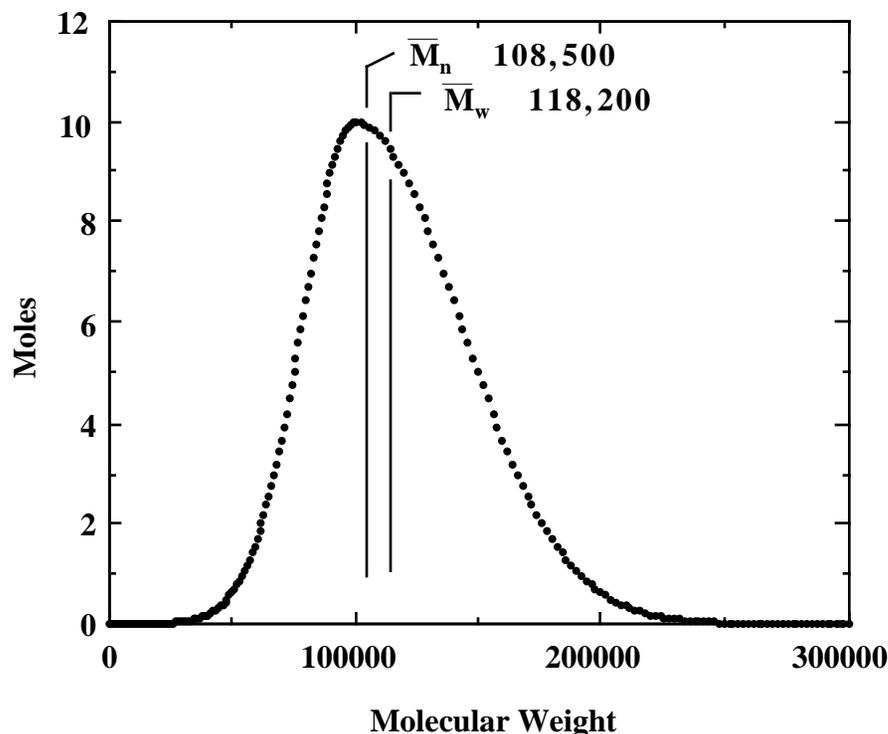


# Molecular Weight and Branching

## Definitions



### Number Average

$$\bar{M}_n = \frac{\sum N_x M_x}{\sum N_x}$$

### Weight Average

$$\bar{M}_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

*"Drop the idea of large molecules.  
Organic molecules with a molecular  
weight higher than 5000 do not exist."  
—Advice given to Hermann Staudinger*

## Methods for the Determination of Molecular Weight

### Number Average—Absolute methods

End group analysis  
Lowering of vapor pressure  
Ebulliometry (elevation of boiling point)  
Cryoscopy (depression of freezing point)  
Osmometry (osmotic pressure)

### Weight Average—Absolute methods

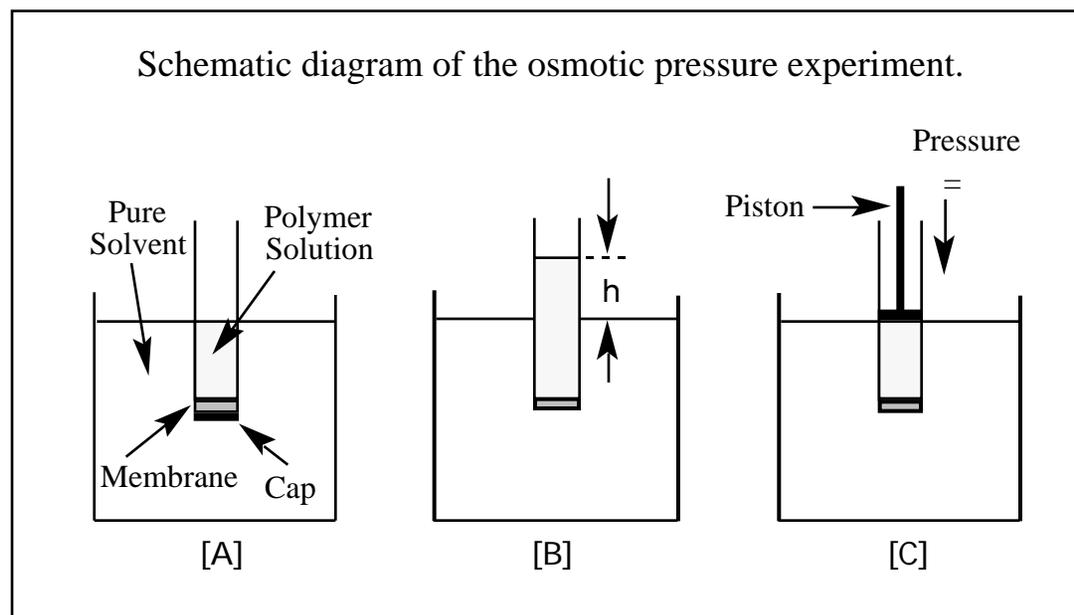
Light scattering  
Neutron scattering  
Ultracentrifugation

### Relative methods

Solution Viscometry  
Size Exclusion Chromatography

# Osmotic Pressure

Osmotic pressure—belongs to a family of techniques that come under the heading of *colligative property measurements*.



# Osmotic Pressure

## Analogy to Ideal Gases and Virial Equations

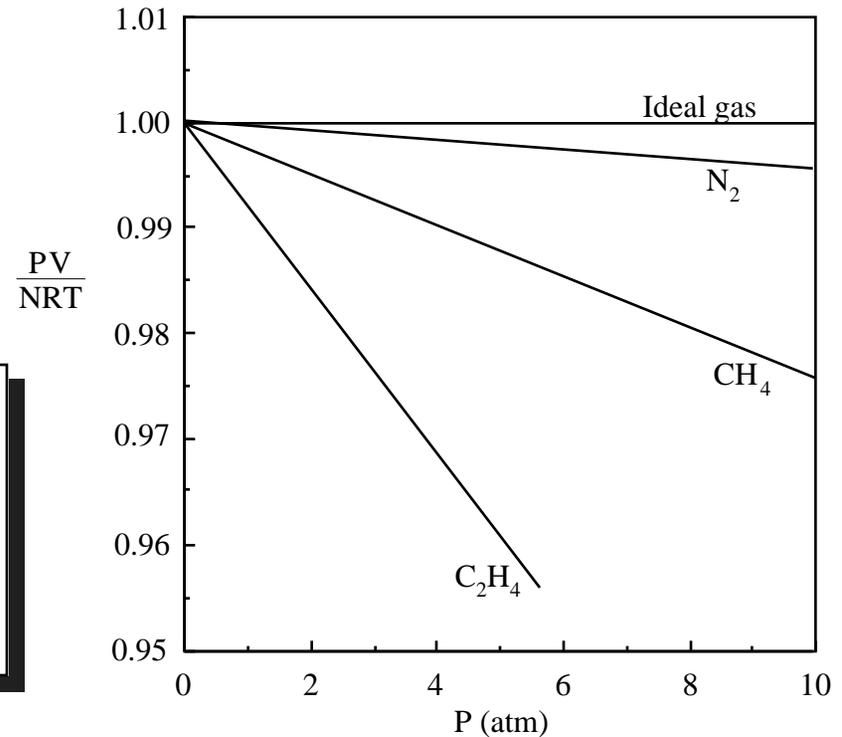
### The Ideal Gas Law

$$\text{or } \frac{PV}{NRT} = 1$$

### The Idea of Virial Equations

$$\frac{PV}{NRT} = 1 + B'P + C'P^2 + D'P^3 + \text{-----}$$

The coefficients B', C', D', etc., are the second, third, fourth, etc., *virial coefficients*.



Schematic plots of  $PV/NRT$  versus  $P$ .

### Relationship to Molecular Weight

$$P \frac{V}{N} = RT$$

and

$$\frac{N}{V} = \frac{\text{\# moles}}{\text{volume}} = \frac{w}{M} \frac{1}{V} = \frac{c}{M}$$

Hence:

$$\frac{P}{c} = \frac{RT}{M}$$

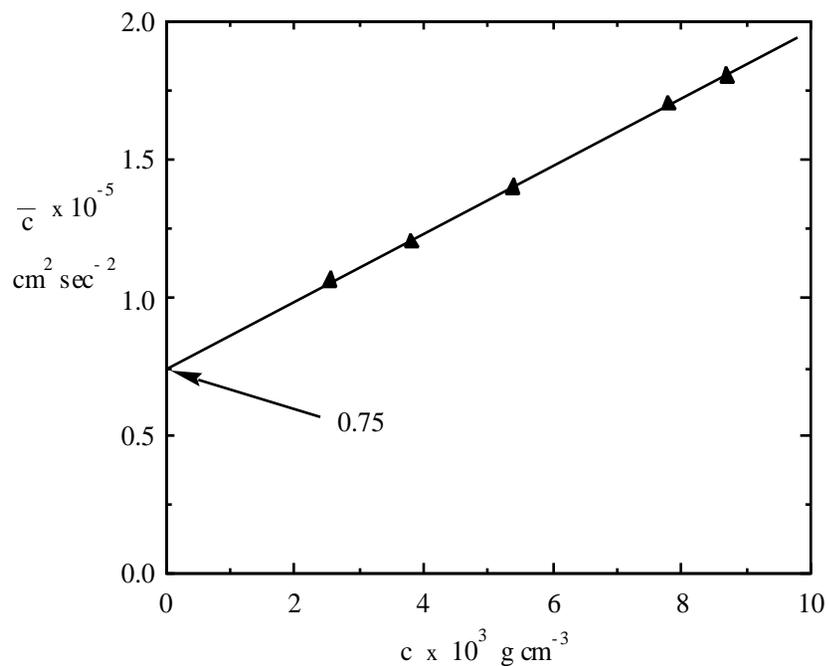
# Osmotic Pressure

**Ideal Solution**

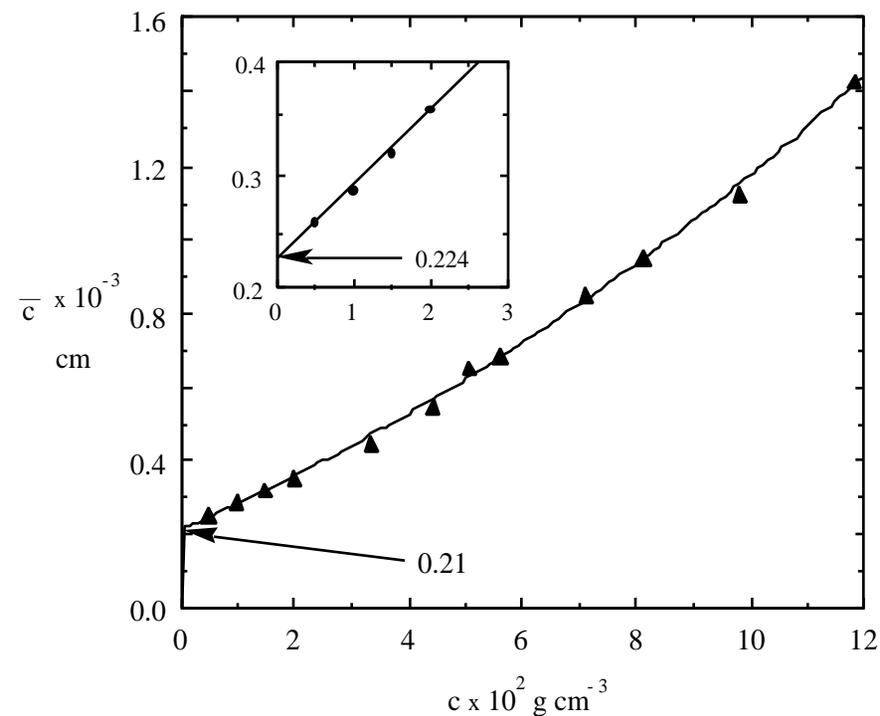
$$\frac{\pi}{c} = \frac{RT}{M}$$

**Not So Ideal Solution**

$$\frac{\pi}{c} = \frac{RT}{M_n} + Bc + Cc^2 + Dc^3 + \dots$$



Graph of  $\pi/c$  versus  $c$  for polystyrene in toluene.



Graph of  $\pi/c$  versus  $c$  for polyisobutylene in chlorobenzene.

# Osmotic Pressure

## Derivation of a Virial Equation from the Flory–Huggins Equation

Osmotic Pressure can be related to the chemical potential via the Flory–Huggins equation:

$$\frac{\mu_s - \mu_s^0}{RT} = \ln \phi_s + \left(1 - \frac{1}{M_n}\right) \phi_p + \frac{2}{p}$$

and:

$$= -\frac{RT}{V_s} \left[ \ln \phi_s + \phi_p \left(1 - \frac{1}{M_n}\right) + \frac{2}{p} \right]$$

Expanding the Ln term:

$$\ln \phi_s = \ln \left(1 - \phi_p\right) = -\phi_p - \frac{\phi_p^2}{2} - \frac{\phi_p^3}{3} - \dots$$

Leads to:

$$= \frac{RT}{V_s} \left[ \frac{\phi_p}{M_n} + \phi_p \left(\frac{1}{2} - \right) + \frac{\phi_p^3}{3} + \dots \right]$$

This has the same form as the virial equation, but uses the concentration variable  $\phi_p$  instead of  $c$ . However, we must be careful because the Flory-Huggins theory does not strictly apply to dilute solutions.

# Light Scattering

Looks fiendishly difficult because of all the equations, but the *Crucial Point* is that we end up with a *Virial Equation* similar to that used *Osmometry*

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

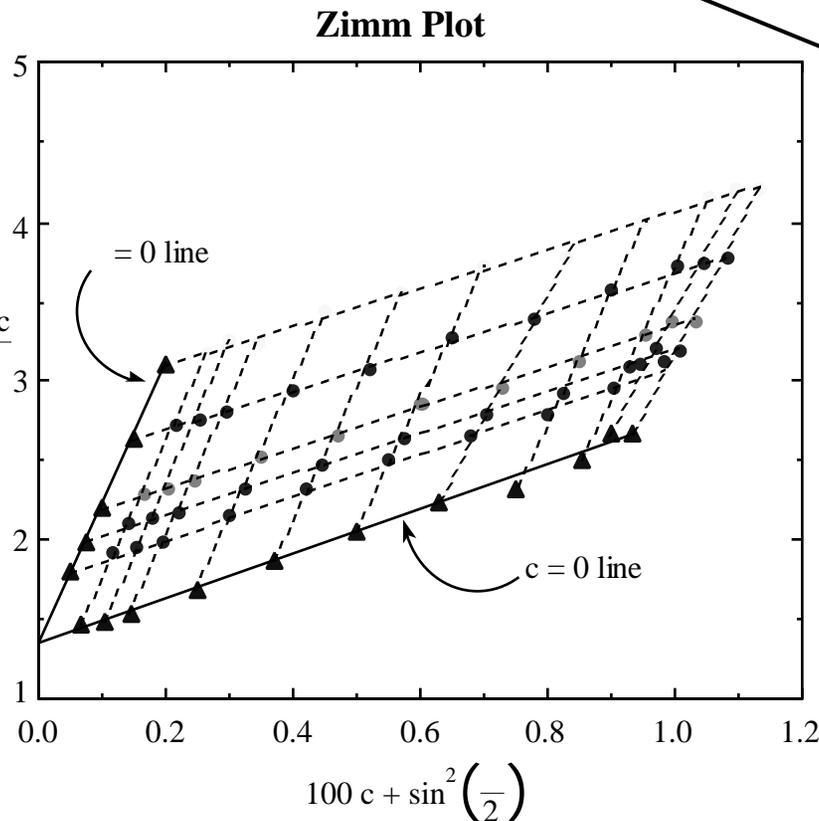
Experimentally measured parameters

Dependence upon angle of observation

Note:  
Weight Average  
Molecular Weight

Virial  
Expansion

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



Double extrapolation

$$c \quad 0$$

$$\theta \quad 0$$

# Measuring the Viscosity of Polymer Solutions

Most common method used to determine the viscosity of a polymer solution is to 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  $\eta$  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.

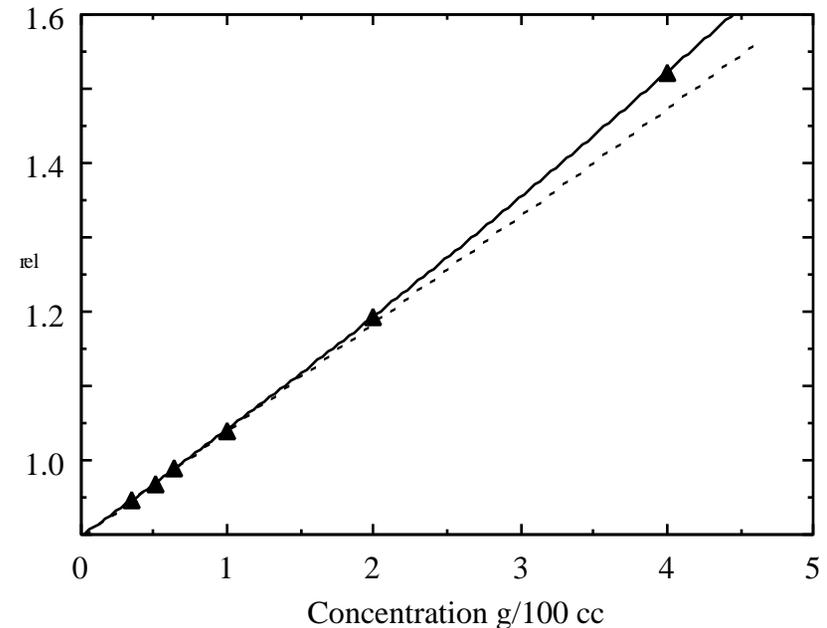
## Relative Viscosity as a Function of Concentration

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  $\eta_{rel}$  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  $c^3$  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  $(\eta_{sp}/c)$  against  $c$  is the intrinsic viscosity,  $[\eta]$ :

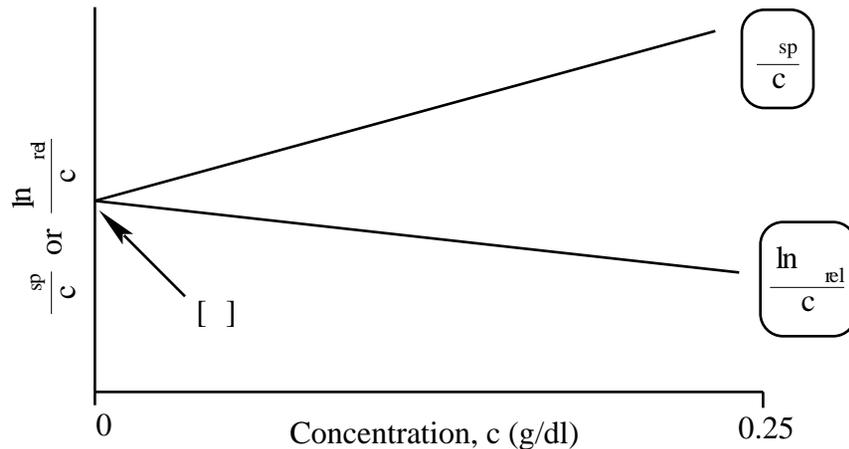
$$[\eta] = \left( \frac{\eta_{sp}}{c} \right)_{c \rightarrow 0}$$

# Measuring the Intrinsic Viscosity

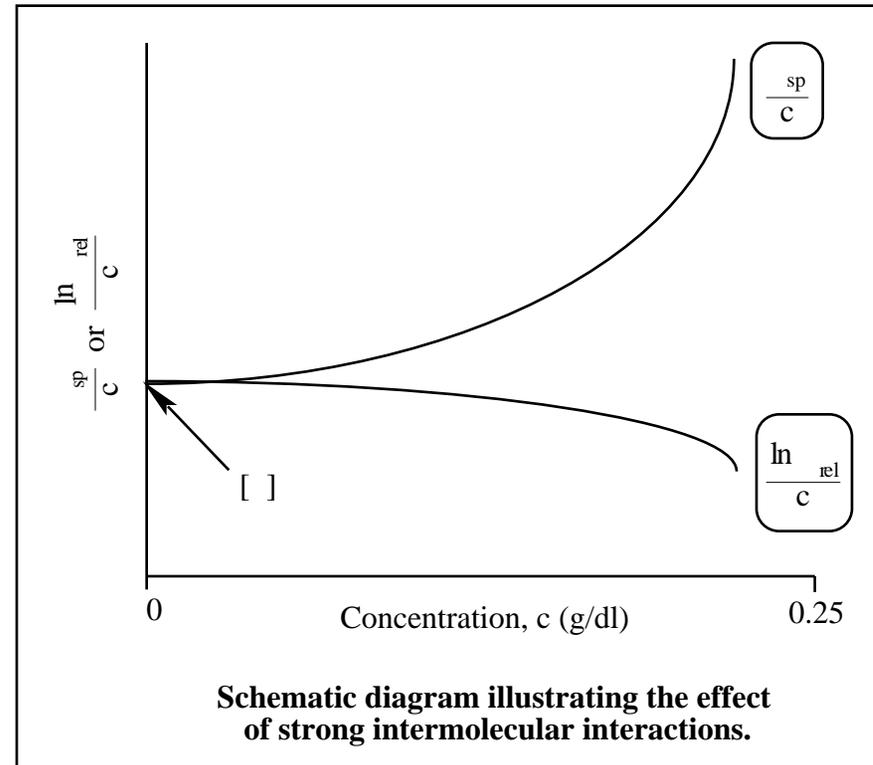
In practice, we use two semi-empirical equations suggested by Huggins and Kraemer

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

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



Schematic diagram illustrating the graphical determination of the intrinsic viscosity.



Schematic diagram illustrating the effect of strong intermolecular interactions.

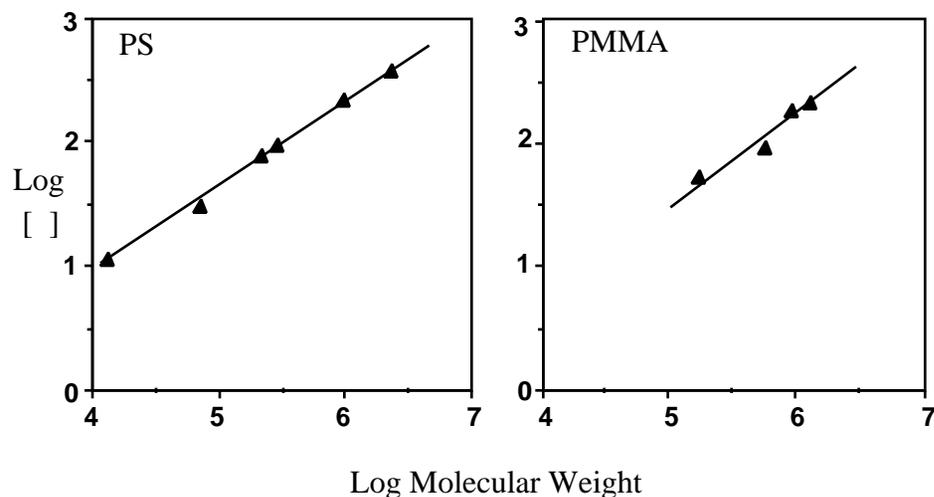
Most "extrapolation to zero concentration" procedures have a serious limitation. Where one would like to perform measurements is at the lowest concentrations possible, but this is generally where the greatest error in measurement occurs.

# The Mark-Houwink-Sakurada Equation

## The Relationship Between Intrinsic Viscosity and Molecular Weight

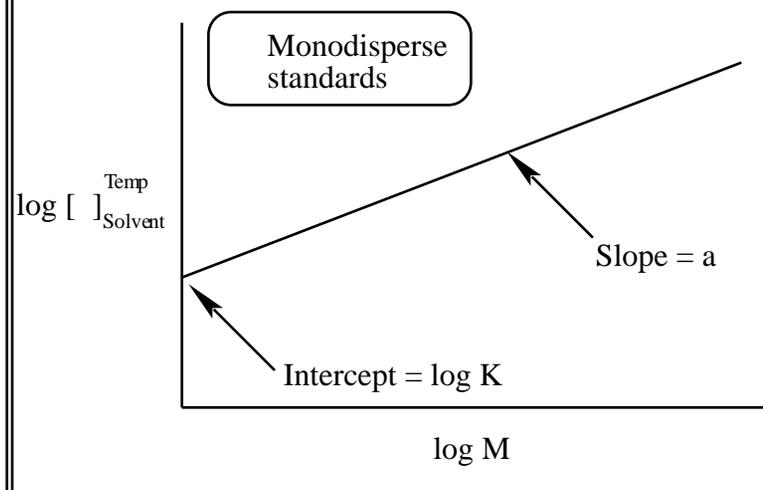
If the log of the intrinsic viscosities of a range of samples is plotted against the log of their molecular weights, then linear plots are obtained that obey equation:

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



Plots of the log [η] 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:  $[\eta] = \frac{\eta_{sp}}{c} = \frac{K \sum_i M_i^a c_i}{c}$

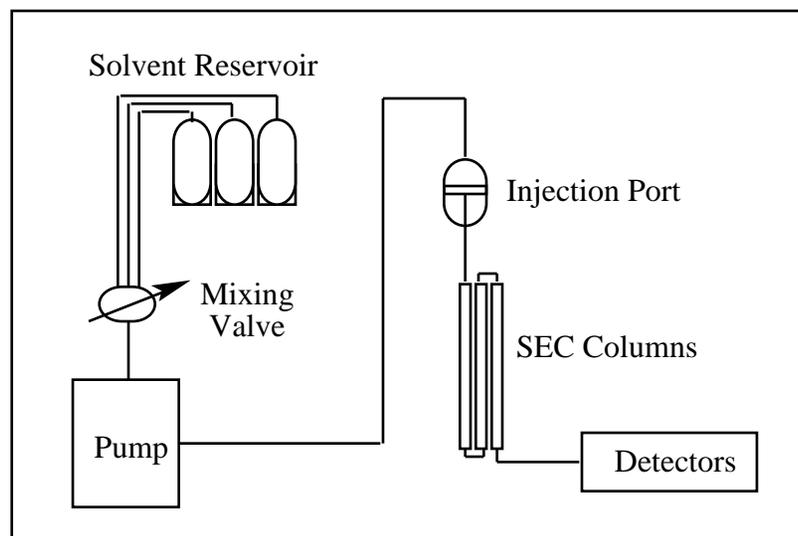
By substitution and rearranging we obtain:

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

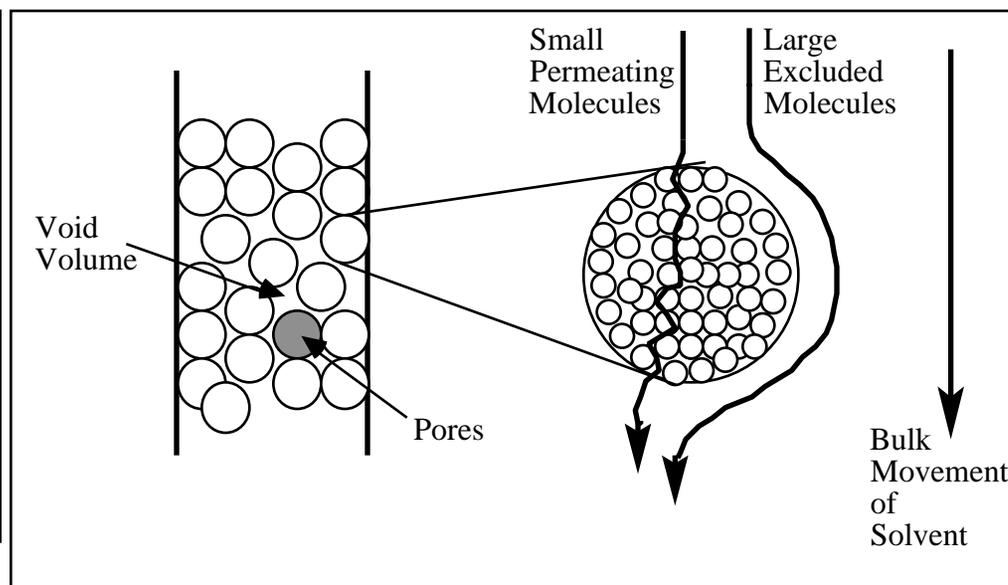
Note that the Viscosity Molecular Weight is **Not** an Absolute Measure as it is a function of the solvent through the Mark-Houwink parameter "a".

# Size Exclusion (or Gel Permeation) Chromatography

Schematic diagram of an SEC instrument.



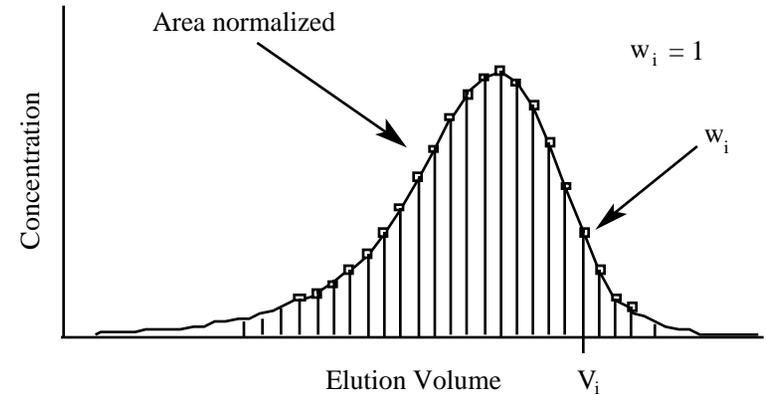
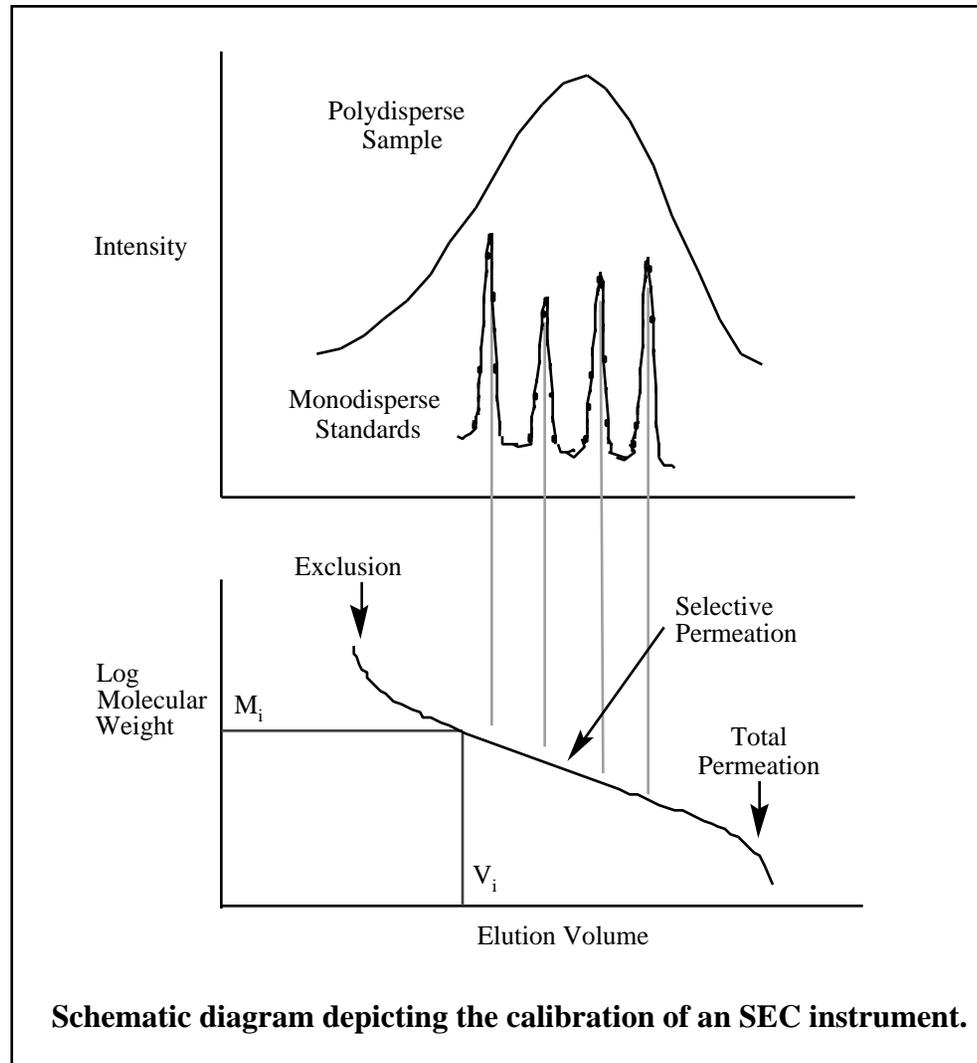
Schematic diagram depicting the separation of molecules of different size by SEC.



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



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

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

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

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

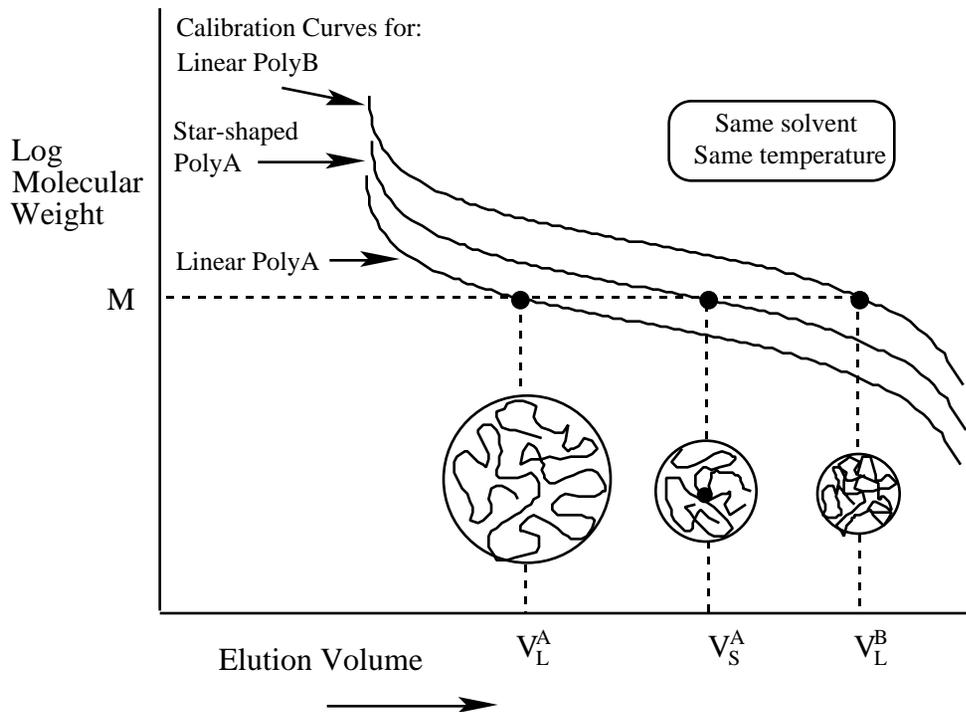
## How Does SEC Separate Molecules ?

If the molecular weight of monodisperse polystyrenes of different molecular architecture (e.g., linear, star-shaped, comb-like, etc.) are plotted against elution volume they do not fall on a single calibration curve.

In other words, if we had three *monodisperse* polystyrenes, one linear, one star-shaped and one comb-like, all with the same molecular weight, they would not come off the column at the same time (elution volume).

Similarly, *different* monodisperse polymers of the same molecular weight generally elute at different times. Thus, for example, monodisperse samples of polystyrene and PMMA having the same molecular weight might come off the column at different times.

In effect, this means we would require different calibration curves for different polymers and even the same type of polymer if the architecture is different.



**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.**

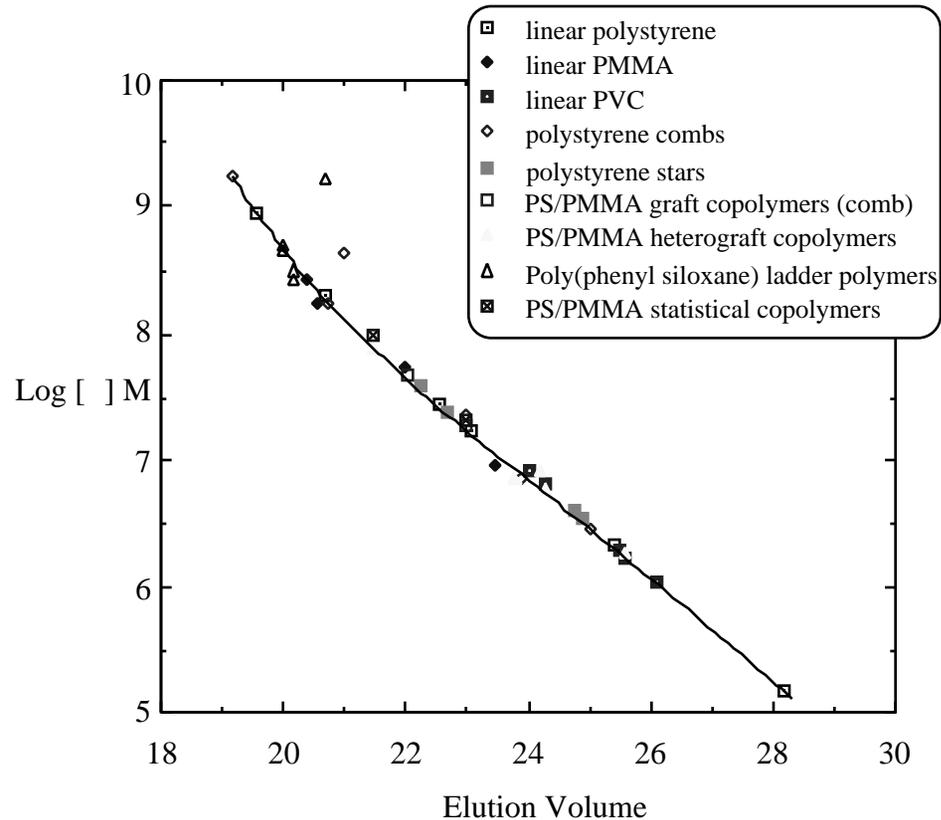
# The Universal Calibration Curve

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.



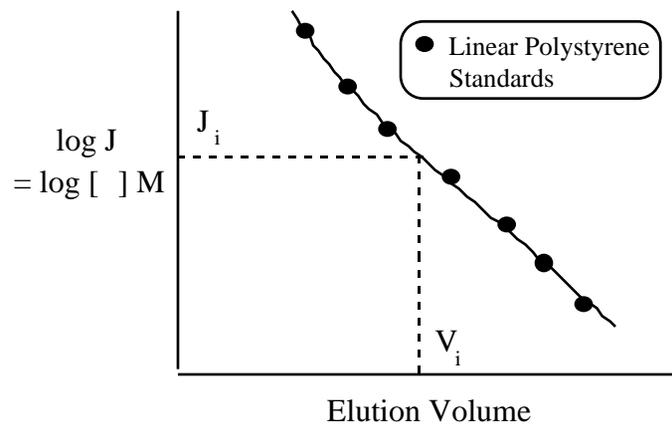
A universal calibration plot of  $\log [\eta]M$  vs elution volume for various polymers.  
Redrawn from the data of Z. Grubisic, P. Rempp and H. Benoit.

# The Calculation of Molecular Weight by SEC

## The Universal Calibration Method

Define:  $J_i = [\eta]_i M_i$

A universal calibration curve is prepared using e.g. monodisperse polystyrene standards



Schematic of a universal calibration plot prepared from linear PS standards.

Note: we can simply calculate the intrinsic viscosity if we can obtain the Mark-Houwink-Sakurada constants,  $K_{PS}$  and  $a_{PS}$ , from the literature for polystyrene in the same solvent at the same temperature as the SEC experiment.

$$J_i = [\eta]_i M_i = K_{PS} [M_i]^{(1 + a_{PS})}$$

Rearranging:  $M_i = \left[ \frac{J_i}{K_{PS}} \right]^{1 / (1 + a_{PS})}$

Important result because it relates the molecular weight of the  $i$ th species to the hydrodynamic volume of that species

Let us assume that the SEC data was obtained from a polydisperse sample of PMMA on an SEC instrument using the same solvent and temperature that was used to prepare the universal calibration curve from PS standards.

If we have  $K$  and "a" for PMMA in the same solvent and temperature then the "true" molecular weights for the polydisperse PMMA may be calculated from:

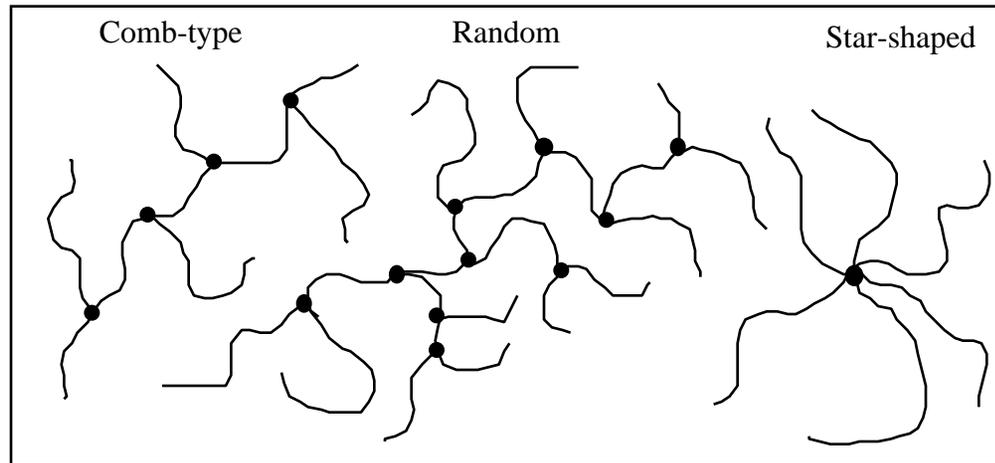
$$M_i = \left[ \frac{J_i}{K_{PMMA}} \right]^{1 / (1 + a_{PMMA})}$$

And:

$$\overline{M}_w = \sum w_i M_i \quad \overline{M}_n = \frac{1}{\sum \frac{w_i}{M_i}}$$

$$[\eta] = \sum w_i [\eta]_i = \sum w_i \left( \frac{J_i}{M_i} \right)$$

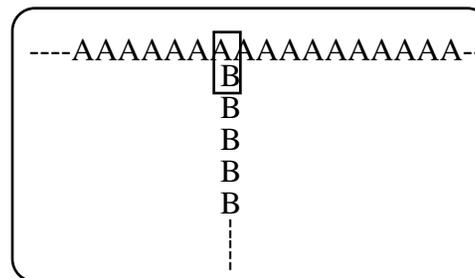
# Long Chain Branching



Schematic representation of different long chain branches.

Long chain branching can have a major effect upon the rheological and solution properties of polymers. Difficult to quantitatively determine the amount of long chain branching using conventional analytical techniques, such as NMR or vibrational spectroscopy.

Very low concentration of any species that can be attributed to the presence of a long chain branch.



# Long Chain Branching and Mean Square Dimensions

The introduction of only one or two long chain branch points leads to a significant decrease in the mean-square dimensions of macromolecules compared to linear molecules of the *same molecular weight*.

This statement may be expressed in terms of the ratio of the respective radii of gyration,  $g$ .

B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, 17, 1301 (1949).

B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, 37, 19 (1959).

$$g = \frac{\langle \bar{S}^2 \rangle_b}{\langle \bar{S}^2 \rangle_l} \quad (\text{for the same molecular weight})$$

Subscripts  $b$  and  $l$  denote branched and linear molecules

$g$  is a function of the *number and type* of long chain branch points in the molecule.

**For Star Shaped Polymers**  
(Functionality  $f$  and Equal Arm Length)

$$g = \frac{3}{f} - \frac{2}{f^2}$$

**For Randomly Branched Monodisperse Polymers**  
(Tetrafunctional)

$$g_4 = \left[ \left( 1 + \frac{\bar{m}_n}{6} \right)^{1/2} + \frac{4 \bar{m}_n}{3} \right]^{-1/2}$$

$\bar{m}_n$  is the number average number of branch points per molecule

# Long Chain Branching—Relation to Intrinsic Viscosity

$g$ , the ratio of the radii of gyration of the branched to linear polymer chain of the *same molecular weight*, is related to the intrinsic viscosity by a branching function,  $g'$  :

$$g' = \frac{[\eta]_b}{[\eta]_l} \quad (\text{for the same molecular weight})$$

**For Star Shaped Polymers**  
(Theoretical Relationship)

$$g' = g^{0.5}$$

**For Randomly Branched Monodisperse Polymers**  
(Empirical Relationship-Kurata et al.)

$$g' = g^{0.6}$$

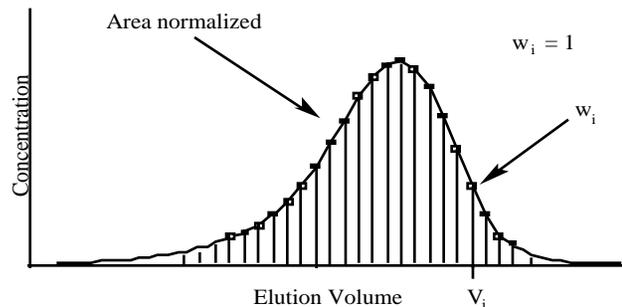
The experimentally determined intrinsic viscosity of a branched polymer will be less than that calculated from the SEC data using the universal calibration curve (which assumes that the polymer chains are perfectly linear).

An appropriate branching function,  $g'(\eta, M)$  that contains a branching parameter,  $a$ , is defined such that:

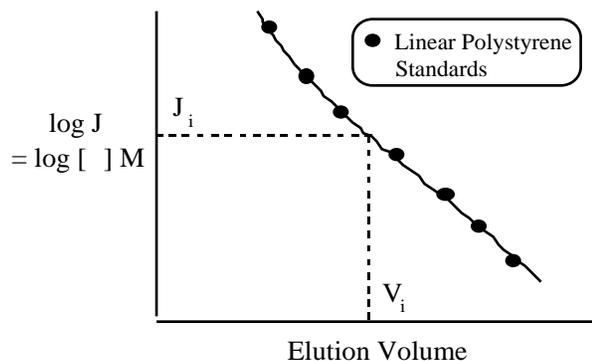
$$[\eta]_b = g'(\eta, M) [\eta]_l = g'(\eta, M) KM^a$$

# SEC and the Determination of Long Chain Branching – I

Lets say this SEC is from a randomly tetrafunctionally branched polydisperse polychloroprene (PC)



Using the universal calibration curve calculate the  $[\eta]$  assuming the polychloroprene is linear



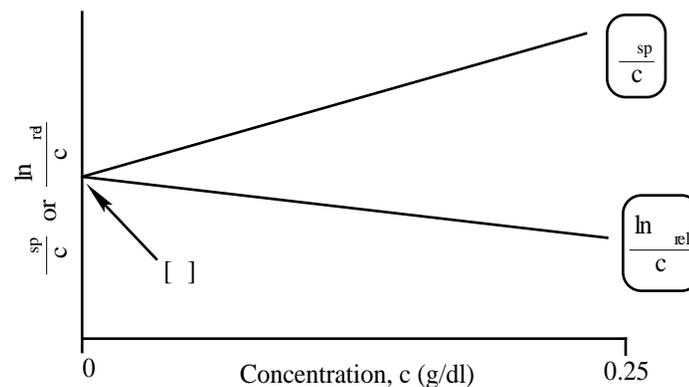
If K and "a" are known for linear PC, then:

$$M_i = \left[ \frac{J_i}{K_{PC}} \right]^{1 / (1 + a_{PC})}$$

And the theoretical  $[\eta]$  for the polydisperse PC assuming it is linear is given by:

$$[\eta] = \sum w_i [\eta]_i = \sum w_i \left( \frac{J_i}{M_i} \right)$$

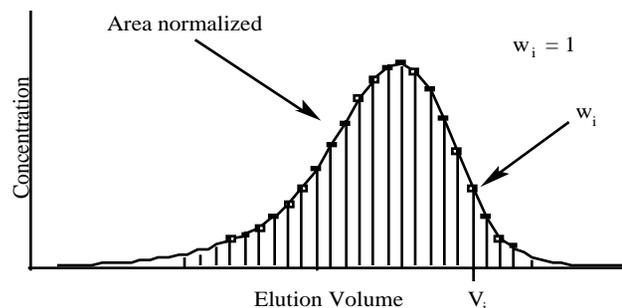
Experimentally determine  $[\eta]$  for the polydisperse PC



The experimentally measured  $[\eta]$  will be *less than* that calculated for a *distribution of linear PC chains*  
*This is the key to a measure of Long Chain Branching*

# SEC and the Determination of Long Chain Branching – II

The same SEC is from a randomly tetrafunctionally branched polydisperse polychloroprene (PC)



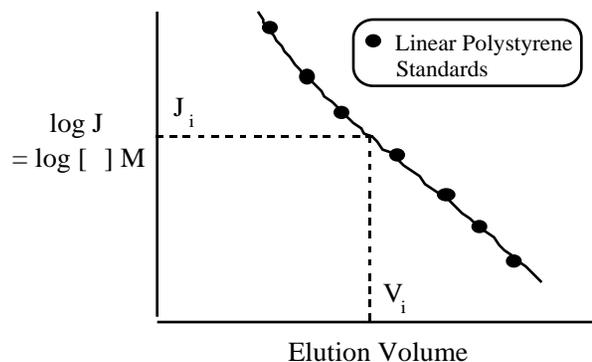
$M_i$  now has to be determined iteratively from:

$$J_i = K M_i^{(1+a)} \left[ \left( 1 + \frac{M_i}{6} \right)^{0.5} + \frac{4}{3} \frac{M_i}{M_i} \right]^{-0.3}$$

And the theoretical  $[ \eta ]$  for the polydisperse PC assuming it is randomly branched with a given value of  $a$  is given by:

$$[ \eta ]_b = K \sum_i w_i M_i^a \left[ \left( 1 + \frac{M_i}{6} \right)^{0.5} + \frac{4}{3} \frac{M_i}{M_i} \right]^{-0.3}$$

Now use the universal calibration curve calculate  $[ \eta ]$  assuming a value of the branching parameter,  $a$



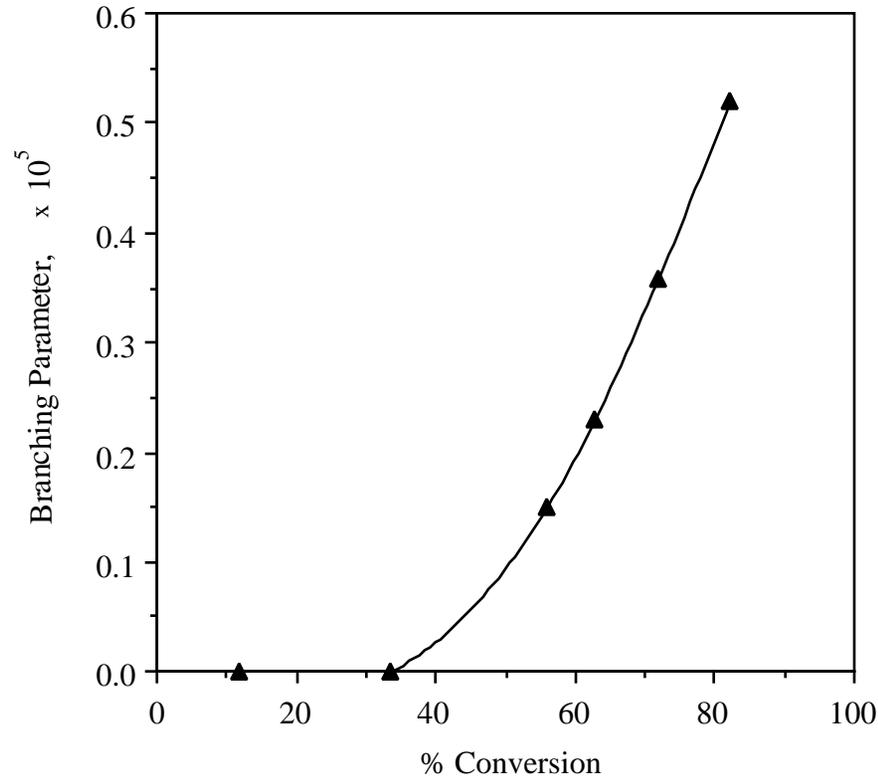
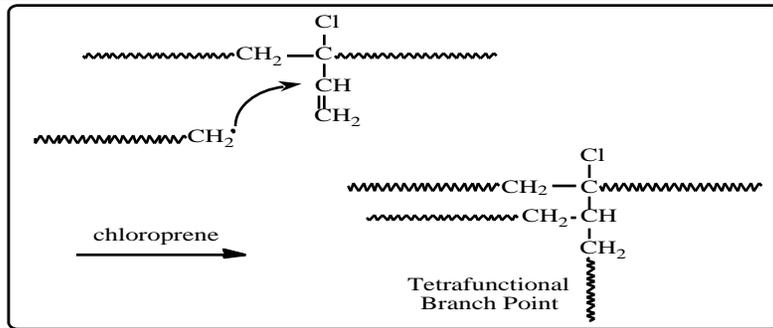
This theoretical value of  $[ \eta ]$  is compared to the experimental  $[ \eta ]$ . The whole procedure is repeated with different values of  $a$  until:

$$[ \eta ]_{\text{calculated}} = [ \eta ]_{\text{observed}}$$

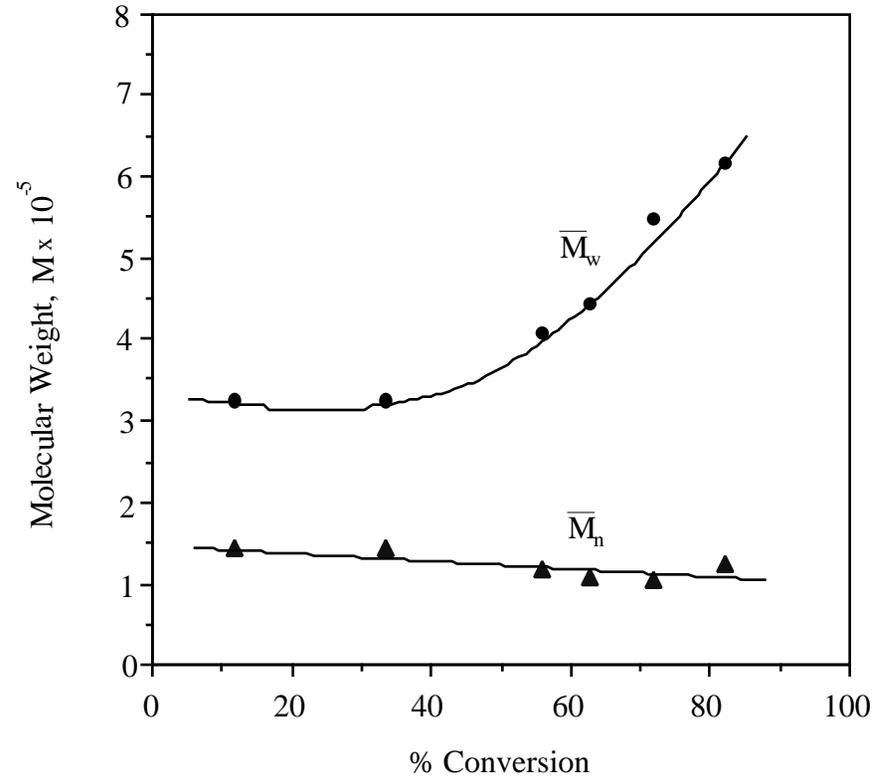
Then:

$$\overline{M}_w = \sum_i w_i M_i \quad \overline{M}_n = \frac{1}{\sum_i \frac{w_i}{M_i}}$$

# Long Chain Branching in Polychloroprene—Experimental



The branching parameter,  $\beta$ , for polychloroprene samples isolated as a function of conversion.



Calculated molecular weight averages for polychloroprene samples isolated as a function of conversion.