Table II
Comparison of Observed Reactivity Ratios for 1-Cyanoethyl and 1-Phenylethyl with Reactivity Ratios Calculated from Copolymerization Kinetic Models

radical	k_A/k_S	k_S/k_A	determinatn method	ref
1-cyanoethyl	0.12 ± 0.03		*a*	this work
$\sim$A$^\bullet$	0.05		*b*	5
$\sim$SA$^\bullet$	0.09		*c*	5
$\sim$AA$^\bullet$	0.04		*c*	5
1-phenylethyl		0.20 ± 0.02	*a*	8
$\sim$S$^\bullet$		0.33	*b*	5
$\sim$SS$^\bullet$		0.23	*c*	5
$\sim$AS$^\bullet$		0.63	*c*	5

[a] ^{13}C NMR method described in present work and in ref 8. [b] Calculated from the best-fit terminal model. [c] Calculated from the best-fit penultimate model.

our previous investigation of the 1-phenylethyl radical,[8] in which k_S/k_A was found to be 0.20 ± 0.02—nearly identical with Hill's r_{SS} and significantly different from the terminal model reactivity ratio r_S. Table II compares the observed reactivity patterns of the 1-cyanoethyl and 1-phenylethyl radicals with those calculated for the analogous macroradicals from the kinetic analyses of Hill and co-workers. The comparison lends support to the penultimate model as a physically meaningful description of the radical copolymerization of styrene and acrylonitrile.

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Registry No. 1, 96837-18-2; (S)(A) (copolymer), 9003-54-7; PS, 9003-53-6; PA, 25014-41-9; S, 100-42-5; A, 107-13-1; (1-^{13}C)-H_3CCHO, 2188-31-0; $H_2NNH_2{\cdot}H_2SO_4$, 10034-93-2; 2,2'-hydrazobis([2-^{13}C]propionitrile), 110774-07-7.

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Miscibility and Phase Separation in Poly(vinyl methyl ether)/Poly(bisphenol A hydroxy ether) Blends

C. Uriarte, J. I. Eguiazábal, M. Llanos, J. I. Iribarren, and J. J. Iruin*

Departamento de Química Física y Macromoléculas, Facultad de Ciencias Químicas, Universidad del País Vasco, San Sebastián, Spain. *Received January 6, 1987*

ABSTRACT: Amorphous blends of poly(vinyl methyl ether) ($\bar{M}_w$ = 63 000 and $\bar{M}_n$ = 37 000) and a copolymer of bisphenol A and epichlorohydrin ($\bar{M}_w$ = 50 400 and $\bar{M}_n$ = 18 000) were found to be miscible over the complete range of compositions at temperatures below 420 K. At higher temperatures, blends separate into two phases, giving a LCST-type phase diagram. Heats of demixing and excess heat capacity of a 50:50 blend have also been measured by DSC. The results have been interpreted in terms of the equation-of-state theory and compared with predictions of a recent model proposed by ten Brinke and Karasz for blends which have direction-specific interactions.

Introduction

The blends of a copolymer of bisphenol A and epichlorohydrin (phenoxy) are among the most studied polymer systems. Harris et al.[1] have described numerous miscible and immiscible blends of this polymer with a series of aliphatic and aromatic polyesters. Robeson et al. have reported miscible blends of this polymer with poly(butylene terephthalate) (PBT)[2] and polyethers,[3] such as poly(ethylene oxide) (PEO) and poly(vinyl methyl ether) (PVME). In all cases the stability of such mixtures has been attributed to the intermolecular interactions between the two components of the blend. These interactions would arise from possible hydrogen bonding between the pendant hydroxyl groups of the phenoxy and the carbonyl and ether groups of the second components. Direct evidence of such a hydrogen-bonding interaction has been found in the result of the Fourier transform infrared studies reported by Moskala and Coleman.[4] Robeson et al.[3] noted that the blends of phenoxy and PVME might separate into phases at temperatures of about 200 °C, but they did not present any experimental data for this.

A necessary and sufficient condition for the miscibility of a two-component system is that the second derivative of the Gibbs free energy with respect to the volume fraction of either component should be positive. The equilibrium-phase behavior of polymer–polymer mixtures is, however, primarily governed by the heat of mixing contribution to the free energy. This follows from the fact that, in mixtures of high molar mass polymers, the entropy of mixing is very small positive or even negative.

An exothermic heat of mixing may be the result of two essentially different properties, as ten Brinke and Karasz[5] have pointed out. Miscible blends of homopolymers of sufficiently high molecular weight can only be obtained if some kind of specific interaction exists. These inter-

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* To whom correspondence should be addressed.

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actions are of highly directionally dependent nature and are supposed to be present in addition to the London dispersion forces. An increasing temperature increases the Brownian motion, which, in turn, reduces the number of favorable directional specific interactions. On the other hand, for random copolymer-homopolymer mixtures, the stability can also arise from the so-called "repulsion effect". This refers to a situation for which the unfavorable exchange interactions between the monomers that make up the copolymer are larger than the two other types of interactions between monomers. All the interactions are unfavorable but the homopolymer "dilutes" the unfavorable intramolecular interactions.

Direct measurements of the heat of mixing of high molar mass polymers are obviously impossible. Mixing polymers in their viscoelastic molten state requires strong mechanical agitation which leads to energy dissipation and an increase in the temperature of the sample. Very recently, Natansohn[6] and Ebert et al.[7] have measured heats of demixing during a DSC scanning in the range of the phase-separation temperature. Ebert et al.[7] have proposed to identify the heat of demixing as a rough approximation of the heat of mixing of a particular blend. This approximation rests on the fact that the phases mainly contain the pure components. This can be achieved by selecting the final temperature of the scanning correctly. It is clear that the flatter the diagram the lower the final temperature.

Various theoretical treatments have been used to describe and predict thermodynamics of polymer mixtures. The Flory–Huggins lattice theory in its simplest form is unable to predict LCST behavior. Various modifications to the lattice theory have introduced lattice site vacancies to take into account volume changes on mixing and empirical temperature and composition-dependent interaction terms. Furthermore, the basic reasons for LCST behavior in polymer solutions may be understood in terms of the well-known solubility parameter model. More quantitative theories take into account the compressibility of both components of the mixture[8]. These are the so-called equation-of-state theory[9] and the Sanchez–Lacombe model.[10] They have shown that the free-volume contributions are unfavorable for mixing, becoming more pronounced at higher temperatures and leading to LCST behavior.

More recently, ten Brinke and Karasz[5] have constructed a theory for blends that have direction-specific interactions, as is predictably the case with our system. Their theory predicts positive excess heat capacities, which, they argued, may be used as a potential tool of testing different theories.

In this work, we have studied miscibility and phase separation of the system constituted by phenoxy and PVME. We have also measured heats of demixing and excess heats capacities which have been confronted with the theoretical predictions of the equation-of-state and ten Brinke and Karasz models.

Experimental Section

Materials. Two commercial phenoxy and PVME samples were used. Phenoxy was obtained from Quimidroga, Barcelona, Spain, and corresponds to the Union Carbide PKHH product. PVME was obtained from Polysciences (catalogue no. 3032). The two samples were previously purified by adequate solution and precipitation.

Molar mass measurements were taken in a GPC/SEC chromatograph (Waters ALC/GPC 150 C) with THF as eluent, relative to polystyrene standards. Given that the Mark–Houwink equation for these polymers in THF is not available in the literature, an iterative procedure,[11] involving intrinsic viscosities in THF and chromatograms, was performed. The final molecular weights of the samples used appear in Table I.

Table I
Molar Mass of the Used Polymers

	$\bar{M}_w$	$\bar{M}_n$
phenoxy	50 800	18 000
PVME	63 000	37 000

Preparation of the Blends. Blends were prepared by solution casting, with dioxane as the solvent. The polymer concentration in the solution was about 10%. Dioxane evaporation was conducted at room temperature under a stream of air. The resulting films were dried in a vacuum oven at 40 °C, until they reached a constant weight, and then stored in vacuo to avoid moisture adsorption.

Phase Diagram Determinations. Location of the phase separation temperatures of the different phenoxy/PVME compositions was investigated by means of thermooptical analysis. The films, which were directly cast onto glass microscope slides from solutions, in a similar manner to that described in the paragraph before, were placed in a Mettler hot-stage device. The system, which we managed to control electrically, was used at a heating rate of 4 °C/min. It was placed under a Zetopan microscope equipped with a photoelectric cell. The appearance of a cloud point was detected as the onset of a transmitted light jump.

Calorimetric Measurements. Glass transition temperatures, heats of demixing, and specific heats of the pure polymers and their blends were determined in a Perkin-Elmer DSC-2C scanning calorimeter. Glass transition temperatures (T_g) were measured in the range 220–400 K, by using the Autocooler device. Samples were heated at a rate of 20 K/min and at a range setting of 5 mcal s^{-1}. The temperatures observed at the midpoint of the heat capacity transition are reported as the glass transition. Each sample was scanned several times to make certain that sample behavior, especially for the blends, was reproducible. The T_g's from the second run are reported. Temperature calibration was made by reference to pure indium.

Demixing heats were measured with samples of about 20 mg. Calibration temperature with indium was carried out at 10 K/min. Corrections were made at other scanning rates. The range was set at 5 mcal s^{-1} for scanning rates of 80 K/min and at 2 mcal s^{-1} for scanning rates of 40 K/min or lower. Areas under the peaks were converted into heats of demixing in the usual way.

Specific heats were measured by using the external standardization method. A reference base line was recorded first. After operating the calorimeter in an isothermal regime for 2 min, there followed a dynamic scanning period during which a deflection was recorded. Similar protocol has been followed with a sapphire sample, which is the external reference, and with the polymer samples. In all cases aluminum pans (pan plus cover) were selected in order to have the same weight (within 5%). Special care was also taken with the platinum cover of the sample holder. In all cases covers were placed in exactly the same position taking a small scratch made on them as a reference. The heat capacity of the samples was obtained by appropriate rationing of the deflections and heat capacities, using previously reported values for the sapphire standard. Samples were heated at 80 K/min, kept at 420 K for 5 minutes, and then cooled at 40 K/min to 320 K before the useful scanning between 320 K and 420 K at 20 K/min.

All theoretical calculations were carried out with an Olivetti M-24 microcomputer and appropriate software.

Results and Discussion

Robeson et al.[3] have reported the miscibility of poly(bisphenol A hydroxy ether) (phenoxy) with water-soluble polyethers, such as poly(ethylene oxide) and poly(vinyl methyl ether) (PVME). In that work, the authors established PVME/phenoxy miscibility as a consequence of the film clarity and of the existence of a single glass transition temperature (T_g) in the complete range of compositions. They also pointed out that their blends became opaque at preparation temperatures or slightly above in a Brabender (150–180 °C). After cooling, transparency appeared rapidly and reheating to the original temperature lead once

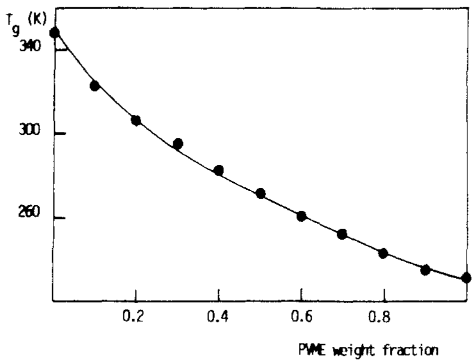

Figure 1. Glass transition temperatures of PVME/phenoxy blends.

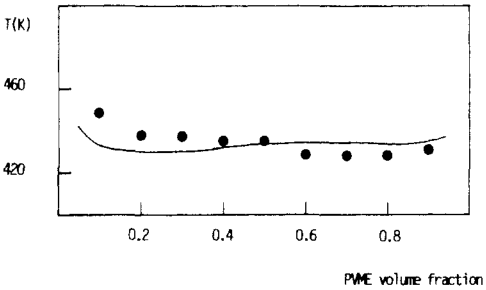

Figure 2. Cloud point curve of blends of PVME with phenoxy. The solid line is the theoretical spinodal (see text).

again to opacity. No more data about the complete phase diagram curve were reported.

Glass Transition Data. Glass transition temperatures (T_g) of PVME and phenoxy blends, covering the whole range of compositions, were measured. Results are shown in Figure 1. Each amorphous blend exhibited a single glass transition whose temperature changes smoothly with composition between the T_g's of the pure components, thus meeting the criterion for a miscible polymer-polymer blend. Results are in a good agreement with those reported by Robeson et al.[3] Slight differences may be attributed to the different preparation modes and to the differences in molecular weight distributions of the PVME samples employed in each work. The solid line in Figure 1 corresponds to the Gordon-Taylor equation:

$$T_g = (w_1 T_{g1} + k w_2 T_{g2})/(w_1 + k w_2) \tag{1}$$

where the semiempirical parameter k has been adjusted to 0.51 in order to match experimental values.

Phase Diagrams. Figure 2 shows the phase diagram found upon heating from homogeneous blends obtained by solution blending. Because of the relatively high value of the temperatures, compared with the T_g of each component, it was possible to observe an equilibrium behavior, i.e., demixing upon heating followed by mixing upon cooling. Another important feature of the phase diagram is the apparent bimodal behavior, but this may not be experimentally significant, giving the errors inherent in this type of measurement.

Heats of Demixing. Very recently, Natansohn[6] has studied the heat of demixing associated with a LCST phase behavior by means of DSC. The systems under study were PS/PVME and PCL/PVC. In a similar way Ebert et al.[7] have applied the same type of experiments to the heat of demixing of PEA/PVDF blends.

When samples of blends that can develop a LCST phase separation are heated in a DSC calorimeter, a thermogram similar to that shown in Figure 3 might be obtained. It is obvious that, in our blend, phase separation is associated with an endothermic process. Different information can be provided by the analysis of such demixing peaks. Our study was confined to the 50:50 blend. Using Ebert et al.[7] terminology, we have denoted the onset temperature as T_E. As in the case of Ebert's work, T_E shifted to larger values with increasing heating rates, as shown in Figure 4. An extrapolation to zero heating rate may be expected to be similar to the phase-separation temperature detected by means of optical microscopy. This is actually the case of our blend. Similar results were obtained by Ebert et al.[7] and Natansohn.[6]

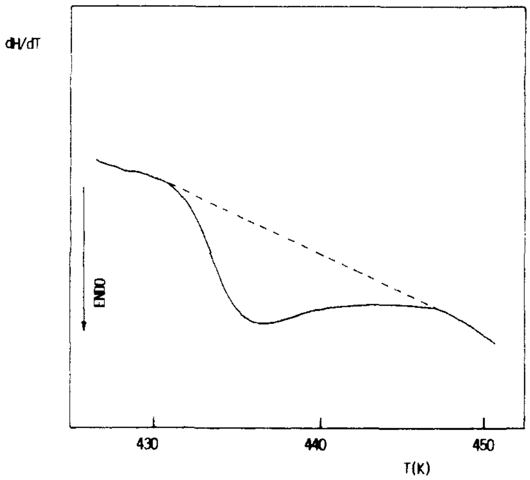

Figure 3. DSC trace characteristic of the phase separation for a 50:50 PVME/phenoxy blend.

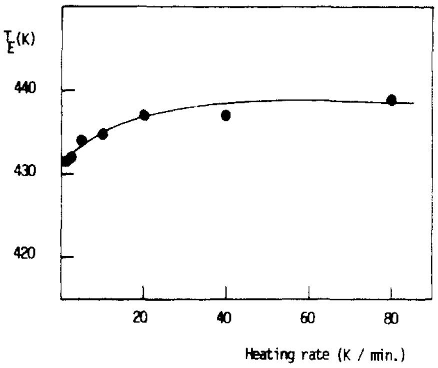

Figure 4. Dependence of the onset temperature T_E on the heating rate for a 50:50 PVME/phenoxy blend.

Heats of demixing have been determined from the area under endotherm peaks. As pointed out by Natansohn,[6] this area increases as the heating rate increases, reaching a plateau in the region between 20 and 80 K/min. However, at lower heating rates the area decreases dramatically. This is not the case of the Ebert et al.[7] system, where the authors have been able to construct master curves of the integral heat of demixing as a function of the difference between the actual temperatures and T_E. The heating rate range in this case goes from 10 to 80 K/min. Consequently, it seems that the heat of demixing does not depend on the heating rate in the PEA/PVDF blend. Natansohn[6] argued that at high heating rates the blend is forced to transform from a single-phase to a two-phase system, giving an endotherm or an exotherm which is a measure of the two components' interaction. At lower heating rates the peak goes unnoticed. His conclusion is that the plateau reflects the nature of such interactions. Our experimental data on heats of demixing are summarized in Table II. The plateau value (~0.48) should be identified as a rough approximation of the total heat of mixing, changing the sign. This approximation becomes more realistic if, as in our system, the two phases obtained

Table II
Heats of Demixing at Different Heating Rates. PVME/Phenoxy 50:50 Blend

heating rate, K/min	heat of demixing, cal/g	heating rate, K/min	heat of demixing, cal/g
80	0.54	10	0.27
40	0.42	5	0.21
20	0.46		

Table III
Heat Capacities of Pure Components and a 50:50 PVME/Phenoxy Blend (in cal/g•K)

PVME	phenoxy	blend
0.604 (±0.003)	0.580 (±0.002)	0.596 (±0.003)

Table IV
Temperature Dependence on the Density, Thermal Expansion Coefficient, and Thermal Pressure Coefficient of Pure Polymers

phenoxy	$1/\rho = 0.83624 + 3.922 \times 10^{-4} (T - 273.2) + 4.84 \times 10^{-7} (T - 273.2)^2$
	$\alpha = 4.911 \times 10^{-4} + 6.77 \times 10^{-7} (T - 273.2)$
	$\gamma = 0.431 - 9 \times 10^{-4} (T - 273.2)$ cal/cm^3·K
PVME	$\rho = 1.05445 - 7.388 \times 10^{-4} \times (T - 298.2) - 2.867 \times 10^{-7} (T - 298.2)^2$
	$\alpha = 7.006 \times 10^{-4} + 3.915 \times 10^{-7} (T - 298.2)$
	$\gamma = 0.301 - 0.00128 (T - 298.2)$ cal/cm^3·K

at the final scanning temperatures correspond to compositions in the vicinity of the pure polymers (see the diagram in Figure 2).

Excess Heat Capacities. Following a suggestion of ten Brinke and Karasz[5] according to which measurements of excess heat capacities of blends over the additive ones might be additional magnitudes to test the potentiality of new theories about polymer/polymer miscibility, Barnum et al.[12] have measured excess heat capacities of poly(α-methylstyrene-*co*-acrylonitrile)/poly(methyl methacrylate) blends and polycarbonate/Kodar mixtures. They reported excess heat capacities which varied according to composition and with a maximum of about 0.02 cal/g·K. The preliminary measurements taken of our PVME/phenoxy blends showed that the excess heat capacities of these blends were lower and very near the experimental error inherent in the experimental determination. For this reason, measurements have only been taken of the 50:50 blend, trying to reduce the errors arising from the low compositions of one of the components and taking into account that, according to Barnum et al.'s work, the maximum deviation is placed in the vicinity of an equimolar mixture. Up to eight experimental determinations have been averaged for each sample investigated. Results are summarized in Table III. From these results, a positive excess heat capacity for the 50:50 blend might be calculated. Its value of 0.004 is within the experimental uncertainty of the measurements, but it seems interesting to take it into account in the following theoretical analysis.

Theoretical Calculations. In the above-mentioned work,[12] Barnum et al. argued that positive values of the excess heat capacity cannot be explained by the modern equation-of-state theories. They appealed for new theories where, as in the case of the ten Brinke and Karasz model, the specific interactions were more emphasized against the role of the free volume effects. In our work, we will discuss the potentiality of the equation-of-state model in matching the experimental results resumed above.

The equation-of-state theory is based on Prigogine's assumption which states that the degree of freedom of a polymer fragment can be separated into internal and external components. The latter number is denoted by $3c$, with $c < 1$. In such a way the equation of state for pure liquids can be written in terms of characteristic and reduced magnitudes T_i^*, P_i^*, v_i^*, $\tilde{T}_i$, $\tilde{P}_i$, $\tilde{v}_i$, available from knowledge of the thermal expansion coefficient α and the thermal pressure coefficient γ.

Extension to mixtures requires a set of combining rules, keeping in mind the model of a random mixture and the additivity of the hard core volumes of both components. Interactions are supposed to take place between the surfaces of adjoining segments. The exchange interactions are described by an interaction parameter X_{12}. The noncombinatorial entropy can be affected by partial order created in the mixture as a consequence of specific interactions. A Q_{12} semiempirical parameter is introduced to adjust theory and experiments. In our work we have introduced a c_{12} parameter which characterizes deviations from additivity of the number of external degrees of freedom per segment in the mixture.[13] The equation of state for the two-component mixture is identical with that of the pure components if we previously calculate the mixture magnitudes in the following way:[13]

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \Theta_2 X_{12} \qquad (2)$$

$$\tilde{T} = T/T^* = (1/P^*)[\phi_1 P_1^* T_1 + \phi_2 P_2^* T_2 - (c_{12}\phi_1\phi_2 kT/v^*)] \qquad (3)$$

where ϕ_i are the segment fractions, Θ_2 is the surface fraction of component 2, calculated as

$$\Theta_2 = (s_2/s_1)\phi_2/[\phi_1 + (s_2/s_1)\phi_2] \qquad (4)$$

where s_2/s_1 is the relation between segment surface areas, k is the Boltzmann constant and, v^* is a segment volume taken as a reference.

Hamada et al.[14] have proposed an expression for the heat of mixing based on a McMaster's type of approach,

$$\Delta H_M = \tilde{r}N[-(3/2)\phi_1\Theta_2 r_1 c_{12} kT + \phi_1 P_1^* v^*/\tilde{v}_1 + \phi_2 P_2^* v^*/\tilde{v}_2 - P^* v^*/\tilde{v}] \qquad (5)$$

and, at atmospheric pressure, the spinodal of a high-molecular weight binary mixture is given by[13]

$$\begin{aligned} &1/r_1\phi_1 + 1/r_2\phi_2 - 6 \ln (m_1/m_2)^{1/2}(c_1 - c_2) + \\ &\quad 6 \ln (m_1/m_2)^{1/2} c_{12}(\phi_2 - 2\phi_1) - \\ &\quad 6c_{12} \ln [[(2\pi m_2 kT)^{1/2}/h](1.3v^*)^{1/3}(\tilde{v}^{1/3} - 1)] \\ &\quad - (2v^*/kT)[(s_2/s)^2(s_1/s)(X_{12}/\tilde{v}) - T\tilde{v}_1 Q_{12}] - \\ &\quad (\delta\tilde{v}/\delta\phi_1)_{P,T}[[c_1 - c_2 + (\phi_1 - \phi_2)c_{12}]/\tilde{v}^{2/3}(\tilde{v}^{1/3} - 1) - \\ &\quad (v^*/kT\tilde{v}^2)[P_1^* - P_2^* - (s_2/s)(\phi_2 - \Theta_1)X_{12}]] = 0 \qquad (6) \end{aligned}$$

where each component has r_i segments of equal volume v^* and s is the average surface. m_i are the segment masses of the two components; h is the Planck constant and $\tilde{v}$ the mixture reduced volume, calculated from $\tilde{T}$ in the usual way in this theory.

Characteristic and reduced magnitudes of the pure components can be calculated from appropriate experimental data of densities and specific volumes at different temperatures and pressures. Data for phenoxy have been taken from the work of Zoller,[15] whereas data for PVME have been extrapolated from data given by Shiomi et al.[16] Table IV resumes the basic data used in the calculations of reduced and characteristic values of the pure components.

In the following calculations we have used c_{12}, X_{12}, Q_{12}, and s_2/s_1 as adjustable parameters, but we have retained some logical conceptions about the physical meaning of such magnitudes. Given that we assume we have specific interactions in the mixtures and consequently exothermic

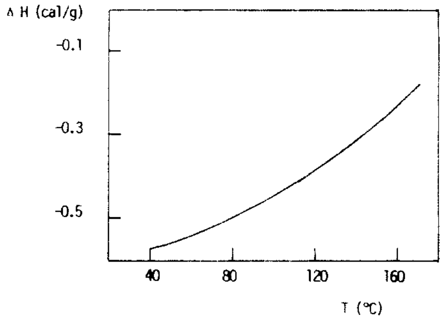

Figure 5. Theoretical heat of mixing against temperature for a 50:50 PVME/phenoxy blend.

heat of mixture, X_{12} must have a negative value. This is also the case of Q_{12} given the decrease in the entropy cause by these specific interactions. Calculations made on the basis of Bondi radii[17] and Sanchez's suggestion[18] about s_2/s_1 both gave values of this parameter close to 1. ten Brinke et al.[13] argued that, in general, specific interactions imply volume contraction on mixing. Therefore, the molecules come closer together in the mixture and the number of external degrees of freedom will be smaller than that obtained by a linear combination of the values for both pure components.[13,14] Hence $c_{12} > 0$ seem to be correct values for polymer/polymer systems.

Spinodals have been simulated for a large number of semiempirical parameter sets, the other magnitudes being introduced in the calculations as variable functions of the temperature. This is a different method if we compare it with other calculations reported in the literature,[13,19] where values at a given temperature are used in the whole range of phase-separation temperatures. We can generally conclude that there are great differences between spinodals generated with not very different semiempirical sets. This behavior differs from that of the interaction parameter–concentration curves. Each set of parameters selected allows us to calculate heats of mixing at different temperatures according to eq 5. Once again, characteristic and reduced magnitudes have been used as temperature-dependent functions, whereas semiempirical parameters have been kept constant. This procedure seems reasonable, at least in a range in the vicinity of 433.2 K, which corresponds to the cloud point of a 50:50 mixture.

The optimum set is that which fits, as well as possible, all the experimental data detailed above. Our proposal is $s_2/s_1 = 1.36$, $X_{12} = -3.38$ cal/cm^3, $Q_{12} = -0.004$ cal/cm^3·K, and $c_{12} = 0$.

Small but negative c_{12} values are needed for simulating the correct shape of the experimental spinodal curve, in spite of the physical meaning explained above. However, such negative c_{12} values gave endothermic heats of mixing. Furthermore, consistency of this negative value would need experimental determinations of specific volumes of the blends, which are not available.

In Figure 2, we have also drawn the theoretical spinodal calculated with the above mentioned set of parameters. Figure 5 illustrates the heat of mixing–temperature relationship. Different features arise from it. For example, theoretical heats of mixing are in the range of those provided by the demixing heat experiments (with the opposite sign). They are exothermic in nature. Furthermore, heat of mixing becomes less negative when the temperature increases. This finding seems to be in agreement with the predictions of Patterson and Robard.[20] However, they concluded that LCST behavior in blends with strong specific interactions is mainly the result of $X_{12}/\tilde{v}$ becoming less negative at elevated temperature. Although this ratio actually becomes less negative when temperature increases, the different terms of eq 5 have different behaviors with temperature. This is not the case of the Patterson and Robard expression where terms related to pure components are kept constant throughout the whole temperature range. Consequently, and in our analysis, it is not possible to conclude that the variation of ΔH_m is primarily due to the exclusive effect of $X_{12}/\tilde{v}$.

The temperature dependence of the heat of mixing is given unambiguously by the excess specific heat of the blend[12]

$$(\delta \Delta H_{\mathrm{mix}}/\delta T)_P = \Delta C_p = C_p - w_1 C_{p1} - w_2 C_{p2} \qquad (7)$$

where w_i are the component mass fraction and both specific heats and the heat of mixing are expressed per unit mass. The theoretical dependence of the heat of mixing on the temperature calculated from Figure 5 can be compared with experimental results obtained from Table III and eq 7. At 390 K the theoretical value was 3.1×10^{-3} cal/g·K, within the range of the excess heat capacity experimentally determined for the 50:50 PVME/phenoxy blend. However, it is also clear from Figure 5 that the derivative of the heat of mixing or ΔC_p, although positive, increases with temperature. This is the opposite behavior to that predicted by the ten Brinke and Karasz model, where the excess specific heat decreased when temperature approached the cloud point temperature. Unfortunately, our system is inadequate for measuring excess heat capacities at different temperatures. Given the phenoxy glass transition temperature and the cloud point temperatures, only a short range of temperatures is appropriate for accurate measurements of ΔC_p. Experimental measurements with other systems or molecular weights are needed in order to achieve a better comparison.

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Registry No. PVME, 9003-09-2; (bisphenol A)(epichlorohydrin) (copolymer), 25068-38-6.

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