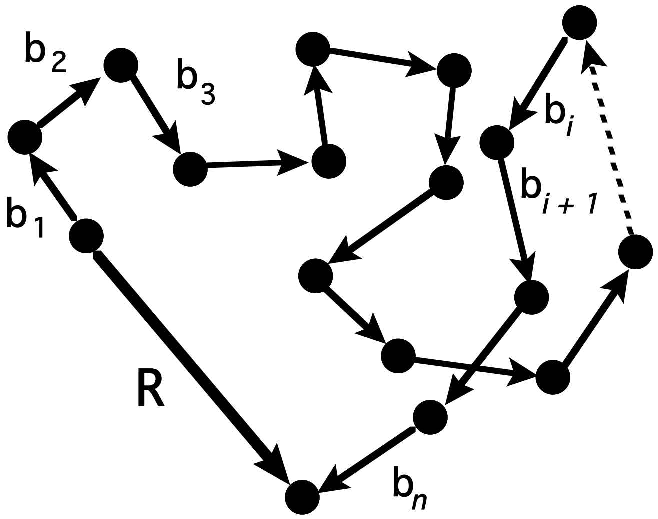
Chapter 3. Properties of Polymers

Hatsuo Ishida
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

3.1. Single Chain Properties

3.1.1. End-to-end Distance

Polymer chains consist of atoms that are connected by covalent bonds. These covalent bonds are usually capable of rotating, creating numerous number of possible conformations. It is, therefore, difficult to define the shape of a polymer chain. It is for this reason that a concept, *end-to-end distance*, R, is introduced. The end-to-end distance is the distance that connect two terminal atoms of the polymer chain. If the chain is forming a tight ball, such as the case in a poor solvent, the S would be small, whereby it is larger in a good solvent as the polymer ball is inflated and the termincal groups are widely separated.



In order to calculate the end-to-end distance, the covalent bonds are regarded as vectors. When many vectors form a closed system, the end-to-end distance R is a vector sum of the all vectors, b_i, along the polymer chain. Thus,

$$R = \sum_{i=1}^{n} b_i \tag{3.1}$$

The distance R varies with time. Therefore, the time average <R> must be considered. However, <R> can be either positive or negative (opposite direction), and therefore <R> is zero over a long time period. In order to avoid this difficulty, $\langle R^2 \rangle$ can be taken as the time average to eliminate the sign and later take $\sqrt{\langle R^2 \rangle}$ as the average distance <R> without the effect of the sign.

$$<R^2> = <R.R> = \sum_{i=1}^{n} <b_i^2> + 2\sum_{i=1}^{n-1} \sum_{i<j}^{n} <b_i.b_j> \tag{3.2}$$

where n is the number of bonds. Since,

$$<b_i^2> = b_i.b_i.\cos\theta_{ij} = b_i^2 \tag{3.3}$$

where θ_{ij} is the angle between two vectors.

A. No restriction in bond angle

In this case, the time average bond angle, $<\cos\theta_{ij}>$, is 0,

$$<b_i.b_j> = b^2<\cos\theta_{ij}> = 0 \tag{3.4}$$

Inserting equations (3.3) and (3.4) into equation (3.2) yields,

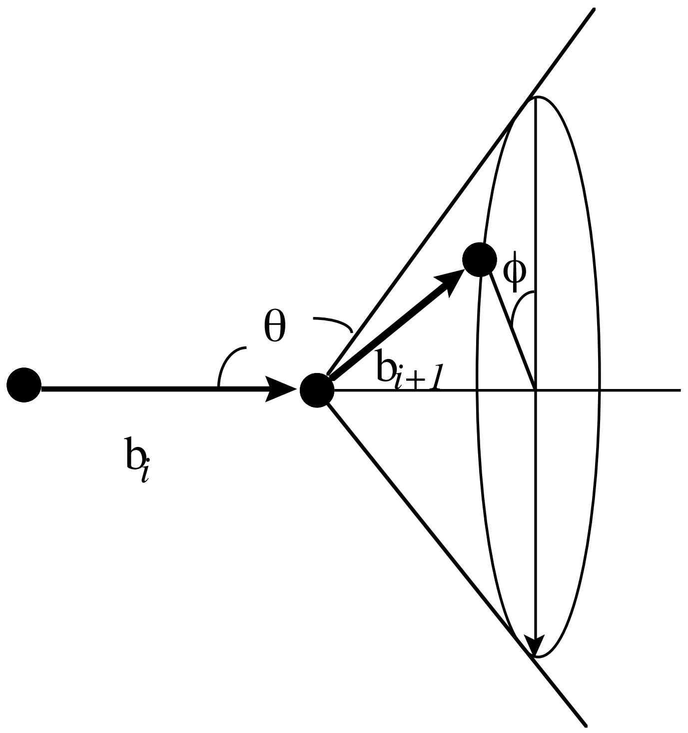
$$<R^2> = nb^2 \qquad (3.5)$$

Thus, the end-to-end distance is,

$$R = \sqrt{<R^2>} = b\sqrt{n} \tag{3.6}$$

B. Fixed bond angle

In this model, the rotation around the bond is unristricted but the rotation must be achieved with a fixed bond angle.



The projected length of b_{i+1} on the direction of b_i is b cos(π-θ). Therefore,

$$<b_i.b_{i+1}> = b^2<\cos(\pi-\theta)> = -b^2\cos\theta \tag{3.7}$$

Then, the next pair, $<b_i.b_{i+2}>$ will be,

$$<b_i.b_{i+2}> = <b_i.b_{i+1}> \cos(\pi-\theta) = b^2\cos^2(\pi-\theta) \tag{3.8}$$

Similarly,

$$<bi.bi+k> = b^2 \cos^k(\pi-\theta) \tag{3.9}$$

We now consider the *i* th bond as reference for the polymer with the total number of bond *n*. If the bond beyond the *i* th is recounted as 1,2,3....*k*, the total number of bonds until *i* th bond is (*n*-*k*). Hence,

$$\sum_{i=1}^{n-1}\sum_{j>i}^{n} <b_i.b_j> = \sum_{i=1}^{n-1}\sum_{k=1}^{n-1} <b_i.b_{i+k}>$$

$$= b^2\sum_{k=1}^{n-1} (n-k)\cos^k(\pi-\theta)$$

$$= b^2 n\sum_{k=1}^{n-1} s^k - b^2\sum_{k=1}^{n-1} ks^k$$

$$= b^2n\frac{s - s^n}{1 - s} - \frac{b^2s}{(1-s)^2}\{1-ns^{n-1} + (n+1)s^n\} \tag{3.10}$$

where $s = \cos(\pi-\theta)$

Therefore,

$$<R^2> = \sum_{i=1}^{n} <b_i^2> + 2\sum_{i=1}^{n-1}\sum_{i<j}^{n} <b_i.b_j>$$

$$= nb^2 + 2[b^2n\frac{s - s^n}{1 - s} - \frac{b^2s}{(1-s)^2}\{1-ns^{n-1} + (n+1)s^n\}]$$

$$= nb^2\left\{\frac{1+s}{1-s} - \frac{2s(1+s^n)}{n(1-s)^2}\right\} \tag{3.11}$$

Since $\frac{2s(1+s^n)}{n(1-s)^2} \approx 0$ for very large n,

$$<R^2> \approx nb^2\frac{1 + \cos(\pi-\theta)}{1 - \cos(\pi-\theta)} = nb^2\frac{1 - \cos\theta}{1 + \cos\theta} \tag{3.12}$$

For the C-C bond, the tetrahedral bond angle = 109°28', and, therefore, $\cos\theta = -1/3$. Accordingly,

$$R = \sqrt{<R^2>} = \sqrt{nb^2\frac{1+\frac{1}{3}}{1 - \frac{1}{3}}} = \sqrt{2nb^2} = \sqrt{2}\ (b\sqrt{n}) \tag{3.13}$$

Thus, the end-to-end distance for the restricted bond angle is $\sqrt{2}$ times larger than unrestricted bond angle case.

C. Barrier for Internal Rotation

If a more accurate calculation is desired, the restriction due to the angle of rotation must be taken into account. After consideration of the energy barrier, ΔE, for internal rotation, the following modified equation is obtained.

$$<R^2> = nb^2\frac{1-\cos\theta}{1+\cos\theta}.\frac{2 + \exp(\frac{-\Delta E}{kT})}{3\exp(\frac{-\Delta E}{kT})} \tag{3.14}$$

3.1.2. Radius of Gyration

The end-to-end distance is difficult to measure. Instead, the radius of gyration, S, is often used since this quantity can be measured by a light scattering technique. The mean-square value of the radius of gyration can be related to the mean-square value of the end-to-end distance by:

$$<S^2> = \frac{1}{6}<R^2> \qquad (3.15)$$

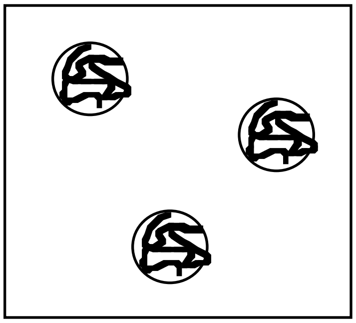
The radius of gyration is the average distance from the center of the gravity to the chain segment. The radius of gyration of a polymer in a poor solvent is smaller than in a good solvent. The radius of gyrations for the same polymer with and without branching are different even for the same molecular weight. The *g-factor* is defined as follows to evaluate the degree of branching.

$$g = \frac{<S^2>\text{(branched polymer)}}{<S^2>\text{(linear polymer)}} \qquad (3.16)$$

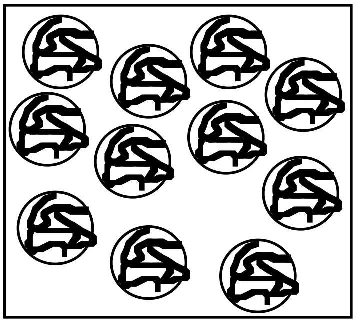
3.2. Solution Properties

3.2.1. Viscosity

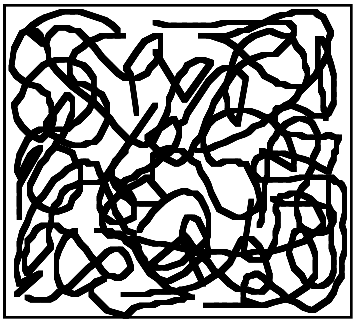
Polymer molecules in a dilute solution exist as ball like with the diameter determined by the radius of gyration. The radius of gyration depends on the interaction of the polymer molecule with the solvent. When the concentration of the polymer increases, the number of balls increases until they start interacting each other. This structure is seen in a semidilute concentration. In a concentrated solution, the polymer molecules no longer exist as separate balls but interact each other. In a sense a polymer chain is a solvent of another chain. As a polymer chain is a good solvent of itself, the polymer chains are much more stretched and sometimes the chains form molecular entanglement if the molecular weight is above a certain value. This special molecular weight is called the *entanglement molecular weight*. For atactic polystyrene, the entanglement molecular weight is around 37,000. A schematic diagram of the polymer molecules in solution is shown below.



Dilute solution



Semi-dilute solution



Concentrated solution

When solvent molecules move through these polymer balls, the solvent receives resistance. The difficulty to flow is expressed by a quantity called *viscosity*, η. The higher the viscosity, the more difficult to move around. Since the viscosity of a polymer solution is a function of the polymer in the solution, the solution viscosity, η, can be expressed in terms of the viscosity of the solvent, η_o, and the concentration of the polymer molecules, C.

$$\eta = \eta_o(1 + aC + bC^2 + \cdots\cdots) \tag{3.17}$$

The coefficient a relates to the properties of the individual polymer chain and the coefficient b relates to the polymer-solvent interaction. In order to obtain the quantity a, the above equation is extrapolated to C=0. Thus, the higher terms can be ignored.

$$\lim \frac{\eta - \eta_o}{\eta_o C} = a \tag{3.18}$$

This quantity a is called intrinsic viscosity, $[\eta]$. The ratio between the solution and solvent viscosities is called *relative viscosity*, $\eta_r = \eta/\eta_o$.

According to Eistein, the viscosity of a very dilute solution with spheres can be expressed as follows.

$$\eta = \eta_o \left(1 + \frac{5}{2}\phi\right) \tag{3.19}$$

where ϕ is the *packing fraction*.

In general, the intrinsic viscosity of a polymer is expressed by the following equation.

$$[\eta] = KM^a \tag{3.20}$$

where $0.5 \leq a \leq 0.8$. This equation is called *Mark-Houwink-Sakurada equation*.

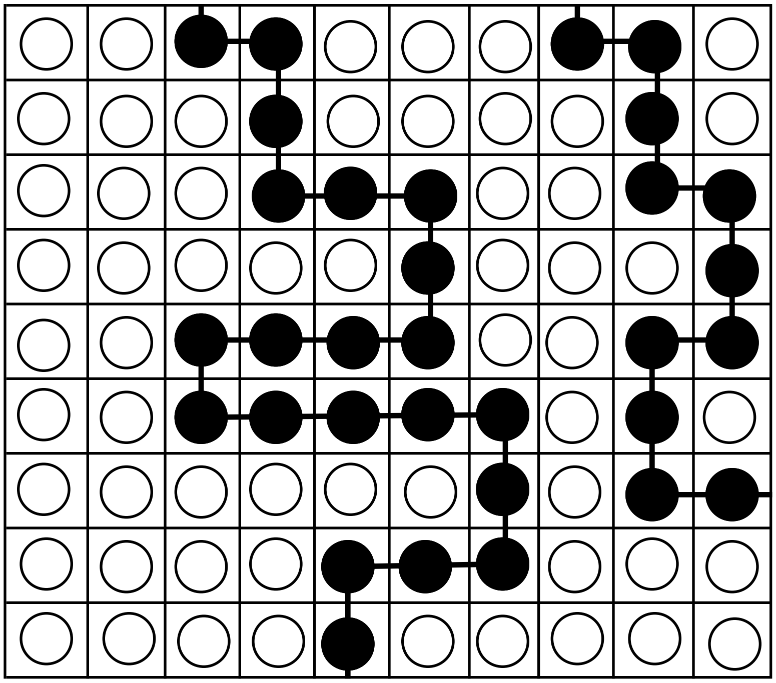
3.2.2. Thermodynamics of Polymer Solution

3.2.2.1. Statistical Theory (Flory-Huggins Theory)

Phase equilibrium, osmotic pressure, vapor pressure and other thermodynamic properties can be studied by obtaining thermodynamic function of the polymer solution. Gibbs free energy provide extra energy that can be utilized and thus is an appropriate function to evaluate the energy obtained by mixing a polymer into a solvent. Those thermodynamic properties of interest are usually the consequence of mixing the polymer into the solvent, the change before and after the mixing should be evaluated. Thus, all thermodynamic properties below indicate those of mixture.

$$G = H - TS = U + PV - TS \tag{3.21}$$

where G is Gibbs free energy, H enthalpy, T temperature, S entropy, U internal energy, and V volume. Flory and Huggins independently calculated ΔS from a lattice model.



The lattice model. The open circle denotes solvent molecule and the closed circle is the chemical repeat unit of a polymer chain.

Following are their assumptions.

i. A polymer solution can be regarded as chemical repeat units of the polymer chain occupying each lattice unit.

ii. The lattice unit has equal size and each lattice unit can be occupied either by a solvent molecule or the chemical repeat unit.

iii. The number of the neiboring chemical repeat units is called valence number.

iv. The number of placement of N_2 polymer chain in N_1 lattice units, $W(N_1, N_2)$, provides entropy of mixing ΔS using the Bolzmann equation shown below.

$$\Delta S = k \log W(N_1, N_2) \tag{3.22}$$

After lengthy calculation, the entropy of mixing can be expressed as:

$$\Delta S = -R\,(\phi_1 \log\phi_1 + \frac{\phi_2}{m_2} \log\phi_2) \tag{3.23}$$

where R is the gas constant, ϕ the volume fraction, m the degree of polymerization, and suffix 1 and 2 express the solvent and polymer, respectively. If the second polymer is regarded as the solvent of the first polymer in place of a small molecular weight solvent, the equation correspond to polymer blend. Thus, the entropy of mixing of a blend is:

$$\Delta S = -R\,(\frac{\phi_1}{m_1}\log\phi_1 + \frac{\phi_2}{m_2}\log\phi_2) \qquad (3.24)$$

If the solvent/solvent interaction energy is defined as ε_{11}, solvent/chemical repeat unit ε_{12}, and chemical repeat unit/chemical repeat unit ε_{22}, the enthalpy of mixing H can be expressed as follows:

$$\Delta H = Q_{12}\,\Delta\varepsilon_{12} \qquad (3.25)$$

where Q_{12} is the number of contact between the solvent molecule and the chemical repeat units and $\Delta\varepsilon_{12} = 0.5\,(\varepsilon_{11} + \varepsilon_{22}) - \varepsilon_{12}$.

Interaction parameter, χ_{12}, is defined as follows:

$$\chi_{12} = \frac{z\Delta\varepsilon_{12}}{kT} \qquad (3.26)$$

where z is the valence number. Accordingly, the Gibbs free energy of mixing, ΔG, is expressed as follows using the interaction parameter:

$$\Delta G = RT\,(\phi_1\log\phi_1 + \frac{\phi_2}{m_2}\log\phi_2 + \chi_{12}\phi_1\phi_2) \qquad (3.27)$$

Again, for polymer blend

$$\Delta G = RT\,(\frac{\phi_1}{m_1}\log\phi_1 + \frac{\phi_2}{m_2}\log\phi_2 + \chi_{12}\phi_1\phi_2) \qquad (3.28)$$

Ordinarily, m is replaced by the number average molecular weight, M_n.

The advantages of Flory-Huggins theory is that he equation is quite simple. Also, m=1 corresponds to small molecular weight compound, and m_1 and m_2 can be used to describe polymer blends. However, this theory does have shorcomings as well. By their assumption that each lattice unit is occupied by either solvent molecule or a chemical repeat unit, the volume of mixing, ΔV, is zero, and the fixed lattice size does not allow to evaluate the thermal expantion.

3.2.2.2. Colligative Properties

A. Vapor Pressure

Vapor pressure lowering can be used to measure molecular weight of polymers. Under *ideal solution assumption*, the activity coefficient, γ, can be ignored. Thus, activity of the solution, a_1, is,

$$a_1 = \frac{P_1\gamma_1}{P_1^o\gamma_1^o} = \frac{P_1}{P_1^o} \qquad (3.29)$$

Also under the ideal solution assumption, a_1 for the gas which is in equilibrium with the solution also holds for the solution, so,

$$a_1 = N_1$$

where suffices 1 and 2 indicate solvent and solute, respectively, and N mole fraction.

$$\frac{P_1}{P_1^o} = N_1 = 1 - N_2 \qquad (3.30)$$

For $N_2 << 1$ (very dilute solution),

$$\ln \frac{P_1}{P_1^o} = \ln (1 - N_2) = - N_2 - \frac{1}{2}N_2^2 - \frac{1}{3}N_2^3.... \quad \text{(this is an exact equation)} \qquad (3.31)$$

while,

$$N_2 = \frac{n_2}{n_1 + n_2} \qquad (3.32)$$

where n is the number of mole of solvent or solute. If we have c grams of solute and w_1 grams of solvent in 1 cc of solution, then,

$$n_1 = \frac{w_1}{M_1} \quad \text{and} \quad n_2 = \frac{c}{M_2}$$

Therefore,

$$\frac{n_2}{n_1} = \frac{c}{w_1}\left(\frac{M_1}{M_2}\right) \qquad (3.33)$$

Also, $v_1 + v_2 = 1$, where v_1 and v_2 are the volume of solvent and solute in 1 cc of solution, respectively.

$$v_1 + v_2 = \frac{w_1}{\rho_1} + \frac{c}{\rho_2} = 1 \qquad (3.34)$$

where ρ is density. Rearranging the above equation yields,

$$w_1 = \rho_1 \left(1 - \frac{c}{\rho_2}\right) \qquad (3.35)$$

Thus,

$$\frac{n_2}{n_1} = \frac{c}{w_1}\left(\frac{M_1}{M_2}\right) = \frac{c}{\rho_1\left(1 - \frac{c}{\rho_2}\right)}\left(\frac{M_1}{M_2}\right)$$

$$= \frac{c}{\left(1 - \frac{c}{\rho_1}\right)}\left(\frac{M_1}{\rho_1}\right)\left(\frac{1}{M_2}\right) \qquad \text{Here, } \frac{M_1}{\rho_1} = V_1^o$$

$$= \frac{cV_1^o}{M_2}\left(\frac{1}{1 - \frac{c}{\rho_2}}\right)$$

$$= \frac{cV_1^o}{M_2}\left(1 + \frac{c}{\rho_2}\right) \qquad (3.36)$$

because,

$$\frac{1}{1 - \frac{c}{\rho_2}} = 1 + \frac{\frac{c}{\rho_2}}{1 - \frac{c}{\rho_2}} = 1 + \frac{c}{\rho_2} \quad \text{Here,} \quad 1 - \frac{c}{\rho_2} \approx 1 \text{ for } c << \rho_2 \qquad (3.37)$$

$$N_2 \approx \frac{n_2}{n_1} = \frac{cV_1^o}{M_2}\left(1 + \frac{c}{\rho_2}\right) \quad \text{since, } N_2 = \frac{n_2}{n_1 + n_1} \approx \frac{n_2}{n_1} \text{ for } n_2 << 1 \qquad (3.38)$$

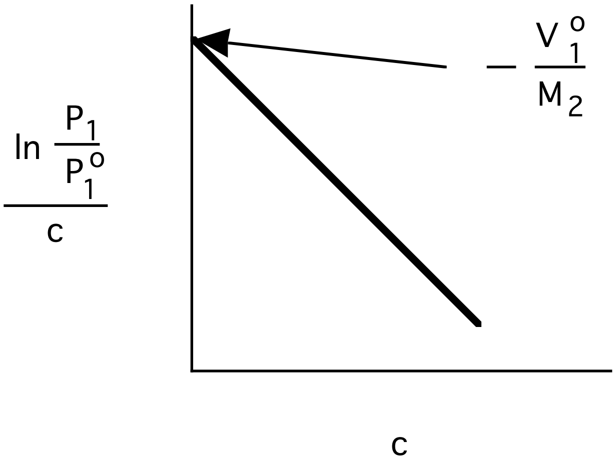
$$\ln\frac{P_1}{P_1^o} = \ln(1 - N_2) = -N_2 - \frac{1}{2}N_2^2 - \frac{1}{3}N_2^3 ....$$

$$= -\left\{\frac{cV_1^o}{M_2}\left(1 + \frac{c}{\rho_2}\right)\right\} - \frac{1}{2}\left\{\frac{cV_1^o}{M_2}\left(1 + \frac{c}{\rho_2}\right)\right\}^2 - \frac{1}{3}\left\{\frac{cV_1^o}{M_2}\left(1 + \frac{c}{\rho_2}\right)\right\}^3 - ......$$

$$= -\left(\frac{V_1^o}{M_2}\right)c - \left(\frac{V_1^o}{M_2\rho_2}\right)c^2 - \frac{1}{2}\left(\frac{V_1^o}{M_2}\right)^2 c^2 - .... c^3 .... c^4 \qquad (3.39)$$

Hence,

$$\frac{\ln\frac{P_1}{P_1^o}}{c} = -\left\{\frac{V_1^o}{M_2}\right\} - \left\{\frac{V_1^o}{M_2\rho_2} + \frac{(V_1^o)^2}{2M_2^2}\right\}c - ..... \qquad (3.40)$$



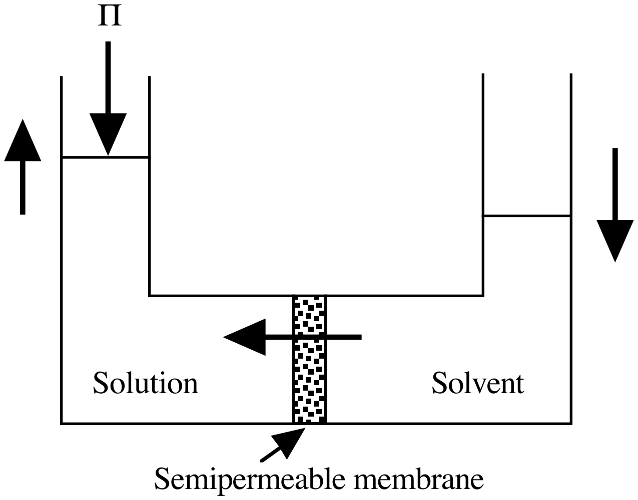
Since $\ln\frac{P_1}{P_1^o} < 0$ for $\frac{P_1}{P_1^o} < 1$, $-\frac{V_1^o}{M_2} > 0$

From the intercept, the molecular weight of the polymer can be calculated.

Colligative properties are proportional to the number of particles while the number of polymer molecules of high molecular weight polymers at the same volume content is very low. Thus, the colligative property measurement is insensitive to high molecular weight polymers.

B. Osmotic Pressure

Osmotic pressure is the pressure needed to equalize the pressure on a semipermeable membrane as a result of the increased Gibbs free energy by mixing polymer with a solvent.



The factors which determine the equilibrium state are:

i. Various porosities of membranes.
ii. The area of the membrane.
iii. The size distribution of capillaries.
iv. The viscosity of the solvent.
v. The distance from the equilibrium.

The advantages of osmotic pressure measurement are that the measurement is very simple and the device is inexpensive. On the other hand, disadvantages of the method are that it takes a long time to approach equilibrium, solvent dilute the solution, and true semipermeable membrane is rarely available.

The Gibbs free energy of mixing, ΔG, can be expressed as the difference between the free energy of the solution, G_1, and that of the solvent, G_1^o.

$$\Delta G_1 = G_1 - G_1^o \quad (3.41)$$

From the thermodynamic law,

$$\left(\frac{\partial G_1}{\partial P}\right)_T = V \qquad (3.42)$$

$$dG_1 = V_1 dP \qquad (3.43)$$

If the free energy increase from G_1 to G_1' requires the pressure to be increased from P_o to P to stop permeation, then,

$$\int_{G_1}^{G_1'} dG_1 = \int_{P_o}^{P} V_1 dP \qquad (3.44)$$

$$G_1' - G_1 = V_1(P - P_o) = V_1\Pi \qquad (3.45)$$

where Π is the osmotic pressure.

$G_1' = G_1^o$ because the G of the solvent is G_1^o at no permeation.

$$G_1' - G_1 = G_1^o - G_1 = V_1\Pi \qquad (3.46)$$

From Eq. (3.41),

$$\Delta G_1 = G_1 - G_1^o = -V_1\Pi \qquad (3.47)$$

The Gibbs free energy is also related to the activation energy:

$$\Delta G_1 = RT \ln a_1 = RT \ln N_1 = -V_1\Pi \qquad (3.48)$$

For very dilute solution,

$$\Delta G_1 = -V_1\Pi = -V_1^o\Pi$$

Therefore,

$$\Pi = -\frac{RT}{V_1^o} \ln N_1$$

$$= -\frac{RT}{V_1^o} \ln (1 - N_2)$$

$$= -\frac{RT}{V_1^o} (-N_2 - \frac{1}{2}N_2^2 - \frac{1}{3}N_2^3 - ....) \qquad \text{from eq. (3.31)}$$

$$= \frac{RT}{V_1^o} (N_2 + \frac{1}{2}N_2^2 + \frac{1}{3}N_2^3 + ...) \qquad (3.49)$$

Substituting eq. (3.36) into eq. (3.49) yields,

$$\frac{\Pi}{c} = \frac{RT}{M_2} + RT\left(\frac{1}{M_2\rho_2} + \frac{V_1^o}{2M_2^2}\right)c + ... \qquad (3.50)$$