Methods to Determine Solubility Parameters of Polymers Using Inverse Gas Chromatography

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ABSTRACT: Experimental values of the Flory–Huggins parameter, χ, between polymers and solvents, are frequently used to determine the solubility parameters of the polymers. A method using nonlinear curve fitting of $RT\chi/V$ was compared to the linear regression method commonly used. It was found that the formulas for the solubility parameter were the same, but the linear method produced a slightly different entropy term. The nonlinear method gave a lower correlation coefficient and wider confidence intervals and was more effective at distinguishing systems than the linear model. The effect of the deviation of probes in the solubility parameter model is discussed. Using probes with low solubility parameters to measure the polymer solubility parameter gave wider confidence intervals. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2894–2902, 2004

Key words: gas chromatography; thermodynamics; solution properties

INTRODUCTION

Knowledge of the interaction parameters between polymers and solvents is very important in the study of their miscibility and the thermodynamic properties of solutions. Inverse gas chromatography (IGC) has been demonstrated to be an effective tool for measuring the thermodynamic properties of solute (probe) vapors in polymers.[1–8] In IGC measurements, a known amount of nonvolatile stationary phase is dissolved in a solvent and coated on a porous, inert support. When a liquid probe is injected into the column, the probe vaporizes and flows with the carrier gas. In order for IGC to be effective, the probes must be volatile and of low molecular weight; the stationary phase is usually a low vapor pressure solvent or a high molecular weight polymer. If the molecular weight of the stationary phase is known, the specific retention volume can be related to the activity coefficient of the probe in the stationary phase.[1–7] Using Flory–Huggins theory[9] the Flory–Huggins interaction parameter between a polymer and probe, χ, can be related to the specific retention volume of the probe, V_g^0, by the following equation[1–7]:

$$\chi = \ln\left(\frac{273.16 R v_2}{V_g^0 P_1^o V_1}\right) - 1 + \frac{V_1}{M_2 v_2} - \frac{P_1^o}{RT}(B_{11} - V_1) \quad (1)$$

where R is the gas constant, T is the column temperature, v_2 is the specific volume, M_2 is the molecular weight of the stationary phase, and P_1^o, V_1, and B_{11} are the vapor pressure, molar volume, and the second viral coefficient of the probe, respectively. In IGC study of polymers, the molecular weight M_2 is large; the $V_1/M_2 v_2$ term is usually small and can be neglected. When χ is less than 0.5, the probe liquid is generally characterized as a good solvent for the polymer, while a value higher than 0.5 designates a poor solvent and may lead to phase separation.[9]

Determination of the solubility parameter

IGC was first applied by Smidsrod and Guillet[10] to study the thermodynamics of probe–polymer interactions using a polymer as the stationary phase. The interaction between a probe and a polymer is usually represented by the value of the Flory–Huggins interaction parameter, χ, and analyzed by the solubility parameters of the polymer and probe. In 1916, Hildebrand pointed out that the relative solubility of a given solute in a series of solvents is determined by the internal pressures of the solvents. Later, Scatchard introduced the concept of cohesive energy density into Hildebrand's theory, identifying this quantity to be the internal pressure. In 1949, Hildebrand proposed the term "solubility parameter" and the symbol "δ," which is defined as the square root of the cohesive energy density[11]:

$$\delta = \left(\frac{\Delta E_{vap}}{V}\right)^{1/2} \quad (2)$$

where ΔE_{vap} is the energy of vaporization and V is the molar volume of the liquid. The cohesive energy den-

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sity represents the energy required to separate the liquid molecules into the ideal gas state. An unambiguous value of solubility parameter can be determined if the material can be vaporized. The heat of vaporization is frequently calculated from the vapor pressure of the saturated liquid by the Clausius–Clapeyron equation. The solubility parameter model has been successful in describing the thermodynamic properties of solutions, especially when the component liquids are nonpolar or slightly polar. It has been shown that the Flory–Huggins interaction parameter can be related to the solubility parameters of the two components by the following relation[11]:

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 \qquad (3)$$

where δ_1 and δ_2 are the solubility parameters of the probe and the polymer, respectively, and V_1 is the volume of the probe. The above equation implies that χ is always positive. A negative experimental value of χ can occur in systems with a specific interaction.

Method of DiPaola–Baranyi and Guillet

Since polymers have no appreciable vapor pressure and their molar volumes are not accurately known, the definition in eq. (2) cannot be used for polymers. Experimental values of χ have been used in the determination of the solubility parameters of polymers. Guillet et al.[12,13] demonstrated the use of IGC in the determination of χ and the solubility parameters of polymers. In their studies, eq. (3) was modified as

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT}\right) \qquad (4)$$

Using a series of probes with different solubility parameters, the solubility parameter of the polymer, δ_2, can be calculated from the slope or the intercept. However, the solubility parameters determined from the slope and intercept terms of eq. (4) are frequently different. A related difficulty associated with this problem is that eq. (3) predicts a positive value for χ. In practice, this is not the case, because specific interactions exist between some probes and the polymer. This is a fundamental problem with the solubility parameter model. One way to overcome this problem is by adding an entropy term into the Flory–Huggins interaction parameter so that $\chi = \chi_H + \chi_S$,[12–16] where the dimensionless χ_S is an entropy term that can be used to accommodate deviation from the original solubility parameter model in eq. (3). When χ_S is added into the equation, the following modified form of the solubility model is obtained:

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 + \chi_S \qquad (5)$$

The Flory–Huggins interaction parameter represents the size-corrected free energy of solution, which is calculated as $RT\chi$.[5–7] The enthalpy of solution is calculated as $RT\chi_H = V_1(\delta_1 - \delta_2)^2$, based on eq. (3). The entropy term can have either a positive or a negative value and represents the deviation from the solubility parameter model. Adding this new term, eq. (4) is changed into the following expression[12,13]:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \eta\right) \qquad (6)$$

where $\eta = \chi_S/V_1$. In the application of eq. (6) to IGC data, it is assumed that the η term depends on the polymer and remains constant for a series of probes. The expression then has a form similar to a linear equation, $y = mx + b$, with the slope $m = 2\delta_2/RT$. A linear regression method is generally used to determine η and δ_2. In the method, δ_1 is used as the independent variable and the left-hand-side, $\delta_1^2/RT - \chi/V_1$, is the subject of observation. Therefore, δ_2 can be determined from the slope term of the plot, and the intercept is used to calculate η after δ_2 is determined. From the χ values and solubility parameters of the probe and polymer, the values of χ_S are determined using eq. (5).[12,13,15,16]

From the standard formula of the linear least square method, the slope and intercept can be obtained based on eq. (6). The slope gives $2\delta_2/RT$, from which the following equation is obtained:

$$\delta_2 = [\Sigma(\delta_i - \bar{\delta})(\delta_i^2 - RT\chi_i/V_i)]/2[\Sigma(\delta_i - \bar{\delta})^2] \qquad (7)$$

where $\bar{\delta}$ is the average value of the solubility parameters of probes, and the summation is taken for all of the probes. The intercept term has the following form:

$$-\left(\frac{\delta_2^2}{RT} + \eta\right) = -\{[(\Sigma\delta_i^2)^2 - \bar{\delta}\Sigma\delta_i^3]/RT - (\Sigma\delta_i^2)(\Sigma\chi_i/V_i)$$
$$+ \bar{\delta}\Sigma\delta_i\chi_i/V_i\}/[\Sigma(\delta_i - \bar{\delta})^2] \qquad (8)$$

from which the following expression is obtained for η:

$$\eta = [\bar{\delta}(\delta_2^2\Sigma\delta_i - \Sigma\delta_i^3)/RT - (\Sigma\delta_i^2)(\Sigma\chi_i/V_i)$$
$$+ \bar{\delta}\Sigma\delta_i\chi_i/V_i]/[\Sigma(\delta_i - \bar{\delta})^2] \qquad (9)$$

Guillet et al.[13] determined χ_S using the above approach for hydrocarbon probes in ethylene–propylene rubber, cis-poly(isoprene), and amorphous poly(propylene). The values were around 0.3 and showed a small probe dependence; they were higher for linear alkanes and lower for aromatic probes. Since then, many studies[16–26] have been conducted using this approach to determine the solubility parameters of polymers. The correlation coefficients based on the plot of

eq. (6) were found to be very close to unity. A collection of studies of the Flory–Huggins interaction parameters and solubility parameters of polymers was published by Barton.[27]

The use of eq. (6) has several complicating questions that require attention: (i) In eq. (6) the observation contains the independent variable, δ_1, and the intercept term contains the slope, δ_2. This is different from a simple linear regression equation. (ii) The observation term is dominated by the δ_1^2/RT term with χ/V_1 contributing only a small portion. This produces a built-in correlation between the observation and the independent variable. (iii) It has been a common practice to use probes with solubility parameters smaller than that of the polymer to make IGC measurements. This is because probes with a high solubility parameter generally participate in polar interactions or hydrogen bonding, and the solubility parameter model may not work properly for them. Using only probes located on one side of χ_2, with a narrow range of solubility parameters, could affect the confidence interval of δ_2. When polar stationary phases were used, upward deviations in the plots of eq. (6) were observed in many systems. Price et al.[28–30] and Voelkel et al.[31,32] have developed a method to determine dispersion, the polar and hydrogen bonding components of solubility parameters. The comparison of a multi-parameter model would require more data. In this study, the original version of DiPaola–Baranyi and Guillet is used. A different approach of fitting the model is proposed and the answers to the above questions are discussed through an analysis using literature data.

Direct curve fitting method using $RT\chi/v$ as the observation

This article proposes a direct curve fitting method using $RT\chi/V$ as the observation in calculating the solubility parameter of a polymer. Eq. (5) can be changed into the following expression:

$$RT\chi/V_1 = (\delta_1 - \delta_2)^2 + RT\chi_S/V_1$$
$$= (\delta_1 - \delta_2)^2 + RT\eta + \lambda_1 \quad (10)$$

where η is the average value of χ_S/V_1 and is assumed to be constant for a polymer, as in the linear plotting method; λ_1 is the error in fitting the model. Eq. (10) is a nonlinear model with two parameters, δ_2 and η. The summation of error square (SS) for a series of probes with solubility parameter δ_i, molar volume V_i and interaction parameter χ_i is

$$SS = \Sigma\lambda_i^2 = \Sigma[RT\chi_i/V_i - (\delta_i - \delta_2)^2 - RT\eta]^2 \quad (11)$$

Setting the partial differentiations $\partial(SS)/\partial\delta_2$ and $\partial(SS)/\partial\eta$ to be zero, the expression for the optimum value of η can be obtained as

$$\eta = [\Sigma\chi_i/V_i - \Sigma(\delta_i - \delta_2)^2/RT]/N \quad (12)$$

where N is the number of probes, δ_2 is the solubility parameter of the polymer, and the summation is taken for all probes. From eqs. (10) and (12) it can be seen that the error term satisfies $\Sigma\lambda_i = 0$, as in the case of a linear model. The expression of δ_2 was found to be identical to eq. (7). This is a gratifying result because the simple method of linear regression can be used to calculate δ_2. The correlation coefficient of the nonlinear model in eq. (10) can be estimated by the standard formula[33]:

$$R^2 = \Sigma(y_{est} - \bar{y})^2/\Sigma(y - \bar{y})^2 \quad (13)$$

where y represents the experimental value of $RT\chi_i/V_i$, $\bar{y}$ is the average value of all probes, and y_{est} is the estimated value of the left-hand side of eq. (10) using the calculated δ_2 and η values. Eq. (13) is a formula for a linear model. In the present study, when eq. (10) is used as y, eq. (13) still represents the portion of the total variance about the mean, $\bar{y}$, explained by the regression calculation. It will be shown later that eq. (13) can provide an estimation of the accuracy of fit of eq. (10).
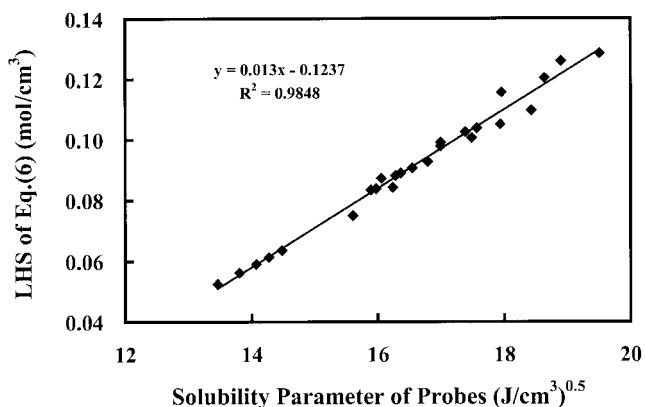
RESULTS AND DISCUSSION

Data reduction

To illustrate the procedure and make a comparison, IGC data for twenty-five probes in poly(ϵ-caprolactone) (PCL) and poly(epichlorohydrin) (PECH), reported by Munk et al.,[34] were used in this study. Their study was chosen because it used a large number of probes with a wide range of polarities. The weight average molecular weights were 37,000 and 700,000 for PCL and PECH, respectively. The authors measured the specific retention volumes of probes in PCL, PECH and blends at volume ratios of 25/75, 50/50, and 75/25 at 80°C. The mixtures were miscible and gave negative polymer–polymer interaction parameters. The interaction parameters of probes with both polymers were used in this study to determine the solubility parameters of the polymers.

The properties of the probes at 80°C are listed in Table I. The solubility parameters of the probes are reported by Munk et al. The values range from 13.46 to 19.51 $(J/cm^3)^{0.5}$. The molar volumes at 80°C were calculated using room temperature density and the method developed by Spencer and Danner and described by Reid et al.,[35] which relates the molar volume of a liquid to its volume at a reference temperature. Figure 1 shows the linear plot of eq. (6) for PCL. The solubility parameter of PCL was determined to be $19.06 \pm 0.49 \, (J/cm^3)^{0.5}$, and the η term was determined to be $7.16 \times 10^{-5} \, mol/cm^3$. Figure 2 shows a similar
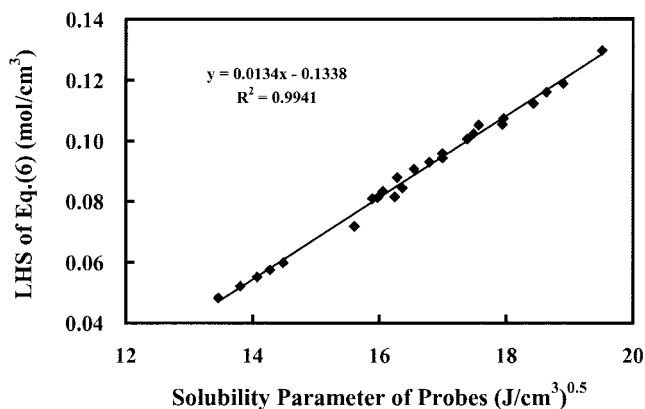
TABLE I
Molar Volume and Solubility Parameter of Probes at 80°C

Probes	Molar volume (cm^3/mol)	Solubility parameter ($J/cm^3)^{0.5}$
n-Pentane	129.5	13.46
n-Hexane	142.3	13.80
n-Heptane	156.4	14.07
n-Octane	171.3	14.27
n-Nonane	186.6	14.48
Cyclohexane	118.5	15.60
Cyclohexene	110.0	16.24
Benzene	96.9	17.38
Toluene	113.7	16.99
Pentyl chloride	135.4	15.89
Butyl chloride	113.8	15.97
Methyl chloroform	107.3	16.05
1,1-Dichloroethane	86.9	16.99
1,2-Dichloroethane	82.8	18.63
Methylene chloride	70.8	18.90
Chloroform	88.1	17.96
Carbon tetrachloride	106.0	16.36
Tetrahydrofuran	88.2	17.57
1,4-Dioxane	91.1	19.51
Acetone	79.9	18.43
2-Butanone	96.2	17.48
Methyl acetate	85.7	17.93
Ethyl acetate	104.7	16.79
Propyl acetate	121.4	16.54
Butyl acetate	138.3	16.28

Figure 2 Plot of left-hand side of eq. (6) versus solubility parameters of probes for PECH.

Difference in the η term

The value of $RT\chi_S/V$ for each probe was calculated using eq. (10) based on experimental values of $RT\chi/V$ and the difference between the solubility parameters of probe and polymer. The results are listed in Tables II and III for PCL and PECH, respectively. The values of $RT\chi_S/V$ were not constant but showed less variation than those of $RT\chi/V$. It can also be seen that, for most probes, the values of $RT\chi_S/V$ were more positive

linear plot of eq. (6) for PECH. The solubility parameter was calculated to be 19.74 ± 0.33 $(J/cm^3)^{0.5}$, and the η term was 1.211×10^{-3} mol/cm^3. In both plots, the correlation coefficients (R^2), based on the linear regression method, were close to unity. The correlation value was 0.9848 for PCL and 0.9941 for PECH. The solubility parameters of both polymers were higher than those of almost all of the probes used. As mentioned previously, this is an example that fits question (iii) in the Introduction.

Figure 1 Plot of left-hand side of eq. (6) versus solubility parameters of probes for PCL.

TABLE II
Comparison of $RT\chi/V$, Square of Difference of Solubility Parameters Between Probes and Polymer, to Entropy Term, $RT\chi_s/V$ of PCL

Probes	$RT\chi/V$ (J/cm^3)	$(\delta_1 - \delta_2)^2$	$RT\chi_s/V$ (J/cm^3)
n-Pentane	26.98	31.31	−4.33
n-Hexane	25.59	27.54	−1.95
n-Heptane	24.59	24.82	0.23
n-Octane	23.82	22.82	1.00
n-Nonane	23.13	20.91	2.22
Cyclohexane	23.29	11.89	11.40
Cyclohexene	16.29	7.92	8.36
Benzene	1.21	2.78	−1.57
Toluene	1.55	4.23	−2.68
Pentyl chloride	7.59	9.99	−2.40
Butyl chloride	9.03	9.48	−0.45
Methyl chloroform	1.64	8.98	−7.34
1,1-Dichloroethane	−2.03	4.23	−6.26
1,2-Dichloroethane	−6.38	0.18	−6.56
Methylene chloride	−12.85	0.02	−12.87
Chloroform	−17.00	1.20	−18.20
Carbon tetrachloride	6.65	7.24	−0.59
Tetrahydrofuran	4.00	2.20	1.80
1,4-Dioxane	3.55	0.21	3.34
Acetone	17.63	0.39	17.24
2-Butanone	10.69	2.45	8.23
Methyl acetate	13.36	1.25	12.11
Ethyl acetate	9.81	5.11	4.70
Propyl acetate	7.74	6.28	1.46
Butyl acetate	6.37	7.69	−1.32
Average	9.050	8.845	0.205

TABLE III
Comparison of $RT\chi/V$, Square of Difference of Solubility Parameters Between Probes and Polymer, to Entropy Term, $RT\chi_S/V$ of PECH

Probes	$RT\chi/V$ (J/cm³)	$(\delta_1 - \delta_2)^2$	$RT\chi_s/V$ (J/cm³)
n-Pentane	39.45	39.35	0.10
n-Hexane	37.55	35.11	2.44
n-Heptane	36.04	32.03	4.01
n-Octane	34.95	29.75	5.20
n-Nonane	33.98	27.56	6.42
Cyclohexane	32.71	17.02	15.69
Cyclohexene	24.56	12.19	12.37
Benzene	6.97	5.50	1.47
Toluene	7.75	7.48	0.27
Pentyl chloride	15.18	14.73	0.45
Butyl chloride	16.77	14.12	2.65
Methyl chloroform	13.40	13.51	−0.10
1,1-Dichloroethane	12.17	7.48	4.69
1,2-Dichloroethane	6.74	1.21	5.53
Methylene chloride	8.29	0.69	7.60
Chloroform	7.33	3.14	4.19
Carbon tetrachloride	20.22	11.34	8.88
Tetrahydrofuran	0.00	4.67	−4.67
1,4-Dioxane	0.00	0.05	−0.05
Acetone	9.92	1.70	8.22
2-Butanone	5.49	5.03	0.46
Methyl acetate	12.33	3.22	9.11
Ethyl acetate	9.25	8.64	0.61
Propyl acetate	7.74	10.14	−2.40
Butyl acetate	7.22	11.90	−4.68
Average	16.242	12.701	3.539

in PECH than in PCL. There are two main sources for the χ_S term: the free volume effect, which is positive,[36] and the specific interaction, which is negative. When the molecular weight of a polymer increases, it becomes more condensed with less free volume, and the free volume contribution to χ_S increases because the difference between the free volume of the probes and the polymer increases. Since PCL has a lower molecular weight than PECH, it is expected to have a lower free volume effect and a lower value of χ_S. The former also has a lower solubility parameter, which indicates that it has a lower cohesive energy density and likely a more expanded structure with more free volume. In addition, the less positive value of χ_S for PCL can also be the result of higher specific interaction between PCL and some of probes, particularly chlorinated compounds. The average values of $RT\chi_S/V_1$ for both polymers were calculated and are listed in Tables II and III. The results were 0.205 and 3.539 J/cm³ for PCL and PECH, respectively. The corresponding values of η were 6.93×10^{-5} and 1.205×10^{-3} mol/cm³ for PCL and PECH, respectively. These values were slightly lower than the values determined from the intercept of eq. (6). This example demonstrates that eq. (6) tends to give a slightly different value in estimating the η term. This difference between results of the two meth-

ods was also noted in an earlier study by Merk et al.[16] The average values of χ_S/V were used as η in the subsequent calculation. Later it will be shown that the difference in the η term between two methods was relatively small and well within the confidence interval of fitting the solubility parameter model.

Apparent high correlation coefficient of the linear plot

In eq. (6), there are two terms on the left-hand side. The typical value of δ_1^2/RT was about 0.1 mol/cm³, while the typical value of χ/V_1 was about 0.01 mol/cm³. To illustrate the effect of the dominating δ_1^2/RT term, a plot using twenty-five probes with solubility parameters ranging from 14.0 to 20.0 (J/cm³)^0.5 at a regular interval of 0.25 (J/cm³)^0.5 was assumed, and the interaction parameter term χ/V_1 was assumed to be zero. Using eq. (6), these hypothetical samples gave a good correlation coefficient of 0.9978, which was even higher than results for PCL and PECH. It is clear that R^2 cannot be effectively used in the linear plot method as evidence of a good fit of the solubility parameter model. From the slope of the hypothetical samples, δ_2 was determined to be 17.00 ± 0.17(J/cm³)^0.5, which was the mean value of the solubility parameters of the probes. Galin[17] and Gray et al.[18] pointed out that, in samples of small χ_i/V_i value, the solubility parameter determined for the polymer would be an average of the probes' solubility parameters. Eq. (7) gives evidence of such dependency. At a value of zero for χ_i/V_i, the solubility parameter of the polymer would be

$$\delta_2 = [\Sigma(\delta_i - \bar{\delta})\delta_i^2]/2[\Sigma(\delta_i - \bar{\delta})^2] \qquad (14)$$

Note that this expression contains only the solubility parameters of the probes. The δ_2 value calculated would be an artifact because it represents an average of δ_i. From the intercept term of the hypothetical samples, η was determined to be -1.1×10^{-3} mol/cm³. The value was lower than the input value, which was zero. It was also noted that when the range of hypothetical samples was reduced to 14.0–18.0 (J/cm³)^0.5, the η term became 5.1×10^{-4} mol/cm³. The sign of the deviation could be either positive or negative. But in both cases the deviations were small.

From the above example, it can be seen that the linear plotting method tends to give a high correlation coefficient and a slight difference in the η term. Also, unless the χ_i/V_i term is sufficiently large, δ_2 could be an average of the solubility parameters of the probes. Therefore, it is important to use probes that give high values of χ_i/V_i and also to employ a different method to compare the accuracy of fit to the solubility parameter model. Obtaining a high value of χ_i/V_i would require probes with solubility parameters different
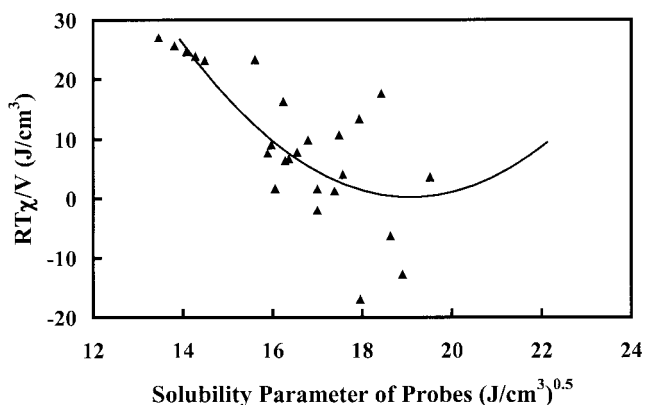
Figure 3 Comparison of experimental $RT\chi/V$ to solubility parameter model using eq. (10) for probes in PCL. Solid curve is the predicted value.

from δ_2. They could be nonpolar probes with low solubility parameters or probes with strong polar characteristics and hydrogen bonding. However, there is a problem with polar probes because the solubility parameter model may not work properly. In the IGC measurement, the selection of probes is further limited by the vapor pressure consideration, which cannot be too low. This leaves probes with low solubility parameters a better choice, as has been shown in many studies.

Figures 3 and 4 compare the experimental values of $RT\chi/V$ with the model in eq. (10) for PCL and PECH, respectively. The predicted values, using eq. (10) and calculated values of δ_2 and η, were plotted as solid curves. It can be seen that the model predicted a similar parabolic function for both systems. The effect of the minimization of SS in the calculation of δ_2 and η was to move the parabolic function horizontally and vertically until the best fit was obtained. The solubility parameter where the minimum occurred was δ_2. The value of χ/V_1 at the minimum point of the parabolic curve was the best value of η. Using eq. (14), the correlation coefficients, R^2, were calculated to be 0.628 and 0.839, for PCL and PECH, respectively. These correlation coefficients were lower than the correlation coefficients in Figures 1 and 2, but values of the non-linear method showed a clear difference between the two polymers. PECH had a higher correlation coefficient with both methods because the data were less scattered. The difference in R^2 between Figures 1 and 2 was small and cannot provide a means of comparison as well as the difference between Figures 3 and 4.

### Sensitivity of δ_2 and η to interaction parameter

In the determination of the solubility parameter of a polymer using an experimentally measured χ value, it is frequently found that some probes deviate from the solubility parameter model. This may be because the probe has a specific interaction in the probe liquid state or with the polymer. In Figures 3 and 4, it can be seen that several probes deviated from the solid curves and accounted for the low R^2 values. Deviation can also occur because of experimental errors. In either case this deviation can affect the computation of δ_2 and η. The effect of the error term, λ_i, on δ_2 can be derived from eqs. (7) and (10):

$$\Delta\delta_2 = -\lambda_i(\delta_i - \bar{\delta})/2[\Sigma(\delta_i - \bar{\delta})^2]$$

$$= \lambda_i(\bar{\delta} - \delta_i)/2(N-1)\sigma^2 \quad (15)$$

where σ^2 is the sample variance. It can be seen that $\Delta\delta_2$ is proportional to $\lambda_i(\bar{\delta} - \delta_i)$. For a probe with $\delta_i < \bar{\delta}$, a positive deviation of χ from the solubility parameter model tends to increase δ_2. This results in a counter-clockwise rotation of the best fit line in Figures 1 and 2 and a small increase in the slope. We can call $\lambda_i(\bar{\delta} - \delta_i)/2(N-1)\sigma^2$ the sensitivity factor of a probe to the value of δ_2. Figure 5 shows a plot of the sensitivity factor versus the solubility parameter of probes for both polymers. It can be seen that probes in PCL had higher sensitivity because their deviations from the solubility parameter model were higher. Also, for both polymers the probes at the left-hand side of the distribution had smaller sensitivity than probes with solubility parameters above 17.0 $(J/cm^3)^{0.5}$.

The relationship between the sensitivity factor to the solubility parameter of the probes is the result of two reasons. First, the probes in the center region of the solubility parameter range had less effect on $\Delta\delta_2$ because $(\bar{\delta} - \delta_i)$ was small. Second, the probes with $\delta_i < \bar{\delta}$ had smaller deviations from the solubility parameter model because these probes usually lacked specific interactions. This gave a small sensitivity factor for probes at the left-hand side of $\bar{\delta}$. Most probes with specific interactions tend to have a high solubility parameter and give a large deviation in χ value. These
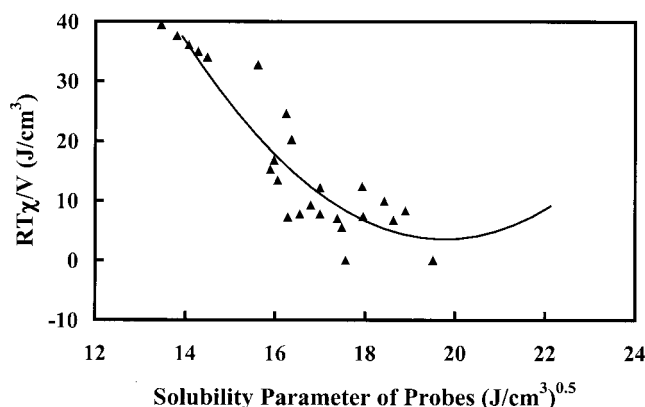
Figure 4 Comparison of experimental $RT\chi/V$ to solubility parameter model using eq. (10) for probes in PECH. Solid curve is the predicted value.
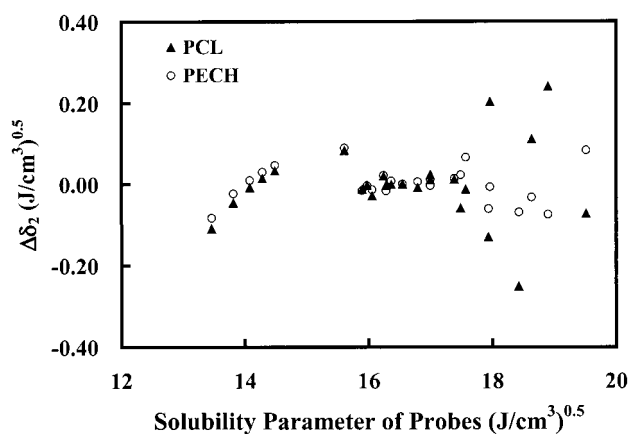
Figure 5 Plot of sensitivity factor, $\Delta\delta_2$, caused by deviation of probes from solubility parameter model versus solubility parameter of probes for PCL and PECH.

probes will have a large effect on δ_2 if they are located near the edge of the right-hand side, where $\delta_i - \bar{\delta}$ is large. Probes with low solubility parameters usually have small $\Delta\delta_2$ values; therefore, they are the preferred samples for IGC measurement. This result supports the earlier conclusion that probes with small solubility parameters are preferred samples with less likelihood of deviation from the solubility parameter model, even though their solubility parameters are farther away from that of the polymer.

In Figure 5, the probe with the highest sensitivity factor shows a value of about ±0.25 $(J/cm^3)^{0.5}$. Since the range of solubility parameters of polymers is about 4.0 $(J/cm^3)^{0.5}$, a difference of 0.25 caused by a single probe is a significant effect, especially when twenty-five probes are used. The best way to reduce the sensitivity factor is to use more probes, especially probes with a wide range of solubility parameters. This is because an increase of N or σ^2 could reduce the level of the sensitivity factor for all probes, as can be seen in eq. (16). Additional probes need to be carefully selected. Adding probes with δ_i close to $\bar{\delta}$ is not very useful in reducing $\Delta\delta_2$. Despite the general belief that an increase in the number of samples can reduce the effect of experimental errors in many measurements, adding a probe with a solubility parameter close to the average value, $\bar{\delta}$, would increase $\Sigma(\delta_i - \bar{\delta})^2$ very little and have little tendency to reduce $\Delta\delta_2$. The use of probes with wide range of solubility parameters is more effective in reducing $\Delta\delta_2$. If the range of solubility parameters of the probes is widened by a factor of two, the variance, σ^2, can be increased by a factor of four, and the sensitivity factor can be reduced by four with the same number of samples. But the selection of probes with high solubility parameters must be carefully weighed against the use of probes with a large deviation from the solubility parameter model.

The effect of the error term on η was derived from eqs. (10) and (12):

$$RT\Delta\eta = \lambda_i/N + 2\Sigma(\delta_i - \delta_2)\Delta\delta_2/N$$
$$= \lambda_i/N + \lambda_i(\bar{\delta} - \delta_2)(\bar{\delta} - \delta_i)/(N-1)\sigma^2 \quad (16)$$

Eq. (16) shows that $\Delta\eta$ depends on two terms. The first term, λ_i/N, is proportional to λ_i, and the effect is gradually diluted by an increase in the number of samples. The second term occurs because there is dependence between η and δ_2 in eq. (12). The deviation term, λ_i, affects δ_2, which in turn affects η. Figure 6 shows the plot of $RT\Delta\eta$ and λ_i/N versus the solubility parameters of probes for both polymers. The difference between $RT\Delta\eta$ and λ_i/N represents the contribution of the last term in eq. (16). The probes in PCL had larger deviations and showed a wider variation of $RT\Delta\eta$ and λ_i/N than those in PECH. In both polymers, the deviation of linear alkanes was small; the deviation was higher for probes with high solubility parameters. The variation of $RT\Delta\eta$ was larger than that of λ_i/N, particularly for probes with high solubility parameters. This indicates that the contribution of the last term is important for those probes. This is because, for those probes, the product $(\bar{\delta} - \delta_2)(\bar{\delta} - \delta_i)$ was positive, and both terms on the right-hand side had the same signs; the effect of λ_i on $\Delta\eta$ was reinforced. Because the second term of eq. (16) was proportional to $\Delta\delta_2$, there was a correlation between $\Delta\eta$ and $\Delta\delta_2$, which can also be seen in the similarity (in spite of opposite signs) between Figure 5 and the open symbols in Figure 6. This is discussed further in the next section.

Correlation between parameters

In Figures 3 and 4, it can be seen that the solubility parameters of most probes are lower than δ_2. Only the
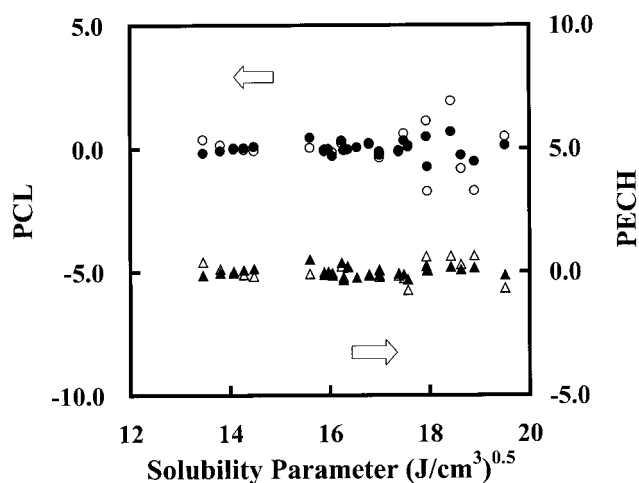
Figure 6 Plot of $RT\Delta\eta$ (open symbols) and λ_i/N (filled symbols) versus solubility parameters of probes for PCL and PECH. Units are J/cm^3.

TABLE IV
Parameters of PCL and PECH

	PCL	PECH
A (J/cm^3)	885	1272
B (J/cm^3)	2389	3142
C (J/cm^3)	9075	9732
S_R (J/cm^3)	341.4	141.8
$\delta_{2,o}$ (J/cm^3)$^{0.5}$	19.06	19.74
$RT\eta_o/\delta_{2,o}$ (J/cm^3)$^{0.5}$	0.0107	0.1793

left halves of the parabolic curves were used to fit eq. (10). Selection of probes with low solubility parameters is a common practice in the literature and was noted as question (iii) in the Introduction. Because only the left-hand portion of the curve was used, one can move the curve to the right and down and still attain a reasonable fit. Mathematically, this indicates a negative correlation between η and δ_2. This is a result of the majority of the probes having solubility parameters lower than the polymer. The effect of such selection can be examined by looking at the joint confidence region of the two parameters. By using a linearization method around the optimum values of the two parameters, $\delta_{2,o}$ and η_o, the approximate joint confident contour of eq. (11) can be expressed in a quadratic form using δ_2 and $\eta RT/\delta_{2,o}$ as the variables[33]:

$$A(\delta_2 - \delta_{2,o})^2 + 2B(\delta_2 - \delta_{2,o})[(\eta - \eta_o)(RT/\delta_{2,o})]$$

$$+ C[(\eta - \eta_o)(RT/\delta_{2,o})]^2 = S_R \frac{p}{N-p} F_\alpha(N, N-p)$$

(17)

where S_R is the sum of error square (SS), calculated at the optimum values $\delta_{2,o}$ and η_o using eq. (11), F_α is the F distribution with confidence level α, p is the number of parameters, and N is the number of samples. The reason that $\eta RT/\delta_{2,o}$ was used as the variable instead of η was to make the dimensions of both variables consistent. For this study, $p = 2$, $N = 25$, and F_α at a 90% confidence level is 2.55. The coefficients A, B, and C can be determined from the partial differentiation with respect to SS using the expression in eq. (11):

$$A = (1/2)\partial^2(SS)/\partial\delta_2^2 = 4\Sigma(\delta_i - \delta_{2,o})^2 \quad (18)$$

$$B = (1/2)(\delta_{2,o}/RT)\partial^2(SS)/\partial\eta\partial\delta_2$$
$$= -2\Sigma(\delta_i - \delta_{2,o})\delta_{2,o} \quad (19)$$

$$C = (1/2)(\delta_{2,o}/RT)^2\partial^2(SS)/\partial\eta^2 = N\delta_{2,o}^2 \quad (20)$$

The parameters for the joint confidence region of PCL and PECH are listed in Table IV. Because $AC - B^2 = 4N(N-1)\sigma^2\delta_{2,o}^2 > 0$, the quadratic form in eq. (17) is an ellipse in a two-dimensional plot of δ_2 and $\eta RT/$

$\delta_{2,o}$. Figure 7 shows the contour of the 90% joint confidence region of parameters δ_2 and $\eta RT/\delta_{2,o}$. The joint confident regions of PCL and PECH are oblique ellipses. A negative correlation between δ_2 and η is clear. This is because $B \neq 0$ in eq. (17). Only when $B = 0$ are the principle axes parallel or perpendicular to the x and y axes, and there is no correlation between η_o and $\delta_{2,o}$. The principle axes of PCL were longer than those of PECH because the former had a higher S_R. The condition $B = 0$ implies that $\bar{\delta} = \delta_2$; in this case the δ_i values of the probes will be distributed on both sides of δ_2, and the condition $\Sigma\delta_i/N = \delta_2$ will be satisfied. From eq. (16), it can also be seen that when $\bar{\delta} = \delta_2$ there is no dependence between $\Delta\eta$ and $\Delta\delta_2$. Thus, this is another advantage of using probes with solubility parameters on both sides of the polymer, besides the increase of σ^2 and decrease of the sensitivity factor mentioned in the previous section.

The main effect of the obliquity in the approximate joint confident region is a decrease in the confidence interval of δ_2 and an increase in the confidence interval of η. The length of the principal axes of the ellipse can be determined from eq. (17) and coefficients A, B, C, and S_R. The values for PCL were 1.17 and 0.18 (J/cm^3)$^{0.5}$ for the long and short axes, respectively. The corresponding values for PECH were 0.72 and 0.11 (J/cm^3)$^{0.5}$. The small angle of obliquity of the joint confident region did not decrease the value of δ_2 much, but the confident interval of $\Delta\eta$ increased by about a factor of two. Assuming an average molar volume of 100 cm^3/mole for the probes, a value of 0.3 (J/cm^3)$^{0.5}$ in $\eta RT/\delta_{2,o}$ represents a difference of 0.19 in the average value of χ_s. This represents a modest fraction compared to the typical value of χ, which usually ranges from -0.5 to 1.5. The 90% confidence intervals of δ_2 using the linear regression method in eq. (6) were 0.80 and 0.51 (J/cm^3)$^{0.5}$ for PCL and PECH, respectively. Compared to the values of 1.17
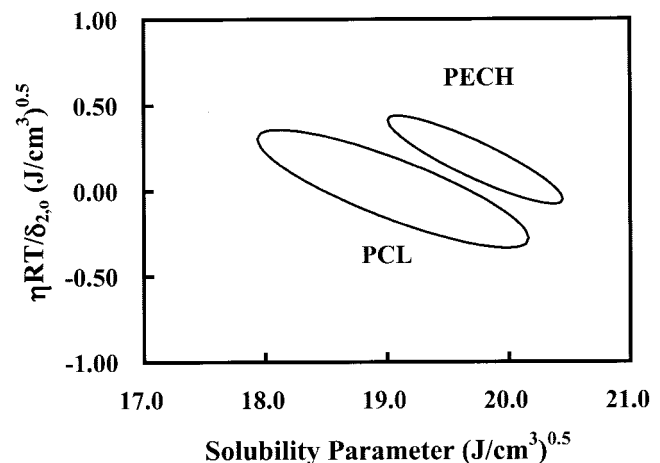

Figure 7 Approximate joint confidence contour of δ_2 and $\eta RT/\delta_2$ at 90% level.

and 0.72 $(J/cm^3)^{0.5}$, the confidence intervals of δ_2 determined by the nonlinear methods were wider. The standard deviation of δ_2 obtained by the linear method could also be affected by the dominating effect of the δ_1^2/RT term. Considering that the range of solubility parameters of polymers is only about 4.0 $(J/cm^3)^{0.5}$, the lengths of the confidence intervals of δ_2 determined by IGC measurement were quite large, especially when twenty-five samples were used. The best method to reduce the confidence interval range is to increase N and σ^2.

Finally, the differences of $\eta RT/\delta_2$ between the linear method and the nonlinear method were 3.5 $\times 10^{-4}$ and 7.4 $\times 10^{-4}$ $(J/cm^3)^{0.5}$ for PCL and PECH, respectively. It can be seen that the numbers were much smaller than the confidence interval of $\eta RT/\delta_2$ in Figure 7, which is in the range 0.20–0.40 $(J/cm^3)^{0.5}$. Therefore, both methods can be used to calculate η and δ_2, but eq. (13) is a preferred method to compare the accuracy of fit of the solubility parameter model.

CONCLUSIONS

A method is proposed to determine the parameters of the solubility parameter model based on direct curve fitting using experimental values of $RT\chi/V$. It was found that the expression of the solubility parameter was the same as that found using the linear plotting method, but the linear method tended to produce a slightly different η term. A different definition of correlation coefficient based on the nonlinear model gave a lower value than the linear model and better accounted for the results. When the solubility parameters of the probes were located predominantly on one side of the polymer, the solubility parameter of the polymer could still be determined, but the joint confident contour was oblique. In this case, values of η and δ_2 were negatively correlated. The use of probes with wider solubility parameter ranges can reduce the influence of deviation of probes from the solubility parameter model. The use of probes on both sides of the polymer with $\bar{\delta} = \delta_2$ can remove the correlation between parameters.

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