Ⅱ. Thermodynamic Properties of Polymers

Chapter 3. The Solubility Parameter

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Chapter 3. The Solubility Parameter

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3.2. The solubility parameter

3.3. Refinements of the solubility parameter concept

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3.3.2 $\delta_v - \delta_h$ diagram

3.4. Solubility of polymers in solvents

3.5. Prediction of solubility parameter components

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Chapter 3. The Solubility Parameter

❑ ***Characteristics***

1) High molecular weight, ranging from 25,000~10^6g/mol or higher
2) Distributed molecular weight
3) Conformations
    - in solution : determined by light-scattering
    - in the bulk : determined by small-angle neutron scattering(SANS)
    - function of temperature, solvent, structure, crystallization, extension, and the presence of other polymer

→ Determination depends on dissolving the polymer in an appropriate solvent and measuring the required properties in dilute solvent

⇒ Solution property must be understood.

3.1. Cohesive Energy

3.1.1. Definitions of Cohesive Energy

- The cohesive properties of a polymer find direct expression in its solubility in organic liquids →expressed quantitatively in the *cohesive energy*

- Definitions of *Cohesive Energy*

  : the increase in internal energy U per mole of substance (if all intermolecular forces eliminated)

the cohesive energy	$E_{coh} = \Delta U$	$(\mathrm{Jmol^{-1}})$
cohesive energy density	$e_{coh} = E_{coh} / V$	$(\mathrm{Jcm^{-3}})$
solubility parameter	$\delta = (E_{coh} / V)^{1/2} = e_{coh}^{1/2}$	$(\mathrm{J^{1/2}cm^{-3/2}})$

- Determination of E_{coh}

  For liquids of low MW, E_{coh} is closely related to the molar heat of evaporation ΔH_{vap}

$$E_{coh} = \Delta U_{vap} = \Delta H_{vap} - p\,\Delta V \approx \Delta H_{vap} - RT$$

  - For low molar mass substances, E_{coh} can easily be calculated from ΔH_{vap}

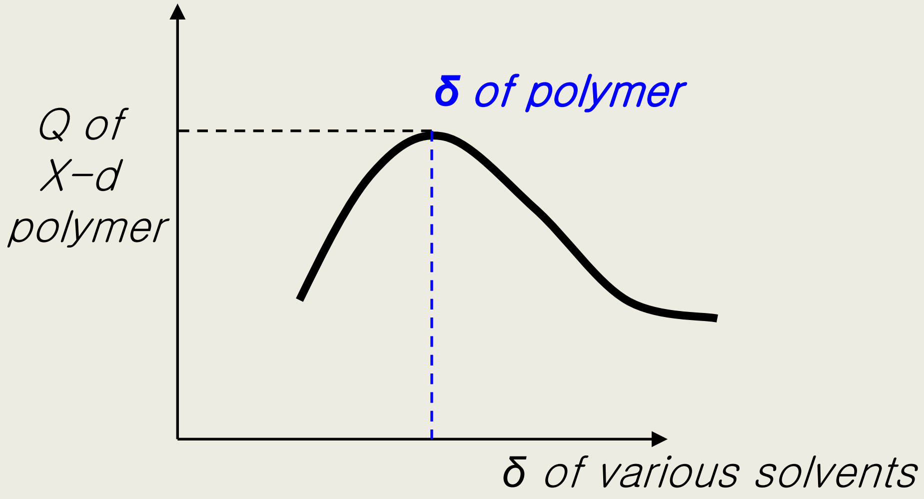
  - As polymers cannot be evaporated, indirect methods have to be used

    (e.g. comparative swelling or dissolving experiments in e_{coh} known liquids)

3.1. Cohesive Energy

3.1.2. Determination of Cohesive Energy

- Determination by swelling experiments for cross-linked polymer



- Theoretical extent of swelling

  : is predicted by the Flory-Rehner theory based on the cross-link density and the attractive forces between the solvent and the polymer.

$$Q = \frac{m - m_0}{m_0} \times \frac{1}{\rho_s}$$

m : the weight of swollen sample
m_0 : the dry weight
ρ_s : the density of swelling agent

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3.1. Cohesive Energy

- Determination by swelling experiments

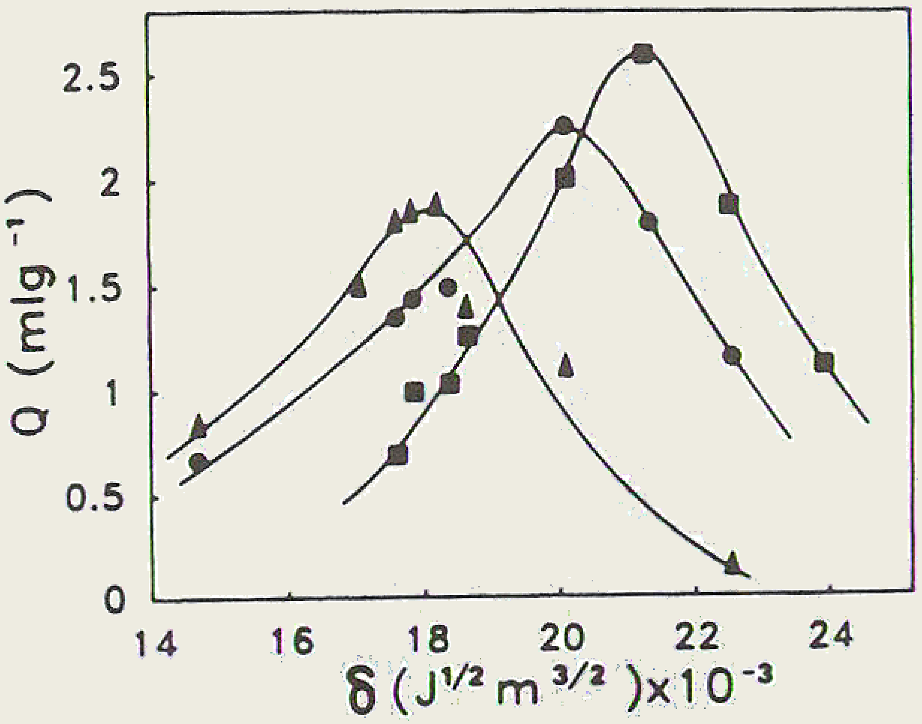


Fig 3.1 The swelling coefficient, Q, reaches a maximum when the solubility parameter of the solvent nearly matches that of the polymer, for several cross-linked systems: polyurethane(■), polystyrene(▲), and a polyurethane interpenetrating polymer networks(●)

3.1. Cohesive Energy

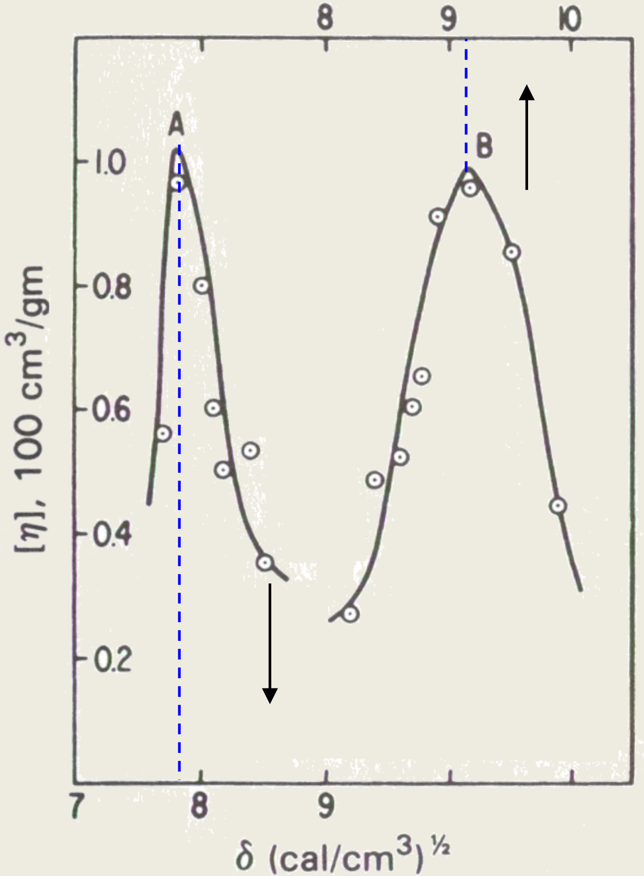
- by measuring the intrinsic viscosity of the polymer in the solvents

: [η] will be highest for the best match in solubility parameter since the chain conformation is most expanded in the best solvent.

$$[\eta] = \Phi\left(\frac{\overline{r_0^{\,2}}}{M}\right)^{\frac{3}{2}} M^{\frac{1}{2}}\alpha^3 = KM^{\frac{1}{2}}\alpha^3$$

Φ : universal constant (2.1×10^{21} dl·mol^{-1}cm^{-3})
$\overline{r_0^{\,2}}$: mean square end-to-end distance of coil
α : expansion coeff. of coil.

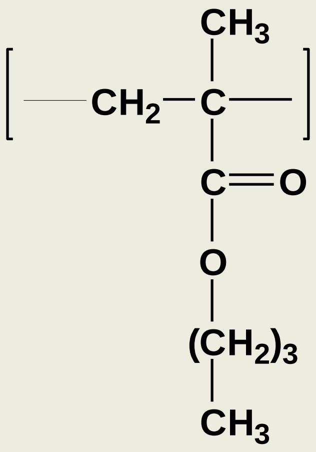
Fig 3.2 Determination of the solubility parameter, using the intrinsic viscosity method, for polyisobutene and polystyrene. The intrinsic viscosity, [η] is a measure of the individual chain size.



3.1. Cohesive Energy

- Theoretical calculation : an example

poly(butyl methacrylate)



$$F = \left(E_{coh}\frac{M}{\rho}\right)^{\frac{1}{2}}$$

ρ : the density
M : the molecular weight
F : group molar attraction constants
= calculated by Small

$\rho = 1.05\ \mathrm{g/cm^3}$
$M = 104\ \mathrm{g/mol}$

Groups	$\sum F_i$
4 $-CH_2-$	1088
2 $-CH_3$	876
1 $>C<$	-190
1 -COO-	634
	F = 2408

$$E_{coh} = F^2\frac{\rho}{M} = 42700\ \mathrm{Jmol^{-1}}$$

cf. experimental value : 43500 – 46500 $\mathrm{Jmol^{-1}}$

3.1. Cohesive Energy

Table. Group contributions to F

Group	Small	Van Krevelen	Hoy
$-CH_3$	438	420	303.4
$-CH_2-$	272	280	269.0
-CH-	57	140	176.0
>C<	-190	0	65.5
$-CH(CH_3)-$	495	560	479.4
$-C(CH_3)_2-$	686	840	672.3
-CH=CH-	454	444	497.4
>C=CH-	266	304	421.5
$-C(CH_3)=CH-$	704	724	724.9
cyclopentyl	-	1384	1295.1
cyclohexyl	-	1664	1473.3
phenyl	1504	1517	1398.4
P-phenylene	1346	1377	1442.2
-F	250	164	84.5
-Cl	552	471	419.6

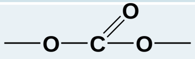
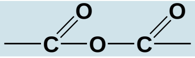
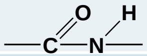
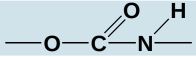
Group	Small	Van Krevelen	Hoy
-Br	696	614	527.7
-I	870	-	-
-CN	839	982	725.5
-CHCN	896	1122	901.5
-OH	-	754	462.0
-O-	143	256	235.3
-CO-	563	685	538.1
-COOH	-	652	1000.1
-COO-	634	512	668.2
	-	767	903.5
	-	767	1160.7
	-	1228	906.4
	-	1483	1036.5
-S-	460	460	428.4

Table. Group contribution to E_{coh} (J/mol)

from "Properties of Polymers", van Krevelen, 1990

- For a prediction of the cohesive energy of substances some group additive methods have been developed.
  - *Dunkel* : derived group contribution for the cohesive energy of liquids at room temperature
  - *Rheineck, Lin* : found that for homologous series of low-molecular-weight liquids, the contribution to the cohesive energy of a methylene group was not constant, but depended on the value of other groups in the molecule
  - *Hayes, Di Benedetto, Van Kreveln and Fedors* : applied Dunkel's original method to polymers
  - *Bunn* : dealt with the cohesive energy at the boiling point
  - *Bondi* : cohesive energy at 0 K

Table. Group contribution to E_{coh} (J/mol) *from “Properties of Polymers”, van Krevelen,* 1990

Group	H_0^0 (0 K)	E_{coh} (298K)					E_{coh} (T_b)	E_{coh} (298K)
	Bondi[1]	Rheineck, Lin[2]	Dunkel[3]	Di Benedetto[4]	Hayes[5]	Fedors[6]	Bunn[7]	van Krevelen[8]
$-CH_3$	10560	4150	7460	-	-	4710	7120	9640
$-CH_2-$	6350	5150	4150	3600	4150	4940	2850	4190
-CH-	-270	4060	-1590	-	-	3430	-1840	420
>C<	-8000	-	-7340	-	-	1470	-6280	-5580
$-CH(CH_3)-$	10290	8210	5870	-	7120	8140	5700	10060
$-C(CH_3)_2-$	13120	-	7580	10390	11900	10890	7960	13700
-CH=CH-	-	-	8300	7210	7500	8620	7120	10200
>C=CH-	-	-	2560	-	-	8620	2940	4860
$-C(CH_3)=CH-$	-	-	10020	10900	11480	13330	10060	14500
Cyclopentyl	33770	-	-	-	-	24240	-	-
Cyclohexyl	38210	29500	-	-	-	29180	-	-
Phenyl	41060	31220	30920	-	-	31940	22630	31000
P-phenylene	35950	-	-	-	23880	31940	16340	25140
-F	-	-	8630	-	-	4190	4730	4470
-Cl	-	11690	14250	-	-	11550	11730	11990
-Br	-	-	-	-	-	15490	12990	15500
-I	-	-	-	-	-	19050	17600	-
-CN	-	-	-	-	-	25530	-	25000
-CHCN	-	-	-	-	24130	28960	-	25420

Table. Group contribution to E_{coh} (J/mol)

from "Properties of Polymers", van Krevelen, 1990

Group	H_0^0 (0 K)	E_{coh} (298K)					E_{coh} (T_b)	E_{coh} (298K)
	Bondi	Rheineck, Lin	Dunkel	Di Benedetto	Hayes	Fedors	Bunn	van Krevelen
-OH	-	32810	30380	-	-	29800	24300	-
-O-	-	-	6830	-	6830	3350	4190	6290
-CO-	-	-	17890	-	-	17370	11150	-
-COOH	-	32810	37580	-	-	27630	23460	-
-COO-	-	19530	16010	-	14160	18000	12150	13410
-O-C(=O)-O-	-	-	-	-	-	17580	-	-
-C(=O)-O-C(=O)-	-	-	-	-	-	30560	16340	-
-C(=O)-NH-	-	-	67880	-	44750	33490	35620	60760
-O-C(=O)-NH-	-	-	-	-	26310	26370	36620	-
-S-	-	-	-	-	-	14150	9220	8800

Ref.

[1] Bondi, A. *J. Polymer Sci.* **A2** (1964) 3159; *"Physical Properties of Molecular Crystals, Liquids and Glasses"*, Wiley, New York, 1968

[2] Rheineck, A. E., Lin, K. F., *J. Paint Technol.* **40** (1968) 611

[3] Dunkel, M. *Z. Physik. Chem.* **A138** (1928) 42

[4] Di Benedetto, A. T. *J. Polymer Sci.* **A1** (1963) 3459

[5] Hayes, R. A. *J. Appl. Polymer Sci.* **5** (1961) 318

[6] Fedors, R. F. *Polymer Eng. Sci.* **14** (1974) 147

[7] Bunn, C. W. *J. Polymer Sci.* **16** (1955) 323

[8] Van Krevelen, D. W., Hoftyzer, P. J. *J. Appl. Polymer Sci.* **11** (1967) 2189

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3.2. The Solubility Parameter

- The definition of solubility parameter (δ) is based on thermodynamic consideration.
- The thermodynamic criteria of solubility are based on the free energy of mixing ΔG_M. Two substances are mutually soluble if ΔG_M is negative.
- "***Like dissolves Like***" : Qualitative description

❖ Quantitatively

$\triangle G_M = \triangle H_M - T\triangle S_M$ (energy of mixing)

$\underline{-\triangle G_M}$: spontaneous process

(-) : depends on $\triangle H_M$

$\triangle H_M$: usually positive

"positive" means opposing mixing

$\triangle H_M$: enthalpy of mixing
$\triangle S_M$: entropy of mixing

❖ ***'opposing mixing'***

: exception for this - the two species in question attract one another in some way, perhaps by having opposite polarities, being acid and base relative to one another, or through hydrogen bonding

3.2. The Solubility Parameter

- ***Hildebrand and Scott equation for regular solutions***

$$\Delta H_M = V_M \left[\left(\frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} - \left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 \nu_1 \nu_2$$

: entropy effect ignored --- (3.1)

where, V_M : the total volume of the mixture

$\triangle E$: the ε of vaporization to a gas at <u>zero pressure</u>

(i.e. infinite separation of molecules)

V : the molar volume of the components

υ : the volume fraction of component in the mixture

$\triangle E/V$: the ε of vaporization per cm^3 = cohesive ε density

1 : solvent

2 : polymer

∴ "***like dissolves like***" means $(\triangle E_1/V_1)^{1/2} \approx (\triangle E_2/V_2)^{1/2}$

∴ solubility parameter : $\delta = \left(\frac{\Delta E}{V} \right)^{1/2}$

∴ $\triangle H_M = V_M[\delta_1 - \delta_2]^2 \upsilon_1 \upsilon_2$

3.2. The Solubility Parameter

- As a requirement for the solubility of a polymer P in a solvent S, the quantity $(\delta_P - \delta_S)^2$ has to be small, as small as possible.

- In the derivation of eq.(3.1), it wad assumed that no specific forces are active between the structural units of the substances involved. Therefore it does not hold for crystalline polymers.

- If one substance contains strongly polar groups or H-bridges, $\triangle H_M$ become higher than predicted by eq.(3.1) → $\triangle G_M$ becomes positive
  →but, dissolution does not occur even for $\delta_1 = \delta_2$.

- For these reasons a more refinement of the solubility parameter is necessary.
  →for the most important application of solubility parameters :
  the prediction of the solubility of polymers in various solvents

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3.3. Refinement of the solubility parameter concept

3.3.1. Hansen Parameter

- In the derivation by *Hildebrand*, only dispersion forces between structural units have been taken into account.
- However, for many liquids and amorphous polymers, the cohesive energy is also dependent on the interaction between polar groups and on H-bonding.

→ the solubility parameter as defined corresponds with the total cohesive energy.

$$E_{coh} = E_d + E_p + E_h$$

where E_d : contribution of dispersion forces
E_p : contribution of polar forces
E_h : contribution of H-bonding

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

$$\Delta H_M = V_M v_1 v_2 \left[(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2\right]$$

- Unfortunately, values of δ_d, δ_p and δ_h cannot be determined directly.

→ Indirect methods for the determination of the solubility parameter components
→ *Hansen*

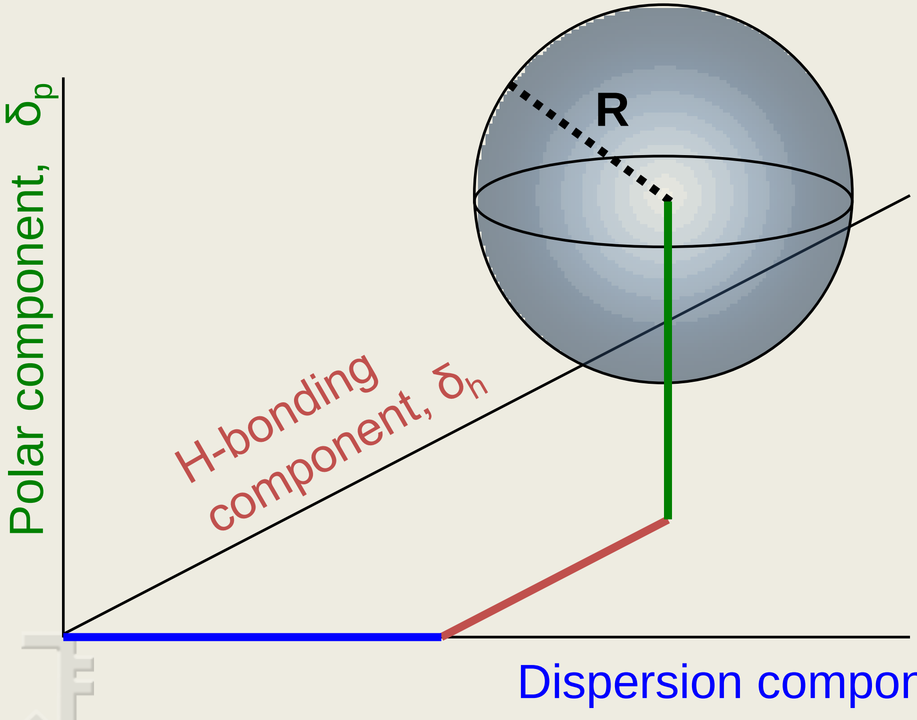
3.3. Refinement of the solubility parameter concept

- The assumption of *Hansen*

: the value of δd of a given solvent was equal to that of a non-polar substance of about same chemical structure.

$$\delta_p^2 + \delta_h^2 = \delta^2 - \delta_d^2$$

- Hansen determined experimentally the solubility of a number of polymers in a series of solvents by a point in a three-dimensional structure.



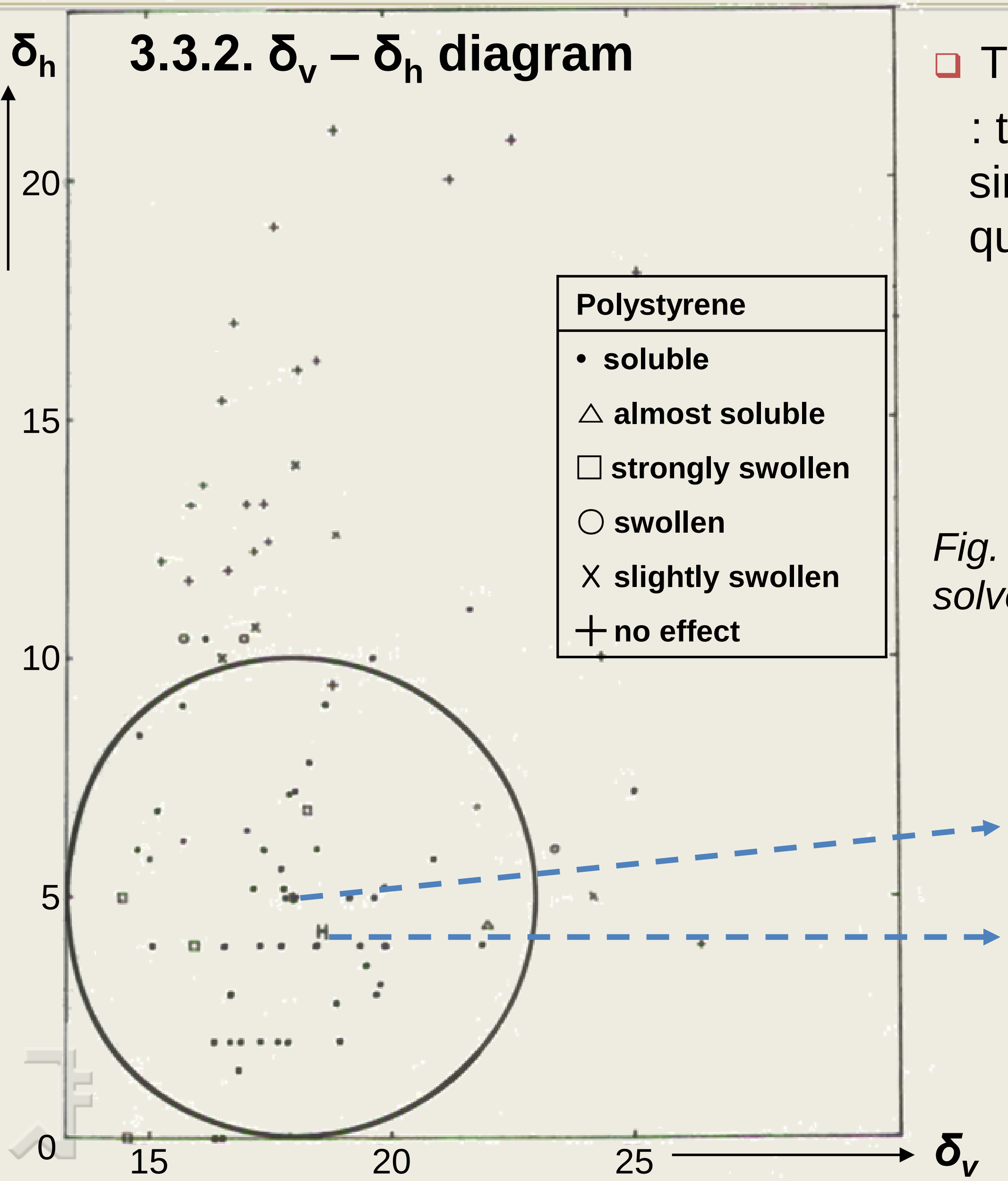
- Disadvantage of *Hansen*'s method

: 3-dimensional structures are necessary for a graphical representation of the interaction between polymers and solvents

→For practical applications, a 2-dimensional method is to be preferred.

3.3. Refinement of the solubility parameter concept

3.3.2. δ_v – δ_h diagram



The center of a circle

The location proposed by Hansen

- The assumption of *Bagley*, δ_v vs. δ_h : the effect of δ_d and δ_p show close similarity, while the effect of δ_h is of a quite different nature.

$$\delta_v = \sqrt{(\delta_d^2 + \delta_p^2)}$$

→ plot δ_v vs. δ_h

Fig. Solubility of polystyrene in various solvent in the δ_v – δ_h diagram.

3.3. Refinement of the solubility parameter concept

- A method proposed by *Chen*, χ_{11}

  : similar to that of Bagley, plot δ_h vs. χ_{11}

$$\chi_{11} = \frac{V_S}{RT}\left[(\delta_{dS}-\delta_{dP})^2 + (\delta_{pS}-\delta_{pP})^2\right]$$

where the subscript S and P denote solvent and polymer, respectively

- Disadvantage of this method

  : the characteristics of the polymer should be estimated beforehand.

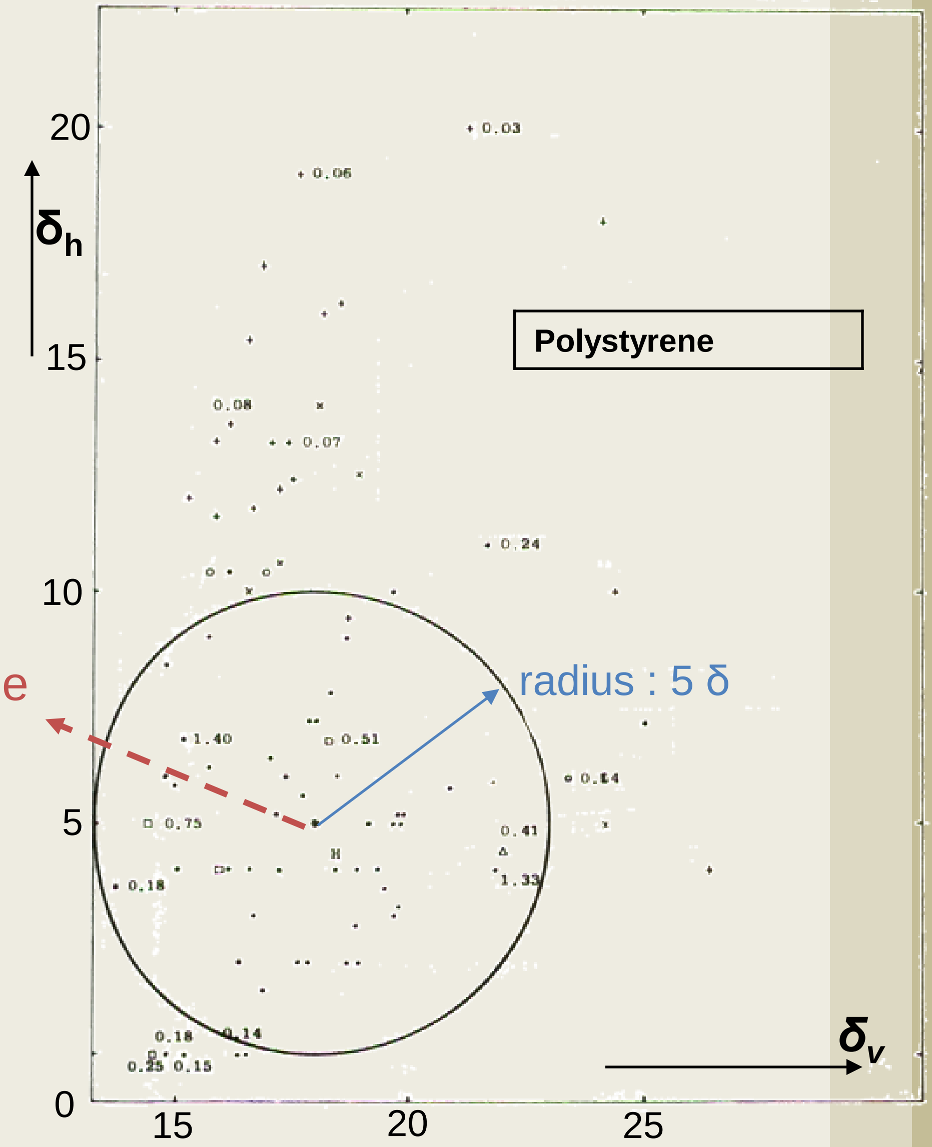
- At the moment the δ_v – δ_h diagram seems to be the most efficient way to represent polymer-solvent interaction.

3.4. Solubility of polymers in solvents

- In the $\delta_v - \delta_h$ diagram, the degree of solubility can be indicated by a number.
  - The degree of solubility = polymer volume / solvent volume

Fig. Solubility of polystyrene in various solvent in the $\delta_v - \delta_h$ diagram.
(numbers : vol. styrene / vol. solvent)

The coordinate value : $\delta_v = 18$; $\delta_h = 5$



- As a general rule, polystyrene is soluble in solvents for which

$$\left|\sqrt{(\delta_v - 18)^2 + (\delta_h - 5)^2}\right| < 5$$

3.5. Prediction of solubility parameter components (δ_d, δ_p and δ_h)

- Some approaches have been published, viz. that of *Hoftyzer and Van Krevelen*

- The basic assumption : Hansen parameters

$$E_{coh} = E_d + E_p + E_h$$

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

- Method of *Hoftyzer and Van Krevelen*

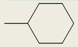
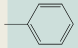
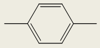
  : predicted from group contribution, using following eqn.

$$\delta_d = \frac{\Sigma F_{di}}{V} \qquad \delta_p = \frac{\sqrt{\Sigma F^2_{pi}}}{V} \qquad \delta_h = \sqrt{\frac{\Sigma E_{hi}}{V}}$$

→ The group contribution for a number of structural groups are given in a table at next page.

3.5. Prediction of solubility parameter components

Table. Solubility parameter component group contributions (Hoftyzer-Van Krevelen)

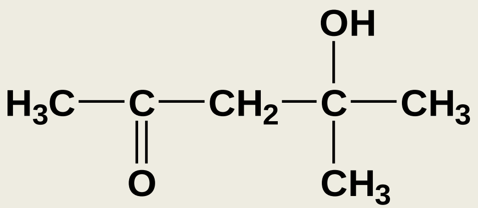
Structural Group	F_{di}	F_{pi}	E_{hi}
$-CH_3$	420	0	0
$-CH_2-$	270	0	0
>CH-	80	0	0
>C<	-70	0	0
$=CH_2$	400	0	0
=CH-	200	0	0
=C<	70	0	0
	1620	0	0
	1430	110	0
 (o.m.p)	1270	110	0
-F	(220)	-	-
-Cl	450	550	400
-Br	(550)	-	-
-CN	430	1100	2500

Structural Group	F_{di}	F_{pi}	E_{hi}
-OH	210	500	20000
-O-	100	400	3000
-COH	470	800	4500
-CO-	290	770	2000
-COOH	530	420	10000
-COO-	390	490	7000
HCOO-	530	-	-
$-NH_2$	280	-	8400
-NH-	160	210	3100
-N<	20	800	5000
$-NO_2$	500	1070	1500
-S-	440	-	-
$=PO_4-$	740	1890	13000
ring	190	-	-

3.5. Prediction of solubility parameter components

- ❑ Theoretical calculation : an example

diacetone alcohol



V=123.8 cm^3/mol

Groups	F_{di}	F_{pi}^2	E_{hi}
3 $-CH_3$	1260	0	0
$-CH_2-$	270	0	0
$>C<$	-70	0	0
-CO-	290	592900	2000
- OH	210	250000	20000
	1960	842900	22000

$$\delta_d = \frac{\Sigma F_{di}}{V} = \frac{1960}{123.8} = 15.8\ J^{1/2}cm^{-3/2}$$

$$\delta_p = \frac{\sqrt{\Sigma F^2_{pi}}}{V} = \frac{\sqrt{842900}}{123.8} = 7.4\ J^{1/2}cm^{-3/2}$$

$$\delta_h = \sqrt{\frac{\Sigma E_{hi}}{V}} = \sqrt{\frac{22000}{123.8}} = 13.3\ J^{1/2}cm^{-3/2}$$

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} = 21.9\ J^{1/2}cm^{-3/2}$$

cf. experimental value : 18.8 – 20.8 $J^{1/2}cm^{-3/2}$

3.5. Prediction of solubility parameter components

- To conclude we give the full equation which determines the solubility of a polymer in an organic liquids :

$$\boxed{\Delta\bar{\delta} = \left[(\delta_{\mathrm{d}.P} - \delta_{\mathrm{d}.S})^2 + (\delta_{\mathrm{p}.P} - \delta_{\mathrm{p}.S})^2 + (\delta_{\mathrm{h}.P} - \delta_{\mathrm{h}.S})^2\right]^{\frac{1}{2}}}$$

- For a good solubility $\Delta\bar{\delta}$ must be small (≤ 5)

Keywords in Chapter 4

- Mean filed lattice theory for mixture

- Flory interaction parameter

- Lever rule

- Spinodal and binodal decomposition in phase diagram

- Ornstein-Zernike scattering function

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