Chapter 3. Conformation, Solutions, and Molecular Weight

3.1 Conformation and chain dimensions

Configuration : stereochemical arrangement of atoms along polymer chain.

cannot be altered without breaking primary bonds.

ex. tactic and geometric isomers

Conformation : stereostructure of a molecule defined by its sequence of bonds and torsion angles.

* **Random flight chain** (or **freely jointed chain**)
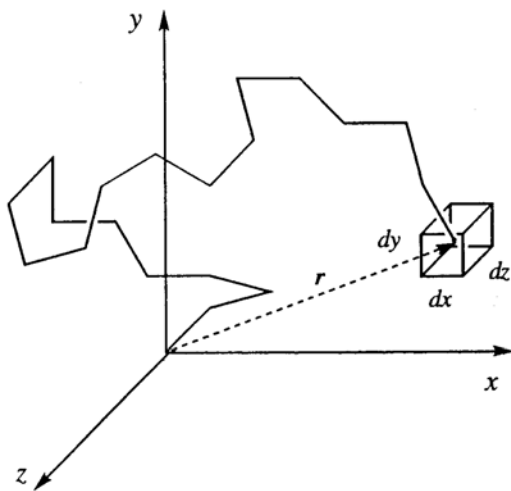
a polymer chain --- n links of length l

Figure 3.1. Illustration of a random conformation of an idealized freely jointed polymer chain having 20 segments of equal length. The end-to-end distance of this conformation is indicated as *r*. With one end of the chain fixed at the origin of the Cartesian coordinate-system, the probability of finding the other end in some infinitesimal volume element (*dV = dx•dy•dz*) is expressed by the Gaussian distribution-function given by eq 3.2.

one end of the chain --- fixed at the origin

end-to-end distance, r

For fully extended chain, r=nl

. Probability of finding one end in infinitesimal volume ($dV = dx \cdot dy \cdot dz$)

---> Gaussian distribution function

$$\omega(x, y, z)\,dx\,dy\,dz = \left(\frac{b}{\sqrt{\pi}}\right)^3 \exp(-b^2 r^2)\,dx\,dy\,dz$$

$$r^2 = x^2 + y^2 + z^2 \quad \& \quad b^2 = \frac{3}{2nl^2}$$

⇓ radial-distribution function

$$\omega(r)\,dr = \left(\frac{b}{\sqrt{\pi}}\right)^3 \exp(-b^2 r^2)\, 4\pi r^2 dr$$
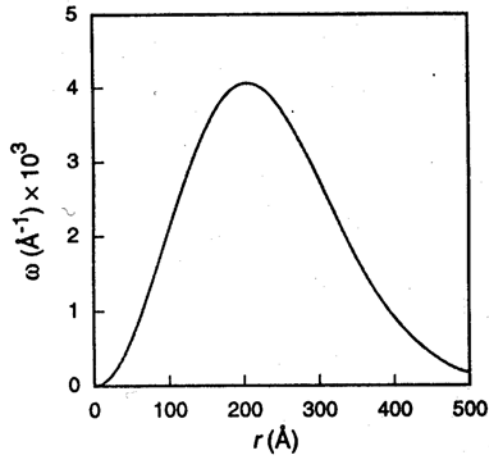

Figure 3.2. The radial-distribution function calculated (eq. 3.5) for a hypothetical polymer chain consisting of 10^4 freely jointed segments of length 2.5 Å.
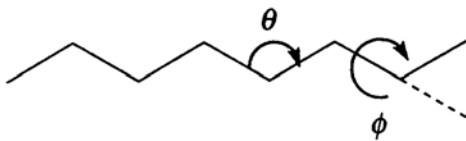
. Mean-square end-to-end distance

$$\langle r^2 \rangle = \frac{\displaystyle\int_0^\infty r^2 \omega(r)\,dr}{\displaystyle\int_0^\infty \omega(r)\,dr} \qquad ===> \qquad \langle r^2 \rangle = nl^2$$

root-mean-square end-to-end distance of freely jointed chain

$$\sqrt{\langle r^2 \rangle} = \sqrt{n}\; l$$

* **Freely rotating chain** (bond angle θ is fixed.)

$$\langle r^2 \rangle = nl^2 \frac{1-\cos\theta}{1+\cos\theta}$$

For the tetrahedral angle, $\theta = 109.28°$ (PE의 경우)

$$\langle r^2 \rangle = 2nl^2$$

* **Hindered rotating chain** (See Fig. 3.4)

$$\langle r^2 \rangle = nl^2 \frac{1-\cos\theta}{1+\cos\theta} \frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle}$$

where $\langle\cos\phi\rangle$: average cosine of bond-rotation angle ϕ
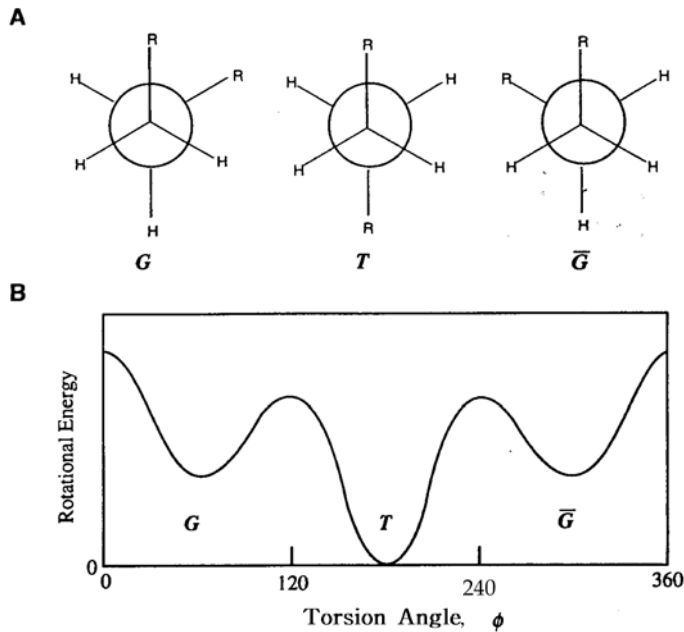
A

B

Torsion Angle, ϕ

Figure 3.4. A. Three low-energy projections of two adjacent bond atoms with substituent group, R. In the case of a polymer chain, R represents all chain segments before and after the bond in question. **B.** Potential-energy diagram illustrating the three lowest energy rotational states — *trans* (T) and the two *gauche* forms, G and $\overline{G}$.

* Size of real polymer chain -- fixed bond angle, restricted rotation, excluded volume

$$\sqrt{\langle r^2 \rangle} = \alpha \sqrt{nC_N} 1$$

    where α : chain expansion factor (or chain expansivity factor)

        <--- effect of excluded volume

      C_N : characteristic ratio

        <--- contribution from fixed bond angle & restricted chain rotation

      $5 \leq C_N \leq 10$ for large polymer chain

      ex.) PE $C_N = 6.7$

           PS $C_N = 10$.   (atactic PS인 경우)

  or

$$\sqrt{\langle r^2 \rangle} = \alpha \sqrt{\langle r^2 \rangle_0}$$

    where $\sqrt{\langle r^2 \rangle_0}$: unperturbed rms end-to-end distance $(= \sqrt{nC_N} 1)$

. *unperturbed dimension*

    --- polymer chain in the absence of excluded volume effects (i.e. $\alpha = 1$)

. *characteristic ratio*

    : the unperturbed mean-square end-to-end distance

      to the mean-square end-to-end distance of the freely jointed model

$$C_N = \frac{\langle r^2 \rangle_0}{nl^2}$$

실험적으로 amorphous solid state에서의 polymer chain

==> unperturbed dimension

==> 이 때의 온도를 θ temperature

cf.) good solvent ($a > 1$)

: polymer-polymer or solvent-solvent interaction보다
polymer-solvent interaction이 강한 경우.

3.2 Thermodynamics of polymer solutions

3.2.1 Flory-Huggins theory

Paul Flory & Maurice Huggins in 1940s.

* Classification of solutions

For *ideal solutions,* $\triangle S_m > 0$, $\triangle H_m = 0$

∵ $\triangle S_m = -R(x_1 \ln x_1 + x_2 \ln x_2) > 0$

$\triangle H_m = 0$

==> $\triangle G_m = RT(x_1 \ln x_1 + x_2 \ln x_2) < 0$: spontaneous mixing

For *regular solutions,* $\triangle S_m = \triangle S_m^{id}$, $\triangle H_m \neq \triangle H_m^{id}$

For *athermal solutions,* $\triangle S_m \neq \triangle S_m^{id}$, $\triangle H_m = \triangle H_m^{id}$

For *irregular solutions,* $\triangle S_m \neq \triangle S_m^{id}$, $\triangle H_m \neq \triangle H_m^{id}$

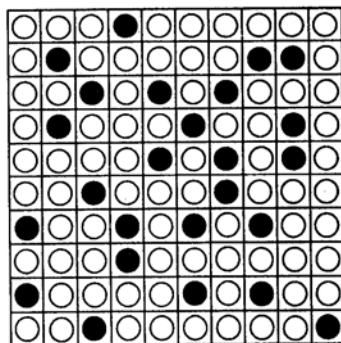*** Simple lattice model (for regular solution)**

Figure 3.7. Representation of two-dimensional Flory–Huggins lattice containing solvent molecules (○) and a low-molecular-weight solute (●).

: mixing of a low molecular weight solvent (comp 1)

with a   "   "   solute (comp 2)

N : total # of lattice sites

n_1 : # of solvent molecules

n_2 : # of solute molecules

$N = n_1 + n_2$

Mixing entropy, $\triangle S_m$

$\triangle S_m = k \ln \varOmega$ by statistical thermodynamics

where   k : Boltzmann's const. ($1.38 \times 10^{-23} J/K$)

$\varOmega$: total number of ways of arranging n_1 solvent molecules

and n_2 solute molecules.

$$\varOmega = \frac{N!}{n_1! \, n_2!}$$

Using *the Stirling's approximation* ($\ln n! = n \ln n - n$),

$\triangle S_m = -k(n_1 \ln x_1 + n_2 \ln x_2)$

or

$\triangle S_m = -R(x_1 \ln x_1 + x_2 \ln x_2)$

: entropy change due to mixing of an ideal mixture

where $R = N_A k$, $x_1 = \dfrac{n_1}{n_1 + n_2}$ <--- 전체수 N이 N_A(1mol)인 경우이므로

Multicomponent system having M components,

$$\triangle S_m^{id} = -R \sum_{i=1}^{M} x_i \ln x_i$$

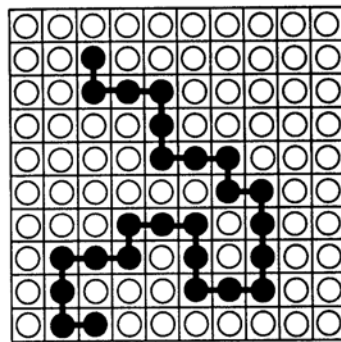* **Lattice model for a polymer chain in solution**

Figure 3.8. Lattice model for a polymer chain in solution. Symbols represent solvent molecules (○) and polymer-chain segments (●).

. **Gibbs energy of mixing** of a polymer solution

$\triangle G_m = \triangle H_m - T \triangle S_m$

$\triangle S_m$ for a high MW polymer in a low MW solvent

$$\triangle S_m = -k(n_1 \ln \phi_1 + n_2 \ln \phi_2)$$

where n_1 : # of solvent molecules, n_2 : # of solute (polymer) molecules

$$N = n_1 + r\, n_2 \qquad N : \text{total \# of lattice sites}$$

r : ratio of polymer volume to solvent volume

ϕ_1, ϕ_2 : lattice volume fraction

$$\phi_1 = \frac{n_1}{n_1 + rn_2}, \quad \phi_2 = \frac{rn_2}{n_1 + rn_2}$$

For a polydisperse polymer,

$$\triangle S_m = -k\left(n_1 \ln \phi_1 + \sum_{i=2}^{M} n_i \ln \phi_i\right)$$

. Enthalpy of mixing

$$\triangle H_m = z n_1 r_1 \phi_2 \triangle \omega_{12}$$

where z : lattice coordination number

r_1 : # of segment in a solvent molecule

$\triangle \omega_{12}$: the change in internal energy for formation of an unlike
molecular pair (solvent-polymer)

$$\triangle \omega_{12} = \omega_{12} - \frac{1}{2}(\omega_{11} + \omega_{22})$$

Flory interaction parameter,

$$\chi_{12} = \frac{z\, r_1 \triangle \omega_{12}}{kT} \qquad : \text{dimensionless}$$

$\therefore \quad \triangle H_m = kT \chi_{12} n_1 \phi_2$

$\Rightarrow \quad \triangle G_m = kT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12} n_1 \phi_2) \qquad$: Flory-Huggins equation

<u>Limitations</u> of Flory-Huggins equation
. applicability only to sufficiently concentrated(semi-dilute or semi-concentrated)
solutions which have uniform segment-density
. no volume change of mixing
. no preferred arrangements of polymer segments & solvent molecules

For dilute polymer solutions $\rightarrow$ Flory-Krigbaum theory
For concentration-dependent interaction energy term $\rightarrow$ Modified Flory-Huggins theory
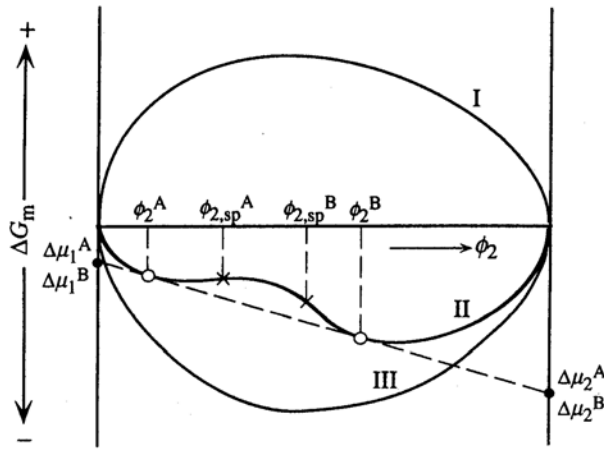
3.2.4 Phase equilibria

Figure 3.9. Idealized representation of three generalized possibilities for the dependence of the Gibbs free energy of mixing, ΔG_m, of a binary mixture on composition (volume fraction of polymer, ϕ_2) at constant pressure and temperature. **I.** Total immiscibility; **II.** partial miscibility; and **III.** total miscibility. Curve II represents the intermediate case of partial miscibility whereby the mixture will separate into two phases whose compositions (○) are marked by the volume-fraction coordinates, ϕ_2^A and ϕ_2^B, corresponding to points of common tangent to the free-energy curve. Spinodal points, compositions $\phi_{2,sp}^A$ and $\phi_{2,sp}^A$, occur at the points of inflection (×).

Conditions for total miscibility over the entire composition range :

i) $\quad \Delta G_m < 0$

ii) $\quad \left(\dfrac{-\partial^2 \Delta G_m}{\partial \phi_2^2} \right)_{p,T} > 0$

Phase equilibrium --- ft'n of *solution T*

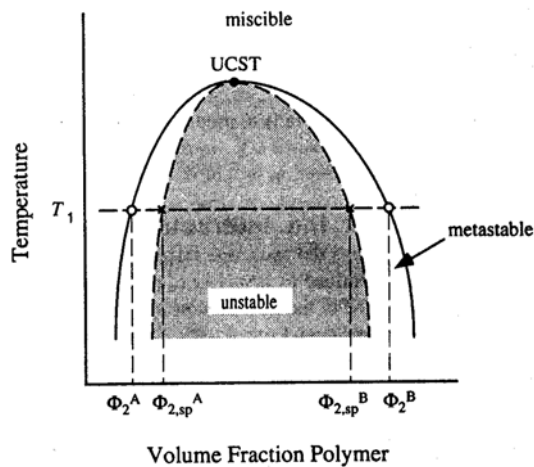In general, solutions of low MW compounds : solubility increases as T increases

Figure 3.10. Representative phase diagrams for a polymer solution showing an upper critical solution temperature (UCST) (•), spinodal curve (– – – –), and binodal curve (———).

Binodal -- loci of points that satisfy the conditions for thermodynamic equilibrium of a binary mixture

Points lying along the **spinodal** -- inflection points,

$$\left(-\frac{\partial^2 \triangle G_m}{\partial \phi_2^{\,2}}\right)_{p,\,T} = 0$$

Critical point : binodal & spinodal coincide,

$$\left(-\frac{\partial^3 \triangle G_m}{\partial \phi_2^{\,3}}\right)_{p,\,T} = 0$$

3.2.6 Prediction of solubilities

* **Solubility parameters**

Estimation of χ_{12} --- based upon the concept of δ (solubility parameter)

$$\delta_i = \sqrt{E_i^{coh}} = \sqrt{-\frac{\triangle E_i^{\,v}}{V_i}} \qquad : \text{units of } [MPa]^{1/2} \text{ or } [cal/cm^3]^{1/2}$$

where $\triangle E^v$: molar energy of vaporization of a pure liquid

E^{coh} : cohesive energy density, V : molar volume

δ of polymer -- δ of solvent giving maximum swelling

. **Small's formula (group contribution method)**

TABLE 3.2 REPRESENTATIVE MOLAR ATTRACTION CONSTANTS AT 25°C

Group	Molar Attraction Constant, F $(MPa)^{1/2}$ cm^3 mol^{-1}		
	Small[17]	Hoy[18]	van Krevelen[19]
–CH$_3$	438	303	420
–CH$_2$–	272	269	280
>CH–	57	176	140
>C<	-190	65.5	0
–CH(CH$_3$)–	495	(479)	560
–C(CH$_3$)$_2$–	686	(672)	840
–CH=CH–	454	497	444
>C=CH–	266	422	304
Phenyl	1504	1398	1517
p-Phenylene	1346	1442	1377
–O– (ether)	143	235	256
–OH	—	462	754
–CO– (ketones)	563	538	685
–COO– (esters)	634	668	512
–OCOO– (carbonate)	—	(904)	767
–CN	839	726	982
–N=C=O	—	734	—
–NH–	—	368	—
–S– (sulfides)	460	428	460
–F	(250)	84.5	164
–Cl (primary)	552	420	471
–Br (primary)	696	528	614
–CF$_3$ (n-fluorocarbons)	561	—	—
–Si–	-77	—	—

$$\delta_i = \frac{\sum F_j}{V_i} = \rho_i \frac{\sum F_j}{M_i} \qquad \text{F}_j : \text{molar attraction constant}$$

ex.) Estimate the solubility parameter for PMMA by the method of Small.

The density of PMMA is $1.188 \, \text{g/cm}^3$ at $25\,℃$.

(Ans.) $\delta_i = 18.9 \, \text{MPa}^{1/2}$

. δ calculation based on the equation of state for polymer

$$\delta \cong \sqrt{\frac{T\alpha}{\beta}} \qquad \alpha : \text{(isobaric) thermal-expansion coefficient}$$

β : (isothermal) compressibility coefficient

$$\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p \qquad \beta = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T$$

. Estimation of $\triangle H_m$ from solubility parameter (by Scatchard-Hildebrand eq'n)

$$\triangle H_m = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2$$

V : volume of the mixture

& $\triangle H_m = kT\chi_{12}n_1\phi_2$

===> $\chi_{12} \cong \frac{V_1}{RT}(\delta_1 - \delta_2)^2$: invalid for exothermic heat of mixing

. Overall solubility parameter (by Hansen)

$$\delta = \sqrt{\delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2}$$

where δ_d, δ_p and δ_h are the dispersive (van der Waals), polar
and hydrogen-bonding solubility parameters, respectively.

3.3 Measurement of molecular weight

$$\overline{M_n}, \; \overline{M_v}, \; \overline{M_w}, \; \overline{M_z}$$

. Primary characterization methods (Absolute methods)
: osmometry, scattering, sedimentation
. Secondary methods (Relative methods)
: GPC (or SEC), viscometry

3.3.1 Osmometry (See Fig. 3.12)

Osmotic pressure, Π, of a polymer solution

$$\triangle \mu_1 = RT \ln a_1 = -\Pi V_1 \qquad \text{(Refer to Chap. 7 of Phys. Chem. by Atkins)}$$

where μ_1 : chemical potential of solvent

$\triangle \mu_1$: μ_1 at solution side $-$ μ_1 at pure solvent side

a_1 : activity of solvent ($\equiv p_1 / p_1{}^0$)
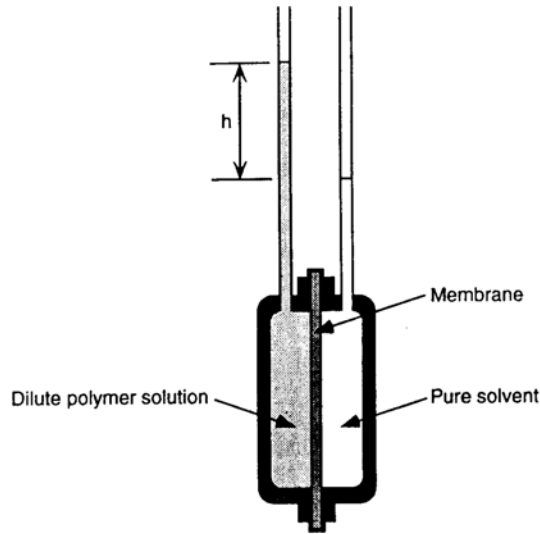
V_1 : molar volume of pure solvent

Figure 3.12. Schematic of a simple membrane osmometer. A dilute polymer solution is located on the left-hand side of the membrane and pure solvent on the right-hand side.

$$\ln a_1 = \ln(1 - \phi_2) + \phi_2 + \chi_{12}\,\phi_2{}^2$$

$$\leftarrow \quad \ln a_1 = \frac{\triangle\mu_1}{RT}\,, \quad \triangle\mu_1 = \mu_1 - \mu_1{}^0 = \left(\frac{\partial\triangle G_m}{\partial N_1}\right)_{T,P}$$

$$\leftarrow \quad \triangle G_m = RT(N_1\ln\phi_1 + N_2\ln\phi_2 + \chi_{12}N_1\phi_2)$$

정리하면,

$$\Pi = -\frac{RT}{V_1}\left(\ln(1-\phi_2) + \phi_2 + \chi_{12}\,\phi_2{}^2\right)$$

$$\leftarrow \quad \text{Taylor series expansion}: \ \ln(1+x) = x - \frac{x^2}{2!} + \frac{x^3}{3!} - \dots$$

$$\leftarrow \quad \phi_2 = cv, \ \text{where} \ \ c : \text{polymer concentration (g/l)}$$

$$v : \text{specific volume of polymer}$$

최종적으로,

$$\frac{\Pi}{c} = \frac{RT}{M}\left[1 + \left(\frac{Mv^2}{V_1}\right)\left(\frac{1}{2} - \chi_{12}\right)c + \frac{1}{3}\left(\frac{Mv^3}{V_1}\right)c^2 + \dots\right]$$

For an ideal, dilute solution,

$$\frac{\Pi}{c} = \frac{RT}{M} \quad ; \text{van't Hoff equation}$$

For high MW, polydisperse polymers,

$$\Pi = RTc\left(\frac{1}{\overline{M}_n} + A_2c + A_3c^2 + \dots\right)$$

where $A_2 = \dfrac{v^2}{V_1}\left(\dfrac{1}{2} - \chi_{12}\right)$: second virial coefficient

In the limit of dilute polymer solution,

$$\frac{\Pi}{RTc} = A_2 c + \frac{1}{M_n}$$

A_2 represents the polymer-solvent interactions.

In good solvents ($\alpha > 1$), A_2 is large & χ_{12} is small (< 0.5)

In θ solvents ($\alpha = 1$), $A_2 = 0$ & $\chi_{12} = 0.5$

Limit for MW by membrane osmometry,

$$20{,}000 < \overline{M_n} < 500{,}000$$

cf.) For $\overline{M_n} < 10{,}000$, vapor-pressure osmometry can be used.

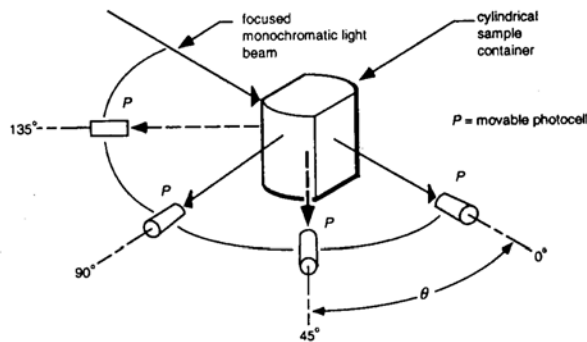## 3.3.2 Light-scattering methods (많은 방법 중에서도 Zimm method에 대해)

Figure 3.15. Conventional light-scattering instrumentation showing incident and scattered light, sample cell, and photomultiplier. (Adapted from *Principles of Polymer Systems*, p. 166, F. Rodriguez, Hemisphere Publishing Corporation, New York, 1989. Reproduced with permission. All rights reserved.)

Fundamental relationship for light scattering,

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

where $P(\theta)$: particle scattering ft'n (effect of chain size and conformation)

In the limit of small angles (i.e., $P(\theta) \rightarrow 1$), a series expansion of $\dfrac{1}{P(\theta)}$ gives

$$\frac{Kc}{R(\theta)} = \frac{1}{M_w}\left[1 + \frac{16}{3}\left(\frac{\pi n}{\lambda}\right)^2 <s^2> \sin^2\left(\frac{\theta}{2}\right)\right] + 2A_2 c$$

where K : optical constant (ft'n of refractive index, n_0)

θ : scattering angle

λ : wave length

$R(\theta)$: Rayleigh ratio (the reduced scattered intensity),

$$R(\theta) = \frac{i(\theta)\,r^2}{I_0 V}$$

I_0 : intensity of incident light

$i(\theta)$: intensity of observed(scattered) light

r : distance between sample & source

V : scattering volume

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

$$\langle s^2 \rangle = \frac{\langle r^2 \rangle}{6} \quad \text{for linear chain polymers}$$

A_2 : second virial coefficient

$$\Downarrow$$

$\overline{M_w}$, $\langle r^2 \rangle$ or $\langle s^2 \rangle$, A_2

이 정보로부터 MW, chain dimension & χ_{12}를 이론적으로 구할 수 있다.

* Separate determination of $\overline{M_w}$, $\langle s^2 \rangle$ & A_2 : Zimm plot
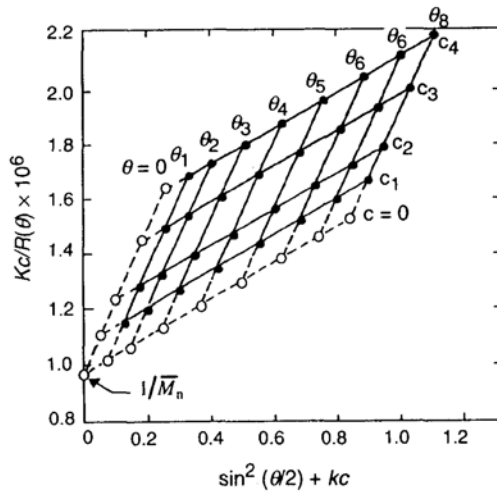

Figure 3.16. Idealized Zimm plot of light-scattering data (●) taken at different angles (θ) and solution concentrations (c). Double extrapolations to zero concentration and zero scattering-angle are represented by broken lines.

$$\lim_{\theta \to 0} \frac{Kc}{R(\theta)} = \frac{1}{M_w} + 2A_2 c$$

$$\lim_{c \to 0} \frac{Kc}{R(\theta)} = \frac{1}{M_w} + \frac{1}{M_w} \cdot \frac{16}{3} \left(\frac{\pi n}{\lambda} \right)^2 \langle s^2 \rangle \sin^2 \frac{\theta}{2}$$

3.3.3 Intrinsic-viscosity measurements

* Mark-Houwink equation,

$$[\eta] = K \, \overline{M_v}^{\,a}$$

where $[\eta]$: intrinsic viscosity

$\overline{M_v}$: viscosity average MW

$$\overline{M_v} = \left(\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right)^{\frac{1}{a}} = \left(\sum w_i M_i^{a} \right)^{\frac{1}{a}}$$

K, a : Mark-Houwink parameters   (See Table 3.6)

0.5 (θ solvent) $< a < 1.0$ (good solvent)

TABLE 3.6 TYPICAL VALUES OF THE MARK–HOUWINK PARAMETERS FOR SOME REPRESENTATIVE POLYMERS AT 25°C[a]

Polymer	Solvent	$K \times 10^3$ mL g^{-1}	n
Polystyrene	Tetrahydrofuran	14	0.70
	Toluene	7.5	0.75
	Benzene	9.2	0.74
Poly(methyl methacrylate)	Benzene	5.5	0.76
Cellulose acetate[b]	Tetrahydrofuran	51.3	0.69
Polycarbonate	Tetrahydrofuran	38.9	0.70
Polydimethylsiloxane	Toluene	2.4	0.84
Poly(2,6-dimethyl-1,4-phenylene oxide)	Toluene	28.5	0.68

[a] Values obtained from light-scattering data.
[b] 55.5 wt % acetal content.

* Huggins equation (implicitly expressed intrinsic-viscosity),

$$\frac{\eta_i}{c} = [\eta] + k_H [\eta]^2 c$$

(See Fig. 3.18)

where $\dfrac{\eta_i}{c}$: reduced viscosity (η_{red})

η_i : relative viscosity-increment (or specific viscosity, η_{sp})

$$= \frac{\eta - \eta_s}{\eta_s} = \eta_r - 1 , \qquad \eta_r : \text{relative viscosity} \left(\frac{\eta}{\eta_s} \right)$$

$$\simeq \frac{t - t_s}{t_s} \qquad \text{by efflux time measurements}\quad \text{(See Fig. 3.19)}$$
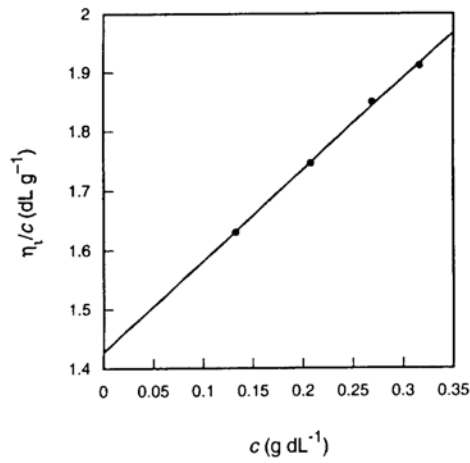
Figure 3.18. Plot of reduced viscosity of a cellulose acetate (intrinsic viscosity of 1.43 dL g^{-1}) in acetone at 25°C.[32]
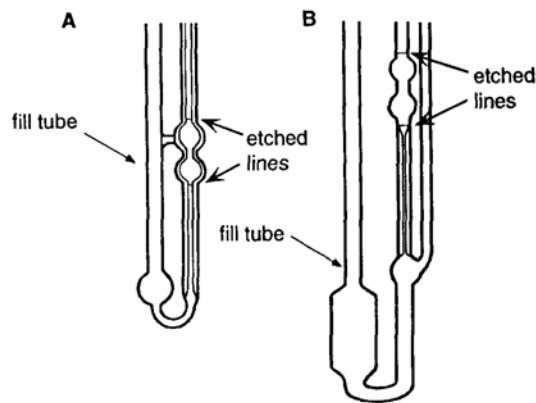

Figure 3.19. Ostwald–Fenske (**A**) and Ubbelohde (**B**) capillary viscometers.

* Estimation of chain dimension by $[\eta]$ measurement

$$[\eta] = \frac{\Phi \langle r^2 \rangle^{3/2}}{M} = (\eta_{red})_{c \to 0} \qquad \text{<-- random coil인 경우}$$

$$\Phi \approx 2.1 \times 10^{21} \, dl/g \, cm^3 \ \text{(Flory constant)}$$

Units : $[\eta]$ in dl/g, r in cm

3.3.4 Gel permeation chromatography (or Size exclusion chromatography)

GPC or SEC

: To separate samples of polydisperse polymers into fractions of narrower MWD.

(See Fig. 3.20)

columns of $30-50$ cm in length

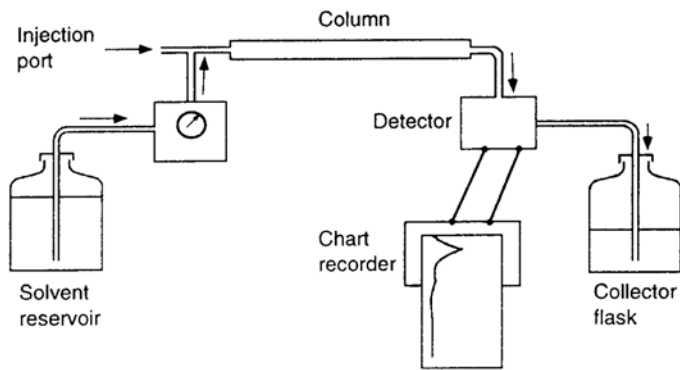highly porous beads of $10-10^7$ Å in pore diameters

Figure 3.20. Basic instrumentation for gel-permeation chromatography (GPC). (Harry Allcock and Frederick W. Lampe, *Contemporary Polymer Chemistry*, 2nd ed., ©1990, p. 396. Reprinted by permission of Prentice-Hall, Englewood Cliffs, NJ.)

Pure prefiltered solvent is pumped through the columns at a rate of $1-2\,\mathrm{ml/min}$, and then $1-5\,\mathrm{ml/min}$ of a dilute polymer solution($< 0.2\,\mathrm{g/dl}$) is injected by syringe into the solvent stream and carried through the columns.

Polymer molecules are eluted out of the column in descending order of MW.

Total elution time in high-resolution columns --- several hours

Measurement of polymer conc. in each fraction --- refractive index or IR absorption

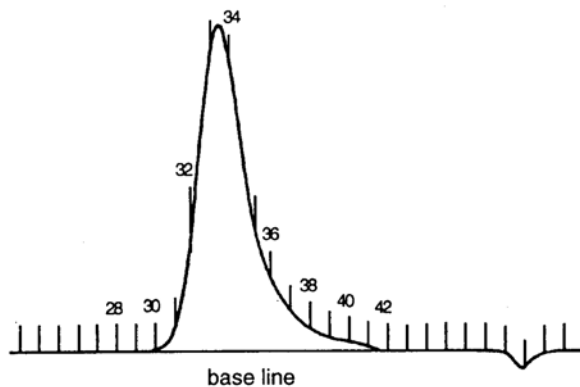Standard polymers : PS or PMMA (MWs from 500 to 2M, PDI of 1.06)

base line

Figure 3.21. GPC chromatogram of a polystyrene sample using tetrahydrofuran as the solvent at a flow rate of 2.0 mL min⁻¹. Vertical marks represent elution counts. The highest-molecular-weight polymer molecules elute at the lowest elution counts (above ca. 29). The negative peak at high elution-volume is usually due to a low-molecular-weight impurity or impurities, such as traces of solvent, stabilizer, water, or dissolved air. (Adapted from L. H. Sperling, *Introduction to Physical Polymer Science*. Copyright ©1986. Reprinted by permission of John Wiley & Sons, Inc.)

* M_2를 알고 M_1을 calibration하는 방법

  같은 시간에서 채취한 elution volume끼리는 molecule의 hydrodynamic volume, V가 동등 (즉, $V_1 = V_2$)하므로 $[\eta]M = \Phi\langle r^2 \rangle^{3/2} \propto V$의 관계식을 이용하면

$$[\eta]_1 M_1 = [\eta]_2 M_2$$

$$K_1 M_1^{1+a_1} = K_2 M_2^{1+a_2} \qquad \text{from Mark-Houwink eq'n}$$

$$\therefore \quad M_1 = \left(\frac{K_2}{K_1} M_2^{1+a_2} \right)^{\frac{1}{1+a_1}} \qquad \text{<---- Mark-Houwink 상수는 문헌에서 구함}$$
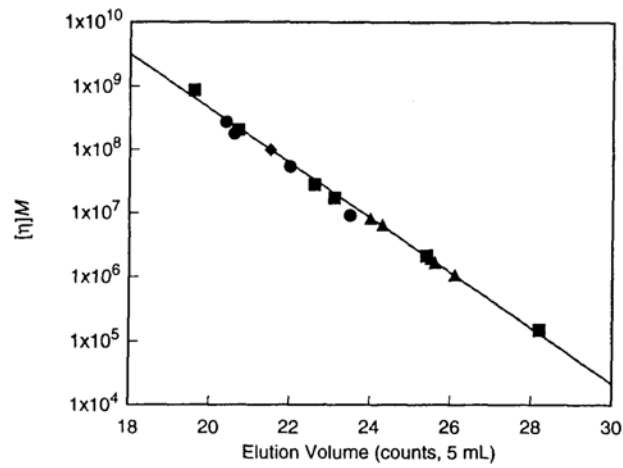
* Universal calibration curve

Figure 3.22. Universal GPC calibration-curve showing data points for polystyrene (■), poly(vinyl chloride) (▲), polybutadiene (◆), and poly(methyl methacrylate) (●) standards in tetrahydrofuran solution. Line gives best fit of polystyrene data.[33]