Miscibility Studies of Poly(styrene-*co*-4-vinylbenzenephosphonic acid diethyl ester) with Poly(*p*-vinylphenol)

Huifang Zhuang, Eli M. Pearce,[*] and T. K. Kwei

Department of Chemistry and Herman F. Mark Polymer Research Institute, Polytechnic University, Six MetroTech Center, Brooklyn, New York 11201

Received May 23, 1994; Revised Manuscript Received August 9, 1994⊛

ABSTRACT: The miscibility of styrene copolymers of 4-vinylbenzenephosphonic acid diethyl ester (PSVBDEP) with poly(*p*-vinylphenol) (PVPh) was studied by using DSC, FTIR, ^{31}P NMR, and ^{13}C NMR. Results indicated that the copolymer containing 4.3 mol % VBDEP units was immiscible with PVPh. For the PSVBDEP-7.5/PVPh blends, a single T_g was observed when the content of PSVBDEP-7.5 was at least 60 wt %. Mixing of PSVBDEP-13.3 with PVPh caused mutual precipitation in tetrahydrofuran. The complexes exhibited a single T_g. Three hydrogen bond donors, hexafluoroisopropyl alcohol, phenol, and *tert*-butyl alcohol, were used to "calibrate" the strength of the $-\ C_6H_4P(O)(OC_2H_5)_2$ group as an acceptor, and the characteristic parameter in the enthalpy–frequency shift relationship was determined. The IR frequency shift of the hydroxyl group of phenol reached 330–350 cm^{-1} when mixed with VBDEP and PSVBDEP-13.3, about the same magnitude as in phenol–DMSO and phenol–DMAc mixtures. Evidence for hydrogen-bonding interaction between the phenol and phosphonate groups was obtained from IR, ^{31}P NMR, and ^{13}C NMR measurements.

Introduction

During the past 20 years, much interest has been shown in miscible polymer blends where a certain specific interaction exists between two components. Many hydrogen-bond-containing polymer blends have been investigated,[1–6] but until recently phosphorus-containing polymers had not received much attention as hydrogen bond acceptors although a number of phosphonate compounds were reported to have strong accepting strengths.[7] Cabasso and co-workers investigated the blends of poly(styrenephosphonate diethyl ester) with cellulose and its derivatives.[8,9] They reported evidence of hydrogen bonding between the hydroxyl group of cellulose acetate and the phosphoryl group (P=O) of poly(styrenephosphonate diethyl ester). The phosphorylated polystyrene derivatives Cabasso used were prepared through polymeric chemical reactions. In our studies, we chose to synthesize a series of styrene copolymers containing 4-vinylbenzenephosphonic acid diethyl ester (PSVBDEP), which was selected as a hydrogen-bonding acceptor. Blends of the copolymers with poly(*p*-vinylphenol) (PVPh), a hydrogen bond donor, were studied by DSC, FTIR, and NMR.

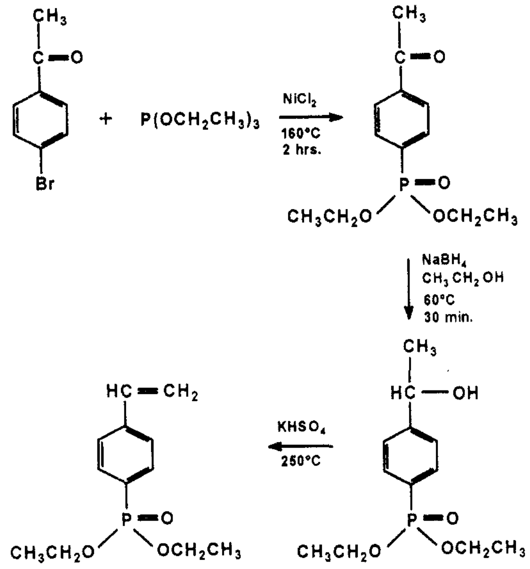
Experimental Section

Materials. The monomer, VBDEP, was synthesized in accordance with a procedure described in the literature (Scheme 1).[10] All the chemicals used for the synthesis were purchased from Aldrich Chemical Co., Inc.

The product of the first step, 4-acetylbenzene phosphonic acid diethyl ester, was collected at 148–150 °C/0.06 Torr. The yield was 87 wt %. The product was characterized by ^{1}H NMR spectroscopy (EM-390) using deuterated chloroform as the solvent. The 90 MHz NMR spectrum included resonances at δ 1.30, 1.37, and 1.44 (3H, triplet, alkoxyl); 2.67 (3H, singlet, acetyl); 4.05, 4.13, 4.22, 4.30, and 4.38 (2H, quintet, alkoxyl); and 7.90, 8.02, 8.13, and 8.19 (4H, multiplet, aromatic).

The product of the second step, 4-(1-hydroxyethyl)benzenephosphonic acid diethyl ester, was collected at 162–165 °C/0.2 Torr. The yield was 70 wt %. The NMR spectrum included resonances at δ 1.22, 1.29, and 1.36 (3H, triplet, alkoxyl); 1.43 and 1.50 (3H, doublet, 1-hydroxyethyl); 3.92, 4.00, 4.08, 4.16, and 4.24 (2H, quintet, alkoxyl); 4.76 (1H, singlet, hydroxyl); 4.83, 4.91, 4.99, and 5.07 (1H, quartet, 1-hydroxyethyl); and 7.51, 7.55, 7.59, 7.63, 7.67, 7.75, 7.82, and 7.90 (4H, multiplet, aromatic).

Scheme 1



The monomer, VBDEP, was collected at 132–134 °C/0.8 Torr. The yield was 65 wt %. The NMR spectrum included resonances at δ 1.26, 1.34, and 1.42 (3H, triplet, alkoxyl); 4.01, 4.09, 4.17, 4.25, and 4.33 (2H, quintet, alkoxyl); 5.35 and 5.47 (1H, doublet, trans to benzene ring); 5.80 and 5.98 (1H, doublet, cis to benzene ring); 6.65, 6.77, 6.85, and 6.97 (1H, quartet, α to benzene ring); and 7.51, 7.55, 7.59, 7.63, 7.71, 7.83, 7.92, and 8.01 (4H, multiplet, aromatic). Further characterization of this monomer will be discussed in the Results and Discussion.

PSVBDEP was prepared by bulk radical copolymerization of styrene with VBDEP at 60 °C under a nitrogen atmosphere. The concentration of the initiator, 2,2′-azobis(isobutyronitrile) (AIBN) (recrystallized from ethanol), was 0.07 wt %. The reaction was quenched after ~10 wt % conversion. The product was purified by precipitation from a chloroform solution into petroleum ether (three times) and then dried in a vacuum oven at 80 °C for 2 days.

PSVBDEP was characterized by 300 MHz ^{1}H NMR spectroscopy (GN-300) using deuterated chloroform as the solvent. The NMR spectrum of the copolymer exhibited broad resonances centered at δ 1.32 (3H, alkoxyl); 1.42 and 1.83 (2H and 1H, aliphatic backbone); 4.09 (2H, alkoxyl); and 6.57 and 7.08 (5H and 4H, aromatic). The ratios of the areas of the OCH$_2$ peak at 4.09 ppm and the phenyl peaks at 6.57 and 7.08 ppm were used

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⊛ Abstract published in *Advance ACS Abstracts*, September 15, 1994.

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for calculation of the copolymer composition. Copolymers containing 4.3, 7.5, and 13.3 mol % VBDEP were synthesized. Further characterization of PSVBDEP will be discussed in the Results and Discussions.

PVPh was received as a courtesy from Hoechst-Celanese Chemical Co. It was purified by precipitation from an acetone solution into water (five times). The purified PVPh was dried in a vacuum oven at 80 °C to constant weight.

Determination of Molecular Weight and Polydispersity. The molecular weights and polydispersities of the three copolymers and PVPh were determined by gel permeation chromatography (GPC) (Waters, Model 590). A solution of 0.2 wt % of polymer in tetrahydrofuran (THF) was prepared and then filtered by a 0.45 μm filter. The column flow rate was 1 mL/min. The GPC 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 and Complexes. Blend films were prepared in two steps: (1) The two polymers were separately dissolved in a common solvent, THF, at a concentration of 1.6 g/100 mL and then mixed in appropriate amounts. (2) Films were cast and dried at room temperature for several days and then further dried at 80 °C in a vacuum oven for at least 2 days.

Three styrene copolymers containing 4.3, 7.5, and 13.3 mol % VBDEP units were mixed with PVPh. For the first two copolymers, films were cast from the mixed solutions. In the case of PSVBDEP-13.3, the mixtures separated into two layers: a gelatinous precipitate and a supernatant clear solution. The precipitate was separated from the solution by centrifugation at 3500 rpm for an hour. The precipitate was then washed twice with THF and dried in a vacuum at 80 °C to constant weight. The precipitate was referred to as a "complex". The complex compositions were determined by 300 MHz ^{1}H NMR spectroscopy with a 50:50 (by volume) mixture of deuterated chloroform and dimethyl sulfoxide (DMSO) as the solvent. Again, the ratios of the areas of the OCH_2 and phenyl peaks were used for calculation.

Determination of Glass Transition Temperature. The glass transition temperatures of polymers and their blends were determined by differential scanning calorimetry (DSC) (DuPont, Model 9900). To remove residual solvent (or moisture) and to standardize its thermal history, the sample was quickly heated (50 °C/min) to a temperature slightly higher than the expected T_g of the sample under nitrogen and then cooled quickly with dry ice prior to the measurement. The heating rate used for each measurement was 20 °C/min under nitrogen. The midpoint of the change in heat capacity with temperature was taken as the T_g.

Infrared Spectroscopy. Hydrogen bonding in polymer blends was studied by FTIR spectroscopy (Perkin-Elmer 1600). For PVPh and PSVBDEP-13.3, the sample films were cast onto NaCl IR windows and dried at room temperature and then at 80 °C in a vacuum for 2 days. For the complexes, 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}.

For the study of enthalpy–frequency shift correlations in VBDEP mixtures with HFIP, phenol, and *tert*-butyl alcohol as acids, carbon tetrachloride was used as the solvent. The concentrations of the acids in solutions were below 0.04 M. A KBr liquid cell was used. With PSVBDEP-13.3 as the base, the copolymer film was cast onto a NaCl plate and dried in a vacuum at 80 °C. Two drops of HFIP or *tert*-butyl alcohol were placed on the film, which was then covered by another NaCl plate. As the acid diffused into the film, the frequency shift of the OH group was monitored until a constant value was reached.

Nuclear Magnetic Resonance Spectroscopy. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a General Electric GN-300 spectrometer. The spectrometer operated at a proton frequency of 300.5 MHz, a carbon frequency of 75.6 MHz, and a phosphorus frequency of 121.6 MHz. For ^{1}H and ^{13}C NMR measurements, tetramethylsilane was used as an internal reference. For ^{31}P NMR studies, the external reference was an 85 wt % phosphoric acid solution in D_2O. The concentration of VBDEP and the acid (phenol, HFIP, or *tert*-butyl alcohol) in $CDCl_3$ was 9 wt %. The concentration of PSVBDEP-13.3 and the acid (phenol, HFIP, or *tert*-butyl alcohol) in $CDCl_3$ was 5 wt %. The molar ratio of the hydrogen-bonding donor to the acceptor was 1:1. In ^{13}C NMR studies, the concentration of VBDEP and phenol was 10 wt %; the concentration of PSVBDEP-13.3 and phenol was 5 wt%. The molar ratio of the hydrogen-bonding donor to the acceptor was 3:1.

Table 1. Molecular Weights and Glass Transition Temperatures of the Polymers Used for Studies

polymer	M_w	M_w/M_n	T_g (°C)
PSVBDEP-4.3	3.01×10^5	1.99	105
PSVBDEP-7.5	3.80×10^5	2.15	107
PSVBDEP-13.3	2.31×10^5	1.88	104
PVPh	8.40×10^4	3.56	190

Table 2. Complex Yields and Compositions of PSVBDEP-13.3 with PVPh

feed comp PSVBDEP/PVPh (by wt)	complex yield	complex comp PSVBDEP/PVPh (by wt)	molar ratio P=O/OH
20/80	20.8	58.6/41.4	0.18
30/70	58.3	73.2/26.8	0.36 (1:3)
40/60	91.7	72.9/27.1	0.35 (1:3)
50/50	87.5	71.6/28.4	0.33 (1:3)
60/40	79.2	83.4/16.6	0.65 (2:3)
70/30	75.0	98.0/2.0	6.37

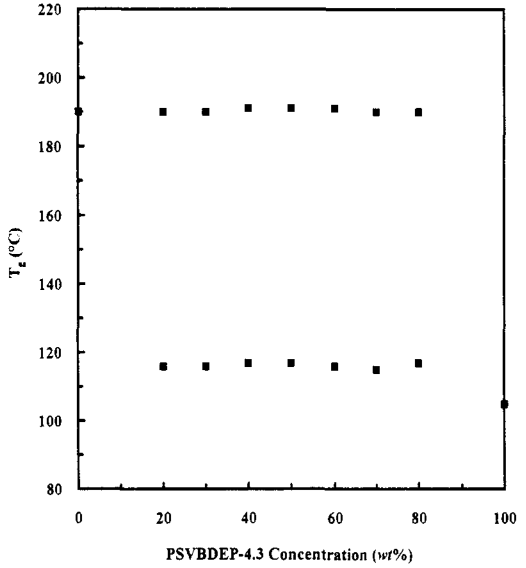

Figure 1. Glass transition temperatures of PSVBDEP-4.3/PVPh blends.

Results and Discussion

The molecular weights and glass transition temperatures of the polymers used for the studies are shown in Table 1.

Three copolymers were mixed with PVPh. As mentioned in the Experimental Section, films were cast from solutions in the cases of PSVBDEP-4.3 and PSVBDEP-7.5. However, mixing of PSVBDEP-13.3 with PVPh caused mutual precipitation in THF. The results of the complex formation are presented in Table 2. The yields of the precipitates indicated that in most cases, the supernatant solution contained only small amounts of polymers. At a feed ratio of 40/60, mixing of PSVBDEP-13.3 and PVPh led to the highest yield of precipitate. The complex compositions were not the same as the feed compositions. In most cases, the complex compositions were close to simple molar ratios of the two interacting groups. The excess PVPh remained in the solution phase.

Miscibility Determination by DSC. Mixtures of PSVBDEP-4.3 and PVPh exhibited two glass transition temperatures over the entire composition range (Figure 1). The higher glass transition temperatures were identical

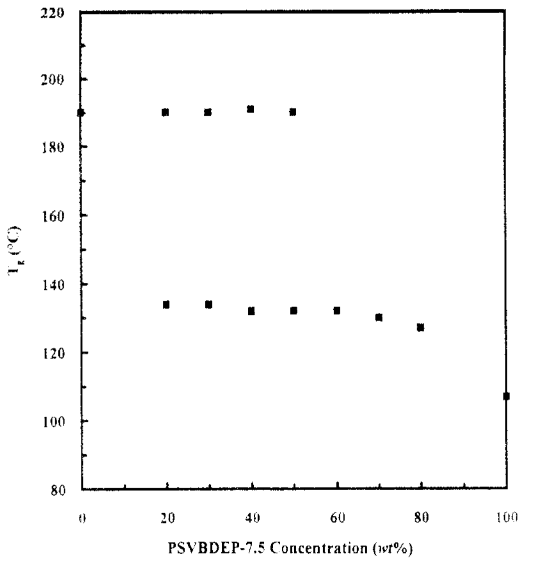

Figure 2. Glass transition temperatures of PSVBDEP-7.5/PVPh blends.

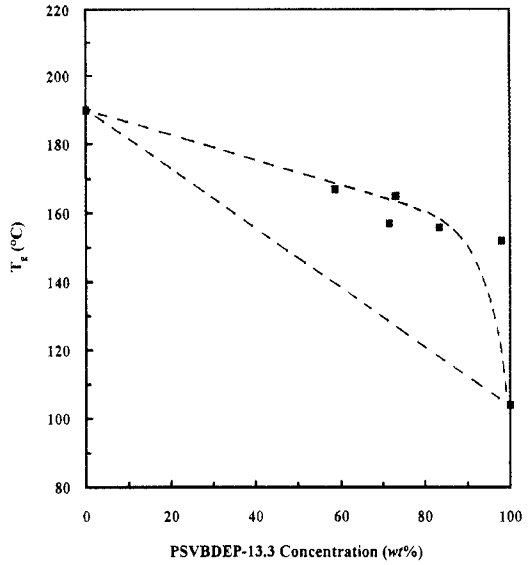

Figure 3. Glass transition temperatures of PSVBDEP-13.3/PVPh complexes. The dashed lines are drawn as visual aids.

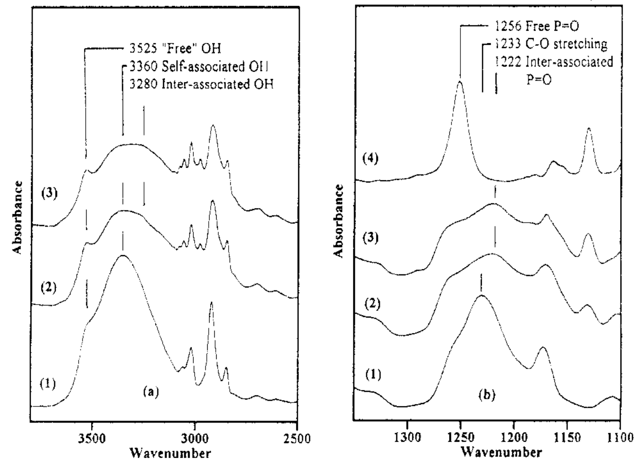

Figure 4. Infrared spectra of PSVBDEP-13.3/PVPh complexes in the (a) 3800–2500 cm^{-1} and (b) 1350–1100 cm^{-1} regions: (1) 0/100; (2) 58.6/41.4; (3) 83.4/16.6; (4) 100/0.

Table 3. IR Frequency Shifts of the OH Group in PVPh Blends

hydrogen bond acceptor	$\Delta\nu$ (cm^{-1})
poly(vinylpyridine)	395
poly(*N*-vinylpyrrolidone)	295
PSVBDEP-13.3	245
poly(ϵ-caprolactone)	105

to that of PVPh, and the lower ones were about 10 °C higher than that of the styrene copolymer. Thus, one of the phases was composed of nearly pure PVPh, and the other contained the styrene copolymer mixed with a very small concentration of PVPh.

When the content of phosphonate units in the styrene copolymer increased to 7.5 mol %, only a single glass transition temperature was observed at each of the copolymer-rich compositions: 60/40, 70/30, and 80/20 (Figure 2). However, the blends showed two glass transition temperatures at compositions of 20/80, 30/70, 40/60, and 50/50. The glass transition temperatures of the miscible blends were close to the weight-average values. In each of the immiscible blends, the higher glass transition temperature was again identical to that of PVPh, while the lower one was about 25 °C higher than that of the styrene copolymer. Thus, these immiscible blends contained two phases: (1) a phase that was nearly pure PVPh; and (2) a second phase which was predominantly the styrene copolymer but contained a higher concentration of PVPh in comparison to PSVBDEP-4.3/PVPh blends. For the 60/40, 70/30, and 80/20 compositions, the as-cast films were not truly transparent. However, heating to a temperature several degrees higher than the glass transition temperature of PVPh enabled these blends to become transparent and exhibit a single T_g after cooling. In addition to the necessary requirement of a favorable polymer–polymer interaction (χ_{23}), a homogenous system is achieved only with a suitably small $|\chi_{12} - \chi_{13}|$ (χ_{12} and χ_{13} are the solvent–polymer interaction parameters).[1,11]

When the styrene copolymer contained 13.3 mol % phosphonate units, all the complexes with PVPh exhibited a single transition temperature (Figure 3), and the T_g values were much higher than the weight-average ones. The high T_g values were consistent with strong hydrogen-bonding interactions in the complexes.[12]

Hydrogen-Bonding Interaction Studies by FTIR Spectroscopy. Hydrogen-bonding interactions in PSVBDEP-13.3/PVPh complexes were first investigated by FTIR spectroscopy. As shown in Figure 4a, there were two types of OH groups in PVPh: "free" OH (3525 cm^{-1}) and self-associated OH (3360 cm^{-1}).[3,4,13] In the complexes, a new absorption peak at 3280 cm^{-1} emerged due to OH groups bonded to phosphonate groups. When the content of phosphonate groups increased, the ratio of the intensities of the interassociated and self-associated OH groups increased. For the OH group bonded to the phosphonate group in the complexes, the frequency shift, $\Delta\nu$, from the "free" OH absorption was 245 cm^{-1} and appeared not to depend on the concentration of PSVBDEP-13.3. In Table 3, the magnitude of the observed frequency shift was compared with literature values reported for other PVPh blends. The acceptor strength of PSVBDEP-13.3 was comparable to that of poly(*N*-vinylpyrrolidone) but much stronger than that of poly(ϵ-caprolactone).[13]

In the 1200–1300 cm^{-1} region, the free P=O absorption peak was located at 1256 cm^{-1} (Figure 4b).[14] The absorption corresponding to the C–O stretching vibration in pure PVPh appeared at 1233 cm^{-1}.[15] In the complexes, an additional peak was observed at 1222 cm^{-1}. Since the C–O absorption peak of phenol should shift, if at all, to a higher frequency because the self-association of PVPh was weakened, the 1222 cm^{-1} peak was attributed to the absorption of hydrogen-bonded P=O groups. The large frequency shift of 34 cm^{-1} from the free P=O group

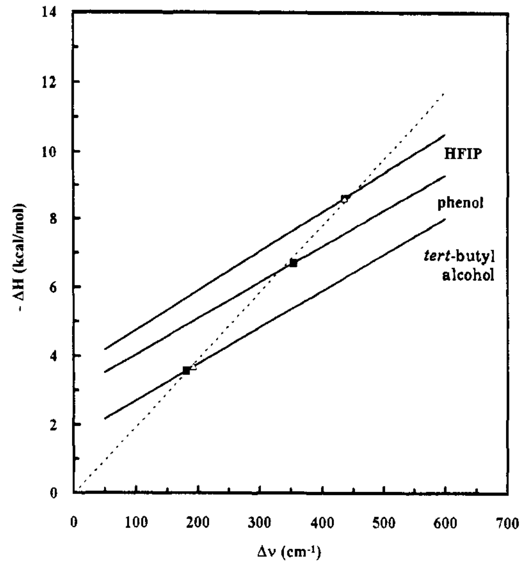

Figure 5. Frequency shifts of hydroxyl groups of HFIP, phenol, and *tert*-butyl alcohol mixed with VBDEP (■) and PSVBDEP-13.3 (▲).

absorption was considered to be indicative of strong hydrogen-bonding interactions.[9]

Frequency Shift–Enthalpy Relationship Determination by FTIR Spectroscopy. To quantitatively "calibrate" the acceptor strength of the $C_6H_4P(O)(C_2H_5)_2$ group, the monomer, VBDEP, was mixed separately with hexafluoroisopropyl alcohol (HFIP), phenol, and *tert*-butyl alcohol. The frequency shifts from the free OH absorption was recorded by FTIR spectroscopy for each acid. In Figure 5, the solid line at the top represented the correlation between the enthalpy of mixing measured calorimetrically, ΔH, and the frequency shift, $\Delta\nu$, when HFIP was mixed with a large number of hydrogen bond acceptors.[16] The middle and bottom solid lines were correlations for phenol and *tert*-butyl alcohol.[17,18] The linear enthalpy–frequency shift correlations for the three hydrogen bond donors, HFIP, phenol, and *tert*-butyl alcohol, are given by eqs 1–3, respectively:

$$-\Delta H = 0.0115\Delta\nu_{OH} + 3.60 \qquad (1)$$

$$-\Delta H = 0.0105\Delta\nu_{OH} + 2.99 \qquad (2)$$

$$-\Delta H = 0.0106\Delta\nu_{OH} + 1.65 \qquad (3)$$

The three straight lines are nearly parallel. When the data for the mixing of a given base, b, with various hydrogen-bonding acids were analyzed, Drago et al. developed the following equation:[17,18]

$$-\Delta H = k_b{}^a\Delta\nu_{OH} \qquad (4)$$

where $k_b{}^a$ was a constant for the base and the superscript, a, indicated that the constant correlated the acid–shift frequency with ΔH. The relationship can be used profitably to calibrate the base strength of a new compound by simply measuring the frequency shifts of hydroxyl groups of HFIP, phenol, and *tert*-butyl alcohol when mixed with that compound, placing the $\Delta\nu$ values on the respective straight lines in Figure 5, and drawing a straight line through the least-mean-square method (the line is usually through the origin). Our experimental data were represented by the dotted line in Figure 5, from which $K_b{}^a$ for VBDEP was obtained as 0.020 kcal/(mol·cm^{-1}). To see if PSVBDEP-13.3 interacted with these acids in a similar manner to VBDEP, HFIP and *tert*-butyl alcohol were separately allowed to diffuse into the copolymer PSVBDEP-13.3 film. The data for the copolymer coincided with the monomer results. The $k_b{}^a$ value of 0.020 kcal/(mol·cm^{-1}) was comparable to literature values of 0.021–0.030 kcal/(mol·cm^{-1}) for other hydrogen-bonding acceptors.[17] For the purpose of comparison, frequency shifts and enthalpies of hydrogen-bond formation of the mixing of various bases with HFIP and phenol are presented in Table 4.[16–19] The IR frequency shift of the hydroxyl group of phenol when mixed with VBDEP and PSVBDEP-13.3 reached 330–350 cm^{-1}, about the same magnitude as in phenol–DMSO and phenol–DMAc mixtures. Thus, it was concluded that VBDEP or PSVBDEP-13.3 was a very strong hydrogen bond acceptor comparable to DMAc and DMSO.

Table 4. IR Frequency Shifts and Enthalpies of Hydrogen-Bond Formation of HFIP and Phenol with Various Bases

	HFIP		phenol	
base	$\Delta\nu_{OH}$ (cm^{-1})	$-\Delta H$ (kcal/mol)	$\Delta\nu_{OH}$ (cm^{-1})	$-\Delta H$ (kcal/mol)
pyridine	417–539[a]	8.4–9.8[a]	465	8.0
DMSO	449	8.7	359	6.8[b]
VBDEP/PSVBDEP-13.3	436	8.6[b]	354/332[c]	6.7/6.5[b]
DMAc	428	8.5	345	6.8
diethyl ether	357	7.2	279	5.9[b]
acetone	280	6.7	193	4.9
ethyl acetate	224	6.5	164	4.8
acetonitrile	208	5.9	150	4.7

[a] Solvent dependent. [b] Calculated from eqs 1 and 2. [c] Estimated from Figure 5.

We have applied the Coleman–Painter model[4] of competing hydrogen-bonding interactions between self-association of the hydroxyl groups and interpolymer interaction for the analysis of our experimental data. Since the two equilibrium constants for the dimerization and multiple association of the phenol group have already been determined by these authors, it is possible to estimate the equilibrium constant K_A for the interpolymer interaction from a knowledge of the miscibility limit. By taking the minimum concentration of the phosphonate ester groups in the styrene copolymer necessary for effecting miscibility with PVPh to be between 8 and 13 mol %, we estimated the equilibrium constant of the $C_6H_4OH/C_6H_4P(O)(OC_2H_5)_2$ interaction to be 60–70. The value is somewhat larger than the constant calculated for the PVPh–poly(*n*-alkyl methacrylate) interaction.[4b] However, since a number of assumptions were used in estimating the solubility parameter and the density of the phosphonate group, the calculated equilibrium constant was only approximate in magnitude.

Hydrogen-Bonding Interaction Studies by ^{31}P and ^{13}C NMR Spectroscopy. We have also applied ^{31}P and ^{13}C NMR spectroscopy to study hydrogen bonding. The monomer, VBDEP, and the copolymer, PSVBDEP-13.3, were mixed separately with *tert*-butyl alcohol, phenol, and HFIP. The molar ratio of the donor to the acceptor was 1:1. Figure 6 indicated that the ^{31}P NMR resonance peak for the free P=O group was located at 21.7 ppm. In the mixtures, the resonance peaks shift downfield as a result of the deshielding effect due to hydrogen-bonding interactions. The shift ranged from 0.3 to 0.7 ppm. The results for the copolymer PSVBDEP-13.3 are shown in Figure 7. In the mixtures, the resonance peaks shifted downfield up to 0.7 ppm, and these peaks were broader compared with that of the free P=O group.

The ^{31}P NMR results suggested that the phosphoryl group was most likely involved in hydrogen-bonding

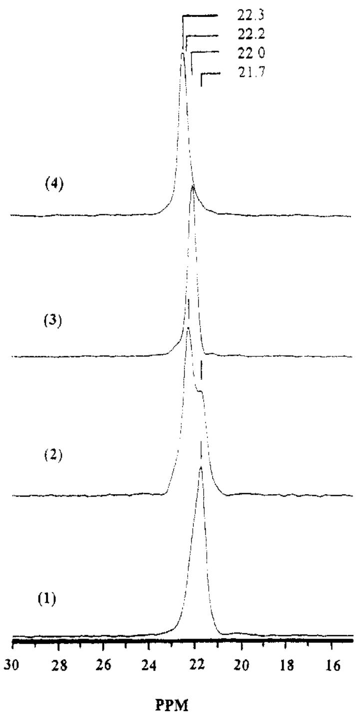

Figure 6. ^{31}P NMR spectra of (1) VBDEP and the mixtures of VBDEP with (2) *tert*-butyl alcohol, (3) phenol, and (4) HFIP.

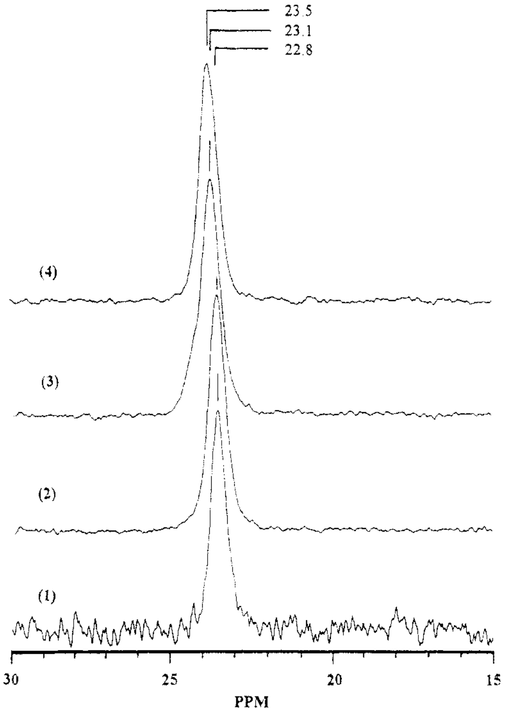

Figure 7. ^{31}P NMR spectra of (1) PSVBDEP-13.3 and the mixtures of PSVBDEP-13.3 with (2) *tert*-butyl alcohol, (3) phenol, and (4) HFIP.

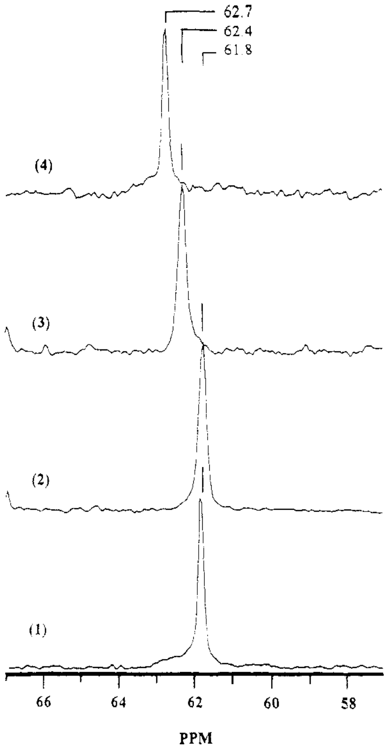

Figure 8. ^{13}C NMR resonance peaks of the carbon of the OCH_2 group for (1) VBDEP, (2) PSVBDEP-13.3, and the mixtures of (3) PSVBDEP-13.3 with phenol and (4) VBDEP with phenol.

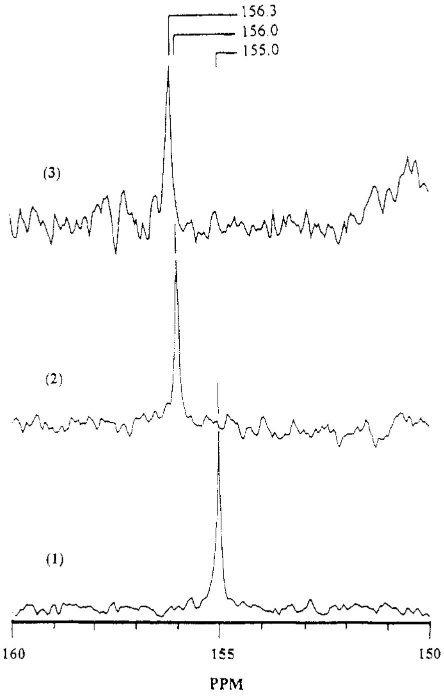

Figure 9. ^{13}C NMR resonance peaks of the phenolic carbon for (1) phenol and the mixtures of phenol with (2) VBDEP and (3) PSVBDEP-13.3.

interactions. Interactions involving the –O– of the alkoxyl groups of the $P(O)(OCH_2CH_3)_2$ were also possible and for this purpose, ^{13}C NMR was used. Both VBDEP and PSVBDEP-13.3 were separately mixed with phenol where the ratio of the donor to the acceptor was 3:1. As shown in Figure 8, the carbon of the OCH_2 group was deshielded in the mixtures of VBDEP and PSVBDEP-13.3, and the shifts were 0.6 and 0.9 ppm, respectively. The phenomena suggest that the –O– of the alkoxyl groups might have also participated in hydrogen-bonding interactions. Correspondingly, the phenolic carbon resonance peak shifted downfield and the shifts were 1.0 and 1.3 ppm in the mixtures with VBDEP and PSVBDEP-13.3, respectively, as would be the expected hydrogen-bonding interactions between hydroxyl and acceptor groups (Figure 9).[20]

Conclusions

Styrene copolymers, PSVBDEP, containing 4.3, 7.5, and 13.3 mol % VBDEP were synthesized and mixed with PVPh. PSVBDEP-4.3 was immiscible with PVPh. PSVBDEP-7.5/PVPh blends were miscible when the concentration of the copolymer was at least 60 wt %. The complexes of PSVBDEP-13.3 with PVPh were miscible.

IR, ^{31}P NMR, and ^{13}C NMR results showed that the driving force for the miscibility was the formation of strong hydrogen-bonding interactions between the phosphonate group of PSVBDEP-13.3 and the hydroxyl group of PVPh. The IR spectra indicated that the frequency shift of the phenolic hydroxyl group when mixed with VBDEP reached 354 cm^{-1}, comparable to the shifts reported for DMSO and DMAc. Thus, VBDEP was a strong base.

Acknowledgment. We wish to acknowledge the National Science Foundation (Grant DMR 9002487) for support of this research. We also wish to acknowledge Dr. Evan Chu and Mr. C. M. Lee for their assistance in NMR measurements. Thanks are also extended to Hoechst-Celanese Chemical Co. for poly(*p*-vinylphenol).

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