Morphological Studies of Lightly-Sulfonated Polystyrene Using ^{23}Na NMR. 1. Effects of Sample Composition

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

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

Received May 23, 1994; Revised Manuscript Received July 13, 1994[®]

ABSTRACT: ^{23}Na nuclear magnetic resonance (NMR) is used to observe the sodium cations in sulfonated polystyrene ionomers (NaSPS). Three NMR peaks are detected, corresponding to isolated ion pairs, aggregated ions, and hydrated ions. Peak intensities vary with sample composition and treatment and provide insight into the effects of these variables on the morphology of the ionomer. Ion distributions are systematically influenced by hydration treatment, sulfonation level, and neutralization level. Fully dried NaSPS at low ion content shows isolated and aggregated sodium ions. Once humidified, the single peak at 0 ppm characteristic of fully hydrated sodium ions indicates that all sodium ions in NaSPS are available for hydration. As the sulfonation level increases, the fraction of sodium ions held in isolated ion pairs decreases while the fraction of ionic species in aggregates increases. This coincides with a shift in the peak position of the aggregated sodium ions to lower frequency, indicative of increased quadrupolar interactions. Finally, as the neutralization level increases at a constant 3.4% sulfonate content, the aggregate peak shifts to higher frequency due to incorporation of the neutralizing agent, NaOH, into the aggregates. At very high neutralization levels, a separate NMR peak characteristic of phase-separated NaOH appears.

Introduction

Ionomers are polymers that contain a small number of ionic repeat units (less than 10–15%) covalently bonded to the polymer backbone. These pendant groups aggregate into ionic domains that form thermally reversible cross-links.[1,2] The presence of these ionic cross-links has a strong influence on the physical properties and dominates the behavior of the polymer. Many ionomers, with different polymer backbones, ionic groups, or cations, have enhanced physical properties due to these cross-links. The improved physical properties include increases in melt viscosity, tear resistance, modulus, impact strength, oil resistance, and glass-transition temperature.[1] Small-angle X-ray studies (SAXS) have shown that the ion pairs aggregate into ion-rich domains that are microphase-separated from the ion-poor matrix.[3-5] This aggregation is due to the incompatibility of the ion pairs and the nonpolar hydrocarbon matrix. However, some of the ion groups remain outside these aggregates as isolated ion pairs. The most direct evidence for these isolated groups comes from electron spin resonance studies (ESR), which show hyperfine structure for polymers with isolated ions of copper(II) or manganese(II).[6,7] No direct evidence has been shown for isolated ions of monovalent cations such as sodium; however, anomalous SAXS (ASAXS) studies have suggested that a low-angle upturn in SAXS patterns of ionomers is due to an inhomogeneous distribution of isolated ions or ionic aggregates.[8,9]

Several nuclear magnetic resonance (NMR) probes have been used to study ionomers, including ^{19}F studies of perfluorosulfonate membranes[10,11] and numerous proton[12-15] and carbon[16,17] studies to determine the effects of ionization, complexation, and water content on the mobility of the ionomer chains. Direct NMR studies of the counterions such as solid-state ^{23}Na NMR have been relatively rare.[18-20] One preliminary study by Dickinson *et al.*[18] examined sodium in Surlyn and 5% sulfonated polystyrene (SPS). In both types of ionomers a broad peak was seen and attributed to the aggregated ions. After humidification or overneutralization, a second, sharper peak appeared downfield.

The ionomer chosen for these studies is sulfonated polystyrene, which has no crystallinity or phase separation in the homopolymer that would serve to complicate the interpretation of spectra. Additionally, the ionic content can be varied readily without changes to molecular weight or matrix composition. The morphology[4,5,8,21-23] and physical properties[21,24] of SPS have been studied in detail, including the effects of ion content,[5,21] water uptake,[4,25] and thermal history.[21,23,26] The strong base of macroscopic results invites studies that focus on the microscopic explanation for these materials' behavior.

Because ionic groups have such a strong effect on the physical properties of ionomers, the nature of the ionic cross-link was the focus of the present study. Among the many compositional and processing parameters that influence the physical properties of ionomers, we have begun with a study of the effects of the number of ionic groups and the percent of neutralization on the local environment of the sodium ion. As described below, ^{23}Na NMR can observe directly the sodium ions held in different environments. Thermal history, solvent treatment, and other sample preparation steps are also major influences on the ionomer microstructure and physical properties, and the effects of these variables will be described in a later communication.[27]

Experimental Section

Polydisperse sulfonated polystyrene (HSPS) and sodium-neutralized sulfonated polystyrene (NaSPS) were provided by Dr. Robert D. Lungberg of the Exxon Research and Engineering Corp. The synthesis of these materials has been described elsewhere.[28] The number average molecular weight of the materials was 106 000 and $M_w/M_n = 2.7$. Unless otherwise specified, all polymer samples and reference compounds were dried under vacuum at room temperature to remove residual water.[29] It is likely that drying below the glass transition temperature (T_g) of the ionomer does not completely remove all water molecules from the aggregates; however, more rigorous drying above T_g affects the local morphology[27] and microstructure[21] of the ionomer. The humidified sample was suspended

---

[*] To whom correspondence should be addressed.

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

[®] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

0024-9297/94/2227-5803$04.50/0

above a beaker of deionized water held at 80 °C, loosely covered, for 72 h. For the samples studied in the section Effect of Neutralization Level, the acid form of SPS (HSPS) was dissolved in a 95% THF/5% water solution, and NaOH(aq) was added dropwise. Sodium content is characterized by the ratio (NaOH/sulfonic acid sites) × 100%; this ratio is labeled percent neutralization even at values greater than 100%. For the highest neutralization levels, above 180%, the solution was cloudy (showing micellar characteristics) but homogeneous. The resulting neutralized ionomers were dried at 65 °C in air for 24 h and then under vacuum at room temperature for 48–168 h. These samples were not precipitated or steam-stripped to ensure that all NaOH remained in the polymer. All other SPS samples were received in the sodium form. Sodium chloride (NaCl), sodium hydroxide (NaOH), sodium nitrite ($NaNO_2$), sodium toluenesulfonate ($CH_3C_6H_4SO_3Na$), sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$), Acid Yellow 29, and Amberlyst-15 ion-exchange resin were obtained from Aldrich.

^{23}Na FTNMR spectra were acquired at 79.2 MHz on a Chemagnetics CMC-300A spectrometer. The frequency axis was set using an external reference of NaCl(s), which has chemical shift $\sigma = 7.1$ ppm 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. 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).[30,31] A pulse delay of 10 s was necessary to obtain fully-relaxed spectra. Supporting data were collected on a Bruker AM-500 spectrometer running at 132 MHz. The spinning speed for these runs was 2.8 kHz.

NMR Background

Nuclei with spin quantum number $I > {}^1/_2$ possess a quadrupole moment (eQ) in addition to a dipole moment. The quadrupole moment interacts with electric field gradients (eq) surrounding the nucleus. The quadrupolar interaction, which generally dominates the line shape and relaxation behavior of the nucleus, is sensitive to the nature of the atomic bonding. This interaction can also be influenced by the presence and structure of nearby molecules, as well as by the formation of complexes. The quadrupolar coupling constant (QCC) = e^2Qq/h,[32] which is a measure of the strength of the interaction, is strongly dependent on the symmetry of the surrounding charge distribution. The asymmetry parameter, η, describes the deviation from axial symmetry. It is defined using the second derivatives of the electric potential.[33,34] More information about quadrupolar nuclei can be found in many reference books and review articles.[34,35] Magic-angle spinning cannot completely remove the effects of the quadrupole interaction, but does reduce the line width substantially.[36,37]

Results and Discussion

Reference Compounds. Several reference compounds were examined to establish characteristic spectral line shapes for different ^{23}Na environments. Figure 1 shows the spectra of solid sodium chloride (a) and sodium nitrite (b). The sodium chloride spectrum is characterized by a Lorentzian line shape with no quadrupolar features present. The sodium nuclei in NaCl are held in symmetric octahedral sites, leading to a cancellation of the electric field gradient. In contrast, $NaNO_2$ has a crystal structure of lower symmetry and shows a distinct powder pattern that can be simulated using the method of Kundla *et al.*,[36] with QCC = 1.5 MHz and $\eta = 0.1$.

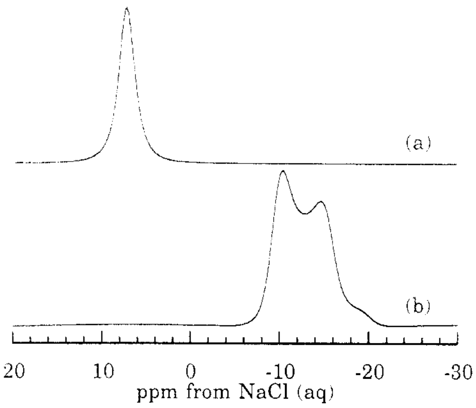

Figure 1. Solid-state ^{23}Na NMR spectra of (a) NaCl and (b) $NaNO_2$.

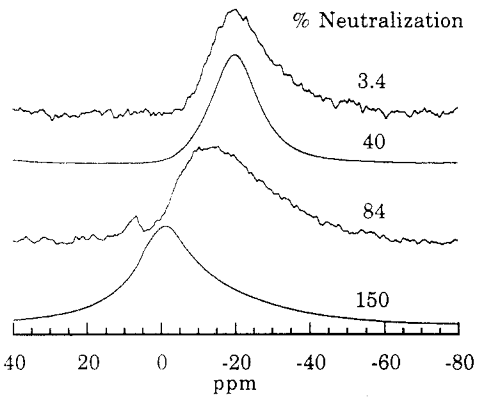

Figure 2. NMR spectra of Amberlyst-15 ion-exchange resin, exchanged with NaOH to 3.4%, 40%, 84%, and 150% neutralization levels.

Amberlyst-15 ion-exchange resin is polymeric and noncrystalline, and thus might be expected to behave similarly to NaSPS. However, it is a covalently cross-linked resin with a much higher sulfonation level than the SPS ionomers. It is expected that the mobility of the polymer chains in the resin would be greatly restricted as compared to NaSPS due to these cross-links. Figure 2 shows the spectra of sodium-neutralized Amberlyst-15. Initially obtained in the acid form, the neutralization level of this resin was varied from 3.4% to 150% of the available sulfonate groups. The spectrum of the 3.4% exchanged resin shows a broad, featureless peak centered around −24 ppm. This peak shifts downfield and broadens with neutralization level; the dramatic shift in the center of gravity seen in the 150% neutralized material is most likely due to excess sodium hydroxide present as amorphous NaOH-rich domains. The peak does not have the obvious quadrupolar features that can be seen in the $NaNO_2$ spectrum. This is probably caused by a combination of factors, the most significant being inhomogeneous broadening due to the distribution of sodium sites and near-neighbor interactions in the sample.

As the sodium content increases the peak breadth increases and the peak begins to shift downfield, particularly above 100% exchange. For a single sodium ion, second-moment calculations using the Van Vleck formula[38] show that the broadening of the sodium line is due to increasing numbers of sodium–sodium interactions. A single sodium ion surrounded by three oxygen atoms at 2.5 Å has a nonspinning width at half-height of 0.2 ppm, while a sodium ion surrounded by three oxygen atoms at 2.5 Å and a second sodium ion at 4 Å has a nonspinning width at half-height of 2.5 ppm—an order of magnitude increase. Also, the broadening due to quadrupolar interactions with like nuclei can be calculated using a modified version of the Van Vleck formula.[35,39] For a sodium–sodium distance of 4 Å this factor would add 2.3 or 2.2 ppm of peak broadening for nuclei in equivalent or inequivalent sites, respectively. The nearby sodium ions

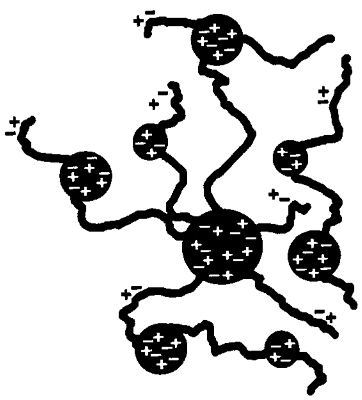

Figure 3. Schematic of the morphology of sodium-neutralized sulfonated polystyrene (NaSPS).

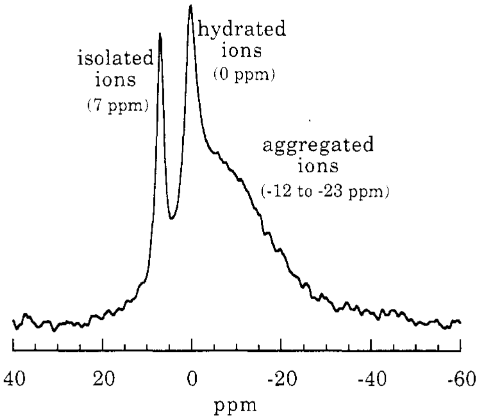

Figure 4. NMR spectrum of NaSPS at 1.7% sulfonation. The ionomer was exposed to the atmosphere before the experiment, and the spectrum is not fully relaxed.

and the presence of trace water of hydration would also increase the asymmetry of the environment surrounding the sodium ion, leading to a wider line. Finally, as was mentioned above, the distribution of sodium cations in the aggregate will cause additional, inhomogeneous broadening.

Peak Identification in NaSPS. Figure 3 shows a schematic diagram of the morphology of NaSPS. The black circles represent ion-rich domains termed aggregates. These aggregates may also contain hydrocarbon chains and trace amounts of water. The aggregates have a distribution of sizes (with an average diameter of 1–2 nm) and have been shown to be spherical in shape.[40] In addition to the aggregates, there are also some isolated ion pairs distributed throughout the hydrocarbon matrix which, in the case of a monovalent cation such as sodium, do not contribute to the cross-linking of the hydrocarbon chains.

Figure 4 shows the spectrum of NaSPS at a sulfonation level of 1.7%. The ionomer was allowed to equilibrate in air for an extended period of time. This spectrum contains three Na^+ species shown by sharp peaks at 0 and 7 ppm and a broad peak at −12 ppm. These are associated with three different sodium environments that have been identified through the use of reference compounds, QCC calculations, and experiments presented later in this paper. The three enviroments seen in this spectrum have been assigned to sodium–sulfonate ion pairs (i) fully hydrated at 0 ppm, (ii) isolated at 7 ppm, and (iii) aggregated at −12 to −23 ppm.

Hydrated Sodium Ions. The peak at 0 ppm is due to hydrated sodium ions. The sodium ion is in a symmetric tetrahedral environment when surrounded by water molecules as $Na(H_2O)_4^+$.[19,41,42] Hydrating the sample resulted in an increase in the intensity of the 0 ppm peak, and drying the sample under vacuum removed the peak completely. When the ion is hydrated, the electric field gradient at the nucleus is zero and the resulting line is narrowed. This peak position is the same as that for aqueous sodium ions.[42,43]

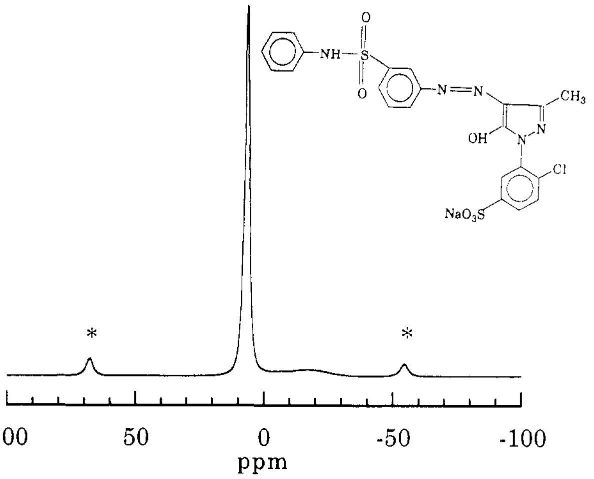

Figure 5. Structure and NMR spectrum of Acid Yellow 29. The peaks at +68 and −55 ppm are spinning sidebands.

Isolated Sodium Ions. The peak at 7 ppm has not been observed previously. We have assigned this peak to isolated sodium ions dispersed throughout the polymer matrix. A reference compound, Acid Yellow 29, supports this assignment. This dye is a large molecule that is only 4% sodium by weight and because of its bulky structure is expected to produce isolated Na^+ ions in the solid state. Acid Yellow 29 shows two peaks (Figure 5), one at 7 ppm and a broad peak of relatively low intensity (10% of the total area) at −20 ppm. The similarity of this spectrum with those of the ionomers is in the positions of the peaks themselves, and the intensities of the peaks in the dye are consistent with the expectation that most sodium ions are isolated in a predominantly hydrocarbon environment.

In the ionomers and Acid Yellow 29, the Na^+ in an isolated ion pair interacts with a single sulfonate group, but the geometry of the $R—SO_3^-$ group produces only a small residual electric field gradient at the sodium site, so the NMR line is narrow. An estimation of the quadrupolar strength, assuming a tetrahedral geometry, is calculated using the following equations:

$$\mathrm{QCC} = \frac{e^2qQ}{h} = \frac{(\mathrm{eQ})(\mathrm{eq})}{h} \qquad (1)$$

$$eq = V_{zz} = \frac{e}{r^3}\left(\frac{3\cos^2\theta - 1}{2}\right) \qquad (2)$$

In these equations h is Planck's constant, e is an elementary charge, Q is the electric quadrupole moment, r is the Na—O distance in the $SO_3^-Na^+$ group, and θ is the angle between the Na—O vector and the principal axis of the SO_3^- group. Typical values of the S—O distance (r = 1.45 Å), angles (θ = 74°), and the Na—O distance (r = 2.26–2.7 Å) were taken from structures of related, well-studied compounds.[44–46] The resulting QCC is approximately 160 kHz and is relatively insensitive to the choice of r within the range given above. Simulations of the MAS quadrupolar line shape of a sodium ion with this QCC were done using a program based on the work of Kundla *et al.*[36] The results are shown in Figure 6, which shows the predicted spectrum, with ~1.1 ppm of additional Lorentzian broadening applied, aligned with the actual NMR spectrum for 1.7% NaSPS. Both the observed and modeled peaks are ~160

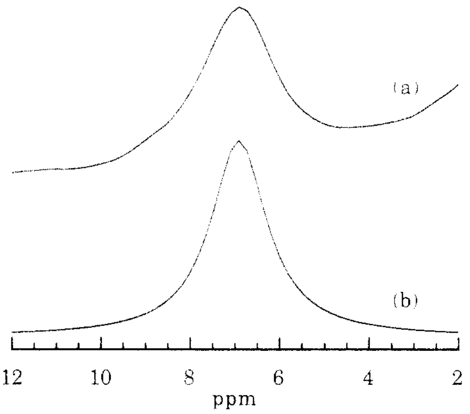

Figure 6. (a) NMR peak due to isolated sodium ions in NaSPS 1.7% and (b) simulated spectrum of an isolated sodium ion, aligned with the peak in NaSPS. The spectrum of NaSPS 1.7% is the same as that in Figure 4; the upward curvature at higher ppm is due to the 0 ppm peak.

Hz (=2 ppm) wide under spinning conditions, indicating that this model for the isolated Na^+–RSO_3^- ion pairs is reasonable. Additional spectra obtained at 132 MHz show no shift in the position of this peak, confirming that the quadrupole coupling is small.

The existence of isolated ions has been reported previously in ESR studies that have probed the local environment of paramagnetic ions.[29,47–50] These studies have concentrated primarily on Mn(II)- and Cu(II)-exchanged ionomers. Ionomers neutralized with divalent ions exhibit behavior very different from ionomers with monovalent ions,[21,51–54] such as longer extension of the rubbery plateau region,[53] better fatigue resistance,[54] and different morphological behavior during annealing.[21] Isolated ions are more likely in a system containing divalent ions, in which the metal ion has two polymer chains tethered to it and is less able to aggregate into ion-rich microdomains.[55] Other authors[56–58] have suggested that there are some differences in ionomer structure for materials neutralized with alkali and alkaline earth metals as compared to those neutralized with transition metals. The support for this view comes primarily from differences in the infrared spectra of ionomers. SPS neutralized with Mn^{2+} showed isolated ions in the ESR spectrum even at 5.5% sulfonation;[29] however, as will be shown in a later section, SPS neutralized with sodium ions contains no isolated ions above about 4% sulfonation. Thus, the data in this paper support the view that monovalent ions (Na^+) and divalent transition-metal ions (studied with ESR) are distributed differently in ionomers.

Aggregated Sodium Ions. The final peak in NaSPS is centered around −17 ppm for NaSPS 4.2% and shifts with ion concentration. This environment is characterized by a broad, asymmetric peak showing a second-order quadrupolar shift. A similar peak was seen in a study by Dickinson *et al.*,[18] in which spectra of 5% NaSPS at 52.9 MHz were reported. The position of the broad peak was ∼−40 ppm, and it was assigned to aggregated sodium ions. This peak shift as a function of spectrometer frequency is due to the strength of the quadrupolar coupling of the sodium ions. The center of gravity of a line shape shifts with frequency as follows:[59]

$$\sigma_{CG} = \sigma_{CS} + \sigma_{QS} \tag{3}$$

with

$$\sigma_{QS} = -\frac{3}{40}\frac{QCC^2}{\omega_L^{\,2}}\frac{I(I+1) - 9m(m-1) - 3}{I^2(2I-1)^2}\left(1 + \frac{\eta^2}{3}\right) \tag{4}$$

where σ_{CG} is the center of gravity of the line shape, σ_{CS} is the true chemical shift, σ_{QS} is the quadrupolar shift, ω_L is the Larmor frequency, I is the spin quantum number of the nucleus ($I = {}^3/_2$ in the case of sodium), m is the transition level, and η is the asymmetry parameter. In the calculations below, η is assumed to be zero for convenience. The maximum possible value of $\eta = 1$ will cause at most a 15% change in the calculated QCC values.

The NaSPS 4.2% sample was run at 132 MHz on a Bruker AM-500 spectrometer and compared to the results obtained at 79.2 MHz. Both are shown in Figure 7. The breadth of the peak base in the spectrum taken at higher frequency is due to spinning sidebands, which could not be spun far enough away from the peak itself due to equipment limitations. However, at the higher magnetic field the aggregate peak is narrowed and less asymmetrical, and so the center of gravity of the peak can be roughly approximated using a Lorentzian peak centered at −10.2 ppm. Using this value in combination with the value of −17 ppm observed at 79.2 MHz, the quadrupolar coupling constant for SPS 4.2% was calculated to be 1.6 MHz. This value is an order of magnitude larger than that found for isolated ions and indicates that the Na^+ ions in aggregates are not merely complexed to a single SO_3^- group in a symmetric geometry.

The width and shift of the peak assigned to aggregated sodium ions can be compared to those of sodium toluenesulfonate (STS) and sodium dodecyl sulfate (SDS), two smaller molecules with chemical structures similar to that of the ionomer. STS was chosen because its chemical structure is nearly identical to that of the SPS monomer, and SDS was chosen for its long-chain hydrocarbon, which may allow for easier aggregation than the bulky ring of STS. Figure 8 shows the spectra of both sodium toluenesulfonate and sodium dodecyl sulfate plotted above a spectrum of NaSPS 6.0%. Both small molecules show distinct line shapes in the range of interest, but with much less homogeneous broadening than was seen in the ionomers and the ion-exchange resins. The STS spectrum can be fitted to a QCC of 2.75 MHz and an η of 0.2. Both the center of gravity and the quadrupolar coupling constant of the broad ionomer peak are in the range of those found for STS and SDS.

The structure of STS is considered to be similar to that of ionic aggregates,[60] and there is a general similarity of the shape, width, QCC, and position of the NaSPS peak with the peak shown for STS. Therefore, as in the study of Dickinson *et al.*,[18] this peak is assigned to sodium ions held in aggregates which are subject to nearby interactions with other sodium ions and sulfonate groups. Different types of aggregated ions, such as dimers, trimers, and larger aggregates, are not resolvable, and all are represented by the broad NMR peak. The interactions lead to increased line width, as was discussed for the ion-exchange resins in the section Reference Compounds. Due to the nature of the material, these interactions are assumed to be ionic, either as ionic bonds or nearby charges that polarize the electrons of the sodium ion. The individual sodium ions exhibit large quadrupolar coupling constants due to the asymmetric environment of the aggregate and the proximity of other ionic species.

Effects of Changing Sample Composition. Effect of Humidification. An NaSPS sample with an ionization level of 1.7% was dried under vacuum to remove residual water. The resultant ^{23}Na NMR spectrum consists of two

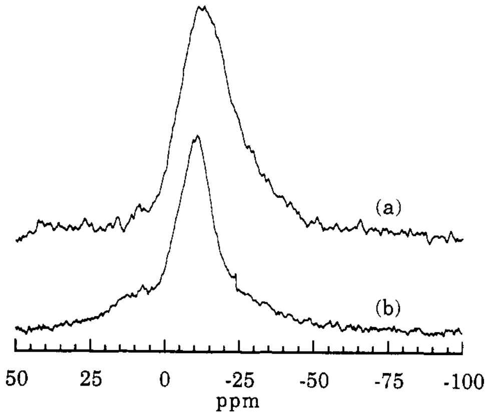

Figure 7. NMR spectrum of NaSPS at 4.2% sulfonation, (a) collected at 79.2 MHz and (b) collected at 132 MHz.

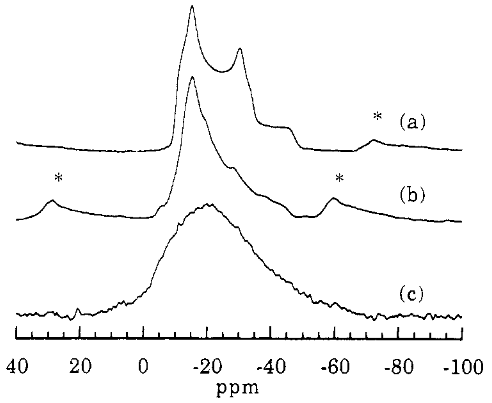

Figure 8. NMR spectra of (a) sodium toluenesulfonate, (b) sodium dodecyl sulfate, and (c) NaSPS 6.0%. Spinning sidebands are denoted by asterisks (*).

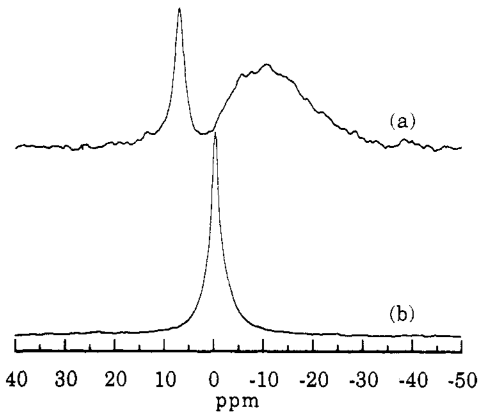

Figure 9. NMR spectra of SPS 1.7% (a) dried under vacuum at room temperature and (b) humidified at 80 °C for 72 h.

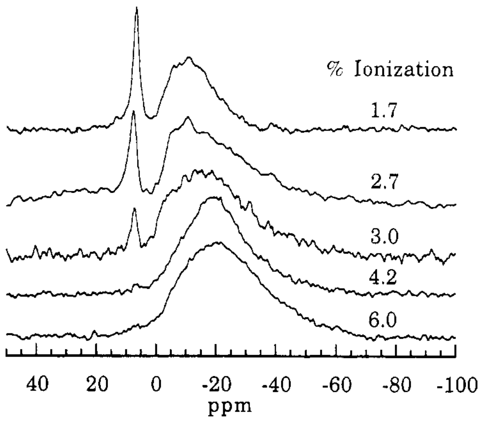

Figure 10. Effect of ionization level on the ^{23}Na NMR spectrum of NaSPS: 1.7%, 2.65%, 3.0%, 4.2%, and 6.0%.

peaks, at +7 and −12 ppm (Figure 9a). The same sample was subsequently humidified, producing a single hydrated NMR peak at 0 ppm, as shown in Figure 9b. With humidification, all sodium ions exist in the fully hydrated form, $Na(H_2O)_4^+$.[19,41] In this form, sodium ions in aggregates are far enough from other sodium ions (>10 Å) that no homonuclear broadening is observed. In addition, all sites have equivalent symmetrical local environments after water has complexed with the Na^+ ions and it is not possible to determine from the spectra whether the species outside the hydration sphere are hydrocarbons (polymer chains) or ionic groups. These results show that even in a glassy matrix such as polystyrene, all sodium ions are available for hydration and that hydration completely frees sodium ions from interactions with any neighboring sulfonate counterions. Whether the aggregates continue to exist in a swollen form or whether they disperse into the matrix, it is clear that hydration greatly weakens the ion–ion interactions and so reduces the accompanying properties of the ionically cross-linked polymer.[27]

Effect of Ionization Level. One of the goals of the present ^{23}Na NMR investigations was to determine a method for producing a mass balance on the sodium ions (i.e. fraction contained in aggregates versus fraction isolated). This has been accomplished by systematically varying the ionic concentration of the material. The effect of ionization level on the fraction of sodium ions in each environment is shown in Figure 10. The ratio of isolated to aggregated sodium ions clearly varies with ionization level; as the sulfonation level increases, fewer isolated ions are present. This is likely because the distance between sulfonate groups decreases at higher ionization levels. The attractive force between dipoles depends inversely on the fourth power of the distance between the ion groups, so the sodium sulfonate ion pairs are more likely to aggregate at higher ion concentrations. Consequently, the number of ion pairs dispersed throughout the hydrocarbon matrix decreases as the ionization level increases. The results of Figure 10 show that at some ionic concentration between 3.0 and 4.2%, the attractive forces are strong enough that all ion pairs are held in aggregates. It should be noted that an "aggregated" sodium ion, as recognized by NMR, is any sodium ion that is not completely isolated from other sodium ions on the NMR length scale of ~10 Å. A recent study has shown a transition point in tensile properties of NaSPS at the same ion concentration where we see the disappearance of isolated ions. Bellinger *et al.*[61] noted a small increase in tensile strength and toughness with increasing ion content to about 4%, and a steeper increase in these properties at 4% and above. It appears that the transition point in the tensile properties is related to the loss of isolated ions, and therefore a greater efficiency of the ions as cross-links.

Figure 11 shows the shift of the center of gravity with sulfonation level for the aggregated sodium ions. The peak shifts gradually upfield with increasing ion content. According to theory (eq 3), a shift to more negative frequency at constant field (ω_L) is due to a higher value of the quadrupolar coupling constant. This is consistent with results from spectra obtained at the higher field of 132 MHz: the aggregate peak in SPS 1.7% shifted less with frequency than did the peak in SPS 4.2%, indicating a lower QCC value for the sample with a lower ionization level. The QCC is dependent on the environment surrounding the sodium ion, such as the symmetry of the site, the number of atoms surrounding the sodium ion, and the

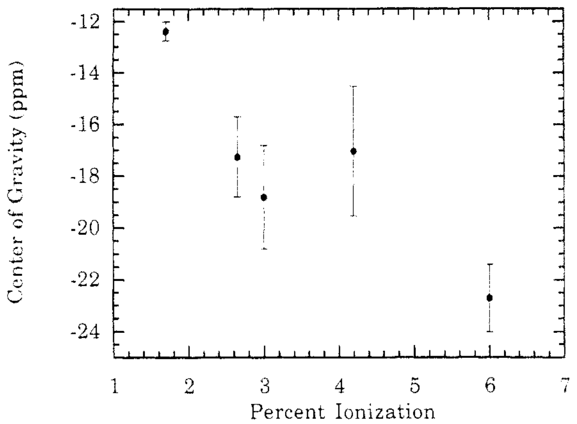

Figure 11. Center of gravity of the aggregate peak versus ionization level for NaSPS.

distances between the sodium ions and the surrounding atoms. Therefore, an increase in the QCC could be due to an increased number of ions held in the aggregate, closer packing between atoms, less symmetrical packing of atoms, or a combination of these factors.

In a previous SAXS study of NaSPS the interparticle aggregate scattering peak was absent for the ionomer at 1.7% sulfonation, but present at ionization levels above 4%.[5] A later study[21] showed relatively weak and broad scattering peaks with a characteristic distance of ~4 nm for ionomers sulfonated to 1.4 and 2.3%. Differences in the results of the two studies may be due to different sample preparation techniques. The scattering peaks are indicative of phase separation in the ionomer. The SAXS and NMR studies indicate that the electron density difference necessary for the formation of the ionomer peak in SAXS is barely present at this low sulfonation level (1.7%) despite the aggregation of 70% of the sodium ions that can be seen with ^{23}Na NMR. The results of even minimal aggregation are apparent in the increases in tensile properties of 1% NaSPS compared to those of unmodified polystyrene.[61]

SAXS results have shown that the scattering peak has more intensity and becomes more well-defined (less broad) as the ionization level increases, indicating better phase separation and less variation in the sizes of the aggregates.[5,21] Our findings are consistent with these results since better phase separation is due to the migration of isolated ions, dimers, and other small multiplets into larger aggregates. In turn, this migration would increase the electric fields and field gradients of the sodium ions involved. Additionally, steric hindrance from the tethered polymer chains would likely prevent symmetric packing inside the aggregate. These effects all increase the QCC and therefore the aggregate peak position and width.

Effect of Neutralization Level. The acid form of 3.4% SPS was neutralized to levels of 30–370%. The resulting ^{23}Na NMR spectra are shown in Figure 12. The spectra show no isolated ions present in NaSPS 3.4%, in contrast to the 3% sample (Figure 10). In addition, the centers of gravity of the SPS 3.4% samples do not fall between the shifts for NaSPS 3.0 and 4.2 in Figure 11. Both deviations are attributed to solvent effects, which will be discussed in future work.[27]

Increasing the neutralization level in NaSPS 3.4% gives results analogous to those seen for the ion-exchange resins (Figure 2); the width of the sodium peak increases with neutralization level and the center of gravity of the NMR line shifts downfield (higher ppm) as neutralization is increased past 100%. Figure 13 shows the shift in the center of gravity of the sodium peak as a function of neutralization level. The 0 ppm peak in the sample with 370% neutralization is due to Na$^+$ in NaOH domains, as discussed below.

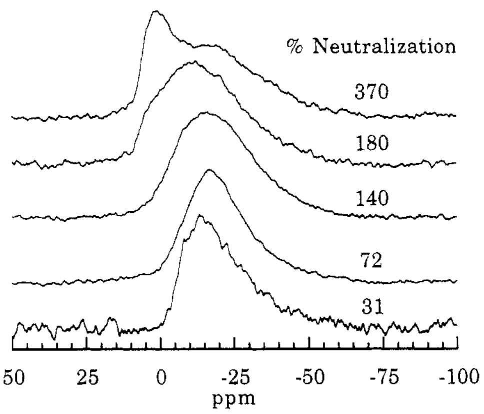

Figure 12. Effect of neutralization level on the ^{23}Na NMR spectrum for NaSPS at the 3.4% sulfonation level: 31%, 72%, 110%, 180%, and 370%.

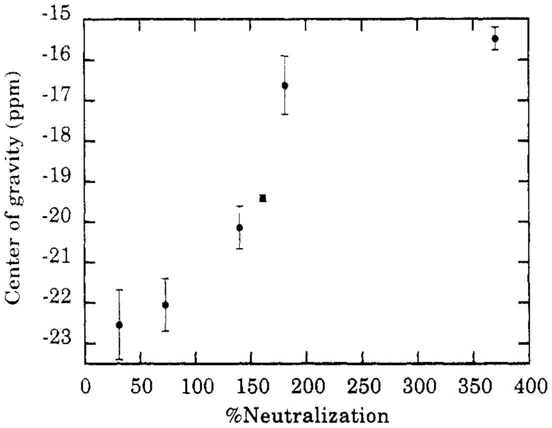

Figure 13. Center of gravity of the aggregate peak versus neutralization level for NaSPS at 3.4% sulfonation.

The level of neutralization has been shown to affect the mechanical[62,63] and rheological[64,65] properties of ionomers. Polymers neutralized below the equvalence point have exhibited poor mechanical properties[62] and increased water uptake.[66] On the other hand, the addition of excess neutralizing agent has been shown to increase the value of the stress at high elongations, while keeping the value of Young's modulus constant. This has been interpreted as an increase in the strength of ionic domains without a corresponding increase in their number. Therefore, it was proposed that the excess neutralizing agent remains trapped in the ionic aggregates and stabilizes the cross-links.[62,65] This view has been supported by EXAFS studies of zinc-neutralized telechelic butadiene, which show no evidence of phase-separated zinc acetate.[67] These EXAFS studies also found no change in the environment of the zinc cation as the percent of overneutralization increased from 10% to 100%. In a study on the fatigue behavior of overneutralized SPS,[63] samples with up to 100% excess NaOH displayed longer fatigue life than those exactly neutralized; however, those samples neutralized to 300% excess showed poor fatigue properties. It was determined that the excess NaOH in these highly overneutralized samples was held in phase-separated particles that were seen in SEM micrographs. Additionally, Weiss *et al.*[68] reported only slight improvement in tensile properties for sulfonated poly(styrene–ethylene/butylene–styrene) neutralized with zinc to 200% and a drastic decrease in properties for the sodium ionomer at the same neutraliza-

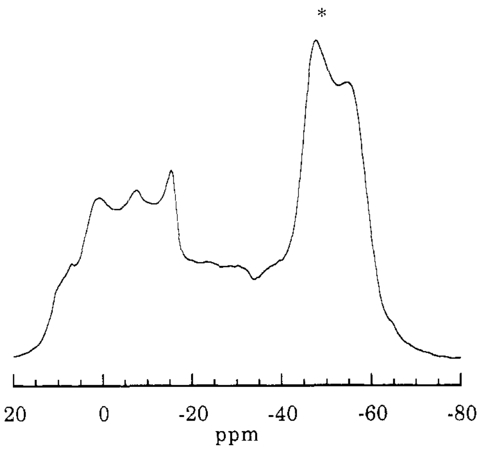

Figure 14. NMR spectrum of crystalline NaOH. A spinning sideband is denoted by an asterisk (*).

tion level. In summary, previous studies have shown that excess neutralizing agent can increase mechanical properties; however, at high enough levels additional agent decreases tensile properties and shortens fatigue life. The question unanswered in prior studies has been exactly where the excess neutralizing agent resides within the ionomer at the different neutralization levels.

The ^{23}Na NMR results for neutralization levels below $\sim$150–200% show that the excess neutralizing agent is within the aggregates, since no additional peak due to NaOH is seen in the spectra; for comparison, a spectrum of crystalline NaOH is shown in Figure 14. However, in this composition range the ^{23}Na NMR data do show some change in the sodium environment with increased amounts of neutralizing agent, as indicated by the changes in peak position and width. Finally, a spectrum of NaSPS 3.4% neutralized to 370% contains an additional peak due to phase-separated NaOH. Although the peak position is nearly the same as that of the fully hydrated sodium ion, the width is 2–3 times larger. The position of the new peak is comparable to bulk NaOH (Figure 14), but the sharp features present in the crystalline NaOH are not observed. Therefore, these new, principally-NaOH domains are not fully crystalline and differ markedly from bulk NaOH. The peak contains roughly 21% of the total amount of sodium in the ionomer. The remainder of the sodium appears in the modified aggregate peak, indicating that these aggregates can contain approximately two NaOH units for every sodium–sulfonate pair before additional NaOH produces this new peak near 0 ppm.

The NMR data reconcile some of the discrepancies among the results of other studies. At low levels of overneutralization, the excess neutralizing agent is held in the ionic aggregates, where it strengthens the cross-links and increases aggregate size. However, at high enough levels the aggregates can no longer contain the additional NaOH, and the excess collects into phase-separated domains that act as defects. For NaSPS 3.4%, the threshold for NaOH defect formation is quite high, occurring between 200% and 370% neutralization.

Conclusions

^{23}Na magic-angle spinning NMR has been used to characterize the environment of sodium ions incorporated into sulfonated polystyrene ionomers. This technique can measure the distribution of sodium ions on the basis of quantitative detection of those held in aggregates and those dispersed throughout the matrix. Different Na$^+$ environments produce characteristic NMR peaks, with a 7 ppm peak due to isolated ions, a 0 ppm peak representing hydrated ions, and a broad peak at −12 to −23 ppm produced by sodium ions in aggregates. Since isolated monovalent ions do not contribute to cross-linking, NMR is a useful technique in determining the efficiency of ionic cross-linking of the pendant sulfonate groups.

^{23}Na NMR can also follow the changes in the ion distribution as a function of humidification, ionization level, and neutralization level. With humidification of 1.7% NaSPS at 80 °C, all sodium ions are held in hydrated sites, Na(H$_2$O)$_4^+$, demonstrating that all ion pairs—isolated or aggregated—are readily hydrated. As the ionization level is increased, the fraction of ions in isolated sites decreases to zero. Finally, as the neutralization level increases at a given sulfonate content, the broadening and downfield shift of the NMR peak assigned to aggregated sodium ions shows that the aggregates continue incorporating sodium well beyond the neutralization equivalence point. At very high levels of overneutralization, a new peak at 0 ppm indicates sodium ions present in domains of excess NaOH that no longer contribute to improved physical properties.

Acknowledgment. The SPS samples used in this work were provided by Dr. Robert D. Lundberg of the Exxon Research and Engineering Corp. The solid-state Chemagnetics CMC-300A NMR spectrometer was purchased with financial support from Shell Oil Foundation. Additional funding for this research was obtained through Grant No. DE-FG02-88ER45370 from the Department of Energy. This study made use of the National Magnetic Resonance Facility at Madison, which is supported by NIH Grant RR02301. Equipment in the facility was purchased with funds from the University of Wisconsin, the NFS Biological Instruction Program, NIH Biomedical Research Technology Program, NIH Shared Instrument Program, and the U.S. Department of Agriculture. E.M.O. also acknowledges the support of the Department of Defense through the National Defense Science and Engineering Graduate Fellowship program.

References and Notes

(1) Eisenberg, A.; King, M. In *Ion-Containing Polymers*; Stein, R. S., Ed.; Academic Press: New York, 1977.
(2) Holliday, L. *Ionic Polymers*; Applied Science: London, 1975.
(3) Yarusso, D. J.; Cooper, S. L. *Macromolecules* **1983**, *16*, 1871.
(4) Yarusso, D. J.; Cooper, S. L. *Polymer* **1985**, *26*, 371.
(5) Peiffer, D. G.; Weiss, R. A.; Lundberg, R. D. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1503.
(6) Bersohn, M.; Baird, J. C. *An Introduction to Electron Paramagnetic Resonance*; W. A. Benjamin, Inc.: New York, 1966.
(7) Westra, S. W. T.; Lyte, J. C. *J. Magn. Reson.* **1979**, *34*, 475.
(8) Ding, Y. S.; Hubbard, S. R.; Hodson, K. A.; Register, R. A.; Cooper, S. L. *Macromolecules* **1988**, *21*, 1698.
(9) Register, R. A.; Cooper, S. L. *Macromolecules* **1990**, *23*, 310.
(10) Schlick, S.; Gebel, G.; Pineri, M.; Volino, F. *Macromolecules* **1991**, *24*, 3517.
(11) Boyle, N. G.; McBrierty, V. J.; Eisenberg, A. *Macromolecules* **1983**, *16*, 80.
(12) Natansohn, A.; Eisenberg, A. *Macromolecules* **1987**, *20*, 323.
(13) Natansohn, A.; Rutkowska, M.; Eisenberg, A. *Polymer* **1987**, *28*, 885.
(14) Nierzwicki, W.; Rutkowska, M. *Polym. Commun.* **1986**, *27*, 327.
(15) Lu, X.; Wang, Y. *Polym. Commun.* **1991**, *32*, 426.
(16) Belfiore, L. A.; Shah, R. J. *Polym. Sci. Mater. Eng.* **1986**, *54*, 490.
(17) Yang, Y.; Wang, D.; Qui, J.; Qian, B.; Wang, H. *Chin. J. Polym. Sci.* **1992**, *10*, 113.
(18) Dickinson, L. C.; MacKnight, W. J.; Connelly, J. M.; Chien, J. C. W. *Polym. Bull.* **1987**, *17*, 459.
(19) Komoroski, R. A.; Mauritz, K. A. *J. Am. Chem. Soc.* **1978**, *100*, 7486.
(20) Park, J. K.; Park, B. K.; Ryoo, R. *Polym. Eng. Sci.* **1991**, *31*, 873.
(21) Weiss, R. A.; Lefelar, J. A. *Polymer* **1986**, *27*, 3.

(22) Galambos, A. F.; Stockton, W. B.; Koberstein, J. T.; Sen, A.; Weiss, R. A. *Macromolecules* **1987**, *20*, 3094.
(23) Register, R. A.; Sen, A.; Weiss, R. A.; Cooper, S. L. *Macromolecules* **1989**, *22*, 2224.
(24) Hara, M.; Jar, P.; Sauer, J. A. *Polymer* **1991**, *32*, 1622.
(25) Yang, S.; Sun, K.; Risen, W. M. *J. Polym. Sci., Part B: Phys. Ed.* **1990**, *28*, 1685.
(26) Hara, M.; Jar, P.; Sauer, J. A. *Polymer* **1991**, *32*, 1380.
(27) O'Connell, E. M.; Root, T. W.; Cooper, S. L. To be submitted.
(28) Makowski, H. S.; Lundberg, R. D.; Singhal, G. S. U.S. Pat. 3,870,841 to Exxon Research and Engineering Co., 1975.
(29) Toriumi, H.; Weiss, R. A.; Frank, H. A. *Macromolecules* **1984**, *14*, 2104.
(30) Samoson, A.; Lippmaa, E. *Phys. Rev. B* **1983**, *28*, 6567.
(31) Lippmaa, E.; Samoson, A.; Magi, M. *J. Am. Chem. Soc.* **1986**, *108*, 1730.
(32) Pfeifer, H. In *NMR-Basic Principles and Progress*: Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1972; Vol. 15.
(33) Slichter, C. P. *Principles of Magnetic Resonance*, 3rd ed.; Springer-Verlag: New York, 1990.
(34) Semin, G. K.; Babushkina, T. A.; Yakobson, G. G. *Nuclear Quadrupole Resonance in Chemistry*; John Wiley & Sons: New York, 1975.
(35) Cohen, M. H.; Reif, F. *Solid State Phys.* **1957**, *5*, 321.
(36) Kundla, E.; Samoson, A.; Lippmaa, E. *Chem. Phys. Lett.* **1981**, *83*, 229.
(37) Samoson, A.; Kundla, E.; Lippmaa, E. *J. Magn. Reson.* **1982**, *49*, 350.
(38) Van Vleck, J. H. *Phys. Rev.* **1948**, *74*, 1168.
(39) Kambe, K.; Ollom, J. *J. Phys. Soc. Jpn.* **1956**, *11*, 50.
(40) Li, C.; Register, R. A.; Cooper, S. L. *Polymer* **1989**, *30*, 1227.
(41) Maeda, M.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3755.
(42) Jardetzky, O.; Wertz, J. E. *J. Am. Chem. Soc.* **1960**, *82*, 318.
(43) Mason, J., Ed. *Multinuclear NMR*; Plenum Press: New York, 1987.
(44) Barnes, C. L.; Hawkinson, S. W. *Acta Crystallogr.* **1980**, *B36*, 2431.
(45) Chetkina, L. A.; Sobolev, A. N. *Acta Crystallogr.* **1977**, *B33*, 2751.
(46) Arora, S. K.; Sundaralingam, M. *Acta Crystallogr.* **1971**, *B27*, 1293.
(47) Pineri, M.; Meyer, C.; Levelut, A. M.; Lambert, M. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 115.
(48) Yamauchi, J.; Yano, S. *Makromol. Chem.* **1978**, *179*, 2799.
(49) Galland, D.; Belakhovsky, M.; Medrignac, F.; Pineri, M.; Vlaic, G.; Jerome, R. *Polymer* **1986**, *27*, 883.
(50) Alonso-Amigo, M. G.; Schlick, S. *J. Phys. Chem.* **1986**, *90*, 6353.
(51) Lefelar, J. A.; Weiss, R. A. *Macromolecules* **1984**, *17*, 1145.
(52) Navratil, M.; Eisenberg, A. *Macromolecules* **1974**, *7*, 84.
(53) Hara, M.; Jar, P.; Sauer, J. A. *Polymer* **1991**, *32*, 1625.
(54) Hara, M.; Jar, P.; Sauer, J. A. *Macromolecules* **1990**, *23*, 4465.
(55) Mattera, V. D.; Risen, W. M. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 753.
(56) Brozoski, B. A.; Coleman, M. M.; Painter, P. C. *Macromolecules* **1984**, *17*, 230.
(57) Brozoski, B. A.; Coleman, M. M.; Painter, P. C. *Macromolecules* **1984**, *17*, 1591.
(58) Han, K.; Williams, H. L. *J. Appl. Polym. Sci.* **1991**, *42*, 1845.
(59) Samoson, A. *Chem. Phys. Lett.* **1985**, *119*, 25.
(60) Sakuri, K.; Douglas, E.; MacKnight, W. J. *Macromolecules* **1993**, *26*, 208.
(61) Bellinger, M.; Sauer, J. A.; Hara, M. *Macromolecules* **1994**, *27*, 1407.
(62) Mohajer, Y.; Bagrodia, S.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *J. Appl. Polym. Sci.* **1984**, *29*, 1943.
(63) Hara, M.; Jar, P.; Sauer, J. A. *Macromolecules* **1990**, *23*, 4964.
(64) Makowski, H. S.; Lundberg, R. D.; Westerman, L.; Bock, J. In *Ions in Polymers*; American Chemical Society: Washington, DC, 1980.
(65) Bagrodia, S.; Pisipati, R.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *J. Appl. Polym. Soc.* **1984**, *29*, 3065.
(66) Williams, C. E.; Russell, T. P.; Jerome, R.; Horrion, J. *Macromolecules* **1986**, *19*, 2877.
(67) Vlaic, G.; Williams, C.; Jerome, R.; Tant, M. R.; Wilkes, G. L. *Polymer* **1988**, *29*, 173.
(68) Weiss, R. A.; Sen, A.; Pottick, L. A.; Willis, C. L. *Polymer* **1991**, *32*, 2785.