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# Effect of Temperature on Local Structure in Poly(ethylene oxide)−Zinc Bromide Salt Complexes

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ABSTRACT: Extended X-ray absorption fine structure (EXAFS) spectroscopy was used to characterize the $(PEO)_n[ZnBr_{2(1-x)}(LiBr)_x]$ system. Values of $n$ and $x$ were chosen so that the average number of nearest-neighbor bromine atoms varied from 2.25 to 3 as determined by Raman spectroscopy. This study determined that the number of nearest-neighbor oxygen atoms was 3, 1, and 0 for zinc with 2, 3, and 4 nearest-neighbor bromine atoms, respectively. Some ambiguity is present in the first case, with four nearest-neighbor oxygen atoms being almost impossible and two being possible but not likely. The mean-squared displacement of the zinc−bromine bond increased almost linearly with absolute temperature, similar to the behavior observed for other covalent or ionic bonds. Interestingly, the strength of the Zn−Br bond, as determined by the change of the mean-squared displacement with temperature, was the same for all samples independent of the degree and nature of coordination. For some samples, there was a clear rise in the mean-squared displacement (MSD) of the Zn−O linkage with temperature. For other samples, the mean-squared displacement at 20 K was extremely large; consequently, the expected increase of the MSD with an increase in temperature was barely noticeable. The MSD showed a relative minimum at a temperature corresponding roughly to the glass transition temperature for all samples where data were collected in an appropriate temperature range. To our knowledge, this study represents the first time a feature in EXAFS spectra has been found to be sensitive to the glass transition temperature. The significance of this observation in terms of local structural changes at the glass transition is discussed.

## Introduction

Poly(ethylene oxide) (PEO)−salt systems have been thoroughly investigated over the past 10−20 years because of their possible use as polymer electrolytes.[1−4] Although most applications envision using a lithium salt, other cations have been investigated as well. One of these cations has been zinc; PEO/zinc salt systems have been studied extensively over the past 15 years. An important issue in many of these studies has been the arrangement of atoms around the zinc cation. This paper will focus on zinc bromide salts dissolved in high molecular weight PEO, with particular attention being paid to the temperature dependence of the zinc coordination. We will significantly extend previous work by other workers and report a novel temperature-dependent effect.

Using theoretical simulations, Xie and Farrington[5] concluded that zinc with one or two nearest-neighbor bromine atoms was present in $(PEO)_{11}ZnBr_2$. The species consisting of a zinc cation with one bromine anion would be positively charged. Although such structures are not common in solids outside of water-containing inorganic compounds, an extra bromide ion could be nearby to maintain charge neutrality. These authors proposed five nearest-neighbor oxygen atoms for zinc with one nearest-neighbor bromine atom and two or three nearest-neighbor oxygen atoms for zinc with two nearest-neighbor bromine atoms. Using extended X-ray absorption fine structure (EXAFS) spectroscopy, McBreen et al.[6] reported that the number of nearest-neighbor bromine and oxygen atoms were 1.8 and 4.16, respectively, for $(PEO)_8ZnBr_2$. However, the fit included a physically impossible negative mean-squared displacement (MSD) and hence should be considered suspect. Einset and Latham et al.[7] reported that $(PEO)_6ZnBr_2$−$(PEO)_{15}ZnBr_2$ had an average number of nearest-neighbor bromine atoms of 2.3−2.4 while the average number of nearest-neighbor oxygen atoms varied widely. The authors realized that the latter was partially due to the fact that bromine backscattering dominated the EXAFS pattern given the $k^3$-weighting scheme the authors used; however, other factors such as sample preparation were also cited.

Our earlier work in this area confirmed the conclusions of Einset et al. regarding the number of nearest-neighbor bromine atoms for systems with similar compositions.[8] Using Raman spectroscopy in combination with EXAFS spectroscopy proved advantageous since Raman and EXAFS spectroscopies were consistent with respect to the number of nearest-neighbor bromine atoms. In our previous paper, we studied systems with the general composition $(PEO)_n[ZnBr_{2(1-x)}(LiBr)_x]$; by varying $n$ and $x$, it was possible to change the number of nearest-neighbor bromine atoms from 2.2 to 4. Because of the different $k$ dependence of the backscattering amplitudes of oxygen and bromine, the statistical error in fitting Zn−O coordination numbers was substantially reduced by using different $k$-weighting schemes, and more consistent oxygen coordination numbers were obtained. The number of nearest-neighbor oxygen atoms was shown to drop with increasing number of nearest-neighbor bromine atoms. However,

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the oxygen coordination number for a given number of bromine nearest neighbors could not be accurately determined because not enough samples were measured.

The effect of temperature on the arrangement of atoms around zinc has also been studied using EXAFS spectroscopy. McBreen et al.[6] found that Zn−Br coordination changed substantially, with a decrease in distance of 0.01 Å and a change in Br speciation from 1.8 to 1.54 as the temperature changed from 25 to 120 °C. A study on $(PEO)_4ZnBr_2$ concluded that the Zn−Br distance did not change with temperature as the temperature dropped from room temperature to −70 K, while the Zn−O distance decreased slightly for most of the samples studied.[9]

The purpose of this present study is to determine more accurately the number of oxygen atoms around zinc as well as to determine the behavior of these systems with changes in temperature over a wide range. The $(PEO)_n[(ZnBr_2)_{1-x}(LiBr)_x]$ system has been studied, with $n = 20{-}80$ and $x = 0{-}0.5$. Compositions were chosen to have a range of average nearest-neighbor bromine atoms from 2.25 to 3, corresponding to the range where the average number of nearest-neighbor oxygen atoms changes most significantly. This choice of materials enables us to take maximum advantage of the ability to determine the number of nearest-neighbor bromine atoms precisely using Raman spectroscopy. During the course of our studies, we discovered a new phenomenon clearly related to the glass transition of the polymer. To our knowledge, this study represents the first time that EXAFS has been used to study the glass transition in any material.

## Experimental Section

**Materials.** PEO (MW 4 × $10^6$, Aldrich Chemical Co.) was dried in a vacuum oven at 50 °C while $ZnBr_2$ and LiBr were dried in a vacuum oven at 100 °C for 48 h prior to use. The appropriate amounts of the salt and polymer were dissolved in acetonitrile and stirred for 24 h. Thin films were cast on Teflon sheets, and the solvent was allowed to evaporate at room temperature for ∼24 h in a nitrogen-atmosphere glovebox. The resultant films were dried in a vacuum oven at 50 °C for 24 h.

**Raman Spectra.** Raman spectra were recorded at room temperature and 10 K using a Jobin-Yvon T64000 triple monochromator Raman system. The 514.5 nm line of an argon ion laser at a power of 300 mW was used for excitation. A 16 s integration time was used, and 10 accumulations were averaged. Spectra were taken at 10 K and room temperature. The cryogenic sample holder was cooled using an Air Products LT-3-110 helium refrigerator. Room temperature spectra were collected both in a 180° (backscattering) geometry under a microscope with an 80× objective and in 90° scattering geometry. Low-temperature spectra were collected only in the 90° scattering geometry because the preferred backscattering geometry was not possible with the cryogenic sample holder. Spectra collected in backscattering geometry were curve fit from 300 and 140 $cm^{-1}$ to determine the percentages of zinc with two, three, and four nearest-neighbor bromine atoms. Spectra were curve-fit (using Galactic Grams ver 5.2) using a straight baseline and one Gaussian−Lorenzian product function for each band.

**EXAFS Spectra.** 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. 5 eV steps were used in the preedge and EXAFS regions, while 2 eV steps were employed from 13 eV below the edge to 41 eV above the edge. A total of 5−7 scans, each lasting 15−20 min, were collected, and the scans were averaged after edge energy determination to improve the signal-to-noise ratio. Only EXAFS region spectra are analyzed and shown; near-edge spectra showed no significant changes with temperature.

**Table 1. Distribution (in %) of Number of Nearest-Neighbor Bromines According to Raman Spectroscopy**[a]

| | $ZnBr_2$ | $ZnBr_3^-$ | $ZnBr_4^{2-}$ |
|---|---|---|---|
| $(PEO)_{20}[ZnBr_2]$ | 74 | 26 | |
| $(PEO)_{60}[ZnBr_2]$ | 71 | 29 | |
| $(PEO)_{80}[ZnBr_2]$ | 77 | 23 | |
| $(PEO)_{40}[(ZnBr_2)_{0.6}(LiBr)_{0.4}]$ | 34 | 66 | |
| $(PEO)_{40}[(ZnBr_2)_{0.5}(LiBr)_{0.5}]$ | 8 | 84 | 8 |

[a] These values were calculated from spectra collected at room temperature in the 180° scattering geometry. The error in the percent of each species is estimated to be ±4%.

Measurements were made over the temperature range 20−443 K. A liquid helium cryostat with a 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. The controller was set to a desired temperature and allowed for a limited time (typically 15 min) to attain that temperature. Temperature variation in the cryostat was ±1 °C, while temperature variation in the heating cell was ±3 °C. For the heating cell, 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 affect data quality for the results presented in this paper.

The theory behind EXAFS is discussed in detail elsewhere[10] 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[11] was used to determine theoretical EXAFS patterns for fitting to experimental data. Atomic arrangements used in FEFF7 were Zn−O with an interatomic distance of 2.10 Å and Zn−Br with a distance of 2.39 Å. Changing these distances in FEFF7 had no significant effect on the quality or results of model fitting. No multiple scattering paths were used. EXAFS oscillations were determined from the raw absorption data using AUTOBK, version 2.65,[12] while FEFFIT, version 2.54,[12] was used to fit expressions generated from FEFF7 to the experimental data.

This version of FEFFIT allows fitting of multiple files at one time, which was very useful for fitting data collected at different temperatures. Error bars shown on plots represent the error in least-squares fitting as determined by FEFFIT. The magnitudes of error bars are sensitive to the number of floating parameters; so for a given plot error bars represent data fitted in the same manner except where noted.

## Results and Discussion

The first part of this paper will be a thorough reexamination of the structure of PEO−$ZnBr_2$ complexes based on EXAFS spectra. Three important and substantial differences between this study and previous studies justify this reexamination:

(1) The average number of nearest-neighbor bromine atoms for each compound is known from Raman spectroscopy as listed in Table 1. Hence, the number of fitted parameters for EXAFS modeling was reduced by one. Further, knowledge of this value allowed for adjustment of the amount of lithium bromide so as to maximize the change in oxygen coordination number. The bromine coordination number was varied between 2.25 and 3 to achieve this goal.

(2) Because multiple files were fit simultaneously, one fitting parameter could be used for interatomic distances

and the edge energy where appropriate. Hence, best-fit parameters were determined from data collected at different temperatures at one time. This approach is inherently better than fitting each file individually.

(3) Instead of trying to determine average oxygen coordination numbers for a set of samples independently of one another, the oxygen coordination number for each $ZnBr_x$ species in different samples was determined by forcing sample-to-sample consistency.

Implicit in the last item is that a given number of nearest-neighbor bromine atoms corresponds to only one given number of nearest-neighbor oxygen atoms. In other words, bromine coordination number uniquely determines oxygen coordination number. This assumption is the simplest one that could be made, and nothing in our measurements argued against the correctness of this assumption. If zinc is only in one phase of the material, then this assumption is almost certainly true. However, if zinc atoms are in both an amorphous and a crystalline phase, then this assumption may not be true if the anion speciations are different and the relative amounts of these two phases differ. Note that a separate PEO/zinc bromide crystalline phase $(PEO)_5ZnBr_2$ has been postulated,[7] meaning that such a situation is theoretically possible. However, because of the rather high PEO/salt ratios used, a significant amount of the postulated mixed-crystalline compound $(PEO)_5ZnBr_2$ was probably not present. Further, other researchers have suggested that this crystalline compound does not even exist.[6] Another question is the structure of the zinc bromide species with three and four bromine atoms; are they isolated as contact ion pairs with a charge of −1 or −2, respectively, or as part of an extended structure? Our work here does not answer that question; either case is possible.

To accurately fit the number of oxygen and bromine atoms, different $k$-weighting schemes should be used as shown previously.[8] Previously, $k$-weighting schemes of −1 and 1 were used to fit the number of oxygen and bromine atoms, respectively, while in this paper weighting schemes of 0 and 2 were used. The reason for this change was that for −1 weighting, a consistent $k$ range could not be found for all samples where the Fourier transform of the isolated $k$-weighted oscillations was zero at a distance of zero given the data reduction procedure used. (This Fourier transform will be termed the radial structure function, or RSF for short, while the distance axis of the RSF will be termed $R_F$ to distinguish this from $R$, which represents a true interatomic distance.) If data could be collected over an infinite energy range (or $k$ range), the RSF must be zero at $R_F = 0$ for the same reason that a radial distribution function is zero at $R = 0$. Since in practice data cannot be collected or analyzed over an infinite range, it is possible for the RSF to be nonzero at $R_F = 0$ depending on the energy (or $k$ range) used and the data reduction procedure. Forcing the $k$-weighted oscillations to be zero at $R_F = 0$ is not necessary if the model perfectly describes the data at low $R_F$ or the EXAFS patterns are all identical at low $R_F$; however, neither was the case in this study. Hence, the purpose of choosing $k = 0$ weighting instead of $k = -1$ weighting, and the purpose of choosing the particular $k$ range used, (2.6−14.5 Å$^{-1}$) was to minimize the effect of truncation errors. Weighting with $k = 2$ was chosen so that the difference in the two $k$-weightings was consistent with the previous paper.

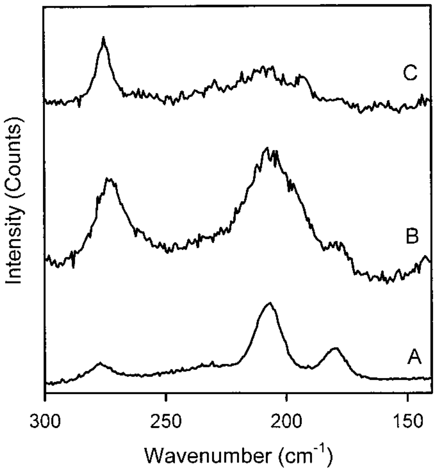

**Figure 1.** Raman spectra for sample $PEO_{20}[ZnBr_2]$: A, room temperature, 180° scattering geometry; B, room temperature, 90° scattering geometry; C, 10 K, 90° scattering geometry. Baselines have been slope adjusted and vertically offset for presentation clarity.

Figure 1 shows representative Raman spectra of the $(PEO)_{20}ZnBr_2$ sample. The curve-fit analysis of the room temperature spectra yields zinc−bromine peaks at 210 and 180 cm$^{-1}$ for all five compositions, and the $(PEO)_{40}$-$[(ZnBr_2)_{0.5}(LiBr)_{0.5}]$ spectrum (not shown) also has a peak at 165 cm$^{-1}$. All spectra also have PEO peaks at 230 and 280 cm$^{-1}$. Peaks at 165, 180, and 210 cm$^{-1}$ have been assigned to zinc with four, three, and two nearest-neighbor bromine atoms, respectively. These assignments are in general agreement with assignments by Macklin and Plane, Yang et al., and others.[13−17] It should be noted that the assignment of the band at 210 cm$^{-1}$ is somewhat ambiguous in the literature. Also, Macklin and Plane and Yang et al. both assign a band at 240 cm$^{-1}$ to $ZnBr^+$; this band does not appear in any of our spectra. Percentages of each species present for each composition as determined from the integrated areas are given in Table 1.

In general, low temperatures are better for determining structural information from EXAFS spectroscopy because mean-squared displacements are smaller, and hence features are better resolved. Since the coordination was determined using Raman spectra collected at room temperature, the first issue to examine was whether the coordination of the zinc changed as the temperature was lowered below room temperature. This determination was not unambiguous, as shown in Figure 1, where fitting spectra to determine integrated areas became impossible. This problem was worsened by the low signal-to-noise ration obtainable through the cryogenic cell due to the loss of scattering intensity through the windows. On the basis of visual inspection, we believe it is appropriate to conclude that Raman spectra were consistent with no change in the coordination of the zinc by bromine as the temperature was lowered; however, it is important to note that small changes would not have been noticed. As the reader will shortly see, changes in mean-squared displacements and distances with temperature support the conclusion of no zinc−bromine coordination change below room temperature.

EXAFS data were fit over three different temperature intervals: below room temperature, room temperature, and above room temperature. Three intervals rather than one were used because the different samples were used for the different intervals, and data were collected during different beamtime assignments. Further, FEFFIT has a limit of 16 spectra at one time, and fitting all three intervals at once would not have been possible for all samples. Because of the different *k*-weighting schemes used, and the fact that the bromine fitting parameters had a large impact on the oxygen fitting parameters, the procedure to fit each set of spectra was the following:

(1) Spectra more sensitive to bromine ($k^2$-weighted spectra) were fit allowing the Zn−Br mean-squared displacements at different temperatures, one Zn−Br distance, and one edge energy to vary. For the higher temperature interval, the Zn−Br distance was allowed to change as well for reasons described shortly. The number of bromine nearest neighbors was fixed by Raman spectra. All mean-squared displacements of oxygen atoms were set at 0.01 Å$^2$, while the number of oxygen nearest neighbors was fixed as described in the Zn−O section. The amplitude reduction factor was set at 1.0 for this and all fits; this value was chosen based on model fits to Zn−O compounds.[18] Note in our previous paper[8] the amplitude reduction factor used was 0.9; however, this change has no effect on the major conclusions of this paper.

(2) Spectra more sensitive to oxygen ($k^0$-weighted spectra) were fit allowing the Zn−O mean-squared displacements to vary at different temperatures, along with one Zn−O distance and one edge energy. The Zn−Br distance and MSD from (1) were input into the fitting file for these spectra. The number of oxygen nearest neighbors was fixed as described in the Zn−O section.

(3) Once again, spectra more sensitive to bromine ($k^2$-weighted spectra) were fit, allowing the Zn−Br mean-squared displacements at different temperatures, one Zn−Br distance, and one edge energy to vary. The number of bromine nearest neighbors was fixed as in (1). The Zn−O distance and mean-squared displacements from (2) were input into the fitting file for these spectra while the number of oxygen nearest neighbors was fixed as in (1) and (2). In all cases, the edge energies from (1), (2), and (3) agreed with one another within the fitting error as output by FEFFIT.

The results of the EXAFS data analysis and consequently the conclusions of this paper depend heavily on the accuracy of the FEFF code. A complete review of this issue is well beyond the scope of this publication. We have measured approximately 10 model compounds in our laboratory and have concluded that FEFF provides an almost exact description of the EXAFS patterns for nearest neighbors using physically reasonable parameters. Therefore, we believe that any errors originate in an incorrect choice of model rather than an erroneous calculation of EXAFS patterns from the FEFF code.

**Zn−Br.** The results for the $k^2$-weighted spectra, i.e., zinc−bromine fits, will be considered first because these results were similar to other systems studied, and the quality of fit was generally very high as shown in Figure 2. Figure 3 shows the change in the Zn−Br mean-squared displacement with temperature. The fits are consistent with one another since the constant mean-squared displacements at low temperatures are roughly identical. No consistent, statistically significant differences exist in the low-temperature mean-squared displacements, a result which was expected since static-disorder terms dominate at low temperature, and the variations in Zn−Br distance should not change sub-

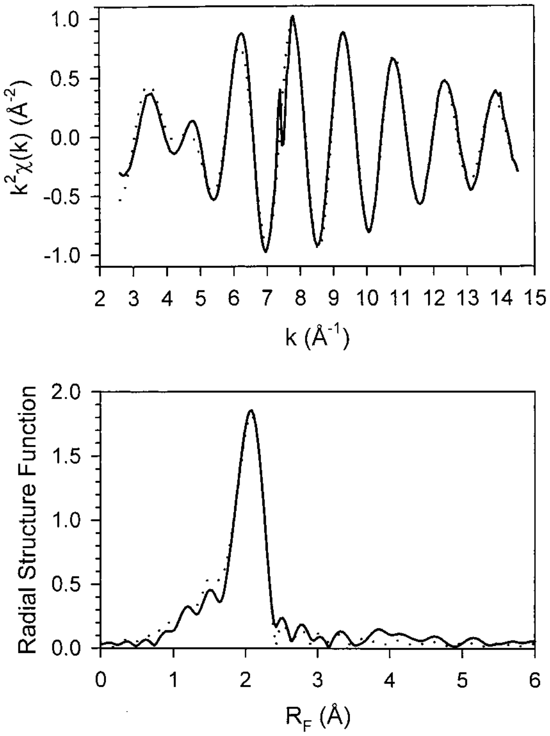

**Figure 2.** Representative $k^2$-weighted spectra measured at 20 K in both *k*-space (top) and $R_F$ space. The solid line represents experimental data, while the dashed line represents the best-fit spectra from FEFFIT.

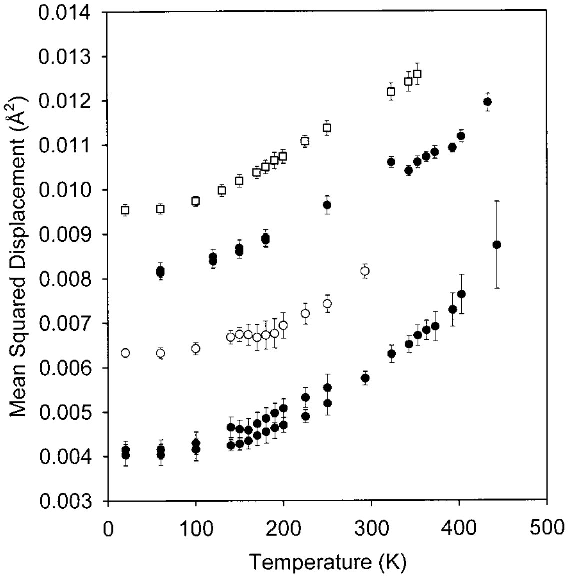

**Figure 3.** Change in Zn−Br mean-squared displacement with temperature. From bottom to top, the average number of nearest-neighbor bromine atoms was 2.25, 2.5, 2.66, and 3 (solid circle, open circle, solid square, open square). From bottom to top, 0.002 Å$^2$ was added successively to the mean-squared displacements (0.000, 0.002, 0.004, and 0.006 Å$^2$) to improve data presentation. For the data at and below room temperature, one Zn−Br distance was used in fitting, while for the data above room temperature, the Zn−Br distance was allowed to float at each temperature. For the latter, the value of the mean-squared displacement changed only in the third significant figure if only one Zn−Br distance was used. However, the error bars were considerably larger if only one Zn−Br distance was used, because the fit quality worsened substantially.

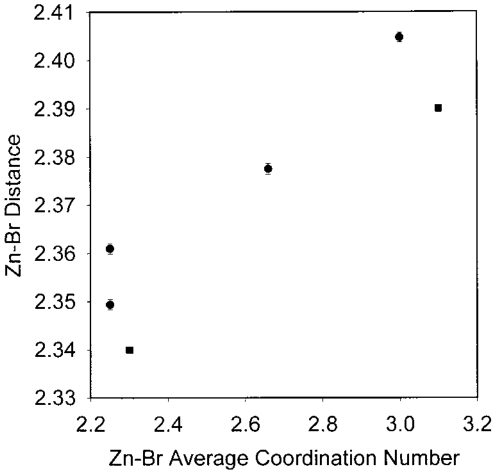

**Figure 4.** Zn−Br distance as a function of number of nearest-neighbor bromine atoms for data collected below room temperature. Circular symbols represent data collected and analyzed for this paper; square symbols represent data taken from ref 8. Data in this paper represent fits using one distance for multiple temperatures, while data from ref 8 represent data from one sample only.

stantially with changes in the number of nearest-neighbor bromine atoms. The values of mean-squared displacements at low temperature are reasonable values for zinc nearest neighbors based on the results for oxygen in carboxylate species[18] and selenium in zinc−selenium alloys.[19] This result suggests that the assignments generated by Raman spectra are reasonable because the mean-squared displacement and number of atoms are highly correlated in any least-squares fit of EXAFS data.

However, the constant value of 0.004 Å$^2$ is slightly higher than the roughly 0.003 Å$^2$ for the compounds listed above. A smaller mean-squared displacement means a smaller number of nearest-neighbor bromine atoms or a smaller amplitude reduction factor; these two variables affect FEFF-calculated spectra identically. Reducing the average number of bromine atoms by 0.25 changes the fitted mean-squared displacement by approximately 0.0005 Å$^2$ while the quality of the fit has little noticeable change. Hence, based on EXAFS data alone a Zn−Br coordination number of 1.8, consistent with McBreen et al.,[6] would be possible.

The number of nearest-neighbor bromine atoms and the distance between zinc and bromine are clearly related. Figure 4 shows the relationship between interatomic distance and the number of nearest-neighbor bromine atoms. The number of nearest-neighbor bromine atoms corresponding to the samples $(PEO)_{20}[ZnBr_2]$ and $(PEO)_{80}[ZnBr_2]$ was assumed to be identical given the estimated error of ±4% in the Raman curve-fitting analysis. According to this graph, a linear relationship exists between Zn−Br coordination number and distance in the range of local environments studied in this paper. Quantitatively, however, the distances here are slightly different than those in the previous publication as shown in the graph. The distances here should be more accurate, since a greater $k$ range was used[20] and multiple files were used in the fits. However, the much different Zn−O distances used, for reasons that will be described shortly, account for most of the differences in Zn−Br distances.

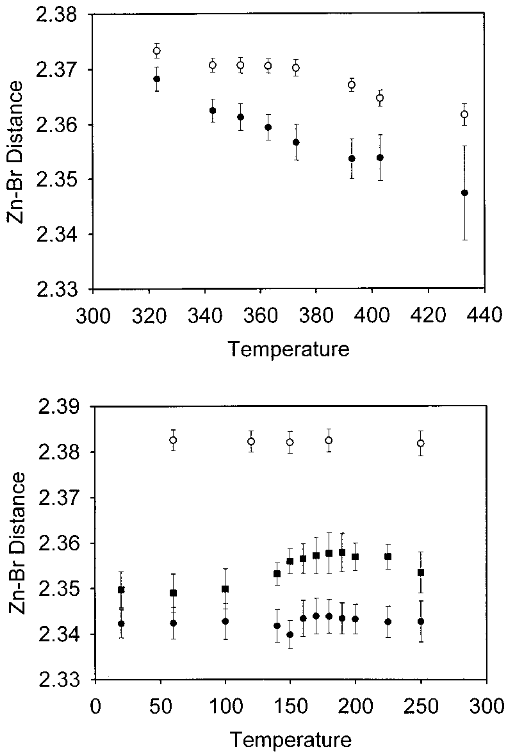

**Figure 5.** Zn−Br distance as a function of temperature. Within a given plot, identical symbols represent data collected from the same sample. Filled symbols represent samples with an average of 2.25 nearest-neighbor bromine atoms, while the filled squares and filled circles in the bottom plot represent data collected from $(PEO)_{20}[ZnBr_2]$ and $(PEO)_{80}[ZnBr_2]$ samples, respectively. A definite drop in mean-squared displacement occurs at higher temperature.

After the EXAFS data had been collected, we realized that morphological changes can occur as samples are stored at room temperature over the period of many days or weeks. Sensitivity to sample preparation conditions has been noted previously.[9] Fortunately, we had made the samples immediately prior to an EXAFS run and were consistent in our sampling handling, so this phenomenon did not seem to substantially affect our results except for one sample. On the basis of data comparison with a sample having the same nominal composition, as well as a clear mismatch in the Zn−Br distance, one $(PEO)_{40}[ZnBr_{2(0.6)}(LiBr)_{0.4}]$ sample did not have 2.66 nearest-neighbor bromine atoms on average. Hence, this sample was treated as an unknown and the number of nearest-neighbor bromine atoms determined from the Zn−Br distance. This sample is shown in Figure 2 as the sample with 2.50 bromine neighbors. The quality of fit with this new bromine coordination environment was equivalent to other samples for both $k^2$ and $k^0$-weighting.

McBreen et al.[6] concluded that the number of nearest-neighbor bromine atoms changed with a temperature change from 25 to 120 °C. This conclusion was based on a decrease in distance of 0.01 Å in the average Zn−Br distance. Within experimental error, our data show a comparable decrease in distance over the same temperature range as shown in Figure 5. Figure 5 also shows that no change in Zn−Br distance occurs below room temperature. Whether any change happens between 250 and 320 K cannot be determined from the data, since the sample-to-sample error in the distance is probably around 0.01 Å. This rather large sample-to-sample error is almost certainly due to morphological changes that occur with aging. The error bars in Figure

5 are probably an overestimate of the error; hence, the decrease at higher temperatures is assuredly real.

There are two possible sources for this drop in Zn−Br distance above room temperature. The first is that higher-order cumulant terms (i.e., the third-order term which is related to thermal expansion) suddenly became important;[21] however, over this temperature range, the drop is too large for thermal expansion. Clearly this drop in distance must represent a reduction in the average number of nearest-neighbor bromine atoms, which is almost certainly accompanied by an increase in the number of nearest-neighbor oxygen atoms. The driving force for these changes is very likely the increased concentration of oxygen atoms available for complexation due to melting of the polymer. Since more oxygen atoms are available, the equilibrium shifts toward more zinc−oxygen coordination and away from zinc−bromine coordination. This observation also probably explains why the environment around zinc can change with aging or with sample preparation, because changes in the fraction of crystalline PEO will change the number of oxygen atoms available for complexation.

A reduction in the number of nearest-neighbor bromine atoms means that the mean-squared displacements in Figure 2 are incorrect for the highest temperatures, since the number of bromine atoms was assumed constant. Based on Figure 4, however, the decrease in coordination implied by the change in radius is approximately 0.15 atoms, and hence the mean-squared displacements are too large by approximately 0.0003 Å$^2$, a difference which was ignored. In fact, the fits used to determine bond strengths (not shown) were too low by approximately this amount in this region; further evidence that the number of nearest-neighbor bromine atoms at the highest temperatures was actually lower than assumed.

The final observation about the Zn−Br bond is that the change in MSD with temperature is independent of the number of nearest-neighbor bromine atoms. Since the change in mean-squared displacement with temperature is proportional to the bond strength, these data show that the Zn−Br bond strength does not depend on the number of bromine atoms. Quantitatively, the respective bond strength can be estimated. The data in Figure 3 can be used to determine an average force constant for the Zn−Br bond if we assume a symmetric pair distribution function for static disorder and harmonic vibration for all bromine atoms in this shell. With these assumptions[10]

$$\sigma^2 = {\sigma_{\mathrm{vib}}}^2 + {\sigma_{\mathrm{stat}}}^2 \tag{1}$$

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

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

where $\mu$ is the reduced mass in atomic mass units (35.96 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 average force constant equals $4\pi^2\mu c^2\nu^2$ and is 1.04 ± 0.04 mdyn/Å. The force constant of gaseous Zn−Br calculated from the frequency obtained from the electronic emission spectrum is 1.03 mdyn/Å.[22]

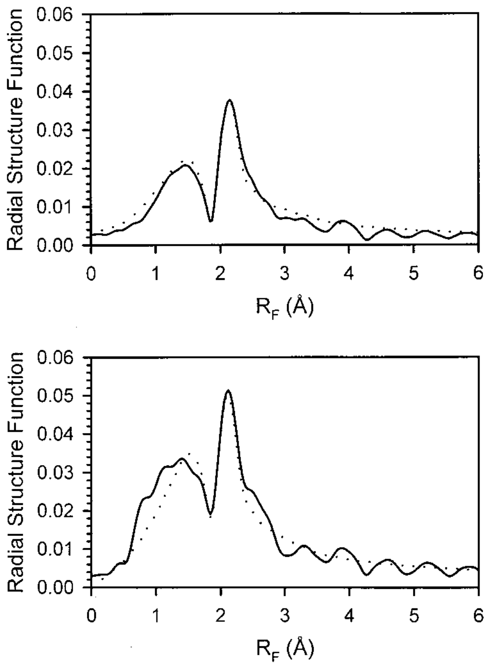

**Figure 6.** Representative $k^0$-weighted spectra measured at 20 K in $R_F$ space. The solid line represents experimental data, while the dashed line represents the best-fit spectra from FEFFIT. The upper plot represents one characteristic type of spectra; the MSD for the oxygen atoms is quite large but the fit is good. The bottom plot represents the second characteristic type of spectra; the MSD for oxygen is much smaller, but features at low $R_F$ are not described well by the model.

**Zn−O.** Fits to Fourier transforms of $k^0$-weighted data were more complicated and can be divided into two qualitatively different cases. The first case is illustrated by the top plot in Figure 6. The fit is satisfactory, and the model used for the simulated structure could be the actual atomic arrangement. The second case is illustrated by the bottom plot in Figure 6, and in this case the model does not fit the data very well. Clear and consistent disagreement occurs between the model and data at low $R_F$. In this case, the model used for the simulated structure is not a good description of the atomic arrangement. Different truncation intervals were chosen, and anomalous features at low $R_F$ consistently occurred, so we are very confident that these features are not artifacts of the data reduction procedures. Further, features at low $R_F$ were noticed in another study of similar materials.[23]

For space-filling reasons, the features at low $R_F$ cannot be due to direct backscattering, since no atoms can get close enough to zinc to backscatter at this distance. One possibility is that these features are due to electronic transitions;[23] however, the fact that these features change substantially in intensity argues against this hypothesis. Interference between two or more backscattered waves is a structural factor that can cause features at low $R_F$. If the low $R_F$ peak was due to interference, then the geometric arrangements must have some specific pattern; such effects were ignored in our analysis. Hence, if the cause really was interference, the descriptions and conclusions that follow are only incorrect with respect to minor details.

The first task in fitting was to determine the number of oxygen atoms for each Zn−Br coordination environment. Given the zinc−bromine distance found in the previous study for zinc with four nearest-neighbor bromine atoms,[8] the size of the bromine anion, and the crystal structure in pure zinc bromide,[24] the only reasonable assignment was to assume that zinc with four nearest-neighbor bromine atoms has no nearest-neighbor oxygen atoms. In fact, zinc with four nearest-neighbor bromine atoms probably has an atomic arrangement equivalent to crystalline zinc bromide.[25] From simple space-filling requirements based on the Zn−O and Zn−Br distances, zinc atoms with three nearest-neighbor bromine atoms could only have one or two oxygen nearest neighbors, while zinc atoms with two nearest-neighbor bromine atoms could only have two or three nearest-neighbor oxygen atoms. The latter could have four oxygen atoms only if the oxygen distances were much larger, which means the Zn−O distances were grossly incorrect. Such a result is possible because of the poor fits to the data but is extremely unlikely.

The task was to determine the best combination of oxygen atoms from the five samples measured at low temperatures. Changing the average number of oxygen atoms by approximately 0.75 changed the oxygen mean-squared displacement by 0.01 Å$^2$; i.e., the best-fit value of the mean-squared displacement was very sensitive to the number of oxygen atoms for $k^0$-weighted spectra. The number of nearest-neighbor oxygen atoms was determined by requiring mean-squared displacements to be positive and as small as possible. On the basis of this analysis, zinc with three bromine nearest neighbors had one oxygen atom, while zinc with two bromine nearest neighbors had three nearest-neighbor oxygen atoms.

This procedure has a number of problems. First, for the samples where the fits are quite good (as represented by the top plot of Figure 6), the mean-squared displacements were quite large, ∼0.02 Å$^2$ at 20 K. Considering only these samples and applying the same criteria gives two as the number of oxygen atoms for zinc with two bromine nearest neighbors. The fact that the MSD for the spectra represented by the bottom part of Figure 6 would have been negative in some cases could reasonably be ignored since the model clearly is not a perfect description of the atomic arrangement anyway. However, changing the amplitude reduction factor to a perfectly reasonable value of 0.8 reduces the mean-squared displacements to perfectly reasonable values 0.003 and 0.013 Å$^2$ for the two cases in Figure 6, which argues that the assignment of three rather than two oxygen atoms is correct. Further, if both the mean-squared displacement and the number of oxygen atoms were varied independently for each sample, the combination of three and one oxygen atoms (for zinc with two and three nearest-neighbor bromine atoms respectively) was the best-fit result more often than any other combination.

These values are not consistent with the average coordination numbers found in our previous publication although those values were based on only two samples.[8] More disconcerting, the Zn−O distance is not the same as found previously, although the distance is consistent with that found by Einset et al.[7] Indeed, researchers have reported Zn−O distances from 1.97 to 2.25 Å in these complexes, attesting to the fact that fitting Zn−O shells is difficult. The correct distance cannot be regarded as being completely settled because the model does not satisfactorily describe the actual spectra. However, we do believe that the distance presented here is most likely correct, since in some cases good fits were obtained.

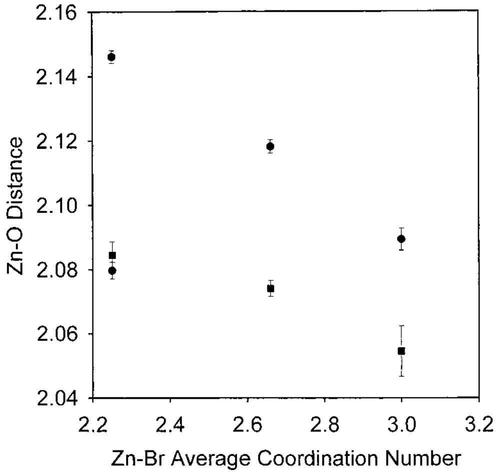

**Figure 7.** Zn−O distance plotted as a function of nearest-neighbor bromine atoms. These distances were determined from sets of data at different temperatures. Square symbols represent sets of data collected above room temperature, while circles represent data collected below room temperature.

The Zn−O distance as a function of bromine coordination number is shown in Figure 7. Clearly, the average distance is around 2.10 Å, which is close to the average distance for oxygen 6-fold coordinated to zinc in compounds such as zinc acetate dihydrate. This result shows that substituting bromine atoms for oxygen atoms, i.e. increasing the Zn−Br coordination number, decreases the Zn−O bond distance; note that decreasing the Zn−O coordination number also decreases the Zn−O bond distance in zinc compounds with only first-shell oxygen atoms.[26] However, the sample-to-sample error is clearly so large as to make such a conclusion tenuous at best. This sample-to-sample error was independent of the two types of spectra shown in Figure 6.

Figure 8 shows the variation in mean-squared displacement with temperature. Ignoring for the moment the drop in mean-squared displacement around 200−250 K, two qualitatively different types of behavior are evident as was previously demonstrated in Figure 6. The first of these occurs when the mean-squared displacement is almost constant within experimental error over the entire temperature range; i.e., the static variation in distance is so large that thermal changes are masked. The second type is when, after a flat region at very low temperatures, the mean-squared displacement rises as thermal vibrations become more important. This second type, as represented by the bottom plot, is typical of most bonds. The rise in mean-squared displacement with temperature for Zn−O is higher than in Zn−Br, which indicates a weaker interaction between zinc and oxygen. Differences in slope at low temperature between the two samples that have nominally the same number of nearest-neighbor oxygen atoms almost certainly represents errors due to fitting inaccuracies rather than real differences in bond strengths.

A significant drop in the mean-squared displacement followed by a rise at higher temperatures is shown in Figure 8. The top and bottom plots of Figure 8 clearly show this behavior; unfortunately, data were not collected at the appropriate intervals to be sure whether such a change occurs with other samples. The bottom plot represents the qualitative behavior where the

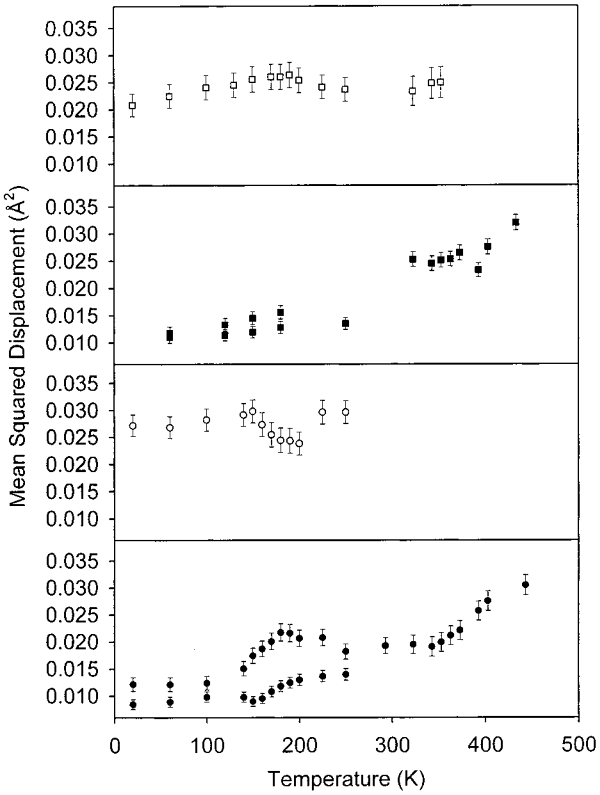

**Figure 8.** Change in Zn−O mean-squared displacement with temperature. From bottom to top, the average number of nearest-neighbor bromine atoms was 2.25, 2.50, 2.66, and 3.00 corresponding to an average number of nearest-neighbor oxygen atoms of 2.50, 2.00, 1.68, and 1.08.

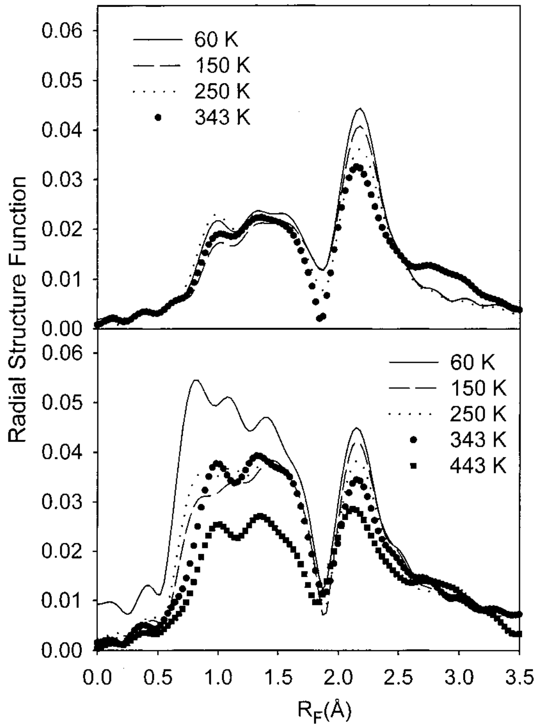

**Figure 9.** Radial structure functions for $k^0$-weighted spectra as a function of temperature. The top plot shows spectra where the fit of the MSD to experimental data was satisfactory, while the bottom plot shows spectra where the fit of the MSD was not satisfactory. The sample represented by the top plot contains zinc with an average of approximately 1 nearest-neighbor oxygen atom and 3 nearest-neighbor bromine atoms, while the sample represented by the bottom plot contains zinc with an average of approximately 2.5 nearest-neighbor oxygen atoms and 2.25 nearest-neighbor bromine atoms.

mean-squared displacement is low at low temperatures, while the top plot represents the qualitative behavior where the mean-squared displacement is high at low temperatures. This drop in mean-squared displacement is at a temperature roughly corresponding to the glass transition temperature of the material.[9] As far as we are aware, this study represents the first time a feature in EXAFS spectra has been found to be sensitive to the glass transition.

Radial structure functions from $k^0$-weighted data at selected temperatures for the top and bottom plots of Figure 8 are shown in Figure 9. The drop in MSD with increasing temperature shown in Figure 8 is reflected as a constant or a slight increase in peak height for the broad peak located between $R_F = 1.0-2.0$. Note that the normal behavior of a nearest-neighbor peak in a RSF is a roughly linear drop in peak height with temperature. The behavior of the peak at $R_F \cong 2.3$ is typical, even though this peak has contributions from both oxygen and bromine. Subtle changes in peak shape for the peak at $R_F = 1.0-2.0$ are present, but understanding these changes is not possible using the current model.

A similar drop in mean-squared displacement followed by a rise was found in the ferroelectric−ferroelectric and ferroelectric−dielectric phase transformation in $Fe_3B_7O_{13}Br$.[27] No detailed morphological explanation was given in that paper to describe this behavior. An apparent drop in the number of nearest-neighbor atoms was found in the melting of elemental lead.[28] However, in that experiment, changes in the number of nearest-neighbor atoms and in the mean-squared displacement could be monitored independently because of the good agreement between the FEFF model and the experimental data. The authors concluded that the drop in the number of nearest-neighbor atoms was not real. Rather, EXAFS is not able to measure the broad structureless component due to diffusion because of the finite energy range available. Hence, the perceived drop in coordination number was actually due to a significant increase in the diffusional hopping rate of lead atoms.

Because the model did not fit the experimental data well, a drop in mean-squared displacement could not be distinguished from an increase in the number of nearest-neighbor oxygen atoms. A drop in MSD or an increase in the number of nearest-neighbor oxygen atoms is counterintuitive. A drop in mean-squared displacement means that either thermal vibrations have decreased or the static variation in distances have decreased. First, a decrease in thermal vibration is probably not the cause because noncovalently bonded interatomic thermal vibrations should either be unaffected by the glass transition or increase dramatically. Second, a decrease in static variation means that ordering occurs with the glass transition, which is certainly possible if nonequilibrium structures were frozen at the glass transition. The third possibility is that an increase in the number of nearest-neighbor oxygen atoms could mean that a substantial change in speciation occurred, which is not supported by any other data and can be rejected. Fourth, an increase in the number of nearest-neighbor oxygen atoms could also be due to a reduction in the number of diffusional hops of oxygen in and out of zinc's coordination environment. Again, such a change is counterintuitive. A fifth possibility is that Figures 8 and 9 represent some subtle change in geometry; however, this explanation is also unlikely since samples with initially high and low mean-squared displacements show this behavior.

We consider the second explanation which postulates freezing-in of nonequilibrium structures at the glass transition to be the most likely. If this explanation is correct, however, then the glass transition represents the formation of nonequilibrium structures at the angstrom scale, which, as far as we are aware, has not been postulated previously. Further, this result would result in a major advancement in our understanding of the glass transition.

## Summary

The arrangements of atoms around zinc, and the changes in those arrangements with temperature, have been investigated in PEO/zinc bromide/lithium bromide complexes with different numbers of nearest-neighbor bromine and oxygen atoms. The relationship between the number of nearest-neighbor bromine and oxygen atoms has been established to a much higher level of accuracy than in previous papers. We have concluded that zinc with four nearest-neighbor bromine atoms has no nearest-neighbor oxygen atoms and zinc with three nearest-neighbor bromine atoms has one nearest-neighbor oxygen atom, while zinc with two nearest-neighbor bromine atoms has three nearest-neighbor oxygen atoms. No evidence of zinc with one nearest-neighbor bromine atom was found. The temperature dependence of the features in EXAFS spectra due to bromine is typical of other strongly bonded nearest-neighbor atoms studied in the literature. However, very unusual behavior was observed in the feature due to nearest-neighbor oxygen atoms, namely a marked decrease in the oxygen atom mean-squared displacements occurring in the vicinity of the glass transition. Several possible explanations for this behavior have been discussed; however, at this point the question must be regarded as open. Further experiments are planned on other bromine-containing polymers to see whether similar behavior at the glass transition might be evident.

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