Chapter 11 – 14

Determination of Molar Mass and MM Distribution

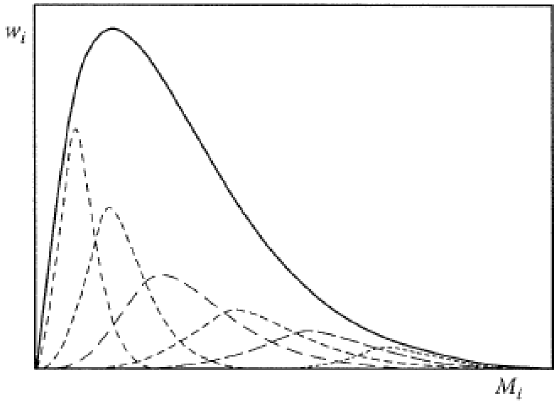
(Average) molar mass determination

- M_n Chapter 11
  - colligative property measurement
    - osmotic pressure, vapor pressure, bp, fp
  - end-group analysis
- M_w Chapter 12
  - light scattering
  - sedimentation (by ultracentrifugation)
- M_v Chapter 13
  - (dilute solution) viscometry
    - volume → mass ~ M_v is a relative MM.
- MMD [MWD] Chapter 14
  - fractionation and GPC
  - mass spectroscopy

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

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

Fig 14.4 p317



Colligative property

= property that depends only on the # of solute

(not on the size or nature)

- measuring gives M_n
  - M_n = total weight / total #

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

- the 4 CP's

as MM ↑, signal ↓

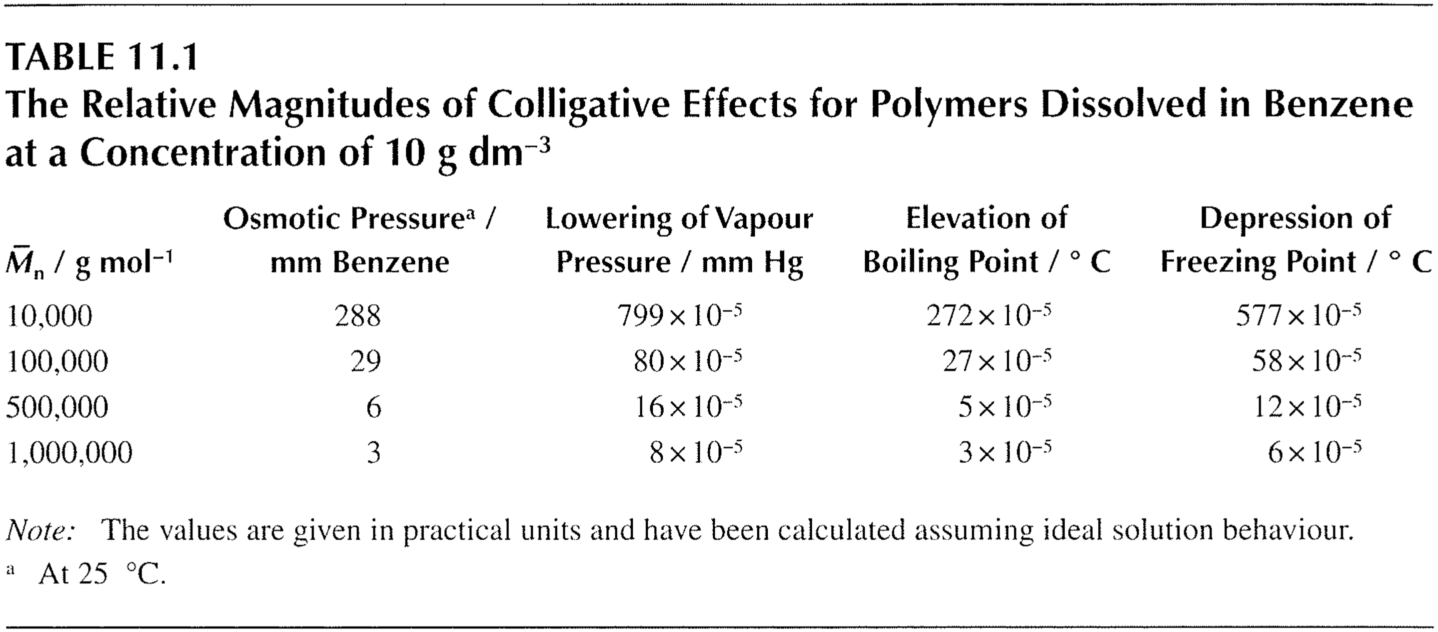


TABLE 11.1
The Relative Magnitudes of Colligative Effects for Polymers Dissolved in Benzene at a Concentration of 10 g dm^{-3}

$\bar{M}_n$ / g mol^{-1}	Osmotic Pressure[a] / mm Benzene	Lowering of Vapour Pressure / mm Hg	Elevation of Boiling Point / ° C	Depression of Freezing Point / ° C
10,000	288	799×10^{-5}	272×10^{-5}	577×10^{-5}
100,000	29	80×10^{-5}	27×10^{-5}	58×10^{-5}
500,000	6	16×10^{-5}	5×10^{-5}	12×10^{-5}
1,000,000	3	8×10^{-5}	3×10^{-5}	6×10^{-5}

Note: The values are given in practical units and have been calculated assuming ideal solution behaviour.

[a] At 25 °C.

Membrane osmometry (MO)

pp269-275

- osmotic pressure π

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

Δc → Δμ → π

$$\pi = \rho g h$$

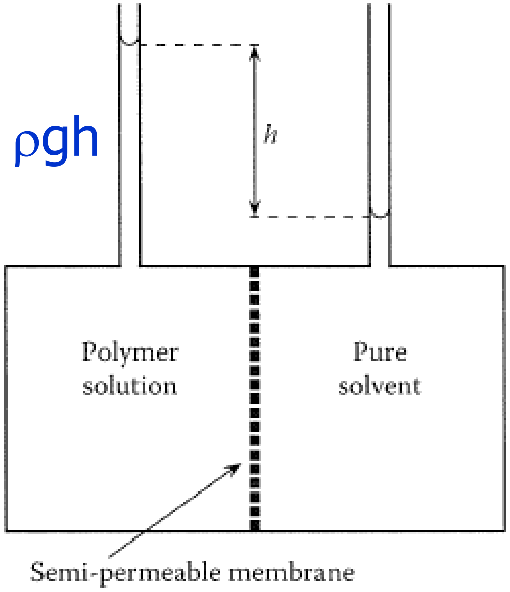


Fig 11.1 p270

$$\mu_1 - \mu_1^{\circ} = \frac{-\mathbf{R}T\phi_2}{x} + \mathbf{R}T\left(\chi - \frac{1}{2}\right)\phi_2^2$$

Eqn (10.48)
F-H for dilute soln

$$\pi = \frac{\mathbf{R}T\phi_2}{x\bar{V}_1} + \frac{\mathbf{R}T(1/2-\chi)\phi_2^2}{\bar{V}_1}$$

$$\leftarrow \quad \frac{\phi_2}{x\bar{V}_1} = \frac{n_2}{V}$$

$$= \mathbf{R}T\left(\frac{n_2}{V}\right) + \mathbf{R}T\left(\frac{1}{2} - \chi\right)x^2 V_1 \left(\frac{n_2}{V}\right)^2$$

for dil soln p271

- $$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{m}{n_2} \rightarrow \frac{n_2}{V} = \left(\frac{m}{V}\right)\left(\frac{n_2}{m}\right) = \frac{c}{\bar{M}_n}$$

- reduced osmotic pressure π/c

$$\frac{\pi}{c} = \frac{\mathbf{R}T}{\bar{M}_n} + \left(\frac{\mathbf{R}T}{V_1}\right)\left(\frac{1}{2} - \chi\right)\left(\frac{xV_1}{\bar{M}_n}\right)^2 c$$

- $$\frac{\pi}{c} = \frac{\mathbf{R}T}{\bar{M}_n} + \left(\frac{\mathbf{R}T}{V_1}\right)\left(\frac{1}{2} - \chi\right)\left(\frac{xV_1}{\bar{M}_n}\right)^2 c$$
  - at θ condition, χ = ½, ideal $$\left(\frac{\pi}{c}\right)_\theta = \frac{\mathbf{R}T}{\bar{M}_n}$$
  - as c → 0 also ideal $$\left(\frac{\pi}{c}\right)_{c\to 0} = \frac{\mathbf{R}T}{\bar{M}_n}$$
- a virial equation
  $$\frac{\pi}{c} = \mathbf{R}T\left[\frac{1}{\bar{M}_n} + A_2 c + A_3 c^2 + \ldots\right]$$
    - A_2 = 2nd virial coeff ~ non-ideality
- MO experiment
  - static or dynamic method
  - for 5E4 < M_n < 1E6
    - diffusion of solute; small signal (π)

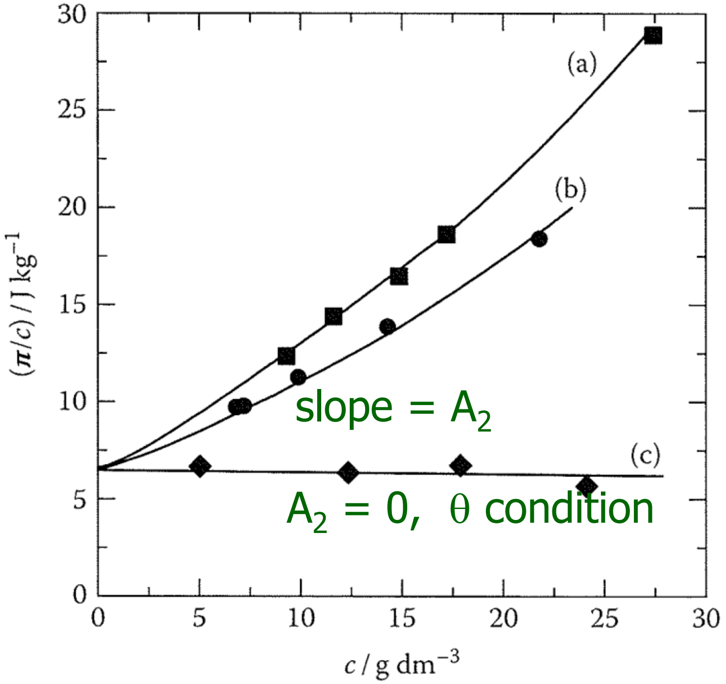


Fig 11.3

Vapor pressure osmometry (VPO)

pp275-277

- lowering of solvent vapor pressure

$$\frac{1}{P}\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)=\frac{\Delta H_\mathrm{v}}{\mathbf{R}T^2}$$

$$\Delta T_\mathrm{e} = -\left(\frac{\mathbf{R}T_0^2}{\Delta H_\mathrm{v}}\right)\ln a_{1,T_0}$$

$$\frac{\Delta T_\mathrm{ss}}{c} = K_\mathrm{ss}\left[\frac{1}{\bar{M}_\mathrm{n}} + A_2^\mathrm{vpo}c + A_3^\mathrm{vpo}c^2 + \ldots\right]$$

$$\frac{\Delta R_\mathrm{ss}}{c} = K_{R\mathrm{ss}}\left[\frac{1}{\bar{M}_\mathrm{n}} + A_2^\mathrm{vpo}c + A_3^\mathrm{vpo}c^2 + \ldots\right]$$

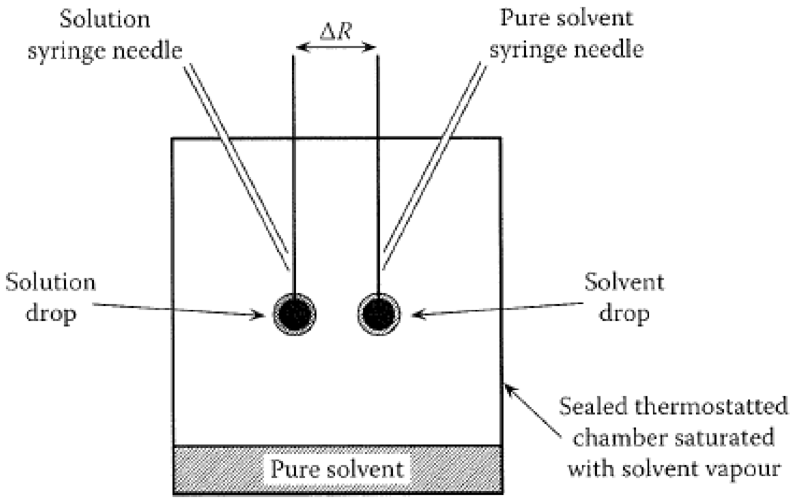


Fig 11.4

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

$\Delta c \rightarrow \Delta \mu \rightarrow \Delta P \rightarrow \Delta H \rightarrow \Delta T \rightarrow \Delta R$

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 MM
  - 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 MM
  - supercooling
- limited by precision of temperature measurement
  - useful only for $M_n < 5000$
  - not used these days

End-group analysis

pp278-279

- step polymers

  HOOC------COOH H_2N-----NH_2 HO-----OH

  - titration or spectroscopic methods
- chain polymers

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

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

Light scattering (LS)

pp281-291

- light scattering
  - 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

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

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

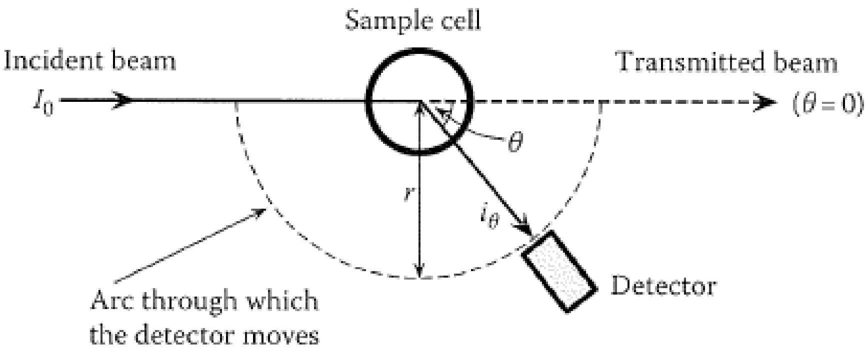


Fig 12.1

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

- LS by gas (cont’d)

molar mass

$$\frac{i_\theta}{I_0} = \frac{2\pi^2 (\mathrm{d}n/\mathrm{d}c)^2 Mc(1+\cos^2\theta)}{\lambda^4 r^2 \mathrm{N_A}} \longrightarrow R = \frac{2\pi^2 (\mathrm{d}n/\mathrm{d}c)^2 \overset{\downarrow}{M}c}{\lambda^4 \mathrm{N_A}}$$

Rayleigh ratio $R = \dfrac{i_\theta r^2}{I_0(1+\cos^2\theta)}$ ~ measuring

- LS by (dilute) solution of small molecules

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

$$\Delta R = \frac{2\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2 c}{\mathrm{N_A}\lambda^4[(1/M)+2A_2c+3A_3c^2+\ldots]}$$

$$\frac{Kc}{\Delta R} = \frac{1}{M} + 2A_2c + 3A_3c^2 + \ldots \longleftarrow K = \frac{2\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2}{\mathrm{N_A}\lambda^4}$$

= optical constant
(exp’tal condition)

then, as c → 0, ΔR/Kc = M?

- LS by sol’n of large molecules (D > $\lambda/20 \approx 20$ nm)
  - asymmetry + interference → angular dependence of i

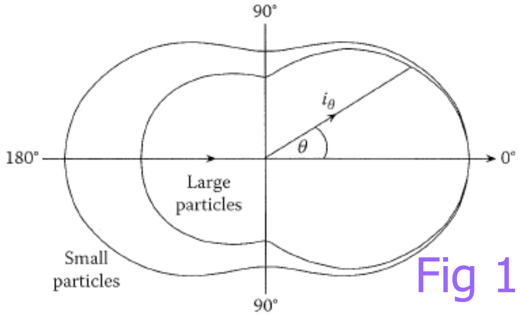


Fig 12.2

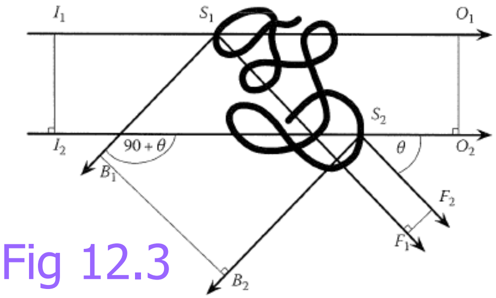


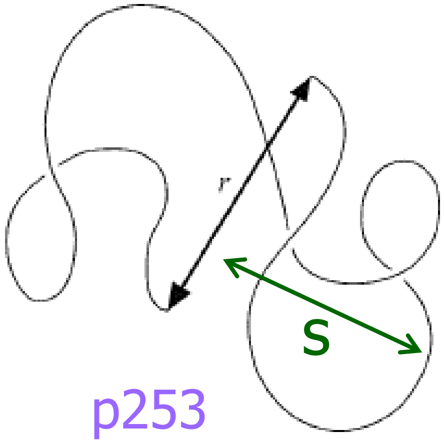
Fig 12.3

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

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

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

q = scattering vector $\propto \sin(\theta/2)$
$\langle s^2 \rangle$ = MS radius of gyration



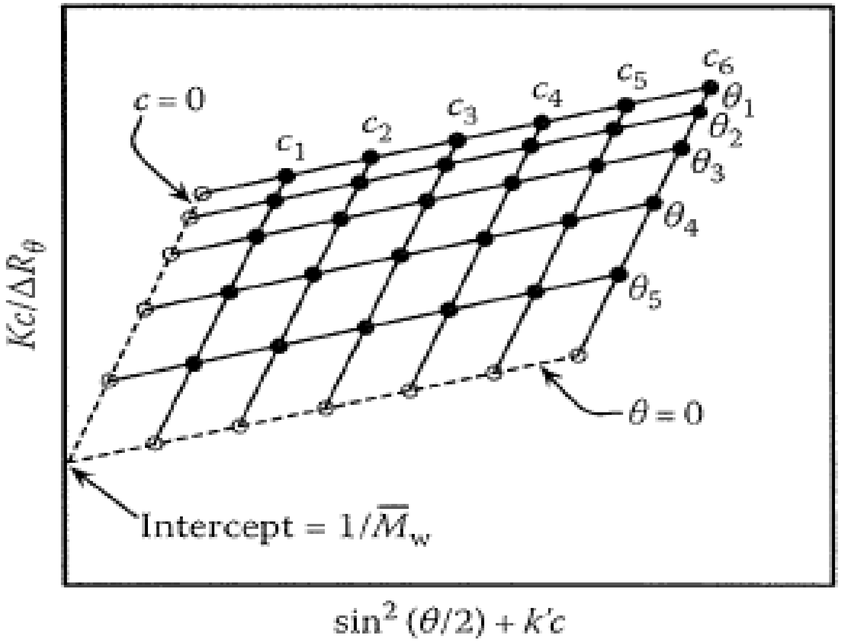
p253

LS by polymer sol'n (cont'd)

$$\frac{Kc}{\Delta R_\theta}=\left[\frac{1}{M}+2A_2c+3A_3c^2+\ldots\right]\left[1+\left(\frac{16\pi^2 n_0^2\sin^2(\theta/2)}{3\lambda^2}\right)\langle s^2\rangle\right]$$

- $$\left(\frac{Kc}{\Delta R_\theta}\right)_{\substack{c\to 0\\ \theta\to 0}}=\frac{1}{\overline{M}_w}$$
- for 2E4 < M_w < 5E6
  - small intensity (i_θ)
  - cancelling if too large
  - sample must be dust-free

Fig 12.4 'Zimm plot'



SAXS and SANS

pp294-296

- LS uses visible light
- XS and NS
    - uses smaller λ
        - smaller scale structure
    - at small angle < 2°
        - to avoid angular dependence P(θ)
    - detector far from sample
        - to separate from θ = 0°
    - high penetration depth
        - can be used for solid polymers
    - SAXS for phase structure
        - morphology of blends, copolymers
    - SANS for dimension of chain in bulk
        - with deuterated sample

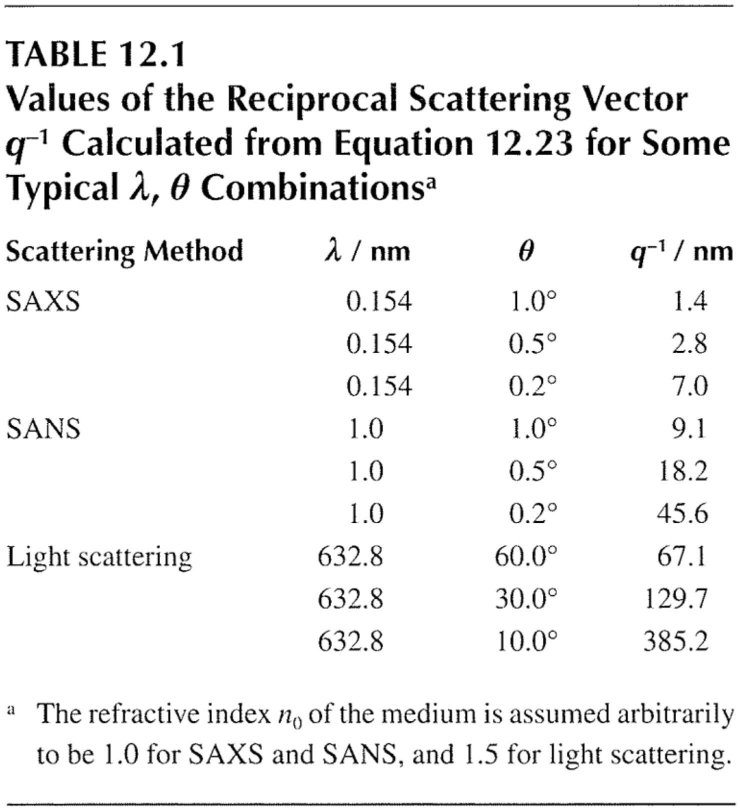
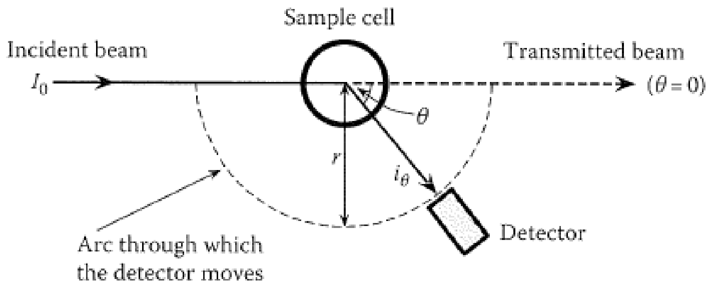


TABLE 12.1
Values of the Reciprocal Scattering Vector q^{-1} Calculated from Equation 12.23 for Some Typical λ, θ Combinations[a]

Scattering Method	λ / nm	θ	q^{-1} / nm
SAXS	0.154	1.0°	1.4
	0.154	0.5°	2.8
	0.154	0.2°	7.0
SANS	1.0	1.0°	9.1
	1.0	0.5°	18.2
	1.0	0.2°	45.6
Light scattering	632.8	60.0°	67.1
	632.8	30.0°	129.7
	632.8	10.0°	385.2

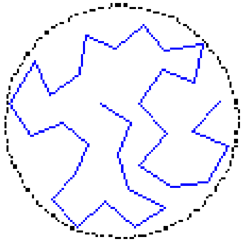
[a] The refractive index n_0 of the medium is assumed arbitrarily to be 1.0 for SAXS and SANS, and 1.5 for light scattering.



Dilute solution viscometry [DSV]

§10.4 pp262-264

- polymer/solvent friction is
  - non-draining = moves together
    - (most) flexible chains
  - free-draining = solvent pass-trough
    - only when very short or rod-like



- volume V_h and viscosity η
  - $\eta = \eta_0 \left[1 + \left(\frac{5}{2} \right) \phi_2 \right]$ Einstein eqn

$$\phi_2 = \left(\frac{c}{M} \right) \mathrm{N_A} V_h \qquad \frac{[\mathrm{g/L}]}{[\mathrm{g/mol}]} [\mathrm{/mol}][\mathrm{L}]$$

  - $\eta_{sp} = (\eta - \eta_0)/\eta_0 = \left(\frac{5}{2} \right) \left(\frac{c}{M} \right) \mathrm{N_A} V_h$

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

- intrinsic viscosity $[\eta]$ and MM
  - $$[\eta] = \lim_{c\to 0}\left(\frac{\eta_{sp}}{c}\right) = \left(\frac{5}{2}\right)\frac{N_A V_h}{M}$$
    $$= \Phi_0^s \alpha_\eta^3 \left(\frac{\langle s^2\rangle_0^{3/2}}{M}\right) = K_\theta \alpha_\eta^3 M^{1/2}$$ Flory-Fox eqn
    $$K_\theta = \Phi_0^s\left(\frac{\langle s^2\rangle_0}{M}\right)^{3/2}$$
  - $[\eta] = KM^a$ Mark-Houwink-Sakurada [MHS] eqn $a = 0.5 + 3\Delta$

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

eqn (10.79) – (10.89)
pp260-262

Common Name	Name Proposed by IUPAC[a]	Symbol and Definition[b]
Relative viscosity	Viscosity ratio	$\eta_r = \eta/\eta_0$
Specific viscosity	—	$\eta_{sp} = \eta_r - 1$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \{\ln(\eta_r)\}/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \lim_{c\to 0}(\eta_{red})$

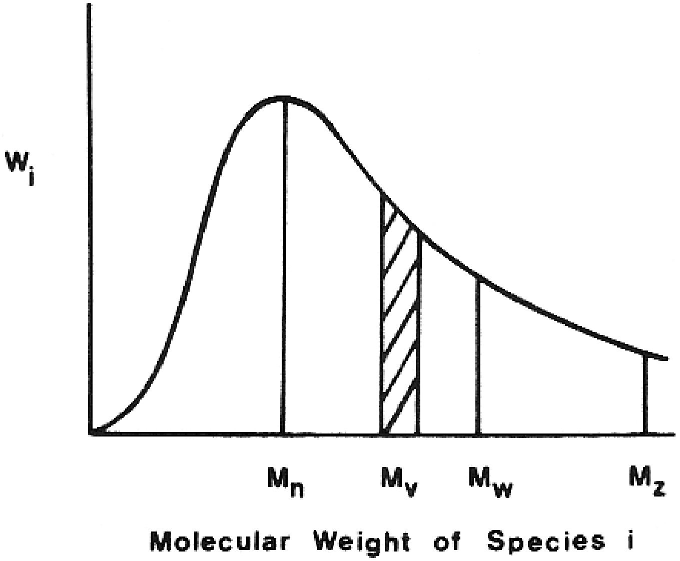
- viscosity-average mol wt, M_v

pp300-301

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

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

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



- DSV experiment pp299-304

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

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

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

- $[\eta] = K\bar{M}_v^a$
  - K, a from handbook Table 13.2
  - at the same solvent and temp
- cautions
  - Temp control < 0.01 °C
  - t_0 > 100 s (laminar)
  - c < 1 g/dL (Newtonian)

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

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

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

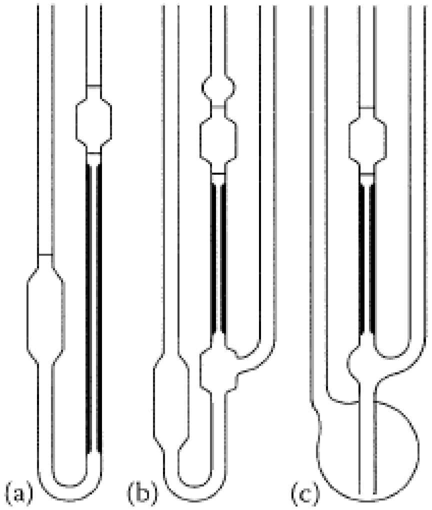


Fig 13.2

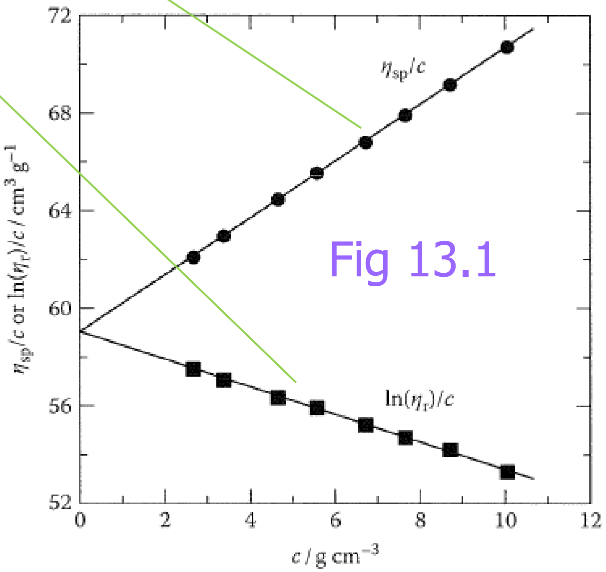


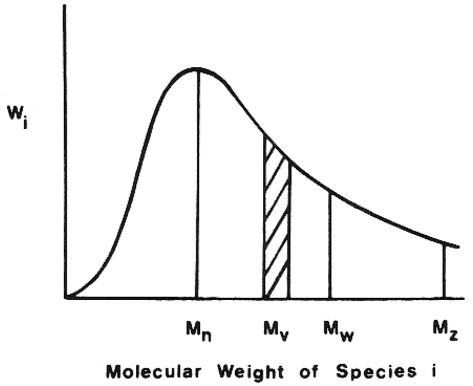
Fig 13.1

Sedimentation (by ultracentrifugation)

- molecule with higher MM sediments faster
  - ultracentrifuge for sedimentation > diffusion
- sedimentation equilibrium exp’t
  - 5000 – 10000 rpm, days for equili
  - refractive index [conc’n] profile
  - M_w and M_z
- sedimentation velocity exp’t
  - 60000 – 70000 rpm, dynamic
  - movement of boundary layer
  - M_w
- MMD?
  - width of boundary layer

MMD and fractionation

- MM of polymers has distribution
  - MM averages
  - MMD [MWD]
    - PDI = M_w/M_n
    - MMD affects property? some on rheology
- fractionation p317
  - separate fractions of narrow(er) distribution
  - by lowering Temp or adding non-solvent
  - manually or (semi-)automatically



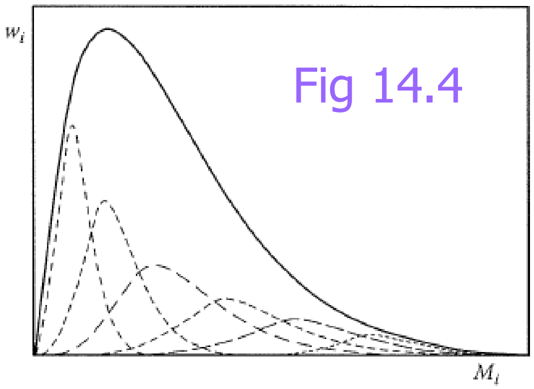


Fig 14.4

Fig 14.2

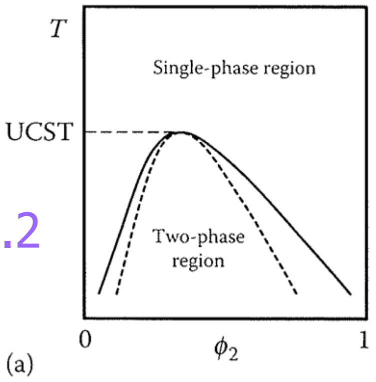
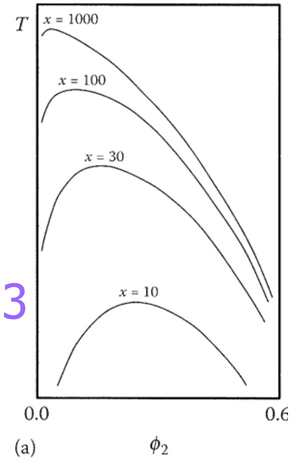


Fig 14.3



Gel permeation chromatography (GPC)

pp318-325

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

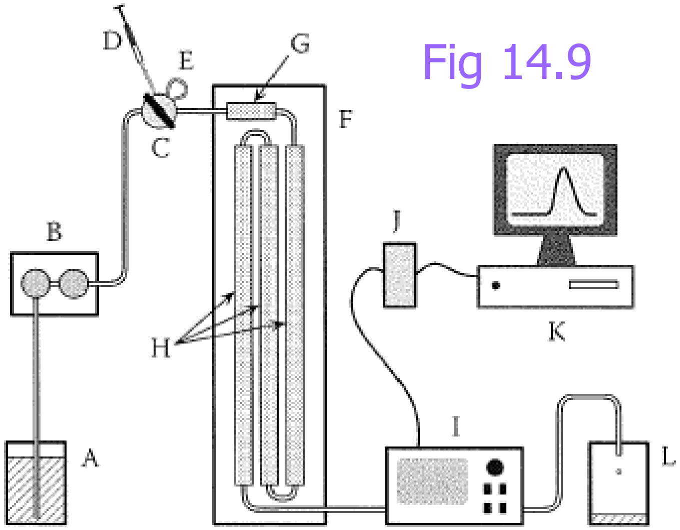


Fig 14.9

- elution volume V_e and size

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

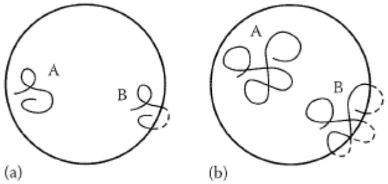
smaller V_e for larger L

L ~ diameter of molecule in sol'n

- V_e to mol wt

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

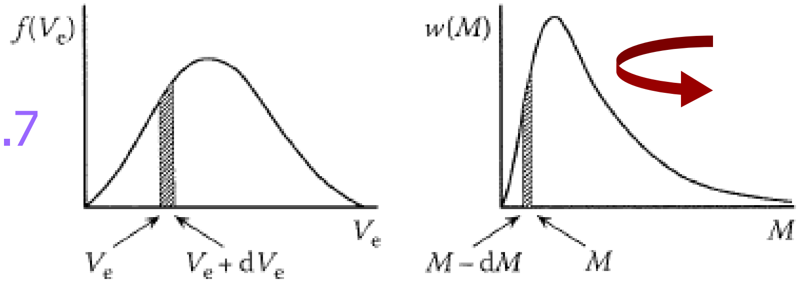
Fig 14.5



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

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

Fig 14.7



- V_e to mol wt (cont'd)
  - 'universal calibration'

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

    - Many polymers fall on the same curve on log$[\eta]$M - V_e plot.

'universal calibration curve'

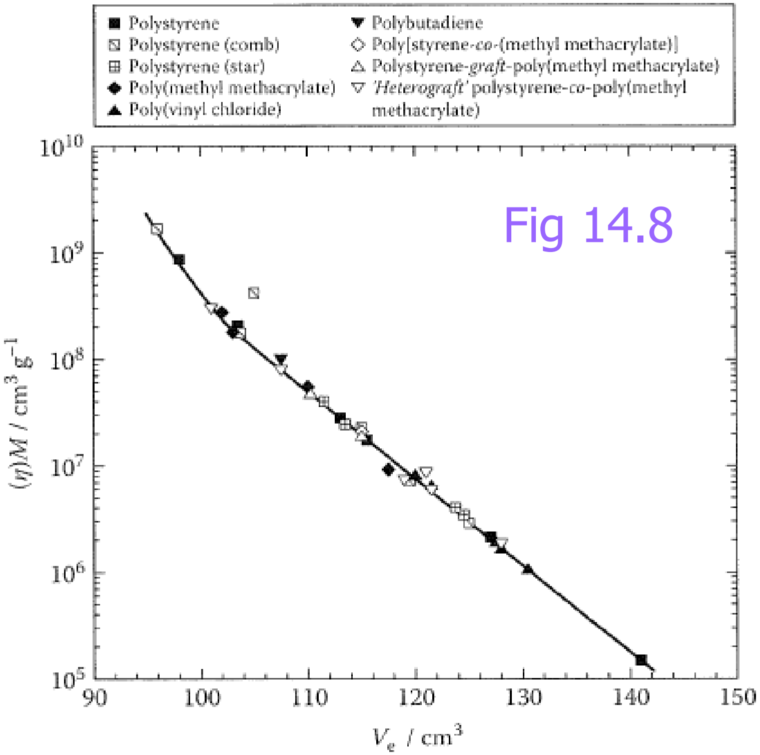


Fig 14.8

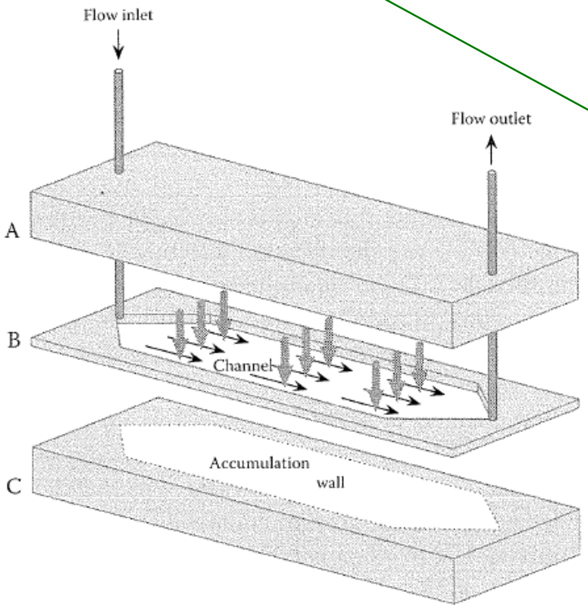
- experiment
  - Run GPC with sample and (anionic PS) standards.
  - For each fraction (V_e), get M.
    - $[\eta]_{PS}M_{PS} = [\eta]_{sample}M_{sample}$
    - $K_{PS}M_{PS}^{a(PS)+1} = K_{sample}M_{sample}^{a(sample)+1}$
  - Calculate M_n, M_w, and MMD.

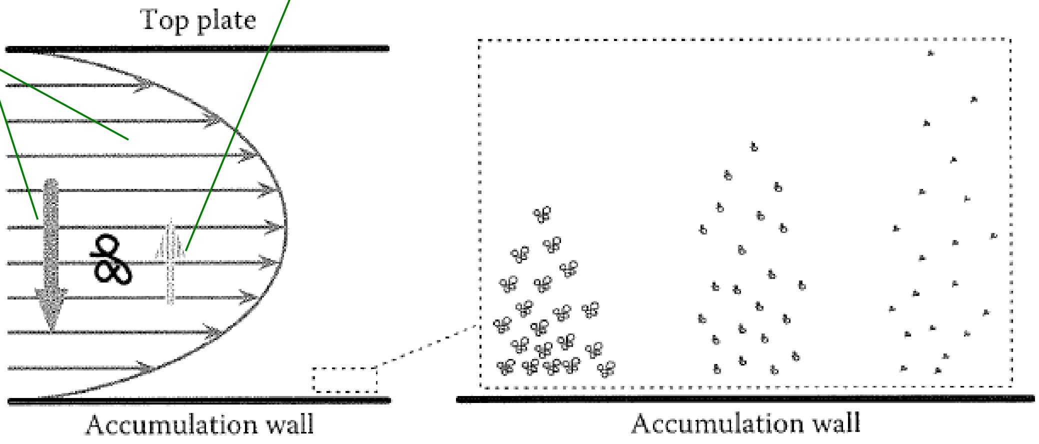
for each 'fraction'
$M \approx M_n \approx M_v \approx M_w$

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

Field-flow fractionation

- forward-flow vs cross-flow and diffusion





cross-flow?
non-solvent, centrifuge, etc

- useful for
  - higher MM (than for GPC)
  - biopolymers
  - sometimes preparatory

Mass spectroscopy [--metry; MS]

pp331-340

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

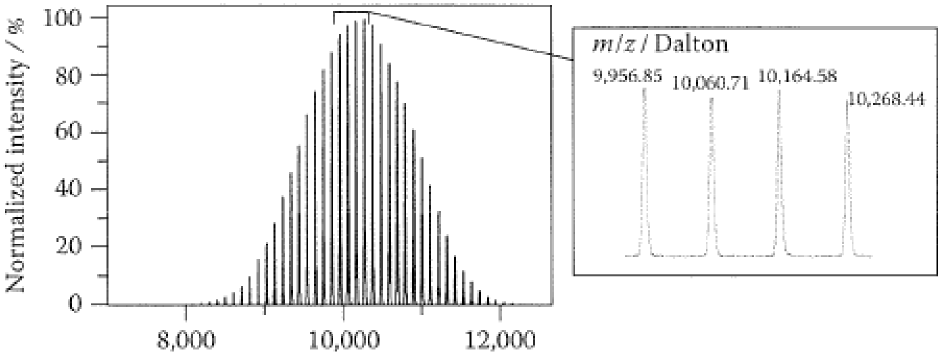


Fig 14.13

Chapter 15

Structure Determination

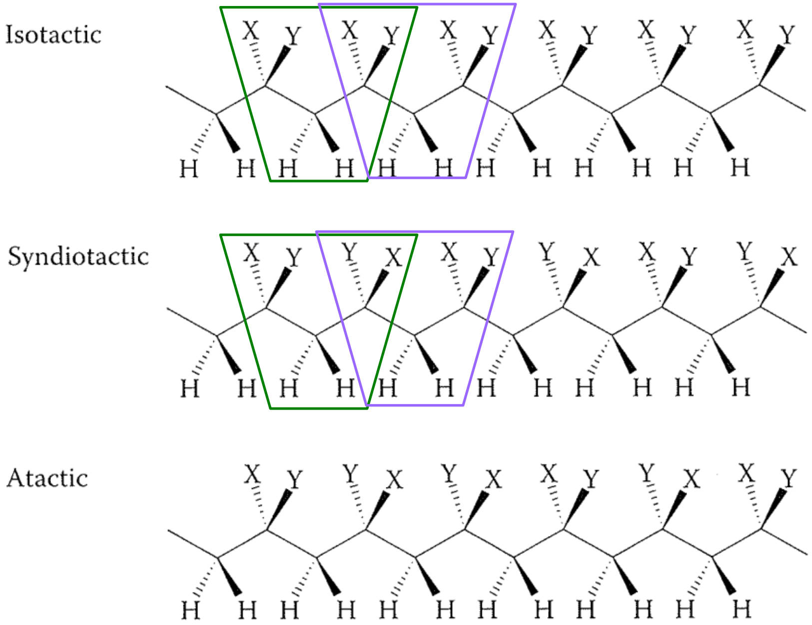
Analysis of
chemical composition and microstructure

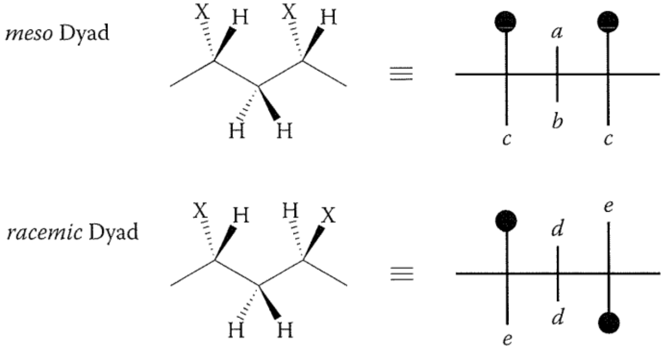
Spectroscopy

- UV/Vis
  - double bonds and conjugations
  - change in structures, especially outdoor
  - additives (with =)
- IR
  - characteristic groups ~ identification
  - copolymer composition, degree of branching, crystallinity, etc
- Raman
  - vibrational spectroscopy detecting change in polarizability
    - IR detects change in dipole moment.
    - mutual exclusion and complementary → application similar to IR
  - sensitive to local environment and orientation of bonds
    - some more applications; LAM, micromechanics, etc

NMR

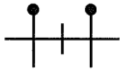
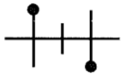
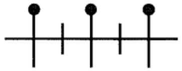
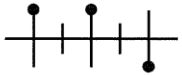
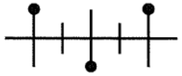
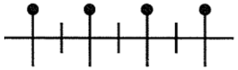
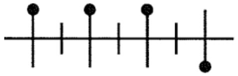
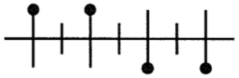
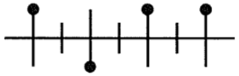
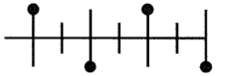
- chemical structure
- chain dynamics and motion
  - using relaxation time and peak width
- sequence distribution in copolymers
- tacticity
  - affects crystallinity
    (and hence properties)





~*mmmmmmmmmmmmmmmmmmrmmmmmmmmmmmmmmmmmmmmmmmmmmmmmm*~

TABLE 15.3
Sequences in Vinyl Homopolymers and Their Mole Fractions according to Bernoullian Statistics

Sequence Type	Designation [a]	Projection	Mole Fraction of Sequence in Terms of P_m [a]
Dyad	*m*		P_m
	r		$1 - P_m$
Triad	*mm*		P_m^2
	mr (and *rm*)		$2P_m(1 - P_m)$
	rr		$(1 - P_m)^2$
Tetrad	*mmm*		P_m^3
	mmr (and *rmm*)		$2P_m^2(1 - P_m)$
	rmr		$P_m(1 - P_m)^2$
	mrm		$P_m^2(1 - P_m)$
	rrm (and *mrr*)		$2P_m(1 - P_m)^2$
	rrr		$(1 - P_m)^3$