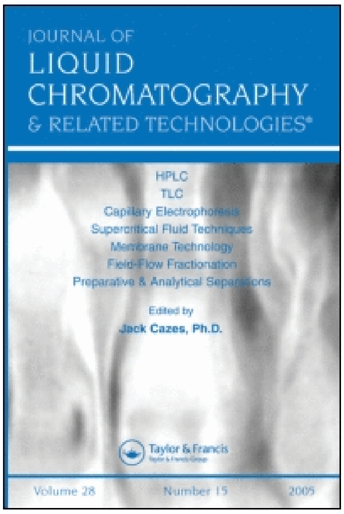

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Estimation of the Compatibility Between Poly(Methylmethacrylate) and Poly(Styrene Co Vinyl Phenol) Blends from Dilute Solution Measurements

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Abstract: The compatibility of poly(methyl methacrylate) (PMMA) with poly(styrene-co-vinyl phenol) (PS-VPh) with two different contents of vinyl phenol, 5.8 and 7.2%, in dilute tetrahydrofuran solutions has been investigated by size exclusion chromatography and fluorescence spectroscopy at 25°C. The chromatographic technique permits the evaluation of the preferential solvation at different PMMA/PS-VPh ratios. Changes in the fluorescence properties of PS-VPh, caused by its association with PMMA, were used to obtain the fraction of copolymer bound to PMMA at diverse PMMA compositions. Both techniques agree quantitatively in every system, indicating that the association increases when the PMMA concentration and the content of the vinyl phenol in the copolymer increase.

Keywords: Size exclusion chromatography, Polymer compatibility, Fluorescence spectroscopy

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INTRODUCTION

The small interaction parameter between polystyrene, PS, and poly (methyl methacrylate), PMMA,[1] is the first indication of the incompatibility between both polymers.[2] Additional proofs are the early phase separation during the polymerisation of styrene monomer in methyl methacrylate[3] and the fact that clear films are not obtained by blending the two polymers,[4–14] or during the extrusion of PS/PMMA blends (5–20% wt PMMA).[15] Moreover, in mixtures of PS and PMMA, two glass transition temperatures (T_g)[10,16] and low solubility of PS in PMMA and, vice versa,[17–19] are noticed. However, PMMA can display compatibility with PS's copolymers such as poly(styrene-co-methyl methacrylate) and poly (styrene-co-acrylonitrile), with no phase separation observed in 1:1 mixtures in cyclohexanone, and clear films have been attained.[7] Homogeneous clear films without evidence of phase separations, at least during a year, have also been observed for different ratios of PMMA/poly(styrene-co-acrylonitrile) mixtures, going from 1/4 to 4/1.[20] Conditional compatibility is observed, however, according to the acrylonitrile content of the PS copolymer. So, in 1/1 mixtures, two opaque samples were obtained when acrylonitrile content in PS was 6.5 and 8% by weight, with phase sizes about 1 μm as shown by electron micrographs, whereas a single Tg, transparent film and no phases in the electron micrographs are observed when acrylonitrile content in PS goes from 9 to 27%.[21] Demixing is observed for copolymers with acrylonitrile content $<9\%$ and $>29\%$ and compatibility at intermediate compositions.[21] At some given compositions, there is also compatibility in the systems poly(styrene-co-maleic acid ester)/poly (methyl methacrylate)[5] and there has been attempts to compatibilize polystyrene and poly(methyl methacrylate) in the presence of inorganic materials such as sepiolite[22] and nanotubes.[23]

On the other hand, the ester group in PMMA is a proton acceptor interacting via hydrogen bonding with proton donors. As a result, PMMA is miscible with many polymers like poly(vinyl chloride), PVC, poly(ethylene oxide), PEO, poly(vinylidene fluoride), PVDF, poly(styrene-co-acrylonitrile), SAN, or with cellulose acetate hydrogen phtalate both in solid state and in solution.[24] Even PMMA and PS, being incompatible in solution,[25] the introduction of interacting groups in PS is an old practice to make them compatible.[26]

In this paper, the compatibility between poly(styrene-co-vinyl phenol), PS-VPh, and PMMA in tetrahydrofuran, THF, solution is tested at different compositions of both components and styrene copolymers with two different contents of vinyl phenol, namely 5.8 and 7.2% in weight. Two techniques such as GPC-SEC and fluorescence spectroscopy have been used. The advantages of the studies in solution are evident, since cristallinity or the morphological states of the polymer blends would not have influence on the results.[27] Also, the retarded diffusion of polymers in the solid state makes it difficult to attain a true thermodynamic equilibrium condition, which is not the case in solution. GPC-SEC yields the preferential solvation parameter that indicates the volume fraction of THF solvent or PMMA preferentially solvated on PS-VPh.

Fluorescence spectroscopy is frequently used[28,29] to study the interaction between polymers and organized media as micelles[30] or liposomes.[31] Here, it is used to determine interactions between two polymers, namely PMMA and PS-VPh. As a result, the fluorescence spectra of two different spectroscopic forms of PS-VPh have been registered. One of both forms $(\text{PS-VPH})_f$ is the free one in solution, the second one $(\text{PS-VPH})_b$ is the form bound to PMMA, which acts as a quencher.

THEORY

Preferential Solvation

A ternary solution solvent (1)/polymer (2)/polymer (3) in which polymer (2) is smaller in size than polymer (3) can approximately be considered as being formed by two coexisting phases in equilibrium: the bulk solvent or a binary phase constituted by solvent (1) and solute (2) and a ternary phase the domain of polymer (3). In order to define the composition in the two phases the following nomenclature will be used throughout the text:

ν_i (i = 1, 2) is the volume fraction of component i in the bulk solvent and it is assumed to be equal to the composition of the solvent mixture $1+2$ prior to the mixing with solute (3) $(\nu_1+\nu_2=1)$; ϕ_i (i = 1, 2, 3) is the volume fraction of component i in the coil domain of polymer (3) $(\phi_1+\phi_2+\phi_3=1)$; u_i (i = 1, 2) is the volume fraction of component 1 in the solvent mixture 1+2 in the ternary phase:

$$u_i = \phi_i/(1-\phi_3),\, u_1 + u_2 = 1.$$

In this ternary polymeric system in thermodynamic equilibrium, the preferential solvation can be defined as the excess volume fraction, ε of component i in the ternary phase with respect to the volume fraction of this component in the binary phase, that is:

$$u_1 = \frac{\phi_1}{1-\phi_3} = \nu_1 + \varepsilon \tag{1}$$

$$u_2 = \frac{\phi_2}{1-\phi_3} = \nu_2 - \varepsilon \tag{2}$$

A positive ε value, $\varepsilon > 0$, indicates that polymer (3) is preferentially solvated by solvent (1).

At dilute solutions, that is when $\phi_3 \to 0$, $u_1 \to \phi_1$ and $\phi_1 = \nu_1 + \varepsilon$ therefore $\varepsilon = \phi_1 - \nu_1 = \Delta\nu_1$ or when $u_2 \to \phi_2$, $-\varepsilon = \phi_2 - \nu_2 = \Delta\nu_2$; then, from these relationships, it yields that:

$$\Delta\nu_1 = \varepsilon = \phi_1 - \nu_1 = 1 - \phi_2 - (1 - \nu_2) = \nu_2 - \phi_2 = -\Delta\nu_2 \quad (3)$$

The preferential solvation coefficient, λ, indicates the volume fraction of solvent (1) or polymer (2) preferentially sorbed on polymer (3) by mass unit of polymer (3). The slope in the origin of the ε variation with polymer (3) concentration, c_3 in g mL^{-1}, is an alternative definition for λ:[32]

$$\lambda = \left(\frac{d\varepsilon}{dc_3}\right)_{c_3\to 0} = \left(\frac{d(\phi_1 - \nu_1)}{dc_3}\right)_{c_3\to 0} \approx \left(\frac{\Delta\nu_1}{c_3}\right)_{c_3\to 0} = -\left(\frac{\Delta\nu_2}{c_3}\right)_{c_3\to 0} \quad (4)$$

A preferential sorption of component (1) on polymer (3) indicates that $\phi_1 > \nu_1$ and therefore $\lambda > 0$. When the component (2) is preferentially solvated onto polymer (3), then $\phi_2 > \nu_2$ and $\lambda < 0$, in agreement with the sign criterion habitually used.[33]

Here, the solvation behaviour of solvent (1)/polymer (2)/polymer (3) ternary systems in dilute solutions of polymer (3) has been studied through GPC/SEC measurements. At such an end and prior to the injection of polymer (3) solutions in the binary solvent (1) + (2) of a given composition, ϕ_1^e, used as eluent, solutions of (1) + (2) of known composition, ϕ_1^i, were injected to construct a calibration curve. Really, ϕ_1^i is volume fraction of component (1) different to that in the eluent, as it also occurs with the component (1) content in the ternary phase when polymer (3) solution is injected. In a certain way, ϕ_1^i simulates ϕ_1, whereas ϕ_1^e indicates the volume fraction of component (1) in the bulk solvent, namely ν_1. If $\phi_1^i > \phi_1^e$, then $\phi_1^i - \phi_1^e = \phi_1 - \nu_1 = \Delta\nu_1^{cal} > 0$. The superscript cal denotes magnitudes obtained from the calibration chromatograms of binary solutions. This injected excess of component (1) with respect to the eluent composition will yield a peak in the chromatogram with height h^{cal}. If the refractive index of solvent 1 is smaller than that of component 2, h^{cal} will be negative with respect to the chromatogram baseline. Therefore, it would result that:

$$\Delta\nu_1^{cal} > 0, \quad h^{cal} < 0 \quad \text{and} \quad \text{a slope } \frac{\Delta\nu_1^{cal}}{h^{cal}} < 0.$$

On the contrary, when:

$$\phi_1^i < \phi_1^e, \quad \text{then } \Delta\nu_1^{cal} < 0, h^{cal} > 0 \quad \text{and}$$

$$\text{the slope will be negative,} \quad \frac{\Delta\nu_1^{cal}}{h^{cal}} < 0.$$

The injection of a polymer (3) solution in the (1) + (2) mixture eluent causes the appearance in the chromatogram of an additional peak, that is the "vacant peak"[34] due to the preferential solvation of polymer (3) by component (1) (or component (2)). If it is the component (1) which is preferentially sorbed, then $\phi_1 > \nu_1$ and, as a result, the bulk solvent would become poor in component (1), appearing as a vacant peak with height $h^{probe} > 0$. The superscript probe denotes magnitudes obtained from the ternary systems chromatograms, which is the problem. So, whereas in the calibration a value $\Delta\nu_1^{cal} > 0$ yields a peak with $h^{cal} < 0$, in the problem case a value $\phi_1 - \nu_1 = \Delta\nu_1 > 0$ should result in a peak with $h^{probe} > 0$. Therefore, the following relationship can be deduced:

$$\frac{\Delta\nu_1^{cal}}{-h^{cal}} = \frac{\Delta\nu_1}{h^{probe}} \tag{5}$$

which allows evaluating the $\Delta\nu_1$ value caused by the preferential sorption through:

$$\Delta\nu_1 = -\frac{\Delta\nu_1^{cal}}{h^{cal}} h^{probe} \tag{6}$$

According to eq. (4), $\lambda = (\Delta\nu_1/c_3)_{c_3 \to 0} > 0$, as expected when the polymer (3) is preferentially solvated by component (1).

On the contrary, if it is component (2), the one preferentially sorbed by polymer (3), the solvent external to coil (3) would become poor in (2), $\phi_2 - \nu_2 = \Delta\nu_2 > 0$, and a negative vacant peak, $h^{probe} < 0$, is obtained. In this case:

$$\Delta\nu_2 = -\frac{\Delta\nu_2^{cal}}{h^{cal}} h^{probe} \tag{7}$$

with slope $(\Delta\nu_2^{calib}/h^{calib}) > 0$ value. Now $\Delta\nu_2 > 0$ and according to eq. (4) $\lambda = -(\Delta\nu_2/c_3)_{c_3 \to 0} < 0$, in agreement with the sign criterion above indicated.

Binding Between PMMA and PS-VPh

Because PMMA is a quencher of PS-VPh, binding isotherms can be determined by assuming that the decrease in fluorescence intensity of the PS-VPh free form, $(\text{PS-VPh})_f$, in the PMMA presence is due to the binding of PS-VPh to PMMA, the $(\text{PS-VPh})_b$ form. From fluorescence measurements, the observed intensity value at a wavelength, I, is due to the emission of both forms of copolymer, free and bound, that are present at a total concentration:

$$(\text{PS-VPh})_t = (\text{PS-VPh})_f + (\text{PS-VPH})_b.$$

When $(\text{PS-VPh})_f = 0$, $(\text{PS-VPh})_t = (\text{PS-VPh})_b$ and

$$I = I_b \frac{[\text{PS-VPh}]_b}{[\text{PS-VPh})_t]} = I_b,$$

where I_b is the fluorescence intensity of a PS-VPh solution in which all the copolymer is bound to PMMA. On the other end, when

$$(\text{PS-VPh})_b = 0, (\text{PS-VPh})_t = (\text{PS-VPh})_f \quad \text{and}$$

$$I = I_0 \frac{[\text{PS-VPh}]_b}{[\text{PS-VPh})_t]} = I_0,$$

where I_0 is the fluorescence intensity of a PS-VPh solution in which all the copolymer is free, as should occur in the absence of PMMA. In any experimental measurement, there is a copolymer fraction bound to PMMA, namely, $[\text{PS-VPh}]_b/[\text{PS-VPh}]_t = \alpha$, which will emit with an intensity proportional to I_b, and a fraction $[\text{PS-VPh}]_f/[\text{PS-VPh}]_t = 1 - \alpha$ which will emit with an intensity proportional to I_0. The experimental I value will be related with α by:

$$I = \alpha I_b + (1 - \alpha) I_0$$

Henceforth, α may be calculated from:

$$\alpha = \frac{I - I_0}{I_b - I_0} \tag{8}$$

I and I_0 are directly obtained from the spectra, whereas I_b is obtained from the intercept in the origin of a double reciprocal plot:[35–37]

$$\left(\frac{I - I_0}{I_0}\right)^{-1} = \frac{I_0}{I_b - I_0} + \frac{I_0}{(I_b - I_0)K_A^{ap}(\text{PS-VPh})_t} R_i^{-1} \tag{9}$$

where K_A^{ap} is an apparent association constant between both polymers and R_i the relationship between total concentrations of the two polymers, namely $R_i = [\text{PMMA}]_t/[\text{PS-VPh}]_t$ in the corresponding solution.

EXPERIMENTAL

Chemicals

A PMMA sample from Aldrich Chemical with nominal molar mass $M_w = 15{,}000\,\text{g/mole}$ has been used. Its characterization by GPC/SEC (equipment and conditions as set below) with a set of three TSK Gel H_{XL} columns in THF as eluent yield:

$$\bar{M}_w = (14{,}500 \pm 2000)\,\text{g mol}^{-1} \quad \text{and}$$

$$\bar{M}_n = (10{,}600 \pm 2000)\,\text{g mol}^{-1}$$

Vinyl phenol was obtained by decarboxilation of p-hydroxicinamic acid[38] and polystyrene-vinyl phenol copolymers (PS-VPh) were synthetized by radical copolymerisation under nitrogen atmosphere at 60°C, using $\alpha\alpha'$-azo-bis-isobutyronitrile (AIBN) as initiator. In a typical experiment, about 40 g of styrene were mixed with the appropriate amount of vinyl phenol in the presence of 0.3 g of AIBN and the polymerization was allowed to run 12 hours for formation of random copolymers. Resulting conversions were about 10%. The obtained copolymers were precipitated twice with ethanol mixtures from their THF solutions and dried under vacuum. Here, two copolymers are used, with VPh contents of 7.2 and 5.8% wt, the respective samples PS-VPh (7.2%) and PS-VPh (5.8%). Characterization by GPC/SEC, in the columns and eluent above indicated, yields

$$\bar{M}_w = (65{,}000 \pm 3000)\,\mathrm{g\,mol^{-1}} \text{ and}$$

$$\bar{M}_n = (37{,}000 \pm 3000)\,\mathrm{g\,mol^{-1}} \text{ for PS-VPh (7.2\%) sample and}$$

$$\bar{M}_w = (63{,}000 \pm 3000)\,\mathrm{g\,mol^{-1}} \text{ and}$$

$$\bar{M}_n = (36{,}000 \pm 3000)\,\mathrm{g\,mol^{-1}} \text{ for PS-VPh (5.8\%) one}$$

Chromatographic grade THF used as eluent was from Scharlau (Barcelona, Spain).

Chromatography

The Waters liquid chromatography equipment consisted of a Model 590 solvent delivery system and a U6K universal injector from Waters (Milford MA, USA). Detection was carried out with a refractive index (R.I.) detector Model 2410 from Waters. Data collection and handling were carried out using Millennium Chromatography Manager from Waters. To study the preferential solvation phenomenon the system was equipped with a set of three columns (each one of 30 cm length × 0.78 cm I.D.) packed with highly crosslinked styrene-divinylbenzene copolymers, namely TSK Gel H_{HR} columns from Tosohaas, Toso Corp. (Tokyo, Japan), with pore sizes: G2500, G4000, and G6000. The mobile phase flow rate was adjusted to $1.0\,\mathrm{mL\,min^{-1}}$ and the injection volume of samples was 100 μL. In all cases, the mobile phases used as eluents consisted of diluted solutions in THF of the PMMA polymer ($M_w \approx 15{,}000\,\mathrm{g\,mol^{-1}}$) and were filtered and degassed through regenerated cellulose 0.45 μm pore diameter filters from Micro Filtration Systems (Dublin, CA, USA). The solutes were the PS-VPh copolymers.

Columns were equilibrated overnight before injection of the analyte solution, which was prepared using as solvent the corresponding mobile phase.

Fluorescence

Emission fluorescence spectra were recorded at 25°C using an Aminco-Bowman Series 2 Luminiscence Spectrometer with a thermostated cell holder and equipped with a Data Station. Throughout the experiments, samples were excited at 280 nm, being the maximum emission wavelength 305 nm. Excitation and emission slits were both set at 5 nm. Samples in THF containing a fixed PS-VPh concentration ($0.05\,\mathrm{g\,dL^{-1}}$ or $7.63\,\mu\mathrm{M}$) and different PMMA concentrations, in order to achieve different

$$R_i = \frac{[\mathrm{PMMA}]_t}{[\mathrm{PS\text{-}VPh}]_t} \text{ molar ratios.}$$

The solutions were annealed at 25°C for 10 min to assure equilibrium conditions before measurements were carried out. Previous kinetic experiments showed us that 10 min was time enough to achieve equilibrium. All emission spectra were corrected for background fluorescence and PMMA and solvent light scattering, by subtraction of the corresponding blanks.

RESULTS AND DISCUSSION

In order to study the preferential solvation phenomenon of a ternary system, THF(1)/PMMA(2)/PS-VPh(3), by injection of PS-VPh samples in different binary eluents THF/PMMA, different calibrations were previously made. Three eluents of $c_2 = 0.05$, 0.10 and $0.20\,\mathrm{g\,dL^{-1}}$ have been investigated by injecting, in every one of them, different PMMA solutions from around 0.02 to $0.20\,\mathrm{g\,dL^{-1}}$. For every solution, a chromatogram is obtained with: i) a negative peak (below the baseline) at a retention volume of 32.2 ± 0.1 mL at injected c_2 values lower than the one of the baseline, which indicates a defect with respect to the eluent (baseline). These negative peaks have been associated with an excess of THF (its refractive index is lower than that of the eluent), since an excess of PMMA has been injected; ii) on the contrary, at injected c_2 higher than the one of the eluent (baseline), positive peaks at (24.3 ± 0.1) mL appear. As an example, Figure 1 depicts elution chromatograms of different PMMA concentrations injected in THF/PMMA $c_2 = 0.20\,\mathrm{g\,dL^{-1}}$. As explained above, negative or defect peaks appear at around 32 mL for PMMA concentrations lower than $0.20\,\mathrm{g\,dL^{-1}}$. These peaks are related with THF excesses in the injected solutions with respect to the baseline. Figure 2 shows "calibration curves" plotted as height of the chromatographic peak, h^{cal}, vs. PMMA concentration, c_2, for the three selected eluents. As can be seen, for every eluent two distinct straight lines corresponding to the positive (excess, solid symbols) and negative (defect, empty symbols) peaks are obtained. Table 1 compiles the linear fits to the calibration data. Next, regarding the ternary systems,

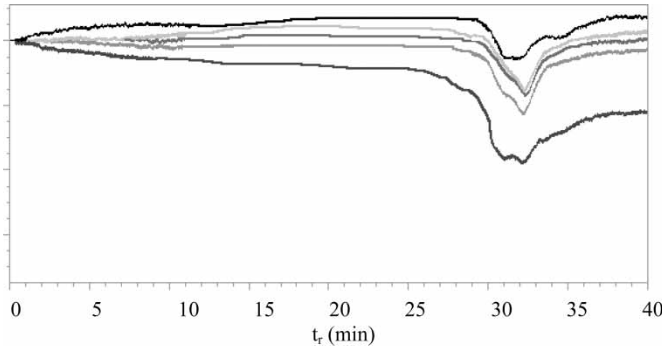

Figure 1. Negative signal deflections from refractive index detector on injection of different PMMA solutions, with respective concentrations: $c_2 = 0.14$, 0.10, 0.08, 0.06 and $0.04\,g\,dL^{-1}$ from the upper to the lowest curve. Baseline corresponds to a mobile phase composition of $0.20\,g\,dL^{-1}$ solution of PMMA in THF.

shown in Fig. 3 as an example, the obtained chromatogram by injection of (PS-VPh 7.2%) in the eluent mixture THF(1)/PMMA ($c_2 = 0.050\,g\,dL^{-1}$) at a concentration of component 3 $c_3 = 0.0050\,g\,dL^{-1}$. As can be seen, a first peak of the PS-VPh copolymer at a retention time 22.7 min with a height about 4276 a.u. and a second vacant peak[39] at a retention time

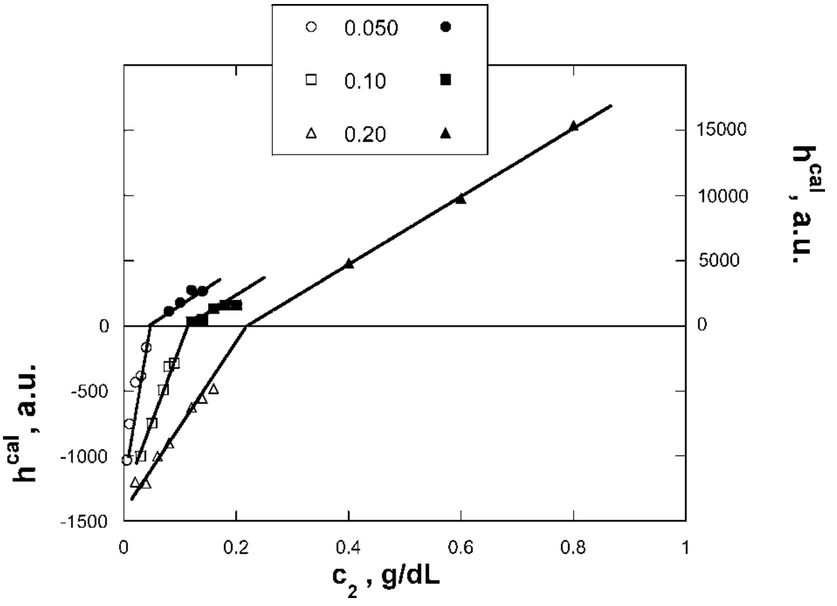

Figure 2. Dependence of the height of PMMA peak on PMMA concentration.

Table 1. Calibration equations of PMMA defects and excesses in three THF(1)/PMMA(2) eluents

	Eluent $c_2 = 0.050\,\mathrm{g\,dL^{-1}}$	Eluent $c_2 = 0.10\,\mathrm{g\,dL^{-1}}$	Eluent $c_2 = 0.20\,\mathrm{g\,dL^{-1}}$
PMMA defect	$h^{cal} = 1.82 \times 10^4\ c_2 - 900$ $R^2 = 0.865$	$h^{cal} = 1.52 \times 10^4\ c_2 - 1525$ $R^2 = 0.980$	$h^{cal} = 8.2 \times 10^3\ c_2 - 1650$ $R^2 = 0.722$
PMMA excess	$h = 3.39 \times 10^4\ c_2 - 1675$ $R^2 = 0.830$	$h = 1.18 \times 10^4\ c_2 - 1800$ $R^2 = 0.882$	$h = 2.51 \times 10^4\ c_2 - 5000$ $R^2 = 0.996$

32.3 min and $h^{probe} = -2411$ a.u. are obtained. In the same figure, as illustrated, is superimposed (at a different height scale) the chromatogram in the same eluent of a PMMA defect, namely an injected concentration $c_2 = 0.020\,\mathrm{g\,dL^{-1}}$ (see Fig. 1), resulting in a peak with $t_r = 32.4$ min and height $= -433$ a.u. The agreement in retention times and in the sign of the vacant peak of polymer 3 with that due to a defect of PMMA, suggests that the PS-VPh copolymer is preferentially solvated by PMMA, probably due to specific interactions via hydrogen bond. Table 2 depicts the results for diverse c_3 injections of the PS-VPh 5.8% and PS-VPh 7.2% copolymers in the three eluents THF(1)/PMMA(2) used for calibrations; in each case, the retention time and peak height (h^{comp}) of the solute peak and the height (h^{probe}) and retention time of the vacant peak are indicated. The plots of h^{comp} against c_3 and h^{probe} against c_3 for both PS-VPh copolymers in the three eluents are linear ($R^2 > 0.99$). In the same way that Fig. 3 illustrates the PMMA defect, in Fig. 4, as an example, is shown the excess chromatogram

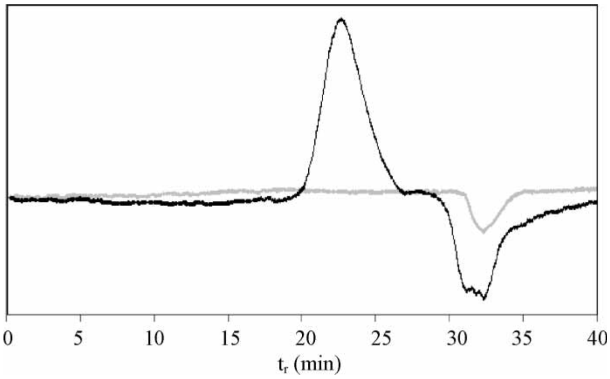

Figure 3. Chromatograms of THF/PMMA/PS-VPh (7.2%) at $c_3 = 0.005\,\mathrm{g\,dL^{-1}}$ (black line) and of the calibration THF/PMMA ($c_2 = 0.02\,\mathrm{g\,dL^{-1}}$) (grey line). Mobile phase THF/PMMA ($c_2 = 0.050\,\mathrm{g\,dL^{-1}}$).

Table 2. Elution behaviour of PS-VPh 5.8% and PS-VPh 7.2% in three THF(1)/PMMA(2) eluents

	PS-VPh 5.8%				PS-VPh 7.2%			
c_3, g dL^{-1}	t_r, min	h^{comp}, au	t_r, min	h^{probe}, au	t_r, min	h^{comp}, au	t_r, min	h^{probe}, au
Eluent $c_2 = 0.050$ g dL^{-1}								
0.005	22.98	3254	31.01	−2000	22.69	4276	32.32	−2411
0.010	22.35	1195	31.11	−1779	22.61	1091	30.86	−1775
0.025	22.34	2201	32.23	−2171	22.24	2721	30.99	−2130
0.050	22.73	6224	31.23	−969	22.77	5534	31.40	−1052
0.10	22.57	7503	31.07	−1677	22.34	5945	31.24	−1767
0.20	22.61	11193	32.32	−366	22.48	11047	31.11	−1845
0.45	23.16	24202	32.06	−511	22.94	21898	34.10	−759
0.75					22.93	48373	32.23	−3174
1.20					23.00	69159	31.37	−1021
Eluent $c_2 = 0.10$ g dL^{-1}								
0.02	22.38	3491	32.27	−9680	22.40	2633	30.36	−28446
0.05	22.35	3945	32.06	−5170	22.44	4286	30.46	−29659
0.10	21.72	6259	31.28	−8050	22.53	6832	30.36	−26213
0.20	22.58	12561	32.22	−2652	22.20	14922	29.97	−28718
0.30	22.74	20860	32.42	−1900	22.50	20041	30.41	−29308
0.40	22.94	24653	32.50	−7723	22.43	23237	30.46	−14708
0.70	23.23	43533	32.34	−10292	22.58	51104	30.53	−14506
0.90	23.07	54823	31.90	−7801	22.60	59897	30.57	−17216
1.10	23.36	66037	32.08	−12269	22.65	69747	30.43	−13961
1.50	23.30	96505	32.64	−4513	22.94	98963	30.51	−16432

(*continued*)

Table 2. Continued

	PS-VPh 5.8%				PS-VPh 7.2%			
c_3, g dL^{-1}	t_r, min	h^{comp}, au	t_r, min	h^{probe}, au	t_r, min	h^{comp}, au	t_r, min	h^{probe}, au
1.90	23.56	104798	32.24	−8974	22.98	104853	30.56	−15636
2.40	23.85	144705	32.81	−6397	23.16	135114	30.59	−15008
Eluent $c_2 = 0.20$ g dL^{-1}								
0.020	22.43	4337	30.86	−3042	22.57	3706	30.87	−3385
0.040	22.43	3284	30.74	−2854	22.59	4724	30.89	−2252
0.100	22.62	7815	30.92	−1372	22.90	9137	31.07	−2024
0.200	22.72	12101	31.35	−858	22.65	11014	31.01	−1984
0.600	23.21	28222	31.24	−1322	23.34	33831	31.29	−3041
1.40	23.47	77779	32.51	−547	23.46	79265	31.64	−2349
2.22	23.80	120736	32.70	−360	23.82	114660	31.14	−2731

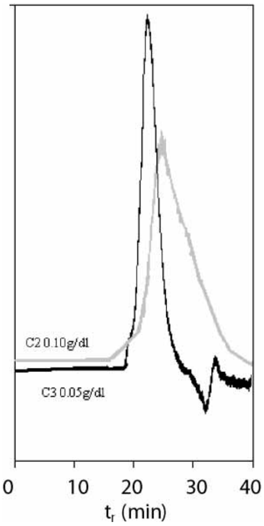

Figure 4. Chromatograms of THF/PMMA/PS-VPh (5.8%) at $c_3 = 0.05\,g\,dL^{-1}$ (black line) and of the calibration THF/PMMA ($c_2 = 0.02\,g\,dL^{-1}$) (grey line). Mobile phase THF/PMMA ($c_2 = 0.10\,g\,dL^{-1}$).

obtained by injecting a $c_2 = 0.020\,g\,dL^{-1}$ in the eluent mixture THF(1)/PMMA(2) ($c_2 = 0.10\,g\,dL^{-1}$), and superimposed to it the chromatogram in the same eluent due to the injection of PS-VPh 5.8% at $c_3 = 0.050\,g\,dL^{-1}$. In the former, the vacant peak with $h^{cal} = 1571$ a.u. appears at a retention time of 24.65 min, due to PMMA. In the latter, the first peak, due to the solvated copolymer, appears at 22.35 min with $h^{comp} = 3945$ a.u. and the second peak at 32.06 min, with a $h^{probe} = -517$ a.u. due to the defect of PMMA (excess of THF). Of course, if THF would preferentially be sorbed on PS-VPh, next to the copolymer peak (22–23 mL) it should appear a PMMA excess peak (24–25 mL) similar to the gray one in Fig. 4. Probably, a comparison on elution behaviour between THF(1)/PMMA(2) ($c_2 = 0.10\,g\,dL^{-1}$)/PS(3) and THF(1)/PMMA(2) ($c_2 = 0.10\,g\,dL^{-1}$)/PS-VPh 7.2% (3) systems would help to understand this better. In Figure 5a, the chromatograms of the former system at diverse PS ($M_w = 106{,}000\,g\,mol^{-1}$) concentrations are shown. As seen, in all cases, a PS peak ($t_r \approx 19.5$ min) appears and overlapped to it a second PMMA peak appears at $t_r \approx 24$ min; this indicates that PS does not interact with PMMA because in no case are THF vacant peaks present. This is not the case when PS-VPh is injected instead of PS as illustrated in Fig. 5b, in which the chromatograms of the THF(1)/PMMA ($c_2^e = 0.10\,g\,dL^{-1}$)/PS-VPH 7.2% (3) system are shown. Here, THF excess peaks at $t_r = 30$–32 min are always present, which indicate a PMMA defect in the solvent due to preferential interaction with PS-VPh. As a conclusion, the results in Fig. 4 (in black) illustrate the

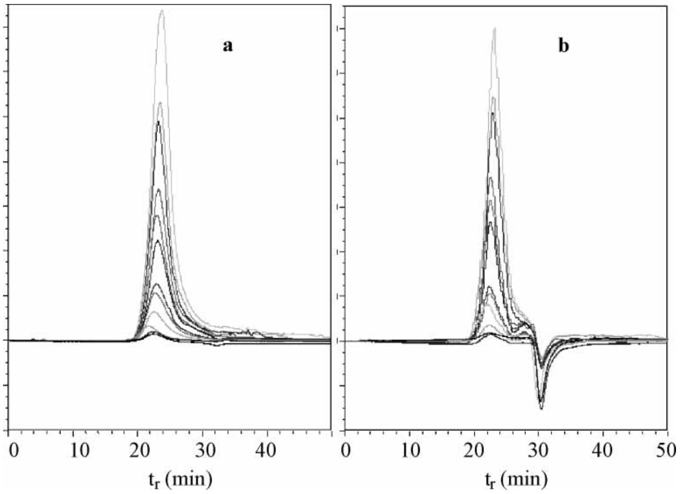

Figure 5. Chromatograms of: a) THF(1)/PMMA(2) ($c_2 = 0.10\,g\,dL^{-1}$)/PS(3) and b) THF(1)/PMMA(2) ($c_2 = 0.10\,g\,dL^{-1}$)/PS-VPh (7.2%)(3) by injection of different c_3 concentrations (increasing concentration from the lowest curve to the upper one). Mobile phase THF/PMMA ($c_2 = 0.10\,g\,dL^{-1}$).

generalized behaviour, that is, in the presence of the binary solvent THF(1)/PMMA(2), the solute PS-VPh interacts preferentially with PMMA.

Quantitative evaluation of preferential sorption is characterized through λ parameter, related to

$$\left(\frac{\Delta\nu_2}{c_3}\right)_{c_3\to 0} \quad \text{by eq. (4).}$$

In turn, $\Delta\nu_2$ can be calculated through eq. (7) with calibration data and h^{probe} gathered in Tables 1 and 2.

In Table 3 ($\Delta\nu_2/c_3$) values are compiled.

As shown in Table 3, at a given c_2 and c_3 concentrations the higher the VPh content in PS-VPh copolymer, the higher the PMMA sorption onto the copolymer

$$\left(\text{more negative}\frac{\Delta\nu_2}{c_3}\text{values}\right),$$

as expected. Moreover, in a given eluent system (at a given c_2 concentration) negative values increase with decreasing c_3, in agreement with found results in similar studies.[33] Finally, from Table 3 it can be observed that the largest λ values

$$\left(\left(\frac{\Delta\nu_2}{c_3}\right)_{c_3\to 0}\text{values}\right)$$

Table 3. ($\Delta\nu_2/c_3$) and R_i dependences with c_3, copolymer content and eluent composition in the systems THF(1)/PMMA(2)/PS-VPh(3)

R_i	c_3, g dL^{-1}	PS-VPh 5.8% $-(\Delta\nu_2/c_3)$	PS-VPH 7.2% $-(\Delta\nu_2/c_3)$
Eluent $c_2 = 0.050$ g dL^{-1}			
43.63	0.005	−17.70	−21.34
21.84	0.010	−7.8	−7.86
8.73	0.025	−3.80	−3.77
4.36	0.050	−0.86	−0.93
2.18	0.100	−0.74	−0.78
1.09	0.200	−0.08	−0.41
0.48	0.450	−0.05	−0.07
0.29	0.750		−0.19
0.18	1.20		−0.04
Eluent $c_2 = 0.10$ g dL^{-1}			
21.83	0.020	−25.6	−75.2
8.72	0.050	−5.40	−31.4
4.36	0.100	−4.3	−13.8
2.18	0.200	−0.70	−7.59
1.45	0.300	−0.30	−5.17
1.09	0.400	−1.0	−1.94
0.62	0.700	−0.70	−1.11
0.48	0.900	−0.45	−1.01
0.40	1.10	−0.54	−0.67
0.29	1.50	−0.16	−0.58
0.23	1.90	−0.25	−0.44
0.18	2.40	−0.14	−0.33
Eluent $c_2 = 0.20$ g dL^{-1}			
43.66	0.020	−14.93	−16.61
21.82	0.040	−7.00	−5.53
8.73	0.100	−1.35	−1.99
4.36	0.200	−0.42	−0.97
1.46	0.600	−0.21	−0.50
0.62	1.40	−0.04	−0.16
0.39	2.22	−0.02	−0.12

are obtained at a PMMA concentration ($c_2 = 0.10$ g dL^{-1}) with both copolymers.

The fluorescence spectrum of the binary solution, THF(1)/PS-VPh(2), shows a maximum fluorescence intensity around 305 nm, characteristic of PS-VPh. This peak decreases for the ternary solutions, THF(1)/PS-VPh(2)/PMMA(3), by increasing the PMMA concentration at a fixed PS-VPh concentration, indicating interaction between both polymers. From the spectra, the fraction of polymer bound can be calculated through eq. (8) by previously determining the value of I_b from a double reciprocal plot (eq. (9)). Table 4 compiles the maximum intensity and α values for the two studied systems at different R_i values or PMMA concentrations. It is noticed that the intensity decreases and α increases upon increasing c_2 or

$$R_i = \frac{[\text{PMMA}]_t}{[\text{PS-VPh}]_t}.$$

The variation of α with R_i expresses the fraction of PS-VPh bound to PMMA. Likewise,

$$\left(-\frac{\nu_2}{c_3}\right)$$

Table 4. I and α variations with R_i in the systems THF(1)/PS-VPh (2)/PMMA(3)

c_2, g dL^{-1}	c_3, g dL^{-1}	R_i	I	α
PS-VPh 5.8%				
0.050	2.00	175	221.5	0.16_4
0.050	1.80	157	224.7	0.14_5
0.050	1.60	139	227.9	0.12_5
0.050	1.40	123	229.5	0.11_5
0.050	1.20	105	231.4	0.10_4
0.050	1.00	87	236.4	0.07_3
0.050	0.80	70	238.5	0.06_0
0.050	0.60	52	241.2	0.04_3
0.050	0.20	18	246.2	0.01_2
0.050	0.00	0	248.1	
PS-VPh 7.2%				
0.050	3.50	306	351.2	0.31_0
0.050	3.00	262	353.1	0.29_7
0.050	2.75	240	354.4	0.28_8
0.050	1.80	157	352.4	0.24_1
0.050	1.60	139	353.3	0.23_4
0.050	1.40	123	357.0	0.20_6
0.050	1.20	104	363.6	0.15_6
0.050	1.00	87	366.8	0.13_1
0.050	0.80	70	368.9	0.11_5
0.050	0.40	35	377.8	0.04_8
0.050	0.10	9	383.4	0.00_5
0.050	0	0	384.0	

dependence with R_i indicates the change in PMMA volume fraction solvated onto PS-VPh by mass unit of the copolymer. Both magnitudes,

$$\left(-\frac{\nu_2}{c_3}\right)$$

and α, show the dependences with R_i of binding, sorption, or compatibility between both polymers, whichever the form under which the interaction between them should take place and, as can be seen, the compatibility increases with R_i at least until $R_i \approx 10$ values (limit imposed by the chromatographic technique). At very high R_i values the increase in compatibility with R_i is doubtful. As ascertained in Tables 3 and 4, PMMA compatibility with PS-VPh 7.2% is higher than with PS-VPh 5.8%, probably due to the larger number of OH groups in the former and, therefore, the larger number of specific interactions via hydrogen bonding between OH groups of PS-VPh and CO groups of PMMA. On the other hand, the increasing compatibility between PMMA and PS-VPh, when R_i increases, i.e., when the PS-VPh concentration decreases at a fixed PMMA concentration, can be related to the PS-VPh autoassociation decrease which takes place when PS-VPh concentration decreases.

In summary, modified polystyrenes, PS-VPh copolymers, strongly interact with PMMA, forming blends in the presence of THF. The interaction increases with the VPh content in the copolymer and with the lesser PS-VPh content in their mixtures with PMMA.

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