

## Phase Behavior of Sulfonated Polystyrene Systems

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### **INTRODUCTION**

Polymer blends are of great interest because they provide an economical route to design and produce novel materials that meet the challenging requirements for industrial applications. Recently, a variety of experimental and theoretical work has been conducted as a means for producing materials with improved properties compared to those of its constituents.<sup>1-4</sup> Some of the findings suggest that the phase behavior in sulfonated polystyrene system require renewed research efforts.<sup>5-8</sup>

Sulfonated polystyrene, P(S-SS<sub>x</sub>), is produced by post-polymerization sulfonation of polystyrene (PS) that attaches sulfonic acid groups at the *para*- positions of the phenyl rings and can result in a nearly random distribution of acid sites along the polystyrene backbone; *x* represents the fractional degree of sulfonation. Besides possible interesting consequences for blend miscibility, other unique properties such as increased strength, hydrophilicity, and proton conductivity arise from incorporation of sulfonic acid at varying levels in polymers.<sup>9</sup> These features are used in a wide range of applications such as adhesives, fuel cell membranes, and ion transfer material in electromigration purification systems.<sup>10</sup>

In this phase behavior study, we examine the miscibility of three different types of blends involving P(S-SS<sub>x</sub>) using ion beam technique forward recoil spectrometry (FRES). This technique uses the mass difference between deuterium and hydrogen to measure depth profiles of the two blend components in an annealed bilayer. The three blend systems are as follows: deuterated polystyrene (dPS) with lightly sulfonated polystyrene, dPS with neutralized P(S-SS<sub>x</sub>) (ionomers), and P(S-SS<sub>x</sub>) with dP(S-SS<sub>y</sub>). Traditional methods such as differential scanning calorimetry (DSC), optical microscopy, etc. suffer from insufficient property contrast at low sulfonation levels and may experience sensitivity issues when detecting a blend of very similar sulfonation levels, deuterium labeling allows FRES to easily distinguish P(S-SS<sub>x</sub>) from dPS or dP(S-SS<sub>y</sub>) at any acid content.

### **EXPERIMENTAL SECTION**

#### **Materials**

Lightly sulfonated polystyrene was prepared by solution sulfonation of polystyrene with acetyl sulfate following a procedure of Makowski et al.<sup>11</sup> The sulfonic acid content was determined by Robertson Microlit Analysis using elemental sulfur analysis via ion chromatography. Neutralized samples of P(S-SS<sub>x</sub>) were prepared by dissolving P(S-SS<sub>x</sub>) in a toluene/methanol solution, and the base dissolved in solution was added dropwise to the agitated solution. The neutralized polymer was recovered by solvent casting the solution. The sample notation used for the ionomers is My-P(S-SS<sub>x</sub>), where M denotes the cation (M = Na<sup>+</sup>, Ba<sup>2+</sup> and Zn<sup>2+</sup> in the case of sodium, barium and zinc salts, respectively), *y* is the neutralization percentage by stoichiometry, and *x* is the degree sulfonation expressed as mole fraction.

Blends of (50/50 wt%) P(S-SS<sub>x</sub>) and P(S-SS<sub>y</sub>) for DSC were prepared by mixing in THF solution and the mixed blend was collected by solution casting. Thin bilayer films were prepared for FRES by lifting the top film off the water with the P(S-SS<sub>x</sub>) or P(S-SS<sub>x</sub>)-M base layer. Each layer thickness is ~ 350 nm, resulting in a total bilayer thickness of ~ 700 nm.

### Forward Recoil Spectrometry:

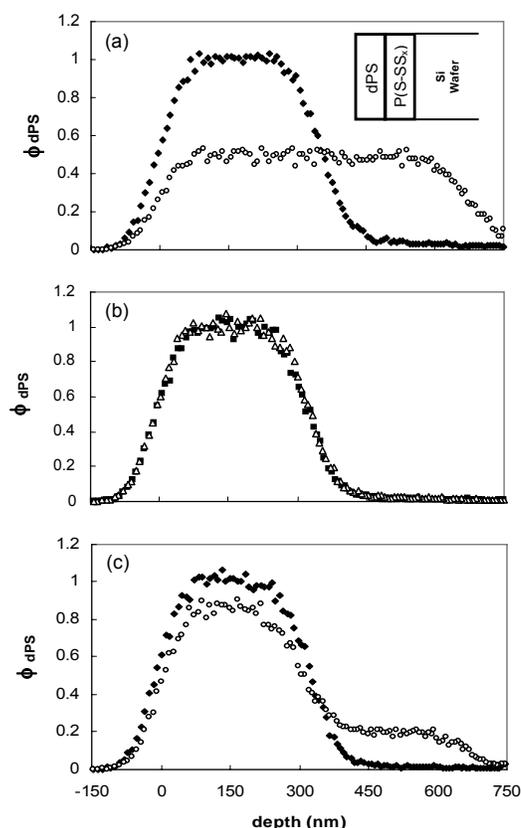
During FRES <sup>4</sup>He ions impact the sample and expel <sup>1</sup>H and <sup>2</sup>D atoms from the sample. Recoiled <sup>1</sup>H and <sup>2</sup>D leave the sample with energies characteristic of their depths and kinematic factors to give concentration profiles of <sup>1</sup>H and <sup>2</sup>D in the polymer sample.<sup>12</sup>

### Viscoelastic Properties

Rheology measurements were performed on a Rheometric Solid Analyzer (RSAII) in oscillatory shear with a sandwich fixture. The samples were run at 170 °C with a strain of 0.5% under nitrogen.

## RESULTS AND DISCUSSION

In the first part of this project, the miscibility between dPS and P(S-SS<sub>x</sub>) was measured as a function of temperature and copolymer composition as given by the mole fraction of sulfonate (x).



**Figure 1.** Concentration of deuterated polystyrene as a function of depth in bilayer samples. The as-cast bilayer is denoted by (■). (a) dPS:P(S-SS) bilayer after annealing indicates complete miscibility (○); inset schematic showing geometry of the bilayer. (b) dPS:P(S-SS) bilayer after annealing indicates complete immiscibility (Δ) and (c) dPS:P(S-SS) bilayer after annealing indicates partial miscibility (○). The annealing condition for these samples is 190 °C for 72 h.

Figure 1 shows FRES spectra as volume fraction of dPS versus depth for initial and annealed dPS:P(S-SS<sub>x</sub>) bilayers. The unannealed profile (Figure 1a) reveals an unmixed bilayer characterized by  $\phi_{dPS} = 1$  at ~ 0 - 350 nm indicating that the dPS layer is on top of the P(S-SS<sub>0.002</sub>) layer.<sup>13</sup> Although the true concentration profile of dPS is a step function, the finite instrumental resolution broadens the surface and back edges. After the dPS:P(S-SS<sub>0.002</sub>) bilayer is annealed (190 °C, 3 days), the volume fraction profile indicates that dPS has diffused into the P(S-SS<sub>0.002</sub>) and dPS is now uniformly distributed throughout the entire sample thickness, ~700 nm. This result indicates complete miscibility for dPS and P(S-SS<sub>0.002</sub>) at 190 °C. In contrast, the dPS concentration profiles for dPS:P(S-SS<sub>0.026</sub>) are indistinguishable before and after annealing (190 °C, 3 days), Figure 1b. The absence of interdiffusion indicates immiscible polymers. Furthermore, we conclude that dPS:P(S-SS<sub>x</sub>) blends with systems with  $x \geq 2.6$  mol% are completely immiscible between 150 °C and 190 °C.

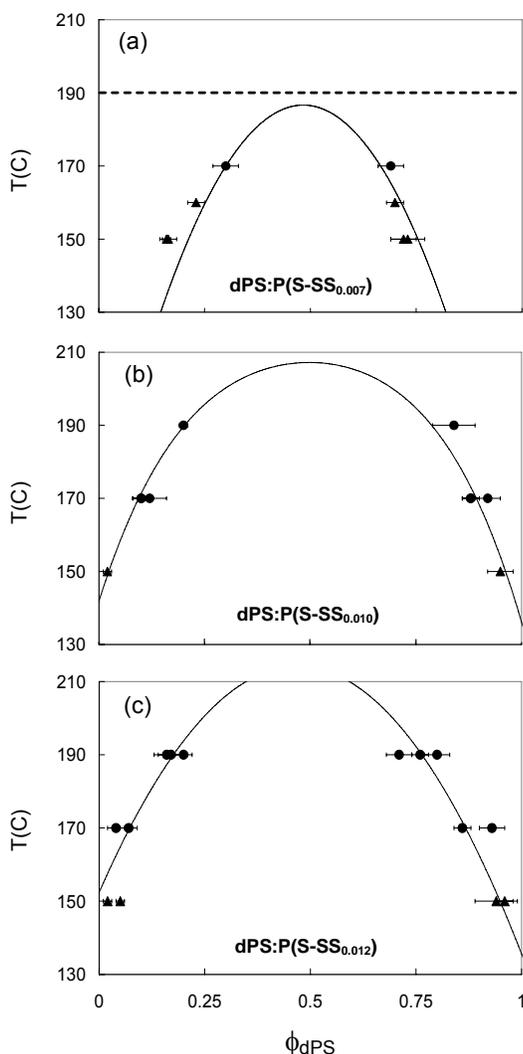
Partial miscibility was observed in PS:P(S-SS<sub>x</sub>) blends with  $x = 0.7$ , 1.0 and 1.2 mol% over the same temperature range as above. Figure 1c demonstrates that after annealing for 3 days at 190 °C, the dPS layer

diffuses into the P(S-SS<sub>0.010</sub>) layer yielding a dPS-rich layer on top of a P(S-SS<sub>0.010</sub>)-rich layer. The dPS concentration profiles for annealed dPS:P((S-SS<sub>x</sub>) bilayers having  $x = 0.7$  or  $1.2$  mol% also display two plateaus that indicate partial blend miscibility and provide values for the coexistence compositions. To ensure that the annealing time used in this study was sufficient

for the bilayer films to reach equilibrium, a control experiment was conducted. The experiment showed that the majority of the intermixing was observed in the first 4 hours whereas the 2- and 3-day profiles were indistinguishable. This confirms that the annealing conditions used in this experiment are sufficient to produce equilibrium conditions.

The coexistence compositions determined from the dPS concentration profiles were used to construct phase diagrams for partially miscible dPS:P(S-SS<sub>x</sub>) blends where  $x = 0.7, 1.0,$  and  $1.2$  mol% (Figure 2). Duplicate bilayer samples were constructed and annealed at selected temperatures, and analysis show good agreement in the coexisting composition. The dPS:P(S-SS<sub>0.007</sub>) blend is partially miscible at  $T \leq 170$  °C; at  $T = 190$  °C the blend is fully miscible, as represented by the dashed line in Figure 2a. The dPS:P(S-SS<sub>0.010</sub>) and dPS:P(S-SS<sub>0.012</sub>) blends are partially miscible across the temperature range tested (Figures 2b and 2c). All of the phase diagrams exhibit an upper critical solution temperature (UCST) behavior in which miscibility is enhanced with increasing temperature. The phase diagrams demonstrate that increasing the sulfonation level leads to a broader two-phase region with a corresponding increase in the critical temperature.

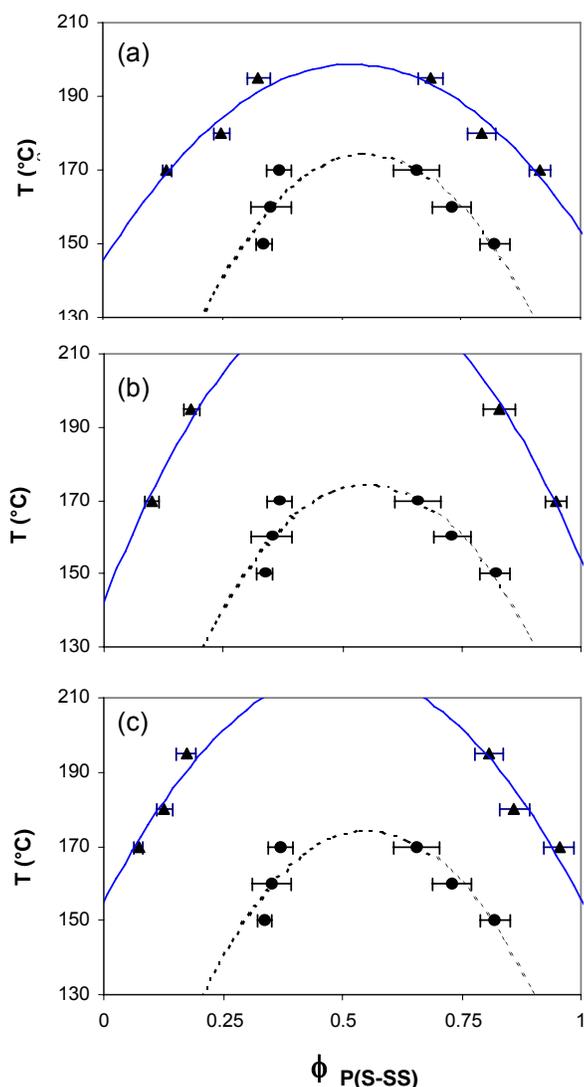
In addition to creating the phase diagrams, the coexistence compositions were also used to calculate the monomer-monomer interaction parameter between styrene and styrene sulfonate and the result is extraordinarily large,  $\chi_{S/SS} \geq 25$ . Such a  $\chi$  value, although built upon mean field assumption, suggests the potential for demixing in P(S-SS<sub>x</sub>) random copolymers that possess even a narrow distribution of compositions.



**Figure 2:** UCST phase diagrams constructed from the coexisting compositions for (a) dPS:P(S-SS<sub>0.007</sub>), (b) dPS:P(S-SS<sub>0.010</sub>), and (c) dPS:P(S-SS<sub>0.012</sub>). Two annealing times are represented: (●) 3 days and (▲) 5 days. The dashed line indicates complete miscibility at that specific temperature and solid curves have been drawn to guide the eye.

The second blend system studied is dPS and P(S-SS<sub>x</sub>)-M ionomers neutralized with M = Na<sup>+</sup>, Zn<sup>2+</sup>, and Ba<sup>2+</sup> counterions. Ionomers are random copolymers with a small amount (<10 mol%) of acid groups partially or fully neutralized by a metal counterion. The phase diagrams in Figure 3 show that the dPS:P(S-SS<sub>0.007</sub>)-M systems have higher UCST than the dPS:P(S-SS<sub>0.007</sub>) system (dashed lines), implying that the neutralization of the acid copolymer

reduces the blend miscibility. For example, previous results indicate that dPS:P(S-SS<sub>0.007</sub>) is fully miscible at annealing temperature of 190°C, however, dPS:P(S-SS<sub>0.007</sub>)-M is now partially miscible at the same temperature. Figure 3 also demonstrates that counterion valency affects the phase diagram for this blend; neutralizing with divalent cations Ba<sup>2+</sup> and Zn<sup>2+</sup> creates a higher UCST than neutralizing with monovalent cation Na<sup>+</sup>.



**Figure 3.** UCST phase diagrams for dPS:M-P(S-SS<sub>0.007</sub>) where M are (a) Na125 (b) Ba125 (c) Zn125 represented by (▲) and the blend of dPS:P(S-SS<sub>0.007</sub>) is represented by (●). The dashed and solid lines have been drawn to guide the eye.

In the case of the blend system involving dPS and P(S-SS<sub>x</sub>), the reduction in miscibility as sulfonation level increases is explained by the complexation of sulfonate groups on one chain with sulfonate groups on the same chain and/or nearby sulfonate groups from a different chain. The attraction of polar groups with other polar groups restricts the conformation the polymer chains, which then reduces the miscibility of homopolymer polystyrene with random copolymer sulfonated polystyrene. However, ionic interactions that result from neutralizing P(S-SS<sub>x</sub>) will create more conformational restrictions and this affects the phase behavior with PS.

The ionic interactions that result from converting P(S-SS<sub>x</sub>) into ionomers is evidenced by rheological results (Figure 4). A typical homopolymer-like terminal behavior with the scaling properties of approximately  $G' \sim \omega^2$  is seen for the measured frequency range at 170°C. However, ionomers have an extended rubbery plateau region and the best interpretation of these data is the result of ionic associations that physically crosslink the polymer.

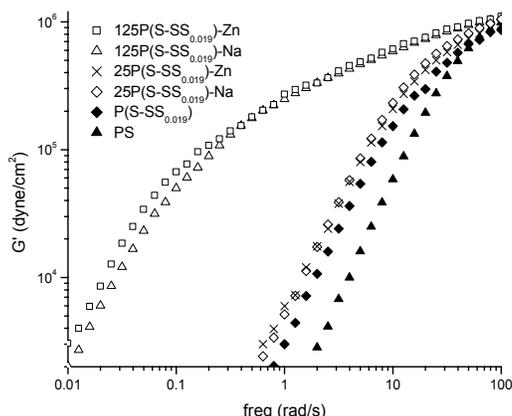
The relaxation time ( $\tau$ ) may be approximated as the reciprocal of the frequency at which a line tangent to the terminal zone intersects a line tangent to the plateau region. The relaxation time at which this dissociation occurs can be directly correlated to the strength of the electrostatic interactions between the ionic groups. The stronger the ionic association, the longer time the ionic domains will require to relax. The relaxation times suggest that the 125%

neutralized sulfonated polystyrene takes the longest to relax, followed by 25% neutralized, acid form, and homopolymer PS. The terminal relaxation time increases relative to an analogous nonionic polymer due to temporary crosslinks that are created after neutralization. The creation of transient crosslinks not only increases the time for the polymer to relax but it also

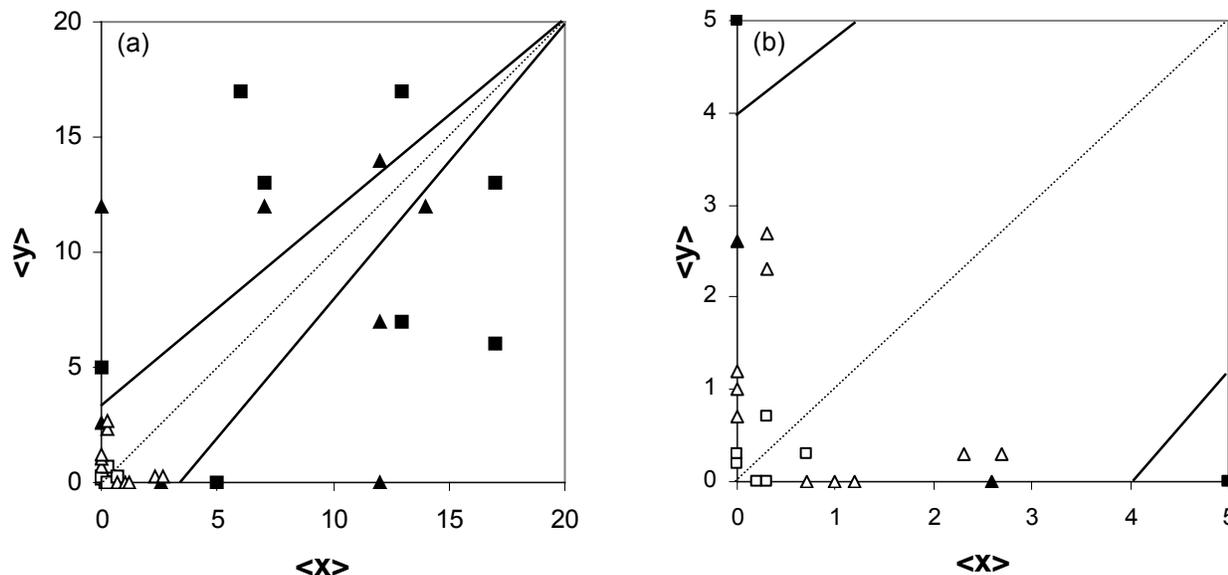
has an effect on the phase behavior. The blend miscibility gap follows the similar trend with the relaxation time; larger miscibility gaps correlate with longer relaxation times.

In general, the effect of blending dPS with P(S-SS<sub>x</sub>) in the acid form has been explored and FRES results indicate full miscibility at  $x \leq 0.2$  mol% and complete immiscibility at  $x \geq 2.6$  mol% for 150 °C to 190 °C. Partial miscibility exists for the PS:P(S-SS<sub>x</sub>) blends with  $x = 0.7$  mol% at  $T \leq 170$  °C and  $x = 1.0$  or 1.2 mol% at  $T \leq 190$  °C. As dPS is blended with P(S-SS<sub>0.007</sub>) ionomers, the miscibility of the blend becomes even less due to the ionic associations in ionomers. The final part of the project will explore the blending of P(S-SS<sub>x</sub>), where the difference in sulfonation level,  $|x-y|$ , varies.

Figure 5a plots the results from blending P(S-SS<sub>x</sub>):P(S-SS<sub>y</sub>) pairs is using DSC and FRES. The dashed line shows the division at which the plot becomes a mirror image of one another. Acid contents above 20 mol% were not used in this experiment because thermogravimetric analysis results show that P(S-SS<sub>x</sub>) with higher sulfonation will thermally degrade. For  $x < 20$  mol%, DSC results can only determine the extent of miscibility in pairs with a large difference in  $T_g$ 's



**Figure 4.** Storage modulus of P(S-SS<sub>0.019</sub>)-Na and P(S-SS<sub>0.019</sub>)-Zn at 25% and 125% neutralization level in comparison to P(S-SS<sub>0.019</sub>) and PS. Rheology was performed at 170°C and 0.5% strain.



**Figure 5.** Blend miscibility summary of sulfonated polystyrene with sulfonated polystyrene samples annealed at 170°C where  $\langle x \rangle$  and  $\langle y \rangle$  represent the average sulfonation levels. (a) DSC was used to determine (■) immiscible P(S-SS<sub>x</sub>):P(S-SS<sub>y</sub>) pairs. FRES was used to determine (▲) immiscible, (△) partially miscible, and (□) miscible pairs. The solid line indicates the boundary between miscible and partially miscible pairs. (b) Results of P(S-SS<sub>x</sub>):P(S-SS<sub>y</sub>) blend pairs at  $\langle x \rangle$  and  $\langle y \rangle \leq 5$ .

such as  $\langle x \rangle = 5$  mol% and  $\langle y \rangle = 12$  mol% with  $T_g$ 's of 122 °C and 135 °C respectively. On the other hand, FRES spectra show blend pair dP(S-SS<sub>0.003</sub>):P(S-SS<sub>0.026</sub>) to be partially miscible whereas earlier results show P(S-SS<sub>0.026</sub>) to be completely immiscible with dPS. Introducing a small quantity of acid groups (~ 0.3 mol%) can convert a completely immiscible blend into a partially miscible blend. Combined results from DSC and FRES were able to predict a window of miscibility region for this blend system. The solid line in Figure 5 indicates the boundary between immiscibility and partially miscibility regions, and information gained from this portion of the study shows that the window of miscibility decreases for P(S-SS<sub>x</sub>):P(S-SS<sub>y</sub>) pairs as  $x$  and  $y$  increases.

## **CONCLUSION**

Polymer-polymer miscibility plays a critical role in determining the final properties of blend systems. The phase behavior of three blend systems involving P(S-SS<sub>x</sub>) was studied using primarily the ion beam technique of forward recoil spectrometry (FRES). FRES results indicate dPS becomes immiscible with P(S-SS<sub>x</sub>) at  $x \geq 2.6$ mol%. When dPS is blended with P(S-SS<sub>0.007</sub>) ionomers, the introduction of ionic interactions hinder the miscibility with dPS thus making the system less miscible. Lastly, the window of miscibility for P(S-SS<sub>x</sub>):P(S-SS<sub>y</sub>) blends decreases as the average sulfonation levels,  $x$  and  $y$ , grow larger. Information gained from a comprehensive phase behavior study of sulfonated polystyrenes will lead to improvements in optimizing and designing future sulfonated polymers.

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