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Miscibility of Polystyrene-Based Ionomers with Poly(2,6-dimethyl-1,4-phenylene oxide)

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ABSTRACT: Sulfonated and carboxylated styrenic ionomers are investigated for their miscibilities with poly(2,6-dimethyl-1,4-phenylene oxide) (PXE), a nonassociating polymer. The nanoscale phase separation in the ionomer component presents a barrier to miscibility, which is nonetheless possible when the functionalization level or PXE content is low. The ionomers absorb PXE up to a certain level, beyond which additional PXE forms a pure phase. As the level of added PXE approaches the saturation limit, ionic groups can be forced from aggregates into the matrix. The saturation limit diminishes as the ionomer's functionalization level increases, but it also depends on the ion type, with ZnSPS showing the highest miscibility of all ionomers studied. The differences in miscibility thus depend on the morphology of the pure ionomer and the strength of the ionic associations.

I. Introduction

Polymer-polymer miscibility has attracted wide interest due to its scientific and technological importance.[1,2] As is well-known, polymer pairs are immiscible at high molecular weight unless the interaction parameter χ is very small or negative, due to the small entropic driving force for mixing long chains. When one component (polymer A) is an ionomer, miscibility can be even more difficult to achieve, due to aggregation of ionic groups producing a nanometer-scale phase separation[3] with a characteristic dimension smaller than the coil size of the other polymer (B). To fit within this fine domain structure, polymer B must lose conformational entropy, a loss which would generally outweigh the small gain in translational entropy produced upon blending. Immiscibility would be the net result for an athermal blend ($\chi = 0$), which has been demonstrated for polystyrene blended with sulfonated polystyrene (SPS) ionomers; the two are immiscible even for sulfonation levels as low as 3 mol %.[4,5]

In order to produce miscible blends containing an ionomer component, two approaches have been considered. The first, which has been employed by several groups, is to use a polymer B which can specifically interact with the ionomer's ionic groups; nitrogen-containing homo- and copolymers have been the most commonly used.[6-9] This approach can be applied to a wide range of base polymers; however, since it relies on the formation of A-B associations which are stronger than the ionic associations in the pure ionomer, such materials can be very difficult to process.[10] Also, this approach tends to destroy the ionic aggregates, which are responsible for many of the unique properties of ionomers.[3] A second approach seeks out systems where the parent polymers have a negative χ, using exothermic mixing of the ionomer's matrix phase with the homopolymer to drive the blending. While the requirement of $\chi < 0$ restricts the scope of this approach, miscible blends produced by this route would be no more difficult to process than the ionomers themselves and could retain the nanophase separation produced by aggregation of ionic groups. The combination of polystyrene ionomers and poly(2,6-dimethyl-1,4-phenylene oxide)—more coveniently referred to as poly(xylenyl ether) (PXE)—may be the most promising candidate for this type of blend because of the unusual exothermic mixing of the base polymers,[11] coupled with the diversity of polystyrene-based ionomers which have been synthesized. Several studies on styrenic ionomers blended with PXE have recently been reported. Up to 15 wt % PXE mixes with poly(styrene-*co*-sodium methacrylate), when the methacrylate content is 6 mol %.[12] Styrene/methacrylic acid/potassium methacrylate terpolymers at a 93.5:4.6:1.9 molar ratio are miscible with PXE for all blend compositions, though other polymers containing 5.6 or more mol % potassium methacrylate produce immiscibility.[13] Several researchers have investigated blends of sulfonated polystyrene (SPS) ionomers blended with PXE. The earliest work[14] showed that adding a small amount of Na^+-neutralized SPS (NaSPS) to unfunctionalized PS/PXE blends was quite effective in retaining an antistatic additive, while having no deleterious effect on mechanical properties. However, no direct measurements of miscibility were made. Both Wong and Weiss[15] and Hseih and Peiffer[16] later found that, for NaSPS, as the sulfonation level was increased, immiscibility was reached soonest for blends that were rich in PXE; for a 50:50 blend, immiscibility appears to occur at 4-5% sulfonation. Comparison of these results with the styrene/methacrylate ionomer case would suggest that sulfonate and carboxylate ionomers have comparable effects on miscibility, an unexpected result. Hseih and Peiffer[16] also found that miscibility was improved somewhat by sulfonating both components but that replacing the methyl groups in PXE with phenyl groups[17] produced immiscible systems in all combinations. Recently, our laboratory has reported investigations of PXE blended with Zn^{2+}-neutralized SPS (ZnSPS), which produced substantially greater misicibility than NaSPS.[18] Steckle et al. have found a similarly large solubility of PXE in block copolymers containing Zn^{2+}-neutralized SPS blocks.[19] The motivation for the present research was to understand how and by how much miscibility could be altered by changing the cation and anion types.

II. Experimental Section

A. Synthesis and Sample Preparation. Sulfonated polystyrene (SPS) was obtained by sulfonation of polystyrene with acetyl sulfate in 1,2-dichloroethane, following the method described in the literature.[18,20] The starting polystyrene (additive-free experimental product of the Dow Chemical Co.) was identical to that used in our previous investigation;[18] a recent molecular weight redetermination via gel permeation chromatography[21] yielded $M_w = 299\,000$, $M_w/M_n = 2.4$. After sulfonation, monomeric

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acid byproducts were removed by Soxhlet extraction with water for about 1 week, until the extract titrated neutral. Sulfonation efficiency based on the amount of sulfuric acid added was found to be 70 ± 3%.

Carboxylated polystyrene (CPS) was synthesized by random copolymerization of styrene and 4-vinylbenzoic acid as described elsewhere;[21] polystyrene homopolymer synthesized by the same method produced $M_w = 161\,000$, $M_w/M_n = 2.1$. The functionalization levels of both types of ionomers were obtained by titration in tetrahydrofuran (THF) to the phenolphthalein end point with a standardized aqueous solution of NaOH. No precipitation was observed during the titrations. The PXE is from the same batch as used previously,[18] with $[\eta] = 0.47$ dL/g ($CHCl_3$, 25 °C), and is estimated to have $M_w = 32\,000$, $M_w/M_n \approx 2$.

Neutralization of the SPS ionomers was accomplished by addition of the stoichiometric amount of aqueous solutions of the hydroxide (Na) or acetate (Zn, Mn, Ni), or a THF solution of tributylamine, to a THF solution of the polymer. CPS ionomers were neutralized similarly except that, for ZnCPS, zinc acetylacetonate (in a 1:9 methanol/THF solution) was used.[21] Neutralized ionomers were recovered by precipitation into heptane. Blends were obtained by an analogous procedure, neutralizing a THF solution in which both the acid ionomer and PXE were dissolved; complete dissolution of the PXE required mild heating (≈50 °C). Precipitated samples were dried in an air oven at 200 °C for 10 h followed by vacuum drying at 180 °C for 24 h. The samples were then compression-molded at 250 °C for 30 min, and the molds were either quenched by immersion in cold water or allowed to cool in ambient air (~5 °C/min). Comparison of samples prepared with the different cooling regimens revealed no discernable miscibility differences. The pure ionomer samples are denoted with a code such as "Ni5.2SPS", indicating a 5.2 mol % sulfonated polystyrene stoichiometrically neutralized with Ni^{2+}. In the same manner, "Na4.5CPS/PXE 60:40" indicates a blend of 60 parts by weight Na4.5CPS and 40 parts PXE.

B. Instrumental Methods. Differential scanning calorimetry (DSC) was carried out at 20 °C/min with a Perkin-Elmer DSC-4 calibrated with indium. Before the actual measurements, samples were scanned to 280 °C, held for 5 min, and quenched to room temperature at 320 °C/min to minimize enthalpy relaxation peaks. The glass transition temperature (T_g) is defined as the midpoint of the heat capacity change, and the transition's breadth (ΔT_g) is defined by the separation of the points where a line tangent to the midpoint intersects the pre- and posttransition base lines. No crystallinity ($T_m = 249$ °C for PXE) was ever observed in the blends. Electron spin resonance (ESR) measurements were performed with a Bruker ER-200D at an X-band frequency of 9.34 GHz. The molded samples were cracked into small pieces to fit into 5-mm sample tubes, which were sealed under nitrogen.

The equipment and data reduction methods used to acquire the SAXS data have been described previously.[18] Desmeared, background-subtracted SAXS intensities are presented as I/I_eV versus q, where I_e is the scattering from a single electron and V is the illuminated sample volume; the scattering vector magnitude $q = (4\pi/\lambda) \sin \theta$, where θ is half the scattering angle and λ is the X-ray wavelength. Because some of the blends show relatively weak scattering, accurate background subtraction is critical. The scattering curve of an unfunctionalized polystyrene was found to be well-described by $I/I_eV = A[\exp(Bq^2)]$, where the exponential term is necessary to account for the leading edge of a polystyrene wide-angle reflection[22] near $q = 7$ nm^{-1}; best-fit values were determined as $A = 231$ nm^{-3} and $B = 0.0376$ nm^2. For the ionomers, we postulated a background of the form $A[\exp(Bq^2)] + C$, where A and B have the same significance and numerical values as for homopolystyrene, and C is introduced to describe the additional scattering in the ionomer due to phase mixing. Best-fit values of C were determined using the high-q region of each curve.

III. Results and Discussion

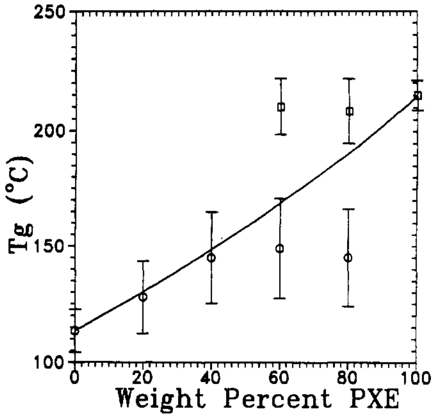

Figure 1. Summary of DSC results for Na2.8SPS/PXE blends: (○) T_g of the mixed phase, (□) T_g of the second phase (essentially pure PXE). Bars denote the onset and end-point of each transition.

Figure 1 summarizes the DSC results for Na2.8SPS blended with PXE in various ratios. At 40 wt % PXE and below, only a single glass transition temperature can be observed. This T_g follows, to a good approximation, the Fox equation,[23] using the measured T_g values of the pure components, further indicating that these blends are miscible.[18] At 60 wt % PXE and above, two glass transitions are observed. The lower T_g corresponds to that found in the 40:60 blend, while the upper T_g is close to that of pure PXE. These results indicate that Na2.8SPS/PXE blends containing more than 40 wt % PXE are phase-separated, with one phase being roughly a 40:60 blend of Na2.8SPS/PXE and the second phase being essentially pure PXE. This behavior was observed in all the blends we examined, although the PXE content dividing the one- and two-phase regions depends on the functionalization level, the bound anion, and the neutralizing cation; for some systems of low functionalization level, only a single T_g, varying in accordance with the Fox equation, was observed over the entire composition range. Wong and Weiss[15] and Hseih and Peiffer[16] found similar results, although the values they reported for the lower T_g vary somewhat more with composition than do ours, perhaps resulting from differences in sample preparation.

Despite the observation of two glass transitions, the Na2.8SPS/PXE blends containing 60 and 80 wt % PXE (indeed, all blends examined in this investigation) were optically clear and had the characteristic amber color of PXE. (Blends containing NiSPS also had a greenish tinge.) Since it is not expected that the refractive indices of the mixed phase and PXE would be identical for all materials examined, this suggests that the phases are dispersed into submicron domains. As shown in Figure 1, careful observation of the breadth of the upper T_g reveals that the end-point temperature was unaltered by blending, while the onset temperature is lower in the blends than in pure PXE. This suggests that the second phase in these materials may be nearly pure PXE but that extensive phase mixing occurs at the domain interfaces. The lower T_g, which broadens with the addition of PXE, achieves a constant breadth at the point where the system moves from homogeneous to two-phase.

Similar behavior has been observed in blends of PXE and styrenic block copolymers, such as styrene/butadiene/styrene, when the styrene block is relatively short.[24-28] At low PXE additions, the styrene phase can absorb all of the PXE, and the material shows a single T_g (in addition to the T_g of the nonstyrenic block). When the PXE concentration exceeds a critical value, a phase which is almost pure PXE appears, while the composition of the mixed styrene/PXE phase remains invariant. In this region of the phase diagram the styrene phase is saturated

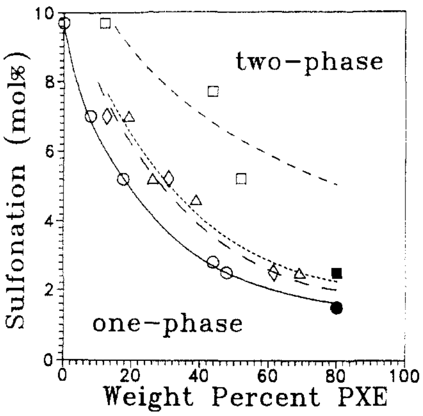

Figure 2. Phase diagram for SPS/PXE blends: (○, —) NaSPS; (◇, – –) MnSPS; (△, · · ·) NiSPS; (□, – –) ZnSPS. Filled symbols denote single-phase blends. Lines are only guides to the eye.

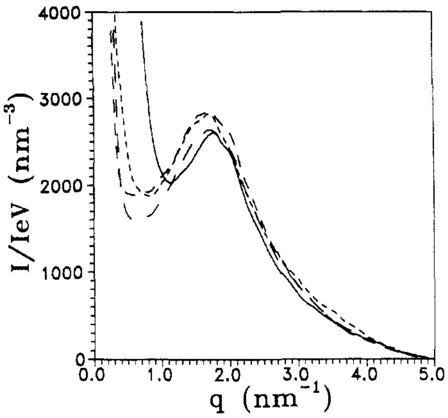

Figure 3. SAXS patterns for pure 5.2SPS ionomers neutralized with different cations: (—) NaSPS, (– –) MnSPS, (· · ·) NiSPS, (- - -) ZnSPS.

with PXE, with the saturation limit imposed by the covalent attachment of the polystyrene segment to a block which is immiscible with PXE. The numerical value of this saturation limit is principally dependent on the chain length of the styrene block;[27] longer styrene blocks can solubilize more PXE of a given molecular weight. Moreover, electron micrographs[28] of PXE blended with a styrene/isoprene diblock show that the excess PXE is present as small domains, with a characteristic size of 1 μm.

Similar behavior would be expected if the styrenic component were chemically cross-linked; that is, it should absorb PXE up to a particular level, but once this saturation limit is exceeded, additional PXE should form a pure phase. In both cases, the principal parameter governing the saturation limit value, for a fixed PXE chain length, is the styrene chain length: the block length in the block copolymer case or the length between cross-links in the network case.

Ionomers bear some resemblance to both these cases, with the ionic aggregates behaving as physical cross-links. Therefore, we expect that the relevant parameter in the ionomer case is the molecular weight between ionic groups, which is inversely related to the functionalization level; in fact, this is the trend we observe. A more interesting question is whether the type of neutralizing cation influences the miscibility.[18] To answer this question, we introduce a different sort of phase diagram, where the ordinate is the functionalization level; an example for the various SPS ionomers is shown in Figure 2. Blends in the lower left of this diagram (low PXE content, low functionalization level) are single-phase, while those in the upper right (high PXE content, high functionalization level) are two-phase. The boundary points were obtained by measuring the lower T_g values for two-phase blends, using the Fox equation to calculate the composition of the mixed phase.

The most interesting feature of the phase diagram is that blend miscibility is strongly influenced by the choice of neutralizing cation, with Na^+ producing the most immiscible system, Zn^{2+} producing the most miscible,[29] and Ni^{2+} and Mn^{2+} yielding intermediate cases. For the NaSPS case, the position of the phase boundary differs somewhat from what would be obtained with the data of Wong and Weiss,[15] which in turn differs from the data of Hseih and Peiffer;[16] however, this may simply be related to differences in the molecular weight of the PXE, as each group obtained its material from a different source.

The striking difference in miscibility shown in Figure 2 begs the question: why does the choice of cation influence the miscibility behavior? One possibility is that the morphology of the neat ionomers is strongly influenced by the cation. Although the nanoscale phase separation in SPS certainly imposes a barrier to miscibility with PXE, the situation might be far worse if the ionic groups were *not* aggregated, since the interaction parameter between PXE and a styrenesulfonate unit is expected to be large and positive. Kressler et al.[30] showed that certain phase-separated styrene/methyl methacrylate (MMA) block copolymers showed no miscibility limit with PXE, while analogous random copolymers became immiscible with PXE at 20 wt % MMA. With ionomers having a random distribution of ionic groups along the chain, such as SPS, it is thought that, due to topological constraints, many of the ionic groups may remain isolated in the polymer matrix.[31,32] If this fraction of isolated ionic groups were to change with the cation, it might influence the miscibility.

Small-angle X-ray scattering (SAXS) patterns for the 5.2SPS ionomers neutralized with various cations are shown in Figure 3. Very little difference is observed between these materials as the neutralizing cation is varied, implying little change in the morphology. Moreover, the SAXS intensity background (see the Experimental Section) varies little with the neutralizing cation. Previously, we suggested that the difference in miscibility between NaSPS/PXE and ZnSPS/PXE may be due to differences in the strength of the ionic associations. Zn^{2+} is known to produce relatively weak associations due to its more covalent binding nature,[33] a feature which is most evident in the lower melt viscosity of ionomers when Zn^{2+} is chosen as the neutralizing cation. Especially when comparing Mn^{2+}, Ni^{2+}, and Zn^{2+}, which have the same charge and very similar ionic radii, the binding chemistry of the cation is the principal difference. If the associations are weaker, then the morphology of a Zn^{2+} ionomer could be more easily rearranged, say, by making smaller aggregates or by dispersing more ionic groups into the polymer matrix, in order to accommodate more PXE. The data in Figure 2 are easily interpreted this way, if Na^+ groups interact the most strongly, followed by Ni^{2+} and Mn^{2+}, and finally by Zn^{2+}. In this context, the PXE is acting as a probe of the association strength of the ionic groups, in particular their desire to associate into nanometer-size aggregates.

Previously, we showed via SAXS that ionic aggregates are still present in ZnSPS/PXE blends, although the extent of phase separation is reduced relative to the pure ionomer.[18] In order to better elucidate the state of the system in the macroscopically single-phase region (which still shows nanophase separation), we performed SAXS and ESR experiments on Mn2.5SPS/PXE blends. SAXS

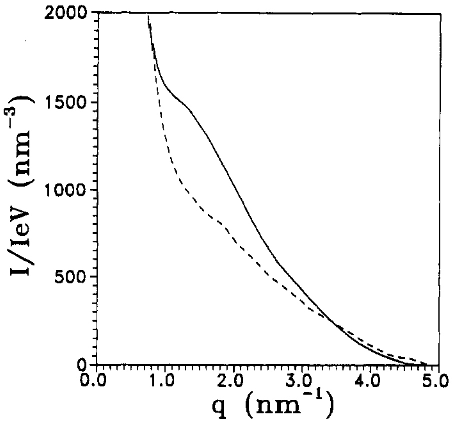

Figure 4. SAXS patterns for (—) Mn4.5SPS and (- - -) Mn4.5SPS/PXE 60:40 showing the diminution of the ionic peak upon blending.

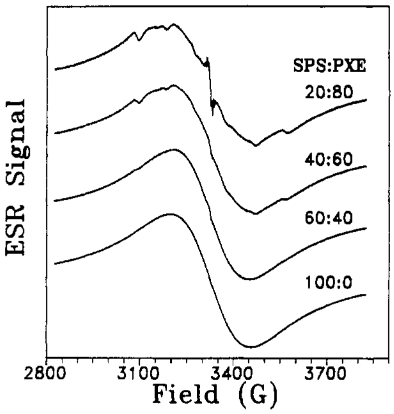

Figure 5. ESR data for Mn2.5SPS/PXE blends (top to bottom): 20:80 w/w Mn2.5SPS/PXE, 40:60, 60:40, 100:0 (pure ionomer).

data for Mn2.5SPS and Mn2.5SPS/PXE 60:40 (a miscible blend) are shown in Figure 4. Upon blending, the intensity of the ionic peak is strongly suppressed, although a hint still remains at the approximate position of the peak in the neat ionomer, similar to previous observations for the ZnSPS/PXE blend system.[18]

Electron spin resonance (ESR) measurements were performed on Mn2.5SPS/PXE blends of varying composition; as Figure 2 shows, DSC indicates that these blends are miscible up to about 62 wt % PXE. The paramagnetic Mn^{2+} cation has proven to be a useful probe of the association state in ionomers.[34-36] Associated Mn^{2+} groups (within about[34] 6 Å of another Mn^{2+}) produce a single broad resonance in the ESR spectrum, while isolated Mn^{2+} produce a six-line hyperfine spectrum. For fully-neutralized ionomers which have been heated above the matrix glass transition temperature, only associated Mn^{2+} are observed,[35] indicating that few ionic groups are normally dispersed in the matrix. Figure 5 shows our ESR data, and, as expected, the pure Mn2.5SPS shows only a single broad resonance. As more PXE is added, the development of the hyperfine pattern characteristic of isolated Mn^{2+} can be seen superimposed on the broad association. (The narrow signal in the center of the blend spectra in Figure 5 is believed to arise from phenolic radicals created in the PXE during molding; it is present in all blends, as well as pure PXE molded in the same way, and absent in all pure ionomers.[37] Comparison with diphenylpicrylhydrazyl (DPPH) indicates that $g_{iso} = 2.004$ for the PXE signal, which is consistent with g values for phenolic radicals.[38]) Since the 40:60 blend is close to the miscibility limit, it is expected that the ratio of isolated to associated Mn^{2+} in the 40:60 and 20:80 blends should be similar; this is approximately observed, though the ratio is somewhat larger for the latter blend. Since a dramatic increase in the fraction of isolated Mn^{2+} occurs on going from the 60:40 to 40:60 blends, the difference between the 40:60 and 20:80 blends may simply reflect that the phase boundary actually occurs at slightly greater than 60 wt % PXE. Note that the increase in isolated Mn^{2+} *cannot* be explained simply by dilution of unpaired Mn^{2+}, which are nonetheless within 6 Å of another Mn^{2+} in the pure ionomer, to an average Mn^{2+}–Mn^{2+} separation at which the exchange interaction is eliminated; Mn0.92SPS, which has an ion content *below* that of the Mn2.5SPS/PXE 40:60 blend, shows only associated Mn^{2+} after heating.[35]

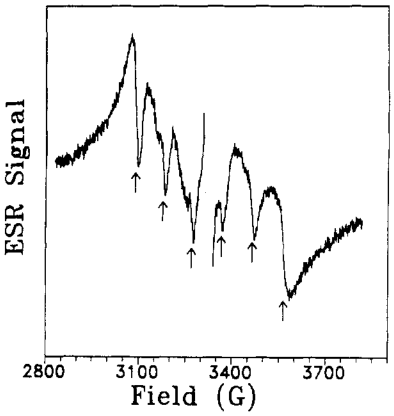

Figure 6. ESR data for a Mn2.5SPS/PXE 20:80 blend, after subtraction of the Mn2.5SPS signal. Arrows mark the positions of the six hyperfine lines.

To better analyze the hyperfine signal, the spectrum of the pure Mn2.5SPS was subtracted from that of the 20:80 blend. Note that this approach is not perfect, as the "broad" signal actually changes its breadth on blending, becoming wider with increasing PXE addition; this broadening is also characteristic of less-highly-associated Mn^{2+}. Figure 6 represents our best effort at subtraction; all six hyperfine lines can be seen, although the central two are somewhat distorted by the PXE signal. The hyperfine splitting is about 100 G, which is typical.[34-36]

Having examined the SPS/PXE blends, we wished to investigate the effect of the anion type on miscibility by comparing the miscibilities of sulfonated and carboxylated polystyrene ionomers with PXE. The CPS ionomers should have an essentially random distribution of carboxylated units along the chain, as discussed previously;[21] a random distribution is also presumed for SPS ionomers, since they are functionalized by a homogeneous post-polymerization reaction. Therefore, the chain topologies in the two cases are very similar, the ionic group placement within the monomer unit is identical, and thus differences in the morphology and miscibility behavior must reflect differences in the strength of the ionic associations. As already demonstrated,[21] the NaCPS ionomers show rather complete nanophase separation and morphologies (as judged by SAXS) very similar to those of SPS ionomers of similar ion content. Figure 7 shows the phase diagram for NaCPS; surprisingly, NaCPS is only slightly more miscible with PXE than NaSPS. NaCPS ionomers similar to ours (though not identical) exhibit viscosities orders of magnitude below those found for analogous NaSPS materials,[20] implying that the carboxylate associations are much weaker. We have also observed that the high-temperature dynamic mechanical relaxation peak in NaCPS occurs at a somewhat lower temperature than in NaSPS.[21,37]

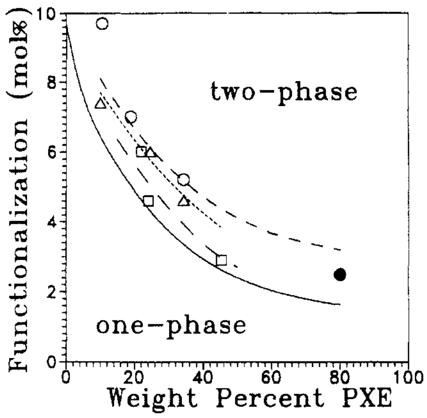

Figure 7. Phase diagram for CPS/PXE and TBASPS/PXE blends: (—) NaSPS, from Figure 2, shown for comparison; (□, – –) NaCPS; (○, - - -) TBASPS; (△, · · ·) ZnCPS. Filled symbol denotes a single-phase blend. Dashed lines are only guides to the eye.

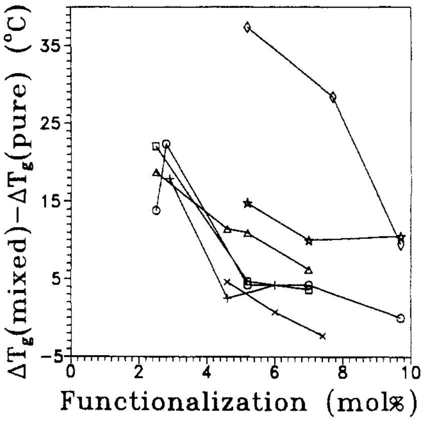

Figure 8. Breadth of the T_g of the blends' mixed phases less the breadth of the corresponding pure ionomer T_g: (○) NaSPS, (□) MnSPS, (△) NiSPS, (◇) ZnSPS, (☆) TBASPS, (+) NaCPS, (×) ZnCPS.

Blending essentially probes the thermodynamics of the system—how strong the ionic associations are—while viscoelastic and rheological measurements probe how quickly an ionic group can move between aggregates, a kinetic quantity. While there is thus no fundamental connection between the two, intuitively one would expect a correlation, and postulating differences between thermodynamics and kinetics to explain the similar miscibilities of NaSPS and NaCPS is not a very satisfying explanation. Another possibility is that, while the ionic groups in NaSPS and NaCPS have different interaction strengths, both interact sufficiently strongly that the PXE is not able to effect much disruption of the morphology in either case, leading to very similar miscibility behavior. Unfortunately, since Na^+ is not paramagnetic, this hypothesis cannot be tested by ESR; solid-state ^{23}Na NMR might prove fruitful.[39]

Comparison of Figures 2 and 7 reveals another unexpected result: the ZnCPS ionomers are far less miscible with PXE than are the ZnSPS ionomers. Fortunately, this result is more easily understood, as ZnCPS does *not* possess a morphology similar to SPS ionomers or to NaCPS; rather, the nanophase separation is much poorer, as evidenced by broad and weak peaks in the SAXS patterns and a greater SAXS background intensity.[21] As already stated, a large fraction of dispersed ionic groups would adversely affect an ionomer's miscibility with PXE, and this is expected to apply to ZnCPS.

To investigate a case where the ionic groups might be highly dispersed, we chose blends of PXE with SPS ionomers neutralized with tributylamine (TBA). TBA-neutralized SPS ionomers have viscosity vs shear rate curves indistinguishable from those of the precursor unfunctionalized polystyrene,[40] which suggests that either the ionic groups are unassociated or the groups can exchange partners very rapidly in the melt. SAXS measurements on a 9.7 mol % sulfonated TBASPS showed no discernable peak,[37] though a substantial low-angle upturn is visible; the TBASPS SAXS pattern resembles many published curves for the acid form of SPS,[31,41–43] which show a weak peak, if any, but a strong low-angle upturn. Since resonant SAXS experiments[42] have shown that the contrast factors for the peak and the upturn are proportional, the inherent ion-polymer contrast in TBASPS should be sufficient to reveal a peak if the morphology of TBASPS corresponds to that of metal-neutralized SPS ionomers. We thus infer that the extent of phase separation in TBASPS is much reduced, although additional confirmation (such as via small-angle neutron scattering from materials with labeled amine) would be desirable.

The phase boundary for TBASPS blended with PXE lies considerably to the left of that for ZnSPS and is not far from the boundaries for MnSPS and NiSPS, even though the ionic associations in TBASPS are expected to be relatively weak. This demonstrates that very weak ionic associations (TBASPS, ZnCPS), yielding many ionic groups dispersed in the matrix, can be nearly as detrimental to miscibility as very strong ionic associations (MnSPS, NiSPS). The greatest miscibility is achieved for an intermediate case (ZnSPS), where phase separation is nearly complete in the pure ionomer, but the morphology is susceptible to disruption by PXE.

A final clue to the origin of the miscibility differences between these similar ionomers lies in how the glass transition of the mixed phase broadens as PXE is added. Figure 8 plots the width of the transition in the mixed phase, less the width of the glass transition in the pure ionomer, vs functionalization level. All the points shown in Figure 8 correspond to *saturated* blends, that is, the mixed phase in two-phase materials. Most of the systems fall in a band where this difference is 0–25 °C. However, the difference for ZnSPS is much greater, followed by TBASPS; recall that the PXE miscibility for the SPS salts varies in the same manner. Since a broad glass transition reflects heterogeneity within a phase, the mixed phase in the ZnSPS/PXE blends must have a spatially inhomogeneous distribution of the PXE; this inhomogeneity is apparently connected with the usually-large solubility of PXE in ZnSPS and the extensive disruption of the ZnSPS morphology which accompanies PXE addition. By contrast, ZnCPS shows essentially no broadening of its glass transition when saturated with PXE; this indicates that what PXE the ZnCPS is able to absorb is distributed very uniformly. Comparing the TBASPS and ZnCPS results in Figure 8 demonstrates that, while they have rather similar miscibility behavior (Figure 7), the way in which the PXE is distributed is very different.

IV. Conclusions

PXE is miscible with a wide range of styrene-based ionomers, provided the functionalization level or PXE content is low. In several respects, the phase behavior of these blends resembles that for block copolymer–homopolymer or cross-linked polymer–homopolymer blends, in that the ionomer will absorb PXE up to a certain level; beyond this saturation limit, additional PXE forms a pure PXE phase. The saturation limit diminshes as the ionomer's functionalization level increases, which corresponds to a decrease in the average topological distance between ionic groups, as well as the average spacing between ionic aggregates. However, the value of the saturation limit also depends on the ion type. From ESR on MnSPS/PXE blends, we demonstrated that, as the level of added PXE approaches the saturation limit, ionic groups are forced from aggregates into the matrix. From this, we infer that the differences in miscibility behavior, among systems where the nanophase separation in the pure ionomer is nearly complete, are due to differences in the ease with which these ionic groups can be forced into the matrix—a measure of the strength of ionic associations.

However, if the nanophase separation in the pure ionomer is poor, as is the case for ZnCPS, miscibility can be severely reduced. Thus, the solubility limit does not increase monotonically as the association strength between ionic groups decreases. The largest solubility limit corresponds to an ionomer (ZnSPS) which has good nanophase separation when pure, but whose morphology can be disrupted by the addition of PXE.

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