Chapter 11 - 14

Measurement of Molar Mass

MM determination

- M_n
  - end-group analysis
  - colligative property measurement
    - osmotic pressure, vapor pressure, bp, fp

$$\bar{M}_n = \sum X_i M_i = \frac{\sum N_i M_i}{\sum N_i}$$

- M_w
  - light scattering
  - sedimentation (by ultracentrifugation) pp306-307

$$\bar{M}_w = \sum w_i M_i = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

- M_v
  - (dilute solution) viscometry
    - volume → mass ~ a relative MM
- MMD
  - fractionation and GPC
  - mass spectroscopy

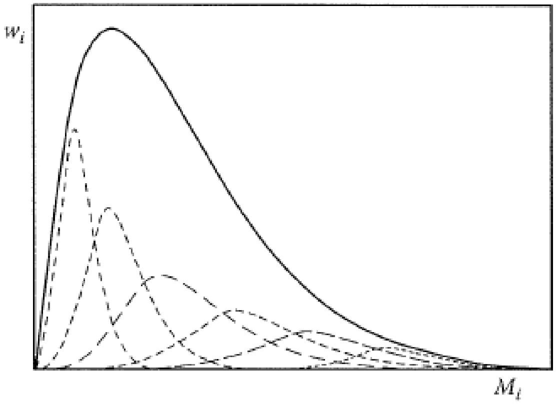


Fig 14.4 p317

End-group analysis

- step polymers

  pp278-279

  -OH, -COOH, $-NH_2$, ---

  - titration or spectroscopic methods
- chain polymers

  RMMMM-----   (R=initiator fragment)

  - spectroscopic methods
- accurate but limited
  - small conc'n of end-group
  - for $M_n < 15000$

Colligative property measurements

- colligative (collective) property
  - property that depends only on the number of molecules
  - osmotic pressure, boiling point, freezing point, etc
  - counting number & measuring weight → M_n
- chemical potential in solution, μ
  - partial molar free energy $$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}$$
  - $\Delta G_1 = \mu_1 - \mu_1^o = RT \ln a_1 = RT \ln \gamma_1 n_1$
  - For dilute polymer solution ($c_2 \rightarrow 0$)

    ↙ solvent behaves ideally, $a_1 \approx n_1$
  - $\mu_1 - \mu_1^o = RT \ln n_1 = RT \ln (1 - n_2)$

    $= -RT[n_2 + n_2^2/2 + n_2^3/3 + \text{-----}]$

a: activity
γ: activity coeff.
n: mol fraction
c: wt conc’n

c: wt conc'n
m: # of moles
V_1^0: molar vol
M: molar mass

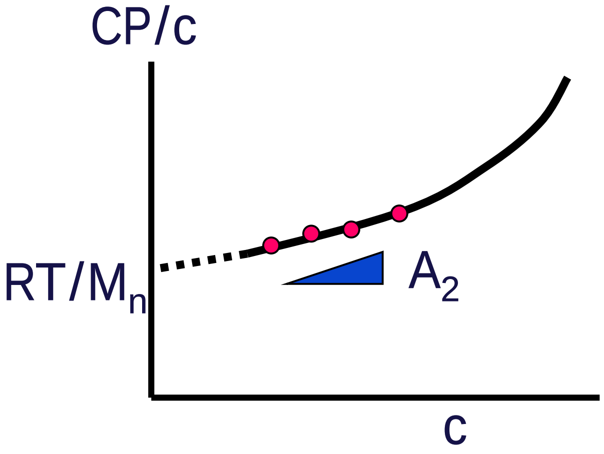
- $n_2 = m_2/(m_1+m_2) \approx m_2/m_1 = (m_2/L)/(m_1/L)$
  $= (c_2/M_2)/(1/V_1^0)$ [(g/L)/(g/mol)]/[(1/(L/mol)]
  $= (c_2V_1^0)/M_2$

- $\mu_1 - \mu_1^o = -RT[n_2 + n_2^2/2 + n_2^3/3 + \text{----}]$
  $= -RTV_1^0[(1/M_2)c_2 + (V_1^0/2M_2^2)c_2^2 + (V_1^{02}/3M_2^3)c_2^3 \text{ --}]$

- $$\underbrace{-(\mu_1 - \mu_1^o)/V_1^0}_{\text{colligative property (CP)}} = RT\ [(1/M_2)\ c_2 + A_2\ c_2^2 + A_3\ c_2^3 + \text{----}]$$
  - a virial equation
    - A_2 ~ 2nd virial coeff, A_3 ~ 3rd virial coeff

- for dilute polymer soln, $c_2 \rightarrow 0$

$$\boxed{[CP/c]_{c \rightarrow 0} = RT/M_n}$$



Membrane osmometry (MO)

- osmotic pressure, π

pp269-275

$$\mu_1 - \mu_1^{\circ} = -\pi\bar{V}_1$$

π = ρgh

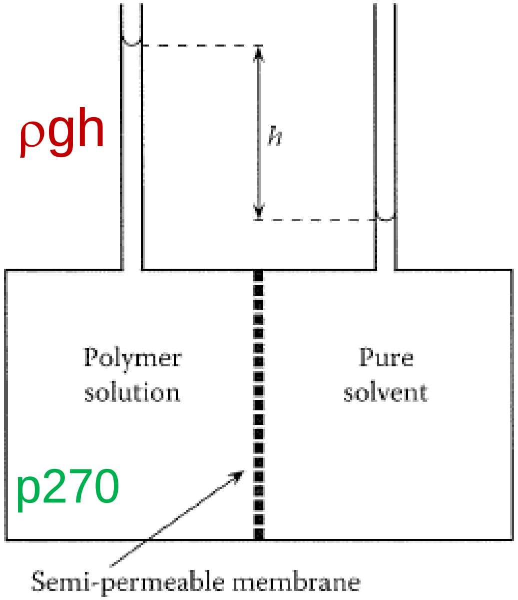


Fig 11.1 p270

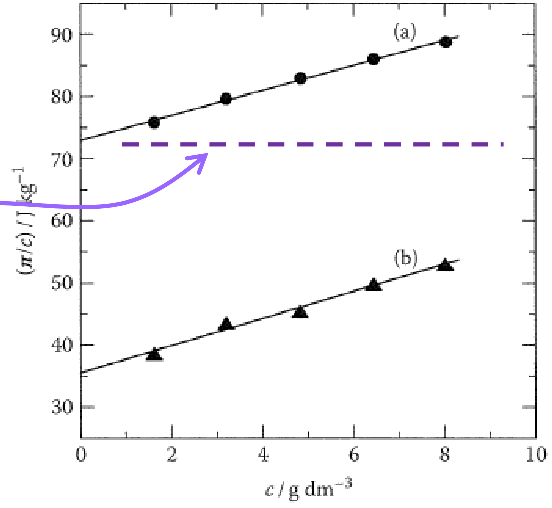
- virial eqn for π

$$\frac{\pi}{c} = \mathbf{R}T\left[\frac{1}{\bar{M}_n} + A_2c + A_3c^2 + \ldots\right]$$

$$\boxed{\left(\frac{\pi}{c}\right)_{c\to 0} = \frac{\mathbf{R}T}{\bar{M}_n}}$$

<cf> also, $\left(\frac{\pi}{c}\right)_{\theta} = \frac{\mathbf{R}T}{\bar{M}_n}$

Fig 11.2 p273



- static or dynamic method
- for 5E4 < M_n < 1E6
  - diffusion of solute; small signal (π)

Vapour pressure osmometry (VPO)

- lowering of solvent vapor pressure

pp275-277

$$\frac{1}{P}\left(\frac{dP}{dT}\right)=\frac{\Delta H_v}{\mathbf{R}T^2}$$

$$\ln\left(\frac{P^0_{1,T_0}}{P_{1,T_0}}\right)=\frac{\Delta H_v \Delta T_e}{\mathbf{R}T_0^2}$$

- the virial eqn

$$\frac{\Delta T_e}{c}=K_e\left[\frac{1}{\overline{M}_n}+A_2c+A_3c^2+\ldots\right]$$

- for $M_n < 15000$
  - small signal (ΔR)
  - complementary to MO

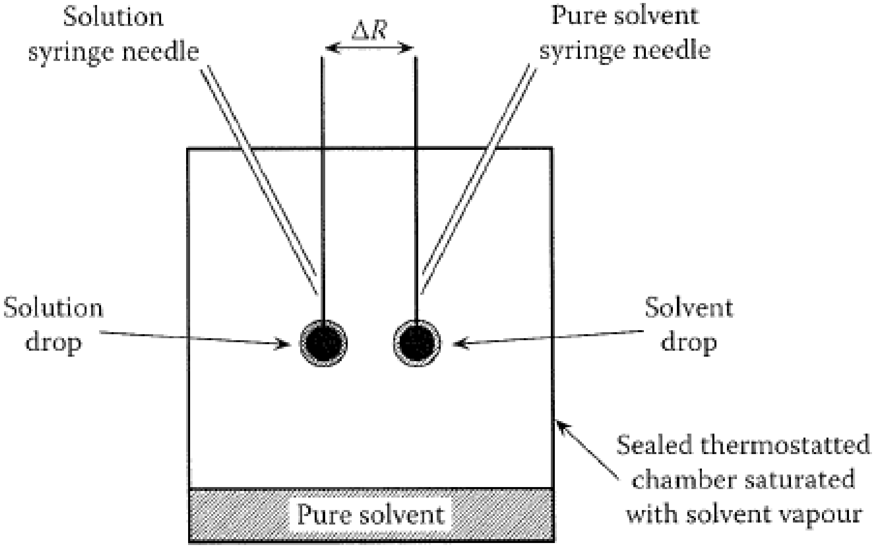


Fig 11.4 p275

Ebulliometry and Cryoscopy

pp277-278

- ebulliometry (bp elevation)
  - $\Delta T_b/c = K_e\ [(1/M_n) + A_2\, c + A_3\, c^2 + \text{----}]$
    - K_e calibrated with known mol wt
    - foaming
- cryoscopy (fp depression)
  - $\Delta T_f/c = K_c\ [(1/M_n) + A_2\, c + A_3\, c^2 + \text{----}]$
    - K_c calibrated with known mol wt
    - supercooling
- limited by precision of temperature measurement
    - useful only for $M_n < 5000$
    - not used these days

Light scattering (LS)

- light scattering

pp281-283

  - static LS ~ time-averaged intensity of light measured
    - elastic [Rayleigh] scattering ~ same freq ~ M_w
    - inelastic [Raman] scattering ~ bond vibration energy
  - dynamic LS ~ movement of particle ~ Doppler effect
- LS by small gas molecule

$$\frac{I_\theta}{I_0} = \frac{8\pi^4\alpha^2(1+\cos^2\theta)}{\lambda^4 r^2}$$

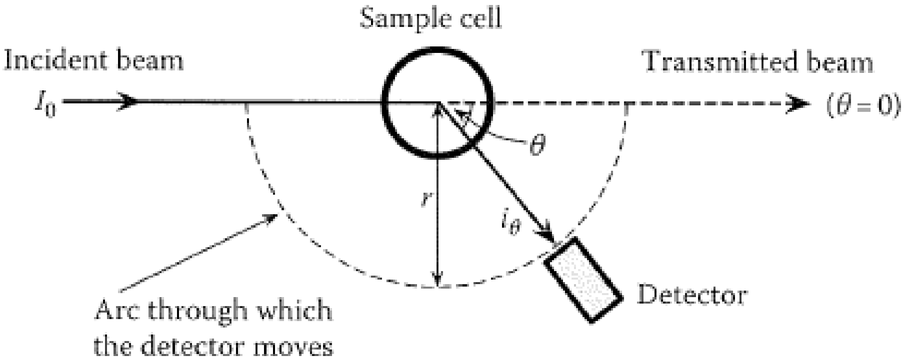


Fig 12.1 p282

  - Rayleigh Eqn
  - α ~ polarizability of molecule
- why M_w?
  - intensity $\propto$ [amplitude]^2 $\propto$ [mass]^2 $\propto$ [polarizability]^2

❑ LS by gas (cont'd)

converting α to refractive index **n** (measurable)

$$\frac{i_\theta}{I_0} = \frac{2\pi^2 (\mathrm{d}n/\mathrm{d}c)^2 c^2 (1+\cos^2\theta)}{\lambda^4 r^2 (N/V)}$$

$N/V = c/(M/\mathbf{N}_A)$ where M is the molar mass of the gas molecules

$$\frac{i_\theta}{I_0} = \frac{2\pi^2 (\mathrm{d}n/\mathrm{d}c)^2 Mc (1+\cos^2\theta)}{\lambda^4 r^2 \mathbf{N}_A} \qquad (12.6)$$

R ~ Rayleigh ratio ~ measuring

$$R = \frac{i_\theta r^2}{I_0 (1+\cos^2\theta)} \longrightarrow \boxed{R = \frac{2\pi^2 (\mathrm{d}n/\mathrm{d}c)^2 Mc}{\lambda^4 \mathbf{N}_A}}$$

LS by (dilute) solution of small molecules pp284-286

$$\Delta R = R_{\text{solution}} - R_{\text{solvent}}$$ by concentration fluctuation

$$\Delta R = \frac{2\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2 \delta V \left\langle (\delta c)^2 \right\rangle}{\lambda^4} \qquad (12.14)$$

from fluctuation theory, $\left\langle (\delta c)^2 \right\rangle = \dfrac{\mathbf{R}Tc}{\delta V \mathbf{N}_{\mathrm{A}} (\partial \pi / \partial c)}$

π ~ osmotic pressure

$$\frac{\partial \pi}{\partial c} = \mathbf{R}T \left[\frac{1}{M} + 2A_2 c + 3A_3 c^2 + \ldots \right] \longleftarrow \frac{\pi}{c} = \mathbf{R}T \left[\frac{1}{\overline{M}_n} + A_2 c + A_3 c^2 + \ldots \right]$$

$$\Delta R = \frac{2\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2 c}{\mathbf{N}_{\mathrm{A}} \lambda^4 [(1/M) + 2A_2 c + 3A_3 c^2 + \ldots]}$$

$$\boxed{\frac{Kc}{\Delta R} = \frac{1}{M} + 2A_2 c + 3A_3 c^2 + \ldots}$$

$$K = \frac{2\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2}{\mathbf{N}_{\mathrm{A}} \lambda^4}$$

K ~ optical constant (exp’t condition)

- LS by sol'n of large molecules (D > λ/20 ≈ 20 nm)
  - asymmetry + interference → angular dependence of i

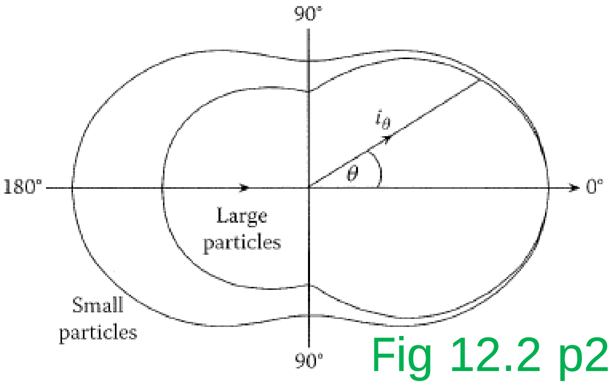


Fig 12.2 p283

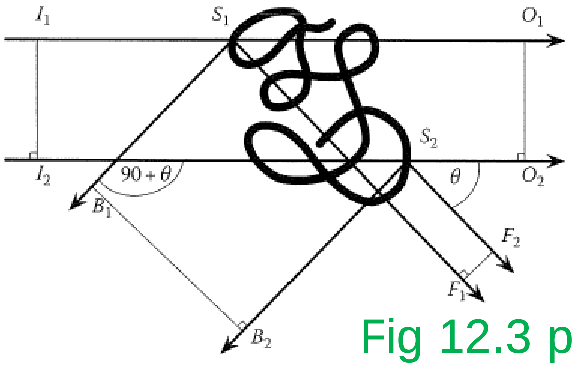


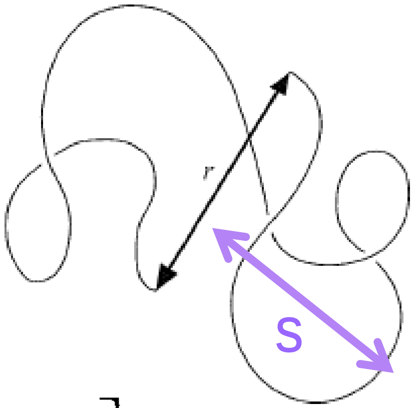
Fig 12.3 p286

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{P(\theta)}\left[\frac{1}{M} + 2A_2c + 3A_3c^2 + \ldots\right]$$

$$P(\theta) = \frac{\Delta R_\theta}{\Delta R_{\theta=0}}$$ ~ scattering factor (angular dependency of ΔR)

LS by polymer sol'n (cont'd)

p253



$$\frac{1}{P(\theta)} \approx 1 + \left(\frac{q^2 \langle s^2 \rangle}{3} \right)$$

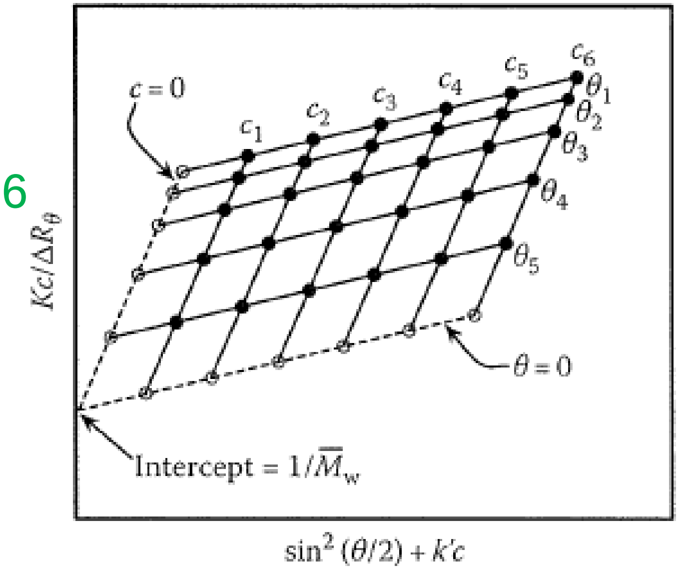
$\langle s^2 \rangle$ ~ mean-square radius of gyration

$$\frac{Kc}{\Delta R_\theta} = \left[\frac{1}{M} + 2A_2 c + 3A_3 c^2 + \ldots \right] \left[1 + \left(\frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2} \right) \langle s^2 \rangle \right]$$

$$\boxed{\left(\frac{Kc}{\Delta R_\theta} \right)_{\substack{c \to 0 \\ \theta \to 0}} = \frac{1}{\bar{M}_w}}$$

'Zimm plot'

Fig 12.3 p286



- must be dust-free
- 2E4 < M_w < 5E6
  - small intensity (i_θ); cancelling

Dilute solution viscometry (DSV)

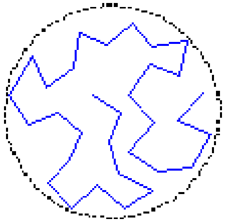
- viscosity η and MM

pp263-264

$$\eta = \eta_0\left[1+\left(\frac{5}{2}\right)\phi_2\right]$$ Einstein eqn

$$\phi_2 = \left(\frac{c}{M}\right)\mathbf{N}_\mathbf{A}V_\mathrm{h}$$

$$\eta_{sp} = (\eta-\eta_0)/\eta_0 = \left(\frac{5}{2}\right)\left(\frac{c}{M}\right)\mathbf{N}_\mathbf{A}V_h$$



η_0 ~ solvent viscosity
ϕ_2 ~ vol fraction of solute
c ~ conc'n of polymer [g/L]
M ~ MM of polymer
V_h ~ hydrodynamic volume
= vol of equiv. sphere
η_{sp} ~ specific viscosity

- intrinsic viscosity [η]

$$[\eta] = \lim_{c\to 0}\left(\frac{\eta_{sp}}{c}\right) = \left(\frac{5}{2}\right)\frac{\mathbf{N}_\mathbf{A}V_\mathrm{h}}{M}$$

$$= \Phi_0^s\alpha_\eta^3\left(\frac{\langle s^2\rangle_0}{M}\right)^{3/2} = K_\theta\alpha_\eta^3 M^{1/2}$$ Flory-Fox eqn

$V_h = (4/3)\,\pi\,R_h^3$
$R_h \propto \alpha_\eta\,\langle s^2\rangle_0^{1/2}$
α_η ~ expansion parameter
$\alpha_\eta \propto x^\Delta \propto M^\Delta$

$$K_\theta = \Phi_0^s\left(\frac{\langle s^2\rangle_0}{M}\right)^{3/2}$$

$$\boxed{[\eta] = KM^a}$$ Mark-Houwink-Sakurada eqn

viscosity-average MM, M_v

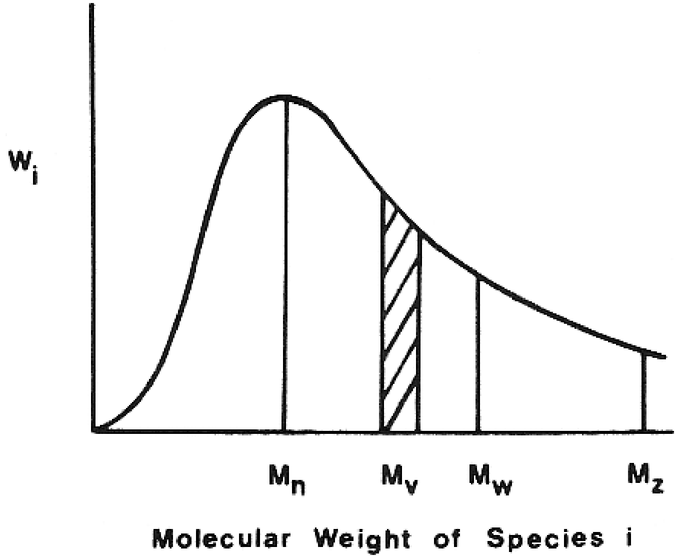
pp300-301

$$\boxed{[\eta] = KM^a}$$

$$[\eta] = \lim_{c\to 0}\left(\frac{\eta_{sp}}{c}\right) = K\left(\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i}\right)$$

$$\boxed{\bar{M}_v = \left(\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i}\right)^{1/a}}$$

- $0.5 \le a \le 0.8$
  - 0.5 at θ-condition; often > 0.7
- $M_n < M_v < M_w$; close to M_w
  - $a = 1 \rightarrow M_v = M_w$
  - $a = -1 \rightarrow M_v = M_n$



- DSV experiment pp299-304

$$\eta_{sp} = k_0[\eta]c + k_1[\eta]^2c^2 + k_2[\eta]^3c^3 + \ldots$$

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c$$ Huggins eqn

$$\frac{\ln(\eta_r)}{c} = [\eta] + k_K[\eta]^2 c$$ Kraemer eqn

$$\frac{V}{t} = \frac{\pi r^4 P}{8\eta l}$$

$$\eta_r = \frac{\eta_s}{\eta_0} = \frac{\rho_s t_s}{\rho_0 t_0}$$

$$\eta_{sp} = \eta_r - 1$$

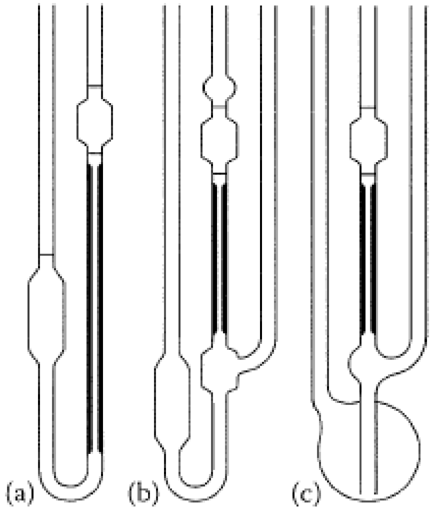


Fig 13.2 p303

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

  - K, a from handbook Table 13.2 p302
    - at the same solvent and temp

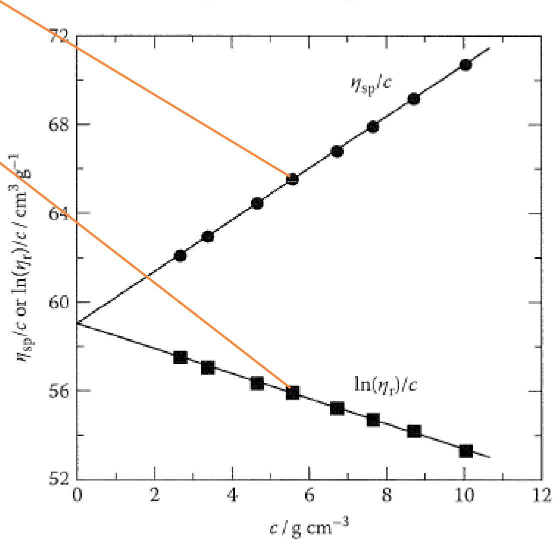


Fig 13.1 p301

- cautions
  - Temp control < 0.01 °C
  - t_0 > 100 s (laminar); c < 1 g/dL (Newt)

Gel permeation chromatography (GPC)

- a size-exclusion chromatography (SEC)
  - separation by size using porous gel
  - Larger molecules elute earlier.

pp318-325

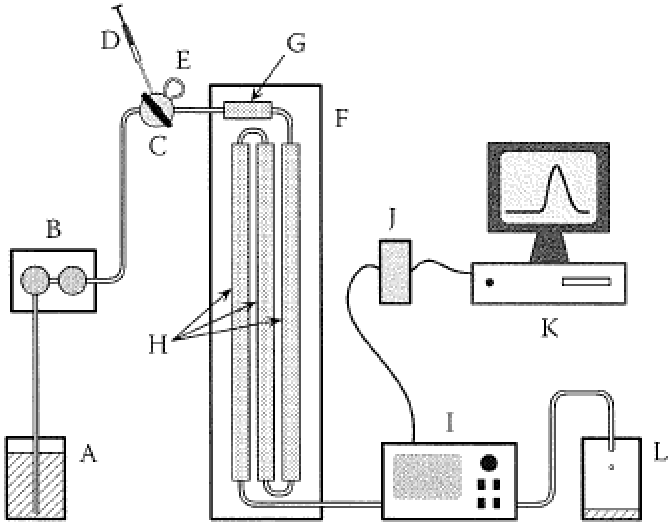


Fig 14.9 p323

Fig 14.5
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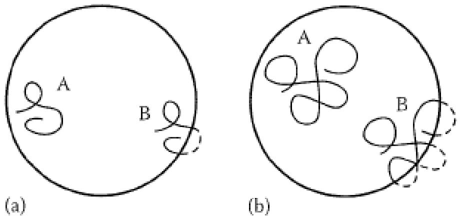


- elution volume V_e and size

$$V_e = V_0 + V_i \exp\left(\frac{-A_s\bar{L}}{2}\right)$$

L ~ diameter of molecule
in sol'n ~ 2 R_h

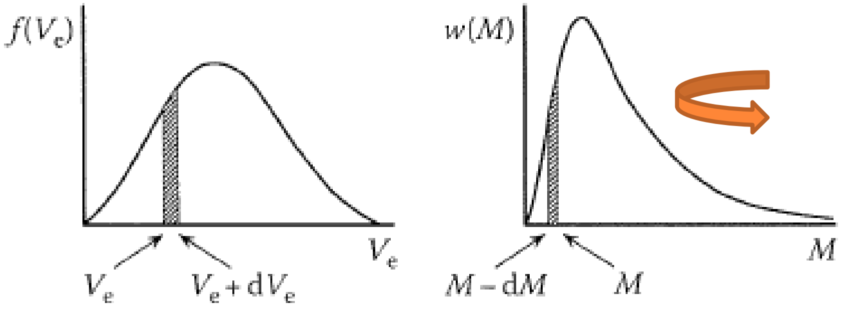


Fig 14.7 p320

- V_e to MM

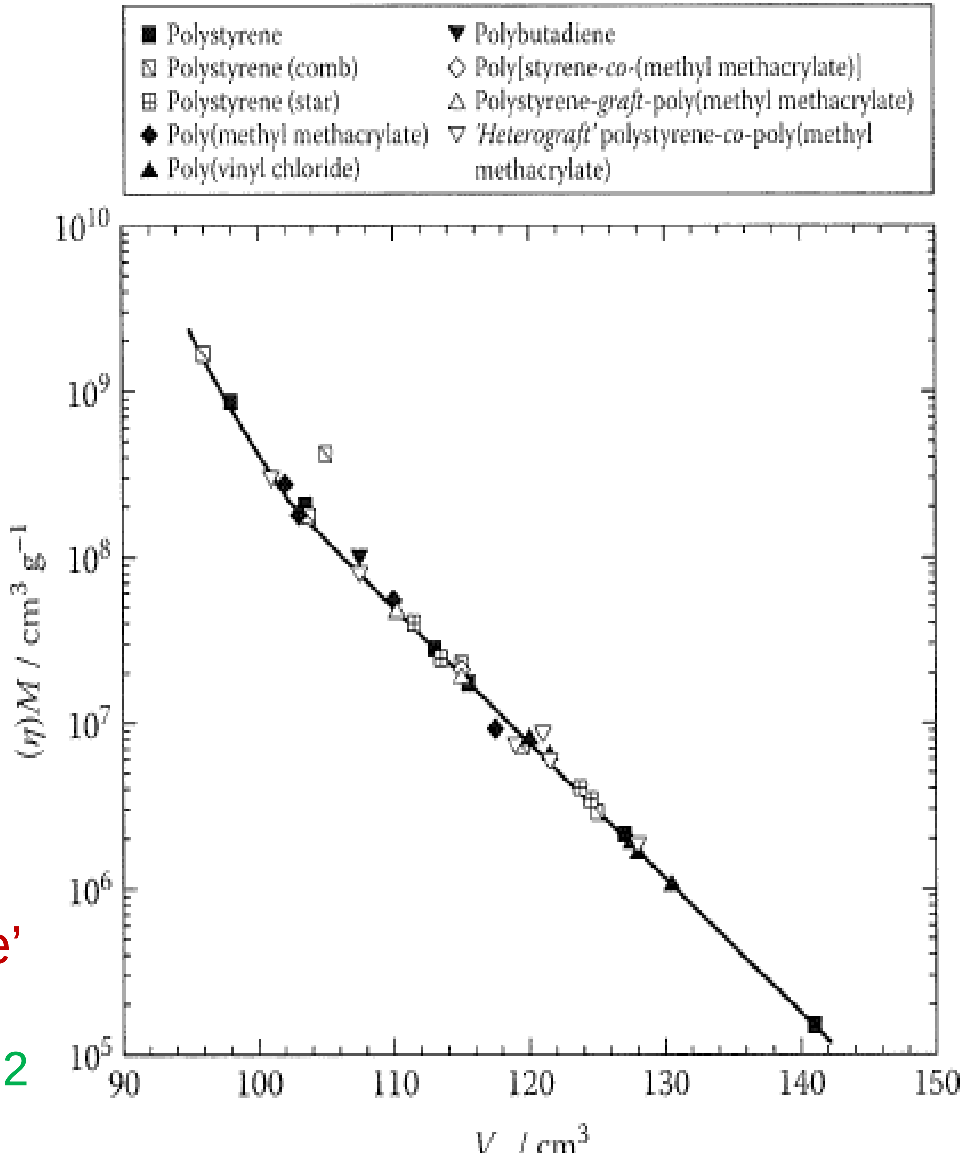
$$[\eta] = \lim_{c\to 0}\left(\frac{\eta_{sp}}{c}\right) = \left(\frac{5}{2}\right)\frac{\mathbf{N_A} V_h}{M}$$

$$V_h = \left(\frac{2}{5}\right)\frac{[\eta]M}{\mathbf{N_A}}$$

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

$$[\eta]M = KM^{1+a}$$

$$M(V_e) = \left[\frac{([\eta]M)_{V_e}}{K}\right]^{1/(1+a)}$$



‘universal calibration curve’

Fig 14.8 p322

- V_e to MM (cont'd)
  - 'universal calibration'
    - With the same instrument, column, and solvent, the same V_e represents the same V_h, regardless of the polymer.
    - Many polymers fall on the same curve on $\log[\eta]M$ - V_e plot.
  - experiment
    - Run GPC with sample and standards (anionic PS).
      - standard with known MM, K, a (sample also with known K, a)
    - For each fraction (V_e), get M.
      - $[\eta]_{PS}M_{PS} = [\eta]_{sample}M_{sample}$
      - $K_{PS}M_{PS}^{a(PS)+1} = K_{sample}M_{sample}^{a(sample)+1}$
    - Calculate M_n, M_w, and MMD.

'fraction' ~
$M \approx M_n \approx M_v \approx M_w$

$$[\eta]M = KM^{1+a}$$

Mass spectroscopy (MS)

pp331-340

- MS determines MM
  - by detecting molecular ion, M^+
  - in vapor phase
  - For polymers;
    - non-volatile ~ ionization
    - fragmentation
- MALDI-ToF technique
  - a soft ionization
    - choice of the matrix critical
  - still for not-too-high MM
    - incomplete ionization, fragmentation, etc

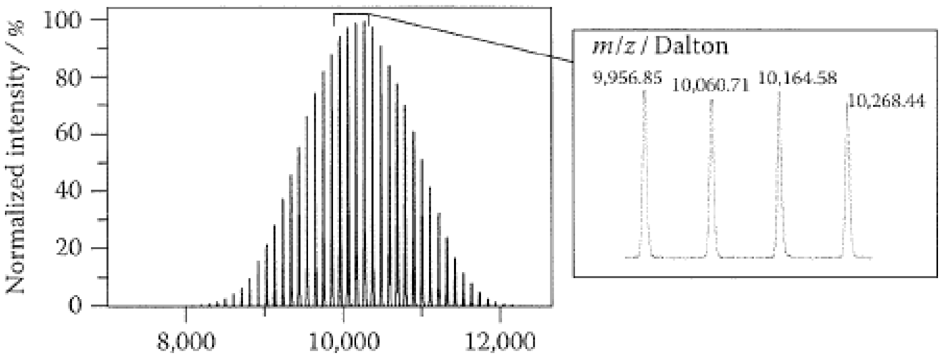


Fig 14.13 p333