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Effects of Temperature on Aggregate Local Structure in a Zinc-Neutralized Carboxylate Ionomer

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ABSTRACT: The aggregate structure of a zinc-neutralized ionomer made from an ethylene−methacrylic acid copolymer was studied as a function of temperature using extended X-ray absorption fine structure (EXAFS) spectroscopy. No gross changes in structure were found in the range 6−450 K, indicating that the aggregate structure remains basically unperturbed over this temperature range under quiescent (no-stress) conditions. Changes in EXAFS spectra were assigned to changes in mean-squared displacement with temperature as expected. At a temperature that corresponds roughly to the melting point of polyethylene, an extremely slight change in EXAFS spectra occurred which might be evidence of minor changes in average aggregate size. No evidence was found for any dramatic changes in structure such as an order−disorder transition or acid salt formation.

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 which will then phase separate into nanometer-size aggregates. These aggregates impart remarkable properties to ionomers including exceptional clarity and toughness.[1]

To characterize structure of ionic aggregates, a technique must be sensitive to the local environment in the aggregates. Extended X-ray absorption fine structure (EXAFS) spectroscopy is utilized to study many types of materials where information on local structure is desired. 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 ($\mu_0(E)$):

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \tag{1}$$

Single-electron single scattering theory[2] relates the normalized absorption coefficient to structural parameters according to the following:

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

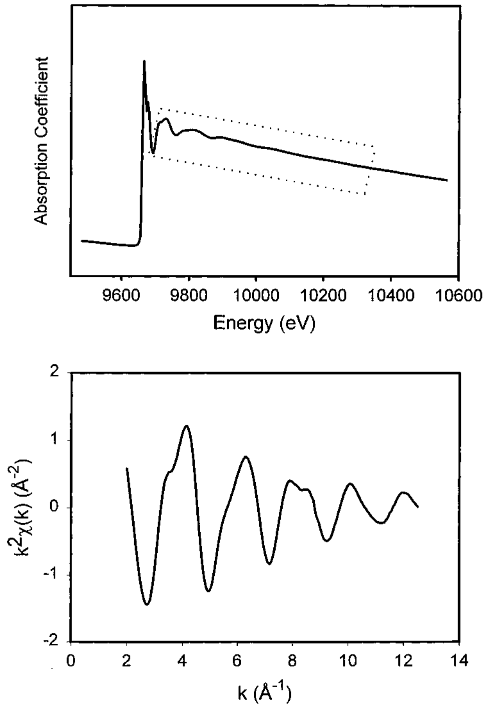

Figure 1. The top plot shows raw data indicating how the absorption coefficient ($\mu(E)$) changes with energy, while the bottom figure represents the oscillations of the absorption coefficient in k space. The energy range of the data in the bottom graph is represented by the data enclosed in the box drawn in the first graph.

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

$$k = \sqrt{\frac{2m}{\hbar^2}(E - E_0)} \tag{3}$$

where k is the wavevector, m is the mass of an electron,

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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. These variations can be due to both differences in the mean distance between the central atom and individual atoms in the coordination shell and also to thermal vibrations of the individual atoms. Finally, 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.

Many groups have studied the effect of temperature on ionic aggregation in zinc-neutralized ethylene–methacrylic acid copolymer ionomers. In a series of papers, Yano et al.[3] investigated the effect of temperature on aggregation in ethylene carboxylate ionomers using a variety of techniques and a variety of cations, including zinc. The main conclusion of this research was defining an order–disorder temperature of ionic aggregates at approximately 50 °C. Below this temperature, these authors concluded that atoms inside aggregates are ordered while above this temperature atoms inside aggregates are disordered. The authors argued that nonionic chain segments are unaffected by this transition. Studies by other groups disagree with this assignment. Using wide-angle X-ray scattering, Biswas[4] and Register et al.[5] have attributed the transition at approximately 50 °C to secondary crystallization of polyethylene segments.

Coleman et al.[6] postulated a different effect that occurs with increasing temperature in zinc ionomers: the formation of acid salts. In commercially available ethylene–methacrylic acid ionomers, only a portion of the acid groups are neutralized with zinc; the remaining acid groups have hydrogen as the counterion. This group studied the vibrations of both neutralized and unneutralized carboxylate groups using Fourier transform infrared spectroscopy (FTIR). Their conclusions were that tetracoordinated zinc carboxylates along with mainly pure acid groups at room temperature transform to hexacoordinated zinc carboxylates and zinc acid salts at high temperature (130 °C). This conclusion was disputed somewhat by Ishioka,[7] who suggested that some of the features in the spectra assigned to species described above were due to water contamination. However, even after reviewing the paper by Ishioka, the authors maintained that their data did suggest acid salt formation.[8]

EXAFS spectroscopy is uniquely suited to study the effect of temperature on aggregate formation. If an order–disorder transition is occurring, then dramatic changes should occur in EXAFS spectra at or near 50 °C. Specifically, the height of the first peak due to zinc–oxygen coordination should drop precipitously. This drop could be due to an increase in mean-squared displacement or a drop in apparent aggregation number. Which possibility is observed depends on the rate of diffusion of oxygen atoms in and out of zinc coordination.[9] If a shift occurs from tetracoordinated zinc to hexacoordinated zinc or acid salts, then dramatic changes in this first peak will occur as well; exactly what occurs depends on the relative amounts of the latter two species.

Experimental Data

Ethylene–methacrylic acid copolymer (EMAA) was graciously supplied by the E. I. DuPont Company and is marketed under the trademark Surlyn. This material is reported to contain 3.9 mol % acid monomer and was 57% neutralized with zinc. Sample preparation is detailed in a previous paper.[10] A liquid helium cryostat with a variable heater was used to cool the sample below room temperature while a specially constructed heating cell was used to heat the sample above room temperature. For the latter, the system was designed to minimize curvature in EXAFS patterns due to sample creep at high temperatures. On the basis of the shape of the EXAFS curves and duplicate measurements, changes in absorption density during an energy scan did not significantly effect data quality for the temperatures presented in this paper. However, at 473 K, sample creep did occur on the basis of curvature in EXAFS spectra, and hence this was the highest temperature used in the experiments. Data collected upon subsequent cooling showed no statistically significant differences versus data collected upon heating except for an irreversible change in thickness.

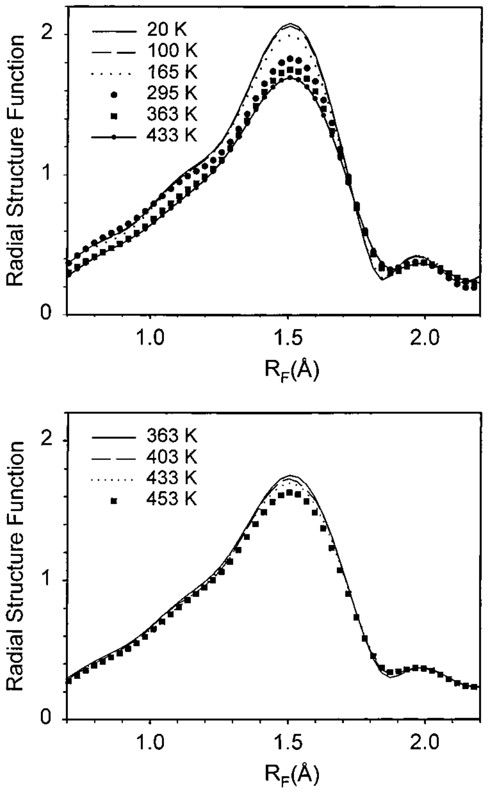

Figure 2. RSF at selected temperatures highlighting features due to the first shell. Compare the bottom plot of Figure 2 with that of Figure 4.

Measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on Beamline 2-3. Three ionization chambers were used to monitor X-ray intensity; the sample was placed between the first and second ionization chambers while a sample of zinc foil was placed between the second and third ionization chambers. The controller was set to a desired temperature and allowed for a limited time (typically 15 min) to attain that temperature. Previous work[10] agrees with the assignment of tetracoordinated zinc postulated by Coleman et al. and showed that the structure of monoclinic zinc acetate[11] described the arrangement of atoms inside the aggregates extremely well. Model fitting using FEFF[12] and the UWXAFS suite of software was performed as described previously.[10] Only two adjustable parameters were used in fitting the model to the experimental data: the mean-squared displacement of the first coordination shell and the edge energy.

Discussion

Figure 2 represents the feature in the radial structure function due to first-shell zinc–oxygen coordination at selected temperatures. The radial structure function is

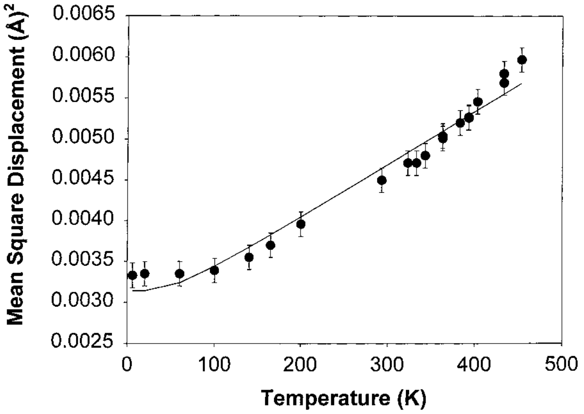

Figure 3. Change with temperature in the mean-squared displacement of zinc coordinated to four oxygens in the first coordination shell. The solid line represents the best fit curve using eqs 4 and 5 to model the temperature dependence of the mean-squared displacement.

similar to a radial distribution function in that peaks in the RSF usually correspond to distinct coordination shells. The abscissa of the RSF has units of angstroms, but the positions of peaks are shifted from the true interatomic distances; hence, a subscript F will be used to distinguish this distance from the actual interatomic distance *R*.

No dramatic changes in spectra occur at 50 °C in Figure 2, indicating that no order–disorder transition is occurring in the ionomer aggregates. Further, no dramatic changes are occurring in local environment with temperature, indicating that no acid salts or hexacoordinated zinc atoms are forming. The decrease in height of the first peak centered at approximately 1.3 Å with increasing temperature represents an increase in mean-squared displacement due to increased thermal vibrations. Figure 3 represents the best-fit mean-squared displacement of the zinc–oxygen distance as a function of temperature. From 100 to 450 K the increase in mean-squared displacement is approximately linear with temperature. The linearity in Figure 3 is apparent in Figure 2; looking carefully it is clear that the decrease of peak height with temperature is approximately the same for equal temperature intervals. (No data are available for 230 K, which is why the gap appears.) The slope of the linear portion of Figure 3 is 7.43×10^{-6} Å^2/K, which is lower than the slope in mean-squared displacement for elemental lead[9] (9.4×10^{-5} Å^2/K) or metal–metal mean-squared displacements (2×10^{-5} Å^2/K) in a zinc–selenium alloy.[13] The fact that no significant changes occur at either the glass transition temperature or the melting temperature of the polymer indicates that the energetics of association are so strong that the physical state of the polymer does not effect the aggregate. Other evidence supporting the independence of aggregate characteristics is the insensitivity of the local structure to neutralization type, method, or free acid content as described previously.[10]

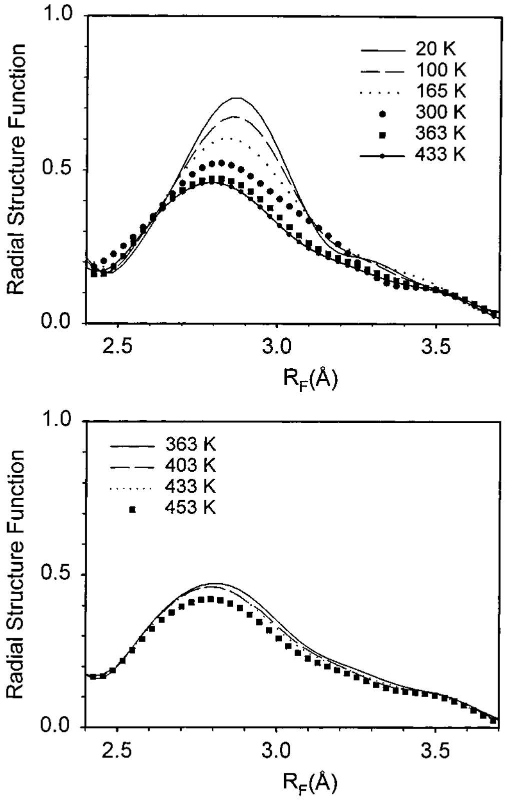

Figure 4. RSF at selected temperatures highlighting features due to the second shell structure. Compare the bottom plot of Figure 2 with that of Figure 4.

The data in Figure 3 can be used to determine an average force constant for the Zn–O bond if we assume a symmetric pair distribution function for static disorder and harmonic vibration for all oxygen atoms in this shell. With these assumptions[2]

$$\sigma^2 = \sigma_{\mathrm{vib}}{}^2 + \sigma_{\mathrm{stat}}{}^2 \qquad (4)$$

where σ_{vib} and σ_{stat} are the vibrational and static contributions to the mean-squared displacement. The vibrational component can be written in the following form:

$$\sigma_{\mathrm{vib}} = 4.106\left(\frac{1}{\mu\bar{\nu}}\coth\left(\frac{x}{2}\right)\right)^{1/2} \qquad (5)$$

where μ is the reduced mass in atomic mass units (12.85 in the present case), $\bar{\nu}$ in cm^{-1} is the vibrational frequency divided by the speed of light, and $x = 1.441\bar{\nu}/T$ with T in kelvin. The fit is shown in Figure 3. The static part of the mean-squared displacement is 0.002 67 Å^2, and the force constant, which equals $4\pi^2\mu c^2\,\bar{\nu}^2$ in mdyn/Å, is 6.01×10^6 mdyn/Å.

The feature shown in Figure 4 represents the only other large peak in the radial structure function. This feature is due to atoms at a distance of about 3 Å from the central zinc atom, which, in the crystal structure of monoclinic anhydrous acetate, include four carbon atoms attached to the four coordinating oxygens and two oxygen atoms coordinated to two other zinc atoms. The fit of the model to either the ionomer or the experimental spectra of the small molecule is not perfect in this region; hence, fitting a mean-squared displacement to this feature would have little value. However, modeling is not necessary to make significant statements about morphology. The peak height does decrease linearly with temperature between 6 and 373 K, while the peak position also shifts linearly with temperature over this same range. Changes in thermal vibrations are undoubtedly responsible for the linear decrease in peak height, while the shift in peak position supports the supposition that more than one atomic species is responsible for this feature.

Above 373 K, there is a qualitative change in the relationship between the first & second peaks. The lack

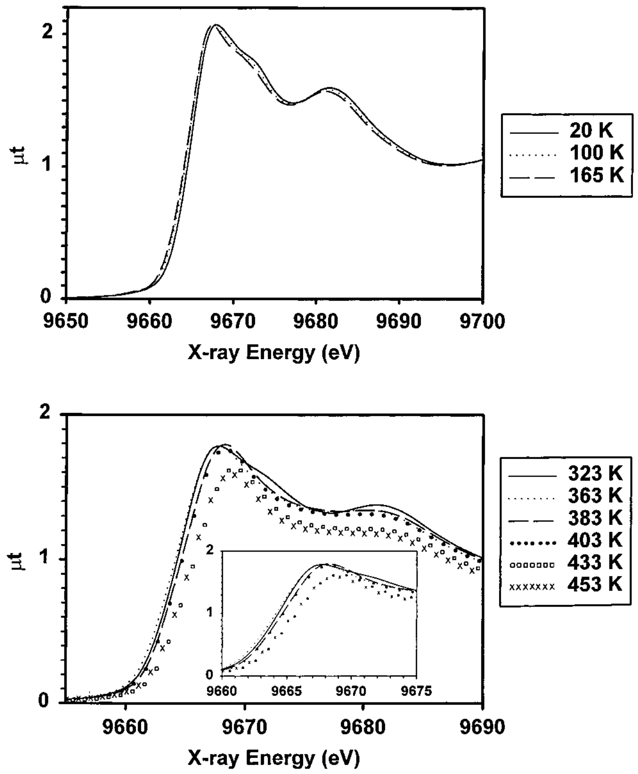

Figure 5. Absorption of selected samples in the near-edge region. The data sets were vertically shifted so that the preedge region had an absorption of zero. The energy scales of each sample were shifted according to zinc foil absorption mounted on a third ionization chamber; therefore, the relative energies shown are consistent although the absolute energy may not be correct.

of any significant changes (peak position shifts, etc.) indicates that no significant structural changes inside the aggregates are occurring at 373 K. However, qualitative difference in linearity between the second and first peak from 373 to 450 K might be evidence of a zinc-backbone carbon distance of around 3 Å, which is possible given a planar aggregate structure and essentially not possible if the structure is three-dimensional (i.e., spherical). In the region from 100 to 373 K, both the first and second peaks decrease linear in height with temperature, indicating that both are due to thermal vibration of atoms. However, this correspondence does not hold beginning at 373 K. It is difficult to understand how motions of either the carbon atom in a carboxylate group covalently bonded to the first-shell oxygen atom or an oxygen atom coordinated to a nearby zinc atom could change its correlation with the motion of the first-shell oxygen atom.[14] On the other hand, backbone chain motions are decoupled from any carboxylic acid movement on a thermal vibration length scale, and inconsistency between features due to zinc coordinated oxygen atom and zinc backbone carbon atom at the melting point of the polymer would not be surprising at all.

Figure 5 represents the near-edge structure of these systems with the energy scale adjusted using the absorption of the zinc foil in front of the third ionization chamber. Two graphs are shown because sample thicknesses were different for the specimens represented by each graph. Up until 403 K, there are no significant changes in either peak shape or edge position, which is consistent with the EXAFS data. The reduction in height and increase in broadness of the peak centered at approximately 9680 eV are probably due to the increase in thermal vibration. There clearly is a step change in near-edge spectra between 403 and 433 K. First, there is a drop in the magnitude of the edge jump, which could be due to a changing thickness. The sample thickness did change during the course of the experiment; however, only data collected at 473 K showed significant curvature characteristic of a changing thickness while data were being collected. It is possible that a thickness change occurred between 403 and 433 K while the sample was heating. The approximately 1 eV shift toward higher binding energies cannot be explained away as artifact however. To our knowledge, the only substantial change occurring in these materials in this temperature range is the onset of anhydride formation; however, this chemical change should involve free acid groups not those coordinated to zinc. Further, if anhydride formation were somehow affecting zinc, it is difficult to understand how the EXAFS spectra would not also show a dramatic change. We are at a loss to explain this observation except to say that we checked our data very carefully to ensure ourselves that this effect is real. This change is reversible: the same near-edge spectra were produced from a cooled sample if the normalized spectra were adjusted to account for the irreversible change in thickness at high temperatures.

Summary

In a zinc-neutralized ionomer where the zinc neutralization level is roughly half of stoichiometric, no evidence was found for an order−disorder transition or acid salt formation as set forth by other researchers. A very slight anomaly in EXAFS spectra occurred near the polymer melting point which might be evidence of a planar aggregate structure. The small changes in EXAFS spectra with changing temperature are consistent with the postulate that the strength of ionic association tends to dominate the behavior of these ionomers. Finally, a significant unexplained change between 403 and 433 K occurred in the near-edge region which was not found in EXAFS spectra.

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(14) From 6 to 100 K, it is fairly easy to imagine how the feature in the EXAFS pattern due to zinc−oxygen coordination would not be affected by temperature, while the feature due to zinc−carbon distance (for example) would be affected.

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