Chromatographic studies of a poly(vinyl methyl ether)/phenoxy resin blend near the lower critical solution temperature

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A blend of poly(vinyl methyl ether) and poly(bisphenol A hydroxy ether) was studied by means of inverse gas chromatography in the vicinity of the lower critical solution temperature. The comparison of the specific retention volume of the mixed polymer system with the average value of the specific retention volumes of the pure components allowed for the detection of the phase separation, which was in reasonable agreement with the phase diagram determined by optical microscopy. Interaction parameters at the cloud-point temperature were negative and far from the critical value obtained from the phase-separation data. They were also probe-dependent. The results have been interpreted on the basis of a ternary g_T parameter similar to that employed in ternary systems of one polymer and two solvents.

(Keywords: inverse gas chromatography; interaction parameter; lower critical solution temperature; phenoxy/poly(vinyl methyl ether) blend)

INTRODUCTION

The study of the interactions between a homopolymer and a volatile probe[1] by means of inverse gas chromatography (i.g.c.) was extended in 1974[2] to the investigation of polymer blends. Starting with the classical Flory–Huggins expression applied to three-component systems, a method of analysis of i.g.c. measurements on polymer blends, which yields the polymer–polymer interaction coefficient, may be proposed. In i.g.c., this interaction coefficient is expressed as:

$$\chi'_{23} = \frac{\chi_{23}}{x_2} = \frac{\chi_{23} V_1}{V_2} \qquad (1)$$

where x_2 is the number of segments in the polymer molecule, V_1 is the molar volume of the solvent injected into the column, V_2 is the molar volume of polymer 2, and χ_{23} or χ'_{23} refer to the interaction between polymer 2 and polymer 3.

In most of the papers devoted to such measurements, the interaction coefficient exhibits a significant dependence on the chemical nature of the probe. Al-Saigh and Munk[3] have analysed the different possible sources of experimental error and concluded that the dependence of the interaction parameter on the nature of the probe seems to be real. In a first approach to the problem they have proposed a similar analysis to that applied to ternary systems constituted by a polymer in a mixed solvent. In these ternary mixtures, it is possible to write a phenomenological relation[4]:

$$\Delta G_m = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1\phi_2 g_{12} + n_1\phi_3 g_{13} + n_2\phi_3 g_{23} + n_1\phi_2\phi_3 g_T] \qquad (2)$$

which expresses the change in the free energy of mixing ΔG_m in terms of the number of moles of the components (n_j), the volume fractions (ϕ_i) and three binary interaction functions g_{ij}, related to the interaction parameter by means of:

$$\chi_{ij} = g_{ij} + \phi_i \, \mathrm{d}g_{ij}/\mathrm{d}\phi_i \qquad (3)$$

In equation (2) g_T is a phenomenological function of the composition of the mixture, while all the other quantities are clearly specified. Al-Saigh and Munk[3] proposed that the i.g.c. method does not measure directly the elusive parameter g_{23} or χ'_{23} but an apparent one, which after some manipulations can be written as:

$$(\chi'_{23})_{app} = \frac{V_1}{V_2}\left(g_{23} + \phi_2 \frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_2}\right) - g_T = (\chi'_{23})_{eff} - g_T \qquad (4)$$

There is a situation where a qualitative idea of the relationship between g_T and the nature of the probe can be experimentally determined. In systems where the mixture presents a lower critical solution temperature (*LCST*), the theory predicts that at this temperature the interaction parameter has almost a zero value[5]:

$$\chi_{crit} = (x_1^{-1/2} + x_2^{-1/2})^2/2 \qquad (5)$$

Consequently for high-molecular-weight polymers, the $(\chi'_{23})_{app}$ measured at temperatures at which the polymer blend shows phase separation can be taken as a first approach to the g_T value of this blend for a given probe.

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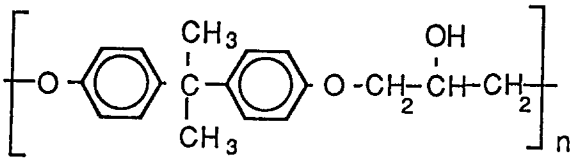
In this work, we have studied by means of i.g.c. the thermodynamics of a mixture constituted by poly(vinyl methyl ether) (PVME) and poly(bisphenol A hydroxy ether), also called phenoxy resin:



This mixture has been stated to be miscible at low temperatures and to exhibit a *LCST*-type phase diagram[6,7].

Phase diagrams obtained by optical microscopy are related to the i.g.c. measurements. The technique is based[8,9] on the observation of the differences of the retention volumes of solvent probes between polymer blends and those of the pure components. Miscible blends have a lower retention volume than the arithmetic average of the values of the homopolymers at the corresponding composition. If the blend is phase-separated, the retention volume should be the same as the average value of the homopolymers.

EXPERIMENTAL

Materials

Phenoxy was obtained from Quimidroga (Barcelona, Spain) and corresponds to the Union Carbide PKHH product. The commercial sample, after being purified by solution in dioxane and precipitation in methanol, had a glass transition temperature of 95°C. Two additional samples (PHA, PHB) described in *Table 1*, prepared by fractional precipitation in the above-mentioned mixture, were used in the determination of the molecular-weight influence on the phase diagrams.

Poly(vinyl methyl ether) ($T_g = -28°C$) was obtained from Polysciences (catalogue no. 3032) and purified in a benzene/iso-octane mixture.

Molecular weights were measured by g.p.c.[7]. They are listed in *Table 1* together with the densities of the polymers[7].

All the solutes were chromatographic quality or reagent grade and were used without further purification.

Apparatus and procedures

In order to determine the phase-separation temperatures of the phenoxy/PVME systems by optical microscopy, several films of variable compositions were prepared by dissolution of the polymers in dioxane and further evaporation of the solvent. The detection of the phase-separation temperatures was carried out by measuring the intensity of the light transmitted in the microscope. The films were deposited onto a hot-stage device (Mettler FP52) and heated from 50°C to the onset of precipitation at a rate of 3°C min^{-1}.

Table 1 Characteristics of the polymers used

		Molecular weights (g mol^{-1})		
		$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_z$
Phenoxy	PHC	50 800	18 000	71 000
	PHA	121 300	45 500	320 000
	PHB	1 700	6 800	23 000
PVME		61 000	29 000	94 300

	Densities (g cm^{-3})^a
Phenoxy	$\rho = 1.199 - 6.363 \times 10^{-4} t$
PVME	$\rho = 1.05445 - 7.388 \times 10^{-4}(t-25) - 2.867 \times 10^{-7}(t-25)^2$

^{a} t in °C

Table 2 Stationary-phase and column parameters

Polymer	Loading (% w/w)	Wt polymer, w_L (g)	Column length (cm)
Phenoxy (PHC)	10.06	0.5028	100
PVME	10.02	0.4415	100
PVME/phenoxy (40/60)	10.04	0.4941	100

Columns for i.g.c. were prepared in the usual manner[9]. The pure polymers and a 40/60 phenoxy/PVME blend were coated from a dioxane solution onto Chromosorb G (AW-DMCS treated, 80/100 mesh). After drying in a vacuum oven for ~48 h at 50°C, the coated support was packed into 1/4 inch o.d. stainless-steel columns by applying a vacuum to one end. Glass wool was used to block the ends of the columns. The relative concentration of the polymers in the blend is assumed to be identical to that in the original solution prior to deposition on the inert support. A summarized description of the columns is given in *Table 2*.

Measurements were taken on a modified Perkin–Elmer Sygma 300 Gas Chromatograph equipped with a flame ionization detector. Nitrogen was used as the carrier gas. Methane was used as a non-interacting marker to correct the dead volume in the column and the retention time was directly measured with the aid of 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^{-1}.

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

Computations

Specific retention volumes were calculated using:

$$V_g^\circ = \Delta t \frac{F}{w_L} \frac{273.16}{T_r} \frac{3}{2} \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \qquad (6)$$

Here, $\Delta t = t_p - t_m$ is the difference between the retention time of the probe and of the marker, F is the flow rate of the carrier gas at room temperature T_r, 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 χ_{1i} can be calculated using:

$$\chi_{1i} = \ln \frac{273.16 R v_i}{V_g^\circ V_1 P_1^\circ} - 1 + \frac{V_1}{M_i v_i} - \frac{B_{11} - V_1}{RT} P_1^\circ \qquad (7)$$

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

A similar equation can be derived for the blend, recognizing that the specific volume of the blend can be replaced by the arithmetic mean of the volumes of the pure polymers. However, it is easily derivable[3] that the apparent $(\chi'_{23})_{\text{app}}$ can be calculated without all auxiliary parameters (P_1°, B_{11}, ...) by means of:

$$(\chi'_{23})_{\text{app}}=\left(\ln\frac{V_{\text{g,blend}}}{w_2v_2+w_3v_3}-\phi_2\ln\frac{V_{\text{g},2}}{v_2}-\phi_3\ln\frac{V_{\text{g},3}}{v_3}\right)(\phi_2\phi_3)^{-1}\quad(8)$$

if three columns, two from homopolymers and a third from a blend, are prepared and retention volumes are measured in identical conditions.

RESULTS AND DISCUSSION

The cloud-point curves of the phenoxy (PH) fractions of high and low molecular weight are presented in *Figure 1*. Owing to the molecular-weight distribution of the polymers, the observed cloud-point curve does not represent coexisting phase compositions. It has been shown that critical points usually shift away from the extreme of the cloud-point curve[10], but can always be found as the point of common tangency of spinodal and cloud-point curve. However, in a first approximation, we can presume that the critical points of our phase-separation curve coincide with the minima of these curves. A second-order polynomial analysis gives us the following critical coordinates:

PVME/PHA	$(\phi_{\text{PH}})_{\text{crit}}=0.32$	$T_c=419$ K
PVME/PHB	$(\phi_{\text{PH}})_{\text{crit}}=0.52$	$T_c=434.2$ K

With these critical data, a first estimation of the variation of the polymer–polymer interaction parameter with temperature and composition can be performed using the classical Flory–Huggins–Staverman model, adequately adapted to deal with molecular polydispersities in two constituent polymers and by the fact that phenoxy and PVME offer different segment surfaces on contact[10].

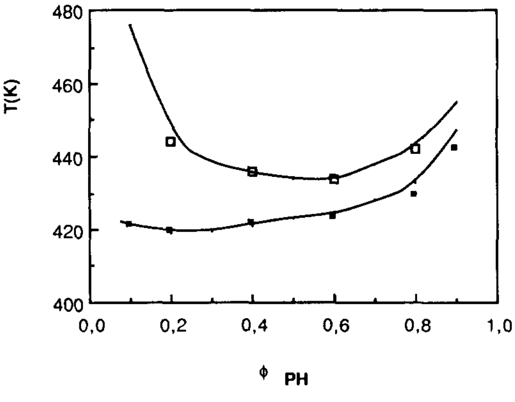


Figure 1 Cloud-point curves of PVME/PHA (■) and PVME/PHB (□) systems and the theoretical spinodals calculated with $\gamma=-0.140$, $\alpha=-0.01$, $\beta_S=0.127$ and $\beta_H=-48.36$

Starting with the free energy of mixing, developed so as to be independent of any model of molecular mixing and applied to a binary mixture of polymeric components, we can obtain the following expression at atmospheric pressure:

$$\frac{\Delta G_m}{NRT}=\frac{\phi_1}{x_1}\ln\phi_1+\frac{\phi_2}{x_2}\ln\phi_2+g(T,\phi)\phi_1\phi_2\qquad(9)$$

where N $(=n_1x_1+n_2x_2)$ is the total number of lattice sites, and n_i and x_i are the number of moles and number of segments per chain respectively. The chemical potential can be derived directly from this expression and, defining χ as in equation (3), equation (9) can be easily transformed in the usual Flory–Huggins expression for a polymer–solvent system.

In equation (9), g is the interaction function, temperature-dependent, which can be written as[10]:

$$g=\alpha+\beta/(1-\gamma\phi_2)\qquad(10)$$

where α is an empirical entropy correction and β accounts for the difference between the interaction energy of unlike neighbours and the average of the value in the pure components. This β term also accounts for the temperature dependence of g:

$$\beta=\beta_S+(\beta_H/T)\qquad(11)$$

and γ introduces the surface areas of the repeat units, σ_1 and σ_2, of the polymers:

$$\gamma=1-(\sigma_2/\sigma_1)\qquad(12)$$

The spinodal and the critical states are determined by[10]:

$$\left(\frac{1}{\phi_1\bar{m}_{w1}}\right)+\left(\frac{1}{\phi_2\bar{m}_{w2}}\right)+\frac{\partial^2(g\phi_1\phi_2)}{\partial\phi_2^2}=0\qquad(13)$$

$$\frac{\bar{m}_{z1}}{\phi_1^2\bar{m}_{w1}^2}-\frac{\bar{m}_{z2}}{\phi_2^2\bar{m}_{w2}^2}+\frac{\partial^3(g\phi_1\phi_2)}{\partial\phi_2^3}=0\qquad(14)$$

where $\bar{m}_w$ and $\bar{m}_z$ are the respective relative weight-average and z-average molecular weights:

$$\bar{m}_w=\bar{M}_w/M_0\qquad(15)$$

$$\bar{m}_z=\bar{M}_z/M_0\qquad(16)$$

M_0 being the molecular weight of the reference segment. In our case the monomeric unit of PVME has been taken as a reference (i.e. $M_0=58$).

The experimental critical data used in conjunction with equations (10)–(16) allow us to calculate α and γ. Consequently β is calculated at the two critical temperatures, from which β_S and β_H are available from equation (11). The final step implies the calculation of g and χ at any concentration and temperature. Our calculations provided us with the following set:

$\gamma=-0.140$ consequently $\sigma_2/\sigma_1=1.14$

$\alpha=-0.01$

$\beta_S=0.127$ $\beta_H=-48.36$

σ_2/σ_1 is in good agreement with the values calculated according to Bondi's radii and Sanchez's suggestion[7].

The model predicts a nearly constant value of g with composition. For instance, at 390 K, the g parameter only varies from $-0.007\,13$ to $-0.007\,15$. Consequently g and χ may be considered to be identical (see equation

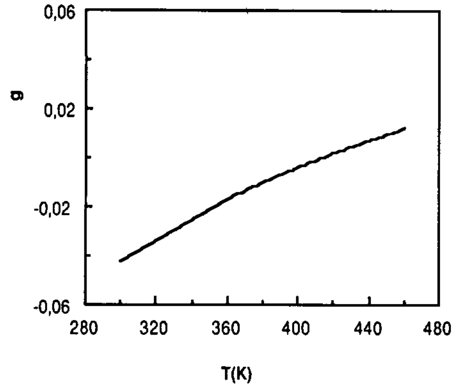


Figure 2 Temperature dependence of *g* in the PVME/PH (40/60) system

(3)). The temperature variation is shown in *Figure 2*. The theoretical spinodals calculated with the above-mentioned set of parameters are also shown in *Figure 1*.

The sample denoted as phenoxy C (PHC) exhibited in its blend with PVME a phase diagram similar to the diagrams of PHA and PHB, with a minimum in the vicinity of $\phi_{PH}=0.4$. For a mixture PVME/PHC (40/60) similar to that used in i.g.c. experiments, the cloud-point temperature was 432 K. This mixture had a glass transition temperature of 303 K. Given the phenoxy T_g (368 K) and the restriction of the i.g.c. measurements at temperatures above T_g+50 K, the temperature range between T_g and phase separation is very short. This temperature range is the only range where thermodynamic measurements of a liquid/liquid mixture can be rigorously taken.

Retention diagrams of the 40/60 blend with several molecular probes were determined in the temperature range between 384 and 480 K far from the glass transition temperature of the blend. In all cases the diagram presented a deviation from strict linearity in the temperature range between 425 and 445 K, as can be seen in *Figure 3* for the case of n-tetradecane. *Table 3* gives the temperatures at which this change in the slope appeared in the different probes investigated.

This change in the slope may be identified with the location of the phase separation in the column. The different values may be considered, at first sight, within the experimental error if we take into account the difficulties in defining the breaking point and the experimental errors inherent to the chromatographic measurements, especially in probes with high volatility where retention times are affected by a great error.

From the chromatographic point of view, the location of the phase-separation temperatures can also be studied by means of the molecular-probe retention volumes on the blend compared to the mean values of the retention volumes of the same molecular probes in the homopolymers. Several authors[8,11–13] have shown that the retention volumes of immiscible blends are a linear combination of the retention volumes of each component:

$$V_g = V_{g,1,2}w_2 + V_{g,1,3}w_3 \qquad (17)$$

Miscible polymer blends have a retention volume lower than the arithmetic average volume of the homopolymers at the corresponding composition because the probe must compete with one of the components for the sites of possible interaction with the other, thus giving a shorter time or volume of elution. In contrast, retention volumes of a phase-separated blend are equal to the linear combination of the retention volumes of the pure constituents.

Figure 4 shows a plot of the experimental retention volumes of the blend against the retention volumes calculated as a linear combination of those of the pure constituents in the investigated temperature range. *Figure 4* corresponds to n-decane. Similar results have been obtained with the remaining molecular probes. It is known[1] that experimental retention volumes are

Table 3 Temperatures where a discontinuity in the retention diagrams is located, temperatures at which experimental and calculated V_g values coincide and polymer–polymer interaction parameter at 432 K of a 40/60 PVME/phenoxy blend

Probes	Temp. where disc. retent. diag. (K)	Temp. where $V_{g,exp}=V_{g,calc}$ (K)	χ'_{23}
Diglyme	445	460	−0.286
Dimethylformamide	436.5	470	−0.153
n-Tetradecane	438.4	480	−0.166
n-Decane	429	468	−0.108
Benzene	425	441	−0.119
Ethyl acetate	430	441	−0.306
n-Propanol	431	460	−0.117
Chlorobenzene	433	441	−0.071
1,2-Dichloroethane	426	470	−0.112
Acetonitrile	443	441	−0.411
Toluene	444	472	−0.102
Dioxane	443	478	−0.322
n-Butanone	428	451	−0.246

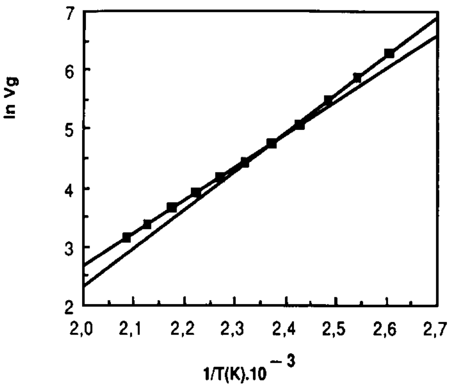


Figure 3 Retention diagram of the 40/60 PVME/PH system with n-tetradecane

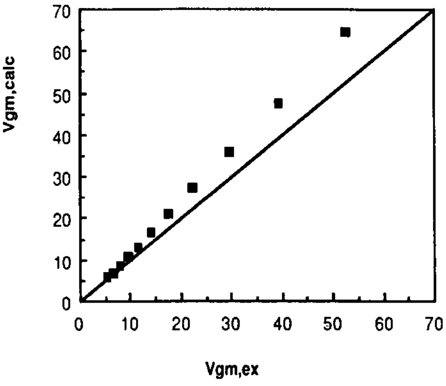


Figure 4 Representation of the n-decane experimental retention volumes vs. the retention volumes calculated as a linear combination of those of the homopolymers

proportional to $1/T$. At low temperatures these experimental retention volumes are smaller than those calculated from a linear combination of the retention volumes of the homopolymers. In all cases, when the temperature increases these values become closer. *Table 3* indicates the temperatures at which experimental and calculated values coincide. These temperatures, in reasonable agreement with those observed in the cloud-point diagram, depend, however, on the nature of the probe.

This well defined difference in the retention conditions of the molecular probes is reflected in the subsequent calculations of the interaction parameter (χ or g) according to equation (8). *Table 3* also gives the value of the interaction parameter between the two polymers at 432 K, the temperature at which the blend separates into phases by means of microscopy.

As can be seen, the interaction parameters corresponding to the different molecular probes are clearly negative and far from the value derived from phase-separation data. According to equation (4), g_T can be evaluated, at least in a first approximation, from the apparent χ'_{23} value predicted by our phase-separation analysis. Whether the g_T calculated in this way is real or a consequence of other experimental uncertainties is not easy to verify. Given the narrow range between the phenoxy T_g and the phase-separation temperature of the blend, it is not possible to calculate interaction parameters at other lower temperatures. An ideal system would be one with a low T_g and a high *LCST* which would give reliable i.g.c. data over an extended range of temperatures.

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