Morphological Studies of Lightly Sulfonated Polystyrene Using ^{23}Na NMR. 3. Effects of Humidification and Annealing

Ellen M. O'Connell, Thatcher W. Root, and Stuart L. Cooper*,†

Department of Chemical Engineering, University of Wisconsin—Madison, Madison, Wisconsin 53706

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ABSTRACT: ^{23}Na nuclear magnetic resonance (NMR) is used to observe the sodium cations in lightly sulfonated polystyrene ionomers (NaSPS). Ion distributions are influenced by humidification and thermal treatment. Fully dried NaSPS at 1.7% sulfonation showed two peaks, indicating isolated and aggregated sodium ions. Once humidified, a new peak appeared at 0 ppm. NaSPS showed a redistribution of ions on subsequent drying, with more ions residing in aggregates. Annealing ionomers at temperatures above the glass transition temperature of the polymer led to an increase in the number of isolated ions and a shift in the peak position of the aggregate peak. A reversible first-order rate expression describes the isolated ion variation with annealing treatment, with a heat of reaction of 6.3 kcal/mol. All sample processing was shown to be reversible to some extent; the distribution of ions could be varied widely using only sample processing.

Introduction

^{23}Na nuclear magnetic resonance (NMR) can be used to study the distribution of ions between aggregated sites and isolated sites in sodium-neutralized lightly sulfonated polystyrene. Previous studies in this laboratory[1] have shown that sodium ions in SPS are found in up to three environments: isolated ions (7 ppm), fully hydrated ions (0 ppm), and aggregated ions (−12 to −23 ppm). The peaks were identified through the use of reference compounds and quadrupolar coupling constant calculations. In the preceding paper,[2] we discussed the effects of solvent casting on the site distributions and local morphology. The largest extent of redistribution occurred for samples cast from more polar solvents, such as dimethylformamide and tetrahydrofuran/water mixtures. Casting from these solvents resulted in a larger fraction of the sodium ions residing in aggregates. Additionally, in an earlier study[1] it was shown that both the isolated and aggregated ions attracted water molecules, and all ions could be held in the fully hydrated state, $Na(H_2O)_4^+$. In this study we show that the effects of other processing variables on the local environment of the sodium ions can be as significant as the effects of composition. Specifically, the effects of humidification and thermal treatment are presented here.

Experimental Section

Polydisperse sodium-neutralized sulfonated polystyrene (NaSPS) ionomers were provided by Drs. Dennis G. Peiffer and Robert D. Lundberg of the Exxon Research and Engineering Co. The number-average molecular weight of the materials was 106 000 and M_w/M_n = 2.7. The synthesis of these materials has been described previously.[3] Samples are identified as NaSPS-*X*, where *X* is the percent of styrene groups that are sulfonated. Before beginning sample processing, polymer samples were dried under vacuum at room temperature for 2–7 days to remove residual water. Drying below the glass transition temperature (T_g) of the ionomer does not completely remove all water molecules from the aggregates;[4] however, drying above at much higher temperatures affects the microstructure[5] and local morphology of the ionomer. To prepare the humidified samples, the ionomers were suspended over beakers of deionized water held at 40, 60, or 80 °C, loosely covered, for 72 h. Solution-cast samples were prepared from ~0.1–2.5 wt % solutions, with the solvent evaporation over 24–72 h (depending on solvent) at 50 °C. Samples were then placed under vacuum at room temperature for complete drying. Heat-treated samples were dried under vacuum at 25 °C before being heated to 140, 160, or 180 °C. Some thermally treated samples showed slight discoloration; however, no evidence of significant degradation was noted. Sodium chloride, toluene, methanol, and tetrahydrofuran (THF) were obtained from Aldrich and used as received.

^{23}Na FTNMR spectra were acquired on a Chemagnetics CMC-300A spectrometer operating at 79.2 MHz. The secondary reference used was NaCl(s) with chemical shift δ = 7.1 ppm. All solid samples were run at room temperature in zirconia rotors using magic angle spinning (typically 5 kHz) and high-power proton decoupling. A single excitation pulse was used with a pulse width of 1.2 μs, corresponding to a 12.7° tip,[6,7] to achieve uniform excitation. A pulse delay of 10 s was necessary to obtain fully relaxed spectra. In general, the reproducibility of the fractions of isolated ions by ^{23}Na NMR was ~10%, but varied with signal-to-noise for each spectrum; for samples with very small fractions of isolated ions, the results in Figure 7 show the extent of the scatter.

Results and Discussion

Effect of Humidification and Drying. One goal of this study is to establish the role of water in ionomer processing and how it relates to the final distribution of ions in a sample. Previous studies have indicated that water remains trapped in the aggregates even after thorough drying.[4] Addition of water also affects the morphology of ionomers, as indicated by a shift of the SAXS scattering peak to smaller angles[8–11] or by the disappearance of the scattering peak.[10,11] The presence of water may also partially dissociate the ions,[12] weakening the ionic cross-links, resulting in decreased mechanical properties.[13] Hydration can also affect the local structure of the aggregates, as has been shown using extended X-ray absorption fine structure (EXAFS),[14] NMR,[15,16] and Fourier transform infrared spectroscopy (FTIR).[17–20]

To better understand the role of water in material processing, humidification experiments have been conducted. The ^{23}Na NMR spectrum of dry NaSPS at 1.7% sulfonation consists of two peaks, at 7 and −12 ppm (Figure 1a). The relaxation times of these two peaks

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* Author to whom correspondence should be addressed.

† Present address: College of Engineering, University of Delaware, Newark, DE 19716.

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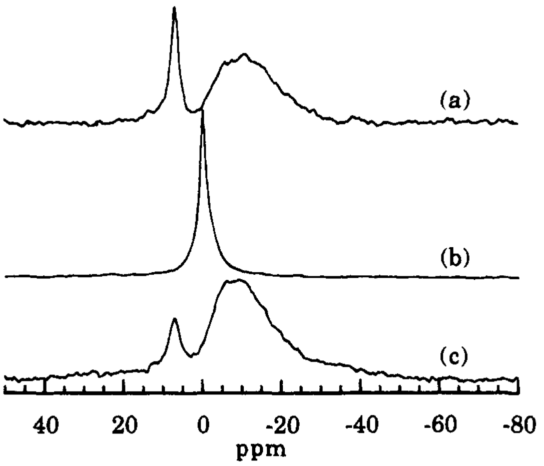

Figure 1. ^{23}Na NMR spectra of NaSPS at 1.7% sulfonation: (a) dried under vacuum at room temperature; (b) hydrated at 80 °C; (c) redried in air at room temperature.

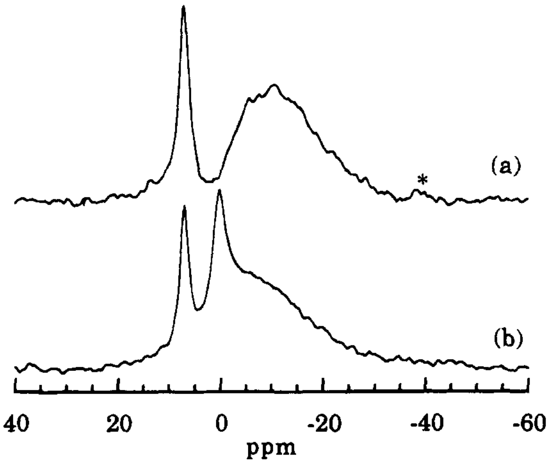

Figure 2. ^{23}Na NMR spectrum of NaSPS-1.7: (a) dried under vacuum; (b) equilibrated with humid room-temperature air. Spinning sidebands are denoted by asterisks.

are roughly 6 and <0.5 s, respectively. Thus, any exchange between these two sites must occur no faster than 1 every 6 s. The same sample subsequently humidified at 80 °C produced a single hydrated NMR peak at 0 ppm,[1] as seen in Figure 1b. Following this, the humidified sample was redried at room temperature in air, producing again isolated and aggregated Na^+ environments (Figure 1c), but with a different distribution among the sites. This redistribution is due to exchange between the isolated and aggregated sodium ions during humidification. With the humidification, all sodium ions are converted to the fully hydrated form, $Na(H_2O)_4^+$. This indicates that all sodium ions, even those bound in aggregates, are available for hydration. A comparison of dry NaSPS-1.7 with a sample equilibrated with humid room-temperature air (Figure 2) shows that the aggregate peak shifts downfield when the ionomer is partially hydrated. This is likely due to swelling of the aggregates by water. Such swelling would decrease the strength of the quadrupolar interaction, both from the increased site symmetry for $Na(H_2O)_4^+$ and because of the increased distance between Na^+ nuclei.

Figure 3 shows NaSPS-1.7 after humidification at three different temperatures: 40, 60, and 80 °C. As the temperature of humidification increases, the fraction of isolated ions decreases until it becomes negligible. At lower temperatures (40 °C), hydration is not complete and the peak due to isolated ions, while decreased in magnitude, is still present. Additionally, the peak corresponding to aggregated ions (initially at −12 ppm) has broadened to include the hydrated ions (the intensity at 0 ppm). Comparison of this spectrum, which is of a sample humidified at 40 °C for 72 h, with that in Figure 2, which is of a sample equilibrated in humid air at room temperature for an extended period of time, indicates that hydration is a slow process and, in the case of the 40 °C sample, is only partially complete after 72 h. The peak indicating isolated ions decreases more quickly than the aggregate peak; unhydrated aggregated sodium ions are still apparent in the 60 °C spectrum (as seen in the inset) but the peak indicating isolated ions has vanished. At this temperature all isolated ions are hydrated, but some small number of the aggregated ions are still unaffected by the humidity. This is particularly interesting since at 60 °C the amount of water present in the sample (calculated from weight loss after drying) corresponds to ~14% of the original sample mass. This mass is more than 10 times the amount of water needed for the stoichiometric level of $Na^+:H_2O = 1:4$. Even with an excess of water, complete hydration of all aggregated ions only occurs above 60 °C. Comparing the widths of the samples humidified at 60 °C and at 80 °C, it is apparent from the broader peak at 80 °C that more exchange between isolated and aggregated sodium ions is occurring in the sample humidified at the higher temperature.

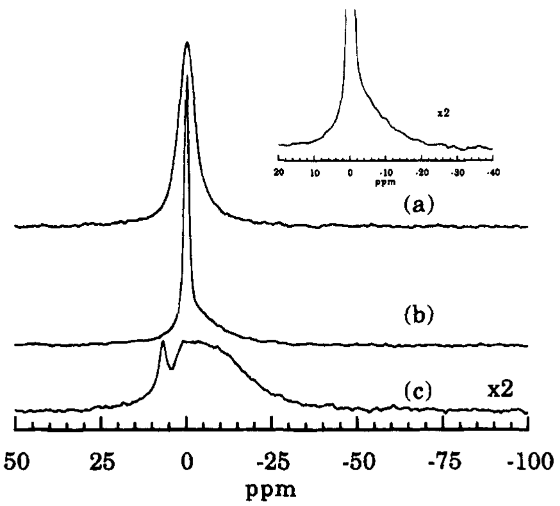

Figure 3. ^{23}Na NMR spectra of NaSPS-1.7 after humidification at three temperatures: (a) 80, (b) 60, and (c) 40 °C. The inset shows (b) on an expanded scale.

Detailed examination of the hydration/dehydration transient provides further insight into changes in NaSPS with humidification. Figure 4 shows the NaSPS sample humidified at 40 °C for the first few hours of the NMR experiment, which is conducted by spinning the sample in dry air. The fraction of isolated sodium ions increases during the first 3 h of the experiment, after which the value is stable. The increase in the number of isolated ions is probably due to drying of the sample by exposure to the air used during sample spinning (MAS). This transient provides insight into the transport of water out of the ionomer. The growth of the isolated ion peak is due to a decrease in the humidified ions, which are held in the broadened, higher-field peak. This fraction of hydrated isolated ions loses waters of hydration readily, and over a fairly short period of time. Thus the isolated ions are both hydrated and dehydrated more readily than ions in

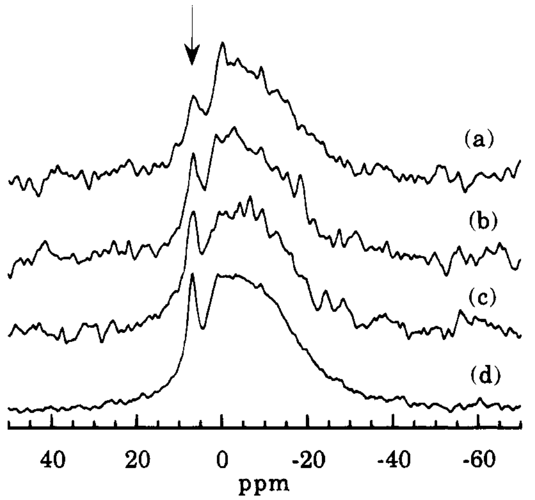

Figure 4. ^{23}Na NMR spectra of the first few hours of the NMR experiment on NaSPS-1.7 humidified at 40 °C: (a) first hour (400 scans); (b) second hour (400 scans); (c) third hour (400 scans); (d) final spectrum (8992 scans). The arrow points to the 7 ppm peak for isolated ions.

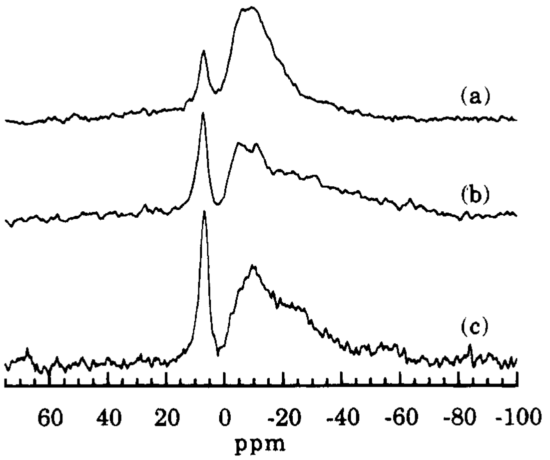

Figure 5. ^{23}Na NMR spectra of NaSPS-1.7 dried at room temperature immediately after humidification at (a) 80 °C (dried in air), (b) 60 °C (dried under vacuum), and (c) 40 °C (dried under vacuum). Each spectrum is scaled by its maximum intensity.

aggregates. The isolated ions appear to be very changeable and readily accessible.

Figure 5 shows the three NaSPS samples when dried at room temperature after humidification at the different temperatures used above. More sodium ions are aggregated in the final dried ionomer for samples humidified at the higher temperatures. At the lower humidification temperature (40 °C), at which hydration of the isolated ions was not complete, there is no noticeable change in the fraction of isolated ions in the final dried sample as compared to the untreated material. Humidification at this temperature apparently hydrates the ions in their environment, but no net transport of ions occurs. Therefore, this distribution of Na$^+$ locations is a reproducible but nonequilibrium state. Above this temperature, the local morphology is altered by humidification and subsequent drying. These results indicate that hydration and disruption of the aggregates is needed to permit global reorganization and to produce the observed aggregation of previously isolated sites. Ishioka[18] also noted reversibility with respect to water content in the FTIR spectra of the carboxylated ionomer ethylene methacrylate partially neutralized with zinc, but at 60 °C. The difference in the temperatures at which the changes are still reversible is probably due to a combination of changes in anion groups, counterions, and backbone polymers. In NaSPS, complete humidification (80 °C) allows for rearrangement of the ions in the polymer matrix. In turn, this rearrangement leads to an increase in the number of aggregated ions on drying. Since the local morphology of the final dried sample depends on the extent of hydration, the amount of physical cross-linking (or aggregation) can be controlled by the choice of humidification temperature.

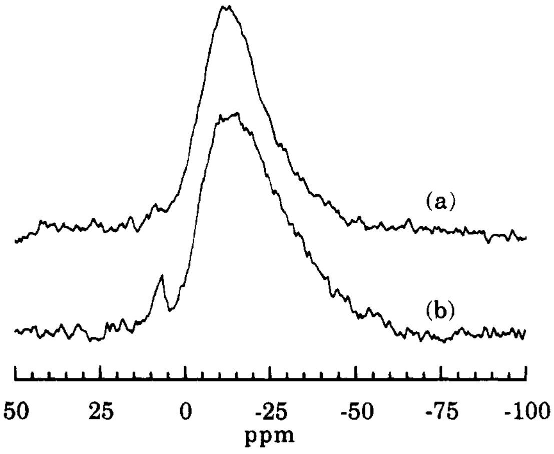

Figure 6. ^{23}Na NMR spectra of NaSPS-4.2 (a) before and (b) after annealing at 160 °C for 24 h.

Cooper *et al.* have presented SAXS results for humidified zinc-neutralized SPS[8] and ethylene methacrylate copolymers.[10] To account for changes such as a peak shift to lower q values on addition of water (where Bragg spacing $d = 2\pi/q$), they postulated that the fraction of aggregated ions might change when the sample is swelled; hydrated ionic species in the matrix would have increased mobility and tend to aggregate. In this study, we have shown that redistribution of the sodium ions is exactly what is occurring during hydration. Complete hydration of isolated ions and some hydration of preexisting aggregates is required to provide this increased mobility.

Effect of Annealing. Previous studies on the thermal treatment of ionomers have shown morphological changes with annealing.[4,5,21] These studies have indicated that the behavior of ionomers is a function of the neutralizing cation. For example, after treatment at temperatures above the matrix glass transition, SAXS patterns of NaSPS showed increased phase separation while SAXS curves of ZnSPS showed increases in phase mixing.[5]

In this study, the NaSPS samples have been subjected to thermal treatment to study more thoroughly the kinetics of formation and dissociation of the aggregates. Samples of NaSPS-4.2 were heated to 140, 160, and 180 °C and quenched to room temperature. NMR spectra of one sample before and after annealing at 160 °C for 24 h are shown in Figure 6. The heat treatment affects the aggregates, as is demonstrated through an upfield shift of the peak's center of gravity from ~ -17 to ~ -23 ppm. This shift indicates a change in the structure of the aggregate. Since the shift is to lower frequency, it is likely that some of the aggregates are becoming more well-ordered.[1] One reason for the improvement in order could be the loss of loosely held interfacial ions from the aggregate.

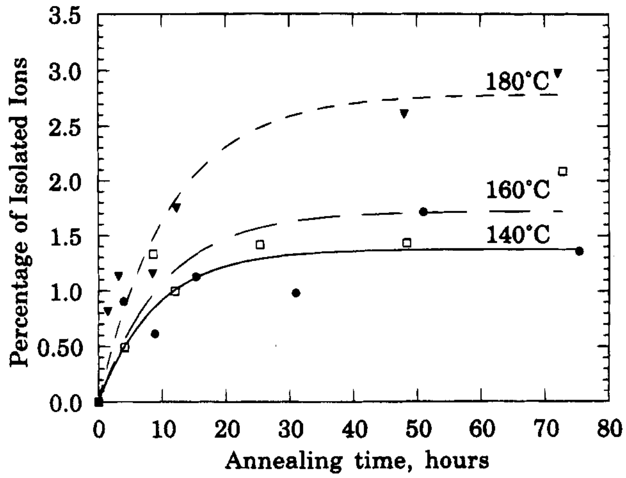

Figure 7. Fraction of total intensity of the NaSPS-4.2 peak from isolated ions as a function of annealing time for three temperatures: 180 °C (▼): 160 °C (□); 140 °C (●). Lines correspond to fitting the data to a first-order expression, as described in the text.

Table 1. Kinetic Parameters for the Association/ Dissociation of Na$^+$ in SPS

temp (°C)	$k_d \times 10^3$ (1/h)	k_a (1/h)	$K_{eq} \times 10^2$
140	1.51 ± 0.64	0.108 ± 0.054	1.4 ± 0.9
160	1.67 ± 0.49	0.095 ± 0.034	1.8 ± 0.8
180	1.91 ± 0.58	0.069 ± 0.027	2.8 ± 1.4

Accompanying the aggregate peak shift is an increase in the intensity of the 7 ppm peak, indicating some dissociation of aggregates and the formation of isolated R$-$(SO)$_3^-$/Na$^+$ ion pairs. This is a different result than was seen in electron spin resonance studies of MnSPS,[4] in which annealing caused increased aggregation, not dissociation. However, SPS ionomers neutralized with Mn^{2+} and Na$^+$ may have qualitatively different behavior as a consequence of the metal valence and the number of polymer-bound anions with which it interacts. Such qualitative differences have also been seen in the effects of solvent casting on these two materials.[2,22] Previous studies have shown differences in behavior between ionomers neutralized with mono- and divalent cations,[19,23-25] and one group of researchers suggested that the behavior could be due to differences in counterion packing within the aggregates.[26]

The fraction of isolated ions, which is a measure of the level of dissociation, can be tracked as a function of annealing time at the three temperatures. This variation in the fraction of isolated ions with annealing time is shown in Figure 7. The rate equation for dissociation of aggregated sodium ions (A) to isolated sodium ions (I), assuming a reversible process and a first-order rate expression, is

$$A \rightleftharpoons I$$

$$dI/dt = -k_a I + k_d A \qquad (1)$$

but $I_0 = 0$ and $I + A = A_0$. The resulting solution is

$$\frac{I(t)}{A_0} = \frac{k_d}{k_d + k_a}(1 - e^{-(k_d+k_a)t}) = \frac{K_{eq}}{1 + K_{eq}}(1 - e^{-k_a(1+K_{eq})t}) \qquad (2)$$

since $K_{eq} = k_d/k_a$. Fitting the data from the annealing experiments ($I(t)/A_0$ vs t) yields the values for K_{eq} and k_a for each of the three temperatures given in Table 1. The heat of reaction for dissociation can be determined from the temperature variation of the equilibrium constant using the Clausius–Clapeyron expression:

$$\ln(K_{eq}) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (3)$$

Since the range of temperatures is limited and there is substantial scatter in the data, the trends should be stressed more than the absolute numbers. The heat of reaction (ΔH) is determined to be +6.3 ± 1.4 kcal/mol, which is stronger than a hydrogen bond but weaker than a primary bond. The formation of isolated ions pairs is thus endothermic, as expected. The entropy change is determined to be +6.7 ± 3.2 cal/mol-K. The Arrhenius activation energies in the forward and reverse directions are $E_{a,d} = 2.2 \pm 0.2$ and $E_{a,a} = -3.9 \pm 1.2$ kcal/mol, respectively. These values are substantially lower than those reported by Hird and Eisenberg (40–54 kcal/mol), who determined activation energies for NaSPS from dynamic storage modulus data at varying frequencies.[27] However, this discrepancy is due to differences in the processes being monitored by each technique. In the mechanical tests, the activation energy for large-scale motion of the polymer chains would be directly measured, and this is certainly expected to be larger than that measured by ^{23}Na NMR, which looks directly at only individual sodium ions.

It is apparent from the data in Figure 7 and Table 1 that the equilibrium constant, K_{eq}, increases with temperature, which is consistent with the endothermic reaction in eq 1. Although there is substantial scatter in the data in Figure 7, it appears that k_a decreases with increasing temperature. This behavior would indicate a negative apparent $E_{a,a}$. Negative activation energies are rare, and this value probably signifies the presence of a multistep process instead of simple association/ dissociation, including such factors as energy of the polymer chains, exclusion of water from the aggregate, or differences in the energy requirements for removing sodium ions from the edge of an aggregate and the energy requirements for removing ions from the center of an aggregate. Higher order reactions do not describe the trends in the data as well as the first-order reaction, nor do they lead to a positive value of $E_{a,a}$.

One possibility for the complexity in the reassociation step involves temperature-dependent levels of water in the aggregates. As was discussed above, the presence of water can affect the local structure,[14,18-20,28] morphology,[8,10,11,29] and physical properties[13] of a sample. Drying NaSPS-4.2 at 25 °C does not lead to any isolated ions, based on NMR results, but probably does not lead to complete drying of the ionomer, either. Heating the sample to a higher temperature, above the glass transition temperature of the ionomer (~120 °C), leads to the presence of a small fraction (~1–4%) of isolated ionic groups. The ionomer matrix has become more mobile at higher temperatures, and allows more ion transport than it did at temperatures below T_g. Therefore, since chain rearrangement occurs at the high temperatures required for complete drying, separating the effects of water removal and chain motion on the local morphology of the cations is not possible.

The fraction of isolated ions created by thermal treatment is small and is unlikely to affect the mechanical properties of these ionomers. However, small changes in the distribution of ions may complicate investigations of the local and larger scale morphology of the ionomer even for the materials with higher sulfonation levels, where most ions are in aggregates.

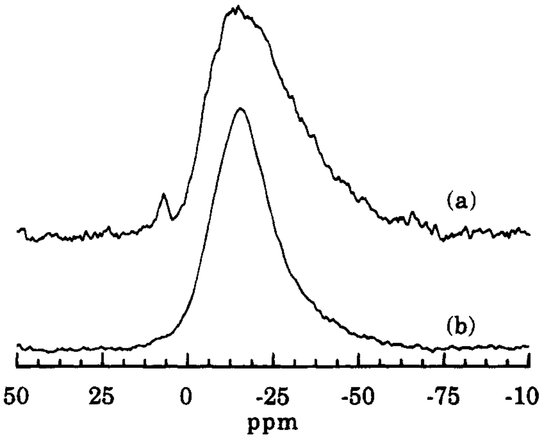

Figure 8. ^{23}Na NMR spectra of NaSPS-4.2: (a) annealed at 160 °C for 24 h; (b) sample (a) cast from a 0.5 wt % solution of 90/10 THF/water.

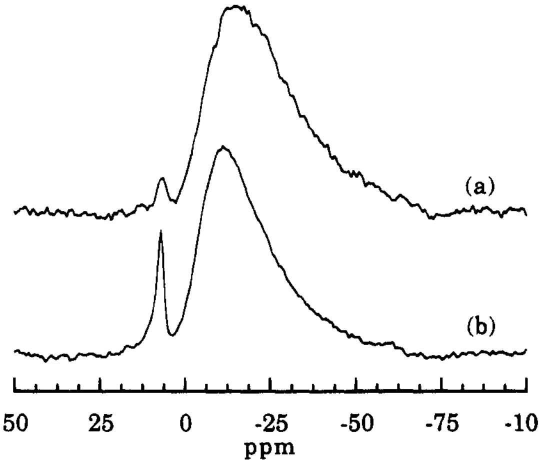

Figure 9. ^{23}Na NMR spectra of NaSPS-4.2: (a) annealed at 160 °C for 48 h; (b) sample (a) cast from a 0.5 wt % solution of 90/10 toluene/methanol.

Cations such as sodium have intrinsically low scattering contrast in SAXS. Therefore, small changes in the number of isolated ions could affect the electron density difference necessary for contrast in SAXS studies. Additionally, small changes could affect the average cation environment as seen in EXAFS studies of these materials, so consistency in sample preparation is of the utmost importance when using sensitive characterization techniques.

Reversibility of the Effects of Sample Processing. Solvent casting, humidification, and thermal treatment have been shown to affect the local morphology of an ionomer through changes in the distribution of sodium ions in different morphological sites and through changes in the aggregate peak shape and position. Our studies have also shown that none of these changes are permanent; original ion distributions can be restored to some extent.

Two of the NaSPS-4.2 samples annealed to high temperature were cast from solution, one from toluene/methanol and one from THF/water, to determine if casting would return the samples to their original morphologies. The results are shown in Figures 8 and 9. In Figure 8, it is apparent that casting an annealed sample from a 90/10 mixture of THF/water at 0.5 wt % completely removes the isolated ions that were created from thermal treatment. Additionally, the aggregate peak is narrowed compared to the thermally treated sample; the center of gravity shifted downfield ~5 ppm followed solvent casting. Comparison of the cast sample with the bulk NaSPS-4.2 (Figure 6a) shows that this treatment returns the aggregated peak to its original position. So, the effects of thermal treatment on the isolated ions can be removed with this solvent. Interestingly, a similar sample cast from a 1 wt % solution of 95/5 THF/water showed narrowing of the aggregate peak but the peak due to isolated ions remained intact. In Figure 9, the annealed sample cast from 90/10 toluene/methanol at 0.5 wt % showed a dramatic increase in the fraction of isolated ions. The aggregate peak also shows less intensity in its low-ppm tail, similar to the result in Figure 8, and the center of gravity of the peak is shifted downfield about 5 ppm. NaSPS-1.7 samples cast from toluene/methanol have also shown an increase in the number of isolated ions; in the preceding paper, the effects of solvent processing on NaSPS-1.7 were presented.[2] For cosolvents in which the polar solvent is the higher boiling component (such as THF/water mixtures), the resulting cast sample contains a larger fraction of aggregated ions. For cosolvents in which the nonpolar component is the higher boiling solvent (such as toluene/methanol mixtures), the polar component evaporates sooner, and the remaining nonpolar solvent prohibits aggregation of "stranded" ions during drying and therefore produces more isolated ions. Figures 8 and 9 show this behavior for annealed NaSPS-4.2. The presence of isolated ions in the sample before casting is an important factor; the original, unannealed NaSPS-4.2 sample contains no isolated ions, and the corresponding sample cast from toluene/methanol also contains no isolated ions.[2]

The effects of sample preparation on the structure of ionomers in toluene solutions has been discussed by Vanhoorne *et al.*[30] The researchers obtained SAXS patterns of barium sulfonato polystyrene ionomers in toluene; the samples were either concentrated from the synthesis solution or isolated from the synthesis solution by distillation of the solvent, dried at 160 °C under vacuum, and dissolved in toluene. The latter sample displayed a more homogeneous solution, i.e., a more narrow distribution of interaggregate spacing. Therefore, the ionomer structure formed in solution is related to the sample processing history.

Thermal treatment has been shown to increase the fraction of isolated ions in the case of NaSPS-4.2, and this treatment should also increase the fraction of isolated ions in a sample cast from a polar solvent, in which the fraction of isolated ions was decreased through the solvent casting procedure. Figure 10 shows NaSPS-2.65 in a series of sequential treatments: as received, cast from 95/5 THF/water, then annealed at 160 °C, and then recast from 95/5 THF/water. The fraction of isolated ions for each step in the processing is given in Table 2. The cast sample shows the expected decrease in the fraction of isolated ions as compared to the original, bulk sample. Following heating, this sample shows a dramatic increase in the fraction of isolated ions, which is much greater than the increase caused by heating the uncast NaSPS-4.2 sample (Figure 6). When the 2.65% sulfonation sample was recast, the fraction of isolated ions again decreased, although not to the amount present in the original sample or after the first casting.

If the ionomer chains in THF/water solution were fully separated and randomly located in solution, then the spectra in Figures 10b and 10d would be equivalent, since the bulk morphology prior to dissolution would be

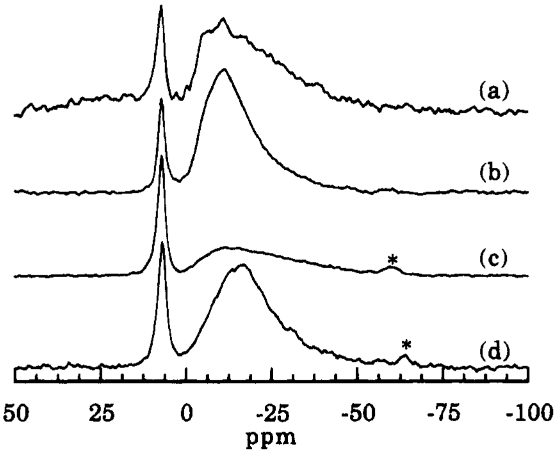

Figure 10. ^{23}Na NMR spectra of NaSPS-2.65: (a) dried under vacuum; (b) cast from a 0.5 wt % solution of 95/5 THF/water; (c) sample (b) annealed at 160 °C for 24 h; (d) sample (c) recast from THF/water. Spinning sidebands are denoted by asterisks. Each spectrum is scaled by its maximum intensity.

Table 2. Fraction of Isolated Ions in Processed Samples of NaSPS-2.65

sample processing	% isolated ions
as received	16
cast from 95/5 THF/water at 0.5 wt %	13
cast, then annealed at 160 °C for 24 h	47
cast, annealed, then cast from 95/5 THF/water at 0.5 wt %	20

inconsequential. However, this is not the case for NaSPS-2.65, and this result leads to the possibility that the chains have a certain degree of order in solution. Ise *et al.*[31-34] have studied ordering in polyelectrolyte solutions using small-angle X-ray scattering (SAXS). These authors propose that the SAXS peak seen for a wide range of polyelectrolyte concentrations (1−16 wt %) is due to interparticle interference. THF/water solutions of ionomers at low concentrations show polyelectrolyte behavior in viscosity experiments.[35] A type of ordering similar to that seen in polyelectrolytes would impose a type of "memory" on the ionomer and could account for the differences in the spectra shown in Figures 10b and 10d.

Both humidification and thermal treatment can allow for variation in the extent of ion aggregation in a given ionomer sample. Subsequent treatments can alter the ionomer local structure to yet another morphology. The effects of these treatments on the local morphology of NaSPS can be restored to some degree. The deliberate manipulation of these treatments produced the large changes seen here, which can be as large as the changes caused by sulfonation level. Inadvertent changes can produce comparable variations in production materials or other experimental studies, and may be a cause of variable behavior in experimental results.

Conclusions

Sample processing (humidification, solvent casting, and thermal history) has a significant effect on the morphology of NaSPS. Humidification can affect the distributions of ions in a sample. At a high enough temperature, all ions are hydrated. All sites have equivalent symmetrical local environments, and it is not possible to determine from the spectra whether the environment outside the hydration sphere is hydrocarbon matrix (polymer chains) or ionic groups. When the temperature is high enough (60 or 80 °C), rearrangement of the polymer-bound ionic groups accompanies humidification. On subsequent drying, the fraction of ions in aggregates is higher than in the unmodified ionomer. Also, isolated ions are more readily hydrated and dehydrated at lower temperatures than are aggregated ions.

Annealing NaSPS at high temperatures leads to some dissociation of the aggregates, which can be seen through the formation of isolated ions. Additionally, the peak position of the aggregated ions shifts about 5 ppm upfield, indicating some restructuring in the aggregates. Measurements of the fraction of isolated ions at different temperatures and times followed a reversible first-order rate expression and yielded a heat of reaction of 6.3 ± 1.4 kcal/mol.

The effects of thermal treatment were shown to be reversible to some degree in this system. Therefore, the local morphology of an ionomer can be tailored to the needs of a specific application. One ionomer can be used repeatedly; its morphology can be altered without variations in the chemistry of the system, allowing for less sample-to-sample variation in a study. Additionally, this preparation-dependent variation and its control are clearly important factors to understand in using ionomers exposed to varying environments.

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