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Phase Behavior of Polystyrene and Poly(styrene-*ran*-styrenesulfonate) Blends

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ABSTRACT: The blend miscibilities of deuterated polystyrene (dPS) and sulfonated poly(styrene-*ran*-styrenesulfonate) (P(S−SS)) are examined by using forward recoil spectrometry (FRES) to probe the intermixing of bilayer films. This method directly determined the equilibrium coexistence compositions for dPS:P(S−SS$_x$) blends where the degree of sulfonation (x) ranged from 0.2 to 2.6 mol %. In the temperature range 150−190 °C, FRES profiles reveal full miscibility for $x \leq 0.2$ mol % and complete immiscibility for $x \geq 2.6$ mol %. Partial miscibility exists in dPS:P(S−SS$_x$) blends with $x = 0.7$, 1.0, and 1.2 mol %, where between 150 and 190 °C the coexisting compositions show upper critical solution temperature (UCST) phase behavior. Blend interaction parameters, χ_{blend}, are calculated using the Flory−Huggins theory and the coexisting compositions of the partially miscible bilayers. The copolymer blend theory estimates the styrene−styrenesulfonate segmental interaction parameter to be extraordinarily large, $\chi_{\text{S/SS}} \geq 25$. While the applicability of mean-field approaches is limited in this profoundly incompatible system, recent theories about random copolymers have established criteria for "self-demixing" due to their inherent compositional variations. Our estimate of the monomer−monomer interaction parameter suggests the potential for demixing in P(S−SS$_x$) random copolymers that possess even a narrow distribution of compositions.

Introduction

Polymer blends are of great interest because they provide a rational route to design and produce novel materials with improved properties compared to those of their constituents. The miscibility of homopolymer blends is fairly well understood in the context of the classic Flory−Huggins theory which accounts for the entropy of mixing and enthalpic contributions arising from interactions between monomers.[1,2] These monomer interactions are represented by the segmental interaction parameter, χ. Monomer pairs that exhibit attractive interactions show a negative χ that promotes miscibility, but it is more common to find positive values.[3−5] Given the small entropy of mixing in polymer blends, even a small positive χ (on the order of 10^{-3}) is sufficient to induce phase separation.

There has been considerable interest in the phase behavior of blends involving random copolymers, where judicious selection of monomers provides the opportunity to manipulate the overall interaction parameter of the blend, χ_{blend}. For instance, incorporating monomers with specific favorable interactions can promote miscibility. A more intriguing route is to combine highly *incompatible* monomers within a copolymer. Since blending this copolymer with another polymer provides a mechanism to dilute the unfavorable intramolecular interactions, such copolymers can form miscible blends in unexpected circumstances, a phenomenon known as the copolymer effect.[6−10]

Studies have shown poly(styrene-*ran*-styrenesulfonate) (P(S−SS$_x$)) random copolymers and their neutralized forms to be good candidates for developing miscible blends with other polymers.[11−14] P(S−SS$_x$) is produced by postpolymerization 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 ionic 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.[15] These features have been utilized in a wide range of applications such as adhesives, fuel cell membranes, and ion transfer material in electromigration purification systems.[16,17]

In a recent study, Beck Tan et al. applied small-angle neutron scattering (SANS) to examine blends of polystyrene and a single sulfonated polystyrene ($x = 0.0167$), concluding that the segmental interaction parameter (χ) between styrene and styrenesulfonate monomers is at least 5.6.[18] Such a value represents an unusually high degree of incompatibility. Given the interest in phase behavior of sulfonated polymers and their range of applications, we have undertaken a systematic study of phase behavior in PS:P(S−SS$_x$) blends, over a broader range of copolymer composition and temperature, to obtain more refined estimates of the segmental interaction parameter between styrene and styrenesulfonate monomeric units. Improved knowledge of blend miscibility should facilitate tailored design of new materials toward specific applications.

We use the ion beam technique forward recoil spectrometry (FRES) to examine the miscibility of deuterated polystyrene (dPS) and lightly sulfonated poly(styrene-*ran*-styrenesulfonate) blends. While traditional methods such as differential scanning

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Table 1. Properties of Deuterated Polystyrene and Poly(styrene-*ran*-styrenesulfonate) Random Copolymers

designation	M_w[a] (kg/mol)	M_w/M_n[a]	x[b]	T_g[c] (°C)
dPS	65.9	1.05	0	107
P(S−SS$_{0.002}$)	65.0	1.06	0.002	109
P(S−SS$_{0.007}$)	65.0	1.06	0.007	110
P(S−SS$_{0.010}$)	65.0	1.06	0.010	110
P(S−SS$_{0.012}$)	65.0	1.06	0.012	110
P(S−SS$_{0.026}$)	65.0	1.06	0.026	112

[a] The weight-averaged molecular weight of dPS and PS prior to sulfonation as determined by SEC. [b] The mole fraction of styrenesulfonate units with a confidence of ±0.001 as determined by elemental analysis. [c] The glass transition temperature is to within ±1.0 °C as determined by DSC.

calorimetry (DSC), optical microscopy, etc., may suffer from insufficient property contrast at low sulfonation levels ($x < 5$ mol %), deuterium labeling allows FRES to easily distinguish P(S−SS$_x$) from dPS at any sulfonation level. This technique uses the mass difference between deuterium and hydrogen to measure depth profiles of the two blend components in an annealed bilayer and has been previously applied to study both PS:brominated polystyrene and PS:poly(styrene-*ran*-methyl methacrylate) blends.[19−21] In this study, equilibrium coexistence compositions are obtained for dPS:P(S−SS$_x$) blends with varying levels of sulfonation ($x = 0.2-2.6$ mol %) and annealing conditions (150−190 °C). For partially miscible blends, phase diagrams are constructed, and the segmental interaction parameter for styrene and styrenesulfonate is estimated.

Experimental Section

Materials. Deuterated polystyrene (dPS) was purchased from Polymer Source ($M_w = 65\,900$ g/mol, PDI = 1.05), and atactic PS was purchased from Pressure Chemical ($M_w = 65\,000$ g/mol, PDI = 1.06). Acetyl sulfate was prepared by combining concentrated sulfuric acid with a solution of acetic anhydride in dichloromethane with acetic anhydride in excess of a 1:1 mole ratio. Freshly prepared acetyl sulfate was combined with a well-stirred solution 10% (w/v) of polystyrene in dichloromethane at 40 °C. The sulfonation reaction proceeded for 4 h and was then terminated by the addition of methanol. The precipitated polymers were washed several times with deionized water until the pH was the same as deionized water. The sulfonated polymers were then dried under vacuum at a temperature above their glass transition temperature (T_g).[22,23] Efforts to assess the randomness of attachment in sulfonated polystyrenes have been complicated by limited solubility; however, it is believed that the acetyl sulfate reaction to low substitutions used here is likely to yield random monomeric sequences.[24]

The level of sulfonation was determined by Robertson Microlit Analysis (Madison, NJ) using elemental sulfur analysis via ion chromatography (Table 1). These sulfonation levels were consistent with the results of titration experiments, performed in our lab, in which methanol solutions of P(S−SS$_x$) were titrated with 6 mM NaOH using the indicator thymol blue. Glass transition temperatures were determined by DSC from 25 to 180 °C at a rate of 20 °C/min using a TA Instruments DSC 2920. The T_g was taken as the inflection point in the DSC thermogram (Table 1). The slight increase in T_g for the P(S−SS$_x$) is consistent with literature reports for this range of sulfonation.[25] Polydispersities and apparent molecular weights were obtained for the P(S−SS$_x$) random copolymers via size exclusion chromatography (SEC) in tetrahydrofuran (THF) and calibrated with polystyrene standards (Table 1). These results demonstrate that the sulfonation reaction does not lead to appreciable chain scission or cross-linking. All polymers were stored in vacuum desiccators.

Sample Preparation. Thin bilayer films were prepared for FRES by dissolving P(S−SS$_x$) in toluene at a concentration of 5.6 wt % [w/w] and then spin-coating onto a silicon wafer. After spin-coating, this base layer was dried in a vacuum oven at 115 °C for 12 h to remove the residual solvent. The thickness of the dried film was determined by ellipsometry. Similar films of dPS were spin-coated on to silicon and then floated onto the surface of ultrafiltered distilled water. The dPS film was then lifted off the water with the P(S−SS$_x$) base layer, and the resulting bilayers were dried in a vacuum at 115 °C for 12 h. To avoid dewetting due to differences in surface energy, dPS films were placed atop P(S−SS$_x$) in all FRES experiments. Each layer thickness is ∼350 nm, resulting in a total bilayer thickness of ∼700 nm.

For the miscibility studies, separate bilayer samples were annealed in a vacuum oven as follows: 150 °C for 5 days, 160 °C for 5 days, 170 °C for 3 days, and 190 °C for 3 days. Only temperatures below 200 °C were selected to prevent dewetting of the polymer films. After annealing, the bilayer samples were removed from the vacuum oven and rapidly cooled to room conditions. For an annealing temperature of 160 °C, the bilayer sample required only ∼10 s to reach the T_g of PS (ca. 100 °C) and ∼30 s to reach room temperature (25 °C). These short times ensure that the annealed bilayers are representative of the phase behavior at the designated annealing temperature. To evaluate the possibility of thermal degradation, a bulk sample of P(S−SS$_{0.026}$) was subjected to the most extreme annealing condition tested in this project, 3 days at 190 °C. DSC data showed that T_g remained the same between the unannealed and annealed bulk P(S−SS$_{0.026}$) sample, indicating the absence of desulfonation. Furthermore, SEC data showed that the average molecular weight and polydispersity remained the same, indicating the absence of chain scission or cross-linking.

Forward Recoil Spectrometry. During FRES ^{4}He ions impact the sample and expel ^{1}H and ^{2}D atoms from the sample. Recoiled ^{1}H and ^{2}D leave the sample with energies characteristic of their depths and kinematic factors to give concentration profiles of ^{1}H and ^{2}D in the polymer sample.[26] For top and bottom layer thickness values of ∼350 nm, the optimum incident beam energy and Mylar stopper foil values were 3 MeV and 10 μm, respectively. The spot size and charge collection were 1×2 mm^2 and 10 μC, respectively.

Raw FRES data are collected as spectra of channel vs counts. The channel corresponds to the energy of the expelled atoms and is converted into a depth scale for deuterium using an in-house software package that includes the stopping power of PS. The counts correspond to the number of expelled atoms and are converted into a deuterium concentration scale using a dPS calibration sample.[19,26] To obtain the volume fraction of dPS (ϕ_{dPS}) across a bilayer, the deuterium counts were divided by the counts collected from a thick dPS calibration sample analyzed under the same experimental conditions.

The resulting volume fraction of dPS vs depth profiles from annealed samples were used to determine the phase behavior of dPS:P(S−SS$_x$) blends. When the blend system is partially miscible, two plateaus are observed in the dPS depth profile. By conservation of mass, the amount of deuterium that has diffused into the P(S−SS$_x$) layer must equal the deuterium that has exited the dPS layer. To meet this criterion, the volume fraction of dPS was scaled until the integrated area of the initial profile equaled the integrated area of the annealed profile; typical scaling factors were 1.05−1.15. After scaling, the coexisting equilibrium compositions in partially miscible blend systems were determined by averaging the volume fraction data of dPS in the dPS-rich and the P(S−SS$_x$)-rich layers.

Results

In this study, the miscibility between dPS and P(S−SS$_x$) was measured as a function of the mole fraction of sulfonate (x) and temperature. FRES results indicate full miscibility at $x \leq 0.2$ mol % and complete immiscibility at $x \geq 2.6$ mol % for 150−190 °C. Partial miscibility exists for the PS:P(S−SS$_x$) blends with $x = 0.7$ mol % at $T \leq 170$ °C and $x = 1.0$ or 1.2 mol % at $T \leq 190$ °C.

Figure 1 shows FRES spectra as volume fraction of dPS vs depth for initial and annealed dPS:P(S−SS$_x$) bilayers. The unannealed profile (Figure 1a) reveals an unmixed bilayer

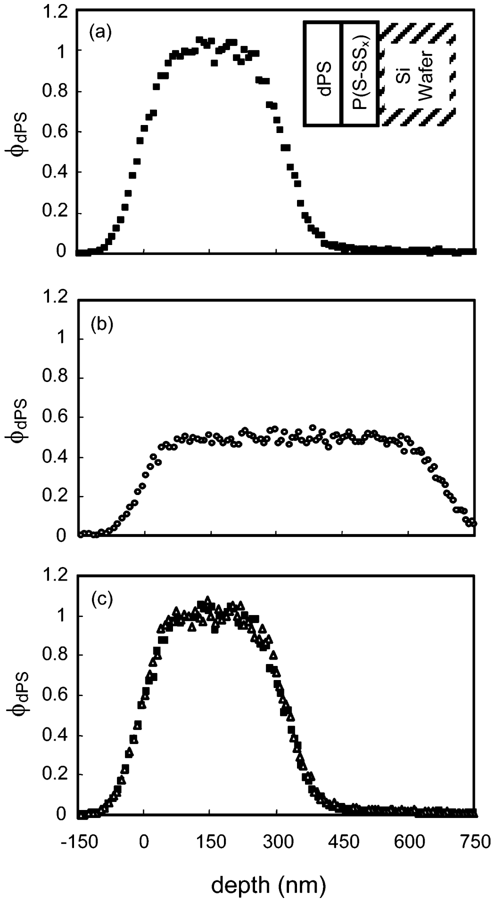

Figure 1. Concentration of deuterated polystyrene as a function of depth in bilayer samples. (a) As-cast bilayer of dPS:P(S−SS$_{0.002}$); inset schematic showing geometry of the bilayer. (b) dPS:P(S−SS$_{0.002}$) bilayer after annealing at 170 °C for 72 h indicates complete miscibility. (c) dPS:P(S−SS$_{0.026}$) bilayer prior to annealing (■) and after annealing at 190 °C for 72 h; (△) indicates complete immiscibility.

characterized by $\phi_{dPS} = 1$ at ∼ 0−350 nm, indicating that the dPS layer is on top of the P(S−SS$_{0.002}$) layer. Although the true concentration profile of dPS is a step function, the finite instrumental resolution broadens the surface and back edges.[26] After the dPS:P(S−SS$_{0.002}$) bilayer is annealed (170 °C, 3 days), the volume fraction profile in Figure 1b indicates that dPS has diffused into the P(S−SS$_{0.002}$), and dPS is now uniformly distributed throughout the entire sample thickness, ∼700 nm. This result indicates complete miscibility for dPS and P(S−SS$_{0.002}$) at 170 °C; complete miscibility was also observed in dPS:P(S−SS$_{0.002}$) bilayers at 150 and 190 °C. In contrast, the dPS concentration profiles for dPS:P(S−SS$_{0.026}$) are indistinguishable before and after annealing (190°C, 3 days) (Figure 1c). The absence of interdiffusion indicates immiscible polymers. The dPS:P(S−SS$_{0.026}$) system is completely immiscible at 190 °C, as well as at 150 and 170 °C (data not shown). Furthermore, we conclude that dPS:P(S−SS$_x$) blends with $x \leq 0.2$ mol % are fully miscible, while systems with $x \geq 2.6$ mol % are completely immiscible between 150 and 190 °C.

Partial miscibility was observed in dPS:P(S−SS$_x$) blends with $x = 0.7$, 1.0, and 1.2 mol % over the same temperature range as above. Prior to annealing, the dPS concentration profile for the dPS:P(S−SS$_{0.010}$) bilayer shown in Figure 2 (filled symbols) is comparable to Figure 1a with a pure dPS layer on top. Upon annealing for 3 days at 170 °C, the dPS layer diffuses into the P(S−SS$_{0.010}$) layer, yielding a dPS-rich layer on top of a P(S−SS$_{0.010}$)-rich layer. This dPS concentration profile corresponds to a partially miscible blend with coexisting compositions of $\phi_{dPS}' = 0.92$ and $\phi_{dPS}'' = 0.10$. At a higher annealing temperature, 190 °C, the coexisting compositions are $\phi_{dPS}' = 0.84$ and $\phi_{dPS}'' = 0.20$, consistent with a greater degree of compatibility. The dPS concentration profiles for annealed dPS:P((S−SS$_x$) bilayers having $x = 0.7$ or 1.2 mol % also display two plateaus that indicate partial blend miscibility for both systems and provide values for the coexistence compositions in the temperature range.

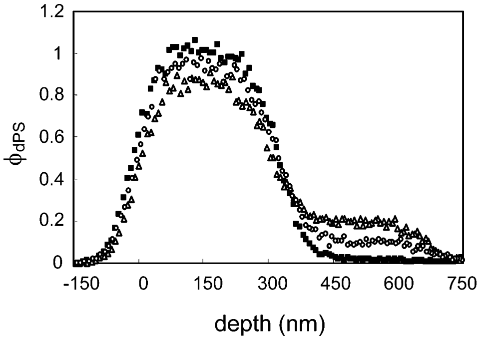

Figure 2. Concentration of deuterated polystyrene as a function of depth in dPS:P(S−SS$_{0.010}$) bilayer samples prior to annealing (■) and after annealing for 72 h at 170 (○) and 190 °C (△). The annealed bilayers indicate partial miscibility as evidenced by dPS-rich and P(S−SS$_{0.010}$)-rich layers, and the coexistence compositions are the averages of the plateaus. At 170 °C $\phi_{dPS}' = 0.92 \pm 0.03$ and $\phi_{dPS}'' = 0.10 \pm 0.02$. At 190 °C $\phi_{dPS}' = 0.84 \pm 0.05$ and $\phi_{dPS}'' = 0.20 \pm 0.01$.

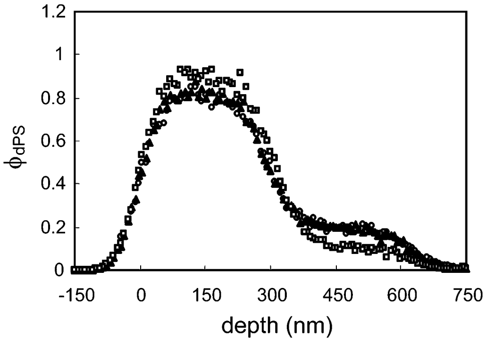

Figure 3. Concentration of deuterated polystyrene as a function of depth in dPS:P(S−SS$_{0.012}$) bilayers after annealing temperature at 190 °C for 4 (□), 48 (▲), and 72 h (○). Partial miscibility is found with coexistence compositions of $\phi_{dPS}' = 0.80 \pm 0.03$ and $\phi_{dPS}'' = 0.21 \pm 0.02$. Concentration profiles after 2 and 3 days of annealing are indistinguishable.

Figure 3 shows results of a control experiment to demonstrate that the annealing times used in this study are sufficient for the bilayer films to reach equilibrium, a condition necessary to accurately determine the coexistence compositions in polymer blends. The sample dPS:P(S−SS$_{0.012}$) was annealed at 190 °C for varying times: 4 h, 2 days, and 3 days. A majority of the intermixing was observed in the first 4 h, whereas the 2- and 3-day profiles were indistinguishable. This confirms that interdiffusion in dPS:P(S−SS$_x$) is very rapid even near the critical temperature, and annealing for 3 days at 190 °C is 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$_x$) blends where $x = 0.7$, 1.0, and 1.2 mol % (Figure 4). Duplicate bilayer samples were constructed, annealed, and analyzed for selected temperatures in the phase diagrams, and the agreement is good. The dPS:P(S−SS$_{0.007}$) 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 4a. The dPS:P(S−SS$_{0.010}$) and dPS:P(S−SS$_{0.012}$)

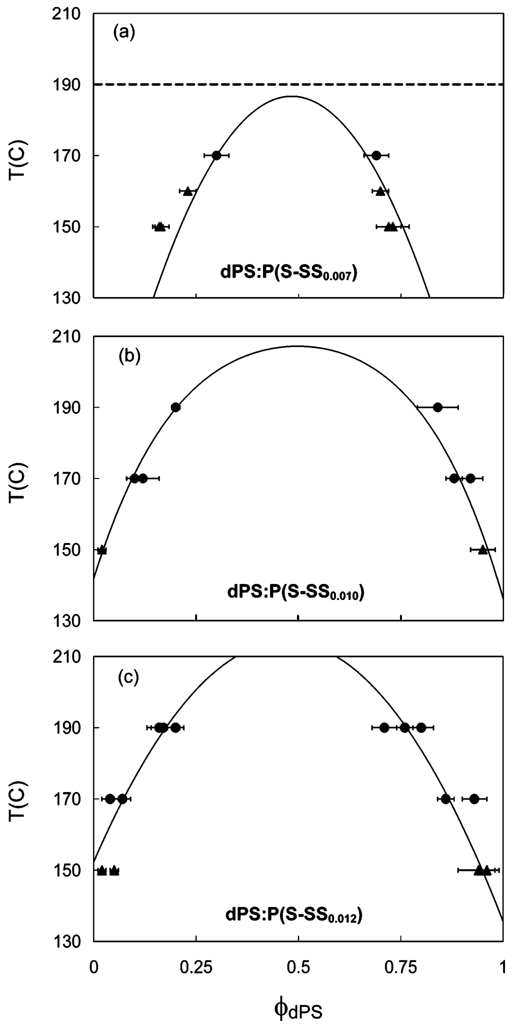

Figure 4. UCST phase diagrams constructed from the coexisting compositions for (a) dPS:P(S−SS$_{0.007}$), (b) dPS:P(S−SS$_{0.010}$), and (c) dPS:P(S−SS$_{0.012}$). Two annealing times are represented: (●) 3 and (▲) 5 days. The dashed line indicates complete miscibility at that specific temperature, and solid curves have been drawn to guide the eye.

blends are partially miscible across the temperature range tested (Figure 4b,c). All of the phase diagrams exhibit an upper critical solution temperature (UCST) behavior in which miscibility is enhanced with increasing temperature. These phase diagrams demonstrate that increasing the sulfonation level leads to a broader two-phase region with a corresponding increase in the critical temperature.

The rapid change in the miscibility of dPS:P(S−SS$_x$) blends with sulfonation, even at the *low* levels considered here, indicates the strong incompatibility between styrene and styrenesulfonate monomeric units. Random copolymers with specific interactions can microphase separate to produce secondary structures; for example, neutralized ionomers typically form metal-rich ionic aggregates. Extensive microphase separation of this type can produce a physical network or gelation that might alter blend miscibility.[27] However, our melt rheological studies on the P(S−SS$_x$) acid copolymers with low sulfonation at the temperatures of interest here show no signs of any network character associated with possible physical associations of the acid groups.[28] Instead, the rheology exhibits classic terminal relaxation characteristic of a viscoelastic liquid. Indeed, the only effect of sulfonation on the viscoelasticity of these materials is a slight shifting of dynamics to longer time scales without any change in the shape of the relaxation spectrum. This shift may be partially explained by a small increase in T_g with degree of sulfonation and might also reflect increased friction induced by SS−SS interactions. This is consistent with published dynamic mechanical analysis studies by Weiss and Lefelar, where P(S−SS$_{0.058}$) behaves as a physical network and P(S−SS$_{0.018}$) behaves as a linear polymer.[29] The absence of microphase separation in P(S−SS$_{0.027}$) acid copolymers with small x is consistent with the absence of a low-angle scattering peak. In contrast, a low-angle scattering peak indicating ionic aggregates appears when P(S−SS$_{0.027}$) is neutralized with metal cations (Na$^+$, Ba^{2+}, Zn^{2+}).[30] In the absence of evidence for both microphase separation and the formation of a physical network in unneutralized P(S−SS$_x$) copolymers with low acid content, the discussion below proceeds by using mean-field theories to interpret the miscibility data, which implies the absence of secondary structures.

Discussion

To further analyze the monomer−monomer interactions, we first analyze the coexistence data using Flory−Huggins theory to determine the blend interaction parameter, χ_{blend}. (Here χ_{blend} represents the effective interaction parameter between homopolymer dPS and the P(S−SS$_x$) copolymer.) According to the Flory−Huggins theory, the Gibbs free energy of mixing, ΔG_m, for a system consisting of two polymers can be written as

$$\frac{\Delta G_m}{kT} = \frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B + \chi_{blend}\phi_A\phi_B \qquad (1)$$

where ϕ_A and ϕ_B are the volume fractions and N_A and N_B are the degree of polymerization for the dPS and P(S−SS$_x$), respectively. At equilibrium the chemical potential of each component must be the same in both phases. Denoting the two conjugate phases by single and double primes, we have

$$\ln\frac{\phi_A'}{\phi_A''} + \left(1 - \frac{N_A}{N_B}\right)(\phi_A'' - \phi_A') + N_A\chi_{blend}[(1-\phi_A')^2 - (1-\phi_A'')^2] = 0 \qquad (2)$$

If N_A, N_B, and the coexistence compositions (ϕ_A', ϕ_A'') are known, eq 2 allows calculation of χ_{blend}. Figure 5 presents χ_{blend} for the three sulfonation levels showing partial miscibility (x = 0.7, 1.0, and 1.2 mol %) against $1/T$ where T is the annealing temperature. The calculated χ_{blend} values are all on the order of 10^{-3}, sufficiently small to allow for partial miscibility at the moderate molecular weights used here. At each sulfonation level, χ_{blend} decreases with increasing temperature, as anticipated from the UCST behavior shown in Figure 4. Also consistent with the phase diagrams in Figure 4, χ_{blend} increases with increasing sulfonation level.

Once χ_{blend} is known, copolymer blending theories can be applied to estimate pairwise segmental interaction parameters.[6,7,10,31] Copolymer blending theories extend the Flory−Huggins theory by accounting for pairwise interactions among the various monomers and have been used to explain the enhanced miscibility found in many systems containing random copolymers. According to the copolymer theory, the interaction parameter for an $A_{1-y}B_y$:$C_{1-x}D_x$ blend of copolymers can be determined from the weighted summation of each of the segmental or monomer−monomer interaction parameters.

$$\chi_{blend} = (1-x)(1-y)\chi_{AC} + (1-x)y\chi_{BC} + x(1-y)\chi_{AD} + xy\chi_{BD} - y(1-y)\chi_{AB} - x(1-x)\chi_{CD} \qquad (3)$$

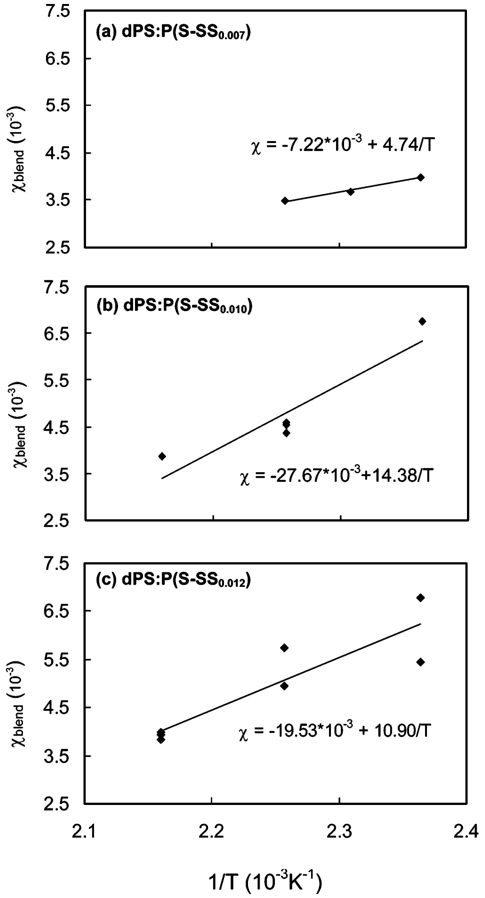

Figure 5. Flory−Huggins interaction parameters, χ_{blend}, for dPS and P(S−SS$_x$) systems as a function of 1/T for (a) 0.7, (b) 1.0, and (c) 1.2 mol %. The lines represent the best fits to $\chi = A + B/T$, and the resulting equations are given.

The six segmental χ parameters represent both intermolecular and intramolecular interactions, while x and y represent the compositions of random copolymers $A_{1-y}B_y$ and $C_{1-x}D_x$. Note that the negative contributions to χ_{blend} from the segmental parameters χ_{AB} and χ_{CD} account for the intramolecular nature of their interactions; this is the root cause of the so-called “copolymer effect” of enhanced miscibility when a copolymer has particularly unfavorable intramolecular interactions.

The copolymer blend theory can be simplified to address blends containing a homopolymer and a random copolymer, (A:$C_{1-x}D_x$), by setting y equal to zero. For this study A represents dPS and $C_{1-x}D_x$ represents P(S−SS$_x$). Thus, eq 3 simplifies to

$$\chi_{\text{blend}} = x\chi_{\text{dS/SS}} + (1 - x)\chi_{\text{dS/S}} - x(1 - x)\chi_{\text{S/SS}} \qquad (4)$$

where χ_{blend} is now a function of only three segmental interaction parameters ($\chi_{\text{dS/SS}}$, $\chi_{\text{dS/S}}$, $\chi_{\text{S/SS}}$) and the copolymer composition (x). An expression for $\chi_{\text{dS/S}}$ was obtained from literature [$\chi_{\text{dS/S}} = 0.2T^{-1} - 2.9 \times 10^{-4}$] and is on the order of 10^{-4} for our experimental temperatures.[32] While this small positive $\chi_{\text{dS/S}}$ is sufficient to induce phase separation in high-molecular-weight blends,[33] this is not expected for the modest molecular weights used here. Indeed, in a control experiment, we found full miscibility between our dPS and PS homopolymers at 170 °C. In light of the near equivalence of dPS and PS, a further reduction in eq 4 is made by assuming that the effect of deuteration is minimal such that $\chi_{\text{dS/SS}} = \chi_{\text{S/SS}}$, and eq 4 reduces to

$$\chi_{\text{blend}} = (1 - x)\chi_{\text{dS/S}} + x^2\chi_{\text{S/SS}} \qquad (5)$$

Table 2. Monomer−Monomer Interaction Parameters for Styrene and Styrenesulfonate Monomeric Units

x	150 °C	160 °C	170 °C	190 °C
0.007	77.7	71.4	68.1	
0.010	65.8		43.4	37.3
0.012	41.2		36.1	26.2

The term χ_{blend} is now a function of only sulfonation level and two segmental interaction parameters, $\chi_{\text{dS/S}}$ and $\chi_{\text{S/SS}}$, of which only $\chi_{\text{S/SS}}$ is unknown.

Despite the small value of $\chi_{\text{dS/S}}$ reported in the literature, the first term contributes appreciably to χ_{blend} owing to the small values of x in this study. However, the second term accounts for the substantial increase in χ_{blend} with degree of sulfonation and the corresponding drop in miscibility found above. Using this simplified equation (eq 5), $\chi_{\text{S/SS}}$ is found to be very large, in fact always greater than 25, and to vary significantly with temperature and sulfonation level (Table 2). The temperature dependence in $\chi_{\text{S/SS}}$ is consistent with the observed UCST behavior. The sulfonation dependence of $\chi_{\text{S/SS}}$ contradicts the copolymer blend theory in which the monomer−monomer interaction parameters are expected to be independent of composition. In fact, eq 3 is based upon the same assumptions as the Flory−Huggins theory, which is a mean-field description of blends with weak dispersive interactions. The polymer blends considered here clearly involve strong repulsions between the hydrophobic styrene monomeric units and the hydrophilic styrenesulfonate monomeric units and specific dipole−dipole attractions between the sulfonic acid groups. The interactions give rise to the increase in glass transition temperature (Table 1). Even in the absence of microphase separation, interactions of this strength almost certainly undermine any mean-field description of blend thermodynamics.

A related way to view this issue is to note the profound effects of even a minute degree of sulfonation. For instance, a sulfonation level of 0.7 mol % corresponds to ∼4−5 sulfonic acid moieties along the polymer that has ∼625 monomeric units at this molecular weight; this small number of sulfonic acid groups is sufficient to drive dPS:P(S−SS$_x$) blends from miscible (at $x = 0$ mol %) to partially miscible. With strong interactions one additional acid group added to the polymer could lead to significant changes in phase behavior. Under such circumstances, a mean-field description cannot be expected to be reliable. Indeed, one might argue that the statement “$\chi_{\text{S/SS}} \approx 25$” is in some sense a contradiction in terms because the magnitude of the monomer−monomer interactions that this represents undermines the very foundation of the Flory−Huggins interaction parameter used to determine the value. Recognizing these limitations, the data in Table 2 are perhaps most useful as a clear indicator of the profound incompatibility between styrene and styrenesulfonate.

The preceding discussion raises the point that, with these strong interactions, very small changes in the degree of sulfonation can have profound effects on blend miscibility. Up to now, the discussion has treated the copolymer as a homogeneous material with a single composition. However, the statistics of random sulfonation will necessarily lead to polymer chains with a distribution of sulfonation about the mean value, just as statistical processes in polymerization lead to a distribution of chain lengths. Because of the polydispersity of composition, a slight difference in the acid content between chains can generate demixing of the system.[34]

According to copolymer blend theory in eq 3, two copolymers of the same type but with different compositions ($A_{1-y}B_y$:$A_{1-x}B_x$) have a χ_{blend} that increases as $(x - y)^2$, specifically χ_{blend}

$= (x - y)^2\chi_{AB}$.[10,31] Immiscibility between copolymers of different compositions is well-known in the literature; for instance, blends of another random copolymer, poly(styrene-*ran*-acrylonitrile), P(S−AN), will phase separate when the nominal composition between the two copolymer samples differs by more than 4 mol %.[35] The monomer−monomer interaction parameter $\chi_{S/AN}$ is reported to be 0.176 at 169 °C, which is substantially smaller than the styrene/styrenesulfonate interaction parameter found here. With such strong unfavorable interactions, it is possible that even a narrow distribution of chain composition in a P(S−SS$_x$) random copolymer may be sufficient to allow phase separation within a single sample.

In the case of a completely random copolymer, Fredrickson et al. computed the stability limit for such "self-demixing" to be given by

$$\chi_s = [2f(1 - f)]^{-1} \tag{6}$$

where f is the nominal fractional composition of the copolymer.[36,37] (Interestingly, the degree of polymerization does not appear in this expression because the statistical narrowing of the composition distribution compensates for the increased tendency for phase separation as the degree of polymerization increases.) According to this expression, random copolymers ($A_{1-f}B_f$) will demix when the composition-dependent χ_s is smaller than the monomer−monomer interaction parameter, χ_{AB}. Symmetric copolymers with $f = 0.5$ provide the smallest χ_s value ($\chi_s(f{=}0.5) = 2$), corresponding to the greatest tendency to phase separate. In contrast, the copolymers considered here are highly asymmetric; for example, the highest degree of sulfonation studied here (corresponding to $f = 0.026$ in eq 6) leads to a value of $\chi_s = 19.7$. Comparing this value to the segmental interaction parameter, $\chi_{S/SS} > 25$, this theory predicts that P(S−SS$_{0.026}$) is, by itself, phase-separated. Furthermore, Nesarikar et al. computed the equilibrium coexistence compositions of phase-separated random copolymers for very large χ_{AB} values.[38] Their calculations show demixing into phases that have quite similar compositions. Thus, one expects significant experimental challenges in detecting phase separation in random copolymers, should it indeed be present. We have no evidence for demixing in our P(S−SS$_x$) random copolymers, though demixing appears likely with such a large segmental interaction parameter. This conclusion should also be tempered with the recognition that, like the Flory−Huggins theory used to extract $\chi_{S/SS}$ from the coexistence data, the demixing theories described here are also based on mean-field descriptions that are suspect in the case of such strong interactions.

While we are unaware of any direct evidence of phase separation in a P(S−SS$_x$) random copolymer, Kirkmeyer et al. have shown evidence suggesting phase separation in a zinc neutralized P(S−SS$_x$) material.[39] In their study, scanning transmission electron microscopy (STEM) detected a heterogeneous distribution of Zn-rich aggregates in a partially (25%) neutralized P(S−SS$_{0.053}$) ionomer; some micron-sized regions exhibit no Zn-rich aggregates while other regions possess numerous Zn-rich ionic aggregates. This heterogeneity might reflect an underlying phase separation in the sulfonate polystyrene. Our ongoing study of P(S−SS$_x$) materials will include blend miscibility studies of dP(S−SS$_y$):P(S−SS$_x$) in which $x \approx y$, where again we use deuterium labeling and FRES to detect subtle phase behavior.

Conclusions

The phase behavior of deuterated polystyrene and poly(styrene-*ran*-styrenesulfonate) random copolymers was studied using the ion beam technique of forward recoil spectrometry to construct dPS composition profiles. In the temperature range 150−190 °C, complete miscibility exists at $x \le 0.2$ mol % and complete immiscibility exists at $x \ge 2.6$ mol %. Partial miscibility exists in dPS:P(S−SS$_x$) blends with $x = 0.7$, 1.0, and 1.2 mol % sulfonation in the same temperature range, and the dPS concentration profiles provide the compositions of the coexisting phases. The coexisting compositions provide phase diagrams for the partially miscible blend systems, all of which demonstrate upper critical solution temperatures (UCST). With increasing levels of sulfonation, the partially miscible dPS:P(S−SS$_x$) blends exhibit increasing UCSTs and broader immiscible regions in the phase diagrams.

A variety of mean-field theories were used to discuss these blend miscibility results. The Flory−Huggins theory was used to calculate χ_{blend} values from the coexisting compositions, and the dependence of χ_{blend} on temperature and sulfonation is consistent with the dPS:P(S−SS$_x$) phase diagrams. From χ_{blend} the copolymer blend theory was used to calculate the styrene/styrenesulfonate segmental interaction parameters ($\chi_{S/SS}$). The calculated values of $\chi_{S/SS}$ are greater than 25 and depend on the copolymer composition; both observations call into question the rigorous application of mean-field approaches in polymers with such strong interactions. Nonetheless, the ramifications of a large monomer−monomer interaction parameter in a random copolymer were discussed particularly with respect to the potential for demixing.

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