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## Chapter 10

# Polymers in Solution

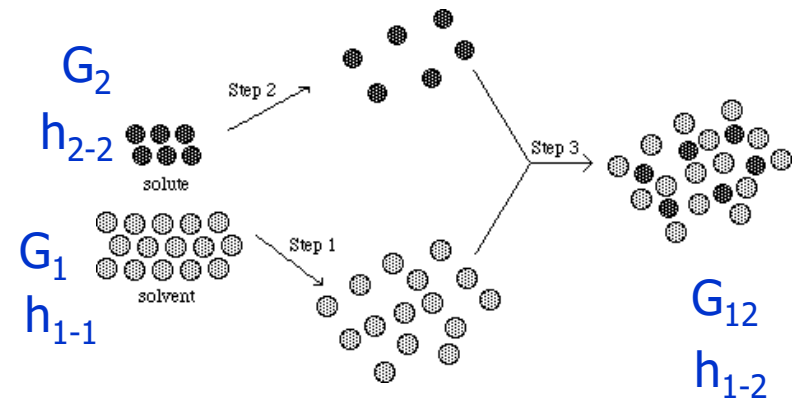
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Thermodynamics of polymer solution

Dimension of single polymer chain

# Solution: thermodynamics

- solution = homogeneous mixture (in molecular level)
  - (dis)solution = mixing solvent [1] and solute [2]
  - $\Delta G_m = G_{12} - (G_1 + G_2)$
- $\Delta G_m = \Delta H_m - T \Delta S_m$ 
  - $\Delta S_m > 0$  always
  - $\Delta H_m > 0$  almost always
    - “like dissolves like”
    - $\Delta H_m = 0$  at best
      - athermal or ideal solution
    - $\Delta H_m < 0$ ? only when specific interaction like H-bonding exists
  - For solution,  $\Delta H_m < T \Delta S_m$



# Ideal solution

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## □ ideal solution

- size of 1 and 2 the same, and
- $\Delta H_m = 0 \leftarrow$  interaction  $h_{1-1} = h_{2-2} = h_{1-2}$

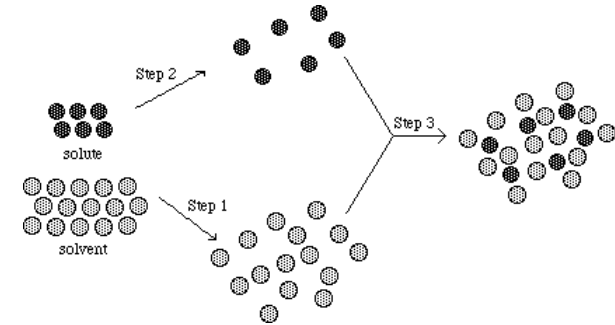
## □ $\Delta G_m$ of ideal solution

- $\Delta G_1 = \mu_1 - \mu_1^0 = RT \ln X_1$   
 $\Delta G_2 = \mu_2 - \mu_2^0 = RT \ln X_2$
- $\Delta G_m = n_1 \Delta G_1 + n_2 \Delta G_2$   
 $= RT (n_1 \ln X_1 + n_2 \ln X_2)$

## □ $\Delta S_m$ of ideal solution

- from  $\Delta G_m$  and  $\Delta H_m (= 0)$
- $\Delta S_m = -R (n_1 \ln X_1 + n_2 \ln X_2)$

$\Delta G_m, \Delta S_m$  from classical thermodynamics  
(Raoult's law for ideal solution)



$\mu \sim$  chemical potential  
 $n \sim$  number of moles  
 $X \sim$  mole fraction  
 $X_1 = n_1 / (n_1 + n_2)$

ideal solution  
athermal solution  
regular solution

# $\Delta G_m$ from statistical mechanics

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- lattice theory
  - filling  $N_1$  and  $N_2$  molecules in  $N_1+N_2=N_0$  cells
    - volume of 1  $\approx$  volume of 2 (for small molecules)
- Boltzmann relation:  $S = k \ln \Omega$ 
  - $k \sim$  Boltzmann constant =  $R/N_A$
  - $\Omega \sim$  number of (distinguishable) ways
- combinatorial  $\Delta S = S_{12} - S_1 - S_2$

$$\Delta S_m^{\text{comb}} = k[\ln \Omega_{12} - (\ln \Omega_1 + \ln \Omega_2)]$$

- $S_{12} = k \ln \Omega_{12} = k \ln [(N_1+N_2)!/N_1!N_2!]$
- $S_1 = k \ln \Omega_1 = k \ln (N_1!/N_1!) = 0 = k \ln \Omega_2 = S_2$

combinatorial  $S =$  configurational  $S$   
other  $S$ ? motion; not usual. So  $S = S^{\text{comb}}$

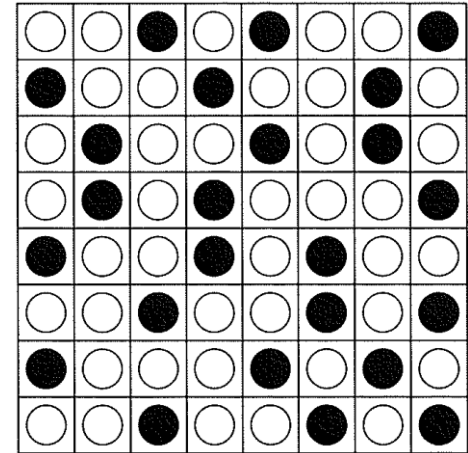


Fig 10.1(a)



$$\Delta S_m^{\text{comb}} = \mathbf{k} \ln \Omega_{12} = \mathbf{k} \ln \left[ \frac{(N_1 + N_2)!}{N_1! N_2!} \right]$$

Stirling's approximation,  $\ln N! = N \ln N - N$  (for large  $N$ ).

$$\Delta S_m^{\text{comb}} = -\mathbf{k} \left\{ N_1 \ln \left[ \frac{N_1}{(N_1 + N_2)} \right] + N_2 \ln \left[ \frac{N_2}{(N_1 + N_2)} \right] \right\}$$

$$\Delta S_m^{\text{comb}} = -\mathbf{R} [n_1 \ln X_1 + n_2 \ln X_2]$$

$$\Delta G_m = \mathbf{RT} [n_1 \ln X_1 + n_2 \ln X_2]$$

- the same to Raoult's law
- for ideal solution of small molecules
  - for real solution,  $\Delta H_m \neq 0 \leftarrow h_{11} \neq h_{12}$
  - for polymer solution,  $\Delta H_m \neq 0$  and different size betw 1 & 2

$X$  = mole fraction  
 $N$  = number of molecules  
 $X_1 = N_1 / (N_1 + N_2)$   
 $n$  = number of moles  
 $\mathbf{k} N_A = \mathbf{R}$

# Flory-Huggins Theory

- for polymer solution
- lattice model
  - filling  $N_1$  solvents and  $N_2$  polymers in  $N_1 + xN_2 = N_0$  cells
    - volume of 1  $\ll$  volume of 2 (segment)
    - how large? by  $x$  (= size 2/1  $\propto$  degree of polym'n)
- $\Delta S_m = S_{12} - S_1 - S_2 = k \ln [\Omega_{12}/\Omega_1\Omega_2] = k \ln [\Omega_{12}/\Omega_2]$ 
  - $\Omega_1 = 1$ ;  $\Omega_2 \neq 1$  ( $\leftarrow$  connected)

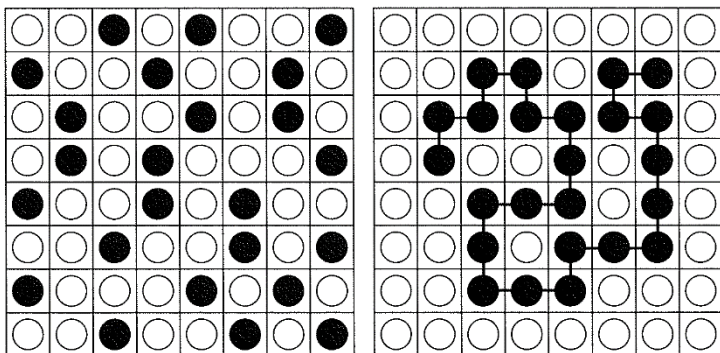
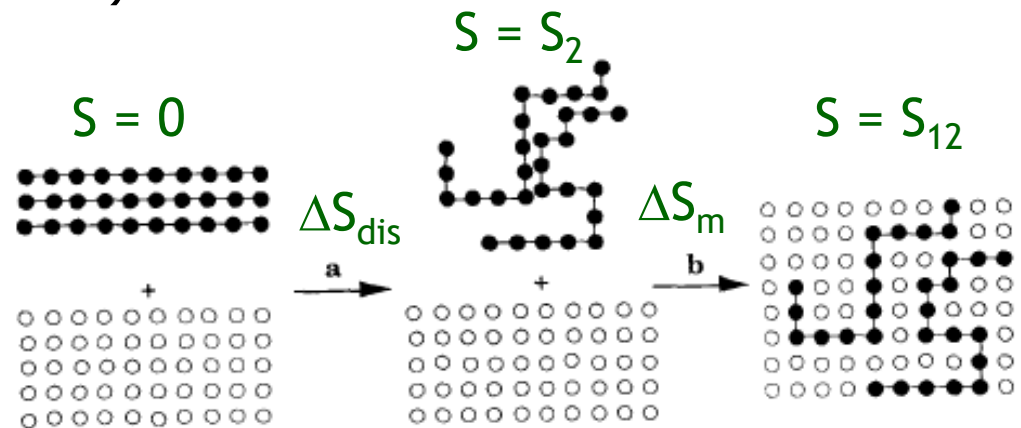


Fig 10.1



$\Delta S$  for disorientation  
[conformation]

- $v_\zeta = \#$  of ways to put  $\zeta^{\text{th}}$  chain (into N cells)

$$v_\zeta = \underbrace{[N - x(\zeta - 1)]}_{\text{1st segment}} \underbrace{\left\{ z \frac{[N - x(\zeta - 1)]}{N} \right\}}_{\text{2nd}} \underbrace{\left\{ (z - 1) \frac{[N - x(\zeta - 1)]}{N} \right\}^{x-2}}_{\text{3rd to } x^{\text{th}}}$$

identical  
( $N_2$ ) chains

$z = \text{coordination number} = \#$  of nearest neighbor

$$v_\zeta = z(z - 1)^{x-2} N^{1-x} [N - x(\zeta - 1)]^x$$

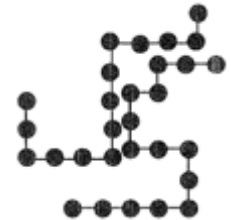
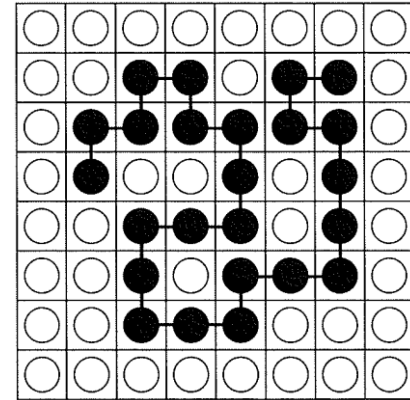
- $\Omega_{12} = \#$  of ways to put  $N_1$  solvents and  $N_2$  chains into N cells

$$\Omega_{12} = \frac{1}{N_2!} \prod_{\zeta=1}^{N_2} v_\zeta = \frac{1}{N_2!} \left\{ z(z - 1)^{x-2} N^{1-x} \right\}^{N_2} \prod_{\zeta=1}^{N_2} [N - x(\zeta - 1)]^x$$

- $\Omega_2 = \#$  of ways to put  $N_2$  chains into  $xN_2$  cells

$$\Omega_2 = \frac{1}{N_2!} \left\{ z(z - 1)^{x-2} (xN_2)^{1-x} \right\}^{N_2} \prod_{\zeta=1}^{N_2} [xN_2 - x(\zeta - 1)]^x$$

polymer only, no solvent  
 $\rightarrow \Omega_{12}$  with  $N_1 = 0$



$$\square \Delta S_m^{\text{comb}} = \mathbf{k} \ln \left( \frac{\Omega_{12}}{\Omega_2} \right)$$

- by expanding and approximations [ $N \gg x$  and Stirling's]

pp241-242 for derivation

$$\Omega_{12} = \Omega_2 \left[ \left( \frac{N}{xN_2} \right)^{N_2} \left( \frac{N}{N_1} \right)^{N_1} \right]$$

$$\Omega_2 = \left\{ \left[ z(z-1)^{z-2} \right]^{N_2} \right\} \left\{ \left[ \frac{x}{e^{x-1}} \right]^{N_2} \right\}$$

$$\Delta S_m^{\text{comb}} = \mathbf{k} \ln \left[ \left( \frac{N}{N_1} \right)^{N_1} \left( \frac{N}{xN_2} \right)^{N_2} \right]$$

$$\square \Delta S_m^{\text{comb}} = -\mathbf{k} [N_1 \ln \phi_1 + N_2 \ln \phi_2]$$

$$\Delta S_m^{\text{comb}} = -\mathbf{R} [n_1 \ln \phi_1 + n_2 \ln \phi_2]$$

$\phi$  = volume fraction  
 $\phi_1 = N_1 / (N_1 + xN_2)$   
 $N$  = # of molecules  
 $n$  = # of moles

- for small molecules, it was  $\Delta S_m^{\text{comb}} = -\mathbf{R} [n_1 \ln X_1 + n_2 \ln X_2]$

- when  $x = 1$ ,  $\phi_1 = X_1$



□ F-H  $\Delta S$   $\Delta S_m^{\text{comb}} = -k[N_1 \ln \phi_1 + N_2 \ln \phi_2]$

□ compare

□ solvent/solvent:  $N_1 = 40, N_2 = 24$

■  $\Delta S_m = -k [40 \ln (40/64) + 24 \ln (24/64)] = 42.3 k$

□ solvent/polymer:  $N_1 = 40, N_2 = 1$  [ $x=24$ ]

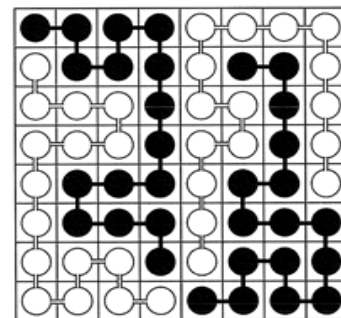
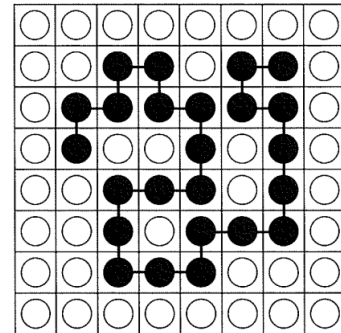
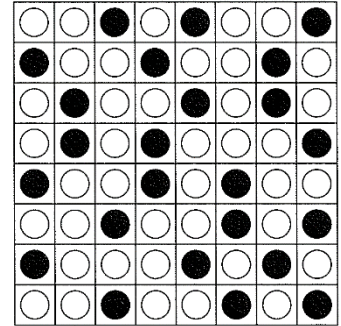
■  $\Delta S_m = -k [40 \ln (40/64) + 1 \ln (24/64)] = 19.8 k$

■ **polymer solution**:  $x \uparrow \rightarrow N_2 \downarrow$

□ polymer/polymer:  $N_1 = 2, N_2 = 2$  [ $x_1 = x_2 = 16$ ]

■  $\Delta S_m = -k [2 \ln (32/64) + 2 \ln (32/64)] = 2.8 k$

■ **polymer blend**: hard to be miscible



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

Fig 18.2 p451

# $\Delta H_m$ in F-H theory

□  $\Delta G_m = \Delta H_m - T \Delta S_m$

□ in original F-H theory

$$\Delta H_m = N_1 z X_2 [h_{12} - \frac{1}{2}(h_{11} + h_{22})]$$

$$= RT n_1 \phi_2 \chi$$

□ modified

← entropy change [non-randomness] with interaction

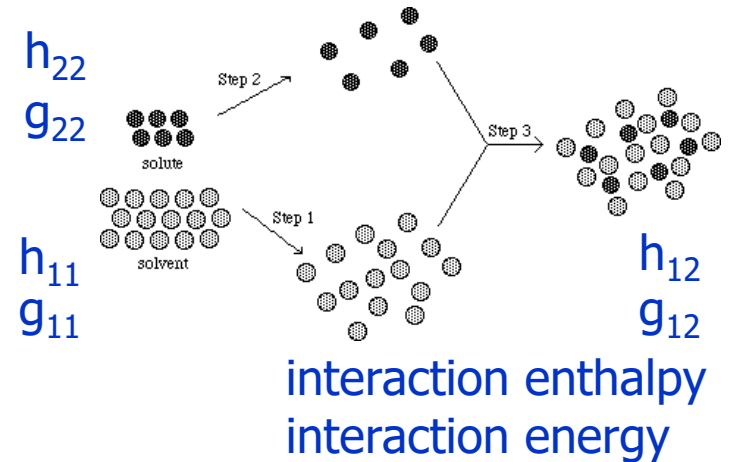
$$\Delta G_m^{\text{contact}} = RT n_1 \phi_2 \chi$$

□  $\chi =$  (F-H polymer-solvent) interaction parameter

□ smaller  $\chi =$  smaller  $\Delta G_m [\Delta H_m] =$  larger solubility

□  $\chi = \chi_S + \chi_H = a + b/T$

■  $\chi_S$  very small (then,  $\Delta G_m^{\text{contact}} \approx \Delta H_m$ )



$\chi = \chi_1 = \chi_{12}$   
all the same

$$\square \Delta G_m^{\text{contact}} = p_{12} \Delta g_{12}$$

$$\square \Delta g_{12} = g_{12} - \frac{1}{2}(g_{11} + g_{22})$$

- two 1-2 contact at the expense of one 1-1 + one 2-2

$$\square p = \# \text{ of contacts}$$

$$p_{12} = N_2(z-2)x\phi_1$$

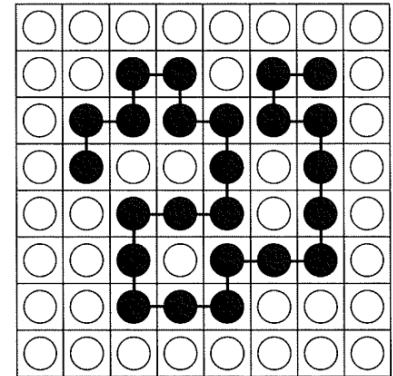
$$p_{12} = (z-2)N_1\phi_2$$

- $(z-2)x+2 \approx (z-2)x$  neighbors for 1 chain
- For  $N_2$  chains, --
- $\phi_1$  of them are solvent
- # of 1-2 contacts =  $xN_2\phi_1 = N_1\phi_2$

$$\square \Delta G_m^{\text{contact}} = (z-2)N_1\phi_2 \Delta g_{12} = \mathbf{RT}n_1\phi_2\chi$$

$$\square \chi = \frac{(z-2)\Delta g_{12}}{\mathbf{k}T}$$

$$n_1 = N_1/N_A \text{ and } \mathbf{R} = \mathbf{k}N_A$$



# F-H equation

□ original  $\Delta G_m = \Delta H_m - T \Delta S_m$   $\Delta H_m = RTn_1\phi_2\chi$

□ modified  $\Delta G_m = \Delta G_m^{\text{contact}} - T \Delta S_m^{\text{comb}}$   $\Delta G_m^{\text{contact}} = RTn_1\phi_2\chi$

$$\Delta S_m^{\text{comb}} = -\mathbf{R}[n_1 \ln \phi_1 + n_2 \ln \phi_2]$$

□  $\Delta G_m = \mathbf{RT}[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1\phi_2\chi]$  **F-H equation**

- predicts polymer solution property
  - solubility, miscibility, phase separation, fractionation, ---
  - vapor pressure, boiling point, ---
- but not that precisely
  - due to drawbacks of theory like
    - no volume change, self-intersection, changing  $\chi$
  - especially for dilute polymer solution
    - Chains are (far-)separated in dilute soln.  
= Chains do not interact. = Mean field theory is not applicable.

MFT? many-body to one-body problem

# Chemical potential $\mu$ in solution

Ch 10 sl 13

□  $\mu$  = partial molar free energy  $\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P,T,n_j}$

□ change in  $\mu_1$  upon mixing (by F-H eqn)

$$\mu_1 - \mu_1^\circ = \left( \frac{\partial \Delta G_m}{\partial n_1} \right)_{P,T,n_2} = \mathbf{RT} \frac{\partial}{\partial n_1} \{ n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi \}_{P,T,n_2}$$

$$\mu_1 - \mu_1^\circ = \mathbf{RT} \left[ \ln \phi_1 + \left( 1 - \frac{1}{x} \right) \phi_2 + \chi \phi_2^2 \right]$$

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Eqn (10.37) = other form of F-H eqn

□  $\mu_1 - \mu_1^\circ = \mathbf{RT} \ln a_1 = \mathbf{RT} \ln X_1 \gamma_1 = \mathbf{RT} \ln X_1 + \mathbf{RT} \ln \gamma_1$  Eqn A

$$(\mu_1 - \mu_1^\circ)^{\text{ideal}} = \mathbf{RT} \ln X_1$$

$$(\mu_1 - \mu_1^\circ)^{\text{E}} = \mathbf{RT} \ln \gamma_1$$

a = activity  
 $\gamma$  = activity coeff.  
X = mole fraction  
E = excess

# Dilute polymer solution

- Polymer chains are separated by solvent.
- F-H theory does not hold.
  - In F-H theory, chains are placed randomly.
  - need modification → Flory-Krigbaum theory

□ in dilute solution

how dilute? < .2 g/mL

$$\phi_2 = \frac{xn_2}{(n_1 + xn_2)} \approx \frac{xn_2}{n_1} \quad \text{and} \quad X_2 = \frac{n_2}{(n_1 + n_2)} \approx \frac{n_2}{n_1} \quad \rightarrow \quad X_2 = \phi_2/x$$

$$\ln \phi_1 = \ln(1 - \phi_2) = -\phi_2 - \frac{\phi_2^2}{2} - \frac{\phi_2^3}{3} - \dots$$

$$\ln X_1 = \ln(1 - X_2) = -X_2 - \frac{X_2^2}{2} - \frac{X_2^3}{3} - \dots = -\left(\frac{\phi_2}{x}\right)$$

Eqn (10.48)

$$\square \text{ Eqn (10.37)} \rightarrow \mu_1 - \mu_1^{\circ} = \mathbf{RT} \left[ \ln \phi_1 + \left(1 - \frac{1}{x}\right)\phi_2 + \chi\phi_2^2 \right] = \frac{-\mathbf{RT}\phi_2}{x} + \underbrace{\mathbf{RT} \left( \chi - \frac{1}{2} \right) \phi_2^2}_{(\mu_1 - \mu_1^{\circ})^E}$$

$$\square \text{ Eqn A} \rightarrow (\mu_1 - \mu_1^{\circ})^{\text{ideal}} = \mathbf{RT} \ln X_1 = \frac{-\mathbf{RT}\phi_2}{x} \quad \text{Eqn (10.49)}$$

# Theta condition

$$\square (\mu_1 - \mu_1^o)^E = \mathbf{RT} \left( \chi - \frac{1}{2} \right) \phi_2^2$$

$$\square \text{ Flory and Krigbaum set 3 parameters } \kappa, \theta, \psi: \kappa = \left( \frac{\theta}{T} \right) \psi$$

$$(\mu_1 - \mu_1^o)^E = \overline{\Delta G}_1^E = \overline{\Delta H}_1^E - T \overline{\Delta S}_1^E$$

$$\overline{\Delta H}_1^E = \mathbf{RT} \kappa \phi_2^2 \quad \overline{\Delta S}_1^E = \mathbf{R} \psi \phi_2^2$$

$$(\mu_1 - \mu_1^o)^E = \mathbf{RT} \psi \left[ \left( \frac{\theta}{T} \right) - 1 \right] \phi_2^2 = \mathbf{RT} \left( \chi - \frac{1}{2} \right) \phi_2^2$$

$$\begin{aligned} \kappa &\sim H \sim \text{interaction} \\ \theta &\sim \text{Temp} \\ \psi &\sim S \sim \text{connectivity} \\ \kappa - \psi &= \chi - \frac{1}{2} \end{aligned}$$

□ When  $T = \theta \rightarrow \chi = 1/2$ ,  $(\mu_1 - \mu_1^o)^E = 0$ , solution becomes **ideal**

□ **theta** [ $\theta$ ] condition;

□  $\theta$  = theta [Flory] temperature

□  $\kappa = \psi \sim$  interaction compensate connectivity

■ not an ideal solution, but the solution **behaves ideally**

- ❑ In  $\theta$  condition
  - ❑ at  $\theta$  temperature in the solvent
  - ❑ the (dilute) solution 'behaves' ideally
    - excess free energy change  $\Delta G_1^E = (\mu_1 - \mu_1^0)^E = 0$
    - by  $\Delta H^E$  and  $T\Delta S^E$  cancelling each other
  - ❑ borderline between good and poor solvent later in EV effect sl#35
    - soluble when  $T > \theta$ ; insoluble when  $T < \theta$
    - (infinitely) high MW fraction precipitates

Table 10.1  
p250

TABLE 10.1  
Values of Theta Temperature for Different  
Polymer–Solvent Systems<sup>a</sup>

Polymer	Solvent	$\theta / ^\circ\text{C}$
Polyethylene	Biphenyl	125
Polystyrene	Cyclohexane	34
Poly(vinyl acetate)	Methanol	6
Poly(methyl methacrylate)	Butyl acetate	-20
Poly(methyl methacrylate)	Pentyl acetate	41
Poly(vinyl alcohol)	Water	97
Poly(acrylic acid)	1,4-Dioxan	29

toluene/methanol (3/1) 25 °C



# Solubility parameter $\delta$

## □ $\Delta H_m$ by Hildebrand

$$\Delta H_m^{\text{contact}} = V_m \phi_1 \phi_2 (\delta_1 - \delta_2)^2$$

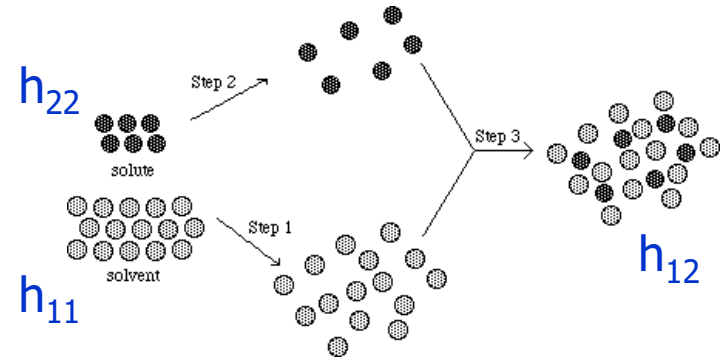
- $V_m \sim$  molar volume (of mixture)

## □ $\delta =$ solubility parameter [溶解度常數]

$$\delta = \left[ \frac{(\Delta H_v - RT)}{V} \right]^{1/2}$$

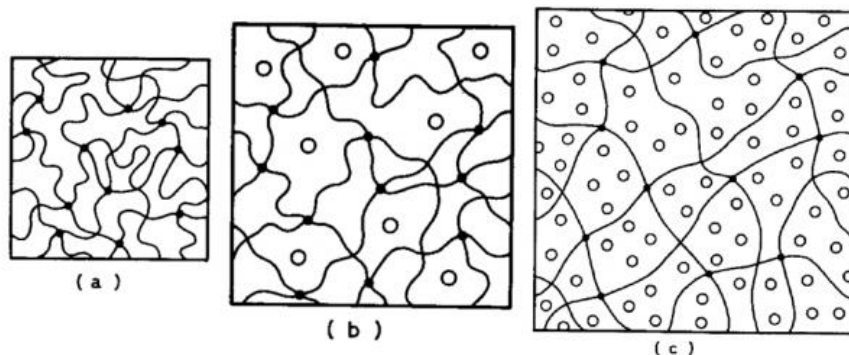
$$[\text{MPa}^{1/2}] = [(\text{J}/\text{cm}^3)^{1/2}] \approx [(1/2)(\text{cal}/\text{cm}^3)^{1/2}]$$

- $\Delta H_{\text{vap}} - RT \approx \Delta H_{\text{vap}} - P\Delta V =$  cohesive energy [J]
- $(\Delta H_{\text{vap}} - RT)/V = \delta^2 =$  cohesive energy density [CED] [ $\text{J}/\text{cm}^3 = \text{MPa}$ ]

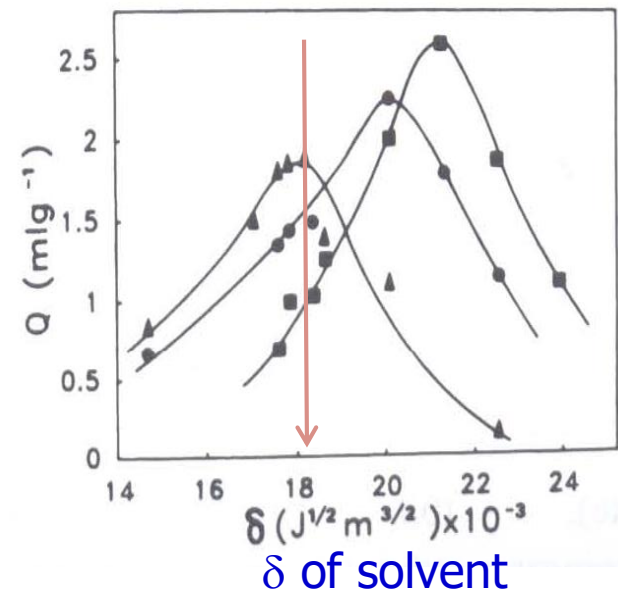
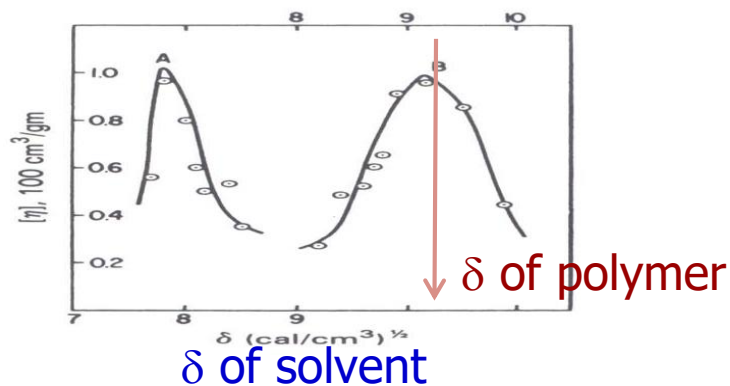


## □ Determination of $\delta$

- from  $\Delta H_{\text{vap}}$  data  $\sim$  for low mol wt, not for polymers
- (experimentally) with solvent of known  $\delta$ 
  - swelling

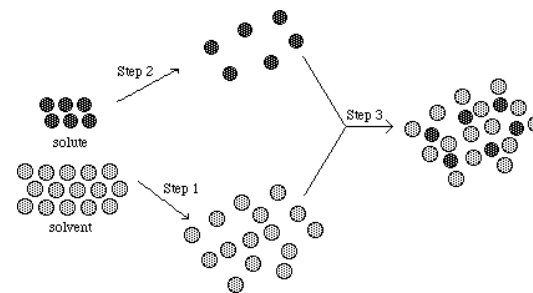


- viscosity



## □ group contribution calculation

$$\delta = \frac{\rho_p \sum_i f_i F_i}{M_0}$$

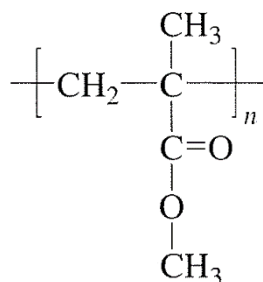


■  $F =$  group attraction constant  $\leftarrow \delta^2 = \delta_{\text{dispersion}}^2 + \delta_{\text{polar}}^2 (+ \delta_{\text{HB}}^2)$

three intermolecular interactions

- (London) dispersion force
- dipole-dipole interaction
- H-bonding

<example> [p252](#) for PMMA



Group	$f_i$	$F_i / (\text{J cm}^3)^{1/2} \text{ mol}^{-1}$	$f_i F_i / (\text{J cm}^3)^{1/2} \text{ mol}^{-1}$
—CH <sub>2</sub> —	1	268	268
—C—	1	65	65
—CH <sub>3</sub>	2	303	606
—C(=O)—	1	669	669

**TABLE 10.2**  
**Solubility Parameters for Common Solvents and Polymers**

Solvent	$\delta / \text{J}^{1/2} \text{cm}^{-3/2}$	Polymer	$\delta / \text{J}^{1/2} \text{cm}^{-3/2}$
Acetone	20.3	Polyethylene	16.4
Carbon tetrachloride	17.6	Polystyrene	18.5
Chloroform	19.0	Poly(methyl methacrylate)	19.0
Cyclohexane	16.8	Polypropylene	17.2
Methanol	29.7	Poly(vinyl chloride)	20.0
Toluene	18.2		
Water	47.9		
Xylene	18.0		

PP soluble in cyclohexane?

*for amorphous state at 25 °C*

- For solution,  $\Delta H_m < T \Delta S_m$ 
  - $\Delta\delta < 20 \text{ MPa}^{1/2}$  for solvent/solvent solution
  - $\Delta\delta < 2 \text{ MPa}^{1/2}$  for solvent/polymer solution **Why?**
  - $\Delta\delta \approx 0$  for polymer/polymer solution
  - when specific interaction like H-bonding,  $\Delta H_m < 0 < T \Delta S_m \rightarrow \Delta G_m < 0$

□ Semicrystalline polymers are not soluble at room temperature.

□  $\Delta H_{\text{fusion}} > 0 \rightarrow \Delta H_{\text{fusion}} + \Delta H_m > T \Delta S_m \rightarrow \Delta G_m > 0$

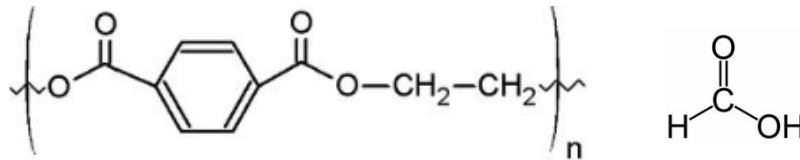
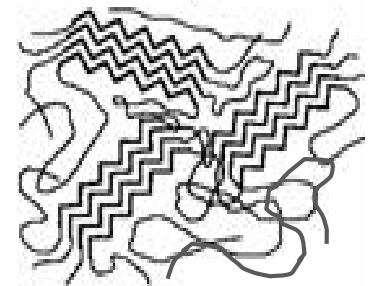
□ to solubilize

■ raise temperature

■ PP in p-xylene at above 100 °C

■ using specific interaction  $\sim \Delta H_m < 0$

■ PET in formic acid (H-bonding)



□  $\chi$  and  $\delta$  both from interaction  $\rightarrow \chi_H = \frac{V_1(\delta_1 - \delta_2)^2}{RT}$

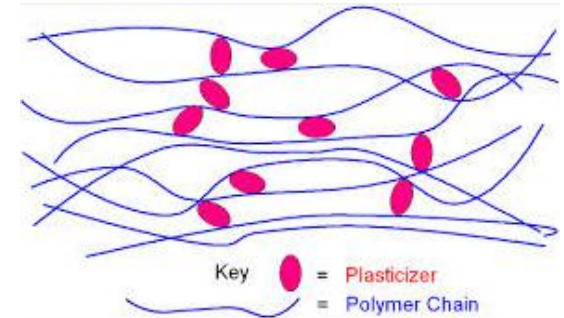
# Additives and $\delta$

## □ stabilizers

- antioxidants, light [UV] stabilizers  $\sim$  radical scavengers
- flame retardants
- has to be fully miscible  $\sim$  small  $\Delta\delta \sim$  usually met

## □ plasticizers

- organic (or polymeric) compound added to improve flexibility [to lower  $T_g$ ]
- $\Delta\delta$  not too large, not too small



## □ antistatic agent, antimicrobials, processing aid

- has to be migrated to or located at the surface
- $\Delta\delta$  moderately large