BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 11, pp. 2237–2241, 1995

0032-3861/95/$10.00 + 0.00

Self-association in poly(styrene-*co*-4-vinylbenzenephosphonic acid) and miscibility of its blends

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(Received 5 July 1994; revised 18 November 1994)

Styrene copolymers containing about 4.3, 7.5 and 13.3 mol% of 4-vinylbenzenephosphonic acid (VBPA) as comonomer units were synthesized. The copolymers were insoluble in common organic solvents, possibly because side reactions involving the phosphonic acid groups had occurred during the drying process. Upon adding a small amount of concentrated hydrochloric acid to tetrahydrofuran, the polymer became soluble. The miscibility of blends of styrene copolymers (PSVBPA) containing VBPA units with poly(n-butyl methacrylate) (PBMA) and with poly(vinyl methyl ether) (PVME) were studied using differential scanning calorimetry and Fourier transform infra-red spectroscopy. All three copolymers were immiscible with PBMA over the entire composition range. Infra-red spectra indicated no observable interactions between the phosphonic acid and –C=O groups in the blends. Blends of PSVBPA-13.3/PVME were also immiscible over the entire composition range. When PSVBPA-7.5 and PSVBPA-13.3 were mixed with styrene copolymers containing 7.5 and 13.3 mol% of 4-vinylbenzenephosphonic acid diethyl ester, the latter being a strong hydrogen-bond acceptor, the blends appeared to be miscible.

(Keywords: hydrogen bonds; blends; miscibility; self-association)

INTRODUCTION

A variety of functional groups including $-C(OH)(CF_3)_2$ (refs 1–5), $-C_6H_5OH$ (refs 1, 5–10), –COOH (refs 5, 6) and $-SO_3H$ (refs 5, 6, 11, 12) have been evaluated as hydrogen-bond donors for miscibility enhancement in polymer blends. However, to our knowledge, phosphonic acids have not been studied in this context. Since many organophosphonic acids are strong acids (e.g. phenylphosphonic acid[13] has $pK_{a1} = 1.83$ and $pK_{a2} = 7.07$), they are potentially effective hydrogen-bond donors. In this report, the miscibility of the styrene copolymers of 4-vinylbenzenephosphonic acid (VBPA) with hydrogen-bond accepting polymers was investigated using differential scanning calorimetry (d.s.c.), Fourier transform infra-red spectroscopy (*FT*i.r.) and ^{31}P nuclear magnetic resonance spectroscopy (^{31}P n.m.r.).

EXPERIMENTAL

Materials

Poly(styrene-*co*-4-vinylbenzenephosphonic acid) (PSVBA) was prepared by hydrolysis of poly(styrene-*co*-4-vinylbenzephosphonic acid diethyl ester (PSVBDEP), which has been reported in a previous paper[14], as follows. PSVBDEP was refluxed in dioxane saturated with concentrated hydrochloric acid at 100°C for 1 day. The product, PSVBPA, was precipitated from its dioxane solution by methanol, and then purified by dissolving in chloroform and precipitating into petroleum ether (twice). The product was dried in a vacuum oven at 50°C for 2 days. Copolymers containing 4.3, 7.5 and 13.3 mol% VBPA were synthesized. After the polymers were dried, redissolution in tetrahydrofuran (THF) required the addition of a small amount of concentrated hydrochloric acid (5% by volume).

Poly(n-butyl methacrylate) (PBMA) was purchased from Aldrich Co. and purified by precipitation of its chloroform solution into methanol (four times), followed by drying in a vacuum oven at 80°C for 2 days. Poly(vinyl methyl ether) (PVME), also purchased from Aldrich Co., was isolated from its aqueous solution by petroleum ether, and then purified by precipitation of its acetone solution into petroleum ether (twice). It was dried at ~40°C in a vacuum oven for 2 days.

Determination of molecular weight and polydispersity

The molecular weights and polydispersities of PBMA, PVME and the precursor copolymer, PSVBDEP, were determined using gel permeation chromatography (g.p.c.) (Waters, model 590). A solution of 0.2 wt% of polymer in THF was prepared and then filtered with a 0.45 μm filter. The column flow rate was 1 $cm^3\ min^{-1}$. The g.p.c. instrument was calibrated with monodisperse polystyrene standards ($M_w/M_n < 1.1$). Thus, the molecular weights measured were 'polystyrene equivalents'.

Preparation of blend films

Blend films were prepared in two steps. (1) The two polymers were separately dissolved in THF at a

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concentration of 1.6 g per 100 ml, and then mixed in appropriate amounts. As already mentioned, the PSVBPA copolymers dissolved completely in THF with the addition of a very small amount of concentrated hydrochloric acid. (2) Films were cast and dried at room temperature for several days and then further dried at 80°C in a vacuum oven for 2 days.

Determination of glass transition temperature

The glass transition temperatures (T_gs) of the polymers and their blends were determined by d.s.c., with the use of a Du Pont instrument model 9900. The heating rate used for each measurement was 20°C min^{-1}. The calorimeter was blanketed by nitrogen during the experiment. The midpoint of the change in heat capacity with temperature was taken as the T_g.

Infra-red spectroscopy

Hydrogen bonding in PSVBPA copolymers and their blends was studied using *FT*i.r. spectroscopy (Perkin–Elmer 1600). For the hydrogen bonding acceptor polymers, films were cast onto NaCl i.r. windows. The films were dried first at room temperature and then at 80°C in a vacuum oven for at least 1 day. For the donor polymers and their blends, the KBr pellet method was used. The spectra were recorded at room temperature under nitrogen. Thirty-two scans were signal-averaged at a resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

The molecular weights and glass transition temperatures of the polymers used for this study are presented in *Table 1*. Since the PSVBPA copolymers were prepared by hydrolysis of their corresponding PSVBDEP phosphonate-containing copolymers, the molecular weights and polydispersities of PSVBPA were assumed to be the same as those of PSVBDEP. Thus, the molecular weights and polydispersities of PSVBPA listed in the table are those of the precursor copolymers.

PSVBPA/PBMA blends – phosphonic acid as a potential donor

Three copolymers, PSVBPA containing 4.3, 7.5 and 13.3 mol% VBPA units, were blended with PBMA in different proportions. All the films were opaque. The blends of PSVBPA-4.3 with PBMA exhibited two T_gs which were close to those of the component polymers in the composition range from 20/80 to 80/20 (by weight). Thus, the pair was considered to be immiscible. When the content of phosphonic acid units in the styrene copolymer was increased to 7.5 or 13.3 mol%, the blends with PBMA were also immiscible.

Table 1 Molecular weights and polydispersities of the polymers used for studies

Polymer	$M_w \times 10^5$	M_w/M_n	T_g (°C)
PSVBPA-4.3	3.01	1.99	123
PSVBPA-7.5	3.80	2.15	140
PSVBPA-13.3	2.31	1.88	166
PBMA	1.89	1.84	30
PVME	1.02	1.80	−19
PSVBDEP-7.5	3.80	2.15	107
PSVBDEP-13.3	2.31	1.88	104

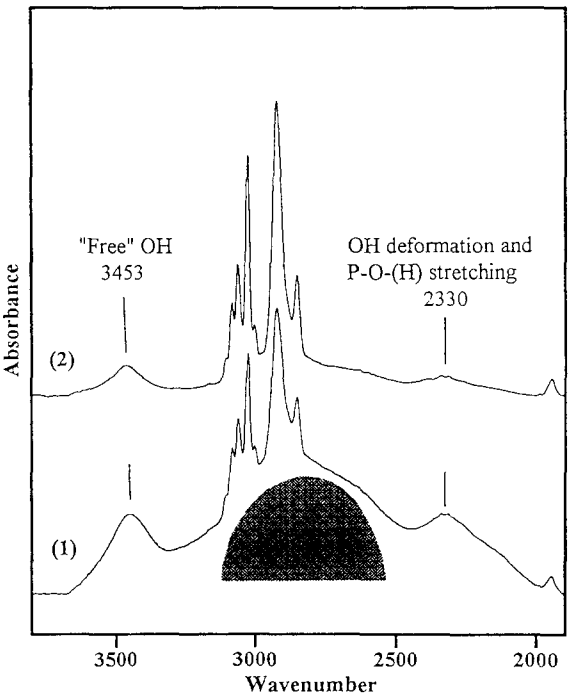


Figure 1 I.r. spectra of (1) PSVBPA-13.3 and (2) PSVBPA-4.3 in the 3800–1900 cm^{-1} region

We are aware of the fact that the miscibility of polymers is strongly affected by the solvent used to prepare the blends[4]. Unfortunately, no alternative solvents, such as methyl ethyl ketone, dimethyl sulfoxide (DMSO) and dimethylformamide, were found to dissolve the copolymers. Thus, based on the present data, we believe that miscibility between polystyrene and PBMA cannot be achieved through incorporation of up to 13 mol% VBPA units into polystyrene. One of the possible reasons is that the self-association of phosphonic acid is very strong and PBMA is not a very strong hydrogen-bond acceptor. As a result, it was very difficult for PBMA to break the self-association in PSVBPA and establish interpolymer hydrogen bonds.

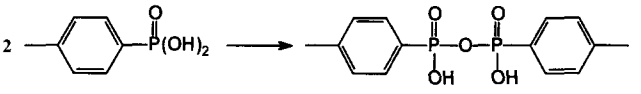
The self-association of hydroxyl groups in PSVBPA-4.3 and PSVBPA-13.3 was studied by *FT*i.r. spectroscopy. The phosphonic acid group had a very broad absorption in the 3680–2000 cm^{-1} region with multiple peaks (*Figure 1*). The peak for self-association of hydroxyl groups overlapped with those for C–H stretching absorptions. Absorption peaks in the region of 2750–2000 cm^{-1} were characteristic of all compounds containing the –P(O)OH group, and the broad peaks were attributed in the literature to strong self-association[15,16]. The very broad absorption under the sharp peaks for C–H stretching absorptions between ~3000–2500 cm^{-1}, i.e. the shaded area in *Figure 1*, was believed to be due to the stretching vibration of the –OH groups involved in self-association (OH···OH and P=O···HO between two phosphonic acid groups). The peak at 2330 cm^{-1} was assigned to a combination of the O–H deformation vibration (~1280 cm^{-1}) and the P–O–(H) stretching vibration (~1000 cm^{-1})[15,16]. On the basis of the above assignment, it then seems reasonable to attribute the peak

at 3453 cm^{-1} to the 'free' OH stretching vibration. To our knowledge, the absorption at 3453 cm^{-1} for phosphonic acids has not been reported in the literature. In *Figure 1*, the ratio of the areas of the free OH and the self-associated OH absorptions can be seen to increase with decreasing concentration of phosphonic acid group in the copolymer, as expected. If the peak assignment is correct, then the frequency of self-associated OH absorptions shifts from the free OH peak by ~450 to ~650 cm^{-1}, which is much larger than those of styrene copolymers of 4-(hexafluoro-2-hydroxyisopropyl)styrene (80 cm^{-1})[1,4], 4-hydroxystyrene (from 113 to 195 cm^{-1})[1,7] and 4-vinylphenyl dimethylsilanol (from 187 to 290 cm^{-1})[17]. It is therefore proposed that the self-association in the PSVBPA copolymers is extraordinarily strong. Thus the tendency for the –OH groups in the copolymers to self-associate renders them ineffective in establishing interpolymer hydroge bonds needed for miscibilization, although the pK_a values ($pK_{a1}=1.83$, $pK_{a2}=7.07$) of phenylphosphonic acid were much smaller than those of phenol ($pK_a=9.9$) and hexafluoroisopropanol ($pK_a=9.3$)[18,19].

In support of this argument, the C=O absorption peak of PBMA at 1730 cm^{-1} did not shift at all (*Figure 2a*). This is in sharp contrast with the behaviour of PBMA blends with styrene copolymers containing $-C(OH)(CF_3)_2$ (refs 1, 4) or $-C_6H_5OH$ (ref. 7) groups. However, as shown in *Figure 2b*, the ratio of the areas of free OH and self-associated OH absorptions increased when the concentration of PBMA increased. Apparently, PBMA functioned as a diluent so that the self-association of PSVBPA-13.3 was weakened and the concentration of the free –OH increased.

One of the difficulties we encountered in this study was the reduced solubility of the copolymers after drying. It was found that the dried copolymers only swelled but did not dissolve in common organic solvents. However, all three copolymers completely dissolved in THF containing a very small amount of concentrated HCl (<5% by volume). Thus, it was suspected at first that a condensation reaction occurred slowly during the drying process (*Scheme 1*)[20], with the reaction of P–O–P with HCl regenerating the phosphonic acid group.

Since the i.r. absorption peak of P–O–P was in the region from 940 to 970 cm^{-1} overlapped by other peaks[16,20], it was not useful in confirming the validity of the postulated reaction in *Scheme 1*. Therefore, we examined the ^{31}P n.m.r. spectrum of a PSVBPA-13.3 gel swollen in deuterated DMSO. In *Figure 3*, the resonance peak at 17.7 ppm was assigned to the self-associated $-P(O)(OH)_2$ group[21] and the small peak at 19.6 ppm was tentatively attributed to the $-P(O)(OH)_2$ group interacting with deuterated DMSO. If the crosslinking reaction occurred as postulated in *Scheme 1*, the resonance peak corresponding to $C_6H_5P(O)(OH)O-$ should be located at 10 ppm in the spectrum[21–23], this was not observed. The resonance peak for $C_6H_5P(O)(O-)O-$, i.e. with both –OH groups participating in crosslinking reactions, should be located at 0 ppm[23]. This was also not observed. Instead, a peak at −15.5 ppm was seen. Thus, more complicated reactions involving the phosphonic acid group might have occurred. The appropriate assignment of this resonance peak needs further study.



Scheme 1

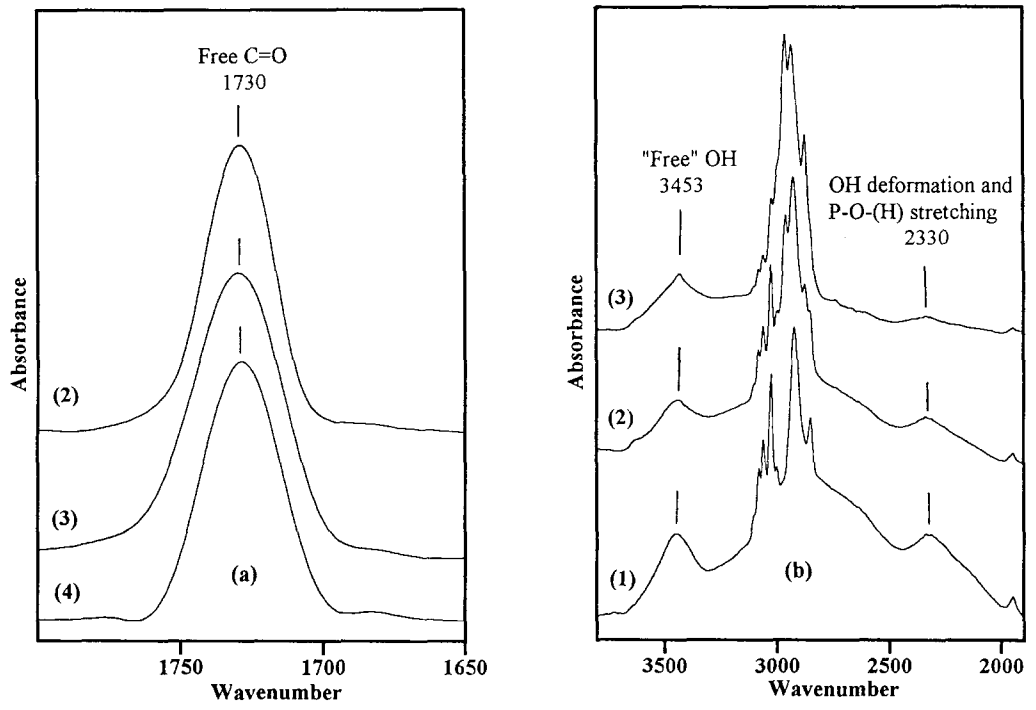


Figure 2 I.r. spectra of PSVBPA-13.3/PBMA blends in the (a) 1800–1650 cm^{-1} and (b) 3800–1900 cm^{-1} regions. Blend composition: (1) 100/0; (2) 70/30; (3) 30/70; (4) 0/100

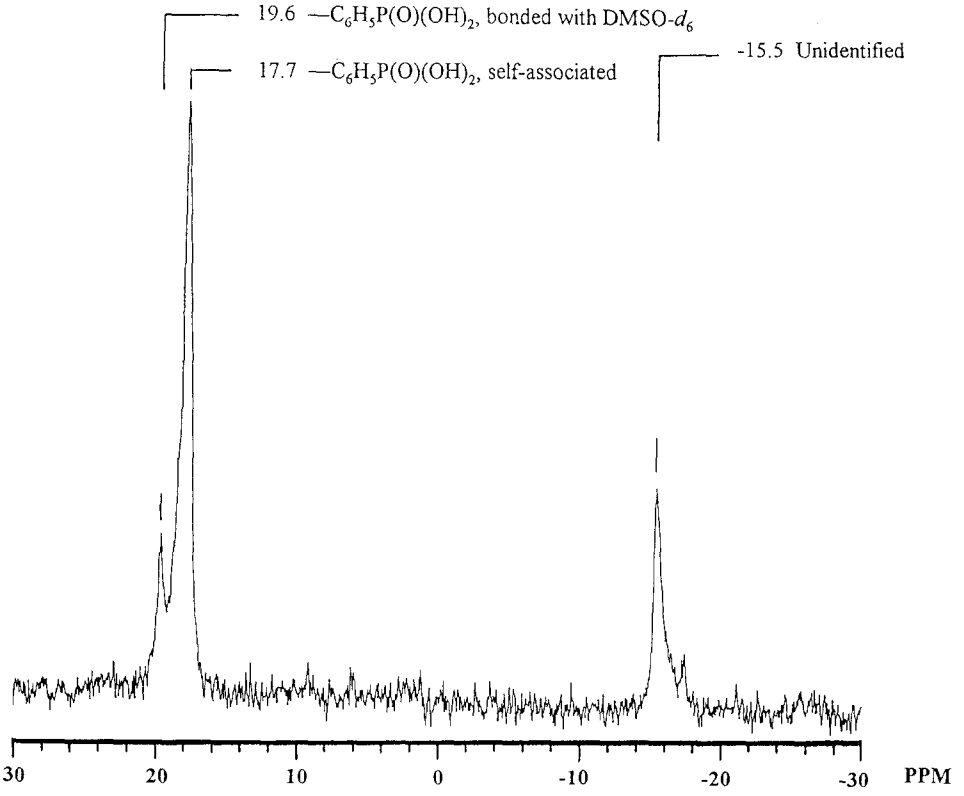


Figure 3 ^{31}P n.m.r. spectrum of PSVBPA-13.3

PSVBPA/PVME blends – phosphonic acid as a potential donor

Polystyrene is known to be miscible with PVME over the entire composition range[24,25]. In addition, since PVME is a strong hydrogen-bond acceptor, we thought that the PSVBPA copolymers should be miscible with PVME with a concomitant increase in the lower critical solution temperature as in the case of $-C(CF_3)_2OH$ copolymers[1,4]. However, when PSVBPA-13.3 was mixed with PVME, all films were opaque. D.s.c. results further indicated that PSVBPA-13.3 was completely immiscible with PVME. We have no explanation for this unexpected result, except to invoke the possibility of the strong self-association of phosphonic acid groups being unfavourable to miscibility.

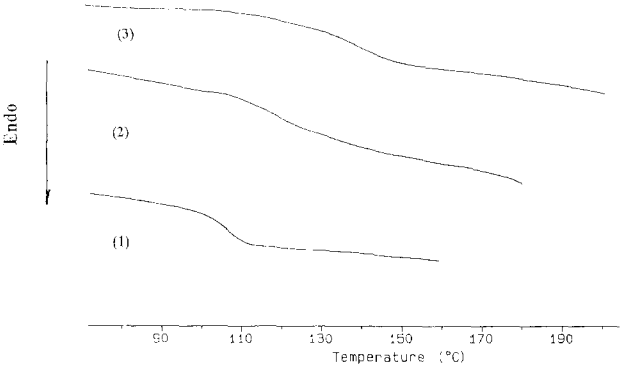


Figure 4 Glass transition temperatures of (1) PSVBDEP-7.5, (2) 50/50 PSVBDEP-7.5/PSVBPA-7.5 blend and (3) PSVBPA-7.5

PSVBDEP/PSVBPA blends – phosphonic acid as a donor and phosphonate as an acceptor

It has been demonstrated above that the phosphonic acid groups are ineffective in promoting miscibility due to strong self-association. Since the parent polymer contains a strong hydrogen-bond acceptor, we studied the miscibility of the PSVBDEP/PSVBPA pair. A 50/50 by weight blend of PSVBDEP-7.5 with PSVBPA-7.5 exhibited a single broad glass transition (*Figure 4*) centred at 133°C, which is about 10°C higher than the weight-average value. PSVBDEP-13.3 was also blended with PSVBPA-13.3 at the same weight ratio. *Figure 5* shows that the blend had a clearly identifiable T_g at 143°C, which is 8°C higher than the weight-average value. The

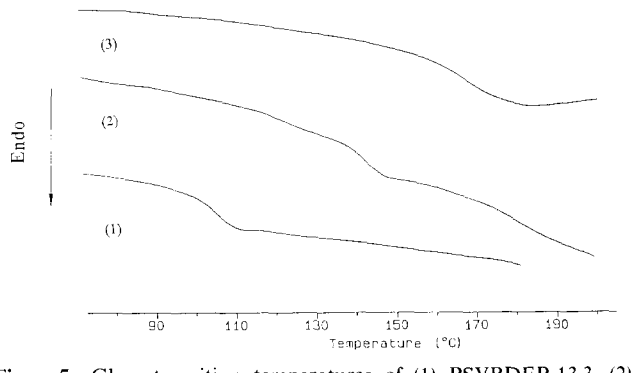


Figure 5 Glass transition temperatures of (1) PSVBDEP-13.3, (2) 50/50 PSVBDEP-13.3/PSVBPA-13.3 blend and (3) PSVBPA-13.3

downward drifts of the thermal scans of the blends at temperatures above 170°C was probably caused by the dissociation of hydrogen-bond interactions, which is always endothermic[26]. These results suggest these two pairs to be miscible. Thus, the diethyl ester of phosphonic acid is a much better hydrogen-bond acceptor than the carbonyl group of PBMA and the ether group of PVME, which is consistent with the i.r. results of model compounds[14]. In addition, PSVBDEP and PSVBPA had similar structures, which might be helpful to miscibility in terms of the matching of physical interactions.

CONCLUSIONS

Styrene copolymers containing 4.3 7.5 and 13.3 mol% 4-vinylbenzenephosphonic acid units were immiscible with PBMA over the entire composition range, and there were no observable interactions between the phosphonic acid and the –C=O groups. PSVBPA-13.3 was also immiscible with PVME over the entire composition range However, PSVBPA-7.5/PSVBDEP-7.5 and PSVBPA-13.3/PSVBDEP-13.3 appeared to be miscible. The phosphonic acid group is not a good hydrogen-bond donor for miscibility enhancement in polymer blends due to its strong self-association.

ACKNOWLEDGEMENTS

The authors acknowledge the National Science Foundation for support of this research under grant DMR 9002487. They also wish to acknowledge Dr Evan Chu for his assistance in n.m.r. measurements.

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