*Macromolecules* **2001,** *34,* 1515−1517

# X-ray Absorption Spectroscopic Studies on Pressure-Induced Coordination−Structural Change of a Zinc-Neutralized Ethylene−Methacrylic Acid Ionomer

**Hideki Hashimoto,[†] Shoichi Kutsumizu,[*,‡] Kenji Tsunashima,[§] and Shinichi Yano[||]**

*Toray Research Center, Sonoyama 3-3-7, Otsu,*
*Siga 520-8567, Japan; Instrumental Analysis Center,*
*Gifu University, Yanagido 1−1, Gifu 501-1193, Japan;*
*Film Research Laboratories, Toray Industries Inc.,*
*Sonoyama 1−1−1, Otsu, Siga 520-0842, Japan; and*
*Department of Chemistry, Faculty of Engineering,*
*Gifu University, Yanagido 1−1, Gifu 501-1193, Japan.*

*Received February 3, 2000*
*Revised Manuscript Received August 28, 2000*

## Introduction

Ethylene−methacrylic acid (E−MAA) ionomers are a representative ion-containing polymer, where a small amount of carboxylic acid groups introduced as MAA comonomers are partially or fully neutralized (i.e., ionized) by metal cations. As a result, the ionic groups associate and form ion-rich domains of nanometer size (hereafter simply called ionic aggregates) in the hydrophobic poly(ethylene) (PE) matrix. The formation of the ionic aggregates markedly improves the material properties compared with the host polymer PE, and thus, E−MAA ionomers are commercially very important for uses of molding and packaging applications. To date, extensive work has been devoted to understand the local environment inside the ionic aggregates as well as the size, shape, and distribution in space of the aggregates.[1,2]

In zinc(II)-neutralized E−MAA ionomers, the local environment around zinc(II) has been investigated primarily by infrared (IR) spectroscopic[3−5] and extended X-ray absorption fine structure (EXAFS)[6−10] analyses. It has been pointed out that the coordination structure around zinc(II) changes depending on temperature[3,5,7] and water absorption,[4,10] but there still remain several controversies. Very recently, we found that the coordination structure around zinc(II) is primarily governed by pressure applied at 130 °C in the melt:[5] When the pressure is zero (i.e., the sample is placed under vacuum) in the melt, the zinc(II) carboxylates preferentially form a hexacoordination structure, which is characterized by two IR carboxylate antisymmetric stretching ($\nu_{as}(COO^-)$) bands at 1624 and 1538 cm$^{-1}$, but increasing the pressure favors a tetracoordination structure with a strong $\nu_{as}(COO^-)$ band at 1585 cm$^{-1}$ (see Figure 1). An important feature is that when the sample is cooled under a constant pressure, it retains the coordination structure determined in the melt to room temperature and remains unchanged upon the release of pressure at room temperature. Furthermore, even exposure to the atmospheric pressure ($P \sim 0.1$ MPa) is enough to change the coordination structure largely. Such a pressure effect on the coordination structure around zinc(II) seems to be characteristic of the zinc(II) carboxylates surrounded by polymer backbone and is quite dependent upon the polymer compositions, most marked for the 60%-neutralized salt of E−MAA with a MAA content of 5.4 mol %, denoted as E-0.054MAA-0.6Zn. Here, an interesting fact is that metal carboxylates incorporated into ionomers in some cases show unusual and intriguing properties not seen for the low-molecular-mass compounds.

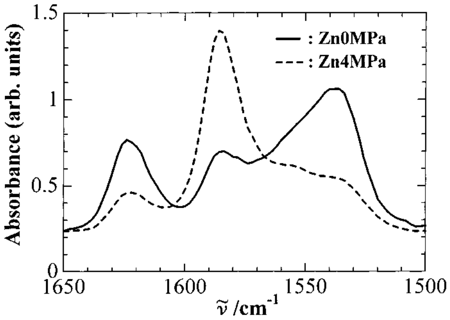

**Figure 1.** Infrared (IR) spectra of Zn0MPa (solid curve) and Zn4MPa (broken curve) in the carboxylate antisymmetric stretching band region at room temperature. Notations “Zn0MPa” and “Zn4MPa” are described in the text.

This paper examines the pressure effect on the coordination structure of zinc(II) carboxylates in E-0.054-MAA-0.6Zn by measuring EXAFS spectra at the zinc absorption edge, which is expected to be complementary with the IR studies.

## Experimental Section

E-0.054MAA-0.6Zn was kindly given to us in pelletized form by Technical Center, Du Pont-Mitsui Polychemicals Co., Ltd., Chiba, Japan. The samples were prepared by a melt reaction of E−MAA with zinc oxide, as described previously.[11] The pellet samples were compression-molded at 130 °C and at 200 kg/cm$^2$ (instrumental value) to transform into $\sim$30-$\mu$m thick films for IR and $\sim$500-$\mu$m thick sheets for EXAFS measurements. These two types of samples were first vacuum-dried at 130 °C for 2 h by using a rotary pump (the pressure $= 7 \times 10^{-4}$ MPa) and cooled to room temperature in 2 h (cooling rate: $\sim$1 °C min$^{-1}$). These samples are denoted as Zn0MPa in this paper, where “Zn” represents the type of neutralizing cation and “0MPa” means the treatment at 130 °C for 2 h under vacuum. Both film and sheet were then cut into two pieces, and to one piece of each a hydrostatic pressure of dry N$_2$ gas was applied using an autoclave and heated at 130 °C for 2 h, followed by cooling to room temperature in 2 h. The pressure at 130 °C was 4 MPa, and the samples are denoted as Zn4MPa. The coordination−structural changes during the processes were also monitored by IR for the film samples, as in ref 5. The sheet samples were stored in a dry desiccator for about 10 days prior to use.

EXAFS spectra were measured using synchrotron radiation at BL-12C of the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK−IMSS−PF), Tsukuba, Japan. The radiation was monochromatized with a double Si(111) crystal. Energy calibration was performed with copper foil. The samples were measured at room temperature under air in the range from $\sim$450 eV below the zinc K-absorption edge of 9660 eV to $\sim$950 eV above. The analytical procedures of the data are described in the Results and Discussion section.

---

[*] To whom correspondence should be addressed. E-mail: kutsu@cc.gifu-u.ac.jp.

[†] Toray Research Center.

[‡] Instrumental Analysis Center, Gifu University.

[§] Film Research Laboratories, Toray Industries Inc.

[||] Department of Chemistry, Faculty of Engineering, Gifu University.

10.1021/ma0001988 CCC: $20.00

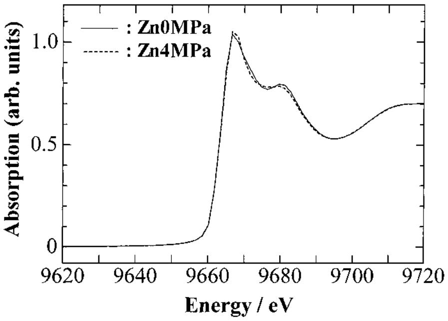

**Figure 2.** XANES spectra of Zn0MPa (solid curve) and Zn4MPa (broken curve). Error bars are roughly equivalent to the line thickness.

## Results and Discussion

Figure 1 shows the IR spectra in the region 1650−1500 cm$^{-1}$ for (a) Zn0MPa and (b) Zn4MPa. Both samples exhibit three $\nu_{as}(COO^-)$ bands at 1624, 1538, and 1585 cm$^{-1}$, but the effect of pressure is evident: As the pressure applied at 130 °C is increased, the intensities of two bands at 1624 and 1538 cm$^{-1}$ decrease while that of the 1585 cm$^{-1}$ band increases. Two isosbestic points at 1605 and 1566 cm$^{-1}$ are visible, which is more clearly shown in Figure 3 of ref 5. If each individual coordination structure around zinc(II) were deformed continuously by pressure, the observed IR spectral change would never show isosbestic points; rather, a gradual peak shift should occur. Therefore, the observed IR spectral change includes an important implication that this pressure-induced transformation occurs between two distinct coordination states and the pressure shifts the equilibrium between the two. The detailed analysis of IR results will be reported separately.[12]

The effect of pressure on the X-ray absorption near edge structure (XANES) spectra at the zinc K edge is shown in Figure 2. It can be seen that in Zn4MPa a peak at 9666 eV is intensified while the high-energy shoulder at ~9680 eV is less evident compared with Zn0MPa. Duplicate measurements confirmed that these changes, although seem subtle in contrast with the change of the IR $\nu_{as}(COO^-)$ band profile (Figure 1), are certainly beyond the experimental errors. Since the XANES region mainly reflects the electronic structure (i.e., valence) of zinc(II), it is reasonable that the difference observed between the two samples is not so large.

The oscillations seen far beyond (>50 eV) the edge are a result of interference between electrons outgoing from zinc(II) and backscattered from neighboring atoms, which provide information on the local structure around zinc(II). According to usual EXAFS data treatments, such oscillations were converted to $k\chi(k)$ vs $k$ curves, where $\chi(k) = [\mu(E)\text{-}\mu_0(E)]/\mu_0(E)$; $\mu(E)$ is the measured absorption coefficient of an atom in the material of interest, and $\mu_0(E)$ is the coefficient of the atom in the free state, both of which are functions of $k$ through the relation, $k = \sqrt{[(2m_e/\hbar^2)(E-E_0)]}$, where $E_0$ is the absorption edge energy, $m_e$ the mass of an electron, and $\hbar$ Planck's constant divided by $2\pi$. After truncation of the $k\chi(k)$ vs $k$ curves to the region $k = 2-14$ Å$^{-1}$, the data were Fourier transformed to obtain the radial structure function (RSF), which are presented in Figure 3. When the pressure in the melt is changed from 0 to 4 MPa, in part a, the RSF value of a peak at $R_F \sim 1.5$ Å is 1% decreased (see the inset). The effect of pressure also is seen in a broad second peak around a distance ($R_F$) of 3.0 Å. These changes were found to be completely reproducible by the duplicate measurements. Therefore, it is suggested that the pressure applied in the melt does affect the coordination structure around zinc(II) in this ionomer, probably not by replacing carboxylate ligands largely but by shifting or rotating them slightly.

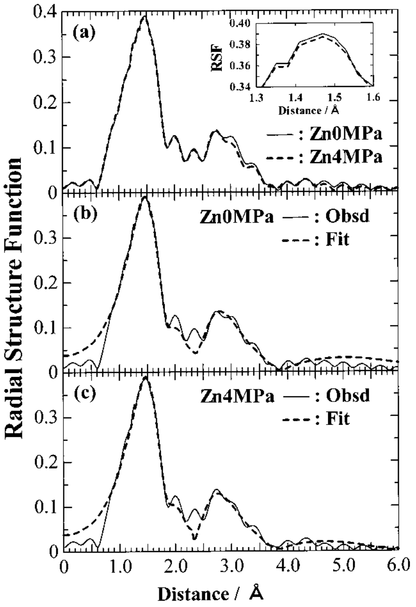

**Figure 3.** (a) Comparison of radial structure functions (RSF) of Zn0MPa (—) and Zn4MPa (– –), and FEFF simulation for (b) Zn0MPa and (c) Zn4MPa, where data (—) and the best-fit result (– –).

To consider this difference quantitatively, the first peak was Fourier transformed again to convert to a $k\chi(k)$ vs $k$ curve and analyzed. On the basis of ionic radii tabulated for Zn(II) and $O^{2-}$,[13] two types of Zn(II)−O bonds with different bond lengths, ~1.98 and ~2.14 Å, were postulated for tetracoordinated and hexacoordinated zinc(II), respectively, both of which are very close to the literature values of low-molecular-mass compounds (e.g., 1.95−1.97 Å for tetracoordinated zinc(II) in monoclinic $Zn(CH_3COO)_2$ [14] and 2.14−2.18 Å for hexacoordinated zinc(II) in $Zn(CH_3COO)_2{\cdot}2H_2O$[15]). The $\chi(k)$ vs $k$ curve was calculated on the basis of the spherical-wave approximation (ab initio code FEFF8),[16] and the optimization of these parameters was performed by fitting to the observed $k\chi(k)$ vs $k$ curve using the nonlinear least-squares method. Here, an important result is that the first peak around $R_F \sim 1.5$ Å cannot be reproduced by one type of Zn(II)−O bonds (Note that the $R_F$ value on RSF and actual bond distance are usually somewhat different.). Thus, by using two positions for the first peak and other three values (2.9, 3.1, and 3.2 Å) for the second peak as the initial parameters, the $k\chi(k)$ vs $k$ curve was calculated to fit the first and second peaks on RSF. The result is shown in Figure 3, parts b and c, and Table 1 lists the obtained parameters by this fitting.

Table 1 clearly reveals that the local environment around zinc(II) in E-0.054MAA-0.6Zn ionomer is dependent on the pressure applied at 130 °C in the melt. As the pressure increases from 0 to 4 MPa, the total number of coordinating oxygens in the first coordination shell (of bond distance range of 1.9−2.3 Å) decreases from 4.8 to 3.0. The error is roughly estimated at ±0.4, and thus, it is certain that the number of coordinating

**Table 1. Structural Parameters for E-0.054MAA-0.6Zn Treated with Different Pressures at 130 °C**

| | Zn0MPa | | Zn4MPa | |
|---|---|---|---|---|
| bond | bond distance/Å | no. | bond distance/Å | no. |
| Zn−O | 1.99 | 3.3 | 1.98 | 2.2 |
| Zn−O | 2.25 | 1.5 | 2.24 | 0.8 |
| Zn···C | 2.86 | 9.5 | 2.81 | 8.5 |
| Zn···C,O | 3.12 | 10.3 | 3.08 | 8.6 |
| Zn···C,O | 3.40 | 1.6 | 3.38 | 0.9 |

[a] Key: − and ··· indicate the distances between two atoms chemically bonded and not bonded, respectively.

oxygens decreases. The number of atoms in the second shell also decreases with increasing the pressure, but the error would be much larger than that of the first shell. Each distance only slightly but did shorten with pressure, as expected. On the other hand, the fraction of shorter Zn(II)−O bonds of ~2.0 Å to the total number of the first shell was 0.69 for Zn0MPa and 0.73 for Zn4MPa, increased only slightly.

Our previous IR studies[5] proposed that the pressure applied in the melt of E-0.054MAA-0.6Zn induces a transformation from hexacoordinated into tetracoordinated zinc(II). More detailed analyses[12] showed that the estimated fraction of the hexacoordinated structure decreases from 0.83 to 0.53 with an increase in the pressure from 0 to 4 MPa. The total coordination number expected should change from 5.5 to 4.9, the trend of which is consistent with the change derived by the present studies. On the other hand, the present EXAFS studies showed that the fraction of longer Zn(II)−O bonds considered to correspond to the hexacoordinated structure changes only from 0.31 to 0.27, and there exists some discrepancy between the two measurements. This discrepancy, however, would be reconciled by considering that each individual coordination structure that is present in the sample is either of tetracoordinated and hexacoordinated zinc(II) but both states in the ionomer are somewhat different from two model structures as seen in monoclinic $Zn(CH_3COO)_2$ and $Zn(CH_3COO)_2{\cdot}2H_2O$, respectively.

At this stage, it is very difficult to understand how and why the coordination structure around zinc(II) is changed with pressure applied in the melt of E-0.054MAA-0.6Zn from these IR and EXAFS results. A plausible hypothesis is that only zinc(II) carboxylates in ionic aggregates are able to change their coordination number without replacing the carboxylate ligands largely. This seems to explain a reason that an interesting phenomenon occurs only in zinc(II)-neutralized E−MAA ionomers, dependent on the MAA content and its neutralization, and **not** in low-molecular-mass analogues.

In conclusion, the present EXAFS studies revealed that the local environment around zinc(II) in E-0.054MAA-0.6Zn ionomer is certainly changed by pressure applied at 130 °C in the melt. This result clearly supports our previous conclusion deduced from the IR studies that the pressure in the melt affects an equilibrium between hexacoordinated and tetracoordinated zinc(II) cations and increasing the pressure favors the presence of the latter species more.

**Acknowledgment.** This study would not have been possible without the extremely helpful personnel at KEK-IMSS-PK. The authors are also indebted to Prof. Yoshihiro Sugi and Yoshihiro Kubota (Gifu University) for permitting us the use of an autoclave, Prof. Norimichi Kojima and Mr. Hiroki Matsumura (Tokyo University) for their helpful discussions, and Mr. Katsuomi Shimabayashi and Daisuke Matsuoka (Gifu University) for assisting the sample preparation.

## References and Notes

(1) For example: *Ionomers: Characterization, Theory, and Applications*; Schlick, S., Ed.; CRC Press: Boca Raton, FL, 1996.
(2) Kutsumizu, S.; Tagawa, H.; Muroga, Y.; Yano, S. *Macromolecules* **2000**, *33*, 3818 and references therein.
(3) Coleman, M. M.; Lee, J. Y.; Painter, P. C. *Macromolecules* **1990**, *23*, 2339 and references therein.
(4) Ishioka, T. *Polym. J.* **1993**, *25*, 1147.
(5) Yano, S.; Nakamura, M.; Kutsumizu, S. *Chem. Commun.* **1999**, 1465.
(6) Yarusso, D. J.; Ding, Y. S.; Pan, H. K.; Cooper, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 2073.
(7) Tsunashima, K.; Nishioji, H.; Hirasawa, E.; Yano, S. *Polymer* **1992**, *33*, 1809.
(8) Grady, B. P.; Floyd, J. A.; Genetti, W. B.; Vanhoorne, P.; Register, R. A. *Polymer* **1999**, *40*, 283.
(9) Grady, B. P. *Macromolecules* **1999**, *32*, 2983.
(10) Welty, A.; Ooi, S.; Grady, B. P. *Macromolecules* **1999**, *32*, 2989.
(11) Hirasawa, E.; Yamamoto, Y.; Tadano, K.; Yano, S. *J. Appl. Polym. Sci.* **1991,** *42*, 351.
(12) Kutsumizu, S.; Nakamura, M.; Yano, S. Submitted to *Macromolecules*.
(13) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
(14) Clegg, W.; Little, I. R.; Straughan, B. P. *Acta Crystallogr.* **1986**, *C42*, 1701.
(15) van Niekerk, J. N.; Schoening, F. R. L.; Talbot, J. H. *Acta Crystallogr.* **1953**, *6*, 720.
(16) Rehr, J. J.; Mustre de Leon, J.; Zabinsky, S. I.; Albers, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 5135.

MA0001988