

MSI 04

Dilute Solution Properties

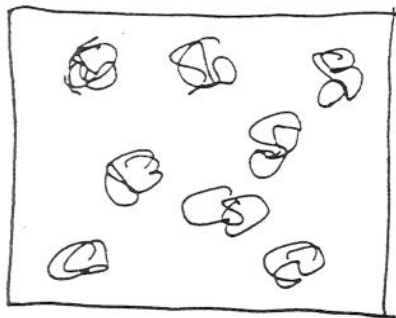
and

Molecular Characterization

Rosen Chapters VI and VII

Polymer Solutions

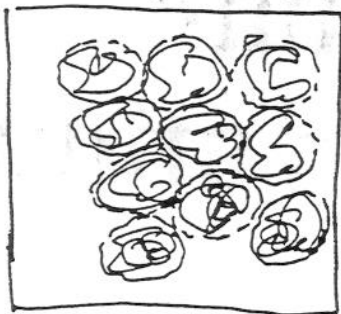
Dilute solution



$$c < c^* \quad (c^* = \frac{1}{[\eta]})$$

polymer / solvent interactions

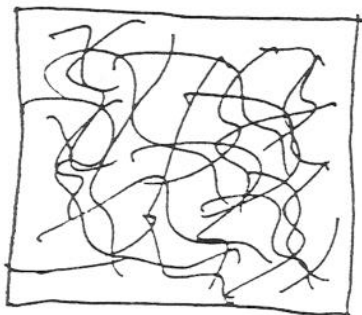
Semi-Dilute solution



$$c = c^*$$

polymer / solvent & polymer / polymer interactions

Concentrated solution \rightarrow Polymer Melt

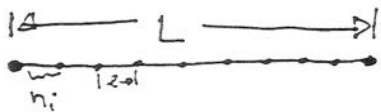


$$c \gg c^* \quad (\text{entangled})$$

- polymer / polymer interactions
- scaling concepts

Solution Viscosity of Polymer/Solvent Systems

Molecular Parameters (Flexible Polymers)



contour length $L = \sum n_i l$

$n_i = \#$ of repeat units
 $l =$ length of a repeat unit

$$L \propto M$$

$$M = \sum n_i m_0$$

↓
repeat unit weight

↓
Add solvent
(single molecule)

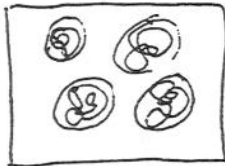


Random coil

$R_g =$ radius of gyration
 ↳ volume perturbed in solution

↓
solution
(concentration of molecules)

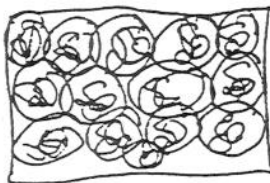
* Intrinsic Viscosity measurements



$c < c^*$ (overlap concentration)
 "dilute" regime

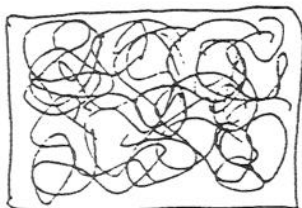
$$\eta = f(\text{solvent, Temp, polymer, concentration, } \eta_s, M)$$

↳ solvent viscosity



$c = c^*$ molecular interactions begin ("semi-dilute" regime)

$$\eta = f(\eta_s, \text{solvent/polymer, } T, c, M)$$



$c \gg c^*$ concentrated regime

$$\eta = f(\eta_s, \text{solvent/polymer, } T, c, M, \text{Entanglements})$$

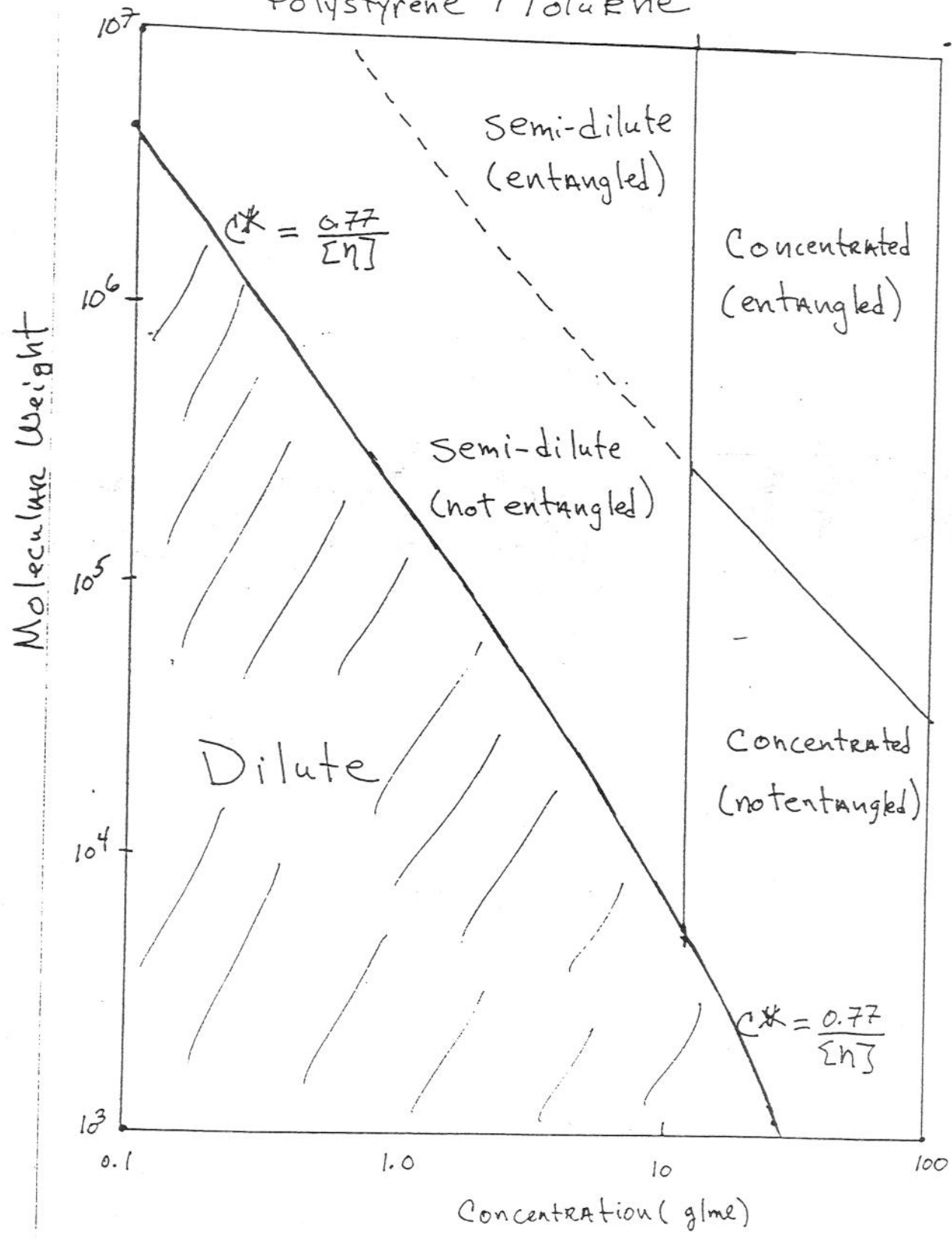
$$\eta = f(\text{Entanglements, } c, M) \quad \text{these dominate}$$

Concentration Regimes for a good solvent system.

Effect of MW on state of solution.

(W.W. Graessley, unpublished data, 19)

Polystyrene / Toluene



Dilute Solution Viscosity ($c \ll c^*$)

$$\eta = f(\eta_s, \text{solvent/polymer}, c, T, M)$$

- pick polymer, solvent, constant T

$$\eta = \text{solution viscosity} \quad \eta_s = \text{solvent viscosity}$$

→ Specific viscosity (eliminates effect of solvent viscosity)

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} = \frac{\eta}{\eta_s} - 1 = \eta_{rel} - 1$$

where $\eta/\eta_s = \eta_{rel}$ (relative viscosity)

→ reduced viscosity (normalize for concentration)

$$\eta_{red} = \eta_{sp}/c = \frac{\eta - \eta_s}{\eta_s c} = \frac{(\eta_{rel} - 1)}{c}$$

→ Intrinsic Viscosity (IV)

- eliminate concentration and entanglement effects

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{sp}/c) = \lim_{c \rightarrow 0} \frac{(\eta_{rel} - 1)}{c}$$

$$\infty \quad [\eta] = f(\text{polymer/solvent}, T, M)$$

- pick polymer/solvent system and constant T

$$[\eta] = f(M)$$

* Notes: Units of $[\eta] \Leftrightarrow \left(\frac{\text{vol}}{\text{wgt.}}\right) \Rightarrow \left(\frac{\text{ml}}{\text{g}}\right) \text{ or } \left(\frac{\text{dl}}{\text{g}}\right)$

↓
inverse
concentration

Common units



Huggins Equation (valid for $\eta_{rel} < 2$)

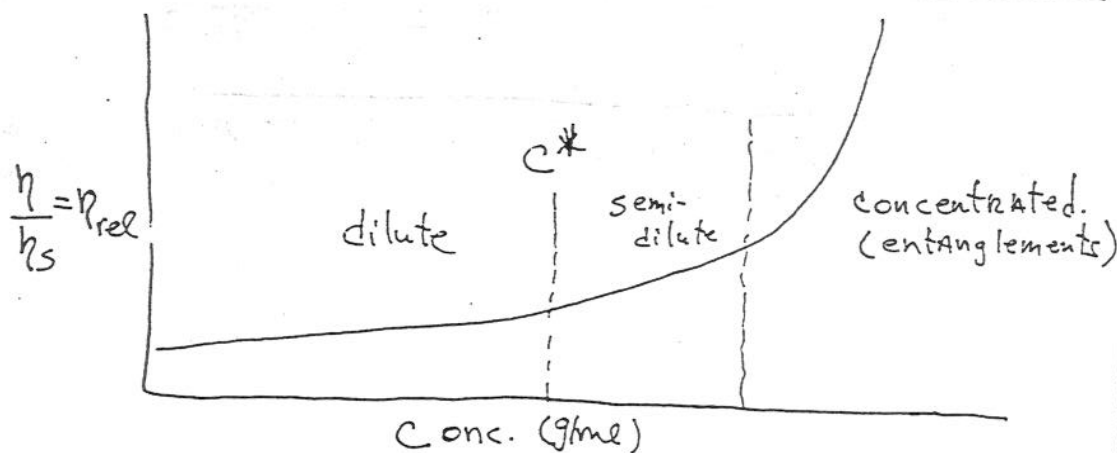
$$\frac{\eta_{sp}}{c} = [\eta] + k' [\eta]^2 c$$

where $k' \approx 0.4$ for many polymer/solvent systems

This provides a method of estimating the solution viscosity for a polymer/solvent system if IV $[\eta]$ is known.

$$\eta_{sp} = \eta_{rel} - 1 = \left(\frac{\eta}{\eta_s}\right) - 1 = [\eta]c + k' [\eta]^2 c^2$$

→ and convenient
Equivalent form for investigating Molecular Interactions



Equivalent form of Huggins Equation (expand natural log in power series)

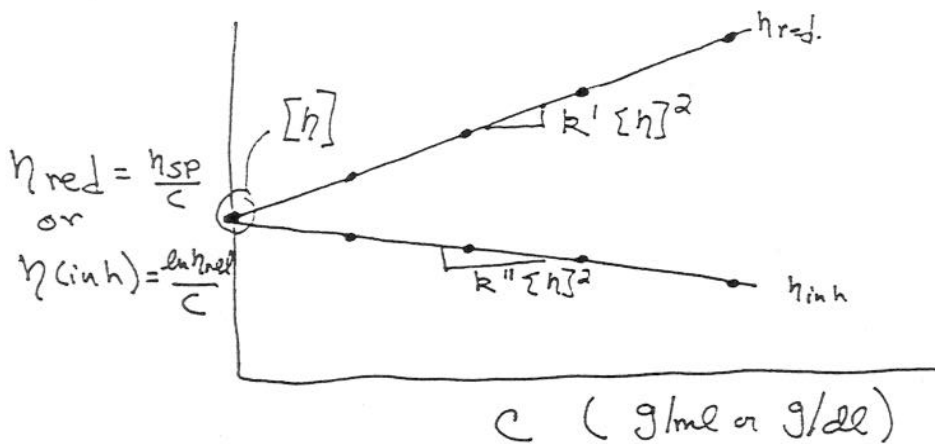
$$\eta_{inh} = \frac{\ln(\eta_{rel})}{c} = [\eta] + k'' [\eta]^2 c$$

η_{inh} = inherent viscosity

$k'' = k' - 0.5$ (so usually negative slope when plotted)

Determination of Intrinsic Viscosity (IV)

- ① Measure solution viscosity in capillary viscometer for a given concentration (c)
- ② Plot according to Huggins' Equation to get $[\eta]$



$$[\eta] = \lim_{c \rightarrow 0} \eta_{red} \quad \text{or} \quad \lim_{c \rightarrow 0} \eta_{inh}$$

Mark-Houwink-Sakurada Equation (MHS)

- developed from solution viscosity measurements for monodisperse (narrow distribution) polymers
- specific for Polymer/Solvent system.

$$[\eta] = K (M)^a$$

$K, a =$ MHS parameters

$a \Rightarrow$ related to "goodness" of solvent

$a = 0.5$ (θ -solvent, poor solvent)

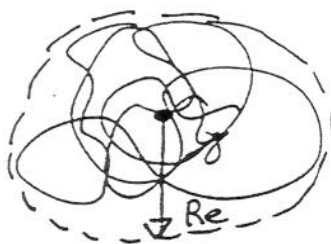
$a = 0.6 - 0.8$ (good solvent)

↑ A few more words on dilute solution intrinsic viscosity $[\eta]$.

- Based on the equivalent (impenetrable) sphere model:

For a "rigid" equivalent sphere flowing in solvent:

$$\text{Stokes Flow: } f_0 = 6\pi\eta_0 R_e$$



equivalent "hard sphere" model.

Einstein Equation:

$$\frac{\eta - \eta_0}{\eta_0} = \eta_{sp} = 2.5 \left(\frac{n_2}{V} \right) V_e$$

where $\frac{n_2}{V} = \# \text{ molecules / volume}$.

$$V_e = \text{equivalent volume} = \left(\frac{4}{3} \right) \pi R_e^3$$

With some manipulation, there leads to the

Mark-Houwink Equation:

$$\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = [\eta] = K M \nu^a$$

$$\text{where } K = \phi \left(\frac{\overline{r_0^2}}{M} \right)^{3/2}$$

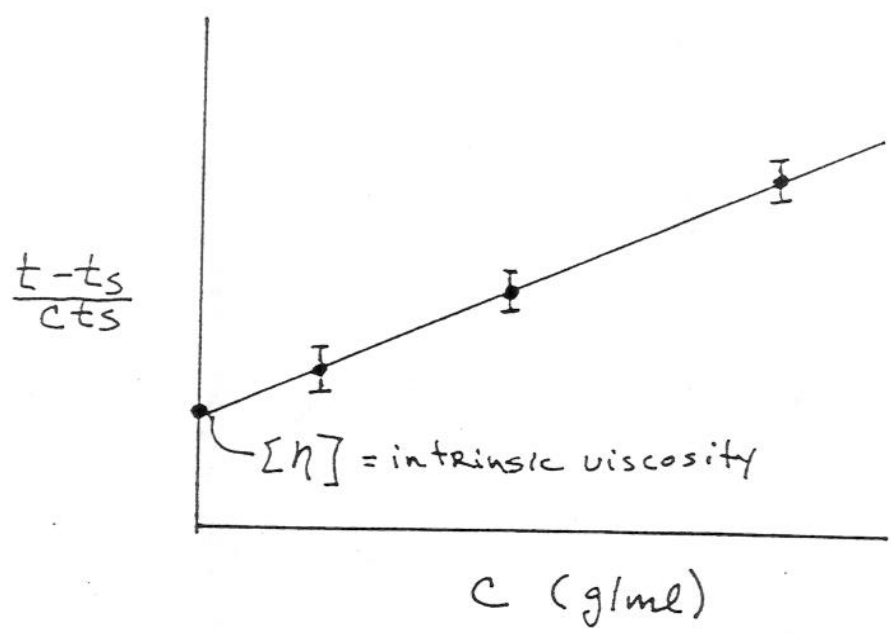
$\overline{r_0^2}$ = mean square end-to-end distance

M = molecular weight

ϕ = universal constant (2.5×10^{21} dl/mol cm³)

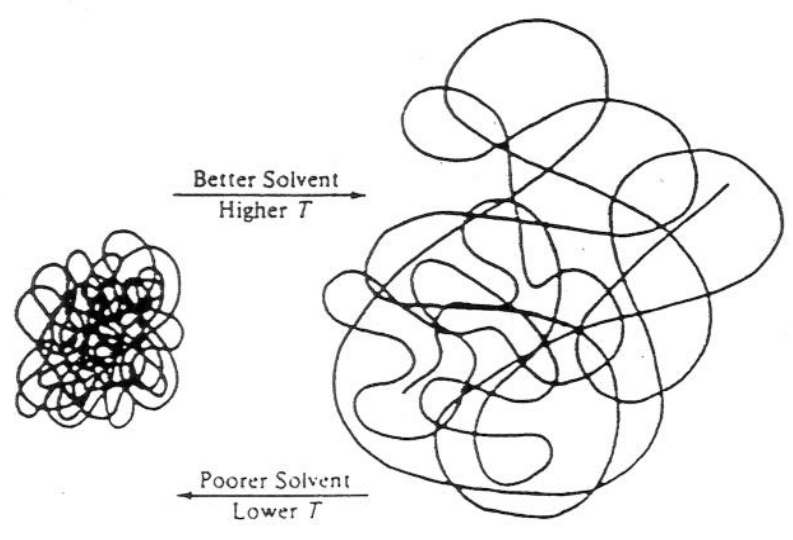
* Reference: Introduction to Polymer Physical Science
L.H. Sperling, Ch. 3, p. 65-121

Intrinsic Viscosity Measurement.



Experimental Considerations

- (1) $t_s > 100$ sec. (no KE correction needed)
 - choose Capillary diameter appropriate for solvent.
- (2) $(t - t_s) > 2$ sec (for increased accuracy at lowest conc.)



$$[\eta] = K(M_r)^a$$

$$0.5 \leq a \leq 1.8$$

typical values

$$0.5 \leq a < 0.8$$

$a > 1.0$ rigid-backbone polymer.
 (i.e. DNA/H₂O $a \approx 1.2-1.4$)

K, a are functions of polymer/solvent system.

- $\left\{ \begin{array}{l} a \approx 0.5 \text{ (theta (poor) solvent)} \\ a = 0.7 - 0.8 \text{ (good solvent - random coil)} \\ a > 1.0 \text{ (good solvent - rigid rod polymer)} \end{array} \right.$

Intrinsic Viscosity Measurements in a Capillary

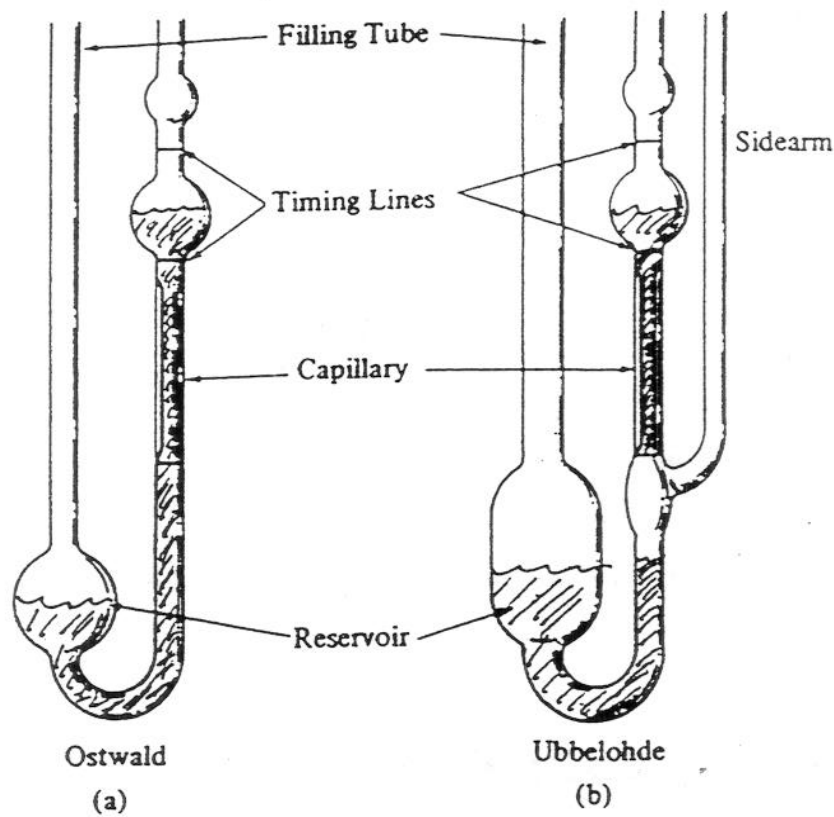


Figure 6.5 Dilute-solution viscometers: (a) Ostwald; (b) Ubbelohde.

Measurement: t_s = solvent flow time

t = polymer soln. flow time at conc. c

Calculation:

$$\eta_{\text{relative}} = \frac{\eta}{\eta_s} = \frac{t}{t_s} \quad (\text{relative viscosity})$$

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} = \frac{(t - t_s)}{t_s} \quad (\text{specific viscosity})$$

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c = \frac{(t - t_s)}{c t_s} \quad (\text{intrinsic viscosity})$$

Mark-Houwink Equation: $[\eta] = K(M_v)^a$

K, a = Mark-Houwink parameters

Molecular Weight from Viscosity Measurements.

Mark-Houwink-Sakurada Equation.

- dilute solution viscosity measured in capillary

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{\text{soln}} - \eta_{\text{solvent}}}{\eta_{\text{solvent}} c} = \text{intrinsic viscosity}$$

$$[\eta] = K (\bar{M}_v)^a$$

where $[\eta]$ = intrinsic viscosity $[\eta] = \frac{\text{ml}}{\text{g}}$ or $\frac{\text{dl}}{\text{g}}$

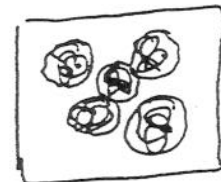
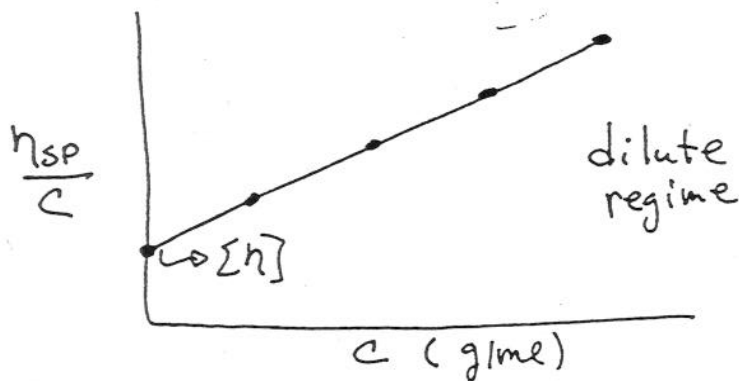
K, a = Mark-Houwink coefficients

$a = 0.65 - 0.8$ in good solvent

$a = 0.5$ in poor solvent

\bar{M}_v = Viscosity Average molecular weight.

Experiment: Cannon-Ubbelohde Viscometers.



polymer-solvent interaction

Note: K, a are for a specific polymer/solvent system.

i.e. PS/toluene ($T=25^\circ\text{C}$) $a \approx 0.76$

PS/cyclohexane ($T=35.5^\circ\text{C}$) $a = 0.5$

\hookrightarrow cyclohexane is a Θ -solvent.

Huggins Equation. (solvent concentration effects)

dilute polymer solutions: $\eta_{rel} < 2$.

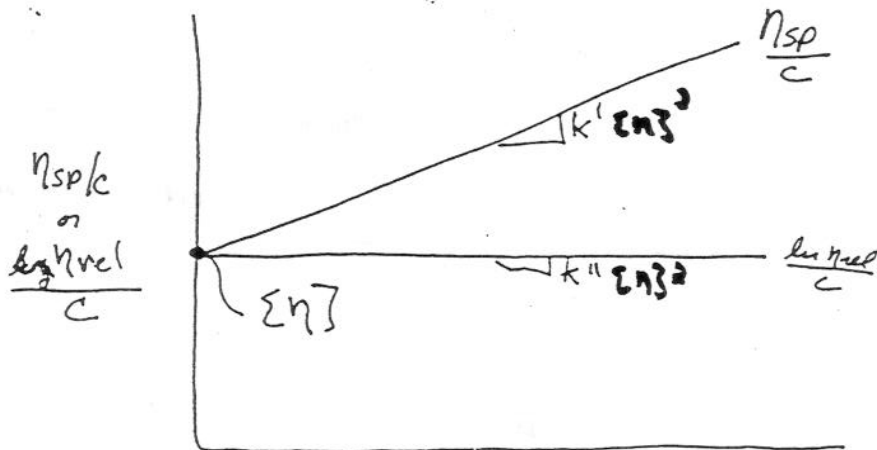
$$\boxed{\frac{\eta_{sp}}{c} = [\eta] + k' [\eta]^2 c}$$

- convenient fact is that $k' \approx 0.4$ for many polymer/solvent systems.
- if $[\eta]$ is known, the solution viscosity vs. concentration can be determined.

Kraemer Equation.

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

and $k' + k'' = 0.5$



Conc.

→ one measurement at low c.

- sometimes $\frac{\ln \eta_{rel}}{c}$ is used in a "singlepoint" measurement because it is slowly changing with concentration. (low slope $k' > k''$)

Relative Methods.

- ① Dilute Solution Viscosity. (M_v)
 - Intrinsic Viscosity Measurement
- ② Gel Permeation Chromatography (GPC)
 - separation by size.
 - MWD - Distribution.

Absolute Methods

- ① Light Scattering (\bar{M}_w, R_g)
 - Low Angle Laser LS (LALLS)
- ② Centrifugation (Sedimentation) (\bar{M}_w, \bar{M}_z)
- ③ End-Group Analysis (\bar{M}_n)
 - IR, NMR (Spectroscopy)
- ④ Colligative Properties (\bar{M}_n)
 - Osmotic Pressure

Methods. Absolute.

① End-Group Analysis (\bar{M}_n)

- if the chemical nature of the END Groups are known, they can be monitored by some spectrographic technique (i.e., IR, NMR)

* **Determination of \bar{M}_n** (number of molecules present).

- DRAWBACK: As M increases, the # of END Groups per unit volume decreases, reducing sensitivity.

→ so **limited to $\bar{M}_n < 10,000$**

② Colligative Property Measurements (\bar{M}_n)

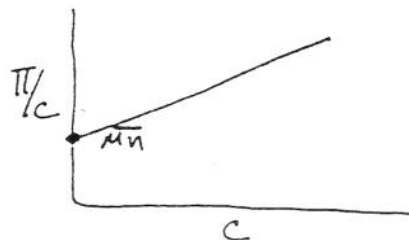
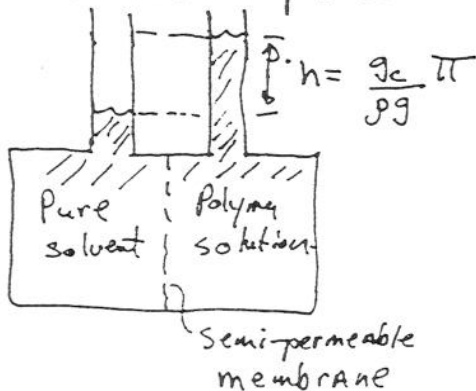
a) boiling-pt elevation. $\lim_{c \rightarrow 0} \frac{\Delta T_{bb}}{c} = \frac{RT_b^2}{\rho \Delta H_b \bar{M}_n}$

b) freezing pt. depression. $\lim_{c \rightarrow 0} \frac{\Delta T_f}{c} = -\frac{RT_f^2}{\rho \Delta H_f \bar{M}_n}$

* c) osmotic pressure: $\lim_{c \rightarrow 0} \frac{\pi}{c} = \frac{RT}{\bar{M}_n}$

a & b are difficult measurements to do.

* osmotic pressure most common method.

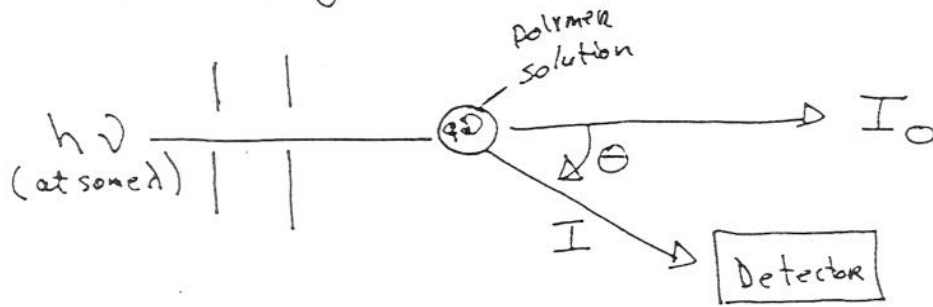


Problem: good "semipermeable" membranes.

Light Scattering.

Reference: T. C. WARD, J. Chem. Ed., 58(4), 867-871 (1981)

Schematic of essential components of light scattering instrument



I_0 = incident radiation (focused, polarized, filtered; or LASER)

$I(\theta)$ = scattered beam intensity as a function of angle

$$R(\theta) = \frac{I(\theta)}{I_0} = \text{Rayleigh Ratio}$$

$R(\theta)_{\text{solvent}}$ = scattering from solvent.

BASIC Light Scattering Equation (small particles $\ll \lambda_0$)

$$\frac{Kc}{R(\theta) - R(\theta)_{\text{solv.}}} = \frac{1}{\bar{M}_w} + 2A_2c + 3A_3c^2 + \dots$$

where $K = \text{optical constant} = \frac{2\pi^2 n_0^2 \left(\frac{dn}{dc}\right)^2}{N_0 \lambda^4}$

n_0 = refractive index at λ

λ = wavelength of incident light

$\frac{dn}{dc}$ = differential refractive index (fct. of polymer/solvent pair)

\bar{M}_w = weight average molecular weight

A_2 = 2nd virial coefficient

(A_2 increases with solvent "goodness")

$A_2 = 0$ (theta solvent)

Light Scattering (large particle $> \lambda/20$)

- with large molecules, there can be scattering from different sections of the same molecule.
- scattering will have an angular dependence which depends upon polymer conformation.

$P(\theta)$ = Angular scattering function
(Accounts for anisotropy in $I(\theta)$)

$$\frac{1}{P(\theta)} = 1 + \frac{16 \pi^2 d^2}{3 \lambda^2} \sin^2(\theta/2)$$

Note: $P(\theta) \rightarrow 1$ as $\theta \rightarrow 0$

* Key Point for Low Angle Light Scattering (LALLS)

Light Scattering Equation (large particles)

$$\frac{Kc}{R(\theta) - R(\theta)_{soln.}} = \frac{1}{M_w P(\theta)} + 2A_2c + \dots$$

Note: as $c \rightarrow 0$, $P(\theta) \neq 0$ } therefore we must
 $\theta \rightarrow 0$, $P(\theta) \rightarrow 1$ } do double extrapolation
 to get $\overline{M_w}$

Zimm Plot - Determination of \overline{M}_w , A_2 , R_g

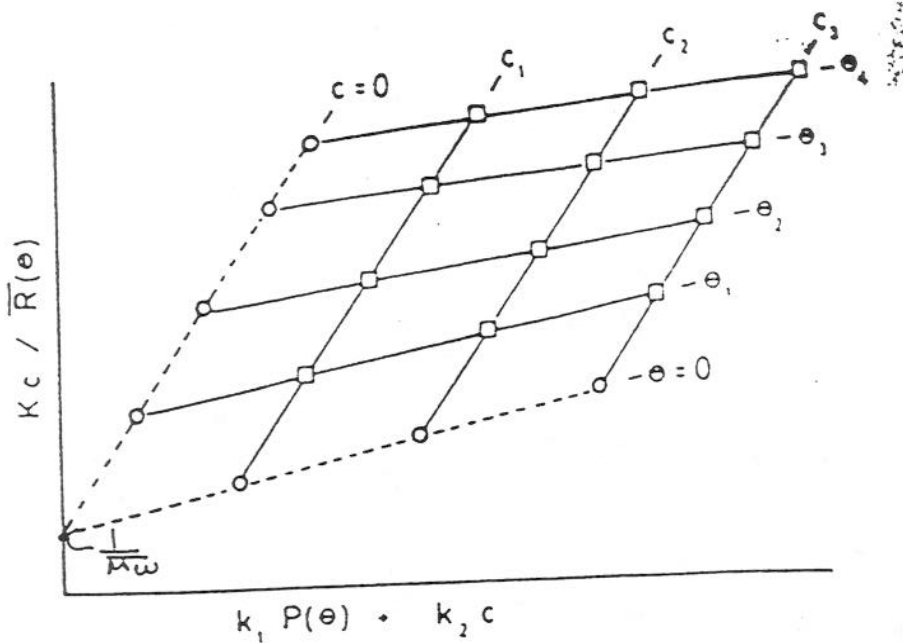


Figure 8. A Zimm-plot double extrapolation procedure. Constants k_1 and k_2 are arbitrary scaling factors. Squares are data points. Circles are extrapolated points.

$k_1, k_2 =$ arbitrary constants

$c=0$ slope determines $\overline{R}_g =$ radius of gyration

$$\overline{R}_g = \left(\frac{\overline{R_0^2}}{6} \right)^{1/2}$$

$\overline{R_0^2}$ = mean square end-to-end distance



$$\overline{R}_g \propto \overline{M}_w$$

$\theta=0$ A_2 - 2nd virial coefficient

intercept = $1/\overline{M}_w$ weight-average molecular weight

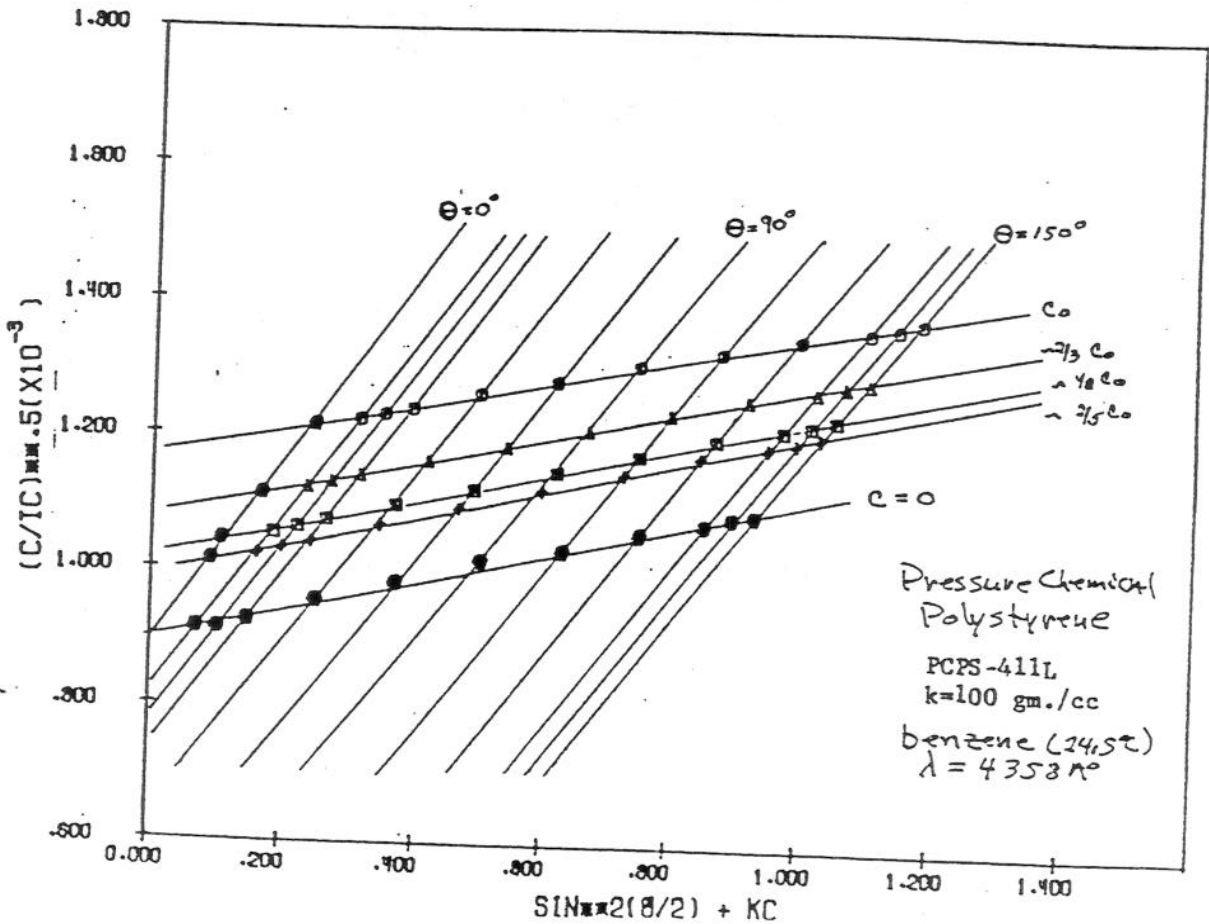
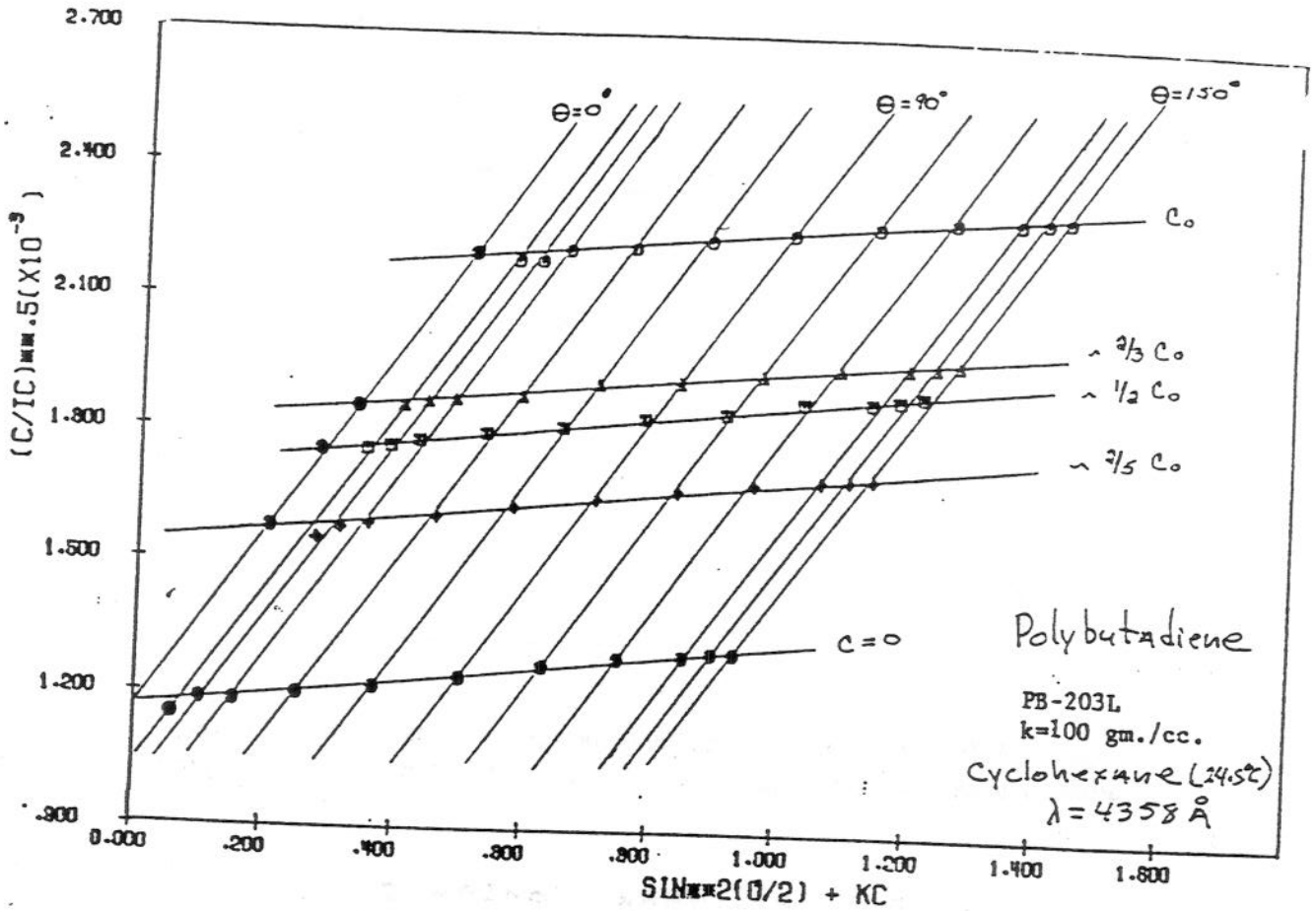
Double extrapolation $c \rightarrow 0$ $\theta \rightarrow 0$ necessary because $P(\theta) \rightarrow 1$ at $\theta=0$

Note: Low ANGLE LASER Light SCATTERING (LALLS)

• important new technique - single point measurement.

Why? $P(\theta) \rightarrow 1$ as $\theta \rightarrow 0$ \therefore no angular dependence to scattering.

Light Scattering - Zimm Plots



Similarities between Osmometry and Light Scattering Theories.

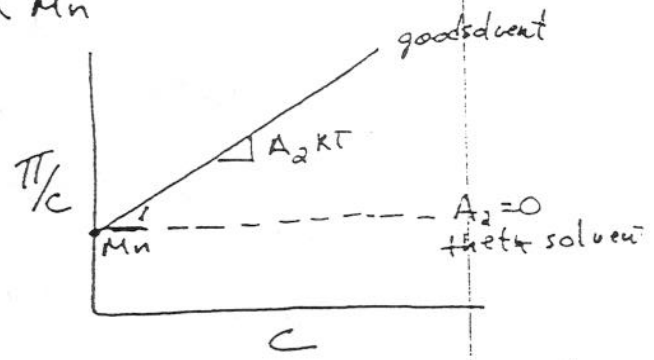
Osmometry:
$$\frac{\pi}{c} = RT \left(\frac{1}{M_n} + A_2 c + \dots \right)$$

π = osmotic pressure

A_2 = 2nd virial coefficient

A_2 is a fct. of solvent quality

$A_2 \uparrow$ with solvent goodness



M_n = number average molecular weight (colligative property)

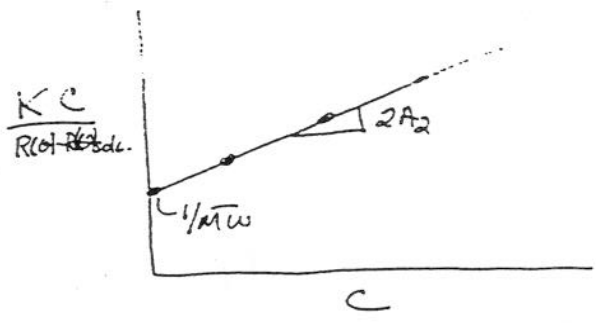
thermodynamic explanation: fluctuation in Gibbs free energy.

Light Scattering

$$\frac{Kc}{R(\theta)_{90}} = \frac{1}{M_w} + 2A_2 c + \dots$$

M_w = weight average molecular weight

A_2 = 2nd virial coefficient.



Scattering: related to fluctuations in polymer segment concentration.

Gel Permeation Chromatography (GPC)

Note:
This technique
Also called
Size Exclusion
Chromatography
(SEC)

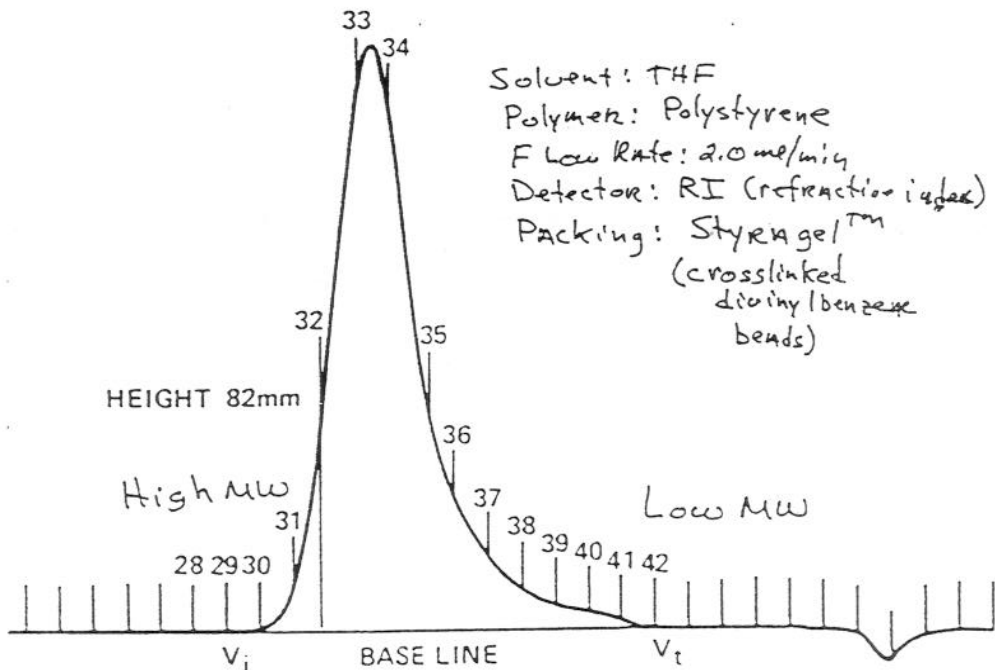
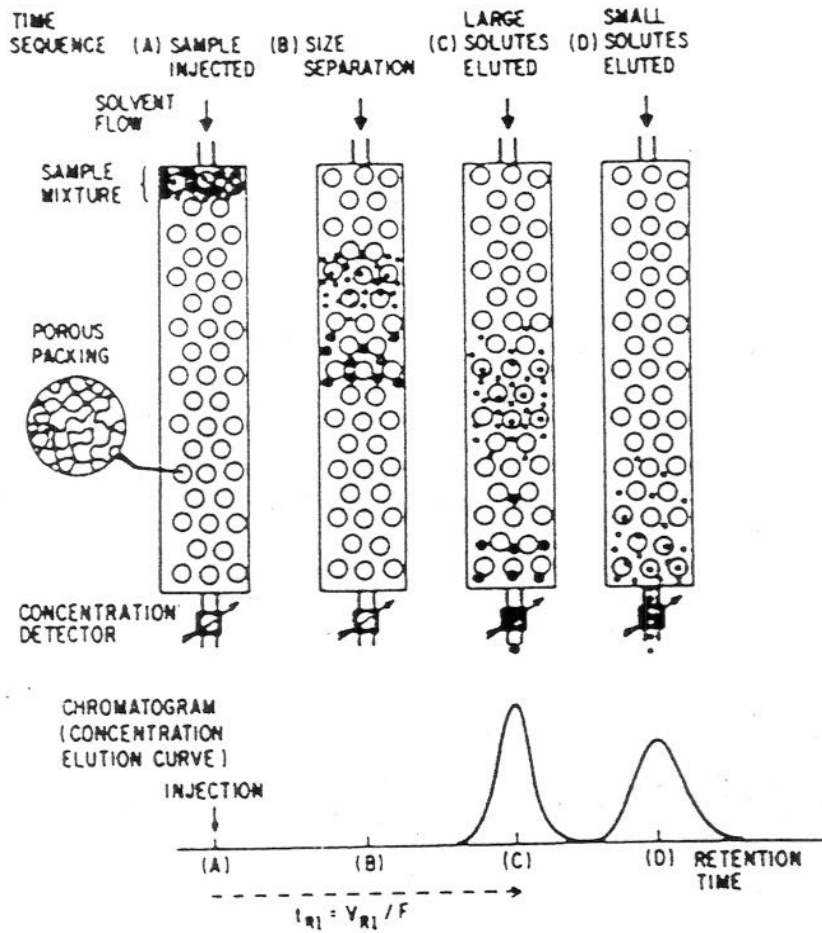


Figure 3.22 A typical GPC chromatogram. The largest molecules appear at the low retention counts. Typical data for polystyrene (66).

Development of a Universal Calibration Curve

Using narrow distribution calibration standards (typically, Anionic PS from Pressure Chemical Co, Pitts).

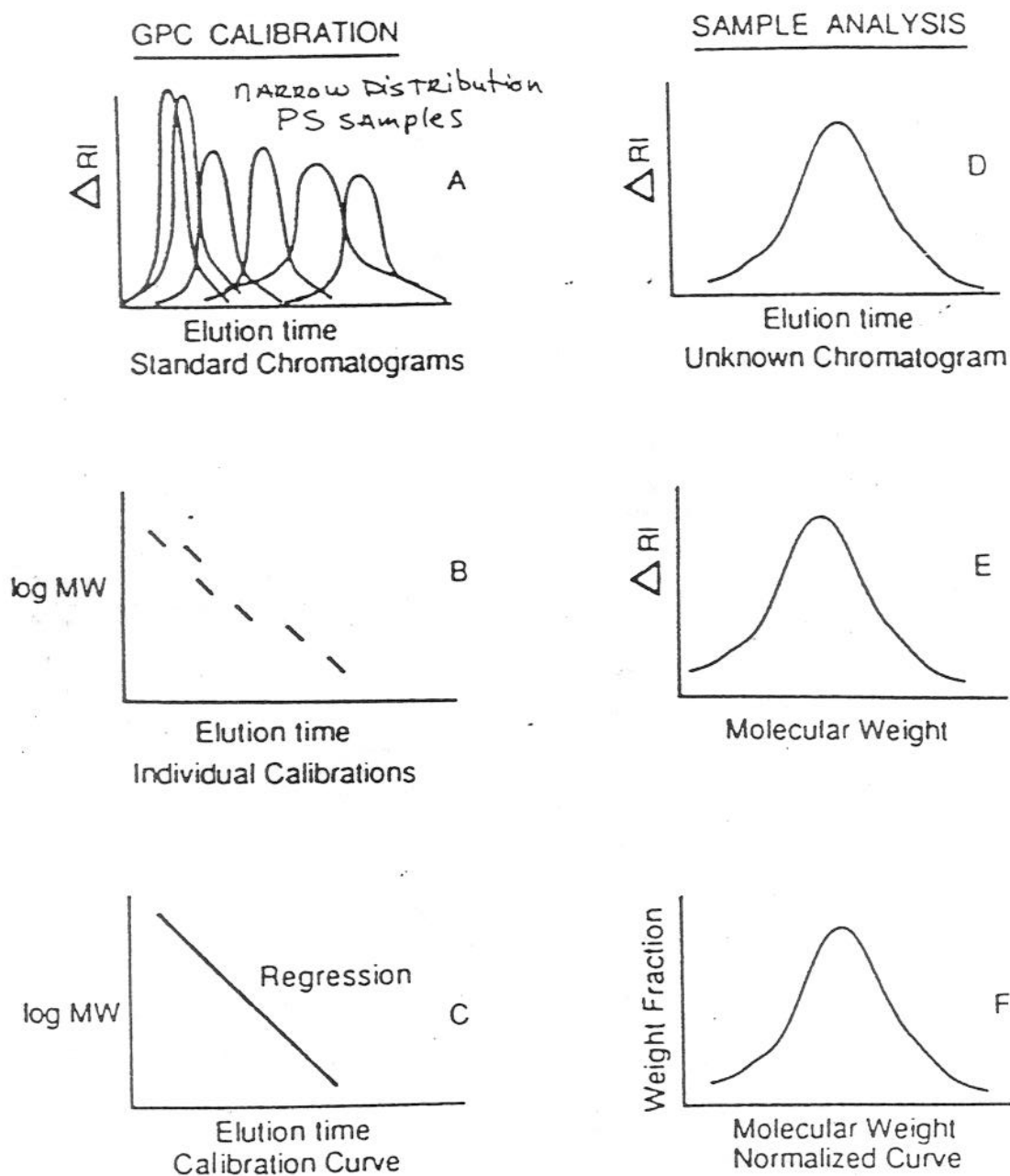


Fig. 2.6. Representation of the stages in the analysis of a sample of a polymer for its weight fraction distribution by gel permeation chromatography (GPC) using a refractive index (RI) detector. A-C represents the establishment of the universal calibration curve of the logarithm of the relative molecular weight ($\log MW$) versus elution time. D represents the detected profile of the difference in RI (ΔRI) compared to the pure solvent versus elution time, from which E and F are derived using calibrations. Reprinted by permission of John Wiley & Sons Inc from Lee, C. H. and Mallinson, R. G. (1989). Molecular weight distribution in continuous stirred tank vinyl acetate emulsion polymerization. *Journal of Applied Polymer Science*, 37, 3315-27. Copyright (1989) John Wiley & Sons Inc.

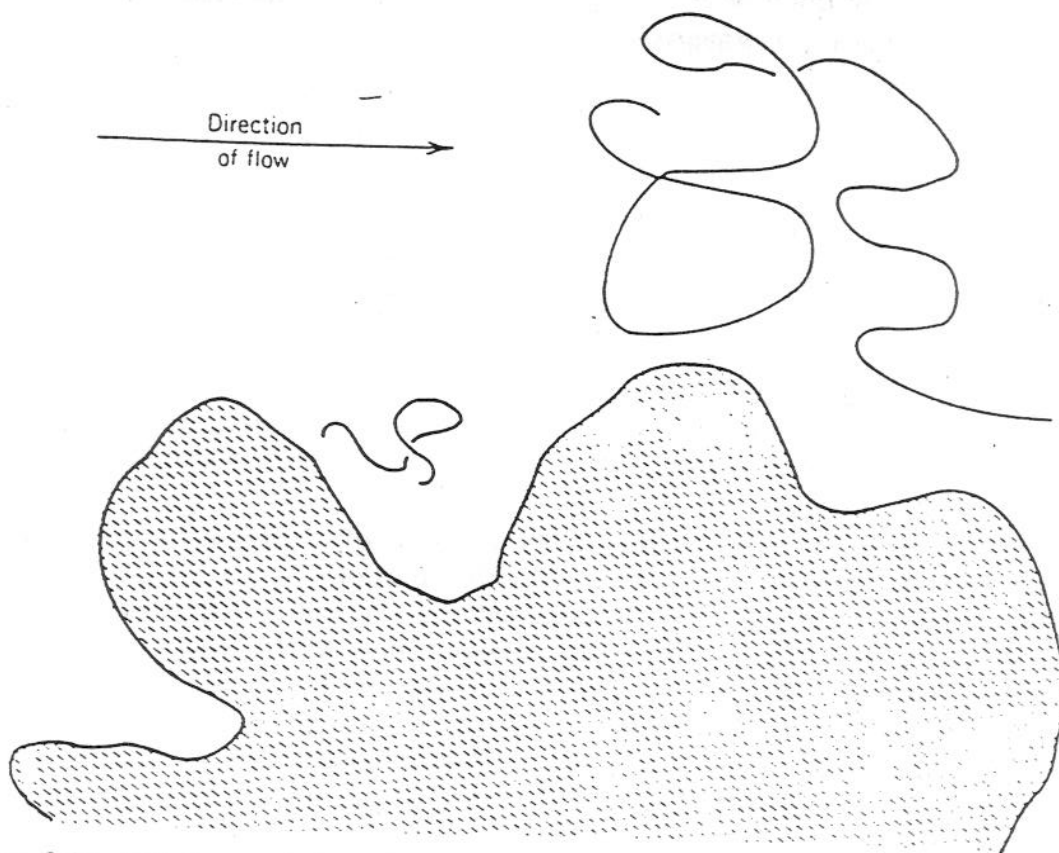
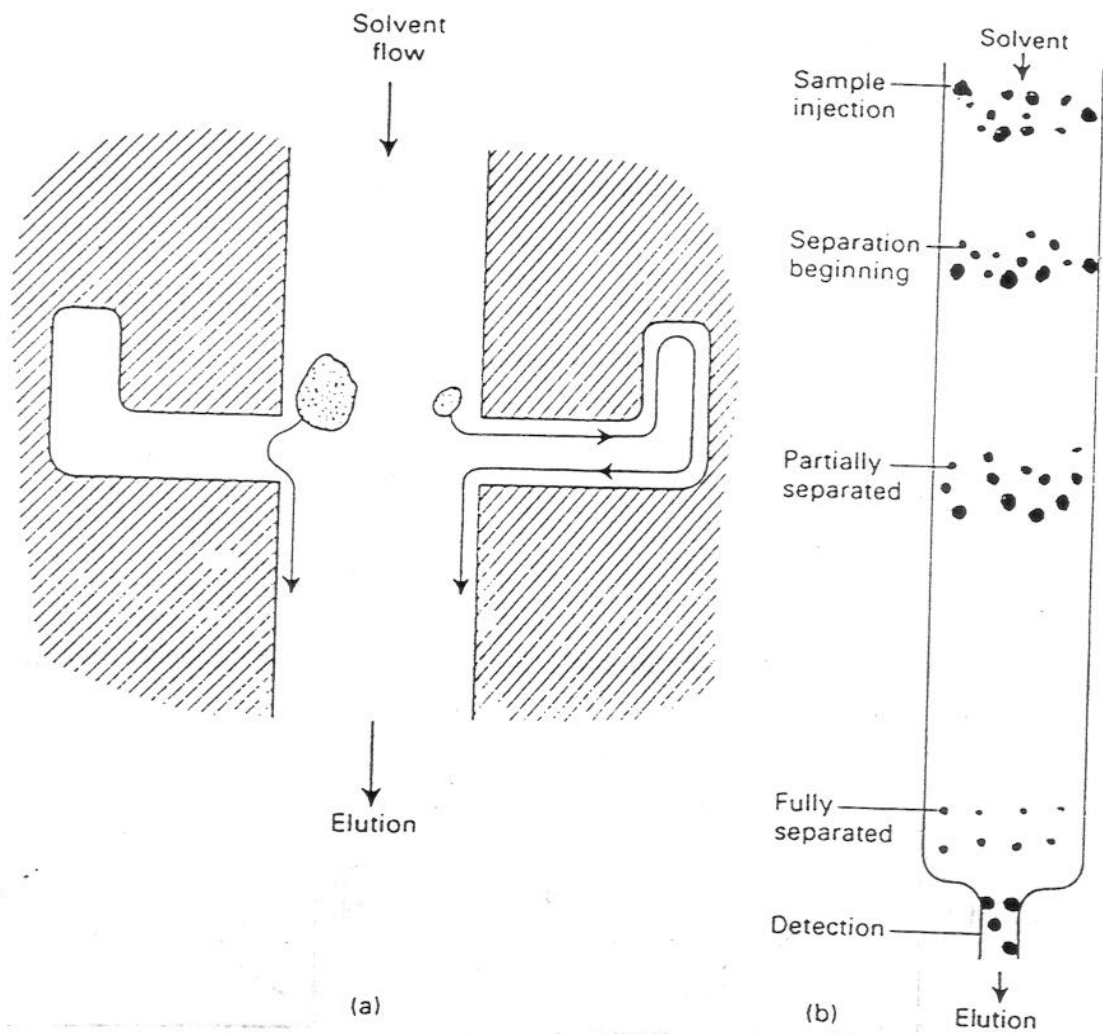


Figure 3.19 The size exclusion effect. The short chain can enter the pore, whereas the long chain passes by.

UNIVERSAL CALIBRATION CURVE

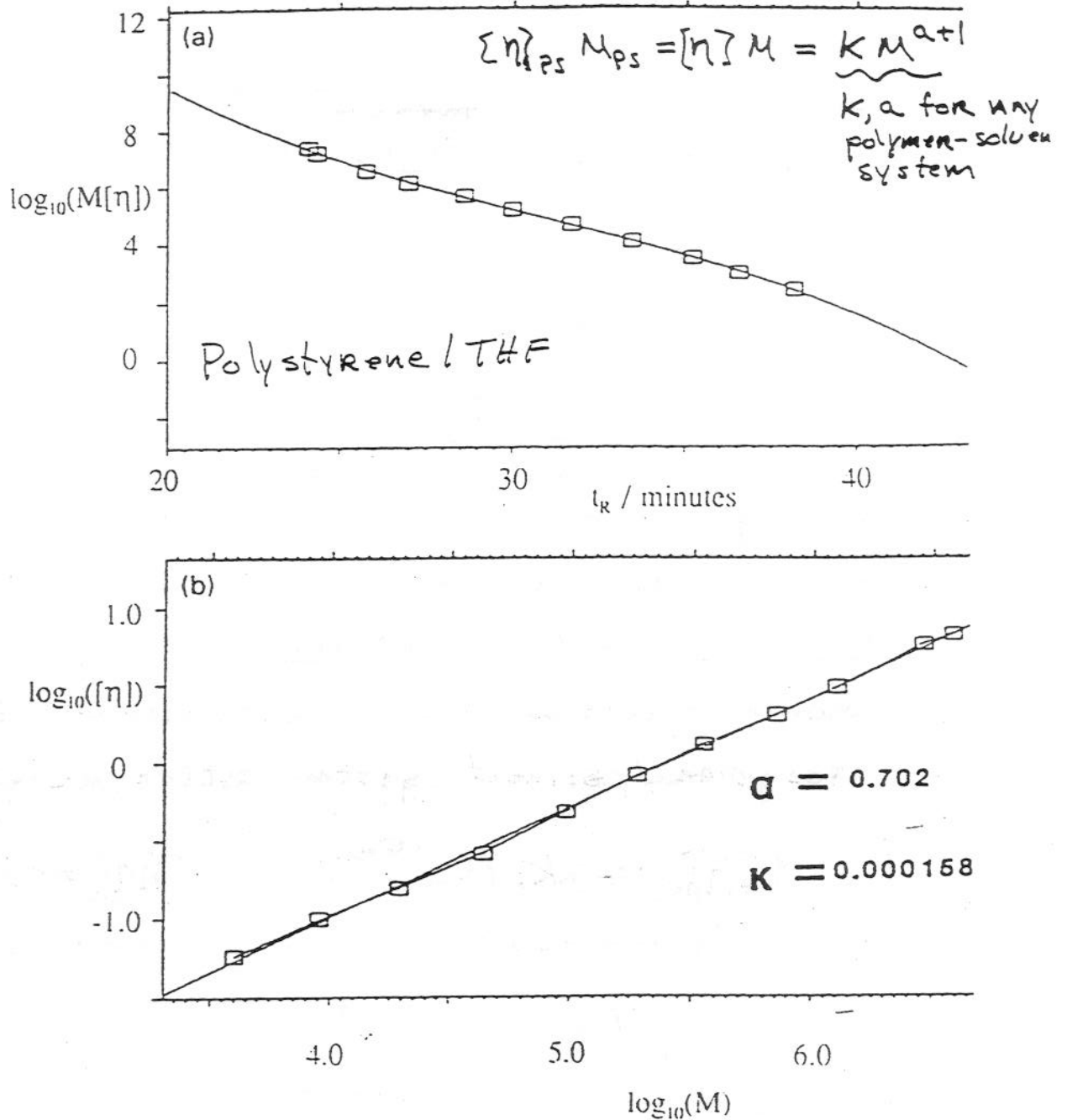


Fig. 2.5. (a) Universal calibration curve on a plot of $\log_{10}(M[\eta])$ versus retention time (t_R), where the locations of the points (empty squares) were determined using polystyrene standards of narrow weight distribution centred on relative molecular mass M . (b) Log-log plot of intrinsic viscosity ($[\eta]$) versus M for polystyrene standards in tetrahydrofuran at 313 K: the resulting values of parameters in the Mark-Houwink-Sakurada equation (eqn (2.4)) are shown within the diagram. Reprinted from Kou, C-Y., Provder, T., and Koehler, M. E., (1990). Evaluation and application of a commercial single capillary viscometer system for the characterization of molecular weight distribution and polymer chain branching. *Journal of Liquid Chromatography*, 13, 3177-99 by courtesy of Marcel Dekker Inc.

Universal Calibration (from Mark-Houwink Eq.)

$$\Sigma \eta^2 M = \phi (\bar{r}_0^2)^{3/2} \alpha^3$$

where $\Sigma \eta^2 M$ = hydrodynamic volume of the molecule

$$\alpha = \Sigma \eta / \Sigma \eta_0 = \text{expansion coefficient}$$

Hydrodynamic Volume Concept for development of the UNIVERSAL GPC CALIBRATION CUR

It can be shown that in Size Exclusion Chromatography (S.C.) that the separation is by size in solution. This is given by the following relationship. ∴

$$\boxed{\text{hydrodynamic volume} = [\eta] M}$$

Using this concept in conjunction with the UNIVERSAL GPC CALIBRATION CURVE and the known values of k, a for PS/solvent and the polymer/solvent system tested, we get.

$$[\eta]_{ps} = k_{ps} M_{ps}^{a_{ps}}$$

polystyrene/solvent

$$[\eta]_x = k_x M_x^{a_x}$$

polymer/solvent.

$$[\eta]_{ps} [M]_{ps} = k_{ps} M_{ps}^{a_{ps}+1}$$

$$\boxed{[\eta]_{ps} [M]_{ps} = [\eta]_x M_x}$$

→ hydrodynamic volume equivalence

$$k_{ps} M_{ps}^{a_{ps}+1} = k_x M_x^{a_x+1}$$

$$\circ \circ \quad M_x = \left[\frac{k_{ps}}{k_x} M_{ps}^{a_{ps}+1} \right]^{1/a_x+1}$$

→ true M of polymer X.

Combined GPC, Light Scattering, and Intrinsic Viscosity Molecular Characterization System

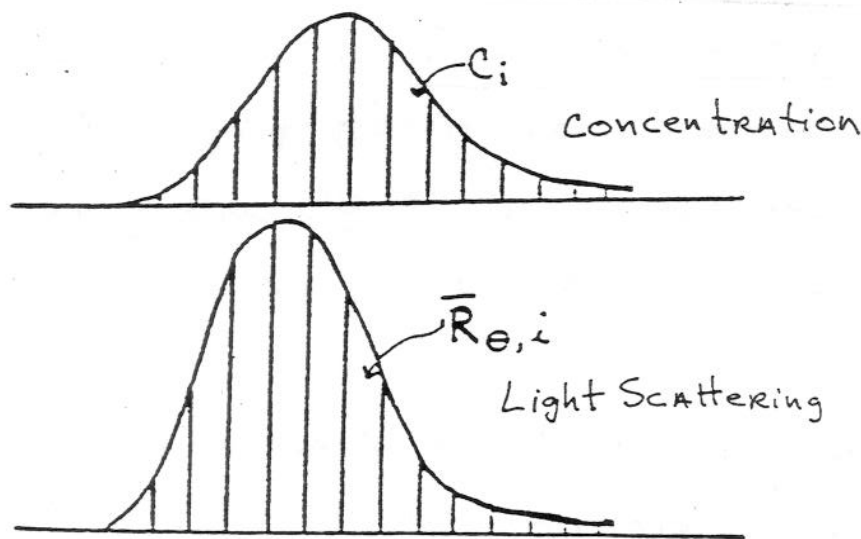
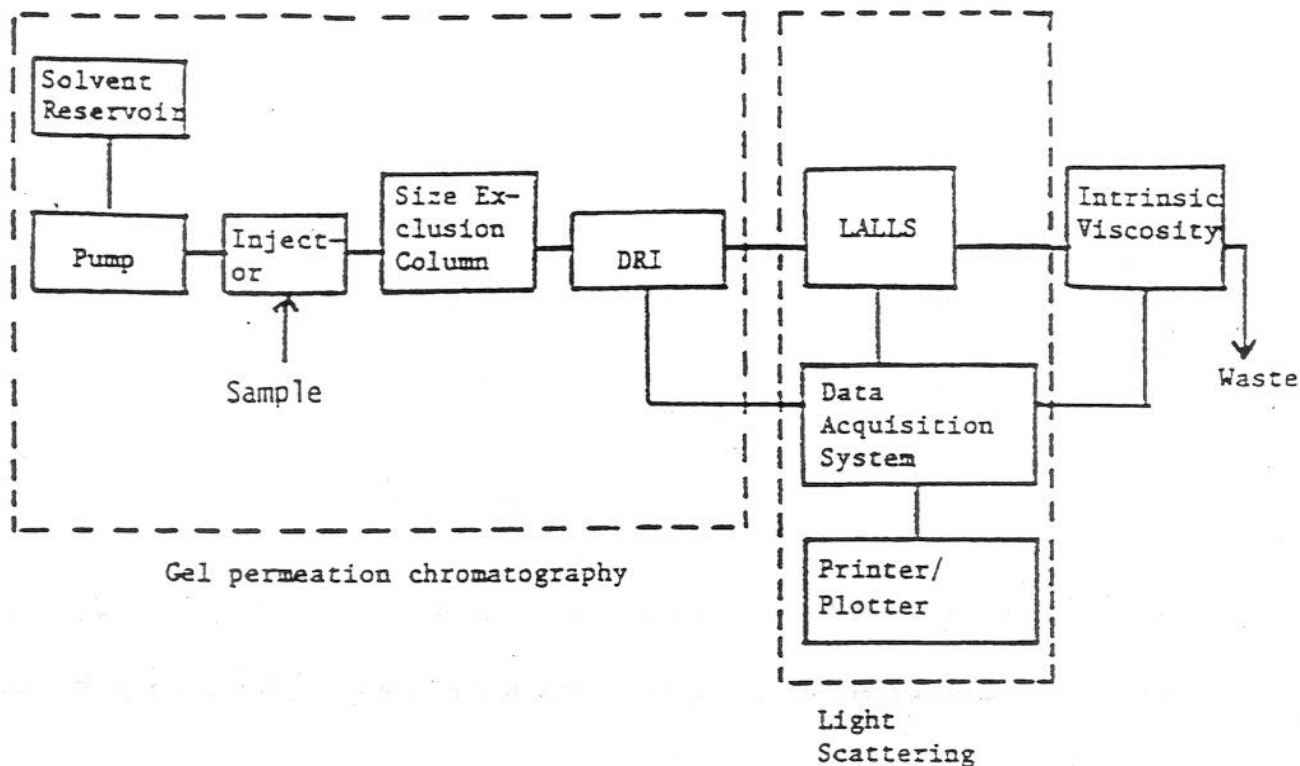


Figure 2. GPC/LALLS data analysis. The excess Rayleigh factor ($\bar{R}_{e,i}$) and concentration (C_i) are evaluated at uniform intervals (i) and used to calculate the molecular weight at i . (R.C. Jordan, J. Liq. Chrom., 3(3), 439 (1980)).

Advantages: \bar{M}_w , MWD, $IV[\eta]$, and MHS Equation in one run

Note: System Calibration curve not necessary.

Advantages of the combined

GPC-IV-LALLS Technique.

I. How do we determine Mark-Houwink parameters.

$$[\eta] = K M^a, \quad K, a = \text{M-H parameters}$$

- ① Series of narrow MWD (< 1.05) polymers.
- ② choose solvent
- ③ capillary viscometry to determine $[\eta]$ for each M .
- ④ Plot of $\log [\eta]$ vs. $M \rightarrow K, a$

II. How do we determine \overline{M}_w ?

- ① Light scattering of dilute solutions \rightarrow various \underline{C} and $\underline{\theta}$
- OR ② Low Angle Light Scattering (LALLS) \rightarrow various \underline{C}

GPC-IV-LALLS

① Gel Permeation Chromatography (GPC)

- separates sample with MWD into narrow fractions of a single M at a very dilute concentration.

② LALLS

- on-line light scattering of each fraction $\rightarrow M_w$

③ Intrinsic Viscosity (IV)

- on-line IV measurement (single point @ low conc)

Results

- \overline{M}_w , $[\eta]$, K, a , and MWD with one pass.

Absolute

solvent independent

for a given polymer/solvent

$$\hookrightarrow [\eta] = k M^a$$

solvent independent

"Molecular Weight and Molecular Weight Distributions in Synthetic Polymers"

Thomas C. Ward, J. Chem. Ed., 58 (11) 1981 p 867-899

- very good article on MW, MWD, Absolute MW methods (Light scattering, membrane osmometry) and Relative MW Methods (GPC).

(1) Molecular Weight Distribution (MWD) for Various Synthesis Techniques

$MWD \text{ (or PDI)} = \bar{M}_w / \bar{M}_n$

Polymerization technique	Typical MWD range.
Addition (Anionic)	1.02 - 1.15
Addition (free radical)	2.0 - 5.0
Addition (heterogeneous catalyst Ziegler-Natta)	2.0 - 25 (or larger)
Step-growth (condensation)	1.5 - 2.0

Molecular Weight Determination Methods

Method.	mol. wgt.	Range	Sample size	Comments
End-Group Analysis	\bar{M}_n	up to 25,000	moderate	need active end groups
membrane osmometry	\bar{M}_n	15,000 - 750,000	moderate	automated, reasonable
Light Scattering	\bar{M}_w	2000 - 10^7	small	Also get conformation info ($R_g \approx A_2$)
ultracentrifuge	$\bar{M}_w, \bar{M}_z, MWD$	2000 - 10^7	small	Costly, time consuming
<u>Relative Techniques.</u>				
Solution viscosity	\bar{M}_v	15,000 - 10^6	small	economical, easy (?)
vapor phase osmometry	\bar{M}_n	up to 25,000	small	moderate cost and time
Size exclusion (GPC)	MWD	up to 5×10^6	small	fast, automated, high temp. • calibration needed.

Molecular Weight and Molecular Weight Distributions

Synthetic Polymers

Thomas Carl Ward

Department of Chemistry and Polymer Materials and Interfaces Lab, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

Polymers distinguish themselves from other species by the presence of a repeating unit or units within a molecular chain. The production of synthetic polymeric materials always involves creation of molecules having varying numbers of these repeating units for both kinetic and thermodynamic reasons. Of those key parameters shown in Table 1 which determine how a polymer will perform in the solid, in solution, or in the melt, molecular weight distribution (MWD) is usually the dominating factor, often influencing the other parameters. The details of semicrystalline polymer morphologies is a good example of MWD playing a role in another parameter. The existence of this distribution of molecular weights has fascinated polymer scientists since the beginning of the quantitative aspects of the discipline in the second quarter of this century. It is hard to overstate the importance of polymer MWD both from an industrial and an academic point of view. To emphasize this point, a few examples will be cited.

Much theoretical attention has been directed toward finding the role of MWD in the rheology of polymer solutions and melts (1). Models of the flow behavior of polymer liquid systems rely heavily on accurate MWD data in order that the predictions of such treatments might be evaluated adequately. On the other hand, on the practical side, it is observed that performance-oriented criteria such as environmental stress resistance and permeability to gases also heavily depend on MWD (2). The scientific literature is filled with examples of both theoretical and applied MWD studies (e.g., see 3, 4). The methods of production (e.g., catalyst type), of processing procedure (e.g., milling, foaming, casting, extruding) and the subsequent environmental exposure (e.g., moisture, radiation) all enter into the shaping of a polymer's MWD. Hence a wide range of scientific groups usually has a keen interest in the subject. It is fair to ask a question concerning the exposure of these persons to such an important area. In the traditional undergraduate curriculum, unfortunately, there is little or no exposure to MWD's. Yet, it should be clear that the ability to describe mathematically, to characterize experimentally, and to correlate physical properties with MWD must be high on any list of skills required in polymer science and engineering.

In this introductory treatment an attempt is made to provide sufficient educational material on MWD's for students interested in polymers without engaging in extensive derivations. Attention is drawn to several of the more prominent models for predicting MWD in a pedagogical way. In addition, the current most popular instrumental methods which might be applied to characterize MWD are reviewed with an emphasis on the physical chemistry of each. The reader interested in more detailed discussions of hardware or in rigor of the theoretical development will find two excellent recent reviews (5, 6). Textbooks in polymer science may be helpful in providing alternative fundamental discussion (7, 8, 9).

The Description of Molecular Weight Averages and Molecular Weight Distribution

Two curves shown in Figure 1, and to be discussed below, illustrate a typical way of presenting MWD data. The ordinate is generally the weight fraction of polymer chains having a certain number of repeating units, denoted here by i , the de-

Table 1. The Polymer Parameters

1. Chemical Composition	Is the polymer a homopolymer or a combination of more than one repeating unit? What is the architecture of chain assembly?
2. Molecular Weight Distribution	What are the proportions of chains having different numbers of repeating units in a sample?
3. Stereochemistry	Do cis/trans isomers exist? Can there be stereoisomers (tacticity), and what is their distribution along the chains?
4. Topology	Are the chains linear, branched or crosslinked?
5. Morphology	What are the details of the structure of the solid polymer?
6. Miscellaneous	Additives, surface features may be present

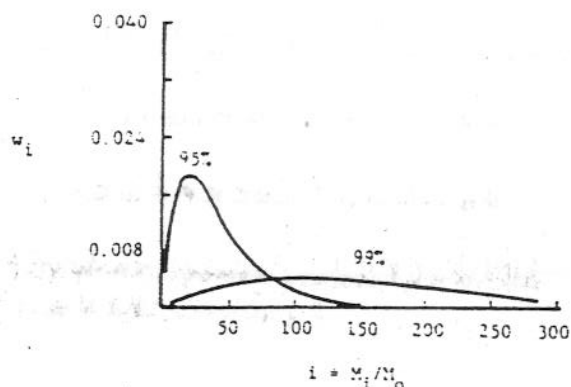


Figure 1. Two molecular weight distributions for random step growth polymerizations having different conversions, ρ , shown in percents.

gree of polymerization. The notation DP is also in common use for degree of polymerization. The abscissa shows the number of these repeating units per chain. If we ignore the chain ends, which are usually chemically different from the repeating units, the DP scale is related to that for molecular weight through the relationship $M_i = iM_0$, where M_0 is the molecular weight of a repeating unit. Although two smooth curves are drawn in Figure 1, polymer DP's and molecular weights must be discrete measures. We find that for visualization purposes and to aid in analytical manipulation of the MWD data the continuous functions which are sketched prove most convenient. The smooth curves also suggest that the ordinate be interpreted as the probability density for finding molecular weights (MW) between MW and $(MW + dMW)$.

Also, it is apparent that it might be appropriate occasionally to plot the mole fraction, n_i , of polymer having i repeating units as the dependent variable, rather than the weight fraction. This comment will be amplified in the paragraphs which follow. In either discrete or continuous presentations of MWD data the areas under the curves should be equal to unity.

While the curves in Figure 1 have actually been drawn from a theory, one would like to establish such information experimentally. An operation of this kind is termed fractionation. In the ideal case we would like to pick apart a sample's MWD in order to identify both the number of molecules of each size and their absolute molecular weight. MWD plots could then be constructed. This concept is illustrated schematically in Figure 2 where the weight fraction of polymer having molec-