A Study of Mixtures of Poly(hydroxy ether of bisphenol A) and Poly(ϵ-caprolactone) by Inverse Gas Chromatography

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ABSTRACT: Inverse gas chromatography (IGC) has been used to calculate polymer–polymer interaction parameters and interaction energy densities in blends of poly(hydroxy ether of bisphenol A) (Phenoxy resin or PH) and poly(ϵ-caprolactone) (PCL). These parameters have been evaluated at three different compositions and a temperature range between 130 and 160 °C from the Scott–Flory–Huggins formalism showing, in all cases, a marked dependence on the probes used. Two data analysis methods have been used, in an attempt to avoid the influence of the probe on the values of the interaction magnitudes. In both methods this influence has been clearly reduced and the trends in the resulting values are quite similar. Both methods give negative values of the polymer–polymer interaction parameter for all compositions and temperatures studied, reflecting the miscibility of the PH/PCL system due to hydrogen-bonding interactions. The values of the experimental interaction parameters obtained from these two methods agree with simulated data resulting from the application of the Coleman, Painter, and co-workers association model and all are in good agreement with the value of the interaction parameter derived from previous melting point depression studies.

Introduction

It has been clearly demonstrated that inverse gas chromatography (IGC) can give, after careful data analysis, such information on polymeric systems as solubility parameters,[1] diffusion coefficients,[2,3] glass transition temperatures,[4] melting temperatures,[5] and interaction parameters.[6–8]

This technique allows the interactions between a polymer blend and a volatile probe injected in extremely low quantities (with respect to the total amount of polymer introduced in the chromatographic column) to be investigated. After adequate data analysis, it gives the polymer–polymer interaction parameter χ_{23}, which is a measure of the thermodynamic miscibility of the two polymers constituting the blend. In addition, when the degree of interaction between two polymers in a blend is being studied, it should depend on the structure of the polymers involved, but not on the nature of the probe injected, which has been found to occur in the majority of the chromatographic investigations of polymer–polymer miscibility. To solve this problem, a number of different methods have been proposed to obtain the true polymer–polymer interaction parameter from measurements of ternary systems (probe–polymer–polymer).

The present work will apply the methods of Prolongo et al.[9] and Farooque and Deshpande[10] to a mixture of poly(hydroxy ether of bisphenol A) (Phenoxy resin, PH, component 2) and poly(ϵ-caprolactone) (PCL, component 3) in the range of temperatures between 130 and 160 °C.

From melting point depression (mpd) studies, it has been found that the PH/PCL system is miscible in all proportions in the melt.[11,12] The value of the so-called interaction energy density (B_{23}) obtained for this blend using this method is close to −2 cal/cm^3. The miscibility is attributed to an intermolecular interaction between the PCL carbonyl group and the Phenoxy hydroxyl group which has been probed by FTIR spectroscopy.[13] The value found for B_{23} and the results obtained by FTIR spectroscopy demonstrate that this interaction is not very strong, although it is enough to be detected by IGC.

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Table 1. Molecular Weight of the Blend Components

polymer	source	M_w	M_n
Phenoxy	Union Carbide (PKHH)	50 700	18 000
PCL	Polysciences, Inc.	17 600	10 800

The main objective of this work was to apply the methods of data analysis mentioned above, in order to obtain a probe-independent interaction parameter for the system. We will compare them with those obtained by the melting point depression method and with the predictions of a recent theoretical association model,[14,15] explicitly designed for application to polymer blends with specific interactions. This model allows us to simulate the relationship between the free energy change upon mixing, ΔG_M, and the temperature and composition, from which other thermodynamic quantities can be derived (interaction parameters, heats of mixing, excess heat capacities, phase diagrams, etc.).

Experimental Section

Materials and Procedures. The Phenoxy resin was purchased from Quimidroga and corresponds to Union Carbide PKHH product. The PCL was supplied by Polyscience. These polymers were purified by solution–precipitation, the solvent–nonsolvent system employed being tetrahydrofuran–hexane. Table 1 summarizes the molecular weight characteristics of the polymers used in this work which have been obtained by GPC, using Mark–Houwink coefficients measured for these polymers.[16,17]

Five chromatographic columns were prepared using a 1 m long $^1/_4$ in. o.d. stainless-steel tube. The columns were washed with diluted nitric acid and prepared in the usual manner. After dissolving known weights of PH and PCL in THF, a specific amount of the support Chromosorb G (AW-DMCS treated, 80/100 mesh) was added to obtain the degree of coating required. The resulting load of the blend on each column was 10%. The solvent was evaporated slowly and finally dried in a vacuum oven for ca. 48 h at 50 °C. The coated support was packed into the column by applying vacuum to one end. The column ends were plugged with glass wool. The relative concentration of the polymer on the support was assumed to be identical to that in the original solution.

Table 2 describes the columns used in this work. Columns were conditioned at temperatures above the T_g of the polymers for ca. 48 h prior to use, while being purged with nitrogen gas. Probes were injected onto the columns containing a small amount

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Table 2. Description of the Chromatographic Columns for the PH/PCL System

column	wt of support, g	PCL, g	PH, g	g of polym
0/100	5.399	0.600	0.000	0.590
25/75	5.400	0.450	0.150	0.591
50/50	5.400	0.300	0.300	0.589
75/25	5.399	0.150	0.450	0.585
100/0	5.397	0.000	0.600	0.582

of a marker (methane) with a 10-μL Hamilton syringe. Three consecutive injections were made for each probe for each set of measurements.

The retention times of the probes were measured by using a modified Sygma 300 Perkin-Elmer gas chromatograph equipped with a flame ionization detector. Nitrogen was used as the carrier gas. Methane was used as a noninteracting marker to correct the dead volume in the column and the retention time was measured directly with the aid of an Olivetti M-24 microcomputer, equipped with a CHROM + card and appropriate software.

Pressures at the inlet and outlet of the column, read from a mercury manometer, were used to calculate corrected retention volumes by the usual procedures. Flow rates were measured at the end of the column with a soap bubble flowmeter.

Results and Discussion

The probe specific retention volumes V_g corrected to 0 °C are commonly used to describe the elution behavior of probes and are defined as

$$V_g^\circ = \Delta t \frac{F}{W} \frac{273.16}{T_r} \frac{3}{2}\left[\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right] \quad (1)$$

where $\Delta t = t_p - t_m$ is the difference between the retention time of the probe t_p and that of the marker t_m, F is the flow rate of the carrier gas measured at room temperature T_r, W is the mass of the stationary phase, and P_i and P_o are the inlet and outlet pressures respectively.

By combination of the Flory–Huggins theory with routine chromatographic calculations, the expression for the residual free energy parameter of binary interaction χ_{1i} applicable for polymers having high molecular weight can be written as[18,19]

$$\chi_{1i} = \ln \frac{273.16 R v_i}{V_g^\circ V_1 P_1^\circ} - 1 - \frac{B_{11} - V_1}{RT} P_1^\circ \quad (2)$$

where R is the universal gas constant, v_i is the specific volume of polymer i, and V_1, B_{11}, and P_1° are respectively the molar volume, the second virial coefficient, and the vapor pressure of the probe at the experimental temperature T.

If a binary polymer blend is used as a stationary phase in a chromatographic column, the interaction parameter between the polymer–polymer pair χ_{23}, can readily be derived from the following equation[20]

$$\chi_{1(23)} = \ln \frac{273.16 R(w_2 v_2 + w_3 v_3)}{V_g^\circ V_1 P_1^\circ} - 1 - \frac{B_{11} - V_1}{RT} P_1^\circ = \left[\left(\frac{\chi_{12}}{V_1}\right)\phi_2 + \left(\frac{\chi_{13}}{V_1}\right)\phi_3 - \left(\frac{\chi_{23}}{V_2}\right)\phi_2\phi_3\right] V_1 \quad (3)$$

where $\chi_{1(23)}$ is the probe–polymer–polymer interaction parameter and w_2 and w_3 and ϕ_2 and ϕ_3 are the weight and volume fractions of the polymers in the blend, respectively.

By study of the columns under experimentally identical conditions of temperature, carrier gas flow rate, and inlet pressure of the carrier gas and use of the same solutes, auxiliary parameters such as P_1°, T, V_1, v_2, v_3, and B_{11} can be eliminated by combining eq 2 applied to the two homopolymers and eq 3 applied to their blends[21]

$$\chi'_{23} = \left[\ln\left(\frac{V_g^\circ}{w_2 v_2 + w_3 v_3}\right) - \phi_2 \ln\left(\frac{V_{g2}^\circ}{v_2}\right) - \phi_3 \ln\left(\frac{V_{g3}^\circ}{v_3}\right)\right]/\phi_2\phi_3 \quad (4)$$

where V_{g2}°, V_{g3}°, and V_g° are the solute specific retention volumes in each column and χ'_{23} is defined as the apparent polymer–polymer interaction parameter referred to the solvent molecule $\chi'_{23} = V_1\chi_{23}/V_2$.

The highest temperature studied was 160 °C due to the thermal instability of PCL at high temperatures, and the lowest (130 °C) was limited by nonequilibrium effects. PCL was heated at 140 °C and kept at that temperature for several days without any significant depolymerization being observed. In Figure 1, the variation of $V_g^\circ{}_{PCL}$ is plotted versus time at which the PCL column has been maintained at 140 °C. If PCL suffered degradation, Figure 1 would show a pronounced decay of $V_g^\circ{}_{PCL}$ with time which does not appear in the study presented in this paper.

Before the study of our system began, several tests were made in order to choose appropriate probes for injection. Initially, columns of pure components were prepared and measured at 135 °C. From 19 probes injected, only 9 were finally selected according to certain criteria. The first criterion was to choose probes with $V_g^\circ{}_{PCL} - V_g^\circ{}_{PH} = \Delta V_g^\circ$ higher than 7 mL/g, because probes with low values of ΔV_g° would give values of χ'_{23} subject to very large error. The second was to select probes with a variety of a chemical structures and polarities. In cases where several members of the same organic family could be used, the most appropriate probe was chosen. For example, in the alkane family *n*-decane was the probe selected. *n*-dodecane gave too high V_g° values, leading to tedious experiments, while in *n*-nonane the error commited when the χ'_{23} parameter is obtained would be higher due to a smaller value of ΔV_g°.

Table 3 summarizes the binary interaction parameters χ_{1i}, the ternary interaction parameters $\chi_{1(23)}$, and the polymer–polymer interaction parameter χ'_{23} for several solutes probing the PH/PCL system at 150 °C. When the hard-core parameters of Flory's equation of state are utilized, χ_{1i}^*, $\chi_{1(23)}^*$, and χ'^*_{23} are obtained.

It can be noticed that the values of χ'_{23} and χ'^*_{23} calculated using eq 4 are almost the same for all the compositions at each temperature. From Table 3, it is quite clear that the polymer–polymer interaction parameters exhibit a marked dependence on the probes, which is the main problem encountered with the IGC technique. This dependence could be due to the different reference volume chosen in the data treatment for obtaining χ'_{23}. Considering the χ_{23} values which are referred to the molar volume of the repeat unit of the PH, the observed tendency is similar. Consequently, this dependence on the probe injected is real and not only due to the experimental error[21] inherent to the technique employed. Henceforward, with the purpose of avoiding the problem of the reference volume, the results will be given in the form of the interaction energy density which is defined as

$$B_{23} = \left(\frac{\chi_{23}}{V_2}\right) RT \quad (5)$$

In addition, the use of B_{23} makes the comparison of the values obtained from the different methods employed here easier.

The Farooque–Deshpande Method. Several authors have attempted to solve the problem of the variation of B_{23} with the vapor probes injected. Farooque and Deshpande[10] tried to develop a method to evaluate the probe-

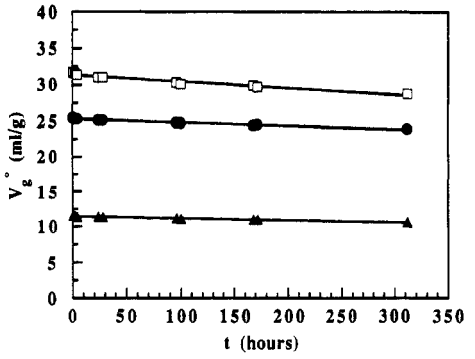

Figure 1. Time dependence of the specific retention volume (V_g°) of PCL at 140 °C for several probes: dioxane (□); 1,2-dichloroethane (●); ethyl acetate (▲).

independent interaction parameter. The method uses the equation

$$\frac{\chi_{1(23)} - \chi_{13}}{V_1} = \phi_2\left[\frac{\chi_{12} - \chi_{13}}{V_1}\right] - \left[\frac{\chi_{23}}{V_2}\right]\phi_2\phi_3 \qquad (6)$$

which is obtained by rearranging eq 3. By plotting $\chi_{1(23)} - \chi_{13}/V_1$ versus $\chi_{12} - \chi_{13}/V_1$, the interaction parameter of the blend, χ_{23}/V_2, is obtained from the intercept.

From the slope, a volume fraction ϕ_2 is obtained which is not the initial composition of the blend. Farooque and Deshpande do not give a physical meaning of this ϕ_2, but following the reasoning proposed by Shi and Schreiber[22] and Etxeberria et al.,[23] ϕ_2 could be considered as the effective blend composition on the column which, as mentioned before, is different from the bulk composition originally prepared. This behavior occurs due to the effect of nonrandom partitioning of the vapor probe into the blend. Following the Farooque–Deshpande treatment, the resultant effective composition is enriched in PCL for all compositions and temperatures studied. This indicates that the solvents interact more with PCL. Table 3 shows that χ_{13} is in all the cases lower than χ_{12}, consistent with this conclusion.

Figure 2 shows a typical plot after applying the method proposed by Farooque and Desphande. To obtain the true interaction parameter with this type of extrapolation, it is convenient to use probes having a wide range of values of $\chi_{12} - \chi_{13}$. This is possible, as mentioned before, working with probes of chemically different natures and polarities. Figure 2 shows a good correlation of the data. However, this success must be treated with caution, since the confidence intervals[24] in the resultant intercepts are around 50%. This behavior has already been found to occur in other blends. In our opinion this good linearity is due only to the small contribution of the χ_{23}/V_2 term to eq 6.

The energy density parameters obtained using this method at several temperatures for three compositions are shown in Table 4. The values of B_{23} are close to −2 cal/cm^3. For compositions of PH/PCL 25/75 and 75/25

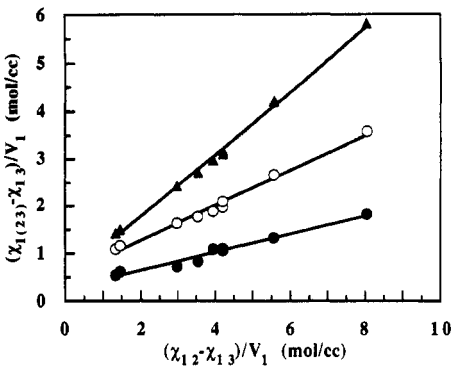

Figure 2. $(\chi_{1(23)} - \chi_{13})/V_1$ vs $(\chi_{12} - \chi_{13})/V_1$ for the PH/PCL system, employing the Farooque–Deshpande method for several blend compositions at 140 °C: 25/75 (●); 50/50 (○); 75/25 (▲).

Table 4. Interaction Energy Densities B_{23} (cal/cm^3) for PH/PCL Blends at Several Temperatures and Various Weight Fractions of PH According to the Methods of Farooque–Deshpande and Prolongo et al.

	by Farooque–Deshpande			by Prolongo et al.		
T (°C)	25% PH	50% PH	75% PH	25% PH	50% PH	75% PH
130	−1.16	−1.78	−1.47	−1.78	−2.72	−2.60
140	−1.37	−1.83	−1.66	−1.63	−2.55	−2.77
150	−1.80	−1.57	−2.17	−2.24	−2.26	−3.70
160	−2.68	−1.62	−2.31	−2.76	−2.26	−3.84

on weight, the value of B_{23} decreases when the temperature is increased, i.e., it becomes more favorable in terms of miscibility, while B_{23} for the 50/50 sample barely changes with temperature.

The Method of Prolongo et al. Prolongo et al.[9] have pointed out that the observed solvent dependence of χ_{23} is largely due to the approximation made in considering the Gibbs mixing function for a ternary polymer–polymer–probe system as additive. The method used here avoids this approximation and yields a value of χ_{23}^* almost independent of the probe injected. The asterisk refers to the fact that the interaction parameter is calculated in the framework of the equation-of-state theory using the characteristic parameters (V^*, P^*, T^*) of the pure components. In this case the volume fraction ϕ_i is redefined as the segment fraction of polymer i, using the surface to volume ratio s_i. Values of the different equation-of-state parameters of the pure components and the probes have been calculated from densities, thermal expansion coefficients, and isothermal compressibilities previously reported.[25-28]

By deriving the expression for the noncombinatorial part of ΔG_M for a ternary system, written according to Flory's equation-of-state theory, eq 7 can be obtained for the extreme case of $\phi_1 \to 0$. This equation can be used to determine the relation χ_{23}^{*T}/V_2^* which, as mentioned before, is directly proportional to B_{23}^*.

Table 3. Interaction Parameters of PH/PHCl 50/50 Blend at 150 °C

probe	χ_{12}	χ_{13}	$\chi_{1(23)}$	χ'_{23}	χ_{12}^*	χ_{13}^*	$\chi_{1(23)}^*$	χ'^*_{23}
n-decane	1.943	1.194	1.566	−0.093	2.070	1.328	1.697	−0.098
1-butanol	0.780	0.488	0.644	−0.078	0.879	0.594	0.746	−0.080
chloroform	0.550	−0.113	0.160	0.143	0.516	−0.139	0.131	0.138
toluene	0.580	0.118	0.320	0.053	0.713	0.258	0.457	0.050
benzene	0.348	−0.076	0.108	0.055	0.649	0.233	0.414	0.052
DC[a]	0.392	−0.092	0.123	0.042	0.598	0.122	0.333	0.039
chlorobenzene	0.430	−0.006	0.186	0.045	0.553	0.125	0.313	0.042
3-pentanone	0.436	0.263	0.384	−0.160	0.591	0.424	0.542	−0.161
propyl acetate	0.529	0.327	0.463	−0.167	0.693	0.498	0.631	−0.169

[a] 1,2-Dichloroethane.

$$\frac{\chi_{23}^{*A} + \kappa}{V_2^* s_1} = \frac{\chi_{23}^{*T}}{V_2^*}\frac{1}{s_3} + \frac{(\chi_{12}^* - \chi_{13}^*)}{V_1^* s_1}\frac{(s_3 - s_2)}{(\phi_2 s_2 + \phi_3 s_3)} \quad (7)$$

In eq 7, χ_{23}^{*T} is the true interaction parameter, χ_{23}^{*A} is the apparent interaction parameter, V_i^* is the characteristic molar volume, χ_{1i}^* is the hard-core binary interaction parameter, s_i is the number of contact sites per segment, estimated from Bondi's radii,[29] θ_i is the surface fraction, calculable form ϕ_i, and κ is a term which includes the free-volume contribution of the pure polymers and their mixtures.

The plot of $(\chi_{23}^{*A} + \kappa)/V_2^* s_1$ versus $(\chi_{12}^* - \chi_{13}^*)/V_1^* s_1$ should be linear, in which χ_{23}^{*T}/V_2^* is calculated from the intercept. As can be seen in Figure 3, the linear correlations are good, which support the validity of eq 7, although the confidence interval is around 50%.

Table 4 shows the density interaction parameters B_{23}^* for all the compositions and temperatures studied. The negative values of B_{23}^* indicate the miscibility of PH and PCL by hydrogen-bonding interaction. The tendency of B_{23}^* is similar to the results obtained using the Farooque–Deshpande method, in spite of the fact that the values of B_{23}^* obtained by the method of Prolongo et al. are slightly higher in absolute value. Furthermore, there is no clear variation of B_{23} with both composition and temperature and this can be indicative of the uncertainty in the calculation of this parameter.

Theoretical Calculations Using an Association Model. Coleman, Painter, and co-workers recently proposed an association model[14,15] for polymer blends with specific interactions, where one polymer self-associates and the second polymer associates with the first. This approach considers both enthalpic and excess entropic contributions to the excess Gibbs energy. According to this treatment, when strong interactions are present in a blend, the free energy of mixing can be written as

$$\frac{\Delta G_M}{RT} = \frac{\phi_2}{x_2}\ln\phi_2 + \frac{\phi_3}{x_3}\ln\phi_3 + \chi^d\phi_2\phi_3 + \frac{\Delta G_H}{RT} \quad (8)$$

where x_i are the degrees of polymerization and ϕ_i the volume fractions. The first two terms are related to the combinatorial entropy, $\chi^d\phi_2\phi_3$ is an unfavorable contribution to the mixing that takes into account the weak dispersive unfavorable interactions, and $\Delta G_H/RT$ is a favorable term representing the enthalpy and entropy of hydrogen bonds. We can include the last two terms in eq 8 in a $g\phi_2\phi_3$ term, where g is the interaction function related to ΔG_M which depends on both temperature and composition. Considering that g is equal to χ in IGC experiments in which $\phi_1 \to 0$, and rearranging eq 8 gives

$$\frac{\Delta G'_M}{V_2} = \frac{RT}{V_2}\left(\frac{\phi_2}{x_2}\ln\phi_2 + \frac{\phi_3}{x_3}\ln\phi_3\right) + \frac{RT}{V_2}g\phi_2\phi_3 \quad (9)$$

where $\Delta G'_M$, V_2, and g are the Gibbs energy expressed in cal/mol, the reference volume, and the interaction function respectively. g is related to χ by

$$\chi_i = g + \phi_i\frac{dg}{d\phi_i} \quad (10)$$

The first term of eq 9 is related to the combinatorial entropy which can be neglected because of the high values of x_2 and x_3. The second term contains, as mentioned before, the favorable and unfavorable contribution to the mixing. The value of $B_{23} = RTg/V_2$ and its variation with temperature and composition can be easily obtained from the values of $\Delta G'_M/V_2$ given by the model.

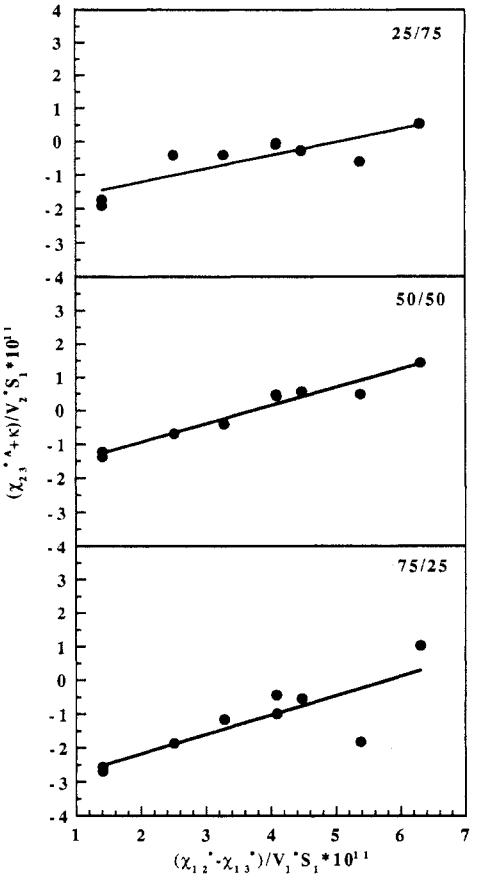

Figure 3. $(\chi_{23}^* + \kappa)/V_2^* s_1$ vs $(\chi_{12}^* - \chi_{13}^*)/V_1^* s_1$ to obtain the true polymer–polymer interaction parameter χ_{23}^{*T}/V_2^* for the PH/PCL system at different compositions at 150 °C according to the method of Prolongo et al.

Table 5. Equilibrium Constants and Enthalpies of Hydrogen Bond Formation for Phenoxy–Polyester Blends at 25 °C

	self-association by			
	dimers	multimers	ether	association
K_i	12.0	19.8	2.9	7.9
h_i (kcal/mol)	−3.6	−3.9	−3.2	−3.9

In order to calculate $\Delta G'_M/V_2$, the application of a commercially available software[14] needs values of the self-association and association constants and enthalpies involved in the equilibria between the interacting functional groups. This information can be obtained from FT-IR studies of the blends or from FT-IR studies of analogue compounds. In the case of the equilibria between Phenoxy and polyesters, all the parameters had been previously determined in our laboratory,[30] although more recently Coleman et al.[31] have introduced some refinements in the model when Phenoxy is used. This polymer can self-associate in three ways: by forming dimers (K_2), by forming multimers (K_B), and by the interaction between its hydroxyl and the aromatic ether groups (K_E). In this work, we will use the parameters obtained by Coleman et al.[31] which are shown in Table 5. In our calculation we have used polymerization degrees which correspond to the experimental molecular weights of our components.

The predictions of the model for the free energy of mixing in PH/PCL mixtures in the temperature range studied show that ΔG_M is negative (Figure 4) for any composition and temperature. As can be seen in Figure 5, the value of B_{23} becomes more negative as the content

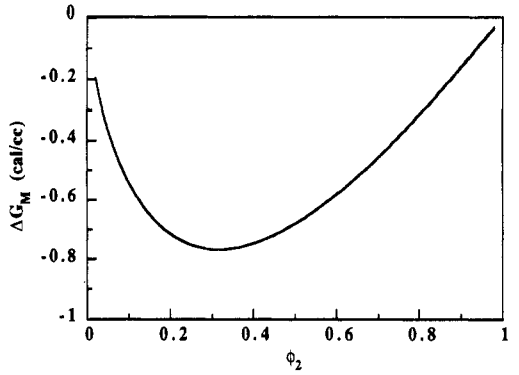

Figure 4. Variation of ΔG_M with composition by applying the Painter, Coleman, and co-workers association model for the PH/PCL system at 140 °C.

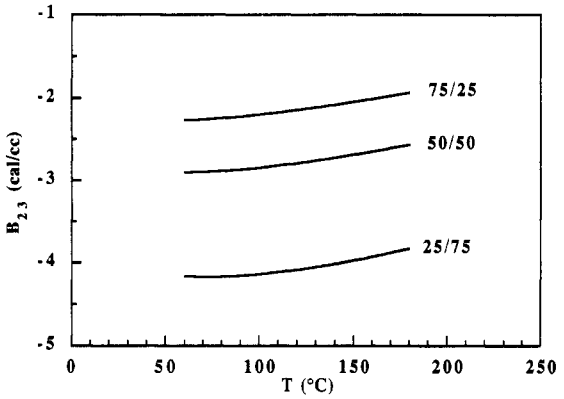

Figure 5. Temperature dependence of B_{23} by the association model for PH/PCL blends at several compositions.

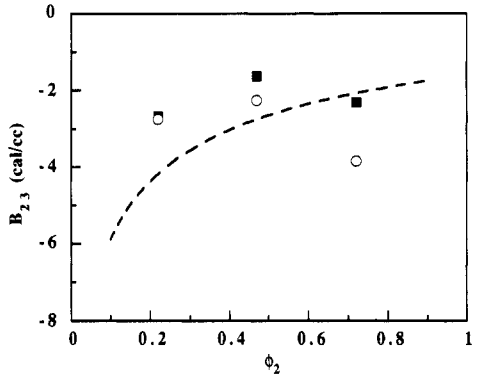

Figure 6. Composition dependence of B_{23} of PH/PCL blends at 160 °C calculated by IGC using the Farooque–Deshpande method (■) and that of Prolongo et al. (○), compared with B_{23} from the association model (- - -).

of PH in the blend is decreased.

The value of B_{23} obtained by using the mpd technique is -2.4 cal/cm^3 as it has been reported in several previous papers.[11,12] The disadvantage of this technique is that it gives the density interaction parameter only at the melting temperature of the semicrystalline component of the blend, which is an important limiting factor.

The results of B_{23} vs blend composition at 160 °C are summarized in Figure 6. The data obtained by IGC from the Farooque–Deshpande method[10] and the method of Prolongo et al.[9] as well as the miscibility prediction of the association model[14,15] are all in good agreement with the value determined by mpd.[11,12] Furthermore, the variation of B_{23} vs temperature (Figure 7) is not very significant.

An interesting point to take into account is that, as has been suggested by Sanchez,[32] there are different kinds of χ or B defining a system, depending on whether they are obtained directly from the free energy of the system (g),

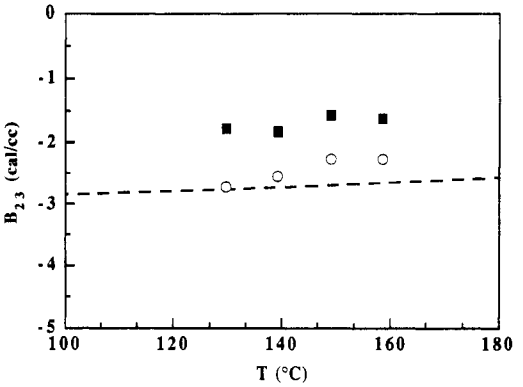

Figure 7. Temperature dependence of B_{23} of PH/PCL blends for the 50/50 composition calculated by IGC using the methods of Farooque–Deshpande (■) and Prolongo et al. (○), compared with B_{23} from the association model (- - -).

from the first derivative or chemical potential (χ_{ij}), or from the second derivative of the free energy (χ_{SC}). When several interaction parameters are to be compared, it is important to consider how they have been obtained. Hence, the value of B obtained from the association model is related to free energy (g), in the melting point depression technique it is related to the PCL chemical potential (χ_{32}), whereas that obtained from IGC experiments is referred to the PH chemical potential (χ_{23}), which, according to eq 10, is equal to g_{23} in IGC experiments in which $\phi_1 \rightarrow 0$. All of them, expressed in cal/cm^3, should be identical, only if there is no concentration dependence. In the present work, the difference in the B_{23} values obtained from different techniques could be due to the concentration dependence that has been observed experimentally.

Conclusions

The miscibility behavior between PH and PCL was investigated by inverse gas chromatography. Gas–liquid chromatographic data were analyzed in terms of Scott's ternary solution treatment of Flory–Huggins theory to study the polymer–polymer miscibility in the molten state and the χ'_{23} parameter obtained was found to be probe dependent. Two methods have been used to avoid the influence of the probe in the value of the polymer–polymer interaction parameter. In both cases, the negative values of χ'_{23} reflect the miscibility of the system by hydrogen-bonding interaction over the entire range of compositions and temperatures studied.

The confidence intervals of the experimental results are in both cases around 50%. Values of B_{23} for PH/PCL blends by the Farooque–Deshpande and the method of Prolongo et al. agree reasonably well with those determined from mpd and a theoretical association model. Although the method of Prolongo et al. is based on the equation of state ternary theory and hence has a more solid thermodynamic background, the Farooque–Deshpande approach allows one to obtain similar trends in the results, in spite of the simplicity of the method. The good correlations obtained by applying both methods support the methods used and the previous choice of probes that were injected.

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