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Miscible Blends of Poly(ethylene oxide) and the Poly(hydroxy ether) of Bisphenol A (Phenoxy)

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ABSTRACT: New experimental data are reported concerning the previously stated miscible mixture constituted by poly(ethylene oxide) (PEO) and the poly(hydroxy ether) of Bisphenol A, also called Phenoxy resin (PH). As in other miscible systems, spin-locking relaxation times $T_{1\rho}$ determined by CP-MAS ^{13}C NMR depend on the blend composition. Mixing volumes, measured by dilatometry, have resulted in a negative excess volume of mixing, usually related to the existence of strong intermolecular interactions between the blend components. A positive excess heat capacity in a 50/50 blend has also been observed. Its magnitude varies with temperature, showing a slightly decreasing tendency. The interaction parameter of a 50/50 blend has been measured by inverse gas chromatography (IGC) at 140 °C, with 13 solvents as probes. A recently reported formulation based on the equation-of-state theory has been applied to eliminate the solvent effect in the apparent interaction parameters experimentally obtained. All experimental data have been used in an attempt to verify the consistency of the Flory-Prigogine-Patterson model for explaining the behavior of such types of mixtures with specific interactions.

Introduction

The miscibility of the poly(hydroxy ether) of Bisphenol A (Phenoxy, PH) with polyethers such as polyoxides and poly(vinyl ethers) was first investigated by Robeson et al.[1] by dynamic mechanical methods. Poly(ethylene oxide) (PEO) was found to be miscible with Phenoxy over the entire composition range. Poly(vinyl methyl ether) (PVME) was also miscible with Phenoxy at low temperatures but exhibited a LCST behavior when the blend was heated to temperatures in the vicinity of 200 °C. However, other related polyethers such as poly(propylene oxide) or poly(vinyl ethyl ether) exhibited a clear two-phase behavior in Phenoxy blends.

Recently, an extensive investigation of the behavior of both PH/PEO and PH/PVME mixtures has been reported.[2-4] Phase diagrams and other thermodynamic magnitudes, such as heat of mixing and excess heat capacities, have been reported for PH/PVME blends.[2] An attempt to determine the interaction parameter by inverse gas chromatography (IGC)[3] was not completely successful because of the difficulties derived from the influence of the nature of the solvent used as a probe in the chromatographic experiment.

The interaction parameter, χ (equivalent to the interaction energy density B), of the PH/PEO blend was studied by means of the melting point depression of the PEO crystals, due to the presence of the amorphous second component.[4] To prevent the influence of the morphological effects in the determination of true (equilibrium) PEO melting points of the different blend compositions, a kinetic study of the crystallization process was carried out. Mixtures crystallized at times where the percentage of crystallinity did not exceed 10% were subsequently melted. The influence of the crystallization temperature on the melting point was also taken into account by using Hoffman-Weeks plots. A large value of the interaction energy density B ($\sim$-6 cal/cm^3) was obtained at 74 °C.

In this work, the PH/PEO interaction parameter was measured by IGC. This technique needs a third component, a solvent, which is used as a "probe" of the interactions between the components of the blend. The solvent is injected at extremely low concentrations with respect to the total amount of polymer introduced in the chromatographic column. However, this low amount complicates the thermodynamic analysis, giving apparent interaction parameters (or B's) clearly dependent on the nature of the injected solvent. These results have frustrated the expectations created by IGC a decade ago as a promising experimental technique in the analysis of polymer blends. Nevertheless, recently, Sanchez,[5] from the point of view of the lattice fluid (LF) theory, and Prolongo et al.,[6] using the equation-of-state theory, have theoretically showed that an appropriate consideration of the ternary systems leads to the obtention of the true interaction parameter (or B) between the two polymers, irrespective of the nature of the solvent used in the chromatographic experiment. The present work is a preliminary test of the feasibility of one of these theoretical approximations.[6]

In addition, the excess volumes and the excess heat capacities of the PH/PEO mixture have also been determined. All the thermodynamic results are consistent with the existence of large intermolecular interactions between poly(ethylene oxide) and Phenoxy.

Experimental Section

Table I summarizes the properties of the polymers used in this work. Phenoxy resin and PEO were commercial samples of PKHH (Union Carbide) and WSR-35 (Union Carbide), respectively. The values of the densities, thermal expansion coefficients, and the temperature coefficients of the pressure have been taken from the literature.[7,8]

Blends were prepared by dissolving the polymers in dioxane and subsequent precipitation in a large excess of isooctane. The samples were dried in a vacuum oven. These samples were used in NMR, excess volume, and excess heat capacity measurements. If necessary, they were milled in a Retsch ZM-1 mill after quenching in liquid nitrogen.

All solid-state NMR experiments were performed by using a Varian VXR-300 spectrometer equipped with a magic angle spinning accessory. Samples were packed in sapphire rotors. Spinning rates were generally 3 kHz. Spinning rate adjustments were made, when necessary, for the removal of the spinning sidebands. A 90° pulse width of 5 μs was employed in conjunction

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Table I
Properties of the Polymers

Phenoxy	PEO
M_w = 50 700 (GPC)	M_v = 335 000 (viscometry)
T_g = 368 K (scanning rate 10 K/min)	T_g = 205 K
ρ (g cm^{-3}) = $1.199 - 6.36 \times 10^{-4}(T - 273.2)$	ρ (g cm^{-3}) = $1.132 - 7.00 \times 10^{-4}(T - 273.2)$
α (K^{-1}) = $4.91 \times 10^{-4} + 6.77 \times 10^{-7}(T - 273.2)$	α (K^{-1}) = $5.04 \times 10^{-4} + 4.17 \times 10^{-7}(T - 273.2)$
γ (cal cm^{-3} K^{-1}) = $0.432 - 1.09 \times 10^{-3}(T - 273.2)$	γ (cal cm^{-3} K^{-1}) = $0.590 - 9.5 \times 10^{-4}T$

Table II
Characteristics of the Chromatographic Columns

column	length, m	coating, %	stationary phase weight, g
PH	1	10.06	0.5028
PEO	1	9.98	0.4966
PH/PEO (50:50)	1	9.89	0.4926

with 256 fid signal accumulations. Adamantane was used to adjust the field homogeneity. Proton spin–lattice relaxation times (in the rotating frame) were measured via carbon signal intensities using a 90_x–τ–spin lock pulse sequence prior to cross-polarization. Data acquisition was performed via ^{1}H decoupling, and delay times (τ) ranged from 0.5 to 15 ms. All spectra were obtained at room temperature.

Columns for IGC were prepared as follows: the pure polymers and a 50/50 Phenoxy/PEO blend were coated from a dioxane solution onto Chromosorb G (AW-DMCS treated, 80/100 mesh). After drying in a vacuum oven for about 48 h at 50 °C, the coated support was packed into $^1/_4$-in.-o.d. stainless steel columns, applying vacuum to one end. Glass wool was used to block the ends of the columns. The relative concentration of the polymers in the blend was assumed to be identical with that in the original solution, namely, prior to deposition on the inert support. A summarized description of the columns is given in Table II.

Measurements were carried out in a modified Sygma 300 Perkin-Elmer gas chromatograph equipped with a flame ionization detector. Nitrogen was used as carrier gas. Methane was used as a noninteracting marker to correct the dead volume in the column, and the retention time was directly measured with an Olivetti M-24 microcomputer, equipped with a CHROM+ card and appropriate software. A minimum of four measurements were taken for every molecular probe and for each temperature in all columns. Pressures at the inlet and outlet of the column, read from a mercury manometer, were used to compute corrected retention volumes by the usual procedures. Flow rates were measured at the end of the column with a bubble flowmeter, and the value was 5 mL/min.

Columns were conditioned at temperatures above T_g for ca. 48 h prior to use, while N_2 was flushed through the column to achieve equilibrium. The oven temperature was measured within ±0.1 °C over the whole temperature range. The molecular probes, including a small amount of methane marker, were injected manually with a 10-mL Hamilton syringe (<0.01 mL).

Specific retention volumes were calculated using

$$V_g^\circ = \Delta t \frac{F}{w_L} \frac{273.16}{T_r} \frac{3}{2} \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \tag{1}$$

where $\Delta t = t_p - t_m$ is the difference between the retention time of the probe and of the marker; F is the flow rate of the carrier gas at a temperature T_r and atmospheric pressure; w_L is the mass of the stationary phase; and P_i and P_o are the inlet and outlet pressures, respectively. Binary interaction parameters between the probe (1) and a polymer i, χ_{1i}, can be calculated as follows:

$$\chi_{1i} = \ln \frac{273.16 R v_i}{V_g^\circ V_1 P_1^\circ} - 1 + \frac{V_1}{M_i v_i} - \frac{B_{11} - V_1}{RT} P_1^\circ \tag{2}$$

where R is the gas constant, M_i and v_i are the molecular weight and the specific volume of polymer i, respectively, 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 experiment temperature, T.

A similar equation can be derived for the ternary χ_{123} parameter of the blend, taking into account that its specific volume can be replaced by the arithmetic mean of the volumes of the pure polymers. Nevertheless, the polymer–polymer interaction parameter referred to the solvent molecule, χ'_{23}, can be straightforwardly calculated without the auxiliary parameters (P_1°, B_{11}, etc.) by means of[9]

$$\chi'_{23} = \left(\ln \frac{V_{g,\mathrm{blend}}}{w_2 v_2 + w_3 v_3} - \phi_2 \ln \frac{V_{g,2}}{v_2} - \phi_3 \ln \frac{V_{g,3}}{v_3} \right) / \phi_2 \phi_3 \tag{3}$$

when three columns, two from the homopolymers and a third one from a blend, are prepared, their retention volumes are measured under identical conditions, and the so-called Scott–Tompa approximation is made.

The specific heats of the pure-component polymers and their blends were determined by a Perkin-Elmer DSC-2C scanning calorimeter, using the external standardization method. A reference baseline was recorded first by operating the calorimeter in an isothermal mode followed by a dynamic scanning period during which a deflection was recorded. Next a sapphire disk, the external reference, was scanned under the same operating conditions. This was followed by the scanning of the polymer sample. In all cases aluminum pans (pan plus cover) were selected to have the same weight (within 5%). The heat capacity of the sample was obtained by appropriate ratioing of the deflections and heat capacities, using previously reported values for the sapphire standard. Samples were heated at 80 K/min, kept at 430 K for 5 min, and then cooled to 330 K at 40 K/min. Finally, the sample was scanned from 330 to 430 K at 10 K/min. Results of excess heat capacities were averaged over ten different samples.

Densities were measured by dilatometry at 122 °C in a silicone bath, using a glass dilatometer which allowed charge and decharge of mercury. Dilatometers were first filled with the polymer samples (0.2–0.3 g), sealed, and degasified in a vacuum line, and then mercury was added to bring the volume up to some reference height. After the height was measured with a cathetometer, the mercury was decharged and the polymer dissolved and evacuated from the dilatometer. After being cleaned, the dilatometer was filled with mercury at several levels in the vicinity of the reference height. This allowed the construction of a calibration relationship $V = V_0 + a\Delta h$, where V_0 was the volume of the arbitrary reference, a the constant section of the capillar, and Δh the different heights measured with the dilatometer.

Densities of the different polymers and blends were calculated according to the equation

$$\rho_p = \{(V_0 + a\Delta h) - (m_{Hg}/\rho_{Hg})\}/m_p \tag{4}$$

where ρ_p and ρ_{Hg} are the densities of the polymer (or blend) and mercury, respectively, and m_p and m_{Hg} the corresponding masses of polymer and mercury. V_0 and a are characteristics for each dilatometer.

Results and Discussion

CP-MAS NMR Miscibility Test. As reported previously,[4] all PH/PEO blends exhibited a single glass transition temperature intermediate between the transitions of the pure components. This is a macroscopic proof of the extensive mixing of the segments of the two polymers. When data reported by Iriarte et al.[4] and those of Robeson et al.[1] are used together in a Gordon–Taylor plot, both series of data are consistent, giving a k parameter of 0.55.

Solid-state CP-MAS ^{13}C NMR provides another approximation to the miscibility of a polymer blend. As is known, the criteria for determination of miscibility rest on the inherent limitations of the technique that is used to characterize the system. When DSC is used for the determination of glass transition temperatures, the distance scale is generally taken to be 20–30 nm. Other techniques such as CP-MAS NMR offer the possibility of

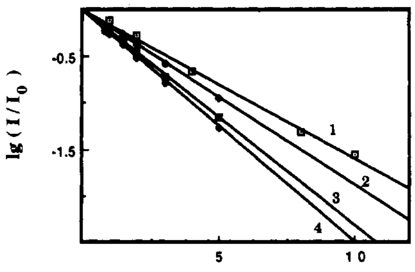

Figure 1. Plot of Phenoxy carbon magnetization at 160 ppm against cross polarization contact time: (1) pure Phenoxy; (2) 75:25 PH/PEO; (3) 50:50 PH/PEO; (4) 25:75 PH/PEO.

Table III
Relaxation Times $T_{1\rho}$ in PH/PEO Blends from the PH Peak at 160 ppm

PH/PEO blend	relax time, ms
100/0	6.34
75/25	5.31
50/50	4.33
25/75	3.96

proving blend miscibility in a much smaller dimensional scale, ranging from a few angstroms to tens of nanometers.

In general, resolution of the various polymer carbon signals in the NMR spectra of pure PH and blends was quite good, without significant problems related with the interference from spinning sidebands. Measurements of rotating frame spin–lattice relaxation times ($T_{1\rho}$) were made by using a 90_x–τ–spin lock pulse sequence, as mentioned above. The carbon signal intensity decay curves were fitted to a standard first-order kinetic expression

$$I = I_0 \exp[-\tau/T_{1\rho}] \qquad (5)$$

which allows the determination of the relaxation times from a plot of the logarithm of the intensity ratio (I/I_0) against the delay time (τ). The slope yields the proton spin–lattice relaxation time in the rotating reference frame. In general, relaxation times should be independent of the carbon peak used to monitor signal decay. In our case, this has been observed when we have calculated relaxation times from the PH peaks of 73, 147, and 160 ppm.

Figure 1 shows the results obtained from the study of the PH peak at 160 ppm at room temperature for pure Phenoxy and PH/PEO 75:25, 50:50, and 25:75 blends. For each blend, single-component relaxation times, which vary with composition, were observed. Increasing the PH content resulted in longer relaxation times, indicative of the efficient spin coupling on the time scale of the relaxation process. Relaxation times are summarized in Table III.

Excess Volumes. Sanchez and Lacombe[10,11] have already emphasized the importance of the excess volumes of mixing on the thermodynamics of systems involving polymers. However, due to the experimental difficulties encountered when one tries to measure excess volumes in polymer/polymer mixtures, scarce experimental studies have been carried out in miscible blends. The importance of this type of measurements has been highlighted by the formulation of new theoretical approaches intending to explain polymer/polymer mixtures with specific interactions.[12]

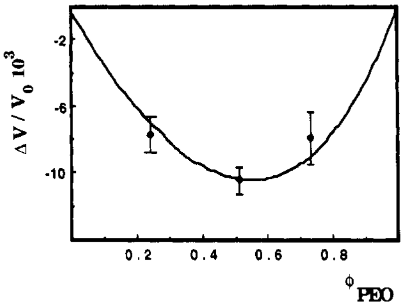

Figure 2. Excess volumes for PH/PEO blends. Symbols are experimental results; the line is theoretical (see text).

Experimental results have been expressed in the form of $\Delta V/V_0$, where V_0 is the additive specific volume of the mixture

$$V_0 = (\phi_1/\rho_1) + (\phi_2/\rho_2) \qquad (6)$$

where ϕ_i is the volume fraction of the components in the blends, and ρ_i their densities in the pure state. ΔV is the difference between the true specific volume of the blends ($1/\rho$) and the additive one. Figure 2 shows the results obtained for three representative blend compositions. Despite the strong intermolecular interactions claimed to be present in this mixture,[13] the excess volume at a PEO weight fraction of 0.5 is not far from that reported for the polystyrene/poly(2-chlorostyrene) miscible blend system.[14] This suggests that specific interactions are not the only factor affecting excess volumes. Other factors such as the very different geometries of PH and PEO may be the origin of such types of differences.

Excess Specific Heats (Δc_p). In general terms, it is nowadays accepted that the enthalpy of mixing plays a dominant role in the phase behavior of polymer blends. Thus, because of the high molecular weights of the components, the simple Flory–Huggins formulation for the free energy of mixing allows us to see that, at high molecular weights of the components, the enthalpic contribution is dominant. However, due to the high viscosity of the polymers and to its viscoelastic character, calorimetric measurement of ΔH_M in polymer blends is a very difficult task that can only be circumvented when oligomeric components are used. The use of the Hess cycle and the use of mixtures of low molecular weight analogues are two reasonable approximations to determine the heat of mixing in polymer blends. However, from a strict thermodynamic consideration of the problem, there is a considerable loss of rigorosity. Heats of mixing have been recently measured[13] in mixtures of a Phenoxy analogue, 1,3-bis[4-(2-propyl)phenoxy]-2-propanol, and a PEO analogue, diethylene glycol diethyl ether. Exothermic heats of mixing were obtained over the entire range of compositions, finding a minimum in the vicinity of a 50:50 blend of about −1.18 cal/cm^3 at 362 K.

Experimental determinations of the variation of ΔH_M with temperature, $\Delta c_p = (\partial \Delta H_M/\partial T)_P$, are also difficult but possible. Recently, theoretical models acknowledging the importance of specific interactions[12,15] have illustrated that excess heat capacity data can provide a useful means of evaluating the importance of various physical issues of polymer blends once these issues have been incorporated into a mathematical model for mixtures.

The temperature dependence of the heat of mixing for blends or, alternatively, the excess specific heat of the blend can be calculated as

$$(\partial \Delta H_M/\partial T)_P = \rho \Delta c_p = \rho[c_p - \omega_1 c_{p1} - \omega_2 c_{p2}] \qquad (7)$$

where ω_i is the mass fraction of component i and c_p and c_{pi} are specific heats of the blend and the pure components,

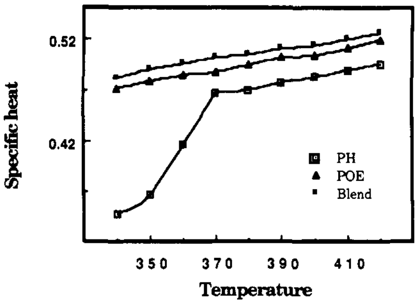

Figure 3. Specific heats (in cal g^{-1} K^{-1}) of pure polymers and a 50:50 blend versus temperature.

Table IV
Evolution of Δc_p with Temperature

T, K	Δc_p, cal g^{-1} K^{-1}	T, K	Δc_p, cal g^{-1} K^{-1}
380	0.0222	410	0.0195
390	0.0210	420	0.0184
400	0.0200		

respectively. The density of the blend ρ should be introduced as a factor which changes units of mass for units of volume. Figure 3 shows specific heats of pure components and of a 50:50 blend in the investigated temperature range.

The discontinuity in the pure Phenoxy behavior corresponds to the glass transition temperature of the pure polymer. This is not observed in the plot of the 50:50 blend, showing, once again, the miscibility of the mixture. Determination of Δc_p has been done in the range 380–420 K, where both pure components and the blend are in the liquid state. Δc_p calculated in this way is representative of the PH/POE (liquid/liquid) mixture. Table IV presents the evolution of the excess heat capacity with temperature. Δc_p slightly decreases when temperature increases, in excellent agreement with existing theories. This type of behavior, empirically described by the equation

$$\Delta c_p = (c_0 + c_1 T)\phi_1\phi_2 \tag{8}$$

allows us to make a phenomenological reformulation of the Flory–Huggins equation that is enough to deal with the occurrence of both upper and lower critical miscibility.[16]

These positive Δc_p values have been interpreted by ten Brinke and Karasz[15] in the framework of their incompressible model of binary mixtures with specific interactions. A compressible version of this model has been proposed by Sanchez and Balasz.[12] In the incompressible model, positive values of Δc_p are indicative of systems with "directional specific" interaction. However, the Sanchez and Balasz analysis shows that there are also compressibility contributions to Δc_p. In general, a positive value of Δc_p is obtained if χ_H (the enthalpic part of the Flory–Huggins parameter) is an increasing function of temperature (i.e., becoming less negative with temperature). This is usually the case when specific interactions are present and likely also for various miscible random copolymer blends, where the miscibility is due to the so-called intramolecular repulsion effect.

Probably, the only examples of a negative Δc_p are miscible polymer blends with a positive interaction parameter, where miscibility is due to entropic reasons (i.e., low enough molecular weights). Although, the subject is open to discussion and needs more experimental evidence, the Δc_p values can be used, at least, as an additional experimental test for proposed theories.

Interaction Parameter by Inverse Gas Chromatography. Inverse gas chromatography (IGC) is one of the experimental methods for studying polymer blends that require the use of a third component, a low molecular weight liquid, which is used as a molecular "probe" of the interactions between the polymeric components. The usual procedure is to study first the polymer–solvent binary systems, and then the analysis of the chromatographic data of the blend column may be used for extracting information about the polymer–polymer interactions. This requires some previous assumptions, usually the Scott–Tompa approximation, on the relationships between the components of the ternary system.

In spite of the linear relationship between the logarithm of the specific retention volume (see eq 1) and $1/T$, which allows extrapolations of $V_g{}^\circ$ data beyond the experimental range, the use of raw experimental data, taken at temperatures at which pure components and the blend were in the liquid state, was preferred. This condition, which in the case of PH requires temperatures at least 40 °C above T_g, and the PEO degradation susceptibility restricted the analysis to a very narrow temperature range in the vicinity of the selected temperature (140 °C).

As previously mentioned, three columns were prepared: two of the pure components and one of a 50:50 blend (by weight). Thirteen solvents of different chemical structure were selected as probes. Solvent data, needed for both the usual chromatographic data reduction[17] and the equation-of-state analysis of the influence of the nature of the probe in the interaction parameter, were taken from different sources.[18–21]

Determination of the polymer–polymer interaction parameter, χ'_{23}, in ternary solvent 1–polymer 2–polymer 3 systems have usually been made by means of the equation

$$\chi_{1p} = \xi_2\chi_{12} + \xi_3\chi_{13} - \xi_2\xi_3\chi'_{23} \tag{9}$$

where χ_{1p} is the interaction parameter measured in the ternary system, $\xi_i = \phi_i/(\phi_2 + \phi_3)$ is the volume fraction of polymer i referred to the total polymer composition, and ϕ_i is the volume fraction of component i in the ternary system. In IGC these two volume fractions are identical, provided that the solvent composition in the ternary system is negligible. The binary polymer–polymer interaction parameter is defined by using the probe molecule as a reference.

To express data according to the Prolongo et al. formulism,[6] the characteristic molar and specific volumes in eq 3 and the characteristic specific volumes were used to calculate the volume fractions ϕ_i. These volume fractions are now called segment fractions. Prolongo et al.'s[6] equations are written in terms of the polymer–polymer interaction parameter with the monomer unit of polymer 2 as a reference, χ_{23}. The interaction parameters are related to each other by

$$\chi'_{23} = \chi_{23}V_1{}^*/V_2{}^* \tag{10}$$

where $V_i{}^*$ are the characteristic molar volumes.

Equation 9 contains, however, important simplifications. Thus, it is assumed that the free energy interaction function g in binary systems is concentration independent. In IGC experiments this assumption can be maintained, given that ϕ_1 tends to zero and g tends to χ. In addition, eq 9 also assumes the interactional part of the Gibbs function of the ternary system to be additive in the binary contributions. This assumption can be the origin of the discrepancies found in the literature among experimental data for ternary systems. This can also be the origin of the nearly unanimous dependence of the interaction parameter on the probe nature reported in IGC papers on polymer blends.

Table V
Binary Polymer–Solvent Interaction Parameters and Polymer–Polymer Interaction Parameters χ'_{23} from Different Probes

probe	χ_{12}	χ_{13}	χ'_{23}
toluene	0.788	0.387	0.184
benzene	0.765	0.263	0.140
chlorobenzene	0.631	0.146	0.348
1,2-dichloroethane	0.677	0.038	0.170
n-decane	2.230	1.780	0.121
tetradecane	2.530	2.198	0.358
DEGDEE	0.097	0.232	−0.284
dioxane	0.154	0.240	−0.302
n-butanone	0.727	0.630	−0.308
ethyl acetate	0.808	0.567	−0.250
1-propanol	1.125	0.634	0.056
acetonitrile	1.055	0.564	0.007
dimethylformamide	−0.218	0.395	−0.245

Table V gives the binary polymer–solvent interaction parameters and the polymer–polymer interaction parameter χ'_{23} in PH/PEO 50:50 blend, which clearly depends on the solvent chemical nature.

Prolongo et al.'s[6] formulism involves the use of the expression of the noncombinatorial part of ΔG_M in a ternary polymer–polymer–solvent system, written in terms of the Flory equation-of-state theory. This allows them to consider the existence of contributions to the interaction parameter other than the additivity in binary interactions. Representing the interaction parameter obtained from eqs 9 and 10 representing the probe-independent, true interaction parameter as $\chi_{23}{}^{app}$ and as $\chi_{23}{}^{T}$, Prolongo et al.[6] have obtained the following equation, which is useful for IGC experiments

$$\chi_{23}{}^{app} = \chi_{23}{}^{T}\frac{s_1}{s_3} + (\chi_{12} - \chi_{13})\frac{(s_3 - s_2)V_2{}^*}{(\phi_2 s_2 + \phi_3 s_3)V_1{}^*} - x \qquad (11)$$

where x can be calculated[6] from equation-of-state theory data of pure components such as characteristic molar volumes $V_i{}^*$, reduced molar volumes V_i, binary interaction parameters χ_{12} and χ_{13}, molecular surface in volume ratios s_i (or number of contact sites per segment), segment fraction (ϕ), and surface fraction (θ, calculable from ϕ and s). x may be calculated for each polymer–polymer–probe system if data of the thermal expansion coefficient and of the temperature coefficient of the pressure for all the components are available (see Table I and refs 17–21). The s ratios can be estimated from Bondi's radii.[22]

From eq 11, the intercept of the $(\chi_{23}{}^{app} + x)/(V_2{}^*s_1)$ against $(\chi_{12} - \chi_{13})/(V_1{}^*s_1)$ plot should give us the probe-independent interaction parameter. Equation 11 predicts, among other effects, a dependence of $\chi_{23}{}^{app}$ on the difference between the binary polymer–probe interaction parameters. This concept was first introduced by Su and Patterson[23] and has been phenomenologically observed, among others, by Galin and Maslinko.[24] This is the so-called "$\Delta\chi$ effect". The Prolongo et al.[6] equation (11) expresses this dependence on rigorous thermodynamic terms, but the number of characteristic parameters necessary to apply this equation may introduce a large uncertainty in the final determination of $\chi_{23}{}^{T}$. Thus, in the present case, the interpolation at a zero value of $\chi_{12} - \chi_{13}$ in Figure 4 gave us a value of -0.98×10^{-11}, certainly negative, but with a standard deviation close to 100%. Perhaps PH/PEO is not the most adequate system for testing eq 11, given the well-known degradation of PEO at temperatures and times in the range employed in the experimental work. Other systems should be studied before concluding the feasibility of this[6] and other approximations[5] that take into account the specific nature of the probe injected in the blend column.

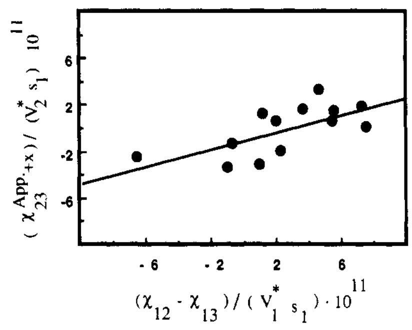

Figure 4. Determination of the probe independent interaction parameter according to the Prolongo et al.[6] equation (11).

Irrespective of the large errors involved in the above-mentioned analysis, we have used the intercept in the calculation of the PH/PEO interaction parameter. We prefer to express it in the form of $\chi_{23}{}^{T}/V_2{}^*$. The result was -1.34×10^{-3} mol/cm^3 at 413.2 K.

When comparing this result with that obtained from previous melting point depression data,[4] one should take into account that these two values may not correspond to the same interaction parameter, as demonstrated by Sanchez.[5] The value extracted from melting point depression is related to the PEO chemical potential (and may be denoted χ_{32}) whereas that extracted from IGC experiments has been defined in terms of the PH chemical potential (χ_{23}). If there is no concentration dependence of the interaction parameter related to the free energy of mixing, then the two interaction parameters (expressed in mol/cm^3) described above are identical.

Using melting point depression data,[4] we can calculate a $\chi_{32}{}^{T}/V_3{}^*$ value of -8.7×10^{-3} mol/cm^3 at 347.2 K. The immediate question is if such a difference is a consequence either of the concentration dependence of the free energy or of the temperature dependence or of both. The good correlation in melting point depression data[4] and the theoretical calculations resumed below seem to support a slight dependence of χ on composition. Therefore, in the following, we will treat the interaction parameters obtained from the two experimental techniques as the same interaction parameter, the difference in values probably arising from the temperature effect.

Theoretical Calculations. Strictly speaking, the Flory-type equation-of-state theory is valid only for dispersion force dominant systems. The specific interactions cannot be expressed by the van der Waals type interaction and also may induce some orientation of molecules or segments, which leads to nonrandom mixing. This has been incorporated in Flory's theory in the form of new adjustable parameters. Given the predictable specific character of the interactions in this system, we have tested the possibilities of this theory to reproduce the experimental results presented above.

Four adjustable parameters can be introduced in theoretical calculations according to different modifications of the equation-of-state model:[25,26] the s_{PH}/s_{PEO} surface ratio; the nonadditive freedom degree parameter, c, which characterizes deviations from additivity of the number of external degrees of freedom per segment in the mixture; the interaction density X; and the entropic correction Q, mainly due to local orders generated in the mixture as a consequence of specific interactions. The set of parameters that gave the best fit of the different experimental results was as follows: $s_{PH}/s_{PEO} = 0.9$, $c = -0.00054$, $X = -23$ cal cm^{-3}, and $Q = -0.031$ cal cm^{-3} K^{-1}. The first adjustable parameter is very close to the value

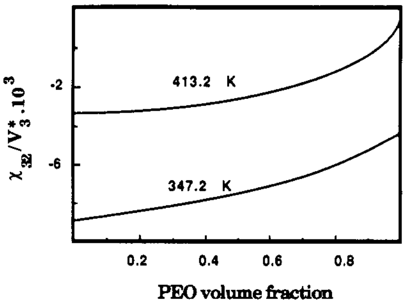

Figure 5. Theoretical evolution of the interaction parameter with the composition at two temperatures.

calculated according to Bondi's surface and volume compilations,[22] which was 0.88. The ratio Q/X is of the same order as the value 2×10^{-3} recently proposed by Rostami[27] as a universal coefficient for adjusting Q once X has been adjusted. The absolute values of both parameters are higher than others reported in the literature, indicating the existence of strong interactions. The total interaction energy density $\bar{X} = X - QT\tilde{v}$ was -8.2 cal cm^{-3} at 395.2 K. This set reproduces the values of the excess volumes (see Figure 2), perhaps the most reliable measurements, and gives a ΔH_M value of -1.68 cal cm^{-3} for a 50:50 blend at 360 K. In addition, it predicts that the interaction parameter depends on the temperature but is rather independent of the concentration (see Figure 5), with reasonable agreement with the experimental results.

The model also predicts positive values for the excess heat capacities with a slight negative slope in temperature. However, the absolute values ($\sim 6 \times 10^{-3}$) are beneath the experimental ones ($\sim 2 \times 10^{-2}$).

It is worth discussing the use of the c parameter. We have analyzed IGC data, according to Prolongo et al.,[6] without any reference to c. However, there is some inconsistency between the quoted values of Q (negative implying more ordering) and the negative value of c (implying more translational degrees of freedom, i.e., less ordering). Some authors[28] consider that the use of c is artificial because it gives a contribution to the interaction parameter proportional to $c \ln (M_1/M_2)$, where M_i denotes the mass per segment of the respective components. Depending on the ratio of M_1/M_2, this contribution will, for a given sign of c, either be favorable or unfavorable.

A zero value of c makes the model less consistent with the experimental results. Figures 2 and 5 do not change in a significant way, but the enthalpy of mixing becomes more negative (-4.15 cal cm^{-3}) and the excess heat capacities change from positive to negative (-1.4×10^{-3}). As in other papers,[12,29] Δc_p seems to be difficult to reproduce by the theoretical models.

Conclusions

Poly(ethylene oxide) and Phenoxy are miscible over the entire range of compositions. The specific interactions between the hydroxyl unit of PH and the ether group of PEO are reflected in the negative excess volume of mixing and in the positive excess heat capacities of the blends. The negative interaction parameter seems to be nearly independent of the composition but temperature dependent. The equation-of-state theory reproduces reasonably well the characteristics of this mixture if a large interaction energy density X and a large entropy correction Q are introduced.

On the other hand, when the characteristics of the injected probes are taken into account, inverse gas chromatography seems to provide reliable data of the polymer–polymer interaction parameter. Other less conflictive systems are under study to verify the preliminary results obtained here.

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References and Notes

(1) Robeson, L. M.; Hale, W. F.; Merriam, C. N. *Macromolecules* **1981**, *14*, 164.
(2) Uriarte, C.; Eguiazábal, J. I.; Llanos, M.; Iribarren, J. I.; Iruin, J. J. *Macromolecules* **1987**, *20*, 3038.
(3) Uriarte, C.; Iruin, J. J.; Fdz-Berridi, M. J.; Elorza, J. M. *Polymer* **1989**, *30*, 1155.
(4) Iriarte, M.; Iribarren, J. I.; Etxeberría, A.; Iruin, J. J. *Polymer* **1989**, *30*, 1160.
(5) Sanchez, I. C. *Polymer* **1989**, *30*, 471.
(6) Prolongo, M. G.; Masegosa, R. M.; Horta, A. *Macromolecules* **1989**, *22*, 4346.
(7) Jain, R. E.; Simha, R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1929.
(8) Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1453.
(9) Al-Saigh, Z. Y.; Munk, P. *Macromolecules* **1984**, *17*, 803.
(10) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352.
(11) Lacombe, R. H.; Sanchez, I. C. *J. Phys. Chem.* **1976**, *80*, 2568.
(12) Sanchez, I. C.; Balasz, A. C. *Macromolecules* **1989**, *22*, 2325.
(13) Fernández-Berridi, M. J.; Martínez de Ilarduya, A.; Valero, M.; Espi, E.; Iruin, J. J. *Polymer*, to be published.
(14) Tsujita, T.; Iwakiri, K.; Kinoshita, T.; Takizawa, A.; MacKnight, W. J. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1987**, *25*, 415.
(15) ten Brinke, G.; Karasz, F. E. *Macromolecules* **1984**, *17*, 815.
(16) Nies, E.; Koningsveld, R.; Kleintjens, L. A. *Prog. Colloid Polym. Sci.* **1985**, *71*, 2.
(17) Fernández-Berridi, M. J.; Guzmán, G. M.; Iruin, J. J.; Elorza, J. M. *Polymer* **1983**, *24*, 417.
(18) Timmermans, J. *Physicochemical Constants of Pure Organic Compounds*; Elsevier: New York, Vol. 1, 1950; Vol. 2, 1965.
(19) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
(20) Olabisi, O. *J. Appl. Polym. Sci.* **1978**, *22*, 1021.
(21) Delzenne, J. *J. Chem. Eng. Data* **1960**, *5*, 413.
(22) Bondi, A. *J. Chem. Phys.* **1964**, *68*, 441.
(23) Su, C. S.; Patterson, D. *Macromolecules* **1977**, *10*, 708.
(24) Galin, M.; Maslinko, L. *Eur. Polym. J.* **1987**, *23*, 923.
(25) ten Brinke, G.; Eshuis, A.; Roerdink, E.; Challa, G. *Macromolecules* **1981**, *14*, 867.
(26) Shiomi, T.; Fujisawa, K.; Hamada, F.; Nakajima, A. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 895.
(27) Rostami, S. *Proceedings of the Third European Symposium on Polymer Blends*, Cambridge, U.K., July 1990.
(28) Referee's comments.
(29) Barnum, R. S.; Goh, S. H.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 395.

Registry No. PEO, 25322-68-3; PH, 25068-38-6; toluene, 108-88-3; benzene, 71-43-2; chlorobenzene, 108-90-7; 1,2-dichloroethane, 107-06-2; *n*-decane, 124-18-5; tetradecane, 629-59-4; dioxane, 123-91-1; *n*-butanone, 78-93-3; ethyl acetate, 141-78-6; *n*-propanol, 62309-51-7; acetonitrile, 75-05-8; dimethylformamide, 68-12-2.