Prediction of solubility parameter from thermal transition behaviour in polymers

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A method of derivation of the solubility parameter $\delta = (h_0/V_0)^{1/2}$ from the thermal transition behaviour is proposed for amorphous and crystalline polymers, where h_0 is the cohesive enthalpy per molar structural unit and V_0 is the molar volume (cm^3). For amorphous polymers, at a temperature T ($< T_g$) h_0 is given as:

$$h_0 \approx h_g + h_s \qquad (h_s \approx h_g + \Delta h)$$

where h_g is the glass transition enthalpy per molar structural unit for a polymer glass, h_s is the transition enthalpy per molar structural unit of the localized solid parts in a polymer glass, and Δh is the enthalpy change per molar structural unit relating to the disappearance of localized solid parts just above T_g. For polystyrene and poly(vinyl acetate), the values of δ from the above equation are in good agreement with reference values. For crystalline polymers, h_0 at T was given by Tanaka as, relating to T_g and T_m^0:

$$T_m^0 > T > T_g, \qquad h_0 \approx h_u + h_x$$
$$T \lesssim T_g, \qquad h_0 \approx h_u + h_x + h_g$$

where h_u is the heat of fusion per molar structural unit and h_x is the heat of transition per molar structural unit due to quasicrystals in the amorphous region. The values of δ from the above equation for poly(ethylene terephthalate) and nylon-6,6 are in good agreement with reference values, and for nylon-6 and nylon-12 almost equal to that of nylon-6,6.

(Keywords: solubility; thermal behaviour; transition phenomena; enthalpy; modelling)

INTRODUCTION

The solubility of a polymer in a solvent can be appraised by the difference in solubility parameter δ between polymer and solvent[1–9]: the smaller the δ difference, the better is the solubility of the polymer. Parameter δ is defined as:

$$\delta = (h_0/V_0)^{1/2} \tag{1}$$

where h_0 is the cohesive enthalpy per molar structural or molecular unit, which contains inter- and intramolecular interactions, and for solvents is nearly equal to the molar enthalpy of vaporization L_v; and V_0 is the molar volume (cm^3). For many solvents, the value of δ is calculated using the experimental value of L_v. However, in the case of polymers, δ is decided directly by measurement of swelling[2,3], dissolution temperature[8] or viscosity[2] of a polymer in several solvents with known values of δ, because a polymer is not vaporized but decomposed at elevated temperatures. However, in order to obtain more accurate δ values, δ should be derived from the experimental value of h_0 as well as in the case of solvent. In this paper, the derivation of δ from h_0 is proposed on the basis of thermal transition behaviour for amorphous and crystalline polymers.

THEORETICAL TREATMENT

Amorphous polymers

For amorphous polymers, the thermal transition behaviour in cooling and heating processes and the derivation of δ are investigated thermodynamically. The configurational partition function Ω normalized per unit volume and taking into account both the conformational character and the free volume of polymer liquid is expressed by[10]:

$$\Omega = \frac{Z^N}{N!}\left(\frac{2\pi mkT}{\hbar^2}\right)^{3Nx/2}\left(\frac{q}{v_f}\right)^{Nx}\exp\left(-\frac{Nxh^v}{RT}\right) \tag{2}$$

where N is the number of polymers, T is the absolute temperature, Z is the conformation partition function for a chain at T, m is the mass of the structural unit, R is the gas constant, k is Boltzmann's constant, $\hbar$ is Planck's constant, h^v is the intermolecular interaction enthalpy per molar structural unit, x is the degree of polymerization and q (<1) is the packing factor of the core. The quantity v_f is the free volume per structural unit and is defined by:

$$\begin{aligned} v_f &= \int_{\text{unit}} \exp\{-[\psi(\rho) - \psi(0)]N_A z/2RT\}\,d\rho \\ &= qv\exp(-h^v/RT) \end{aligned} \tag{3}$$

with $h^v = -N_A\psi(0)z/2$ and the apparent volume v per structural unit given by:

$$v = \frac{1}{q}\int_{\text{unit}} \exp\{[-\psi(\rho)]N_A z/2RT\}\,d\rho \tag{4}$$

Here N_A is Avogadro's number, z is the coordination number and $\psi(\rho)$ is the potential energy at a vector ρ from the centre of the core. From equation (2), the

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enthalpy H_l and entropy S_l per molar chain for the polymer liquid are derived as:

$$H_l = RT^2 \frac{\mathrm{d}\ln Z}{\mathrm{d}T} + \tfrac{3}{2}RxT - RxT^2 \frac{\mathrm{d}\ln v_f}{\mathrm{d}T} + xh^v \qquad (5)$$

$$S_l = \left(R\ln Z + RT\frac{\mathrm{d}\ln Z}{\mathrm{d}T}\right) + \tfrac{3}{2}Rx - x\left(R\ln v_f + RT\frac{\mathrm{d}\ln v_f}{\mathrm{d}T}\right) + xS_d \qquad (6)$$

with

$$S_d = \tfrac{3}{2}R\ln\left(\frac{2\pi mkT}{h^2}\right) - \frac{R}{Nx}\ln N! + R\ln q$$

In the vicinity of the glass transition temperature T_g (here it is defined as the starting temperature of the isobaric specific heat C_p jump[11])* during the cooling process, it is hypothesized that the heterogeneous structure composed of frozen solid parts and still unfrozen flow parts generates the free-energy difference Δf ($= f_{\text{solid}} - f_{\text{flow}}$) per molar structural unit. Here f_{solid} is the free energy per molar structural unit for solid parts; f_{flow} ($= h_{\text{flow}} - Ts_{\text{flow}}$) is the free energy per molar structural unit for flow parts, with h_{flow} ($= H_l/x - \tfrac{3}{2}RT$) the enthalpy per molar structural unit for flow parts and s_{flow} ($= S_l/x - \tfrac{3}{2}R$) the entropy per molar structural unit for flow parts. Here it is assumed that solid parts generated near T_g achieve a quasistable thermodynamic state. The minimum thermodynamic condition for stability is $f_{\text{solid}} = 0$ as in nucleation[12]. A polymer liquid generated from solid parts with $f_{\text{solid}} = 0$ can be taken as a liquid composed of only flow parts. When $f_{\text{solid}} = 0$ and $f_{\text{flow}} \neq 0$, Δf is given as[10]:

$$\Delta f = -(h^c - Ts^c) - h^v - RT\ln v_f + TS_d \qquad (7)$$

with

$$h^c = \left(RT^2\frac{\mathrm{d}\ln Z}{\mathrm{d}T}\right)\Big/x$$

$$s^c = \left(R\ln Z + RT\frac{\mathrm{d}\ln Z}{\mathrm{d}T}\right)\Big/x$$

where h^c and s^c are the conformational enthalpy and entropy per molar structural unit, respectively. At T_g, assuming that the cohesive state of all polymer chains is frozen in quasiequilibrium, the minimum conditions $\Delta f = 0$ ($f_{\text{flow}} = 0$) and $s_{\text{flow}} = 0$ ($= -\Delta S_g$ in ref. 10) should be accepted as the criterion of T_g for a polymer liquid with homogeneous structure or containing solid parts with $f_{\text{solid}} = 0$ (ref. 10). The value $s_{\text{flow}} = 0$ means the freezing of flow parts. In this case, h^c and s^c at T_g are represented by:

$$h^c = RT_g^2\frac{\mathrm{d}\ln v_f}{\mathrm{d}T} - h^v \qquad (8)$$

$$s^c = RT_g\frac{\mathrm{d}\ln v_f}{\mathrm{d}T} + R\ln v_f - S_d \qquad (9)$$

From equation (8), the glass transition enthalpy h_g per molar structural unit is given as:

$$h_g = RT_g^2\frac{\mathrm{d}\ln v_f}{\mathrm{d}T} = h^c + h^v \qquad (10)$$

Using:

$$\frac{\mathrm{d}\ln v_f}{\mathrm{d}T} \approx \frac{\alpha_f}{\varphi_g} \approx \frac{1}{C_2'} \qquad \text{(ref. 10),}$$

$$h_g \approx \frac{RT_g^2}{C_2'} \qquad (11)$$

where α_f is the difference between the volume expansion coefficient below T_g and that above T_g, φ_g is the free-volume fraction at T_g, and C_2' is the constant in the WLF equation[13]. In equation (10), h^v corresponds approximately to the molar cohesive energy[14] of a functional group in a polymer, e.g. 4300 cal mol^{-1} for $-CH(C_6H_5)-$ in polystyrene (PS), 3500 cal mol^{-1} for $-CH(OCOCH_3)-$ in poly(vinyl acetate) (PVAc), 3900 cal mol^{-1} for $-C_6H_4-$ in poly(ethylene terephthalate) (PET) and 8500 cal mol^{-1} for -CONH- in polyamide. The value of h^c is calculated from the equation for h^c in equation (7). For the solid parts generated in the vicinity of T_g, the transition enthalpy h_s per molar structural unit in f_{solid} ($= h_s - Ts_s$) is given as:

$$h_s \approx h_g + \Delta h \qquad (12)$$

with

$$\Delta h \approx \int_{T_g}^{T_l} C_p\,\mathrm{d}T - \int_{T_g}^{T_l} C_p^g\,\mathrm{d}T$$

where h_s is the transition entropy per molar structural unit for solid parts, and Δh is the enthalpy change per molar structural unit relating to the disappearance of solid parts just above T_g in the heating process. Also in equation (12), C_p is the observed isobaric specific heat, C_p^g is the isobaric specific heat of a superheated polymer glass (hypothesized), and T_l is the temperature at which C_p in the heating process from a temperature below T_g coincides with that of pure liquid. The reason for equation (12) to be valid is as follows. At an elevated temperature T in the range of $T_g < T \lesssim T_l$, the free energy f_m per molar structural unit for a polymer liquid containing solid parts is represented by:

$$f_m \approx f_{\text{solid}}X_s + f_{\text{flow}}(1 - X_s) \qquad (13)$$

where X_s is the mole fraction of solid parts. Here it is assumed that in this temperature range the thermodynamic equilibrium condition $f_{\text{solid}} = f_{\text{flow}}$ (>0) holds under the release of freezing ($s_{\text{flow}} \neq 0$ at $T > T_g$), by which the solid parts fixed in the glass are mobilized. In this case from equation (13) the next relation is derived:

$$f_m = f_{\text{solid}} = f_{\text{flow}} \qquad (14)$$

The isobaric specific heat C_p is represented as:

$$C_p = (\partial H_q/\partial T)_p \qquad (15)$$

with

$$H_q = f_q - T(\partial f_q/\partial T)_p, \qquad q = m\text{, solid or flow}$$

From equations (14) and (15), it is understood that C_p

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* The well-known T_g is defined as the temperature at which the heat capacity is half-way between the liquid and the glass. However T_g in this case is understood to be for the ideal glass predicted from the C_p jump curve. For the ideal glass, the C_p jump occurs vertically at T_g. For the unideal glass, which shows the C_p jump curve in *Figure 1*, it is observed[11] that annealing at a temperature from the initial temperature to the final temperature on the C_p jump curve does not give any enthalpy relaxation to the polymer, except for below the starting temperature. Therefore in this paper, the starting temperature of the C_p jump is defined as T_g

values for solid parts and flow parts are the same in this temperature range. This result leads equation (12) to be valid, because Δh can be taken as the enthalpy change per molar structural unit only for solid parts. *Figure 1* shows the schematic curves of C_p and enthalpy H in the vicinity of T_g for non-annealed and annealed polymer glasses. *Figure 2* shows the structural models of amorphous polymer in the ranges of $T < T_g$, $T_g < T < T_l$ and $T_l < T$. Thus for amorphous polymers, h_0 at a temperature T ($<T_g$) is taken as:

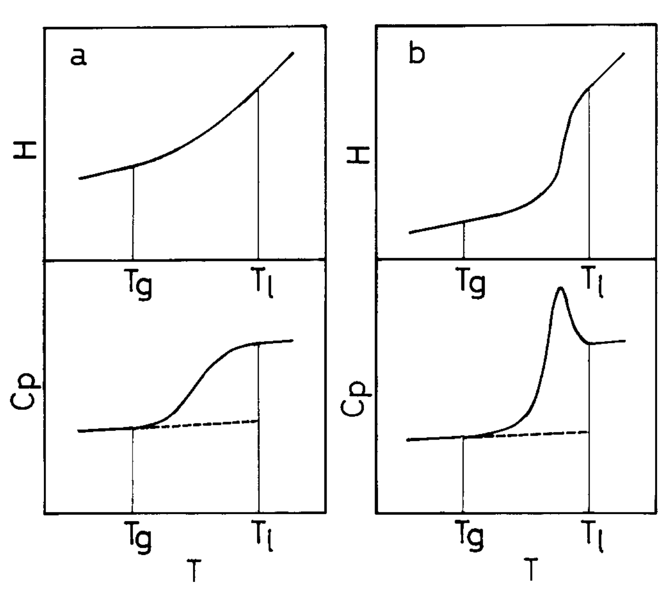

Figure 1 Schematic curves of C_p and H in the vicinity of T_g for (a) non-annealed and (b) annealed polymer glasses. The C_p^g curve for a superheated polymer glass (hypothesized) is also shown (------)

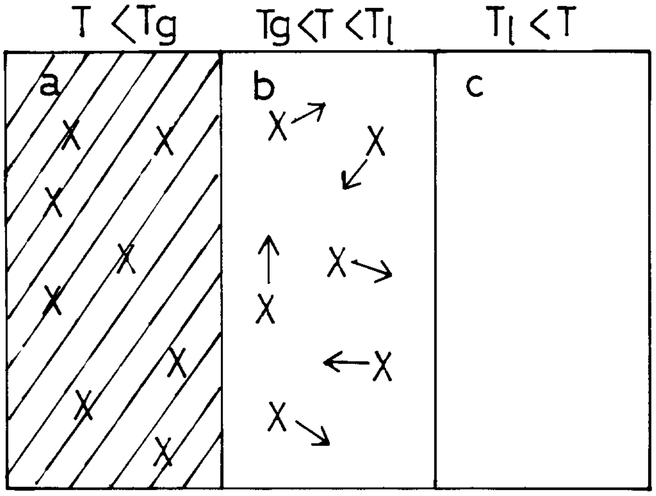

Figure 2 Structural models of an amorphous polymer in the temperature ranges of (a) $T < T_g$, (b) $T_g < T < T_l$ and (c) $T_l < T$: hatching, glass parts; crosses, solid parts; white, flow parts. The arrows show the mobility of solid parts

$$h_0 \approx h_g + h_s \tag{16}$$

where h_g is regarded as the energy spent on the mobilization of solid parts at T_g. *Table 1* shows the values of h_0 and δ for PS and PVAc glasses with known C_2' (refs 13, 15), together with T_g, C_2', h_g, Δh, h_s and δ^* (reference value). The values of Δh, 80–150 cal mol^{-1} for PS and 100–130 cal mol^{-1} for PVAc, were adopted on the basis of the jump behaviour of C_p near T_g (refs 11, 16). The values of h_g were calculated from equation (11).

As shown in *Table 1*, the values of δ for PS and PVAc are in good agreement with δ^*, respectively. Accordingly, equation (16) may be supported.

Crystalline polymers

The derivation of δ for crystalline polymers is now discussed. For crystalline polymers, h_0 at T is given as[9], relating to T_g and the melting temperature T_m^0:

$$\begin{aligned} T_m^0 > T > T_g, \quad & h_0 \approx h_u + h_x \\ T \lessgtr T_g, \quad & h_0 \approx h_u + h_x + h_g \end{aligned} \tag{17}$$

where h_u is the heat of fusion per molar structural unit and h_x is the heat of transition per molar structural unit due to quasicrystals in the amorphous region. For crystalline polymers, Δh in equation (12) must be rewritten as:

$$\Delta h \approx (h_u + h_x) - h_g \tag{18}$$

For polymers such as PET, nylon-6, nylon-6,6 and nylon-12, h_x is given as[9]:

$$h_x \approx 2h_u(1 - 1/a) \tag{19}$$

where a is the coefficient in the following modified Flory's equation on melting of a random copolymer[9]:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{aR}{h_u}\ln X_A \tag{20}$$

where T_m is the melting temperature of the copolymer, T_m^0 is the melting temperature of the major component homopolymer and X_A is the mole fraction of the major component. The experimental value of a is about 2 for nylon-6, nylon-6,6 and nylon-12 copolymers[9,17], and about 2.5 for PET copolymers[9]. Therefore from equation (19), values $h_x \approx h_u$ for nylon-6, nylon-6,6 and nylon-12, and $h_x = 6600$ cal mol^{-1} ($>h_u$) for PET are derived. Thus the values of h_0 and δ for PET, nylon-6, nylon-6,6 and nylon-12 are calculated from equations (1) and (17), using the values of h_x. The value of h_g is derived from equation (10), using the computed values of h^c at T_g and

Table 1 The numerical values of T_g, C_2', h_g, Δh, h_s, h_0, δ and δ^* for PS and PVAc

Polymer	T_g (K)	C_2' (K)	h_g (cal mol^{-1})	Δh (cal mol^{-1})	h_s (cal mol^{-1})	h_0 (cal mol^{-1})	δ ((cal cm^{-3})$^{1/2}$)	δ^* ((cal cm^{-3})$^{1/2}$)
PS	359[b]	56.6	4520 (4840)[a]	80–150	4600–4670	9120–9190	9.55–9.59	8.5–10.3
PVAc	305[b]	46.8	3950	100–130	4050–4080	8000–8030	9.64–9.66	8.8–11.1

[a] From equation (10)
[b] See footnote on previous page

Table 2 The numerical values of T_g, h_g, h_0, δ and δ^* for PET, nylon-6, nylon-6,6 and nylon-12

Polymer	T_g (K)	h_g (cal mol^{-1})	h_0 (cal mol^{-1})	δ ((cal mol^{-1})$^{1/2}$)	δ^* ((cal mol^{-1})$^{1/2}$)
PET[9]	342	4180 (4200)[a]	16300	10.7	10.7[b]
Nylon-6	323	8990	19190	13.7	–
Nylon-6,6[9]	323	17970	38000	13.6	13.6[b]
Nylon-12	315	10120	31320	12.6	–

[a] From equation (11)
[b] From ref. 21

Bunn's data[14] on h^v of $-C_6H_4-$ and $-CONH-$ groups. *Table 2* shows the values of h_0 and δ for PET, nylon-6, nylon-6,6 and nylon-12 at T ($< T_g$), together with h_g and δ^*.

The value of h_g in parentheses for PET was calculated from equation (11), using $C_2' = 55.3$ K[18] for amorphous PET. This value is almost equal to 4180 cal mol^{-1} from equation (10). Each value for nylon-12 was calculated using $h_u = 10120$ cal mol^{-1} (refs 17, 19) and amorphous density $\rho_a = 1.00$ g cm^{-3} (ref. 20). For other polymers, the values of h_u and ρ_a listed in ref. 21 were used. As shown in *Table 2*, the values of δ for PET and nylon-6,6[9] are in good agreement with δ^*, respectively, and for nylon-6 and nylon-12 almost equal to that of nylon-6,6.

REFERENCES

1 Nakanishi, K. *Netsusokutei* 1982, **9** (2), 61
2 Barton, M. *Chem. Rev.* 1975, **75**, 731
3 Bristow, G. M. and Watson, W. F. *Trans. Faraday Soc.* 1958, **54**, 1742
4 Lee, W. A. and Sewell, J. H. *J. Appl. Polym. Sci.* 1968, **12**, 1397
5 Small, P. A. *J. Appl. Chem.* 1953, **3**, 71
6 Moore, W. R. *J. Soc. Dyers Colourists* 1957, **73**, 500
7 Maloney, D. P. and Prausnitz, J. M. *J. Appl. Polym. Sci.* 1974, **18**, 2703
8 Michaels, A. S., Vieth, W. R. and Alcalay, H. H. *J. Appl. Polym. Sci.* 1968, **12**, 1621
9 Tanaka, N. *Sen-i Gakkaishi* 1988, **44**, 541
10 Tanaka, N. *Polymer* 1978, **19**, 770
11 Yoshida, H. *Netsusokutei* 1986, **13** (4), 191
12 Mandelkern, L. 'Crystallization of Polymers', McGraw-Hill, New York, 1964, p. 242
13 Ferry, J. D. 'Viscoelastic Properties of Polymers', Wiley, New York, 1960
14 Bunn, C. W. *J. Polym. Sci.* 1955, **16**, 323
15 Adam, G. and Gibbs, J. H. *J. Chem. Phys.* 1965, **43**, 139
16 Sharonov, Y. *Sov. Phys.* (*Tech. Phys.*) 1957, **1**, 2138
17 Carner, D. P. and Fasulo, P. D. *J. Appl. Polym. Sci.* 1988, **36**, 495
18 Sasabe, H., Sawamura, K., Saito, S. and Yoda, K. *Polym. J.* 1971, **2**, 518
19 Goodmann, I. and Kehayoglou, A. H. *Eur. Polym. J.* 1983, **19** (4), 321
20 Gogolewski, S., Czerniawska, K. and Gasiorek, M. *Colloid Polym. Sci.* 1980, **258**, 1130
21 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', Wiley, New York, 1989