

$\langle r^2 \rangle = cnl^2$, freely jointed, rotating, hindered rotation models)

4. Chain conformation depends on temperature, solvent structure, crystallization, orientation, presence of other polymers.

Molecular weight determination

◆Gaseous molecules: By IG law

Molecules must be separated (diluted→ideal gas law)

$PV=nRT \rightarrow n \rightarrow MW = \text{weight}/n$

◆Polymer: By dilute solution law (Solution thermodynamics)

Polymer chains must be separated in solvent

< Sperling Ch 4: Concentrated solution, phase separation, diffusion >

3.1.2 How does a polymer dissolve?

▶ Amorphous polymer at $T > T_g$ (Polymer melts);

Follow Fick's law of diffusion, 4.4)

$J_A = -CD\nabla x_A = -D\nabla C_A$ <Flux is directly proportional to the gradient>

$C = C_A + C_B$, $D = D_{\text{diffusivity}}$

▶ $T < T_g =$ Non-Fickian <Diffusion depends on (relaxation) time>

Slow diffusion of solvent into the polymer→ Plasticizes

polymers → Lowers the T_g below ambient temperature → Swelling occurs rapidly in rubbery state → Swollen-unswollen boundary moves inward (Stress at the swelling boundary causes craze or fracture: ESCR) → Polymers diffuse out of swollen mass into solvent to follow Fickian diffusion.

- ▶ Cross-linked polymer only swells to equilibrium, not dissolved.
- ▶ Also, polymers with high T_m , or strong secondary bonds (PAN) are not dissolved without degradation → MW cannot be determined directly.

3.2 The solubility parameter

Solubility of A in B is governed by the free energy of mixing

$$\Delta G_M = \Delta H_M - T\Delta S_M \quad (3.1)$$

$\Delta G_M < 0$: Solution occurs spontaneously.

$\Delta G_M > 0$: Separation occurs spontaneously.

$T\Delta S > 0$: ∴ Entropy increases upon mixing → Entropy drives mixing.

- ▶ $\Delta H_M > 0$ (Endothermic) for nonpolar organic compounds.
- ▶ Exception is found when the two species attract one another by having opposite polarities (acid and base), or hydrogen bonding.

► For regular solutions, (No specific interactions; Moderately diverges from the ideal solution) Hildebrand and Scott:

$$\Delta H_M = V_M \left[\left(\frac{\Delta E}{V_1} \right)^{\frac{1}{2}} - \left(\frac{\Delta E}{V_2} \right)^{\frac{1}{2}} \right]^2 v_1 v_2 \quad (3.2)$$

V_M = Total volume of mixture

ΔE = (Molar) Energy of vaporization at zero pressure (infinite separation)

V = Molar volume of each component (1=Solvent, 2=Polymer)

v = Volume fraction of each component (1=Solvent, 2=Polymer)

$\Delta E/V$ = Cohesive energy density (Energy of vaporization per unit volume) [=] (cal/cm³), (MPa)

Solubility parameter is defined as

$$\delta = \left(\frac{\Delta E}{V} \right)^{\frac{1}{2}} \quad (3.3)$$

When the components have identical/essentially identical δ values, they are dissolved, miscible (compatible), where the solution process is spontaneous due to the positive ΔS_M . (Eq 3.1)

<Note Eqs. (3.2) and (3.3) are invalid for negative heat of mixing>

3.2.1 SP Tables

Scan Tables 3.1 and 3.2

Table 3.1 Solubility parameters of some common solvents

Solvent	δ		H-bonding ^a Group	Specific Gravity ^b 20°C (g/cm ³)
	(cal/cm ³) ^{1/2}	MPa ^{1/2}		
Acetone	9.9	20.3	m	0.7899
Benzene	9.2	18.8	p	0.87865
<i>n</i> -Butyl acetate	8.5	17.4	m	0.8825
Carbon tetrachloride	8.6	17.6	p	1.5940
Cyclohexane	8.2	16.8	p	0.7785
<i>n</i> -Decane	6.6	13.5	p	—
Dibutyl amine	8.1	16.6	s	—
Difluorodichloromethane	5.5	11.3	p	—
1,4-Dioxane	7.9	16.2	m	1.0337
Low odor mineral spirits	6.9	14.1	p	—
Methanol	14.5	29.7	s	0.7914
Toluene	8.9	18.2	p	0.8669
Turpentine	8.1	16.6	p	—
Water	23.4	47.9	s	0.99823
Xylene	8.8	18.0	p	0.8611

Source: J. Brandrup, E. H. Immergut, and E. A. Gruike, eds., *Polymer Handbook*, 4th ed., Wiley-Interscience, New York, 1999.

^aHydrogen bonding is an important secondary parameter in predicting solubility. p, Poorly H-bonded; m, moderately H-bonded; and s, strongly H-bonded.

^bJ. Brandrup and E. H. Immergut, *Polymer Handbook*, 3th ed., Wiley-Interscience, New York, 1989, sec. III, p. 29.

Note: 1 (cal/cm³)^{1/2} = 2.046 × 10³ (J/m³)^{1/2}.

Table 3.2 Solubility parameters and densities of common polymers (6)

Polymer	δ (cal/cm ³) ^{1/2}	δ (MPa) ^{1/2}	Density (g/cm ³)
Polybutadiene	8.4	17.2	1.01
Polyethylene	7.9	16.2	0.85 (amorphous)
Poly(methyl methacrylate)	9.45	19.4	1.188
Polytetrafluorethylene	6.2	12.7	2.00 amorphous, estimated
Polyisobutene	7.85	16.5	0.917
Polystyrene	9.10	18.6	1.06
Cellulose triacetate (56% ac groups)	13.60	27.8	1.28 ^a
Cellulose tributyrate	—	—	1.16 ^a
Polyamide 66	13.6	22.9	1.24
Poly(ethylene oxide)	9.9	20.0	1.20
Poly(ethylene terephthalate), partly crystalline	10.7	21.9	1.38
Poly(ethylene terephthalate), amorphous	10.7	21.9	1.34
Poly(vinyl alcohol)	12.6	25.8	1.26
Poly(vinyl chloride)	9.6	19.8	1.39

Note: 1 (cal/cm³)^{1/2} = 2.046 × 10³ (J/m³)^{1/2}.

^aC. J. Malm, C. R. Fordyce, and H. A. Tanner, *Ind. Eng. Chem.*, **34**, 430 (1942).

Why methanol ($\delta=14.5$ (cal/cm³)^{1/2}) or water (23.4) does not dissolve polybutadiens (8.4) or polystyrene (9.1)? Why benzene (9.2) and toluene (8.9) dissolve these polymers?

Rule of thumb

Polymers will dissolve in solvents having δ_p within about one unit of their own, in $(\text{ca}/\text{cm}^3)^{1/2}$.

3.2.2 Experimental determination of δ_p (See SY Lee)

The δ_p of a new polymer is determined by several means.

► **Cross-linked polymers** by swelling test.

Define the **swelling coefficient** (Q).

$$Q = \frac{m - m_0}{m_0} \times \frac{1}{\rho_s} \quad (3.4)$$

m = Weight of the swollen polymer

m_0 = Weight of the dried polymer

ρ_s = Density of the swelling agent

Plot Q vs δ_p of various solvents (Figure 3.1)-The **maximum** defines the **solubility** of the polymer. *<The best solvent swells the polymer the most>*

► The theoretical extent of swelling is predicted by the **Flory-Rehner** theory *<Cross-link density and solvent-polymer attractions are considered>*.

Scan Figure 3.1 here

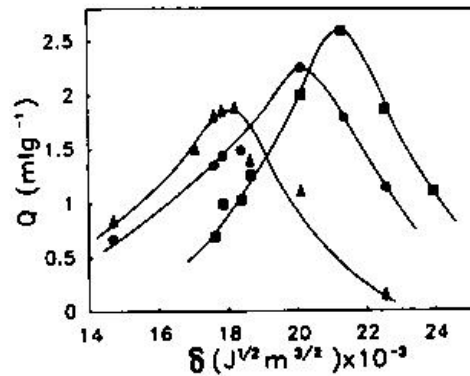


Figure 3.1 The swelling coefficient, Q , reaches a maximum when the solvent nearly matches that of the polymer, for several cross-linked systems: polyurethane (■), polystyrene (▲), and a polyurethane-polystyrene interpenetrating polymer networks (●). Solvents having solubility parameters near $2 \times 10^4 \text{ (J/m}^3\text{)}^{1/2}$ will swell the IPN best.

sp of PS=?

sp of PU=?

sp of PU-PS IPN= $2 \times 10^4 \text{ (J/m}^3\text{)}^{1/2}$

The peak for the IPN is broader and appears in-between the two.

►Soluble polymers

The intrinsic viscosity of the polymer in several solvents is measured and plotted $[\eta]$ vs sp of solvents. Since, chain conformation is most expanded in the best solvent (To be seen w/ Eq 3.82), the intrinsic viscosity is the highest for the best polymer-solvent match.

Scan Figure 3.2 here.

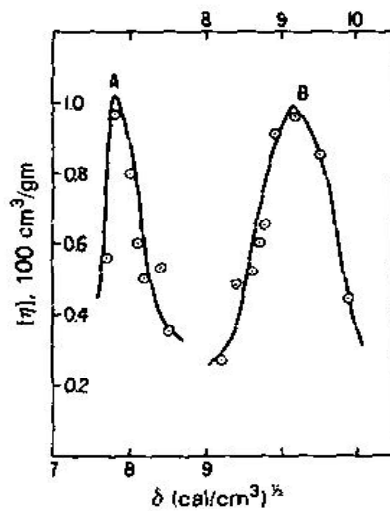


Figure 3.2 Determination of the solubility parameter, using the intrinsic viscosity method (B), for polyisobutene (A) and polystyrene (B). The intrinsic viscosity, $[\eta]$, is a measure of the individual chain size. See Section 3.8.

3.2.3 Theoretical calculations of δ : An example

Chemical structure \rightarrow Estimate δ (Group contribution theory)

Define the **molar attraction constants, G** for each group,

$$\delta = \frac{\rho \sum G}{M} \quad (3.5)$$

ρ =Density

M = Molecular weight (of repeat unit, mer)

Group molar attraction constant (**G**) by Small and Hoy (Table 3.3)