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Miscibility and interactions in poly (vinyl methyl ether)/poly(4-hydroxystyrene) blends

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Differential scanning calorimetry, (DSC) and inverse gas chromatography, (IGC) were used to analyze the miscibility and interactions in the poly(4-hydroxystyrene)/poly(vinyl methyl ether) (P4HS/PVME) system. The miscibility was assessed by the measurement of a single glass transition temperature, T_g, for each blend composition. The T_g–composition curve was analyzed in terms of Fox, Gordon–Taylor and Kovacs theories. The influence of molecular weight of P4HS in the presence of a cusp in the T_g–composition curve was discussed by comparison with previous T_g data. The IGC retention behaviour of the homopolymers and three blends (0.25, 0.5 and 0.75 P4HS volume fractions) was realized at 190°C using selected probes. The polymer–polymer interaction parameters χ_{23} calculated from the Scott–Flory–Huggins formalism showed an apparent dependence on the probes. This dependence was analyzed using Horta's method based on the equation-of-state theory and a more simplified method proposed by Desphande. Negative values of χ_{23} confirmed the miscibility of the system. A blend composition dependence of χ_{23} was found, mainly determined by differences in the molecular surface-to-volume ratio of the polymers. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: glass transition temperature; interactions; inverse gas chromatography)

INTRODUCTION

Miscible polymer blends have become important technologically because they represent an easy way to optimize properties and cost. Owing to the low values of combinatorial entropy of mixing, miscibility in polymer–polymer systems requires the existence of strong specific interactions between the components, such as hydrogen bonding[1–4]. There is an intensive interest in identifying the nature and strength of intermolecular interactions in miscible polymer blends, in this sense IR spectroscopy is very useful, thus the presence of strong hydrogen bond interactions between poly(4-hydroxystyrene), P4HS, and other polymers containing carboxyl or ether groups has been clearly identified[5–12].

On the other hand, the thermodynamic characterization of the interactions has been the subject of extensive studies[1–4,13–27]. Based on the Flory–Huggins theory the polymer (2)–polymer (3) interaction parameter, χ_{23}, has been chosen to describe the interaction between the two components, which takes into account the enthalpic and non-combinatorial entropy of mixing contributions. Inverse gas chromatography (IGC) has been widely used to obtain the χ_{23} parameter; it requires the determination of the interaction of several probes or solvents (1) with each polymer, χ_{12} and χ_{13} and with the blend, χ_{1p}. With these parameters and applying the Scott–Flory–Huggins treatment to ternary systems, which assumes that the Gibbs mixing function is additive with respect to the binary contributions, χ_{23} is obtained. However, it has been recognized that χ_{23} could depend on the chemical nature of the probe[13–27]. This solvent dependence has been attributed to the inability of the Scott–Flory–Huggins treatment to account for all the interactions present in the polymer–polymer–solvent ternary systems[14,18,20,24]. The variation of χ_{23} with the probe arises from the different interactions between the probe and each polymer. The easiest way to avoid this problem is to choose probes that give similar interactions with each polymer ($\chi_{12} = \chi_{13}$). In the cases in which this is not possible, other methods can be used to obtain non-probe-dependent interaction parameters. The method proposed by Horta *et al.*[20] based on the equation-of-state theory and the more simplified Desphande's[24] method which can be derived from Horta's method, have been applied to several systems[20,23–26]; they give χ_{23} values in which the solvent dependence has been eliminated. Particularly, we have studied the systems formed by P4HS + poly(vinyl acetate)[23] and P4HS + poly(ϵ-caprolactone)[26]. A good concordance was found between the interaction parameters calculated by the two methods, and in the P4HS/PCL blends with those obtained from the melting point depression of PCL.

The present study aimed to analyse the miscibility of the system P4HS + poly(vinyl methyl ether) (PVME) by IGC. For this system, the presence of hydrogen bond interaction involving the phenolic hydroxyl group of P4HS with the ether group of PVME from is known from Fourier transform IR spectroscopy (FTIR)[7]. The IGC retention behaviour was realized for three blend compositions (0.25, 0.50 and 0.75 P4HS volume fractions) at 190°C using selected probes. The dependence of χ_{23} on the nature of the probes was analysed using Horta's and Desphande's methods. In addition the glass transition temperature was determined by differential scanning calorimetry (DSC). The compositional variation of

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the glass transition temperature was analysed in terms of Fox[28], Gordon–Taylor[29] and Kovacs' theories[30,31]. The results obtained were compared with those previously reported[32] using polymer samples of different molecular weight.

EXPERIMENTAL DETAILS

Materials

The PVME and P4HS samples were purchased from Polysciences (UK). The PVME was purified by precipitation into heptane from its toluene solutions and vacuum dried. The average molecular weight of PVME, $M_n = 9.8 \times 10^4$, and the polydispersity index, $M_w/M_n = 2$, were obtained from GPC. The P4HS was used without further purification as in previous papers. The average molecular weight of P4HS was $M_n = 1.5 \times 10^3$ determined by vapour pressure osmometry, and $M_w/M_n = 2$ determined by GPC.

Glass transition temperature measurements

The polymer blends were prepared by mixing 3% (w/v) solutions in acetone and slowly casting films. They were kept at room temperature for 3 weeks and finally dried under vacuum for 24 h at a temperature 30°C higher than the glass transition temperatures T_g.

The T_g values were determined using a Perkin-Elmer DSC-4 differential scanning calorimeter calibrated with indium. The heating rate was 20°C min^{-1} and the sample weight ranged from 5–10 mg. The T_g was taken at the midpoint of the heat capacity transition. At least three scans were performed for each sample. Second and subsequent scans were identical indicating an accuracy in the T_g data of $\pm$ 1 K.

Chromatographic measurements

Chromatographic columns were prepared for each of the pure components and their mixtures with the following compositions $w_3 = 0.25$, 0.50 and 0.75, w_3 being the weight percent of P4HS in the mixture. The stationary phases were coated onto Chromosorb W by dissolution in acetone.

All details about the apparatus, materials, column preparation and procedure were described elsewhere[23,26]. The measurement temperature was 463 K, well above the glass transition of the homopolymers and blends. This temperature ensured that the system exhibited ideal chromatographic behaviour over the entire composition range. The characteristics of the columns are given in *Table 1*.

Table 1 Polymer mixtures and polymer loading in the columns

Column	ω_3	T_g (°C)	Polymer loading (%)
1	0	−22.2	6.7
2	0.25	4.5	13.5
3	0.50	42.0	5.3
4	0.75	85.1	8.9
5	1	138.2	7.7

The net retention time of each probe t_n was measured at 463 K and the specific retention values V_g were calculated from the expression

$$V_g = t_n \frac{F}{W}\left(\frac{3}{2}\right)\left[\frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1}\right]\left(\frac{P_0 - P_w}{P_0}\right)\frac{273.15}{T_r} \qquad (1)$$

where w is the mass of the polymer in the column P_i and P_0 are the inlet and outlet pressures, F is the carrier gas flow rate at room temperature T_r and atmospheric pressure P_0, and P_w is the water vapour pressure at T_r. The retention volumes were independent of the gas flow rate within the range 15–30 ml min^{-1}. Values of V_g were in the range 1–10 ml g^{-1}.

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 PVME 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_{ij} ($j = 2, 3$), which can be calculated from IGC experiments with the relationship[13]:

$$\chi_{ij} = \ln\left(\frac{273.15 R \nu_j}{V_g^0 P_1^0 V_1}\right) - \left(1 - \frac{V_1}{V_j}\right) - \frac{P_1^0(B_{11} - V_1)}{RT} \qquad (2)$$

where ν_j and V_j refer to the specific volume and molar volume of the polymer, V_1 and P_1^0 represent the probe molar volume in the liquid phase and its saturated vapour pressure respectively, and B_{11} is the second virial coefficient of the probe in the gas phase. All other symbols have their usual meaning.

For solvent (1) + polymer (2) + polymer (3) ternary systems, it has been shown[13] that the overall interaction parameter between the volatile probe (1) and the binary stationary phase (2–3) is given by

$$\chi_{1p} = \ln\left(\frac{273.15 R(\omega_2 \nu_2 + \omega_3 \nu_3)}{V_g^0 P_1 V_1}\right) - \left(1 - \frac{V_1}{V_2}\right)\varphi_2 - \left(1 - \frac{V_1}{V_3}\right)\varphi_3 - \frac{P_1^0(B_{11} - V_1)}{RT} \qquad (3)$$

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

The vapour pressures P_1^0, were calculated from the Antoine equation, taking the Antoine constants from the Reid–Prausnitz–Sherwood compilation[33]; the molar volumes of the probes, V_1, were calculated using Bensons's method[33]. Second virial coefficients were calculated from the Pitzer–Curl–Tsonopoulos correlation[34]. The density, thermal expansion coefficient and critical parameters for the solvents were taken from references[35,36]. Data for the polymer were $\nu_2 = 0.862$ and 0.948 cm^3 g^{-1} for P4HS and PVME respectively and thermal expansion coefficients were $\alpha_2 = 8.95 \times 10^{-4}$ and 7.01×10^{-4} K^{-1} for P4HS and PVME respectively at 25°C[17,37,38].

RESULTS AND DISCUSSION

Glass transition temperatures

PVME + P4HS blends were found to be miscible over the whole composition range. They exhibit a single T_g intermediate between values of the pure components. The variation of T_g with the blend composition displays a downward curvature as can be seen in *Figure 1*. In a first aproximation this T_g–ω curve could be considered to follow a simple monotonic function that could be described by the ideal rule of Fox[28]:

$$\frac{1}{T_g} = \frac{\omega_2}{T_{g2}} + \frac{\omega_3}{T_{g3}} \qquad (4)$$

where T_{g2}, T_{g3} and T_g refer to the glass transition temperatures of PVME, P4HS and the blend of composition ω

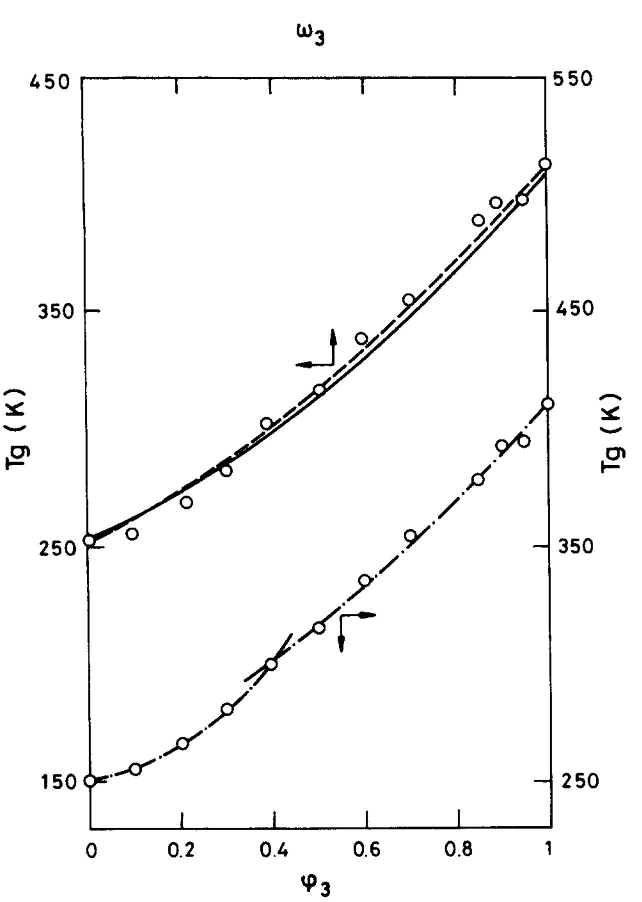

Figure 1 Composition dependence of T_g for PVME (2)/P4HS (3) blends: (O) experimental data, (———) Fox equation, (- -) Gordon–Taylor equation, (– • –) prediction from Kovacs' theory

respectively. This behaviour is similar to that found in other related systems[10,11], such as P4HS + poly(methyl acrylate), P4HS + poly(ethyl acrylate) and P4HS + poly(vinyl acetate). Coleman *et al.*[39] have studied several systems containing P4HS, indicating that those that are miscible present T_g that seem to follow the Fox rule. In the systems before mentioned, strong hydrogen bond interactions between components are present, as has been proved through the FTIR spectra[5–7,10,11]. These interactions do not produce an increase in stiffness as reflects the downward curvature of the T_g–ω curve because the destruction of the self-association of P4HS[11] by the other component produces the opposite effect.

A more close description of the T_g–ω_3 curve could be obtained through the Gordon–Taylor[29] equation:

$$T_g=\frac{\left(\omega_2 T_{g2}+K'\omega_3 T_{g3}\right)}{\omega_2+K'\omega_3} \tag{5}$$

where $K' = \rho_3\Delta\alpha_2/\rho_2\Delta\alpha_3$, $\Delta\alpha_i = (\alpha_L - \alpha_G)_i$ being the difference of the coefficients of expansion at T_g of the glassy (G) and liquid (L) states, and ρ_i the density of the i component. equation (5) reduces to the Fox rule when $K=\frac{T_{g2}}{T_{g3}}$. Usually K' is taken as an arbitrary adjustable parameter. The application of the Gordon–Taylor equation to the system here studied gives the best prediction taking $K' = 0.7$ as shown in *Figure 1*.

However, miscible blends with very large differences between the T_g values of the pure components frequently show unusual non-monotonic T_g–ω dependence. It appears to be described by two well defined regions separated by a singular point or cusp[32,40–42]. This is the case reported by Pedrosa *et al.*[32] for P4HS + PVME blends, using a PVME sample of similar T_g to that we have used but a P4HS sample of higher molecular weight which has a T_g 17°C higher. In addition, they cast the blends from tetrahydrofuran, THF, solutions while we used acetone. They reported the presence of a cusp in the T_g–composition curve located at $\omega_3 \approx 0.5$. In the blends here studied, the presence of a cusp at $\omega_3 \approx 0.4$ can also be observed (see *Figure 1*), although the non-monotonic behaviour is less pronounced.

Often the equilibrium miscibility of a system is very influenced by the method of blending; this is particularly true in systems having strong interactions between components, when the blends are prepared from casting. The limit result is solvent induced phase separation when the solvent interacts more strongly with one component of the blend than with the other[43,44]. This effect has been detected in some systems involving P4HS like P4HS + poly(methyl methacrylate)[10], P4HS + polyesters[45], and P4HS + polyphosphazenes[46], which showed tendencies to phase separate when casting from THF, but appeared to be miscible when acetone was used. The differences in the T_g–ω_2 curves for PVME + P4HS reported here and by Pedrosa *et al.*[32] could be attributed to a solvent effect. Nevertheless both kinds of blend (cast from THF or acetone) show clear miscibility behaviour and since the interaction of THF and acetone with P4HS is similar to the interaction with PVME (see *Figure 3*), it seems more likely that those differences will be caused by the different molecular weight and T_g of P4HS used.

In order to clarify this effect we have applied Kovacs' theory[30,31] which is based on the hypothesis that the fractional free volume of the mixture f is given by the weighted sum of the fractioned free volumes of pure components f_i plus an interaction term:

$$f=\varphi_2 f_2+\varphi_3 f_3-g\varphi_2\varphi_3 \tag{6}$$

where φ_i is the volume fraction of the component i and the term, $g\varphi_2\varphi_3$, represents the fraction of excess volume in the mixture

$$g\varphi_2\varphi_3=V_e/V \tag{7}$$

In the original theory[31], the excess volume is defined as $V_e = V_2 + V_3 - V$, with V_2, V_3, V the volumes of the components (2) and (3) and the blend volume respectively. According to this theory if the difference $T_{g3} - T_{g2}$ is large, the free volume of polymer 3 becomes zero at a critical temperature T_c:

$$T_c=T_{g3}-f_{g3}/\Delta\alpha_3 \tag{8}$$

where the polymer with higher T_g in the blend is denoted with the number 3 and f_{g3} is its fractional free volume at T_{g3}.

The composition dependence of T_g above T_c is given by

$$T_g=\frac{\varphi_2 T_{g2}+K\varphi_3 T_{g3}+(g/\Delta\alpha_2)\varphi_2\varphi_3}{\varphi_2+K\varphi_3} \tag{9}$$

with $K = \Delta\alpha_3/\Delta\alpha_2$ and $\Delta\alpha_i$ the difference between the volume expansion coefficient in the liquid and glassy states of the i component.

Below T_c, T_g is given by

$$\frac{T_g-T_{g2}}{\varphi_3}=\frac{g}{\Delta\alpha_2}+\left(\frac{f_{g3}}{\Delta\alpha_2}\right)\frac{1}{\varphi_2} \tag{10}$$

Then for $T < T_c$ a plot of $(T_g - T_{g2})/\varphi_3$ vs. $1/\varphi_2$ should give a straight line of slope $f_{g3}/\Delta\alpha_2$ and intercept $g/\Delta\alpha_2$.

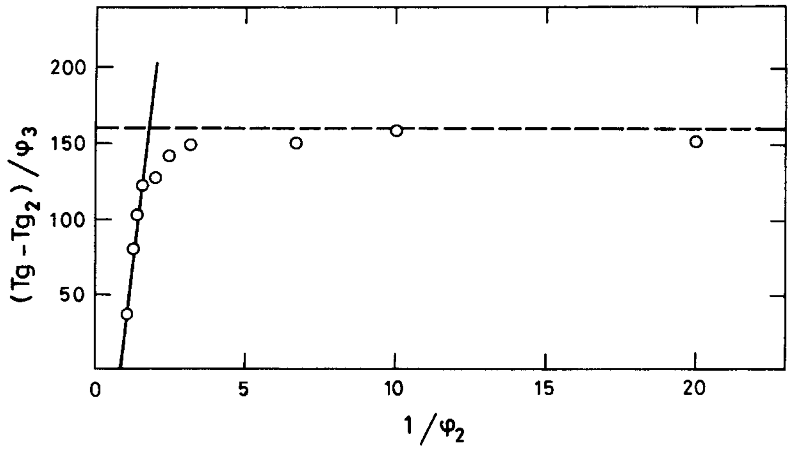

Figure 2 Representation of the T_g–composition data according to Kovacs' theory (———) and the additivity rule (- - -)

Table 2 Parameters of Kovacs' theory for PVME (2) + P4HS (3) blends

System	$\Delta\alpha_3$ (K^{-1})	$\Delta\alpha_2$ (K^{-1})	g	T_c (K)	ϕ_C
PVME ($T_g = 251$ K) + P4HS ($T_g = 411$ K)	2.21×10^{-4}	1.8×10^{-4}	− 0.018	298	0.4
PVME ($T_g = 250$ K) + P4HS ($T_g = 428$ K)[32]	2.97×10^{-4}	2.02×10^{-4}	− 0.011	344	0.49

In *Figure 2* it is shown that the data corresponding to $\varphi_3 \leq 0.4$ can be fitted to a straight line from which the parameters g and $\Delta\alpha_2$ are obtained taking $f_{g3} = 0.0025$ as usual[47,48]. In order to calculate T_c from equation (8) it is necessary to know $\Delta\alpha_3$ which can be obtained from the expression

$$\Delta\alpha_3 = K\Delta\alpha_2 \qquad (11)$$

where K is derived from equation (9) using the value of $g/\Delta\alpha_2$ previously determined. Values of Kovacs' parameters are given in *Table 2* together with those reported by reference[28] for comparative purposes.

Negative values of the Kovacs' g parameter reflect an increase in the free volume in the polymer mixture. The lower g value here obtained can be explained taking into account the lower molecular weight of the P4HS used. A lower P4HS molecular weight in this case means a T_g closer to that corresponding to PVME, as a consequence the difference of free volume between both polymers is reduced. This is associated with a less unfavourable contribution to the mixing entropy and consequently with a higher free volume. The ϕ_C comparative values are also different (see *Table 2*) because this parameter is highly sensitive to the ($T_{g3} - T_{g2}$) value; in our system the P4HS molecular weight gives a ($T_{g3} - T_{g2}$) 18°C degrees lower, so the appearance of the break in the T_g–composition curve is located at a smaller concentration.

Polymer–polymer interaction

Specific retention volumes of eleven probes were obtained for homopolymers PVME, P4HS and three blends of 0.25, 0.50 and 0.75 P4HS volume fractions. The probes selected were acetone, butan-2-one, pentan-3-one, ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, ethanol, propan-1-ol, propan-2-ol, tetrahydrofuran and chlorobencene. From V_g values and following the procedure given by equations (2) and (3), the χ_{1i} parameters, characterizing the interactions of the vapour-phase probe with each of the two polymers χ_{12} and χ_{13} and with their mixture, χ_{1p}, were obtained. These results are plotted as a function of the blend composition in *Figure 3*. As apparent in this figure, all the curves, except that corresponding to ClBz, exhibited the upward curvature which reflects favourable interaction between the two polymers which confirms the miscibility of PVME/P4HS blends inferred from T_g data.

The polymer–polymer interaction parameter, χ_{23}, according to Flory–Huggins treatment applied to ternary systems is determined using the relation

$$\chi_{1p} = \varphi_2\chi_{12} + \varphi_3\chi_{13} - \varphi_2\varphi_3\chi_{23}' \qquad (12)$$

where χ'_{23} is defined in the form $\chi'_{23} = \chi_{23}(V_1/V_2)$.

Values of χ'_{23} are presented in *Table 3* for all the blend compositions. As is usual in IGC experiments, χ'_{23} is probe dependent; this cannot only be attributed to the difference between molar volumes of the probes. As in other systems, which we have studied previously, this dependence is not due to the experimental artifacts. In a first approximation the χ'_{23} mean value for each blend composition could be used for comparative purposes and they are also included in *Table 3*. These values show a blend composition dependence; negative values of $\langle\chi'_{23}\rangle$ reflect a favourable interaction between polymers, the positive $\langle\chi'_{23}\rangle$ value obtained for $\varphi_2 = 0.75$ means that the interaction becomes unfavourable when the concentration of P4HS increases. It should be noted that in this kind of system in which a component has a very low molecular weight (P4HS), small negative values of the polymer–polymer interaction parameter are compatible with miscibility because the combinatorial entropy ensures that the blend does not phase separate.

In order to provide probe-independent interaction parameters we applied a theoretical method proposed by Horta *et al.*[20] based on the equation-of-state ternary theory. According to this method the solvent–blend interaction parameter χ_{1p} can be obtained as an additive combination of binary interaction parameters, which in the case of IGC, where $\varphi_1 \rightarrow 0$ is given by

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

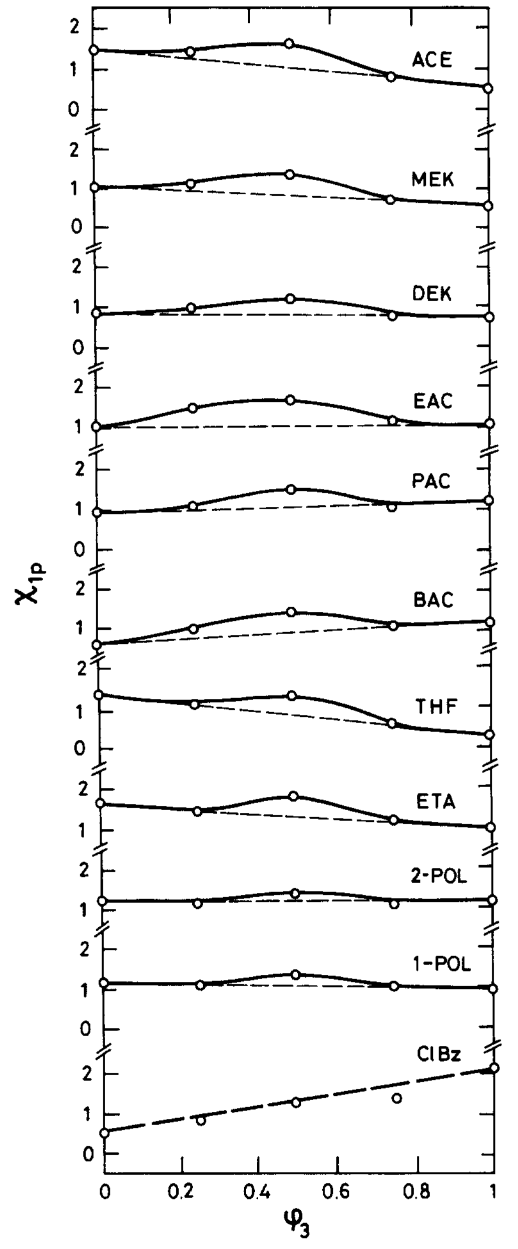

Figure 3 Dependence of χ_{1p} on the P4HS volume fraction for each probe, (- - -) hypothetical average χ_{1p} for non-interacting ($\chi_{23} = 0$) blends

Where Γ is a free-volume term, ϕ_i and θ_i are the segment and molecular surface fractions, $\tilde{V}_i$ and $\tilde{V}_{ij}$ the reduced volumes of the *i*th component and the binary *i*–*j* system, and s_i the molecular surface-to-volume ratio of the *i*th component. All the interaction parameters, χ_{ij}, in equation (13) are defined in terms of segments fractions, and $\chi'^{\mathrm{T}}_{23} = \chi^{\mathrm{T}}_{23} V_1^*/V_2^*$, V_i^* being the reduced molar volume of the *i*th component, χ^{T}_{23} is considered the polymer–polymer probe-independent interaction parameter.

By comparing equation (13) with the additivity relation equation (12), written in segment fraction that reads

$$\chi_{1p} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi_{23}'^{\mathrm{A}} \qquad (14)$$

the following equation is obtained:

$$\frac{\chi^{\mathrm{A}}_{23} + \kappa}{V_2^* s_1} = \frac{\chi^{\mathrm{T}}_{23}}{V_2^* s_3} + \frac{s_3 - s_2}{(\phi_2 s_2 + \phi_3 s_3) V_1^* s_1}(\chi_{12} - \chi_{13}) \qquad (15)$$

Table 3 Polymer–polymer interaction parameters, χ'_{23}, for the system PVME (2) + P4HS (3) at 463 K

Solvent	χ'_{23}		
	$\varphi_3 = 0.25$	$\varphi_3 = 0.5$	$\varphi_3 = 0.75$
Acetone (ACE)	−0.71	−2.14	0.12
Butan-2-one (MEK)	−0.60	−2.18	0.17
Pentan-3-one (DEK)	−0.40	−1.36	0.40
Ethyl acetate (EAC)	−2.55	−2.74	−0.44
n-Propyl acetate (PAC)	−0.19	−1.52	0.66
n-Butyl acetate (BAC)	−1.08	−1.82	0.17
Ethanol (ETA)	0.29	−1.40	−0.13
Propan-1-ol (1 POL)	0.13	−1.04	−0.02
Propan-2-ol (2 POL)	0.40	−1.76	0.40
Tetrahydrofuran (THF)	−1.53	−2.22	−0.54
Chlorobenzene (ClBz)	0.57	0.10	1.67
$\langle\chi'_{23}\rangle$	−0.61	−1.63	0.21

with

$$\kappa = \left(\frac{V_2^*}{V_1^*}\right)\left[\left(\frac{\Gamma}{\phi_2\phi_3}\right) + \chi_{12}\left(\frac{\tilde{V}_2}{\tilde{V}_{23}} - 1\right) \times \left(\phi_3^{-1} + \frac{s_2 - s_3}{\phi_2 s_2 + \phi_3 s_3}\right) + \chi_{13}\left(\frac{\tilde{V}_3}{\tilde{V}_{23}} - 1\right) \times \left(\phi_2^{-1} - \frac{s_2 - s_3}{\phi_2 s_2 + \phi_3 s_3}\right)\right] \qquad (16)$$

and

$$\Gamma = \frac{P_1^* V_1^*}{RT}\left[\Gamma_{1p} - \frac{\tilde{V}_2}{\tilde{V}_{23}}\theta_2\Gamma_{12} - \frac{\tilde{V}3}{\tilde{V}_{23}}\theta_3\Gamma_{13}\right] + \frac{p_2^* V_1^*}{RT}\frac{s_1}{s_2}\frac{\theta_2}{\theta_3}\Gamma_{23} \qquad (17)$$

where

$$\Gamma_{ij} = \tilde{V}_i^{-1} - \tilde{V}_{ij}^{-1} - 3\tilde{T}_i \ln\frac{\left(\tilde{V}_{ij}^{1/3} - 1\right)}{\left(\tilde{V}_{\mathrm{i}}^{1/3} - 1\right)} \qquad (18)$$

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

In order to apply this method complete information on the components is needed. The parameters V_i^*, P_i^*, T_i^*, and s_i were calculated as is described in previous papers[23,26]. These values together with the molar volumes and reduced volumes at 463 K for the probes and P4HS are included in those papers. *Table 4* shows the corresponding equation-of-state parameters for PVME and P4HS.

Figure 4 displays the $(\chi^{\mathrm{A}}_{23} + \kappa)/V_2^* s_1$ versus $(\chi_{12} - \chi_{13})/V_1^* s_1$ for each blend composition. As can be seen, an acceptable linear correlation is obtained, the scattering of the data being highest for $\phi_3 = 0.23$. The slopes of the lines are almost independent of the blend composition, giving values around −0.6. The corresponding theoretical values calculated as $(s_3 - s_2)/(\phi_2 s_2 + \phi_3 s_3)$ are three times higher (−0.17). These differences are not significant taking into account the standard deviations of the linear correlation and the uncertainty in the values of s_2 and s_3 calculated through a geometrical model[26].

The polymer–polymer interaction parameters, $\chi^{\mathrm{T}}_{23}/V_2^*$ were obtained from the intercepts of the straight lines and are given in *Table 5*; the negative values indicate miscibility of the P4HS and PVME, the interaction becoming more favourable for intermediate compositions. Finally we applied the more simple Desphande method[24] which gives a mean value of the interaction parameter, χ^{D}_{23}, by using the

Table 4 Equation-of-state parameters for polymers, $T = 463$ K

Polymer	v^{*a}(cm^3 g^{-1})	p^*(J cm^{-3})	T^*(K)	v^a(cm^3 g^{-1})	$\tilde{V}$	s(10^{-8} cm^{-1})
PVME	0.801	525	6450	1.081	1.349	0.64
P4HS	0.703	602	5570	0.989	1.406	0.54

[a] v is the specific volume and v^* the reduction parameter (per gram) for volume.
v^*, P^*, and T^* data calculated from thermal expansion isothermal compresibility coefficients and density at 298 K.

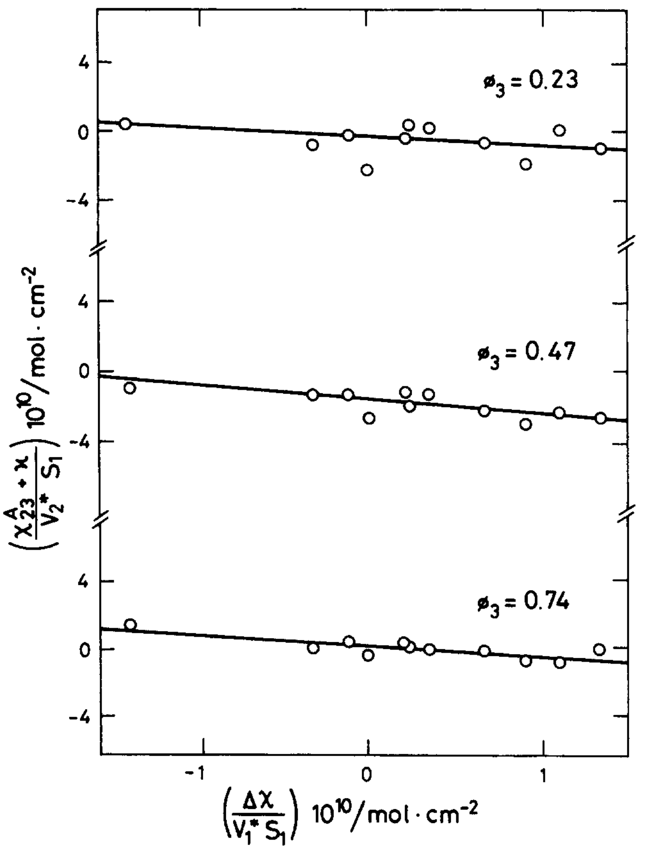

Figure 4 Polymer–polymer interaction parameter $(\chi_{23}^A + \kappa)/V_2^* s_1$ against $(\chi_{12} - \chi_{13})/V_1^* s_1$ for PVME/P4HS blends

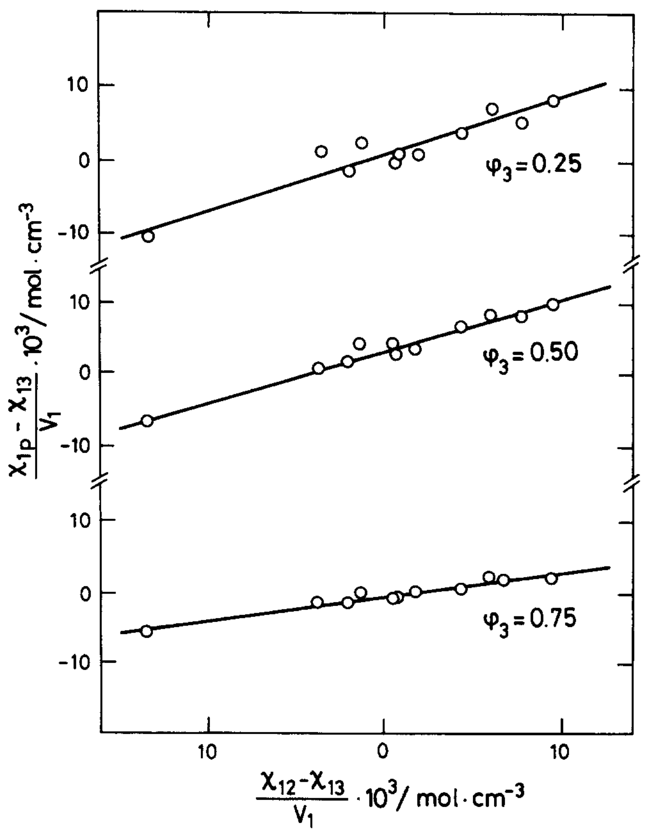

Figure 5 $(\chi_{1p} - \chi_{13})/V_1$ against $(\chi_{12} - \chi_{13})/V_1$ for PVME/P4HS blends according to Desphande's method

Table 5 Interaction parameters of PVME (2) + P4HS (3) at 463 K

	$\phi_3 = 0.23$	$\phi_3 = 0.47$	$\phi_3 = 0.74$
χ_{23}^T/V_2^* (cm^{-3} mol)	-0.2×10^{-2}	-0.8×10^{-2}	0.1×10^{-2}
χ_{23}^D/V_2 (cm^{-3} mol)	-0.1×10^{-2}	-0.3×10^{-2}	0.0

equation:

$$\frac{\chi_{1p} - \chi_{13}}{V_1} = \varphi_2\left(\frac{\chi_{12} - \chi_{13}}{V_1}\right) - \left(\frac{\chi_{23}^D}{V_2}\right)\varphi_2\varphi_3 \qquad (19)$$

Figure 5 shows the corresponding plot for each blend composition and the polymer–polymer interaction parameters, χ_{23}^D/V_2, are listed in *Table 5*.

As was expected, the values of χ_{23}^D/V_2 are higher than χ_{23}^T/V_2^*. The reason is that equation (19) can be derived from equation (15). Making $K = 0$, which means that the free volume differences between polymers are neglected, and assuming $s_2 = s_3$, an equation similar to equation (15) but written in segment fraction is obtained, in which $\chi_{23}^T s_1/s_2$ is replaced by χ_{23}^D. Then taking into account that in general $s_1/s_3 \sim 2$ the differences found between χ_{23}^T and χ_{23}^D could be explained.

The negative values of the interaction parameters obtained for P4HS + PVME are the consequence of the hydrogen bond interaction between the hydroxyl groups of P4HS and the methoxy groups of PVME. This behaviour is similar to that found in other related systems P4HS + PVA[23] and P4HS + PCL[26]. All these systems are formed by a polymer highly autoassociated by hydrogen bonds (P4HS), plus another non-associated polymer that has chemical groups capable of establishing hydrogen bonds with P4HS, which ensures the miscibility of the two polymers. The corresponding polymer–polymer interaction parameters that we obtained for the mentioned systems are included in *Table 6*, for comparative purposes. In these systems the free volume differences are not very important, then the concentration dependence of χ_{23}[17] is mainly determined by the differences in the molecular surface-to-volume ratio of the polymers. Thus in the P4HS + PVA system, for which s_2/s_3 is close to unity, almost no variation of χ_{23} with composition is obtained, but for P4HS + PCL and P4HS + PVME the dependence of χ_{23} with composition is clear. Finally, it is interesting to notice that in this kind of system the increase in P4HS content in the blends provokes a rise in the polymer–polymer interaction parameters which means that when the autoassociated polymer is in majority, the blend becomes less thermodynamically compatible.

Table 6 Dependence of the interaction parameters, χ^T_{23}/V^*_2, on the blend composition, ϕ_3, for polymer (2) + polymer (3) systems, determined by IGC

System	s_2/s_3	χ^T_{23}/V^*_2 (cm^{-3} mol)					
PVA (2) + P4HS (3) (443 K)		$\phi_3 = 0.25$	$\phi_3 = 0.37$		$\phi_3 = 0.5$		$\phi_3 = 0.75$
	1.04	-0.1×10^{-2}	-0.2×10^{-2}		-0.1×10^{-2}		0.1×10^{-2}
PCL (2) + P4HS (3) (463 K)		$\phi_3 = 0.23$		$\phi_3 = 0.47$		$\phi_3 = 0.72$	
	1.46	-0.9×10^{-2}		-0.5×10^{-2}		-0.2×10^{-2}	
PVME (2) + P4HS (3) (463 K)		$\phi_3 = 0.23$		$\phi_3 = 0.47$		$\phi_3 = 0.74$	
	1.19	-0.2×10^{-2}		-0.8×10^{-2}		0.1×10^{-2}	

CONCLUSIONS

The miscibility behaviour between poly(4-hydroxystyrene) + poly(vinyl methyl ether) was investigated. The measurement of a single glass transition temperature for each blend composition confirmed the miscibility of the system. The presence of a cusp in the T_g–composition curve was analysed in terms of the Kovacs' theory, giving a Kovacs' parameter g lower than that previously reported in the literature; we attribute this fact to the lower P4HS molecular weight used here.

The negative values of the polymer–polymer interaction parameters χ'_{23} reflected the miscibility of the system by hydrogen-bond interactions. The probe dependence of χ'_{23} was eliminated applying the theoretical methods of Horta *et al.* and Desphande. A blend composition dependence of χ'_{23} was found, which was explained taking into account the difference in the molecular surface-to-volume ratio of the polymers.

Finally, the comparison with other systems containing P4HS such as P4HS + poly(vinyl acetate), P4HS + poly(vinyl methyl ether), confirms that in this kind of system the increase in the composition of the autoassociated polymer P4HS worsens the miscibility.

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