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Notes

Conductivity Anomaly in the Zinc(II) Complex Salts of Ethylene–Methacrylic Acid Copolymer with 1,3-Bis(aminomethyl)cyclohexane

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Ionomers are polymers having ionic side groups attached to hydrophobic organic backbones. The hydrophilic ionic groups tend to separate from the hydrophobic polymer matrix and frequently condense to form ionic aggregates such as multiplets and ionic clusters.[1] The formation of ionic clusters not only gives substantial changes in polymer properties such as mechanical strength, elasticity, etc.[2] but also sometimes produces new functional properties such as ionic transport[3] and O_2 molecule sorption.[4,5] To date, various ionomers neutralized by metal cations have been extensively studied in order to clarify the formation and morphology of ionic clusters.

Recently, a new type of ionomer, ethylene–methacrylic acid copolymers (EMAA) partly neutralized by Zn(II) and/or an organic amine, 1,3-bis(aminomethyl)cyclohexane [1,3-$(H_2NCH_2)_2C_6H_{10}$] (BAC), have been developed.[6–9] We abbreviate hereafter these ionomers as EMAA–xZn–yBAC, where x is the degree of neutralization by Zn and y is the molar equivalent ratio of BAC to carboxylic acid (where BAC is divalent). Although there have been various studies such as small-angle X-ray scattering (SAXS),[6] differential scanning calorimetry (DSC),[8] dielectric[6,7] and mechanical[9] measurements, etc. on this EMAA–Zn–BAC system, no dc conductivity studies have been made on it. The conductivity of the ionomers should be subject to a transport of carriers through the polymer matrix, presumably in cooperation with molecular motions in it. Thus, the conductivity measurements may provide us with new information on the formation and structure of the ionic cluster and on its effect on the polymer properties. This paper reports the presence of an anomaly in the conductivity of the EMAA–Zn–BAC system. It is pointed out that this anomaly may be connected with the order–disorder transition associated with the ionic clusters in the present system.

EMAA is ACR-1560 of Du Pont–Mitsui Polychemicals, Co. Ltd., whose MAA content is 5.4 mol %. EMAA–xZn–yBAC copolymers were prepared by the melt reaction procedure described previously.[6–9] Dc conductivity measurements were performed by measuring the current through the sample sheet under a steady constant voltage (up to 3000 kV/m) with a Keithley 610C electrometer (its sensitivity is ca. 10^{-14} A). To exclude the surface current from the measured one, a three-terminal electrode system was used as described previously.[10] The samples were circular sheets of 50-mm diameter and 0.05–0.8-mm thickness. Gold was carefully deposited in vacuo on the surface of the sheets to ensure electrical contact between the electrode and the sample. The diameter of the electrode was 37 mm. The samples of this system nearly obeyed Ohm's law. The measurements as a function of temperature were carried out at a constant heating or cooling rate (ca. 0.5 K/min) under dry N_2 gas atmosphere. Here, the rates of the thermal cycles were confirmed to be slow enough to prevent the artificial thermal hysteresis. The temperature was measured by an Fe–constantan thermocouple in good thermal contact with the electrode.

The temperature dependence of the conductivity for EMAA–0.6Zn–0.4BAC is shown in Figure 1. The most striking feature is that the conductivity in the first heating shows an unusual peak near 325 K. Moreover, this anomaly is not observed in the first cooling and second heating (which was run soon after the first cooling) but again begins to appear on heating after storing at room temperature and gradually shifts to higher temperatures with increasing the storage duration, indicating that this anomaly is not due to the so-called thermal stimulated depolarization currents. These observations remind us of the DSC results of this system (e.g., EMAA–0.6Zn–0.97BAC) as reported previously;[8] in the first heating of the DSC, an endothermic peak has been found near 325 K (T_i), below the melting point of the polyethylene crystallites (T_m = ca. 363 K), but it is not seen in the first cooling and second heating and begins to appear on heating after storing at room temperature. This phenomenon in DSC can be explained by an order–disorder transition associated with the ionic clusters, which was recently proposed by us:[8] The ionic clusters are in an ordered state at room temperature. This ordered state is transformed into a disordered one above T_i. When the sample is cooled from a temperature above T_i to room temperature, the ionic clusters are still in the disordered state but gradually

Table I
Physical Data for Various Samples Examined

samples	deg of crystallinity,[a] %	from conductivity: σ(350 K), S cm^{-1}	T_i, K	E_a ($T > T_i$), eV	from DSC: T_i,[c] K	T_m,[c] K
EMAA	19	(0.3–3) × 10^{-16} [b]	ca. 325	1.0–1.3[b]	325	364
EMAA–0.6Zn	17	(1–6) × 10^{-16} [b]	ca. 320	1.0–1.2[b]	329	362
EMAA–0.4BAC	12	(1–2) × 10^{-14} [b]	ca. 310	2.0–2.1[b]	327	363
EMAA–0.6Zn–0.4BAC	11	(2–3) × 10^{-15} [b]	ca. 325	2.4–2.8[b]	333	363

[a] The data were estimated from the heat of fusion by assuming that the heat of fusion of polyethylene crystallites is 290.4 J/g. [b] Range for the sample examined. [c] Peak temperature (T_{max}).

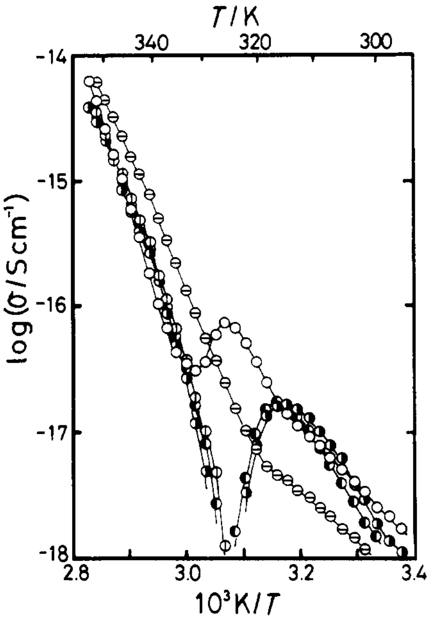

Figure 1. Temperature dependence of the conductivity for EMAA-0.6Zn-0.4BAC: first heating (○); first cooling (⊖); second heating processes run soon after the first cooling (⦶) and after storing for 3 days (◑) and 10 days (◐).

reconstruct the ordered structure with a long relaxation time of about 40 days at room temperature.[8] In conjunction with these DSC results, the anomalous conductivity-temperature relationships for EMAA-0.6Zn-0.4BAC appear to be related to this transition.

Figure 2 shows the temperature dependence of the conductivities for (a) EMAA, (b) EMAA-0.6Zn, and (c) EMAA-0.4BAC. Conductivity data for all the samples, including EMAA-0.6Zn-0.4BAC, are listed in Table I, together with other physical data. All the samples exhibit an anomaly around 320 K in the first heating process: In both EMAA (Figure 2a) and EMAA-0.6Zn (Figure 2b) the conductivity-temperature plots show a bend near 320 K, while the plots for EMAA-0.4BAC show a small hump near 310 K (Figure 2c). In EMAA-0.6Zn-0.4BAC, this anomaly is especially conspicuous and is observed as a peak, as already indicated in Figure 1. In contrast to the data in the first heating process, those in the first cooling and second heating processes for each sample show no anomaly around this temperature. On the other hand, previous SAXS[6] and dielectric[6,7] results have indicated that the ionic clusters are scarcely formed in EMAA and EMAA-0.6Zn but are formed by the addition of BAC. The above anomaly in the conductivity seems to reflect the formation of the ionic clusters by the addition of BAC. Consequently, these results support that the anomaly may come from the order-disorder transition associated with the ionic clusters.

In the higher temperature region have T_i, the plots of $\log \sigma$ versus $1/T$ are curved for the EMAA-Zn-BAC system as seen in Figures 1 and 2b,c, which may be explained by the Vogel-Tamman equation, substantially equivalent to the WLF equation. On the other hand, the plots for EMAA are nearly the Arrhenius type (Figure 2a). Similar results were also reported in the styrene-methacrylic acid copolymer and its Na salt.[11] The magnitude of the conductivity at a given temperature, e.g., σ(350 K), is in the following order: EMAA-0.4BAC > EMAA-0.6Zn-0.4BAC > EMAA-0.6Zn > EMAA. The activation energies E_a in the high-temperature region above T_i were obtained by using the relation $\sigma(T) = \sigma_0 \exp(-E_a/k_B T)$ and are listed in Table I. From the values of E_a, the four samples are classified into two groups; the values of E_a for EMAA-0.4BAC and EMAA-0.6Zn-0.4BAC are 2-3 eV (193-289.5 kJ/mol), while those for EMAA and EMAA-0.6Zn are near 1 eV (96.5 kJ/mol). On the other hand, as mentioned above, it has been pointed out that BAC promotes the formation of the ionic clusters and that the ionic clusters

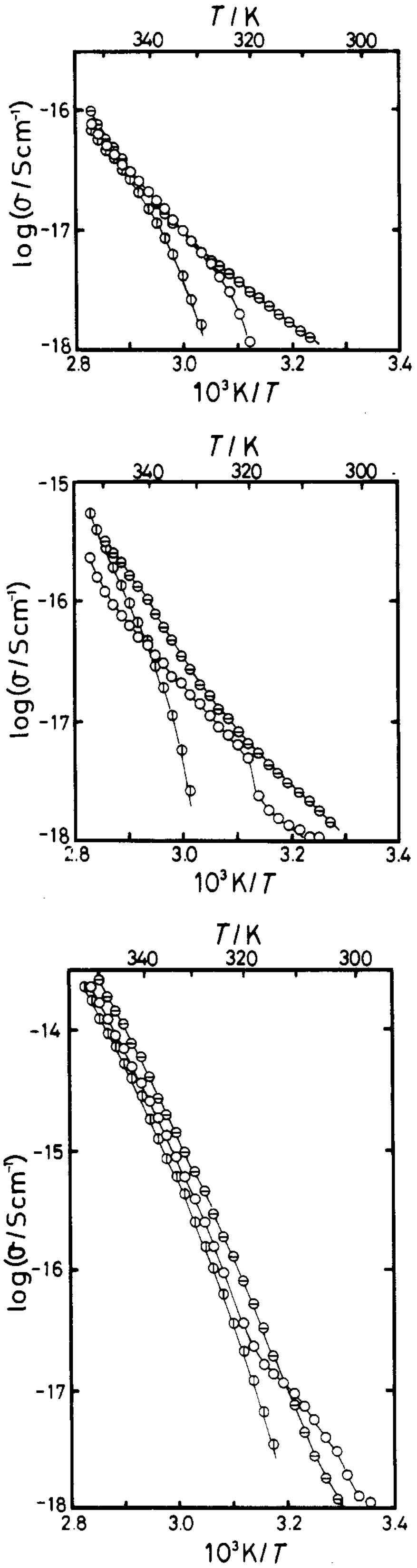

Figure 2. Temperature dependence of the conductivities for various samples: (a, top) EMAA, (b, middle) EMAA-0.6Zn, and (c, bottom) EMAA-0.4BAC. First heating (○); first cooling (⊖); second heating (⦶).

are formed in both EMAA–0.4BAC and EMAA–0.6Zn–0.4BAC but not so in EMAA and EMAA–0.6Zn. Hence, these results show that E_a seems to be connected with the degree of formation of the ionic clusters. Provided that the hopping of the ionic carriers governs the conductivity in the high temperature region, the apparent E_a may reflect the easiness of the hopping, which is closely related to the degree of freedom of the molecular motions. Therefore, the formation of the ionic clusters may restrict the molecular motions and lead to the increase in E_a. Accordingly, our conductivity results show that the formation of the ionic clusters significantly influences the transport of the carriers in the polymer matrix.

It is a topic for further discussion to clarify the origin of the anomaly found in the conductivity for the EMAA–Zn–BAC system. Further detailed studies are in progress in our laboratory and will be reported elsewhere.

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Registry No. (EMAA)·*x*Zn·*y*BAC (copolymer), 108644-30-0; (EMAA)·*x*Zn (copolymer), 28516-43-0; (EMAA)·*x*BAC (copolymer), 108338-54-1.