Effect of Coneutralization on Internal Aggregrate Structure in Ethylene-Based Ionomers

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ABSTRACT: Local aggregate structures in ethylene−methacrylic acid (E−MAA) and ethylene−acrylic acid (E−AA) ionomers were studied using extended X-ray absorption fine structure spectroscopy (EXAFS). In the case of pure zinc neutralization, E−AA and E−MAA ionomers showed very minor differences in EXAFS spectra. These small differences were statistically significant, however, and almost certainly a result of the structural differences between the acid repeat units. Overneutralization with zinc acetate dihydrate caused significant changes in the EXAFS pattern which could not be attributed to a linear combination of EXAFS spectra from the ionomer and zinc acetate dihydrate. Coneutralization with either lithium or sodium also changed the local environment around zinc. Zinc/sodium ratios were systematically varied in both E−AA and E−MAA. In the former, the local environment around zinc changed as the Zn/Na mole ratio changed from 1:0 to 1:1; at ratios between 1:1 and 1:9 the local environments were identical. Therefore, at low Zn/Na ratios only one type of zinc-containing aggregate exists in the system, and this aggregate probably contains both sodium and zinc. A partial list of properties for this mixed-cation aggregate was generated, and possible structures were proposed. For E−MAA ionomers, zinc local environment changes continuously as Zn/Na ratio changes. Hence, more than one type of aggregate exists at all Zn/Na ratios, and the relative distribution of these aggregates changes with this ratio. The implications of the differences in aggregate structure on the rheological behavior of these mixed-cation systems are discussed.

Introduction

The remarkable improvement in mechanical properties of polymers having a small fraction of ionic groups covalently bonded to the polymer backbone is due to phase separation of the ionic groups into nanometer-size ionic-rich aggregates. The aggregates act as both reinforcing filler and cross-links, leading to improvement in such properties as abrasion and tear resistance and impact strength[1] as well as profoundly affecting the rheological properties.[2] Important commercial ionomers include copolymers of ethylene and methacrylic acid (E−MAA) and copolymers of ethylene and acrylic acid (E−AA). In these two commercial systems, neutralization of carboxylate groups usually occurs with either sodium, zinc, or a combination of these cations.

In E−MAA ionomers, the melt index (MI) of an ionomer neutralized with a combination of sodium and zinc shows only very small deviations from an empirical log mixing rule according to a recent international patent application.[3] In other words, the melt index can be predicted from the following:

$$\log[\mathrm{MI}_{\text{mixed ionomer}}] = w_{\mathrm{Na}} \log[\mathrm{MI}_{\mathrm{Na}}] + w_{\mathrm{Zn}} \log[\mathrm{MI}_{\mathrm{Zn}}] \tag{1}$$

where MI_x is the melt index of the ionomer equivalently neutralized with cation x (the weight percent of cation remains the same, but neutralization only occurs with x) and w_x is the weight fraction of x relative to the total weight of cation in the mixed ionomer. However for E−AA ionomers, the melt index of the mixed-cation ionomer is significantly higher than the MI calculated from the mixing rule; in fact, the MI of the mixed-cation ionomer can be significantly higher than either of the pure components. This “MI uplift” has been confirmed by measurements of the zero-shear viscosity: the zero-shear viscosity of a mixed sodium−zinc ionomer is lower than the zero-shear viscosities of the ionomer neutralized with only sodium or only zinc.[4] A higher melt index/lower viscosity improves processibility for many applications, since lower viscosities mean faster mold filling at equivalent pressures, etc.

This study examines atomic-scale internal structure of the aggregates by measuring extended X-ray absorption fine structure (EXAFS) spectra at the zinc absorption edge. EXAFS is the measure of oscillations in the X-ray absorption coefficient on the high-energy side of an absorption edge. An absorption edge occurs when the energy of the X-ray is just sufficient to cause the ejection of an electron from an atom in the material. Oscillations occur due to interference between the outgoing photoelectron waves and photoelectron waves backscattered by nearby atoms. The shape and period of the oscillations are functions of the absorbing atom (in this paper, zinc) as well as the type, distance, and number of atoms around the absorbing atom. Hence, EXAFS offers a means to probe the local atomic arrangement of materials. The maximum distance probed by this technique is 5−6 Å; in ionomers information is typically limited to nearest and next-nearest neighbors of the absorbing atom because of the low atomic number atoms and hence weak backscatterers in polymers. The information from EXAFS is similar to that available from wide-angle X-ray diffraction; however, long-range translational symmetry is not required for EXAFS. Further information about the theoretical basis of EXAFS can be found in previous publications by the authors[5,6] and a treatise on the subject.[7]

This study uses EXAFS to probe the average local environment around zinc atoms in E−AA and E−MAA ionomers. A previous study of dried zinc-neutralized E−MAA ionomers showed that the local environment around zinc was well-described by the arrangement of atoms in crystalline monoclinic anhydrous zinc acetate.[8]

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In this structure, zinc is coordinated to four oxygen atoms from four different carboxylate groups at an average distance of 1.96 Å.[9] The features in EXAFS patterns attributed to backscattering from the first coordination shell were independent of neutralization level if the neutralization level was greater than about 30%. The EXAFS patterns were identical when different neutralizing agents and/or neutralizing procedures were used. In the study described in this paper, this arrangement of atoms around zinc was changed by the use of acrylic acid instead of methacrylic acid, by overneutralization with zinc acetate dihydrate, and finally by neutralization with a combination of zinc and either sodium or lithium.

Experimental Section

Samples were graciously supplied by DuPont as pellets. E−MAA samples were made from a copolymer with 3.9 mol % acid monomer, while E−AA copolymers were made from a copolymer with 8.9 mol % acid monomer. Acid copolymers were neutralized in a twin-screw extruder with either sodium hydroxide or zinc oxide; then these single cation ionomers were blended to produce the mixed-cation ionomers. For E−AA mixed-cation ionomers, a sodium ionomer with 39% acid group neutralization was blended at the appropriate ratios in a twin-screw extruder with a zinc ionomer having 25% acid group neutralization. One sample (Zn/Na = 1:9) was made via blending in a roll mill. E−MAA mixed-cation ionomers were made by blending in a twin-screw extruder sodium and zinc ionomers 57% neutralized with the metal cation. Differences in percent acid groups neutralized or acid content should not affect the conclusions presented in this paper since these variations produce almost negligible variations in cation local structure for zinc E−MAA ionomers[8] and because these factors do not seem to affect "MI uplift" substantially.

Pellets were compression molded at 700 bar into 32 mm disks. Precise atomic compositions for all samples were not provided prior to forming the pellets into disks; however, the absorbances were all between 0.5 and 2 at 100 eV above the zinc absorption edge. Compression molded samples were dried in a vacuum oven for approximately 1 week at 70 °C and then transferred into a special shipping liquid nitrogen dewar for transport to the Stanford Synchrotron Research Laboratory (SSRL).

EXAFS measurements were made at SSRL on Beamline 2-3 using a double crystal monochromator tuned to the Si(111) reflection. Five electronvolt steps were used in the preedge and EXAFS regions, while 1 eV steps were used from 16 eV below the edge to 40 eV above the edge. Two different entrance slit widths were used (0.7 and 1 mm); however, this difference was found to have a negligible effect on EXAFS spectra. Energy calibration was performed with zinc foil. Incoming and outgoing X-ray intensities were monitored using nitrogen-filled 15 and 30 cm ionization chambers, respectively. A third chamber of 30 cm length was placed after the second chamber, and zinc foil was mounted between the second and third chambers to provide an energy reference for all samples. Five scans (each lasting approximately 20 min) were collected and added together after edge energy determination before further analysis to improve the signal-to-noise ratio. Samples were mounted in an Oxford Instruments continuous-flow liquid helium cryostat with the sample maintained at 20 K to reduce the mean-squared displacement. The data presented in this paper represent results from two experiments carried out at different times on the same beamline.

AUTOBK,[10] a commercial software package available from the University of Washington UWXAFS project, was used to convert the measured absorbance vs X-ray energy (E) curves to $k^2\chi(k)$ vs k according to the formula

$$\chi(k) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \qquad (2)$$

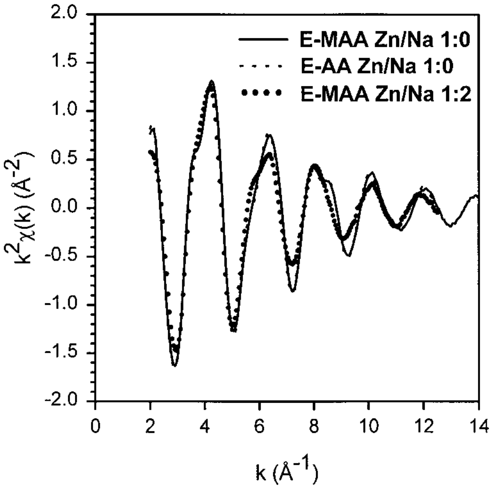

Figure 1. Plots of $k^2\chi(k)$ vs k for three ionomers: a zinc-neutralized E−MAA ionomer, a zinc-neutralized E−AA ionomer, and an E−MAA ionomer neutralized with equimolar amounts of zinc and sodium.

where $\mu(E)$ and $\mu_0(E)$ are the measured and mean absorption coefficients, respectively, at energy E. k is termed the wavevector and is given by

$$k = \sqrt{\frac{2m_e}{h^2}(E - E_0)} \qquad (3)$$

where E_0 is the absorption edge energy, m_e is the mass of an electron, and h is Planck's constant divided by 2π.

After isolation of the EXAFS oscillations and truncation of a spectrum to the region $k = 2-12.5$ Å^{-1}, the data set was Fourier transformed to obtain the radial structure function (RSF). The radial structure function is similar to a radial distribution function since peaks in the RSF usually correspond to distinct coordination shells. The abscissa of the RSF has units of angstroms, but locations of peaks are shifted from true interatomic distances; hence, a subscript F will be used to distinguish this distance from the actual interatomic distance R. Fitting of the data to model structures was performed using FEFFIT from UWXAFS in combination with FEFF7.[11] Error ranges on fitted parameters are outputs from FEFFIT. On the basis of experiments described in a previous publication,[8] the amplitude reduction parameter was set to 1.0 for all samples in this study.

Results and Discussion

Representative $k^2\chi(k)$ vs k spectra for three different samples shown in Figure 1 indicate a clear difference between the E−MAA ionomer neutralized with sodium and zinc relative to the two ionomers neutralized with just zinc. Figure 1 also shows the high data quality achieved in this experiment. To better visualize how changes in structure affect the arrangement of atoms around zinc, radial structure functions were calculated and will be presented throughout the remainder of this paper.

Figure 2 shows RSFs for the zinc-neutralized ionomers of Figure 1. Error bars represent one standard deviation calculated by averaging standard deviations for three different E−MAA ionomer samples measured at least three times each.[12] The errors in these experiments have the same functional dependence and slightly lower magnitude compared to the error calculate by Vaarkamp for PtO_2.[13] Since the peaks centered at $R_F \approx 1.5$ Å are identical, E−MAA and E−AA zinc ionomers both are 4-fold coordinated to oxygen. Qualitative differences exist between E−MAA and E−AA radial

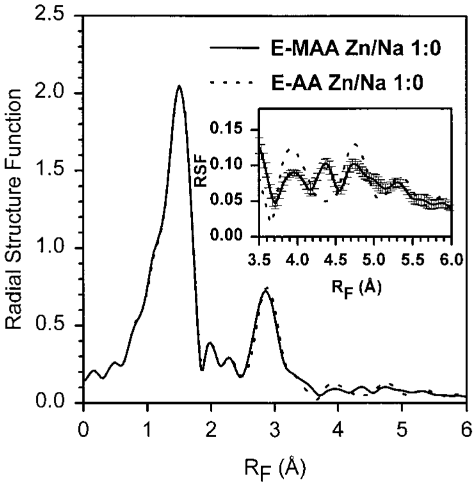

Figure 2. Radial structure functions of a zinc-neutralized E–AA ionomer and a zinc-neutralized E–MAA ionomer. Error bars in the inset represent one standard deviation calculated from 12 different spectra as described in the text. On the larger scale, error bars are roughly equivalent to the line thickness.

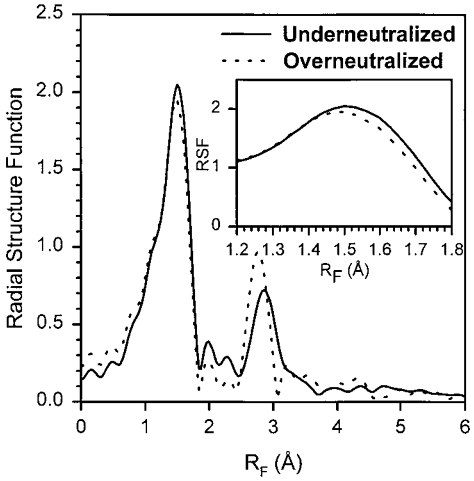

Figure 3. Radial structure function of E–MAA neutralized with 57% of the stoichiometric amount of zinc compared to RSF of E–MAA overneutralized with zinc acetate dihydrate to 170% of stoichiometric. The inset highlights the shift of the first-shell peak position toward lower R_F with overneutralization.

structure functions at higher R_F. These variations are most likely not due to differences in acid content or neutralization level since similar variations in zinc-neutralized E–MAA ionomers do not produce the qualitative differences shown in Figure 2. Almost certainly, the radial structure functions in Figure 2 are not identical because the acid structures are different, and hence the aggregate packing is affected slightly. These variations in RSFs are minor, and only very careful procedures enabled this variation to be distinguished from experimental error.

A more significant change in the arrangement of atoms occurs when the ionomer is overneutralized with zinc acetate dihydrate as shown in Figure 3. Using Excel Solver, the *k*-space spectrum of the overneutralized material was fit using linear combinations of the following experimental spectra: ionomer + zinc acetate dihydrate, ionomer + dried zinc acetate dihydrate, and ionomer + monoclinic anhydrous zinc acetate.[14] None of these combinations gave an acceptable fit to the data. Examining the RSF closely allows some quantitative observations, even if a detailed structural description for the overneutralized material cannot be provided. The very slight change in first-shell peak position indicates that the average first-shell zinc–oxygen distance is approximately 0.01 Å smaller in the overneutralized ionomer. The slight reduction in first-shell peak height for the overneutralized material indicates larger static (as opposed to thermal) variations in Zn–O distances. In other words, the four oxygen atoms coordinated to one zinc atom are at slightly different individual average distances, and/or different zinc atoms have different average zinc–oxygen distances. The change in peak position for the peak centered at $R_F \approx 3$ Å indicates a change in the average position of carboxylate anions. The significant increase in height and shift to lower R_F suggests more uniform carbon and noncoordinating oxygen distances. This latter conclusion is more speculative since changes in interference effects and multiple scattering can cause nonintuitive changes in next-nearest-neighbor spectral features.

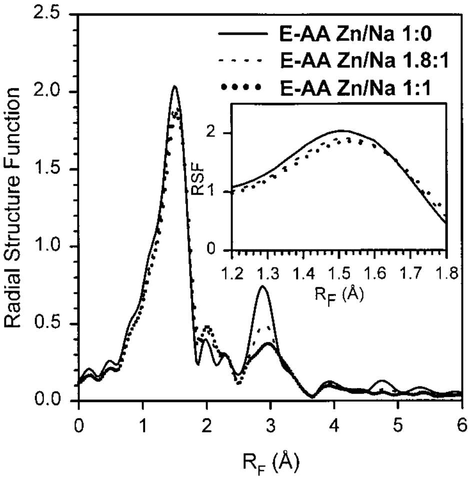

Figure 4. Radial structure functions for three E–AA ionomers at Zn/Na ratios indicated in the legend. The inset highlights the shift of the first-shell peak position toward higher R_F with increasing sodium content.

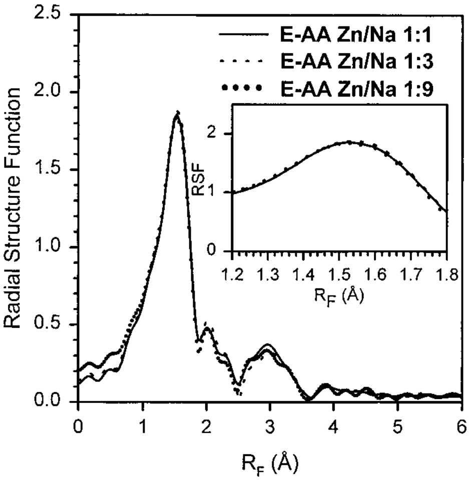

Figure 5. Radial structure functions for three E–AA ionomers at Zn/Na ratios indicated in the legend. The curves are essentially identical, indicating the arrangements of atoms around zinc in these materials are also identical.

Even more dramatic shifts in radial structure functions are found in Figures 4–7. Figure 4 shows the effect of an increase in sodium content on the RSF for E–AA ionomers. Two features require special mention: the

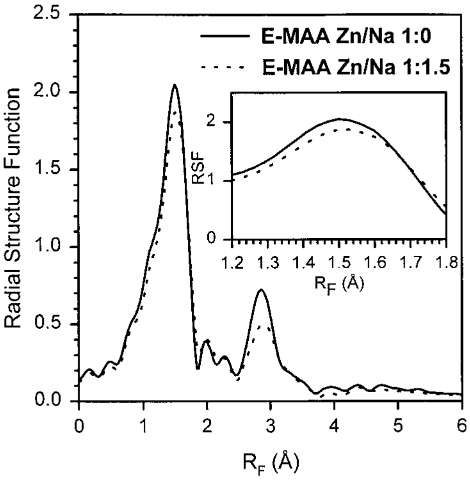

Figure 6. Radial structure function of E−MAA ionomer neutralized with only zinc compared to radial structure function of E−MAA ionomer with equimolar amounts of zinc and sodium. Compare Figure 6 and Figure 4.

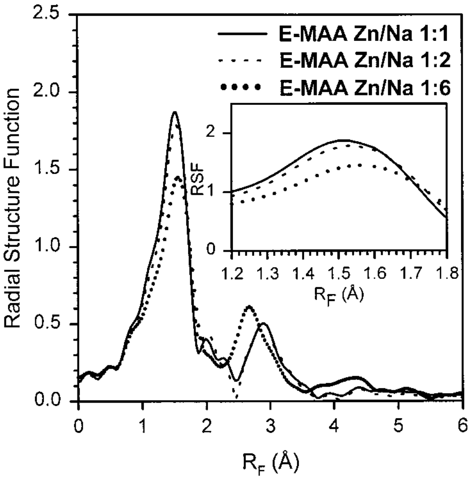

Figure 7. Radial structure functions for three E−AA ionomers at Zn/Na ratios indicated in the legend. Compare Figure 7 and Figure 5.

peak due to first-shell oxygen atoms clearly shifts toward higher distances and decreases in height while the peak centered at $R_F \approx 3$ Å decreases in height. Figure 5 indicates no alteration in local environment around zinc as the Zn/Na mole ratio varies from 1:1 to 1:9. Figures 6 and 7 show the same patterns, but for E−MAA ionomers. Comparing Figures 4 and 6, qualitative changes for the two ionomers are identical at comparable cation ratios. Figures 5 and 7 provide a stark contrast: no change in local environment for E−AA ionomers as the Zn/Na ratio varies from 1:1 to 1:9 and dramatic changes for E−MAA ionomers as the Zn/Na ratio varies over a similar range.

If two cations are mixed in the same ionomer, the EXAFS patterns of one cation (in this case Zn^{2+}) will exhibit one of three possible alternatives as the cation ratio varies. The first possibility is that the two cations do not mix and the EXAFS pattern does not change. This situation occurs when the two cations are Zn^{2+} and H^+ in E−MAA as shown in a previous publication.[8] The second possibility is that spectra change over some continuum; i.e., the cation is in many different environments, and the sum of the EXAFS patterns from each of these environments weighted appropriately yields the resultant EXAFS pattern. Since the relative distribution of the different arrangements changes as the cation ratio changes, the RSFs are different at all cation ratios. This situation is represented by E−MAA neutralized with Na^+ and Zn^{2+} as shown in Figures 6 and 7. The third and final possibility is the formation of a new aggregate, which most likely contains both cations. As the concentration of the absorbing cation decreases, EXAFS spectra change over a continuum as the pattern shifts from one characteristic of the pure aggregate to one characteristic of the mixed-cation aggregate. Eventually, the pattern does not change because all the absorbing atoms are contained within the new aggregate. This situation is represented by E−AA neutralized with Na^+ and Zn^{2+} as shown in Figures 4 and 5.

Because E−MAA neutralized with Zn^{2+} and Na^+ has a mixture of many different types of aggregates, only semiquantitative information is available about internal aggregate morphology. The shift in first-shell peak position toward higher R_F indicates the presence of 5-fold and 6-fold oxygen coordination, since in zinc−oxygen compounds an increase in coordination number is coupled with an increase in average zinc−oxygen distance.[15] The dramatic increase in height and the shift toward lower R_F for the peak at $R_F \approx 3$ Å in 1:9 Zn/Na seemingly indicates a substantial decrease in the variation of carboxylate positions, which would seem to be contradictory to the increase in variation of first-shell zinc−oxygen distances. However, the crystal structure of monoclinic anhydrous zinc acetate has large variations in average carboxylate positions; therefore, reducing this variation even while introducing disorder in the first coordination shell is not impossible.

The very large variation in zinc−oxygen distances for the 1:9 Zn/Na material can only mean that the number of coordinating oxygen atoms varies from zinc atom to zinc atom. The change was so dramatic that modeling was necessary to be sure that a reasonable combination of zinc−oxygen distances with reasonable mean-squared displacements could produce this pattern. Atomic positions were taken from the structure of monoclinic anhydrous zinc acetate[9] (4-fold oxygen coordination), monoaquobis(acetylacetonato)zinc (5-fold oxygen coordination),[16] and zinc acetate dihydrate (6-fold oxygen coordination).[17] The relative weights of the three different oxygen coordination structures were allowed to vary in FEFFIT as follows:

$$\text{spectra}_{\text{E-MAA Zn:Na 1:9}} = x_1\text{FEFF}_{4\text{ oxygen atoms}} + x_2\text{FEFF}_{6\text{ oxygen atoms}} + (1 - x_1 - x_2)\text{FEFF}_{5\text{ oxygen atoms}}$$

Mean-squared displacements were fixed at the average value for E−MAA pure zinc ionomers since fitting of experimental spectra from zinc oxide, monoclinic anhydrous zinc acetate, and zinc hydroxide indicates that the best-fit mean-squared displacement does not vary substantially for a zinc−oxygen first coordination shell at 20 K. With three adjustable parameters (x_1, x_2, and the edge energy E_0), the best-fit result is displayed in Figure 8. The generally correct description shows that the EXAFS pattern for E−MAA Zn/Na 1:9 could be produced by many different oxygen coordination environments for zinc. The model was not expected to be perfect since more than three different environments might exist for zinc in this system. Further, even if only three environments existed, the position of the oxygen atoms might not be described by the positions given by the three compounds.

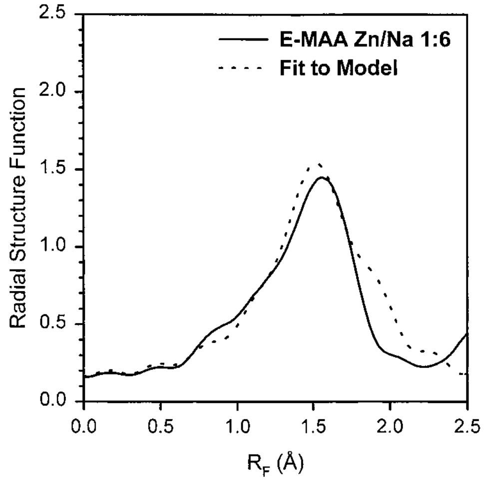

Figure 8. Radial structure function for E−MAA Zn/Na 1:9 along with best-fit spectrum. The fitting structures and the meaning of *x* are given in the text; for the theoretical RSF above $x_1 = 0.40 \pm 0.33$, $x_2 = 0.34 \pm 0.18$.

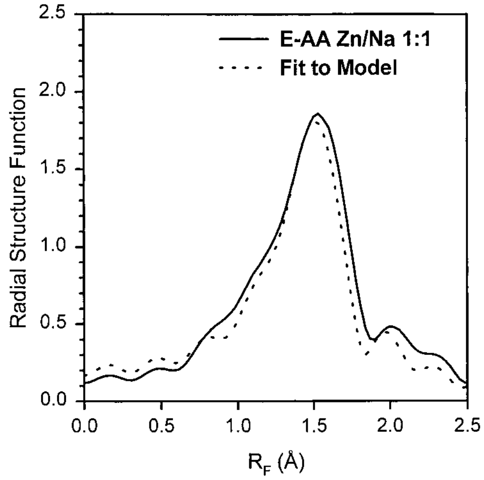

Figure 9. Radial structure function for E−AA Zn/Na 1:1 along with best-fit spectrum using a combination of 4-fold and 6-fold coordinating oxygens. For the theoretical RSF above, the fraction of 4-fold coordinated oxygen was 0.92 ± 0.04.

Modeling also gives substantial insight into the new coordination structure present in the mixed-cation E−AA ionomer represented by the radial structure functions displayed in Figure 5. One possibility is that a new 4-fold oxygen coordination environment exists around zinc. On the basis of modeling, the average zinc−oxygen distance in this new environment would be about 1.99 Å. The static variation in zinc−oxygen distances must be larger than in monoclinic anhydrous zinc acetate. In other words, zinc−oxygen distances in this new structure vary more than from 1.949 to 1.965 Å. EXAFS cannot distinguish between the possibility that zinc has one coordination environment with four different distances or multiple 4-fold coordination environments with varying distances.

Another possibility, supported by modeling as shown in Figure 9, is that zinc has two different coordination environments: one with 4-fold oxygen coordination and another with 6-fold oxygen coordination. Atomic positions used in modeling were described previously. The pattern cannot be described by five oxygen atoms with a physically reasonable mean-squared displacement, nor can it be described by a combination of four and five oxygen atoms or five and six oxygen atoms. As indicated in the caption of Figure 9, the ratio of atoms in a 4-fold coordination environment to those in a 6-fold coordination environment is roughly 10:1.

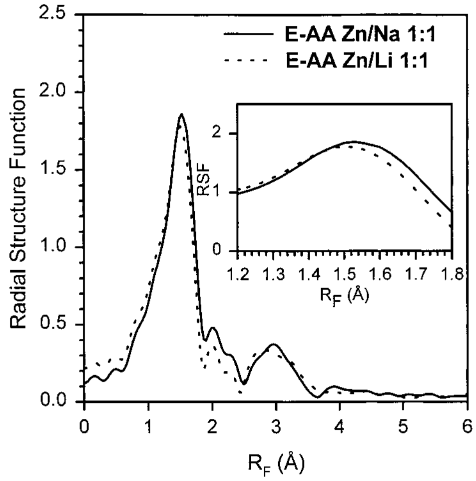

Figure 10. Radial structure function for E−AA ionomer neutralized with equimolar amounts of zinc and lithium compared to RSF for E−AA ionomer neutralized with zinc and sodium.

Zinc-edge EXAFS is not sensitive enough to conclude Na^+ is in the same aggregate with Zn^{2+} in E−AA ionomers, because sodium is not a strong backscatterer. Unless bridging oxygens are present, Na^+ would be at least 5−6 Å away from its nearest zinc atom. However, the addition of Na^+ leads to the formation of a new aggregate, which is the only zinc-containing aggregate in the system at Zn/Na ratios less than 1:1. This observation almost certainly means that the two cations are contained within the same aggregate. Further, lithium also disrupts the local structure as shown in Figure 10 but differently than sodium. The difference between sodium and lithium's effect on the local structure of zinc supports the conclusion that monovalent and divalent cations are in the same aggregate.

A complete description of this behavior must also include why this structure forms in E−AA ionomers, but not in E−MAA ionomers. The most likely reason is that the methyl groups interfere with atomic packing, not allowing the mixed-cation structure to form. One potential structure, supported by the data but definitely not the only possibility, consists of a central 6-fold coordinated zinc atom surrounded by sodium atoms. The sodium atoms would be in turn surrounded by zinc atoms 4-fold coordinated to oxygen, with carboxylate groups between each layer and perhaps waters of hydration where necessary. This structure is consistent with the dramatic changes in the RSF peak at $R_F \approx 3$, since the introduction of sodium atoms would significantly perturb the positions of the carboxylate anions.

A small molecule with the formula $Zn(C_2H_3O_2)\cdot 2Na(C_2H_3O_2)\cdot 4H(C_2H_3O_2)$[18] does exist, and its structure would serve as an excellent model for the partially neutralized mixed-cation ionomer. Unfortunately, the crystal structure for this material could not be located. In a previous paper examining E−MAA mixed-cation ionomers based on IR spectroscopy,[19] a possible structure with four oxygen atoms around zinc and six oxygen atoms around sodium was proposed. This structure is clearly not the only structure in mixed-cation E−MAA ionomers; however, for mixed-cation E−AA ionomers this arrangement offers intriguing possibilities. This structure is consistent with EXAFS data presented here, and sodium EXAFS could determine whether the 6-fold coordination structure to sodium is correct.

Differences in aggregate structure also provide insight into the observed differences in rheological behavior between E−AA and E−MAA ionomers. Adding ionic groups to an un-ionized polymer increases the viscosity significantly, in many cases orders of magnitude. Hence, the strength of ionic associations significantly influence melt viscosity. For E−MAA ionomers, the ability of the mixing rule to describe the viscosity behavior suggests that a significant amount of pure Zn aggregates and pure Na aggregates is present at all Zn/Na ratios, consistent with EXAFS results. In fact, the mixing rule is not obeyed exactly for E−MAA ionomers, and some small "MI uplift" can be measured.[20] This behavior is consistent with EXAFS as well, since EXAFS results indicate some new structures must be forming. For E−AA ionomers, EXAFS results indicate clearly that the system is not a mixture of pure zinc and pure sodium aggregates, and hence the mixing rule will fail. Changes in MI indicate that the new aggregate in the mixed-cation system is weaker than either a pure Zn or pure Na aggregate. In other words, the synergistic viscosity behavior in mixed-cation E−AA ionomers occurs because a weak sodium−zinc aggregate forms.

As the Zn/Na mole ratio decreases in E−AA, the mole ratio at which the EXAFS pattern becomes only that of the new aggregate (Zn/Na = 1:1) could represent the mole ratio of cations inside the mixed-cation aggregate if the minimum in viscosity occurs at this mole ratio. The minimum in viscosity does in fact occur at a Zn/Na mole ratio of 1:1;[3,5] however, this fact does not absolutely prove that the zinc:sodium ratio inside the new aggregate is 1:1. Sodium-edge EXAFS can be used to determine this mole ratio absolutely, and experiments are currently planned. However, whether sodium EXAFS will be useful in these mixed-cation systems is not certain, since L absorption edges from zinc could interfere with sodium EXAFS spectra.

Summary

The local environment around zinc in ethylene-based ionomers differed with carboxylate anion repeat structure, overneutralization, and coneutralizing cation. The difference was shown to be very small in the former and was probably due to the small difference in acid repeat unit structure. The effects of overneutralization with zinc acetate dihydrate were much larger and were not simply a linear combination of the ionomer structure and the structure of the neutralizing salt.

A qualitative difference between E−AA and E−MAA ionomers neutralized with zinc and sodium was found. In E−AA ionomers at Zn/Na mole ratios from 1:1 to 1:9, the arrangements of atoms around zinc were identical, indicating the formation of a new type of aggregate. This aggregate probably contains both sodium and zinc and, on the basis of rheological behavior, is significantly weaker than either a pure sodium or pure zinc aggregate. In contrast, the arrangement of atoms around zinc in E−MAA mixed-cation ionomers over this cation range changes with Zn/Na ratio. Most likely significant amounts of zinc are contained within pure zinc aggregates at most mole ratios; however, zinc exists in other coordination environments as well.

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References and Notes

(1) Eisenberg, A., King, M., Eds. *Ion Containing Polymers*; Halsted-Wiley: New York, 1975.
(2) Register, R. A.; Prud'homme, R. K. Melt Rheology. In *Ionomers: Synthesis, Structure, Properties and Applications*; Tant, M. R., Mauritz, K. A., Wilkes, G. A., Eds.; Blackie Academic and Professional: New York, 1997.
(3) Permentier, D.; Jozef, C.; Tengkumahamad, M. International Patent Application 94/01469, 1994.
(4) Register, R. A., unpublished data.
(5) Grady, B. P.; Cooper, S. L. *Macromolecules* **1994**, *27*, 6627.
(6) Grady, B. P.; Moore, R. B. *Macromolecules* **1996**, *29*, 1685.
(7) Teo, B. K. *EXAFS: Basic Principles and Data Analysis*; Springer-Verlag: New York, 1986.
(8) Grady, B. P.; Floyd, J. A.; Genetti, W. B.; Vanhoorne, P.; Register, R. A. *Polymer* **1999**, *40*, 283.
(9) Clegg, W.; Little, I. R.; Straughan, B. P. *Acta Crystallogr.* **1986**, *C42*, 1701.
(10) Newville, M.; Līviņš, P.; Yacoby, Y.; Rehr J. J.; Stern, E. A. *Phys. Rev. B* **1993**, *47*, 14126.
(11) Zabinsky, S. I.; Rehr, J. J.; Ankudinov, A.; Albers R. C.; Eller, M. J. *Phys. Rev. B* **1995**, *52*, 2995.
(12) Data points having the same x value were averaged in R space because error bars are simple to calculate and have clear meaning. However, data should **only** be averaged in R space if the radial structure functions are identical. In other words, the radial structure function calculated by averaging radial structure functions from two different compounds is meaningless. EXAFS data from different local environments can be linearly combined, but the mathematical operation must be performed in k space, not in R space.
(13) Vaarkamp, M. *Catal. Today* **1998**, *37*, 271.
(14) The RSF for dehydrated zinc acetate dihydrate was not identical to the RSF for monoclinic anhydrous zinc acetate. Drying of the former was not necessarily complete; further complete drying under the conditions described in the paper will not necessarily yield monoclinic anhydrous zinc acetate.
(15) Pan, H. K.; Knapp, G. S.; Cooper, S. L. *Colloid Polym. Sci.* **1984**, *262*, 734.
(16) Montgomery, H. A.; Lingafelter, E. C. *Acta Crystallogr.* **1963**, *16*, 748.
(17) Van Niekerk, J. N.; Schoening, F. R. L.; Talbot, J. H. *Acta Crystallogr.* **1953**, *6*, 720.
(18) Davidson, A. W.; McAllister, W. H. *J. Am. Chem. Soc.* **1930**, *52*, 519.
(19) Tachino, H.; Hara, H.; Hirasawa, E.; Kutsumizu, S.; Yano, S. *Macromolecules* **1994**, *27*, 372.
(20) Hall, M., private communication.

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