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Structures and Properties of Hydrocarbon Ionomer Membranes. 2. Polystyrene-Based Cation Exchangers

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ABSTRACT: The structural properties of the polymers poly(methyl methacrylate-*co*-methacrylic acid) P(MMA-*co*-MAA), poly(styrene-*co*-methacrylic acid) P(S-*co*-MAA), and poly(styrene-*co*-*p*-sulfonic acid) P(S-*co*-SSA) were studied using small-angle X-ray scattering methods. Evidence for ionic aggregation in the dry state and phase separation in the wet state is found for some of the systems. The thin film membrane properties of these polymers as well as poly(styrene-*co*-acrylic acid) P(S-*co*-AA) and poly(vinylcyclohexane-*co*-acrylic acid) P(VCH-*co*-AA) were evaluated. The conductivity and the properties of sorbed water were evaluated as a function of increasing ionic content. For each polymer system, an abrupt insulator to conductor transition was found, at water contents which indicate that ionic–aqueous conducting regions in the polymers are randomly distributed whether or not the polymer is phase-separated. The hydrogen bonding of sorbed water in these polymers was studied using near-infrared spectroscopy and compared to that in other hydrophilic polymers.

Introduction

Synthetic ionomers have many important practical applications, and their use as membranes in several technologies is now widespread. In particular, the perfluorinated ionomers have widespread applications due to their good ionic conductivity, high inherent permselectivity, and excellent chemical stability. High permselectivity in favor of one ionic charge type over another is due not only to Donnan exclusion of electrolyte but also to a kinetic limitation of the diffusion of ions based on size and charge for these ionomers. Their complex microphase-separated morphology has been implicated as the underlying cause of this enhanced permselectivity.[1] This research is focused on the development of a better understanding of the relationship between polymer morphology and ionic permselectivity for hydrocarbon ionomer membranes. Our approach is to prepare and characterize several classes of hydrocarbon ionomers with increasing morphological complexity and to correlate structural features with the nature of sorbed water and their membrane transport properties. For each class of ionomer, a series of polymers with increasing ionic content is prepared and evaluated, since there are often abrupt changes in both structural and transport properties at certain ion contents, as discussed previously.[2]

In the first paper of this series, we reported a study of poly(methyl methacrylate-*co*-methacrylic acid) [P(MMA-*co*-MAA)] polymer membranes.[2] Samples of increasing ion content were solution cast into films. At a certain ion (and water) content, a sharp insulator to conductor transition is exhibited which is accompanied by the appearance of strongly hydrogen bonded sorbed water. Three spectroscopically distinct types of water exist in the polymers after this transition, and two of these types appear to comprise the ion conducting pathways, as inferred using site percolation theory. These polymers are morphologically simple, which correlates with the close correspondence of this transition to ideal percolation behavior. In this paper we report the extension of this research to four classes of ionomers, three of which are based on polystyrene and are somewhat more complex morphologically. Our overall goal is to understand how the structural properties of water swollen ionomer membranes affect ionic and small molecule transport properties in membrane applications.

The polymers studied here are poly(styrene-*co*-methacrylic acid) [P(S-*co*-MAA)], poly(styrene-*co*-acrylic acid) [P(S-*co*-AA)], poly(styrene-*co*-*p*-sulfonic acid) [P(S-*co*-SSA)], and poly(vinylcyclohexane-*co*-acrylic acid) [P(VCH-*co*-AA)]. The polymer backbones are more hydrophobic than the first polymer studied, which is expected to yield more complex morphological properties, which may be reflected in their membrane properties as well.

Extensive morphological and mechanical studies of the three polystyrene systems and the vinylcyclohexane ionomers in the dry state have been performed in the past in several laboratories.[3–25] According to a recent model of ionomer morphology,[25] ions in materials of this type aggregate to form multiplets, which are features containing several ion pairs in a rigid noncrystalline form. It is postulated that these multiplets are surrounded by a region of chain material of reduced mobility. However, since the multiplets, along with the surrounding material, are less than 30 Å in diameter, they do not exhibit an independent glass transition temperature. As the number density of these multiplets increases, the regions of restricted mobility begin to overlap, and when these overlapping regions of restricted mobility reach dimensions of ca. 100 Å or more, the material exhibits two glass transitions, that of the matrix and that of the clustered regions. All of the materials which are discussed here show two loss tangent peaks in their dynamic mechanical behavior (above some minimum ion concentration), which reflects the presence of the clustered regions. The double-peak behavior extends up to some maximum ion concentration at which the material can be thought of as being made up entirely of clustered regions. In the poly(styrene-*co*-sodium methacrylate) [P(S-*co*-MANa)] ionomers, for example, the two-peak behavior extends from ca. 1 to ca. 15 mol %.[23]

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In addition, all four systems, above some minimum ion concentrations, show a small-angle X-ray peak at characteristic q [$=4\pi(\sin\theta)/\lambda$] values. This is frequently true of clustered ionomers. For example, for an ion content of ca. 7 mol % in a styrene–cesium methacrylate copolymer, the q(maximum) value is seen at ca. 0.32 Å^{-1}, which reflects an intermultiplet distance of ca. 20 Å. In the case of styrene–cesium acrylate copolymers with the same ion content,[24] the q(maximum) is seen at ca. 0.29 Å^{-1}, and the Bragg spacing (d_{Bragg}) is ca. 22 Å, while for vinylcyclohexane–cesium acrylate copolymer, it is also found to be ca. 22 Å.[24] For the styrene–cesium styrenesulfonate ionomers q(max) = ca. 0.17 Å^{-1} and d_{Bragg} = ca. 37 Å.[7,15] An illustrative calculation gives some idea of the size of the multiplets. For the purpose of such a calculation, all of the ion pairs are assumed to form aggregates on a cubic lattice. In a methacrylate ionomer, at a concentration of 7 mol % of ions, with a Bragg spacing of 20 Å, each ionic core (multiplet) contains an average of 4.5 ion pairs. At the same ion content, in an acrylate ionomer, each multiplet contains an average of 5.2 ion pairs, while in the p-sulfonate ionomer the number is 17. All the random styrene-based ionomers have identical backbone flexibility between the functional groups. Thus, the thickness of the layer of restricted mobility surrounding the multiplets is taken to be the same. If this is the case, then the volume fraction of material in the restricted mobility region increases with increasing number of multiplets, while the number of the multiplets is inversely related to the size of the multiplets. Hence, the volume fraction of material of restricted mobility is higher in systems containing smaller multiplets.[22]

In the case of sulfonate ionomers, the electrostatic interaction between the sulfonate ion and its counterion is stronger than that for the carboxylate systems.[22] Also, the ion pairs in the p-sulfonate ionomers have a lower steric hindrance to aggregation than those in the methacrylate ionomers, since the ion is located in the *para*-position of the benzene ring, while in the methacrylates case it is right on the backbone.[22] The steric hindrance to multiplet formation is, therefore, larger in the methacrylate case. Thus, the p-sulfonate ionomers form larger multiplets with a larger intermultiplet distance than is seen in the methacrylate ionomers. Comparing the methacrylate and acrylate ionomers,[24] one finds that the only difference in the chemical structures of these two families is the presence of the methyl group on the methacrylate. Therefore, for the methacrylates, the contact surface area of the chain[26] is bigger due to the presence of the methyl group, and thus the multiplets are smaller than in the acrylates. Therefore, the Bragg spacing for the methacrylates is marginally smaller than that for the acrylates. Thus, among the three polystyrene-based samples in this study at the same ion content, the order in increasing size of multiplets is methacrylates, acrylates, and sulfonates. Therefore, the order of increasing volume fraction of materials of restricted mobility is exactly the opposite, i.e., p-sulfonates, acrylates, and methacrylates.

The P(VCH-*co*-AA) polymer exhibits higher matrix and cluster glass transition temperatures compared to the styrene-based ionomers, which is likely due to the greater bulkiness of the pendant cyclohexyl group relative to that of a phenyl group.[24] This increases the stiffness of the chain relative to the styrene-based materials. As a consequence, P(VCH-*co*-AA) shows smaller multiplets, a smaller percentage of ions in multiplets, and a lower volume fraction of clustered material, for comparable ion contents, compared to the styrene-based ionomers.[24]

The study of water in ionomers is of obvious importance to commercial applications and started about 3 decades ago. Longworth and Vaughan first mentioned that the SAXS peak was sharpened and intensified upon the introduction of a small amount of water, while water saturation reduced the peak intensity.[27] A more extensive SAXS study of poly(ethylene-*co*-cesium methacrylate) [P(E-*co*-MACs)] containing 3.8 mol % of ions was performed by MacKnight et al.[28] It was found that in the dry state the peak maximum occurred at ca. 35 Å, while in the water-saturated state water completely destroyed the ion peak and only broad small-angle upturn (SAUT) was observed.[28] Also, the effect of water sorption on the SAXS profiles of the P(E-*co*-MANa) ionomer containing 5.4 mol % of ions was studied by Katsumizu et al.[29] It was found that, as the water content increased, the small-angle ionic peak moved to lower q values, i.e., a larger Bragg spacing, and its intensity decreased. It was suggested that the shift of the peak was due to the swelling of the ionic clusters by water; both the number of the ionic aggregates and the number of ion pairs per cluster were thought to remain unchanged by hydration. Also, it was suggested that the decrease in the peak intensity by hydration was due to the decrease of the electron density difference between the ionic cluster and surrounding matrix regions by hydration. These studies were performed for polymers with ion contents which are much smaller than those needed for membrane applications.

Small-angle X-ray scattering (SAXS) studies of perfluorinated ionomer membranes in the water-swollen state were performed by Fujimura et al.,[30] Roche et al.,[31] and Gierke et al.[1,31] It was found that, with increasing water uptake, the SAXS peak maximum shifted to lower q or smaller angles and that the intensities of the peaks increased. The shift of the scattering maximum was ascribed to increasing intercluster distances, and the increase in the intensity, to the increase in the electron density difference between the clusters and their surrounding medium. The effect of water on the SAXS profiles of poly(butadiene-*co*-sodium methacrylate) ionomers was studied by Mark et al.[32] It was also found that the ionomer peak shifted to lower q values, corresponding to larger Bragg spacings, as water was added. The effect of water on the SAXS profiles of styrene-zinc styrenesulfonates [P(S-*co*-SSZn)] was studied by Yarusso and Cooper.[8] It was found that for the samples containing ca. 3 or 7 mol % of ions, with increasing water content, the SAXS peak again shifted to lower q values and its intensity increased. They suggested that a morphological rearrangement occurs upon swelling and that the rearrangement results in the change in the fraction of the ions which form aggregates as well as in the number of aggregates in the material as the water content increases. At low water contents, the water is absorbed by the ionic groups which exist in the matrix. Then, at higher water contents, those hydrated species tend to aggregate. Thus, the intensity of the SAXS peak increases.

However, Fitzgerald[33] found that when sufficient amounts of water were absorbed by neutralized P(S-*co*-SSA) ionomers, the intensity of the SAXS peak decreased and its position shifted to lower angle. He suggested that since Yarusso and Cooper[8] used a pressure cooker to diffuse the water into the ionomers, the samples might be supersaturated. Therefore, it might be possible that the SAXS peak of Yarusso and Cooper actually arose from the water clusters. Also, it was pointed out that the water can be absorbed into the polystyrene matrix under such conditions, and thus it might be also possible that the water swells the hydrocarbon and disrupts the ionic association. This might allow those ion pairs which exist in the matrix without association to become incorporated into the aggregates. Since the size of the scattering entity (aggregates) would increase with increasing water content, there would be a decrease in the electron density contrast. Therefore, the intensity of the peak decreased and the peak shifted to lower q values, with increasing water content.

The effect of polar diluents, i.e., methanol or glycerol, on the SAXS profiles of P(S-*co*-SSZn) ionomers was studied by Fitzgerald et al.[10,11,19] It was found that the position of the scattering maximum moved to slightly lower q and that the intensity of the SAXS peak decreased with increasing amounts of methanol. The decrease in the peak intensity was ascribed to a decrease in the scattering invariant upon addition of methanol. Also, in the case of the styrene–manganese styrenesulfonates [P(S-*co*-SSMn)] (1.6 mol %), the addition of 5% methanol lowered the SAXS peak intensity and shifted the SAXS peak maximum to lower q. However, further addition of methanol (to 10%) rendered the peak invisible. It was also found that the small-angle upturn (SAUT) shifted to slightly higher q values. The addition of glycerol to P(S-*co*-SSMn) also shifted the SAXS peak to a lower q value and increased the peak intensity. It was suggested that the glycerol swelled the aggregate, which enhanced the scattering invariant and increased the volume fraction of these regions, and thus the intensity of the SAXS peak increased with increasing amount of the added glycerol.

Experimental Section

Synthesis. The preparation of the materials has been described elsewhere.[3,6,24] Therefore, for the convenience of the reader, only brief summaries of the procedures are given here. For the synthesis of poly(styrene-*co*-methacrylic acid) [P(S-*co*-MAA)], the two purified monomers, i.e., styrene and methacrylic acid, were copolymerized by free-radical bulk polymerization at 60 °C using benzoyl peroxide as the initiator. After the predetermined polymerization time (set to achieve a conversion of ca. 5–15%), the reaction solution was cooled and diluted with 20 volumes of tetrahydrofuran (THF). For materials containing less than 20 mol % of methacrylic acid, the copolymer was recovered by precipitation into excess methanol, while for systems with acid contents higher than 20 mol %, the copolymer was precipitated into a mixture of methanol/water (80/20, v/v). The precipitated copolymer was filtered and dried in a vacuum oven at 60 °C for 2 days. To determine the acid concentration, polymers were dissolved in a benzene/methanol (90/10, v/v) mixture to make a 5% (w/v) solution and were then titrated with a standard methanolic sodium hydroxide to the phenolphthalein end point. For synthesis of the random poly(styrene-*co*-acrylic acid) [P(S-*co*-AA)] ionomers, the same procedure was used as for the P(S-*co*-MAA) samples, as was briefly described elsewhere.[24]

For the preparation of P(S-*co*-SSA) copolymers, the polystyrene was synthesized by anionic polymerization. The number-average molecular weight and the polydispersity index of the polystyrene were 220 000 and 1.6, respectively, as determined using a Varian 5010 liquid chromatograph with THF as the eluent. Polystyrene standards of narrow molecular weight distribution were used for calibration. The polystyrene was sulfonated using the method of Makowski et al.[34] The sulfonation level was also determined by titration with methanolic NaOH to the phenolphthalein end point. The details of the synthesis of the poly(methyl methacrylate-*co*-methacrylic acid) [P(MMA-*co*-MAA)] ionomers were given in the first publication in this series.[2]

The synthesis of P(VCH-*co*-AA) was performed by the copolymerization of styrene and methyl acrylate and its subsequent hydrogenation using a modification of Osada's method.[24,35]

Sample Preparation. For the samples in the dry state, the copolymers were first dissolved in a benzene/methanol (90/10, v/v) mixture to give a 5% (w/v) solution. A predetermined quantity of methanolic CsOH was added to neutralize the acid groups. The solutions were freeze dried and then dried further under vacuum at 160 °C for at least 1 day. The sample notation used for the ionomers is P(MMA-x-MACs) for P(MMA-*co*-MAA), P(S-x-SSCs) for P(S-*co*-SSA), and P(S-x-MACs) for P(S-*co*-MAA), where x is the mol % of the cesium neutralized anionic groups. Powdered polymer samples were processed into membrane films by dissolution in dimethylformamide 2 w/v % solutions and casting on glass plates at ca. 60 °C. Uniform transparent films were obtained with an average thickness of about 0.25 mm. These films were used for transport studies and for SAXS measurements with water-equilibrated samples.

For the SAXS studies, the cesium neutralized samples were compression molded at 240 °C under a pressure of ca. 20 MPa. The pressure was applied for 5 min and then it was slowly released, the mold was cooled slowly to below the matrix T_g and subsequently removed from the mold. The molded samples, in thin disk forms with dimensions of 12 mm (diameter) × 0.6 mm (thickness), were stored under vacuum at 100 °C for 24 h.

Small-Angle X-ray Scattering (SAXS) Measurement. The small-angle X-ray scattering (SAXS) experiments for the ionomers in the dry and equilibrated water-swollen states were conducted at station D-22 of the LURE, Orsay, France, using a synchrotron as the radiation source. A detailed description of the instrument is given elsewhere.[36] The sample-to-detector distance of 597 mm allowed SAXS data to be obtained in the q range of 0.018–0.37 Å^{-1} (where q is the scattering vector, equal to $4\pi(\sin\theta)/\lambda$, where θ is half the scattering angle, and λ is the X-ray wavelength). For dry samples, the thin disks were mounted directly in the sample holder which had a hole with a diameter of ca. 2 mm for the beam. For wet samples, the solution-equilibrated sample films were placed in a sealed cell with Kapton windows, which were moisturized with a few drops of the mother solution to maintain the equilibrated water-swollen state of the sample during the measurement. In order to prevent any possible loss of solvent during the measurement, the sample chamber was not kept under vacuum during the measurement. For the purpose of valid comparison between the dry and wet samples, the measurements on the dry materials were also performed under atmospheric pressure. The counting time was ca. 5 min. The SAXS data were plotted as intensity vs q after correction for background scattering. In that procedure, the SAXS profile of pure polystyrene or poly(methyl methacrylate) was subtracted from that of each ionomer sample. If the polymer was measured in a cell with Kapton windows, data for polystyrene or poly(methyl methacrylate) homopolymers kept between Kapton windows under experimental conditions were used for the subtraction. All samples were normalized to a thickness of 1 mm.

Membrane Properties. Membrane equilibration, electrolyte and water sorption, equivalent weight determination, and self-diffusion measurements were made using the same methods as described in ref 2. All films, obtained in acid form, were generally hydrophobic and much less conductive than the neutralized Na^+ forms. Membrane resistances were measured in a 0.1 M NaCl/0.005 M NaOH solution using a GenRad 1689 RLC Digibridge; and specific conductivities were calculated as described in ref 2.

In order to gain some insight into the character of sorbed water in the membranes, near-infrared spectra were obtained for the solution-cast membrane films. All samples were equilibrated in a mixture solution of 0.1 M NaCl/0.005 M NaOH before infrared absorbance studies. Samples were blotted and quickly introduced into a Nicolet 8000 FTIR spectrometer, and the averaged spectra of 50 scans were then obtained. The OH combination band between 5400 and 4700 cm^{-1} was decomposed into Gaussian component peaks using the commercial software program Spectra Calc. The goodness of the fit was satisfactory in all cases, as judged by the computed statistical fitting parameter (χ^2).

Results and Discussion

SAXS Measurements. As was mentioned before, the first publication in this series dealt with membranes made of P(MMA-*co*-MAA) ionomers.[2] The morphology of that system was also investigated as part of the present study.

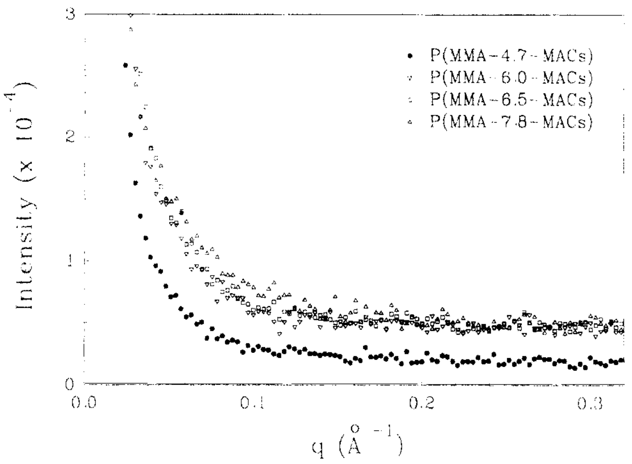

Figure 1. Small-angle X-ray scattering profiles for P(MMA-*co*-MACs) in the water-swollen case.

The results of the small-angle X-ray scattering (SAXS) study on the water-equilibrated samples of P(MMA-*co*-MACs) are shown in Figure 1. As can be seen, a small-angle upturn (SAUT) is the only characteristic feature of this family of materials, with no trace of a typical "ionomer peak". In a large number of dry ionomers, a small-angle peak is seen at a q value which is characteristic of a distance between the scattering centers. Most recently, this peak has been interpreted as reflecting the distance between centers of multiplets.[25,37] The absence of the peak suggests that in these materials no scattering centers are present in the range of distances covered by a value of q between 0.02 and 0.32, i.e., a Bragg spacing on the order of 300 Å down to 20 Å. It should be mentioned that the absence of a SAXS peak does not automatically exclude the possibility of ionic aggregation. It is possible for aggregation to be present without giving rise to a SAXS peak, if the contrast (electron density difference) between ion-rich and ion-poor regions is too low.[30] This is occasionally encountered for ionomers with ions of low electron density, i.e., Na^+ or Li^+. This is not likely to be the case here, since we are dealing with Cs^+ ions which show high contrast relative to hydrocarbon or water. A SAUT is prominent; however, very few conclusions can be drawn from the SAUT because the interpretation of that feature has been a subject of some controversy.[12,13,38] A previous study of the materials in the dry state also failed to detect any peaks.[39]

While the SAXS patterns of several polystyrene-based ionomer systems have been published at low ion contents,[7,8,10,12,13,15,17,20] those for the P(S-*co*-SSCs) system have not been published in the range of 10–20 mol %. These are shown in Figure 2a. For the P(S-*co*-MACs) ionomers at high ion content in the dry state, the SAXS profiles are shown in Figure 2b; it is seen that the positions of the q maxima are independent of the ion content. For the acrylates in the dry state, the SAXS profiles, which are shown elsewhere,[24] also showed that the positions of the q maxima remain constant with changing ion content. It should be mentioned that the SAXS profile for the P(S-*co*-MACs) containing a low ion content, e.g., ca. 7.6 mol %, also showed a small but clean peak at the same position as for the higher ion content samples. For the sulfonate ionomers, it is seen that, as the ion content increases, the peak position shifts to a slightly larger q value. This means that, with increasing ion content, the intermultiplet distance decreases and thus the size of multiplets decreases.

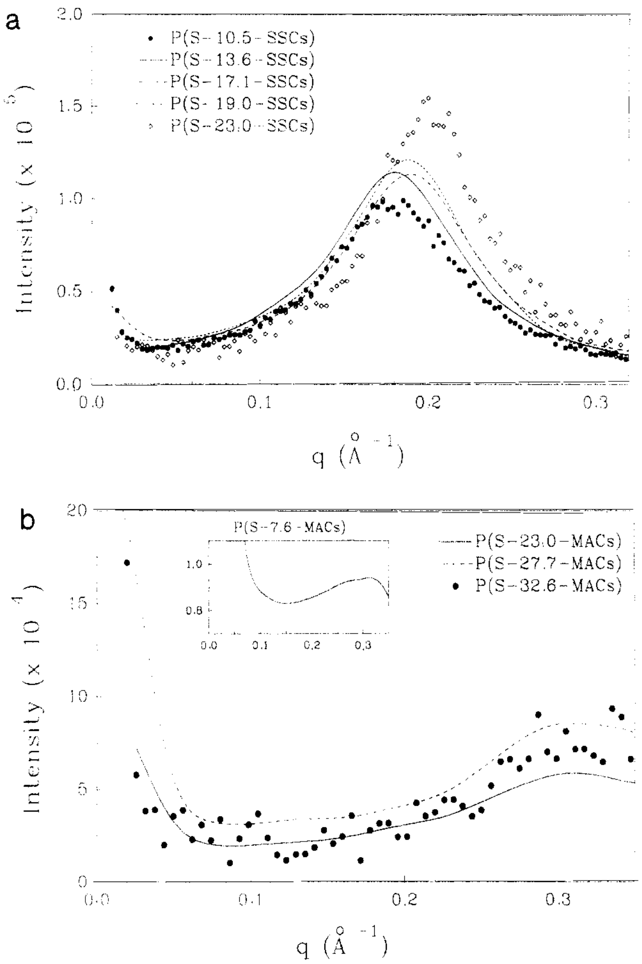

Figure 2. Small-angle X-ray scattering profiles (a) for P(S-*co*-SSCs) ionomers in the dry state and (b) for the P(S-*co*-MACs) ionomers in the dry state. For some of the plots, only smooth lines are shown for clarity. For those, the Fast Fourier Filter smoothing program in the PeakFit computer software package was utilized and the experimental points are omitted.

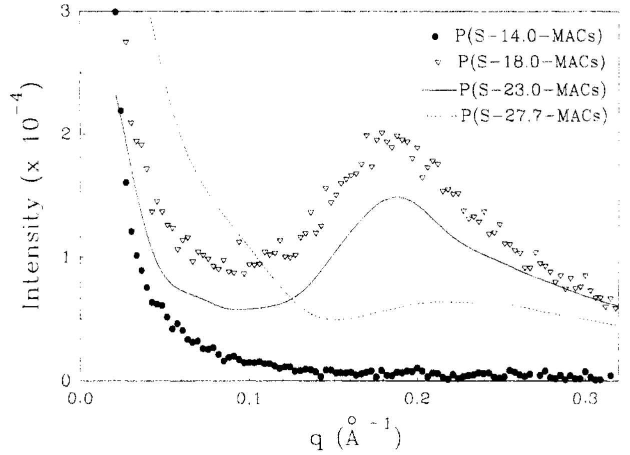

Figure 3. Small-angle X-ray scattering profiles for P(S-*co*-MACs) ionomers in the water-swollen state. Again, for some of the concentrations, only smooth lines are shown to improve clarity of presentation.

The results of SAXS study of the P(S-*co*-MACs) ionomers in the equilibrated water-swollen state are shown in Figure 3, and a comparison of the dry and wet profiles for the 23 mol % sample is shown in Figure 4. It is clear that while the wet sample containing 14 mol % of ions shows no peak, above ca. 18 mol % of ions a distinct peak becomes visible, the strength of which rises at some threshold value and then decreases in intensity with increasing ion content. This behavior is most unusual and might be of great relevance in understanding transport

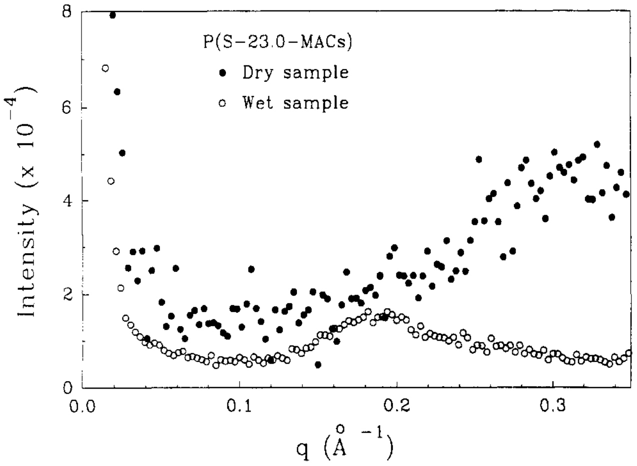

Figure 4. Small-angle X-ray scattering profiles for P(S-23.0-MACs) in the dry state (●) and in the water swollen state (○).

properties. In terms of the difference between the wet and dry samples, it is clear that the Bragg spacing increases upon swelling, which means that the distance between the scattering centers increases.

The absence of the small-angle peak in the X-ray data for the dry P(MMA-*co*-MACs) ionomers stands in marked contrast to the presence of a peak in the P(S-*co*-MACs) ionomers of a comparable cesium carboxylate content. While the peak intensity in the styrenes is low, it is, nonetheless, clear that there are scattering centers at a preferred distance. The absence of the peak in methyl methacrylate ionomers makes it clear that in these materials phase separation of the type encountered in the styrene-based ionomers is not present. These results are consistent with the differences in viscoelastic results on the methyl methacrylate-based ionomers and styrene-based ionomers at comparable ion contents, which also illustrate the differences between the two families. The mechanical behavior of P(MMA-*co*-MAA) ionomers (Figure 2 of the previous study)[2] shows only an increase in the glass transition temperature rather than the appearance of the second phase usually associated with the presence of the SAXS peak. It should be recalled that the SAXS peak and a second dynamic mechanical peak, the so-called cluster peak, are usually present together, especially in the simple ionomer system. Also, in the ethyl acrylate ionomers which were studied over a wide ion content range, clustering becomes evident only above a concentration of ca. 12 mol %.[40] By contrast, for the P(S-*co*-MAA) ionomers, the phase inversion due to clustering already occurs at ca. 5 mol %.[18,23] All these results suggest that the methyl methacrylate and styrene ionomers are different in their dry state behavior. The differences are, most probably, due to the differences in the dielectric constant of the materials and possibly also to the differences in the persistence length of the polymer.[22,25] While in the styrene-based ionomers ion aggregation is important, in the methyl methacrylate-based ionomers it is much less so at ion concentrations of 0–10 mol %.

The SAXS results on the P(MMA-*co*-MACs) ionomers in the water-swollen state also show absolutely no feature associated with phase separation over distance scales of 20–300 Å. Therefore, it seems reasonable to suggest that, just as in the dry samples, the ions are dispersed singly and randomly in the material, a situation analogous to aqueous salt solutions. Thus, the SAXS results are completely consistent with the results of the transport study of the first publication of this series.[2]

For the P(S-*co*-MACs) system in the dry state, the SAXS peak arises from intermultiplet interferences. The intermultiplet scattering is ascribed to phase separation between the ionic aggregates and the matrix, which is driven primarily by the attraction of the ion pairs for each other via dipolar interactions.

In the case of these materials in the water-swollen state, the SAXS profiles show very different features from those in the dry state. The SAXS profile for the sample containing 14 mol % of ions (~2 water molecules/ion pair) shows absolutely no peak. This suggests, most probably, that there are no scattering centers of a sufficiently high electron density to give rise to a peak. This in turn means that the ions, because of ionic hydration, attract each other only very weakly and suggests that the hydrated ions are dispersed more or less uniformly in the polymer. A similar effect, i.e., the absence of the SAXS peak, has been observed in the poly(styrene-*co*-4-vinylpyridinium methyl iodide) copolymers, in which the ion pairs are believed to be too large to aggregate at or above the glass transition temperature of the polystyrene matrix. Since the ion pairs are distributed singly and randomly throughout the material, no SAXS peak is to be expected in the q region normally associated with ion aggregation.[41] At this concentration, therefore, the water molecules weaken the interactions, reducing its strength to below that required for aggregation. However, since the volume fraction of (hydrated) ions plus water is ca. 6%, it is apparently insufficient to phase separate as a result of the dissimilarity between water and styrene. It should be recalled that such a phase separation would involve appreciable chain deformations, which carry with it an entropic penalty. The enthalpic compensation for such a process from the aggregation of the hydrated ions is, apparently, insufficient to induce phase separation.

As the ion content increases from ca. 14 to ca. 18 mol %, the equilibrated water content rises from ca. 6 to ca. 13 wt % (from 2 to 5 water molecules/ion pair); this is accompanied by a remarkable morphological change in the sample, i.e., the appearance of a well-defined peak in the SAXS profile. This peak with a q(max) of 0.19 Å^{-1}, is associated with a Bragg spacing of 34 Å. A possible explanation for this phenomenon is the onset of phase separation between regions of high hydrocarbon content and regions containing an aqueous solution of high ion content on a size scale of ca. 34 Å. As ion content increases further, e.g., to 28 mol %, the water content increases dramatically, which reduces the concentration of cesium ions in the water. Thus, the contrast between hydrocarbon and aqueous regions decreases, and the intensity of the SAXS peak decreases in parallel. It is interesting to note that the size scale of the phase-separated regions changes only very slightly. This is not surprising, because a cube root dependence is operative between volumes and linear dimensions. It should be stressed that the peak position does not necessarily measure directly the size of either the hydrocarbon domains or the aqueous domains but is a function of periodicity of these two regions. The other point to make is that the driving force for the phase separation is now no longer ionic aggregation but unfavorable interaction between the polystyrene phase and the aqueous solution phase, with the ions serving to hold the water in the polymer. Apparently a minimum quantity of aqueous ionic solution is necessary for the onset of this type of phase separation to be manifested, and this onset occurs at a volume fraction of (hydrated) ions plus water above 6%. The difference between the styrene-based ionomers and the methyl methacrylate-based ionomers is undoubtedly due to the higher dielectric constant and hydrophilicity of methyl methacrylate relative to styrene.

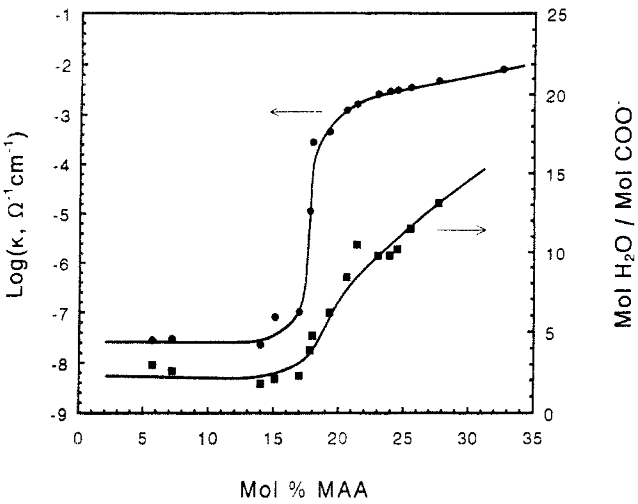

Figure 5. Specific conductivity and the water to ion exchange site ratio of poly(styrene-*co*-methacrylic acid) as a function of ionic content.

Furthermore, it is likely that in the water-swollen methyl methacrylate polymer, well beyond the percolation threshold, the chains may be present at a molecularly dispersed level rather than in an aggregate form as in the styrene.

Another interesting feature is seen in the SAXS profile for the P(S-27.7-MACs) ionomer in the wet state. The profile shows that there is one well-defined peak at a q of ca. 0.22 Å^{-1}, which reflects a Bragg spacing of ca. 29 Å, and a shoulder at a lower q value, ca. 0.08 Å^{-1}, representing a Bragg spacing of ca. 80 Å. An attempt was made to fit this SAXS profile with the shape factor for spheres,[42] but it was unsuccessful. Therefore, no spherical features are present which are consistent with this profile. At present, we have no explanation for this shoulder, because not enough data are available to come to an unambiguous conclusion.

No SAXS data were obtained for the other ionomers in the water-swollen state. However, because in the dry state the morphologies and mechanical properties of the acrylates are similar to those of the methacrylates,[24] the P(S-*co*-AACs) and the P(VCH-*co*-AACs) ionomers in the wet state are believed to be similar morphologically to the P(S-*co*-MACs) ionomers.

As for the sulfonate system, the very small number of published studies[1,8,30,31,33] on the SAXS of the materials in the water-swollen state suggests that, with increasing water content, the peak moves to lower q values and eventually merges with the SAUT. The P(S-*co*-SSCs) ionomers present us a situation in which the ion is highly hydrophilic, but the polystyrene is highly hydrophobic. The increased hydrophilicity of the ions, i.e., sulfonate relative to carboxylate, may render the entire chain hydrophilic enough to mimic the SAXS behavior of the P(MMA-*co*-MACs) series to some extent in spite of the hydrophobicity of the styrene. If a SAXS peak is found to be present in the water-equilibrated state at percolation, then it will suggest that the styrene is still sufficiently hydrophobic to phase separate to some extent from the aqueous ionic solution, possibly in the form of elongated micelles observed in the perfluorosulfonates,[43] and that a sufficiently strong driving force for the phase separation is provided by the difference in the interaction between the styrene phase and the aqueous solution phase. If no peak is seen, it will suggest that a more nearly molecular level dispersion of the chain is taking place. This remains to be determined in the future.

Membrane Properties. Figure 5–8 show the specific conductivities and the ratio of water to exchange site vs mol % of ionic comonomers for P(S-*co*-MAA), P(S-*co*-AA), P(S-*co*-SSA), and P(VCH-*co*-AA), respectively. These plots reveal the existence of abrupt transitions from insulator to ionic conductor with increasing ion and water content for each type of membrane. These transitions are quite similar to that seen earlier for P(MMA-*co*-MAA) membranes[2] and for each polymer occur at specific ion contents where a sufficiently large volume fraction of the polymer is conductive to enable macroscopic transport of ions. This insulator to conductor transition was found to occur at 6.5 mol % of ionic comonomer for the rather polar P(MMA-*co*-MAA) ionomer, due to the extensive water swelling even at low ion contents. For the styrene–carboxylate ionomers a greater ion content is required to enable conductivity. Further, the transition from an insulator to conductor occurs at a lower ion content (ca. 15 mol %) for P(S-*co*-AA) membranes than for P(S-*co*-MAA) (ca. 18 mol %), which is likely due to the lower polarity of the ionic site for the latter polymer. The transition for P(S-*co*-SSA) occurs at a much lower ion content, about 7 mol %. This is due in part to the greater hydrophilicity of the sulfonate ion exchange site compared to the carboxylate group, which is observed for both conventional ion exchange resins and for perfluorinated ionomers.[44,45] A much larger ion content is required to

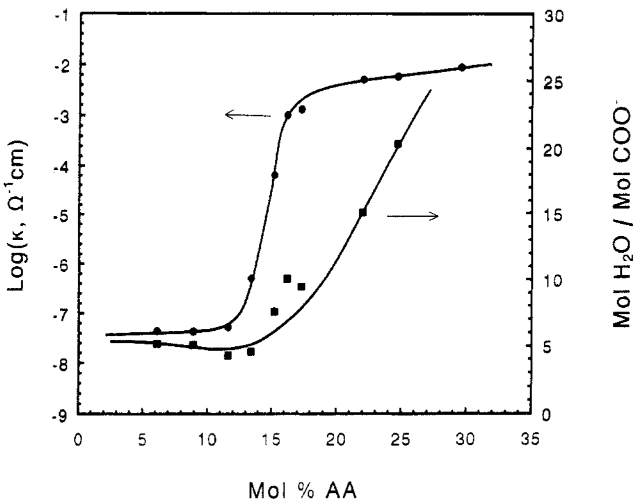

Figure 6. Specific conductivity and the water to ion exchange site ratio of poly(styrene-*co*-acrylic acid) as a function of ionic content.

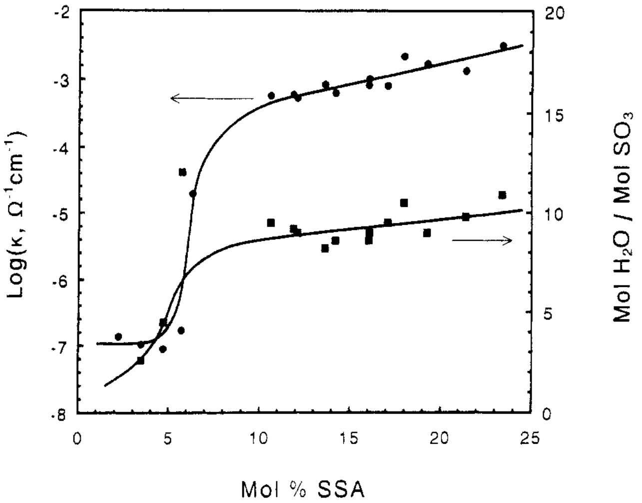

Figure 7. Specific conductivity and the water to ion exchange site ratio of poly(styrene-*co*-*p*-sulfonic acid) as a function of ionic content.

Table 1. Water Sorption and Component Peaks of the OH Near-Infrared Band of Sorbed Water, for Sodium Ion Forms

					peak position (cm^{-1}) and area (%)			
polymer class	EW	ion content (mol %)	% water (w/w)	mol H_2O/mol exch site	center	peak 1	peak 2	peak 3
P(S-*co*-MAA)	617	17.0	6.4	2.3	5235	5244 (23)	5182 (25)	5085 (52)
	583	18.0	12.9	4.8	5215	5238 (19)	5156 (34)	5030 (47)
	510	20.6	22.9	8.4	5215	5239 (17)	5164 (32)	5041 (51)
P(S-*co*-AA)	888	11.6	8.0	4.3	5235	5246 (19)	5183 (32)	5085 (49)
	675	15.2	16.8	7.6	5221	5240 (17)	5169 (30)	5055 (53)
	592	17.3	22.4	9.5	5215	5239 (16)	5165 (32)	5047 (52)
P(S-*co*-SSA)	3090	3.5	1.5	2.6	5207	5246 (14)	5180 (38)	5084 (47)
	1901	5.7	10.3	12.3	5227	5241 (19)	5181 (34)	5093 (47)
	1064	10.6	14.5	10.0	5217	5239 (18)	5169 (42)	5066 (41)
P(VCH-*co*-AA)	489	21.5	4.8	1.4	5274 5157	5275 (7)	5205 (30)	5096 (63)
	429	24.3	16.1	4.6	5271 5167	5274 (6)	5197 (32)	5071 (62)
	380	27.3	29.2	8.7	5167	5267 (5)	5189 (35)	5061 (60)
water[a]					5175	5297 (13)	5200 (42)	5038 (45)

[a] References 51 and 55.

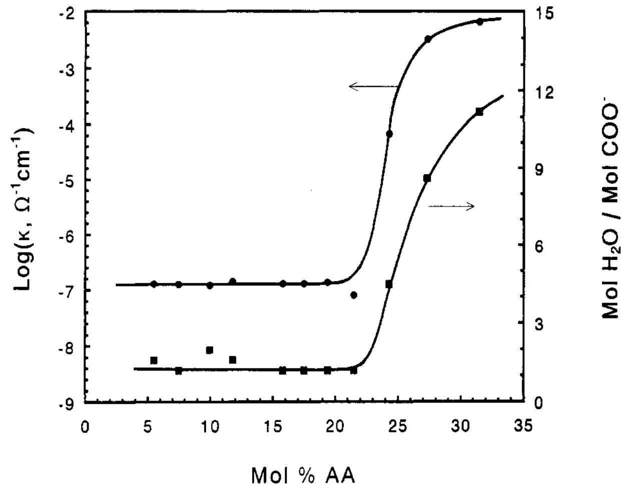

Figure 8. Specific conductivity and the water to ion exchange site ratio of poly(vinylcyclohexane-*co*-acrylic acid) as a function of ionic content.

reach the insulator to conductor transition for the saturated analog of P(S-*co*-AA), P(VCH-*co*-AA), as shown in Figure 8.

Table 1 shows the water sorption of membrane samples at ion contents just before, at, and after the conductor transition. The ion contents of the membranes are also expressed in terms of equivalent weight (EW) in the Na^+ form. The water contents are reported as weight percent and mole ratio of water to ion exchange site for the wet polymer. As seen from the table and figures, the water to ion exchange site ratio remains fairly small before the onset of ionic conductivity, at values too low for even primary hydration of the anionic exchange site and counterion pair. This indicates that ion association predominates at these low ion contents. During the transition, the water to ion ratio increases abruptly. Finally, this ratio continues to rise until eventually the water content is so large that the highly swollen polymers begin to dissolve. These observations are generally similar to those for P(MMA-*co*-MAA). The only exception here is the water to ion ratio for P(S-*co*-SSA), which remains relatively constant after the polymer reaches the conduction plateau. This polymer shows relatively lower water uptakes compared to P(MMA-*co*-MAA). Thus for a given ion content, the order of hydrophilicity for these polymers is P(MMA-*co*-MAA) > P(S-*co*-SSA) > P(S-*co*-AA) > P(S-*co*-MAA) > P(VCH-*co*-AA).

As discussed previously, these abrupt transitions from insulator to ionic conductor are critical phenomena which can be analyzed using a percolation theoretical framework. The primary goal of such a treatment is to determine whether the spatial distribution of the conducting sites within the partially swollen polymer is random or ordered in some manner. Site percolation theory has been used to analyze the insulator–conductor transition for P(MMA-*co*-MAA)[2] and for perfluorinated sulfonate ionomer membranes.[46–48] The analysis of the results was based on the following general equation:

Table 2. Percolation Analysis of Conductivity Data, Sodium Ion Forms

membrane	c_0	n	correl coeff
P(S-*co*-MAA)	0.16	1.60	0.987 (n = 7)
P(S-*co*-AA)	0.15	1.46	0.976 (n = 5)
P(VCH-*co*-AA)	0.15	1.54	0.999 (n = 3)

$$\kappa = \kappa_0(c - c_0)^n$$

where κ and κ_0 are the specific conductivities of the membrane and the conducting phase elements, respectively, c is the volume fraction of this conducting phase, and c_0 is its volume fraction at the threshold of conductivity. The exponent n is essentially a function of the dimensionality of the system, in our case three dimensions. Its theoretical value has been given as 1.5–2.0, depending on the treatment. Site percolation theory predicts that, for a three-dimensional system, c_0 should be about 15 vol % for an infinite array of randomly distributed conduction sites in a matrix of nonconducting material. A way to apply this theory is to estimate c as the volume percent of sorbed water in the polymer and to evaluate the other parameters in the above equation using this assumption.

The results for three of the studied polymers are listed in Table 2. For these systems, percolation analyses indicate that the distribution of conducting elements is completely random, so that the systems are percolatively "ideal". Unlike the P(MMA-*co*-MAA) system, P(S-*co*-MAA) ionomers (and likely at least the analogous P(S-*co*-AA) system) are microphase separated, as indicated by SAXS. Thus, unlike the perfluorinated ionomers, percolative ideality is retained even though microphase separation exists; i.e., these regions themselves are randomly distributed. This highlights an important unusual characteristic of the perfluorinated ionomers which is not reproduced with these hydrocarbon systems, that of percolative nonideality. The insulator to conductor transition for the perfluorinated ionomers occurs at or below 10 vol % of conducting phase.[46–49] This unusual behavior, which is technologically valuable, can be due to

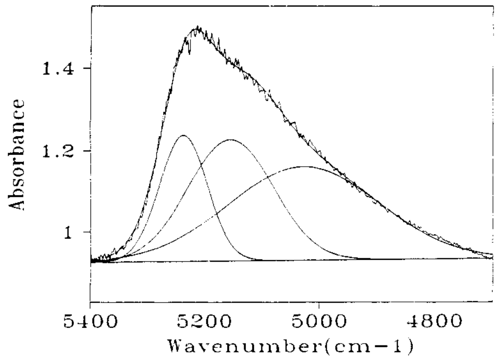

Figure 9. OH near-infrared band of sorbed water, P(S-*co*-MAA) 18.0 mol % MAA, and component peaks.

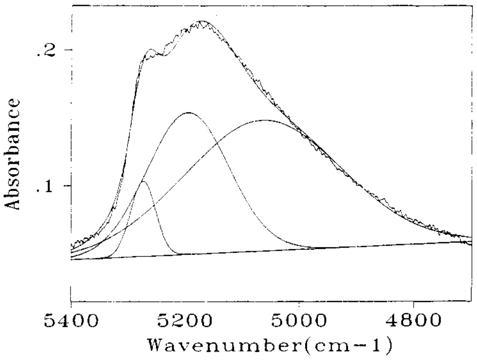

Figure 10. OH near-infrared band of sorbed water, P(VCH-*co*-AA) 24.3 mol % AA, and component peaks.

several possible morphological configurations. The essential feature is that the volume elements of the conducting phase spatially correlate to produce quite low critical volume fractions for macroscopic conduction. This does not occur for these phase-separated hydrocarbon polymers. It was not possible to perform percolation analysis for the fourth polymer P(S-*co*-SSA), because insufficient samples had been prepared in the insulator to conductor region. However, we estimate that the transition occurs somewhere between 10 and 12 vol % of conducting phase, which suggests that these regions are spatially correlated as with the perfluorinated systems.

The previous analysis of the percolation behavior of P(MMA-*co*-MAA) suggests that not all sorbed water is in conductive pathways.[2] For this polymer, analysis indicated that some of the weakest hydrogen-bonded water was not part of the conducting volume elements. This was not seen in the percolation analysis of the polymers studied here; that is, these polymers showed ideal percolative behavior only when all sorbed water was taken into account. We conclude that hydration of the methyl esters in P(MMA-*co*-MAA), which are absent from the current polymers, accounts for this difference.

Figure 9 shows the near-infrared combination band absorbance of sorbed water in P(S-*co*-MAA) with 18.0 mol % ionic repeat units, which is rather typical of the observed bands for all the polystyrene-based polymers studied here. This band arises from the combination of the asymmetric stretch and the bending fundamental bands of water. As discussed previously[2,50–52] analysis of this band can yield important information about the range of molecular environments of sorbed water in polymer systems. The band can be decomposed into three Gaussian components, as shown in Figure 9. In pure water, it has been suggested that the component peaks represent, in order of decreasing frequency, OH groups which are not hydrogen bonded, weakly hydrogen bonded, and strongly hydrogen bonded.[51] Of course, a wide range of OH environments exists, and so this interpretation (as well as the separation of the overall asymmetric band into these components) is somewhat oversimplified. Since the molar absorptivities of each type of water are expected to be quite similar, the area percents of the component peaks can be related to the relative amounts of OH group involved in each general environment though. These component peaks and their relative area percents are listed in Table 1 for polymers in the insulator to conductor transition region, with the results for pure water also listed for comparison.

In the case of sorbed water, the physical significance of three component peaks is even less straightforward than for liquid water. Little strongly hydrogen bonded extended water structure can be expected in these cases, since most of the sorbed water is likely involved with ionic hydration as well as with interactions with polar groups in the polymer. For the low ion and water content samples, we expect that virtually all water molecules fall within the Coulombic fields of sodium ion and/or the anionic exchange sites. In general, the result will be to shift the band to lower frequencies, which is dominated by anion–water interactions.[51,53] With increasing water content after the conductor transition, secondary ionic hydration and water–water interactions are possible.

For the polystyrene-based ionomers, there appears to be considerably less non-hydrogen-bonded OH for sorbed water than is present in liquid water, from the positions of peak 1 listed in Table 1. The other components are rather similar to those for water however. It is rather surprising that there is relatively little change in the spectral properties of sorbed water even though the water to ion exchange site ratios increase by 2–4 here. The positions of these peaks 2 and 3 are 20–40 cm^{-1} higher than for P(MMA-*co*-MAA), in reflection of the lower polarity environment for the polystyrene-based ionomers.

P(VCH-*co*-AA) shows some interesting differences in its near-infrared water bands. The band separates into two peaks for lower water content samples, as shown for the 24.3 mol % sample in Figure 10. This is due to a much higher frequency of peak 1, a characteristic of the perfluorinated ionomers.[52] As well, a much greater proportion of the sorbed water is found in peak 3, the most strongly hydrogen-bonded water. These results are suggestive of a clustering of water for this saturated ionomer, with a small proportion of OH groups exposed to the hydrocarbon ring perhaps (peak 1).

This near-infrared combination band of sorbed water has been studied for a series of nonionic hydrophilic polymers, including poly(methyl methacrylate) and photopolymerized hexamethylene dimethylacrylate and ethoxylated Bisphenol A dimethacrylate.[54] Equilibrium water sorptions for these polymers are all less than 2 wt %, and the near-infrared combination bands have peak maxima at 5243, 5243, and 5233 cm^{-1}, respectively. These are only somewhat higher than the peak centers of the sorbed water bands for the ionomers studied here, as seen in Table 1. By comparison, the peak centers for isolated water molecules, liquid water, and ice are at 5332, 5175, and 5040 cm^{-1}, respectively.[55] Thus the overall effect of the presence of ion exchange sites and counterions does not dramatically affect the overall hydrogen bond strength of sorbed water in these polymers. Even though the water to ion exchange site ratio and the overall water contents of the polymers increase substantially in the insulator to conductor regions, the spectral properties of sorbed water only undergo relatively minor shifts. It is in this region that ion pairs dissociate, ions become fully hydrated, and water–water interactions become more significant. These

Table 3. Ionic Diffusion Coefficients for P(S-*co*-MAA) Membranes

medium	mol % ionic comonomer	$D \times 10^6$, cm^2 s^{-1}			D ratios		
		Na^+	Cs^+	Cl^-	Na^+/Cs^+	Na^+/Cl^-	Cs^+/Cl^-
water		13.3	20.6	20.3	0.65	0.66	1.02
P(S-*co*-MAA)	23.0	0.365	1.03	1.79	0.35	0.20	0.58
	27.7	1.29	3.20	3.35	0.40	0.38	0.96

all have only minor effects on the combination band, which always remains significantly higher in frequency than pure water with its extended hydrogen-bonded structure.

Finally, the self-diffusion coefficients of sodium ion, cesium ion, and the co-ion chloride ion are reported for two ion contents of P(S-*co*-MAA) in Table 3. This polymer was chosen for the study of individual ionic diffusion coefficients because the SAXS results confirm that it is microphase separated. As noted above, the ion-clustered perfluorinated ionomers exhibit the property of "superselectivity", which means that the ratios of diffusion coefficients in the polymer are significantly altered from those in water. For example, the Na^+/Cs^+, Na^+/Cl^-, and Cs^+/Cl^- ratios for a 1200 EW Nafion membrane are 5.2, 2.0, and 0.38 compared to 0.65, 0.66, and 1.0 in water, while for a 1050 EW Nafion carboxylate the Na^+/Cl^- ratio is 7.0.[45] The corresponding values in Table 3 do not reflect this phenomenon; they likely differ from solution values only because of a small amount of ion pairing of the sodium ion. From these results we conclude that the phenomenon of superselectivity is induced not only by microphase separation but also by other factors in the morphologically complex perfluorinated ionomers.

Conclusions

The SAXS properties of P(MMA-*co*-MAA), P(S-*co*-MAA), and P(S-*co*-SSA) show that only the latter two polymers are ion aggregated in the dry state, which is in agreement with their respective mechanical properties. This aggregation disappears upon hydration for P(S-*co*-MAA), and with increasing ion content a new SAXS peak related to phase separation appears. At this point, about 17 mol % of ionic repeat units, the water to exchange site ratio increases, and the polymer undergoes a sharp insulator to ionic conductor transition with further increases in ion content. Thus we find excellent correlation among the SAXS, water sorption, and conductivity properties of this polymer. We previously found that P(MMA-*co*-MAA) also undergoes a sharp transition of the same type, and for each of these polymers the transition occurs at 15 vol % of conducting phase, which indicates that the conducting regions are randomly distributed throughout the polymer. The SAXS properties of P(MMA-*co*-MAA) show no phase separation in the wet state, so that these polymers behave percolatively ideal whether or not they are phase separated in the hydrated state. The ionic diffusional properties of P(S-*co*-MAA) show little sign of the superselective properties of the perfluorinated ionomers. We conclude that structural elements in addition to microphase separation are responsible for the unusual transport properties which are exhibited by the latter, percolatively nonideal, polymers. These in turn are likely to arise not just from phase separation but from subtle differences in the microenvironments of ions of different charge type and size.[49,56] Future research will focus on hydrocarbon carboxylate ionomers which have pendant side chains like the perfluorinated ionomers and also some polystyrene-based vinylpyridine containing anion exchange ionomers.

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