

Surface enrichment in PS/PVME blends:

2. The effect of specific interactions in the bulk mixture

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The surface composition of blends of styrene copolymers, containing a hydrogen-bonding comonomer, with poly(vinyl methyl ether) has been estimated using infra-red reflectance spectroscopy. Surface enrichment by the polyether, which has the lower surface energy, is markedly less than that observed previously for poly(vinyl methyl ether)/polystyrene homopolymer blends. The extent of this effect depends on the strength of the hydrogen bond involved, and this in turn can be correlated with the degree of blend miscibility as determined by lower critical phase separation temperatures and heats of mixing. The findings confirm that surface enrichment depends not simply on surface energy differences but also on bulk mixing thermodynamics.

(Keywords: surface enrichment; PS/PVME blends; hydrogen bond)

INTRODUCTION

The surface of a two-phase polymer mixture should consist predominately of one component, namely that having the lower surface free energy, since thermodynamics already favour complete demixing. Real systems certainly approximate to this expectation^{1,2} but are limited presumably by constraints associated with phase domains having a finite size and an equilibrium composition. In miscible blends lower surface energies may also be achieved by preferential placement of one component at the surface. However this requires a composition gradient to be maintained between the surface and the bulk, and consequently the equilibrium surface composition is determined by the minimization of the total system free energy. Theoretical treatments along these lines have been presented using mean-field formalisms³⁻⁵.

In principle a blend surface may be varied by changing either the relative surface tensions (γ_i) or, alternatively, the mixing thermodynamics; the latter is the subject of this present investigation. Targeting one variable alone may prove difficult since chemical modification will usually affect both and may effectively change the original system to another, albeit related, one. This problem is overcome by the choice of a blend in which small chemical changes bring about significant effects at the segmental level, such as the introduction of specific interactions which enhance miscibility. Polystyrene/poly(vinyl methyl ether) (PS/PVME) is one such system, in which the introduction of hydroxyl substituents results in hydrogen bonding to the polyether^{6,7}.

Surface enrichment in PS/PVME blends has been demonstrated by X-ray photoelectron spectroscopy (X.p.s.) and surface tension measurements^{8,9}. The former

technique has a high surface sensitivity and returns information from the topmost 6 nm or so, but has certain drawbacks in terms of the ease of application and in cost, whereas the latter is limited to the study of polymer melts. In a previous paper¹⁰ we demonstrated that surface enrichment in PS/PVME blends may be observed using attenuated total reflectance Fourier transform infra-red (ATR FTi.r.) spectroscopy. Despite the surface depth sensitivity of this technique being of the order of 0.5–3 μm , the results in terms of the apparent surface fraction of PVME parallel those from X.p.s. and surface tension measurements. In this paper we utilize the convenience of ATR FTi.r. to examine the effect of specific interactions on the surface composition in four blend systems.

EXPERIMENTAL

Preparation of monomers

Styrene and *p*-chlorostyrene were obtained from the Aldrich Chemical Company and were freed from inhibitor by standard techniques. 4-Vinylacetophenone (4-VA) was prepared by the pyrolysis of poly(vinylacetophenone), obtained by the complete acylation of polystyrene, according to the method described by Kenyon and Waugh¹¹. The crude distillate from the pyrolysis was purified on a silica column, using chloroform as the eluant, to give a fraction boiling at 342 ± 1 K. 4-Vinyltrifluoroacetophenone (4-VTA) was synthesized from *p*-chlorostyrene by a Grignard reaction with trifluoroacetic acid in tetrahydrofuran (THF), as described by Cheng and Pearce⁶. The crude product was chromatographed as above and adjudged to be pure by proton magnetic resonance and infra-red spectroscopy.

4-(Hexafluoro-2-hydroxy isopropyl)styrene (4-HFHS) was similarly synthesized from *p*-chlorostyrene and

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hexafluoroacetone. The procedures described by Pearce *et al.* were followed⁷ but analysis of the notionally purified product indicated the presence of THF, presumably due to a strong association between the alcohol and THF. The product was finally isolated by washing a chloroform solution of the THF 'complex' with 10% aqueous sodium hydroxide, separating the aqueous layer and subsequently treating it with 10% HCl to yield a yellow organic layer. This was taken up in CCl₄, washed with water till neutral, dried and the solvent evaporated to yield a product with the expected spectroscopic characteristics. The procedure adopted for the synthesis of 4-hydroxystyrene (4-HS) from 4-hydroxy cinnamic acid was that described by Sovish¹². The pure product was fractionally recrystallized from cold hexane.

Copolymerizations

All copolymerizations were carried out under vacuum, using toluene as the solvent and 0.3 mol% 2,2'-azobisisobutyronitrile (AIBN) as the initiator, at 333 K, and were terminated at low conversion by precipitation into cold methanol. Purification was by three reprecipitations from toluene solution into methanol, followed by drying under vacuum at 333 K for 36 h. The copolymerization details are shown in *Tables 1* and *2*.

Copolymers of styrene with 4-vinylacetophenone and with 4-vinyltrifluoroacetophenone were reduced with lithium aluminium hydride using standard techniques to give the corresponding structures containing 4-(2-hydroxyethyl)styrene (4-HES) and 4-(1,1,1-trifluoro-2-hydroxyethyl)styrene (4-TFHS), respectively. The reduced copolymers were isolated and purified by repeated reprecipitations into methanol. Copolymer molecular weights were determined by gel permeation chromatography in THF solution in terms of polystyrene equivalents. All copolymer compositions are assumed equal to that of their respective comonomer feeds. This would seem a quite reasonable approximation for the feeds used here where the maximum mole fraction is 0.06.

Table 1 Details of the copolymerization of 4-vinylacetophenone (4-VA) and of 4-vinyltrifluoroacetophenone (4-VTA) with styrene and the characteristics of the reduced copolymers

Mol% in feed	Polymerization time (h)	Conversion (wt%)	$M_n \times 10^3$ (g mol ⁻¹)	M_w/M_n	T_g (K)
2.2 4-VA	4.5	19	28	1.7	368
6.0 4-VA	4.0	15	28	1.7	368
0.6 4-VTA	4.0	10	28	1.6	371
1.1 4-VTA	4.0	12	45	2.1	371
2.8 4-VTA	3.5	9	34	1.8	377

Table 2 Details of the copolymerization of 4-hydroxystyrene (4-HS) and of 4-(hexafluoro-2-hydroxy isopropyl)styrene (4-HFHS) with styrene and the characteristics of the copolymers obtained

Mol% in feed	Polymerization time (h)	Conversion (wt%)	$M_n \times 10^3$ (g mol ⁻¹)	M_w/M_n	T_g (K)
0.5 4-HS	4.0	4	39	1.5	372
1.0 4-HS	4.0	10	35	1.6	372
2.0 4-HS	4.0	12	30	2.3	375
0.3 4-HFHS	5.0	10	37	1.6	372
0.7 4-HFHS	5.0	9	43	1.6	375
1.4 4-HFHS	5.0	13	42	1.6	375
2.7 4-HFHS	5.0	11	40	1.6	369

Blend preparation and characterization

Films of the blends were prepared from 5% toluene solutions on aluminium foil stretched over levelled glass plates by using a bar spreader with an extrusion height of 200 μ m. Nominal film thicknesses were therefore 10 μ m. Films were vacuum dried at 333 K for 24 h and then cut to the appropriate size (on the aluminium backing) for the infra-red studies.

ATR FTi.r. spectra of the polymer-air interface of PS/PVME blends were obtained as before¹⁰ using a Perkin Elmer 1720X FTi.r. spectrometer. The extinction coefficient of the ether stretching mode (ϵ_{PVME} at 1084 cm⁻¹) and the styrene ring deformation (ϵ_{PS} at 699 cm⁻¹) have been determined previously¹⁰. The copolymer extinction coefficients were calculated as styrene mole-fraction proportions of ϵ_{PS} .

Glass transition temperatures (T_g) were measured using a Perkin-Elmer DSC-2 differential scanning calorimeter at a scanning rate of 20 K min⁻¹, and the values obtained are shown in *Tables 1* and *2*. The cloud-point temperatures (CPTs) of the blends were determined as the temperatures at which the first visible signs of turbidity occurred on heating 50/50 wt% blends, cast onto cover slips, using a Linkam PR600 variable temperature microscope hot-stage.

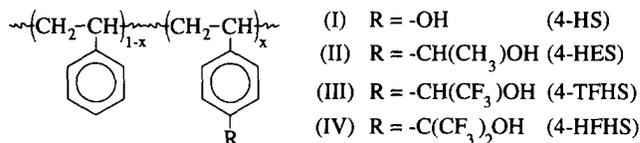
RESULTS AND DISCUSSION

The apparent PVME surface-volume fraction, ϕ_s , is estimated from the ATR FTi.r. measurements as^{10,13}

$$\phi_s = C_{PVME} / (C_{PVME} + C_{PS}) \approx A_{PVME} / (A_{PVME} + \lambda A_{PS}) \quad (1)$$

where dp_i is the depth of penetration and $\lambda = dp_{PVME} \epsilon_{PVME} / dp_{PS} \epsilon_{PS}$. $dp_{PVME} = 1.33 \mu$ m at 1084 cm⁻¹, $dp_{PS} = 2.04 \mu$ m at 699 cm⁻¹, C_i are volume fractions, A_i are the measured absorbances, and the extinction coefficients are in units of μ m⁻¹. By using the ratio of two absorbances problems associated with imperfect or irreproducible contact of sample and reflection element are minimized.

In blends with PS homopolymer, ϕ_s was found to be appreciably greater than ϕ_B (the PVME bulk-volume fraction) over the range $0 < \phi_B < 0.6$. Here we examine similar blends with styrene copolymers, where the comonomer substituent R is one of the hydroxyl moieties (I)-(IV).



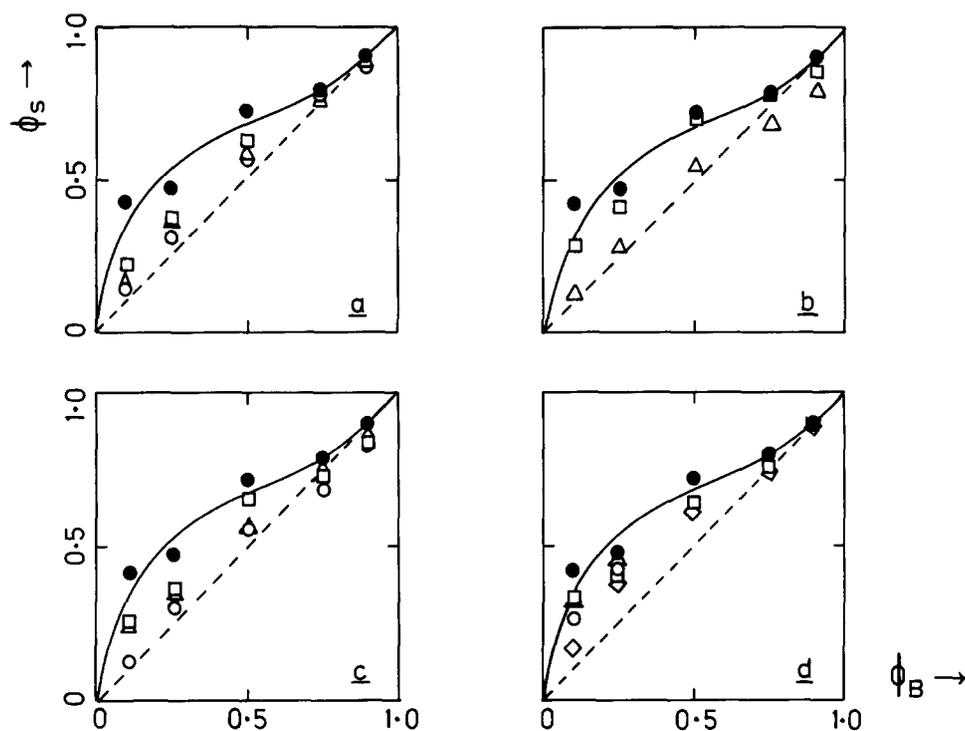


Figure 1 Apparent PVME surface-volume fraction (ϕ_s) plotted against PVME bulk-volume fraction (ϕ_B) in various PS-copolymer/PVME blends: (a) 4-HS, with feed mol% of 0.5 (\square), 1.0 (\triangle) and 2.0 (\circ); (b) 4-HES, with feed mol% of 2.2 (\square) and 6.0 (\triangle); (c) 4-TFHS, with feed mol% of 0.5 (\square), 1.1 (\triangle) and 2.8 (\circ) and; (d) 4-HFHS, with feed mol% of 0.3 (\square), 0.7 (\triangle), 1.4 (\circ) and 2.7 (\diamond). The data for PS/PVME blends, shown by filled circles and a full line, are taken from ref. 10

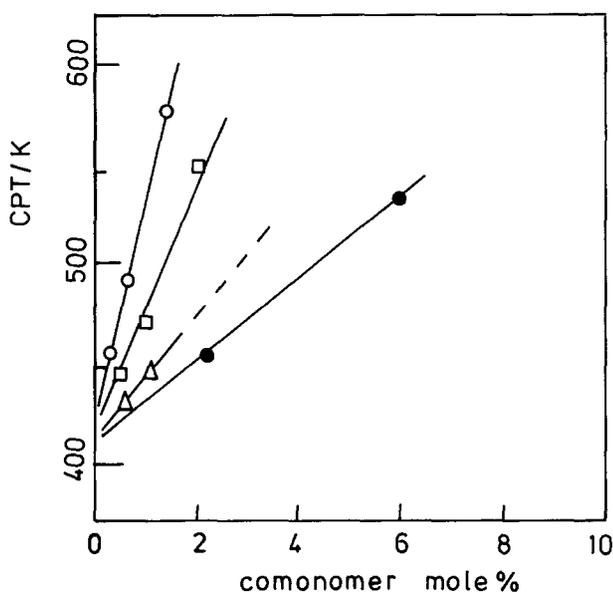


Figure 2 Variation in the cloud-point temperature of various PS-copolymer/PVME (50/50 wt%) blends as a function of comonomer content (mol%): (\square) 4-HS; (\bullet) 4-HES; (\triangle) 4-TFHS and; (\circ) 4-HFHS

Their effect is seen from the plots of ϕ_s vs. ϕ_B , which are shown in *Figure 1*. The surface excess is successively reduced with increasing comonomer content indicating a reduced tendency for surface enrichment by PVME, and in three of the systems the measurable surface excesses have been all but eliminated within the range of copolymer compositions examined. Changes in γ_i , estimated by using the parachor¹⁴, turn out to be minimal. For example, $\gamma_{PS}(\text{calc})$ is $43.0 \text{ dyne cm}^{-1}$

whereas $\gamma(\text{calc})$ for a 2 mol% 4-HFHS/styrene copolymer is $42.9 \text{ dyne cm}^{-1}$. We can conclude that the reason for the reduced surface enrichment derives from changes in bulk thermodynamics and not from any change in surface energy.

PS/PVME is a well-studied blend¹⁵⁻¹⁹; infra-red spectroscopy reveals a weak interaction involving the aromatic ring and the oxygen of the ether which promotes miscibility²⁰. This, however, is both molecular-weight and solvent dependent, with single-phase blends demixing just above a temperature of 400 K. PS/PVME is thus best described as 'marginally' miscible, and changes due to hydrogen bonding are readily discerned by examining the effects on the CPT (see *Figure 2*), where all four comonomers cause demixing to move to higher temperatures, giving evidence of enhanced miscibility. Since here the sample molecular weight range is limited, a comparison between the copolymers seems to be in order, giving an increase in the CPT (per mole% comonomer) in the order, 4-HFHS > 4-HS > 4-TFHS > 4-HES.

The copolymers display distinctive O-H stretching bands (see *Figure 3*). The -OH region of the unblended copolymers exhibits both a free -OH stretching component and an 'intramolecular' self-association component, whereas 10/90 wt% PVME/copolymer blends show only a single broad band displaced to lower wavenumbers, suggesting that in this case all bonded structures are intermolecular with PVME as the acceptor. A correlation between the -OH band shifts and the enthalpy of hydrogen bond formation has been proposed by several investigators²¹⁻²³ and these spectra can be used to estimate heats of mixing for the systems in the following way.

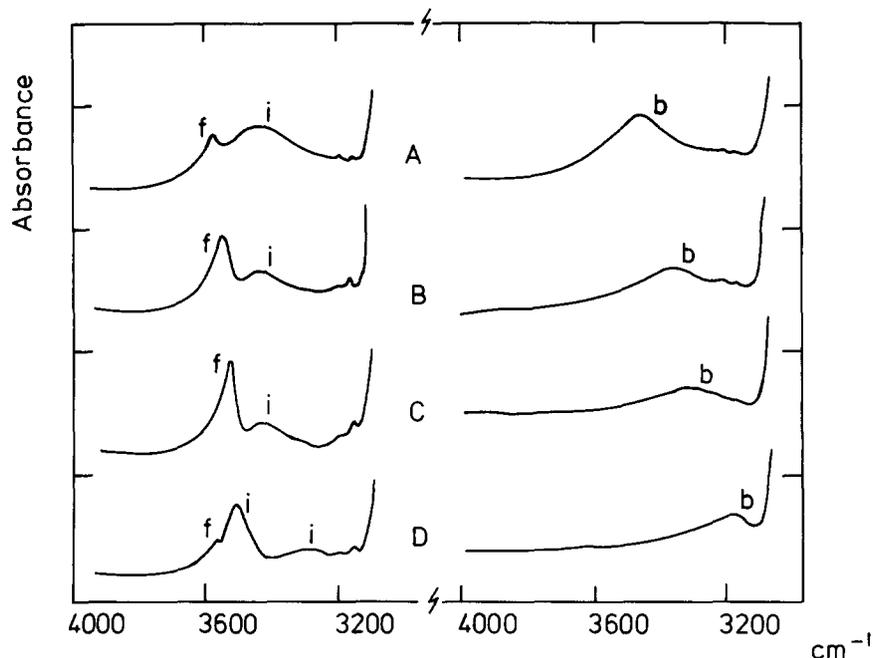


Figure 3 The infrared O-H stretching region for the styrene copolymers (left hand set) and for blends (10/90 wt%) with PVME (right hand set), with comonomer feeds (mol%): (A) 2.2 4-HES; (B) 2.8 4-TFHS; (C) 2.0 4-HS and; (D) 2.7 4-HFHS. The band types are: (f) free; (i) intramolecular and; (b) intermolecular

Table 3 Infrared free -OH stretching (f) and intramolecular self-associated stretching (i) frequencies in PS copolymers, and intermolecularly associated -OH frequencies (b) in blends (10/90 vol%) with PVME

System	Mol% in feed	ν (cm ⁻¹)			$\Delta\nu$ (cm ⁻¹)		Area ^a (f:i)	$-\Delta H_{HB}^b$ (kJ mol ⁻¹)
		(f)	(i)	(b)	(f-b)	(i-b)		
4-HS	2.0	3545	3440	3320	225	120	2:1	23
4-HES	2.2	3582	3460	3440	140	20	1:5	5
4-TFHS	2.8	3556	3440	3390	266	50	1:1	13
4-HFHS	2.7	3580	3513	3200	380	313	1:6:1	35
			3300			100		

^a Relative area of free band to intramolecular self-association band

^b Using the correlation $-\Delta H = \Delta\nu/8.5$ suggested in ref. 21 and weighting the (f-b) and (i-b) contributions according to the relative areas (f:i)

We may regard PS/PVME mixtures as athermal (literature estimates of the Flory χ -parameter range from small negative to small positive values¹⁵) and the heat of mixing of a copolymer/PVME blend to therefore result solely from hydrogen bond formation. However, in the unmixed (reference) state, the -OH groups are both intramolecularly bonded and unbonded (free). Although the ratio of these environments is dependent on the copolymer composition, over the present limited range this is relatively minor, and so it is assumed constant. A far more adventurous assumption is that the relative areas of the intra and free bands can be taken as a measure of the relative proportions of intra and free -OH environments. On this basis, and using the spectra in *Figure 3*, the various peak shifts and the corresponding values of the enthalpies of intermolecular hydrogen bond formation, relative to the ratio-weighted pure component -OH environments, are shown in *Table 3*.

The situation for 4-HFHS is more complex than just a simple equilibrium between free and intra environments. The major -OH environment corresponds to the band at 3513 cm⁻¹ with the (minor) free component^{7,24} at ~3580 cm⁻¹, plus yet one further environment at even lower wavenumbers. However, if the spectrum is accepted

as characterizing the reference state of the copolymer, it is not at all necessary to assign the molecular nature of these environments, other than on the basis of their relative energies.

The ΔH_{HB} entries in *Table 3* are in line with the abilities of the various comonomers to raise the CPT of the blend, a parameter which might be expected to relate to the hydrogen bond strength. The comonomer concentrations at which $\phi_S \sim \phi_B$ likewise may be expected to show some correlation, and this may be put on a semi-quantitative basis in terms of the heat of mixing, since ΔH_B refers to an equilibrium (equation (2)) characterized by an equilibrium constant K_{HB} :



A is a PVME repeat unit, D a comonomer unit and DA is a vinyl methyl ether/styrene hydrogen bonded unit. If V_{PS} is the molar volume of a styrene unit and x is the mole fraction of comonomer D, then the heat of mixing per cm³ of blend due to hydrogen bond formation is given by:

$$\Delta H_M = \alpha x(1 - \phi_B)\Delta H_{HB}/V_{PS} \quad (3)$$

The equilibrium shown in equation (2) may be considered in the standard manner, with α as the extent of the equilibrium, and it was found that the following holds when x is small:

$$K_{\text{HB}} = \alpha V_{\text{PVME}} / [V_{\text{PS}} \phi_{\text{B}} (1 - \alpha)] \quad (4)$$

Solving for α and substituting the result into equation (3) then gives

$$\Delta H_{\text{M}} = x \phi_{\text{B}} (1 - \phi_{\text{B}}) K_{\text{HB}} \Delta H_{\text{HB}} / (V_{\text{PS}} \phi_{\text{B}} K_{\text{HB}} + V_{\text{PVME}}) \quad (5)$$

Equation (5) requires a value of K_{HB} to be assigned, and here we have chosen a value of $K_{\text{HB}} \sim 10$, as obtained for the interassociation of 4-HFHS with the methacrylate repeat unit²⁴, as being numerically reasonable for these calculation purposes.

A short extrapolation of the trends indicated in Figure 1 enables the comonomer mole fractions at which $\phi_{\text{S}} \sim \phi_{\text{B}}$ to be estimated as 3.5 (4-HS), 4.0 (4-TFHS) and 8.0 (4-HES). (A corresponding value for 4-HFHS is too far outside the range synthesized to be chosen with any certainty.) From equation (5) now, at $\phi_{\text{B}} = 0.5$, the corresponding estimates of ΔH_{M} are -3.9 , -3.3 and -2.0 J cm^{-3} , suggesting that quite small exothermic heat of mixings (i.e. about 3 J cm^{-3}) will ensure a nil overall drive for measurable surface enrichment. This fine balance could be quite common; the components of a miscible blend will generally have rather similar γ_i values (since these reflect the same molecular basis as the miscibility), and so the magnitude of the driving force for surface enrichment will never be large. Surface phenomena are just as likely, therefore, to respond to the influences of bulk properties as to surface or interfacial properties.

Although the 4-HFHS system falls within the generality of these last remarks, it is less affected than would be expected by the introduction of the strongest hydrogen bond in this series of blends. The reason for this is not obvious, as is the apparent surface excess of polystyrene at ϕ_{B} in the range 0.75–0.90 in two of the blends (see Figure 1). There may indeed be matters of detail not brought to light by this present examination; nevertheless, judicious modification of blend thermodynamics has been shown to bring about changes in the observed surface excess of the lower surface energy component. We emphasize the word 'observed', especially in the context of this FTi.r. method, which returns an integral effect

over a 'near-surface', which is roughly equivalent to the depth of penetration. The possibility of examining the concentration profile in this region by reflectance spectroscopy will be addressed in a future paper.

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