Sulfonated Polystyrene Ionomers Neutralized by Bi- and Multifunctional Organic Cations. 1. An Infrared Spectroscopic Study

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ABSTRACT: An infrared spectroscopic investigation of lightly sulfonated polystyrene blended with ten different organic small molecules containing bi-, tri-, and quadrifunctional amine or pyridine groups was undertaken. Proton transfer from the sulfonic acid moieties of the polymer to the nitrogen functions of the small molecules, giving rise to ion pairs and hence ionic cross-linking, was clearly detected. The extent of proton transfer was correlated qualitatively with the relative basicity of the small molecule. A quantitative calculation of the degree of proton transfer was performed, based primarily on the normalized area of the absorption band and shoulder at 900–906 cm^{-1}. The results range from about 50% proton transfer or less to purine, 2,2′-pyridil, and *N*-phenyl-1,4-phenylenediamine to almost complete proton transfer to 1,6-hexanediamine and 1,4-phenylenediamine.

Introduction

It is well-known that ionomer morphology and properties are influenced by various factors, notably ion content, type and position of ionic group, type of counterion, type of backbone, thermal history, and solvation conditions.[1] All of these affect the tendency of the ionic groups to aggregate in a low-polarity matrix, and hence to form multiplets and clusters, the latter being the source of the unique properties of ionomers.[1] Among the factors, we wish to point out the attention given to the role of counterions. Numerous series of ionomers with different counterions have been studied, several of which are found in refs 1–7. For anion-containing ionomers, in particular, they include alkali, alkaline earth, transition, and rare earth metal cations. In general, the ionic interactions involving inorganic cations are strong, and therefore significant aggregation of the ionic units is observed. Because the ionic aggregates are at the heart of the formation of the cluster phase, the cation strongly affects its characteristics, depending on both the charge and size of the cation, as well as on the packing structures of the ionic aggregates involving those cations. Consequently, various ionomer properties are strongly affected. Thus, the choice of counterion is an important, and relatively simple, element in obtaining desired characteristics in ionomer materials.

As an alternative to inorganic cations, organic cations (generally larger than inorganic cations) are also of interest. In fact, appropriate small molecules of various types and numbers of functionality are readily available, adding significantly to the palette from which the polymer chemist can choose to neutralize ionomers and tailor their properties.

To date, relatively few studies of anion-containing ionomers neutralized by low molecular weight organic cations have been published. Those reported generally involve the creation of ion pairs following proton transfer from acid groups to bases that usually contain amine or pyridine moieties. Weiss et al.[8] described thermal, mechanical, and rheological properties of poly[styrene-*co*-(styrenesulfonic acid)] ionomers (PS-SSA) neutralized by a series of alkylamines, all monofunctional but with varying numbers and lengths of alkyl branches. The authors demonstrated that the properties of these ionomers are primarily a function of amine size, with increase in size reducing the strength of the interactions among ion pairs due to steric hindrance and increase in tail length causing plasticization effects. Smith and Eisenberg[9] used rigid as well as flexible low molecular weight amines, also monofunctional, to neutralize sulfonated polystyrene. Neutralization with the flexible (singly-branched) amines was found to result in a decrease in the glass transition temperature, T_g, by an amount proportional to the number of carbon atoms in the alkyl chain of the amine (plasticization), while neutralization with rigid amines results in an increase in the T_g (antiplasticization).

Salts of carboxylic acid-containing ionomers with monofunctional amines have also been investigated. Weiss and Agarwal[10] noted that the tributylamine salt of a propylene–acrylic acid copolymer has a lower viscosity than the copolymer by itself, suggesting that the ionic interactions are shielded by the bulky amine groups. Smith and Goulet[11] studied the effect of flexible and rigid amines (monofunctional) on copolymers of methyl methacrylate and methacrylic acid and concluded that the plasticization and antiplasticization effects of carboxylate–ammonium ion pairs are somewhat weaker than those of the sulfonate–ammonium ion pairs.

Organic molecules with more than one functional group can, potentially, introduce direct ionic cross-linking sites among the polymer chains (much like inorganic cations which are bi- or multivalent) and thereby give additional control of the physical properties of the resulting ionomers. This was actually recognized many years ago by Brown,[12] who prepared salts of carboxylic acid-containing elastomers with hexamethylenediamine for other purposes. Rees[13] compared aliphatic diamines to metal cations as ionic cross-links in ethylene–methacrylic acid (PE-MAA) ionomers, focusing on physical properties like tensile modulus, yield point, ultimate strength, and melt viscosity; he concluded that the diamine salts provided weaker ionic interactions than the metal salts. Plante[14] examined

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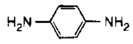
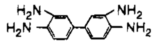
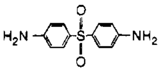
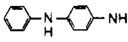
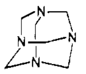
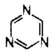
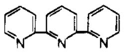
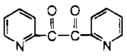
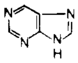
Table 1. Characteristics of the Small Molecules

Small Molecule (purity)	Acronym	Structure	T_m / °C	T_b / °C
1,6 - Hexanediamine (98%)	HDA	$H_2N-(CH_2)_6-NH_2$	42-45	204-205
1,4 - Phenylenediamine (99%)	PDA		143-145	267
3,3' - Diaminobenzidine (99%)	DAB		175-177	--
4 - Aminophenylsulfone (98%)	APS		175-177	—
N - Phenyl - 1,4 - phenylenediamine (98%)	PPD		73-75	—
Hexamethylenetetramine (99%)	HMT		280	—
1,3,5 - Triazine (97%)	TAZ		81-83	—
2,2' : 6 ,2" - Terpyridine (98%)	TPY		89-91	-
2,2' - Pyridil (97%)	PYR		154-156	—
Purine (99%)	PUR		214-217	—

the dynamic mechanical properties of blends of 1,10-decanediamine with various PE-MAA ionomers, and in some cases, he observed increases in transition temperatures; however, the presence of crystallinity and the fact that the ionomers were only partially neutralized by Na complicated the interpretation of the data obtained.

Apart from a series of investigations by Yano and coworkers[15] of PE-MAA copolymers and metal (primarily Zn) ionomers mixed with 1,3-bis(aminomethyl)cyclohexane, also a complex system, there are no in-depth studies of ionomers neutralized by multifunctional organic molecules. This is the focus of this paper and the following one. We have chosen ten bi-, tri-, and quadrifunctional small organic molecules containing amine or pyridine moieties for blending with sulfonated polystyrene to produce organically neutralized ionomers. In this paper, we present an infrared spectroscopic analysis of the series of ionomers. Our primary interest is to detect and quantify the extent of proton transfer depending on the small molecule used and to qualitatively correlate that with its basicity. The next paper will present molecular orientation and dynamic mechanical properties of these ionomers and correlate the trends observed with the extent of proton transfer determined in this paper.

Experimental Section

Poly[styrene-*co*-(styrenesulfonic acid)] (PS-SSA) of 5.0 mol % SSA content (PS-0.050SSA) was synthesized according to literature procedures.[16,17] The parent polystyrene was purchased from Aldrich, its average molecular weight reported to be about 280 000. The acid content of the product was determined by titration using a standardized solution of NaOH in methanol with phenolphthalein as the indicator. The ten organic molecules chosen were all obtained from Aldrich and were used as received. Their acronyms, reported purities, molecular structures, and reported melting and boiling points (when available) are listed in Table 1.

Blending of the sulfonated polystyrene with the small organic molecules was effected in solution, using a 10–20 wt % excess of small molecules compared to the amount necessary for exact stoichiometry between the number of nitrogens in the small molecules and the sulfonic acid moieties in the polymer (except for purine, as will be seen). First, a calculated quantity of small molecule was accurately weighed into small glass vials to which 2–3 mL of methanol was added. Because hexanediamine and diaminobenzidine are not soluble in methanol alone, several drops of water and *N,N*-dimethylformamide, respectively, were added prior to the methanol. The copolymer was separately dissolved to a 5% concentration in THF/methanol (90/10 v/v). The small molecule solution was then added with a pipet to the vigorously stirred copolymer solution. Stirring was continued for 1 h, following which the neutralized solution was cast onto a glass plate and the solvent evaporated in air over a 48-h period.

The resulting films were detached, cut into strips, taped down to aluminum foil at their extremities to avoid deformation, and dried under reduced pressure at room temperature for 1 day and 120 °C for 3 days. Those drying conditions were considered to be an optimal compromise between sufficient drying and the risk of losing some of the small molecule through evaporation or sublimation. As far as drying is concerned, no peaks due to solvent were observed in the infrared spectra of the films; furthermore, the glass transition temperatures measured by differential scanning calorimetry were constant in repeated scans. The small molecule content in the blends after drying was evaluated through elemental analysis of the nitrogen content, although, because the total nitrogen content is very small (0.62 ± 0.02 wt % for all of the blends at stoichiometry), the results are only indicative. In most cases, a value of 0.7 ± 0.1 wt % was obtained for each sample (based on 2 determinations per sample) using a Carlos Erba 1106 CHN elemental analyzer; 0.4 wt % was obtained for the sample with pyridil and 1.4 wt % for the one with purine. This analysis was confirmed for selected samples by Guelph Chemical Laboratories (Guelph, Ontario): nitrogen contents of 0.66, 0.56, and 1.51 wt % were obtained for the samples with 1,4-phenylenediamine, *N*-phenyl-1,4-phenylenediamine, and purine, respectively, via the Kjeldahl method using the ammonia electrode finish, and 1.42 was obtained for the sample with PUR via the dynamic flush combustion method using the EA1108 elemental analyzer. These results suggest that no significant amount of small molecule was lost during the drying process; however, the sample with purine apparently contains more than twice the stoichiometric quantity of small molecule.

The solution-cast films were about 70–80 μm in thickness. For some of the analyses, these were too thick, and thus a series of samples were also prepared by compression-molding these "thick films" to thicknesses of 20–30 μm ("thin films") in a SPECAC IR film-making mold at 200 °C for 3 min. After drying and before IR analysis, the films were stored in a desiccator containing $CaCl_2$.

A Mattson Sirius 100 FTIR spectrometer was used to obtain the infrared spectra. One hundred scans were taken at a resolution of 4 cm^{-1}. The spectroscopic analyses and data treatment were conducted using the program Spectra-Calc (Galactic Industries).

Results and Discussion

1. Selection of the Small Organic Molecules.

The basic prerequisite in selecting the ten small organic molecules in Table 1 was that they possess at least two functional groups with sufficiently strong basicity so that, as potential cations for PS-SSA, proton transfer and hence ionic cross-linking interactions are in principle possible. Furthermore, it was desirable that the range of basicities be sufficiently large that different degrees of proton transfer take place. Various structural factors, such as degree of functionality, flexible vs rigid molecules, and linear vs cyclic functionalities, were also considered of interest.

The expected order of basicity of the compounds chosen can be partially evaluated from organic chemistry principles,[18] at least for the addition of the first proton. The addition of the second, and in some cases

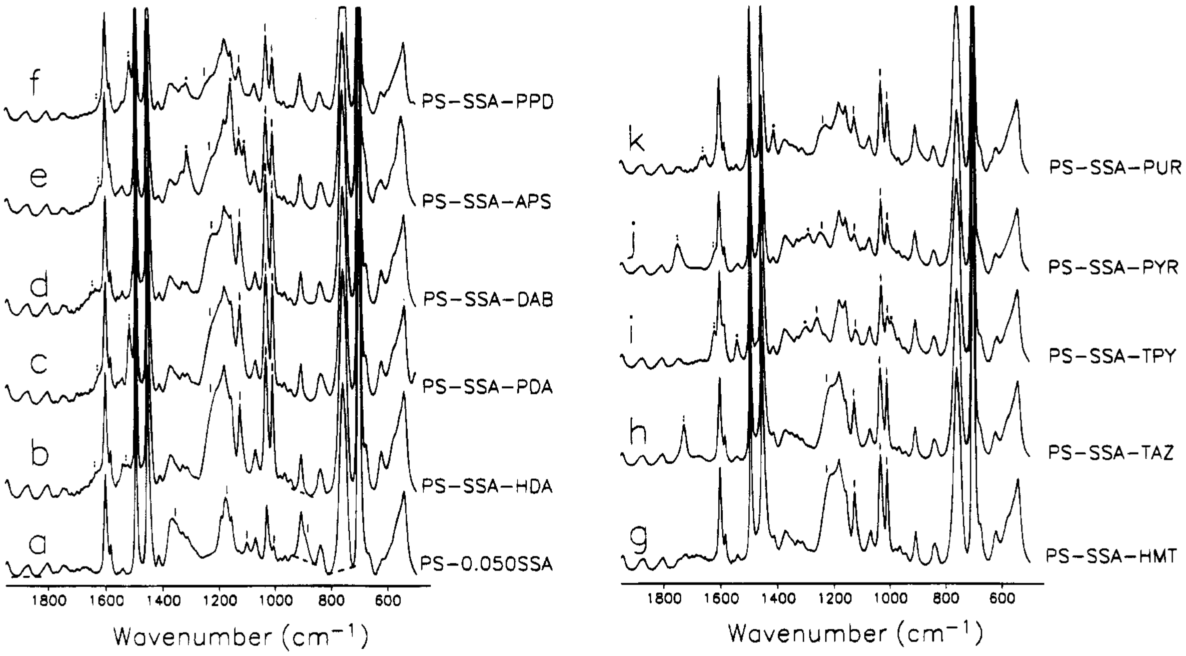


Figure 1. Infrared spectra in the 500−1950 cm^{-1} region of PS-0.050SSA and the ten ionomers resulting from (full or partial) neutralization of the copolymer by the organic small molecules indicated. The main absorption bands referred to in the text are indicated, with the vertical dashes referring to sulfonate-related bands (sulfonic acid in PS-SSA), the double dots to amine- or pyridine-related bands, and the single dots to unidentified small molecule bands. The base lines used for the proton transfer calculations are also shown.

of the third and fourth protons, is much more difficult if not impossible to evaluate: in most of the compounds chosen, the basic sites are interconnected through resonance (there are also statistical and coulombic effects that play an important role)[18c] so that the ionization of one site can strongly affect the basicity of the other site(s). For a few of the compounds, aqueous pK_a values are known, and these will be mentioned in what follows; however, they are only indicative, since basicities determined in aqueous solution cannot be extrapolated with certainty to organic media.

The compounds chosen can be classified into four categories. In the first category, 1,6-hexanediamine (HDA), represents aliphatic amines with a flexible chain structure and very strong basicity (the two reported pK_a constants are 10.93 for the first protonation and 9.83 for the second.[19] The second category possesses aromatic primary amines, whose basicities are normally lower than that of aliphatic amines, because of resonance stabilization provided by the aromatic groups. Among these, we have chosen 1,4-phenylenediamine (PDA), 3,3′-diaminobenzidine (DAB), 4-aminophenyl sulfone (APS), and *N*-phenyl-1,4-phenylenediamine (PPD). (The pK_a values reported for PDA are 6.08 and 3.29.[19] In comparison, benzidine, which possesses two amine groups rather than four as does DAB, has reported pK_a values of 4.70 and 3.63.[19]) A difference between PDA and DAB is that one is bifunctional and the other quadrifunctional, although they have the same ratio of functional groups to benzene rings. APS is expected to be less basic than PDA and DAB, due to the electron-withdrawing substituent (O=S=O) between the two benzene rings. PPD possesses two types of amine groups, one being a primary amine which should be stronger than that of APS, the other being a secondary amine located between two rings, probably much weaker than that of APS (the pK_a in water of ϕ_2NH is reported[18] to be only 1.0 compared to 4.6 for ϕNH$_2$, where ϕ represents an aromatic group). In the third category, hexamethylenetetramine (HMT), with tertiary aliphatic amines and a cyclic structure, is in principle quite basic. It is to be noted that it is not necessarily stable: it is subject to hydrolysis and thus may give rise to bifunctional primary amines as well as to monofunctional secondary amines,[20] which are also quite basic. Finally, 1,3,5-triazine (TAZ), 2,2′:6′,2″-terpyridine (TPY), 2,2′-pyridil (PYR), and purine (PUR) were selected to represent aromatic, heterocyclic amine structures. Compared with primary amines, the basicities of these compounds are normally weaker, since the pair of free electrons that gives them basicity occupies an sp^2 orbital, causing them to be held more tightly and therefore to be less available for sharing with acids than the pair of electrons of primary amines. The order of basicity of these molecules is difficult to guess a priori, as they are affected by a variety of steric and resonance effects. However, TAZ is expected to be the most basic, since there is only one ring to delocalize three pairs of free electrons. PUR may be the least basic (the reported pK_a constant for single protonation is 2.52),[19] given the variety of resonance forms it possesses, with PYR possibly being less basic than TPY due to extra stabilization of the free electron pairs by the carbonyl groups.

2. Band Assignments for the Organic Salts of PS-0.050SSA. The infrared spectra of PS-0.050SSA and the ten organically neutralized ionomers, in the 500−1950 cm^{-1} region, are shown in Figure 1. In order to identify changes in the spectra upon blending the acid copolymer with the small molecules, it is useful to review first the IR absorption bands related to the SSA group in PS-SSA. According to Zundel,[21] for thoroughly dried samples of poly(styrenesulfonic acid), there are two bands at 1172 and 1350 cm^{-1}, assigned, respectively, to the symmetric and antisymmetric stretching vibrations of the two SO bonds with double-bond character (O=S=O). A band at 1097 cm^{-1} is attributed[22] to in-plane skeleton vibrations of the benzene ring with strong participation of the substituents, whereas a weak band near 1005 cm^{-1} (the exact position being sensitive to hydration) is assigned to in-plane bending vibrations of the benzene ring substituted in the para position. A fairly broad band at about 900

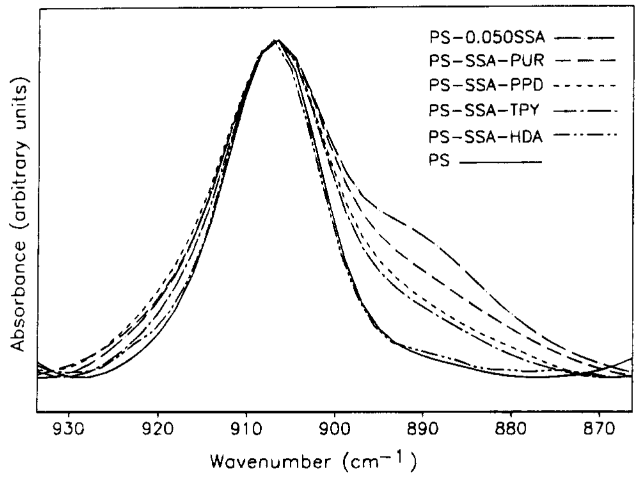


Figure 2. Variations in the intensity of the shoulder to the 906 cm^{-1} absorption for the samples indicated.

cm^{-1}, which overlaps a polystyrene band at 906 cm^{-1}, is assigned to the stretching vibration of the SO bond with single-bond character. In the spectrum for PS-0.050SSA (Figure 1a), bands at 1102 and 1004 cm^{-1} and a shoulder at 900 cm^{-1} are clearly evident; the bands at 1350 and 1172 cm^{-1} are also present, although overlapped with polystyrene bands.

When PS-0.050SSA is blended with the small molecules, a number of spectral changes occur, generally similar to what is observed in hydrated PS-SSA,[17,21,25] in metal-neutralized PS-SSA,[3,21,25] and in PS-SSA blended with pyridine-containing copolymers.[24,26] These changes reflect the occurrence of proton transfer from the SSA unit to the base (amine, pyridine, water, etc.), thus transforming the acid into the SO_3^- ion. One obvious change is the disappearance of the 900 cm^{-1} shoulder for the most basic small molecules, in particular, PS-0.050SSA-HDA (b), PS-0.050SSA-PDA (c), PS-0.050SSA-DAB (d), and PS-0.050SSA-HMT (g). For these ionomers, the original polystyrene band at 906 cm^{-1} has become sharp and symmetric again. However, for PS-0.050SSA-PPD (f), PS-0.050SSA-PYR (j), and PS-0.050SSA-PUR (k), involving molecules with relatively weak basicity, a weak shoulder to the 906 cm^{-1} band is still evident, although less intense than for the copolymer. The progressive decrease in the intensity of the shoulder with increasing basicity of the small molecule is shown qualitatively for selected counterions in Figure 2, where the maximum intensities have been made coincident in order to highlight the effect. Ionization of SSA following proton transfer to the small molecule eliminates the single-bond character of the acid group, and therefore the band at 900 cm^{-1}. Hence, the intensity of this band reflects the extent of proton transfer from the acid sites in PS-SSA to the small molecules. This suggests the possibility of quantifying the proton transfer in these materials, an operation which will be effected in a later section.

Another significant change in the spectra of the organically neutralized ionomers is the intense band which appears around 1008 cm^{-1}. As above for the (weak) 1004 cm^{-1} absorption, this band is assigned to the in-plane bending vibrations of the para-substituted benzene ring,[21] this time substituted by the sulfonate group. The intensity of this band is greatest for the blends with the most basic small molecules (Figure 1). Furthermore, the band position is generally 2 cm^{-1} higher in wavenumber for these blends compared to those with the more weakly basic molecules (1009 cm^{-1} for the HDA, PDA, DAB, HMT, and TAZ ionomers, 1007 cm^{-1} for the APS, PPD, PYR, and PUR ionomers, and 1005 cm^{-1} for the TPY ionomer). Thus, this band also reflects the degree of ionization of the acid groups present.

In addition, a rather intense new band appears at 1125 or 1126 cm^{-1} (1121 cm^{-1} for the TPY ionomer), assigned to the in-plane skeleton vibrations of the benzene ring with strong participation of the sulfonate groups.[21,22] Again, there is a correlation between the intensity of this band and the basicity of the small molecule, the band being the least intense for the TPY, PYR, PPD, and PUR ionomers. The band at 1102 cm^{-1} in PS-SSA disappears with the more basic small molecules, although a hint of it remains for TPY, PYR, PPD, and PUR.

Parallel to the above changes are those related to the antisymmetric and symmetric stretching vibrations of the sulfonic acid group and the sulfonate ion, respectively. The acid vibrations are expected to decrease significantly in intensity in the spectra of the ionomers, which indeed seems to be the case for the 1350 cm^{-1} antisymmetric vibration. The trend for the 1172 cm^{-1} symmetric vibration of the acid is obscured by the appearance of a doublet around 1200 cm^{-1}, related to the antisymmetric vibration of the $-SO_3^-$ ion. According to Zundel,[21] when a proton is removed from a sulfonic acid group, the resulting $-SO_3^-$ anion with its three identical bonds has a pyramidal structure, and C_{3v} "local" symmetry would be expected, giving a doubly degenerate antisymmetric stretching vibration. However, the symmetry can be perturbed by the electrostatic field of the cation, which can polarize the $-SO_3^-$ anion and thus change the C_{3v} symmetry to C_s symmetry; as a result, the degeneracy is removed and the vibration splits into a doublet that absorbs in the vicinity of 1200 cm^{-1}.[21] The same effects are observed in metal-neutralized ionomers.[3,25] In our case, the higher wavenumber antisymmetric vibration is clearly evident as a broad band, especially for the more basic molecules, in the region generally between 1210 and 1240 cm^{-1}; it tends to be closer to 1210 cm^{-1} for the NH_3^- salts and at higher wavenumbers for the others (noting also that in blends of PS-SSA with vinylpyridine-containing polymers, this band is located at 1248 cm^{-1}).[24,26] The lower wavenumber antisymmetric vibration, expected to be located at somewhat below 1200 cm^{-1},[21] is more difficult to localize with certainty (and is therefore not indicated in Figure 1), being obscured by PS- and SSA-related bands, as well as in some cases by additional absorbances related to the small molecules.

The symmetric $-SO_3^-$ stretching vibration is found in the region of 1040 cm^{-1} generally.[21,22] For completely sulfonated polystyrene neutralized by metal cations, this band is located anywhere from 1030 to 1052 cm^{-1}, depending on the cation.[21] In the spectra of Figure 1, there is no additional band (nor detectable shoulder) between the polystyrene bands at about 1030 and 1070 cm^{-1}. However, in checking the intensity ratio of the 1030 cm^{-1} band to the 1945 cm^{-1} polystyrene band (one of the four weak bands between 1700 and 2000 cm^{-1} attributed to combination or overtone vibrations of the CH groups of the benzene ring),[21] which should be constant if there is no overlap with bands from the sulfonate or sulfonic acid group or from the small molecules, it was noticed that the ratio is significantly higher in spectra (b) through (k) than in spectrum (a) or in that for pure polystyrene, ranging from about 3.5 for (a) to about 6.0 for the systems with the most basic small molecules (exceptionally 7.1 for DAB). Since this trend could not be accounted for by overlap from small-

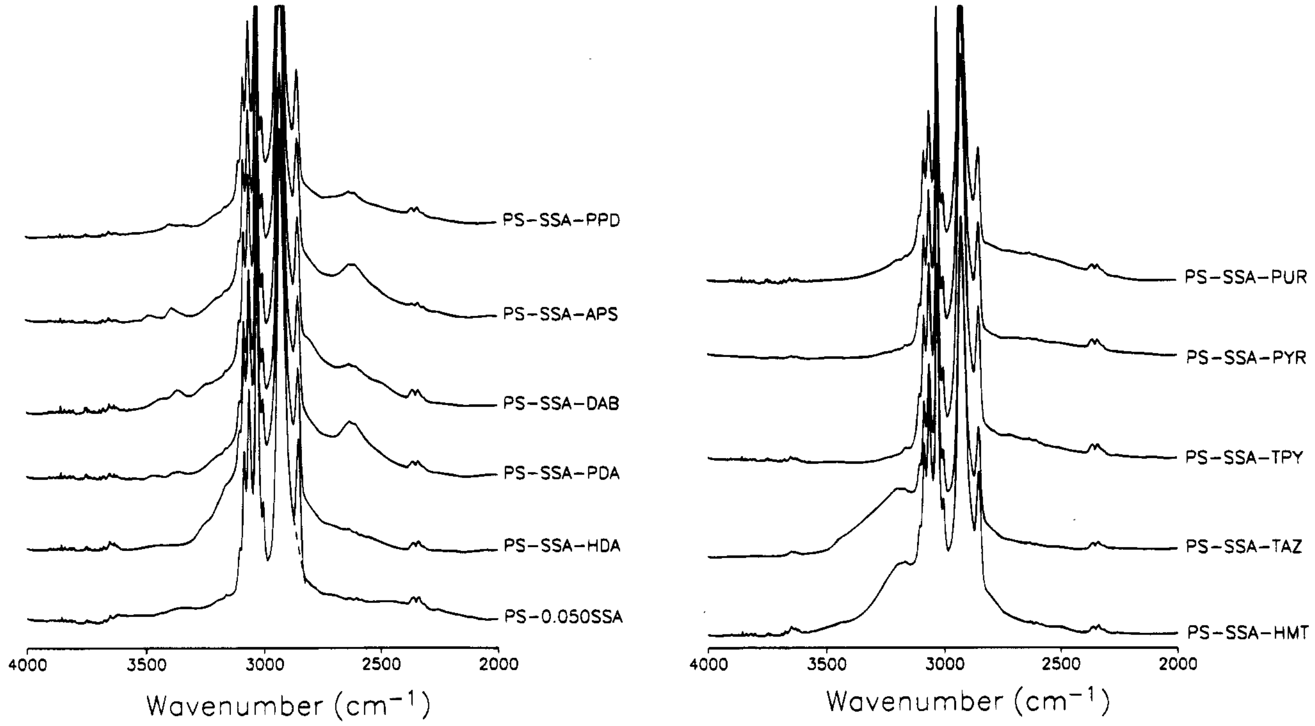


Figure 3. Infrared spectra in the 2000–4000 cm^{-1} region of PS-0.050SSA and the ten ionomers resulting from neutralization of the copolymer by the organic small molecules indicated.

molecule bands, we conclude that the symmetric $-SO_3^-$ stretching vibration and the PS band at 1028 cm^{-1} (attributed to in-plane bending vibrations of the benzene ring)[21] are coincident. This conclusion was also reached for hydrated PS-SSA copolymers.[17] It is also noteworthy that the maximum is actually located at 1032 cm^{-1} for the most basic small molecules (HDA, PDA, DAB, HMT, TAZ), at 1030 cm^{-1} for most of the others (APS, PYR, PPD, PUR), and at 1028 cm^{-1} for TPY.

The above analyses focus on the changes in the spectra that are related to the polymer functional group. Parallel changes must occur that are related to the formation of ammonium and pyridinium salts in the small molecules. However, because the functional groups are not all identical and are affected by variable structural and resonance effects, band assignments of the functional groups in the small molecules, both pure and as counterions, are a difficult enterprise. The small molecules by themselves may also be partially protonated by H_2O in some cases. Furthermore, the small-molecule bands are generally weak in the spectra of the ionomers, thus making identification of changes in the bands upon neutralizing still more arduous. Only the more obvious bands will therefore be considered, and the analysis will necessarily remain qualitative and incomplete.

Protonated primary amine salts, $-NH_3^+$, are expected to have asymmetric and symmetric deformations in the regions of 1625–1560 and 1550–1500 cm^{-1}, respectively.[27,28] Indeed, weak bands or shoulders are observed at about 1515–1530 and 1620–1640 cm^{-1}, for the ionomers with HDA, PDA, DAB, APS, and PPD [spectra (b) to (f) of Figure 1]. However, for spectra (c) to (f), a peak at about 1625 cm^{-1} is present in the spectra of the small molecules alone, probably due to the NH_2 scissors vibration reported to be in the region of 1640–1600 cm^{-1} for aromatic amines.[28] Furthermore, rather broad, intense peaks for the same small molecules are located at about 1500–1520 and 1580–1600 cm^{-1}. Thus, the aforementioned bands can be assigned with good assurance to $-NH_3^+$ for the ionomer with HDA (b) only, the NH_2 scissors vibration of neat HDA being located at about 1570 cm^{-1}, the most intense peak in its spectrum, and where there is no band between 1600 and 1700 cm^{-1}. It is noteworthy that the HDA ionomer has no absorption band at 1570 cm^{-1}, which concords with the analysis above that there is essentially complete proton transfer in this material. [A weak (broad) band near 1630 cm^{-1} and possibly a shoulder on the lower wavenumber side of the 1570 cm^{-1} band in pure HDA may be ascribed to H_2O-protonated $-NH_3^+$, this substance being particularly hygroscopic due to its high basicity.] As for the pyridinium salts in the midspectral region, a new weak band appears at about 1620 cm^{-1} for the ionomers with TPY (i) and PYR (j), one at 1726 cm^{-1} for TAZ (h), and a weak doublet at 1647 and 1663 cm^{-1} for PUR (k): all of these may be due to vibrations of the rings in ionized form.[27] Furthermore, the two C=O bands at 1695 and 1720 cm^{-1} for pure PYR are apparently shifted to 1748 cm^{-1} in the ionomer (j), probably reflecting protonation of the pyridine ring to which the carbonyls are coupled by resonance. No clear changes involving tertiary amines can be identified in the spectra of the HMT ionomer (g). A few additional bands, marked by dots in Figure 1, are attributed to the small molecules, although in some cases this means small displacements in position relative to bands in the small molecules alone; we have not attempted to identify these bands in greater detail.

Frequently, the high wavenumber region of the IR spectra also contains evidence of ammonium or pyridinium salt formation. Figure 3 shows that a weak, broad band at about 2630 cm^{-1} appears in the spectra of ionomers with primary aromatic amine counterions (PDA, DAB, APS, and PPD). This band has been assigned by Joesten and Schaad[29] to an N–H stretching vibration in hydrogen-bonded protonated amines, but has also been attributed to overtone and combination frequencies[27,30] enhanced by Fermi resonance and involving deformation vibrations.[28] This band is about twice as intense for PDA and APS as for DAB and PPD. It is not present for the aliphatic salt, HDA, which is sometimes the case for amine salts.[27] A hint of a weak broad band at about 2050 cm^{-1}, another combination band frequently present for primary amine salts, is present for HDA, PDA, and APS. For the heterocyclic counterions, TPY, PYR, and PUR, there appears to be a much broader and weaker band at about 2600 cm^{-1}, although pure PUR itself absorbs broadly in this region. The shoulder at about 3200 cm^{-1} for the HMT ionomer is attributed to the tertiary amine salt stretching frequency.[28] That for TAZ may arise from protonated N−H stretching frequencies that are not hydrogen-bonded to the anion.[26]

3. Quantitative Analysis of Proton Transfer. As described above, there appears to be a correlation between the intensity of the shoulder to the 906 cm^{-1} band and the extent of proton transfer to the small molecules. When the proton transfer is complete, the shoulder disappears and the 906 cm^{-1} band becomes the same as that in PS. Since the 906 cm^{-1} band is constant in intensity for all the ionomers and only the absorption of the shoulder varies in proportion to the amount of non-neutralized SSA groups remaining, it is possible to quantify the proton transfer by determining the area under the absorption comprised of 906 cm^{-1} band plus the 900 cm^{-1} shoulder and normalize this to an isolated polystyrene band. The boundaries are fixed by PS, for which the corresponding values represent 100% proton transfer, and by unneutralized PS-0.05SSA, for which there is necessarily 0% proton transfer (when thoroughly dried).

Initially, the area under the 906−900 cm^{-1} band was normalized to the polystyrene band at 758 cm^{-1} (out-of-plane bending vibrations of the monosubstituted benzene ring),[21] as was done in ref 24 for determining the extent of proton transfer in ionomer blends of PS-SSA and ethyl acrylate−vinylpyridine copolymers. For this purpose, the films analyzed above had to be remolded into thinner samples, in order that the intense 758 cm^{-1} peak be within the range of the Beer−Lambert law. Since there is overlap, in some cases, from a small-molecule band, the procedure was repeated using two other polystyrene bands as internal standards, namely, 1875 and 1945 cm^{-1} (combination vibrations or overtones of the out-of-plane vibrations of the benzene ring).[21] Because these are weak absorbances, it was appropriate to use the thicker films for the latter calculations, although they were also checked in the thin samples. It was noted that, in most cases, the ratio of the intensities of the 1875−1945 cm^{-1} bands is 0.71 ± 0.01, as was noted also by Smith and Eisenberg for blends of PS-SSA with styrene−vinylpyridine copolymers.[26] To establish the 0% and 100% limits, three PS films and two samples of PS-0.050SSA were measured. The minor number of determinations for which there was clearly significant overlap of the internal standard by a small-molecule band were eliminated. Otherwise, the various calculations were evaluated to establish the degree of proton transfer and to estimate its error. The error estimate takes into account any detectable overlap of the 906−900 cm^{-1} band by small-molecule bands that could be detected, which appeared to be the case only for PUR. In any case, as mentioned above, the small molecule content in the samples is low, and therefore only very intense bands from the small molecules will affect the ionomer spectra significantly.

The above calculations assume that the PS-SSA copolymer and all the ionomers are dried thoroughly, since H_2O also induces proton transfer.[17,21,25] The bands at 1102 and 1004 cm^{-1} in spectrum (a) of Figure 1, which are present only for dried samples,[25] and the weak intensity of the 1004 cm^{-1} absorption, coupled with the absence of any significant absorption at 1125 cm^{-1}, assure us that the copolymer is essentially dry (certainly to within the experimental error established above). Since the PS-SSA film was prepared in the same way as the organically neutralized ionomers, we assume that the latter are dry to the same extent. Even if not, the proton transfer values would contain only a systematic error which decreases with increasing proton transfer, such that the trends observed are unlikely to be affected.

Table 2. Calculated Degrees of Proton Transfer (PT) in PS-SSA Ionomers Neutralized by the Organic Cations Indicated[a]

cation	PT/%	cation	PT/%
HDA	98 ± 2	APS	77 ± 4
PDA	97 ± 2	TPY	60 ± 4
DAB	96 ± 2	PYR	50 ± 10
HMT	94 ± 4	PPD	46 ± 5
TAZ	85 ± 3	PUR	40 ± 10

[a] Determined from the normalized area under the 906−900 cm^{-1} infrared absorption bands.

The final results of the above analyses are listed in Table 2.

The trends observed should also be reflected in the relative intensities of the bands at 1125 and 1008 cm^{-1}. Thus, these bands were also analyzed quantitatively as best as possible, again using the 758 and the 1875 or 1945 cm^{-1} bands as internal standards. However, consistent base lines for the 1125 and 1008 cm^{-1} bands for the entire series are difficult to establish, as they experience significant overlap with neighboring bands; this problem is especially serious for the 1125 cm^{-1} band of the ionomers with APS, TPY, PYR, PPD, and PUR, and for the 1008 cm^{-1} band for the ionomer with TPY. Taking the highest relative intensities of the 1125 and 1008 cm^{-1} bands as representing essentially complete proton transfer, consistent with that established based on the 900−906 cm^{-1} band, the degrees of proton transfer for the various ionomers determined from the 1125 and 1008 cm^{-1} bands concord with those given in Table 2 in most cases. The main inconsistency lies with the TPY ionomer, for which the degree of proton transfer appears to be as low as 30% (half that given in Table 2); however, as noted above, the base lines for this sample are particularly ambiguous at the 1125 and 1008 cm^{-1} bands. It is also noteworthy that the degree of proton transfer for the PYR ionomer, based on the latter bands, appears to be at the lower end of the range given in Table 2 and that for PUR at the higher end.

It is clear from Table 2 that the degree of proton transfer to the ten small molecules has correlation with their relative basicities, as analyzed above. The greatest degree of proton transfer is observed with the most basic molecules, namely, HDA, PDA, DAB, and HMT. The proton transfer is virtually complete for these. Clearly, whether the primary amine is aliphatic or aromatic makes little difference, in contrast to the basicities determined in aqueous media. Thus, it can be stated that all four molecules are above or at the lower limit of basicity for obtaining complete proton transfer in the PS-SSA matrix (it is to be noted, in this connection, that the relatively low aqueous pK_a constant of 3.29 reported for the second protonation of PDA does not correspond to lesser proton transfer from PS-SSA). The expected reduction in basicity caused by the central O=S=O substituent in APS clearly diminishes the degree of proton transfer. Of the nonheterocyclic molecules, it is PPD which experiences the least amount of proton transfer, similar to that of the heterocyclic TPY, PYR, and PUR molecules; this may well reflect the very weak basicity of the secondary amine between two aromatic groups compared to the primary amine attached to a single aromatic group (and as reflected in the aqueous pK_a values noted above). The fact that the degree of proton transfer to PPD is close to 50% may well imply that it is essentially the primary amine which is protonated. Of the heterocyclic molecules, it is TAZ which experiences the greatest amount of proton transfer, corresponding to its expected higher basicity. Given the high error for the degrees of proton transfer to TPY, PYR, and PUR, it is not possible to distinguish between them, although it is clear that the relatively low degrees of proton transfer correspond to the expected weaker basicity of these heterocyclic molecules. It may also be noted that the indication from elemental analysis that PUR is present to about twice the stoichiometry of SSA groups supports its being a weak base, since the degree of proton transfer to PUR would likely be even less than that measured if less purine were present.

The degree of proton transfer in these ionomers will obviously affect the extent of ionic cross-linking in these materials. When proton transfer is virtually complete, the number of direct ionic cross-linking sites will be at their maximum. When protonation is far from complete, two different situations can be envisaged, which cannot be distinguished in the present study. On the one hand, singly-charged molecules may predominate over doubly- or multiply-charged molecules, particularly if one potential protonation site is sufficiently basic to provoke proton transfer and the other(s) is (are) not. In the extreme situation, a system involving a bifunctional molecule which is 50% protonated or less will have only singly-charged cations, as was suggested above for PPD. On the other hand, if protonation of one of the N's enhances the basicity or the availability of the other, formation of direct ionic cross-links is favored, with a fraction of the small molecules simply remaining unprotonated.[31]

Superimposed on direct ionic cross-links caused by doubly- or multiply-charged organic counterions may be some ionic aggregation, as is observed in metal-neutralized ionomers. This factor may also contribute to an effective cross-link network in these materials. These aspects will be considered in the following paper, where molecular orientation and dynamic mechanical results are reported.

Conclusions

An IR spectroscopic investigation, at ambient temperature, of PS-0.050SSA blended with ten different organic small molecules containing bi-, tri-, and quadrifunctional amine or pyridine groups was presented. A detailed band analysis correlated the changes observed in the spectra with variable degrees of proton transfer from the acid to the small molecules in accordance with the estimated order of basicity of the latter, with essentially complete proton transfer occurring for both the aliphatic and aromatic primary amines studied. The degree of proton transfer was quantified based primarily on the normalized area of the band and shoulder at 906−900 cm^{-1}. Thus, different organic cations provide different extents of direct ionic cross-linking in these ionomers.

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