Macromolecules **2001,** *34,* 7108−7112

EXAFS Spectroscopy Studies of Cation Local Environment in Sodium-Neutralized Ethylene Copolymer Ionomers

K. V. Farrell and B. P. Grady*

School of Chemical Engineering and Materials Science, University of Oklahoma, 100 East Boyd, Norman, Oklahoma 73019-0628

Received December 7, 2000; Revised Manuscript Received April 23, 2001

ABSTRACT: Extended X-ray absorption fine structure (EXAFS) spectroscopy was used to study the local environment around sodium in ethylene−methacrylic acid (E−MAA) and ethylene−acrylic acid (E−AA) copolymer ionomers. Substantial changes occur in the arrangement of atoms around sodium as the neutralization level changes from ∼20% to 80%, unlike zinc ionomers where the arrangement basically does not change over this range of neutralization levels. In E−MAA ionomers, changes in EXAFS patterns were consistent with the environment around sodium becoming less uniform with increasing neutralization level while the reverse was true for E−AA ionomers. This difference in the sodium ionomers was unexpected and surprising, particularly since the amount of water absorbed per sodium cation did not depend on acid comonomer identity. In E−AA ionomers neutralized with both zinc and sodium, the environment around sodium becomes substantially more ordered vs the environment of the equivalent material neutralized only with sodium. This result is consistent with the formation of a single type of zinc−sodium mixed aggregate consistent with EXAFS studies at the zinc edge. In E−MAA mixed-cation ionomers, the environment becomes more disordered upon addition of zinc, also consistent with studies at the zinc edge.

Introduction

Ionomers have hydrophobic polymer structures with ionic groups randomly located along the hydrocarbon backbone. The number, type, and locations of these charged groups are based on the monomer composition and polymerization process used to produce the copolymer. To form an ionomer from a polymer containing acid groups, part or all of the copolymer's acid groups are neutralized with a cation. These species form ion pairs that will phase separate into nanometer-size aggregates. These aggregates impart remarkable properties to ionomers including exceptional clarity and toughness.[1]

The materials studied here are copolymers of ethylene and either acrylic or methacrylic acid (E−AA or E−MAA). Both have significant commercial applications, including food packaging materials, automobile parts, and golf ball covers. The vast majority of commercial E−AA or E−MAA ionomers are neutralized with zinc, sodium, or both zinc and sodium. The properties of zinc-neutralized and sodium-neutralized carboxylate copolymer ionomers are very different; these differences include the following:

(1) Sodium-neutralized ionomers absorb significantly more water.

(2) Sodium-neutralized ionomers are typically harder than the zinc counterparts, which is a result of higher fractional crystallinities. This crystallinity difference is also typically reflected in a higher melting point for the sodium-neutralized material, although the melting points of both ionomers are typically very low (90 °C) compared to polyethylene homopolymer.

(3) Zinc ionomers show excellent adhesion to a variety of solid surfaces, while sodium ionomers do not.

These differences are the result of differences in aggregate characteristics, i.e., size, shape, and composition. Our group has extensively studied the zinc aggregate in both E−MAA and E−AA copolymer ionomers.[2,3,4,5] Our studies, as well as the properties listed above, are consistent with the conclusion that zinc aggregates are thermodynamically highly favored. Experimental evidence from our studies to support this conclusion are the following:

(1) Adding water does not break the aggregate apart when absorption is carried out at room temperature. A recent study from Ishioka et al. confirmed this observation.[6] Through detailed inductive analysis, we concluded that water absorbs only at the edges of aggregates.

(2) Heating the material to near the degradation temperature of the polymer without any applied stress does not significantly affect the aggregate structure.

(3) Aggregates in E−AA and E−MAA ionomers have essentially the same structure.

(4) A significant amount of isolated zinc ions appear only at neutralizations less than about 20% of stoichiometric. The structure of the aggregate does not change as a function of neutralization; however, the average size increases with increasing neutralization amount.

These conclusions have been arrived at through the careful application of extended X-ray absorption fine structure (EXAFS) spectroscopy. EXAFS spectroscopy is the measure of the oscillations in absorption coefficient at energies above the absorption edge as shown in Figure 1. The dramatic increase in the absorption coefficient at the absorption edge is due to a single type of atom (in this study zinc) absorbing X-rays. Equation 1 describes the normalized absorption coefficient ($\chi(E)$) in terms of the measured absorption coefficient ($\mu(E)$) and the absorption coefficient if no oscillations were present ($m_0(E)$):

$$\chi(E) = \frac{\mu(E) - m_0(E)}{m_0(E)} \qquad (1)$$

Single-electron single scattering theory[7] relates the

---

* Corresponding author.

10.1021/ma002081p CCC: $20.00

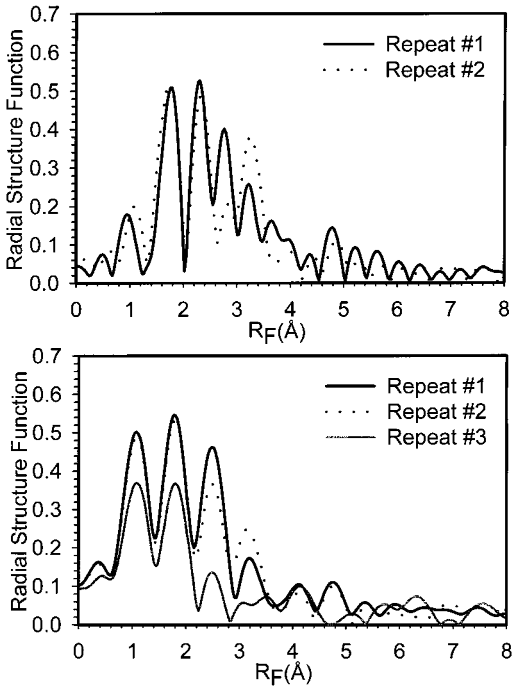

Figure 1. Graph showing reproducibility of radial structure functions. Black lines represent data taken during the higher-quality run, while gray lines represent data collected during the lower-quality run. Note that a black line in the top or bottom plot for a given repeat represent one set of raw data; the difference between the top and bottom is the energy range used in data reduction procedures. The convention that the top plot represents data with the larger *k* range (or energy range) will be used throughout this paper.

normalized absorption coefficient to structural parameters according to

$$\chi(k) = \sum_j N_j S_j(k) F_j(k) e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda_j}(k) \frac{\sin(2kr_j + \Phi_{jk}(k))}{kr_j^2} \tag{2}$$

where $F_j(k)$ is the backscattering amplitude from each of the N_j neighboring atoms of the jth type around the absorbing atom, $\Phi_{jk}(k)$ is the total phase shift, λ_j is a term representing inelastic losses in the scattering process, $S_j(k)$ is the amplitude reduction factor due to many-body effects of the absorbing atom, and

$$k = \sqrt{\frac{2m}{\hbar^2}(E - E_o)} \tag{3}$$

where k is the wavevector, m is the mass of an electron, and $\hbar = h/2\pi$. The mean squared displacement σ_j^2 in eq 2 represents the variation in average distance between atoms in a particular coordination shell and the central absorbing atom. If a specific type of atom is in more than one environment, then the observed EXAFS spectrum is an average of the individual spectra weighted appropriately.

This papers details EXAFS spectroscopy studies at the sodium K-edge, which occurs at 1070 eV. This energy is experimentally difficult to reach; UV beamlines typically have a higher-energy cutoff around 1000 eV and hard X-ray beamlines typically have a lower energy cutoff around 2000 eV. A number of synchrotrons are adding facilities to access this edge, but at the time these experiments were performed, only one beamline in the United States had the capability of performing EXAFS studies at this energy. To our knowledge, this study represents the first time that EXAFS spectroscopy has been conducted at the Na edge in ionomers and the first Na-edge EXAFS conducted in transmission for any system.

Experimental Section

Materials. Experimental and commercial grades of ethylene−methacrylic acid (E−MAA) and ethylene−acrylic acid (E−AA) copolymer ionomers were graciously supplied by the E. I. DuPont Co. The former contained approximately 4.0 mol % acid repeat unit while the latter contained 5.2 mol % acid repeat unit. The E−MAA copolymer ionomer conneutralized with both zinc and sodium had a significantly higher acid content; approximately 7.6 mol % of the polymer repeat units were acid groups. Percent neutralizations in this paper represent percent of stoichiometric; i.e., 100% neutralized would mean that all acid groups had a counterion, and no excess counterions were present.

Samples were compression molded into extremely thin sheets in a 32.5 mm diameter mold. The disks were heated and drawn into films using a home-built apparatus and then thoroughly dried in a vacuum oven. The desired thickness was 10 μm, but the thickness was not measured because the film was easily damaged. Instead, multiple films were made for each sample and inserted into the synchrotron beam. Once a good sample was found, i.e., the absorption was in the right range, the spectrum was recorded. Generally, samples with an absorption at 1000 eV less than 3 were used. The beam changed its vertical position at the sample by approximately 2 mm as the energy was scanned between 1000 and 1500 eV. If the sample is of nonuniform thickness, the movement leads to changes in the thickness of the sample in the beam. This change was estimated by comparing measured absorptions with calculated values from Victoreen coefficients and the maximum variation found was 20%. Sample-to-sample differences in thickness nonuniformities certainly contributed to the poor reproducibility relative to other EXAFS experiments done at higher energies by our lab; however, beamline issues and difficulties with background subtraction as described below were probably much larger contributors.

Data Collection and Treatment. Data presented in this paper were from 2 different trips to the Stanford Synchrotron Radiation Laboratory (SSRL). The beamline behaved much differently between the two runs, and the data quality was much higher for one of the runs. On the basis of different samples that were measured during both runs, as well as our own visual inspection, the usable energy range for the lower-quality run extended roughly only 230 eV ($k = 7.7$ Å^{-1}) above the edge. A comparison of radial structure functions (RSFs) is shown in Figure 1. RSFs can be thought of as radial distribution functions, except peak positions are shifted from interatomic distances and areas under peaks cannot be used without modification to calculate the number of atoms in a particular coordination shell. Figure 1 shows spectra for three samples of the same material measured at different times and can be used to estimate the error associated with these experiments. Throughout this document, the top plot presents data calculated from the larger *k* range and only represents samples from the higher-quality run. The bottom plot presents data calculated from the smaller *k* range and represents samples from both the higher-quality and lower-quality run. In theory, differences between the bottom plots should only be a result of a different *k* range in the Fourier transform. However, background subtraction almost certainly plays a role as well as described in the Supporting Information. The effect of background subtraction is particularly acute for the bottom plots since the energy range was so limited. Hence, conclusions will be drawn only from the top plots, and the bottom plots will only be used to confirm these conclusions. We believe most, if not all, of the problems with lack of reproducibility, both run-to-run and sample-to-sample, were due to design problems

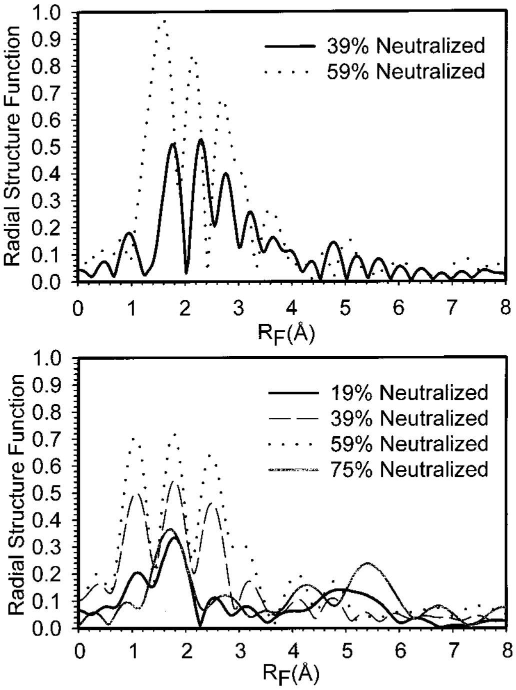

Figure 2. Effect of neutralization level on RSFs in sodium-neutralized E−AA ionomers.

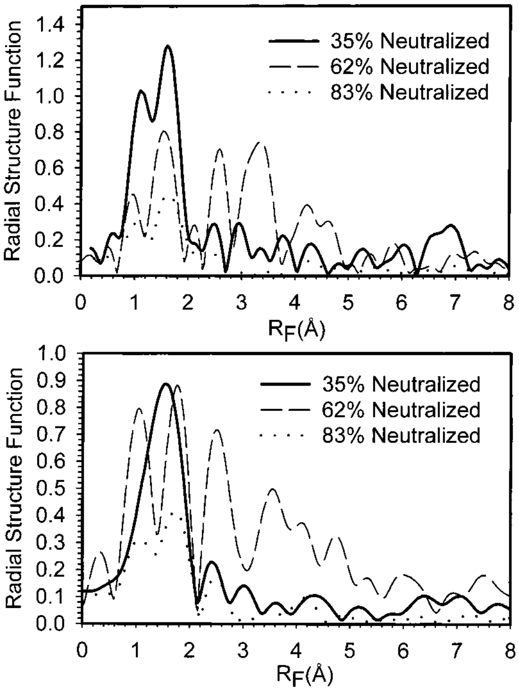

Figure 3. Effect of neutralization level on RSFs in sodium-neutralized E−MAA ionomers.

in the monochromating elements, and these problems are being addressed by SSRL. More details regarding data collection and treatment are given in the Supporting Information.

Results and Discussion

Figures 2 and 3 represent changes in local environment around Na in E−AA and E−MAA ionomers as a function of neutralization level. In both cases, differences in RSFs are extremely large, which suggest substantial changes in the local environment around sodium with neutralization level. By way of contrast, in zinc ionomers, the change in RSF from the fully aggregated state to one where the ions were totally isolated caused a change in RSF peak height of only 33%,[8] and no changes were seen in the peak at lowest R_F between neutralization levels of 30 and 90%.[2] Changes in the sodium spectra shown in Figures 2 and 3 indicate dramatic shifts in environment for the sodium atoms. Such changes in this system can only be due to dramatic changes in the number of atoms around sodium and/or changes in the distribution of distances of atoms around sodium. The latter is more likely, since the number of nearest-neighbor atoms should not depend on the structure or size of sodium aggregates. With this interpretation, an increased amplitude presumably means that sodium is more ordered in an average sense, i.e., sodium is in a smaller number of different environments.

These two plots indicate that the qualitative behaviors of the two ionomers are very different. In E−AA ionomers, peaks become more intense at higher neutralization levels, where the converse is true for E−MAA ionomers. Hence, for E−AA ionomers the arrangement of atoms around sodium have less variation at higher neutralization levels; hence, presumably the aggregate structure is either more uniform, or the distribution of sodium atoms in and outside of aggregates has changed. For E−MAA ionomers the converse is true: the arrangements of atoms around sodium have more variation at higher neutralization levels. This difference was unexpected, since the difference in structure between AA and MAA repeat units is quite small. Comparisons of the effect of neutralization level in sodium-neutralized E−AA and E−MAA do not exist in the open literature to our knowledge. One reason for the lack of investigations is that the parent copolymers cannot be identical to each other in structure or molecular weight; hence, differences in rheological behavior, for example, will not be due only to differences in aggregate characteristics. Infrared spectroscopic measurements might give some insight; however, to our knowledge measurements have not been made at different neutralization levels for both E−AA and E−MAA using the same parent copolymers.

A more quantitative description of the environment around sodium could not be given for the samples measured in this study. First, model compounds could not be measured in transmission because of much too high absorption, and the beamline could not be configured for fluorescence. We expected modeling with FEFF[9] to assist in interpretation; however, using six first-shell oxygen atoms at a reasonable distance with reasonable mean-squared displacement gives RSF peak heights which are approximately 0.5 on the *y*-scale shown in the figures. This height is much too low for some samples in Figures 1−3, and hence, this result indicates that the FEFFIT model cannot be used with any level of confidence to model these spectra. We are confident that the substantial disagreement between the experimental data and the FEFFIT model is not in the data reduction procedures, because the background subtraction procedures will not cause a factor of 2 (or more) error in RSF peak intensity. We believe that the difference was either beamline-related or FEFF software-related. The software must be considered to be unproven in this instance since the software has never been shown to successfully predict EXAFS patterns for an atomic number this low. However, the author of the fitting program believes that the software should work and is also is very puzzled with this result.[10] Beamline errors

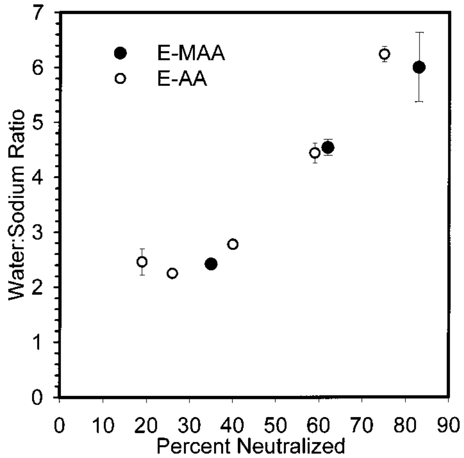

Figure 4. Water absorption as a function of neutralization level for ethylene copolymer ionomers.

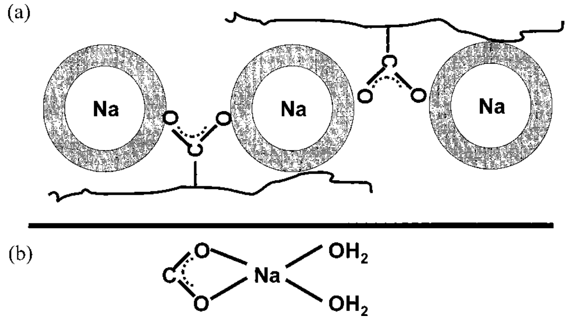

Figure 5. Rough schematic showing how water molecules might associate with aggregated sodium ions (top) and with isolated sodium ions (bottom).

are another possible cause of this disagreement; however, most beamline inaccuracies such as changes in absorption caused by movement of the beam across the sample and broad energy band-pass should cause artificially small, not artificially large, RSF peaks. We would like to emphasize that all conclusions in this paper are based on relative differences and hence will still be correct even if beamline problems are consistently causing peak heights that are too large.

To help better understand differences in EXAFS spectra, sample disks were molded and dried at 70 °C in a vacuum oven until constant weight was achieved. The amount of water adsorbed was monitored and is plotted in Figure 4. The amount of water adsorbed per cation increased with increasing neutralization level, unlike in zinc where the amount of water adsorbed per cation decreased as the neutralization level increased.[3] This behavior indicates that having sodium ions in close proximity to one another stabilizes full hydration of the cation. The simplest explanation for this behavior is that a repeating structure, schematically illustrated in Figure 5, can occur only if the sodium ions are in close proximity. Full hydration is presumably six nearest-neighbor water atoms according to the results in Figure 5.

One might reasonably interpret the apparent plateau at low neutralization levels in Figure 4 as indicating that ions are unaggregated for all neutralization levels below ~35% in the dry structure. However, some critical aggregation number might be required to produce structures such as those found in the bottom schematic of Figure 5, so it is very possible for small aggregates in the dry state to appear unaggregated in the wet state.

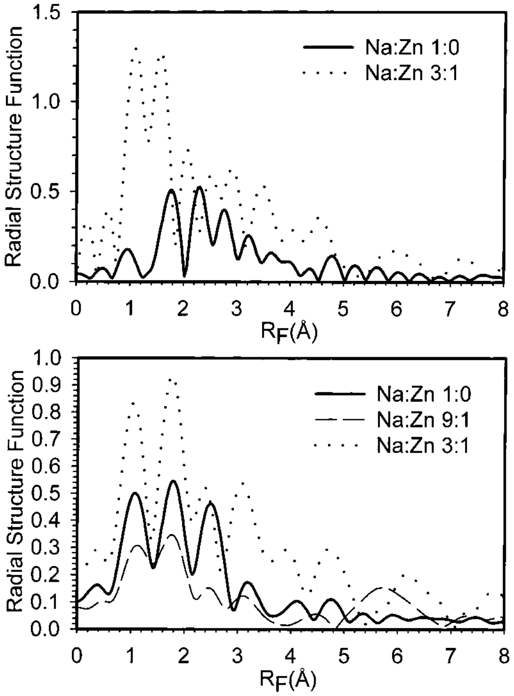

Figure 6. Radial structure functions for E−AA ionomers as a function of Na:Zn ratio. The overall neutralization level varied from 39% for the pure sodium sample to 35% for the Na:Zn 3:1 sample.

Further, the amount of water absorption does not depend on whether the comonomer is acrylic or methacrylic acid. This result indicates that unaggregated cations, as measured by water absorption, are more ordered than aggregated ions for E−MAA copolymer ionomers and less ordered for E−AA copolymer ionomers.

In a previous paper,[11] the effect of co-neutralization with zinc was studied. Very different behavior was found for the two types of ionomers. For E−AA, the arrangement of atoms around zinc did not change from a Na:Zn ratio of 1:1 to a ratio of 1:0. This behavior was unimpeachable evidence that a new aggregate formed, and almost certainly this aggregate contained both zinc and sodium. On the other hand, for E−MAA the arrangement of atoms changed continuously as the Na:Zn ratio changed, indicating that zinc resided in a distribution of different environments. As noted previously, this qualitative difference in local environmental change was consistent with the qualitative difference in viscosity behavior noted in a recent patent.[12] The results of EXAFS studies at the sodium edge on the same ionomers are shown in Figures 6 and 7. The range of compositions was limited to Na:Zn ratios greater than 3:1, because the L_{III} edge of zinc at approximately 1200 eV is clearly noticeable at lower ratios.

Qualitatively, the behaviors of the two ionomers were opposite. In E−AA copolymer ionomers, peaks in the RSF become much more intense with the addition of zinc, consistent with more ordering around the sodium atom. Ordering is expected if a single type of zinc−sodium aggregate is forming. In E−MAA copolymer ionomers, the environment becomes more disordered with increasing zinc content, consistent with the disordering that occurred in zinc spectra. Hence, the results of EXAFS measurements at the sodium edge are consistent with those made at the zinc edge.

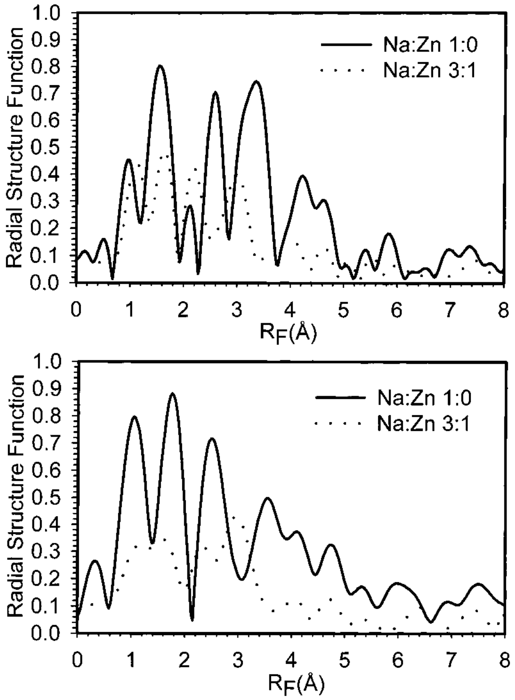

Figure 7. Radial structure functions for E−MAA ionomers as a function of Na:Zn ratio. The neutralization level was 62% for all samples.

Summary

For the first time, EXAFS spectroscopy at the sodium-edge was used to measure the arrangement of atoms around sodium in sodium-neutralized ionomers. Two different types of ionomers were measured: copolymers of ethylene with methacrylic and acrylic acid, respectively. In E−MAA ionomers, the environment around sodium became less uniform with increasing neutralization level, while the reverse was true for E−AA ionomers. This finding indicates a qualitative difference between the aggregate structures for the ionomers made with the two comonomers, which is quite surprising given the small difference in monomer structure. Our studies also confirmed results from studies at the zinc edge for the ionomers neutralized with both zinc and sodium; namely, in E−AA ionomers, a new aggregate forms which presumably contains both zinc and sodium, while in the E−MAA ionomers a distribution of different environments exist. Finally, water absorption studies carried out to help in the interpretation of EXAFS spectra showed that the amount of water absorbed per sodium atom increased with increasing neutralization level and was not dependent on acid comonomer identity.

Acknowledgment. Samples were kindly supplied by Dr. John Paul, Dr. Matt Hall, and Dr. John Chen of the DuPont Sabine Research Laboratory. Aaron Lowe and Chris Rhodes helped perform EXAFS experiments. The efforts of the SSRL staff, in particular Curtis Troxel, Piero Pianetta, and especially Jeff Moore (who has since moved on to KLA-Tracor), are acknowledged. Financial support for this project was provided by the DuPont Sabine Research Laboratory and an NSF CAREER Grant DMR-9733068. This paper was written while B.P.G. was at the Max Planck for Colloid and Interface Science in Golm supported by a Humboldt Fellowship; this support is gratefully acknowledged. Finally, an anonymous reviewer deserves thanks for making suggestions to improve the manuscript. SSRL is operated by the Department of Energy, Office of Basic Energy Sciences. The SSRL Biotechnology Program is supported by the NIH, Biomedical Research Technology Program, National Center for Research Resources. Further support for SSRL is provided by the Department of Energy, Office of Health and Environmental Research.

Supporting Information Available: Text giving a detailed description of data collection and reduction procedures, including figures showing plots of the data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Eisenberg, A.; Kim, J.-S. *Introduction to Ionomers*; Wiley-Interscience: New York, 1998.
(2) Grady, B. P.; Floyd, J. A.; Genetti, W. B.; Vanhoorne, P.; Register, R. A. *Polymer* **1999**, *40*, 283.
(3) Welty, A.; Ooi, S.; Grady, B. P. *Macromolecules* **1999**, *32*, 2989.
(4) Grady, B. P. *Polymer* **2000**, *41*, 2325.
(5) Farrell, K. V.; Grady, B. P. *Macromolecules* **2000**, *33*, 7122.
(6) Ishioka, T.; Shimuzu, M.; Watanabe, I.; Kawauchi, S.; Harada, M.; *Macromoleules* **2000**, *33*, 2722.
(7) Teo, B. K. *EXAFS: Basic Principles and Data Analysis*; Springer-Verlag: New York, 1986.
(8) Grady, B. P. Unpublished data.
(9) Zabinsky, S. I.; Rehr, J. J.; Ankudinov, A.; Albers, R. C.; Eller, M. J. *Phys. Rev. B* **1993**, *52*, 2995.
(10) Newville, M. Private communication.
(11) Grady, B. P. *Macromolecules* **1999**, *32*, 2983.
(12) Permentier, D.; Jozef, C.; Tengkumahamad, M. U.S. Patent 5,929,174, 1999.

MA002081P