Dielectric Relaxations of Ethylene Ionomers

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Received April 9, 1991; Revised Manuscript Received September 16, 1991

ABSTRACT: Dielectric relaxation studies were performed for the alkali (Na, K), alkaline earth (Mg, Ca), and transition [Cu(II), Mn(II), Co(II)] metal salts of the ethylene–methacrylic acid (5.4 mol%) copolymer (EMAA), and for the transition metal complexes with 1,3-bis(aminomethyl)cyclohexane (BAC) of EMAA. It was pointed out that the dielectric relaxations of the ethylene ionomers are sensitive to the formation of ionic clusters. When the ionic clusters are formed, the β' relaxation related to a glass–rubber transition above T_g was depressed and there appeared two relaxations, the α relaxation above T_i, due to a micro-Brownian molecular motion of long segments containing the salt groups incorporated into the ionic clusters, and the β relaxation below T_i, due to a molecular motion of short segments containing the isolated salt groups. From this relationship between dielectric relaxations and the formation of ionic clusters, it was concluded that the Na, K, Ca, Mg, and Co(II) salts of EMAA form the ionic clusters at higher neutralization above about 30%, but the Cu(II) and Mn(II) salts do not form clusters even at 60% neutralization. In the transition-metal complexes with BAC, the formation of ionic clusters was drastically promoted by the addition of BAC.

Introduction

Functional properties of ionomers are mainly derived from the existence of a small amount of ionic groups attached pendantly to the backbone chains. The ionic groups tend to aggregate in the hydrophobic polymer matrix to form ionic aggregations such as multiplets and clusters. During the past decades, considerably scientific effort has been devoted to clarifying the structure of ionic clusters by many researchers,[1-5] since the formation of ionic clusters influences physical properties. However, no satisfying answer has yet been obtained on the structure of the ionic clusters, because the colloidal size of the ionic clusters stands in the way of elucidating the structure.

How the segmental molecular motions of ionomers are affected by ionic aggregation has been extensively studied by means of mechanical[2-4,6] and dielectric measurements.[7-20] Briefly speaking about past work, the ionic clusters act as cross-links in the ionomers, and so the formation of ionic clusters increases the glass-transition temperature (T_g). Dielectric spectroscopic data show how the dipole moments of the polar groups are oriented by the applied alternating-current electric field. In ethylene ionomers, the polar groups are only in the ionic groups and not in the hydrophobic polymer matrix. Moreover, the functional properties of ionomers are mainly caused by ionic groups associated in ionic aggregations. Since the molecular motion of segments in ionomers can be detected through the orientation of the polar ionic groups, dielectric relaxation spectroscopy should be one of the most powerful methods to examine the structure–property relationships of ionomers.

In ethylene–methacrylic acid (MAA) (or acrylic acid) copolymers neutralized with metal cations, β' and γ relaxations were observed at low contents of the metal carboxylate, and α, β, and γ relaxations at high content.[9] The β' and γ relaxations were assigned to a micro-Brownian molecular motion of long segments above T_g and a local molecular motion of short segments below T_g, respectively. When the ionic clusters were formed at high contents of metal carboxylates, the β' relaxation was depressed and there appeared the α and β relaxations, which are attributed, respectively, to a glass–rubber transition of the ionic clusters and to a motion of short hydrocarbon chains containing the isolated salts not incorporated into the ionic clusters. In previous works,[16,17] we demonstrated that these changes in the dielectric relaxations by the formation of ionic clusters are so drastic that the dielectric relaxation can provide evidence for the formation of ionic clusters.

This work presents dielectric relaxations of ethylene–methacrylic acid copolymers (EMAA) neutralized with various metal cations and their complexes with 1,3-bis(aminomethyl)cyclohexane (BAC) and clarifies how and why the segmental molecular motions of the ethylene ionomers change by the formation of ionic clusters.

Experimental Section

Materials. The metal salts of EMAA used here are listed in Table I. Here the metal salts are denoted as EMAA-xM (M, metal cation; x, degree of neutralization). The EMAA is ACR-1560 of Du Pont-Mitsui Polychemicals Co. Ltd., whose MAA content is 5.4 mol %. The metal salts of EMAA were prepared by a melt reaction of EMAA with a stoichiometric quantity of cation sources in an extruder at 450–530 K.[21] Here Na_2CO_3, K_2CO_3, $Mg(OH)_2$, $Ca(OH)_2$, ZnO, $Cu(CH_3COO)_2$, $Mn(CH_3COO)_2 \cdot 4H_2O$, and $Co(CH_3COO)_2$ were used as the cation sources. Volatile byproducts such as H_2O, CO_2, and CH_3COOH were eliminated by a vacuum pump attached to the extruder. The melt strands from the extruder die were cooled in water and pelletized. The pellet samples obtained were compression molded into sheets at 430 K and cooled to room temperature at the rate of about 30 K/min by circulating cold water in the press jacket. The transition-metal complexes with BAC of EMAA were prepared by a melt reaction of EMAA-xM and BAC in the extruder at 410–490 K in the same procedure as that for EMAA-xM.[22,23] The sheet samples were prepared from the pellet samples in the same way as described for the metal salts. These samples are also listed in Table I. Hereafter, the transition-metal complexes with BAC are denoted as EMAA-xM-yBAC (y, equivalent ratio of BAC to carboxylic acid, where BAC is a divalent base).

The formation of the metal salts and their complexes with BAC was confirmed by IR spectra. In EMAA, the absorption peak corresponding to the stretching vibration of COOH groups was observed near 1700 cm^{-1}, as is well-known.[7,24,25] When EMAA

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0024-9297/92/2225-0368$03.00/0

Table I
List of Samples[a]

sample, EMAA-*x*M-*y*BAC	T_i, K	ΔH_i, J/g	T_m, K	ΔH_m, J/g	X_c, %	MFR, dg/min	V, cm^3/g	ν_{asym} cm^{-1}	ν_{sym}, cm^{-1}
EMAA	315	5.3	365	61.6	21.2	60	1.0679		1425
EMAA-0.20Na	318	7.9	365	67.0	23.1	18	1.0584	1529	1402
EMAA-0.40Na	321	9.4	364	45.3	15.6	4.6	1.0540	1540	1400
EMAA-0.60Na	323	13.7	362	36.7	12.6	1.0	1.0510	1558	1405
EMAA-0.80Na	323	11.8	362	26.8	9.2	0.23	1.0484		
EMAA-0.90Na	327	13.3	360	23.5	8.1	0.18	1.0466	1556	1411
EMAA-0.20K	318	6.9	365	61.4	21.1	17	1.0586	1529	1400
EMAA-0.40K	320	10.8	365	54.0	18.6	4.7	1.0478	1540	1395
EMAA-0.60K	372	15.6	362	32.2	11.1	1.3	1.0374	1551	1397
EMAA-0.80K	331	32.3	362	54.3	18.7				
EMAA-0.90K	332	29.0	362	45.7	15.7				
EMAA-0.20Mg	324	12.5	364	55.6	19.1	18	1.0601	1544	1397
EMAA-0.40Mg	329	14.2	362	38.1	13.1	4.5	1.0697	1547	1395
EMAA-0.60Mg	330	16.5	360	21.6	7.4	0.8	1.0600	1544	1397
EMAA-0.80Mg	329	14.5	357	14.7	5.1	0.06	1.0581		
EMAA-0.90Mg	331	12.6	357	11.4	3.9	0.06	1.0576		
EMAA-0.02Ca	320	8.7	364	59.0	20.0	10	1.0560	1554	1407
EMAA-0.40Ca	324	11.2	359	40.0	14.1	1.5	1.0527	1560	1406
EMAA-0.60Ca	326	12.5	356	24.0	8.1	0.13	1.0524	1567	1406
EMAA-0.20Cu	322	10.0	365	60.3	20.8	23	1.0531	1600	1407
EMAA-0.20Cu-0.16BAC	324	10.9	365	56.5	19.5	17	1.0533	1603, 1530 (w)	1405
EMAA-0.20Cu-0.46BAC	325	14.6	364	46.4	16.0	26	1.0523	1605 (w), 1532 (b)	1405
EMAA-0.20Cu-0.74BAC	328	19.7	364	33.6	11.6	33	1.0531	1544 (b)	1398
EMAA-0.40Cu	324	11.5	364	56.1	19.3	9.9	1.0448	1603	1406
EMAA-0.40Cu-0.16BAC	326	14.3	364	46.7	16.1	11	1.0472	1602, 1529 (w)	1405
EMAA-0.40Cu-0.40BAC	326	15.4	364	41.2	14.2	15	1.0457	1602, 1536 (w)	1404
EMAA-0.40Cu-0.62BAC	326	17.0	363	40.2	13.8	18	1.0443	1606 (w), 1544 (b)	1396
EMAA-0.40Cu-0.87BAC	328	21.7	363	30.5	10.5	24	1.0446	1605 (w), 1544 (b)	1392
EMAA-0.60Cu	328	14.3	364	51.1	17.6	5.7	1.0385	1603	1405
EMAA-0.60Cu-0.16BAC	329	16.6	364	48.5	16.7	5.3	1.0371	1603, 1528 (w)	1406
EMAA-0.60Cu-0.40BAC	329	17.3	364	47.7	16.4	8.1	1.0362	1604, 1536 (w)	1405
EMAA-0.60Cu-0.59BAC	327	17.1	363	40.9	14.1	13	1.0355	1605 (w), 1534 (b)	1400
EMAA-0.60Cu-0.97BAC	326	17.4	364	38.0	13.1	22	1.0368	1542 (b)	1392
EMAA-0.20Mn	314	9.1	365	61.7	21.2	31	1.0613	1589	1400
EMAA-0.20Mn-0.24BAC	316	11.6	366	50.7	17.5	17	1.0579	1590, (w) 1535	1405
EMAA-0.20Mn-0.57BAC	319	16.0	365	37.1	12.8	20	1.0572	1527 (b)	1399
EMAA-0.20Mn-1.09BAC	318	11.3	363	20.3	7.0		1.0609	1522 (b)	1396
EMAA-0.40Mn	317	9.1	366	58.2	20.0	18	1.0513	1588	1397
EMAA-0.40Mn-0.16BAC	318	12.0	366	50.6	17.4	12	1.0524	1588, 1536 (w)	1404
EMAA-0.40Mn-0.40BAC	325	17.5	365	45.3	15.6	16	1.0519	1527 (b)	1402
EMAA-0.40Mn-0.94BAC	324	12.6	363	25.5	8.8	28	1.0507	1518 (b)	1394
EMAA-0.40Mn-1.42BAC	321	7.6	362	34.1	11.7	37	1.0439	1526 (b)	1393
EMAA-0.60Mn	322	14.8	365	48.1	16.6	10	1.0444	1584	1397
EMAA-0.60Mn-0.16BAC	322	15.7	364	44.3	15.3	7.5	1.0437	1584, 1542 (w)	1406
EMAA-0.60Mn-0.40BAC	323	17.0	363	39.3	13.5	8.6	1.0443	1528 (b)	1406
EMAA-0.60Mn-0.83BAC	324	14.8	363	26.3	9.1		1.0477	1524 (b)	1408
EMAA-0.60Mn-1.25BAC	324	10.8	361	17.0	8.8	23	1.0410	1525 (b)	1400
EMAA-0.20Co	322	9.3	365	53.2	18.3	16	1.0517	1598	1402
EMAA-0.20Co-0.21BAC	322	19.5	363	47.7	16.4	21	1.0495	1600, 1540 (w)	1400
EMAA-0.20Co-0.48BAC	319	16.5	363	46.2	15.0	25	1.0496	1600 (w), 1535 (b)	1395
EMAA-0.20Co-0.71BAC	322	20.9	362	34.5	11.9	30	1.0513	1530 (b)	1395
EMAA-0.40Co	324	12.7	363	50.7	17.5	9.8	1.0433	1596	1397
EMAA-0.40Co-0.26BAC	322	21.2	363	47.0	16.2	15	1.0433	1595, 1535 (w)	1395
EMAA-0.40Co-0.42BAC	321	20.3	363	39.9	13.7	17	1.0430	1595, 1535 (w)	1400
EMAA-0.40Co-0.51BAC	322	19.9	363	43.1	14.8	13	1.0399	1595 (w), 1535 (b)	1400
EMAA-0.60Co	326	20.0	362	39.8	13.7	5.2	1.0396	1599	1400
EMAA-0.60Co-0.08BAC	325	18.0	362	40.3	13.9	5.8	1.0413	1600, 1560 (w)	1400
EMAA-0.60Co-0.35BAC	325	20.2	364	36.9	12.7	9.2	1.0378	1600, 1550 (b)	1400
EMAA-0.60Co-0.62BAC	325	21.6	364	34.8	12.0	11.0	1.0355	1600 (w), 1540 (b)	1402

[a] x: degree of neutralization by metal cation. y: equivalent ratio of BAC as divalent base to carboxylic acid. T_i and ΔH_i: order–disorder transition temperature of ionic clusters and its enthalpy change. T_m and ΔH_m: melting point of polyethylene crystallites and its enthalpy change. X_c: degree of crystallinity. MFR: melt flow rate. V: specific volume. ν_{asym} and ν_{sym}: antistretching and stretching vibration of COO^-, respectively, and w and b: weak and broad absorption bands, respectively.

was neutralized by metal cation, the 1700 cm^{-1} peak was depressed and a new absorption due to the antisymmetric stretching vibration of COO^- (ν_{asym}) appeared in the range of 1500–1600 cm^{-1} (see Table I). The addition of BAC to the transition-metal salts shifted ν_{asym} to lower wavenumbers (see Table I). Previous ESR and UV spectral results also indicated the formations of the transition-metal salts[26-28] and their complexes with BAC.[29-31]

Measurements. Dielectric measurements were carried out with a multifrequency LCR meter (Yokogawa-Hewlett Packard, type 4274A) in a temperature range of 85–390 K at several frequencies between 100 Hz and 100 kHz. The three-terminal electrode system was used as previously described.[32] The sheets for dielectric measurements were about 0.5 mm thick and the diameter of the main electrode was 37 mm, where gold was

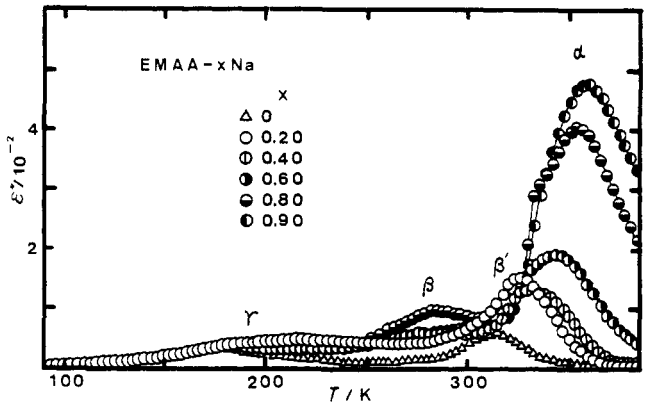

Figure 1. Temperature dependence of dielectric loss (ϵ'') at 1 kHz for EMAA-xNa.

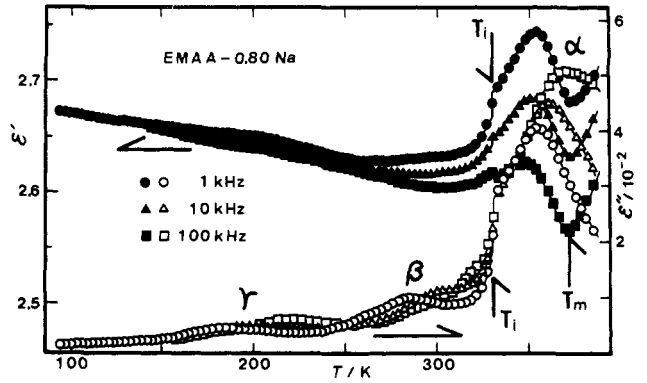

Figure 2. Temperature dependences of dielectric constant (ϵ') and the loss (ϵ'') at a few frequencies for EMAA-0.80Na.

carefully deposited in vacuo on the surface of the sheet to ensure electrical contact between electrode and sample. Melt flow rate (MFR) was measured as weight of flow in grams per 10 min from a melt indexer at 463 K and under a 2160-g load. Differential scanning calorimetric (DSC) measurements were made by a Du Pont DSC-990 calorimeter at the heating/cooling rate of 10 K/min. The temperature (T_i) of the order–disorder transition of ionic clusters and its enthalpy change (ΔH_i) and melting point (T_m) of polyethylene crystallites and its enthalpy change (ΔH_m) were obtained from the DSC data. The degree of crystallinity in the polyethylene region (X_c) was calculated from the value of ΔH_m by assuming that the heat of fusion of polyethylene crystallites is 290.4 J/g.[33] Specific volume (V) at 298 K was obtained by a buoyancy method with benzene. IR spectra were recorded by use of a Shimadzu IR-435 spectrometer for the thin films at room temperature.

Results and Discussion

Alkali and Alkaline Earth Metal Salts of EMAA. Figure 1 shows the temperature dependence of dielectric loss (ϵ'') at 1 kHz for EMAA-xNa. EMAA exhibits the β' near 315 K and γ relaxations near 182 K which are related, respectively, to a micro-Brownian molecular motion of long segments above T_g and to a local molecular motion of short segments below T_g, being consistent with those reported by several workers.[7,8] In EMAA-0.20Na, the β' relaxation locates near 326 K at 1 kHz, which means that T_g increases by about 10 K by the neutralization of 20%. On the other hand, at x values higher than 40%, the β' relaxation is depressed and there appear the α and β relaxations which are related, respectively, to a molecular motion associated with the ionic clusters and to a motion of hydrocarbon chains containing a small amount of salt groups not incorporated into the ionic clusters, as already mentioned. Figure 2 shows the temperature dependences of dielectric constant (ϵ') and the loss (ϵ'') for EMAA-0.80Na at different frequencies. It is here emphasized that one abrupt change in both ϵ' and ϵ'' is observed near 330 K for the highly neutralized samples such as 0.80 and 0.90 of x, being independent of frequency (see also Figure 1). Recently we proposed the presence of the order–disorder transition inside of ionic clusters,[34,35] at room temperature, the ionic clusters are ordered assemblies of ionic groups. With increasing temperature, the inside ordered ionic clusters transform into disordered ones near 330 K (T_i) below T_m of polyethylene crystallites, although the ionic clusters themselves are sustained even above T_m. The abrupt changes of ϵ' and ϵ'' are considered to correspond to this order–disorder transition, because the temperature exhibiting the abrupt change coincides with T_i (see Table I). On the other hand, the bend of ϵ' near 370 K apparently corresponds with the melting of polyethylene crystallites; the increase of ϵ' above 370 K is caused by the decrease of sample thickness with melt flow above T_m during the dielectric measurements. Since the ordered ionic clusters act as rigid cross-links, the micro-Brownian molecular motion of long segments should be hindered by the rigid cross-links. Therefore, the formation of the ionic clusters depresses the β' relaxation and causes appearances of the α and β relaxations: below T_i, the motion of long segments is restricted by a cross-linking effect of the rigid ionic clusters and the β relaxation, a local motion of hydrocarbon chains containing the salt groups not incorporated into the ionic clusters, is seen. Above T_i, the disordered ionic clusters are soft enough to participate in the micro-Brownian molecular motion of long hydrocarbon chains and this softening results in the appearance of the α relaxation.

However, we must consider whether the α relaxation comes from an interfacial polarization of the Maxwell–Wagner type[36] or not, since the ionomers can be regarded as a heterogeneous system in which spherical ionic clusters disperse in polyethylene matrix. First, it can be considered that the ionic clusters are too small to cause the interfacial polarization, since the diameter of ionic clusters has been reported to be around 10 Å for ethylene ionomers.[16] Second, in the Maxwell–Wagner theory, the relaxation time (τ) is expressed as $(2\epsilon_1 + \epsilon_2)\epsilon^*_0/(2\sigma_1 + \sigma_2)$, where ϵ_1 and ϵ_2 are the relative dielectric constants, and σ_1 and σ_2 are the conductivities, respectively, for polyethylene matrix and ionic clusters, and ϵ^*_0 is the dielectric constant of a vacuum. Here ϵ_1 and ϵ_2 are 2–80, and $\sigma_1 \simeq 0$, while σ_2 would be assumed to be smaller than 10^{-14} S/m, because the salt groups would not dissociate into the ions in the polyethylene solvent and the ionic clusters would act as an insulator in the solid state, similar to a metal carboxylate. Therefore, we can assume $\tau \gg 1$ s and the relaxation frequency $\ll 1$ Hz. Thus, even if an interfacial polarization is active in the present ionomers, it would exist at much higher temperatures than the α relaxation or would be at much lower frequencies than 1 Hz. Consequently, the α relaxation is concluded to be unrelated to an interfacial polarization. This conclusion seems to be qualitatively supported by the facts that the α relaxation appears at the nearly same temperature range regardless of the cation species and especially that the addition of BAC did not change the relaxation temperature of the α relaxation in EMAA-xM-yBAC systems much, as described later.

Figure 3 shows the temperature dependence of ϵ'' at 1 kHz for the K, Ca, and Mg salts of EMAA. In EMAA-xK, EMAA-0.20K shows the β' and γ relaxations near 323 and 205 K at 1 kHz, respectively, while EMAA-0.40K has the α relaxation near 325 K and one peak near 270 K. In the highly neutralized K ionomers ($x \geq 0.40$), a very fast uptake

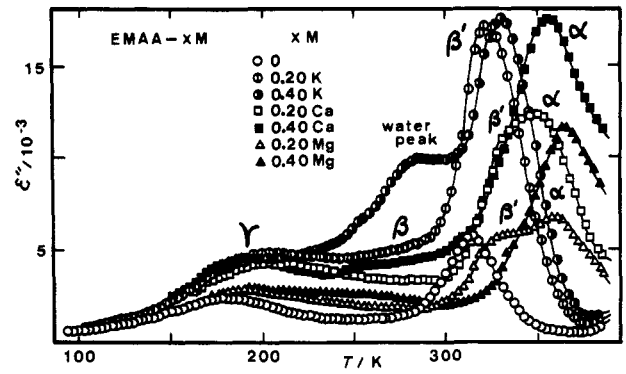

Figure 3. Temperature dependence of dielectric loss (ϵ'') at 1 kHz for the K, Ca, and Mg salts of EMAA.

of water occurred and its amount increased with increasing x, although we carefully treated the samples to avoid the water uptake. From this fact, the peak near 270 K can be ascribed to the water peak caused by water absorbed.[7] On the other hand, steep increases of ϵ'' originating in a direct-current (dc) electric conduction were seen above 360 K for EMAA-0.80K and 330 K for EMAA-0.90K, respectively. In fact, a dc electric conduction in potassium–ethylene ionomers was reported to increase rapidly by the uptake of water by Hirasawa and Yano.[37]

In EMAA-xCa and -xMg, the β' relaxation is depressed and the α and β relaxations appear where the β relaxation is not obviously seen in Figure 3 but was clearly observed for the more highly neutralized samples. With increasing x, the α relaxation shifts to higher temperatures and becomes bigger. These results, essentially consistent with those for EMAA-xNa, can be also explained by the cross-linking effect of ionic clusters containing Ca/Mg cations. It is noted that the β' relaxation still exists with the α relaxation in both EMAA-0.20Ca and -0.20Mg. This fact suggests that the ionic groups begin to cluster from around $x = 0.20$.

Consequently the dielectric relaxation behavior of ethylene ionomers neutralized by alkali and alkaline earth metal cations faithfully reflects how the ionic groups are aggregated in the polymer matrix. When the ionic groups are not aggregated, the β' and γ relaxations exist above and below T_g, respectively, as conventionally seen in viscoelastic polymers.[38,39] However, once the ionic clusters are formed, the β' relaxation is depressed and the α and β relaxations appear above and below T_i, respectively. The formation and structure of ionic clusters in ethylene ionomers have been extensively studied by use of various experimental techniques such as mechanical, dielectric, small angle X-ray scattering ones, and so on.[1-5] It has been pointed out that ethylene ionomers neutralized by alkali and alkaline earth metal cations change the physical properties near 33% neutralization during increase of the degree of neutralization.[21,40,41] In the alkali metal–ethylene ionomers, for example, the mechanical stiffness shows a maximum near 33% neutralization, which suggests that the alkali metal ions form an octahedral coordination with three carboxyl groups to construct the ionic clusters. From the relationships between dielectric relaxations and ionic aggregations, the dielectric relaxation results obtained in this study also support the speculation that the ionic clusters are constructed with higher degrees of neutralization than 20–40%, maybe about 33%, in alkali and alkaline earth metal salts of EMAA.

In Figure 4, data points of relaxation temperature (T_{max}) at 1 kHz and dielectric increament ($\Delta\epsilon$) are plotted against the degree of neutralization (x) for the α (β'), β, and γ

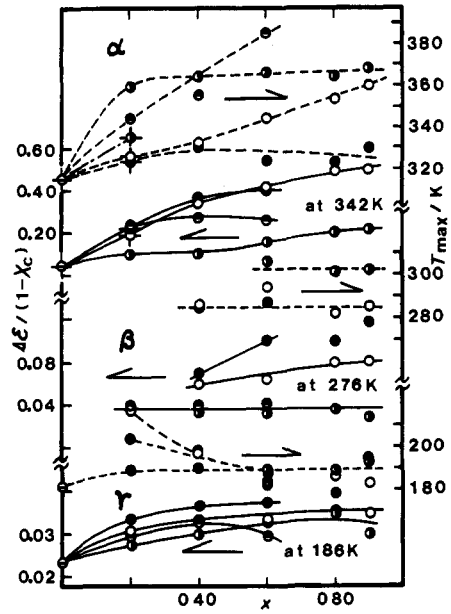

Figure 4. Plots of T_{max} at 1 kHz and $\Delta\epsilon/(1 - X_c)$ versus x for EMAA-xM (M = Na, K, Ca, Mg): Na, ○; K, ●; Ca, ⊖; Mg, ◑; EMAA, ⊖; data of β' relaxation, -◇-; T_{max} at 1 kHz, – –; $\Delta\epsilon/(1 - X_c)$, —.

relaxations in all the samples. Here, the value of $\Delta\epsilon$ is obtained from the Cole–Cole plots.[42] The Cole–Cole distribution parameters of relaxation time (β) are estimated to be 0.2–0.4 for the three relaxations ($\beta = 1.0$ means a single relaxation time), indicating a wide distribution of relaxation time (see Table III). In the monovalent Na and K salts, both values of T_{max} and $\Delta\epsilon/(1 - X_c)$ for the α relaxation increase almost proportionally to x, where X_c is degree of crystallinity of polyethylene region. The values of T_{max} for the β and γ relaxations are almost independent of x, except for those of the γ relaxation in the 0.20Na and 0.20K salts. In the 0.20Na and 0.20K salts, in which the ionic clusters may not be formed, T_{max} for the γ relaxation is relatively higher than that of EMAA. This suggests that the γ relaxation, the local molecular motion of short segments, is more hindered by the isolated salt groups not incorporated into the ionic clusters. The values of $\Delta\epsilon/(1 - X_c)$ gradually increase with increasing x for the α relaxation but scarcely change both for the β and γ relaxations.

Dielectric relaxation behavior of the divalent Ca and Mg salts somewhat differs from that of the monovalent Na and K salts. In EMAA-xMg, T_{max} for the α relaxation remains constant up to the 90% neutralization after about a 45 K jump seen in the 20% neutralization. On the other hand, T_{max} for the α relaxation of EMAA-xCa increases almost proportionally to x. The increase of T_{max} by x is larger for the divalent metal salts than for the monovalent metal salts. However, T_{max}'s for the β and γ relaxations are independent of x in the divalent metal salts as well as the monovalent metal salts. With increasing x, the value of $\Delta\epsilon/(1 - X_c)$ for the α relaxation increases for EMAA-xCa and EMAA-xMg, but the magnitude of the increase is smaller than that of EMAA-xNa. In the β and γ relaxations, the values of $\Delta\epsilon/(1 - X_c)$ remain almost constant, regardless of x.

Table II shows the activation enthalpies (ΔH) for the relaxations obtained from the Arrhenius plots. The values of ΔH lie between 250 and 300 kJ/mol for the β' relaxation in EMAA, EMAA-0.20Na, and -0.20K. The values of ΔH for the α and β relaxations clearly differ by the valence of metal cation; in the monovalent cations (the Na and K

Table II
Relaxation Parameters of Various Samples

	α relaxation		β′ relaxation		β relaxation		γ relaxation	
sample	T_{max}, K	ΔH, kJ/mol	T_{max}, K	ΔH, kJ/mol	T_{max}, K	ΔH, kJ/mol	T_{max}, K	ΔH, kJ/mol
EMAA			315	251			182	51
EMAA-0.20Na			326	348			217	39
EMAA-0.40Na	333	396			285	67	197	40
EMAA-0.60Na	344	301			294	66	182	42
EMAA-0.80Na	353	328			282	85	186	42
EMAA-0.90Na	360	321			285	74	183	44
EMAA-0.20K			323	293			205	44
EMAA-0.40K	330	356			285	85	198	32
EMAA-0.60K	324	314			287	71	188	37
EMAA-0.80K	323	333			269	108	178	40
EMAA-0.90K	330	369			278	148	195	67
EMAA-0.20Mg	359	172	335	157			189	50
EMAA-0.40Mg	364	137				96	190	33
EMAA-0.60Mg	366	163			306	105	189	40
EMAA-0.80Mg	364	135			301	117	189	42
EMAA-0.90Mg	368	184			302	114	194	43
EMAA-0.20Ca	344	233				180	189	41
EMAA-0.40Ca	355	289				123	190	33
EMAA-0.60Ca	385	128				184	183	32
EMAA-0.20Cu			318	205			186	36
EMAA-0.20Cu-0.16BAC	340	303					184	38
EMAA-0.20Cu-0.46BAC	346	287					189	50
EMAA-0.20Cu-0.74BAC	357	256			288	76	187	43
EMAA-0.40Cu			324	265			185	36
EMAA-0.40Cu-0.16BAC	345	261					186	37
EMAA-0.40Cu-0.40BAC	348	262					183	41
EMAA-0.40Cu-0.62BAC	351	234			289	76	187	45
EMAA-0.40Cu-0.87BAC	354	260			285	69	183	44
EMAA-0.60Cu			333	287			187	38
EMAA-0.60Cu-0.16BAC	351	353					181	35
EMAA-0.60Cu-0.40BAC	351	314					180	30
EMAA-0.60Cu-0.59BAC	351	287			284	68	183	38
EMAA-0.60Cu-0.97BAC	353	279			282	66	184	41
EMAA-0.20Mn			330	207			186	42
EMAA-0.20Mn-0.24BAC	339	232					184	37
EMAA-0.20Mn-0.57BAC	349	288			273	57	180	41
EMAA-0.20Mn-1.09BAC	357	367			270	61	183	46
EMAA-0.40Mn			335	180			185	42
EMAA-0.40Mn-0.16BAC	347	229					182	40
EMAA-0.40Mn-0.40BAc	354	287			277	48	182	40
EMAA-0.40Mn-0.94BAC	351	355			270	55	181	45
EMAA-0.40Mn-1.42BAC							177	38
EMAA-0.60Mn			348	279			187	42
EMAA-0.60Mn-0.16BAC	354	224					186	42
EMAA-0.60Mn-0.40BAC	362	243			276	58	184	41
EMAA-0.60Mn-0.83BAC	357	227			274	62	181	45
EMAA-0.60Mn-1.25BAC							180	44
EMAA-0.20Co	355	253	328	225			190	50
EMAA-0.20Co-0.21BAC	342	229			275	58	183	39
EMAA-0.20Co-0.48BAC	344	274			275	71	187	41
EMAA-0.20Co-0.71BAC	352	247			273	62	183	41
EMAA-0.40Co	354	287					185	42
EMAA-0.40Co-0.26BAC	349	218			276	60	184	41
EMAA-0.40Co-0.42BAC	350	264			277	74	186	38
EMAA-0.40Co-0.51BAC	352	233			278	73	180	40
EMAA-0.60Co	360	356					176	35
EMAA-0.60Co-0.08BAC	358	256			283	98	183	41
EMAA-0.60Co-0.35BAC	354	265			277	58	184	42
EMAA-0.60Co-0.62BAC	354	258			275	64	183	40

salts), ΔH lies between 300 and 400 kJ/mol for the α relaxation and between 65 and 85 kJ/mol for the β relaxation (the values of ΔH for EMAA-0.80K and -0.90K may be much affected by the water absorbed). In the divalent cations (the Mg and Ca salts), the values of ΔH are between 125 and 290 kJ/mol for the α relaxation and between 100 and 180 kJ/mol for the β relaxation. This difference of ΔH by the cation valence is consistent with the previous results by MacKnight et al.[9] We can possibly explain this difference as follows: (1) Since the divalent cations prefer to bond intermolecularly with two COO^- groups to form a network in the matrix, the ΔH value of the β relaxation may be bigger for the divalent cations than for the monovalent ones. (2) The rigid ordered ionic clusters are softened above T_i although the ionic clusters themselves still remain. As already described, the α relaxation is related to the micro-Brownian molecular motion of long segments containing the metal salt groups of the softened ionic clusters above T_i. By inference from the value of ΔH for the α relaxation, the interaction between the cations inside of the softened ionic clusters appeared to be stronger in the monovalent cations than

Table III
Values of Static Dielectric Constant (ϵ_0), High-Frequency Limiting Dielectric Constant (ϵ_∞), Dielectric Increment ($\Delta\epsilon$), Cole–Cole Distribution Parameter of Relaxation Time (β), and Dipole Moment of COOM (μ_2) at 342 K for α/β' Relaxation

sample	ϵ_0	ϵ_∞	$\Delta\epsilon$	β	μ_2, D	μ_{2d}, D
EMAA	2.3528	2.3158	0.0370	0.47	$\mu_1 = 0.45$	
EMAA-0.20Na	2.5877	2.4438	0.1439	0.33	1.7	
EMAA-0.40Na	2.6182	2.3323	0.2859	0.27	1.9	
EMAA-0.60Na	2.7241	2.3623	0.3618	0.17	1.7	
EMAA-0.80Na	2.8908	2.4508	0.4400	0.20	1.7	
EMAA-0.90Na	2.9633	2.5097	0.4536	0.20	1.6	
EMAA-0.20K	2.5794	2.4059	0.1735	0.33	1.6	
EMAA-0.40K	2.7225	2.4215	0.3010	0.31	1.9	
EMAA-0.60K	2.8779	2.5298	0.3418	0.39	1.7	
EMAA-0.20Mg	2.3823	2.4135	0.0768	0.26	1.1	1.6
EMAA-0.40Mg	2.5013	2.4135	0.0878	0.21	0.93	1.3
EMAA-0.60Mg	2.6012	2.4568	0.1444	0.22	1.1	1.5
EMAA-0.80Mg	2.5695	2.3830	0.1865	0.23	1.1	1.5
EMAA-0.90Mg	2.6002	2.3998	0.2004	0.16	1.1	1.5
EMAA-0.20Ca[a]	2.6012	2.4132	0.1880	0.18	2.0	2.9
EMAA-0.40Ca[a]	2.6249	2.4114	0.2135	0.18	1.6	2.2
EMAA-0.60Ca	2.6416	2.4128	0.2288	0.17	1.4	1.9
EMAA-0.20Cu	2.4684	2.4220	0.0464	0.33	0.63	0.89
EMAA-0.40Cu	2.5962	2.5350	0.0612	0.27	0.68	0.96
EMAA-0.60Cu	2.3890	2.3260	0.0630	0.20	0.67	0.94
EMAA-0.20Mn	2.5270	2.4250	0.1020	0.35	1.4	1.9
EMAA-0.40Mn	2.4828	2.3210	0.1618	0.29	1.4	2.0
EMAA-0.60Mn	2.6148	2.3920	0.2228	0.25	1.4	1.9
EMAA-0.20Co	2.4712	2.4045	0.3528	0.35	0.97	1.4
EMAA-0.40Co	2.4902	2.4057	0.3494	0.35	0.90	1.3
EMAA-0.60Co	2.5957	2.4899	0.3562	0.36	0.87	1.2

[a] Values at 343 K.

in the divalent cations. This reason may come from the difference in electrostatic interaction between the cations. (3) The ΔH values of the γ relaxation are comparatively small and are scarcely affected by both ionic aggregations and cation species. This is because the γ relaxation is due to a local motion of short segments in amorphous hydrocarbon chains.

Generally, the relative static dielectric constant (ϵ_0) of solution is represented by the Onsager equation[43]

$$\epsilon_0 - 1 = \sum [(N_i\mu_i^2/9kT\epsilon^*_0)\{\epsilon_0(\epsilon_{\infty i} + 2)^2 + (2\epsilon_0 + 1)/(2\epsilon_0 + \epsilon_{\infty i})\} + \{4\pi\epsilon_0(\epsilon_{\infty i} - 1)/(2\epsilon_0 + \epsilon_{\infty i})\}a_i^3N_i] \quad (1)$$

Here, N_i, a_i, $\epsilon_{\infty i}$, and μ_i are the number of dipole moments per unit volume, molecular radius, high-frequency limiting dielectric constant, and dipole moment of the i component, respectively. ϵ^*_0, k, and T are the permittivity of a vacuum, the Boltzmann constant, and absolute temperature, respectively. The Onsager equation is essentially derived from liquids in which the dipoles are not correlated, but is known to be frequently applicable even for solids. We can regard the present ionomers as a solution in which the polar solute, COOM(I)/$(COO)_2$M(II) groups, is dissolved in nonpolar polyethylene solvent. Although the polar groups would be correlated, we posulated that the Onsager equation is applicable for the α above T_i or β' relaxation above T_g in the present systems, because the content of polar groups is low (smaller than 5.4 mol % of MAA in EMAA) and the present ionomers are in a rubbery (liquid) state at the higher temperatures above T_g/T_i. Then, in eq 1, we denoted $i = 0$, 1, and 2 to polyethylene matrix, COOH, and COOM(I)/$(COO)_2$M(II), respectively. Assuming that both dipoles of COOH and COOM(I)/$(COO)_2$M(II) contribute to one same relaxation (this assumption seems to be reasonable, because the α relaxation is associated with the motion of long segments containing both the dipoles, and the Cole–Cole distribution parameter of the relaxation time as shown in Table III is considerably broad), we obtained $\epsilon_0 \simeq \epsilon_{\infty 1} \simeq \epsilon_{\infty 2} = \epsilon_\infty$. From $\mu_0 = 0$, $N_0 \gg N_1$, N_2, and $^4\pi/_3a_0^3 = N_0$, we obtained

$$\epsilon_0 - 1 = (^1/_9kT\epsilon^*_0)[(\epsilon_\infty + 2)^2(2\epsilon_0 + 1)/(2\epsilon_0 + \epsilon_\infty)](N_1\mu_1^2 + N_2\mu_2^2) + 2\epsilon_0(\epsilon_\infty - 1)/(2\epsilon_0 - \epsilon_\infty) \quad (2)$$

where

$$N_1 = (1 - x)N \quad (3)$$

$$N_2 = xN \quad (4)$$

when x is degree of neutralization by metal cation and N is the total number of MAA (COOH groups) per unit volume. Consequently, we obtained

$$\mu_2^2 = (9kT\epsilon_0/N)[(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)/\epsilon_0(\epsilon_\infty + 2)^2](1/x) - [(1 - x)/x]\mu_1^2 \quad (5)$$

The calculated values of μ_2 for the α relaxation are listed in Table III. Here, the μ_2 values for the divalent salts are estimated as those per COOM(II)$_{1/2}$, and μ_{2d} is the dipole moment per $(COO)_2$M(II) which was calculated by replacing x in eq 5 by $x/2$. The dipole moment (μ_1) of COOH in EMAA was calculated to be 0.45 D by assuming the Onsager equation as listed in Table III. This low value can be explained by the presence of dimer ($\mu = 0$) as previously pointed out by MacKnight et al.[7,8] The μ_2 values for COOM(I)/$(COO)_2$M(II) groups clearly depend on the metal cation species. This difference of μ_2 among the metal cations should be explained by the electronegativity of the metal cations and/or the coordination structure of COOM groups. Although the μ_2 value involves some error owing to the assumptions on the calculation, it may be worthwhile to notice that the μ_2 value of COONa (around 1.7 D) unexpectedly coincides with that of free COOH groups of alkanoic acids such as acetic acid ($\mu = 1.75$ D).[44] Another interesting point is that the μ_2 values show no

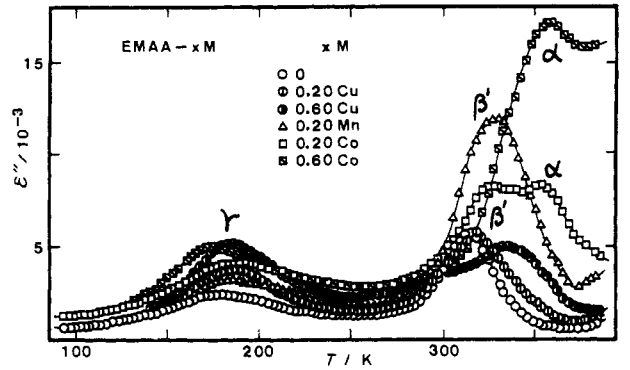

Figure 5. Temperature dependence of dielectric loss (ϵ'') at 1 kHz for the Cu(II), Mn(II), and Co(II) salts of EMAA.

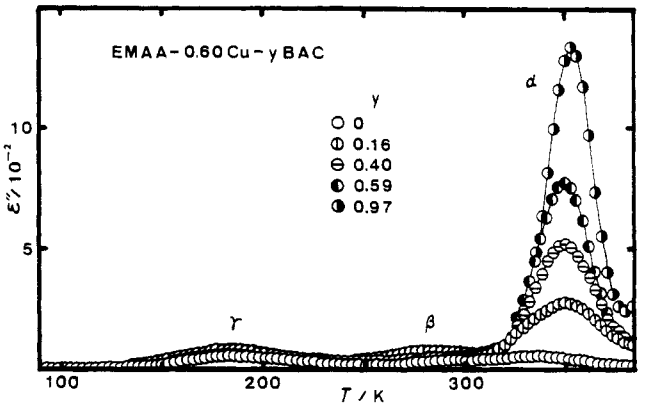

Figure 6. Temperature dependence of dielectric loss (ϵ'') at 1 kHz for EMAA-0.60Cu-yBAC.

dependency on the degree of neutralization (x). In EMAA-xNa, for example, the x = 0.20 compound shows the β' relaxation above T_g, while the α relaxation is observed above T_i instead of the β' relaxation when x is larger than 0.40. Nevertheless, the μ_2 is almost the same in all the Na salts, regardless of x. These results lead to one conclusion—that the dielectric contribution of the COONa groups in the disordered state of the ionic clusters is almost the same as that of the isolated COONa groups not incorporated into the ionic clusters, or in other words, that the molecular motion of long segments containing the COONa groups inside of the ionic clusters above T_i (α relaxation) is similar to the micro-Brownian molecular motion of long segments in the rubbery state above T_g as conventionally seen in viscoelastic polymer systems.[38,39]

In conclusion, the present dielectric results suggest that the inside of ionic clusters is rigid in the ordered state below T_i but soft in the disordered state above T_i.

Transition-Metal Salts of EMAA and Their Complexes with BAC. Previously we reported dielectric properties of the Zn(II) salts of EMAA and their complexes with BAC.[16,17] In EMAA-xZn (x = 0–0.60), the β' and γ relaxations were observed near 330 K above T_g and 190 K below T_g, respectively. The β' relaxation gradually shifted to higher temperatures with increasing x, but both α and β relaxations were not seen, even at x = 0.60. These dielectric results indicated no formation of ionic clusters, which was also confirmed by small angle X-ray scattering, DSC, and thermal expansion measurements.[16,34,35] When BAC was added to EMAA-xZn, it was found that the ionic clusters were formed by the increase of ionic nature of the Zn(II)$(BAC)_n$–$(COOR)_2$ bond; a covalent nature prevails in the Zn(II)–$(COOR)_2$ bond of EMAA-xZn, which does not tend to form the ionic aggregations, but in EMAA-xZn-yBAC, the ionic nature in the Zn(II)$(BAC)_n$–$(COOR)_2$ bond produces ionic aggregations such as ionic clusters. This section presents further dielectric studies on various transition metal [Cu(II), Mn(II), Co(II)] salts of EMAA and their complexes with BAC.

Figure 5 shows the temperature dependence of ϵ'' at 1 kHz for various transition-metal salts of EMAA (see Table II). In EMAA and EMAA-xMn (x = 0.20–0.60) as well as EMAA-xZn, the β' and γ relaxations were observed above and below T_g, respectively. With increasing x, the β' relaxation shifts to higher temperatures and becomes bigger, while the γ relaxation remains almost constant, regardless of x. In EMAA-xCo, EMAA-0.20Co exhibits both β' and γ relaxations in the higher temperature range above 300 K, as seen in Figure 5, and only the α relaxations are seen for EMAA-0.40Co and -0.60Co. In EMAA-xCu (x = 0.20–0.60), the β' and γ relaxations were observed above the below T_g, respectively, but the α relaxation is seen as a small shoulder on the β' relaxation for EMAA-0.60Cu. The coexistence of the β' and α relaxations suggests a partial clustering of the ionic groups. Namely, the clusterings of the ionic groups seem to begin from around x = 0.20 for the Co(II) salts and x = 0.60 for the Cu(II) salts. Whether the ionic clusters are formed is governed by the ionic nature of the COO–metal bond. The ionic tendency increases in order of Cu(II), Co(II), Zn(II), and Mn(II). However, most of Cu(II) salts exist in the dimers in the polymer matrix,[26,27,30] and hence the formation of ionic clusters may be suppressed. Therefore, it may be true that the Co(II) salts tend to form the ionic clusters most strongly among the four transition-metal salts. In fact, it is reported that the Co(II)–$(COO)_2$ bond in cobalt(II) stearate is considerably ionic.[45]

The values of ϵ'' for EMAA-0.60Cu-yBAC are plotted as a function of temperature at 1 kHz in Figure 6. The β' relaxation seen in EMAA-0.60Cu is depressed by the addition of BAC, and the α and β relaxations are observed near 350 and 280 K, respectively. The intensity of the α relaxation becomes very large as y increases. The ϵ''-temperature curves for EMAA-Mn–BAC and EMAA-Co–BAC systems are similar to those for EMAA-0.60Cu-yBAC (Figure 6). As BAC is added, the β' relaxation is replaced by the α and β relaxations and the intensities of the α and β relaxations also increase in both systems. These dielectric results indicate that the addition of BAC to the transition-metal salts promotes the formation of ionic clusters as previously reported for EMAA-xZn-yBAC.[16,17] Plots of T_{max} at 1 kHz and $\Delta\epsilon/(1-X_c)$ versus BAC content (y) for all the relaxations are shown in Figure 7 for EMAA-xCu-yBAC, in Figure 8 for EMAA-xMn-yBAC, and in Figure 9 for EMAA-xCo-yBAC. In EMAA-xCu-yBAC, T_{max} of the β' relaxation exists at 318–330 K for EMAA-xCu (y = 0), but the α relaxation appears by the addition of BAC and its T_{max} value remains almost constant regardless of y. T_{max}'s for both β and γ relaxations seems to be independent of either BAC content (y) or Cu content (x). In EMAA-xMn-yBAC, with increasing x, T_{max} for the α relaxation gradually increases at lower contents of BAC, but inversely decreases at higher contents of BAC and so has a maximum value at one point of x. The decrease of T_{max} suggests that BAC acts as a plasticizer at higher content, which suggests that the coordination of BAC to Mn(II) is not so strong. In EMAA-xCo, both α and β' relaxations are seen in EMAA-0.20Co, and only the α relaxation is observed at the higher contents above x = 0.40, as already described. In EMAA-xCo-yBAC, T_{max} of the α relaxation remains constant, regardless of x and y, and locates at a higher temperature than that of the β' relaxation. In both the EMAA-Mn–BAC and -Co–BAC

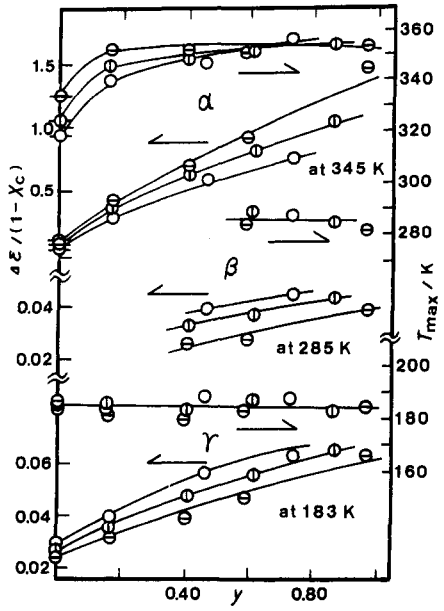

Figure 7. Plots of T_{max} at 1 kHz and $\Delta\epsilon/(1 - X_c)$ versus BAC content (y) in EMAA-xCu-yBAC: $x = 0.20$, ○; $x = 0.40$, ⊙; $x = 0.60$, ⊖; data of β' relaxation, -◇-.

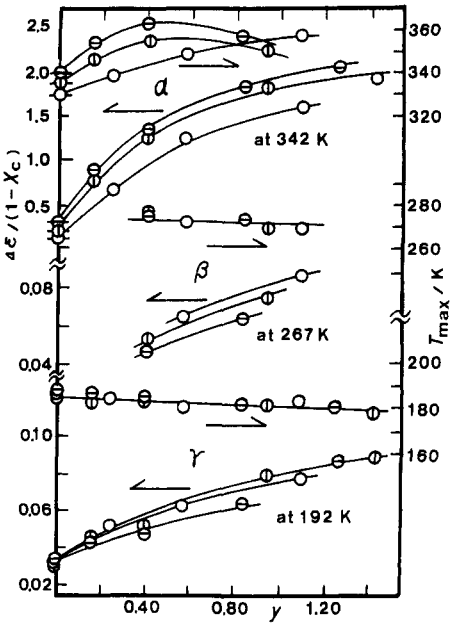

Figure 8. Plots of T_{max} at 1 kHz and $\Delta\epsilon/(1 - X_c)$ versus BAC content (y) in EMAA-xMn-yBAC: $x = 0.20$, ○; $x = 0.40$, ⊙; $x = 0.60$, ⊖; data of β' relaxation, -◇-.

systems, as well as the EMAA-Cu-BAC system, T_{max}'s for the β and γ relaxations show no dependence on BAC content (y). Consequently, the change of T_{max} with the addition of BAC reflects whether the ionic groups are clustered: the α relaxation appears with clustering of ionic groups, and its T_{max} values are located at higher temperatures, compared with that of the β' relaxation. On the other hand, T_{max}'s for the β and γ relaxations scarcely respond to the clustering of ionic groups, because these relaxations are due to the molecular motion of short segments containing the isolated salt groups not incorporated into the ionic clusters, as already described. As BAC content (y) increases, the values of $\Delta\epsilon/(1 - X_c)$ increase to a great extent for the α relaxation in all the samples, and gradually increase for the β and γ relaxations. However, as the content of transition-metal cation (x) is increased at a constant value of y, $\Delta\epsilon/(1 - X_c)$ becomes larger for the α relaxation but inversely smaller for both

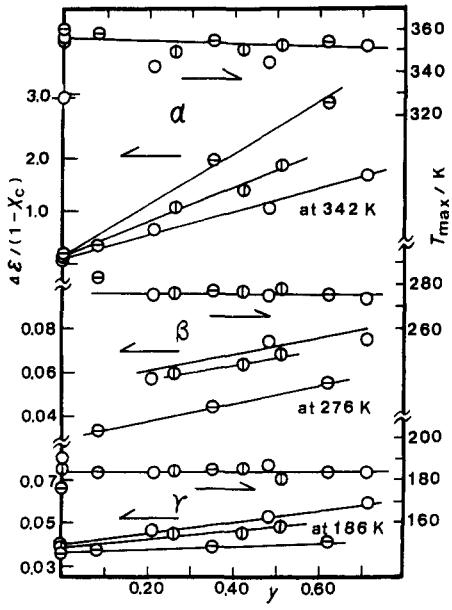

Figure 9. Plots of T_{max} at 1 kHz and $\Delta\epsilon/(1 - X_c)$ versus BAC content (y) in EMAA-xCo-yBAC: $x = 0.20$, ○; $x = 0.40$, ⊙; $x = 0.60$, ⊖; data of β' relaxation, -◇-.

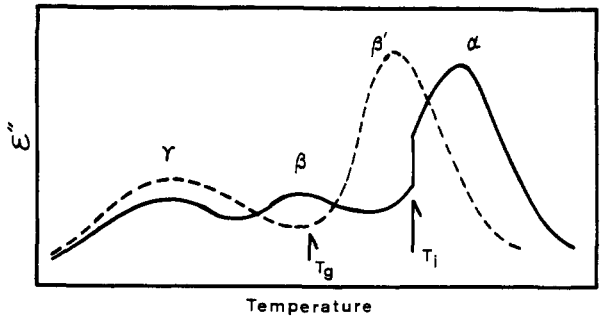

Figure 10. Schematic figure of dielectric relaxation behavior in ethylene ionomer when ionic clusters are not formed (– –) and when ionic clusters are formed (—).

β and γ relaxations. The addition of BAC to the transition-metal salts increases the ionic nature of the metal cation–COO bond to form the ionic clusters. The polar salt groups incorporated into the ionic clusters are rigid below T_i and inactive for both β and γ relaxations below T_i, but are softened above T_i to become active for the α relaxation above T_i. With increasing x at a constant value of y, the number of isolated polar salt groups not incorporated into the ionic clusters may decrease, because as the value of x is larger, the ionic clustering may be more accelerated with the addition of BAC to the transition-metal salts. This decrease of the isolated polar salt groups leads to the decrease of $\Delta\epsilon/(1 - X_c)$ for both β and γ relaxations by the increase of x at a constant value of y.

Remarks on the Relationships between Dielectric Relaxation and Formation of Ionic Clusters. In the present work, we indicated that the dielectric relaxation drastically changes by the formation of ionic clusters, as demonstrated in Figure 10. Conversely speaking, the formation of ionic clusters is monitored by examining the dielectric relaxations. Namely, when the ionic clusters are formed, the ionomers show the α relaxation above T_i and the β relaxation below T_i, instead of the β' relaxation.

To date, we have proposed the existence of the order–disorder transition of the first-order inside the ionic clusters of ethylene ionomers.[34] The present dielectric data also support this model. Dynamic mechanical relaxation studies are in progress on the present ethylene

ionomers. At present, we can say that the mechanical results are similar to the dielectric results described here. The mechanical results will be reported elsewhere in the near future.

Acknowledgment. We thank Mr. Hitoshi Tachino of Du Pont-Mitsui Polychemicals Co. Ltd. for critically reading the manuscript.

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Registry No. EMMA–Na (copolymer), 25608-26-8; EMMA–K (copolymer), 26376-80-7; EMMA–Mg (copolymer), 75062-18-9; EMMA–Ca (copolymer), 26702-73-8; EMMA–Cu (copolymer), 120751-20-4; EMMA–Mn (copolymer), 76522-88-8.