Morphological Studies of Lightly Sulfonated Polystyrene Using ^{23}Na NMR: Effects of Polydispersity in Molecular Weight

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ABSTRACT: Ion content and molecular weight have been shown to affect the ^{23}Na NMR spectra of monodisperse sodium-neutralized sulfonated polystyrene ionomers (MNaSPS). A new NMR peak at −2.7 ppm appears at ionization levels above 1.2% and molecular weights of a least 35 000; this peak is not present in polydisperse NaSPS. The fraction of NMR intensity due to this peak is relatively constant above $M_n \sim 100\ 000$. It is proposed that this peak is due to a distorted version of an isolated site. Along with the new −2.7 ppm peak, the monodisperse materials also have far fewer isolated ions than the corresponding polydisperse ionomers. It is possible that the greater chain uniformity of the monodisperse ionomers eliminates plasticization of the aggregates by the low molecular weight components and steric hindrances from the high molecular weight components and permits more complete aggregation of the ionic groups. The new NMR peak can be removed by casting from a cosolvent of THF/water, but not by casting from THF/methanol. Blending of two or more monodisperse materials in solution followed by annealing resulted in an NMR spectrum similar to that of a polydisperse material; however, the behavior of the blend without annealing did not replicate that of polydisperse NaSPS.

Introduction

Ionomers are polymers that contain a small mole fraction of ionic groups incorporated into the polymer backbone. Ionomers have been studied frequently due to their enhanced physical properties, such as modulus, impact strength, and melt viscosity, compared to those of the un-ionized parent polymer. The enhanced physical properties as compared to those of the unmodified parent polymer are because of the phase separation of the ionic groups into ionic microdomains. These ionic domains, or aggregates, act as physical cross-links and reinforcing filler.

One of the most commonly studied ionomers is sulfonated polystyrene (SPS); the morphology[1−10] and physical properties[4,11−14] of this ionomer have been studied in detail. Many of the previous studies of SPS have been completed using polydisperse ionomers. However, more recently monodisperse SPS ionomers have been studied, particularly in the investigation of the solution behavior of these systems using viscometry, light scattering, and neutron scattering techniques.[15−21] A recent small-angle X-ray scattering (SAXS) study[22] has indicated differences in solid-state morphology between SPS samples of different polydispersities.

The viscoelastic[23−31] and tensile[32,33] behavior of linear, monodisperse polymers has been the subject of numerous studies. However, the behavior of polydisperse materials is less well understood. Many researchers have chosen to study blends of two or more well-characterized monodisperse materials to understand the effects of polydispersity.[24,28,34−37] In many cases, the relaxation behavior was simply the superposition of the viscoelastic behavior of the two monodisperse materials. Jackson and Winter[34] have reviewed a number of models used for predicting the behavior of bidisperse blends and used a generalized linear blending rule to describe data on polystyrene blends.

Polydispersity has been shown to affect shear moduli (G', G''),[24,26,38,39] stress relaxation moduli,[28] compliance,[24,36,40] dielectric spectra,[41] melt viscosity,[24−27,30,33,37] tensile properties,[32,33,38] and self-diffusion.[42,43] Researchers have also investigated the effects of molecular weight and dispersity of polymer chains between cross-links in network systems.[44−46] Above the critical entanglement molecular weight, narrow-distribution polystyrenes show two distinct relaxations in shear experiments, while polydisperse materials show only a broad distribution of relaxation times.[23,24] Materials with very broad molecular weight distributions exhibit non-Newtonian flow at lower shear rates than the corresponding narrow-distribution polymers.[27,30,39] In terms of bulk properties, the tensile strengths and elongations of monodisperse polystyrenes are higher than those of polydisperse materials at the same weight-average molecular weights (M_w); the reverse behavior is seen with respect to M_n.[32,33]

Influences of molecular weight in telechelic ionomers have also been studied.[47−49] Telechelic ionomers contain two ionic groups per chain, placed at either end of the polymer chain. The effects of changing molecular weight are more complicated in these systems because varying the molecular weight in a telechelic ionomer also changes the ion content. Additionally, different ion types will play varied roles in viscoelastic and mechanical behavior. Jérôme and Broze[47] studied telechelic Mg-neutralized polyisoprene ionomers and reported decreases in G' as the molecular weight increased from 7000 to 36 000, as would be expected since the ion content decreases in this range. However, as the molecular weight was increased further to 69 000, the values of G' increased. They attributed this behavior to an increased density of entanglements. Tant *et al.*[48] reported increases in the measured values of mechanical properties (stress−strain properties) and decreases in creep rates as molecular weight increased for Ba-

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neutralized polyisoprene telechelic ionomers. The authors concluded that, in this case, the effects of ionic groups are less significant than the effects of entanglements.

The effects of molecular weight on properties in random ionomer systems have received less attention than similar studies looking at the effects of ion content or ion type. However, investigations on the rheological[50,51] and dynamic mechanical properties[51] of ionomers have been reported. Erhardt *et al.*[50] reported the effects of molecular weight on the zero-shear viscosity of styrene/butyl methacrylate/potassium methacrylate terpolymers. An ionomer with M_w of 34 000 showed a greater dependence of viscosity on ion content than did a material with M_w of 145 000. The authors concluded that the ions are much less effective at increasing viscosity when polymer chains are already entangled; the entanglements control the viscous behavior of the material more than do the ionic groups. Kim *et al.*[51] reported changes with molecular weight in the high-temperature region of dynamic mechanical and rheological experiments of sodium-neutralized sulfonated polystyrene and poly(styrene−sodium methylacrylate). As molecular weight increased, the high-temperature loss peak (termed “ionic” or “cluster” glass transition) became more well developed and the onset of flow was delayed to higher temperatures. These changes were particularly noticeable for very low molecular weights (M_n = 21 000) and were much less dramatic in the sulfonated ionomer than in the carboxylated material.

A previous study in this laboratory[52] showed that sodium ions are found in up to three NMR environments in polydisperse NaSPS: isolated ions (7 ppm), fully hydrated ions (0 ppm), and aggregated ions (−12 to −23 ppm). The relative amounts of each type of sodium ion were found to be a function of sample composition, i.e., ionization and neutralization levels. Two subsequent studies[53,54] showed that the effects of processing on the local environments of the sodium ions are as significant as the effects of composition. Changes in local morphology were seen for materials cast from solvents of differing polarity, humidified at several temperatures, and annealed at temperatures above the glass transition temperature of the ionomer. The purpose of this study is to determine the differences in local morphology of ionomers of differing molecular weights and polydispersities.

Experimental Section

Monodisperse sodium-neutralized sulfonated polystyrene (MNaSPS) ionomers were synthesized as described in the literature.[55] Sulfonation of monodisperse polystyrene (M_w/M_n = 1.1) was carried out for 1 h at 50 °C in a strictly homogeneous solution containing 7 wt % polystyrene. Acid forms of the ionomers were neutralized with NaOH at 50 °C; the caustic solution was added slowly with vigorous stirring to ensure even distribution throughout the dilute solution. The ionomer was isolated via steam stripping, dried under air for 12 h, and dried under vacuum at 60 °C for 24 h. Sulfur content was determined through Dietert sulfur analysis. The sulfonation level reported here is based on this analysis. The molecular weights, sulfonation levels, and sample identification for the monodisperse SPS samples used in this study are shown in Table 1. Polydisperse sodium-neutralized sulfonated polystyrene ionomers (NaSPS) were synthesized similarly. The number-average molecular weight of the polydisperse materials was 106 000, and M_w/M_n = 2.7. Polydisperse materials are identified as NaSPS-*X*, where *X* is the mole percent of styrene groups that are sulfonated; NaSPS-2.7 is a sample having 2.7% of the total styrene groups sulfonated. Unless otherwise specified, all polymer samples and reference compounds were dried under vacuum at room temperature to remove residual water.[56] It is likely that drying below the glass transition temperature (T_g) of the ionomer dehydrates isolated ions[54] but does not completely remove all water molecules from the aggregates; however, it has been shown that more rigorous drying above T_g affects the local morphology[54] and microstructure[4] of the ionomer. Solutions were made with 95/5 tetrahydrofuran (THF)/water to a concentration of 0.5 wt % or, in the case of the ionomer blends, in 90/10 THF/methanol or 90/10 THF/water at ≤0.1 wt %. Solutions were blended dropwise and stirred for several hours following blending. The drying conditions, concentrations, and THF/water ratios used for the ionomers and blends were chosen on the basis of the results of previous studies.[53,54] NaSPS polyelectrolyte, PE-100 (M_n = 77 400, M_w/M_n = 1.10, ion content 4.7 mequiv/g) was obtained from Polysciences, Inc. Sodium chloride, THF, and methanol were obtained from Aldrich.

Table 1. Number-Average Molecular Weights and Ionization Levels for Monodisperse Sulfonated Polystyrene Materials

sample name	M_n	% sulfonation	number of entanglements/chain
M1-100	105 000	1.2	5.5
M2-100	105 000	2.7	5.5
M3-100	105 000	3.6	5.5
M5-100	105 000	5.1	5.5
M2-1.8m	1800 000	2.3	95
M3-900	900 000	3.2	47
M4-35	35 000	4.2	1.8
M6-9	9 000	5.9	0.5
PE-100	77 400	100	4.6

^{23}Na FTNMR spectra were acquired at 79.2 MHz on a Chemagnetics CMC-300A spectrometer. The frequency scale was set by using an external reference of NaCl(s), which has a chemical shift of δ = 7.1 relative to the standard NaCl(aq) solution. All solid samples were run in zirconia rotors using magic angle spinning (typically 5 kHz) and high-power proton decoupling. Dry air was used to spin the rotors, limiting the level of humidity during the course of the NMR experiment. The presence of residual water or solvent was evident in the NMR spectrum as a peak at roughly 0 or −1 ppm, respectively, which could be removed with further drying. To achieve uniform excitation, which permits quantitative analysis of the peak areas, the samples were run with a pulse width of 1.2 μs (corresponding to a 12.7° tip).[57,58] A pulse delay of 10 s was necessary to obtain fully relaxed spectra. Some spectra were obtained by using shorter pulse delays so that more scans could be acquired, and these spectra are labeled as such in the figure captions. The number of acquisitions needed when the pulse delay was 10 s ranged from 10 000 to 20 000 scans. In figures with multiple spectra, individual spectra have been scaled to conveniently show spectral detail, although the actual areas of fully relaxed spectra do scale with sodium content in each sample.

Results and Discussion

The sodium-neutralized sulfonated polystyrene materials studied previously were complicated systems. These were ionically cross-linked, polydisperse, entangled materials. It is possible to reduce the number of parameters by choosing monodisperse polymers above and below the molecular weight at which entanglements occur in polystyrene ($M_c \sim$ 31200−38000).[26] In this way, the effects of molecular weight and polydispersity on the fraction of sodium ions participating in cross-linking can be determined. The effect of polydispersity on the local environments of the sodium ions in sulfonated polystyrene (termed “local morphology” in this report) has not been studied previously. In fact, if SPS is a random ionomer with the ionic groups randomly spaced along the hydrocarbon chain, the initial expecta-

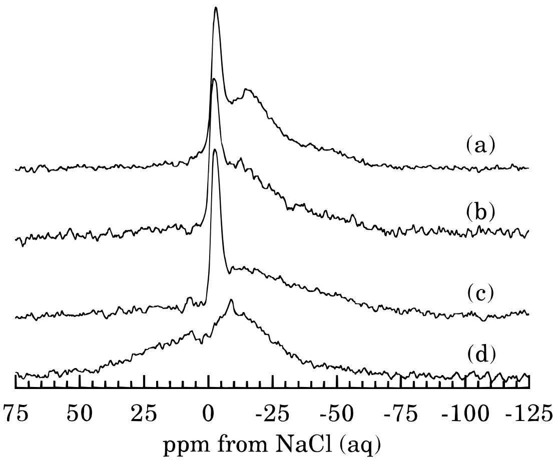

Figure 1. ^{23}Na NMR spectra of MNaSPS with M_n = 105 000. Ion contents are (a) 5.1%, (b) 3.6%, (c) 2.7% and (d) 1.2%. Part d was acquired with a pulse delay of 0.5 s so that more scans, and therefore a better signal-to-noise ratio, could be obtained.

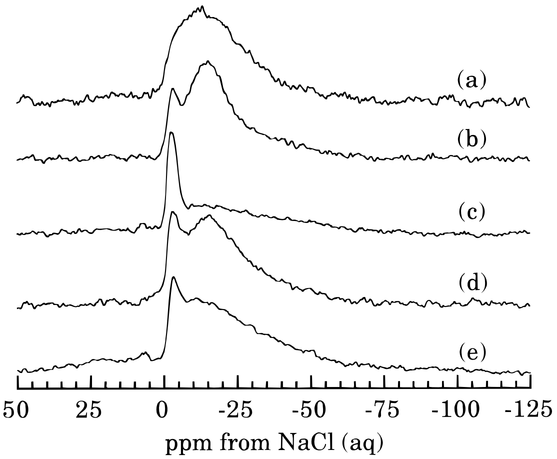

Figure 2. ^{23}Na NMR spectra of MNaSPS at five different ion contents and molecular weights: (a) M6-9, (b) M4-35, (c) M2-100, (d) M3-900, (e) M2-1.8m. Part e was aquired with a pulse delay of 1 s. A spectrum with a pulse delay of 10 s showed similar features.

tion would be that chain polydispersity should have very little effect on aggregate morphology. However, a previous SAXS study[22] showed differences in the breadth and position of the SAXS interference peak for samples of differing polydispersity. Since the SAXS peak is generally attributed to the presence of ionic domains, it appears that the domains are different in these two materials.

Effects of Molecular Weight and Ion Content in Monodisperse NaSPS. Figure 1 shows the NMR spectra of monodisperse NaSPS samples with $M_n \sim$ 105 000 and a range of ion contents. Each spectrum shows a distinct peak at −2.7 ppm. The fraction of the total intensity in this peak decreases slightly as ion content increases for materials of constant molecular weight. The broad peak due to aggregated ions becomes more distinguishable as ion content increases, probably signifying more order in the aggregates at higher ion contents. The 1.2% sulfonated sample does not show enough resolution to determine the fraction of intensity in any peak. However, it is interesting to note that only at this low ion content is a substantial amount of the NMR intensity present around 7 ppm, which is the chemical shift assigned to isolated sodium ions. At this ion content, many ions are too far apart to aggregate together and are left dispersed throughout the polystyrene matrix as isolated $Na^+SO_3^-$ ion pairs. The intensity at this chemical shift dramatically decreases as ion content increases, and isolated sites are barely observed at 2.7% ion content. In contrast, isolated ions persist past 3.0% ion content in polydisperse NaSPS.[52]

Figure 2 shows the spectra of the NaSPS samples with different molecular weights. The lowest molecular weight ionomer, M_n = 9000, shows no distinct −2.7 ppm peak at all. Additionally, the ionomer with M_n = 35 000 has less intensity in the narrow peak than the other ionomers studied. The fraction of intensity represented by the −2.7 ppm peak for all monodisperse samples is plotted as a function of ionization level and molecular weight in Figure 3. The peak appears only above the entanglement length of polystyrene, and it accounts for 15−18% of the overall sodium intensity of the sample for molecular weights above 35 000. Kim *et al.*[51] have shown that molecular weight effects in ionomers are less apparent above $M_n \sim$ 100 000, which is similar to the behavior reported here. Erhardt *et al.*[50] have suggested that the effects of chain entanglements and ionic groups on ionomer behavior are interrelated. Additionally, Tant *et al.*[48] have stated that, at high enough molecular weights, the effect of molecular weight (or more precisely, entanglements) on telechelic ionomers outweighs the effects of ionic interactions. Finally, Onogi *et al.* showed that properties of unsubstituted polystyrene become less sensitive to molecular weight above $M_n \sim$ 100 000.[23,32,36] In summary, the effects of molecular weight begin to outweigh the effects of ion contents at high enough M_n and plateau at $M_n \geq$ 100 000. These conclusions are consistent with the data presented here; it appears that once the molecular weight of the polymer is high enough for entanglements, the effect of ion content on the ^{23}Na NMR spectra is less significant. In this case, the presence or absence of entanglements causes changes in the environments in which the sodium ions reside. Much larger effects of ion content were seen for polydisperse NaSPS materials,[52] in which a portion of polymer chains are below the entanglement molecular weight.

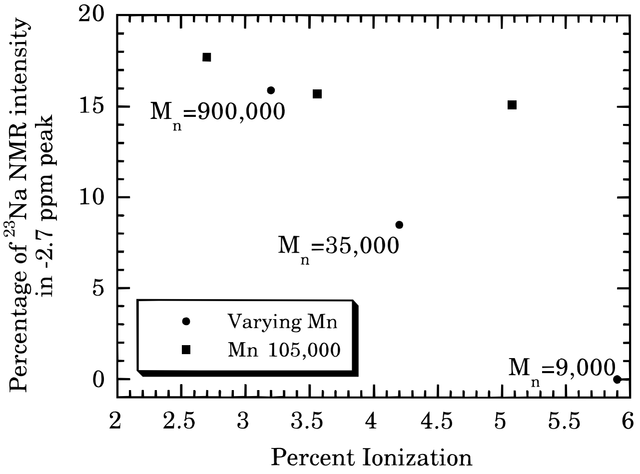

Figure 3. Fractions of NMR intensity due to the −2.7 ppm peak for several monodisperse sulfonated polystyrene ionomers.

Effects of Polydispersity in NaSPS. Molecular weight has been shown to affect ionomer properties,[50,51] particularly below the molecular weight needed for entanglements. Therefore, it is not unexpected that polydispersity would play a role as well. To determine the effects of polydispersity on the local environment

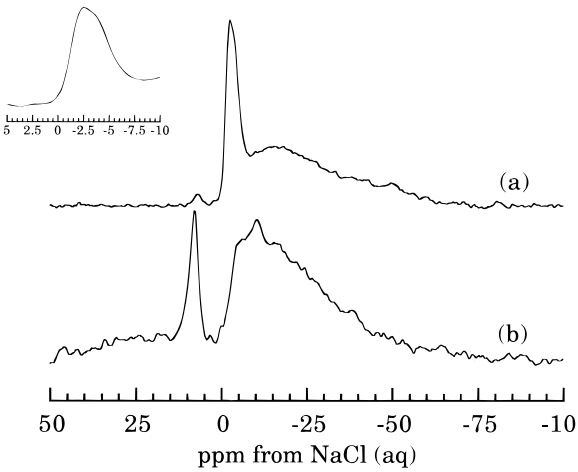

Figure 4. Comparison of (a) monodisperse and (b) polydisperse NaSPS at 2.7% ionization and $M_n \sim 105\,000$. The M2-100 spectrum used a pulse delay of 1 s; the increased number of scans improved the resolution. The inset is the −2.7 ppm peak in (a).

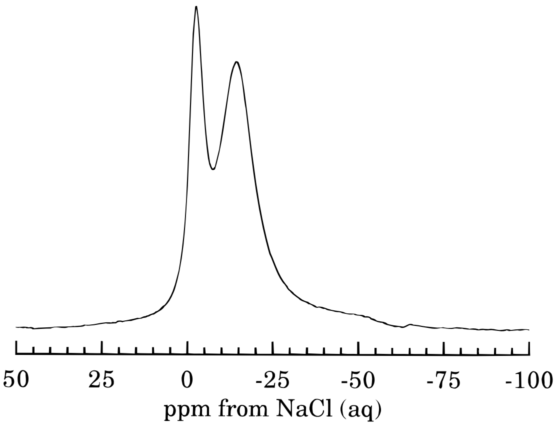

Figure 5. NMR spectrum of a sodium-neutralized sulfonated polystyrene polyelectrolyte ($M_n = 77\,400$).

of the sodium ions, ^{23}Na NMR studies of poly- and monodisperse polystyrene were undertaken.

^{23}Na NMR spectra of polydisperse NaSPS have been reported previously.[52−54] The NMR spectrum of monodisperse NaSPS at 2.7% ionization (M2-100) is shown in Figure 4 with the corresponding spectrum of polydisperse NaSPS ionized to 2.7% (NaSPS-2.7). The materials have similar values of M_n and have most of their sodium cations in aggregates, as seen from the broad peak near −15 ppm. The most noticeable difference between the two spectra is the presence of a relatively narrow (∼5−5.5 ppm wide) peak at −2.7 ppm only in the monodisperse sample. Also, the fraction of isolated ions, represented by the intensity at 7 ppm, is much lower in the monodisperse material.

The ^{23}Na NMR spectrum of a sulfonated polystyrene polyelectrolyte (PE-100) is shown in Figure 5. This polyelectrolyte is equivalent to a fully sulfonated monodisperse polystyrene sample. It is apparent from the spectrum that at complete ionization this additional NMR peak at −2.7 ppm persists. The fraction of sodium ions represented by this peak is ∼18%, which is at the upper end of the range shown in Figure 3.

The origin of this −2.7 ppm peak certainly is of interest. In principle, the peak could be due to differences in chemistry (initiators or contaminants) between the monodisperse and polydisperse ionomers or due to differences between the morphologies of the two materials. On the basis of a number of reasons, we believe that this peak has a morphological cause.

There are several possible explanations for the presence of the −2.7 ppm peak in the monodisperse sample. The first is the presence of excess neutralization agent, excess water, or an extraneous product. However, the sample is neutralized with NaOH, and in a previous study[52] we identified the peak for excess NaOH near 0 ppm. The ionomers are dried under vacuum, and in the previous study[52] the peak due to humidified sodium ions appeared at 0 ppm and did not appear in samples dried under vacuum. The asymmetry present in the −2.7 ppm peak (Figure 4, insert) is not apparent in the peak due to hydrated sodium ions. This −2.7 ppm peak was also seen for the commercial polyelectrolyte, which was synthesized in a manner different from our procedure. Additionally, as we will discuss shortly, the peak can be removed through solvent casting. Therefore, the peak is not due to excess NaOH, water, or an additional component.

The second possibility is that the differences in the polymerization of the two types of polystyrene affect the ionization reaction. The particular initiator in the monodisperse polystyrene might contribute to preferential sulfonation of the chain ends. If this were the case, however, the difference in the intensities of the −2.7 ppm peaks in the samples with $M_n = 105\,000$ and $M_n = 900\,000$ should be much greater than it is, since the former has 9 times as many chain ends per unit mass as the latter. Most likely, then, the peak is not due to chain ends.

The last possibility to consider is that the origin of the peak is due to morphological changes in material structure. This is the most likely for two reasons. The peak does not appear in materials below the entanglement length of polystyrene and is of lower intensity in materials near the entanglement length. Also, as is shown in the following, the peak is not removed through casting from THF/methanol, but can be removed by casting from a THF/water solution. Each of these factors indicates that this peak is due to morphological constraints, such as the steric hindrance of isolated ions, in the as-prepared monodisperse sulfonated polystyrene. This is considered further in the Discussion section.

Effects of Sample Preparation. The effects of solvent casting on the local morphology of polydisperse SPS ionomers have been studied in detail in this laboratory (Na^{+}-neutralized)[53] and by other researchers (Mn^{2+}-neutralized).[59] Casting of NaSPS samples from low concentrations of 90/10 or 95/5 THF/water mixtures resulted in dramatic decreases in the fraction of isolated ions present in the material. In these solvents and at these concentrations, the ionic groups are fully solvated[60] and the ionomers exhibit polyelectrolyte behavior, as indicated by a sharp increase in reduced viscosity at decreasing concentrations.[61] Slow evaporation of the solvent allows for rearrangement of the chains and the formation of a new morphology. Presumably, similar morphological changes will occur when MNaSPS is cast from similar solvent mixtures. Two ionomer systems, M1-100 and M2-100, were cast from 95/5 THF/water to determine the effects of the polar cosolvent on the morphology of these ionomers. The results are shown in Figures 6 and 7 for the 1.18% and 2.7% sulfonated ionomers, respectively. Additionally, the monodisperse ionomers are compared to the corresponding polydisperse ionomers prepared by similar casting procedures. It is apparent that solvent effects are substantial in

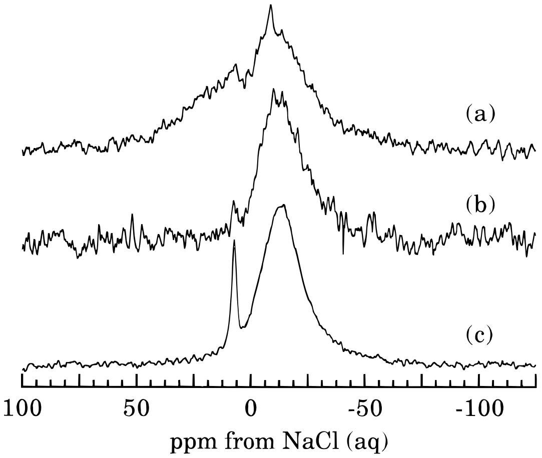

Figure 6. NMR spectra of (a) M1-100 as synthesized, (b) M1-100 after casting from 95/5 THF/water at 0.5 wt %, and (c) NaSPS-1.7 after casting from 0.5 wt % 90/10 THF/water.

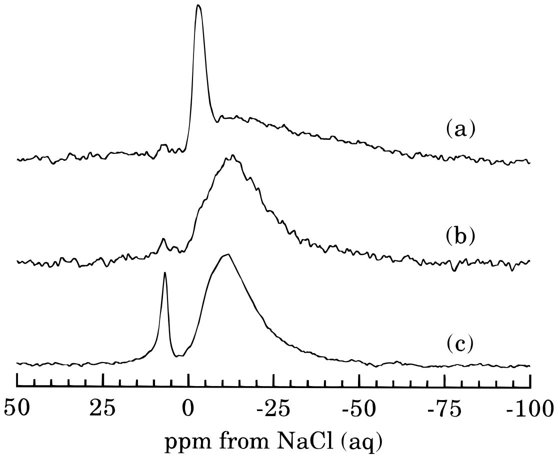

Figure 7. NMR spectra of (a) M2-100 as synthesized, (b) M2-100 after casting from 95/5 THF/water at 0.5 wt %, and (c) NaSPS-2.7 after casting from 0.5 wt % 90/10 THF/water.

these systems: the peak at −2.7 ppm is reduced to a shoulder in the case of M2-100, and the fraction of the signal near 7 ppm is reduced considerably for M1-100. Similar results were seen in an earlier study of solvent effects on polydisperse NaSPS,[53] in which casting from THF/water permitted local rearrangement of the sodium ions into aggregates. Therefore, the THF/water cosolvent appears to be an effective medium for permitting the local rearrangement of sodium ions in mono- and polydisperse NaSPS ionomers.

It is particularly interesting to note the differences between cast samples of the monodisperse and polydisperse NaSPS at equivalent ionization and molecular weight, NaSPS-2.7 and M2-100 (Figure 7). In parallel with the results for the uncast samples, the monodisperse ionomer has substantially fewer isolated ions than the polydisperse material, as shown by the intensities at 7 ppm. This indicates that the cast monodisperse samples have more sodium ions in aggregates, where they participate in cross-linking. Previous studies[53,54] have indicated that differences in ion distributions in NaSPS could be due to different sample histories. In this case, the different local morphologies seen here are not due to material processing since the preparations were equivalent.

Blends of Monodisperse NaSPS. The monodisperse ionomers were mixed to determine whether blending would remove the −2.7 ppm peak and create

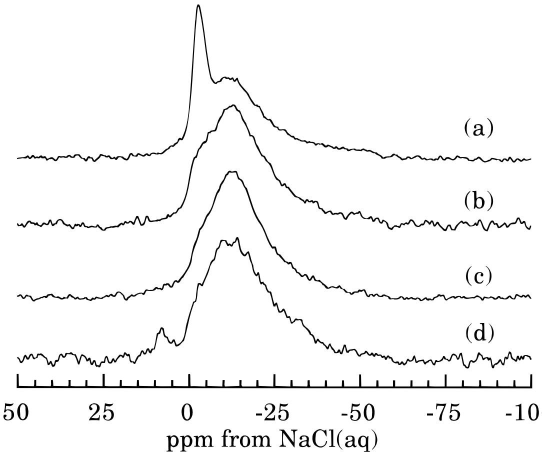

Figure 8. NMR spectra of the following: (a) 1/1 blend of M4-35 and M3-900 blended in THF/methanol solutions and cast; (b) sample (a) redissolved in THF/water and cast; (c) 2/1/1 blend of M1-100/M3-900/M4-35 cast from THF/water; (d) sample (c) annealed at 155 °C for 24 h.

a spectrum more similar to that seen for the polydisperse ionomers, i.e., containing more isolated ions. Figure 8a,b shows the result when the ionomers M3-900 and M4-35 were blended in a 1/1 ratio using THF/methanol and THF/water solutions, respectively. The result from the first cosolvent is essentially the sum of the spectra of the individual components, while the result from the THF/water solution shows dramatic changes. Apparently, the THF/methanol solution is not an effective solvent in terms of allowing complete mixing of the components. Similar results were shown in an earlier study on polydisperse NaSPS,[53] in which THF/methanol cosolvents did not permit extensive redistribution of the sodium ions in and out of aggregates. Methanol solvates the sodium ions less completely than does water,[62] so that the aggregates are not fully dissociated in the solution.

The lack of intensity around 7 ppm for the blend could be due to the high sulfonation level, which is close to the point at which all ions become aggregated in NaSPS.[52] Figure 8c shows a blend with three monodisperse ionomers, in which the ratio of M1-100/M3-900/M4-35 is 2/1/1, compared with the previous two-component blend. There is no increase in intensity around 7 ppm. It is likely that the concentrations in solution used in the blends are too low to permit the presence of isolated ions;[53] however, low concentrations were needed to fully separate the ionomer chains and to ensure complete blending.

The three-component blend was then annealed at 155 °C for 24 h, a treatment that has been shown to create isolated ions in the polydisperse samples.[54] The results of this treatment are shown in Figure 8d. The fraction of isolated ions has indeed increased, as evidenced by the increase in intensity of the 7 ppm peak. However, this treatment noticeably discolored the blend of monodisperse ionomers and to a higher degree than was observed for the polydisperse materials. These ionomers made from monodisperse polystyrene are more sensitive to annealing for long periods of time, perhaps because of the particular initiator used. Nevertheless, the similar behavior of monodisperse and polydisperse ionomers when subjected to both solvent casting and heat treatment shows that they are indeed chemically similar and that the new Na^+ environment (−2.7 ppm peak) present in the monodisperse ionomers has a morphological cause related to different chain responses to sample processing for the monodisperse material. A possible cause is discussed in the following section.

Discussion. The precise identification of the −2.7 ppm peak is not possible at this time. However, some observations on the characteristics of this new NMR peak are in order. The peak is narrow relative to those of the aggregated ions, but not compared to those of the isolated ions.[52] By using the method of Kundla *et al.*,[63] an upper limit on the quadrupolar coupling constant (QCC) can be determined. The maximum QCC is ~900 kHz, which is significantly greater than the value reported for isolated ions (~160 kHz), but still substantially less than the value observed for aggregated ions (1.6 MHz).[52] Additionally, while relatively narrow, the peak is not Lorentzian. As shown in the inset to Figure 4, there are several inflection points along the peak, indicating that this line is a heavily broadened quadrupolar powder pattern. Also, the spin−lattice relaxation time (T_1) of the −2.7 ppm peak (2.3 s) is between the T_1's of the isolated (~6 s) and aggregated (<0.5 s) ions. The position of the peak is intermediate as well, and since the second-order quadrupole shift is at most 3.3 ppm,[64] the main factor determining this peak position is the chemical shielding.

From the preceding considerations, it could be postulated that the environment represented by this peak is a distorted version of the isolated site, with the sodium ion becoming more shielded, causing an upfield shift. One possibility would be an isolated ion close to an aggregate or another isolated ion, but sterically hindered from being incorporated into an aggregate. This would show increased shielding from the higher electron density of another ion pair or aggregate nearby, compared to the shift observed for Na^+ isolated in a pure hydrocarbon environment.

The two phenomena, the −2.7 ppm peak and the lower fraction of isolated ions in cast MNaSPS, are interesting because the sulfonate groups are located randomly on the polymer chain, so that the distance between ionic groups should not vary with chain length. However, it is also apparent that both phenomena are functions of chain length; in Figure 2 the −2.7 ppm peak in MNaSPS is not present for the ionomer of $M_n = 9000$, and this peak is only beginning to appear for the ionomer near the critical molecular weight for entanglements of polystyrene ($M_n \sim 35\,000$). Additionally, casting from the relatively polar cosolvent THF/water can remove the peak almost completely with only a shoulder of intensity remaining, and annealing of a blend of several monodisperse components allows this peak to entirely disappear.

These NMR results indicate that polydispersity affects the distribution of ions in sulfonated polystyrene, so that more isolated ions are present in polydisperse NaSPS. Williams *et al.*[65] have compared SAXS patterns of monodisperse Mg-neutralized telechelic polyisoprenes and polydisperse Mg-neutralized telechelic polybutadienes. They reported higher levels of electron density fluctuation in the polydisperse samples, which they attributed to a larger number of isolated ionic groups dissolved in the matrix of the polydisperse material. This is consistent with the results reported here.

It is likely that, at constant ion content, entanglements or molecular weight plays a role in the ionomer local morphology, particularly in the fraction of isolated ions seen in mono- and polydisperse materials. Table 1 shows the number of entanglements per chain (assuming an entanglement molecular weight $M_e = M_c/2 \sim 18\,000$) for each material. In M4-35, all chains should have approximately 2 entanglements and 14 ion groups. In contrast, for polydisperse NaSPS-2.7, a polymer chain in the high molecular weight tail might have an $M \sim 900\,000$ and therefore would have about 47 entanglements. The large number of entanglements may prevent some of the ionic groups from aggregating into domains.

In addition to the effects of high molecular weight fractions, the lower molecular weight chains may also play a role in the appearance of isolated ions in polydisperse NaSPS. Plante *et al.*[66] studied the effects of low molecular weight ionic oligomers (MW = 800) on the morphology and dynamic mechanical properties of carboxylated polystyrene (CPS) neutralized with either Cs or Ba. Addition of about 10 wt % of the Cs-neutralized oligomer to CsCPS caused the aggregate peak in the SAXS pattern to disappear; the peak reappeared at lower scattering angles (higher Bragg spacings) at higher oligomer content. Similar behavior was seen for BaCPS; the SAXS peak gradually shifted to lower scattering angles as the amount of oligomer increased. The authors suggested that the slight decrease in intensity of the SAXS peak with increasing oligomer content could be due to the destabilization of aggregates, leading to dispersion of some ionic groups into the matrix as oligomer content increases. It appears that the addition of low molecular weight oligomers can alter the morphology of the aggregate. In a SAXS study comparing NaSPS of narrow and broad molecular weight distributions,[22] the SAXS peak of the narrow molecular weight sample is centered around 37 Å, while the SAXS peak of the polydisperse NaSPS is at 42 Å, indicating a shift to lower scattering angle as dispersity increases. If in polydisperse NaSPS the lower molecular weight chains disrupt some of the aggregates, more isolated (unaggregated) ions would be expected. This is consistent with the NMR results.

The monodisperse (and polydisperse) materials are precipitated from the dichloroethane sulfonation medium into boiling water. It is likely that entangled chains prevent the arrangement into a more preferred morphology on such a short time scale. Dissolution in THF/water at these low concentrations allows the aggregates to be fully dissociated[53,60,61] and separates the entangled chains. Slow evaporation of the solvents permits rearrangement of the chains and ionic groups into a new, more preferred morphology. This local morphology primarily consists of aggregates. The greater chain uniformity of the monodisperse ionomers limits the plasticization of the aggregates by any low molecular weight components and permits more complete aggregation. In general, it appears that ionic aggregation in NaSPS is affected by ion concentration, molecular weight, and polydispersity, among other factors. Various sample treatments such as solution casting and annealing affect the ionic group and polymer chain mobility during processing, which in turn affects the extent of aggregation achieved.

Conclusions

Ion content and molecular weight affect the ^{23}Na NMR spectra of monodisperse sulfonated polystyrene ionomers. At low ion contents, the fraction of NMR intensity due to isolated sodium ions is larger than that at higher ionization levels, just as is seen in polydisperse NaSPS. Many ions are too far apart to aggregate together and are left dispersed throughout the polystyrene matrix. A new NMR peak at -2.7 ppm appears at ionization levels $\geq 2.3\%$ and molecular weights $\geq 35\,000$; this peak is not present in the spectra of polydisperse NaSPS, but is present in those of the fully sulfonated NaSPS polyelectrolyte. The effects of molecular weight on the NMR spectra are not noticeable below $M_\mathrm{n} \sim 100\,000$; below this point, the fraction of intensity in the -2.7 ppm peak is less than what is seen in materials with larger molecular weights. The peak at -2.7 ppm is identified as being due to morphological constraints, since its intensity is a function of molecular weight and sample preparation. Casting from 95/5 THF/water cosolvents removed the -2.7 ppm peak from the NMR spectrum. Differences were apparent in the ^{23}Na NMR spectra of mono- and polydisperse materials due to the effects of entanglements and molecular weight on ionic aggregation. Blending of two or more monodisperse materials did not replicate the NMR spectrum of a polydisperse material; however, the behavior of the blend with annealing paralleled that of polydisperse NaSPS.

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