

Chapter 7. Polymer Solubility and Solutions

-Three factors are of general interest:

1. What Solvents will dissolve what polymer?
2. How does the polymer-solvent interaction influence the solution properties/
3. To what applications do the interesting properties of polymer solutions lead?

-General rules for polymer solubility:

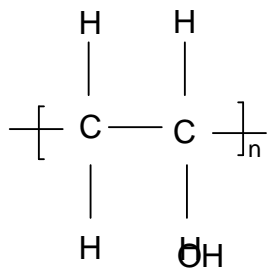
1. Like dissolve like;

Polar polymers - polar solvents

Nonpolar polymer - nonpolar solvent

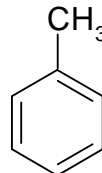
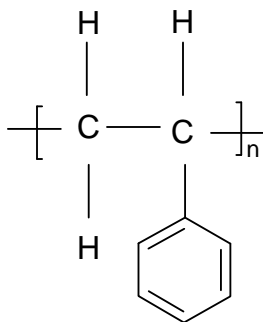
(e.g.)

poly(vinyl alcohol)



: H₂O

polystyrene



:

2. Solubility will decrease with increasing molecular weight at const. temp.
3. Crystallinity decreases solubility.

4. Crosslinking eliminates solubility.
5. The rate of solubility increases with short branches, allowing the solvent molecules to penetrate more easily.
6. The rate of solubility decreases with longer branches, because the entanglement makes it harder for individual molecules to separate.

-The thermodynamic basis

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0$$

Where ΔG_m = the change in Gibbs free energy in the process

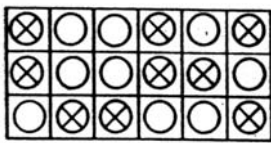
ΔH_m = the change in enthalpy in the process

ΔS_m = the change in entropy in the process

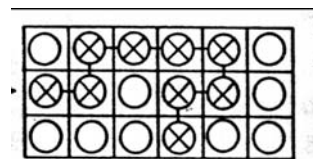
Only if ΔG_m is negative will the solution process be feasible.

A positive ΔH – solvent and polymer “prefer their own company”, the pure materials are in a lower energy state.

A negative ΔH – the solution is in the lower energy state, specific interactions are formed between the solvents and polymer molecules.



(a)



(b)

Fig. Lattice model of solubility.

Solvent, open circles ; solute, filled circles.

(a) Low -molecular -weight solute

(b) polymeric solute.

-for(a): non polymer liquids:

free energy of dilution of a solution

$$\Delta G_m = RT \ln \left(\frac{P_A}{P_{A^0}} \right) \quad (1)$$

where ΔG : free energy of dilution resulting from the transfer of one molecule of liquid A from the pure liquid state with vapor pressure P_{A^0} to a large amount of solution with vapor pressure P_A .

when the solution is ideal -Rault's law is obeyed.(mixing of A and B), $P_A =$

$$P_{A^0} \frac{N_A}{N_A + N_B} = P_{A^0} n_A \quad (2)$$

n_A : mole fraction of A

then Eq(1) becomes : $\Delta G_A = RT \ln(n_A)$ (3)

The total free energy of mixing is

$$\begin{aligned} \Delta G_m &= N_A \Delta G_m + N_B \Delta G_B \\ &= RT(N_A \ln(n_A) + N_B \ln(n_B)) \end{aligned} \quad (4)$$

For ideal mixing $\Delta H = 0$, since $\Delta G = \Delta H - T\Delta S$

$$\therefore \Delta S_m = -R(N_A \ln(n_A) + N_B \ln(n_B)) \quad (5)$$

For (b): a polymer molecule located in the liquid lattice

- The Flory -Huggins model uses a simple lattice representation for the polymer solution and calculates the total number of ways the lattice can be occupied by small molecules and by connected polymer segments.

$$\Delta S_m = -R(N_1 \ln(\phi_1) + N_2 \ln(\phi_2)) \quad (6)$$

$$\Delta H_m = RT\chi_{12}N_1\phi_2 \quad (7)$$

$$\Delta G_m = \Delta H_m - T\Delta S_m = RT(N_1 \ln(\phi_1) + N_2 \ln(\phi_2) + \chi_{12}N_1\phi_2) \quad (8)$$

, N_i = number of moles of the i th component

ϕ_i = volume fraction

- for a system consisting of two polymers

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12} \phi_1 \phi_2 (m_1 n_1 + m_2 n_2) \quad (9)$$

(ref) H.Tompa; polymer solutions, Butterworths, London, 1956, chapter 7

where

$$\phi_i = m_i n_i / (m_i n_i + m_j n_j)$$

(i, j = 1, 2 and i ≠ j),

χ_{12} = polymer-polymer interaction parameter.

m_i = degree of polymerization

$$m_1 = v_1 / v_0, \quad m_2 = v_2 / v_0$$

chemical potential of mixing of component 1 : partial derivative of (eq.9) with respect to n_1

$$\Delta \mu_1 / RT = \ln \phi_1 + (1 - m_1 / m_2) \phi_2 + m_1 \chi_{12} \phi_2^2 \quad (10)$$

$$\Delta \mu_2 / RT = \ln \phi_2 + (1 - m_2 / m_1) \phi_1 + m_2 \chi_{12} \phi_1^2 \quad (11)$$

At equilibrium the chemical potential of each component must be the same in both phase.

$$\Delta \mu_1' = \Delta \mu_1''$$

$$\Delta \mu_2' = \Delta \mu_2''$$

From eqs. (10), (11), (12), and (13),

$$\chi_{12} = \frac{\{(\phi_1'^2 - \phi_1''^2)[m_2 \ln(\phi_1'' / \phi_1') + (m_1 - m_2)(\phi_2'' - \phi_2')] + (\phi_2'^2 - \phi_2''^2)[m_1 \ln(\phi_2'' / \phi_1') + (m_2 - m_1)(\phi_1'' - \phi_1')]\}}{2m_1 m_2 (\phi_1'^2 - \phi_1''^2)(\phi_2'^2 - \phi_2''^2)}$$

Assumptions : 1. χ_{12} is taken to be constant

2. both components of the mixtures are considered to be monodisperse.

To examine χ_{12} as a function of concentration (or compositions), χ_{12} is a linear function of

$$\frac{\Delta\mu_1}{RT} = \ln \phi_1 + \left(1 - \frac{m_1}{m_2}\right)\phi_2 + m_1 g_0 \phi_2^2 + m_1 g_1 (1 - 2\phi_1)\phi_2^2$$

2,

$g_{12}(\phi_2) = g_0 + g_1 \phi_2$ is employed.

The (eq.9) becomes:

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + (g_0 + g_1 \phi_2)\phi_1 \phi_2 (m_1 n_1 + m_2 n_2) \quad (14)$$

Partial differentiation of eq.(14) with respect to n_i :

$$\frac{\Delta\mu_1}{RT} = \ln \phi_1 + \left(1 - \frac{m_1}{m_2}\right)\phi_2 + m_1 g_0 \phi_2^2 + m_1 g_1 (1 - 2\phi_1)\phi_2^2 \quad (15)$$

$$\frac{\Delta\mu_2}{RT} = \ln \phi_2 + \left(1 - \frac{m_{12}}{m_1}\right)\phi_{12} + m_{12} g_0 \phi_1^2 + 2m_2 g_1 \phi_1^2 \phi_2 \quad (16)$$

At equilibrium;

$$\Delta\mu_1' = \Delta\mu_1''$$

$$\Delta\mu_2' = \Delta\mu_2''$$

Eq(15) will give,

$$\ln(\phi_1' / \phi_1'') + \left(1 - \frac{m_1}{m_2}\right)(\phi_2' - \phi_2'') + m_1 g_0 (\phi_2'^2 + \phi_2''^2) + m_1 g_1 [(1 - 2\phi_1')\phi_2'^2 - (1 - 2\phi_1'')\phi_2''^2] = 0 \quad (17)$$

Similarly Eq(16) yields,

$$\ln(\phi_1' / \phi_1'') + \left(1 - \frac{m_2}{m_1}\right)(\phi_1' - \phi_1'') + m_2 g_0 (\phi_1'^2 + \phi_1''^2) + 2m_2 g_1 (\phi_1'^2 \phi_2' - \phi_1''^2 \phi_2'') = 0 \quad (18)$$

Using eqs.(17) and (18), $g_{12} = g_0 + g_1 \phi_2$ is obtained.

• The solubility parameter

- the estimation of ΔH_m in regular solutions :

(those in which solute and solvent do not form specific interactions)

$$\Delta H_m = \phi_1 \phi_2 [\delta_1 - \delta_2]^2 * V_m \cong \Delta E$$

where ϕ = volum fractions

δ = solubility parameter

subscripts 1 = polymer , 2=solvent

ΔE = the change in internal energy

$$\delta = (\text{CED})^{1/2} = \left(\frac{\Delta E_v}{V} \right)^{1/2} [(\text{cal/cm}^3)^{1/2}] \Rightarrow \text{Hildebrand}$$

where (CED)=cohesive energy density, a measure of the strength of the intermolecular forces holding the molecules together in the liquid state.

(ΔE_v) =molar change in internal energy on vaporization,cal/g*mol

V = molar volume of liquid, cm³/g*mol

- The cohesive of a volatile liquid can be estimated from the work required to vaporize unit amount of the material.

The molecules are transported from their equilibrium distances in the liquid to an infinite separation in the vapor.

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

$$\Delta H_m = \phi_1 \phi_2 [\delta_1 - \delta_2]^2 * V$$

where V is total volume of the mixture.

ΔH_m is always positive.

$$|\delta_1 - \delta_2| < 0.5 \quad (\text{solubility})$$

- Measuring the solubility parameter of a low -molecular -weight solvent is no problem.
- Polymers degrade long before reaching their vaporization temp, making it impossible to evaluate ΔE_v directly.
- The greatest tendency of a polymer to dissolve occurs when its solubility parameter matches that of the solvent.
- For the crosslinked polymers, the value of the solvent at which maximum swelling is observed is taken as the solubility parameter of the polymer.

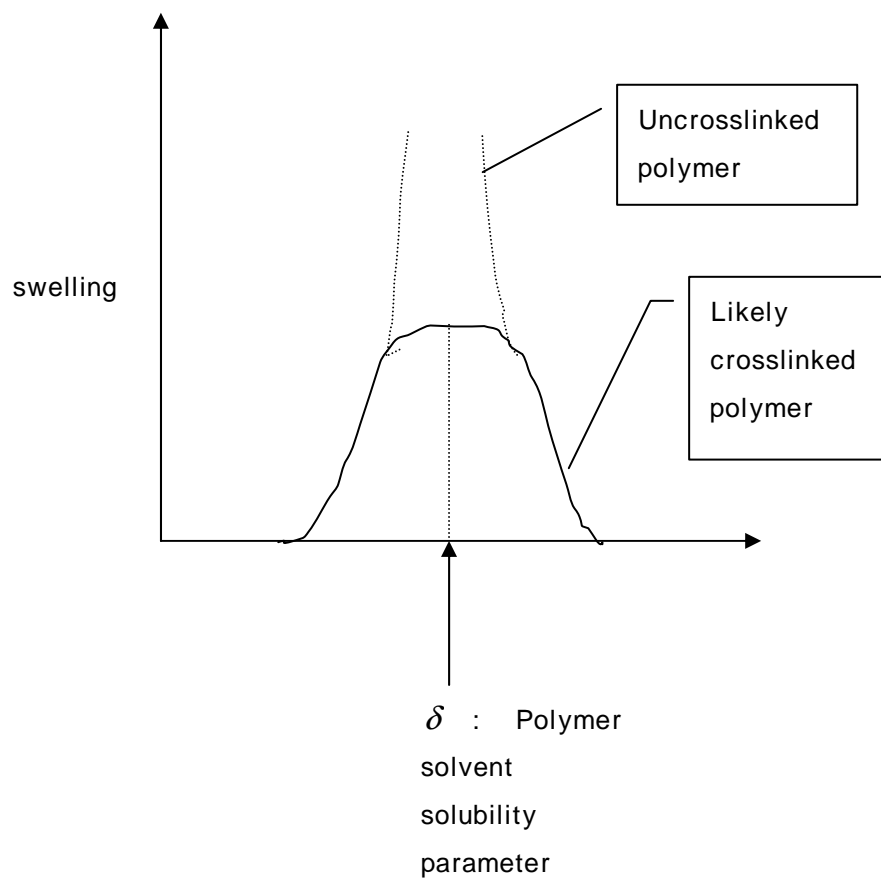


Fig. Determination of δ (polymer) by swelling

- solubility parameter of solvent mixture

$$\delta_{\text{mixture}} = \frac{\chi_1 v_1 \delta_1 + \chi_2 v_2 \delta_2}{\chi_1 v_1 + \chi_2 v_2} = \delta_A \phi_A + \delta_B \phi_B$$

where χ =mole fraction

- Estimation of solubility parameter by
Group Molar Attraction Constants:

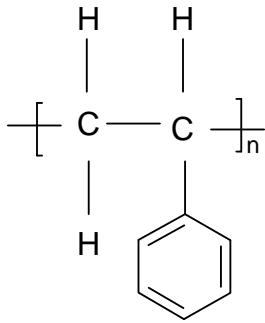
$$\delta = \sigma \sum F_i / M_0 \quad (\text{By van Krevelen -"Properties of Polymer"})$$

where σ = density of the amorphous polymer

M_0 = formula molecular weight of the repeating unit

$\sum F_i$ = sum of all the molar attraction constants

(ex) polystyrene



Group	F_i	No.group	$\sum F_i$	Description
CH ₂	131.5	1	131.5	Density=1.05g/cm ³
CH	85.99	1	85.99	M=104g/mol
-C= (aromatic)	117.12	6	702.72	$\delta = 1.05(896.77)/104=9.0(\text{cal}/\text{cm}^3)^{1/2}$
6 - MEMBERED RING	-23.44	1	-23.44	$896.77 \left(\frac{\text{cal} * \text{cm}^3}{\text{mol}} \right)^{1/2}$

- Hansen's Three -dimensional solubility Parameter

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_H^2$$

-The cohesive energy, δ^2 , is divided into three parts:

- 1) dispersion forces (δ_d)
- 2) polar forces (δ_p)
- 3) hydrogen bonding (δ_H)

ex)

solvent	δ_d	δ_p	δ_H	δ
Chloroform	808	1.5	2.8	9.36
THF	802	2.8	3.9	9.50
MEK	7.77	4.4	2.5	9.27
m-cresol	8.8	2.5	6.3	11.1
Methanol	7.4	6.0	10.9	14.5
Toluene	8.82	0.7	1.0	8.91
H ₂ O	6.0	15.3	16.7	23.5
PS	8.6	3.0	2.0	9.33
Styrene	9.09	0.49	2.0	9.32

- Properties of dilute solutions

-Good solvent : Solubility parameter closely matches that of the polymer. The secondary forces between polymer segments and solvent molecules are strong, and the polymer molecules are strong, and the polymer molecules will assume a spread-out conformation in solution.

- poor solvent : the attractive forces between the segments of the polymer chain are greater than those between the chain segments and the solvent.

Ex) polystyrene ($\delta = 9.0 \sim 9.3$)

Chloroform ($\delta = 9.2$)

Then non-solvent is added , methanol($\delta = 14.5$),the mixed solvent(Chloroform + methanol) becomes too"poor" to sustain solution, and the polymer precipitates out.

When $\Delta G = 0$ and $\Delta H = T\Delta S$ (θ condition)

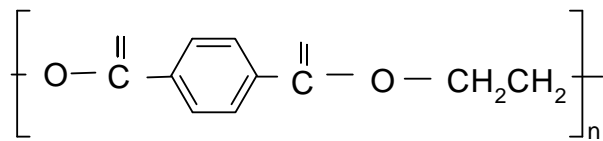
- Paint Industry

-By adding non-solvent into the polymer solution, the solution viscosity will decrease.

-the viscosity for optimum spraying or brushing characteristics might be obtained with a mixed solvent, with the poorer component the more volatile.


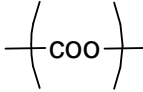
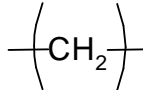
- the poorer component evaporates first, leaving a high viscosity and, therefore, sag -and run -resistant film on the substrate.

Ex 4.1) Estimate the densities of amorphous PET and crystalline PET.



Sol) Molecular weight of repeating unit = 192.2

At room temperature, amorphous PET is in the glassy state. (see Table 4.9,p 87)

group	$V_g(298)$	$V_c(298, \text{cm}^3/\text{mol})$
1* 	65.5	59.0
2* 	46.0	43.0
2* 	32.7	29.4
	144.2	131.4

$$\text{So, } \sigma_g(298) = \frac{192.2}{144.2} = 1.33 \text{ (g/cm}^3\text{)}$$

$$\sigma_g(298) = 1.33$$

$$\text{For } \sigma_c(298) = \frac{192.2}{131.4} = 1.465 \text{ (g/cm}^3\text{)}$$

$$\sigma_c(298) = 1.477$$

$$\text{The ratio } \Rightarrow \frac{\sigma_c}{\sigma_g} = \frac{1.465}{1.33} \cong 1.10$$