

# Three-Dimensional Solubility Parameters of Poly( $\epsilon$ -Caprolactone)

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**ABSTRACT:** The three-dimensional solubility parameter model was applied to analyze solution thermodynamic data of 27 solutes in poly( $\epsilon$ -caprolactone) (PCL) between 70 and 110 °C. A linear regression method was compared with a nonlinear least square regression method, which searches solubility parameter components by minimization of the sum of error squares. The parameters of polymers were the same by both methods. When compared with the error in predicting  $\chi RT/V$ , the data showed a different slope from the simple three-dimensional model. These deviations were reduced by a different model using a smaller weight on the polar and hydrogen bonding components. In the new model, the solubility parameter components were closer to

the value of a structure analogue of PCL. The confidence intervals for the parameters were estimated from a linearized equation based on the sum of error squares. The solubility parameter components obtained were different from the average values of the five solutes with the smallest  $\chi$ . The inclusion of solutes with high hydrogen bonding components contributed to the increase of the component in the nonlinear regression method. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2002–2009, 2006

**Key words:** solution properties; thermodynamics; chromatography; solubility parameters; interaction parameter

## INTRODUCTION

In 1916, Hildebrand<sup>1</sup> pointed out that the solubility of a given solute in a series of solvents is determined by the internal pressures of the solvents. Later, Scatchard<sup>2</sup> introduced the concept of cohesive energy density into Hildebrand's theory, identifying this quantity with the internal pressure. In 1949, Hildebrand proposed the term "solubility parameter" and the symbol " $\delta$ ," which is defined as<sup>3</sup>

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

where  $\Delta E_{\text{vap}}$  is the energy of vaporization and  $V$  is the molar volume of the solvent. The ratio  $\Delta E_{\text{vap}}/V$  is the cohesive energy density; it 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 usually calculated from the vapor pressure of a saturated liquid by the Clausius–Clapeyron equation.

The solubility parameter model has been successful in describing thermodynamic properties of polymer solutions. It has been shown that the Flory–Huggins

interaction parameter can be related to the solubility parameters of two components by<sup>4</sup>

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2, \quad (2)$$

where  $\delta_1$  and  $\delta_2$  are the solubility parameters of the solvent and polymer, respectively, and  $V_1$  is the volume of the solvent. When  $\chi$  is less than 0.5, the solvent is generally characterized as a good solvent for the polymer, while a value higher than 0.5 is a poor solvent and may lead to phase separation.<sup>5</sup> Equation (2) implies that  $\chi$  is always positive. A negative experimental value of  $\chi$  can occur in systems with a specific interaction. One way to overcome this problem is by adding an entropy term into the Flory–Huggins interaction parameter so that  $\chi = \chi_H + \chi_S$ , where the dimensionless  $\chi_S$  is a residual entropy term that can be used to accommodate the deviation from the original solubility parameter model in eq. (2).<sup>6,7</sup> The Flory–Huggins interaction parameter represents the free energy of solution without the combinatorial portion. The enthalpy of solution is calculated using eq. (2). The residual entropy term can have either a positive or a negative value and represents the deviation from the solubility parameter model. When  $\chi_S$  is added into the equation the following modified form of the solubility model is obtained:

$$\chi = \chi_H + \chi_S = (V_1/RT)(\delta_1 - \delta_2)^2 + \chi_S. \quad (3)$$

Since polymers have no appreciable vapor pressure and their molar volumes are not accurately known,

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the experimental values of  $\chi$  have been used in the estimation of the solubility parameters of polymers. Inverse gas chromatography (IGC) has been shown to be an effective tool for measuring the thermodynamic properties of solute (probe) vapors in polymers.<sup>8–11</sup> Guillet and colleague<sup>10,11</sup> demonstrated the use of IGC in the determination of  $\chi$  and the solubility parameters of polymers. In their studies, eq. (3) was changed into the expression<sup>10,11</sup>

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \eta\right), \quad (4)$$

where  $\eta = \chi_S/V_1$ . In the application of eq. (4) to experimental results of  $\chi$  it is assumed that the  $\eta$  term depends on the polymer and remains constant for a series of probes. A linear regression method is generally used to determine  $\eta$  and  $\delta_2$ . In this method  $\delta_1$  is used as the independent variable and the left-hand-side,  $\delta_1^2/RT - \chi/V_1$ , is treated as the observation. Therefore,  $\delta_2$  can be determined from the slope term of the plot, and the intercept is used to calculate  $\eta$  after  $\delta_2$  is determined. From  $\chi$  and solubility parameters of the probes and polymer the values of  $\chi_S$  are determined using eq. (3).<sup>10,11</sup>

The solubility parameter concept is quite general and has many applications. Several authors have tried to look at the components of the cohesive energy density. The cohesive energy of organic compounds may be divided into three parts, corresponding with three types of interaction forces: dispersion, polar, and hydrogen bonding.<sup>12</sup> Blanks and Prausnitz<sup>13</sup> considered the cohesive energy as the sum of a polar part and a nonpolar part and proposed a two-dimensional solubility parameter model. The nonpolar part of cohesive energy is estimated from the heat of vaporization of a straight-chain hydrocarbon compound with the same molar volume and reduced temperature. The remainder of the cohesive energy is assigned to the polar component. The concept of three-dimensional solubility was proposed by Hansen<sup>14</sup> and the corresponding solubility parameter expression is

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2, \quad (5)$$

where  $\delta_d$  = the dispersion component of  $\delta$ ,  $\delta_p$  = the polar component of  $\delta$ , and  $\delta_h$  = the hydrogen-bonding component of  $\delta$ . A revised and expanded table of solubility parameter components was published by Hansen and Beerbower.<sup>15</sup> Methods to estimate temperature dependency of each component were also given. The dispersion component was estimated from a hydrocarbon with a similar molar volume and reduced temperature as described by Blanks and Prausnitz.<sup>13</sup> The polar and hydrogen bonding components were then made on an empirical basis.

A combination of eq. (3) and the method of Hansen<sup>14–16</sup> gives the following equation for the three-dimensional solubility parameter model:

$$\chi = (V_1/RT)[(\delta_{1,d} - \delta_{2,d})^2 + (\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,h} - \delta_{2,h})^2] + \chi_S. \quad (6)$$

Using the above equation the three-dimensional form of eq. (4) can be obtained:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_{d,2}}{RT}\right)\delta_{d,1} + \left(\frac{2\delta_{p,2}}{RT}\right)\delta_{p,1} + \left(\frac{2\delta_{h,2}}{RT}\right)\delta_{h,1} - \left(\frac{\delta_{1,2}^2}{RT} + \eta\right). \quad (7)$$

Note that the left-hand side can be obtained from experimental results and it is a linear function of the three solubility parameters components. From a regression calculation, the solubility parameters of polymers can be determined. Because of the dominating effect of the  $\delta^2/RT$  term on the left hand side of eq. (4), high correlation coefficients were generally observed. Huang<sup>17</sup> noted this and proposed a nonlinear regression method by minimizing the error in the prediction of  $\chi RT/V$  to calculate the solubility parameter of a polymer for the one-dimensional model. For the three-dimensional case the corresponding expression is

$$RT\chi_i/V_1 = [(\delta_{1,d} - \delta_{2,d})^2 + (\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,h} - \delta_{2,h})^2] + RT\eta, \quad (8)$$

where  $\eta$  is represents  $\chi_S/V_1$  and is treated as a constant. In the calculation experimental values of  $RT\chi_i/V_1$  were considered a function of  $\delta_{1,d}$ ,  $\delta_{1,p}$ ,  $\delta_{1,h}$  with four parameters:  $\delta_{2,d}$ ,  $\delta_{2,p}$ ,  $\delta_{2,h}$ , and  $\eta$ , which were determined by the minimization of sum of error square in eq. (8). For the one-dimensional case an analytical expressions for  $\delta$  was derived<sup>17</sup> and it was concluded that the solubility parameters calculated by two methods were the same. For the three-dimensional case, a comparison of the solubility parameter components was made using PVC and poly(tetrahydrofuran) (PTHF) with 25 solutes. The results were the same as the linear regression method.<sup>18</sup> In this study the similar approach is extended to poly( $\epsilon$ -caprolactone) (PCL) at different temperatures. The method to estimate the confidence interval is also discussed.

## RESULTS AND DISCUSSION

### Determination of solubility parameters of probes

Tian and Munk<sup>19</sup> used the IGC method to determine the specific retention volume of a series of solutes in PCL. Forty-three solutes were studied at temperatures

TABLE I  
Molar Volume  $V$  ( $\text{cm}^3/\text{mol}$ ) and Solubility Parameter Components of Probes at  $70^\circ\text{C}$

Solutes	$V$	$\delta_r(\text{J}/\text{cm}^3)^{0.5}$	$\delta_d(\text{J}/\text{cm}^3)^{0.5}$	$\delta_p(\text{J}/\text{cm}^3)^{0.5}$	$\delta_h(\text{J}/\text{cm}^3)^{0.5}$
1. Pentane	123.7	13.44	13.44	0.00	0.00
2. Hexane	138.7	13.98	13.98	0.00	0.00
3. Heptane	154.5	14.47	14.47	0.00	0.00
4. Octane	170.6	14.74	14.74	0.00	0.00
5. Nonane	187.0	14.98	14.98	0.00	0.00
6. Decane	203.4	15.03	15.03	0.00	0.00
7. Cyclohexane	113.5	15.89	15.89	0.00	0.18
8. Benzene	93.2	17.56	17.47	0.00	1.78
9. Toluene	111.0	17.31	17.16	1.40	1.79
10. Ethylbenzene	127.6	17.07	17.01	0.60	1.25
11. Chloroform	84.5	17.78	16.80	3.00	4.98
12. Carbon tetrachloride	101.3	16.89	16.88	0.00	0.54
13. <i>n</i> -Butyl chloride	109.7	16.48	15.47	5.40	1.78
14. 1,1-Dichloroethane	82.9	17.72	15.98	6.59	3.91
15. Methylchloroform	83.0	19.71	18.00	7.20	3.56
16. Trichloroethylene	105.0	16.70	16.06	4.20	1.78
17. Chlorobenzene	105.7	18.80	18.23	4.22	1.79
18. Acetone	78.0	18.75	14.56	10.16	6.03
19. Methyl ethyl ketone	94.4	17.98	15.04	8.79	4.45
20. Tetrahydrofuran	85.5	18.19	15.85	5.60	6.95
21. Dioxane	89.1	19.30	18.11	1.81	6.43
22. Methyl acetate	84.0	17.89	15.12	6.97	6.56
23. Ethyl acetate	103.6	16.86	14.79	5.19	6.22
24. <i>n</i> -Butyl acetate	138.1	16.34	14.95	3.61	5.53
25. Ethanol	61.8	23.93	14.70	8.56	16.83
26. Propanol	79.1	22.26	14.97	6.58	15.10
27. Butanol	95.8	21.13	15.07	5.60	13.71
Variance			1.70	10.97	21.94

between  $70$  and  $110^\circ\text{C}$ . Specific retention volumes and interaction parameters of solutes were reported. The probes in the study covered a wide range of interaction characteristics. This offered the opportunity to explore the components of the solubility parameters of polymers using the three-dimensional approach. In the present study the solubility parameter components of probes at  $25^\circ\text{C}$  were taken from Hansen and Beerbower.<sup>15</sup> Several probes were excluded from this study because of their low critical temperatures and high vapor pressures. Parameters of 27 solutes were available for this study. The molar volumes of probes were calculated using the method of Spencer and Danner described by Reid et al.<sup>20</sup> The solubility parameter components decreased when temperature increased. They were adjusted for temperature by the method given by Hansen and Beerbower.<sup>15</sup>

$$d\delta_d/dT = -1.25\alpha\delta_d \quad (9)$$

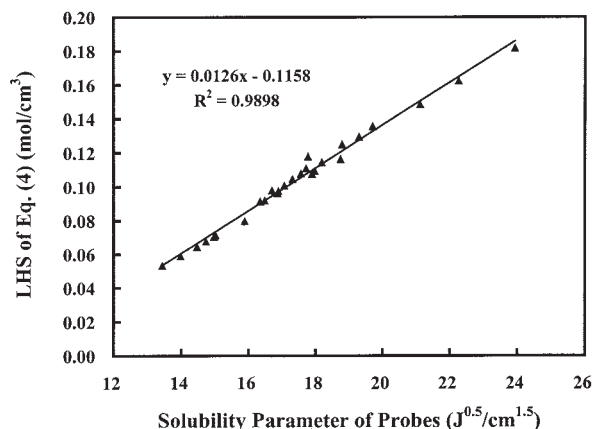
$$d\delta_p/dT = -\alpha\delta_p/2 \quad (10)$$

$$d\delta_h/dT = -(1.22 \times 10^{-3} + \alpha/2)\delta_h \quad (11)$$

The thermal expansion coefficients,  $\alpha$ , were calculated using the molar volume of probes at  $25^\circ\text{C}$  and the experimental temperatures. The resulting solubility

parameter components at  $70^\circ\text{C}$  are shown in Table I. It can be seen that the dispersion components of probes covered a range from  $13.44$  to  $18.23 \text{ J}^{0.5}/\text{cm}^{1.5}$ . Polar components had a wider range from  $0$  to  $10.16 \text{ J}^{0.5}/\text{cm}^{1.5}$ . Hydrogen bonding components had the widest range from  $0$  to  $16.83 \text{ J}^{0.5}/\text{cm}^{1.5}$ . These ranges are important in determining the confidence interval of each parameter. Huang<sup>17,18,21</sup> has shown that the coefficient of the joint confidence region is proportional to the variance of the solubility parameters of probes. This leads to an inverse relationship between the variance and the square of the confidence interval of the solubility parameters of polymers. This applies to the one-dimensional case and is expected to apply to higher dimension cases also. A wide range of probes can reduce the confidence interval of the solubility parameters of polymers, which will be discussed later. The variances of three components are also shown in Table I.

Figure 1 shows the plot of the left-hand side of eq. (4) vs. the solubility parameter of the probes using data at  $70^\circ\text{C}$ . A straight line with a high correlation coefficient was obtained. When polar probes and stationary phases were used, increased deviations in the plotting of eq. (4) were observed in some systems. Price et al.<sup>22</sup> and Voelkel and Janas<sup>23</sup> developed a method to determine the dispersion, polar, and hydro-



**Figure 1** Plot of the left-hand side of eq. (4) vs. the solubility parameter of probes for PCL at 70 °C.

gen bonding components of the solubility parameters. Their method used nonpolar probes to determine dispersion components and used probes with either a polar or a hydrogen bonding nature to determine the other components. Since no clear trend of increased deviation was observed for solutes with hydrogen bonding this method was not used to determine the components in this study. In the present study the linear method was first used for the three-dimensional model based on eq. (7). With this method the solubility parameter components of the probes were treated as independent variables and the components of the polymer were obtained as the unknown coefficients. The calculation was made using the Microsoft Excel program.<sup>24</sup> The results of solubility parameters of polymers are shown in Table II. After the components of the polymers were determined, the values of  $\eta$  were determined from the intercept term. The values of components and  $\eta$  are listed in Table II. The parameters were also calculated by direct minimization of the sum of error squares. The sum of error squares in fitting the model was calculated as

$$S_R = \sum [RT\chi_i/V_i - (\delta_{1,d} - \delta_{2,d})^2 - (\delta_{1,p} - \delta_{2,p})^2 - (\delta_{1,h} - \delta_{2,h})^2 - RT\eta]^2. \quad (12)$$

In the nonlinear regression method, the sum of error squares was calculated and the solubility parameter components of the polymer were changed at an interval of  $0.01 \text{ J}^{0.5}/\text{cm}^{1.5}$  each time until a minimum was reached. It was found that the solubility parameter components were the same as the linear regression method as was concluded in a previous study.<sup>17,21</sup> The difference in  $RT\eta$  between the two methods was very small. From these values, the sum of error square,  $S_R$ , was calculated and these are also listed in Table II. It can be seen that the dispersion component showed a clear decreasing trend when temperature increased. The value of hydrogen bonding components was higher than polar components for the temperatures studied. The values of both generally decreased when temperature was increased. The value of  $S_R$  decreased steadily when temperature increased. The value of  $\eta$  was negative and the magnitude decreased steadily when temperature increased.

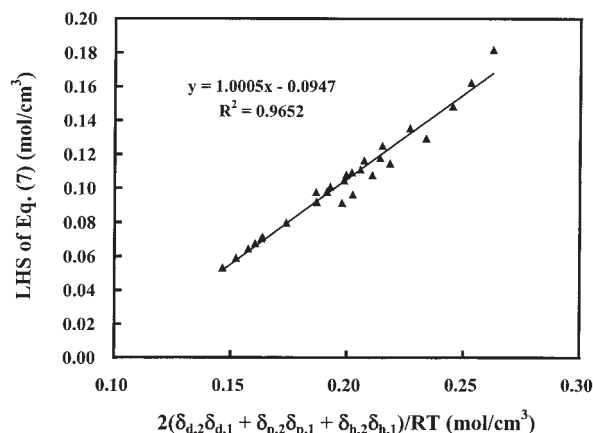
### Comparison between data and models

After the solubility parameter components of PCL were determined, a comparison was made between experimental values of  $\chi RT/V_1$  and the predicted values based on the solubility parameter model. The plot of eq. (4) is shown in Figure 1 for 70 °C. Similar results were obtained at all temperatures. In the previous study<sup>18</sup> it was pointed out that these apparent high correlations were due to the dominating effect of the  $\delta^2/RT$  term on the left-hand side of the equation. In this study a similar effect was demonstrated in the three-dimensional situation. Figure 2 shows the plot of eq. (7) for PCL at 70 °C. It can be seen that the plot has a slope close to unity, which was the theoretical value. The data points were more scattered than the plot of eq. (4). This reflected the inadequacy of the three-dimensional model, which will be discussed again later.

A different comparison method can be made by comparing the prediction of  $RT\chi/V_1$  without the inclusion of the  $\delta^2/RT$  term. This was shown in Figure 3 using results of 70 °C. In the figures a plot was made

**TABLE II**  
Parameters of Three-Dimensional Solubility Parameter Model as in Eq. (6) for PCL between 70 and 110 °C (Units:  $\delta = \text{J}^{0.5}/\text{mol}^{1.5}$ ,  $RT\eta = \text{J}/\text{cm}^3$ , and  $S_R = \text{J}^2/\text{cm}^6$ )

	Temperature (°C)				
	70	80	90	100	110
$\delta$	17.39	16.78	16.43	16.10	15.79
$\delta_d$	15.53	14.90	14.52	14.15	13.83
$\delta_p$	2.42	2.57	2.28	2.24	2.21
$\delta_h$	7.44	7.28	7.35	7.34	7.29
$RT\eta$ by Eq. (4)	-32.69	-32.00	-31.86	-31.38	-31.07
$RT\eta$ by Eq. (7)	-32.64	-32.02	-31.84	-31.30	-31.13
$S_R$	7013.5	6819.8	6798.3	6742.8	6481.2



**Figure 2** Plot of the left-hand side of Eq. (7) vs.  $2[(\delta_{d,2}/RT)\delta_{d,1} + (\delta_{p,2}/RT)\delta_{p,1} + (\delta_{h,2}/RT)\delta_{h,1}]$  for PCL at 70 °C.

by plotting  $RT\chi/V_1$  versus  $\Sigma(\delta_1 - \delta_2)^2 + \eta RT$ . If the three-dimensional model was perfect the plot should give a straight line with slope equal to unity. This line was also plotted in Figure 3. It can be seen that for probes with solubility parameters near those of the polymers, i.e., when the abscissa was small, the value of  $RT\chi/V_1$  tended to be higher than the theoretical value, while for probes away from the polymers the value tended to be lower. In the previous study the similar trend were also observed on PVC and PTHF using 25 solutes.<sup>21</sup>

The trend in Figure 3 indicated that the three-dimensional model did not properly predict the value of  $RT\chi/V_1$ . The reason for these deviations was that experimental results had a narrower range of  $RT\chi/V_1$  than those provided by the three-dimensional model. In this respect, solubility parameter components defined in eq. (5) might have much higher polar and/or hydrogen bonding components than were necessary to fit the experimental results of  $RT\chi/V_1$  through eq. (6). Because the polar components contributed a wider range than the dispersion components, it has been proposed to multiply the former by a factor less than unity, by Weimer and Prausnitz<sup>25</sup> in their study of hydrocarbon solutes (component 1) in several polar solvents (component 2). In their study the energy of mixing had the form

$$\Delta U/V_1 = (\delta_{1,d} - \delta_{2,d})^2 + \delta_{2,p}^2 - 2\psi_{12} \quad (13)$$

where  $\psi_{12} = 0.396 \delta_{2,p}^2$  for 7 hydrocarbons in 25 polar solvents. The first two terms on the right-hand side were the expression of a two-dimensional solubility model when solutes are nonpolar and the solvents are polar. The third term was used to correct the difference between the model and experimental results. This term was explained as an induction term between polar and nonpolar species. Helpinstill and Van Win-

kle<sup>26</sup> also proposed the use of a similar factor in polar-polar systems. In their expression the energy of mixing had the form

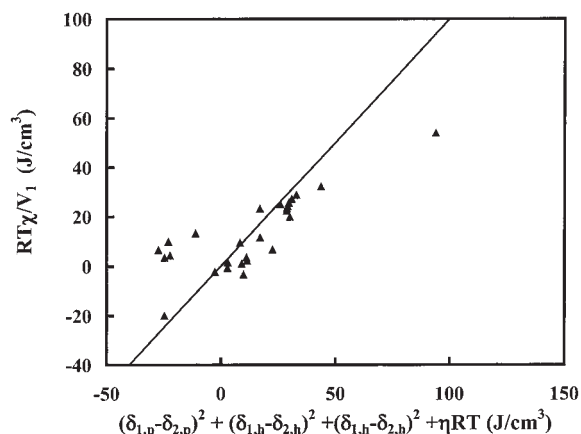
$$\Delta U/V_1 = (\delta_{1,d} - \delta_{2,d})^2 + (\delta_{1,p} - \delta_{2,p})^2 - 2\psi_{12}, \quad (14)$$

where  $\psi_{12} = k(\delta_{1,p} - \delta_{2,p})^2$  with  $k$  varying from 0.399 to 0.447. Because the value of  $k$  was near 0.5, the last term in eqs. (13) and (14) significantly reduced the contribution of the polar term. Judging from the trend in Figures 2 and 3 the prediction of the three-dimensional model could be improved by a similar approach. Therefore, Huang and Deanin<sup>18</sup> suggested modifying eq. (8) into the following form:

$$RT \chi_i/V_i = (\delta_{1,d} - \delta_{2,d})^2 + b[(\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,h} - \delta_{2,h})^2] + RT\eta. \quad (15)$$

Here the constant  $b$  modifies the weighting of the polar and hydrogen bonding interactions. Note that in this form the summation of polar and hydrogen bonding components is multiplied by the same constant. One could use a different constant for each term if enough data could justify its use.

After the parameter  $b$  was included eq. (15) became nonlinear and the direct minimization method was used to determine parameters. The results for the solubility parameter components are listed in Table III. It can be seen that when temperature increased both  $\delta_d$  and  $\delta_p$  decreased but  $\delta_h$  increased slightly.  $\delta_h$  was higher than  $\delta_p$  but the difference between  $\delta_p$  and  $\delta_h$  was smaller than that in Table II. The relative values of solubility parameter components were similar to *n*-butyl acetate, which is a structure analogue to PCL. The component values of PCL were higher because it is more condensed than *n*-butyl acetate. This suggested that the new values probably were closer to the



**Figure 3** Plot of  $\chi RT/V_1$  versus  $\Sigma(\delta_1 - \delta_2)^2 + \eta RT$  for PCL at 70 °C. Solid line is  $\Sigma(\delta_1 - \delta_2)^2 + RT\eta$  using parameters in Table II.

**TABLE III**  
Parameters of Three-Dimensional Solubility Parameter Model as in Eq. (15) for PCL between 70 and 110 °C (Units:  $\delta = \text{J}^{0.5}/\text{mol}^{1.5}$ ,  $RT\eta = \text{J}/\text{cm}^3$ , and  $S_R = \text{J}^2/\text{cm}^6$ )

	Temperature (°C)				
	70	80	90	100	110
$\delta$	19.77	19.15	18.73	18.36	18.03
$\delta_d$	18.47	17.80	17.37	16.97	16.59
$\delta_p$	4.24	4.23	3.99	3.93	3.98
$\delta_h$	5.64	5.65	5.76	5.78	5.82
$RT\eta$	-6.80	-5.93	-4.99	-3.60	-3.24
$b$	0.310	0.301	0.294	0.280	0.276
$S_R$	651.8	596.0	579.6	506.2	481.9

true values of PCL than those in Table II. There was also an increase in  $\eta$  and the values now are closer to zero. The sum of error squares is also listed in Table III. From  $S_R$  it can be seen that the agreement with the model was much improved compared to that in Table II. The value of  $b$  was smaller at high temperature. This indicated that at high temperature the effect of polar and hydrogen bonding assumed an even smaller weight. A plot was made to compare  $RT\chi/V_1 - (\delta_{1,d} - \delta_{2,d})^2$  vs.  $(\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,h} - \delta_{2,h})^2$  in Figure 4 for PCL 70 °C. It can be seen that the data exhibited a linear trend and the magnitude of deviation was much smaller compared with Figure 3.

In Figure 4, a sample on the left-hand side of the data had a particularly low value of  $\chi RT/V$ . This solute was identified as chloroform. It has a specific interaction between its hydrogen atom and the esters groups of PCL. This type of interaction accounted for the miscibility of many poly(vinyl chloride) (PVC) blends. Based on the amount of deviation the magnitude of interaction was estimated to be about  $-19 \text{ J}/\text{cm}^3$  or  $-4.5 \text{ cal}/\text{cm}^3$ . This was near the values reported for several polyester-PVC blends.<sup>27,28</sup>

### Confidence interval of solubility parameters

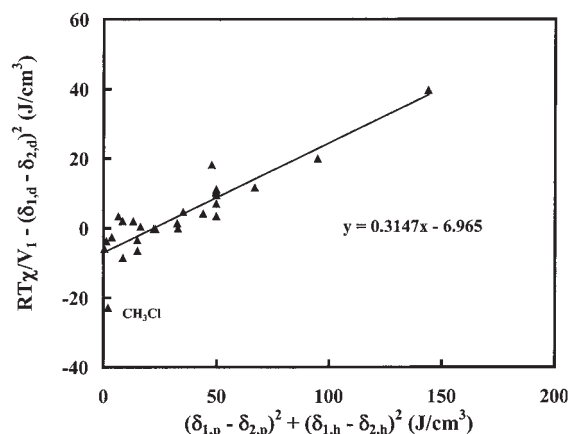
In previous studies a method to examine the confidence interval for the one-dimensional solubility parameter model was discussed.<sup>18,22</sup> The method used a linearized expression for  $S_R$  around the optimum values of parameters. This method can be extended to a three-dimensional situation and is illustrated here using the three-dimensional model with the parameter "b." The joint confidence region was made based on five parameters:  $\delta_{2,d}$ ,  $\delta_{2,p}$ ,  $\delta_{2,h}$ ,  $b$ , and  $RT\eta$ . By using a linearization method around the optimum values of the five parameters, the approximate joint confident contour of eq. (12) can be expressed as a quadratic form using the relative values of  $\delta$ 's,  $b$ , and  $RT\eta$  to their optimum values as the variables,<sup>17,18,29</sup>

$$XAX^T = \sum_i \sum_j A_{ij} X_i X_j = S_R \frac{p}{N-p} F_\alpha(N, N-p), \quad (16)$$

where  $X$  is a vector defined as the deviation of the five parameters from the optimum parameter values [ $\delta_{2,d} - \delta_{2,d0}$ ,  $\delta_{2,p} - \delta_{2,p0}$ ,  $\delta_{2,h} - \delta_{2,h0}$ ,  $b - b_0$ ,  $(\eta - \eta_0)RT$ ],  $A$  is a coefficient matrix,  $S_R$  is the sum of error square calculated at the optimum values of solubility parameter components and  $\eta$  using eq. (12),  $F_\alpha$  is the  $F$  distribution with confidence level  $\alpha$ ,  $p$  is the number of parameters, and  $N$  is the number of samples. For this study  $p = 5$ ,  $N = 27$ , and the  $F_\alpha$  at 90% confidence level was 2.13. The components of the coefficient matrix  $A$  can be determined from the partial differentiation of  $S_R$  with respect to the component of the vector  $X$  using the expression:

$$A_{ij} = (1/2)\partial^2(SS)/\partial x_i \partial x_j. \quad (17)$$

The expressions of the diagonal elements of  $A$  are given in the Appendix. Equation (16) is a canonical form; it represents a hypoelliptic in five dimensions. The value of confidence interval can be determined by a diagonalization process, which turns the matrix  $A$  into a diagonalized matrix.<sup>30</sup> This was demonstrated in the one-dimensional case.<sup>17</sup> When the solubility parameters components of probes were distributed on both sides of these of polymers the cross terms  $A_{ij}$  ( $i \neq j$ ) were small and the correlation between parameters was low. The confidence interval of each parameter could then be approximated as the square root of the ratio between the right-hand side of eq. (16) and the corresponding coefficients of each  $A_{ii}$  term. The results are listed in Table IV. The confidence interval of polar and hydrogen bonding components was higher than the dispersion component despite the former two having higher variances. The effect of higher variances was somewhat reduced because both components were weighted by the factor  $b^2$  as can be seen the formulae in the Appendix. Finally, the confidence interval of  $b$  was small and clearly indicated



**Figure 4** Plot of  $RT\chi/V_1 - (\delta_{1,d} - \delta_{2,d})^2$  vs.  $(\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,h} - \delta_{2,h})^2$  for PCL at 70 °C. Solid line is the linear regression result.

**TABLE VI**  
**90% Confidence Interval for Parameters for Three-Dimensional Solubility Parameter Model as in Eq. (15) of PCL between 70 and 110 °C (Units:  $\delta = \text{J}^{0.5}/\text{mol}^{1.5}$ )**

	Temperature (°C)				
	70	80	90	100	110
$\delta_d$	0.56	0.56	0.58	0.56	0.56
$\delta_p$	1.66	1.65	1.70	1.69	1.68
$\delta_h$	1.14	1.13	1.14	1.12	1.11
$b$	0.073	0.072	0.073	0.069	0.069

that the value of  $b$  was below unity at statistically significant levels. This indicated the importance of using the parameter and supported the use of eq. (15).

#### Estimation of solubility parameters based on probe with lowest $\chi$

A different method to estimate the components of three-dimensional solubility parameters was proposed by Choi et al.<sup>31</sup> Their method took the average of the corresponding components of probes that had negative  $\chi$  in a particular polymer and treated the average as the solubility parameter component of the polymer. The concept behind this procedure was the simple "like dissolves like" argument. Not every polymer produced enough negative interaction parameters for probes. Among the data used in this study only four probes gave a negative interaction parameter at 70 °C. However, the value of  $\chi RT/V$  generally reached a minimum when the probes' solubility parameters were near that of the polymer as can be seen in Figures 3 and 4. Therefore, the averaging method was used to estimate the components. In this study five probes that had the lowest interaction parameter were initially used for averaging and the results are given in Table V. The same five solutes had the lowest  $\chi$  values for all temperatures; they were chloroform, chlorobenzene, 1,1-dichloroethane, trichloroethylene, and benzene. The components of the solubility parameter estimated by this method were lower than those from the results of the nonlinear regression method. Also included in Table V is the averaging result of the lowest 10 solutes. It can be seen that the results of  $\delta_p$  were similar and a small increase in  $\delta_h$  was seen but they were still different from the results by the nonlinear regression method. It appeared that the inclusion of several highly polar and hydrogen bonding solutes in the nonlinear regression method brought a large increase in polar and hydrogen bonding components. The use of solutes with low  $\chi RT/V$  emphasized solutes with properties closer to the polymer while the use of solutes with properties away from the polymer could have an effect in distorting the values of the

parameters because of their large error in fitting a model.

In the past, there were many studies on the determination of solubility parameter components of polymers by different techniques but little was mentioned on the overall data fit of the model when the difference of solubility parameter components between solvents and the polymer increased. The difference could affect the values of parameters of polymers in a model fitting. This study showed that the three-dimensional model in the form of eq. (6) overpredicted the interaction parameter. Despite the difference in eqs. (6) and (15) the success of a three-dimensional solubility parameter model in predicting solubility can be explained in Figures 3 and 4. For systems with small predicted values of  $RT\chi/V_1$  based on eq. (7), they usually correctly gave low values of  $RT\chi/V_1$ . Hence, the prediction of good solvents of polymers was still valid. This explains the widespread use of the three-dimensional model in the literature.

## CONCLUSIONS

The three-dimensional solubility parameter model was used to analyze solution thermodynamic data of several solutes in PCL. The previous method to determine solubility parameter based on direct minimization of the sum of error squares was extended to the three-dimensional model. The results of solubility parameter components of PCL were the same as the linear regression method. The simple three-dimensional model was found to have large error in fitting the model. The error was reduced by using a smaller weight on the polar and hydrogen bonding components. The confidence interval of each parameter was estimated. The solubility parameter components obtained were different from the average values of the five solutes with the smallest  $\chi$ . The inclusion of solutes with high hydrogen bonding components con-

**TABLE V**  
**Solubility Parameter Components of PCL for Temperatures between 70 and 110 °C Determined by the Method of Choi Using Solute with the Smallest  $\chi$  (Units:  $\delta = \text{J}^{0.5}/\text{mol}^{1.5}$ )**

	Temperature (°C)				
	70	80	90	100	110
$\delta$ (5 samples)	17.50	16.97	16.69	16.40	16.10
$\delta_d$ (5 samples)	16.91	16.35	16.07	15.78	15.48
$\delta_p$ (5 samples)	3.60	3.55	3.53	3.50	3.47
$\delta_h$ (5 samples)	2.74	2.81	2.79	2.77	2.75
$\delta$ (10 samples)	17.76	17.21	16.93	16.65	16.36
$\delta_d$ (10 samples)	17.07	16.52	16.24	15.96	15.67
$\delta_p$ (10 samples)	3.46	3.42	3.39	3.37	3.34
$\delta_h$ (10 samples)	3.47	3.38	3.35	3.33	3.30

tributed the increase of the hydrogen bonding component in the nonlinear regression method.

## APPENDIX

### Diagonal elements of coefficient matrix A

$$\begin{aligned} A_{11} &= 4\sum(\delta_{i,d} - \delta_{2,do})^2 \\ A_{22} &= 4\sum(\delta_{i,p} - \delta_{2,po})^2 b^2 \\ A_{33} &= 4\sum(\delta_{i,h} - \delta_{2,ho})^2 b^2 \\ A_{44} &= \sum [(\delta_{i,p} - \delta_{2,po})^2 + (\delta_{i,h} - \delta_{2,ho})^2]^2 \\ A_{55} &= N \end{aligned}$$

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