Macromolecules **2004,** *37,* 2287−2293

Novel Miscible Blends Composed of Poly(ether sulfone) and Poly(1-vinylpyrrolidone-*co*-styrene) Copolymers and Their Interaction Energies

J. H. Kim, M. S. Whang, and C. K. Kim*

Department of Chemical Engineering, Chung-Ang University, 221 Huksuk-Dong, Dongjak-Gu, Seoul, 156-756, Korea

Received October 27, 2003; Revised Manuscript Received January 16, 2004

ABSTRACT: The miscibility of poly(ether sulfone), PES, with various hydrophilic copolymers containing 1-vinylpyrrolidone or vinyl alcohol as a repeat unit was explored. Among these blends, PES formed homogeneous mixtures with poly(1-vinylpyrrolidone-*co*-styrene) copolymers, P(VP-S), containing VP from 59 to 92 wt %. Miscible PES blends with P(VP-S) copolymers underwent phase separation on heating caused by lower critical solution temperature type phase behavior. The phase separation temperature of miscible blends first increases gradually with VP content, goes through a broad maximum centered at about 77 wt % VP, and then decreases just prior to the limiting content of VP for miscibility with PES. The calculated interaction energies of PES/P(VP-S) blends indicated that miscibility of these blends stemmed from the intramolecular repulsion between VP and styrene.

Introduction

Polymer blends have been widely investigated because of their simplicity and their efficiency in developing new high-performance materials. By blending, one may be able to achieve useful combinations of the advantage of each material into a single product. However, most of polymer blends are immiscible because of their endothermic heat of mixing and the small increase of entropy on mixing.[1,2] The application of immiscible blends is often limited because of their poor interfacial properties. A major concern in designing blends with useful properties is the relationship between polymer structure and blend thermodynamics. Quantitative information about polymer−polymer interactions is an important element for controlling phase behavior of blends since phase behavior of blends is dominated by these interactions.[3−6]

Poly(ether sulfone) (PES) is used in a variety of applications because of its excellent balance of properties.[7−10] It is a transparent, rigid, and tough thermoplastic with chemical inertness. It also has excellent thermal oxidative stability and hydrolytic stability. Applications particularly suited for PES include molded articles and extrusion for which hydrolytic stability and good electrical properties are required. However, the hydrophobic properties of PES and its relatively high melt viscosity and price often deter its applications.[7−10]

In this study, to broaden applications of PES by proving hydrophilic property or by reducing melt viscosity, blends of PES with hydrophilic polymers were explored. Since poor interfacial properties of immiscible blends limited their applications, it is essential to develop miscible PES blends with hydrophilic polymers. It was recently reported that PES formed miscible blend with polyimide.[11] However, PES does not form a miscible blend with hydrophilic polymers such as poly(1-vinylpyrrolidone) (PVP) and poly(vinyl alcohol) (PVA). Common polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) also do not form miscible blends with PES. Small variations in the molecular structure of one component may cause large changes in the phase behavior of blends. According to a simple binary interaction model for describing how the net interaction energy depends on copolymer composition, copolymerization can be an effective strategy to produce a new miscible blend.[12−14] Miscibility of various hydrophilic copolymers with PES was examined. In this study, we focused on fabrication of the miscible blends having hydrophilic properties. Phase behavior of the developed miscible blends was also examined, and then interaction energies of the binary pairs involved in the blends were quantified from the phase boundaries using lattice fluid theory[15−18] combined with the binary interaction model.[12−14]

Materials and Procedures

Most of the polymers used in this study are listed in Table 1. PES (Ultra-son E) was purchased from ICI Americas Inc. Copolymers containing 1-vinylpyrrolidone as hydrophilic component such as poly(1-vinylpyrrolidone-*co*-styrene) [P(VP-S)] and poly(1-vinylpyrrolidone-*co*-methyl methacrylate) [P(VP-MMA)] were synthesized at various copolymer compositions. Copolymers containing vinyl alcohol such as poly(vinyl alcohol-*co*-styrene) [P(VA-S)] and poly(vinyl alcohol-*co*-methyl methacrylate) [P(VA-MMA)] were also prepared in our laboratory. Copolymerization was performed in the bulk at 80 °C with AIBN (azobis(isobutyronitrile)) as the initiator. The conversion for the synthesis of the copolymers was kept at about 10 wt % to avoid composition drift. The resulting solution was poured into a large excess of *n*-hexane to precipitate the polymer. The precipitated polymer was vacuum-filtered, dried in an air circulating oven at 80 °C for 24 h, and dried in a vacuum oven at 100 °C for a day. Molecular weight information on polymers was obtained using GPC calibrated with polystyrene standards, and monomer content of copolymers was determined by elemental analysis. The numerical value included as part of the code for these copolymers indicates the weight percent of VP or VA.

Blends were prepared from four different methods coded P_1, P_2, P_3, and P_4. The details of each are described below. P_1: The blend was prepared in film form by casting solutions containing 5 wt % total polymer in methylene chloride into a Petri dish. The cast solutions were dried at 60 °C until most solvent

---

* To whom all correspondences should be addressed.

10.1021/ma0356156 CCC: $27.50

Table 1. Polymers Used in This Study

abbreviation[a]	VP contents (wt %)[b]	T_g (°C)	$\bar{M}_w$[c]	$\bar{M}_w/\bar{M}_n$[c]	source
PES		229	70 000	1.92	ICI Americas Inc. Ultra-son E
P(VP-S) 24	24	107	65 000	2.02	synthesized
P(VP-S) 32	32	109	42 000	2.10	Aldrich
P(VP-S) 36	36	115	70 500	1.87	synthesized
P(VP-S) 49	49	123	62 000	1.79	synthesized
P(VP-S) 59	59	130	71 000	2.12	synthesized
P(VP-S) 65	65		59 000	2.25	synthesized
P(VP-S) 69	69	134	79 000	1.97	synthesized
P(VP-S) 72	72	137	75 000	1.81	synthesized
P(VP-S) 77	77	140	80 500	1.97	synthesized
P(VP-S) 81	81	148	77 000	2.01	synthesized
P(VP-S) 88	88		69 000	2.18	synthesized
P(VP-S) 92	92	153	61 000	1.88	synthesized
P(VP-S) 96	96	155	67 000	1.71	synthesized

[a] The numerical value included as part of the code for copolymers indicates the weight percent of VP. [b] The VP content in the copolymer was determined by elemental analysis. [c] Molecular weights were determined by GPC with polystyrene standards.

evaporated in an air circulating oven. The blends were finally dried in a vacuum oven at 130 °C for a week. P_2: This method followed the same procedure as P_1 except that the solvent was 1-methyl-2-pyrrolidone (NMP), and most solvent was evaporated at 100 °C. P_3: This method also followed the same procedure as P_1 except that most solvent was evaporated at 130 °C. P_4: In this method, PES and copolymer were precipitated simultaneously from the NMP solution using the nonsolvent water. The precipitate was allowed to dry in an air-circulating oven and then further dried in a vacuum oven at 130 °C for a week.

Glass transition temperatures were measured at a heating rate of 20 °C/min by using a DSC (TA Instrument, model DSC-2010). The first scan was run to 200 °C to erase previous thermal history during sample preparation, and then the sample was quenched to room temperature to start the second scan. The glass transition temperature, T_g, was defined as the onset of the change in heat capacity during the second heating from room temperature to 250 °C. The phase separation temperature caused by the lower critical solution temperature (LCST) type phase behavior was measured by an annealing technique to access the closest true equilibrium temperature.[19-23] The detailed explanation for this technique is described in the next section.

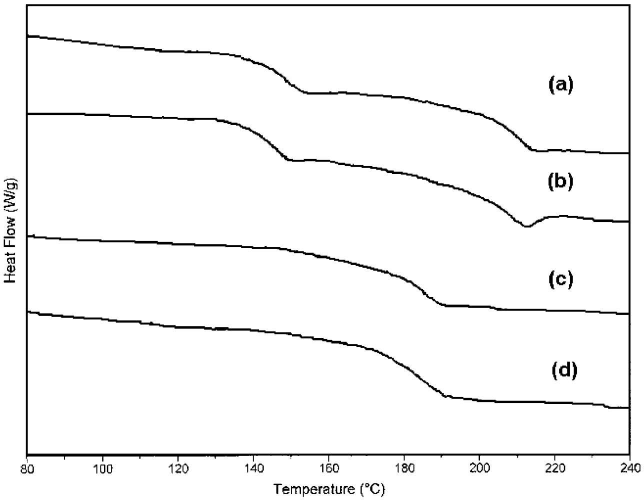

Figure 1. DSC thermograms for PES/P(VP-S) 72 = 5/5 blends: (a) blend cast from dichloromethane at 60 °C; (b) cast from NMP at 100 °C; (c) cast from NMP at 130 °C; (d) precipitated simultaneously from the NMP solution using the nonsolvent water.

Results and Discussion

Phase Behavior of Blends. The blends of PES with P(VP-MMA), P(VA-S), or P(VA-MMA) were immiscible regardless of blend compositions and copolymer compositions. The blends were translucent, and their thermograms reveal two T_gs. However, P(VP-S) copolymers containing a certain amount of VP formed miscible blends with PES. Because of these, P(VP-S) copolymers were only used for further study. Miscibility of PES blends with P(VP-S) copolymers containing VP from 24 up to 96 wt % was examined. Figure 1 shows the DSC thermograms of PES/P(VP-S) 72 = 5/5 blends prepared by four different preparation methods. The blend cast from dichloromethane at 60 °C and that cast from NMP at 100 °C (methods P_1 and P_2) were translucent and visually heterogeneous. DSC thermogram revealed two T_gs for these specimens (Figure 1a,b). However, the PES/P(VP-S) 72 = 5/5 blend cast from NMP at 130 °C (method P_3) was transparent, and its thermogram revealed a single T_g (Figure 1c). The T_g behavior of the PES/P(VP-S) 72 blend prepared by precipitation method (P_4) was similar to that prepared by method P_3 (Figure 1d). PES blends containing various amounts of P(VP-S) 72 copolymer also show similar T_g behavior that depends on preparation methods. Because of this, blend samples were prepared by methods P_3 or P_4 for further study. Blends of PES with copolymers having VP contents from 59 to 92 wt % were transparent and showed a single T_g that varied regularly with overall blend composition. PES blends with the P(VP-S) copolymers containing less than 59 wt % VP and those with the P(VP-S) copolymers containing more than 92 wt % VP were opaque and showed two T_gs, indicating that phase separation occurred. Figure 2 shows T_g behavior for PES blends with selected P(VP-S) copolymers prepared by method P_3. The glass transition behavior for blends containing 50% of PES, which prepared by method P_3, is summarized in Figure 3 by plotting the observed glass transitions vs content of VP of the copolymers. Blends of PES with copolymers having VP contents from 59 to 92 wt % were transparent and showed a single T_g that varied regularly with overall blend composition. From these results, it was concluded that PES and P(VP-S) copolymers prepared by methods P_3 and P_4 formed miscible blends when copolymers contain VP from 59 to 92 wt % and beyond these critical limits to form immiscible blends.

The miscibility of the PES/P(VP-S) blend depends on preparation methods of blends. Even though each binary pair in casting solution is miscible, asymmetry in the molecular interaction, the so-called $\Delta\chi$ effect or solvent effect,[24-27] can lead to the region of immiscibility. On the other hand, when copolymer composition is near the

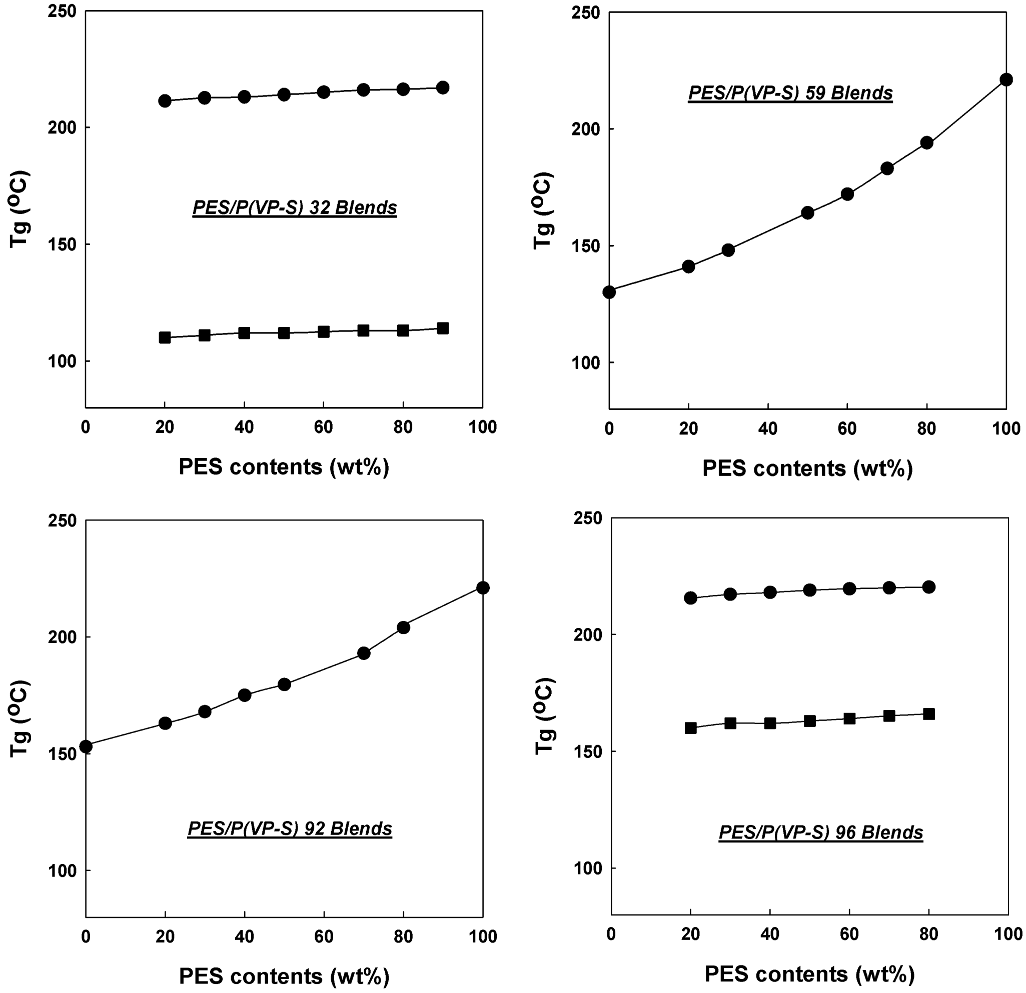

Figure 2. Glass transition temperatures of PES blends with selected P(VP-S) copolymers.

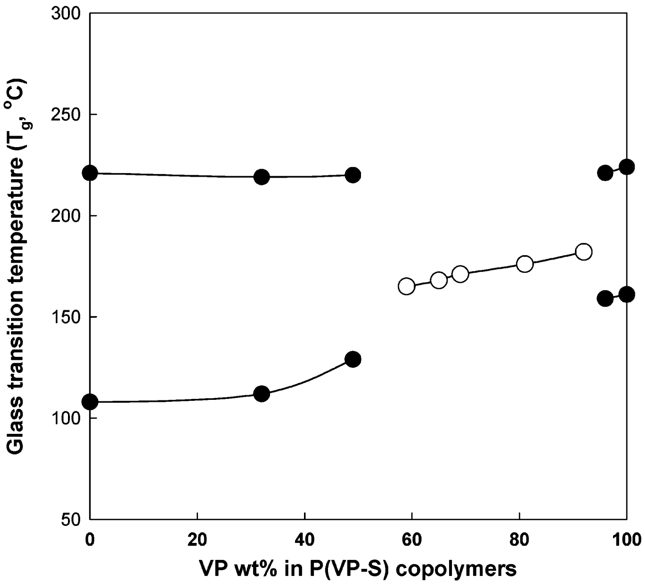

Figure 3. Glass transition temperatures vs contents of VP in the P(VP-S) copolymers for PES/P(VP-S) = 5/5 blends.

boundary of miscibility window, the kinetics of the phase separation process may be very slow because of rate effects as reported previously.[22,28] The miscible region might be underestimated in the former case while it might be overestimated in the latter case. To avoid misleading results, isothermal annealing was performed to get a true equilibrium phase boundary and to determine the phase separation temperature.

Phase separation temperature caused by LCST-type phase behavior was measured by an annealing technique[19−23] to access the closest true equilibrium temperature. For example, the PES/P(VP-S) 59 = 5/5 blend was heated rapidly to a temperature about 180 °C and then heated at a rate of 2 °C/min. Changes in the image with temperature were observed as the specimens were heated at a rate of 2 °C/min. Changes in the image were observed at 220 °C. After determining the approximate temperature at which phase separation occurred, blend specimens were annealed in the hot stage at a fixed temperature for 30 min. The blend annealed at 210 °C was still clear, and changes in the morphology of the blend were not observed while that annealed 220 °C became opaque and changes in the morphology were observed during annealing. The presence of a separated phase structure implies that phase separation occurred by the LCST-type phase separation behavior. The phase boundary would appear to lie between 210 and 220 °C for this blend. By successively repeating the annealing process within the determined temperature range, the location of the phase boundary was determined. Phase separation temperature might be affected by annealing because of thermal degradation at these temperatures. Thermal decomposition of the blend at high temperature (about 350 °C) comes from the thermal instability of P(VP-S) copolymer, as shown in Figure 4. Since phase separation temperatures of miscible blends are lower

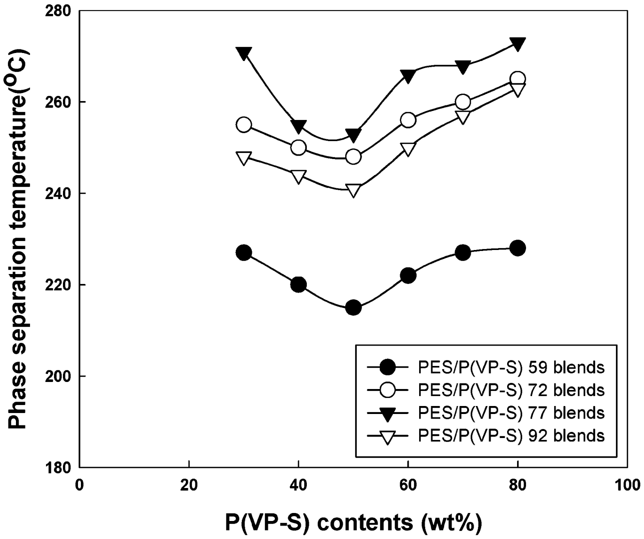

Figure 4. Phase separation temperatures of PES blends with various P(VP-S) copolymers

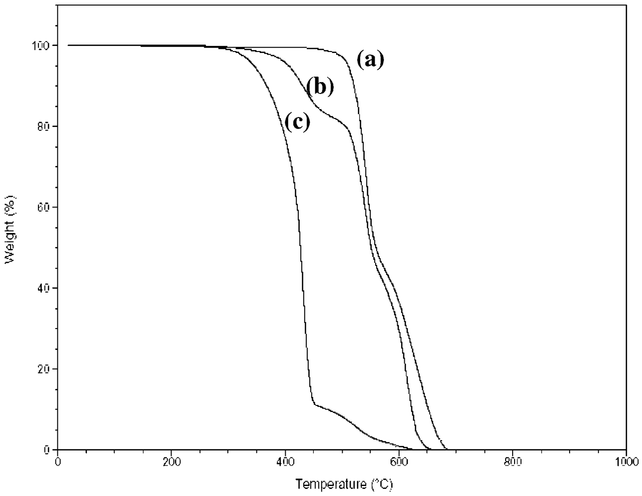

Figure 5. TGA traces of blends and each component using a heating rate of 5 °C/min: (a) PES; (b) PES/P(VP-S) 69 = 5/5; (c) P(VP-S) 69.

than 280 °C regardless of blend compositions and copolymer compositions, blends are chemically stable at around the phase separation temperature.

Figure 5 shows phase separation temperatures for miscible blends of PES with four selected P(VP-S) copolymers. The phase separation temperature curves are all very similar, with each showing a minimum at 50 wt % PES. The effect of VP content can be exhibited more easily with a plot of the phase separation temperature for a fixed PES content of the blend vs the VP content of the copolymer, as shown in Figure 6. PES/P(VP-S) blends became miscible by increasing VP content up to 59 wt %. The phase separation temperature of miscible blend first increases gradually with VP content, goes through a broad maximum centered at about 77 wt % VP, and then decreases just prior to the limiting content of VP for miscibility with PES.

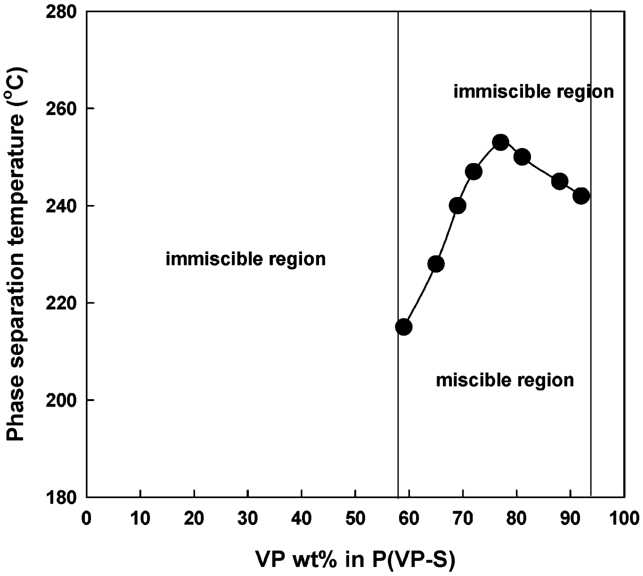

Figure 6. Miscibility map and phase separation temperatures for 50/50 blends of PES with P(VP-S) copolymers

Interaction Energies. Homopolymer pairs involved in the PES and P(VP-S) blends such as PES−PVP, PES−PS, and PVP−PS are immiscible. To explore copolymerization effects on the miscibility, interaction energies of binary pairs involved in the PES/P(VP-S) blends were calculated from phase boundaries using the lattice-fluid theory combined with the binary interaction model. The detailed background for the lattice-fluid model and binary interaction model was described previously.[21,22] To extract information about interaction energy from the liquid−liquid phase boundaries, it is assumed that to a good approximation these data correspond to the spinodal curve. As reported elsewhere,[22,23,29] the morphology of the PES/P(VP-S) blend observed with an image analyzer at the reported phase separation temperature could be also characterized by a high level of phase interconnectivity in both the minor and major phase caused by spinodal decomposition.

For the evaluation of the interaction energies responsible for the equilibrium phase behavior using an equation-of-state theory, pressure−volume−temperature data for each polymeric component are required so that characteristic parameters can be determined. The characteristic parameters of P(VP-S) were obtained by using the mixing rule with those of PS and PVP obtained from *PVT* data of each polymer.[30−35] To obtain the characteristic parameters of PES, the changes in the density of PES as a function of temperature and pressure were measured using a density gradient column and a Genimix PVT apparatus. Starting at 30 °C, PES was compressed along with 28 isotherms, spaced about 10 °C apart, up to about 300 °C, with volume data recorded at pressure intervals of 10 MPa between 0 and 100 MPa along with each isotherms. The specific volume at zero pressure for each isotherm was obtained by extrapolation using the Tait equation.[30−35] Pressure−volume−temperature data of PES homopolymer above the glass transition temperature are listed in Table 2. The characteristic parameters of the lattice-fluid theory were obtained by the nonlinear least-squares methods of fitting *PVT* data to the equation of state. While the equation of state proposed by Sanchez and Lacombe has a simpler and more convenient closed mathematical form than many others, it shows systematic deviations in the regression at very high pressure.[19,32] Thus, only low-pressure data (0−50 MPa) where this is not a problem were used. The characteristic parameters for PES obtained from the data are listed in Table 3.

Table 2. Density (g/cm^3) of PES as a Function of Pressure and Temperature

P (MPa)	223.9 (°C)	231.1 (°C)	240.8 (°C)	249.8 (°C)	259.5 (°C)	268.9 (°C)	277.9 (°C)	287.1 (°C)	296.2 (°C)
0	1.2966	1.2890	1.2823	1.2753	1.2691	1.2597	1.2513	1.2427	1.2265
10	1.3049	1.2973	1.2913	1.2845	1.2787	1.2700	1.2620	1.2533	1.2424
20	1.3131	1.3056	1.3001	1.2935	1.2882	1.2802	1.2720	1.2637	1.2587
30	1.3199	1.3122	1.3072	1.3007	1.2956	1.2880	1.2807	1.2718	1.2671
40	1.3262	1.3186	1.3140	1.3078	1.3027	1.2952	1.2881	1.2801	1.2751
50	1.3323	1.3245	1.3205	1.3143	1.3093	1.3021	1.2953	1.2876	1.2832
60	1.3378	1.3304	1.3268	1.3206	1.3158	1.3087	1.3019	1.2945	1.2903
70	1.3432	1.3362	1.3327	1.3268	1.3219	1.3149	1.3083	1.3015	1.2970
80	1.3483	1.3418	1.3383	1.3328	1.3277	1.3209	1.3145	1.3081	1.3039
90	1.3531	1.3470	1.3439	1.3387	1.3334	1.3268	1.3204	1.3145	1.3102
100	1.3575	1.3522	1.3491	1.3444	1.3389	1.3325	1.3264	1.3208	1.3167

In the lattice-fluid theory, the characteristic pressure of a mixture, P^*, is related to that of each component and the interaction energy, $\Delta P^*_{(ij)}$, by[12−14,18−23]

$$P^* = \sum_i \phi_i P_i^* - \sum_{i<j}\sum \phi_i \phi_j \Delta P^*_{(ij)} \qquad (1)$$

For a binary blend of a random copolymer composed of units 1 and 2 units and a homopolymer of 3, the interaction energy between copolymer and homopolymer is given by in terms of monomer unit pair interactions, ΔP^*_{ij}

$$\Delta P^*_{(ij)} = \Delta P^*_{13}\phi_1' + \Delta P^*_{23}\phi_2' - \Delta P^*_{12}\phi_1'\phi_2' \qquad (2)$$

where ϕ_i' indicates the close packed volume fraction of component i in the copolymer. The free energy of mixing per unit volume, g, is given by

$$g = g_{\mathrm{nc}} + g_{\mathrm{c}} \qquad (3)$$

where g_{c} is the combinatorial entropy

$$g_{\mathrm{c}} = RT\sum_i \frac{\phi_i}{v_i^* r_i} \ln \phi_i \qquad (4)$$

and g_{nc} is the noncombinatorial free energy represented by

$$g_{\mathrm{nc}} = -\tilde{\rho}P^* + P\tilde{v} + \frac{RT}{v^*}\left(\frac{1-\tilde{\rho}}{\tilde{\rho}}\ln(1-\tilde{\rho}) + \frac{\ln\tilde{\rho}}{r}\right) \qquad (5)$$

Finally, the spinodal condition for a compressible mixture can be written

$$\frac{\mathrm{d}^2 g}{\mathrm{d}\phi^2} = g_{\phi\phi} - \frac{(g_{\tilde{\rho}\phi})^2}{g_{\tilde{\rho}\tilde{\rho}}} = 0 \qquad (6)$$

where the subscripts ϕ and $\tilde{\rho}$ indicate partial derivatives with respect to ϕ or $\tilde{\rho}$. In terms of the Sanchez−Lacombe theory, the indicated derivatives for binary mixture are given by[18,38]

$$g_{\phi\phi} = -2\tilde{\rho}\Delta P^* + RT\left(\frac{1}{\phi_1 r_1 v_1^*} + \frac{1}{\phi_2 r_2 v_2^*}\right) \qquad (7)$$

$$g_{\tilde{\rho}\phi} = -(P_1^* - P_2^* - (1-2\phi_1)\Delta P^*) + \frac{RT}{\tilde{\rho}}\left(\frac{1}{r_1 v_1^*} - \frac{1}{r_2 v_2^*}\right) - RT\left(\frac{1}{v_1^*} - \frac{1}{v_2^*}\right)\left(\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\right) \qquad (8)$$

$$g_{\tilde{\rho}\phi} = \frac{RT}{v^*}\left(\frac{2\ln(1-\tilde{\rho})}{\tilde{\rho}^3} + \frac{1}{\tilde{\rho}^2(1-\tilde{\rho})} + \frac{1}{\tilde{\rho}^2}\left(1 - \frac{1}{r}\right)\right) \qquad (9)$$

Table 3. Characteristic Properties of Polymers

abbreviation	T^* (K)	P^* (bar)	ρ^* (g/cm^3)
PES	797.8	5820	1.4721
PS	810	3730	1.0920
PVP	810	5650	1.0904

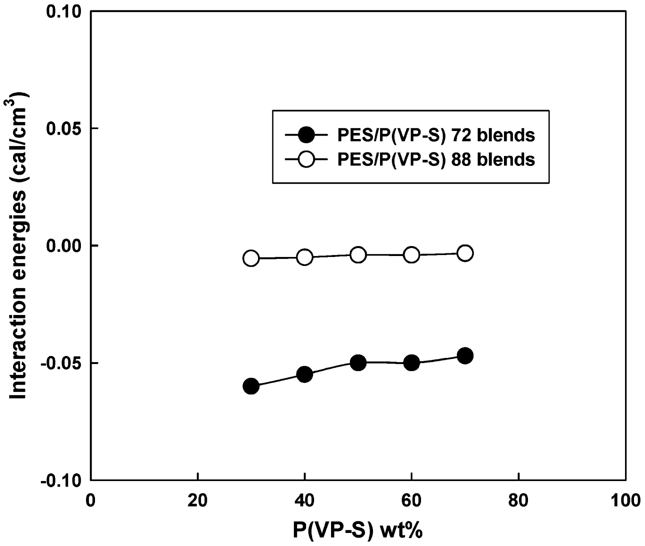

Figure 7. Interaction energies for blends of PES with selected P(VP-S) copolymers.

The ΔP^* values ($\Delta P^*_{\mathrm{PES-P(VP-S)}}$) for blends of PES with P(VP-S) copolymers were calculated from phase boundaries shown in Figure 5 using eq 6. Figure 7 shows that the $\Delta P^*_{\mathrm{PES-P(VP-S)}}$ values obtained for blends of PES with specific P(VP-S) copolymers are essentially composition independent as described in the lattice-fluid theory.[15−23] The average value of interaction energies for PES/P(VP-S) blends was used further calculation.

Figure 8 shows the change in the interaction energies of PES/P(VP-S) blends as a function of VP content in the copolymers. The curve presenting interaction energy for PES/P(VP-S) blends was convex down. As predicted with the binary interaction model (eq 2), the curve shape for the interaction energies of PES/P(VP-S) pairs might stem from the intramolecular repulsion between VP and styrene, i.e., the positive interaction energy between VP and styrene. Interaction energies for miscible blends were negative, but they were nearly zero. Weak favorable interactions for the miscibility of the PES/P(VP-S) blend might result in the dependence of miscibility on the preparation methods.

The binary interaction energies involved in the PES/P(VP-S) blends, i.e., $\Delta P^*_{\mathrm{PES-VP}}$, $\Delta P^*_{\mathrm{PES-S}}$, and $\Delta P^*_{\mathrm{VP-S}}$, were obtained by the least-squares methods of fitting $\Delta P^*_{\mathrm{PES-P(VP-S)}}$ data to eq 2. The interaction energy of each binary pair was $\Delta P^*_{\mathrm{PES-VP}} = 0.11$ cal/cm^3,

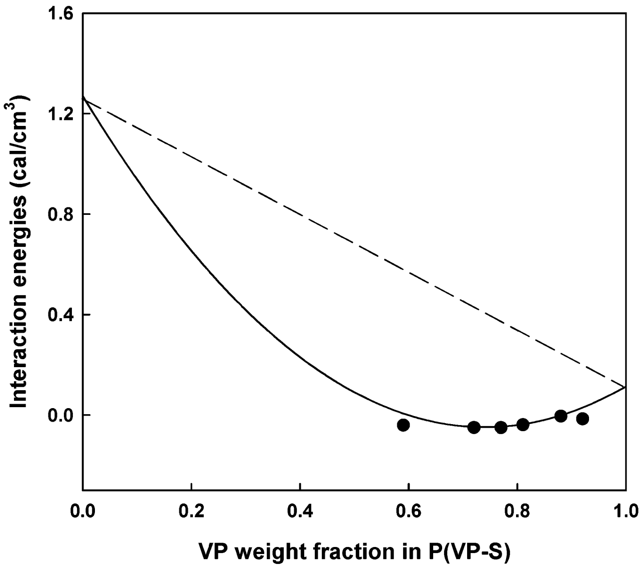

Figure 8. Interaction energies as a function of VP content in P(VP-S) copolymers. Note that solid line was obtained by the least-squares methods of fitting $\Delta P^*_{\mathrm{PES-P(VP-S)}}$ data to eq 2.

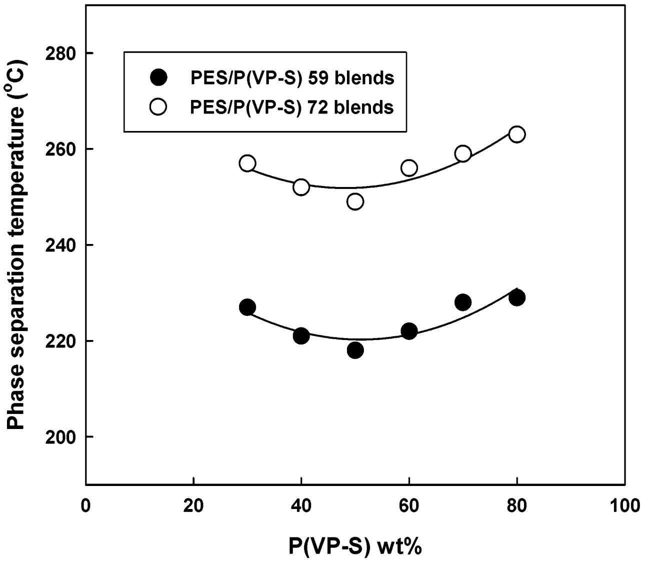

Figure 9. Experimental phase separation temperatures of PES/P(VP-S) blends. Note that the corresponding spinodal curves were calculated from eq 6 with interaction energies obtained here.

$\Delta P^*_{\mathrm{PES-S}} = 1.27$ cal/cm^3, and $\Delta P^*_{\mathrm{VP-S}} = 2.40$ cal/cm^3. Interaction energies of the binary pairs calculated here indicate that the homopolymer blends such as PES/PVP, PES/PS, and PVP/PS blends are immiscible. Figure 9 showed that experimental phase separation temperatures and the spinodal curve calculated from eq 6 and a fixed $\Delta P^*_{\mathrm{PES-P(VP-S)}}$ value for each PES/P(VP-S) blend. The curves agreed with the experimentally determined phase separation temperatures.

Summary

The miscibility of PES with various hydrophilic copolymers such as (VP-S), (VP-MMA), P(VA-S), and P(VA-MMA) was examined. Various methods have been used in preparing blends. Except PES blends with P(VP-S) containing a certain amount of VP, blends of PES with other copolymers were always immiscible. The miscibility of PES/P(VP-S) blends was affected by the preparation method of blend. On the basis of the phase separation temperatures caused by LCST-type phase behavior, it was concluded that copolymer of P(VP-S) containing between 59 and 92 wt % VP gave homogeneous mixtures with PES. The phase separation temperature of the miscible blend first increases gradually with VP content, goes through a broad maximum centered at about 77 wt % VP, and then decreases just prior to the limiting content of VP for miscibility with PES. To understand phase behavior of blends examined here, interaction energies were calculated from phase boundaries using lattice-fluid theory combined with the binary interaction model. The results indicated that the miscibility of PES with P(VP-S) copolymers stemmed from intramolecular repulsion between VP and styrene. It also suggested that the miscibility changes of PES/P(VP-S) blends with preparation methods stemmed from the nearly zero but negative interaction energies.

Acknowledgment. This research was supported by the Chung-Ang University Research Grants in 2003.

References and Notes

(1) Paul, D. R.; Bucknall, C. B. *Polymer Blends*; Paul, D. R., Bucknall, C. B., Eds.; John Wiley & Sons: New York, 1999; Vol. 1, Chapter 1.
(2) Brown, H. R. *Polymer Blends*; Paul, D. R., Bucknall, C. B., Eds.; John Wiley & Sons: New York, 1999; Vol. 2, Chapter 23.
(3) Paul, D. R.; Walsh, D. J.; Higgins, J. S. In *Polymer Blends and Mixtures*; Maconnachie, A., Ed.; NATO ASI Series E, Applied Science, No. 89; Martinus Nijoff Publishers: Dordrecht, The Netherlands, 1985; p 1.
(4) Olabisi, O.; Robenson, L. M.; Shaw, M. T. *Polymer−Polymer Miscibility*; Academic Press: New York, 1979; Chapters 2, 3.
(5) Freitag, D.; Grigo, U.; Muller, P. R.; Nouvertne, W. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; John Wiley: New York, 1988; Vol. 11, 48.
(6) Paul, D. R.; Barlow, J. W.; Keskkula, H. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; John Wiley: New York, 1988; Vol. 12, p 399.
(7) Harris, J. E.; Johnson, R. N. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; John Wiley: New York, 1988; Vol. 13, p 196.
(8) Klaus, C. B.; Susana, V. P.; Nuns, P. *J. Membr. Sic.* **1993**, *79*, 83.
(9) Robison, L. M.; Crisafulli, S. T. *J. Appl. Polym. Sci.* **1983**, *28*, 2925.
(10) Boom, R. M.; Boomgaard, T. V. D.; Smolders, C. A. *J. Membr. Sci.* **1994**, *90*, 231.
(11) Kapantaidakis, G. C.; Koops, G. H.; Wessling, M. *Desalination* **2002**, *145*, 353.
(12) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(13) Kambour, R. P.; Bendler, T. J.; Bopp, R. C. *Macromolecules* **1983**, *16*, 1827.
(14) Brinke, G. T.; Karasz, F. E.; Macknight, W. J. *Macromolecules* **1983**, *16*, 1827.
(15) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2568.
(16) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2358.
(17) Sanchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145.
(18) Sanchez, I. C. *Encyclopedia of Physical Science and Technology*; Academic Press: New York, 1987; Vol. XI, p 1.
(19) Kim, C. K.; Paul, D. R. *Polymer* **1992**, *33*, 4941.
(20) Callaghan, T. A.; Takakuwa, K.; Paul, D. R.; Padwa, A. R. *Polymer* **1993**, *34*, 3796.
(21) Gan, P. P.; Paul, D. R. *Polymer* **1994**, *35*, 1487.
(22) Kim, M. H.; Kim, J. H.; Kang, Y. S.; Park, H. C.; Won, J. O. *J. Polym. Sci., Polym. Phys. Ed.* **1999**, *37*, 2950.
(23) Kim, Y.; Yoo, J. E.; Kim, C. K. *Polymer* **2003**, *44*, 5439.
(24) Brannock, G. R.; Paul, D. R. *Macromolecules* **1990**, *23*, 5240.
(25) Robard, A.; Patterson, D. *Macromolecules* **1977**, *10*, 1021.
(26) Su, S. C.; Patterson, D. *Macromolecules* **1977**, *10*, 709.

(27) Kim, C. K.; Kim, J. J.; Paul, D. R. *Polym. Eng. Sci.* **1994**, *34*, 1788.
(28) Nishimoto, M.; Keskkula. H.; Paul, D. R. *Polymer* **1991**, *32*, 272.
(29) Park, D. S.; Kim, J. H.; Kim, C. K.; Lee, J. W. *J. Polym. Sci., Part B* **2001**, *39*, 1948.
(30) Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1261.
(31) Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1453.
(32) Rodgers, P. A. *J. Appl. Polym. Sci.* **1993**, *18*, 1061.
(33) Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *20*, 157.
(34) Kim, C. K.; Paul, D. R. *Polymer* **1992**, *33*, 1630.
(35) Kim, J. H.; Kim, C. K.; Lee, J. W.; Seo, S. B. *J. Polym. Sci., Polym. Phys. Ed.* **2003**, *41*, 1401.

MA0356156