Thermodynamic Study of Poly(4-hydroxystyrene)/Poly(vinyl acetate) Blends by Inverse Gas Chromatography

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ABSTRACT: The poly(4-hydroxystyrene) (P4HS)–poly(vinyl acetate) (PVA) system was studied at 170 °C by inverse gas chromatography. Specific retention volumes of several probes in the homopolymers and four blends (0.26, 0.38, 0.51, and 0.76 P4HS volume fractions) were used to measure the thermodynamic interaction between the polymers. The polymer–polymer interaction parameter χ_{23} calculated from the Scott–Flory–Huggins formalism showed an apparent dependence on the probes. This dependence seemed to be related with the strength of the probe interaction with the homopolymers and is believed to result from inappropriate application of the Scott–Flory–Huggins treatment to ternary systems. A method based on the equation-of-state theory was applied to eliminate the influence of the probe on χ_{23}. Negative values of the polymer–polymer interaction parameter confirm the miscibility of the system, and only a slight variation with the blend composition was found. This variation reveals that the maximum trend in miscibility is achieved at intermediate blend compositions.

Introduction

For the past few years there has been intensive interest in polymer blends because they represent a faster and less expensive way to improve properties than developing new polymers. The characterization of the blends at a basic stage involves the study of the miscibility of the pair. Miscible blends exhibit strong intermolecular interaction between dissimilar chains, which provides a favorable energetic contribution to the mixing process.[1-3] In this respect, hydrogen bonding between polymers is particularly attractive as a potential way to achieve miscibility in many cases.

Although there are a large number of techniques enabling the characterization of miscible blends, only a few of them allow the interactions to be quantified. The more frequently used techniques are those in which the polymer–polymer interaction parameter, χ_{23}, is obtained from measurements performed on a ternary polymer–polymer–solvent system. Among them, the inverse gas chromatography (IGC) method has turned out to be popular because of its rapidity (the characterization of the probe solvent is vanishingly small, which results in fast establishment of equilibrium) and the general availability of GC equipment.

In general, the polymer–polymer interaction parameter obtained from IGC exhibits a significant dependency on the chemical nature of the probe.[4-14] Munk et al.[13] suggested that the apparent variability in χ_{23} with the probe could be partly caused by uncontrolled experimental artifacts and errors, so they investigated the IGC technique itself to improve the experimental procedure and the data analysis methods. Nevertheless, they further pointed out that part of the observed variation was real. The χ_{23} probe dependence has been frequently related with probe structure and solvent strength,[4-15] but it was believed that the Scott–Flory–Huggins treatment had been inappropriately applied to ternary systems[7,13,16] and that the weakness was to assume that the Gibbs mixing function for the ternary polymer–polymer–solvent system is additive with respect to the binary contributions. Recently, a method has been proposed to calculate a "true" polymer–polymer interaction parameter, χ_{23}^{T}, based on the equation-of-state ternary theory[16] that should be not probe dependent. As far as we know, it has been only applied

to the polystyrene + poly(vinyl methyl ether)[16] and poly(ethylene oxide) + Phenoxy[14] systems.

In the present work, we have selected the poly(4-hydroxystyrene) + poly(vinyl acetate) system. The miscibility in this system arises from the intermolecular hydrogen-bonding interactions involving the phenolic hydroxyl group with the acetate carbonyl groups. This has been previously proved by Coleman et al.'s infrared studies.[17-20] Furthermore, our glass transition measurements also show that this blend is miscible at all compositions.[21,22] The blend has been studied at 170 °C, and the IGC retention behavior was measured for four blend compositions (0.26, 0.38, 0.51, and 0.76 P4HS volume fraction) using nine solvent probes. The experiments were carried out trying to minimize experimental errors[12] to determine the polymer–polymer interaction parameter χ_{23} and its dependence on blend concentration and probe. In addition, we have applied the method proposed by Horta et al.[16] that leads to χ_{23}^{T} for each blend composition.

Experimental Section

Materials. Poly(4-hydroxystyrene) (P4HS) and poly(vinyl acetate) (PVA) were purchased from Polysciences (U.K.).

The molecular weight of PVA determined by light scattering was $M_w = 200\,000$. The polydispersity index $M_w/M_n = 2$ and $M_n = 90\,000$ were obtained from GPC. The average molecular weight of P4HS was $M_n = 1500$ by vapor pressure osmometry, and GPC experiments revealed $M_w/M_n = 2$.

The solvents used were Carlo Erba RPE. Chromosorb W (AW-DMCS, treated, 80–100 mesh) was obtained from Sigma. The carrier gas was 99.99% helium from C.M. (Spain).

Column Preparation. All stationary phases were coated onto Chromosorb W by dissolution in acetone, stirring for 4 h, and slow evaporation of the solvent (in a rotary evaporator). Previous studies[21,22] showed that this solvent gave blend solutions which were homogeneous at all compositions; thus no demixing of the polymers occurs during the evaporation of the solvent. The stationary phase was finally dried in a vacuum oven at 50 °C for 1 day and packed by a gentle tapping procedure in a stainless steel column (inner diameter 0.6 cm, length 1.5 m), the end of which was loosely plugged with glass wool. The columns were purged at 150 °C for 5 h under dry nitrogen. The percentage loading was determined twice by the calcination method (0.5 h at 300 °C and 2 h at 800 °C) with the usual blank correction. The blend composition on the support was assumed to be the same as in the solutions used to coat the support. The weight support

Table I
Polymer Mixtures and Polymer Loading in the Columns

column	$w_3{}^a$	$T_g{}^b$ (°C)	% polymer loading
1	0	44	7.3
2	0.25	72	10.2
3	0.37	76	9.5
4	0.50	80	7.4
5	0.75	110	13.9
6	1	130	9.7

^{a} w_3 = weight percent of P4HS in the mixture. ^{b} From refs 21 and 22.

in the columns was between 6 and 7.3 g. Column characteristics are listed in Table I.

Instrumentation and Measurements. Measurements were made on a Varian gas chromatograph Model 3300 equipped with a flame ionization detector. Carrier gas (helium) flow rate was measured from the end of the column with a soap bubble flowmeter at room temperature. The measurement temperature was 170 °C, well above the glass transition of the homopolymers and blends, as can be seen in Table I. This condition ensured that the system exhibited ideal chromatographic behavior over the entire composition range. Flow rate and room temperature were checked frequently. The range of flow rates (five were selected) was 15–30 mL/min (±0.2 mL/min). Column inlet pressures (range 1000–1300 mmHg) were monitored with a Druck pressure transducer with an accuracy of 0.2 mmHg, and outlet pressures (atmospheric) were read from a mercury manometer (±0.5 mmHg).

Five or more consecutive injections of 1 μL were made for each probe. The net retention times of a probe were determined from the peak's maxima of retention times for the probe and the methane marker (±5 × 10^{-3} min).

Data Treatment. Specific retention volumes, V_g, were calculated from the expression

$$V_g = t_n \frac{F}{w} \left(\frac{3}{2} \right) \left[\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \right] \left(\frac{P_o - P_w}{P_o} \right) \frac{273.15}{T_r} \quad (1)$$

where t_n is the net retention time of each probe, w is the mass of the polymer in the column, P_i and P_o are the inlet and outlet pressures, F is the carrier gas flow rate at room temperature T_r and atmospheric pressure P_o, and P_w is the water vapor pressure at T_r. The values of V_g are usually extrapolated to zero flow rate to obtain $V_g{}^\circ$. In this work, V_g values were (in most of the cases studied) independent of the gas flow rate within the range 15–30 mL/min. Only a slight flow dependence was found for the column of P4HS with probes that showed small retention times. Values of $V_g{}^\circ$ were in the range 2–10 mL/g.

Throughout this paper, subscript 1 will be used to denote the probe or solvent, while the polymer will be denoted by 2 or 3, corresponding to PVA and P4HS, respectively. From the Flory–Huggins treatment of solution thermodynamics, the reduced residual chemical potential of the solvent in the mixture (solvent + polymer) is defined as the solvent–polymer interaction parameter, χ_{1j} (j = 2, 3), which can be calculated from IGC experiments with the relationship[4]

$$\chi_{1j} = \ln \frac{273.15 R v_j}{V_g{}^\circ P_1{}^\circ V_1} - \left(1 - \frac{V_1}{V_j} \right) - \frac{P_1{}^\circ}{RT}(B_{11} - V_1) \quad (2)$$

where v_j and V_j refer to the specific volume and molar volume of the polymer. V_1 and $P_1{}^\circ$ represent the probe molar volume in the liquid phase and saturated vapor pressure, respectively, and B_{11} is the second virial coefficient of the probe in the gas phase. All other symbols have their usual meanings.

For solvent (1) + polymer (2) + polymer (3) ternary systems, it has been shown[4] that the overall interaction parameter between the volatile probe (1) and the binary stationary phase (2–3) is

given by

$$\chi_{1p} = \ln \frac{273.15 R(\omega_2 v_2 + \omega_3 v_3)}{V_g{}^\circ P_1{}^\circ V_1} -$$
$$\left(1 - \frac{V_1}{V_2} \right) \varphi_2 - \left(1 - \frac{V_1}{V_3} \right) \varphi_3 - \frac{P_1{}^\circ(B_{11} - V_1)}{RT} \quad (3)$$

where ω_2, ω_3 and φ_2, φ_3 refer to the weight fractions and volume fractions of PVA and P4HS in the blend.

The vapor pressures, $P_1{}^\circ$, were calculated from the Antoine equation:

$$\log P_1{}^\circ = A - B/(t + C) \quad (4)$$

where t is the temperature in °C and the constans A, B, and C were taken from the Reid–Prausnitz–Sherwood compilation.[23]

The molar volumes of the probes, V_1, were calculated using Benson's method.[23]

$$V_1 = M_1/\rho_L \quad (5)$$

$$\rho_L - \rho_V = 2\rho_c + \frac{T - T_c}{T_c - T_B}(2\rho_{LB} - 2\rho_c) \quad (6)$$

$$\rho_V = P_1{}^\circ M_1/RT \quad (7)$$

where ρ_L and ρ_V are the densities of the liquid probe and its saturated vapor at temperature T. M_1 is the molecular weight. ρ_c is the density at the critical temperature T_c, and ρ_{LB} is the liquid density at the normal boiling temperature T_B.

Second virial coefficients B_{11} were calculated from the Pitzer–Curl–Tsonopoulos correlation:[24]

$$\frac{B_{11} P_c}{RT_c} = \mathcal{F}^{(0)}\left(\frac{T}{T_c}\right) + \omega \mathcal{F}^{(1)}\left(\frac{T}{T_c}\right) + \mathcal{F}^{(2)}\left(\frac{T}{T_c}\right) \quad (8)$$

$$\omega = -\log\left(\frac{P_1{}^\circ}{P_c}\right)_{T_R=0.7} - 1000 \quad (9)$$

where $\mathcal{F}^{(i)}$ are known functions of $(1/T_R)$ and $T_R = T/T_c$.

The density, thermal expansion coefficient, and critical parameters for the solvents were taken from references.[25,26]

Data used for polymers were v_2 = 0.840 cm^3/g, v_3 = 0.862 cm^3/g, α_2 = 6.76 × 10^{-4} K^{-1}, and α_3 = 8.95 × 10^{-4} K^{-1} at 25 °C.[27-29]

Results and Discussion

Specific retention volumes $V_g{}^\circ$ of nine probes were obtained for homopolymers PVA and P4HS and blends. The probes—toluene, acetone, 2-butanone, 3-pentanone, tetrahydrofuran, ethyl acetate, propyl acetate, n-butyl acetate, and isopropyl alcohol—were selected in such a way that they present different strengths of interaction with the polymers. Previous studies[30,31] have shown that the retention volumes of immiscible blends should be a linear combination of retention volumes of the pure polymers. On the other hand, for a miscible blend the probe gives a smaller volume of retention than the one corresponding to the linear combination of retention volumes of the pure constituents. As can be seen in Figure 1, the curves exhibited the downward curvature in the $V_g{}^\circ$ values, which gave the strength of the interaction between the two polymers in the blend; this is in concordance with the compatibility of the blend found by DSC measurements which already reflected a unique T_g value for each blend (Table I) and by infrared spectral studies that reflect the intermolecular hydrogen-bonding interactions involving the phenolic hydroxyl group with the acetate carbonyl group.[17,20]

Using $V_g{}^\circ$ values and following the procedure given by eqs 2 and 3, the χ parameters characterizing the interactions of the vapor phase probe with each of the two polymers, χ_{12} and χ_{13}, and with their mixtures, χ_{1p}, have been obtained and are plotted as a function of the blend composition in Figures 2 and 3 for all the probes studied
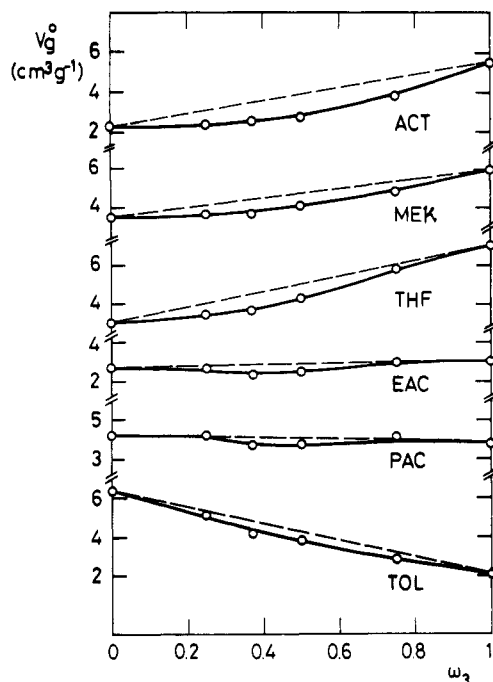
Figure 1. Dependence of V_g° on the P4HS weight fraction for selected probes. (– – –) Hypothetical average for nonmiscible blends.
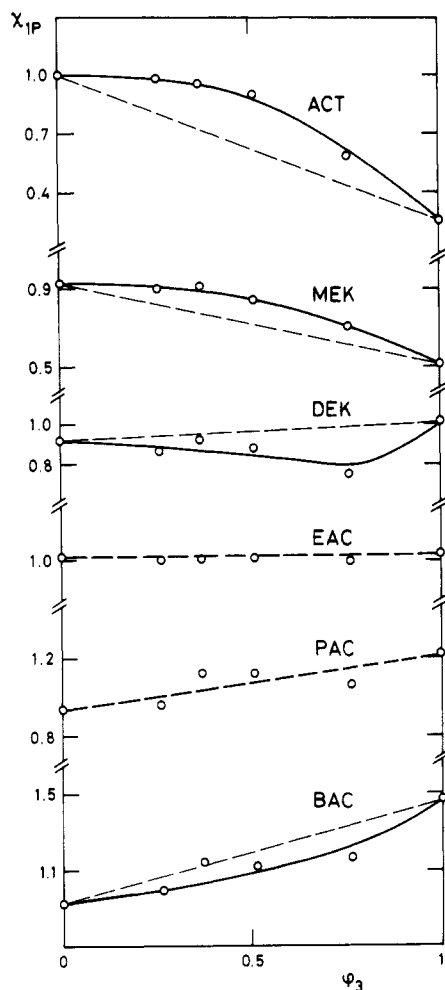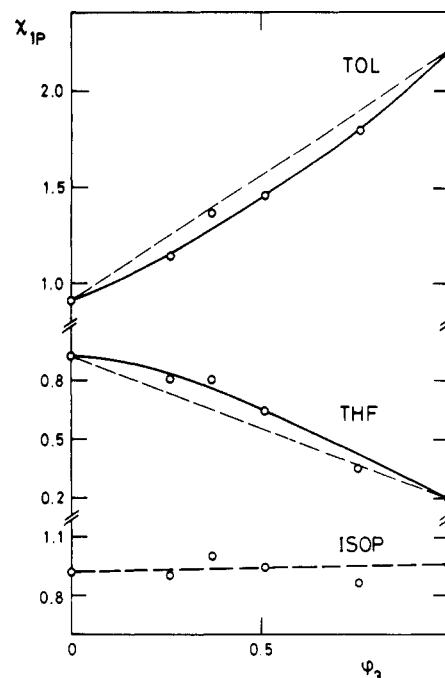

Figure 3. Variation of χ_{1p} with P4HS volume fraction for probes. (– – –) Hypothetical average for noninteracting ($\chi_{23} = 0$) blends.

polymer–polymer interaction parameter is usually obtained from measurements in polymer (2) + polymer (3) + solvent (1) ternary systems using the relation

$$\chi_{1p} = \varphi_2\chi_{12} + \varphi_3\chi_{13} - \varphi_2\varphi_3\chi'_{23} \tag{10}$$

where $\chi'_{23} = \chi_{23}V_1/V_2$ and χ_{23} is the polymer (2)–polymer (3) interaction parameter taking as reference the volume V_2.

The linear behavior in Figures 2 and 3 represents a blend with $\chi_{23} = 0$. Upward curvatures will give $\chi_{23} < 0$, whereas the downward curvatures will correspond to $\chi_{23} > 0$.

Values of χ'_{23} calculated from eq 10 are given in Table II for all the blend compositions, together with the polymer–solvent interaction parameters for the pure components. Munk et al.[12,13] have suggested calculating χ'_{23} from a simpler procedure, assuming that the columns are under identical conditions and combining eqs 2, 3, and 10; in our case this gives results identical to the corresponding ones reported in Table II.

For compatible polymer–polymer systems, negative values of χ'_{23} may be expected, reflecting a favorable interaction between the polymers. Positive values of χ'_{23} may reflect an unfavorable interaction between polymers, but in these cases the blend would be miscible if the components had a sufficiently low molecular weight, so that the combinatorial entropy ensures that the mixture does not phase separate. In the PVA/P4HS system one of the polymers, P4HS, has a low molecular weight (M_n = 1500); then slightly positive values of χ'_{23} would be in accordance with the blend compatibility obtained by DSC. As we can see in Table II, χ'_{23} values are, in general, negative or small and positive, except for the blend composition with the highest content in P4HS ($\varphi_3 = 0.76$), where the very positive values of χ'_{23} indicate an unfavorable interaction between polymers that could cause an incipient phase separation. In this kind of system where the compatibility is achieved by hydrogen bond interaction, it should not be strange that at high temperatures (170 °C) the interaction will be weakened, so that the blends having a very high concentration of the component that present autoassociation by hydrogen bond, i.e., P4HS, will become less compatible and even phase separate.

Figure 2. Variation of χ_{1p} with P4HS volume fraction for probes. (– – –) Hypothetical average for noninteracting ($\chi_{23} = 0$) blends.

(χ_{12} and χ_{13} are given by the intercept of the curves with the two ordinate axes). The χ_{1p} parameter is affected by the interaction between the polymers themselves. According to the Scott–Flory–Huggins[32] treatment, the

Table II
Interaction Parameters χ_{ij} Referred to V_i for the System Solvent (1) + P4HS (3) + PVA (2) at 443 K

| | | | | χ'_{23} | | | |
probe (code)	χ_{12}	χ_{13}	$\chi_{12} - \chi_{13}$	$\phi_3 = 0.26$	$\phi_3 = 0.38$	$\phi_3 = 0.51$	$\phi_3 = 0.76$
toluene (TOL)	0.92	2.20	−1.29	0.57	0.14	0.44	0.53
acetone (ACT)	1.00	0.25	0.75	−0.95	−1.07	−1.15	−0.88
2-butanone (MEK)	0.93	0.52	0.41	−0.43	−0.63	−0.47	−0.39
3-pentanone (DEK)	0.92	1.08	−0.16	0.45	0.21	0.44	1.58
tetrahydrofuran (THF)	0.93	0.21	0.72	−0.30	−0.61	−0.30	0.18
ethyl acetate (EAC)	1.01	1.05	−0.033	0.06	−0.50	−0.52	0.14
propyl acetate (PAC)	0.94	1.22	−0.28	0.31	−0.33	−0.14	0.53
n-butyl acetate (BAC)	0.92	1.47	−0.55	0.39	−0.04	0.30	0.95
isopropyl alcohol (ISOP)	0.92	0.96	−0.044	0.11	−0.30	−0.002	0.50

The χ'_{23} values depend on the P4HS/PVA composition, being smaller for intermediate volume fractions; this indicates that the miscibility of P4HS + PVA is more likely to be achieved when the blend mixture is around $\varphi_3 \approx 0.5$.

Usually in IGC experiments the polymer–polymer interaction parameter χ'_{23} is probe dependent. The values in Table II show a strong variation with the kind of probe, leading to positive and negative results for the same blend composition; this fact cannot be exclusively imputed to experimental errors but is probably due to the deficiency in the Scott–Flory–Huggins treatment as has been pointed out in several works.[7,13,16] Furthermore, if a more appropriate value of χ'_{23}/V_1 is calculated, the differences between probes will remain about equal in importance; on the other hand, the variation of χ'_{23} with probes seems not to be random; as can be seen in Table II, χ'_{23} values are more negative when χ_{12} is higher than χ_{13}.

Theoretical Calculations

To obtain χ'_{23}, eq 10 is frequently used. The approximations involved in such an equation are quite drastic as discussed by Pesci and Freed[33] and have recently been relaxed in an off-lattice discussion of the Flory–Huggins interaction parameter by Schweizer and Curro.[34] A very important consequence of the rigid-lattice derivation leading to eq 10 is the frequent assumption that the interactional part of the Gibbs function of the ternary system is additive in the binary contributions. This can cause the interaction parameter obtained for polymer mixtures by IGC to be strongly probe dependent.

The shortcomings of rigid-lattice models to describe phase-equilibria data of polymer solutions were pointed out years ago.[35] The use of generalized van der Waals models[36] or lattice-with-holes models[37,38] has allowed the description of basic phenomenology[37,38] such as lower critical solution temperatures.

Using the equation of state proposed by Flory[39] and Patterson,[40] Horta et al.[16] have proposed a method to calculate the so-called Flory interaction parameter, which, besides making use of the free-volume concept, does not assume the additivity hypothesis.

By deriving the expression for the noncombinatorial part of the Gibbs mixing function, ΔG_M, for a ternary polymer (2) + polymer (3) + solvent (1) system, written according to Flory's equation-of-state theory, one can obtain the residual potential of the solvent, χ_{1p}, as an additive combination of binary interaction parameters. In the case of IGC where $\phi_1 \to 0$, it reads

$$\chi_{1p} = \chi_{12}\frac{\tilde{V}_2\theta_2}{\tilde{V}_{23}} + \chi_{13}\frac{\tilde{V}_3\theta_3}{\tilde{V}_{23}} - \chi'_{23}{}^{\text{T}}\phi_2\phi_3\frac{s_1}{s_3} + \Gamma \quad (11)$$

where Γ is a free-volume term, ϕ_i and θ_i are the segment and molecular surface fractions, with $\tilde{V}_i$ and $\tilde{V}_{ij}$ the reduced

volumes of the ith component and the binary i–j system, and s_i is the molecular surface to volume ratio. It is probably useful to comment that all the interaction parameters χ in eq 11 are defined in terms of segment fractions instead of volume fractions, and $\chi'_{23}{}^{\text{T}} = \chi_{23}{}^{\text{T}}V_1^*/V_2^*$, with V_i^* the reduced molar volume of the ith component. $\chi_{23}{}^{\text{T}}$ must be considered as more reliable than the χ_{23} obtained from the additivity approximation.

By comparing eq 11 with the additivity relation now written in segment fractions

$$\chi_{1p} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi'_{23}{}^{\text{A}} \quad (12)$$

the following equation can be obtained:

$$\frac{\chi_{23}{}^{\text{A}} + \kappa}{V_2^*s_1} = \frac{\chi_{23}{}^{\text{T}}}{V_2^*s_3} + \frac{s_3 - s_2}{(\phi_2s_2 + \phi_3s_3)V_1^*s_1}(\chi_{12} - \chi_{13}) \quad (13)$$

with

$$\kappa = \left(\frac{V_2^*}{V_1^*}\right)\left[\left(\frac{\Gamma}{\phi_2\phi_3}\right) + \chi_{12}\left(\frac{\tilde{V}_2}{\tilde{V}_{23}} - 1\right)\left[\phi_3^{-1} + \frac{s_2 - s_3}{\phi_2s_2 + \phi_3s_3}\right] + \chi_{13}\left(\frac{\tilde{V}_3}{\tilde{V}_{23}} - 1\right)\left[\phi_2^{-1} - \frac{s_2 - s_3}{\phi_2s_2 + \phi_3s_3}\right]\right] \quad (14)$$

and

$$\Gamma = \frac{P_1^*V_1^*}{RT}\left[\Gamma_{1p} - \frac{\tilde{V}_2}{\tilde{V}_{23}}\theta_2\Gamma_{12} - \frac{\tilde{V}_3}{\tilde{V}_{23}}\theta_3\Gamma_{13}\right] + \frac{P_2^*V_1^*}{RT}\frac{s_1}{s_2}\frac{\theta_2}{\theta_3}\Gamma_{23} \quad (15)$$

where

$$\Gamma_{ij} = \tilde{V}_i^{-1} - \tilde{V}_{ij}^{-1} - 3\tilde{T}_i\ln\frac{(\tilde{V}_{ij}^{1/3} - 1)}{(\tilde{V}_i^{1/3} - 1)} \quad (16)$$

and P_i^* and T_i^* are the reduced parameters of the components for the pressure and temperature, respectively.

Although eq 13 allows the conversion of the additive interaction parameter $\chi_{23}{}^{\text{A}}$ in $\chi_{23}{}^{\text{T}}$, complete information of equation-of-state parameters of the components is necessary, which explains why this method has been only applied so far to polystyrene + poly(vinyl methyl ether)[16] and Phenoxy + poly(ethylene oxide)[14] systems, even though it gives satisfactory results in the PS + PVME system, where there is no interaction by hydrogen bonding.

To obtain a probe-independent interaction parameter for P4HS + PVA blends, thermal expansion coefficient, isothermal compressibility, and density data were needed for calculating the characteristic parameters of the components. These parameters, V^*, P^*, and T^*, were con-

Table III
Equation-of-State Parameters for Probes

probe	$V_1{}^a$ (cm³/mol)	$V_1{}^{*b}$ (cm³/mol)	$\tilde{V}_1{}^c$	$P_1{}^{*d}$ (J/cm³)	$T_1{}^{*e}$ (K)	$s_1 \times 10^{-8}{}^f$ (cm⁻¹)
toluene (TOL)	128.87	84.74	1.5208	555	5051	1.25
acetone (ACT)	96.78	55.47	1.7447	599	4337	1.50
2-butanone (MEK)	114.34	68.91	1.6593	554	4551	1.46
3-pentanone (DEK)	133.01	82.21	1.6179	504	4680	1.44
tetrahydrofuran (THF)	101.11	63.78	1.5853	550	4853	1.34
ethyl acetate (EAC)	127.29	74.21	1.7153	600	4394	1.48
propyl acetate (PAC)	145.86	88.14	1.6549	628	4518	1.45
n-butyl acetate (BAC)	162.19	103.15	1.5724	556	4778	1.43
isopropyl alcohol (ISOP)	99.92	61.03	1.6372	378	5060	1.49

[a] Calculated at 443 K by Benson's method with data from ref 23. [b] Calculated at 298 K from thermal expansion coefficients. [c] $\tilde{V}_1 = V_1(443\ K)/V_1{}^*(298\ K)$. [d] Calculated from isothermal compressibility at 298 K. [e] Calculated from $\tilde{V}_1$ at 298 K. [f] According to Bondi.[41]

Table IV
Equation-of-State Parameters for Polymers

	v^b (cm³/g)	v^{*a} (cm³/g)	$\tilde{V}^b$	P^{*a} (J/cm³)	T^{*a} (K)	$s \times 10^{-8}$ (cm⁻¹)
P4HS	0.974	0.703	1.385	602	5570	0.54
PVA	0.923	0.714	1.293	607	6631	0.56

[a] Data calculated from thermal expansion, isothermal compressibility coefficients, and density at 298 K. [b] Data calculated at 443 K from the thermal expansion coefficient and density.
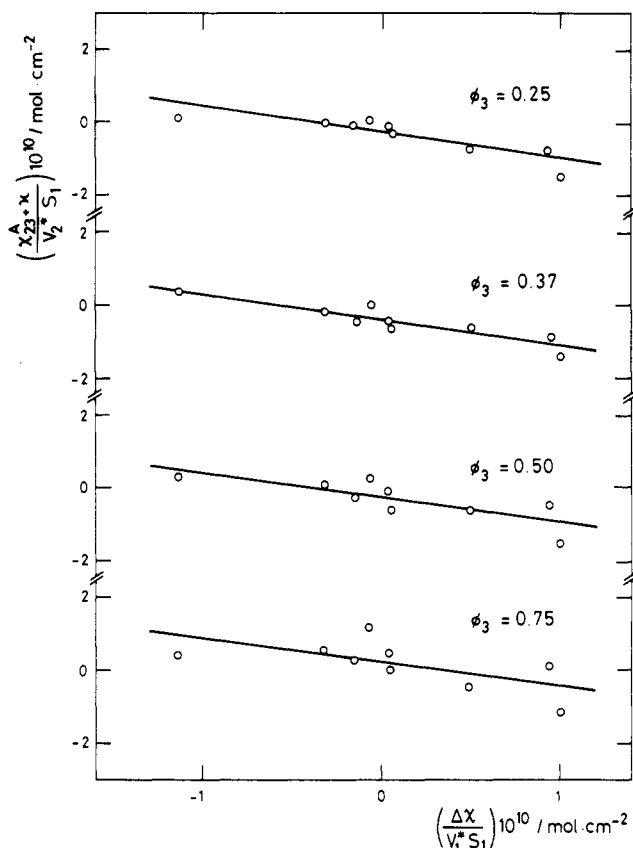

Figure 4. Polymer–polymer interaction parameter, $(\chi_{23}{}^A + \kappa)/V_2{}^* s_1$, vs $\Delta\chi/V_1{}^* s_1$ ($\Delta\chi = \chi_{12} - \chi_{13}$) for PVA/P4HS blends.

sidered temperature independent and are given in Tables III and IV for probes and polymers, respectively. Molar volume and reduced volume at 443 K are also included. The molecular surface to volume ratios were calculated for solvents according to Bondi[41] and they are also shown in Table III. The values of s_3 and s_2 have been estimated using a cylinder model for the polymer units, with a radius calculated from V^* and a length obtained from structural parameters of vinyl polymers; the results are shown in Table IV.

Figure 4 shows $(\chi_{23}{}^A + \kappa)/V_2{}^* s_1$ vs $(\chi_{12} - \chi_{13})/V_1{}^* s_1$ for each composition of the blend; according to eq 13, a linear plot should have been obtained. As we can see, an acceptable linear correlation is obtained for the three

compositions having the lower P4HS content. Equation 13 predicts that the slope of these straight lines should be $(s_3 - s_2)/(\phi_2 s_2 + \phi_3 s_3)$. Taking into account that s_3 and s_2 have similar values (between 0.5 and 0.6 for vinyl polymers), the slopes of the lines will depend slightly on the blend composition, as is illustrated in Figure 4. The values obtained for these slopes, around −0.6, are an order of magnitude higher than the corresponding theoretical values if s_3 and s_2 are estimated using a cylinder model. Irrespective of the experimental error, it must be noted that deviations in s_2 and s_3 of 20% can cause such high differences between theoretical and experimental slope results. From the intercepts of the straight lines shown in Figure 4, the following values have been obtained for the probe-independent interaction parameters, $\chi_{23}{}^T/V_2{}^*$ = −0.1 × 10⁻², −0.22 × 10⁻², −0.1 × 10⁻², and 0.1 × 10⁻² mol·cm⁻³ for ϕ_3 = 0.25, 0.37, 0.50, and 0.75, respectively, with standard deviations around 50% or even more as in the case of the column with ϕ_3 = 0.75. Although these are important errors, it should be noted that the additive interaction parameters χ'_{23} given in Table II show a very noticeable spread, in such a way that the average values of the magnitude of $\chi'_{23}/V_1{}^*$ are −0.6 × 10⁻² and −0.3 × 10⁻² mol·cm⁻³ for ϕ_3 = 0.37 and 0.5, showing standard deviations of 100% and about 300%, respectively, with even larger errors for the other compositions. The negative values of $\chi_{23}{}^T/V_2{}^*$ indicate the miscibility of the PVA and P4HS by hydrogen bond interaction, and the variation of $\chi_{23}{}^T/V_2{}^*$ as a function of blend composition shows that the blend becomes more miscible at intermediate P4HS contents. The positive value obtained at ϕ_3 = 0.75 indicates an unfavorable interaction at the study temperature 170 °C for this composition, which could be the beginning of an incipient phase separation.

Finally, if we apply eq 13 in the simplified case of κ = 0, which means that free-volume differences between polymers and their mixtures are neglected, the values obtained for $\chi_{23}{}^T/V_2{}^*$ are 0, −0.18 × 10⁻², −0.1 × 10⁻², and 0.1 × 10⁻² mol·cm⁻³ for ϕ_3 = 0.25, 0.37, 0.50, and 0.75, respectively. These values are slightly more positive than the corresponding values calculated from eq 13 without any simplification; then the free-volume contribution included in the term κ is not very significant in this system.

Conclusions

In our system, poly(4-hydroxystyrene)/poly(vinyl acetate), χ'_{23} is probe-dependent; although the magnitude of this variation is comparable with those reported for other systems, χ'_{23} is not fully satisfactory for quantitative measurement of the polymer–polymer interaction. Minimizing the probe dependence on χ'_{23} has been attempted by applying a method based on the equation-of-state ternary theory. The $\chi_{23}{}^T$ values obtained from this method seem to be more reliable than the average values of χ'_{23}. In both cases the negative values of χ'_{23} reflect the miscibility of the system by hydrogen bond interaction, until compositions around 0.7 in P4HS at 170 °C. A slight variation for the interaction parameter with blend composition has been found and indicates that the system becomes more miscible at intermediate P4HS content.

References and Notes

(1) Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: New York, 1978.
(2) Olabisi, O.; Roberson, L. M.; Shaw, M. T. *Polymer–Polymer Miscibility*; Academic Press: New York, 1979.
(3) Walsh, D. J.; Rostami, S. In *Advances in Polymer Science*; Springer-Verlag: Berlin, Heidelberg, 1985; Vol. 72, p 119.
(4) Deshpande, D. D.; Patterson, D.; Schreiber, H. P.; Su, C. S. *Macromolecules* 1974, *7*, 530.
(5) Su, C. S.; Patterson, D. *Macromolecules* 1977, *10*, 708.
(6) Su, C. S.; Patterson, D.; Schreiber, H. P. *J. Appl. Polym. Sci.* 1976, *20*, 1025.
(7) Olabisi, O. *Macromolecules* 1975, *8*, 316.
(8) Dipaola-Baranyi, G.; Degre, P. *Macromolecules* 1981, *14*, 1456.
(9) Dipaola-Baranyi, G. *Macromolecules* 1981, *14*, 683.
(10) Walsh, D. J.; McKeown, J. G. *Polymer* 1980, *21*, 1335.
(11) Walsh, D. J.; Higgins, J. S.; Rostami, S.; Weerapereruma, K. *Macromolecules* 1983, *16*, 391.
(12) Al-Saigh, Z. Y.; Munk, P. *Macromolecules* 1984, *17*, 803.
(13) El-Hibri, M. J.; Cheng, W.; Munk, P. *Macromolecules* 1988, *21*, 3458.
(14) Iriarte, M.; Espi, E.; Etxeberria, A.; Valero, M.; Fernández-Berridi, M. J.; Iruin, J. J. *Macromolecules* 1991, *24*, 5546.
(15) Al-Saigh, Z. Y.; Chen, P. *Macromolecules* 1991, *24*, 3788.
(16) Prolongo, M. G.; Masegosa, R. M.; Horta, A. *Macromolecules* 1989, *22*, 4346.
(17) Coleman, M. M.; Painter, P. C. *Appl. Spectrosc. Rev.* 1984, *20*, 255.
(18) Moskala, E. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* 1984, *17*, 1671.
(19) Coleman, M. M.; Lichkus, A. M.; Painter, P. C. *Macromolecules* 1989, *22*, 586.
(20) Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* 1985, *26*, 228.
(21) Palanco, J. M. G.; Sanchis, A.; Prolongo, M. G.; Masegosa, R. M.; Rubio, R. G. Abstracts, 3rd European Polymer Federation Symposium on Polymeric Materials, Oct 1–5, 1990, p 350.
(22) Sanchis, A.; Prolongo, M. G.; Masegosa, R. M.; Salom, C.; Rubio, R. G., to be published.
(23) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
(24) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1986.
(25) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Techniques of Chemistry. Organic Solvents*, 4th ed.; John Wiley & Sons: New York, 1986; Vol. II.
(26) Kumagai, A.; Iwasaki, H. *J. Chem. Eng. Data* 1979, *24*, 261.
(27) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; Wiley-Interscience: New York, 1975.
(28) Luengo, G.; Rojo, G.; Rubio, R. G.; Prolongo, M. G.; Masegosa, R. M. *Macromolecules* 1991, *24*, 1315.
(29) Luengo, G.; Sanchez, I. C., private communication.
(30) Riedl, B.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* 1986, *24*, 2565.
(31) Mandal, B. M.; Bhattacharya, C.; Bhattacharyya, S. N. *J. Macromol. Sci., Chem.* 1989, *A26* (1), 175.
(32) Scott, R. L. *J. Chem. Phys.* 1949, *17*, 249.
(33) Pesci, A. I.; Freed, K. F. *J. Chem. Phys.* 1989, *90*, 2017.
(34) Schweizer, K. S.; Curro, J. G. *J. Chem. Phys.* 1989, *91*, 5059.
(35) Patterson, D.; Robard, A. *Macromolecules* 1978, *11*, 690.
(36) Vera, H. J.; Prausnitz, J. M. *Chem. Eng. J.* 1972, *3*, 1.
(37) Sánchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* 1976, *80*, 2352.
(38) Lacombe, R. H.; Sánchez, I. C. *J. Phys. Chem.* 1976, *80*, 2568.
(39) Flory, P. J. *J. Am. Chem. Soc.* 1965, *87*, 1833.
(40) Biros, J.; Zeman, L.; Patterson, D. *Macromolecules* 1971, *3*, 4.
(41) Bondi, A. *Physical Properties of Molecular Crystals, Liquids and Glasses*; Wiley: New York, 1968.