The Effect of Diluents on the Ionic Interactions in Sulfonated Polystyrene Ionomers

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INTRODUCTION

The unique mechanical and rheological properties of ionomers are a consequence of strong associations between the ionogenic groups. These interactions result in microphase separated morphologies. One important question yet to be studied in any detail is the effect of polar and nonpolar diluents and plasticizers on the morphology and properties of ionomers. A useful strategy for studying this question is to employ a combination of instrumental techniques that probe different aspects of the ionomer microstructure. For example, infrared spectroscopy (IR) and electron spin resonance (ESR) monitor local interactions, while small angle x-ray scattering (SAXS) provides information on the bulk microstructure and dynamic mechanical analysis (DMA) measures molecular relaxation processes.

ESR is useful for studying cation-cation interactions in ionomers with paramagnetic cations such as Cu(II) or Mn(II). Fitzgerald and Weiss have recently shown that for a dilute solution of Mn(II)-neutralized sulfonated polystyrene in a polar solvent, the Mn(II) cations exist mostly as isolated ions or ion-pairs. However, in a relatively nonpolar solvent the cations are associated. Furthermore, upon the addition of a polar cosolvent to the nonpolar solvent (e.g., methanol to toluene), the cations can be solvated so that predominately isolated species are present.

The interaction between the anion and cation can be studied using Fourier Transform Infrared Spectroscopy (FTIR). The frequencies of the sulfonate stretching modes provide information on the local environment of the anion. For example, when a metal neutralized sulfonated polystyrene ionomer (SPS) is hydrated there is a shift in both the asymmetric and symmetric SO\textsubscript{3}\textsuperscript{-} M\textsuperscript{+} IR bands to lower wave-numbers. This indicates that water is able to dissociate the ion pair, thus weakening the polarization of the sulfonate anion by the cation.

Microphase separation in ionomers can be characterized by small angle x-ray scattering (SAXS). A maximum in the scattering vector \( k \) (\( k = 4\pi \sin \theta / \lambda \), where \( 2\theta \) is the scattering angle and \( \lambda \) is the wavelength of the radiation) is typically observed between 1.5 nm and 2.5 nm. The origin of this scattering peak has not yet been definitively established, but it is generally agreed that it is a consequence of the existence of ion-rich domains. The position of the scattering maximum has been found to be very sensitive to thermal history, and the addition of water.

This communication presents some preliminary results on the effect of diluents (plasticizers) and sample preparation on the morphology of ionomers. SPS was chosen as a model system because it is noncrystalline and soluble in a wide variety of organic solvents. Materials were characterized by SAXS, ESR, and DMA. FTIR studies of these ionomers are described in detail in ref. 7.
The preparation of SPS has been reported elsewhere. The neutralized ionomers were recovered by steam distillation, washed with methanol, and dried for 72 h under vacuum between 120–130°C. Films were prepared for the SAXS studies by compression molding at 180°C. Cast films of Mn-SPS ionomers were prepared from dimethylformamide (DMF), tetrahydrafuran (THF), a mixture of 90% toluene + 10% methanol, and a mixture of 90% THF + 10% water. The solvent was allowed to evaporate at room temperature for 48 h and final drying was accomplished in a vacuum oven at 45°C for 72 h. No residual solvent was detected either gravimetrically or by FTIR. Samples containing methanol or dodecane were prepared by suspending films above the solvent or immersing them in the solvent at 25°C in closed glass vials. The concentration of solvent was determined gravimetrically. Less volatile diluents such as glycerol and dioctyl phthalate (DOP) were mixed with the polymer on a heated two-roll mill.

SAXS studies were performed at the National Center for Small Angle Scattering Research at Oak Ridge National Laboratory using the 10 m camera. This apparatus utilizes a rotating anode x-ray source (λ = 0.1542 nm), crystal monochromatization of the incident beam, pin-hole collimation, and a two-dimensional position sensitive detector.

ESR spectra were obtained with a Varian E-3 spectrometer operating at x-band frequency. A quartz solution cell made by Wilmad Glass Co. was used for measurements on solutions.

DMA was carried out with a Rheometrics System 4 mechanical spectrometer using rectangular or parallel plate geometries in torsion. A frequency of 1 Hz was used and the temperature was varied from 25°C to 250°C.

RESULTS AND DISCUSSION

The viscoelastic behavior of the neat 1.82 mol% Na-SPS and the same material plasticized with 10% (wt) glycerol and 10% (wt) DOP is shown in Figure 1. The unplasticized ionomer exhibits a distinct plateau region in $G'$ and a loss peak in $G''$ above the primary glass transition temperature (Tg). Both of these features are

![Fig. 1. Dynamic and loss moduli for 1.82 mol% NaSPS with and without plasticizers.](image-url)
absent in the unmodified polystyrene. The rubbery plateau is due to the formation of an ionic network, and the loss peak has been attributed to the glass transition of the ionic clusters in other ionomers.\textsuperscript{12} Previously reported data\textsuperscript{9} for SPS ionomers showed that a significant change in the SAXS curve and the SAXS invariant occurred at about the same temperature as this mechanical loss, which indicates that it is indeed a consequence of local motions in the ionic clusters.

The addition of DOP lowers $T_g$ and shifts the entire modulus versus temperature curve to lower temperature, a result typically observed for plasticized polymers. Although the plateau in $G'$ and the loss peak in $G''$ move to lower temperature, these features, which are characteristic of ionic aggregation, remain. For the case of the ionomer containing glycerol, however, only a small decrease in $T_g$ was observed, and the rubbery plateau and the high-temperature loss peak disappeared. These results clearly indicate the preferential plasticization of the two phases of an ionomer by polar and nonpolar diluents as predicted by Lundberg, Makowski, and Westerman\textsuperscript{13} who measured the viscosity of similar ionomer compositions but only at a single temperature, 220°C. The polar glycerol preferentially partitions into the ionic domains and solvates the ionic interactions, thus influencing primarily that part of the viscoelastic behavior due to the ionic aggregation. The relatively nonpolar DOP affects only the polystyrene matrix, leaving the ionic associations intact.

An unanswered question arising from these data is why DOP should shift the ionic transition in an identical manner as it does $T_g$. This may be related to the competition between electrostatic and elastic forces that affect the stability of the ionic clusters as proposed by Eisenberg.\textsuperscript{14} Alternatively, the effect of a "matrix plasticizer" on the ionic cluster transition may be due in part to the presence of a significant hydrocarbon component in the cluster. Although the integrity of the ionic associations are preserved, the additional free volume of the cluster that may occur by some partitioning of the DOP into the cluster plasticizes the cluster glass transition. Why both the matrix and cluster transitions should be affected in the same manner is not clear. Additional studies are obviously needed before any explanation of this phenomenon may be considered conclusive.

![ESR spectra of 3% (w/v) solutions of 2.65 mol % MnSPS at room temperature.\textsuperscript{16}](image)
Direct evidence of the selective solvation of the different components of the SPS ionomer was obtained using ESR spectroscopy. Figure 2 shows the ESR spectra of solutions of Mn-SPS in a polar and nonpolar solvent. In a dilute solution of DMF, a polar solvent, the ESR spectrum exhibits six hyperfine lines characteristic of isolated Mn(II) ions. The ESR spectrum of the same polymer in THF, a relatively nonpolar solvent, is a single broad line, which indicates that the Mn(II) ions are predominantly associated. DMF is able to effectively solvate the Mn(II) ions while THF cannot. Other evidence that polar solvents interact preferentially with the ionic groups was previously published by Fitzgerald and Weiss. They showed that in a nonpolar solvent it was possible to solvate Mn(II) ions by the addition of a polar co-solvent such as methanol. Upon addition of methanol to a solution of Mn-SPS in toluene, the ESR signal changed from one broad absorption line into six hyperfine lines characteristic of isolated Mn(II) ions. A similar result is shown in Figure 2 for mixed solvents of THF and water.

The effect of polar diluents on the morphology of SPS ionomers was characterized by SAXS. Figure 3 shows the SAXS curves for a 3.85 mol% Zn-SPS that contains varying amounts of methanol. The addition of methanol reduces the intensity of the peak characteristic of ionic clusters and shifts the peak to lower scattering vector. Complementary ESR measurements on Mn-SPS have shown that the addition of methanol solvates the dipole-dipole interactions. Taken together, these results indicate that the methanol partially destroys the structural heterogeneity responsible for the peak, i.e., the ionic cluster. The scattering invariant decreased by a factor of about 3 from the dry ionomer to that containing 6.3% methanol. This indicates that the addition of methanol leads to phase mixing. These results are consistent with the ESR data that show that methanol weakens the interactions between the ionic entities. The shift of the SAXS peak to lower \( k \) corresponds to a larger characteristic distance. The origin of this characteristic distance, however, is not clear in that models that attribute it to interparticle and intraparticle interference have been proposed in the ionomer literature.

The effect of a nonpolar solvent, dodecane, on the SAXS curve of the same Zn-SPS sample is shown in Figure 4. The addition of 3.4% (wt) has no effect on the scattering curve. If the dodecane were present in the ionic clusters a reduction in the electron density difference between the ionic aggregates and the hydrocarbon matrix would be expected, which should result in a decrease in the intensity of the scattering peak. This and the fact that no change in the position of the SAXS peak
was observed indicate that the dodecane must be absent from the scattering entity, or in other words, it partitions into the hydrocarbon matrix.

The data presented here show that diluents can have a dramatic effect on the ionic associations in ionomers. This suggests that sample preparation, specifically the solvent from which the ionomer is isolated, may also affect these associations and the final ionomer morphology. Figure 5 compares samples of 7.6 mol% MnSPS that were compression molded and cast from various solvents. The sample cast from THF/water showed no scattering peak and the intensity was comparable to that of polystyrene. The samples cast from DMF and THF exhibited no scattering maximum; however, the intensity of the scattered radiation was significantly higher than for the THF/water system. The sample cast from toluene/methanol exhibited a
small scattering peak, but at a lower scattering vector than the heat pressed sample. It is apparent that specific solvation and evaporation effects are very important in understanding how the ionic associations form and this is currently being studied in more detail. The interpretation of these SAXS results is not straightforward due to the ambiguities involved with ascribing a specific model to the SAXS data. This will be discussed in more detail in another paper. It is interesting to note, however, that the ESR spectra of all of these samples indicate that the Mn(I1) ions are predominately associated. Therefore, even though the microstructure is affected by sample preparation, in all samples dipole-dipole or higher multiplet interactions are favored over isolated ion pairs.

CONCLUSIONS

We have established that it is possible to control the level of ionic associations and the microstructure of ionomers by means of sample preparation and/or the addition of low molecular weight diluents. Using a variety of techniques that probe the local environment of the ions, the higher order cluster morphology, and the molecular relaxation processes, we have clearly demonstrated that nonpolar diluents preferentially interact with the hydrocarbon matrix and polar diluents with the ionic-rich regions of the ionomer. A more detailed study of the effects of other solvent systems and other cations, as well as a more complete description of the changes in cluster microstructure, will be published elsewhere.

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