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Characterization of the interactions in the poly(4-hydroxystyrene)/poly(ε-caprolactone) system by inverse gas chromatography

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Inverse gas chromatography has been used to measure the thermodynamic interaction between poly(4-hydroxystyrene) (P4HS) and poly(ε-caprolactone) (PCL) at 190°C. The retention behaviour of the homopolymers and three blends (0.25, 0.5 and 0.75 P4HS volume fraction) was characterized for 13 probes. The polymer–polymer interaction parameter χ_{23} calculated from the Soctt–Flory–Huggins formalism showed an apparent dependence on the probes. The method based on the equation-of-state theory given by Horta *et al.* and a more simplified method recently proposed by Deshpande were applied to eliminate the influence of the probe on χ_{23}. The results of these methods were closely similar to the one obtained by melting-point depression of the PCL in the binary blends. Negative values of χ_{23} confirm the miscibility of the system. A blend composition dependence of χ_{23} has been found, leading to more miscible blends when the PCL content increases. This behaviour was related to the differences in the surface-to-volume ratio of both polymers.

(Keywords: thermodynamic interaction; P4HS/PCL blend; inverse gas chromatography)

INTRODUCTION

As polymer blends are becoming important technologically, the interest in their thermodynamic characterization is increasing. Based on the classical theory of Flory and Huggins 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 the non-combinatorial entropy-of-mixing contributions. Owing to the extremely low values of the combinatorial entropy of mixing, miscible polymer blends generally require the existence of strong specific interactions (such as hydrogen bonding) between polymers, expecting as a consequence negative values of χ_{23}; however specific interactions bring non-randomness, so that a negative entropic contribution arises and small positive values of χ_{23} could also be found even when the enthalpic contribution is negative.

Inverse gas chromatography (i.g.c.) has been widely used to determine the χ_{23} parameter[1–15]. This rapid and available technique involves the determination of retention volumes of volatile probes (1) that are carried through columns containing the polymers and their blends by a flow of an inert gas. The retention volume is related to the activity coefficient of the probe in the stationary phase, from which the interaction parameter χ_{1i} between the probe (1) and the stationary phase (i) can be calculated.

From these determinations and applying the Scott–Flory–Huggins treatment to a ternary system, which assumes that the interactional part of the Gibbs function for the ternary system is additive in the binary contributions, the χ_{23} parameter can be determined. In general this parameter exhibits a significant dependence on the probe; particularly it seems that large values of χ_{23} are obtained with probes that interact preferentially with one of the polymers. As a consequence, doubts were expressed about the quantitative validity of the χ_{23} i.g.c. results. In order to obtain a solution to this problem Munk *et al.*[8,9] carried out a critical examination of the i.g.c. experimental aspects and pointed out that there was a definitive dependence of χ_{23} on the nature of the probe, which could not be caused by uncontrolled experimental errors. Furthermore they pointed out that Scott–Flory–Huggins treatment did not account for all the interaction present in the polymer–polymer–solvent ternary system and this deficiency could be responsible for the probe dependence of χ_{23}.

Thus, the variation of χ_{23} with the probe arises from the different interaction between the probe and each polymer, described as $\Delta\chi$ effect[3]. Therefore it was suggested to select probes that gave similar interaction ($\chi_{12} = \chi_{13}$) with each polymer[16]. Since this is not always

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possible, several methods have been independently proposed, in order to obtain a probe-independent interaction parameter. Horta's group[16] have proposed a method based on the equation-of-state theory, which gives a polymer–polymer interaction parameter χ_{23}, named 'true', because the assumption that the Gibbs mixing function for the ternary polymer–polymer–solvent system is additive with respect to the binary contributions is avoided. Other more simplified methods[11,15] can be derived from that of Horta's group, taking into account some approximations.

The aim of this work was to carry out a thermodynamic study of poly(4-hydroxystyrene)/poly(ε-caprolactone) system by i.g.c. The miscibility in this system arises from a favourable interaction due to the intermolecular hydrogen bonding[17,18]. The i.g.c. retention behaviour was measured for three blend compositions (0.25, 0.50, 0.75 P4HS volume fractions) at 190°C using 13 selected probes. The experiments were carried out trying to minimize experimental errors to determine the polymer–polymer interaction parameter χ_{23} and its variation with the blend composition. The dependence of χ_{23} on the nature of the probes was analysed using Horta's method and the more simplified Deshpande's method, which so far has been applied only to a few systems[13,14,16]. We have compared the χ_{23} i.g.c. results with that obtained by measuring the melting-point depression of the PCL in the binary blends[18,19].

EXPERIMENTAL

Materials

Poly(4-hydroxystyrene) (P4HS) and poly(ε-caprolactone) (PCL) were purchased from Polysciences (UK). The average molecular weight of PCL, $M_n = 5.0 \times 10^4$, and the polydispersity index $M_w/M_n = 1.6$ were obtained from g.p.c. The average molecular weight of P4HS was $M_n = 1.5 \times 10^3$ by vapour pressure osmometry, and g.p.c. 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.

Column preparation

Chromatographic columns were prepared for each of the pure components and their mixtures, using Chromosorb W as support. The method of coating the polymer onto the inert support was described in a previous work[14]. Tetrahydrofuran (THF) was the solvent used for making solutions of the polymer blends. The columns (inner diameter 0.6 cm, length 1.5 m) were purged at 15°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 in the columns was around 6.5 g. Column characteristics are detailed in *Table 1*.

Table 1 Polymer mixtures and column characteristics

Column	ω_3[a]	T_g[b] (°C)	Polymer loading (%)
1	0	−62	11.5
2	0.25	−38	9.6
3	0.50	21.2	10.1
4	0.75	66	10.8
5	1	130	9.6

[a] ω_3 = weight per cent of P4HS in the mixture
[b] From ref. 18

Instrumentation and procedure

Measurements were carried out on a Varian gas chromatograph (model 3300) equipped with a flame ionization detector. Dried helium was used as a carrier gas. Flow rates were conventionally measured with a soap-bubble flowmeter at the detector outlet. The column oven temperature was 190 ± 0.05°C, well above the glass transition (T_g) of the homopolymers and blends, as can be seen in *Table 1*. This condition ensured that the system exhibited ideal chromatographic behaviour over the entire composition range. Flow rate and room temperature were checked frequently. The range of flow rates (four were selected) was 15–30 ml min^{-1} (± 0.2 ml min^{-1}). The inlet pressures (range 1000–1300 mmHg) were monitored by 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

The specific retention volumes V_g, were calculated according to the usual relation:

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

where t_n is the net retention time for each probe, m 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 vapour pressure at T_r. The values of V_g are usually extrapolated to zero flow rate to obtain V_g^0. In this work, V_g values were independent of the gas flow rate within the range 15–30 ml min^{-1}. Values of V_g^0 were in the range 1–13 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 PCL 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 i.g.c. experiments with the relationship[1]:

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

where v_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[1] that the overall interaction parameter between the volatile probe (1) and the binary stationary phase (2–3) is given by:

$$\chi_{1p}=\ln\left(\frac{273.15R(\omega_2 v_2+\omega_3 v_3)}{V_g^0 P_1^0 V_1}\right)-\left(1-\frac{V_1}{V_2}\right)\varphi_2 -\left(1-\frac{V_1}{V_3}\right)\varphi_3-\frac{P_1^0(B_{11}-V_1)}{RT} \quad (3)$$

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

The vapour pressures P_1^0 were calculated from the Antoine equation:

$$\log P_1^0 = A - B/(t+C) \quad (4)$$

where t is the temperature (°C) and the constants A, B and C were taken from the Reid–Prausnitz–Sherwood compilation[20].

The molar volumes V_1 of the probes were calculated using Benson's method[20]:

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

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

$$\rho_V = P_1^0 M_1/RT \quad (7)$$

where ρ_L and ρ_V are the densities of the liquid probe and its saturated vapour 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[21]:

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

$$\omega = -\log(P_1^0/P_c)_{T_R=0.7}-1.000 \quad (9)$$

where $\mathscr{F}^{(i)}$ 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 refs. 22 and 23.

Data used for polymers were $v_2 = 0.925\ \mathrm{cm^3\ g^{-1}}$, $v_3 = 0.862\ \mathrm{cm^3\ g^{-1}}$, $\alpha_2 = 6.50\times10^{-4}\ \mathrm{K^{-1}}$ and $\alpha_3 = 8.95\times10^{-4}\ \mathrm{K^{-1}}$ at 25°C (refs. 24–26).

RESULTS AND DISCUSSION

The probes, selected in such a way that they present different strengths of interaction with the polymers, were n-butyl acetate, n-propyl acetate, ethyl acetate, 2-methyl propan-1-ol (isobutyl alcohol), propan-1-ol, propan-2-ol, pentan-3-one, butan-2-one, acetone, chlorobenzene, toluene, dioxane and tetrahydrofuran. The specific retention volumes V_g^0 of these probes were obtained for homopolymers PCL, P4HS and its blends. As is known for a miscible blend, the probes should give a smaller retention volume than that corresponding to the linear combination of retention volumes of the pure components. This effect is shown in *Figures 1* and *2*,

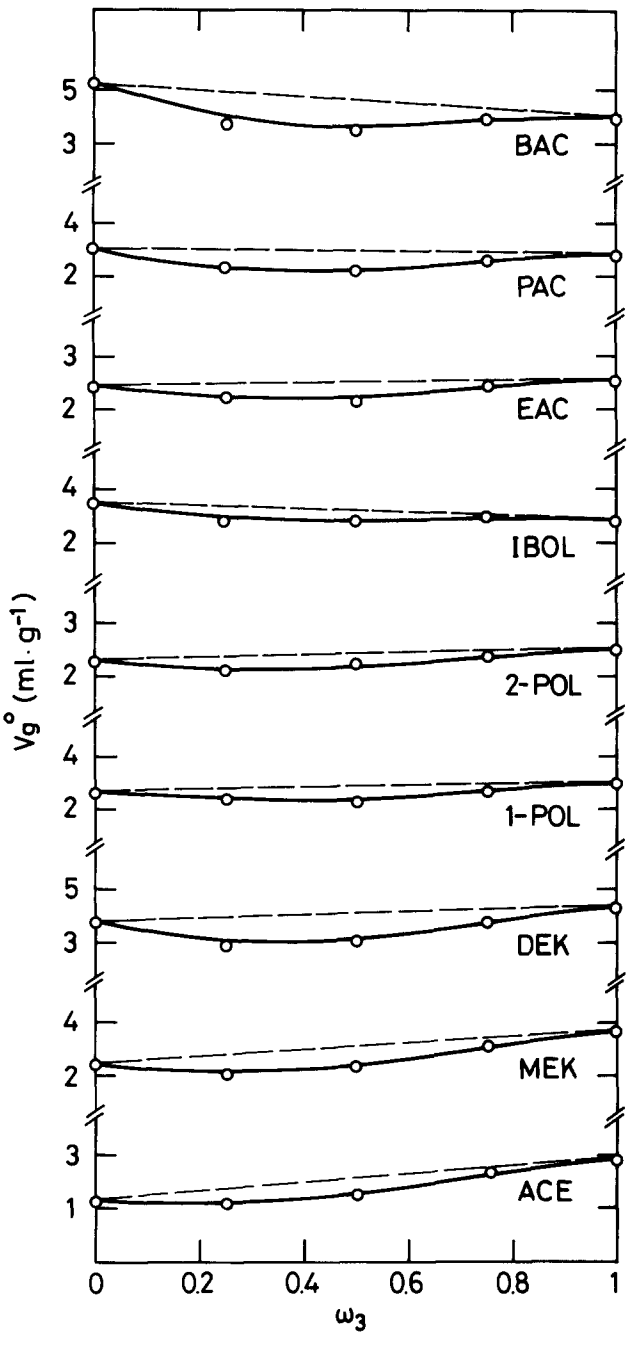

Figure 1 Dependence of V_g^0 on the P4HS weight fraction for selected probes; (– – –) hypothetical average for non-miscible blends

where the curves exhibit the downward curvature in the V_g^0 values, related to the strength of interaction between the two polymers, which reduces the ability of the mixture to interact with the selected probes. From V_g^0 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 mixtures, χ_{1p}, have been obtained. They are plotted as a function of the blend composition in *Figures 3* and *4* for all the probes studied. According to the Scott–Flory–Huggins treatment, the polymer–polymer interaction parameter is usually obtained from measurements in polymer (2)+polymer (3)+solvent (1) ternary systems, using the relation:

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

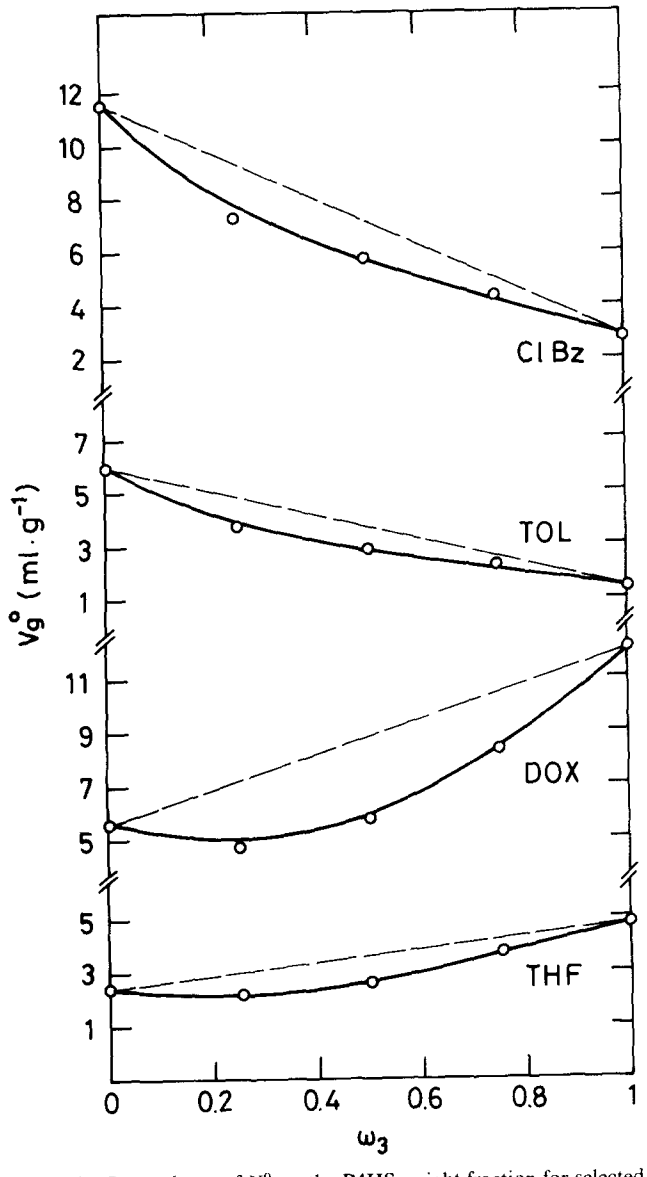

Figure 2 Dependence of V_g^0 on the P4HS weight fraction for selected probes; (---) hypothetical average for non-miscible blends

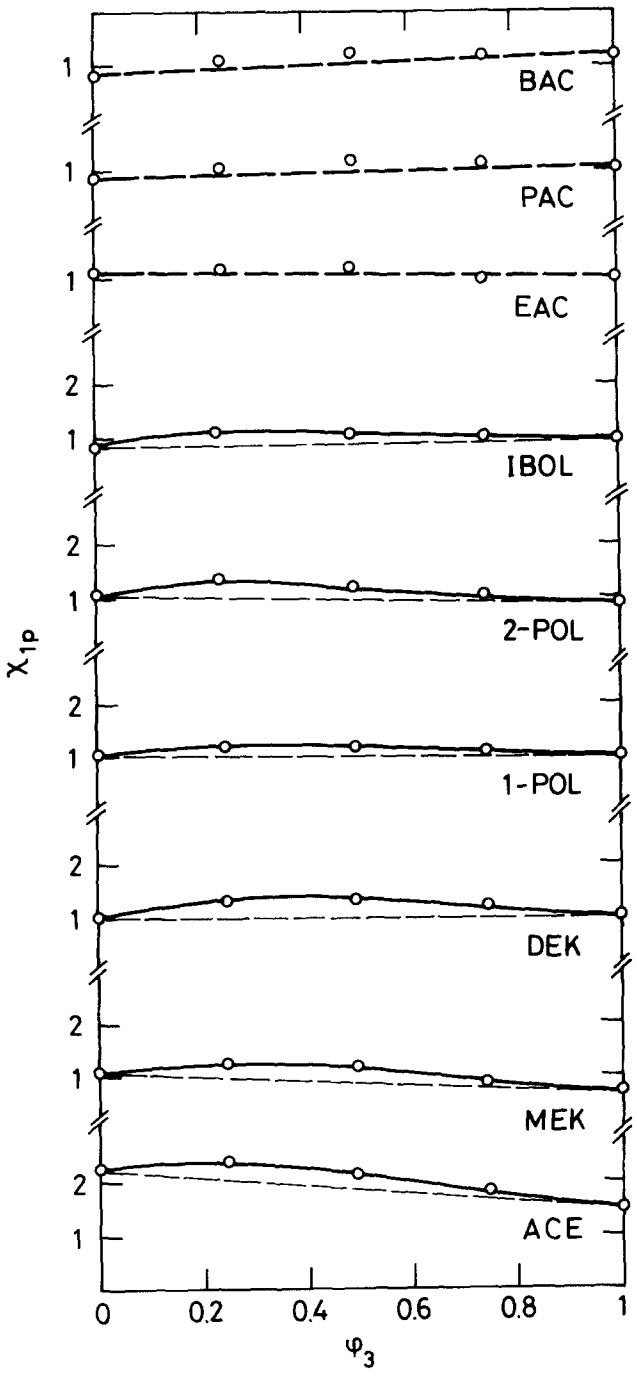

Figure 3 Variation of χ_{1p} with P4HS volume fraction for probes; (---) hypothetical average for non-interacting ($\chi_{23}=0$) blends

where $\chi'_{23}=\chi_{23}(V_1/V_2)$ and χ_{23} is the polymer (2)–polymer (3) interaction parameter taking as a reference the volume V_2. The linear behaviour in *Figures 3* and *4* represents a blend with $\chi_{23}=0$, whereas the upward curvatures will correspond to $\chi_{23}<0$.

Values of χ'_{23} calculated from equation (10) are given in *Table 2* for all the blend compositions, together with the polymer–solvent interaction parameters for the pure components. As can be seen in *Table 2*, χ'_{23} values are in general negative, reflecting that a favourable hydrogen-bond interaction between both polymers is present, even at high temperatures (190°C). As is usual in i.g.c. experiments, χ'_{23} is probe-dependent, and a mild variation with the molar volume of the probe should be expected. However, the large variation of χ'_{23} found is higher than that expected from the differences in molar volume of the probes. On the other hand, taking into account that the probes used have been carefully selected to span a wide range of interaction with both polymers, the average values of χ'_{23} have been calculated because they may still be used for comparative purposes, and these results are included in *Table 2* as $\langle\chi'_{23}\rangle$. These values depend on the PCL/P4HS composition, being more negative when the PCL content in the blend increases, indicating that in these cases the miscibility of PCL + P4HS is more likely achieved.

Theoretical calculations

In order to minimize the solvent effect in the polymer–polymer interaction parameter obtained for polymer mixtures by i.g.c., Horta's group[16] have proposed a method based on the equation-of-state ternary theory[27,28]. This method leads to the calculation of a 'true', χ^T_{23}, interaction parameter, which, besides making use of the

free-volume concept, does not assume the additivity hypothesis (discussed by Pesci and Freed[29]). To follow the formalism used by those authors, it is necessary to substitute the volume fractions φ_i in the Flory–Huggins theory by segment fractions ϕ_i according to:

$$\phi_i = \frac{w_i v_i^*}{\sum w_i v_i^*} \tag{11}$$

where v_i^* and w_i represent respectively the characteristic specific volume and the weight fraction of the ith component. In agreement with Flory's equation-of-state theory, the non-combinatorial part of the Gibbs mixing function ΔG^M is not a sum of binary contributions. All terms depend simultaneously on the properties of the ternary system because the variable on which ΔG^M depends is the reduced temperature of the ternary system.

By deriving the expression for the non-combinatorial 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, the residual chemical potential of the solvent, χ_{1p}, can be obtained as an additive combination of binary interaction parameters. In the case of i.g.c. where $\phi \to 0$, it reads:

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

where Γ is a free-volume term, $\tilde{V}_i$ and $\tilde{V}_{ij}$ the reduced volumes of the ith component and the binary i–j system, and θ_i is the molecular surface fraction defined as:

$$\theta_i = \frac{w_i v_i^* s_i}{\sum w_i v_i^* s_i} \tag{13}$$

with s_i the molecular surface-to-volume ratio of the ith component. All the interaction parameters χ in equation (12) are defined in terms of segment fractions instead of volume fractions, and:

$$\chi'^{T}_{23} = \chi^{T}_{23}(V_1^*/V_2^*) \tag{14}$$

with V_i^* the reduction molar volume of the ith component. χ^{T}_{23} must be considered as more reliable than the χ_{23} obtained from the additivity approximation.

By comparing equation (12) with the additivity relation now written in segment fractions:

$$\chi_{1p} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi'^{A}_{23} \tag{15}$$

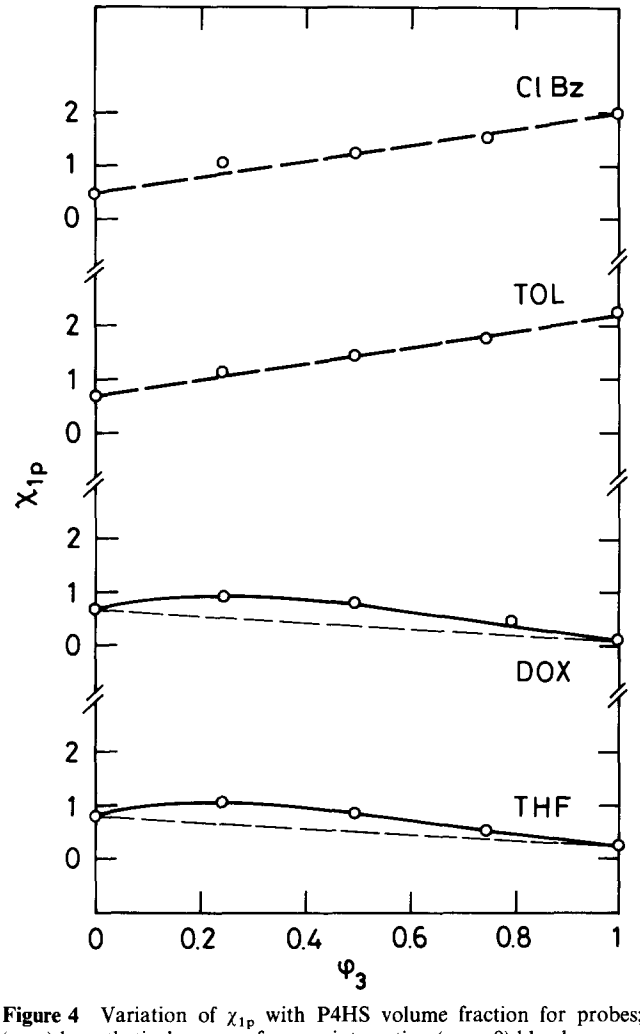

Figure 4 Variation of χ_{1p} with P4HS volume fraction for probes; (– – –) hypothetical average for non-interacting ($\chi_{23}=0$) blends

Table 2 Interaction parameters χ_{ij} referred to V_j for the system solvent (1)+PCL (2)+P4HS (3) at 463 K

Probe (code)	χ_{12}	χ_{13}	$\chi_{12}-\chi_{13}$	χ'_{23}		
				$\varphi_3=0.24$	$\varphi_3=0.49$	$\varphi_3=0.74$
Acetone (ACE)	1.309	0.577	0.73	−1.640	−0.825	−0.185
Butan-2-one (MEK)	1.051	0.622	0.43	−1.612	−0.842	−0.331
Pentan-3-one (DEK)	0.842	0.765	0.07	−1.710	−1.188	−0.584
Propan-1-ol (1-POL)	1.125	1.013	0.11	−0.717	−0.756	−0.448
Propan-2-ol (2-POL)	1.096	0.843	0.25	−1.153	−0.565	−0.163
Isobutyl alcohol (IBOL)	0.838	1.097	−0.26	−0.882	−0.439	0.061
Ethyl acetate (EAC)	1.117	1.070	0.05	−0.902	−0.560	−0.115
n-Propyl acetate (PAC)	0.964	1.096	−0.013	−1.186	−0.831	−0.461
n-Butyl acetate (BAC)	0.864	1.202	−0.34	−1.352	−0.956	−0.392
Tetrahydrofuran (THF)	0.895	0.272	0.62	−1.554	−0.974	−0.487
Dioxane (DOX)	0.713	−0.013	0.74	−1.980	−1.385	−0.968
Toluene (TOL)	0.684	2.226	−1.54	−0.449	0.095	0.045
Chlorobenzene (ClBz)	0.527	1.994	−1.46	−0.639	0.017	0.464
$\langle\chi'_{23}\rangle$	–	–	–	−1.2	−0.7	−0.2

the following equation can be obtained:

$$\frac{\chi_{23}^{A}+\kappa}{V_2^* s_1}=\frac{\chi_{23}^{T}}{V_2^* s_3}+\frac{s_3-s_2}{(\phi_2 s_2+\phi_3 s_3)V_1^* s_1}(\chi_{12}-\chi_{13}) \quad (16)$$

with

$$\kappa=\left(\frac{V_2^*}{V_1^*}\right)\left[\left(\frac{\Gamma}{\phi_2\phi_3}\right)+\chi_{12}\left(\frac{\tilde{V}_2}{\tilde{V}_{23}}-1\right)\left(\phi_3^{-1}+\frac{s_2-s_3}{\phi_2 s_2+\phi_3 s_3}\right)+\chi_{13}\left(\frac{\tilde{V}_3}{\tilde{V}_{23}}-1\right)\left(\phi_2^{-1}-\frac{s_2-s_3}{\phi_2 s_2+\phi_3 s_3}\right)\right] \quad (17)$$

and

$$\Gamma=\frac{P_1^* V_1^*}{RT}\left(\Gamma_{1p}-\frac{\tilde{V}_2}{\tilde{V}_{23}}\theta_2\Gamma_{12}-\frac{\tilde{V}_3}{\tilde{V}_{23}}\theta_3\Gamma_{13}\right)+\frac{P_2^* V_1^*}{RT}\frac{s_1}{s_2}\frac{\theta_2}{\theta_3}\Gamma_{23} \quad (18)$$

where

$$\Gamma_{ij}=\tilde{V}_i^{-1}-\tilde{V}_{ij}^{-1}-3\tilde{T}_i\ln\left(\frac{\tilde{V}_{ij}^{1/3}-1}{\tilde{V}_i^{1/3}-1}\right) \quad (19)$$

and P_i^* and T_i^* are the pressure and temperature reduction parameters of the components.

Equation (16) allows one to obtain χ_{23}^{T} from the additive interaction parameter χ_{23}^{A}, but complete information of equation-of-state parameters of the components is necessary, which explains why this method has only been applied so far to a few systems[13,16]. As a consequence Deshpande *et al.*[15] have recently suggested another more simplified method, which is a rearranged form of the basic Su and Patterson i.g.c. equation[1] and allows one to evaluate a mean value of the interaction parameter, χ_{23}^{D}, by plotting the l.h.s of equation (20) vs. $(\chi_{12}-\chi_{13})/V_1$:

$$\frac{\chi_{1p}-\chi_{13}}{V_1}=\varphi_2\left(\frac{\chi_{12}-\chi_{13}}{V_1}\right)-\left(\frac{\chi_{23}^{D}}{V_2}\right)\varphi_2\varphi_3 \quad (20)$$

As interesting observation is that Deshpande's method can be derived from Horta's one after introducing some approximations. In effect, starting from equations (15) and (16), making the free-volume term κ vanish, and assuming $s_2=s_3$ it leads to:

$$\frac{\chi_{1p}-\chi_{13}}{V_1^*}=\phi_2\frac{(\chi_{12}-\chi_{13})}{V_1^*}-\frac{\chi_{23}^{T}\phi_2\phi_3}{V_2^*}\left(\frac{s_1}{s_3}\right) \quad (21)$$

This equation is similar to equation (20), but equation (20) is written in volume fractions and leads to a polymer–polymer interaction parameter χ_{23}^{D} higher than χ_{23}^{T} becuase the s_1/s_3 ratio has in general a value close to 2.

Now we will discuss and compare for the PCL (2)/P4HS (3) system, the values of χ_{23} calculated through these theoretical methods with those obtained by the additivity approximation (*Table 2*) and also with those determined from the measurements of the melting-point depression of PCL in binary blends[18,19], which obviously does not require the presence of a solvent and as a consequence avoids the additivity approximation.

In order to obtain χ_{23}^{T} from equation (16), the characteristic parameters of the solvents and polymers are needed. *Tables 3* and *4* include these parameters, which were calculated as mentioned before from thermal expansion, isothermal compressibility coefficients and density at 298 K[22-26]. These parameters V^*, P^* and T^* were considered temperature-independent. Molar volumes and reduced volumes at 463 K are also included. The molecular surface-to-volume ratios were calculated for solvents according to Bondi[30], and they are also shown in *Table 3*. The values of s_3 and s_2 have been estimated using a cylinder model for the polymer, with a radius r calculated from V^* and a length L obtained from structural parameters of the polymers:

$$s_i=\frac{2\pi rL+2\pi r^2}{\pi r^2 L}=2\left(\frac{1}{r}+\frac{1}{L}\right)\sim\frac{2}{r} \quad (\text{if } L\to\infty)$$

$$r=\left(\frac{V^*}{L\pi N_A}\right)^{1/2}$$

Figure 5 shows $(\chi_{23}^{A}+\kappa)/V_2^* s_1$ against $(\chi_{12}-\chi_{13})/V_1^* s_1$ for each composition of the blend. It can be noted that in general an acceptable linear correlation is obtained.

Table 3 Equation-of-state parameters for solvents

	$T=298$ K			$T=463$ K		
Solvent	V_1^* (cm^3 mol^{-1})	P_1^* (J cm^{-3})	T^* (K)	V_1[a] (cm^3 mol^{-1})	$\tilde{V}_1$[b]	s (10^8 cm^{-1})
ACE	55.47	599	4337	101.95	1.8384	1.50
MEK	68.91	554	4551	120.06	1.7423	1.46
DEK	82.21	504	4680	139.64	1.6986	1.44
1-POL	60.22	454	5227	97.33	1.6112	1.49
2-POL	61.03	378	5060	106.52	1.7454	1.49
IBOL	74.92	281	5334	119.34	1.5928	1.45
EAC	74.21	600	4394	133.80	1.8030	1.48
PAC	88.14	628	4518	152.37	1.7287	1.45
BAC	103.15	556	4778	168.32	1.6317	1.43
THF	63.78	550	4853	105.12	1.6481	1.34
DOX	67.27	738	4899	105.05	1.5616	1.37
TOL	84.74	555	5051	133.27	1.5725	1.25
ClBz	82.12	594	5269	123.87	1.5084	1.23

[a] Calculated by Benson's method with data from ref. 20
[b] $\tilde{V}_1=V_1$ (463 K)$/V_1^*$ (298 K)

Table 4 Equation-of-state parameters for polymers

Polymers	$T=298$ K			$T=463$ K		
	v^{*a} ($cm^3\,g^{-1}$)	P^* ($J\,cm^{-3}$)	T^* (K)	v^a ($cm^3\,g^{-1}$)	$\tilde{V}$	s ($10^8\,cm^{-1}$)
PCL	0.790	479	6805	1.025	1.297	0.79
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

Table 5 Interaction parameters of PCL/P4HS determined by melting-point depression (d.s.c.) at 335 K and by i.g.c. at 463 K, at different blend compositions φ_3

φ_3	D.s.c. (335 K) 0.7–1	I.g.c. (463 K) 0.24	0.49	0.74
χ_{23}/V_2 ($cm^{-3}\,mol$)	-1.1×10^{-2}	–	–	–
χ^T_{23}/V^*_2 ($cm^{-3}\,mol$)	–	-0.9×10^{-2}	-0.5×10^{-2}	-0.2×10^{-2}
χ^D_{23}/V_2 ($cm^{-3}\,mol$)	–	-1.0×10^{-2}	-0.8×10^{-2}	-0.2×10^{-2}

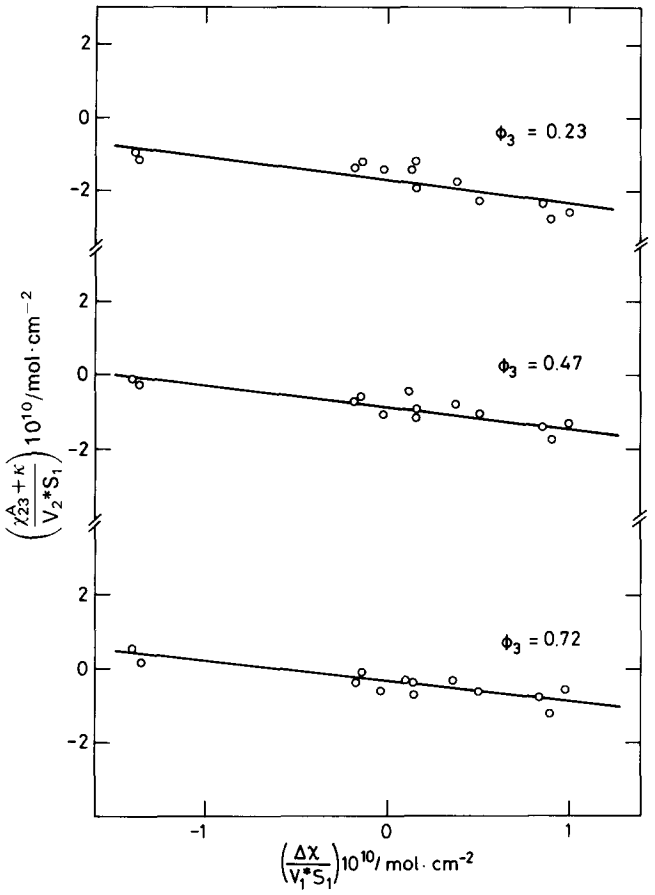

Figure 5 A plot of the quantity $(\chi^A_{23}+\kappa)/V^*_2 s_1$ against $\Delta\chi/V^*_1 s_1$ ($\Delta\chi=\chi_{12}-\chi_{13}$) for PCL/P4HS blends

According to equation (16) the slopes of these straight lines should be $(s_3-s_2)/(\phi_2 s_2+\phi_3 s_3)$; the values of these slopes are around -0.6, varying slightly with composition. These values are one order of magnitude higher than the corresponding theoretical ones, probably due to the uncertainty in the values of s_2 and s_3 estimated through the cylinder model. That discrepancy is reasonable if we consider that deviations in s_2 and s_3 of 20% can cause such high differences between theoretical and experimental slope results. Following from *Figure 5* the polymer–polymer interaction parameter χ^T_{23}/V^*_2 for each composition can also be obtained from the intercepts of the straight lines. The values for compositions $\phi_3=0.23$, 0.47 and 0.72 are respectively -0.9×10^{-2}, -0.5×10^{-2} and $-0.2\times10^{-2}\,mol\,cm^{-3}$, with standard deviations around 50%. These negative values indicate the miscibility of the P4HS and PCL by hydrogen-bond interaction, and the variation of χ^T_{23}/V^*_2 as a function of blend composition shows that the blend becomes more miscible at high PCL contents. Applying equation (16) in the simplified case of $\kappa=0$, which means that free-volume differences between polymers and their mixtures are neglected, the values obtained for χ^T_{23}/V^*_2 are -0.7×10^{-2}, -0.3×10^{-2} and $-0.1\times10^{-2}\,mol\,cm^{-3}$ for $\phi_3=0.23$, 0.47 and 0.72 respectively. These values are less negative than those calculated without any simplification. Nevertheless the differences are quite small compared with the standard deviations, so the free-volume contribution included in the κ term is not very significant in this system and hence the interactional term of χ_{23} seems to be dominant.

Furthermore, we have applied the extremely simple Deshpande method, which provides a probe-independent interaction parameter χ^D_{23} (see equation (20)). *Figure 6* shows $(\chi_{1p}-\chi_{13})/V_1$ against $(\chi_{12}-\chi_{23})/V_1$ for each composition of the blend. A very good linear correlation is obtained. The slopes of these straight lines are 0.92, 0.66 and 0.36 for $\varphi_3=0.24$, 0.49 and 0.74 respectively. According to equation (20), the slopes should be φ_2, but the values obtained are $\simeq 1.3\varphi_2$ in all cases. This discrepancy is not surprising because making only $\kappa=0$ in Horta's method (equation (16)) leads to an equation similar to Deshpande's, with a slope:

$$\phi_2\left(1-\frac{(s_3-s_2)\phi_3}{(\phi_2 s_2+\phi_3 s_3)}\right) \qquad (22)$$

instead of ϕ_2. Neglecting the differences between volume and segment fractions and considering the corresponding

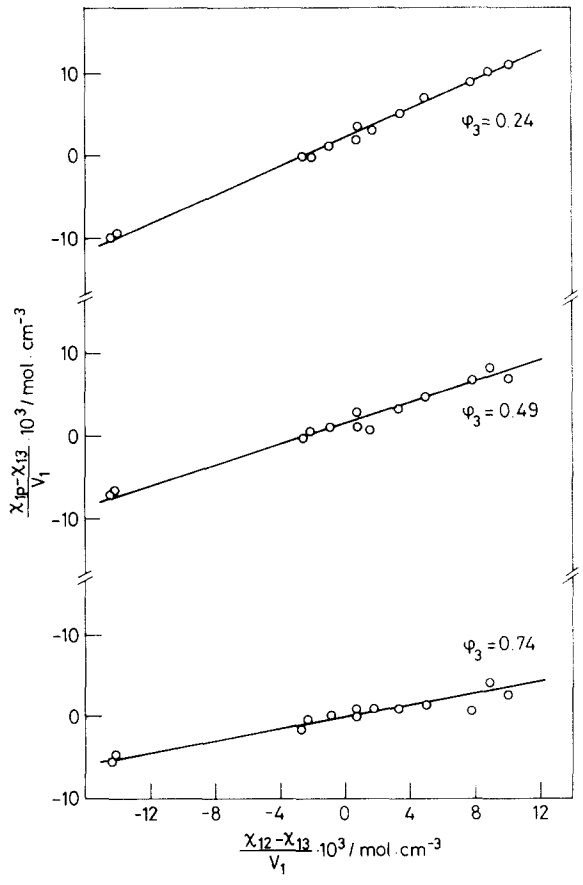

Figure 6 A plot of the quantity $(\chi_{1p}-\chi_{13})/V_1$ against $(\chi_{12}-\chi_{13})/V_1$ for PCL/P4HS blends

values of s_2 and s_3, a value of $1.2\phi_2$ for the slope is predicted.

The average values of χ'_{23} are similar to the corresponding ones obtained from Horta's and Deshpande's extrapolations. This is due to having chosen a group of solvents that cover a wide range of $\Delta\chi$ with negative and positive values. As a consequence it should not be surprising that, in a set of solvents where the $\Delta\chi$ is more restricted, the average values of χ'_{23} differ considerably with those extrapolated ones.

All of the i.g.c. results of the PCL/P4HS interaction parameter are compiled in *Table 5* together with the interaction parameter determined by measuring the melting-point depression of PCL in the binary blends[18]. There is good correlation between Horta's and Deshpande's values and, what is more, with the d.s.c. value, which supports the validity of these methods.

The negative values of χ_{23} confirm the miscibility of PCL with P4HS arising from strong specific interactions between the two polymers. The χ_{23} values show a systematic variation with composition; such concentration dependence has also been found in other systems[6,31,32]. In the PCL/P4HS blends the χ_{23} vs. φ_2 dependence indicates that the blend becomes more miscible at high PCL content, in accordance with the behaviour reported in the literature for polymer blends in which the PCL is involved[26,33].

The concentration dependence of the interaction parameter χ_{23} can be analysed in terms of the Flory equation-of-state theory. That dependence is determined by the free-volume contribution and by the ratio s_2/s_3. For the PCL/P4HS system the differences between the free volume of the components are almost negligible, so the χ_{23} vs. φ_2 dependence should come from the differences in the surface-to-volume ratio of the components ($s_2/s_3 \simeq 1.5$). In the poly(vinyl acetate)/P4HS system, which we have previously studied[14,18], there are no differences in free volume, and the surface-to-volume ratios of both polymers are quite similar, and as a consequence did not show a significant composition dependence.

CONCLUSIONS

The miscibility behaviour between poly(4-hydroxystyrene)/poly(ε-caprolactone) was investigated. The negative values of χ'_{23} in the binary P4HS/PCL blends reflect the miscibility of the system by hydrogen-bond interaction in all the composition range.

A variation for the interaction parameter with the blend composition has been found and indicates that the blend becomes more miscible at high PCL contents. To minimize the probe dependence on χ'_{23}, two theoretical methods have been applied to calculate the polymer–polymer interaction parameter: Horta's method based on the equation-of-state ternary theory and a more simplified one recently proposed by Deshpande. The values of χ_{23} obtained from these methods are more reliable than the average values of χ'_{23}. A good concordance has been found between the interaction parameters calculated by the two theoretical methods and those obtained by measuring the melting-point depression of PCL in binary blends. These results, together with those found before for the P4HS/PVA system, confirm these methods as good approaches to get probe-independent interaction parameters.

As Deshpande's method can be derived from that of Horta and because it is simpler, it could be preferentially used in systems in which the surface-to-volume ratios of the polymers are similar and no large differences in the free volumes are present.

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