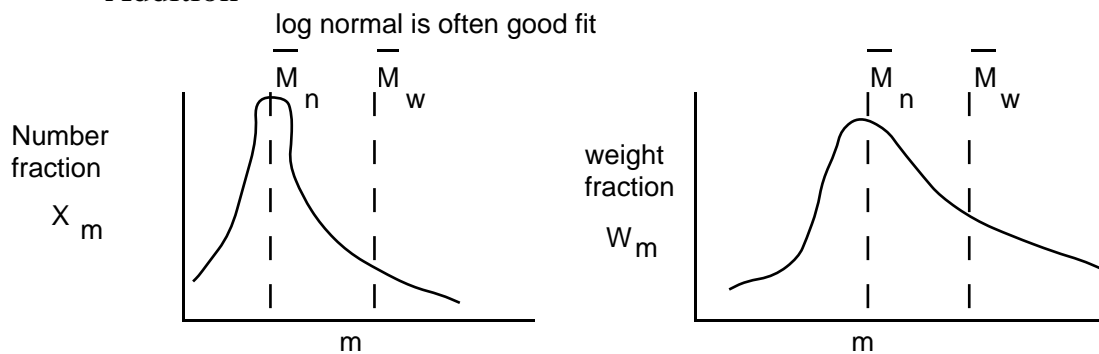
$$\frac{\bar{M}_{z+1}}{\bar{M}_z} = \frac{\bar{M}_w}{\bar{M}_n} = \exp(\beta^2/2)$$

Many additional polymerisations model using this.

Stepwise



Addition



$$\bar{M}_3 > \bar{M}_w > \bar{M}_v > \bar{M}_n$$

Viscosity Ave

Ratio

$$\frac{\bar{M}_w}{\bar{M}_n} = \text{Polydispersity index}$$

if $\frac{\bar{M}_w}{\bar{M}_n} = 1$ Monodisperse
 $\frac{\bar{M}_w}{\bar{M}_n} \approx 2$ typical for stepwise
 $\frac{\bar{M}_w}{\bar{M}_n} \sim 5$ typical for addition

2.3.7 Useful notes for Tripos manipulation

Worked example. Express \bar{M}_n in terms of the number fraction x_m .

$$\bar{M}_n = \frac{\sum N_m m}{\sum N_m} \quad \text{Definition}$$

$$x_m = \frac{N_m}{\sum N_m} \quad \text{Definition}$$

manipulate x_m to get x_m in form of \bar{M}_n define.

$$\text{So } x_m m = \frac{N_m m}{\sum N_m}$$

Take sum of both sides

$$\sum x_m m = \frac{\sum N_m m}{\sum N_m}$$

This is a number and can be taken outside 1st \sum

$$\sum x_m m = \frac{\sum N_m m}{\sum N_m} = \bar{M}_n \quad \text{QED}$$

$$\bar{M}_n = \sum x_m m$$

Now you show,

$$\bar{M}_n = \frac{1}{\sum \frac{w_m}{m}}$$

Summary.

Why are MMD important?

Can you define the number and weight average molecular mass without looking at notes?

Can you express the above averages in terms of weight fractions?

Can you define cumulative number and weight fraction in terms of r ?

Why do we use normalised moments?

What other areas of Chem Eng, other than the ones already given, utilise/ need to be described by moments?