

Miscibility Enhancement of Polystyrene and Poly(alkylene Oxide) Blends Using Specific Intermolecular Interactions

R. A. WEISS,^{1,2} C. BERETTA,¹ S. SASONGKO,¹ and A. GARTON^{1,3}

¹*Polymer Science Program, ²Dept. of Chemical Engineering, and ³Dept. of Chemistry, University of Connecticut, 97 N. Eagleville Road, Storrs, Connecticut 06269-3136*

Synopsis

Acid–base interactions were used to enhance the miscibility of blends of polystyrene and oligomeric poly(alkylene oxide). The polystyrene was modified by sulfonation of less than 5% of the styrene rings. The poly(alkylene oxides) were low molar mass polyethylene oxide chains ($M = 900$ and 6000) that were end capped with propyl amine groups. Blends of the poly(alkylene oxide) diamines with polystyrene were immiscible. Blends with the sulfonated polystyrenes were miscible due to proton transfer from the sulfonic acid groups to the basic amino groups of the functionalized poly(alkylene oxide). This was confirmed by FTIR. DSC and dynamic mechanical analyses were used to verify the one- or two-phase nature of the blends.

INTRODUCTION

Various types of specific interactions have been employed to enhance the miscibility of polymer–polymer blends. These include crosslinking,¹ hydrogen bonding,² dipole–dipole interactions,³ acid–base interactions,⁴ ion–dipole interactions,⁵ charge-transfer complexes,⁶ transition metal complexation,⁷ and interpenetrating networks.⁸

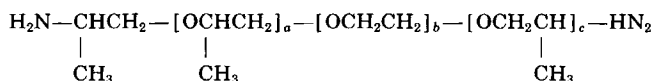
In most of the previous work, the interacting functional groups were randomly placed on both polymer backbones. A notable exception to this is the study by Horrian et al.,⁹ who prepared blends of end-functionalized polystyrene and polybutadiene, two polymers that are immiscible. In their study, the polymers were end terminated with either carboxylic acid groups or tertiary amines such that an acid–base interaction occurred when the polymers were mixed. Although a multiphase system was obtained, the properties of the blend led the authors to speculate that a multiblock copolymer was formed by chain extension. More recent results indicate that this approach may yield miscible or microphase-separated morphologies.¹⁰

In our laboratory, we have been studying the use of acid–base interactions and transition metal complexation to either improve polymer–polymer miscibility or to prepare grafted-block copolymers.¹¹ This article describes the preparation and characterization of blends of lightly sulfonated polystyrene and amine-terminated poly(alkylene oxide) oligomers.

EXPERIMENTAL SECTION

Materials. Lightly sulfonated polystyrene (SPS) was prepared from a commercial atactic polystyrene homopolymer (Montedison Chemical Co.) with $M_n = 86,000$ and $M_w = 230,000$ as determined by gel permeation chromatography. Sulfonation was carried out using acetyl sulfate as the sulfonating reagent following the method of Makowski et al.¹² This procedure results in little change of the polymer molar mass and in random attachment of the sulfonic acid group at the para-position of the phenyl ring. Two SPS samples were prepared, containing 1.35 and 4.51 mol % SO_3H , hereafter referred to as 1-SPS and 4-SPS, respectively (mol % is defined here as the percentage of the styrene repeat units sulfonated).

The poly(alkylene oxide) diamines (PAODA), trade name Jeffamines, were obtained from the Texaco Chemical Co. These consisted of a poly(ethylene oxide), PEO, chain with propylene oxide terminal groups that were capped by an amine group:



The values of $(a + c)$ and b for the materials used in this study were taken from the manufacturer's literature and are given in Table I along with their thermal transitions as determined by differential scanning calorimetry (DSC). The percent crystallinities were calculated from the ratio of the heat of fusion measured by DSC to 47.0 cal/g, the heat of fusion of 100% crystalline poly(ethylene oxide).¹³

Blends were prepared by adding dropwise a 10% solution of the PAODA in tetrahydrofuran (THF) to a vigorously stirred 10% solution of SPS in THF. The polymer blends were recovered either by precipitation in methanol or by evaporating the solvent. Blends of the unmodified polystyrene (PS) and the PAODAs were also prepared in the same way. All samples were dried under vacuum at 70°C for 48 h. A summary of the blends studied is given in Table II. The notation for the blend samples is xxyy-zz where xx is the styrenic polymer used (PS, 1S, or 4S, representing polystyrene, 1-SPS, and 4-SPS, respectively), yy is the PAODA used (E9 or E60 representing E-900 and E-6000, respectively), and zz is the weight percent of PAODA. For example, 1SE9-10 corresponds to a blend of 10% ED-900 PAODA and 90% 1-SPS. The

TABLE I
Poly(alkylene Oxide) Diamine Oligomers

Sample designation	b	$(a + c)$	T_g (°C)	T_m (°C)	Crystallization (%)
ED-900	15.5	2.5	-59	16	57
ED-6000	131.5	2.5	-54	54	8
Poly(ethylene oxide) ^a			-41	69	

^a Data from Ref. 13.

TABLE II
 Blend Samples (Mass Fraction)

Sample designation	PS	1-SPS	4-SPS	ED-900	ED-6000	NH ₂ /SO ₃
PSE9-10	0.897			0.103		
PSE9-25	0.750			0.250		
PSE60-25	0.750				0.250	
1SE9-10		0.897		0.103		2.0
1SE9-25		0.750		0.250		5.8
1SE60-25		0.750			0.250	0.86
1SE60-43		0.565			0.435	2.0
4SE9-25			0.726	0.274		2.0
4SE60-25			0.750		0.250	0.26
4SE60-72			0.285		0.715	2.0

last column in Table II corresponds to the molar ratio of amine groups to sulfonic acid groups. Thus twice the stoichiometric ratio of NH₂/SO₃H corresponds to one PAODA chain per sulfonic acid group.

Infrared Spectroscopy. Infrared spectroscopy characterizations of the amine-sulfonic acid interactions were carried out with a Nicolet Model 60SX Fourier transform infrared (FTIR) spectrometer. The samples were cast from dilute chloroform solutions onto KBr plates and dried under vacuum at 70°C to remove all traces of the solvent.

Differential Scanning Calorimetry (DSC). Thermal analyses were performed with either a Perkin-Elmer DSC-2 or a DSC-7 over the range of -90–190°C. Indium and cyclohexane were used for temperature calibration. Subambient measurements (-90–20°C) were made under a helium atmosphere using liquid nitrogen to cool the DSC cell. A nitrogen atmosphere and a mechanical cooling accessory were used for measurements from -30 to 190°C. A heating rate of either 10 or 20°C/min and a sample size of about 5–10 mg were used. The glass transition temperatures (T_g) were often difficult to detect for blends with relatively high crystallinity, and in these cases larger samples, 15–20 mg, and a faster heating rate, 40°C/min, were used. T_g was taken as the midpoint of the specific heat change and T_m was defined as the peak in the melting endotherm.

Dynamic Mechanical Analysis (DMA). Dynamic mechanical properties were measured with a Rheometrics System-4 mechanical spectrometer. Compression-molded rectangular bar specimens, 0.7 × 10 × 63 mm, were used for torsion experiments from -120°C to the transition region of the PS-rich phase. Measurements above the PS T_g were made with a parallel plate fixture using disk specimens, 25 mm diameter and about 1 mm thick. A constant frequency of 1 Hz and a heating rate of about 3°C/min were used for all measurements.

RESULTS AND DISCUSSION

For blends of two amorphous polymers, opacity is an indication of immiscibility, while optical clarity is a necessary, but insufficient, indication of mis-

cibility. (Clarity may also result if the refractive indices of the two polymers are similar or if the dispersed phase size is too small to scatter light.) When one of the components is crystallizable, as was the PAODA used in this study, the conclusions to be drawn from sample clarity are even more ambiguous. Opacity of the material may result from crystallization of the crystallizable component, which is not by itself evidence for immiscibility. Many systems have been reported in which the crystallizable component retained the ability to crystallize, but the amorphous fractions of the blended polymers were judged to be miscible.¹⁴ Where crystallization occurs in a miscible polymer blend, the crystallization kinetics generally differ from that of the unblended crystalline material, and the melting point is depressed in a manner similar to that resulting from plasticization of the crystallizable polymer with a low molar mass diluent.¹³ In the present study, thermal and mechanical measurements were used along with visual observations of sample clarity to assess blend miscibility.

Sample Clarity

The relative clarity of the blends of the PAODA and the styrenic polymers is shown by the photographs in Figure 1. The line grid is beneath the sample disks so that the grid becomes more visible as the sample becomes more optically clear. Figure 1(a) shows a series of blends involving the lower molar mass PAODA, ED-900. A blend of 10% ED-900 with polystyrene, i.e., blend PSE9-10, was opaque, which, as will be demonstrated by the DSC and DMA results discussed, was consistent with the fact that these materials were immiscible. A similar blend of ED-900 with 1-SPS, blend 1SE9-10, in which 1.35 mol % sulfonic acid groups were incorporated into the PS, was optically clear. In-

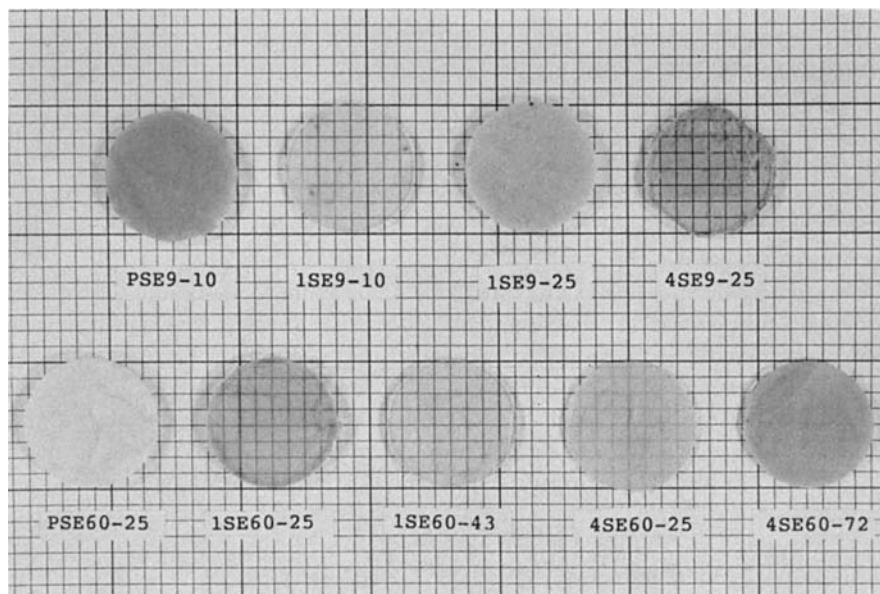


Fig. 1. Optical clarity of SPS/PAODA blends: (a) (top row) with ED-900; (b) (bottom row) with ED-6000; sample notation is explained in the text.

creasing the concentration of ED-900 in a blend with 1-SPS to 25%, sample 1SE9-25, resulted in an opaque material, but then increasing the sulfonation level to 4.51 mol %, i.e., substituting 4-SPS for 1-SPS, again yielded a clear material. It will be shown in the discussion to follow that these latter three blends were one phase, two phase, and one phase, respectively.

The relative clarities of the blends using the higher molar mass PAODA, ED-6000, are shown in Figure 1(b). A blend of 25% ED-6000 with PS, sample PSE60-25, was opaque. Blends with 1-SPS containing 25 and 43% PAODA were clear. 1SE60-43 exhibited a slight haze that is not visible in Figure 1. This may have been due to some crystallinity of the PAODA component, though this was not clearly detected by DSC. In contrast, the blends of 25 and 72% ED-6000 with 4-SPS were translucent and opaque, respectively. The blends with 1-SPS were single-phase systems, while the blends containing PS or 4-SPS formed two-phase, immiscible mixtures.

Thermal Analyses (DSC)

DSC thermograms of the starting materials and the blends are given in Figures 2–5 and the transition temperatures are summarized in Table III. The results for blends of ED-900 with PS are shown in Figure 2. Blend PSE9-10 exhibited two T_g s, which indicated a two-phase morphology. The lower temperature T_g corresponded within experimental error to the T_g of pure ED-900. The T_g of the polystyrene phase, however, was depressed by about 20°C from that of the starting PS, which suggests limited solubility of the ED-900 in the PS. No crystallinity was detected by DSC. This may have been due to depression of the melting point or crystallization rate of the PAODA due to either partial miscibility or a small phase size. The T_m of the starting ED-900 (16°C) was already below room temperature and depression of the crystallization temperature may have precluded crystallization occurring under the experimental conditions used.

TABLE III
Transition Temperatures for PS/PAODA and SPS/PAODA Blends

Sample	T_g (°C)	T_m (°C)
PS	88	
PSE9-10	-58/66	
PSE9-25	-57/76	18
PSE60-25	-46/82	51
1-SPS	91	
1SE9-10	103	
1SE9-25	-61/73	21
1SE60-25	104	
1SE60-43	104	
4-SPS	100	
4SE9-25	78	
4SE60-25	-41/50	57
4SE60-72	-57/92	56

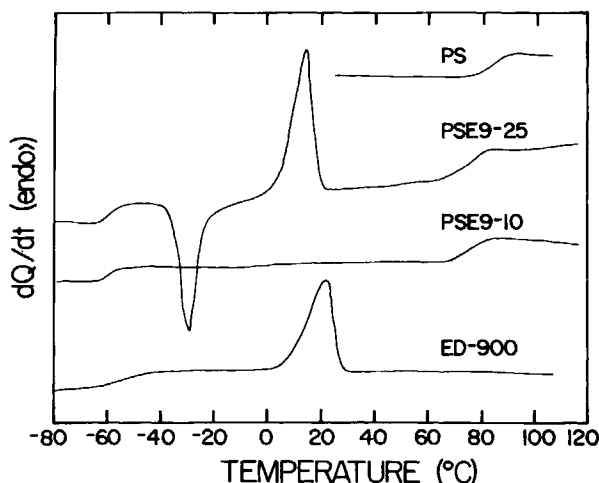


Fig. 2. DSC thermograms of PS, ED-900, and their blends.

PSE9-25 also exhibited two T_g s, with the lower one corresponding to that of the PAODA and the higher one depressed from that of the PS. In this case, the T_g depression was only about 15°C. The crystalline melting transition of the PAODA was observed with this sample, but as evident by the low-temperature exotherm in the DSC thermogram, the material actually crystallized during the heating experiment and not during cooling of the sample from room temperature. Therefore, it appeared that the cooling rates used, 10–20°C/min, were sufficiently rapid to quench the PAODA into an amorphous state.

These results show that ED-900 and PS were immiscible for the blend compositions studied. Since it is well known that PS and PEO form immiscible blends,¹⁵ it is clear that the addition of propylene oxide amine groups to the ends of the PEO chains had no significant influence on the phase behavior of PEO/PS blends. The partial miscibility of the polymers, evident from the depression of the PS T_g , was most likely due to the low molar mass of the PAODA and not any specific interactions between the polymers.

The effect on the DSC thermograms of substituting 1-SPS for PS in blends with ED-900 is shown in Figure 3. Blend 1SE9-10 formed a miscible, single phase system as evident from the single T_g . Interestingly, the T_g was about 10°C higher than that of the neat 1-SPS. This result was surprising in that for a miscible polymer blend, T_g is expected to be intermediate between the T_g s of the individual pure components. A T_g greater than that of either component, however, is not without precedence. For example, Smith et al.¹⁶ observed that the addition of up to 12% PEO to poly(acrylic acid) resulted in an increase in T_g . In that study and in the present one, the increase in T_g may be due to the formation of a network through physical interactions between the two polymers. Since the PAODA were difunctional, proton transfer between the terminal amines on both ends of a PAODA chain with sulfonic acid groups on different SPS chains crosslinks the SPS. Although 1SE9-10 contained an excess of the amine functionality (amine/sulfonic acid = 2.0), there is no reason to believe that this type of physical crosslink did not occur. As will be shown later in this

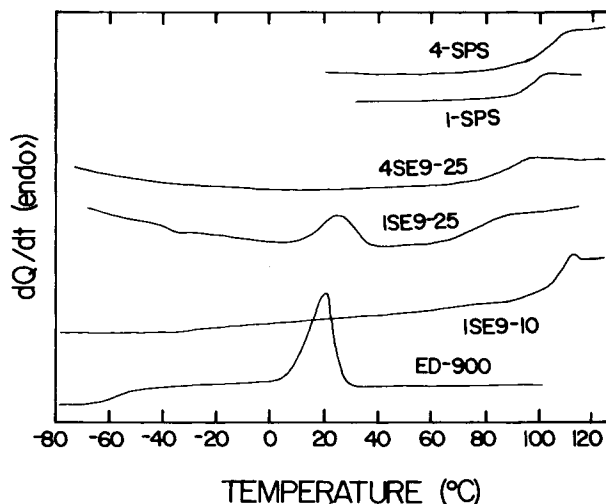


Fig. 3. DSC thermograms of 1-SPS, 4-SPS, ED-900, and their blends.

article, proton transfer in these systems was confirmed by FTIR. As with the blend of ED-900 and PS that contained 10% of the PAODA, no crystallinity was observed in the 1SE9-10. This may be due to a depression of the crystallization kinetics, or more likely, it may be a result of the miscibility of the components, which would change the crystallization behavior of the PAODA.

When the concentration of ED-900 was increased to 25% in a blend with 1-SPS, that is, blend 1SE9-25, two changes were noticeable. First, the blend became opaque and two T_g s were observed. (The lower T_g is not clearly resolved in the DSC thermogram shown in Fig. 3, but it was clear at higher attenuation of the signal.) Second, although the lower temperature T_g was identical with that of the pure ED-900, the higher temperature T_g was depressed about 20°C from that of the pure 1-SPS. Thus, increasing the ED-900 concentration resulted in a two-phase system with a pure PAODA phase dispersed in a matrix of a mixture of 1-SPS and ED-900. However, in progressing from 10% to 25% ED-900, the T_g of the SPS-rich phase decreased by about 30°C. This behavior was unusual in that if phase separation occurred simply as a result of reaching the miscibility limit of the PAODA in SPS, one would expect the temperature of the SPS-rich phase T_g to have been unaffected. It appears, therefore, that the depression of the higher temperature T_g was a consequence of the six-fold excess of amine groups at this concentration, which probably inhibited formation of the physical crosslinks. That is, the lower probability that both ends of a PAODA molecule would react with sulfonic acid groups most likely yielded a branched or comb-like molecular architecture instead of a network.

Holding the ED-900 concentration at about 25%, but increasing the sulfonation level of the SPS to 4.51 mol %, i.e., substituting 4-SPS for 1-SPS, resulted again in a miscible blend, sample 4SE9-25. This blend had only a single T_g and was a clear yellow glass, cf. Figures 1 and 3. In contrast to the miscible blend of 1-SPS and ED-900, sample 1SE9-10, which had a higher T_g than that of either polymer component, the T_g of 4SE9-25 was about 22°C lower than that of 4-SPS. Although the blend compositions were different, both of these blends

had twice the stoichiometric ratio of amine to sulfonic acid groups. As will be discussed, an increase in T_g was observed in other blends involving the PAODA and 1-SPS, but not for blends with 4-SPS. It appears that the explanation is related to the sulfonation level of the SPS, and it is perhaps an influence of the SPS microstructure. Although the PAODA/SPS blends were prepared in solution, infrared and electron spin resonance spectroscopy results have indicated that associations of the sulfonate groups in SPS-salts persist in dilute solution when a relatively low dielectric constant solvent such as THF is used.¹⁷ Comparable evidence for the persistence of hydrogen bonded supramolecular structure in SPS solutions has not been reported. Nevertheless, the strikingly different T_g behavior of PAODA/SPS blends prepared from 1-SPS and 4-SPS suggests that this may have resulted from differences in the distribution, or availability, of the sulfonic acid groups for the two polymers in the THF solutions used to prepare the blends.

Similar improvements in miscibility were observed with blends of the sulfonated polystyrenes and the higher molar mass PAODA, ED-6000. DSC thermograms of ED-6000, PS, and blend PSE60-25 are given in Figure 4. The blend exhibited two T_g s, indicating that the components were immiscible. The lower T_g was somewhat diffuse, which was probably due to the high degree of crystallinity of the PAODA, but it was consistent with the T_g of pure ED-6000. As with the blends of PS and ED-900, the upper T_g was depressed from that of the starting PS, but in this case by only about 8°C. Again, this suggested that some of the PAODA, most likely the lower molar mass fraction, was miscible with the PS. The sharp endotherm for the blend at about 49°C represented the melting transition of crystalline PAODA, which was depressed by about 5°C from the T_m of the pure ED-6000. An unusual result was found for the cooling thermograms of the PSE60-25 in that two exotherms were observed at 30 and 5°C (see curve PSE60-25C in Fig. 4). This may indicate two different environments of the PAODA, which further supports the conclusion of partial miscibility of these polymers.

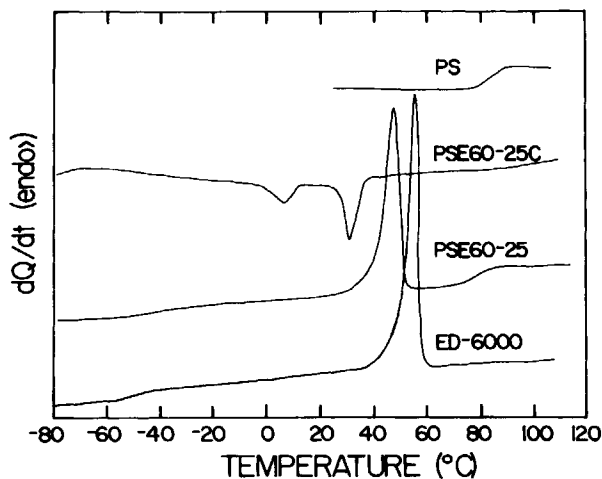


Fig. 4. DSC thermograms of PS, ED-6000, and their blends.

Blends of ED-6000 with 1-SPS containing 25 and 43.5% PAODA, samples 1SE60-25 and 1SE60-43, respectively, exhibited one T_g and no melting transition (Fig. 5). The thermogram of 1SE60-43 was consistently rough with various undulations (see Fig. 5). Although the positions of these "thermal events" were not reproducible, it was not possible to obtain a smooth thermogram. These events may represent small amounts of crystallization and melting, but no reasonable estimate of the amount or the transition temperatures was possible. The sample appeared clear (see Fig. 1), though a slight haze was visible when compared with 1SE60-25. This haze may have been a consequence of minute amounts of crystallinity.

The amine/sulfonic acid ratio was nominally 1 : 1 for 1SE60-25 and 2 : 1 for 1SE60-43. For both blends the T_g was higher than that of either pure component, about 10°C above that of 1-SPS. As with blend 1SE9-10, it appeared that the PAODA molecules acted as crosslinks. The T_g s of all three blends, 1SE9-10, 1SE60-25, and 1SE60-43, were essentially identical, which indicated equivalent crosslink densities. This is somewhat surprising in that one expects that the acid-base reaction between the terminal amine groups of the PAODA and the sulfonic acid groups of SPS should proceed randomly. When the amine/sulfonic acid ratio is greater than one, the blend may contain some PAODA chains in which both amine groups have reacted, others in which only one has reacted, and still others in which neither have reacted. On the other hand, when a stoichiometric amount of the two functional species are used, all the amine groups should react. Only chains in which both amine groups have reacted can function as crosslinks, and then only if the terminal groups react with sulfonic acid groups on different chains. Intuitively, one would not expect the concentration of PAODA crosslinks to be the same when different amine/sulfonic acid ratios were used. Therefore, the T_g results for the three miscible blends based on 1-SPS raise an interesting, though unanswered, question as to the origin of the T_g rise and/or the distribution of the reacted amine groups.

The miscibility and T_g behavior of the blends of ED-6000 with 1-SPS and 4-SPS were very different. The mixture of 27% ED-6000 and 73% 4-SPS, sample

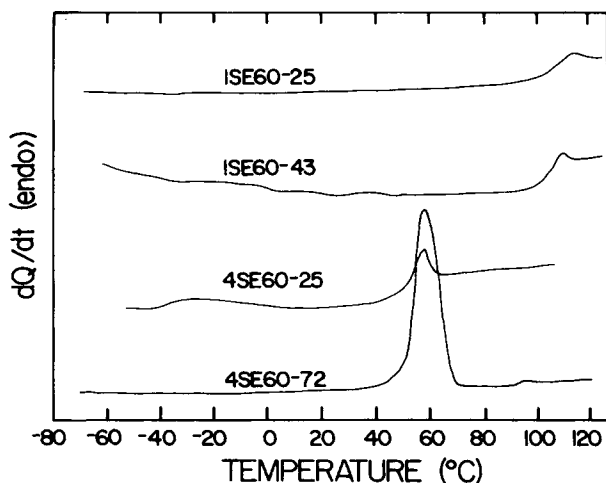


Fig. 5. DSC thermograms of blends of ED-6000 with 1-SPS and 4-SPS.

4SE60-25, was translucent (Fig. 1) and formed an immiscible system as evident by the two T_g s at -41 and 50°C (Fig. 5). A small crystalline melting endotherm was superimposed on the higher T_g , with the peak position at 57°C , which was comparable to that of the pure ED-6000. The immiscibility result was surprising in view of the improvement in miscibility that was observed in the ED-900 containing blends when the sulfonation level was increased. These data do, however, support the conclusion of a fundamental difference in the effect of the acid-base interaction or the availability of the sulfonic acid groups for complexation in the two ionomers.

For 4SE60-25, the amine/sulfonic acid ratio was only 0.26 : 1. Whereas the addition of 25% ED-6000 to 1-SPS raised the T_g by 13°C , the T_g of 4SE60-25 was 46°C lower than that of 4-SPS. Because of the relatively low amine/sulfonic acid ratio for this blend, the probability of forming an effective network was low. The large depression of the higher T_g indicated that although a two-phase system was formed, there was considerable mixing of the PAODA in the styrene-rich phase. This conclusion of a relatively high degree of phase mixing was also supported by the fact that this material was translucent rather than opaque (see Fig. 1).

When the amine/sulfonic acid ratio was raised to 2 : 1 for a blend of ED-6000 and 4-SPS, sample 4SE60-72, a poorly resolved T_g at about -60°C , a broad melting transition centered at 56°C , and a second T_g at about 92°C were observed by DSC. Because of the high degree of crystallinity of this sample, the T_g s were difficult to detect. The facts that this material was opaque and had two T_g s, however, indicated that this material was phase separated.

Dynamic Mechanical Analyses (DMA)

A limited check on the conclusions drawn from the DSC experiments was made using DMA. Because this technique probes molecular motions of local segments of the chain, it is somewhat more sensitive than DSC at detecting the existence of small domains. Dynamic storage and loss moduli as a function of temperature are given for blends PSE9-10 and 1SE9-10 in Figure 6 and for blends PSE60-25 and 1SE60-25 in Figure 7. The blends with PS exhibited two T_g s and the blends with 1-SPS exhibited only a single T_g , which confirmed the

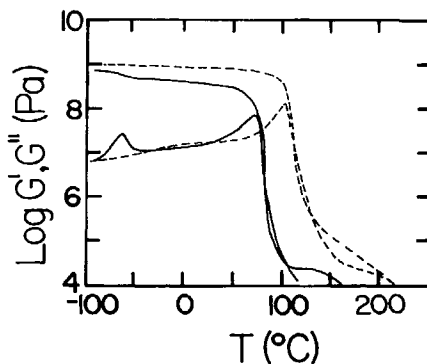


Fig. 6. $\log G'$ and $\log G''$ versus temperature for (—) PSE9-10 and (---) 1SE9-10.

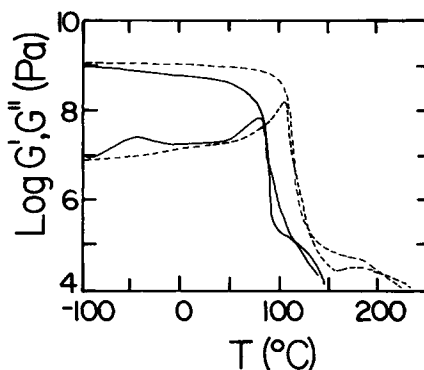


Fig. 7. $\log G'$ and $\log G''$ versus temperature for (—) PSE60-25 and (---) 1SE60-25.

conclusions regarding miscibility discussed previously. Like the DSC data, the DMA results gave a T_g for the blends containing 1-SPS that was higher than the T_g of either component.

Origin of Miscibility

Specific intermolecular interactions were responsible for the miscibility of these blends. Two interactions were possible: (1) proton transfer from the basic amino-terminal group of the PAODA to the acidic sulfonic acid group of the

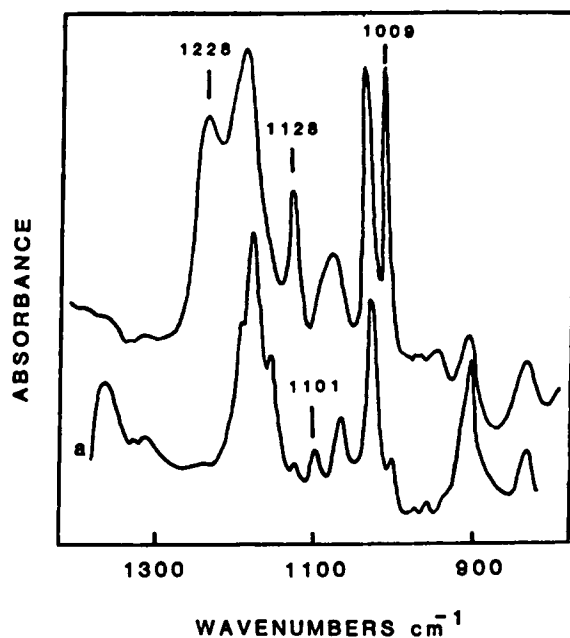


Fig. 8. FTIR spectra of (a) 4-SPS and (b) difference spectrum of a blend of 77% 4-SPS/23% ED-900 minus ED-900, scaled to remove the characteristic CH bending absorptions. Reprinted from Ref. 18 with permission.

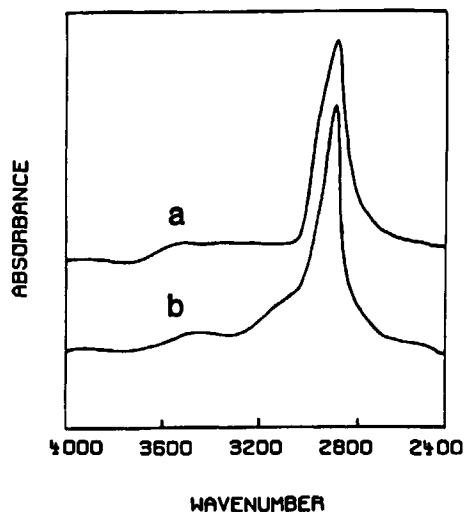


Fig. 9. FTIR spectra of (a) ED-900 and (b) difference spectrum of a blend of 77% 4-SPS/23% ED-900 minus 4-SPS.

modified polystyrene and (2) hydrogen bonding between the ether oxygens of the PAODA and the sulfonic acid groups. Figure 8 shows the 1400–800 cm^{-1} FTIR spectral region for 4-SPS and the difference spectrum for a blend of 23% ED-900 and 77% 4-SPS minus the ED-900 contribution. The difference spectrum represents the sum of the SPS contribution to the blend spectrum plus any changes due to interactions of the components. Salt formation in the blend was confirmed by the disappearances of the 1101 cm^{-1} absorption characteristic of the sulfonic acid groups and the appearance of strong absorptions at 1009, 1128, and 1228 cm^{-1} characteristic of the sulfonate salt.¹⁸ Figure 9 shows the 4000–2200 cm^{-1} FTIR spectra of ED-900 and the difference spectrum for the blend minus the 4-SPS. This difference spectrum gives the sum of the PAODA contribution and any changes associated with interactions. The broad absorption at ca. 3050 cm^{-1} was due to the N–H stretching mode of the amine salt. The higher frequency absorption at ca. 3450 cm^{-1} was due to absorbed water.¹⁸

Attempts to determine shifts of the sulfonic acid absorbances due to hydrogen bonding were not successful, largely because of the relatively low concentration of these groups and the interference of styrene absorbances in the same spectral regions. In addition, even qualitative assessments of hydrogen bonding in lightly sulfonated polystyrene was hindered by the complexity of the IR spectra of these polymers.¹⁹ In the “dry” bulk state, the absorption bands due to styrene sulfonic acid were broad, and multi-peaked absorptions were often observed. This probably arose from the difficulty in removing all water from these materials, even at elevated temperatures under vacuum. In addition, aggregation of the sulfonic acid groups is known to occur in the neat material,²⁰ and this is believed to result from hydrogen bonding. Thus, the starting SPS polymers probably already contained a finite concentration of sulfonic acid groups that were hydrogen bonded by water and other sulfonic acid groups.

CONCLUSIONS

It has been shown that miscible blends of what are essentially poly(ethylene oxide) oligomers and polystyrene may be prepared by introducing specific interacting functional groups on the two chains. In this case, the polystyrene was randomly functionalized with sulfonic acid groups attached to the phenyl ring. The poly(alkylene oxide) was end terminated by amino-propylene oxide groups. Miscibility resulted at least in part from proton transfer from the sulfonic acid to the amine end groups. Distinctive, though as yet unexplained, differences were observed in the miscibility and T_g behaviors of the blends prepared from two different levels of substitution for the sulfonated polystyrene. It was suggested that these differences might be a result of differences in the aggregation of the sulfonic acid groups in the solutions used to prepare the blends.

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References

1. N. Yoshimura and K. Fujimoyo, *Rubber Chem. Tech.*, **42**, 1009 (1968).
2. F. Cangelosi and M. T. Shaw, *Polym. Plast. Tech. Eng.*, **21**, 13 (1983).
3. E. M. Woo, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **28**, 1347 (1983).
4. A. L. Zhou and A. Eisenberg, *J. Polym. Sci. Polym. Let. Ed.*, **21**, 223 (1983).
5. M. Hara and A. Eisenberg, *Macromolecules*, **17**, 1335 (1984).
6. N. Ohno and J. Kumanotani, *Polym. J.*, **11**, 947 (1979).
7. A. Sen and R. A. Weiss, *Polym. Preprints*, **28**(2), 220 (1987).
8. L. H. Sperling, D. W. Taylor, M. L. Kirkpatrick, H. F. George, and D. R. Bardman, *J. Appl. Polym. Sci.*, **14**, 73 (1970).
9. J. Horrian, R. Jerome, and P. Teyssie, *J. Polym. Sci. Part C Polym. Let.*, **24**, 69 (1986).
10. R. Jerome, personal communication.
11. A. Sen, R. A. Weiss, and A. Garton, in *Multiphase Polymers: Blends and Ionomers*, R. A. Weiss and L. A. Utracki, Eds., ACS Symp. Ser., Amer. Chem. Soc., Washington, DC, to appear.
12. H. S. Makowski, R. D. Lundberg, and G. H. Singhal, U.S. Pat. 3,870,841 (1975), assigned to Exxon Res. and Eng. Co.
13. B. Wunderlich, *Macromolecular Physics*, Academic Press, New York, 1980, Vol. 3.
14. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979.
15. S. Krause, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978, Vol. 1, Chap. 2.
16. K. L. Smith, A. E. Winslow, and D. E. Petersen, *Ind. Eng. Chem.*, **51**, 1361 (1959).
17. J. J. Fitzgerald and R. A. Weiss, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, **C28**(1), 99 (1988).
18. A. Garton, S. Wang, and R. A. Weiss, *J. Polym. Sci. Polym. Phys. Ed.*, **26**, 1545 (1988).
19. J. J. Fitzgerald and R. A. Weiss, *Columbic Interactions in Macromolecular Systems*, ACS Symp. Ser. **302**, Amer. Chem. Soc., Washington, DC, 1986, p. 35.
20. R. A. Weiss and J. A. Lefelar, *Polymer*, **27**, 3 (1986).

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