dc Electrical Conduction Studies on Ethylene Ionomers

Shoichi Kutsumizu,*,† Yoshio Hashimoto,† Yukiyoshi Sakaida,† Hisaaki Hara,‡ Hitoshi Tachino,‡ Eisaku Hirasawa,‡ and Shinichi Yano†

Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-11, Japan, and Technical Center, DuPont-Mitsui Polychemicals Company, Ltd., 6 Chigusa-Kaigan, Ichihara, Chiba 299-01, Japan

Received March 28, 1994; Revised Manuscript Received June 23, 1994®

ABSTRACT: dc conductivity (σ) studies were carried out for various types of ethylene ionomers in the temperature range from room temperature to 400 K. Ionomers used in this study are metal salts (Na, K, Mg, Ca, Co, Cu, Mn, and Zn) of poly(ethylene-*co*-methacrylic acid) (EMAA) and transition-metal complexes with 1,3-bis(aminomethyl)cyclohexane (BAC). It was revealed that the conduction behaviors certainly reflect the state of ionic aggregation. In particular, the σ vs the reciprocal of temperature plots for all the ionomers studied exhibited a maximum peak or an inflection near 325 K. The temperature exhibiting this anomaly coincided with an order–disorder transition temperature of ionic aggregates (T_i), and moreover, the anomaly was observed as a peak for ionomers with a microphase separation of the ionic aggregates from the polymer matrix, while it was observed as an inflection for ionomers without the microphase separation. Thus, this study uncovered an interesting fact that the σ anomaly near 325 K is widely observed for EMAA ionomers and the appearance of the anomaly is markedly dependent upon a microphase structure of the ionomers.

Introduction

Ionomers are polymers functionalized by a small amount of ionic groups attached to the backbone chains, where polar ionic groups frequently aggregate in the hydrophobic polymer matrix to form ionic aggregates. The formation of ionic aggregates characterizes the physical properties of ionomers.[1-9] For a decade, we have been investigating the structure and properties of ethylene ionomers, which are copolymers of ethylene and methacrylic acid (EMAA) neutralized by metal cations and are typical ionomers practically used worldwide. Although ethylene ionomers are ion-containing polymers, they are electrical insulators because ions in ionomers are tightly bound to the side groups. However, the conductivity increases by water uptake, and by taking advantage of this, anti-electrostatic ethylene ionomers have been recently developed.[10] From these viewpoints, fundamental studies on dc ionic conduction are important and worthy, but unexpectedly, few papers have dealt with this subject.[11-14] On the contrary, dielectric relaxational studies have been extensively performed, because microscopic information on the molecular motions can be obtained through the orientation of the polar ionic groups under an alternating electric field.[1-4,15-17]

In our preceding work,[18] we studied the dc electrical conduction behavior of a model ethylene ionomer and uncovered marked evidence that the dc conduction mainly comes from ionic conduction and, moreover, an anomaly seen near 325 K in the dc conductivity vs the reciprocal of temperature plots, which is followed by a thermal hysteresis, corresponds to an order–disorder transition of ionic aggregates. In this paper, we will extend our dc conduction study over various types of ethylene ionomers to more fully understand the effect of ionomer structure upon temperature-dependent dc conductivity. Samples used in this study are EMAA ionomers neutralized with various metal cations (Na, K, Mg, Ca, Co, Cu, Mn, and Zn) at different degrees of neutralization and transition-metal complexes of EMAA with 1,3-bis(aminomethyl)cyclohexane (BAC). It is revealed that the conduction behaviors certainly reflect the state of ionic aggregation and the appearance of the conductivity anomaly near 325 K is clearly related to a microphase structure of EMAA ionomers.

Experimental Section

Materials. The starting EMAA polymer was from DuPont-Mitsui Polychemicals Co. Ltd., whose MAA content was 5.4 mol % in the experiments of Figures 1–6 and 13.3 mol % in the experiment of Figure 7. The metal salts of EMAA and the transition-metal complexes of EMAA with BAC were prepared by a melt reaction in an extruder at 410–530 K according to the method described in the previous papers.[19,20] We denote the metal salts of EMAA and the transition-metal(II) complexes as EMAA-*x*M and EMAA-*x*M-*y*BAC, respectively, where M is the metal cation, x is the degree of neutralization, and y is the equivalent ratio of BAC to carboxylic acid (BAC is a divalent base). The pellet samples obtained were compression-molded into sheets at about 430 K and stored at room temperature in a vacuum desiccator for more than 1 month. We used these samples as dry samples, although they still contained 0.1–0.5 wt % residual water.

Differential scanning calorimetric (DSC) thermograms were recorded using a Seiko Denshi DSC-210 at a heating/cooling rate of 5 K/min. At the first heating, EMAA ionomers aged at room temperature for more than 1 month exhibited two endothermic peaks near 325 and 365 K. The peaks near 325 and 365 K were assigned to an order–disorder transition of ionic aggregates (T_i), in the context of our proposed model,[21-23] and the melting of polyethylene crystallites (T_m), respectively. The polyethylene crystallinity (X_c) was calculated from the area of the 365 K peak by assuming that the heat of fusion of polyethylene crystallites is 290.4 J/g. The physical properties of all samples examined are listed in Table 1.

Measurements. dc conductivity measurements were performed by measuring the current through the sample under a steady constant voltage (up to 3000 kV/m) with a Keithley 610C electrometer (the sensitivity is ca. 10^{-14} A). To ensure electrical contact between the electrode made of stainless steel and the surface of the samples, gold electrodes were carefully deposited in vacuo on the surface of the sample sheets, and the sheets were stored at room temperature for 30–60 days before use. The change of the dc current with the applied field strength nearly obeyed Ohm's law within the field strength up to 3000 kV/m. Variation of the current with temperature change was measured at a heating/cooling rate of ca. 0.6 K/min under a dry N_2 atmosphere,

* To whom correspondence should be addressed.
† Gifu University.
‡ DuPont-Mitsui Polychemicals Co. Ltd.
® Abstract published in *Advance ACS Abstracts*, August 1, 1994.

0024-9297/94/2227-5457$04.50/0

Table 1. Physical Data for Various Samples Examined

samples	from DSC				from conductivity		
	T_i, K	ΔH_i, J/g	T_m, K	X_c, %	σ(350 K), S^{-1} cm^{-1}	T_i,[a] K	E_a, eV
EMAA (5.4 mol % MAA) Ionomers							
EMAA	320	12	363	21	8.6×10^{-17}	328	1.3
EMAA-0.08BAC	324	12	364	23	1.9×10^{-16}		1.8
EMAA-0.24BAC	325	15	364	20	4.9×10^{-15}	315	2.0
EMAA-0.40BAC	324	11	364	14	1.6×10^{-14}	318	2.0
EMAA-0.97BAC	333	29	361	10	3.2×10^{-14}	329	2.8
EMAA-0.20Zn	326	13	363	20	3.9×10^{-17}	326	1.2
EMAA-0.20Zn-0.08BAC	328	19	364	20	1.1×10^{-16}	319	2.8
EMAA-0.20Zn-0.24BAC	328	17	364	18	9.1×10^{-16}	320	2.0
EMAA-0.20Zn-0.40BAC	330	21	363	16	3.9×10^{-15}	330	2.0
EMAA-0.20Zn-0.97BAC	334	29	361	10	2.8×10^{-14}	333	3.0
EMAA-0.20Zn-1.21BAC	337	30	362	8	8.9×10^{-14}	336	2.7
EMAA-0.40Zn	329	13	364	20	2.1×10^{-16}	326	1.2
EMAA-0.40Zn-0.08BAC	330	21	364	22	1.7×10^{-16}	322	2.8
EMAA-0.40Zn-0.24BAC	333	23	363	13	2.3×10^{-15}	330	2.5
EMAA-0.40Zn-0.40BAC	333	24	363	13	2.3×10^{-15}	328	2.3
EMAA-0.40Zn-0.97BAC	334	25	362	8	2.6×10^{-14}	328	2.5
EMAA-0.60Zn	328	15	363	17	3.1×10^{-16}	324	1.3
EMAA-0.60Zn-0.08BAC	334	21	362	14	5.0×10^{-16}	320	2.6
EMAA-0.60Zn-0.24BAC	336	27	362	13	8.7×10^{-16}	330	2.5
EMAA-0.60Zn-0.40BAC	335	26	362	11	1.9×10^{-15}	327	2.7
EMAA-0.60Zn-0.97BAC	335	26	362	8	3.5×10^{-14}	329	2.5
EMAA-0.60Zn-1.21BAC	339	29	362	7	6.0×10^{-15}	341	2.5
EMAA-0.60Cu	330	17	364	19	2.6×10^{-17}	331	1.1
EMAA-0.60Cu-0.16BAC	332	26	363	15	6.5×10^{-17}	323	1.8
EMAA-0.60Cu-0.59BAC	334	29	363	14	1.4×10^{-15}	317	2.1
EMAA-0.60Cu-0.97BAC	335	28	363	12	4.8×10^{-15}	323	2.1
EMAA-0.40Mn	328	18	364	22	1.8×10^{-17}	313	1.8
EMAA-0.60Mn-0.40BAC	329	18	363	15	2.7×10^{-13}	324	2.6
EMAA-0.60Mn-1.25BAC	332	14	360	7	8.5×10^{-13}	328	2.6
EMAA-0.60Co	327	16	361	14	6.3×10^{-16}	323	2.4
EMAA-0.60Co-0.62BAC	328	20	363	12	1.2×10^{-12}	328	2.2
EMAA-0.20Na	325	13	364	16	3.6×10^{-17}		1.4
EMAA-0.60Na	333	27	362	14	1.0×10^{-16}	319	1.9
EMAA-0.90Na	337	29	360	8	8.5×10^{-16}	332	2.1
EMAA-1.0Na	331	21	~350	~1	5.8×10^{-14}	321	2.0
EMAA-0.80K	328	14	362	11	7.9×10^{-14}	326	2.1
EMAA-0.60Mg	338	32	359	7	1.7×10^{-17}	323	1.1
EMAA-0.90Mg	339	30	362	4	8.9×10^{-18}	327	0.6
EMAA-0.40Ca	325	17	361	16	1.3×10^{-18}	321	1.4
EMAA (13.3 mol % MAA) Ionomers							
EMAA-0.60Na	344	6		0	4.5×10^{-16}	344	2.4
EMAA-0.60Zn	335	2		0	2.7×10^{-16}	340	1.8

[a] Temperature exhibiting the conductivity anomaly.

where the rate of thermal cycle was found to be slow enough to prevent a spurious thermal hysteresis. In this paper, only first heating processes are discussed, and a thermal hysteresis intrinsic in the EMAA ionomers and details of the experimental setup and the procedure can be found elsewhere.[18,24]

Thermally stimulated depolarization current (TSDC) measurements were performed by the following procedure: A dc electric field of 270 kV/m was applied at 385 K above T_m, and then, the sample was cooled to room temperature at a rate of ca. 1 K/min under the field of 270 kV/m. After the circuit was made short, the TSDC generated was monitored during heating at a rate of ca. 0.6 K/min using a Keithley 610C electrometer.

Results and Discussion

Zinc(II) Salt and Zinc(II)–BAC Complex Salt. Figure 1 shows the temperature (T) dependence of the dc conductivity (σ) for EMAA and its Zn(II) salts. All four samples exhibit an inflection between 325 and 335 K in the σ–$1/T$ curves. The temperatures showing the inflection almost agree with the order–disorder transition temperatures of ionic aggregates (T_i) measured by DSC (see Table 1). In the preceding paper,[18] the σ anomaly is observed as a peak at T_i, and the difference in the appearance of the anomaly will be discussed later.

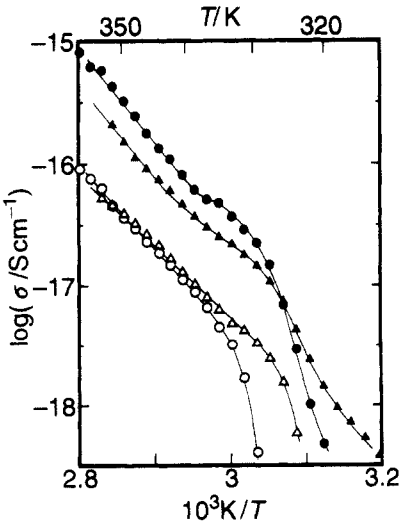

Figure 1. Temperature dependence of the conductivity in the first heating for EMAA-xZn: (○) x = 0; (△) x = 0.2; (▲) x = 0.4; (●) x = 0.6.

Plots above 340 K appear to obey the Arrhenius equation

$$\sigma(T) = \sigma_0 \exp(-E_a/k_B T) \quad (1)$$

where k_B and σ_0 are the Boltzmann constant and a

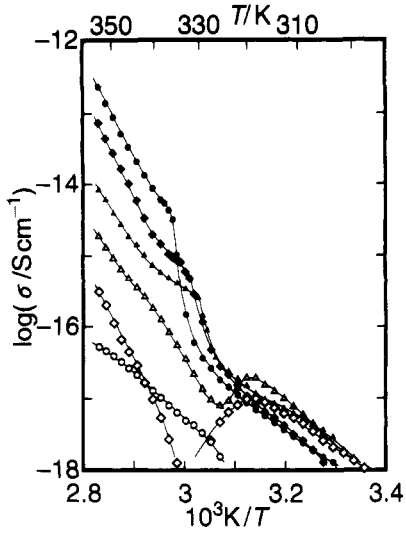

Figure 2. Temperature dependence of the conductivity in the first heating for EMAA-0.20Zn-yBAC: (○) y = 0; (◇) y = 0.08; (△) y = 0.24; (▲) y = 0.40; (◆) y = 0.97; (●) y = 1.21.

proportionality constant, respectively. From the slope of the σ–$1/T$ curves above 340 K, the activation energy, E_a, is estimated to be ca. 1.2 eV for all four samples and is independent of the neutralization degree (x), while the conductivity at 350 K (σ(350 K)) slightly increases with the increasing neutralization degree. This increase, however, is not due to the decrease in the polyethylene crystallinity (X_c) because the X_c values for these samples are almost equal (about 20%, see Table 1). In poly(styrene-*co*-methacrylic acid) ionomers, it has been pointed out that the conductivity decreased with the increasing neutralization degree by the cross-linking effect of ionic aggregates.[13] The Zn(II) salts of EMAA show no signs of such a decrease up to the neutralization of 60%.

Figure 2 shows the effect of the amount of BAC (y) on the temperature-dependent conductivity for EMAA-0.20Zn-yBAC. The coordination of BAC to the Zn(II) cation substantially changes the conductivity–temperature behavior; both σ(350 K) and E_a above 340 K remarkably increase with increasing BAC content (y). In particular, a distinct difference is found between EMAA-0.20Zn and EMAA-0.20Zn-0.08BAC, suggesting that the coordination of BAC to the Zn(II) cation facilitates some structural change in the ionic aggregates. In addition, all EMAA-0.20Zn-yBAC with $y > 0$ exhibit a σ peak at 319–336 K, while the σ anomaly of EMAA-0.20Zn is observed as an inflection near T_i. The temperatures exhibiting these anomalies almost agree with T_i, as shown in Table 1. This allows the speculation that the σ peak is related to the order–disorder transition of ionic aggregates at T_i, as discussed in the preceding paper.[18] The difference in the conductivity behavior observed seems to be related to the following facts: The small-angle X-ray scattering (SAXS) results[25] showed that EMAA-0.20Zn-yBAC comes to exhibit the so-called *ionomer peak* with increasing y, indicating that addition of BAC to EMAA-0.20Zn promotes the formation of ionic aggregates because the *ionomer peak* is generally taken as evidence for ionic aggregation. Dielectric[16] and dynamic mechanical[22] measurements also revealed that EMAA-0.20Zn-yBAC with $y > 0$ exhibit microphase separation of ionic aggregates from the polyethylene phase, namely the formation of the *ionic cluster* phase in Eisenberg's terminology,[9] which is detected by the appearance of two individual relaxations assigned to a glass trasition of both phases. Infrared[16] and extended X-ray absorption fine structure (EXAFS)[26] studies suggested that the coordination of BAC to the Zn(II) carboxylate groups increases the ionic nature of the COO–Zn bond, which explains the effect of the addition of BAC to EMAA-0.20Zn on the ionic aggregation. From these results, it is concluded that the difference in the conductivity–temperature behavior between EMAA-0.20Zn and EMAA-0.20Zn-yBAC with $y > 0$ well corresponds to the difference in the microphase structure. Moreover, as seen in Table 1, the ΔH_i on DSC increases from 13 to 30 J/g as the amount of BAC, y, increases from 0 to 1.21, and we interpreted this increase as an increase of order inside the ionic aggregate regions.[21-23] Advancing this interpretation, it is probable that the formation and ordering of the ionic cluster phase in EMAA-0.20Zn-yBAC ($y > 0$) also enhances the magnitude and sharpness of the anomaly near T_i.

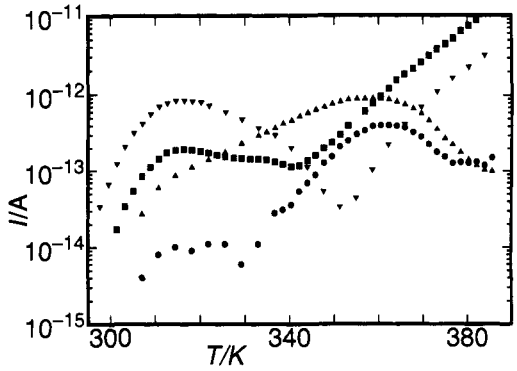

Figure 3. TSDC curves for various EMAA-Zn-BAC ionomers: (●) EMAA; (▲) EMAA-0.60Zn; (■) EMAA-0.40BAC; (▼) EMAA-0.60Zn-0.40BAC.

Figure 3 shows the TSDC curves for EMAA ionomers. EMAA and EMAA-0.60Zn exhibit a single current peak near 360 K, while EMAA-0.40BAC and EMAA-0.60Zn-0.40BAC show a current peak near 320 K and an abrupt increase above ca. 350 K. In general, TSDC peaks on heating usually originate from the release of charges or from the thermal reorientation of dipoles, which are, during the preceding cooling process under a dc electric field, trapped and frozen out, respectively.[27] The peak near 360 K can be assigned to a release of charges trapped at the interface between the crystalline and amorphous regions of the polyethylene backbone chains. In fact, a similar current peak has been observed near T_m in a low-density polyethylene (LDPE).[28] The abrupt increase above ca. 350 K in EMAA-0.40BAC and EMAA-0.60Zn-0.40BAC apparently has the same origin as the 360 K peak in EMAA and EMAA-0.60Zn. On the other hand, our SAXS[25] and dielectric[16] studies indicated that the microphase separation occurs in both EMAA-0.40BAC and EMAA-0.60Zn-0.40BAC, but not in EMAA and EMAA-0.60Zn. Therefore, we attribute the 320 K peak to a release of charges trapped at the interface between the ionic cluster phase and the polyethylene amorphous phase or to a depolarization of the ionic groups oriented in the ionic cluster phase.

Other Transition-Metal(II) Salts and Transition-Metal(II)–BAC Complex Salts. Figure 4 shows the σ–$1/T$ curves for various transition-metal(II) salts of EMAA. All the five samples exhibit an anomaly near 320 K: EMAA-0.40Mn and EMAA-0.60Co exhibit a peak at 313 K and 322 K, respectively, and EMAA, EMAA-0.60Zn, and EMAA-0.60Cu show a bend near 325 K. As already described for EMAA-xZn, these anomalies are related to the order–disorder transition of ionic aggregates at T_i. In addition, in the temperature region above 340 K, all the σ–$1/T$ plots show a bend or a hump near 360 K, which

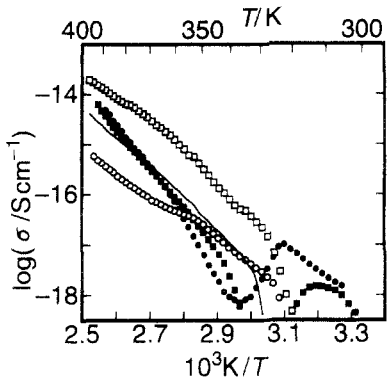

Figure 4. Temperature dependence of the conductivity in the first heating for various transition-metal(II) salts of EMAA: (—) EMAA; (□) EMAA-0.60Zn; (●) EMAA-0.60Co; (■) EMAA-0.40Mn; (○) EMAA-0.60Cu.

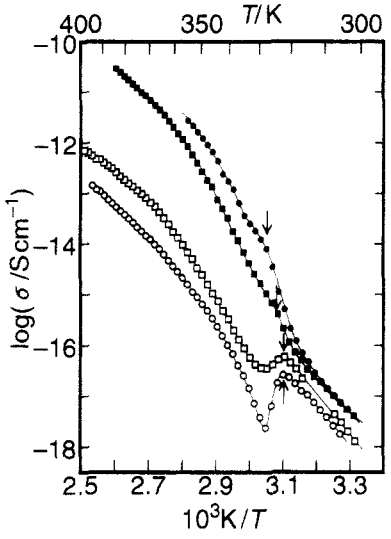

Figure 5. Temperature dependence of the conductivity in the first heating for the transition-metal(II) complexes with BAC: (□) EMAA-0.60Zn-0.40BAC; (●) EMAA-0.60Co-0.62BAC; (■) EMAA-0.60Mn-0.40BAC; (○) EMAA-0.60Cu-0.59BAC. Arrows indicate the order–disorder transition temperature of ionic aggregates at T_i (see text).

corresponds to the melting of the polyethylene crystallites at T_m. Between 340 and 360 K, all the σ–$1/T$ plots show a straight line, and calculated E_a values in that region are 2.0–2.5 eV for EMAA-0.40Mn and EMAA-0.60Co and 1.0–1.5 eV for EMAA, EMAA-0.60Zn, and EMAA-0.60Cu. The differences in the appearance of the anomaly and the E_a value strongly suggest that some difference in the state of ionic aggregation exists between the former ionomers (EMAA-0.40Mn and EMAA-0.60Co) and the latter ionomers (EMAA, EMAA-0.60Zn, and EMAA-0.60Cu).

Figure 5 shows the temperature dependence of the conductivity for the BAC-coordinated transition-metal(II) complex ionomers. The coordination of BAC to the Cu(II), Mn(II), and Co(II) salts increases both σ(350 K) and E_a between 340 and 360 K, compared with the values of the precursor ionomers. All the complex ionomers used in this experiment are known to have a microphase-separated ionic cluster phase.[15,17] Therefore, changes observed upon the coordination of BAC to the transition-metal(II) carboxylate groups can be explained as a result of the formation of such an ionic cluster phase. In the temperature region near T_i, EMAA-0.60Cu-0.59BAC and EMAA-0.60Zn-0.40BAC exhibit a peak near 322 K, while comparatively high conductivities of EMAA-0.60Co-0.62BAC and EMAA-0.60Mn-0.40BAC tend to obscure their σ anomaly peaks. The TSDC measurements were

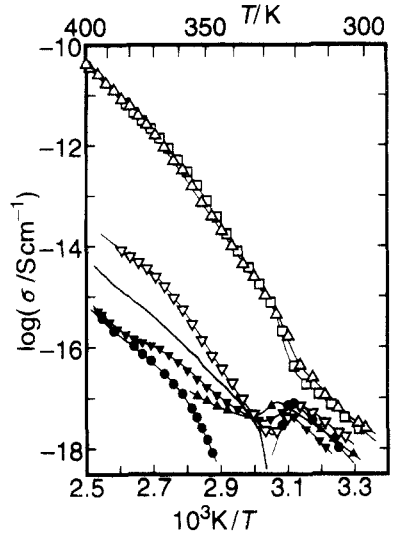

Figure 6. Temperature dependence of the conductivity in the first heating for some alkali-metal and alkaline-earth-metal salts of EMAA: (—) EMAA; (▽) EMAA-0.6Na; (△) EMAA-1.0Na; (□) EMAA-0.8K; (▼) EMAA-0.6Mg; (▲) EMAA-0.9Mg; (●) EMAA-0.4Ca.

also carried out on the EMAA-0.60Cu-yBAC ionomers. A chart of the results is not included, but they followed the same trend as shown for EMAA-xZn-yBAC ionomers in Figure 3.

Alkali-Metal and Alkaline-Earth-Metal Salts. Figure 6 shows the temperature dependence of the conductivity for alkali-metal and alkaline-earth-metal salts of EMAA. All the samples including monovalent Na and K salts and divalent Mg and Ca salts exhibit a σ peak at 319–327 K in the σ–$1/T$ plots. EMAA-1.0Na and EMAA-0.8K show a very high conductivity even near T_i, which seems to obscure the σ peak. In this experiment, a good relationship between the appearance of the σ peak and a microphase structure is again demonstrated because all the ionomers examined in this experiment are known to have microphase-separated ionic clusters.[1,2,15,17]

From the Arrhenius plots in the temperature range above T_i, the E_a's for the alkali-metal salts are 2–3 eV, whereas those of the alkaline-earth-metal salts are around 1 eV. This difference probably has no relationship to the polyethylene crystallinity (X_c) (see Table 1). Phillips et al.[15] and we[17] reported that the activation enthalpies for the dielectric β relaxation are 125–290 kJ/mol for the divalent Mg and Ca salts and are larger than those for the monovalent Na and K salts (100–185 kJ/mol). The β relaxation is attributed to a micro-Brownian segmental motion containing isolated ionic groups in the amorphous polyethylene phase. Taking these dielectric results into consideration, we interpreted the difference in E_a as follows: The divalent cations rather serve for interchain bonding to form a complicated network in the matrix,[17] which would hinder the thermal motion of chain segments. According to the free-volume model for ionic conduction,[29] the hopping of ions necessitates a void, the so-called *free volume*, which is produced by the thermal motion of chain segments. Therefore, the probability of hopping of ions would be substantially reduced in the alkaline-earth-metal salt compared to that in the alkali-metal salts. In other words, the number of ionic carriers that can contribute to the conduction, and hence σ_0 in eq 1, would be diminished in the alkaline-earth-metal salts. On the other hand, the phase boundary between the ion-rich phase and the surrounding hydrophobic amorphous phase would be more obscure in the alkaline-earth-metal salts than in the alkali-

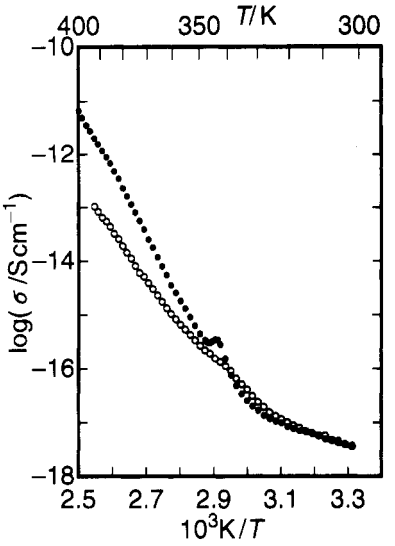

Figure 7. Temperature dependence of the conductivity in the first heating for the Na and Zn salts of EMAA containing 13.3 mol % MAA: (●) 60% neutralized Na salt; (○) 60% neutralized Zn salt.

metal salts, and hence the trapping effect on the ionic carriers would also be reduced. As a result, the alkaline-earth-metal salts show values of σ(350 K) and E_a smaller than the alkali-metal salts.

Effect of Crystallinity on the dc Conduction. The EMAA ionomers used in the experiments of Figures 1–6 contain 5.4 mol % MAA units and are semicrystalline, whereas the DSC, dilatometry, and SAXS measurements[30] revealed that the ionomers containing 13.3 mol % MAA are almost amorphous. In order to investigate the effect of polyethylene crystallinity on the conduction behavior, the temperature dependence of the conductivity for the latter amorphous ionomers was observed. The samples used in this experiment are the Na and Zn(II) salts, and the results are shown in Figure 7. Both salts exhibit no anomaly around 360 K in the σ–$1/T$ plots. This is not surprising because they scarcely contain the polyethylene crystallites. However, near 340 K, the Na and Zn(II) salts show a noticeable sharp peak and a very broad peak, respectively. The DSC thermograms showed that the order–disorder transition temperature (T_i) of ionic aggregates is 344 K for the Na salt and 335 K for the Zn salt.[30] Therefore, these results evidence that the σ anomaly near T_i is not related to the melting of the polyethylene crystallites but to the order–disorder transition of ionic aggregates.

Mechanism of the dc Conduction Behaviors. Figure 8 graphically summerizes how (a) the σ(350 K) and (b) the E_a above T_i depend upon the type of neutralizing cations and the degree of neutralization. With increasing neutralization, the conductivity, σ(350 K), decreases a little bit for the Mg and Cu(II) salts and slightly increases for the Zn(II) salts. For the Na salts, the conductivity almost remains constant at x = 0–0.6 but rapidly increases at $x \geq 0.9$. The conductivity for the BAC salt increases with increasing y and reaches a constant value above $y \sim 0.5$. Figure 8 also shows that E_a depends upon the type of neutralizing cation. Values of E_a for both the Na (x = 0.6–1.0) and BAC (y = 0.08–0.97) salts are relatively large (2–3 eV), while those of the other salts and EMAA are around 1 eV.

In our preceding paper,[18] we showed that the dc conduction of EMAA ionomers above T_i mainly comes from ionic conduction; under a dc electric field, a small amount of dissociated protonic carriers and/or an unavoidable amount of ionic impurities migrate in the amorphous regions, as in most of the insulating polymers.[29,31] In this case, the E_a values are determined mainly by the potential barriers for hopping of the ionic carriers (i.e. mobility of carriers). Therefore, the E_a values rather than the σ(350 K) values elucidate the conduction processes in ionomers; the difference in the E_a values should reflect a difference in the conduction path in ionomers. Regarding the microphase structure of the ionomers, microphase-separated ionic clusters exist in the Na (x = 0.6–1.0) and BAC (y = 0.08–0.97) salts but not in the Cu(II) and Zn(II) salts.[15–17] In the former ionomers, formation of an ionic cluster phase would require the existence of a sharp phase boundary between the ionic cluster phase and the polyethylene amorphous phase, acting as a trapping effect on the ionic carriers, and also would restrict the conduction path in ionomers. As a result, the former ionomers show a larger E_a than the latter. Consequently, whether the ionic cluster phase is formed would be a dominant factor in determining the E_a value. The only exception is the Mg salts (x = 0.6 and 0.9), which are known to form the ionic cluster phase[1,2,15,17] but show a low E_a of ~1 eV. As discussed in Figure 6, the bonding character of the Mg cation may be responsible for the small E_a value.

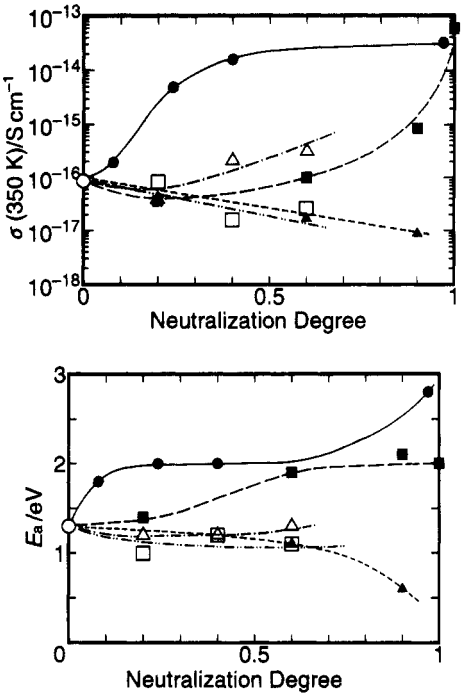

Figure 8. (a, top) Conductivity at 350 K (σ(350 K)) and (b, bottom) activation energy (E_a) between 340 and 360 K vs the degree of neutralization for EMAA ionomers: (—●—) EMAA-yBAC; (-■-) EMAA-xNa; (-▲-) EMAA-xMg; (-·-△-·-) EMAA-xZn; (-··-□-··-) EMAA-xCu.

To conclude this study, it is important to elucidate why and how the σ T_i anomaly appears as a peak or an inflection. In the preceding paper,[18] we intensively investigated the σ T_i peak of EMAA-0.60Zn-0.40BAC and proposed an explanation based on the following two mechanisms: (a) Above T_i, some of the ionic carriers are trapped at the interface between the disordered ionic cluster and amorphous regions, leading to a discontinuous decrease in the conductivity and, hence, to an apparent σ peak near T_i in the σ–$1/T$ plots. (b) This mechanism is based on the assumption that permanent dipoles or ionic groups inside the ionic aggregates form some ordered arrangement at room temperature and that, at T_i (ca. 325 K), the disordering of the permanent dipoles or the displacement of the ionic groups takes place, on the analogy of the

observations of some polymers near T_g.[32-34] The change at T_i would give rise to an induced current and causes an apparent σ peak near T_i in the σ–$1/T$ plots. A very important finding of this study is that a σ T_i peak appears when EMAA ionomers form microphase-separated ionic clusters. Such phase separation would require the existence of a sharper phase boundary between the ion-rich phase and the surrounding amorphous region. Therefore, in mechanism a, the formation of the ionic cluster phase favors trapping of the ionic carriers. On the other hand, under the assumption of our order–disorder transition model of ionic aggregates,[21-23] the increase in size of ionic aggregates and the formation of the ionic cluster phase also promotes the ordered arrangement of the ionic groups inside the ionic aggregates. Therefore, in mechanism b, the enhanced order increases the induced current at T_i, resulting in a sharp σ T_i peak. Consequently, all the results obtained in this study are consistent with either of the two mechanisms proposed, and further works are apparently needed to reach a definitive conclusion.

Acknowledgment. The authors very much thank Prof. Kenji Tadano of Gifu College of Medical Technology for valuable discussions. S.K. wishes to acknowledge the support of the Ministry of Education, Science, and Culture of Japan (Grant-in-Aid for Scientific Research No. 03750645).

References and Notes

(1) Holliday, L., Ed. *Ionic Polymers*; Applied Sciences: London, 1975.
(2) Eisenberg, A., King, M., Eds. *Ion-Containing Polymers, Polymer Physics*; Academic Press: New York, 1977; Vol. 2.
(3) Pineri, M.; Eisenberg, A., Eds. *Structure and Properties of Ionomers*; NATO ASI Series C, Mathematical and Physical Sciences; D. Reidel Co.: Dordrecht, The Netherlands, 1987; Vol. 198.
(4) Utracki, L. A., Weiss, R. A., Eds. *Multiphase Polymers: Blends and Ionomers*; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989.
(5) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.
(6) MacKnight, W. J.; Taggart, W. P.; Stein, R. S. *J. Polym. Sci., Polym. Symp.* **1974**, *45*, 113.
(7) Moudden, A.; Levelut, A. M.; Pineri, M. *J. Polym. Sci., Polym. Phys.* **1977**, *15*, 1707.
(8) Yarusso, D. J.; Cooper, S. L. *Macromolecules* **1983**, *16*, 1871.
(9) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.
(10) Tachino, H.; Hara, H.; Hirasawa, E.; Kutsumizu, S.; Yano, S. *Polym. J.*, in press.
(11) Rees, R. W.; Vaughan, D. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1965**, *6*, 296.
(12) Hirota, S. *Rep. Prog. Polym. Phys. Jpn.* **1973**, *13*, 437.
(13) Arai, K.; Eisenberg, A. *J. Macromol. Sci., Phys.* **1980**, *B17*, 803.
(14) Kutsumizu, S.; Hashimoto, Y.; Yano, S.; Hirasawa, E. *Macromolecules* **1991**, *24*, 2629.
(15) Phillips, P. J.; MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1970**, *8*, 727.
(16) Yano, S.; Yamamoto, H.; Tadano, K.; Yamamoto, Y.; Hirasawa, E. *Polymer* **1987**, *28*, 1965.
(17) Yano, S.; Nagao, N.; Hattori, M.; Hirasawa, E.; Tadano, K. *Macromolecules* **1992**, *25*, 368.
(18) Kutsumizu, S.; Hashimoto, Y.; Hara, H.; Tachino, H.; Hirasawa, E.; Yano, S. *Macromolecules* **1994**, *27*, 1781.
(19) Hirasawa, E.; Yamamoto, Y.; Tadano, K.; Yano, S. *J. Appl. Polym. Sci.* **1991**, *42*, 351.
(20) Hirasawa, E.; Tadano, K.; Yano, S. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 753.
(21) Tadano, K.; Hirasawa, E.; Yamamoto, Y.; Yamamoto, H.; Yano, S. *Jpn. J. Appl. Phys.* **1987**, *26*, L1440.
(22) Tadano, K.; Hirasawa, E.; Yamamoto, H.; Yano, S. *Macromolecules* **1989**, *22*, 226.
(23) Hirasawa, E.; Yamamoto, Y.; Tadano, K.; Yano, S. *Macromolecules* **1989**, *22*, 2776.
(24) Koizumi, N.; Yano, S. *Bull. Inst. Chem. Res., Kyoto Univ.* **1969**, *47*, 320.
(25) Yano, S.; Tadano, K.; Sugiura, T.; Hirasawa, E. Ref 3, p 481.
(26) Tsunashima, K.; Nishioji, H.; Hirasawa, E.; Yano, S. *Polymer* **1992**, *33*, 1809.
(27) Mort, J., Pfister, G., Eds. *Electronic Properties of Polymers*; John-Wiley & Sons: New York, 1982.
(28) Suh, K. S.; Damon, D.; Tanaka, J. *IEE Conf. Publ.* **1988**, *289*, 17.
(29) Miyamoto, T.; Shibayama, K. *J. Appl. Phys.* **1973**, *44*, 5372.
(30) Kutsumizu, S.; Tadano, K.; Tachino, H.; Matsuda, Y.; Hara, H.; Hirasawa, E.; Yano, S. To be published.
(31) Saito, S. *Koubunshi* **1968**, *17*, 672 (in Japanese).
(32) Munick, R. J. *J. Appl. Phys.* **1956**, *27*, 1114.
(33) Ieda, M.; Kosaki, M.; Ohshima, H.; Shinohara, U. *J. Phys. Soc. Jpn.* **1968**, *25*, 1742.
(34) Kosaki, M.; Sugiyama, K.; Ieda, M. *J. Appl. Phys.* **1971**, *42*, 3388.