

4.3 Flory-Huggins theory

regular solution approximation \rightarrow not valid for polymer solution

※ **Mixing entropy**

- Assumptions

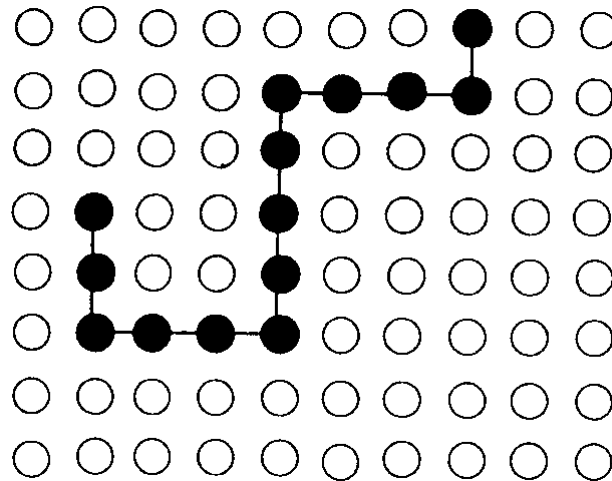
1. The components of the mixture are placed in “lattice”.
2. Volume is unchanged during mixing.
3. Mixing entropy is strongly influenced by the chain connectivity of the polymer component.
4. Mixing enthalpy for polymer-small molecule mixtures is similar to that for regular solutions.
5. Each repeating unit of the polymer (“segment”) occupies one position.

6. n lattice positions are partitioned.

(n_1 solvent molecules & n_2 polymer solute molecules)

7. each polymer molecule occupies x lattices.

8. i polymer molecules have already been placed in the lattice.



The number of vacant positions : $n - xi$

→ 즉, $(i+1)$ th molecule의 1st segment를 위치시킬 방법의 수

of ways of arranging the next segment :

$$= z \cdot (1 - f_i) \quad z : \text{coordination \# of the lattice}$$

$$(1 - f_i) : \text{fraction of remaining vacant position} \left(= \frac{(n - xi)}{n} \right)$$

of ways of arranging the 3rd (& all the rest) segment :

$$= (z - 1) \cdot (1 - f_i)$$

∴ The number of different ways of arranging the $(i+1)$ th molecule :

$$v_{i+1} = (n - xi)z(z - 1)^{x-2}(1 - f_i)^{x-1}$$

of arranging all the polymer molecules :

$$P_2 = \frac{v_1 v_2 \cdots v_{n_2}}{n_2!}$$

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Polymer molecules cannot be distinguished.

$$P_2 = \left(\frac{z-1}{n}\right)^{n_2(x-1)} \frac{1}{n_2!} \frac{(n-x)!}{(n-(n_2+1)x)!} \approx \left(\frac{z-1}{n}\right)^{n_2(x-1)} \frac{n!}{(n-n_2x)! n_2!}$$

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← Stirling's approximation & $n = n_1 + n_2x$

$$S = k \left\{ -n_1 \ln \left(\frac{n_1}{n_1 + n_2x} \right) - n_2 \ln \left(\frac{n_2}{n_1 + n_2x} \right) + n_2(x-1) \ln \left(\frac{z-1}{e} \right) \right\}$$

▷ *Disordering & dissolution* of a polymer

- 1) Formation of an amorphous polymer (disorientation) $\rightarrow S_a$
- 2) Dissolution of the amorphous polymer in the solvent $\rightarrow \Delta S_{mix}$

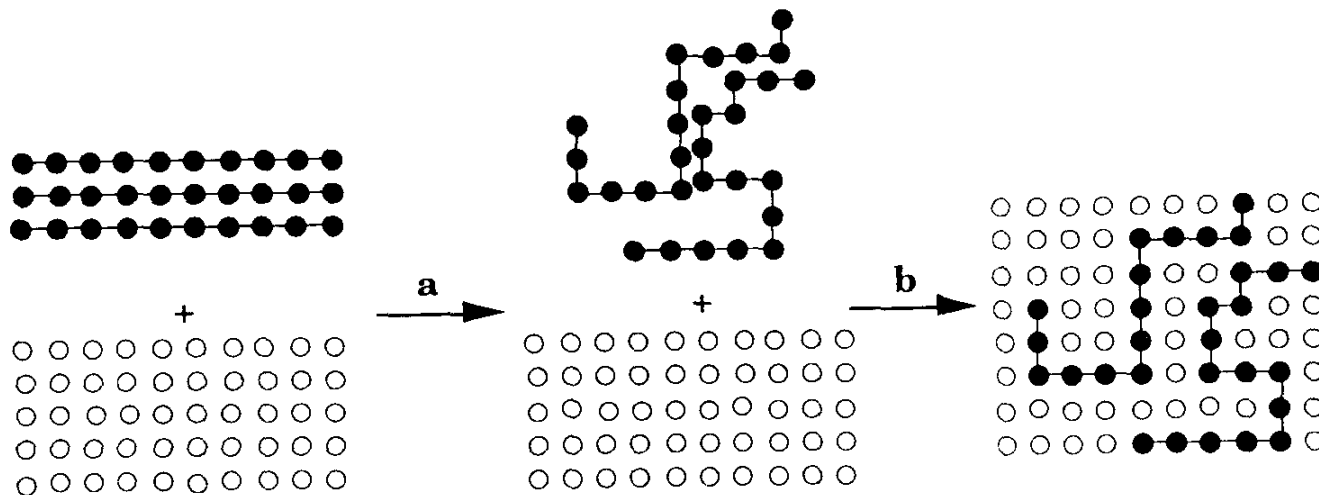


Figure 4.7 Schematic representation of steps a and b in the disordering and dissolution of a polymer.

S_a : entropy of the amorphous state prior to mixing

$$= kn_2 \ln x + kn_2(z-1) \ln \left(\frac{z-1}{e} \right)$$

$$\therefore \Delta S_{mix} = S - S_a$$

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$$= -k(n_1 \ln v_1 + n_2 \ln v_2) \quad v : \text{volume fraction}$$

$$\Rightarrow \boxed{\frac{\Delta S_{mix}}{N} = -R \left(v_1 \ln v_1 + \frac{v_2}{x} \ln v_2 \right)}$$

where, $N = N_1 + xN_2$, $kN_A = R$, $n_1 = NN_A v_1$, $n_2 = NN_A \frac{v_2}{x}$, $n = NN_A$

※ **Mixing enthalpy**

: interaction energy between solvent molecules & solute segments

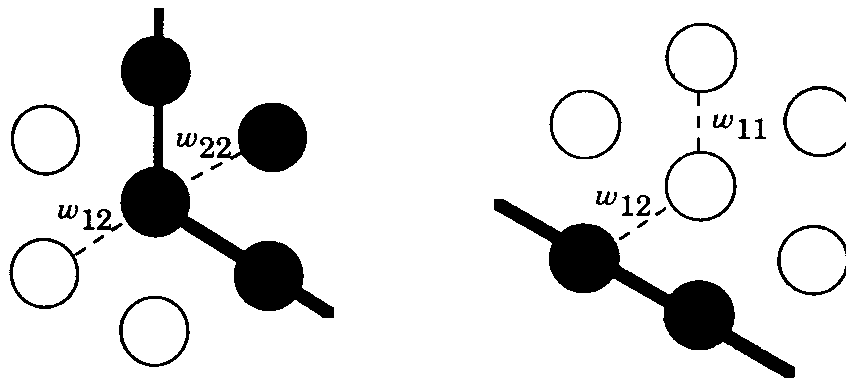


Figure 4.8 Schematic illustration of the interactions between solvent (unfilled) and solute= polymer (filled) molecules.

$$\Delta H_{mix} = \{ \text{Interaction energy for the solute segments} \\ + \text{Interaction energy for the solvent molecules} \\ - 11 \ \& \ 22 \text{ interaction energies of pure states} \} / 2$$

$$= (H_1 + H_2) - (H_{01} + H_{02})$$

$$H_2 = \frac{1}{2} n v_2 (v_1 z w_{12} + v_2 z w_{22})$$

$$H_1 = \frac{1}{2} n v_1 (v_1 z w_{12} + v_2 z w_{12})$$

$$H_{01} = \frac{1}{2} n v_1 z w_{11}$$

$$H_{02} = \frac{1}{2} n v_2 z w_{22}$$

$$= n_1 z v_2 \frac{\Delta w_{12}}{\quad} \quad \leftarrow \quad \Delta w_{12} = w_{12} - \frac{1}{2} (w_{11} + w_{22})$$


 energy change associated with the formation of one solvent-solute contact

$\Delta H_{mix} < 0$: exothermal
 > 0 : endothermal
 $= 0$: athermal mixing

$$\rightarrow \frac{\Delta H_{mix}}{N} = RT\chi_{12}v_1v_2$$

χ_{12} : interaction parameter, $\chi_{12} = z\Delta w_{12} / RT$

※ **Change in free energy on mixing**

$$\frac{\Delta G_{mix}}{N} = \frac{\Delta H_{mix}}{N} - T \frac{\Delta S_{mix}}{N}$$

$$\frac{\Delta G_{mix}}{N} = RT \left(v_1 \ln v_1 + \frac{v_2}{x} \ln v_2 + \chi_{12}v_1v_2 \right)$$

※ Chemical potentials

: μ_i (1: solvent, 2: solute)

$$\mu_1 = \mu_1^0 + RT \ln a_1$$

activity, ideal solution인 경우 $a_1 = x_1$

$$\frac{\Delta G_{mix}}{N} = RT \left(v_1 \ln v_1 + \frac{v_2}{x} \ln v_2 + \chi_{12} v_1 v_2 \right) \text{ 을}$$

$$\mu_1 - \mu_1^0 = \frac{\Delta G_{mix}}{N} + x_2 \frac{d(\Delta G_{mix}/N)}{dx_1} \text{ 에 대입하여 정리하면,}$$

$$\begin{aligned} \rightarrow \frac{\mu_1 - \mu_1^0}{RT} &= \ln a_1 \\ &= \ln v_1 + (1 - 1/x)v_2 + \chi_{12} v_2^2 \end{aligned}$$

$\mu_2 = \mu_2^0 + RT \ln a_2$ 에 대해서도 같은 방법으로 정리하면,

$$\begin{aligned} \rightarrow \frac{\mu_2 - \mu_2^0}{RT} &= \ln a_2 \\ &= \ln v_2 + (1 - x)v_1 + x\chi_{12} v_1^2 \end{aligned}$$

- Phase (spinodal) separation occurs when

$$\frac{d^2(\Delta G_{mix} / N)}{dx_1^2} = 0 \Rightarrow \frac{d\mu_1}{dx_1} = 0$$

- Critical temperature : $\frac{d^3(\Delta G_{mix} / N)}{dx_1^3} = 0 \Rightarrow \frac{d^2\mu_1}{dx_1^2} = 0$

- Critical values for phase separation

위의 두 조건을 적용시켜 해를 구하면,

$$v_{2,c} = \frac{1}{1 + \sqrt{x}}$$

$$\chi_{12,c} = \frac{1}{2} + \frac{1}{2x} + \frac{1}{\sqrt{x}}, \quad T_c = \frac{B}{R\chi_{12,c}}$$

For a polymer of infinite molar mass,

$$\chi_{12,c} = \frac{1}{2}, \quad T_c = \frac{2B}{R}$$

- χ_{12} calculation by measuring osmotic pressure

$$-\Pi V_1 = RT \ln a_1 = -\mu_1^0 + \mu_1$$

← V_1 : molar volume of the solvent

$$\ln\left(\frac{a_1}{v_1}\right) - \left(1 - \frac{1}{x}\right)v_2 = \chi_{12}v_2^2$$

→ χ_{12} as a slope in plot of $\ln\left(\frac{a_1}{v_1}\right) - \left(1 - \frac{1}{x}\right)v_2$ against v_2^2

- Modified Flory - Huggins theory (χ_{12} 에 관련된 결정 보완)

$$\frac{\Delta S_{mix}}{N} = -R \left(v_1 \ln v_1 + \frac{v_2}{x} \ln v_2 + v_1 v_2 \left(\frac{\partial(\chi_{12}T)}{\partial T} \right) \right)$$

$$\frac{\Delta H_{mix}}{N} = -RT^2 \left(\frac{\partial \chi_{12}}{\partial T} \right) v_1 v_2$$

4.5 Solubility parameter concept

$$w_{12} = -\sqrt{w_{11}w_{22}} \quad \text{for non-specific attraction forces}$$

$$\Delta w_{12} = w_{12} - \frac{1}{2}(w_{11} + w_{22}) = \frac{(\sqrt{|w_{11}|} - \sqrt{|w_{22}|})^2}{2} > 0$$

When specific interactions are involved, this eq'n is not applicable.

$$\text{CED (cohesive energy density)} \equiv \frac{\Delta E_V}{V_1}$$

↗ molar energy of vaporization
 ↘ molar volume

: a measure of the intermolecular energy

$$\sqrt{\text{CED}} : (\text{Hildebrand}) \text{ solubility parameter } \delta \quad \therefore \delta^2 = \frac{\Delta E_V}{V_1}$$

Polymers degrade prior to vaporization.

$\therefore \delta$ is indirectly determined.

δ of best solvent $\approx \delta$ of polymer

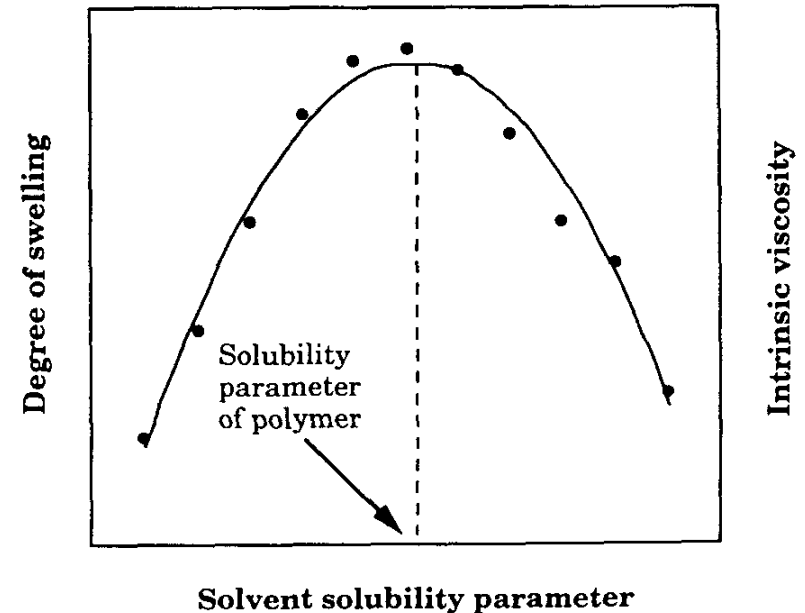
Theoretically,

$$\delta = \frac{\rho \Sigma G}{M} : \text{Small's formula}$$

G : molar attraction const. of the groups
of the repeating unit

Multi-dimensional δ (by Hansen)

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$



4.7 Polymer-polymer blends

Miscibility ~ a single phase system at a molecular level

⇒ System appears to be homogeneous at a level assessed by the particular test performed.

ex. T_g method.

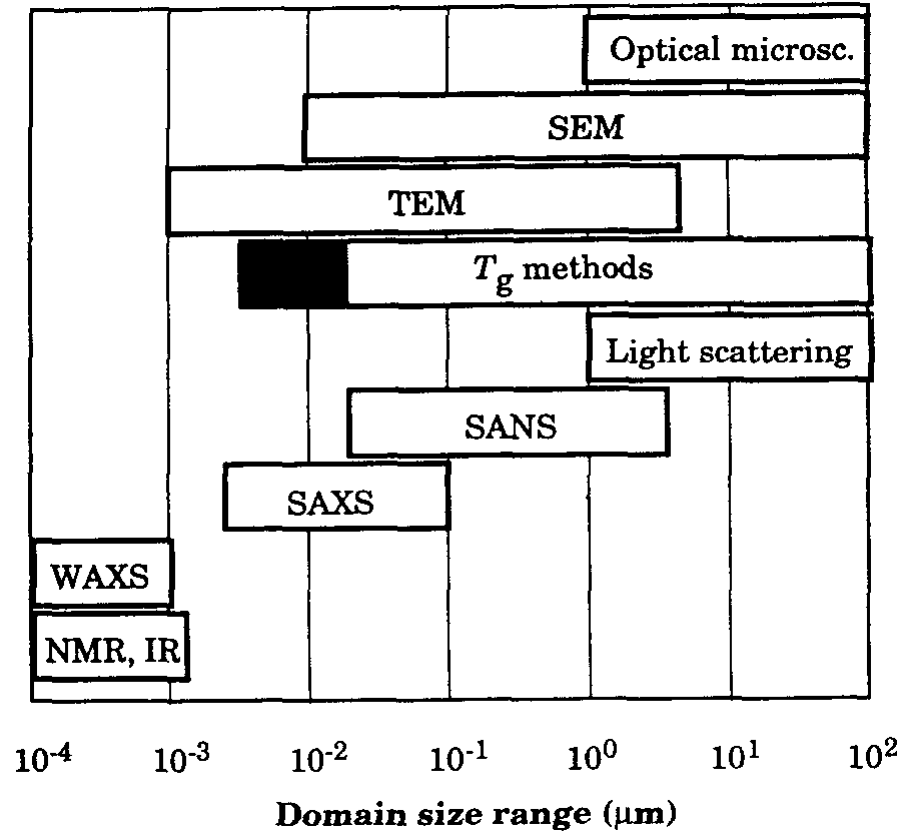
resolution : 2 ~ 15 nm,

T_g in binary systems > 20 K

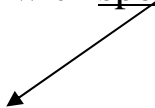
. T_g of miscible blend

$$\frac{1}{T_g} = \sum \frac{w_i}{T_{gi}} : \text{Fox equation}$$

Size range for the assessment of miscibility



- Making stable and reproducible blends of immiscible polymers
 - by introducing a third component (“compatibilizer”)
 - by promoting co-reactions between polymers
 - by modification of the polymers (introducing groups with specific interaction)



acid/base groups
hydrogen-bonding group
& charge-transfer complexes