

# Multiparameter Solution Model and Evaluation of Polymer–Polymer Miscibility Using Inverse Gas Chromatography Data

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**ABSTRACT:** Inverse gas chromatography (IGC) has been widely used to determine the Flory–Huggins parameters,  $\chi$ , between solutes (probes) and polymers. This study correlated the Flory–Huggins parameter data using a multiparameter model, which included dispersion, polarity, acidity, and basicity components. The parameters of poly( $\epsilon$ -caprolactone) (PCL) and polyepichlorohydrin (PECH) were calculated from IGC data using a series of probes. The parameters of the polymers were used to evaluate mutual miscibility between PCL and PECH. The

results predicted miscibility in agreement with the conclusion of an IGC study using blends of PCL and PECH. A method to estimate the confidence interval of polymer parameters was proposed. The anomalous solubility parameter of polymer mixtures previously reported was also explained using this model. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 4085–4091, 2009

**Key words:** inverse gas chromatography; interaction parameter; solubility parameter; acid–base interaction

## INTRODUCTION

The knowledge of the interaction parameters between polymers and solvents is very important in the study of their miscibility and 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.<sup>1–4</sup> In IGC measurement, a known amount of nonvolatile stationary phase is dissolved in a volatile solvent and coated on a porous inert support. In the operation of IGC, a carrier gas is passing through the column continuously. When a liquid probe is injected into the column, the probe vaporizes and flows with the carrier gas, and a characteristic specific retention volume can be measured. Using Flory–Huggins theory,<sup>5</sup> the Flory–Huggins interaction parameter between a polymer and probe,  $\chi$ , can be related to the specific retention volume of probes,  $V_g^0$ , by the following equation<sup>1–4</sup>

$$\chi = \ln\left(\frac{273.16Rv_2}{V_g^0 P_1^0 V_1}\right) - 1 - \frac{P_1^0}{RT}(B_{11} - V_1) \quad (1)$$

where  $R$  is the gas constant,  $T$  the column temperature,  $v_2$  the specific volume of the stationary phase,

and  $P_1^0$ ,  $V_1$ , and  $B_{11}$  are the vapor pressure, the liquid molar volume, and the second virial coefficient of the probe at column temperature, respectively. When  $\chi < 0.5$ , the probe liquid is generally characterized as a good solvent for the polymer, whereas  $\chi > 0.5$  indicates a poor solvent and may lead to phase separation.<sup>5</sup> In the case of a polymer blend, the parameter  $\chi$  can still be defined and the miscibility generally occurs when  $\chi < 0$ , because the high molar volume of both components diminishes the combinatorial entropy.

When a polymer blend is used in an IGC study, the corresponding specific retention volume and density data of blends can be used in eq. (1). The interaction parameter obtained is called  $\chi_{1(23)}$ . Applying the Flory–Huggins equation of polymer solutions<sup>5</sup> to a ternary system with two polymers and one probe, the interaction parameter  $\chi_{1(23)}$  can be related to the difference between pair interactions of probe polymers,  $\chi_{12}$  and  $\chi_{13}$ , and polymer–polymer  $\chi_{23}$ <sup>1–4,6–9</sup>:

$$\chi_{1(23)} = \phi_2 \chi_{12} + \phi_3 \chi_{13} - \phi_2 \phi_3 \chi_{23}' \quad (2)$$

Here  $\phi$  is the volume fraction of the two stationary phases and  $\chi_{23}' = \chi_{23}(V_1/V_2)$ .

Equation (2) was frequently used to study the interaction parameter between two stationary phases using the IGC method. In examining literature data, it was found that, in many miscible systems,<sup>1–4,6–9</sup>  $\chi_{23}'$  values were probe dependent. The values of  $\chi_{23}'$

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were positive when  $\chi_{12}$  and  $\chi_{13}$  were positive, and decreased when  $\chi_{12}$  and  $\chi_{13}$  decreased to negative. Some negative  $\chi_{23}'$  values were generally observed for probes with low  $\chi_{12}$  and  $\chi_{13}$ . This trend caused the slope of the  $\chi_{1(23)}/V_1$  vs.  $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$  plot to deviate slightly from unity.<sup>8,9</sup> It has been pointed out that  $\chi_{23}'$  contains  $V_1$ , which is probe dependent. What the literature referred to is the probe dependency of  $\chi_{23}$  or  $\chi_{23}/V_2$  for a solvent mixture. The comparison of  $\chi_{23}$  or  $\chi_{23}/V_2$  will be more appropriate for studying probe dependency.<sup>8,9</sup> The probe dependency indicated that probing the binary mixtures by a third component might not be a satisfactory method.

### MULTIPARAMETER SOLUTION MODELS

Ideally, one way to avoid the probe dependency of polymer–polymer interaction parameters is to use a binary solution model for the polymer–polymer system to estimate miscibility. By using the same binary solution model to probe–polymer system, the parameters of a polymer could be estimated using IGC data from a series of probes in the polymer. The parameters of two polymers could then predict the miscibility between the two polymers in the absence of the probes. The conclusion of this approach would be closer to probe independent. Many solution models could be used for this purpose.<sup>10,11</sup> One of the early solution models was the Hildebrand regular solution theory. Hildebrand proposed the term “solubility parameter” and the symbol “ $\delta$ ,” which is defined as<sup>10–12</sup>

$$\delta = \left(\frac{\Delta E_{\text{vap}}}{V}\right)^{1/2} \quad (3)$$

where  $\Delta E_{\text{vap}}$  is the energy of vaporization and  $V$  the molar volume of the liquid. 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 the saturated liquid by the Clausius–Clapeyron equation. For polymers the method of DiPaola-Baranyi and Guillet<sup>13,14</sup> was commonly used to estimate the solubility parameter using probes with a range of  $\chi$  values.

Using the Hildebrand–Scatchard equation, the internal energy change of mixing is related to the solubility parameter of two components by the following equation<sup>12</sup>

$$\Delta U = (x_1V_1 + x_2V_2)(\delta_1 - \delta_2)^2\phi_1\phi_2 \quad (4)$$

where  $V$  is the molar volume and  $\phi$  the volume fraction. If there is a specific interaction that produces

negative heat of solution, the value of  $\Delta U$  will be lower than the prediction of eq. (4) and may be negative. In the regular solution, it was assumed that the entropy of solution and excess volume of solution are zero. When a polymer system is considered, the entropy term is determined from the Flory–Huggins combinatorial formula, whereas the enthalpy of solution is represented by the Flory–Huggins interaction parameter,  $\chi$ . The interaction parameter  $\chi$  can be related to the solubility parameters of two components by<sup>13,14</sup>

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 \quad (5)$$

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. The above equation implies that  $\chi$  is always positive. Without a specific interaction, two polymers are generally immiscible. A negative value of  $\chi$  can occur in systems with a specific interaction. One would need a multiparameter solution model, which can include the specific interaction between probe–polymer and polymer–polymer, to obtain an expression for a negative  $\chi$  value. The ultimate goal is to be able to estimate the polymer–polymer interaction parameter using the parameters obtained from the probe–polymer interactions of the two polymers.

There are several types of intermolecular interactions. The Hildebrand solubility parameter model aggregates all interactions into one parameter. The Hansen solubility parameter is a model that extends the one-dimensional solubility parameter model into three dimensions with dispersion, polar, and hydrogen bonding components.<sup>15</sup> Both Hildebrand and Hansen models give a positive value for  $\chi$ . Several studies<sup>16–19</sup> have shown that multidimensional solubility parameter models overpredict  $\chi$ , and there was a need to place a smaller weight on the polar and hydrogen components. In searching the literature, it is noted that the model of Karger et al.<sup>20</sup> can give a negative enthalpy of mixing. Their model considered the cohesive energy as the sum of dispersion, polar, and hydrogen bondings. The expression for the cohesive energy density is

$$E_{\text{vap}}/V = \lambda^2 + \tau^2 + \sigma\tau + \alpha\beta \quad (6)$$

where  $\lambda$  is the dispersion component,  $\tau$  the polar component,  $\sigma$  the polar-induced interaction,  $\alpha$  the acidity, and  $\beta$  the basicity component. The major difference between this model and the Hansen solubility parameter method is that the hydrogen bonding has direction, i.e. an acceptor (acid) and a donor (base). These parameters were derived from several correlations but their total is related to the heat of vaporization or cohesive energy density. Furthermore, for alcohols, the value of  $\alpha$  and  $\beta$  were

assumed to be the same. The expression for the activity coefficient of a solute is<sup>20</sup>

$$\ln \gamma_1^\infty = (V_1/RT)[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 + (\sigma_1 - \sigma_2)(\tau_1 - \tau_2) + (\alpha_1 - \alpha_2)(\beta_1 - \beta_2)] \quad (7)$$

where subscript 1 indicates the solute and 2 indicates the solvent. The expression in the bracket represents the multiparameter form of  $\chi$ . The last two terms make it possible to obtain a negative value for  $\chi$ . When this happens, the system is having some sort of specific interactions. Several modifications<sup>21,22</sup> have been developed based on the model in eq. (7). The polar-induced term is usually not included in these modifications. The expression of Thomas and Eckert<sup>21</sup> has the following form:

$$\ln \gamma_1^\infty = (V_1/RT)[(\lambda_1 - \lambda_2)^2 + q_1^2 q_2^2 (\tau_1 - \tau_2)^2 / \psi_2 + (\alpha_1 - \alpha_2)(\beta_1 - \beta_2) / \xi_2] + d_{12} \quad (8)$$

where subscript 1 indicates the solute and 2 indicates the solvent. Parameters  $\lambda$ ,  $\tau$ ,  $\alpha$ , and  $\beta$  are defined similar to eq. (7). The parameter  $d_{12}$  is the combinatorial part, which is calculated by the Flory-Huggins method with a correction in molar volume. The parameter  $q$  is a measure of the dipole-induced dipole energy. The value of  $q$  is unity for a saturated compound. Its value decreases when the amount of unsaturated bonds increases. A value of 0.9 was given for many aromatic compounds.

Equation (8) also included additional parameters  $\psi_2$  and  $\xi_2$  to take into account the receptor difference between two molecules. Note that the solubility parameter models and eq. (7) predict that  $\chi_1/V_1 = \chi_2/V_2$ , which was not followed in many alkane-alcohol solutions. The purpose of using parameters  $\psi$  and  $\xi$  was to overcome the failure of this symmetric relation. When a solvent has functional groups that can form specific interactions, these functional groups will interact with each other and show less interaction with the solute molecules. The result is that the solute feels the solvent is less polar or interactive. Alcohol is one example where hydrogen bonding is extensive. The mixtures of alcohols and alkanes have been successfully described as a mixture of alkanes and a polymer formed by alcohols connected by hydrogen bonding.<sup>23</sup> When an infinitely small amount of alkane molecule is dissolved in alcohol, the hydrogen bonding could be shielded away from solute molecules. But when an infinitely small amount of alcohol is dissolved in alkane solvents, the hydrogen bonding of alcohol molecules is broken. The result is that the activity coefficients for alcohols in alkanes are higher than alkanes in alcohols. Thomas and Eckert used parameters  $\psi$  and  $\xi$  to account for the asymmetry effect for a polar solvent.

For a nonpolar solvent, they are unity, and for polar solvent the values are higher.

In a more recent study, Eckert et al.<sup>22</sup> proposed the following expression:

$$\ln \gamma_1^\infty = (V_1/RT)[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 + (\alpha_2 - \alpha_{1,\text{eff}})(\beta_2 - \beta_{1,\text{eff}})] + d_{12} \quad (9)$$

The effective parameters  $\alpha_{1,\text{eff}}$  and  $\beta_{1,\text{eff}}$  are modified from  $\alpha_1$  and  $\beta_1$ , respectively, to account for the asymmetric effect of solutes. This again relates to the fact that the functional groups of solvents can interact with each other before interacting with the solute molecules. This is more important for highly associated solvents, such as alcohols as mentioned above. In the study of Eckert et al.,<sup>22</sup> the parameters of solutes are established from spectroscopic method and the values of  $\alpha$  and  $\beta$  are no longer equal for alcohols.

#### PARAMETERS OF PCL AND PECH

Tian and Munk<sup>24</sup> reported an extensive measurement of interaction parameters for several polymers over a wide temperature range using more than 40 probes. In that study, the specific retention volumes of the polymers were reported for temperatures between 70 and 110°C and interaction parameters were determined from the IGC method using eq. (1). Among them, the combination of poly( $\epsilon$ -caprolactone) (PCL) and polyepichlorohydrin (PECH) was particularly interesting because their mixture was separately studied and concluded to be miscible.<sup>25</sup> A table of polarity, acidity, and basicity components was available from Eckert et al.,<sup>22</sup> which enabled the use of eq. (9). The dispersion component was calculated by the correlation methods given by Thomas and Eckert.<sup>21,22</sup> The probes whose parameters are available are listed in Table I. In this study, it is assumed that the polymer stationary phase is not as interactive as alcohols and that  $\alpha_{1,\text{eff}}$  and  $\beta_{1,\text{eff}}$  can be treated as constants of the polymers for all the probes used. From eq. (9), the interaction parameter can be written as

$$\chi RT/V_1 = (\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 + (\alpha_1 - \alpha_2)(\beta_1 - \beta_2) \quad (10)$$

This equation is a simplified form of eqs. (8) and (9) for solvents that are not highly associated. For each polymer, there are four parameters:  $\lambda_2$ ,  $\tau_2$ ,  $\alpha_2$ , and  $\beta_2$ . These parameters were determined by minimization of the square of error in the prediction of  $\chi RT/V_1$ . The sum of error square is defined as

$$SS = \sum [\chi RT/V_1 - (\lambda_1 - \lambda_2)^2 - (\tau_1 - \tau_2)^2 - (\alpha_1 - \alpha_2)(\beta_1 - \beta_2)]^2 \quad (11)$$

**TABLE I**  
Parameters of Probes. Units = Cal<sup>0.5</sup>/cm<sup>1.5</sup>

Solutes	$\lambda$	$\tau$	$\alpha$	$\beta$
Heptane	7.81	0.072	0	0
Octane	7.91	0.048	0	0
Nonane	8.00	0.04	0	0
Decane	8.07	0.032	0	0
Benzene	8.49	1.96	0	0.458
Toluene	8.45	1.59	0	0.425
Ethylbenzene	8.49	1.45	0	0.401
Methylene chloride	8.20	2.75	2.77	0
Chloroform	8.43	2.04	2.861	0
Carbon tetrachloride	8.58	1.12	0	0
Butyl chloride	7.96	1.47	0	0.199
Chlorobenzene	8.71	1.93	0	0.444
Acetone	7.49	2.95	0.594	1.86
Methyl ethyl ketone	7.71	2.62	0.488	1.695
Tetrahydrofuran	8.02	2.06	0	1.902
1,4 -Dioxane	8.08	3.01	0	1.749
Methyl acetate	7.52	3.13	0	1.331
Ethyl acetate	7.64	2.58	0	1.216
<i>n</i> -Butyl acetate	7.96	1.85	0	1.047
Ethanol	7.51	0.435	5.882	1.912
Propanol	7.79	0.321	5.216	1.689
Butanol	7.93	0.146	4.716	1.527

where the summation runs through all the probes. In the process the values of the parameters were changed by 0.01 each time and the sum of square of error was compared until the minimum was reached. This is similar to the process of determination of multiparameter solubility parameter in previous papers.<sup>18,19</sup> The parameters of PCL and PECH are listed in Table II. It can be seen that PECH has slightly higher dispersion and polar component than PCL. PCL has more basicity than acidity, while PECH has more acidity than basicity. These opposite properties provide interaction between the two polymers and make them miscible. It is also noted that PECH has some basicity in addition to acidity. When a polymer contains several functional groups, it is expected that the characteristics of each type of functional group will be retained in the polymer. For PCL, it contains only the ester group besides methylene units. It can be seen that the ester group provides only basicity but no acidity component as compared with the ester probes in Table I. For PECH, it contains chlorinated hydrocarbon and ether. The former, similar to methylene chloride and

**TABLE II**  
Parameters of PECH and PCL at 90°C

Parameters	PCL	PECH
$\lambda$ (cal <sup>0.5</sup> /cm <sup>1.5</sup> )	9.1	9.5
$\tau$ (cal <sup>0.5</sup> /cm <sup>1.5</sup> )	2.1	2.4
$\alpha$ (cal <sup>0.5</sup> /cm <sup>1.5</sup> )	0	1.6
$\beta$ (cal <sup>0.5</sup> /cm <sup>1.5</sup> )	1.2	0.4
$S_R$ (cal/cm <sup>3</sup> )	13.1	21.4

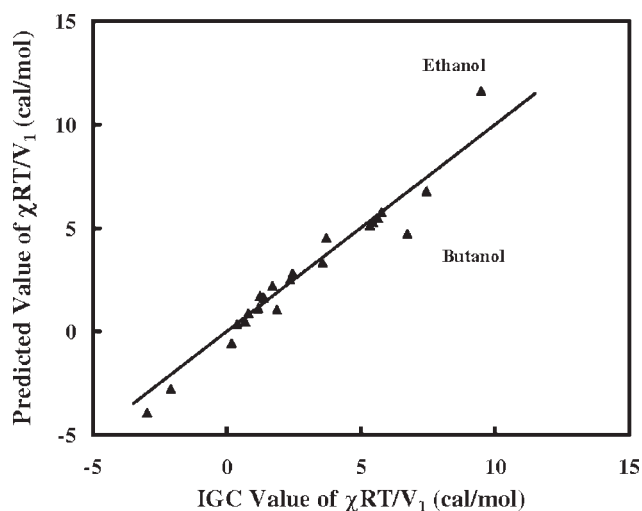
**TABLE III**  
Covariances Between Parameters of Solutes

	$\lambda$	$\tau$	$\alpha$	$\beta$
$\lambda$	1.00	-0.02	-0.25	-0.59
$\tau$	-0.02	1.00	-0.30	0.34
$\alpha$	-0.25	-0.30	1.00	0.35
$\beta$	-0.59	0.34	0.35	1.00

chloroform in Table I, provides acidity, whereas the ether group provides basicity.

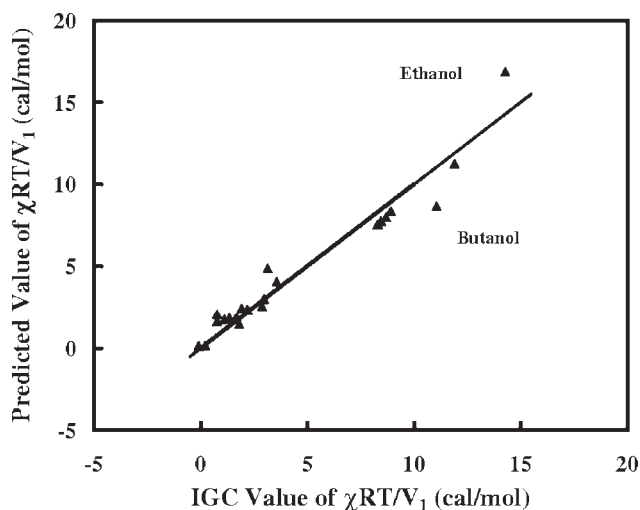
Note that eq. (10) can be written with only  $\chi$  on the left-hand side and  $V_1/RT$  multiplying the right-hand side. The results of the minimization gave parameters very near that in Table II. In a regression study of data, it is possible that more than one objective function could be used. The best objective function would be the one that has wide variation and small correlation between the independent variables. Huang<sup>19</sup> has noted the importance of using probes with a wide range of properties to lower the confidence interval in the estimation of the solubility parameters of polymers. In another study, Huang<sup>26</sup> also noted that parameters of many organic molecules were not varied independently, which might affect the conclusion about the dependency of solution properties on probe parameters. The covariances of the four parameters of solutes are shown in Table III. It can be seen that the covariances between parameters were low. The only pair with absolute value higher than 0.5 was between  $\tau$  and  $\beta$ , which was -0.59. All other pairs had correlations below 0.4.

For comparison, the plot of predicted values of  $\chi$  vs. the values of Tian and Munk<sup>24</sup> are shown in Figures 1 and 2 for PCL and PECH, respectively. It can be seen that the correlation was good for most



**Figure 1** Plot of calculated values of  $\chi RT/V_1$  from IGC vs. predicted values for PCL at 90°C. Solid line indicates perfect prediction.





**Figure 2** Plot of calculated values of  $\chi RT/V_1$  from IGC vs. predicted values for PECH at 90°C. Solid line indicates perfect prediction.

probes. Two probes had more deviation in Figures 1 and 2. They were ethanol and butanol. Alcohols seemed to have a separate trend with a slope higher than unity. Between each member of the alcohols, the difference in predicted values was higher than the experimental value. Similar results were also observed in Figure 2. This suggested that there might be some room for adjusting parameters for alcohols in Table I. With parameters for the two polymers, the interaction parameters between the two polymers can be estimated as

$$\chi_{ab}RT/V = (\lambda_a - \lambda_b)^2 + (\tau_a - \tau_b)^2 + (\alpha_a - \alpha_b)(\beta_a - \beta_b) \quad (12)$$

This quantity alone can be used to estimate their miscibility because the combinatory entropy for the polymer mixture is small. Note that in eq. (12), the value of  $\chi_{ab}/V$  is taken as a single value because the molar volume of the polymer is not known but the ratio  $\chi_{ab}/V$  is treated as a parameter. The value of  $\chi_{ab}RT/V$  is the interaction energy per unit volume. By using the parameters of the two polymers, the value of  $\chi_{ab}RT/V$  was calculated to be  $-1.0 \text{ cal/cm}^3$ , which indicated that the two polymers should be miscible. In this study and the study based on IGC study using blends,<sup>25</sup> PCL and PECH are concluded to be miscible.

#### CONFIDENCE INTERVAL OF PARAMETERS

In previous studies, a method to examine the confidence interval for parameters of a nonlinear multi-parameter model was discussed.<sup>18,26,27</sup> The method used a linearized expression for SS around the optimum values of the parameters. In this study, this method was applied to eq. (11). The joint confidence

region was made based on four parameters:  $\lambda_2$ ,  $\tau_2$ ,  $\alpha_2$ , and  $\beta_2$ . By using a linearization method around the optimum values of the four parameters, the approximate joint confident contour of eq. (12) can be expressed as a quadratic form using the relative values of parameters to their optimum values as the variables<sup>18,27,28</sup>:

$$XAX^T = \sum_i \sum_j A_{ij} X_i X_j = S_R \frac{p}{N-p} F_\alpha(N, N-p) \quad (13)$$

where  $X$  is a vector defined as the deviation of the four parameters from the optimum parameter values [ $\lambda_2 - \lambda_{2,o}$ ,  $\tau_2 - \tau_{2,o}$ ,  $\alpha_2 - \alpha_{2,o}$ ,  $\beta_2 - \beta_{2,o}$ ],  $A$  is a coefficient matrix,  $S_R$  is the sum of error square calculated at the optimum values of solubility parameter components using eq. (11),  $F_\alpha$  is the  $F$  distribution with confidence level  $\alpha$ ,  $p$  is the number of parameters, and  $N$  is the number of samples. For this study,  $p = 4$ ,  $N = 22$ , and the  $F_\alpha$  at 90% confidence level was 2.22. The components of the coefficient matrix  $A$  can be determined from the partial differentiation of SS with respect to the component of the vector  $X$  using the following expression

$$A_{ij} = (1/2) \partial^2(SS) / \partial x_i \partial x_j \quad (14)$$

The expressions of the diagonal elements of  $A$  are given in the Appendix. Equation (13) is a canonical form; it represents a hypoelliptic in four dimensions. The value of confidence interval (CI) can be determined by a diagonalization process, which turns the matrix  $A$  into a diagonalized matrix. This was demonstrated in the one-dimensional case.<sup>27</sup> When the solubility parameters components of probes were distributed on both sides of these 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. (13) and the corresponding coefficients of each  $A_{ii}$  term. The results are listed in Table IV. It can be seen that the confidence intervals of  $\alpha$  and  $\beta$  were wider than the dispersion and polar components. The basicity parameter had a much wider CI than basicity. This was because, in eq. (10), the acid and base parameters were multiplied together. An accurate determination of acid parameter required a

**TABLE IV**  
90% Confidence Interval (CI) of Parameters of PECH and PCL at 90°C

CI of Parameters	PCL	PECH
$\lambda$ (cal <sup>0.5</sup> /cm <sup>1.5</sup> )	0.24	0.23
$\tau$ (cal <sup>0.5</sup> /cm <sup>1.5</sup> )	0.22	0.25
$\alpha$ (cal <sup>0.5</sup> /cm <sup>1.5</sup> )	0.64	0.81
$\beta$ (cal <sup>0.5</sup> /cm <sup>1.5</sup> )	0.25	0.35

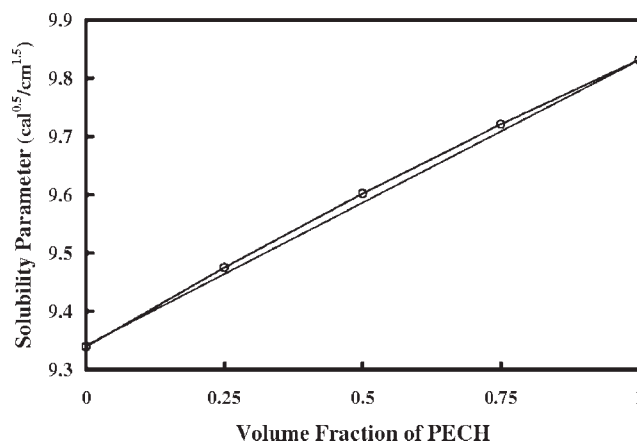
selection of base probes with wide range of basicity, and vice versa for basic parameter. The alcohol probes provided high acidity but their basicity was similar to the strength of esters. The variance of  $\beta$  was small compared with  $\alpha$ . Finally, the difference ( $\alpha_a - \alpha_b$ ) and ( $\beta_a - \beta_b$ ) between PCL and PECH were different from zero at a statistically significant level, and provided a negative value of  $-0.64 \text{ cal/cm}^3$  for  $(\alpha_a - \alpha_b)(\beta_a - \beta_b)$ . This indicated the acid–base interaction in eq. (10) provides a source of miscibility.

### EXPLANATION OF ANOMALOUS SOLUBILITY PARAMETER OF POLYMER MIXTURES

In recent articles,<sup>29,30</sup> it was shown that using the method of DiPaola-Baranyi and Guillet, the solubility parameters of polymer miscible mixtures were lower than the prediction of the regular solution model. If there were a specific interaction that produced negative enthalpy of solution, the solubility parameter of the mixture would be higher than the volume average to account for the separation of the additional specific interaction of the mixtures in the vaporization process. However, the solubility parameters calculated using IGC data of blends turned out to be lower than the volume average. This led to a conclusion that when specific interactions occur between two polymers the probes have less probability to contact the functional groups of the polymers, leading to a lower apparent solubility parameter for the polymer mixture in IGC measurement. The solubility parameter of the mixtures measured by the IGC method also reflects the change in the interaction between the probe and the polymer mixtures. It can no longer be related only to the cohesive energy density by eq. (3). The increase of solubility parameter of blends can be demonstrated using the multiparameter model for PCL and PECH. The true cohesive energy density of a polymer mixture still contains four components: dispersion, polarity, acidity, and basicity components. A first approximation is that they can be added up by the volume fraction. From these mixture properties, the cohesive energy density was estimated using the following expression

$$\delta^2 = \left(\frac{\Delta E_{\text{vap}}}{V}\right) = \lambda_m^2 + \tau_m^2 + \alpha_m \beta_m \quad (15)$$

The plot of  $\delta$  vs. the volume fraction of PCL for PCL–PECH mixtures is shown in Figure 3. It can be seen that the calculated solubility parameter now has a positive deviation from the linear rule. This plot showed the variation of solubility parameter of polymer mixtures based on the cohesive energy calculation. It was different from the IGC measurement of the polymer mixture, which has negative deviation.<sup>29</sup> From the above comparison, it could be concluded



**Figure 3** Plot of calculated values of solubility parameter of PCL–PECH system vs. volume fraction at 90°C. The linear line is the volume average.

that the interaction between acidity and basicity of the two polymers not only brings the polymer into a miscible system, but also creates a negative deviation in polymer solubility parameter and probe-dependent interaction parameter in an IGC study.

### CONCLUSIONS

The interaction between probes and a polymer is usually represented by the values of the Flory–Huggins interaction parameters,  $\chi$ , and analyzed through the solubility parameters of the polymer and probes. This study correlated the Flory–Huggins parameter using a multiparameter model, which included dispersion, polarity, acidity, and basicity components. The parameters of PCL and PECH were obtained from IGC data using a series of probes. The parameters of the polymers were then used to evaluate miscibility. The results predicted them to be miscible in agreement with other evidences. The anomalous solubility parameter of polymer mixtures measured by IGC method could be explained through this model.

### APPENDIX: DIAGONAL ELEMENTS OF COEFFICIENT MATRIX A

$$A_{11} = 4\Sigma(\lambda_2 - \lambda_{2o})^2$$

$$A_{22} = 4\Sigma(\tau_2 - \tau_{2o})^2$$

$$A_{33} = \Sigma(\beta_2 - \beta_{2o})^2$$

$$A_{44} = \Sigma(\alpha_2 - \alpha_{2o})^2$$

### References

- Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley: New York, 1979.
- Lloyd, D. R.; Ward, T. C.; Schreiber, H. P., Eds. *Inverse Gas Chromatography: Characterisation of Polymers and Other*

- Materials (ACS Symposium Series, No. 391); American Chemical Society: Washington DC, 1989.
- Al-Saigh, Z. Y.; Guillet, J. E. In *Encyclopedia of Analytical Chemistry: Instrumentation and Applications*; Meyers, R., Ed; Wiley: Chichester, 2000; p 7759.
  - Vilcu, R.; Leca, M. *Polymer Thermodynamics by Gas Chromatography* (transl. V. Vasilescu); Elsevier: Amsterdam, 1990.
  - Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1953.
  - Deshpande, D. D.; Patterson, D.; Schreiber, H. P.; Su, C. S. *Macromolecules* 1974, 7, 530.
  - Su, C. S.; Patterson, D.; Schreiber, H. P. *J Appl Polym Sci* 1976, 20, 1025.
  - Huang, J. C. *J Appl Polym Sci* 2003, 89, 1242.
  - Huang, J. C. *J Appl Polym Sci* 2003, 90, 671.
  - Null, H. R. *Phase Equilibrium in Process Design*; Wiley: New York, 1970.
  - Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; 4th ed.; McGraw-Hill: New York, 1987.
  - Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand Reinhold Co.: New York, 1970.
  - Dipaola-Baranyi, G.; Guillet, J. E. *Macromolecules* 1978, 11, 228.
  - Ito, K.; Guillet, J. E. *Macromolecules* 1979, 12, 1163.
  - Hansen, C. M. *J Paint Technol* 1967, 39, 104.
  - Weimer, R. F.; Prausnitz, J. M. *Hydrocarbon Process* 1965, 44, 237.
  - Helpinstill, J. G.; Van Winkle, M. *Ind Eng Chem Proc Des Dev* 1968, 7, 213.
  - Huang, J. C.; Deanin, R. D. *Fluid Phase Equilib* 2005, 227, 125.
  - Huang, J. C.; Lin, K. T.; Deanin, R. D. *J Appl Polym Sci* 2006, 100, 2002.
  - Keller, R. A.; Karger, B. L.; Synder, L. R. *Gas Chromatography, Proceedings of the International Symposium on Gas Chromatography*; 1970; 125.
  - Thomas, E. R.; Eckert, C. A. *Ind Eng Chem Proc Des Dev* 1984, 23, 194.
  - Hait, M. J.; Liotta, C. L.; Eckert, C. A.; Bergmann, D. L.; Karachewski, A. M.; Dallas, A. J.; Deikens, D. L.; Li, J. J.; Carr, P. W.; Poe, R. B.; Rutan, S. C. *Ind Eng Chem Res* 1993, 32, 2905.
  - Chen, S. A.; Bagley, E. B. *Chem Eng Sci* 1978, 33, 153.
  - Tian, M.; Munk, P. J. *Chem Eng Data* 1994, 39, 742.
  - El-Hibri, M. J.; Cheng, W.; Munk, P. *Macromolecules* 1988, 21, 3458.
  - Huang, J. C. *Fluid Phase Equilib* 2005, 237, 186.
  - Huang, J. C. *J Appl Polym Sci* 2004, 91, 2894.
  - Draper, N. R.; Smith, H. *Applied Regression Analysis*; 2nd ed.; John Wiley & Sons: New York, 1981.
  - Huang, J. C. *Eur Polym J* 2006, 42, 1000.
  - Huang, J. C. *J Appl Polym Sci* 2007, 106, 4110.