

LIQUIDS

$$i' = \left(\frac{N}{V}\right) \left(\frac{I_0 \lambda^4}{4}\right) \left(\frac{1}{2}\right) \left(\frac{1 + \cos^2 \theta}{r^2}\right)$$

scatterers per unit volume

Characteristics of the incident beam

Polarizability

Geometry of observation

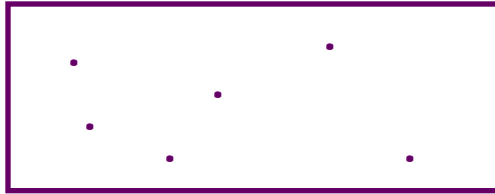
TO A FIRST APPROXIMATION

$$= \frac{1}{2} \left(\frac{dn}{dc}\right) \frac{M}{A}$$

HENCE PURE LIQUIDS SHOULD NOT SCATTER LIGHT !!!

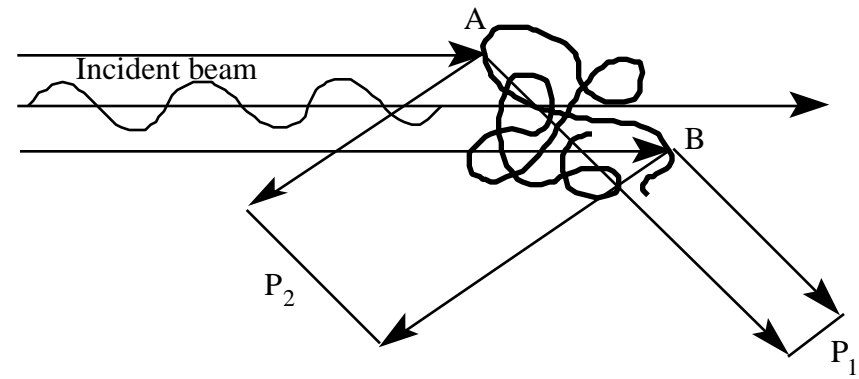
FLUCTUATIONS

Pure liquids - density
Solutions - concentration



$$\frac{K (1 + \cos^2 \theta) c}{R^0} = \frac{1}{M_w} (1 + 2 \cos^2 \theta c + \dots)$$

But a polymer is too large to
Be considered a single oscillator
(ie a point source of radiation).
Must consider interference
effects



ZIMM PLOT

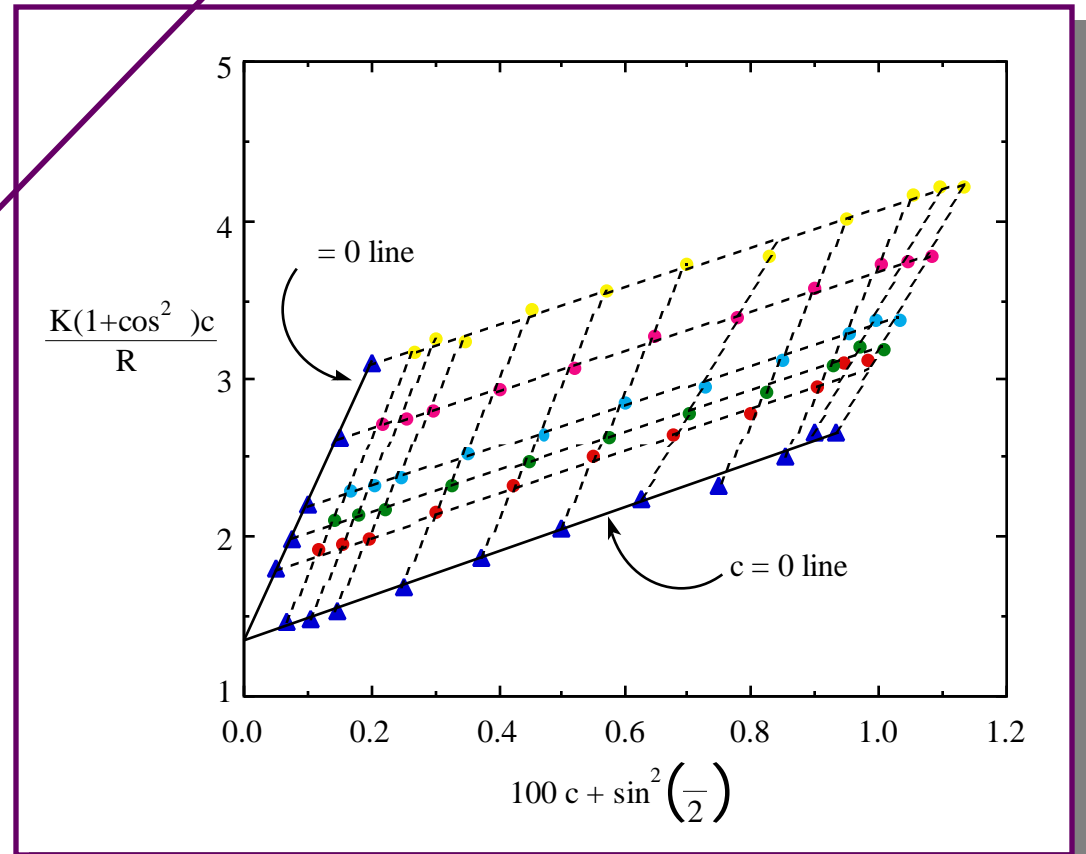
$$\frac{K(1 + \cos^2 \theta) c}{R} = \frac{1}{M_w} (1 + 2 A_2 c + \dots) \left(1 + S \sin^2 \left(\frac{\theta}{2} \right) \right)$$

Experimentally measured parameters

Weight Average Molecular Weight

Virial Expansion

Dependence upon angle of observation



THE VISCOSITY OF POLYMER SOLUTIONS

Measure the time taken to flow between fixed marks in a capillary tube under the draining effect of gravity. The (volume) rate of flow, Q , is then related to the viscosity by Poiseuille's equation:

$$Q = \frac{P r^4}{8 \eta l}$$

where P is the pressure difference maintaining the flow, r and l are the radius and length of the Capillary and η is the viscosity of the liquid.

Relative Viscosity

Defined as the viscosity of a polymer solution divided by that of the pure solvent and for dilute solutions:

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0}$$

where t is the time taken for a volume V of solution (no subscript) or solvent (subscript 0) to flow between the marks.

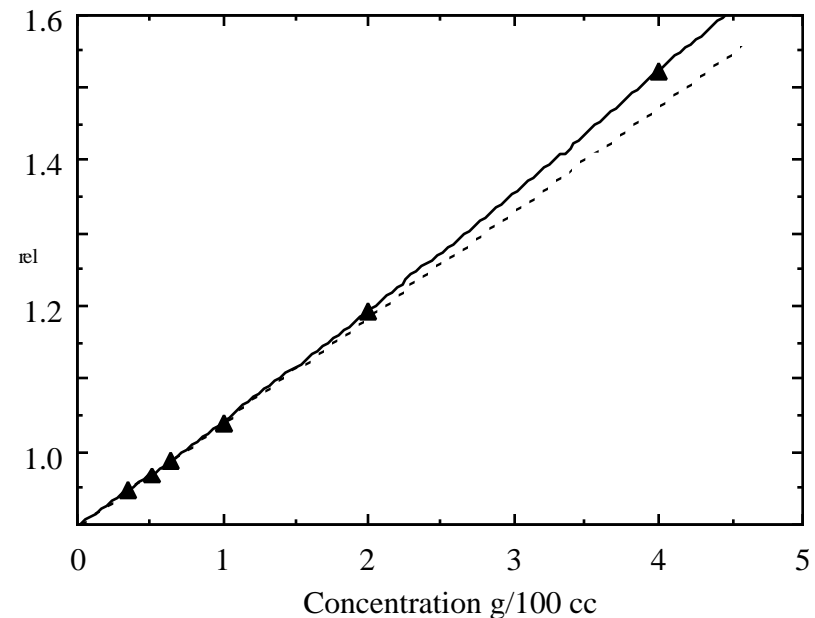
Relative Viscosity as a Function of Concentration

A power series, similar to that used in the treatment of osmotic pressure and light scattering data, is commonly used to fit relative viscosity data:

$$\eta_{rel} = \frac{\eta}{\eta_0} = 1 + [\eta]c + kc^2 + \dots$$

Both $[\eta]$ and k are constants.

$[\eta]$ is called the *intrinsic viscosity*



Plot of η_{rel} versus c for PMMA in chloroform.
Plotted from the data of G. V. Schultz and F. Blaschke.

If viscosity measurements are confined to dilute solution, so that we can neglect terms in c^2 and higher:

$$\left(\frac{\eta_{rel} - 1}{c} \right) = \frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) = [\eta] + kc$$

The *Specific Viscosity* is defined as: $\eta_{sp} = \eta_{rel} - 1$

Note also that as c goes to zero (infinite dilution), then the intercept on the y-axis of a plot of (η_{sp}/c) against c is the intrinsic viscosity, $[\eta]$:

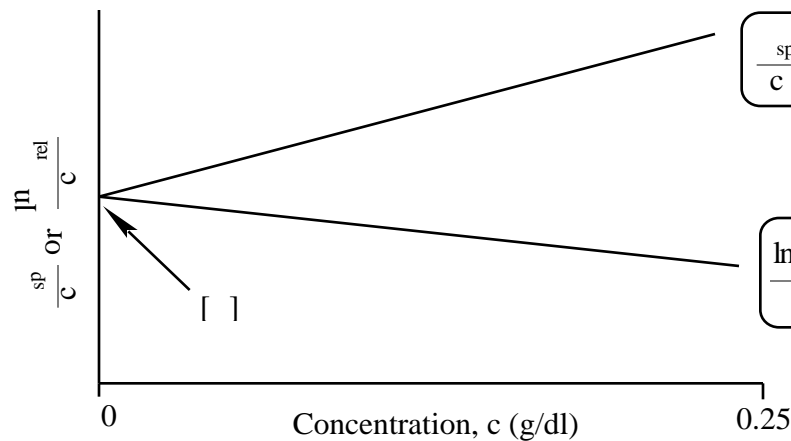
$$[\eta] = \left(\frac{\eta_{sp}}{c} \right)_{c \rightarrow 0}$$

MEASURING THE INTRINSIC VISCOSITY

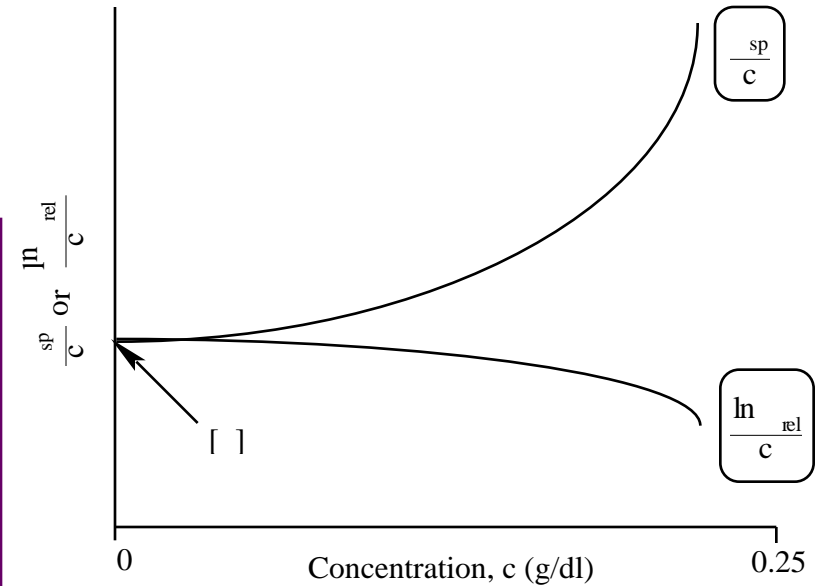
In practice, we use two semi-empirical equations suggested by Huggins and Kraemer

$$\frac{sp}{c} = [\eta] + k'[\eta]^2 c$$

$$\frac{\ln_{rel}}{c} = [\eta] + k''[\eta]^2 c$$



Schematic diagram illustrating the graphical determination of the intrinsic viscosity.



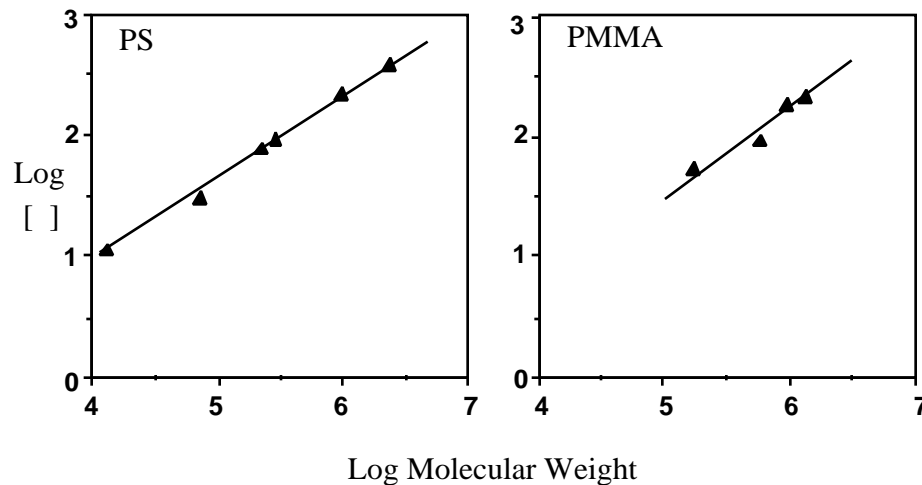
Schematic diagram illustrating the effect of strong intermolecular interactions.

THE MARK-HOUWINK-SAKURADA EQUATION

The Relationship Between Intrinsic Viscosity and Molecular Weight

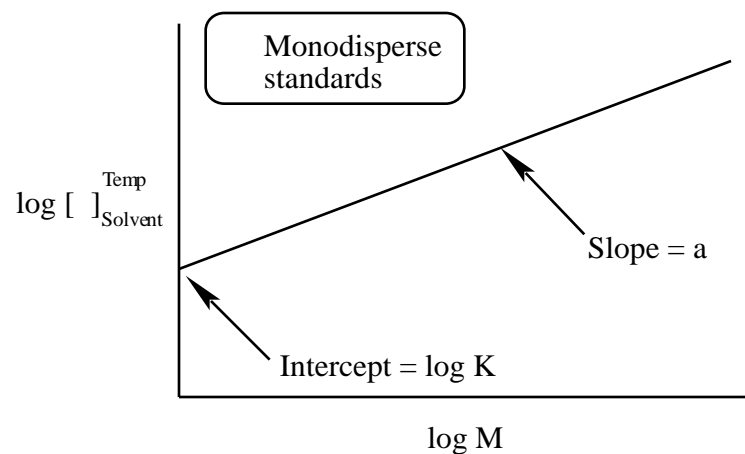
If the log of the intrinsic viscosities of a range of sample is plotted against the log of their molecular weights, then linear plots are obtained that obey equation:

$$[\eta] = KM^a$$



Plots of the log $[\eta]$ versus log M for PS and PMMA.
Replotted from the data of Z. Grubisic, P. Rempp and H. Benoit

Schematic diagram of the Determination of the Mark-Houwink-Sakurada constants K and " a ".



Note that K and " a " are not universal constants, but vary with the nature of the polymer, the solvent and the temperature.

THE VISCOSITY AVERAGE MOLECULAR WEIGHT

For Osmotic Pressure and Light Scattering we saw that there is a clear relationship between experimental measurement and the number and weight molecular weight average, respectively. Viscosity measurements are related to molecular weight by a semi-empirical relationship and a new average, the Viscosity Average for polydisperse polymer samples is defined.

In very dilute solutions $\eta_{sp} = \sum_i (\eta_{sp})_i$

Now: $\frac{(\eta_{sp})_i}{c_i} = K M_i^a$ Hence: $\eta_{sp} = K \sum_i M_i^a c_i$ And: $[\eta] = \frac{\eta_{sp}}{c} = \frac{K \sum_i M_i^a c_i}{c}$

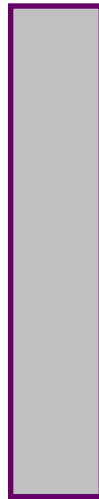
By substitution and rearranging we obtain:

$$\bar{M}_v = \left[\frac{\sum_i N_i M_i^{(a+1)}}{\sum_i N_i M_i} \right]^{\frac{1}{a}}$$

Note that the Viscosity Molecular Weight is Not an Absolute Measure as it is a function of the solvent through the Mark-Houwink parameter "a".

FRACTIONATION

POLYMER SOLUTION



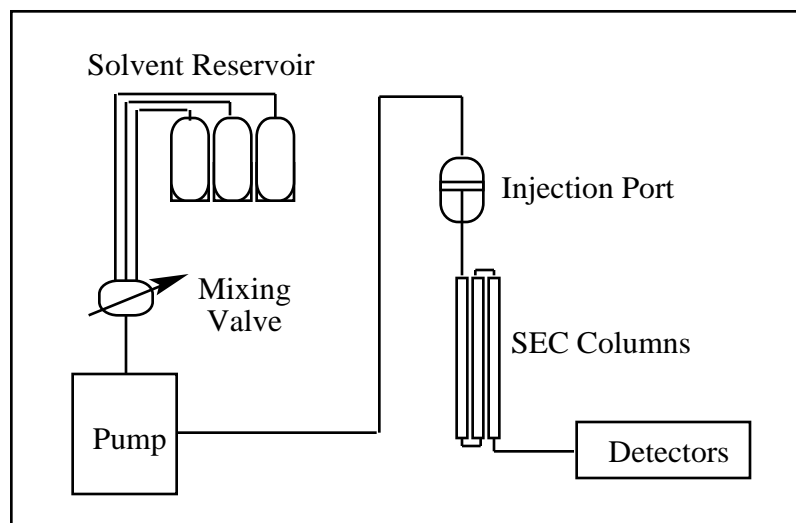
COLUMN



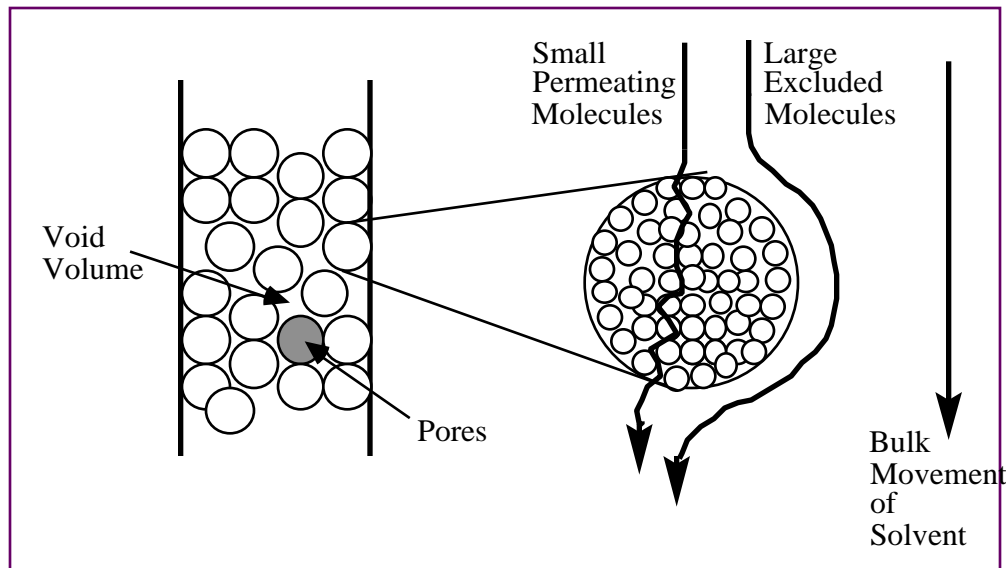
Collect fractions.
Measure how much
Polymer is in each
fraction

SIZE EXCLUSION (OR GEL PERMEATION) CHROMATOGRAPHY

Schematic diagram of an SEC instrument.



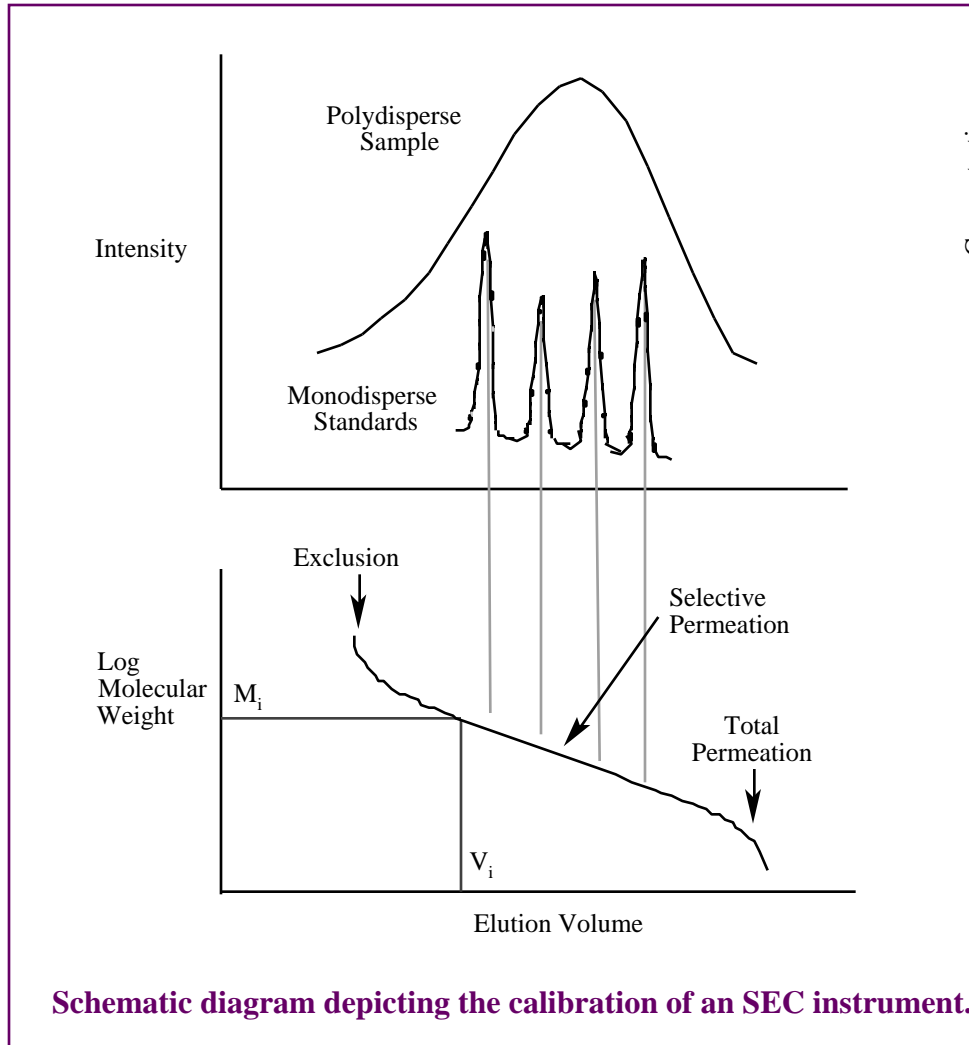
Schematic diagram depicting the separation of molecules of different size by SEC.



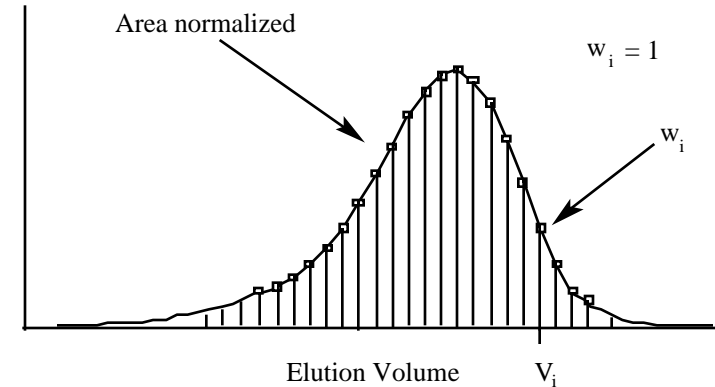
For a given volume of solvent flow, molecules of different size travel different pathlengths within the column. The smaller ones travel greater distances than the larger molecules due to permeation into the molecular maze. Hence, the large molecules are eluted first from the column, followed by smaller and smaller molecules.

THE CALCULATION OF MOLECULAR WEIGHT BY SEC

The Simplest Case where Monodispersed Standards of the Polymer are Available



Schematic diagram depicting the calibration of an SEC instrument.



$$w_i = \frac{h_i}{h_i}$$

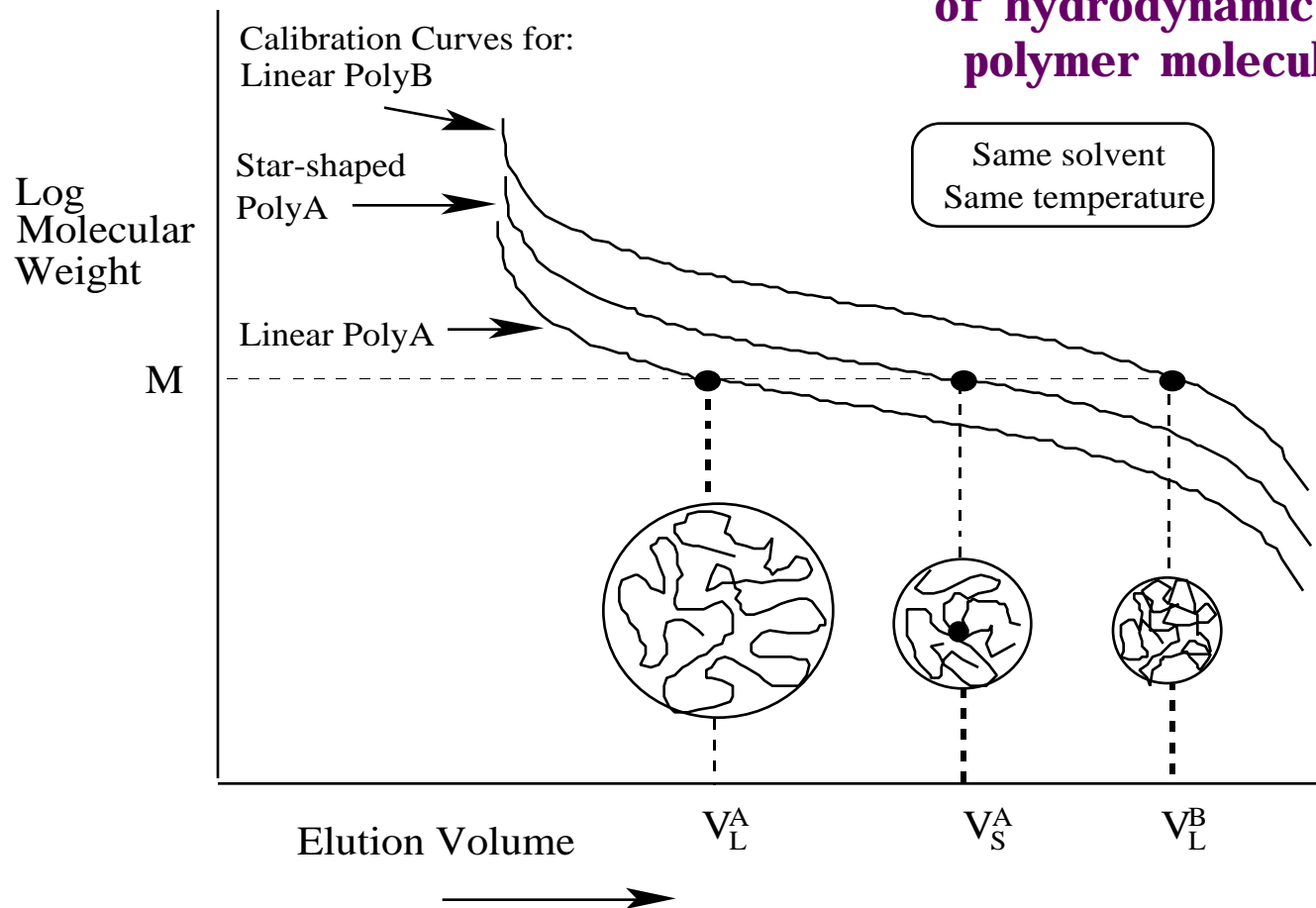
$$\bar{M}_w = \sum w_i M_i$$

$$\bar{M}_n = \frac{1}{\sum \frac{w_i}{M_i}}$$

$$[\eta] = \sum w_i [\eta_i] = K \sum w_i M_i^a$$

HOW DOES SEC SEPARATE MOLECULES ?

Benoit and his coworkers recognized that SEC separates not on the basis of molecular weight but rather on the basis of hydrodynamic volume of the polymer molecule in solution.



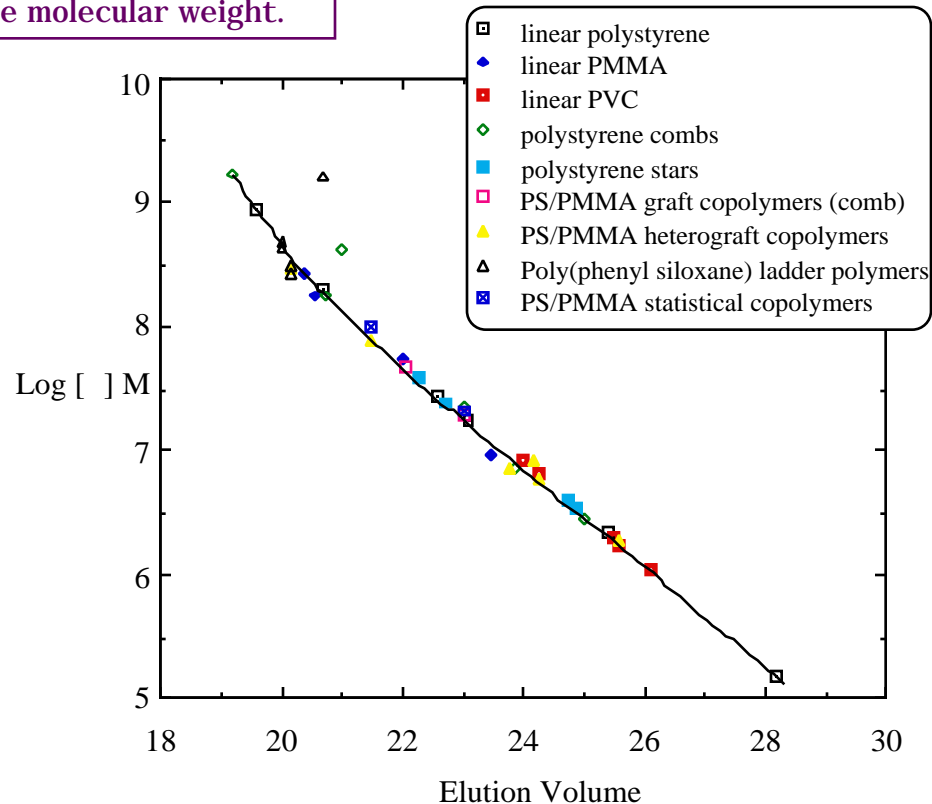
The Universal Calibration Curve

If we model the properties of the polymer coil in terms of an equivalent hydrodynamic sphere, then the intrinsic viscosity, $[\eta]$, is related to the hydrodynamic volume V_h via the equation:

$$[\eta] = \frac{2.5 A V_h}{M}$$

A is Avogadro's number and M is the molecular weight.

Benoit and his coworkers recognized that the product of intrinsic viscosity and molecular weight was directly proportional to hydrodynamic volume.



A universal calibration plot of $\log [\eta]M$ vs elution volume for various polymers. Redrawn from the data of Z. Grubisic, P. Rempp and H. Benoit.