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Morphology of Zinc-Neutralized Maleated Ethylene−Propylene Copolymer Ionomers: Structure of Ionic Aggregates As Studied by X-ray Absorption Spectroscopy

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ABSTRACT: X-ray absorption spectroscopy (EXAFS) was used to characterize zinc-neutralized ionomers made from ethylene−propylene copolymers with grafted maleic anhydride units (Zn-MAn-*g*-EPM). The structure of the zinc moieties in the dry system consisted of two chelating carboxylate groups around one zinc atom—a structure much different than if the carboxylate anions come from acrylic or methacrylic acid. These self-contained zinc−two chelating carboxylate structures assemble into a larger superstructure as shown in a previous SAXS study, which indicated that the microphase-separated ionic aggregates are ~2 nm. This superstructure must therefore contain significant amounts of nonionic material, consistent with the observation that the superstructure also forms in the unneutralized maleic anhydride precursor. After addition of water, zinc atoms in the sample with 10% of the carboxylate groups neutralized were fully solvated, i.e., zinc was surrounded by six water molecules. Zinc atoms in samples with higher neutralization levels had two carboxylate oxygens replaced by water oxygens, which in turn maintained the zinc coordination number at four.

Introduction

Ionomers are polymers with a small mole fraction of chemically bonded ionic moieties attached as side chains to the polymer backbone. The ionic groups can be based on either anions, such as carboxylate or sulfonate groups, or cations, such as quaternary amine groups. In the case of anionic groups, a metal cation must be neutralizing at least some of the anions in order for the material to be termed an ionomer. The most important commercial examples of ionomers are copolymers of ethylene and either acrylic or methacrylic acid neutralized with zinc or sodium. The ionic groups microphase separate into ionic-rich domains, which typically cause an increase in clarity, toughness, and viscosity in comparison to the unneutralized copolymer.

The ionomers that are the focus of this study are similar to ethylene−carboxylate ionomers discussed above in that carboxylic acid groups are distributed along a polyolefin backbone. However, in this study the ionomers are made from noncrystalline copolymers of ethylene and propylene followed by postpolymerization grafting with maleic anhydride. Subsequent hydrolysis of the maleic anhydride functionality leads to the formation of two carboxylic acid moieties on the propylene,[1] and these carboxylate groups can in turn be neutralized with a metal cation. 100% neutralization would imply that all acid groups have an associated metal cation, i.e., no neutralizing hydrogen atoms.

Ionomers made from zinc-neutralized maleic anhydride grafted ethylene−propylene copolymers (Zn-MAn-*g*-EPM) were part of an extensive small-angle X-ray scattering (SAXS) and NMR study by two of the coauthors of this paper.[1,2] These materials had a qualitative change in the scattering pattern between 25 and 50% neutralization. Samples with 25% neutralization and below had a maximum in intensity of the scattering peak due to the ionic aggregates at one constant scattering vector q while this peak shifts to a second, constant, and lower q for 50, 75, and 100% neutralization. The Yarusso−Cooper[3] model was used to fit the data, and the observed shift was associated with larger values of the ionic aggregate radius and the closest approach radius in the model.

The maximum of the scattering peak for the Zn-MAn-*g*-EPM was at q values as small as $q = 0.05$ Å^{-1}, which is at much lower q than in most ionomers. For example, in copolymers of ethylene and methacrylic acid neutralized with zinc, the maximum of the scattering peak was found around $q = 0.3$ Å^{-1}, while for the noncrystalline carboxylated polystyrene neutralized with zinc, the q values were between 0.15 and 0.2 Å^{-1}.[4] The difference between the Zn-MAn-*g*-EPM ionomers and these two ionomers was not due to differences in ionic contents; the equivalent acid values per weight of polymer (χ) were in the same ranges for all materials. Modeling with the Yarusso−Cooper model supports the hypothesis that the scattering entities in Zn-MAn-*g*-EPM were on the order of 3−6 times larger than the scattering entities in these other carboxylate-containing ionomers. This size range was further supported by solid-state NMR results.[1]

The arrangement of atoms inside the aggregate must allow for large aggregates in Zn-MAn-*g*-EPM ionomers. The arrangement of atoms inside the aggregates for the ethylene−methacrylic acid ionomers, as well as the

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ethylene−acrylic acid ionomers, was extensively studied by one of the coauthors using X-ray absorption spectroscopy (XAS).[5−8] Zinc atoms are 4-fold coordinated to oxygen, with each oxygen coming from a different carboxylate group. For a given carboxylate group, the other oxygen coordinates to a second zinc atom, and the result is a planar-type structure where all zinc atoms lie (or nearly lie) in a plane and oxygen atoms lie above and below the plane.[5] This structure is similar to that of monoclinic anhydrous zinc acetate,[9] and the tightness of this structure implies that polymer chains cannot be part of the aggregate; rather, they are found above and below the plane of the zinc atoms. The overall size was found to be on the order of a few nanometers, consistent with recent transmission electron microscopy data.[10] The addition of water causes only a very slight change in the aggregate structure, which was attributed to the replacement of a coordinating carboxylate group at the edge of an aggregate with a coordinating water molecule.[6] In other words, adding water does not seriously disrupt the arrangement of atoms inside the zinc aggregate. This situation is in direct contrast to the situation in zinc-neutralized sulfonated polystyrene ionomers, where the addition of water causes the complete solvation of zinc so that zinc becomes surrounded by six water molecules[6] as in zinc benzenesulfonate hexahydrate.[11]

Although the carboxylate anion is the same, Zn-MAn-*g*-EPM ionomers are different from the ethylene−carboxylate ionomers in that two carboxylate groups are nearby to one another, i.e., on the same repeat unit. At neutralization levels greater than 50%, the energy involved in having these two nearby anions involved in a “planar” structure like that of monoclinic zinc acetate would very likely be high, to the point where such an arrangement is expected to be highly unfavorable. Another difference is that in the unneutralized (i.e., the neutralizing cation is hydrogen or the groups exist as anhydride linkages) Zn-MAn-*g*-EPM polymer the carboxylate anions are microphase separated according to SAXS experiments, while no evidence supports the carboxylate anions being microphase separated in the ethylene−carboxylate ionomers. The purpose of this current study is to explore the arrangement of atoms inside the Zn-MAn-*g*-EPM ionomers as a function of neutralization level and water content and interpret this information in light of results from SAXS experiments as well as studies of other ionomers.

Experimental Section

Materials. Synthesis and detailed characteristics of the materials are found in ref 2. The parent copolymers contain 45 wt % ethylene and 55 wt % propylene, and the degree of grafting (DG) represents the weight fraction of maleic anhydride/total weight of polymer. To convert to equivalent acid per unit weight, the following equation applies:

$$\chi = \frac{\text{DG}}{100\%} \frac{1000}{M_{\text{MAn}}} \times 2$$

The degree of neutralization (DN) represents the fraction of acid groups neutralized with zinc cations, assuming all of the anhydride moieties are converted to acid groups.

To prepare the samples for EXAFS measurement, the samples were dried overnight under vacuum at 80 °C, after which the samples were compression-molded at 150 °C. The samples were then placed back in the vacuum oven. The thus obtained dry samples were quenched in liquid nitrogen before packaging the samples in a shipping dewar at ∼79 K for shipment to the Stanford Synchrotron Radiation Laboratory (SSRL). Upon arrival at SSRL, these dry samples were warmed under vacuum where they remained until measurement. Wet samples were prepared in exactly the same manner, except that after removal from the vacuum oven the samples were immediately immersed in water and remained there until removal immediately before measurement. The time of immersion was long enough to produce a sample with the equilibrium level of water absorption unless otherwise indicated.[12] Wet samples with varying immersion times were shipped to the synchrotron in the same manner as the dry samples and then were immersed in 18 MΩ water for the time indicated immediately prior to measurement.

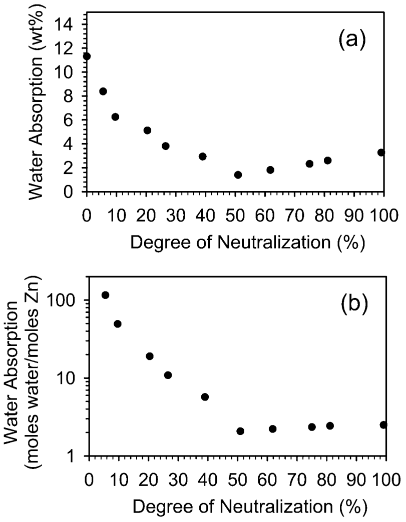

Figure 1. Equilibrium water absorption as a function of degree of neutralization for zinc ionomers based on MAn-*g*-EPM (DG = 7.33 wt %): (a) water absorption expressed in wt % and (b) water absorption expressed in mol water/mol Zn.

One important issue related to these materials is the state of the unneutralized acid groups; some of the acid groups could actually be anhydride moieties. The state of these groups depends on the treatment applied. Certainly for the wet samples, i.e., the samples with added water, hydrolysis has occurred and acid groups are present. During neutralization, water is used, and at the end of the neutralization procedure unneutralized acid groups are probably present as well. However, this neutralization procedure is followed by a drying step at 80 °C, which converts some of the unneutralized acid groups back to the anhydride, depending on the neutralization level. Figure 1 shows that for the unneutralized sample the amount of water absorbed is much greater than the amount necessary to hydrolyze the anhydride moieties, and hence the carboxylic acids must be absorbing water. Note that this behavior is very different than in the ethylene−carboxylate materials; the amount of absorbed water is negligible when only carboxylic acids are present.

XAS Measurements. Measurements were performed at the SSRL on beamline 2-3 in transmission at a temperature of ∼20 K. Three ionization chambers were used to monitor the X-ray intensity; the sample was placed between the first and second ionization chambers while zinc foil was placed between the second and third ionization chambers. A total of 5−10 scans, each lasting approximately 30 min, were collected, and the scans were averaged after edge energy determination to improve the signal-to-noise ratio. The number of scans was adjusted so that more scans were collected for samples with less zinc content. Only the EXAFS region (greater than ∼10 eV above the edge) spectra are analyzed and shown; near-edge spectra showed no significant changes.

The theory behind EXAFS is discussed in detail elsewhere[13] and will not be described here. Model fitting has an extremely important role in this study, and important issues will be highlighted throughout the presentation and discussion of results. The program FEFF7[14] was used to determine theoreti-

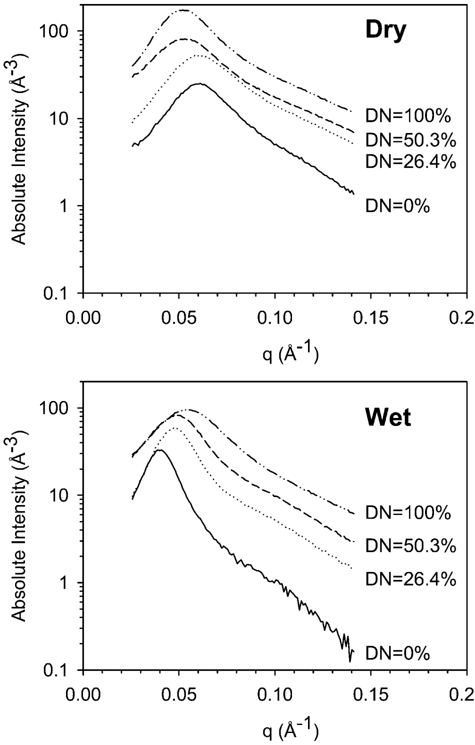

Figure 2. SAXS patterns for dry samples and samples swollen to their equilibrium states. The numbers to the right of the curves refer to neutralization levels. All samples have a degree of grafting (DG) of 7.33 wt %.

cal EXAFS patterns for fitting to experimental data. EXAFS oscillations were determined from the raw absorption data using AUTOBK, version 2.65,[15] while FEFFIT, version 2.54,[15] was used to fit expressions generated from FEFF7 to the experimental data. The amplitude reduction factor was set to 1.0 based on fits to molecules with known crystal structures. The EXAFS oscillations are not shown in this paper; rather, the Fourier transform of these oscillations is shown, which has been termed the radial structure function. Radial structure functions are similar to radial distribution functions; however, peak heights and positions in the former depend on many factors, including the identity of the particular atom.

SAXS Measurements. SAXS data of fully hydrated samples were collected at beamline 8.2 of the Synchrotron Radiation Source (SRS) at the CLRC Daresbury Laboratory, Warrington, UK. A complete description of the details regarding measurement protocol and experimental setup is given in ref 2. The Yarusso−Cooper model was used to analyze the resulting scattering patterns. This model is based on a liquidlike interference between spherical scattering objects, where the radius of closest approach (R_{CA}) is different than the radius of the scattering object (R_1). The two other fitted parameters in this model are the volume per aggregate (V_p), which is the inverse of the number density of aggregates, and the electron density difference between the scattering object and the matrix ($\rho_1 - \rho_0$).

Results and Discussion

There were two main objectives of this work: a study of Zn-MAn-*g*-EPM polymers as a function of molar degree of substitution and neutralization level and a study of these same materials after the addition of water. Figure 2 shows SAXS patterns of the ionomers after full water hydration; there are significant changes compared to the patterns of the dry ionomers, which are also shown and appeared previously in ref 2. The scattering peak shifts to lower q values with added water for all samples. For 100% neutralization, there is a large drop in scattered intensity with added water while the shift of the peak is marginal. Such a drop is most likely due a decrease in electron density with little other effect, and the modeling shown in Table 1 supports this conclusion. For 50% neutralization, the intensity of the peak is almost constant, while the peak position shows a shift from $q = 0.053$ Å^{-1} to $q = 0.048$ Å^{-1}. The peak shift with added water toward lower q values continues with the 25% and 0% neutralized samples. Application of Bragg's law as well as more sophisticated modeling represented by Table 1 suggests that the distance between aggregate centers is becoming larger with added water. This observation probably implies that more ionic material is becoming part of the matrix and/or smaller aggregates are coalescing into larger ones.

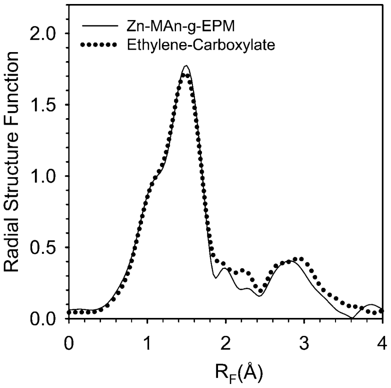

Figure 3. Comparison of the EXAFS patterns of a zinc ethylene−methacrylic acid copolymer ionomer containing 11 wt % methacrylic acid neutralized to 1% of stoichiometric with the Zn-MAn-*g*-EPM ionomer having a DG of 7.33 wt % and neutralized to 50% of stoichiometric. The data for the Zn-MAn-*g*-EPM ionomers shown in Figures 3 and 5 are not the same because the data reduction procedures were different. Data from the ethylene−carboxylate sample required a different reduction procedure because of the low zinc content. To eliminate differences due to this procedure, data from the Zn-MAn-*g*-EPM ionomer were treated identically to the ethylene−carboxylate data for this plot only.

Table 1. Best-Fit Parameters of the Yarusso−Cooper Model for DG = 7.33 wt % Material

water saturated	DN (%)			
	0	25	50	100
q_{peak} (Å^{-1})	0.041	0.048	0.048	0.051
R_1 (Å)	41.11	30.23	30.34	25.99
R_{CA} (Å)	69.72	59.21	56.89	50.2
V_p (Å^3)	1.76×10^6	1.11×10^6	1.40×10^6	1.08×10^6
ρ (e$^-$ Å^{-3})	0.024	0.059	0.092	0.141
$R_{CA} - R_1$ (Å)	28.61	28.98	26.55	24.21
dry				
q_{peak} (Å^{-1})	0.061	0.061	0.053	0.052
R_1 (Å)	23.96	21.63	24.78	25.3
R_{CA} (Å)	46.04	25.77	52.06	53.41
V_p (Å^3)	6.18×10^5	6.71×10^5	1.32×10^6	1.06×10^6
ρ (e$^-$ Å^{-3})	0.062	0.13	0.162	0.187
$R_{CA} - R_1$ (Å)	22.08	24.14	27.28	28.11

EXAFS is typically used to determine the arrangement of atoms around a central atom, in this case zinc. Figure 3 shows that the 50% neutralized sample with a DG of 7.33 wt % has an EXAFS spectrum identical to the spectrum of an ethylene−carboxylate ionomer at a very low neutralization level, within the experimental error of the latter. As shown previously,[5] at neutralization levels used commercially zinc atoms in ethylene carboxylate ionomers are "associated" via oxygen atoms from the same carboxylate anion, i.e., two oxygen atoms from the same carboxylate group are attached to two

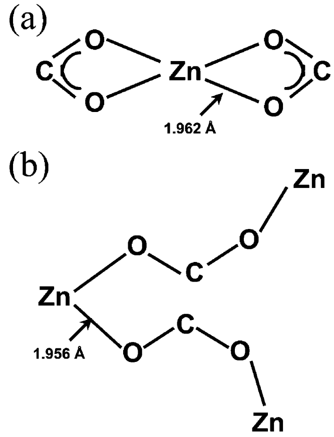

Figure 4. Schematic representations of (a) nonassociated and (b) associated zinc atoms. The former represents the structure of the ionomers represented in this study, while the latter represents the structure of ethylene−carboxylate ionomers at sufficiently high neutralization levels. Although there is a small difference in the average Zn−O distance for the two structures, the more substantial difference according to EXAFS is the variation of this distance; in the nonassociated structure the variation is much larger than in the associated structure. For a more detailed version of the associated structure, see ref 5.

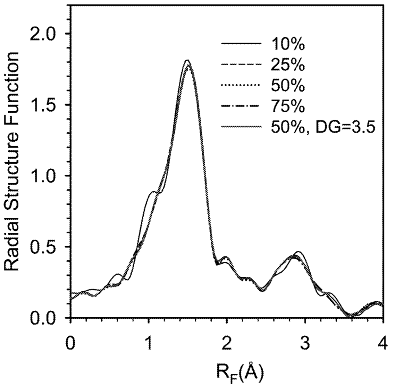

Figure 5. EXAFS patterns for dry Zn-MAn-*g*-EPM samples. The legend refers to the neutralization level. All samples have a degree of grafting (DG) of 7.33 wt % except where indicated.

different zinc cations. At low enough neutralization levels, however, zinc cations in ethylene−carboxylate ionomers must be “nonassociated” in the sense that the zinc atom is coordinated to two chelating carboxylate cations if no water is present. These two situations are represented schematically in Figure 4. The question to be asked is the following: is the composition low enough in the ethylene−carboxylate ionomer sample represented in Figure 3 so that only nonassociated zinc cations are present? Two different low neutralization levels (0.5 and 1%) had identical EXAFS patterns within experimental error, which were different than the patterns for samples at higher neutralization levels, indicating that the zinc-neutralized ethylene carboxylate ionomer spectrum shown in Figure 3 does represent only nonassociated zinc cations. Hence, Figure 3 shows conclusively that at sufficiently high neutralization levels four oxygen atoms from two chelating carboxylate anions surround zinc in the Zn-MAn-*g*-EPM ionomers.

Figure 5 shows how the EXAFS patterns are identical for all the materials except for the material with 10% neutralization, and the change at this low neutralization level is very slight. This identification is consistent with the hypothesis above, namely a chelated structure will have no change in EXAFS pattern with neutralization level. A change with neutralization level does occur with the structure shown in Figure 4b, which was attributed to a change in aggregate size with neutralization level (which in turn changes the fraction of zinc atoms at the edge of an aggregate and hence the average EXAFS pattern).[8] The difference between the 10% neutralized materials and the others is almost certainly in the nature of the chelation. Figure 6 shows the six different possibilities for the immediate environment around zinc. Structure **1** is not possible because the bond angles and distances would be too distorted. At low enough neutralization levels, possibility **2a** will occur since all of the other possibilities require nearby zinc atoms. **2b** and **2c** allow for optimal hydrogen bonding since, as shown by the dotted line, the O· · ·H distance can be set independently from Zn−O distances. In structure **2a**, the O· · ·H and Zn−O distances cannot be set independently of one another. Hence, **2b** and **2c** should be preferred at sufficiently high neutralization levels. Hence, the small difference between 10% neutralization and other samples is almost certainly due to the fact that some of structure **2a** occurs in the former but not in the latter. This argument implies that the driving force to optimize hydrogen bonding in structure **2a** has a small, but noticeable, effect on Zn−O coordination—a conclusion that is not unreasonable. EXAFS cannot be used to distinguish between possibilities **2b** and **2c**, nor can it distinguish between possibilities **3a** and **3b**. EXAFS does indicate that at least one between **2b** and **2c**, and one between **3a** and **3b** has the same arrangement of atoms around zinc since the EXAFS pattern does not change as the neutralization level varies toward 100%.

The difference in spectra between these Zn-MAn-*g*-EPM ionomers and commercial ethylene−carboxylate ionomers presented previously[5] has important implications. Essentially, the aggregate structure has been altered simply by altering the placement of ionic groups; the equivalent weight, the ionic moiety, and the degree of neutralization are identical or nearly identical. As an example of the importance of this statement, this work indicates that if partially neutralized ethylene−carboxylate ionomers contain adjacent acrylic or methacrylic acid units, then these units should have at most one of the carboxylate anions neutralized since the preferred arrangement cannot be formed. As another example, this difference shows that one way to alter aggregate size without changing neutralization level or amount of acid repeat units is to alter the placement of those units along the polymer backbone.

The structure of two chelated carboxylate anions to one tetrahedrally coordinated zinc cation has not been found in any small molecule to our knowledge, and hence modeling must be used to determine the characteristics of this structure. To determine the Zn−O bond distance and the mean-squared displacement (MSD, the square of the average variation in Zn−O bond distance), FEFF7 was used to model the system assuming all four oxygen atoms are at the same distance and in a tetrahedral arrangement. The Zn−O bond distance was determined to be 1.9617 Å, which is a bit longer than the average Zn−O bond distance of 1.9564 Å in anhydrous monoclinic zinc acetate.[9] The error in the determination due to fitting uncertainties is roughly 0.005 Å. The peak height at $R_F \approx 1.5$ Å is much smaller for nonassociated zinc cations (Figure 4a) vs zinc cations contained in the extended zinc structure (Figure 4b),

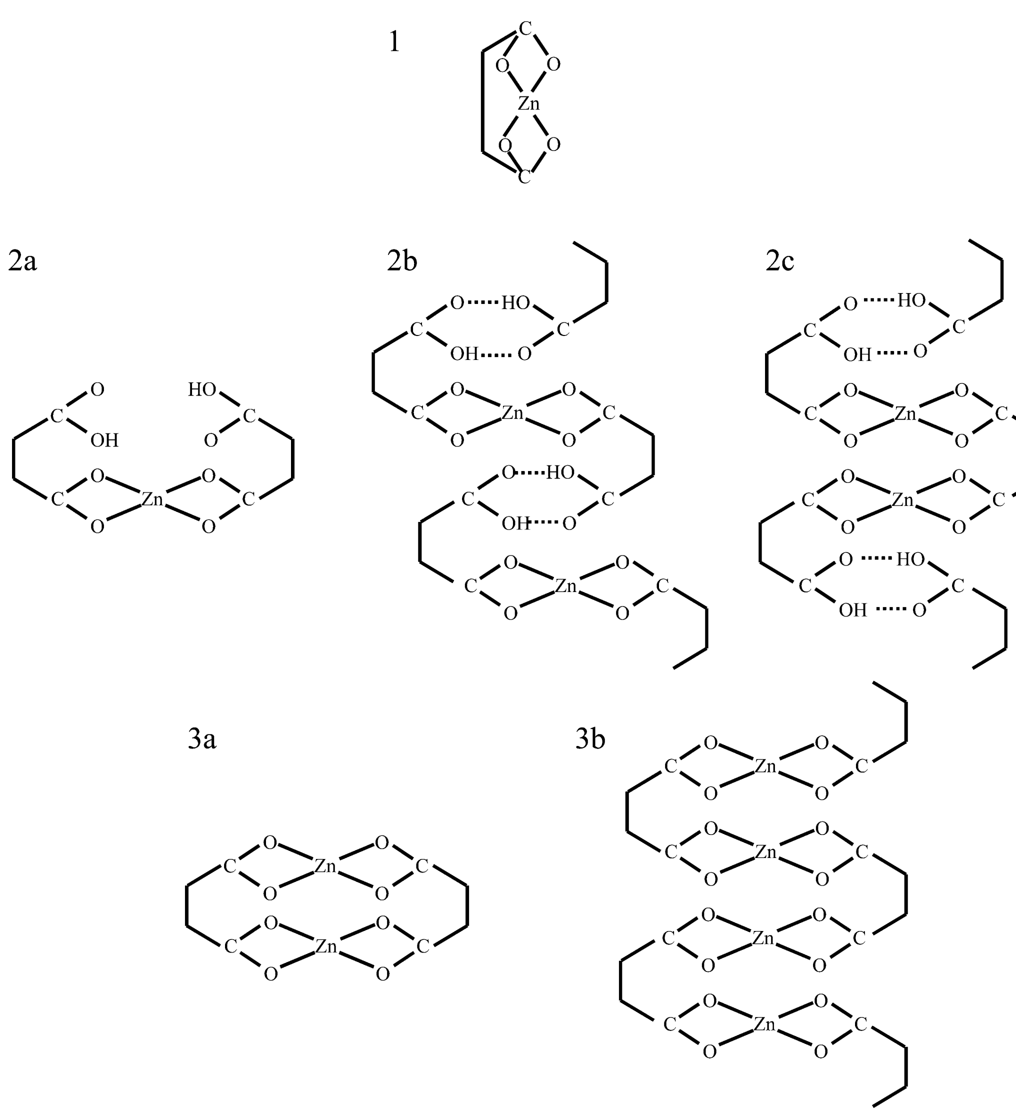

Figure 6. Six schematic possibilities for the structure around zinc in this system. Dotted lines represent hydrogen bonds. The lines do not imply that hydrogen bonding is necessarily occurring in all situations, just that such bonding is possible. Unneutralized closed anhydride structures are not shown in this schematic, depending on the neutralization level such structures do exist in this system.

indicating a significantly larger mean-squared displacement for nonassociated zinc cations. Since thermal vibrations are suppressed at 20 K, the large MSD corresponds to a large spread in Zn−O distances, and hence the assumption of a uniform Zn−O distance used to model the system is certainly incorrect.

The geometry of two carboxylate anions chelated to one zinc cation requires some discussion. Without any changes in bond angles, a coordinated, chelated carboxylate group would require a 50% lengthening of the C−O bond length. Almost certainly, the maximum change in bond length is only a few hundredths of an angstrom. Assuming tetrahedral coordination of the oxygen atoms to zinc, it is not possible for the carboxylate to chelate even with an O−C−O angle of 180° since the distance between the oxygen atoms using the measured bond distance is greater than twice the C−O bond distance.[16] Clearly oxygen atoms are not tetrahedrally arranged around zinc; in other words, a significant reduction in the O−Zn−O bond angle must be occurring. In zinc acetate dihydrate where zinc is coordinated to four oxygens from two chelating carboxylates and two oxygens from water, a significant reduction in O−Zn−O bond angle occurs without substantial distortion of the acetate bond distances or angles.[17] Unfortunately, we are not able to determine the actual value of the O−Zn−O bond angle or, equivalently, the value of the O−C−O bond angle.

Figure 7a shows the water absorption as a function of time. The nominal thicknesses of the two samples were the same for the samples represented by the line and square symbols,[18] but the surface areas were not. The water contents represented by the line were measured on samples with large enough weight changes so that the error in the change in weight measurement was small. The open square symbols were measured on samples at the beamline immediately prior to EXAFS measurement, and hence the samples were quite small (25×5 mm^2) in order to fit in the sample holder. The estimated error in the measurement of samples measured at the beamline was 0.2 wt %, which does not account for the much larger difference between the line and symbols at high weight fractions. At this time, we do not have a good explanation for the differences in Figure 7a; perhaps some of the samples absorbed water as they traveled from the laboratory to the beamline.

Figure 7b shows the EXAFS patterns taken at the times and water contents indicated for the sample with

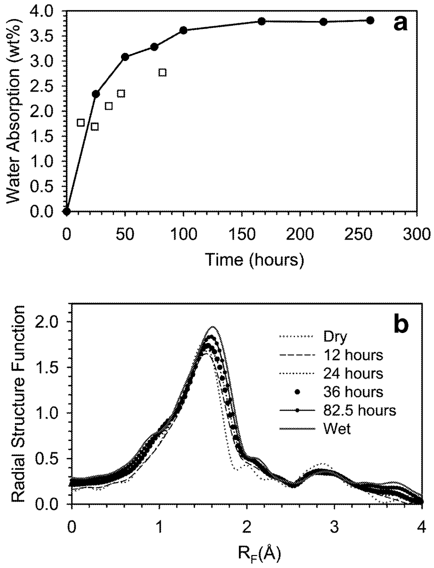

Figure 7. Effect of water absorption on the Zn-MAn-*g*-EPM ionomer with a DG of 7.33 wt % and neutralized to 25% of stoichiometric. Part a shows the kinetics of water absorption as measured by the change in weight relative to the initial weight, while part b shows the EXAFS patterns at various water absorption levels. In (a), the dots connected with the lines (line drawn to guide the eye) represent data collected in the laboratory, with samples designed to minimize measurement uncertainty. The open squares on the graph represent the measured change in weight on samples actually used for collecting EXAFS patterns.

25% DN. The general shift of the peak position located at approximately $R_F = 1.5$ Å to the right indicates that the average Zn−O bond distance is increasing. Modeling showed that the distance increased from an average of 1.9617 Å to an average of 2.0321 Å. Since thermal vibrations should be totally suppressed at the EXAFS measurement temperature, the initial decrease in peak height means the variation in the Zn−O distance increased. The relative minimum in the peak height with added water coupled with the continuous variation in the EXAFS pattern strongly suggests that zinc atoms are in at least two different environments. The increase in peak height coupled with the aforementioned shift of the peak position to the right indicates that the average coordination number of the Zn−O increased from 4 to a value near 5[19] after the addition of water for the ionomer neutralized to 25% of stoichiometric. One cannot be more quantitative about this number without assuming a value for the MSD, which we have no ability to do.

The EXAFS pattern with equilibrium water absorption for the 10% neutralized material is shown in Figure 8 along with a pattern from a zinc sulfonated polystyrene (ZnSPS) ionomer with 100% water absorption. This sample was previously shown to contain six water molecules in the coordination shell of zinc.[6] Although the EXAFS patterns for the 10% neutralized material and the ZnSPS ionomer are not identical, the two are close enough to conclude that the 10% neutralized material with maximum water absorption also corresponds to zinc with six water molecules in its coordination shell. The minor differences are undoubtedly due to the difference between sulfonate and carboxylate anions; the nature of the nearby counterion would be expected to have a small, but not negligible, effect on the position of the water molecules around zinc.

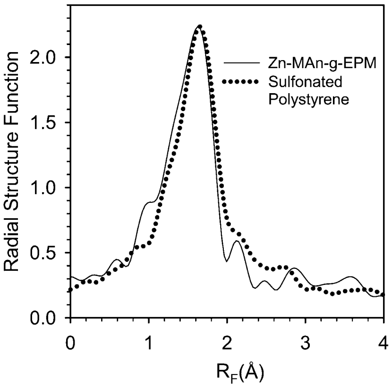

Figure 8. EXAFS patterns of two samples saturated with water that correspond to six waters of hydration around the zinc cation. The first pattern represents data from a sulfonated polystyrene sample published previously,[6] while the second pattern represents data from the sample with DG equal to 7.33 wt % and 10% neutralized with zinc. The average Zn−O distance was 2.0700 Å.

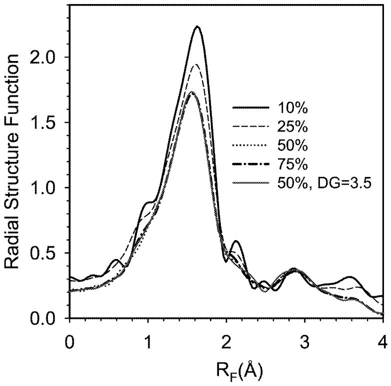

Figure 9. EXAFS patterns of samples after immersion in room temperature water for a time long enough to achieve maximum absorption. The legend refers to the neutralization level. All samples have a DG of 7.33 wt %, except where indicated.

EXAFS patterns for the remaining ionomers with maximum water absorption are shown in Figure 9, along with other ionomers shown previously to facilitate comparisons. Clearly these other ionomers do not show EXAFS patterns that are consistent with six water molecules around the zinc; the patterns for the samples with a neutralization level above 50% are consistent with 4-fold oxygen coordination around zinc. Above 50% neutralization, the amount of adsorbed water was 2 water atoms per zinc atom as shown in Figure 1. The simplest explanation for these observations is that the structure of the ionomer with maximum water absorption at neutralization levels greater than 50% consists of zinc coordinated to two oxygen atoms from water and two oxygen atoms from neutralizing carboxylate anions. Intuitively, this picture is quite appealing because the O−Zn−O and O−C−O bond strains are removed.

The effect of added water at different neutralization levels, i.e., 4-fold vs 6-fold coordination to zinc, is almost certainly a result of the difference in structure between **2a** vs **2b** and **2c**, at least for the 10% sample. However, another factor must be playing a role as well. Both SAXS and NMR experiments show that the ionic moieties in this system are much larger than zinc with two chelating carboxylates, indicating that microphase-separated domains contain a great deal of non-zinc-containing material.[1,2] One obvious difference between materials below and above 50% neutralization is that the former must contain anhydride groups if a sample is fully dry, while the latter might not. If zinc/chelated carboxylates and anhydride moieties are found in the same aggregate superstructure, i.e., the larger structure containing ionic groups and at least some polymer material, then conversion of the anhydride to two carboxylic acids would by necessity swell the aggregate and possibly cause the zinc/carboxylate to become much more susceptible to further hydration.

Comparing changes in EXAFS patterns with changes in SAXS patterns after water absorption gives very important clues regarding the morphology of these systems. The idea of two different effects of added water, one at low neutralization levels and another at high neutralization levels, is consistent to both measurements. Further, in samples with less than 50% neutralization, the shift of the SAXS peak toward lower q values and the modeling results indicate the breakup of some superstructures with added water. This breakup is consistent with EXAFS results since zinc becoming fully hydrated is the expected response if a superstructure containing zinc is broken apart. Superstructure breakup would not be expected to occur with the replacement of two carboxylic acids oxygen with two water oxygens as happens with samples at high neutralization levels, and none was suggested by SAXS measurements. The reduction in electron density at 100% neutralization is entirely consistent with two molecules of added water to the coordination environment of zinc. One result not as easily explainable is the fact that the sample with 100% neutralization had a qualitatively different change in SAXS pattern with added water vs the 50% neutralized sample, yet the changes in EXAFS patterns are identical. Perhaps zinc atoms are not equally distributed across all superstructures, and the ones without zinc atoms are more likely to break apart with added water. Clearly not all superstructures break up with added water since the sample with no zinc atoms still has a SAXS peak. An equally plausible explanation is that water does not cause the breakup of aggregates per se, but the coalescence of aggregates into larger sizes. Either or both of these phenomena could be occurring.

Conclusions

Dry zinc-neutralized ionomers made from ethylene−propylene copolymers with grafted maleic anhydride units (Zn-MAn-*g*-EPM) have a total of four oxygen atoms surrounding zinc, with one pair of oxygen atoms from a single (chelating) carboxylate group and another pair of oxygen atoms from another chelating carboxylate group. This arrangement is much different then in random copolymers of ethylene and either acrylic or methacrylic acid, where the four oxygens are from four different carboxylate anions. This difference must be due to the fact that in the Zn-MAn-*g*-EPM ionomers all carboxylate groups have another closely spaced carboxylate group, while in the ethylene−carboxylate ionomers only a small fraction of carboxylate ions are located on adjacent repeat units. In other words, this work shows that the aggregate structure changes with changes in the placement of ionic groups along the polymer backbone. The addition of water causes different changes in the Zn-MAn-*g*-EPM ionomers; at low neutralization levels the structure is transformed to that of zinc fully hydrated by water, i.e., six surrounding oxygen atoms, while at higher neutralization levels zinc is coordinated to two oxygen atoms from water and two oxygen atoms from different carboxylate groups. SAXS patterns were mostly consistent with this observation; at 100% zinc neutralization superstructures containing zinc atoms seemed to change only with regards to electron density, while at 25% neutralization level definite evidence was found for more dramatic changes in morphology. The 50% zinc-neutralized samples showed a response intermediate to the two extremes in SAXS measurements, while EXAFS measurements showed a response identical to that at 100% neutralization.

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(18) It would have made little sense to go through the effort of making the thicknesses of the two samples identical. The surface area of the edges was not insignificant compared to the surface area of the faces for the EXAFS sample, so a simple 1-D diffusion model could not be applied. We could have compensated for this effect; however there is no guarantee that Fickian diffusion would apply.
(19) For the zinc−oxygen bond, a bond distance of 1.95−1.98 Å is typical of 4-fold coordination, while a bond distance of 2.00−2.03 Å is typical of 5-fold coordination, while a bond distance of 2.06−2.12 Å is typical of 6-fold coordination.

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