Molecular Weights, Polymers, & Polymer Solutions (Part I - Chapter 2 in Stevens)[1]

I Number and Weight Average Molecular Weight - An Introduction

A) Importance of MW and MW Distribution

1) Optimum MW, MW Distribution, etc.

a) depends upon application via processing and performance tradeoffs

2) Typical MW values for commercial polymers

a) Vinyl polymers in the 10^5 and 10^6 range

b) Strongly H-bonding polymers in the 10^4 range

i) e.g., 15,000 - 20,000 for Nylon

3) MW Determinations (many more details later in chapter)

a) We wish to determine both average values of MW and information about MW distribution

b) Some Important Methods

i) Gel Permeation Chromatography, GPC

ii) Light Scattering

iii) Viscometry

iv) Mass Spectroscopy

v) End Group Analysis (Chemical & Spectroscopic)

vi) Colligative Properties (P-Chem Methods)

- Boiling Point Elevation
- Freezing Depression (Cryoscopy)

[1] The graphics in these notes indicated by "Figure/Table/Equation/Etc., x.x in Stevens" are taken from our lecture text: "Polymer Chemistry: An Introduction - 3rd Edition" Malcolm P. Stevens (Oxford University Press, New York,

- Osmometry, etc.

B) Number Average Molecular Weight, M_n bar

1) This term is very sensitive to the total number of molecules in solution and hence is especially sensitive to the low molecular weight monomers and oligomers
   a) Determined by End Group Analysis and Colligative Properties
2) M_n bar = $\Sigma N_i M_i / \Sigma N_i$
3) Example
   a) 9 moles of MW = 30,000 and 5 moles of MW = 50,000 $\Rightarrow$ M_n bar $\approx$ 37,000

C) Weight Average Molecular Weight, M_w bar

1) This term is sensitive to the mass of the molecules in solution and hence is especially sensitive to the very highest MW species present in the system
   a) Determined by Light Scattering and Ultracentrifugation
2) M_w bar = $\Sigma W_i M_i / \Sigma W_i = \Sigma N_i M_i^2 / \Sigma N_i M_i$
3) Example
   a) 9 moles of MW = 30,000 and 5 moles of MW = 50,000 $\Rightarrow$ M_w bar $\approx$ 40,000
4) Note:
   a) M_w bar $\geq$ M_n bar (Draw MW distribution chart)
   b) M_w bar/M_n bar = Polydispersity Index
   c) M_w bar/M_n bar = 1, M_w bar = M_n bar for a sample having a single MW (Monodisperse)

1999).

d) M_w bar/M_n bar ≥ 1 is Polydisperse

D) General Molecular Weight Expression & M_z bar and M_v bar

1) M bar = $\Sigma N_i M_i^{(a+1)} / \Sigma N_i M_i^a$

2) A Higher Order MW, called the Z average, is closely related to processing characteristics ⇒ a = 2

a) M_z bar = $\Sigma N_i M_i^{(2+1)} / \Sigma N_i M_i^2 = \Sigma N_i M_i^{3)} / \Sigma N_i M_i^2$

3) A viscosity based MW, M_v bar, has $0 \le a \le 1$ and closer to 1 (i.e., to M_w bar)

a) M_V bar = $\Sigma N_i M_i^{(1.x)} / \Sigma N_i M_i^{0.x}$

i) Where x is typically close to 1 and ∴ 1.x is typically close to 2

ii) ∴ M_V bar = $\Sigma N_i M_i^{(1.9)} / \Sigma N_i M_i^{0.9}$ in a typical case

b) M_z bar ≥ M_w bar ≥ M_v bar ≥ M_n bar

II Polymer Solutions

A) Steps Dissolving a Discrete Molecule and a Polymer

1) Discrete Molecule Dissolution Steps for a Crystalline Sample

a)

2) Polymer Dissolution Steps

a) solvent diffusion

i) solvation & swelling

ii) ⇒ Gel formation

iii) network polymers stop at this stage, degree of swelling correlated with crosslink density

b) True dissolution

i) untangling of chains

ii) very slow process and may not occur on timescale of real world

B) Thermodynamics of Polymer Dissolution

1) Choosing a Solvent for Polymers

a) Polymer Handbook!!!!! lists solvents and nonsolvents for common polymers

b) Rule of Thumb: Like dissolves Like

2) $\Delta G = \Delta H - T\Delta S$

a) ΔG must be negative for spontaneous (but not necessarily fast) dissolution

b) ΔS will be positive because of greater mobility in solution

c) $\therefore$ need ΔH to be negative or at least not too positive

3) $\Delta H_{mix} \propto (\delta_1 - \delta_2)^2$

a) ΔH_{mix} is the Enthalpy of mixing (dissolution)

b) δ_1 is the Solubility Parameter of one component

c) δ_2 is the Solubility Parameter of the other component

4) In practice, ΔH is seldom negative and we simply try to keep it from getting too positive

5) $\therefore$ we see that we want the polymer and the solvent to have as similar of Solubility Parameters as possible

C) Solubility Parameters, δ

1) The δ Parameters is related to the heat of vaporization of the sample

2) For small molecules these can be measured experimentally

3) ∴ the δ Parameters of solvents are tabulated

   a) multiple parameter expressions can also be used for more precision

4) For conventional polymers these can be estimated using tables

   a) Group Molar Attraction Constants

   b) Table 2.1 in Stevens

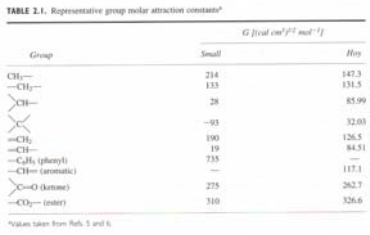

TABLE 2.1. Representative group molar attraction constants[a]

Group	G [(cal cm³)^½ mol⁻¹] Small	Hoy
CH_3—	214	147.3
—CH_2—	133	131.5
>CH—	28	85.99
>C<	−93	32.03
=CH_2	190	126.5
=CH—	19	84.51
—C_6H_5 (phenyl)	735	—
—CH= (aromatic)	—	117.1
>C=O (ketone)	275	262.7
—CO_2— (ester)	310	326.6

[a]Values taken from Refs. 5 and 6.

   c) $\delta = d \Sigma G / M$

      i) G = the individual Group Molar Attraction Constants of each structural fragment

      ii) d = density

      iii) M = molecular weight

D) Hydrodynamic Volume in Solution

1) The apparent size of the polymer in solution

2) Reflects both the polymer chain itself and the solvating molecules in inner and outer spheres

3) Figure 2.1 in Stevens

4) Hydrodynamic Volume is related to an Expansion Factor, α

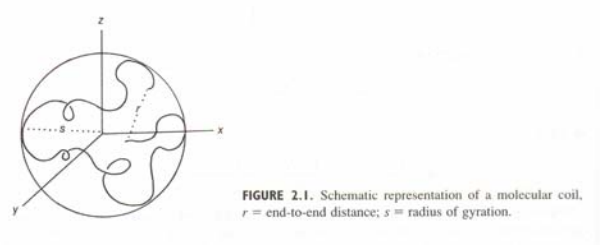

FIGURE 2.1. Schematic representation of a molecular coil. r = end-to-end distance; s = radius of gyration.

   a) α = 1 is the value for the "non-expanded" polymer in the "ideal" statistical coil having the smallest possible size

   b) as α increases, so does the Hydrodynamic Volume of the sample

E) The *Theta* State (θ)

1) Solubility varies with temperature and the nature of the solvent

2) ∴ there will be a minimal dissolution temperature call the *Theta Temperature* and at that point the solvent is said to be the *Theta Solvent*

3) The *Theta State* at this point is the one in which the last of the polymer is about to precipitate

4) Compilations of Theta Temperatures & Solvents are available in the literature

F) Intrinsic Viscosity & Molecular Weight

1) $[\eta]$ = Intrinsic Viscosity (i.e., the viscosity in an "Ideal Solution")

2) Mark- Houwink-Sakurada Equation

   a) $[\eta] = K (M_v \text{ bar})^a$

   b) K and a are characteristic of the particular solvent/polymer combination (more later)

   c) M_v bar = the Viscosity Average Molecular Weight

III Measurement of Number Average Molecular Weight

A) General Considerations

1) Ideal Instrument

   a) Gives full information on the molecular weight distributions for sample

      i) Reliable for all species in sample from monomers to crosslinked polymers

      ii) From this MW distribution can be extracted mathematically for the various types of MW averages (M_w bar, M_n bar, M_v bar, etc.)

iii) Highly sensitive so can use small & very dilute samples

iv) Data quality

- highly accurate
- highly precise

b) Requires no calibration

i) Neither at the start of each run nor for different types of samples

c) Cost and convenience

i) low cost to buy and maintain

ii) highly reliable/robust

iii) easy to operate

2) Real Instruments

a) Most methods give only averages

i) exceptions are: GPC, Light Scattering, & MS

b) Most methods' results vary depending on the structure of the sample

i) ∴ need to calibrate each sample and/or know some structural information such as branching

c) Most methods have limited sensitivities and/or linear ranges

d) Most methods require expensive instrumentation

e) There can be substantial disagreements between the results of different techniques

f) However, many methods are improving in these areas rapidly

B) End-Group Analysis

1) Basic principles

a) The structures of the end groups must be different from that of the bulk repeating units (e.g., CH_3 vs. CH_2 in an ideal polyethylene)

b) ∴ If you detect the concentration of the end group and know the total amount of sample present you can calculate the average MW, M_n bar

i) need to have either a perfectly linear polymer (i.e., two end groups per chain) or need to know information about the amount of branching

ii) ∴ the Mn bar values that come out for "linear" polymers must typically be considered an upper bound since there may be some branching

c) Detection of concentrations of end groups

i) Spectroscopy - IR, NMR, UV-Vis

ii) Elemental Analysis

iii) Radioactive or Isotopic labels

2) Strengths

a) The requisite instruments are in any department

b) can be quite quick

c) Sometimes this information comes out "free" during polymer structural studies

3) Weaknesses

a) does not give MW distribution information

b) need to know information about the structure

i) identity and number of end groups in each polymer molecule

c) limited to relatively low MW for sensitivity reasons

i) 5,000 - 10,000 is typical MW range

ii) Can be high with some detections types

- radioactive labeling of end groups
- fluorescent labeling of end groups

C) Colligative Properties - Membrane Osmometry

1) Figures 2.2, 2.3, & 2.4 in Stevens

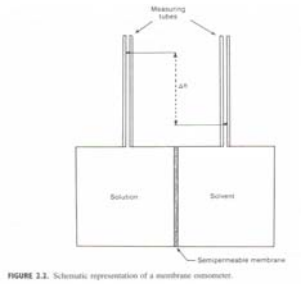

FIGURE 2.2. Schematic representation of a membrane osmometer.

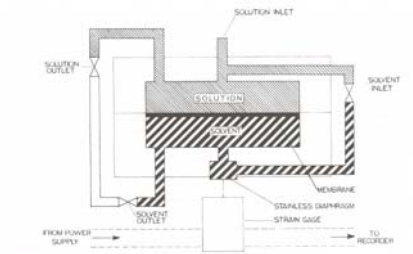

FIGURE 2.3. Automatic membrane osmometer [Courtesy of Wescan Instruments, Inc.]

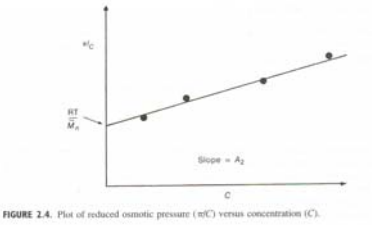

FIGURE 2.4. Plot of reduced osmotic pressure (π/C) versus concentration (C).

2) Basic principles

a) molecules dissolved in solvents change the structure of the solution

b) solvent molecules want to diffuse into the solution with the highest solute concentration (in terms of moles)

c) Figure 2.3 in Stevens

3) Strengths

a) quick

4) Weaknesses

a) does not give MW distribution information

b) range of 50,000 to 2,000,000 limited by low molecular weight species present and sensitivity, respectively

D) Colligative Properties - Vapor Pressure Osmometry

1) Basic principles
   a) Diagram
   b) Same physical chemistry principles as membrane osmometry except that the solvent molecules move through gas phase instead of membrane
2) Strengths
   a) quick
   b) not hurt by low MW species as is membrane Osmometry
   c) home-made systems can be very inexpensive
3) Weaknesses
   a) does not give MW distribution information
   b) while can be used up to MW of 40,000 is more typically used for MW below 25,000

E) Colligative Properties - Cryoscopy & Ebulliometry

1) Basic principles
   a) changes in solution structures upon dissolution decrease mp and increase bp
2) Strengths
   a) can be quick and inexpensive
3) Weaknesses
   a) does not give MW distribution information
   b) mostly limited to MW below 20,000

IV Measurement of Weight Average Molecular Weight

A) Light Scattering

1) Basic Principles - Static and Dynamic

a) Instrumentation

i) Figures 2.7 in Stevens

ii) Moving detector

iii) Multiple Solid State Detectors

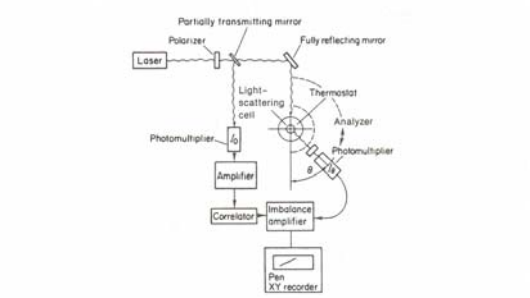

FIGURE 2.7. Schematic of a laser light-scattering photometer. [From Rabek,[94] copyright 1980. Reprinted by permission of John Wiley & Sons, Ltd.]

b) each polymer molecule in solution (and its associated solvent molecules) has a different refractive index than neat solvent

c) ∴ they behave as tiny lenses and scatter light

i) scan detector over a range of angles or use multiple detectors

ii) measure scattered intensity as a function of angle and concentration

iii) Use "Zimm" plot to extrapolate to infinite dilution and to zero degrees

iv) Figure 2.6 in Stevens

d) Brownian motion effects and dynamic light scattering

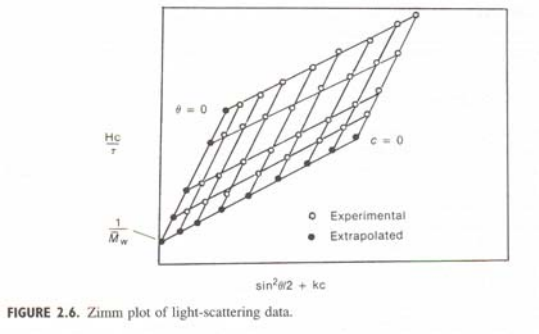

FIGURE 2.6. Zimm plot of light-scattering data.

2) Strengths

a) an absolute method that does not need calibration

b) can give shape information as well as MW information

c) quite sensitive and easy to couple to an LC

3) Weaknesses

a) cost!

B) Ultracentrifugation

1) Basic Principles

   a) each polymer molecule in solution (and its associated solvent molecules) has a different density than neat solvent

   b) ∴ if one has a density gradient in the solution (ultracentrifuge generates this from the salt solution) the polymers will settle to their optimum levels

   c) measure sedimentation height/velocity

2) Strengths

   a) excellent for polymers having a variety of specific MWs, e.g., proteins

3) Weaknesses

   a) does not give MW distribution information

   b) costly if don't have an ultracentrifuge for other reasons

   c) time consuming

   d) not as useful with true "bell curve" MW distributions

V Viscometry

A) Viscosity Measurement

1) Table 2.2 in Stevens

TABLE 2.2. Dilute Solution Viscosity Designations[a]

Common Name	*IUPAC Name*	*Definition*
Relative viscosity	Viscosity ratio	$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0}$
Specific viscosity	—	$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_{rel} - 1$
Reduced viscosity	Viscosity number	$\eta_{red} = \frac{\eta_{sp}}{C} = \frac{\eta_{rel} - 1}{C}$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \frac{\ln \eta_{rel}}{C}$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \left(\frac{\eta_{sp}}{C}\right)_{C=0} = (\eta_{inh})_{C=0}$

[a]Concentrations (most commonly expressed in grams per 100 mL of solvent) of about 0.5 g/dL.

2) Basic Principles

   a) Math & Mark-Houwink-Sakurada Equation

      i) $[\alpha] = K (M_v \text{ bar})^a$

ii) K and a are characteristic of the particular solvent/polymer combination (more later)

iii) M_v bar = the Viscosity Average Molecular Weight

b) Measurement of [η]

i) Make up 5-6 solutions at different concentrations of the same sample and of pure solvent

ii) measure the time it takes each of them to flow through the viscometer

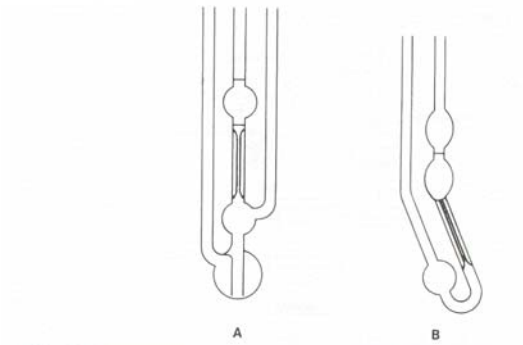

FIGURE 2.8. Capillary viscometers: (A) Ubbelohde, and (B) Cannon–Fenske.

iii) extrapolate to viscosity at zero concentration which gives the intrinsic viscosity

c) Measurement of [η] K and a

i) Plot the [η] values against the MW values from another technique and get K and a from the intercept and slope

d) MW determination for a polymer of known structure

i) Look up K and a in the Polymer Handbook

- Table 2.3 in Stevens

ii) Use the [η] values to calculate M_v bar directly

TABLE 2.3. Representative Viscosity-Molecular Weight Constants[a]

Polymer	Solvent	Temperature, °C	Molecular Weight Range × 10^{-4}	$K^b \times 10^3$	a^b
Polystyrene	Cyclohexane	35[c]	8–42[e]	80	0.50
(atactic)[d]	Cyclohexane	50	4–137[e]	26.9	0.599
	Benzene	25	3–61[f]	9.52	0.74
Polyethylene (low pressure)	Decalin	135	3–100[g]	67.7	0.67
Poly(vinyl chloride)	Benzyl alcohol	155.4[g]	4–35[e]	156	0.50
	Cyclohexanone	20	7–13[f]	13.7	1.0
Polybutadiene					
98% *cis*-1,4, 2% 1,2	Toluene	30	5–50[g]	30.5	0.725
97% *trans*-1,4, 3% 1,2	Toluene	30	5–16[g]	29.4	0.753
Polyacrylonitrile	DMF[h]	25	5–27[e]	16.6	0.81
	DMF	25	3–100[g]	39.2	0.75
Poly(methyl methacrylate-*co*-styrene)					
30–70 mol %	1-Chlorobutane	30	5–55[e]	17.6	0.67
71–29 mol %	1-Chlorobutane	30	4.8–81[e]	24.9	0.63
Poly(ethylene terephthalate)	*m*-Cresol	25	0.04–1.2[g]	0.77	0.95
Nylon 66	*m*-Cresol	25	1.4–5[f]	240	0.61

[a] Values taken from Ref. 4e.
[b] See text for explanation of these constants.
[c] Atactic defined in Chapter 3.
[d] θ temperature.
[e] Weight average.
[f] Number average.
[g] N,N-dimethylformamide.

e) Bootstrapping for a new polymer

i) make 3 or more samples of your polymer having different average MWs

- measure the viscosities of each of these

ii) go to Polymer Handbook or your own research and find K and a values for the most closely related polymer

- these are a 1st guess/estimate of those for your polymer

iii) use these K and a values and the experimental [η] values to give a 1st estimate of the MW values for your polymer

iv) use these 1st estimate MW values and the experimental [η] values to calculate new K and a values

v) use these new K and a values and the experimental [η] values to get a better estimate of the MW values

vi) use these 2nd estimate MW values and the experimental [η] values to calculate new K and a values

vii) use these new K and a values and the experimental [η] values to get a better estimate of the MW values

viii) continue until these results converge

3) Strengths

a) very quick and reliable

b) no expensive equipment required

4) Weaknesses

a) does not give MW distribution information

b) need good values for K and a

VI Molecular Weight Distribution

A) Gel Permeation Chromatography, GPC

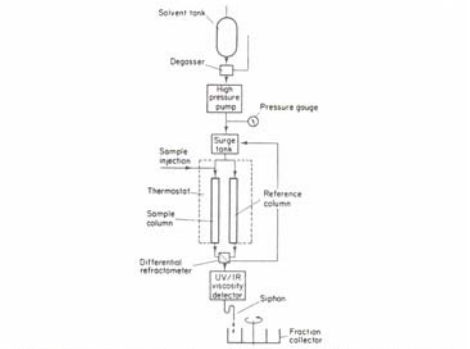

FIGURE 2.9. Schematic representation of a gel permeation chromatograph. [From Rabek,[78] copyright 1980. Reprinted by permission of John Wiley & Sons, Ltd.]

1) Basic Principles

a) Figure 2.9 in Stevens

b) this is a type of liquid chromatography (also called size exclusion chromatography)

c) one uses a different type of column for separation

i) NOT affinity but rather via the residence time in different sized pores of the packing material

ii) the beads are made from styrene and divinyl benzene copolymer where the exact conditions and the nature of the template molecules allows the vendors to make packing beads of controllable diameters

iii) High MW samples come through first (they don't fit in the pores)

iv) Low MW samples come through last

v) Figure 2.10 in Stevens

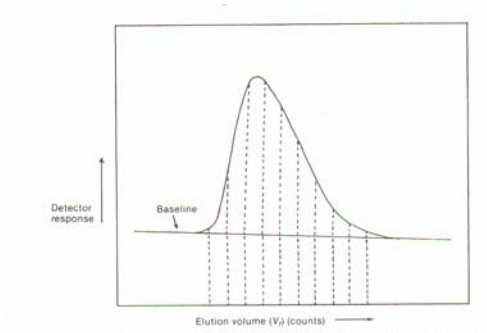

FIGURE 2.10. Typical gel permeation chromatogram. Dotted lines represent volume "counts."

d) The Chromatogram is a graph of intensity vs. time

e) Calibration curve

i) Figure 2.12 in Stevens

ii) this needs to be calibrated wrt.

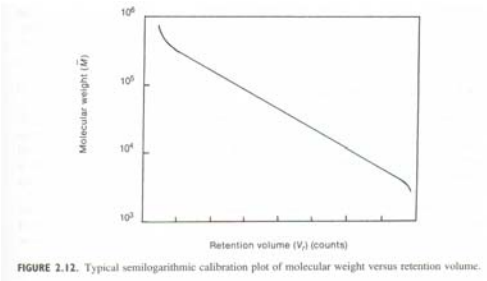

FIGURE 2.12. Typical semilogarithmic calibration plot of molecular weight versus retention volume.

standards to put MW on bottom axis

- typically monodisperse polystyrene or poly(vinyl alcohol)

iii) want a perfectly linear calibration chart for MW from 0 to 100,000,000

- however, it curves up at high MW because all of the large polymers are excluded from the pores and ∴ come strait through
- also, it curves down at low MW because to all of the small molecules the pores are equally oversized

iv) need to do a calibration curve for each polymer/solvent combination

v) Gives Polystyrene (or Poly(vinyl alcohol)) Equivalent MWs

f) Universal calibration

i) Figure 2.11 in Stevens

ii) log([η]M) is plotted with time on the x axis

iii) All or almost all polymers then fit on the same curve as the intrinsic viscosity acts as a "fudge factor"

iv) Gives Polystyrene (or Poly(vinyl alcohol)) Equivalent MWs

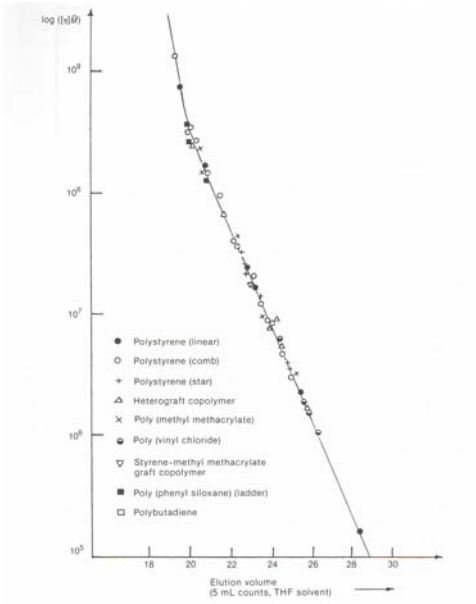

FIGURE 2.11. Universal calibration for gel permeation chromatography. THF, tetrahydrofuran. [From Grubisic, Rempp, and Benoit,[24] copyright 1976. Reprinted by permission of John Wiley & Sons, Inc.]

2) Strengths

a) gives a full molecular weight distribution

3) Weaknesses

a) costs

b) need to calibrate

c) ∴ use an online absolute detector such as a light scattering detector

B) Mass Spectrometry

1) Basic Principles

a) sample volatilization

i) Field Desorption, FD

ii) Fast Atom Bombardment, FAB

iii) Laser Desorption, LD

iv) Matrix Assisted Laser Desorption, MALDI

v) Electrospray, ESI

b) ion separation by mass

i) Ion Traps / Ion Cyclotron Resonance, IT/ICR

ii) Quadrupole, Q

iii) Time of Flight, TOF

c) Combinations of different components, e.g., MALDI-TOF

i) Figure 2.5 in Stevens

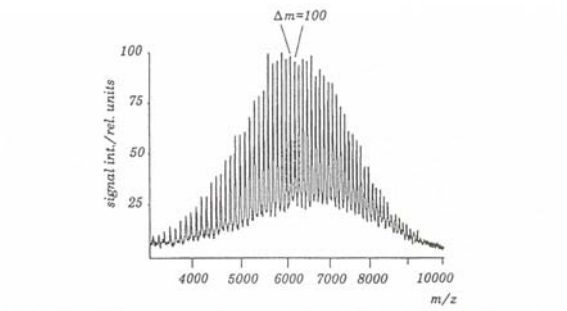

FIGURE 2.5. MALDI mass spectrum of low-molecular-weight poly(methyl methacrylate). [From Bahr, Deppe, Karas, and Hillenkamp,[13] copyright 1992. Reprinted by permission of the American Chemical Society.]

d) Rapidly improving due to proteomics/genomics research

2) Strengths

a) One often has the equipment for other purposes

b) Can give MW distributions, especially when coupled to an LC

c) Can give structural information

3) Weaknesses

a) cost

b) time to optimize conditions

C) Fractional Solution & Fractional Precipitation

1) Basic Principles

2) Strengths

3) Weaknesses