EXAFS studies on Zn(II) complexes with 1,3-bis(aminomethyl)cyclohexane of ethylene–methacrylic acid copolymer

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(Received 26 November 1990; revised 3 June 1991; accepted 1 July 1991)

Extended X-ray absorption fine structure (EXAFS) experiments were performed at 25 and 105°C for Zn(II) salts of ethylene–methacrylic acid (5.4 mol%) copolymer and their complexes with 1,3-bis(aminomethyl)cyclohexane (BAC) (EMAA-Zn-BAC). The zinc carboxylate in EMAA-Zn-BAC systems was in a four-fold coordination at room temperature. The Zn–O distance increased with increasing BAC content, and became smaller at 105°C than at room temperature for EMAA-0.60Zn and EMAA-0.60Zn-0.40BAC but scarcely changed with temperature for EMAA-0.60Zn-0.97BAC. The fluctuation factor (σ) was larger at 105°C than at room temperature for all the samples, due to thermal vibration. In this paper, it is pointed out that these EXAFS results support the presence of an order–disorder transition in ionic clusters.

(Keywords: EXAFS; ethylene ionomer; Zn(II) complexes with BAC; temperature dependence)

INTRODUCTION

Recently, we pointed out the presence of a first-order order–disorder transition in ionic clusters of ethylene ionomers[1,2]. For example, in Zn(II) complexes with 1,3-bis(aminomethyl)cyclohexane (BAC) of ethylene–methacrylic acid copolymer (EMAA) (hereafter denoted as EMAA-xZn-yBAC, where x is the degree of neutralization by Zn and y is the equivalent ratio of divalent BAC to COOH), the ionic clusters are in an ordered state like ionic crystallites at room temperature, and with increasing temperature, they transform into a disordered state at the transition temperature (T_i), ~60°C. This order–disorder transition has a few peculiar features: the transformation from the disordered state to the ordered state obeys a relaxational process with a very long relaxation time, for example 38 days at 28°C; and the volume of ionic clusters is smaller in the disordered state than in the ordered state. This was explained by the voluminous ionic clusters formed by the bulky Zn(II) complexes with BAC.

Generally, extended X-ray absorption fine structure (EXAFS) analysis gives information about the number of nearest neighbours around an X-ray absorbing atom, their atomic nature, their distance from the absorbing atom and their distribution. Therefore, EXAFS spectroscopy is one of the most powerful methods used to clarify the coordination structure of ionic groups such as metal carboxylates and how the ionic groups aggregate to form ionic clusters. A lot of elaborate EXAFS work by Ding and Cooper[3] suggested that ionic clusters have an internal structure and their results seem to support our model of an order–disorder transition[1,2]. However, to our knowledge, EXAFS measurements on ionomers have not yet been conducted as a function of temperature, although they are very important for examining how the structure and thermal vibrations of ionic groups change with temperature.

This work examines how the local structure inside ionic clusters changes with temperature using EXAFS studies of EMAA-Zn-BAC systems.

EXPERIMENTAL

The EMAA is ACR-1560 (Du Pont-Mitsui Polychemicals Co. Ltd) with a methacrylic acid content of 5.4 mol%. The Zn(II) salts and their complexes with BAC used

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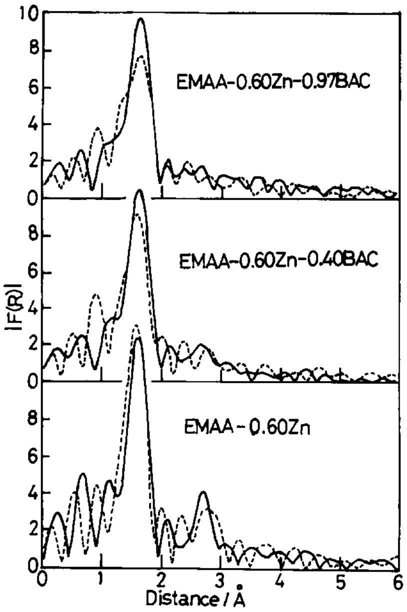

Figure 1 Radial structure function $|F(R)|$ *versus* distance from the Zn atom: (——) room temperature; (– – –) 105°C

here are the same as those prepared previously[2,4,5]. They were prepared by melt reactions of EMAA and zinc oxide or of the Zn(II) salts and BAC. The formation of Zn(II) salts/Zn(II) complexes with BAC was confirmed by i.r. spectra[5].

EXAFS measurements were carried out using synchrotron radiation from the EXAFS facilities at BL-10B of the Photon Factory in the National Laboratory for High-Energy Physics (KEK-PF), Japan[6]. The radiation was monochromatized with a channel-cut Si(311) crystal and an entrance slit. The measurements at room temperature were done under air. For the measurements at 105°C, the sample was set up at the head of an electric heater which was kept under a reduced pressure using a rotary pump in a box with Kapton-film windows. Data were collected in the range from ~400 eV on the lower energy side of the Zn absorption K-edge of 9.659 keV to ~10.7 keV on the higher energy side.

RESULTS AND DATA ANALYSES

The extracted EXAFS function $[\chi(k)]$ from the observed absorption coefficient was generally expressed as

$$\chi(k) = [\mu(k) - \mu_0(k)]/\mu_0(k) \qquad (1)$$

Here, $\mu_0(k)$ is the absorption coefficient of the free atom which was estimated by using a cubic spline function, and k is the wave number of the photoelectrons expressed as $k = (2m/h^2)^{1/2}(E - E_0)^{1/2}$ (where E_0 is the energy at the absorption edge of the phonon and E is the energy of the incident X-ray). The radial structure function $(F(R))$ was obtained by Fourier transformation from k-space to R-space:

$$F(R) = (2\pi)^{-1/2} \int_{k_{\min}}^{k_{\max}} k^3\chi(k)\exp(-2ikR)\,dk \qquad (2)$$

where $\chi(k)$ is multiplied by k^3 to cancel the diminution of the wave amplitude with increasing k. The relation of $F(R)$ *versus* distance from the Zn atom (R) was calculated in the range of k from 4 Å $(k_{\min})$ to 15 Å $(k_{\max})$. *Figure 1* shows $|F(R)|$–R curves for EMAA-Zn-BAC systems. At room temperature, the first peak is observed near 1.6 Å for EMAA-0.6Zn. As the BAC content increases, the peak becomes broader. At 105°C, the first peak slightly shifts to lower R values for EMAA-0.60Zn. At 105°C, as BAC is added to EMAA-0.60Zn, the peak around 1.6 Å becomes considerably broader and a new peak appears near 1.4 Å as a shoulder of the first peak. In the EMAA-Zn-BAC system, the Zn(II) complexes with BAC are bonded to COO^- and hence the first peak near 1.6 Å may come from the scatterings at the O atom neighbouring the Zn atom. The shoulder peak near 1.4 Å might come from the scatterings at the N atom of BAC coordinated near the Zn atom.

The $k^3\chi(k)$ for the first peak was obtained by reverse Fourier transformation of equation (2):

$$k^3\chi(k) = (2\pi)^{-1/2} \int_{R_{\min}}^{R_{\max}} W(R)F(R)\exp(2ikR)\,dR \qquad (3)$$

Here, the first peak was extracted by a window function,

$$W(R) = \begin{cases} \{1 - \cos[\pi(R - R_{\min})/D]\}/2, & \text{when } R_{\min} \leqslant R < R_{\min} + D \\ 1, & \text{when } R_{\min} + D \leqslant R \leqslant R_{\max} - D \\ \{1 - \cos[\pi(R_{\max} - R)/D]\}/2, & \text{when } R_{\max} - D \leqslant R \leqslant R_{\max} \end{cases}$$

where $D = 0.1$ Å. Assuming that one electron scatters only once at one kind of O atom and is in a plane wave, we obtain

$$k^3\chi(k) = A(k)\sin[2kr + \phi(k)] \qquad (4)$$

$$A(k) = S_0k^2/r^2NF(k)\exp(-2\sigma^2k^2)\exp(-2r/\lambda) \qquad (5)$$

where $A(k)$ and $\sin[2kr + \phi(k)]$ are contributions from the amplitude and phase shift parts, respectively, r is the distance from the absorbing atom to the coordination shell, N is the coordination number of atoms at r, σ is the fluctuation factor, $F(k)$ is the backscattering amplitude, $\phi(k)$ is the phase shift function, λ is the mean free path of the phonon and S_0 is a factor of non-elastic scatterings. Using the theoretical values of Teo and Lee[7] for $F(R)$ and $\phi(k)$, and assuming $\lambda = 5$ Å and $S_0 = 1$, the fittings for the $k^3\chi(k)$–k curves were done for EMAA-0.60Zn by the non-linear least squares method. The fitting curves for the first peak are shown in *Figure 2*. The values of r, N and σ obtained are listed for EMAA-0.60Zn in *Table 1*. The Zn–O distance (r) and the coordination number (N) are 1.967 Å and 4.0, respectively, at room temperature, which are well consistent with the values of Ding and Cooper[3]. Therefore, the zinc carboxylate of EMAA is in a four-fold coordination.

Generally, the values of $\phi(k)$ should change in both nature and ionization of chemical bond but this is ignored in the theoretical values of $\phi(k)$ used in the above calculation. Therefore the values of r, N and σ calculated above sometimes involve errors originating in $\phi(k)$. To avoid errors, the values of r, N and σ were calculated using the data of EMAA-0.60Zn at room temperature as a standard as follows.

Determination of r. The phase shift term,

$$\sin[2kr + \phi(k)],$$

in equation (4) is expressed as

Table 1 Structural parameters for EMAA-*x*Zn-*y*BAC

Sample	Temperature (°C)	Coordination no.		Distance of Zn-O (Å)		Fluctuation factor (Å)	
		N	Δ	r	Δ	σ	Δ
EMAA-0.60Zn	25	4.0		1.967		0.047	
	105	5.0	0.1	1.947	0.014	0.056	0.001
EMAA-0.60Zn-0.40BAC	25	4.0	0.1	1.979	0.002	0.055	0.001
	105	4.1	0.1	1.968	0.015	0.065	0.001
EMAA-0.60Zn-0.97BAC	25	4.1	0.1	1.997	0.009	0.061	0.001
	105	4.3	0.2	1.996	0.019	0.068	0.002

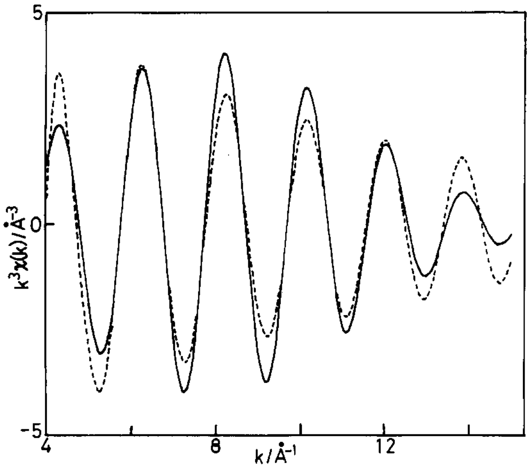

Figure 2 Fit (---) of the Fourier-filtered $k^3\chi(k)$ *versus* k curve for the first peak in EMAA-0.60Zn, assuming that the contribution is due to the O atom

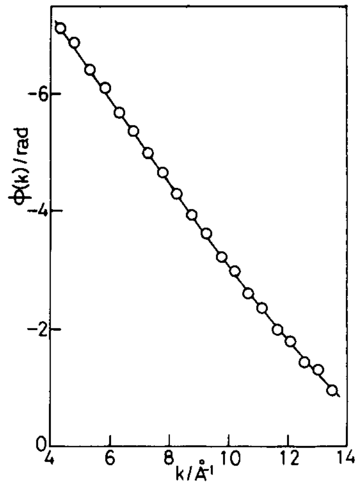

Figure 3 Plots of $\phi(k)$ *versus* k

$$\phi(k) = n\pi - 2kr, \text{ at } k^3\chi(k) = 0 \quad [\text{the end of } k^3\chi(k)] \qquad (6)$$

and

$$\phi(k) = (n+2)\pi/2 - 2kr, \text{ at } k^3\chi(k) = \pm 1 \quad [\text{the loop of } k^3\chi(k)] \qquad (7)$$

Using the values of k at $k^3\chi(k) = 0$ and ± 1 (*Figure 2*) and r (*Table 1*) for EMAA-0.60Zn at room temperature, $\phi(k)$ was obtained and is plotted against k in *Figure 3*. The plots are slightly curved, although they should be linear on the assumption that one electron scatters only once at one kind of scattering O atom and is in a plane wave. The values of $k^3\chi(k)$ for the other samples except EMAA-0.60Zn at room temperature were calculated by the reverse Fourier transformation of the first peak [equation (3)] as already described, and the values of k were obtained by equations (6) and (7). The experimental values of $\phi(k)$ were obtained from the $\phi(k)$–k plots in *Figure 3*. By using both values of k and $\phi(k)$ obtained above, the values of r were obtained by equations (6) and (7) and are listed in *Table 1*.

Determination of N and σ. In equation (5), $k^3\chi(k) = A(k)$ when $\sin[\phi(k) + 2kr] = \pm 1$ and then equation (5) is consistent with the envelope curve in the $k^3\chi(k)$–k curves. The envelope curve for the standard sample (EMAA-0.60Zn at room temperature) is denoted as $A(k)$. Since the values of S_0, $F(k)$ and λ are common in all the samples, the following equation is obtained:

$$\log(A/A_0) = -2(\sigma^2 - \sigma_0^2)k^2 + X$$
$$X = 2\log(r_0/r) + \log(N/N_0) - 2(r - r_0)/\lambda \qquad (8)$$

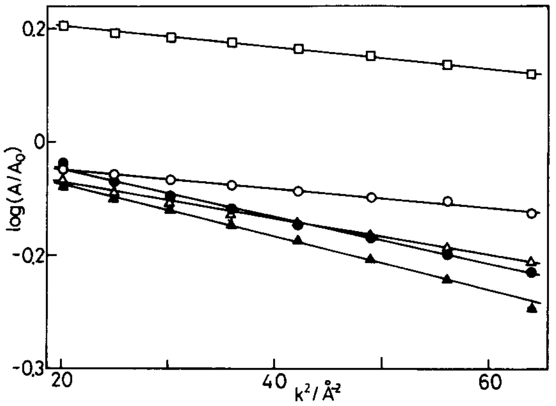

Figure 4 Plots of $\log(A/A_0)$ *versus* k^2: (□) EMAA-0.60Zn at room temperature: (○) and (●) EMAA-0.60Zn-0.40BAC at room temperature and 105°C, respectively; (△) and (▲) EMAA-0.60Zn-0.97BAC at room temperature and 105°C, respectively

where N_0, r_0 and σ_0 are for EMAA-0.60Zn at room temperature (*Table 1*) and the values of r have already been calculated. *Figure 4* shows plots of $\log(A/A_0)$ *versus* k^2, from which both values of $(\sigma^2 - \sigma_0^2)$ and N were obtained. The values of N/N_0 and $\sigma^2 - \sigma_0^2$ should be correctly obtained using this calculation, since it minimizes the contribution of the difference in $F(k)$ between theoretical and experimental values to N and σ.

DISCUSSION

Table 1 lists values of r, N and σ. Zinc carboxylate of EMAA is in a four-fold coordination at room temperature as already described, since r and N are estimated to be 1.967 Å and 4.0, respectively, at room temperature. At 105°C, however, the value of N was estimated to be 5.0. I.r. spectral studies on EMAA-0.60Zn are in progress in our laboratories. At room temperature, one absorption peak was observed near $1584\,\mathrm{cm}^{-1}$ assigned to the antisymmetric stretching vibration of COO^- in a four-fold coordination. With increasing temperature above T_i, a peak near $1565\,\mathrm{cm}^{-1}$ appears and increases and the $1584\,\mathrm{cm}^{-1}$ peak decreases. The $1565\,\mathrm{cm}^{-1}$ peak is assigned to the antisymmetric stretching vibration of COO^- in a six-fold coordination. Therefore, the i.r. results suggest that the structure of zinc carboxylate in EMAA tends to transform from four-fold to six-fold coordination with increasing temperature above T_i. In the present EXAFS data, N of EMAA-0.60Zn increases from 4.0 to 5.0 with increasing temperature from room temperature to 105°C and this increase can be explained by the transformation from four-fold to six-fold coordination. As BAC is added to EMAA-0.60Zn, the values of r and σ gradually increase at room temperature, but the value of N scarcely changes. Therefore, the coordination of BAC to $\mathrm{Zn(\text{–}COO)_2}$ broadens the Zn–O distance and increases the degree of fluctuation but does not change the coordination structure of $\mathrm{Zn(\text{–}COO)_2}$.

Previously, we proposed the order–disorder transition model of ionic clusters as already described in the Introduction. At room temperature below the transition temperature (T_i was ~50°C for the present samples[2]), the ionic clusters are in an ordered state inside, but with increasing temperature above T_i, the inside of the ionic clusters is transformed into a disordered state. Therefore, it is interesting to note how the order–disorder transition affects the EXAFS data. When the temperature is increased from room temperature to 105°C, the value of r decreases in EMAA-0.60Zn and EMAA-0.60Zn-BAC but scarcely changes in EMAA-0.60Zn-0.97BAC, while the value of σ increases in all the samples. The temperature dependence of σ has been reported for a few inorganic compounds[8–11]. The increase in σ, of course, comes from both the thermal vibration of the lattice and the structural changes with temperature. A structural change such as a transformation from a crystalline to an amorphous state generally causes a large increase in σ. On the other hand, the contribution of the thermal lattice vibration to σ is connected with the Einstein temperature (θ_E), where the increase of σ with increasing temperature is expressed by the relation $[\theta_E(T_1)/\theta_E(T_2)]^2 = \tanh(\theta_E/2T_1)/\tanh(\theta_E/2T_2)$. As already described, the zinc carboxylate of EMAA-0.60Zn tends to undergo a transformation from four-fold to six-fold coordination around T_i. In EMAA-Zn-BAC systems, the Zn-BAC salts retain a six-fold coordination over a wide temperature range from room temperature to 105°C. However, the value of $\sigma^2(105°\mathrm{C}) - \sigma^2(\text{room temperature})$ is around 0.01 regardless of the coordination structure in these systems, and this result suggests that the increase in σ with temperature comes from an enhancement of thermal vibration which is connected with the order–disorder transition. Our recent dielectric relaxation results[5,12] indicate that the Zn(II) salts and Zn(II)-BAC complexes in EMAA are rather flexible at 105°C and so vibrate enough to cooperate with the so-called micro-Brownian molecular motion of long segments in the rubbery state. When ionic clusters are not formed, the β' relaxation, assigned to micro-Brownian molecular motion of long segments, appears above T_g and the γ relaxation, assigned to the local molecular motion of short segments, occurs below T_g. When the ionic clusters are formed, the β' relaxation is replaced by two relaxations, an α relaxation above T_i and a β relaxation below T_i, which are attributed to micro-Brownian molecular motion of long segments including the Zn(II)/Zn(II)-BAC carboxylates and to a local molecular motion of short segments including Zn(II)/Zn(II)-BAC carboxylates not incorporated into the ionic clusters, respectively. Hence, when the ionic clusters are formed, they are in an ordered and rigid state below T_i and act as crosslinks which disturb the appearance of the β' relaxation, but above T_i, they are in a disordered and rather flexible state and so the ionic groups inside the ionic clusters take part in the α relaxation. However, we cannot state here how the value of σ is affected by the order–disorder transition of ionic clusters, because we have only two data values at room temperature and 105°C. Nevertheless, the increase of σ with temperature can enhance the thermal vibration of the Zn–O bond and this indicates that the ionic groups inside the ionic clusters vibrate more at 105°C than at room temperature in the EMAA-Zn-BAC systems.

EXAFS measurements give us information on the structure and thermal fluctuations around the Zn cation, but the information seems to be sometimes too local to examine the structure and state of ionic clusters as a whole. Further EXAFS studies are in progress in our laboratories.

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