# Morphological Studies of Lightly Sulfonated Polystyrene Using $^{23}$Na NMR. 2. Effects of Solution Casting

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ABSTRACT: $^{23}$Na nuclear magnetic resonance (NMR) is used to study the local environment of sodium cations in lightly sulfonated polystyrene ionomers (NaSPS). Solution casting is shown to have a significant effect on the local morphology of NaSPS. NaSPS with 1.7% styrenesulfonate groups cast from solutions of DMF or THF/water at low concentrations showed more aggregated ions than those samples cast from relatively nonpolar solvents such as THF and THF/methanol mixtures. No changes due to sample history were seen for more highly sulfonated samples (4.2% styrenesulfonate groups). The changes in morphology due to solution casting were shown to have some reversible character.

## Introduction

Ionomers are polymers that contain a small number of ionic repeat units. Incorporation of the ionic groups into the polymer leads to increases in physical properties, such as modulus, impact strength, melt viscosity, and tear resistance.[1] These increases in properties are due to the aggregation of the ion pairs into physical cross-links. One of the most commonly studied ionomers is the random copolymer of styrene and sulfonated styrene.[2] Among the advantages of using this ionomer for morphological studies are a lack of complexity from crystallinity or phase separation from the polystyrene backbone and the ability to vary the ionic content without changes to molecular weight or matrix composition. The morphology[3−8] and physical properties[6,9] of SPS have been studied, including the effects of water uptake,[3,10] casting solvent,[7,11] and thermal history.[6,8,12] Since the morphology and physical properties of ionomers are due to the presence and aggregation of the ion pairs, the local structure of the ions is the focus of this research.

Many solution studies have been done on SPS ionomers in solvents of varying polarity.[2,13−23] In these studies, polymer solutions in low-polarity solvents show association behavior while those in high-polarity solvents do not. Electron spin resonance (ESR) studies of manganese-neutralized SPS (MnSPS) at 2.25% sulfonation showed both isolated and associated $Mn^{2+}$ ions when the polymer was in a THF solution (primarily associated), but only isolated ions in a DMF solution.[13,14] Also, increasing the amount of methanol in a toluene/methanol solution of MnSPS, or adding water to a THF solution, increased the fraction of noninteracting (isolated) $Mn^{2+}$ ions.[13] The presence of isolated ions indicates that the polar solvent (DMF, water, or methanol) was able to solvate the cation, removing all associations with other $Mn^{2+}$ ions.

Although the ESR data indicate that DMF and the cosolvents toluene/methanol and THF/water are able to solvate cations, of the three only DMF and THF/water solutions show polyelectrolyte behavior for ionomers.[15,16] A THF/methanol solution has been shown to lack polyelectrolyte behavior as well.[17] The existence of polyelectrolyte behavior in the THF/water cosolvent also depends on the ratio of the solvents; polyelectrolyte behavior is seen when the volume fraction of water is greater than 3%.[15,17] The investigators proposed that solvation results in an equilibrium between dissociated and aggregated ions.[21−23] In this proposal, the equilibrium focuses solely on the interaction between the solvent and the ionic groups. The direction in which the equilibrium shifts will therefore depend on the strength of the solvent−ionic group interaction and the concentration of polar cosolvent. For example, Lantman *et al.*[18−20] have shown that dissolving NaSPS in DMF leads to dissociation of the sodium from the sulfonate group; in THF the $Na^+SO_3^-$ group remains primarily associated.

In this study we are interested in the ion distribution in the solid polymer film following casting from solvents of differing polarity. Since the distribution of ions in solution is a function of the solvent polarity, it would be expected that the distribution in the resulting cast film would also be affected by the choice of solvent. Similar work was done by Weiss *et al.*,[7,11] who showed changes in the SAXS patterns of MnSPS at 7.6% sulfonation cast from solvents of increasing polarity. The intensity of the SAXS peak decreased as the polarity of the casting solvent increased, and the scattering peak completely disappeared in a sample cast from a 90/10 THF/water cosolvent. In all samples, however, the ESR spectra indicated that all $Mn^{2+}$ ions were fully aggregated, even in the absence of the SAXS peak.

Previous $^{23}$Na nuclear magnetic resonance (NMR) studies in this laboratory[24] 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 relative amounts of each type of sodium ion were found to be functions of sample composition, i.e., ionization and neutralization level. As the sulfonation level increased, the fraction of sodium ions held in isolated ion pairs decreased while the fraction of ionic species in aggregates increased. This coincided with a shift in the peak position of the aggregated sodium ions to lower (more negative) ppm values, indicative of increased quadrupolar interactions. As the neutralization level was increased at a constant sulfonate content, the aggregate peak shifted to higher ppm due to incorporation of the neutralizing agent, NaOH, into the aggregates. At very high neutralization

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levels (>180%), a separate NMR peak appeared due to phase-separated NaOH. Additionally, it was shown that both the isolated and aggregated ions were susceptible to water vapor, and all ions could be held in the fully hydrated state, $Na(H_2O)_4^+$. In this study we report that the effects of processing, particularly of solvent casting, are as significant as the effects of composition on the local environment of the sodium ions. In a comparison study,[25] we examine the effects of thermal processing on aggregate dissociation.

## Experimental Section

Polydisperse sodium-neutralized sulfonated polystyrene (NaSPS) samples were provided by Drs. Robert D. Lundberg and Dennis G. Peiffer of the Exxon Research and Engineering Co. The synthesis of these materials has been described elsewhere.[26] The number-average molecular weight of the materials was 106 000 and $M_w/M_n = 2.7$. Samples are identified as NaSPS-*X*, where *X* is the percent of styrene groups that are sulfonated; NaSPS-1.7 is a sample having 1.7% of the available styrene groups sulfonated. Samples studied as received from Exxon, without any additional processing, are identified as the "original, uncast" samples, or "bulk" samples. Unless otherwise specified, all 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;[27] however, more rigorous drying above the $T_g$ affects the microstructure[6] and local morphology[25] of the ionomer. The cast samples were dissolved to form ~0.1−2.5 wt % solutions and the solvent was allowed to evaporate slowly. The presence of residual solvent (e.g., tetrahydrofuran) was apparent in the NMR spectrum as a sharp peak at roughly −1 ppm, which could be removed by drying. Sodium chloride, toluene, methanol, dimethylformamide (DMF), and tetrahydrofuran (THF) were obtained from Aldrich and used as received.

Small-angle X-ray scattering (SAXS) samples were either compression molded for 4 min at 190 °C and 9000 psi or were cast from a 2.5 wt % solution onto a liquid gallium surface. SAXS patterns were acquired using a Kratky camera with Cu Kα X-rays from an Elliot GX-21 rotating-anode generator with a nickel filter; data were collected using a Braun OED-50M linear position detector. The data were corrected for sample absorption of X-rays, parasitic scattering, detector sensitivity, and detector linearity. Low count rates were used so no correction for dead time was necessary. Sample intensities were converted to an absolute scale using a Lupolen standard; cholesterol myristate was used to determine the sample-to-detector distance. The data were desmeared using the method of Lake,[28] and background scattering was accounted for using the Bonart method.[29] The data are presented as $I/I_eV$ versus the scattering vector $q$, where $I$ is the scattered intensity, $I_e$ is the scattered intensity of a single electron, $V$ is the scattering volume, and $q = 4\pi \sin \theta/\lambda$ ($2\theta$ is the scattering angle; $\lambda$ is the wavelength of the X-rays, 1.54 Å).

$^{23}$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 $\delta = 7.1$ ppm. All solid samples were run at room temperature in zirconia rotors using magic angle spinning (typically 5 kHz) and high-power proton decoupling. To achieve uniform excitation, the samples were run with a pulse width of 1.2 $\mu$s (corresponding to a 12.7° tip).[30,31] A pulse delay of 10 s was necessary to obtain fully relaxed spectra. The relative uncertainty in the peak areas is ±15%.

## Results and Discussion

**Effect of Solvent Casting.** The concentration of polymer in the casting solution affects the fraction of isolated ions found in the cast sample. Figure 1 shows samples cast from 90/10 THF/water solutions at 2.5, 1.0, 0.5, and 0.1 wt %. In all cast samples the final fraction of isolated ions is lower than in the original, uncast (bulk) sample. The two samples cast from higher concentration solutions have nearly the same fraction (~19%, compared to 30% in the original material), while the sample cast from the solution of lowest concentration shows far fewer isolated ions (Table 1). Lundberg and Phillips[17] have presented plots of reduced viscosity versus polymer concentrations for NaSPS-1.7 in THF/water solutions of varying ratios. Increases in reduced viscosity at low concentrations were seen for a 90/10 mixture of THF and water. The upward curvature began between 0.5 and 1 wt % solutions, which is the same point at which the significant decrease in the fraction of isolated ions is seen in Figure 1. A dependence of ionomer properties on sample history has been reported previously.[32] Solutions of NaSPS-1.7 isolated (freeze-dried) from dilute solutions of dioxane displayed lower melt viscosities and higher solubilities in xylene than solutions of NaSPS-1.7 isolated from more highly concentrated solutions. These freeze-dried samples are expected to retain the morphology of NaSPS in solution, while the solution-cast samples in this study do not.

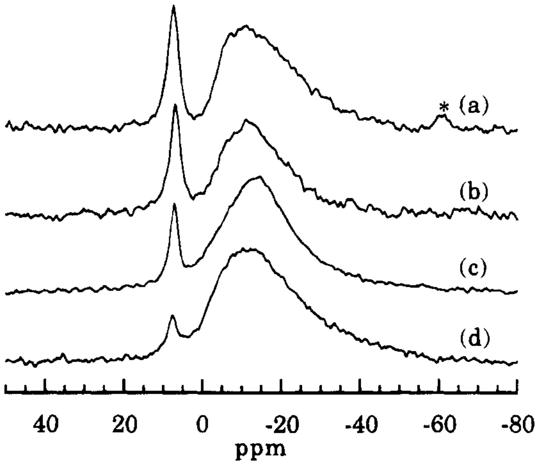

**Figure 1.** NMR spectra of NaSPS-1.7 cast from solutions of 90/10 THF/water at several polymer concentrations: (a) 2.5, (b) 1.0, (c) 0.5, and (d) 0.1 wt %. A spinning sideband is denoted by an asterisk.

**Table 1. THF/Water Influence on Isolated Na$^+$ on Films**

| 90/10 THF/water | | 1 wt % NaSPS in solution | |
|---|---|---|---|
| NaSPS concn (wt %) | % isolated ions | THF/water ratio | % isolated ions |
| 2.5 | 22 | 99/1 | 28 |
| 1.0 | 19 | 95/5 | 20 |
| 0.5 | 11 | 90/10 | 19 |
| 0.1 | 6 | | |

The effect of the ratio of polar to nonpolar components to the cosolvent was studied for the samples cast from THF/methanol and THF/water. Figure 2 shows NaSPS-1.7 cast from a 1 wt % solution of THF/water at different cosolvent ratios. The fraction of isolated ions decreases as the percentage of water in the solution increases (Table 1). The sample cast from 99/1 THF/water has approximately the same fraction of isolated ions as the original, uncast sample. Comparison of the fractions of isolated ions in a sample cast from a 95/5 cosolvent and in one cast from a 90/10 cosolvent shows them to be nearly identical. This is consistent with results from reduced viscosity studies.[15,17] A solution of 97/3 THF/water showed no polyelectrolyte behavior, but solutions of 95/5 and 90/10 THF/water showed the distinct increases in reduced viscosity at low concentrations. THF/methanol samples (95/5 and 90/10), which do not

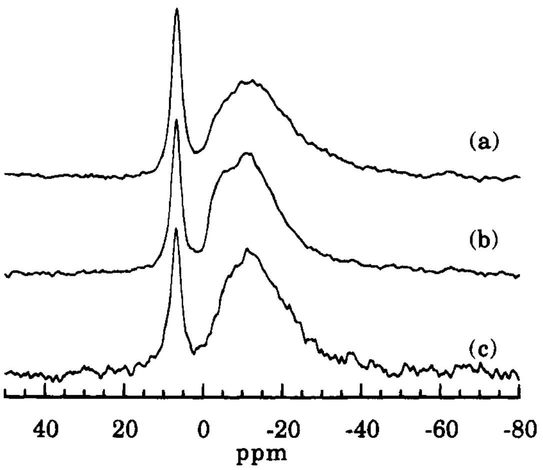

**Figure 2.** NMR spectra of NaSPS-1.7 cast from a 1.0 wt % solution of THF/water at several cosolvent ratios: (a) 99/1, (b) 95/5, and (c) 90/10.

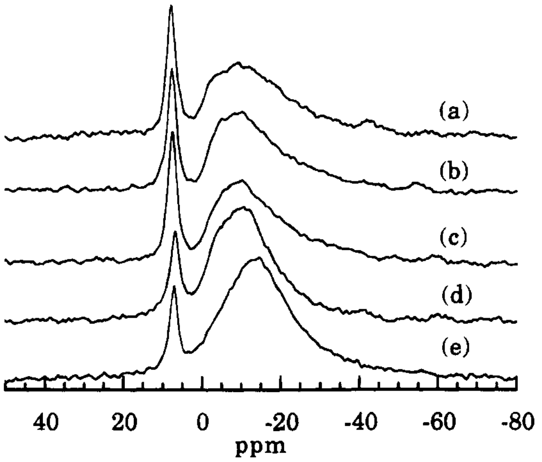

**Figure 3.** NMR spectra of NaSPS-1.7 cast from 0.5 wt % solutions of (a) 90/10 toluene/methanol, (b) THF, (c) 90/10 THF/methanol, (d) DMF, and (e) 90/10 THF/water.

**Table 2. Fractions of Na$^+$ Ions for NaSPS-1.7% Cast from Different Solvents**

| solvent[a] | eff dielec const[b] | isolated ions (7 ppm) | aggregated ions (−12 ppm) |
|---|---|---|---|
| no treatment | | 0.30 | 0.70 |
| 90% toluene/10% methanol | 5.4 | 0.36 | 0.64 |
| THF | 7.6 | 0.27 | 0.73 |
| 90% THF/10% methanol | 10.1 | 0.27 | 0.73 |
| 90% THF/10% water, 1 wt % | 14.7 | 0.19 | 0.81 |
| 90% THF/10% water | 14.7 | 0.11 | 0.89 |
| DMF | 36.7 | 0.11 | 0.89 |

[a] 0.5 wt % except as indicated. [b] For mixed solvents, this is estimated as the average of the dielectric constants of the pure solvents weighted by the volume fractions.

show polyelectrolyte behavior,[17] produced cast samples with NMR spectra that showed nearly identical amounts of isolated ions (30 and 27%, respectively). These quantities were nearly equivalent to the value for the original, uncast sample (30%).

Figure 3 shows NaSPS-1.7 cast from several different solvents: toluene/methanol, THF, THF/methanol, DMF, and THF/water. Table 2 contains the fractions of isolated and aggregated ions in these samples as well as the "average" dielectric constant of the solvents used. The value of the dielectric constant for the mixtures is only a guide; it is likely that specific interactions between the polar cosolvent and the ionic groups overwhelm the effect of overall solvent polarity.[17] The samples cast from THF and THF/methanol show few changes compared to the 30% isolated ions seen for the uncast sample, while NaSPS cast from toluene/methanol actually shows a slight increase in the fraction of isolated ions. The samples cast from the more polar solvents show substantially fewer ions in isolated sites. As the polarity of the casting solvent increases, the fraction of isolated ions in the cast material decreases by 2/3. The more polar solvents dissociate the aggregates and solvate the isolated ions. During the evaporation of the solvent or cosolvent, the chains are able to rearrange and form new aggregates. This results in a decrease in the fraction of isolated sodium ions. Additionally, in the sample cast from THF/water solution, the aggregate peak has shifted to higher frequency. This shift has been found to be smaller for samples cast from solutions of higher concentration (1 wt % or higher).

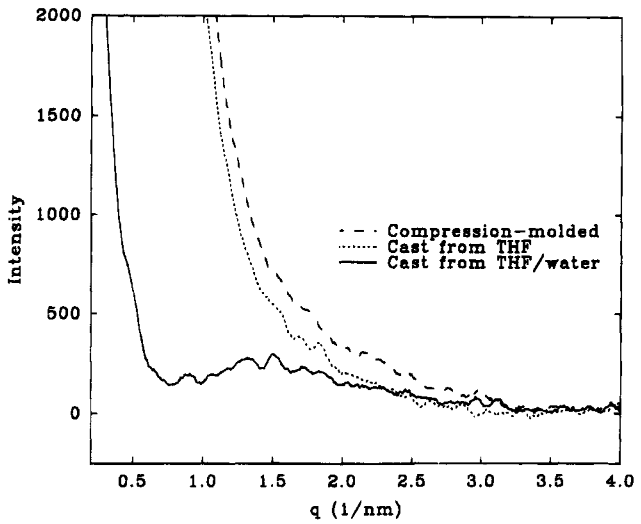

**Figure 4.** SAXS patterns for NaSPS-1.7 compression molded, cast from a 2.5 wt % solution of THF, and cast from a 2.5 wt % solution of 95/5 THF/water.

SAXS patterns for NaSPS-1.7 compression molded and cast from THF and THF/water are shown in Figure 4. At this sulfonation level it is difficult to obtain the electron density contrast necessary to see a scattering peak,[4] and no peak is seen for the compression-molded sample or the sample cast from THF, which, from our previous arguments, should have a morphology nearly identical to that of the bulk ionomer. There is scattered intensity over the $q$-range of interest, but the pattern decays smoothly with no evidence of an interference peak. The sample cast from THF/water, however, does show changes in the SAXS pattern, with some evidence of a scattering peak being formed in the range $q = 1-2$ nm$^{-1}$. It is possible that the change in the SAXS pattern is due to a change in electron density difference between the aggregates and the matrix, which in turn is due to the increased aggregation of the sodium ions upon casting from THF/water.

At higher sulfonation levels more complete aggregation is obtained, and solvent casting appears to have less of an effect on the local morphology. Figure 5 shows the NMR spectra of bulk NaSPS-4.2, cast from DMF, cast from a toluene/methanol solution, and cast from a 90/10 THF/water mixture. The resulting spectra show the same features for all samples. No isolated ions are created by casting, and there is no substantial shift in the aggregate peak. At this ion content, ion-pair

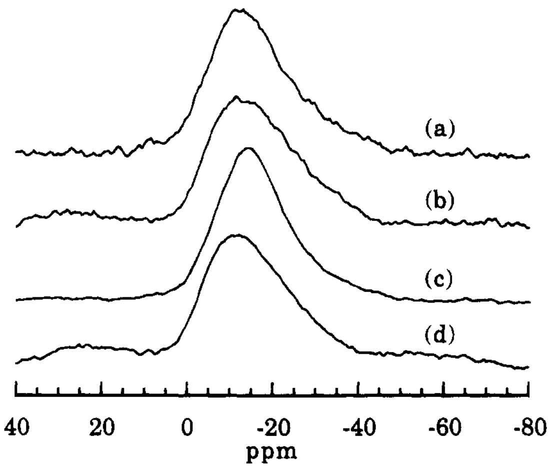

**Figure 5.** NMR spectra of NaSPS-4.2: (a) dried under vacuum, (b) cast from 90/10 toluene/methanol, (c) cast from DMF, and (d) cast from 90/10 THF/water.

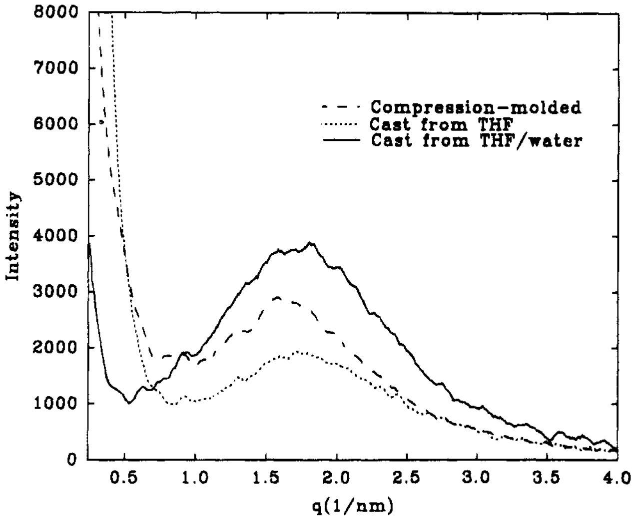

**Figure 6.** SAXS patterns for NaSPS-4.2 compression molded, cast from a 2.5 wt % solution of THF, and cast from a 2.5 wt % solution of 95/5 THF/water.

interactions are strong enough to ensure that all ions reside in aggregates regardless of solvent history. Therefore, in terms of the local morphology probed by NMR, there is no difference between casting NaSPS-4.2 from a nonpolar solvent and a polar solvent. Fitzgerald and Weiss[2] reported that NaSPS cast from several solvents retained the characteristic SAXS scattering peak, in contrast to their work on MnSPS. The SAXS patterns of NaSPS-4.2 compression molded and cast from THF and 95/5 THF/water solutions are shown in Figure 6. All samples show the characteristic interference peak.

The structure of the ionomer in solution is quite different in the solvents THF (relatively nonpolar) and DMF (polar). In THF, the ionomer mimics its bulk conformation, and most of the ions are associated.[18-20] When the THF is evaporated, the distribution of ions will remain mostly unchanged from the bulk. In DMF, the ions are fully solvated, the aggregates are dissociated, and the ionomer acts like a polyelectrolyte.[15,18-20] As the polar solvent is evaporated, the ions are driven into the polar environment of the aggregates.

In the THF/water cosolvent, the water solvates the cations and evaporates more slowly than THF, permitting the ions to reaggregate. Water also solvates $Na^+$ ions much more easily than methanol, which would lead to more mobility in the cations in THF/water solutions compared to THF/methanol solutions; Lundberg found that more than 10 wt % methanol was needed for 50% solvation of NaSPS-4.2 while only 0.6 wt % water in THF was required.[33] In the equilibrium of aggregated and dissociated species proposed by Lundberg[21,22] he states that only when the alcohol–ionic group association is stronger than the ionic group self-association will the addition of alcohol dissociate the aggregates. In this case, methanol in moderate amounts is not enough to dissociate the aggregates; however, the more strongly solvating cosolvent water is. Lundberg also reported more isolated sodium ions in THF/water solutions than in toluene/methanol solutions,[17] indicating that more ion pairs are fully dissociated when water is the cosolvent.

**Table 3. Boiling Points for Solvents Used in Mixed-Solvent Systems**

| solvent | bp (°C) |
|---|---|
| methanol | 65 |
| THF | 66 |
| water | 100 |
| toluene | 110 |

The rate of evaporation of the two solvents may also affect the final aggregation of the sodium ions. Table 3 shows the boiling points for the two polar and two nonpolar solvents. In mixtures of methanol and toluene the polar solvent evaporates much faster than the nonpolar solvent, and the solvated chains transport ions into the organic phase. In mixtures of THF and water, the polar solvent evaporates much slower than the nonpolar solvent and solvated ionic groups will be driven to aggregate. In the case where the boiling points of the cosolvents are nearly identical, such as in THF/methanol mixtures, in which the methanol weakly solvates the ionic groups, the final cast sample will show little change from the original ionomer.

The NaSPS samples that show the largest extent of redistribution are those cast from the more polar solvents. Ionomers solvated by these solvents show both isolated ions in ESR studies and polyelectrolyte behavior in viscometric and light scattering studies. Therefore, the ion pairs must be completely dissociated from any other ion pairs in order to permit local rearrangement of the pairs during solvent evaporation. When the polar solvent is the highest boiling component, NMR spectra of the cast samples show the lowest quantities of isolated ion pairs remaining in the solid state, so the polar cosolvent can cause tremendous changes in aggregation or distribution.

**Reversibility of the Effects of Solution Casting.** Sample processing can lead to changes in the distribution of sodium ions among different morphological sites in the ionomer and to changes in the aggregate peak position of the processed ionomer compared to the original sample. Our studies indicate that all changes are reversible to some degree.

The sample cast from 1 wt % 90/10 THF/water (Figure 2c) was recast from several solvents to determine if the changes in morphology were reversible. Casting from THF and THF/methanol did not substantially affect the local morphology of the ionomer; as was seen in the study on the original, uncast NaSPS, these solvents produce cast samples that mimic the bulk morphology of the ionomer before it is put into solution. However, the samples recast from toluene/methanol and DMF showed distinct changes (Figure 7). Casting from DMF decreased the fraction of isolated ions, similar to what was seen in Figure 3, but the fraction of isolated ions

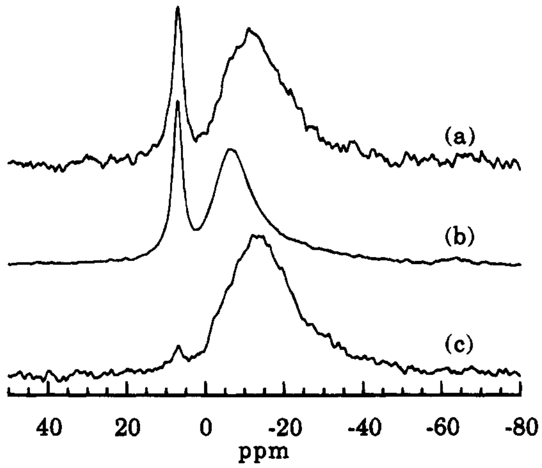

**Figure 7.** NMR spectra of NaSPS-1.7: (a) cast from a 1 wt % solution of 90/10 THF/water, (b) sample (a) recast from a 1 wt % solution of 90/10 toluene/methanol, and (c) sample (a) recast from a 1 wt % solution of DMF.

decreased to 3%. Casting from toluene/methanol increased the fraction of isolated ions to 29%, similar to the results seen in Figure 3, and also shifted the position of the aggregate peak. The peak is much more narrow than in the uncast sample, and its center of gravity is at a higher ppm value. It appears that the upfield shift in the aggregate peak caused by casting from THF/water can be reversed by this choice of solvent.

## Conclusions

Solution casting has a significant effect on the morphology of NaSPS at low sulfonation levels. The distribution of ions shifts for samples cast from relatively polar solvents (DMF, THF/water), in which the aggregates are dissociated and the isolated ions are solvated while in solution. Upon slow evaporation of the solvent the ions form new aggregates and substantially fewer isolated ions are present. Casting from relatively nonpolar solvents (THF, THF/methanol) did not drastically change the morphology of the original, uncast ionomer, although casting from toluene/methanol mixtures slightly increased the fraction of isolated ions.

The effects of solution casting on the local morphology of NaSPS appear to be reversible; the choice of casting solvent can allow for variation in the extent of ion aggregation in a given ionomer sample. These findings suggest that the local morphology of the ionomer at low sulfonation levels can be tailored to the desired specifications solely through sample processing. At higher sulfonation levels (4.2%), ion proximity is high enough that aggregation is seen for all processing conditions tested, and solvent character has no detectable effect on local morphology.

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