

# Development of Miscible Blends of Bisphenol A Polycarbonate and Lightly Sulfonated Polystyrene Ionomers from *Intrapolymer* Repulsive Interactions

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**ABSTRACT:** Differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the phase behavior and interactions of blends of the free acid derivative and lithium and sodium salts of lightly sulfonated polystyrene (MSPS) with Bisphenol A polycarbonate (PC). The blends exhibited upper critical solution temperature (UCST) phase behavior and a miscibility window with respect to the sulfonation level. At a fixed blend composition, a minimum in the cloud point temperature occurs at the sulfonation level marking the middle of the miscibility window. The miscibility window depended on the sulfonate cation used. No interactions involving either the carbonate carbonyl group or the sulfonate groups were detected for any of the blends. Miscibility was attributed to intramolecular repulsive interactions within the ionomer.

## Introduction

A requirement for achieving miscibility of a mixture is that the free energy of mixing,  $\Delta G_m$ , be zero or negative. Because the combinatorial entropy of mixing for high molecular weight polymers is very small, it is often thought that a negative enthalpy of mixing, i.e., exothermic intermolecular interactions, is necessary for attaining a homogeneous mixture. Various strategies for promoting exothermic interactions in binary polymer blends have been commonly employed. These include the development of attractive interactions by hydrogen bonding,<sup>1,2</sup> proton transfer,<sup>3</sup> charge-transfer,<sup>4</sup> transition metal complexation,<sup>5</sup> and ion–dipole interactions.<sup>6</sup> A second, relatively unexploited approach for attaining miscibility in the absence of specific attractive interactions is to employ intrapolymer repulsive interactions of the different species in a random copolymer.<sup>7–10</sup> In that case, miscibility of the copolymer with another homopolymer usually occurs only for a narrow composition range of the copolymer. In essence, the “copolymer” approach to achieving miscibility uses the small, but finite, entropy of mixing to balance the dispersive interactions between the two polymers.

Ionomers are particularly attractive molecules for promoting miscibility with a wide range of other polymers. On the one hand, the ionic functional group may be used to achieve specific attractive interactions with complementary functional groups on another polymer, e.g., hydrogen bonding, ion–dipole, or transition metal complexation. On the other hand, the strong repulsive interactions between the ionic and nonionic species of the ionomer, which is a random copolymer, suggest that charged polymers may mix with other polymers through a “copolymer” effect.

Polystyrene-based ionomers have been very effective at producing new miscible blends. Examples include styrene–methacrylic acid/poly(alkylene oxide),<sup>11,12</sup> SPS/ethyl acrylate–vinylpyridine copolymer,<sup>13</sup> SPS/polyamide,<sup>14–18</sup> SPS/polyurethane,<sup>19</sup> SPS/polypeptide,<sup>20</sup> and SPS/polycarbonate.<sup>21</sup> With the exception of the last system, in all the previous blend studies with polysty-

rene ionomers miscibility was attributed to specific interactions between the ionic groups of the ionomer and polar groups on the other polymer. One prominent advantage of this approach is that the strength of the specific interactions and, as a result, the phase behavior of the blend can be tailored by varying the acid group, the level of functionality, or the counterion used.<sup>22</sup>

Relatively little effort has been made to employ the repulsive interactions between the ionic and nonionic groups in an ionomer to promote miscibility with another polymer. Although repulsive interactions in copolymers containing polar and nonpolar groups have been used for achieving miscibility of nonionic blends, the interactions between the ionic and nonionic species in an ionomer are expected to be much stronger than what is usually observed in other common copolymers. In fact, the repulsive intramolecule interactions in ionomers are the major driving force for microphase separation of ionic aggregates in ionomers.<sup>23</sup> The intensity of these repulsive forces and the possibility of controlling them by judicious choice of their concentration and/or the counterion used suggest that intrapolymer repulsive interactions of an ionomer may be an especially effective method for achieving miscibility of polymer blends or promoting compatibilization of binary or ternary mixtures.

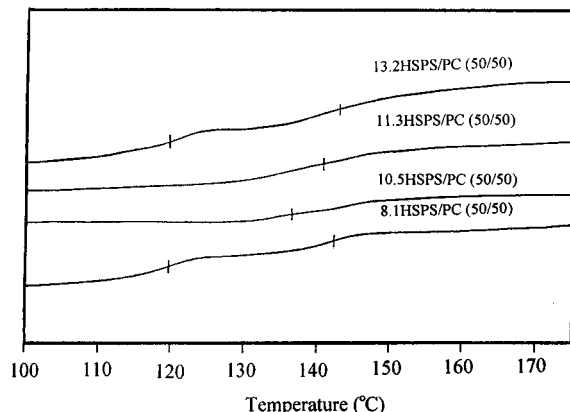
In a previous communication,<sup>21</sup> we reported that blends of lightly sulfonated polystyrene ionomer (SPS) and Bisphenol A polycarbonate (PC) were miscible for a narrow range of the sulfonation of the ionomer. In the present paper, we provide a more complete description of the miscibility and interactions between SPS and PC as a function of temperature, the extent of sulfonation, and the cation used. Infrared spectroscopy was used to look for specific interactions that may occur between the two polymers.

## Experimental Details

**Materials.** SPS was prepared by solution sulfonation of polystyrene with acetyl sulfate following the procedure of Makowski et al.<sup>24</sup> This method substitutes a sulfonic acid group at the para-position of the phenyl ring, and sulfonation is random along the chain. The molecular weights determined by gel permeation chromatography (GPC) were  $M_n = 100\,000$  and  $M_w = 280\,000$ . The sulfonation level was determined by titration of the sulfonic acid derivative, HSPS, in a mixed

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**Figure 1.** DSC heating thermograms of 50/50 blends of  $x,y$ -HSPS/PC blends annealed at 170 °C.

solution of toluene/methanol (90/10 v/v) with methanolic sodium hydroxide. The lithium and sodium salts of SPS were prepared by neutralizing a solution of HSPS with the appropriate metal hydroxide. The nomenclature used for the ionomers was  $x,y$ -MSPS, where  $x,y$  and M denote the sulfonation level in mol % of styrenes substituted and the cation, respectively. Bisphenol A polycarbonate (PC) was obtained from General Electric Co. and had a  $M_n = 48\,000$ .

**Blend Preparation.** Blends with various compositions were prepared by adding a 4% (w/v) PC solution in tetrahydrofuran (THF) dropwise to a stirred 4% solution of MSPS in a mixture of THF and methanol (90/10, v/v). Blend samples for thermal analysis were obtained by casting the blend solutions at 60 °C and drying under vacuum at 100 °C for 1 day. Thin films of the blends for Fourier transform infrared spectroscopy (FTIR) measurements were prepared by casting ~1% solutions onto glass plates at 60 °C and drying in a vacuum oven at 100 °C for 1 day.

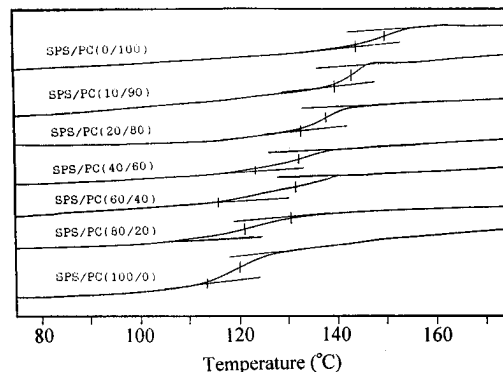
**Differential Scanning Calorimetry (DSC) Analysis.** Glass transition temperatures ( $T_g$ ) were measured with a Perkin-Elmer DSC-7. The samples were first held at 170 °C for 1 h and then quickly quenched to 0 °C before the DSC scan was run at 20 °C/min.  $T_g$  was defined as the midpoint of the change in the heat capacity at the transition.

Miscibility of the blends at various temperatures was assessed by annealing the blend at the desired temperature for 20–60 min (a shorter annealing time was used as the temperature increased) and quenching rapidly to 0 °C before running the DSC scan. The cooling rate was assumed to be fast enough so that the subsequent heating thermogram represented the morphology of the blend at the annealing temperature. The blend was considered to be miscible at the annealing temperature if the subsequent heating thermogram exhibited a single  $T_g$  and phase-separated if the thermogram showed two  $T_g$ 's.

**FTIR Analysis.** FTIR spectra were measured with a Nicolet Model 60SX spectrometer with a resolution of 1  $\text{cm}^{-1}$ . A total of 256 scans were signal averaged for each spectrum. The films for FTIR analysis were thin enough to be within the absorbance range where the Beer–Lambert law was obeyed.

## Results and Discussion

**Miscibility of HSPS and PC.** Representative DSC thermograms for 50/50 HSPS/PC blends as a function of the degree of sulfonation of the HSPS are shown in Figure 1. The samples were first annealed at 170 °C under nitrogen for 1 h to eliminate any possible effect of the solvent used and were then quenched rapidly to 0 °C before recording the DSC thermograms. It was assumed that the cooling of the sample was rapid enough to preserve the equilibrium blend morphology at the annealing temperature, so that the thermograms in Figure 1 represent the phase behavior of the blends at 170 °C. The data indicate that the 50/50 HSPS/PC blends exhibit a narrow *miscibility window* between



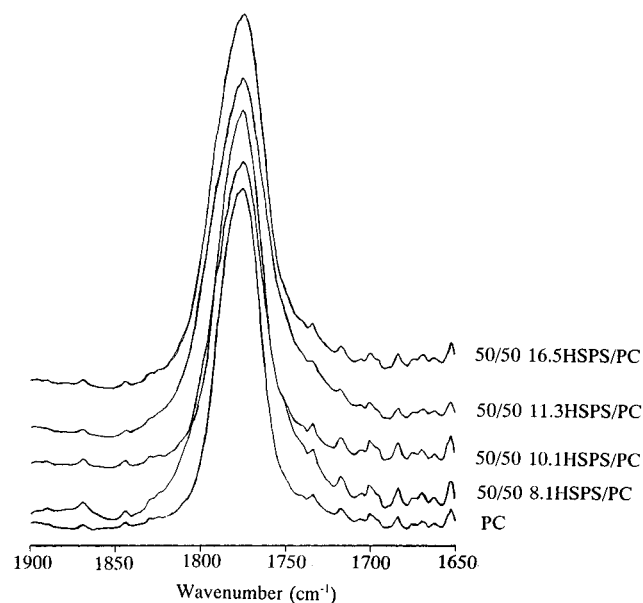
**Figure 2.** DSC heating thermograms of 11.3-HSPS/PC blends annealed at 170 °C.

10.1 and 11.3 mol % sulfonation. At lower or higher sulfonation levels, the 50/50 blends were immiscible, as evident from the two  $T_g$ 's and the fact that they were cloudy in appearance. The turbidity of the immiscible blends is noteworthy in that the refractive index difference between PS and PC is too small to detect cloudiness in an immiscible blend. Sulfonation of the PS sufficiently enhanced the difference in the refractive indices so that turbidity was observed.

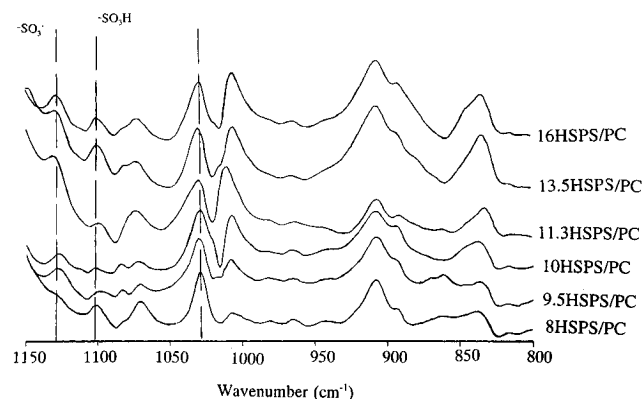
Figure 2 shows the composition dependence of the DSC thermograms for 11.3-HSPS/PC blends annealed at 170 °C. The blends exhibit a single composition-dependent  $T_g$  over the entire composition range. Similar data were obtained for 10.1-HSPS/PC blends. These results indicate that the HSPS/PC blends are miscible at all compositions at 170 °C when the sulfonation level of the HSPS is within the range of 10.1–11.3 mol %.

The miscibility window indicated by Figure 1 is rather narrow, which is often the case for homopolymer/copolymer blends in which no specific attractive interaction occurs between the two polymers. The mechanism of miscibility in this case is generally attributed to the repulsive forces between dissimilar groups in the random copolymer, sometimes called the *copolymer effect*.<sup>7–9</sup> The behavior of the HSPS/PC blends is distinct from other blends containing SPS ionomers, where enhanced miscibility arises from hydrogen bonding interactions.<sup>14,19,22</sup> For the latter systems, miscibility usually increases as the sulfonation level increases. That is, miscibility is favored by increasing the concentration of interacting functional groups. To understand the phase behavior of the HSPS/PC blend, it is essential to know which type of interaction, intrapolymer repulsive or interpolymer attractive interaction, is primarily responsible for the miscibility enhancement.

If specific attractive interactions occur between HSPS and PC, the most likely candidate is hydrogen bonding between the carbonate carbonyl groups of PC and the sulfonic acid groups of HSPS, i.e.,  $-\text{C}=\text{O}\cdots\text{H}-\text{OO}_2\text{S}-$ . FTIR measurements were used in an attempt to identify this interaction. Figure 3 shows the FTIR spectra in the carbonyl stretching region, 1900–1650  $\text{cm}^{-1}$ , for the pure PC and 50/50 HSPS/PC blends with different sulfonation levels. The absorption at 1775  $\text{cm}^{-1}$  is due to the stretching vibration of the carbonate carbonyl group, and its position is known to be sensitive to specific interactions involving that group.<sup>1</sup> No change of either the position or the band width of the C=O band for the blends compared with that for the pure PC was observed over the sulfonation range from 8.1 to 16 mol %, which includes both miscible and immiscible blends. This result indicates that the miscibility observed in the DSC experiments does not arise from an interaction involving the carbonate carbonyl group.



**Figure 3.** FTIR spectra of the carbonate carbonyl stretching region of 50/50 *x,y*-HSPS/PC blends.



**Figure 4.** Double difference (blend - PS - PC) FTIR spectra of the sulfonate stretching region of 50/50 *x,y*-HSPS/PC blends.

A similar result was obtained from the examination of the carbonate carbonyl band as a function of the composition for the 10.1-HSPS/PC blends. DSC indicated that the 10.1-HSPS/PC blends were miscible over the entire composition region, but the carbonate carbonyl infrared absorption band was insensitive to the addition of 10.1-HSPS. These FTIR results lead us to conclude that any specific interactions involving the carbonate carbonyl group are, at best, extremely weak, and intrapolymer repulsive interactions represent a more plausible explanation for miscibility of HSPS/PC blends.

Additional evidence to support the above conclusion is provided by the FTIR spectra in Figure 4, which show the absorption region characteristic for the sulfonic acid group, 800–1150  $\text{cm}^{-1}$ , for a series of 50/50 HSPS/PC blends with sulfonation levels ranging from 8 to 16 mol %. To isolate the bands due to the sulfonic acid groups and to remove any interference of bands arising from polystyrene (PS) and PC in this region, the double difference spectra (blend - PS - PC) were calculated and are shown in Figure 4. A complete description of the sulfonate absorbances for fully sulfonated polystyrene and the effects of specific interactions on those bands is given by Zundel.<sup>25</sup> Absorption bands at 1034, 1127, and 1192  $\text{cm}^{-1}$  are associated with the sulfonate anion,  $-\text{SO}_3^-$ , and are sensitive to interactions of the sulfonate with its environment, e.g., hydration by moisture<sup>25</sup> or

hydrogen bonding by a second component in a polymer blend.<sup>26</sup> Bands at 900, 1097, and 1360  $\text{cm}^{-1}$  arise specifically from the sulfonic acid group,  $-\text{SO}_3\text{H}$ . Any interaction that polarizes the acid proton will decrease the intensity of the sulfonic acid bands and increase the sulfonate anion absorbances. For example, the addition of a polyamide, which strongly hydrogen bonds with the sulfonic acid groups, causes a complete disappearance of the sulfonic acid absorbances in HSPS ionomers.<sup>27</sup> It is clear from the data in Figure 4 that the addition of PC has no influence on the sulfonate and sulfonic acid absorbances in HSPS, which further supports our contention that no specific intermolecular interaction occurs between HSPS and PC and miscibility results from the strong repulsive interactions between the styrenesulfonic acid and styrene groups within the ionomer.

When only weak dispersion forces occur between a copolymer and a homopolymer, the intramolecular repulsion models<sup>7–9</sup> reduce to an equation relating the  $\chi$  interaction parameter to the Hildebrand solubility parameter.<sup>1</sup> For the HSPS/PC blends,

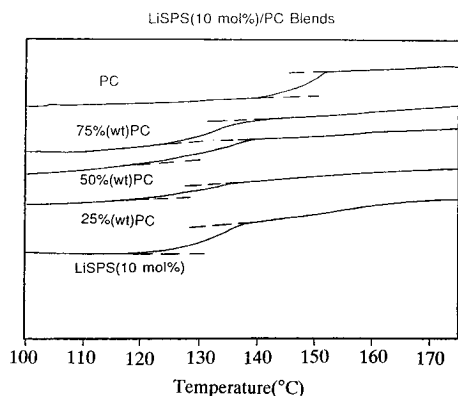
$$\chi = V_r[\delta_{\text{pc}} - \delta_{\text{sps}}]^2/RT \quad (1)$$

$$\delta_{\text{sps}} = f_s\delta_s + (1 - f_s)\delta_{\text{ps}} \quad (2)$$

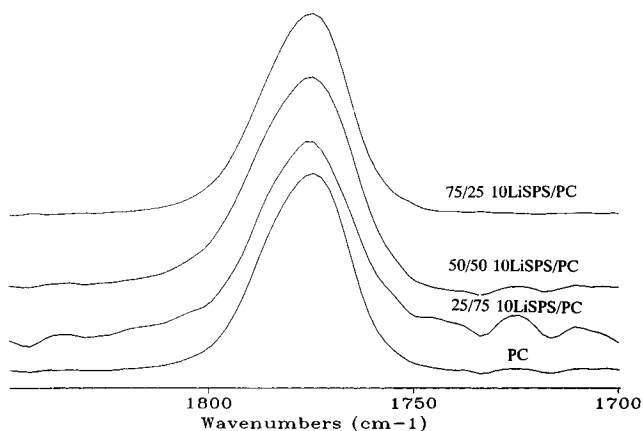
where  $\delta_{\text{pc}}$ ,  $\delta_s$ , and  $\delta_{\text{ps}}$  are the solubility parameters for PC, fully sulfonated PS, and PS,  $f_s$  is the volume fraction of the sulfonated styrene monomer in HSPS, and  $V_r$  and  $T$  are the reference volume and temperature. The solubility parameters of PS and PC from the literature<sup>27</sup> are  $\delta_{\text{pc}} = 9.9$  ( $\text{cal}/\text{cm}^3$ )<sup>0.5</sup> and  $\delta_{\text{ps}} = 9.1$  ( $\text{cal}/\text{cm}^3$ )<sup>0.5</sup>. A value for  $\delta_s$  was not found in the literature, but it was estimated by assuming that  $\chi$  was a minimum, i.e.,  $\chi = 0$ , at the sulfonic acid concentration in the middle of the observed miscibility window. Then, according to eq 1,  $\delta_{\text{pc}} = \delta_{\text{sps}}$  and from eq 2,  $\delta_s = \sim 16.6$  ( $\text{cal}/\text{cm}^3$ )<sup>0.5</sup>. In the absence of attractive specific interactions, the miscibility of HSPS and PC generally requires that  $[\delta_{\text{pc}} - \delta_{\text{sps}}]^2 \leq 0.01$  for high molecular weight polymers. Substitution of this requirement into eqs 1 and 2 provides an estimate of the range of sulfonation of 9.0–12.0 mol % required for miscibility of HSPS/PC, which, considering the assumptions made, is in reasonable agreement with the experimental result of 10.1–11.3 mol %.

The solubility parameter of the HSPS ionomer can vary between the values for polystyrene and fully sulfonated polystyrene, i.e., 9.1–16.6 ( $\text{cal}/\text{cm}^3$ )<sup>0.5</sup>, by varying the degree of sulfonation. This wide range of solubility parameters encompasses the values for most polar polymers, e.g., polyesters, polyamides, polyethers, polysulfones, and polyacrylates, and suggests that SPS ionomers may be particularly effective for achieving miscibility via the *copolymer effect* with a variety of polymers even when no specific attractive interactions occur. That is, one may tailor-make the ionomer needed for a miscible blend by choosing the appropriate sulfonation level required to match the solubility parameter of the other polymer. Although such a strategy can be employed, in principle, by varying the composition of any copolymer, the range of solubility parameters that may be achieved with SPS is unusually broad. In addition, further adjustments in the solubility parameter of SPS may be possible by neutralizing the sulfonic acid and varying the cation.

**Miscibility of PC with LiSPS and NaSPS.** Previous studies<sup>11–21</sup> showed that miscibility of an ionomer with another polymer is often very sensitive to the counterion chosen for the ionomer if the miscibility is completely or partially due to specific attractive interac-



**Figure 5.** DSC heating thermograms of 10.1-LiSPS/PC blends annealed at 170 °C.



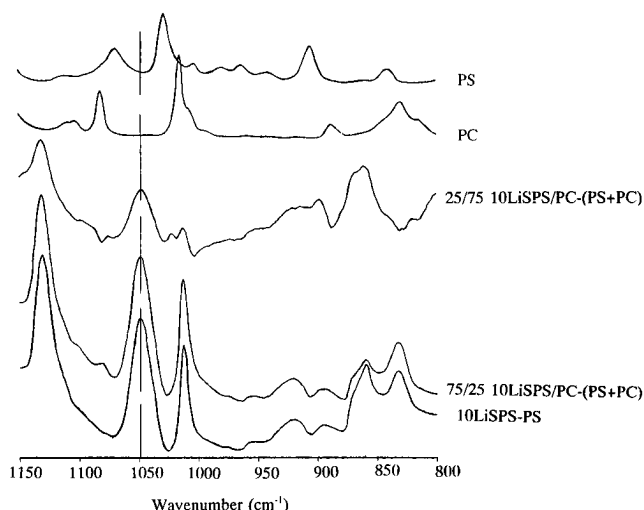
**Figure 6.** FTIR spectra of the carbonate carbonyl stretching region of 10.1-LiSPS/PC blends.

tions. Some metal cations such as  $\text{Li}^+$  are well-known to complex with carbonyl oxygen in small molecule mixtures or in polymer blends.<sup>28</sup> To assess specific ion effects on the phase behavior of SPS/PC blends, blends of LiSPS and NaSPS with PC were investigated.

Figure 5 shows the DSC thermograms for 10.1-LiSPS/PC blends annealed at 170 °C as a function of composition. A single composition-dependent  $T_g$  was observed for all the blends, indicating that the two polymers were miscible at 170 °C. As with the HSPS/PC system, a narrow miscibility window was observed for LiSPS/PC as the sulfonation level was varied. For 50/50 blends at 170 °C, the miscibility window covered a range of sulfonation of 8.1–13.5 mol %, which is slightly wider than that for the HSPS/PC blends.

Infrared spectra for the carbonyl stretching region of PC and three 10.1-LiSPS/PC blends are shown in Figure 6. The peak position and shape of the  $\text{C=O}$  stretching band for the PC at 1775  $\text{cm}^{-1}$  did not change upon the addition of 10.1-LiSPS, which indicates little or no interaction between the carbonate carbonyl and the  $\text{Li}^+$ –sulfonate groups. In blends of LiSPS with polyamides<sup>28</sup> and poly(ethylene oxide),<sup>26</sup> relatively strong ion–dipole interactions were observed between the  $\text{Li}^+$  ion and the oxygen of the amide carbonyl and the ether, respectively. It is not apparent why  $\text{Li}^+$  and the carbonyl oxygen of the carbonate did not interact, but this may be a consequence of the symmetry and a more stable resonance structure of the carbonate group ( $\text{—O—C(O)—O—}$ ).

The lack of a specific interaction between LiSPS and PC was also confirmed by comparison of the anion symmetric stretching vibrations of the 10.1-LiSPS/PC blends with the neat ionomer, Figure 7. The  $\text{—S—O—}$

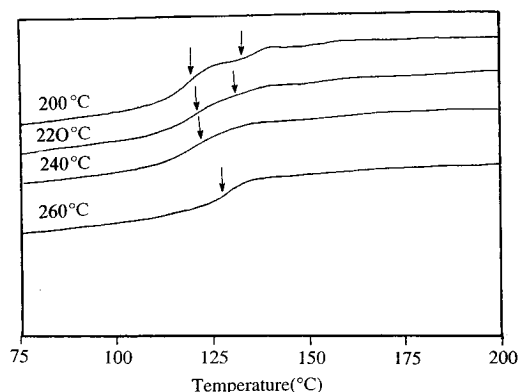


**Figure 7.** Double difference (blend - PS - PC) FTIR spectra of the sulfonate stretching region of 10.1-LiSPS/PC blends.

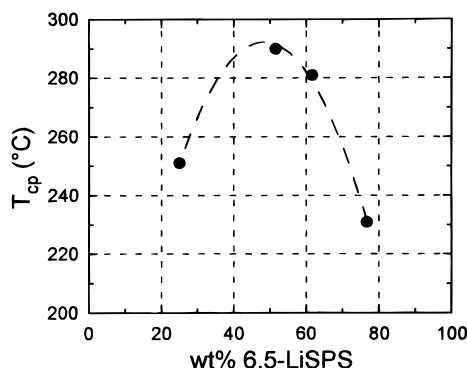
symmetric stretching band of the sulfonate anion appears at  $\sim 1059 \text{ cm}^{-1}$ . The position of this band is very sensitive to the local environment of the sulfonate anion, and any weakening of the anion–cation interaction, such as would occur if the  $\text{Li}^+$  complexed with the carbonate group, would shift the anion symmetric stretching vibration to a lower frequency.<sup>25</sup> That result is what is observed when LiSPS is mixed with a polyamide,<sup>23</sup> but the addition of PC had no effect on this vibration. This result confirms the absence of an interpolymer interaction, and it, again, leads us to believe that miscibility between 10.1-LiSPS and PC arises from intrapolymer repulsive interactions within the ionomer.

The metal salts of the neat SPS ionomers usually exhibit microphase separation of the ionic species. The evidence for this is a broad peak observed in small angle X-ray scattering (SAXS).<sup>29</sup> When a strong specific interaction occurs between the two polymers, such as in blends of an SPS ionomer with a polyamide, the microphase separation is disrupted by solvation of the sulfonate groups by the polyamide. In that case, the SAXS peak disappears.<sup>15</sup> For an ionomer blend involving weak or no specific interactions, such as between a ZnSPS ionomer and poly(2,6-dimethylphenylene oxide) (PPO), ionic aggregation persists even in a miscible blend.<sup>30</sup> SAXS experiments were not done for the LiSPS/PC blends, but the insensitivity of the infrared stretching vibrations of the sulfonate groups to the addition of PC suggests that the microphase separation in the ionomer also persists in these blends.

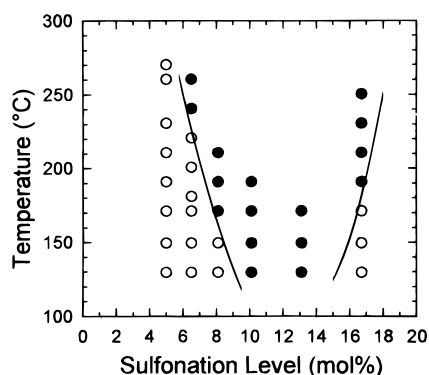
An athermal blend described by eq 1 is expected to exhibit upper critical solution temperature (UCST) behavior. The liquid–liquid phase separation temperature for the LiSPS/PC blends was determined as a function of blend composition and sulfonation level using DSC analysis. Samples were first annealed at an elevated temperature and then quenched to 0 °C prior to running a DSC scan. If the subsequent thermogram showed one  $T_g$ , the blend was presumed to be miscible at the annealing temperature and immiscible if two  $T_g$ 's were observed. Figure 8 shows the DSC thermograms for the 75/25 6.5-LiSPS/PC blend annealed at four different temperatures. The blend was miscible above 240 °C, but immiscible below 220 °C, which indicates that a UCST-type phase boundary exists somewhere between 220 and 240 °C. Similar DSC data were collected for several other compositions, and a phase



**Figure 8.** DSC heating thermograms of a (75/25) 6.5-LiSPS/PC blend annealed at 200, 220, 240, and 260 °C.



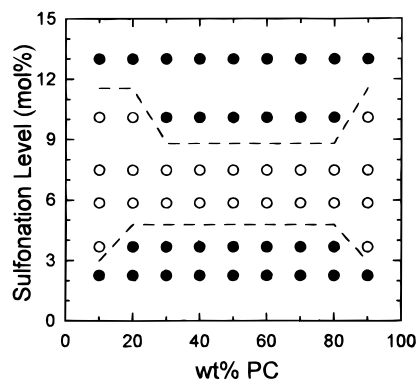
**Figure 9.** Cloud point vs composition for 6.5-LiSPS/PC blends.



**Figure 10.** Temperature vs sulfonation level miscibility map for (75/25) LiSPS/PC blends. The open circles denote immiscible blends; the filled circles denote miscible blends. The dotted line represents the locus of phase separation temperatures.

diagram constructed from that data is given in Figure 9. The points in Figure 9 correspond to the middle of the temperature interval between the highest temperature for which two-phase behavior was observed by DSC and the lowest temperature for which single-phase behavior was found. The uncertainty in the liquid-liquid phase boundary in Figure 9 is  $\pm 10$  °C. The observation of UCST-type phase behavior and a miscibility window is relatively rare with polymer blends. One other system that exhibits these characteristics is a blend of poly(styrene-*co*-methacrylic acid) and PC,<sup>31</sup> which is very similar to the present blend.

The phase boundary was also dependent upon the sulfonation level of the SPS. Figure 10 shows a miscibility map for 75/25 LiSPS/PC mixtures. The open points in Figure 10 denote DSC scans exhibiting two  $T_g$ 's, and the filled points represent a scan showing only a single  $T_g$ . The solid line represents the locus of phase



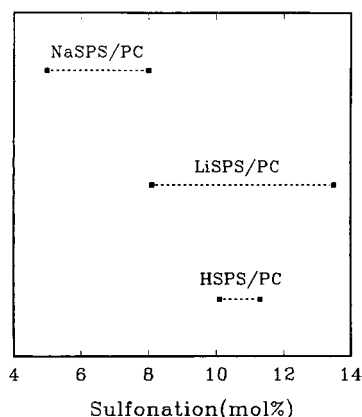
**Figure 11.** Sulfonation level vs composition miscibility map for NaSPS/PC blends at 170 °C. The filled circles denote immiscible blends; the open circles denote miscible blends. The area between the dotted lines represents the locus of miscibility windows at 170 °C.

separation temperatures for a 75/25 LiSPS/PC blend as a function of sulfonation level. The transition temperature, i.e., UCST, was calculated as the middle of the temperature interval between the highest temperature immiscible blend and the lowest temperature miscible blend for a specific sulfonation level, and it, therefore, has an uncertainty of  $\pm 10$  °C. For a specific blend composition, the UCST first decreases as the sulfonate concentration is increased from zero, reaches a minimum at the middle of the miscibility window, and then increases as the sulfonation level is increased further.

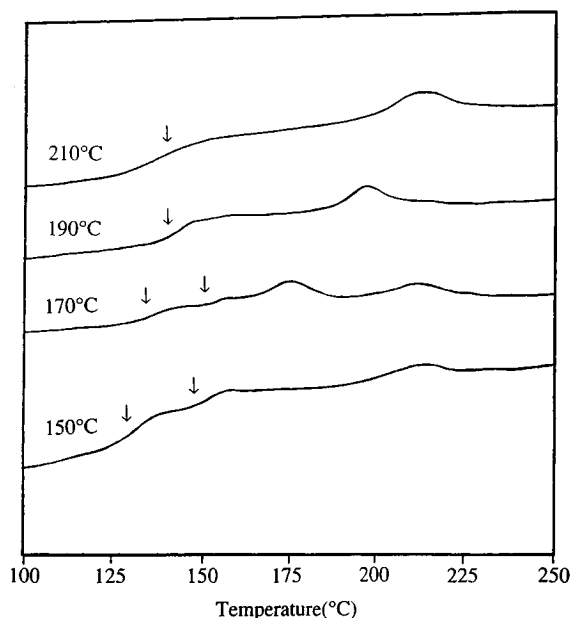
Changing the cation from  $\text{Li}^+$  to  $\text{Na}^+$  affected the sulfonation range of the miscibility window, but the same features of the phase behavior that were observed with the HSPS and LiSPS were qualitatively preserved in the NaSPS/PC blends. A miscibility map for the NaSPS/PC blends at 170 °C is given in Figure 11. Here, the open points denote miscible blends and the closed circles denote immiscible blends. The miscibility window at 170 °C at any blend composition is given by the sulfonation range of a vertical chord connecting the two dotted lines. For example, the miscibility window for a 50/50 blend at 170 °C corresponds to ca. 5–8 mol % sulfonation. A possible problem with the NaSPS/PC data is that DSC analysis of the miscible blends indicated that their  $T_g$ 's were lower than would be expected from the  $T_g$ 's of the component polymers. The blends containing NaSPS were prepared from dimethylformamide (DMF) solutions rather than THF/methanol, and one concern is that the PC may have degraded in the presence of a  $\text{Na}^+$  salt and the polar solvent at the temperatures used to cast films, ca. 110 °C, or that not all the DMF was removed during drying of the films. DMF has a relatively high boiling point and may also complex with ionomers which makes it difficult to completely remove.

A comparison of the miscibility windows of the 50/50 blends at 170 °C prepared from HSPS, LiSPS, and NaSPS is given in Figure 12. This figure shows that even when miscibility is due to intramolecular repulsive effects, there are significant ion effects that influence the phase behavior, though, again, we note the potential problem with interpreting the NaSPS/PC data as explained in the paragraph above.

**Crystallization of PC.** PC is usually considered a noncrystalline polymer, but it is crystallizable. In the bulk, the crystallization kinetics are sufficiently slow that under normal circumstances, crystallization of PC does not occur. Crystallization may, however, occur when PC is precipitated from solution in certain solvents. No evidence for crystallization was found in this



**Figure 12.** Width of miscibility windows at 170 °C for 50/50 MSPS/PC blends, where M = H<sup>+</sup>, Li<sup>+</sup>, and Na<sup>+</sup>.



**Figure 13.** DSC heating thermograms of a (50/50) 17.1-LiSPS/PC blend annealed at 150, 170, 190, and 210 °C.

study for PC cast from THF. However, for the LiSPS/PC blends, when the sulfonation level was 17.1 mol %, the PC crystallized at the elevated temperatures used for annealing the blends. This is evident from the high-temperature endotherms observed in DSC thermograms following annealing, as shown for 50/50 blends in Figure 13. For that particular composition, the UCST was between 170 and 190 °C. For the sample annealed at 150 °C, which was in the glass transition region for PC, a melting endotherm was observed at ca. 210 °C, which is consistent with the reported melting point for PC. When annealed above 150 °C, the blend exhibited a melting endotherm close to the annealing temperature, though the sample annealed at 170 °C also had a melting endotherm at 210 °C. The characterization of the nucleation of PC crystallinity by the SPS ionomers is incomplete and is only included in this paper because it was unexpected and may warrant a separate investigation.

### Conclusions

Lightly sulfonated polystyrene ionomers are miscible with Bisphenol A polycarbonate, though no specific interaction occurs between the two polymers. Miscibility arises as a result of intramolecular repulsive interactions within the ionomer, the so-called *copolymer effect*. A suitable criterion for miscibility was when the

solubility parameters of the ionomer and the PC were matched within ca. 1%. The blends exhibit UCST phase behavior and a miscibility gap with respect to the sulfonate concentration. The miscibility window widens with temperature and is also dependent on the ionomer cation. The UCST is also a function of the cation, and for a specific blend composition and cation, the UCST first decreases with increasing sulfonation and then goes through a minimum and increases again as the sulfonation level increases. In other words, the solubility parameter of sulfonated polystyrene increased with the sulfonation level and matched well with the solubility parameter of polycarbonate in a particular range of sulfonation level.

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### References and Notes

- (1) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing Inc.: Lancaster, PA, 1991.
- (2) Pearce, E. M.; Kwei, T. K.; Min, B. Y. *J. Macromol. Sci., Chem.* **1984**, *A21*, 1181.
- (3) Zhou, Z. L.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 223.
- (4) Rodriguez-Parada, J. M.; Percec, V. *Macromolecules* **1986**, *19*, 55.
- (5) Sen, A.; Weiss, R. A.; Garton, A. In *Multiphase Polymers: Blends and Ionomers*; Utracki, L. A., Weiss, R. A., Eds.; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989; p 353.
- (6) Eisenberg, A.; Hara, M. *Polym. Eng. Sci.* **1984**, *24*, 1306.
- (7) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
- (8) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
- (9) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
- (10) Cowie, J. M. G.; Reid, V. M. C.; McEwen, I. J. *Polymer* **1990**, *31*, 905.
- (11) Hara, M.; Eisenberg, A. *Macromolecules* **1984**, *17*, 1335.
- (12) Hara, M.; Eisenberg, A. *Macromolecules* **1987**, *20*, 2160.
- (13) Smith, P.; Hara, M.; Eisenberg, A. In *Current Topics in Polymer Science, II*; Ottenbrite, R. M., Utracki, L. A., Inoue, S., Eds.; Hanser: New York, 1987; p 255.
- (14) Lu, X.; Weiss, R. A. *Macromolecules* **1991**, *24*, 4381.
- (15) Lu, X.; Weiss, R. A. *Macromolecules* **1992**, *25*, 6185.
- (16) Kwei, T. K.; Dai, Y. K.; Lu, X.; Weiss, R. A. *Macromolecules* **1993**, *26*, 6583.
- (17) Molnar, A.; Eisenberg, A. *Polym. Commun.* **1991**, *32*, 1001.
- (18) Gao, Z.; Molnar, A.; Morin, F. G.; Eisenberg, A. *Macromolecules* **1992**, *25*, 6460.
- (19) Tannenbaum, R.; Rutkowska, M.; Eisenberg, A. *J. Polym. Sci., Polym. Phys.* **1987**, *25*, 663.
- (20) Weiss, R. A.; Shao, L.; Lundberg, R. D. *Macromolecules* **1992**, *25*, 6370.
- (21) Lu, X.; Weiss, R. A. *Proc. Annu. Tech. Conf., Soc. Plast. Eng.* **1993**, 684–686.
- (22) Weiss, R. A.; Lu, X. *Polymer* **1994**, *35*, 1963.
- (23) Eisenberg, A.; King, M. *Ion Containing Polymers: Physical Properties and Structure*; Academic Press: New York, 1977.
- (24) Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U.S. Patent 3,870,841, 1975.
- (25) Zundel, G. *Hydration and Intermolecular Interaction*; Academic Press: New York, 1969.
- (26) Lu, X.; Weiss, R. A. Unpublished work.
- (27) Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers. Correlations with Chemical Structure*; Elsevier: New York, 1972; Chapters 6 and 8.
- (28) Rajagopalan, P.; Kim, J.-S.; Lu, X.; Eisenberg, A.; Weiss, R. A.; Risen, W. M., Jr. *J. Polym. Sci., Polym. Phys.* **1995**, *33*, 495.
- (29) Peiffer, D. G.; Weiss, R. A.; Lundberg, R. D. *J. Polym. Sci., Polym. Phys.* **1982**, *20*, 1563.
- (30) Register, R. A.; Bell, T. R. *J. Polym. Sci., Polym. Phys.* **1992**, *30*, 569.
- (31) Akiyama, S.; Ishikawa, K.; Fujishi, H. *Polymer* **1991**, *32*, 1673.