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An Infrared Spectrocopic Study of a Polyester Copolymer Ionomer Based on Poly(ethylene oxide)

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ABSTRACT: A molecular level understanding of the properties of polymer electrolytes can only be obtained through an identification of the types of ionic structures formed in these materials and their relationship to the motion of ions in these systems. Vibrational spectroscopy has proved to be a powerful tool in characterizing such local structures, and a detailed study of the infrared spectrum of a set of sulfonated PEO/aromatic polyesters is presented here. An analysis of the symmetric SO_3^- stretching mode revealed no detectable amounts of "free" SO_3^- ions in any of the ionomers, but bands due to ion pairs and aggregates were identified. The band due to aggregates increased in intensity relative to the band due to ion pairs as the temperature increased. Vibrational modes due to the poly(ethylene oxide) segments of the copolymers were characteristic of chains in the amorphous state. However, bands due to sequences of trans and gauche O−C−C−O−C−C−O conformations characteristic of the ordered state appeared to be favored upon complexation with ions. The interaction between cations and PEO portions of the chain "locks" the segments in their preferred structure to a large degree, so that compared to non-sulfonated copolymers there are relatively small changes in the relative intensities of conformationally sensitive bands with temperature.

Introduction

At the heart of an understanding of the properties of polymer electrolytes is a molecular level knowledge of the types of ionic structures formed in these materials and their relationship to the motion of ions in these systems. Ionic conductivity depends on both the number of charge carriers and their mobility, which in turn depends on complex relationships between the types of ionic groups present (e.g., single or "free" ions, triplets, etc.), how they are coordinated to polymer functional groups, and how ion motion is coupled to chain dynamics.

Recent work has revealed a particular conundrum.[1−4] Older studies aimed at separating the contributions of mobile ion concentration and ion mobility to conduction indicated that there was a significant concentration of "free" ions in the systems studied.[5−11] However, more recent dielectric spectroscopic studies, employing a model of electrode polarization to determine ion mobility and mobile ion concentration,[3] indicates that most ions exist in a bound state with only a very small fraction of free ions contributing to dc conduction.[1,2] It was suggested that one possible cause of this discrepancy is that different definitions of "free" or "mobile" ions apply to different techniques. However, there is another difference in the systems studied that needs to be addressed. Much of the earlier work involved mixtures of salts such as lithium or sodium triflate ($LiCF_3SO_3$, $NaCF_3SO_3$) with polymers such as poly(ethylene oxide), PEO. On the other hand, the dielectric work involved single ion conductors based on PEO/aromatic polyester or PEO/polyurethane ionomers, where the aromatic rings were sulfonated to various degrees. There is a very rich and extensive literature involving the application of vibrational spectroscopy to the characterization of salt/polymer complexes involving sulfonate groups and assignments of specific infrared bands and Raman lines to "free" ions, and various types of associated structures have been made.[12−27] Accordingly, in this article we will apply FTIR to a study of an ionomer that was the subject of previous dielectric spectroscopic studies.

Experimental Section

Materials. This study concerns an ionomer synthesized from a melt condensation of poly(ethylene glycol) (PEG, molecular weight 600) with the sodium salt of dimethyl 5-sulfoisophthalate and dimethyl isophthalate, the latter components being present in the proportions x:1−x, with x being the mole fraction of the sulfonated species, as illustrated in Figure 1. These polymers will be designated PEO600-x%Na, with the neutral polymer synthesized using dimethyl isophthalate designated PEO600-0%Na and the fully sulfonated ionomer PEO600-100%Na.

Synthesis of these polymers was accomplished using a step growth procedure described in detail in ref 1. These sodium polyester ionomers were then dissolved in water and diafiltered with deionized water using an Amicon 1000 molecular weight cutoff membrane. In ref 1 the Na cations in the ionomers were ion exchanged for Li, but this step was omitted in the materials under consideration here.

In addition to the ionomers, we also investigated the FTIR spectra of the following model compounds: Dimethyl isophthalate (DMIP, 99%) and sodium salt of dimethyl 5-sulfoisophthalate (DM5SIP-Na, 98%) were supplied by Sigma-Aldrich, and poly(ethylene glycol) (PEG400, M_n = 400 g/mol) was supplied by TCI America, Inc.

Specimen Preparation. DMIP and DM5SIP-Na are solid powders at room temperature. They were ground thoroughly with KBr powder at ∼3 wt % and pressed into pellets with thicknesses of about 1 mm. Ionomer and PEG400 specimens were prepared by spreading them directly on KBr windows with a spatula. After preparation, all specimens were transferred to a

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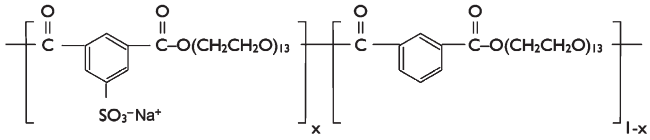

Figure 1. Chemical structure of the polyester random copolymer ionomersPE600-*x*Na, where *x* is the fraction of ionic isophthalate groups.

vacuum desiccator to remove residual moisture for at least 12 h before FTIR spectra were recorded.

Fourier Transform Infrared Spectroscopy. Infrared absorption spectra were collected using a Thermo Scientific Nicolet 6700 FTIR spectrometer in the range of 4000−400 cm^{-1}. A resolution of 2 cm^{-1} was used in the acquisition of all spectra, and 100 scans were signal-averaged. Spectra recorded at elevated temperature were obtained by using a Harrick high-temperature cell mounted in the spectrometer and a Harrick temperature controller having a reported accuracy of ±0.1 °C. Films were heated to selected temperatures and held for 5 min before spectra were recorded. Films used in this study were sufficiently thin to be within an absorbance range where the Beer−Lambert law is obeyed. A custom-made horizontal sample holder was used to prevent specimen flow at elevated temperatures. A dry atmosphere was maintained during collection of spectra for all materials.

Results and Discussion

We will focus mainly on a comparison of the spectra of fully sulfonated polymers to those that are not sulfonated at all. Samples with an intermediate degree of sulfonation will only be considered when the spectra show important additional features.

It is useful to start by considering the 2000−500 cm^{-1} region of the FTIR spectra of the PEO600-0%Na and PEO600-100%Na polymers, which are compared in Figure 2. In both spectra the PEO bands are characteristic of chains in the amorphous state. Some differences are immediately apparent, particularly in the 1000−500 cm^{-1} regions of the spectra. The most prominent of these involve the different pattern of substitution on the aromatic ring of the polymers, but there are other differences associated with both the sulfonate groups and PEO chains. We will first consider regions of the spectrum associated mostly but not exclusively with sulfonated aromatic ester groups, followed by a discussion of regions of the spectrum where PEO bands dominate. We will conclude by discussing some interesting changes that occur as a function of temperature.

Sulfonated Aromatic Ester Bands. Figure 3 shows the 1800−1550 cm^{-1} region of the spectra of the PEO-0%Na and PEO600-100%Na polymers, characterized by a strong ester carbonyl stretching mode centered near 1722 cm^{-1}. There are relatively small changes in this region of the spectrum with sulfonation, but we used the carbonyl band to establish criteria for obtaining difference spectra, two of which are shown in the figure. The films were not exactly the same thickness, and we found that subtracting 0.9 times the spectrum of PEO600-0%Na from that of PEO600-100%Na largely eliminated the carbonyl absorption from the spectrum. Not exactly, because there is a small shift in the frequency of this mode with sulfonation, giving rise to slight negative and positive lobes near 1730 and 1710 cm^{-1}, together with a weak positive lobe near 1705 cm^{-1}. The latter is probably due to a difference in asymmetry between the bands in the two spectra that is apparent in the "under-subtracted" spectrum, also shown in this figure (obtained by subtracting 0.7 times the spectrum of PEO600-0%Na from PEO600-100%Na). Comparing difference spectra with different degrees of subtraction often helps in deciding which features are real differences and which are artifacts of subtraction that are a consequence of band shifts or changes in shape. We will return to the ester group later, but the immediate point is that subtracting 0.9 times one spectrum from the other essentially eliminates a common contribution to both spectra. It can be seen that there is also a clear change in weak bands near 1600 cm^{-1}. These are in-plane aromatic ring breathing modes, and this difference is a consequence of the different degree of substitution on the aromatic rings between sulfonated and non-sulfonated polymers.

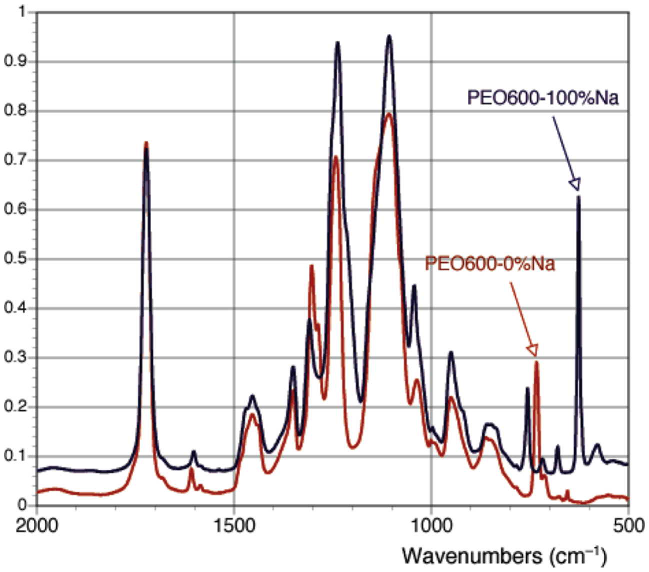

Figure 2. Comparison of the infrared spectrum of PEG600-100%Na to that of PEG600-0%Na in the range 2000−500 cm^{-1}.

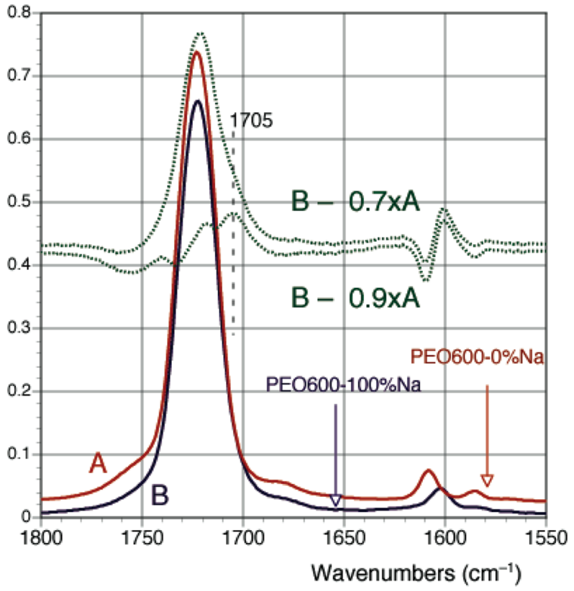

Figure 3. Comparison of the infrared spectrum of PEG600-0%Na (A) to that of PEG600-100%Na (B) in the carbonyl stretching region of the spectrum. Also shown are two difference spectra.

Far more significant changes can be seen in the 1400−1150 cm^{-1} region of the spectrum, as shown in Figure 4. Working from higher wavenumbers to lower, the band near 1350 cm^{-1} has been assigned to the CH_2 wagging vibration of PEO.[28−30] In their detailed analysis of the conformational dependence of infrared bands and Raman lines in this polymer, Matsuura and Fukuhara[30] associated gauche conformations of the C−C bond with bands between 1360 and 1350 cm^{-1}, while bands assigned to the trans conformation of this bond usually

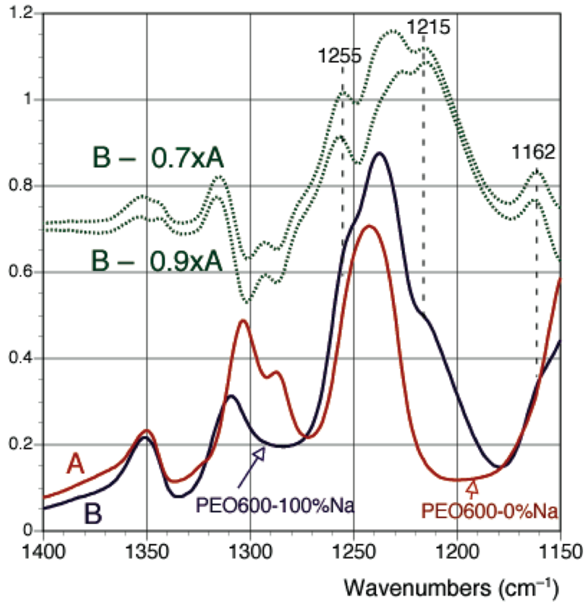

Figure 4. Comparison of the infrared spectrum of PEG600-0%Na (A) to that of PEG600-100%Na (B) in the 1400−1150 cm^{-1} region of the spectrum. Also shown are two difference spectra.

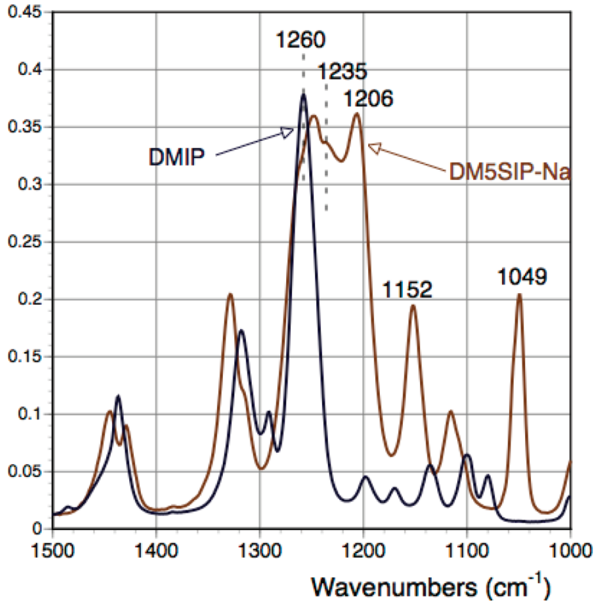

Figure 5. Comparison of the infrared spectra of the isophthalate model compounds dimethyl isophthalate (DMIP) and the sodium salt of dimethyl 5-sulfoisophthalate (DM5SIP-Na).

give rise to an infrared band between 1340 and 1320 cm^{-1}. Prominent infrared bands near 1305 and 1310 cm^{-1} can be observed in the spectra shown in Figure 4, but these bands are also observed in the spectra of the model compounds, dimethyl isophthalate (DMIP) and the sodium salt of dimethyl 5-sulfoisophthalate (DM5SIP-Na) (i.e., simply the methylated ester part of the isophthalate structures shown in Figure 1), as can be seen in Figure 5. These bands are most likely aromatic ring modes and unfortunately mask any contributions from trans CH_2 wagging modes. The features that can be observed in the difference spectra can be attributed to the subtraction of bands of different frequency.

The bands between 1300 and 1200 cm^{-1} in both the spectra of the polymers and model compounds are intriguing. The strong band near 1260 cm^{-1} in DMIP is observed near 1242 cm^{-1} in PEG600-0%Na and is characteristic of modes that have a large contribution from the single bond C−O stretching vibration of the ester group. When the aromatic ring to which the ester groups are attached is also substituted with the sodium salt of a sulfonate group, various other strongly absorbing modes become apparent. In the spectrum of DM5SIP-Na, the 1260 cm^{-1} band remains as a shoulder, while a more prominent mode centered near 1250 cm^{-1} appears. Two additional strong modes also become apparent near 1235 and 1206 cm^{-1}. In the spectra of the polymers, a band centered near 1238 cm^{-1} that has a shoulder near 1255 cm^{-1} replaces the 1242 cm^{-1} band of PEG600-0%Na. A shoulder near 1215 cm^{-1} can also be clearly seen. It is well-known that strongly absorbing infrared bands due to the asymmetric SO_3^- stretching mode appear near 1200 cm^{-1}. Normal coordinate calculations have shown that modes observed between 1206 and 1186 cm^{-1} in the spectrum of sodium benzenesulfonate can be assigned to the asymmetric SO_3^- stretching mode, coupled to some degree to aromatic ring modes.[31−33] However, this mode is doubly degenerate, and when it is involved in a strong, asymmetric interaction with a cation, this degeneracy is lifted and two bands are observed, with the degree of splitting (frequency separation) of these bands depending on the strength of the interaction. This doublet is observed near 1214 and 1242 cm^{-1} in the infrared spectrum of sodium bis(2-ethylhexyl)sulfosuccinate,[34,35] suggesting that the bands near 1215 and 1255 cm^{-1} that appear in the spectrum of the sulfonated polymer and near 1250 and 1206 cm^{-1} in the spectrum of DM5SIP-Na can be assigned to asymmetric SO_3^- stretching modes.

In the spectrum of the sulfonated model compound, DM5SIP-Na, there is a band near 1235 cm^{-1} that is not present in the spectrum of its non-sulfonated counterpart, DMIP. One possibility is that this mode is due to "free" SO_3^- anions. However, an analysis of the symmetric SO_3^- stretching mode, discussed below, indicates that such groups are not present in these materials. Another possibility is that the ester group interacts with the sulfonate oxygen atoms and the cation. The shoulder near 1260 cm^{-1} would then represent those ester groups that are not involved in such interactions, while the band near 1235 cm^{-1} would be assigned to those modes that are involved in such interactions. In the polymer, sulfonation results in a shift of the ester band from about 1242 cm^{-1} to about 1238 cm^{-1}. This shift could be simply a result of factors such as a change in vibrational coupling upon sulfonation, but the presence of an unshifted band in the model compounds indicates that this is a less likely explanation than some sort of electrostatic interaction. However, the small shift in frequency relative to that observed in DM5SIP-Na suggests that any such interaction in the polymer is much weaker than the model compound, as also indicated by the small differences in the carbonyl stretching region, discussed above. This is presumably because the cation prefers to interact with ether oxygen groups.

There is a band near 1162 cm^{-1} that appears as a shoulder in the sulfonated polymer that is absent in the PEG600-0%Na (and is more clearly revealed in the difference spectra) that appears as a well-resolved mode near 1152 cm^{-1} in the spectrum of DM5SIP-Na. This is most likely a ring mode.

The 1200−1000 cm^{-1} region of the spectrum, shown in Figure 6, has strong bands centered between 1150 and 1100 cm^{-1} that can be assigned to PEO modes and a weaker set of bands near 1045 cm^{-1}. There are very interesting changes in the former with sulfonation, but we will defer a discussion of these until later. Here our focus is on the modes near 1045 cm^{-1}, as the SO_3^- symmetric stretching mode absorbs in this

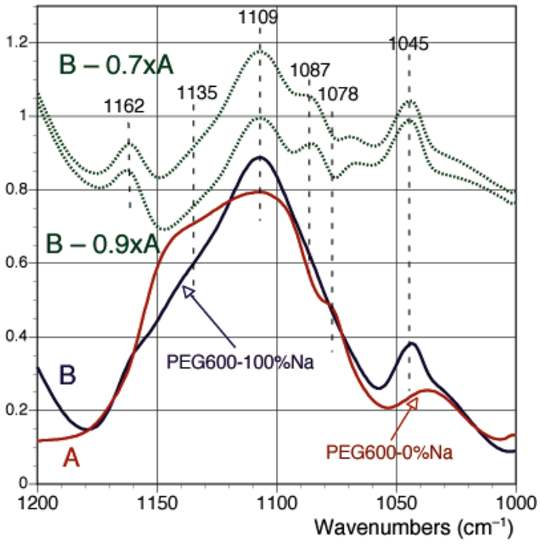

Figure 6. Comparison of the infrared spectrum of PEG600-0%Na (A) to that of PEG600-100%Na (B) in the 1200−1000 cm^{-1} region of the spectrum. Also shown are two difference spectra.

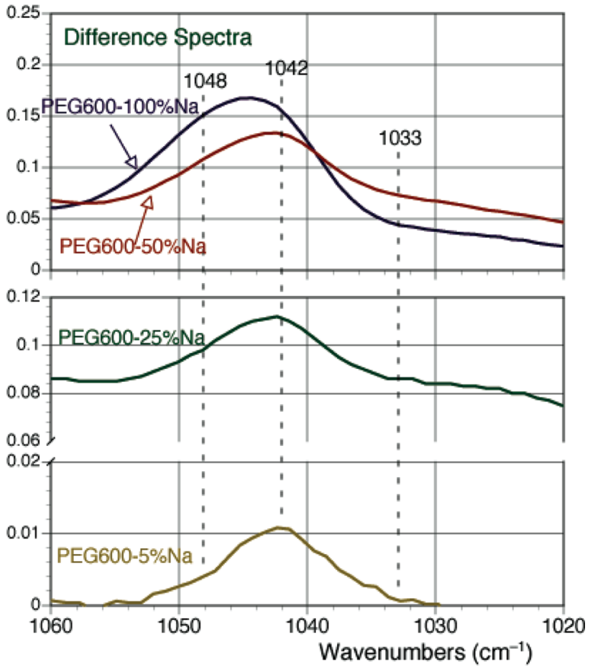

Figure 7. Comparison of infrared difference spectra of PEG600-*x*Na in the SO_3^- symmetric stretching region of the spectrum. Spectra corresponding to *x* values of 5%, 25%, 50%, and 100% are shown.

region of the spectrum. However, in the spectrum of the nonsulfonated PEG600-0%Na polymer there is a broad band centered near 1030 cm^{-1}. This is a mixed PEO mode associated with various conformations of C−C−O−C−C units.[30] Superimposed upon this in the spectrum of the fully sulfonated polymer, PEG600-100%Na, is a band centered near 1043 cm^{-1} that can be assigned to the symmetric SO_3^- stretching vibration. This mode is very sensitive to the state of this anion, so in Figure 7 we consider a scale-expanded region of the difference spectra obtained by subtracting the spectrum of PEG600-0%Na from samples with various degrees of sulfonation. A sample with just 5% of the aromatic units substituted (i.e., PEG600-5%Na) displays what appears to be a single band centered near 1042 cm^{-1}.

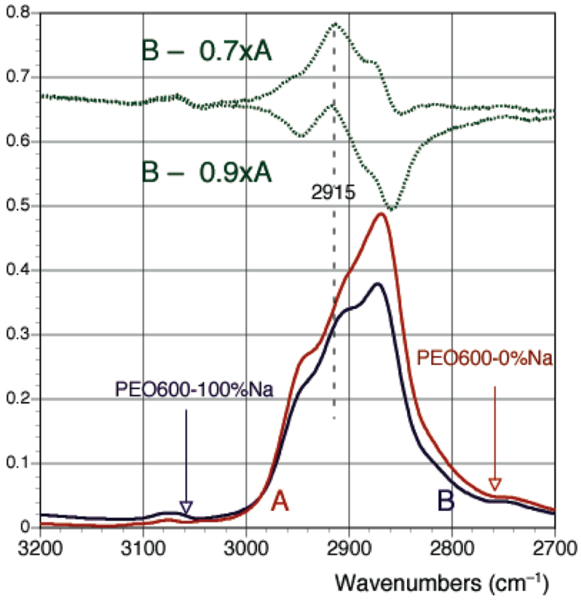

Figure 8. Comparison of the infrared spectrum of PEG600-0%Na (A) to that of PEG600-100%Na (B) in the C−H stretching region of the spectrum. Also shown are two difference spectra.

As the concentration of sulfonate groups increases, this band appears to shift to higher wavenumbers as a result of the increasing intensity of a mode near 1048 cm^{-1} that is clearly evident as a shoulder in the PEG600-100%Na spectrum.

Raman lines and infrared bands due to “free“ SO_3^- ions, ion pairs, and aggregates have been assigned in the spectra of $CF_3SO_3^-$ (triflate) salts, most often $LiCF_3SO_3$ but also $NaCF_3SO_3$, in various solvents and in complexes with PEO and its oligomers.[12−27] Essentially, the frequency of the SO_3^- stretching mode increases with the number of SO_3^- oxygen atoms that are coordinated to cations.[25] In both the infrared and Raman spectra of solutions, a band assigned to the free anion is observed at the lowest frequency, near 1033 cm^{-1} for the triflate anion. No such band is evident in the spectra shown in Figure 7. Bands and lines observed between 1037 and 1043 cm^{-1} have been assigned to contact ion pairs, the precise frequency depending on the nature of the cation and the nature of the solute (e.g., polymer or oligomer). Assignments are to some degree complicated because of interactions and symmetry-imposed selection rules. This results in Raman lines that can be observed at somewhat different frequencies than infrared bands assigned to the same structure.[21,24] However, taking the work reported in the literature as a whole, we assign the band near 1042 cm^{-1} to a contact ion pair, while the shoulder near 1048 cm^{-1} can be assigned to some form of aggregate where the species vibrate as $(2Na^+)SO_3^-$ units (i.e., triple ions). These could be in the form of dimers (quadrupoles) or present as extended chain-like structures.

PEO Bands. In considering the bands due to PEO vibrational modes, we will proceed systematically from high to low wavenumbers, starting with the CH stretching region of the spectrum. Spectra and difference spectra (based on subtraction criteria used in the carbonyl stretching region, described above) plotted in the range 3200−2700 cm^{-1} are shown in Figure 8. Aromatic CH stretching modes give rise to the weak absorptions between 3100 and 3000 cm^{-1}, while the CH aliphatic modes from the PEO portions of the chain result in the far more intense bands observed at wavenumbers below 3000 cm^{-1}. PEO and various low molecular weight model compounds have been the subject of a number of normal coordinate calculations, whose goal has to been to assign bands to conformations in both the ordered and disordered states.[28−30] The CH stretching region has been neglected in some of these studies, and the only assignments are infrared bands near 2950 cm^{-1} to asymmetric CH_2 stretching vibrations and bands near 2890 cm^{-1} to symmetric stretching CH_2 stretching modes of chains in the *TGT* (trans−gauche−trans) conformation of the O−C−C−O sequence of bonds characteristic of the ordered chain conformation in the crystalline state.[28] However, in the spectra of both molten high molecular weight PEO samples and low molecular weight PEO liquids there is a prominent shoulder near 2900 cm^{-1}. This can be seen in the spectra of both PEO600-0%Na and PEO600-100%Na but is more prominent relative to the mode near 2890 cm^{-1} in the latter and is revealed as a band near 2915 cm^{-1} in the difference spectra. In their original normal coordinate analysis of PEO, Matsuura and Miyazawa[28] observed that repulsive interactions involving O−C−C groups influences the CH stretching frequencies, suggesting that such interactions are more pronounced in chain segments involved in interactions with cations.

The CH_2 wagging modes near 1350 cm^{-1} were discussed above (Figure 4), so we now turn our attention to the strong PEO bands observed between 1200 and 1000 cm^{-1}, shown in Figure 6. There is an intense band near 1109 cm^{-1} in the nonsulfonated polymer, together with prominent shoulders near 1135 and 1078 cm^{-1}. These are mixed C−O, C−C, and CH_2 rocking modes.[28−30] Although there are significant changes in this region of the spectrum upon melting the PEO homopolymer, it has not been possible to assign modes to specific structures, as various combinations of gauche and trans conformers all make contributions to individual bands. However, it can be clearly seen that sulfonation results in the strongest band, near 1109 cm^{-1}, becoming more intense relative to its neighbors.

The 1000−600 cm^{-1} region of the spectrum is shown in Figure 9. Bands near 625 and 760 cm^{-1} in the spectrum of PEO600-100%Na and near 730 cm^{-1} in the spectrum of PEO600-0%Na are assigned to out-of-plane CH deformation modes of the aromatic ring and will be considered no further. The most interesting differences are in the 1000−800 cm^{-1} range, shown on an expanded scale in Figure 10, where the spectra of the polymers are compared to a low molecular weight (400) poly(ethylene glycol) sample, PEG400. The spectra of the model compounds (DMIP and DM5SIP-Na, not shown) indicate that the only ring or ester modes that contribute significantly to this region of the spectrum give rise to bands near 920 cm^{-1} in the spectrum of PEG600-100%Na and near 866 cm^{-1} in the spectra of both polymers. The remaining PEO bands can be assigned to mixed C−C stretch, C−O stretch, and CH_2 rocking modes. All three spectra have a band near 950 cm^{-1} that can be assigned to a mixed C−O stretching and CH_2 rocking modes.[28−30] All three spectra also display a shoulder near 940 cm^{-1}. The relative intensity of the 950 cm^{-1} mode to the 940 cm^{-1} shoulder is greater in the spectrum of the fully sulfonated sample than in the spectra of the non-sulfonated polymer and PEG400. Normal mode calculations indicate that the band near 950 cm^{-1} is due to vibrations of O−C−C−O−C−C−O PEO sequences in the *TGT-TGT* conformation, while the band near 940 cm^{-1} can be assigned to *xTx-xTx* conformations, where *x* can be *T* or *G*.[30] The *TGT-TGT* sequences are characteristic of the ordered state, and it appears that complexation with ions favors this conformation.

The band near 886 cm^{-1} in the spectrum of the PEG400 sample can be assigned to an OH end-group mode, which brings us to the bands near 844 and 835 cm^{-1}. Both bands have been assigned to adjoining conformational sequences, *xGx-xGx*.[30] This observation is consistent with the observation made above that the formation of complexes with cations involves *TGT-TGT* conformations of the PEO chain. The 835 cm^{-1} band appears to be more intense relative to the mode near 844 cm^{-1} in the spectrum of the sulfonated polymer than in the spectrum of its non-sulfonated counterpart, and we presume that this is related to a difference in conformations of the C−O bonds adjacent to the gauche C−C bonds.

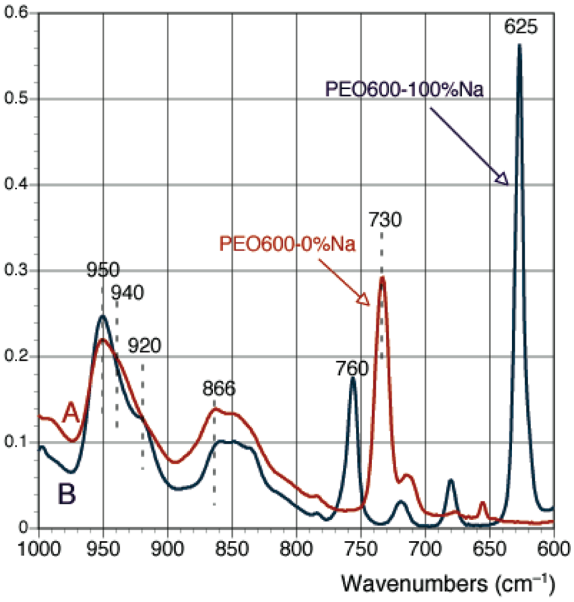

Figure 9. Comparison of the infrared spectrum of PEG600-0%Na (A) to that of PEG600-100%Na (B) in the 1000−600 cm^{-1} region of the spectrum.

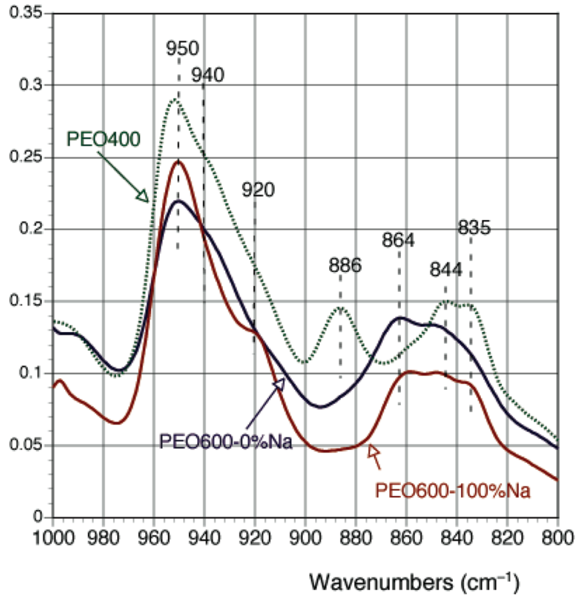

Figure 10. Comparison of the infrared spectrum of PEG600-0%Na to that of PEG600-100%Na and PEO400 in the 1000−800 cm^{-1} region of the spectrum.

Changes with Temperature. There are interesting changes in both bands due to sulfonate groups and bands due to PEO segments as the temperature of the samples is increased. We

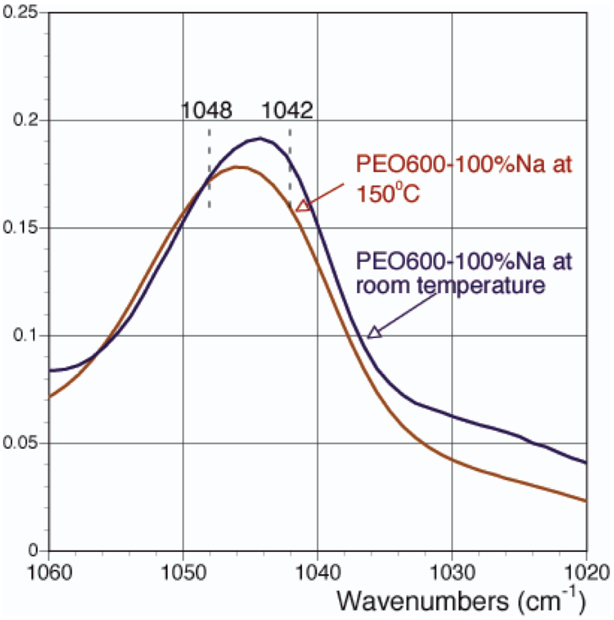

Figure 11. Comparison of difference spectra obtained from the fully sulfonated polymer PEO600-100%Na at room temperature and at 150 °C.

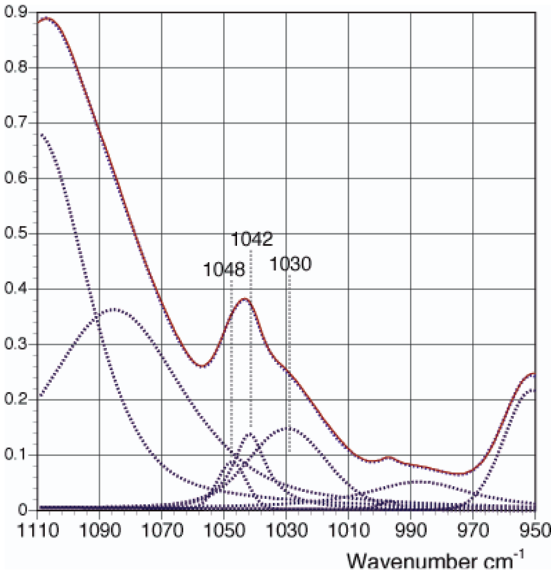

Figure 12. Results of curve-resolving the spectrum of PEO600-100% Na obtained at room temperature in the 1110−950 cm^{-1} region of the spectrum.

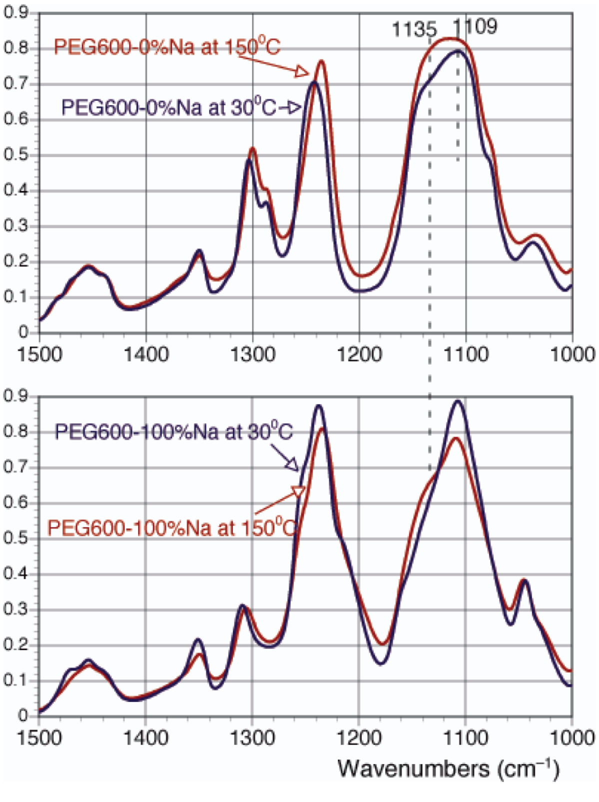

Figure 13. Comparison of spectra PEO600-100%Na and PEO600-0% Na at room temperature and at 150 °C.

will first consider the SO_3^- symmetric stretching mode. Difference spectra obtained by subtracting the spectrum of PEO-0%Na from that of PEO600-100%Na (each at the same temperature) so as to remove the contribution of a PEO mode near 1030 cm^{-1} are shown in Figure 11. Spectra were taken at ∼10 °C intervals up to a maximum temperature of 150 °C. Only the ambient and highest temperature spectra will be considered here.

The peak position of the asymmetrically broadened sulfonate band shifts from about 1043 cm^{-1} in the spectra obtained at room temperature to about 1046 cm^{-1} in the spectrum obtained at 150 °C. As discussed above, in the fully sulfonated sample this band profile is due to overlapping contributions from a mode near 1042 cm^{-1} assigned to ion pairs and a mode near 1048 cm^{-1} assigned to some form of aggregate where the species vibrate as $2(Na^+)SO_3^-$ units. The apparent shift to higher wavenumber as the temperature of the sample is raised is a result of an increasing contribution from the latter band. This result is consistent with a small-angle X-ray scattering (SAXS) study of this sample by Wang et al.[36] It was observed that a scattering peak appears and grows as the temperature is increased from 27 to 150 °C, presumably as a result of the formation of ionic domains of some description. It would therefore be useful to obtain a rough idea of the relative contribution of bands due to ion pairs and higher aggregates by curve-resolving this region of the spectrum. Unfortunately, it is not clear where to place a baseline in the difference spectrum. A baseline can be placed with more certainty in the spectrum of the polymer, however, by examining the spectrum over the entire mid-infrared range, but the accuracy of resolving the 1042 and 1048 cm^{-1} modes is compromised by the intense PEO modes that overlap the SO_3^- symmetric stretching mode. This is illustrated in Figure 12, where the 1110−950 cm^{-1} region of the spectrum obtained at 25 °C is resolved into its component bands. (The methodology we use to set baselines and the function used to describe band shapes is described in detail in refs 37 and 38.) The spectrum obtained at 150 °C was curve resolved in a similar manner. The fraction of the total area of the two bands occupied by the 1048 cm^{-1} mode increases from about 27% to 38%. But it should be kept in mind that although the fit between the calculated and observed spectrum is excellent (see Figure 12), these numbers are probably subject to considerable error. Nevertheless, it is clear that a band due to aggregates at the expense of a band due to ion pairs does increase in intensity as the temperature is raised, and this correlates well with SAXS data on the identical polymer.

Bands due to PEO segments also show some interesting differences between sulfonated and non-sulfonated samples as a function of temperature. As an example, the 1200–1000 cm^{-1} region of the spectrum is shown in Figure 13. In the spectrum of the non-sulfonated sample, PEG600-0%Na, the prominent shoulder near 1135 cm^{-1} observed at room temperature increases in intensity with increasing temperature, and at 150 °C it is essentially equal in intensity to the 1109 cm^{-1} mode, resulting in what appears at first sight to be a very broad single band. In the completely sulfonated sample, however, the shoulder near 1135 cm^{-1} increases in intensity to a much smaller extent. It would appear that the interaction between PEO segments and the ions present in the system perturbs the intensity of the 1109 cm^{-1} mode significantly, presumably as a result of an interaction with the ether oxygen. Equivalent changes are seen in other regions of the spectrum (e.g., the CH stretching region), and it appears that the interaction between cations and PEO portions of the chain "locks" the segments in their preferred structure to a large degree, so that there are relatively small changes with temperature and those presumably involve those PEO segments that are left out of these interactions.

Conclusions

FTIR has been used to characterize a set of PEO/aromatic polyester based ionomers, where the aromatic rings have been sulfonated to various degrees. Previously reported dielectric spectroscopic studies of these polymers indicated that most ions exist in a bound state with only a very small fraction of free ions contributing to dc conduction.[1,2] This is in contrast to studies of other ionic systems that suggested the presence of a significant concentration of "free" ions. An analysis of the symmetric SO_3^- stretching mode revealed no detectable amounts of "free“ SO_3^- ions in any of the ionomers studied here, in agreement with the dielectric spectroscopy work. Bands due to ion pairs and aggregates were identified, however. The band due to aggregates increased in intensity relative to the band due to ion pairs as the temperature increased, consistent with a small-angle X-ray scattering (SAXS) study of this sample.[36]

Bands assigned to the poly(ethylene oxide) segments of the copolymers were characteristic of chains in the amorphous state. However, bands due to sequences of trans and gauche O–C–C–O–C–C–O conformations characteristic of the ordered state appeared to be favored upon complexation with ions. The interaction between cations and PEO portions of the chain "locks" the segments in their preferred structure to a large degree, so that compared to non-sulfonated copolymers there are relatively small changes in the relative intensities of conformationally sensitive bands with temperature.

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