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Blend Miscibility of Sulfonated Polystyrene Ionomers with Polystyrene: Effect of Counterion Valency and Neutralization Level

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ABSTRACT: Elastic recoil detection (ERD) was used to characterize the phase behavior of blends involving neutralized poly(styrene-*ran*-styrenesulfonate) ionomers (P(S-SS$_x$)-M) and deuterated polystyrene (dPS). The lightly sulfonated ionomers (acid mole fraction $x = 0.007$) were neutralized with various cations (M): sodium (Na^+), barium (Ba^{2+}), and zinc (Zn^{2+}). The dPS:P(S-SS$_{0.007}$)-M blends have a higher upper critical solution temperature (UCST) than the dPS:P(S-SS$_{0.007}$) blends, indicating that neutralizing the acid copolymer reduces blend miscibility. The UCST is higher when P(S-SS$_{0.007}$) is neutralized (125%) with divalent cations, Ba^{2+} and Zn^{2+}, rather than with a monovalent cation, Na^+. In addition, as the level of neutralization increases from 25% to 125%, the miscibility in the dPS:P(S-SS$_{0.007}$)-Zn blends decreases; this was not observed in the dPS:P(S-SS$_{0.007}$)-Na blends. Complementary linear viscoelastic measurements were performed on a copolymer and ionomers with a higher acid content. Upon neutralization, the storage moduli at lower frequencies indicate slower polymer chain relaxations and the self-assembly of ionic functional groups. The specific interactions that produce these physical cross-links also impede blend miscibility.

Introduction

Ionomers are random copolymers with a small fraction (<10 mol %) of acid groups partially or fully neutralized by a metal counterion. Unique properties such as improved mechanical strength, hydrophilicity, and proton conductivity arise from the incorporation of ionic functional groups into hydrophobic polymers. Because of these characteristics, ionomers are utilized in a wide range of applications such as adhesives, fuel cell membranes, and ion exchange resins.[1−3] Much commercial and scientific attention has been focused on polymer blends involving ionomers as a means for producing materials with new or improved properties compared to those of its constituents. In particular, sulfonated polystyrene P(S-SS$_x$) ionomers are effective at producing new miscible blends.[4−6] For example, researchers found that P(S-SS$_x$) ionomers form miscible blends with nylon, polyurethane, and poly(dimethylphenylene oxide) at specific acid mole fractions (x) and blend compositions.[7−9] Miscibility is achieved through attractive interactions between the ionic groups of the ionomer and the polar groups on the other polymer in the blend.

Recently, efforts have also been made to examine blend systems without specific attractions between the constituent polymers, such as blending polystyrene with a sulfonated polystyrene ionomer. Hara et al. studied the mechanical properties and morphology in blends of sulfonated polystyrene ionomer with polystyrene.[10−12] Transmission electron micrographs of a 70/30 wt % solution-cast film PS:P(S-SS$_{0.026}$)-Na sample showed micron-size ionomer-rich phases dispersed in the sample, which were absent in the PS:P(S-SS$_{0.011}$)-Na sample. Hara et al. concluded that, given the absence of macrophase separation at the lower acid content, there is a considerable degree of homopolymer:ionomer miscibility. In addition to phase separation observed in sulfonated polystyrene blends, our lab has shown evidence suggesting macrophase separation in a zinc neutralized P(S-SS$_x$) material.[13] In that study, scanning transmission electron microscopy (STEM) detected a heterogeneous distribution of Zn-rich nanoaggregates in a partially (25%) neutralized P(S-SS$_{0.053}$) ionomer. Some micron-sized regions do not exhibit Zn-rich aggregates, while other regions contain numerous aggregates. These morphological results indicate macrophase separation in a P(S-SS$_x$) ionomer; therefore, the phase behavior of these materials requires further examination.

Previously, we have obtained phase diagrams for blends of lightly sulfonated P(S-SS$_x$) in the free acid form with deuterated PS (dPS) and found the partially miscible blends exhibited upper critical solution temperature (UCST) behavior.[14] The phase diagrams show an increase in UCST as sulfonation level increases until the blend becomes immiscible at $x > 2.6$ mol % from 150 to 190 °C. The intramolecular and intermolecular complexation of the sulfonate groups reduces the dPS:P(S-SS$_x$) miscibility as the sulfonation level increases.

In the present study, we explore how ionic interactions that result from neutralizing P(S-SS$_x$) will impact its blend miscibility with dPS. Phase diagrams of dPS and neutralized acid copolymer (P(S-SS$_{0.007}$)-M), where the cation (M) is sodium (Na^+), barium (Ba^{2+}), or zinc (Zn^{2+}), are constructed using the ion beam technique of elastic recoil detection (ERD), also known as forward recoil spectrometry (FRES). The rheological behavior of P(S-SS$_{0.019}$) ionomers will also be examined, and a comparison is made between these linear viscoelastic results and the phase diagrams obtained by ERD.

Experimental Section

Materials. Lightly sulfonated polystyrene P(S-SS$_x$) was prepared according to the procedure described in our previous paper.[14] Two

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sulfonation levels of P(S-SS$_x$) were used in this study: $x = 0.007$ for the ERD experiments and $x = 0.019$ for the rheological measurements.

Both levels of P(S-SS$_x$) were neutralized by first dissolving the copolymer in a mixture of toluene/methanol (90/10 v/v). A stoichiometric amount of base (vacuum-dried metal acetate) was dissolved in 50/50 v/v toluene/methanol and added dropwise to the agitated P(S-SS$_x$) solution. The combined solution was stirred for 1 h at ~40 °C. The neutralized polymer was recovered by solvent-casting the solution in a Teflon Petri dish for 2 days and then dried under vacuum for 12 h at 115 °C. The stoichiometric neutralization level is denoted by y as either 25 or 125 mol %, P(S-SS$_x$)-yM. All polymers were stored in vacuum desiccators.

The sulfonic acid content was determined by Robertson Microlit Analysis (Madison, NJ) using elemental sulfur analysis via ion chromatography. These sulfonation levels were consistent with the results of titration experiments performed in our lab. Infrared spectra of polymer films were determined using the NaCl disk method. The films for FTIR were made by melt-pressing at 160 °C and 15 000 psi for 5 min and then slowly cooled to room temperature. FTIR spectra were recorded using a Perkin-Elmer System 2000 FTIR spectrometer at a resolution of 2 cm^{-1}, and each film was scanned 64 times at room temperature.

FTIR spectra indicate the successful sulfonation of PS and subsequent neutralization of P(S-SS$_x$). Relative to the PS spectrum, the P(S-SS$_{0.007}$) spectrum exhibits a small peak at 1102 cm^{-1}, corresponding to the in-plane bending vibration of the benzene ring substituted by $-SO_3H$ (Figure 1a). At the higher level of sulfonation ($x = 0.019$), vibrations from both $-SO_3H$ and $-SO_3^-$ groups are evident in the acid copolymer (Figure 1b). Our results are consistent with previous FTIR data for comparable materials.[15-17] Upon complete neutralization with Na$^+$ or Zn^{2+}, the $-SO_3H$ peak disappears, while both $-SO_3^-$ and $-SO_3M$ peaks increase (Figure 1a). These assignments are also evident when comparing P(S-SS$_{0.019}$), P(S-S$_{0.019}$)-25Zn, and P(S-S$_{0.019}$)-125Zn, where the $-SO_3^-$ and $-SO_3M$ peaks exhibit intermediate intensities when partially neutralized (Figure 1b).

Viscoelastic Properties. Rheology measurements were performed on a Rheometrics Solid Analyzer (RSAII) with a shear sandwich fixture in oscillatory shear. The solvent-cast ionomer was compression molded at 160 °C into rectangular films with dimensions 12.5 mm × 16 mm × 0.5 mm. In some cases, the solvent-cast material had to be remolded to obtain homogeneous, bubble-free samples. Frequency sweeps were collected under nitrogen at 170 °C with a strain of 0.5%, which is in the linear viscoelastic regime as determined by strain sweeps. A second frequency sweep recorded the same storage and loss moduli, which suggests the absence of polymer degradation. Time–temperature superposition methods failed because there are multiple activation energies for the terminal processes, as previously reported.[18,19]

Elastic Recoil Detection (ERD). Thin bilayer films were prepared for ERD by dissolving solvent-cast P(S-SS$_{0.007}$) ionomers in a mixture of toluene/THF (80/20 v/v) at a concentration of 4 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 residual solvent. The thickness of the dried film was determined by ellipsometry. Similar films of dPS were spin-coated on 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$_x$)-M base layer and allowed to dry. The bilayer films for ERD were annealed at 170–195 °C for 5 days to allow interdiffusion. Our previous paper evaluated the possibility of thermal degradation by subjecting a bulk sample of P(S-SS$_{0.026}$) to the most extreme annealing conditions, and no evidence for desulfonation or chain scission was found by DSC or GPC.[14] In addition, thermal gravimetric analysis was performed on bulk P(S-SS$_{0.026}$)-M (M = Na, Zn, or Ba), and these ionomers exhibited better thermal stability than the acid copolymer as denoted by a higher onset thermal degradation temperature.[20]

During ERD, ^{4}He ions impact the sample and expel ^{1}H and ^{2}D atoms from the bilayer with energies characteristic of their original depths to provide ^{1}H and ^{2}D concentrations as a function of depth in the bilayer. As described earlier, the hydrogen concentration profiles from dPS:P(S-SS$_x$)-M bilayers provide the coexisting equilibrium compositions with an accuracy of 2 vol % P(S-SS$_x$).[14] In contrast to traditional methods like differential scanning calorimetry, where miscibility is determined by the number of glass transition temperatures, ERD determines the extent of miscibility by directly measuring the coexistence compositions that denote the phase boundaries between one- and two-phase regions.

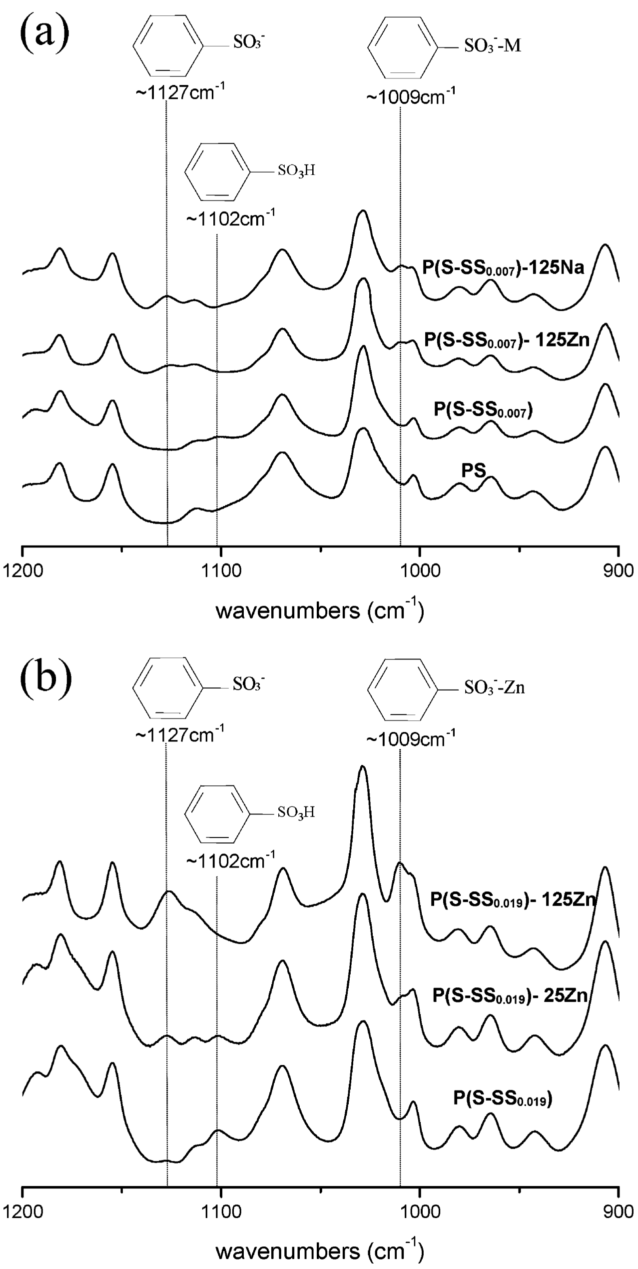

Figure 1. FTIR spectra from compression molded films of (a) P(S-SS$_{0.007}$) and (b) P(S-SS$_{0.019}$) at various neutralization levels.

Results and Discussion

Melt Rheology. In P(S-SS$_x$)-M ionomers, the ionic groups associate into nanometer-size aggregates due to electrostatic attractive forces and act as temporary cross-links that greatly impact their viscoelastic properties.[21-23] Rheological results in Figure 2 show that the P(S-SS$_{0.019}$) acid copolymer and its ionomers exhibit typical terminal behavior ($G' \sim \omega^2$) at 170 °C, where G' and ω are the storage modulus and frequency, respectively. At a frequency of ~100 rad/s the storage moduli

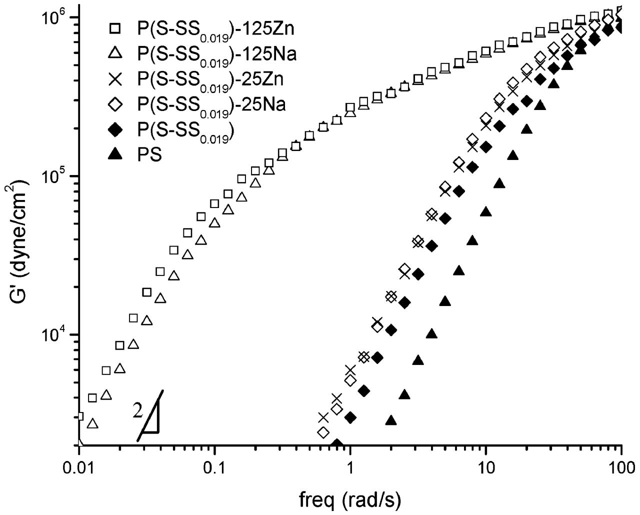

Figure 2. Storage modulus of P(S-SS$_{0.019}$)-Na and P(S-SS$_{0.019}$)-Zn at 25% and 125% neutralization level in comparison to P(S-SS$_{0.019}$) and PS. Rheology was performed at 170 °C and 0.5% strain.

Table 1. Relaxation Times for PS, P(S-SS$_{0.019}$), and P(S-SS$_{0.019}$)-M as a Function of Cation and Neutralization Level at 170 °C

M	neutralization level (%)	relaxation time (s)
PS	0	0.1
P(S-SS$_{0.019}$)	0	0.4
Na	25	0.5
Zn	25	0.6
Na	125	42
Zn	125	53

are comparable for P(S-SS$_{0.019}$)-Na and P(S-SS$_{0.019}$)-Zn ionomers with both 25% and 125% neutralization levels. This suggests that the cross-link densities are independent of ion type, Na$^+$ or Zn^{2+}, and neutralization level.

In contrast, the terminal relaxation times (τ) are strongly dependent on the neutralization level. The relaxation times of the 125% neutralized ionomers are orders of magnitude greater than PS, P(S-SS$_{0.019}$), and the 25% neutralized P(S-SS$_{0.019}$) ionomers. Introducing sulfonic acid groups to PS slightly extends the storage modulus of P(S-SS$_{0.019}$) when compared to homopolymer PS due to the hydrogen bonding between sulfonate groups. Neutralizing these acid groups to 25% provides only a marginal increase in the terminal relaxation time, but neutralizing to 125% significantly extends the storage modulus. The relaxation time is determined by

$$\tau = \lim_{\omega \to 0} \frac{G'}{\omega G''} \qquad (1)$$

where ω, G', and G'' are frequency, storage modulus, and loss modulus, respectively.[24] In Table 1, the relaxation time for P(S−SS$_{0.019}$) is 0.4 s, which is 4 times slower than PS, due to the hydrogen bonding between the sulfonic acid groups. When P(S-SS$_{0.019}$) is neutralized to 25%, τ increases only slightly, while τ increases by a factor of 100 for the 125% neutralized ionomers. From this data, it is apparent that, even at a low sulfonation level ($x = 0.019$), neutralization creates substantial changes in the rheological behavior.

A smaller difference in τ is observed between Na$^+$ and Zn^{2+} neutralized P(S-SS$_{0.019}$) ionomers, where the ionomers neutralized with a divalent cation exhibit a 20% increase in τ relative to those with a monovalent cation. The longer relaxation times exhibited by Zn^{2+} ionomers indicate stronger electrostatic interactions relative to Na$^+$. These results are consistent with previous dynamic mechanical analysis of fully neutralized P(S-SS$_x$) ionomers demonstrating stronger electrostatic interactions for divalent cations.[25−27] Lefelar et al. found that while the moduli of the storage modulus remained the same, the rubbery plateau of P(S-SS$_{0.018}$)-Zn persists to higher temperatures than P(S-SS$_{0.018}$)-Na.[23,28] Similarly, Hara et al. observed a longer rubbery plateau when P(S-SS$_{0.041}$) samples were neutralized with divalent calcium (Ca^{2+}) as compared to monovalent potassium (K$^+$) and cesium (Cs$^+$).

This dynamical mechanical behavior is understood in terms of the electrostatic interactions and coordination between the anions and cations in ionomers. FTIR studies have probed the local acid group environment in neutralized poly(ethylene-*ran*-methacrylic acid) and suggest acid groups have different interactions with monovalent or divalent cations.[25−27] Using a crystal closest packing model, Lefelar and Weiss showed that monovalent Na$^+$ ion pairs can be added more readily to a multi-ion aggregate due to the availability of unshared oxygens from $-SO_3^-$ as compared to divalent Zn^{2+} ion pairs.[29] This model indicates that Zn^{2+} is more tightly bound in the ionic aggregates than Na$^+$ and is consistent with the longer relaxation times found in our Zn^{2+} neutralized materials. However, the extent of neutralization plays a more profound role in determining the relaxation time.

Phase Behavior. Most blend miscibility studies examine the physical properties of two or more phases in a blend by detecting differences in the indices of refraction or glass transition temperatures. However, our bilayer blend samples are annealed so that two partially miscible polymers intermix until thermodynamic equilibrium is reached at which point the coexistence compositions are directly determined.

We have previously used this method to probe the miscibility of dPS:P(S-SS$_x$) blends.[14] Here, our interest is dPS:P(S-SS$_x$)-M blend systems where we expect the diffusion of dPS into P(S-SS$_x$)-M ionomers to be slower due to the presence of ionic aggregates. Scanning transmission electron microscopy (STEM) has been conducted on P(S-SS$_{0.019}$) ionomer spin-cast thin films (50 nm). These images show nanoscale aggregates that are spherical, monodisperse, and uniformly distributed throughout the polymer matrix.[20] Colby et al. found that the self-diffusion coefficient of P(S-SS$_{0.085}$)-Na is slower than that of homopolymer PS by a factor of 30.[30] This retardation is mainly ascribed to the association of ion pairs, which Colby et al. refer to as “stickers”, and the effect is increased as more stickers are added. In light of Colby’s work, we used longer annealing times and higher annealing temperatures for these dPS:P(S-SS$_x$)-M ionomer blend systems. Concentration profiles are indistinguishable for bilayers annealed at 170 °C for 5 and 10 days, confirming that our annealing conditions are sufficient to reach equilibrium.

The coexistence compositions determined from the ERD concentration profiles are used to construct phase diagrams for the partially miscible dPS:P(S-SS$_{0.007}$)-M blends. The phase diagrams (Figure 3) show that the dPS:P(S-SS$_{0.007}$)-M ionomer systems (solid lines) have a higher UCST than the dPS:P(S-SS$_{0.007}$) systems (dashed lines). This shows that the neutralization of an acid copolymer reduces its miscibility. For example, previous results indicate that dPS:P(S-SS$_{0.007}$) is fully miscible at 190 °C,[14] while dPS:P(S-SS$_{0.007}$)-Na, dPS:P(S-SS$_{0.007}$)-Zn, and dPS:P(S-SS$_{0.007}$)-Ba are partially miscible at the same temperature. Partial miscibility is the equilibrium condition in which a two-component system exhibits two distinct phases with coexistence compositions (ϕ', ϕ'') that satisfy $0 < \phi'' < \phi' < 1.0$. Reduced dPS miscibility with P(S-SS$_{0.007}$) ionomers as

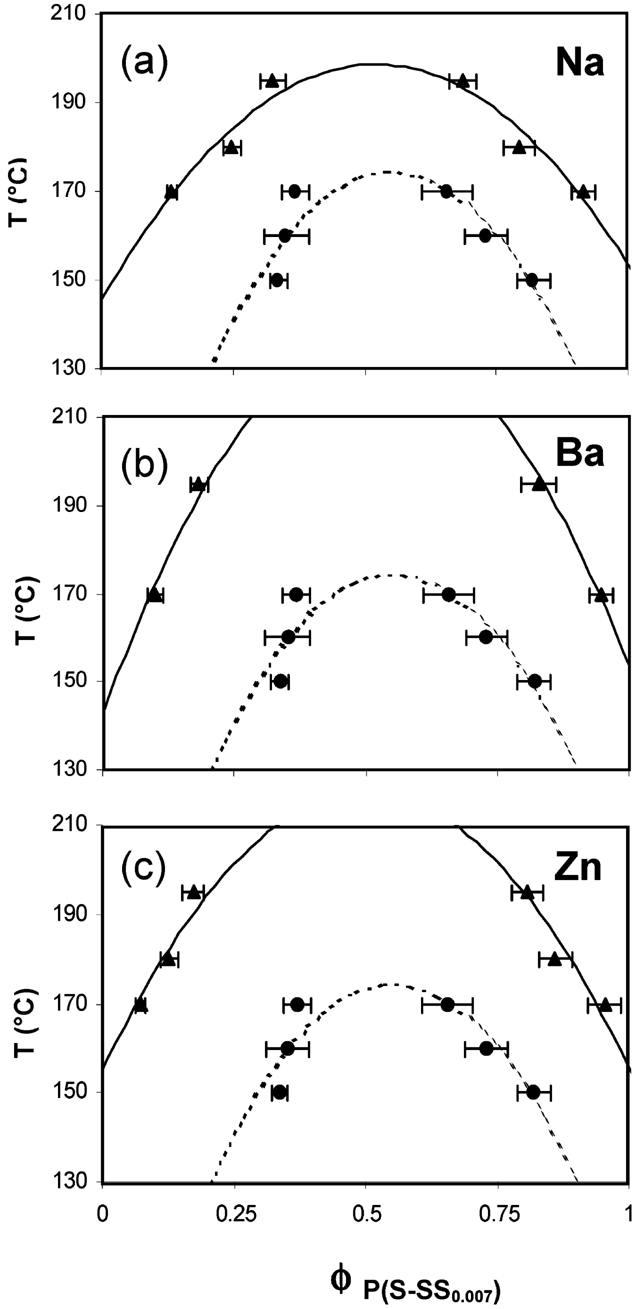

Figure 3. UCST phase diagrams for dPS:P(S-SS$_{0.007}$)-125M where M are (a) Na, (b) Ba, and (c) Zn represented by (▲) and the blend of dPS:P(S-SS$_{0.007}$) is represented by (●). The dashed and solid lines have been drawn to guide the eye.

compared to P(S-SS$_{0.007}$) acid copolymers is expected because miscibility is limited by the ionic aggregates.

Figure 3 also demonstrates that counterion valency affects the phase diagrams for these blends, where neutralizing with divalent cations Ba^{2+} and Zn^{2+} creates a higher UCST than neutralizing with monovalent cation Na^{+}. This finding is consistent with our rheological behavior observed in P(S-SS$_{0.019}$) ionomers. The longer relaxation times of P(S-SS$_{0.019}$)-Zn relative to P(S-SS$_{0.019}$)-Na at both 25% and 125% neutralization indicate the stronger ionic association in P(S-SS$_x$)-M^{2+} ionomers. The stronger ionic associations in P(S-SS$_x$)-M^{2+} ionomers relative to P(S-SS$_x$)-M^{+} ionomers limits the miscibility of dPS.

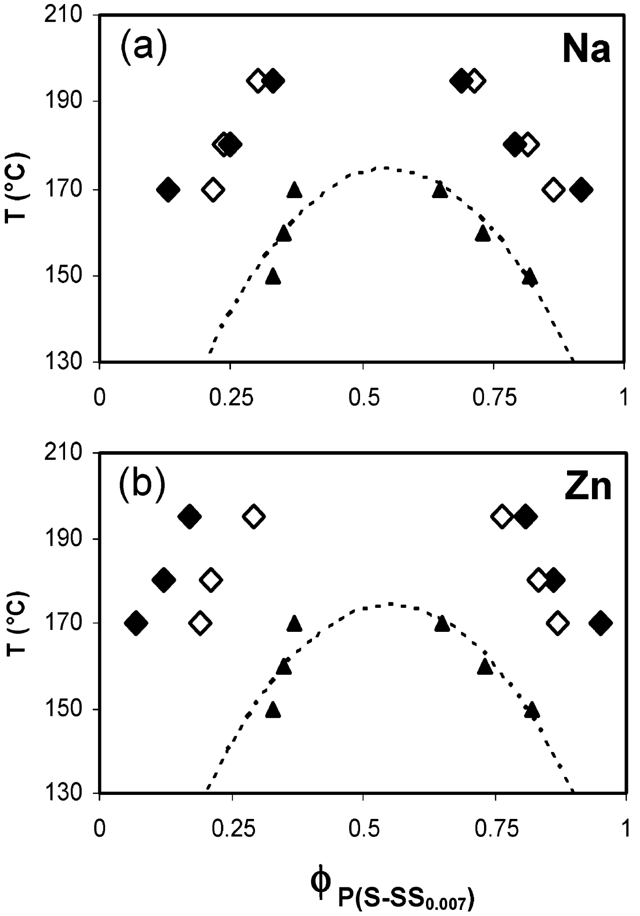

Figure 4. UCST phase diagrams for (a) dPS:P(S-SS$_{0.007}$)-Na and (b) dPS:P(S-SS$_{0.007}$)-Zn where the neutralization levels are 25% (◇) and 125% (◆). The blend of dPS:P(S-SS$_{0.007}$) is represented by (▲).

In addition to the effect of cation on dPS:P(S-SS$_x$) ionomer blend miscibility, the level of neutralization also has an effect. Figure 4 compares the phase diagrams of dPS:P(S-SS$_{0.007}$)-Na and dPS:P(S-SS$_{0.007}$)-Zn blends with 25% and 125% neutralization. At these levels of neutralization, the dPS:P(S-SS$_{0.007}$)-Na phase diagrams are comparable, while the dPS:P(S-SS$_{0.007}$)-Zn blends exhibit less miscibility at higher neutralization. This effect of neutralization is modest compared to the dramatic (~100 times) increase in relaxation time associated with increasing from 25 to 125% neutralization. Equally puzzling is the fact that 25% neutralization has a profound effect on miscibility relative to its comparatively modest effect on relaxation time.

Rheology probes the process of ion hopping in which repetitious breaking and re-forming of cross-links occur during the melt flow of polymer.[1] The propensity for ion hopping and thereby interchange of ionic groups between aggregates increases at higher temperatures. While rheology detects the dynamics of ion hopping, the dPS:P(S-SS$_{0.007}$)-M blend phase diagrams indicate the extent to which the ionomer morphology can accommodate homopolymer PS. Our main finding is that P(S-SS$_{0.019}$) ionomers exhibit longer relaxation time than its acid copolymer, and this corresponds to a reduction in the blend miscibility of dPS:P(S-SS$_{0.007}$)-M systems as compared to the dPS:P(S-SS$_{0.007}$) system. Stronger ionic interactions make for longer relaxation times, and stronger ionic interactions make it more difficult for dPS to penetrate the P(S-SS$_x$)-M ionomer morphology, which reduces the blend miscibility. The strength of ionic interactions per ionic group increases with cation valency from monovalent to divalent, and the magnitude of ionic interactions increases with the level of neutralization.

To further discuss our results, we hypothesize how the ionomer morphology changes when blended with homopolymer. For this discussion, let us assume that the number density of ionic aggregates is comparable at both 25% and 125% neutralization and ionic aggregates contain both unneutralized and neutralized acid groups. Consequently, the 25% neutralized ionomer has fewer metal cations in each ionic aggregate, which might account for the observed absence of a X-ray scattering peak in this ionomer while IR spectroscopy indicates partial neutralization. This scenario is consistent with the minor effect of neutralization level on blend miscibility and the dramatic effect on the relaxation time. In the case of miscibility, the inclusion of PS into a partially or fully neutralized ionomer occurs by the swelling of the ionomer matrix by the homopolymer. The extent of swelling depends on the elastic restoring force as determined by the number density of ionic aggregates (that is the separation between the ionic aggregates), such that with the proposed morphology the extent of miscibility will be only slightly influenced by the level of neutralization. Interestingly, this hypothesis suggests a strong effect from the level of acid comonomer because this strongly influences the number density of ionic aggregates. In contrast, the rheological response depends on the strength of the ionic aggregates, which is slightly different for Na^+ and Zn^{2+} neutralized materials but significantly different for 25% and 125% neutralized as the metal content of the ionic aggregates increases. When partially neutralized, applied strain can readily remove (unneutralized) acid groups from the ionic aggregates, but this becomes more difficult in a fully neutralized ionomer when every acid group is associated with a metal cation. The purpose of this hypothesis is to direct future studies.

Conclusion

The terminal relaxation time increases as the material changes from PS to P(S-$SS_{0.019}$), P(S-$SS_{0.019}$)-25Na, P(S-$SS_{0.019}$)-25Zn, P(S-$SS_{0.019}$)-125Na, and P(S-$SS_{0.019}$)-125Zn, with the most dramatic difference occurring between the 25% and 125% neutralized ionomers. The small differences in τ between Na^+ and Zn^{2+} neutralized ionomers indicate that divalent cations provide a stronger ionic interaction within the ionic aggregates. The blend miscibility of dPS:P(S-$SS_{0.007}$)-M blends were measured by ERD, which provides the coexistence compositions. Relative to homopolymer:acid copolymer blends of dPS: P(S-$SS_{0.007}$), the homopolymer:ionomer blends show less miscibility and the UCSTs are comparable when the ionomers are 25% and 125% neutralization. The dPS:P(S-$SS_{0.007}$)-M blends neutralized with divalent cations are less miscible than those neutralized with monovalent cations, which we discuss in terms of the stronger ionic interactions for divalent cations. We propose a morphology that is consistent with both the dramatic effect of neutralization level observed in the rheology and the subtle effect observed in the blend miscibility.

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References and Notes

(1) Eisenberg, A.; Kim, J.-S. *Introduction to Ionomers*; John Wiley & Sons: New York, 1998; p 352.
(2) Elabd, Y. A.; Napadensky, E.; Sloan, J. M.; Crawford, D. M.; Walker, C. W. *J. Membr. Sci.* **2003**, *217*, 227−242.
(3) Yarusso, D.; Cooper, S. L. *Macromolecules* **1983**, *16*, 1871−1880.
(4) Eisenberg, A.; Hara, M. *Polym. Eng. Sci.* **1984**, *24*, 1306−1311.
(5) Hara, M.; Eisenberg, A. *Macromolecules* **1984**, *17*, 1335.
(6) Hara, M.; Eisenberg, A. *Macromolecules* **1987**, *20*, 2160.
(7) Lu, X.; Weiss, R. A. *Macromolecules* **1992**, *25*, 6185−6189.
(8) Rutkowska, M.; Eisenberg, A. *Macromolecules* **1984**, *17*, 821−824.
(9) Tomita, H.; Register, R. A. *Macromolecules* **1993**, *26*, 2796−2801.
(10) Bellinger, M. A.; Sauer, J. A.; Hara, M. *Macromolecules* **1994**, *27*, 6147−6155.
(11) Bellinger, M. A.; Sauer, J. A.; Hara, M. *Polymer* **1997**, *38*, 309−315.
(12) Hara, M.; Bellinger, M.; Sauer, J. A. *Polym. Int.* **1991**, *26*, 137−141.
(13) Kirkmeyer, B. P.; Weiss, R. A.; Winey, K. I. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 477−483.
(14) Zhou, N. C.; Xu, C.; Burghardt, W. R.; Composto, R. J.; Winey, K. I. *Macromolecules* **2006**, *39*, 2373−2379.
(15) Atorngitjawat, P.; Klein, R.; Runt, J. *Macromolecules* **2006**, *39*, 1815−1820.
(16) Li, H.-M.; Liu, J.-C.; Zhu, F.-M.; Lin, S.-A. *Polym. Int.* **2001**, *50*, 421−428.
(17) Fitzgerald, J.; Weiss, R. A. *Columbic Interactions in Macromolecular Systems*; American Chemical Society: Washington, DC, 1986; pp 35−47.
(18) Tierney, N.; Register, R. A. *Macromolecules* **2003**, *36*, 1170−1177.
(19) Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 99−185.
(20) Zhou, N. C. Phase Behavior and Morphology of Sulfonated Polystyrene Systems. Thesis, University of Pennsylvania, Philadelphia, 2007.
(21) Douglas, E. P.; Waddon, A. J.; MacKnight, W. J. *Macromolecules* **1994**, *27*, 4344−4352.
(22) Eisenberg, A.; Navratil, M. *Macromolecules* **1973**, *6*, 604−612.
(23) Weiss, R. A.; Fitzgerald, J. J.; Kim, D. *Macromolecules* **1991**, *24*, 1071−1076.
(24) Tant, M. R.; Mauritz, K. A.; Wilkes, G. L. *Ionomers, Synthesis, Structure, Properties and Application*; 1997.
(25) Walters, R. J.; Sohn, K. E.; Winey, K. I.; Composto, R. C. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *41*, 2833−2841.
(26) Coleman, M. M.; Lee, J.-Y.; Painter, P. C. *Macromolecules* **1990**, *23*, 2339−2345.
(27) Page, K. A. C. K. M.; Moore, R. B. *Macromolecules* **2005**, *38*, 6472−6484.
(28) Weiss, R. A. *Polym. Prepr.* **1985**, *26*, 21−22.
(29) Lefelar, J. A.; Weiss, R. A. *Macromolecules* **1984**, *17*, 1145−1148.
(30) Colby, R. H.; Zheng, X.; Rafailovich, M. H.; Sokolov, J.; Peiffer, D. G.; Schwarz, S. A.; Strzhemechny, Y.; Nguyen, D. *Phys. Rev. Lett.* **1998**, *81*, 3876−3879.

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