Structure and Properties of the Neodymium(III) Salts of Poly(ethylene-*co*-methacrylic acid)

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ABSTRACT: Neodymium(III) (Nd(III)) salts of poly(ethylene-*co*-5.4 mol% methacrylic acid) (EMAA) were synthesized in the neutralization range from 0 to 100%. The coordination structure, the formation and structure of ionic aggregates and their microphase separation were investigated. The infrared spectral results suggested that local environments around Nd(III) ions significantly change near 50% neutralization. Above this degree of neutralization, the X-ray scattering and visible spectral results indicated the presence of ionic aggregates. Interestingly, almost simultaneously with the ionic aggregation, a microphase separation of ionic aggregates from the polymer matrix (the formation of *ionic cluster phase* in Eisenberg's terminology) was found to take place by dynamic mechanical and dielectric relaxational measurements. The activation energy for the α relaxation (340–420 kJ mol⁻¹), which is attributed to the glass transition of the ionic cluster phase, and the melt flow rate revealed that the Nd(III) ionomers were densely cross-linked by either isolated or aggregated ions. The stiffness also indicated the existence of the densely cross-links, and the Nd(III) ionomers exhibited the higher stiffness compared with the monovalent and divalent salts of EMAA.

KEY WORDS Ethylene Ionomer / Neodymium Salt / Microphase Separation / Ionic Aggregate / Coordination Structure /

Since the pioneer work by Rees *et al.*^{1,2} in the mid-1960's, poly(ethylene-*co*-methacrylic acid) (EMAA) ionomers have been used for packaging, extrusion coating, and molding applications because of their glass-like high clarity and high modulus superior to those of conventional polyethylene. These ionomer characteristics are known to arise from ionic crosslinking effects by aggregation of ionic groups in the hydrophobic polymer matrix.^{3–6} The structure and properties of ionic aggregates have been extensively studied by many researchers, and several different types of ionomers other than EMAA ionomers have been developed and characterized. Moreover, several morphological models have been proposed to date,^{5,7–11} but the structure of the ionic aggregates and their arrangement in the polymer matrix still remain as an open question.

In general, the nature of neutralizing cation, the degree of neutralization, the flexibility of backbone chains, and the degree of crystallinity of hydrophobic chain segments are important factors in controlling ionic aggregation and designing ionomer properties. In particular, the nature of neutralizing cation such as size, valence, ionicity, or coordination number is a key factor to determine the formation and structure of ionic aggregates. Lefelar and Weiss¹² proposed a conceptual model based on a crystal closest packing approach, and showed that in carboxylated ionomers such as EMAA ionomers the packing of anionic side groups is determined by the neutralizing cation while in sulfonated ionomers such as sulfonated polystyrene ionomers the anion packing is independent of cations. Experimentally, the effects of cation type on ionic aggregation and the

relevant properties has been extensively studied using various physical techniques.^{13–22} In ethylene ionomers, Bonotto and Bonner,²⁰ and we²¹ investigated the mechanical properties for several salts of ethylene ionomers and found that the K, Na, and Mg salts showed a maximum stiffness near 33% neutralization while in the Zn salts, the stiffness initially increased with increasing the neutralization but the increase is saturated at ~80% neutralization. These degrees of neutralization correspond with each minimal degree of neutralization causing a microphase separation of ionic aggregates from the polymer matrix, which have been found in the mechanical^{21,23,24} and dielectric^{25–28} relaxational studies. Moreover, very recently, we investigated the structure and physical properties of the binary systems of EMAA ionomers neutralized with two types of metal cations, and found that in the Na/Zn binary cation system, the stiffness showed a maximum value near 50 mol% of Na.²² All these studies clearly indicate that the formation and structure of ionic aggregates and the physical properties are closely connected with the strength of ionic interactions and the coordination structure of metal cations. Therefore, cation chemistry is certainly important in designing ionomer properties.

In ethylene ionomers, the structure–property relationships of the trivalent metal salts are unknown, though a wealth of studies has been made on the monovalent and divalent metal salts. Only one paper by Straus²⁹ dealt with the trivalent salts of EMAA, where he chose Al(III) as a trivalent neutralizing cation. Nevertheless, he only obtained the crude Al(III) salts of EMAA because of the synthetic difficulties, which made it impossible to study the structure and physical properties of these materials. On the other hand, a few reports have been published

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on the rare-earth(III) salts of poly(ethylene-*co*-acrylic acid) (EAA) by Li *et al.*,^{30,31} but the neutralization level was under 20%, because their interest was focused on the catalytic activity in butadiene polymerization and not the ionomer properties. From these points of view, the structure and physical properties of EMAA ionomers neutralized with trivalent metal cations are interesting.

In this work, we choose rare-earth(III) ions as a trivalent neutralizing cation, and we succeed in synthesizing the neodymium(III) (Nd(III)) salts of EMAA with various degrees of neutralization up to 100% by use of the melt reaction process.³³ This melt reaction method^{21,32,34} has been found to be very useful to obtain various salts of EMAA ionomers thoroughly purified (*e.g.*, free from organic solvents that often influence the structure and properties of ionomers³⁵). The purpose of this work is to clarify the structure and physical properties of the Nd(III) salts of EMAA. The coordination structure, the formation of ionic aggregates and the microphase separation, and the relevant physical properties were investigated from X-ray scattering, visible and infrared (FT-IR) spectroscopic, differential scanning calorimetric (DSC), dilatometric, dynamic mechanical and dielectric relaxational, and melt viscosity (melt flow rate) studies.

EXPERIMENTAL

Preparation of the Nd(III) Salts of EMAA

The starting EMAA polymer was a random ethylene copolymer made by Du Pont–Mitsui Polychemicals Co., Ltd., whose MAA content was 5.4 mol%. Neutralization of EMAA by Nd(III) was accomplished by a melt reaction of EMAA and (CH₃COO)₃Nd(III)·3H₂O at 453–473 K for 30–45 min using a Brabender PLE 651 plasti-corder with a rotor turning of 40 rev min⁻¹. During the reaction, the mixing bowl was degassed by a rotary pump to maintain the reduced atmosphere of 250–600 mmHg. The products obtained were compression-molded into 0.5-mm-thick sheets at 423 K and were dried under a reduced pressure of 5–10 mmHg at 413 K for 1 hour to remove residual water and acetic acid; the vacuum-drying frequently altered the IR spectral pattern, and so, this procedure was repeated (usually 2 or 3 times) until no alteration was observed in the spectral pattern. Elemental analyses were performed in the Laboratory for Organic Elemental Microanalysis of Kyoto University, and the results indicate that the neutralization reaction proceeded stoichiometrically, as shown in Table I. The Nd(III) ionomers are hereafter denoted as EMAA-*x*Nd, where *x* (0 ≤ *x* ≤ 1) is the degree of neutralization by Nd(III). As reported previously,^{36,37} a small amount (0.5–3 wt%) of water uptake profoundly, in general, changes the structure and physical properties of EMAA ionomers. The dry samples were stored at room temperature in a vacuum dessicator before use, but absorbed a very small amount of water within the level of residual water as seen in Table I, where the amount of absorbed water was determined from the weight loss by vacuum-drying at about 413 K for 1 hour, and these data are also included.

Table I. Elemental analysis data of EMAA-*x*Nd

Sample	C%		H%		Residual water
	Clacd	Found	Calcd	Found	
	%	%	%	%	%
EMAA	81.2	80.7	13.3	13.4	0.10
EMAA-0.1Nd	80.5	79.9	13.2	13.6	
EMAA-0.2Nd	79.9	79.3	13.0	13.3	0.08
EMAA-0.3Nd	79.3	78.9	12.9	12.3	
EMAA-0.4Nd	78.6	78.0	12.8	12.8	<0.01
EMAA-0.5Nd	78.0	77.2	12.7	12.8	
EMAA-0.6Nd	77.4	77.3	12.6	12.6	0.12
EMAA-0.8Nd	76.2	75.7	12.3	12.5	0.27
EMAA-1.0Nd	75.1	74.3	12.1	12.2	

Physical Measurements

X-Ray scattering measurements were performed with a Mac Science X-ray generator (MXP³ system) operated with a copper target at a 50-kV accelerating potential and 40-mA emission current. The Cu-*K*_α radiation ($\lambda = 1.54050 \text{ \AA}$) was selected with a graphite monochromator. The divergence and scattering slits were 1°, and the receiving slit was 0.15 mm. Samples were scanned at 2.0° min⁻¹ at room temperature.

Visible spectra were measured using a Hitachi 330 or a Shimadzu UV-2100 PCS recording spectrophotometer at room temperature. The thickness of the samples used were 0.2–0.5 mm.

IR spectra were measured for *ca.* 50 μm -thick films with a Perkin Elmer 1640 FT-IR spectrometer at room temperature, where 64 scans at a resolution of 4 cm⁻¹ were signal averaged.

DSC measurements were carried out with a Seiko Denshi DSC-210 differential scanning calorimeter (SSC-5000 system) at a heating/cooling rate of 10 K min⁻¹ under a dry N₂ flow of *ca.* 40 mL min⁻¹. The instrument was calibrated by indium (mp 156.6°C, $\Delta H = 28.458 \text{ cal g}^{-1}$) and tin (mp 231.9°C, $\Delta H = 59.5 \text{ cal g}^{-1}$). *ca.* 10 mg of the samples weighed to 10⁻² mg were heated to 433 K and then cooled to room temperature at a rate of 10 K min⁻¹. After this, the samples were stored at room temperature for 30 days in a vacuum dessicator until used. The temperature (*T*_i) of the order-disorder transition of ionic aggregate regions^{38–40} and its enthalpy change (ΔH_i) and melting point (*T*_m) and crystallization temperature (*T*_c) of polyethylene crystallites and their enthalpy changes (ΔH_m and ΔH_c) were obtained from the DSC data. The weight fraction of crystallinity (*X*_c) was calculated from the value of ΔH_c by assuming that the heat of fusion of polyethylene crystallites is 290.4 J g⁻¹.

Thermal expansions were measured at a heating/cooling rate of *ca.* 0.5 K min⁻¹ using a glass capillary dilatometer (0.6-mm i.d.). A compression-molded sheet of ~1 g was aged at room temperature for more than 1 month, and then carefully immersed in liquid mercury *in vacuo* to avoid the formation of voids on the surface of the sheet. The volume change of the sample with temperature was calculated from a reading of the height of mercury in the capillary of the dilatometer. The density at 298 K was obtained by a buoyancy method with benzene.

Dynamic mechanical properties were measured using a Rheospectroler Model DVE-V4 (Rheology Co., Ltd.) attached to a NEC PC9801EX computer. A compression-molded sheet was cut into a specimen of approximately 20-mm length, 6-mm width, and 2-mm thickness, and then aged at room temperature for 30–40 days before the measurements. The tensile mode was analyzed under a constant tension, at a heating rate of 3 K min^{-1} in the temperature range from 123 to 393 K and at frequencies of 1, 10, and 100 Hz.

Dielectric measurements were carried out with a multifrequency LCR meter (Yokogawa-Hewlett Packard, type 4274A) attached to a NEC PC9801F2 computer, by use of the three terminal electrode system described previously⁴¹; the outer diameter of the guarded electrode was 37 mm, and those of the unguarded electrode and the guard electrode were 50 mm, while the inner diameter of the guard electrode was 39 mm. The specimens for dielectric measurements were circular sheets of 50-mm diameter and about 0.5-mm thickness. To ensure electrical contact between the electrode and specimen, gold was carefully deposited *in vacuo* on the surface of the specimen, and then the specimen was aged at room temperature for 30–50 days. The measurements were made under N_2 atmosphere in the temperature from 90 to 400 K and at several frequencies between 100 Hz and 100 kHz. The temperature was measured by a calibrated Fe-constantan thermocouple touched with the guard electrode.

The melt flow rate (MFR) was measured as the weight of polymer flow (g/10 min) from a melt indexer at 463 K under a 2160-g load.

Stiffness was measured at room temperature using a Toyoseiki stiffness tester according to ASTM D-747. The specimens of 100-mm length and 20-mm width were stamped out from a 3-mm thick compression-molded sheet and aged at 296 K for 2 months before the measurements.

Tensile properties were tested using an Intesco Model 201 at room temperature and with a crosshead speed of 200 mm min^{-1} . The specimens, stamped out from a 2-mm thick compression-molded sheet, were in the shape of a dogbone according to JIS K-6760 and aged at 296 K for a few days before the measurements.

RESULTS AND DISCUSSION

X-Ray Scattering

Figure 1 shows X-ray scattering patterns of EMAA- $x\text{Nd}$. When the degree of neutralization (x) is 0.5 or less, two peaks near $2\theta = 21$ and 23° (2θ is the scattering angle) are clearly visible, riding on a broad amorphous halo near 19° . The 21 and 23° peaks are assigned to the (110) and (200) diffractions from the polyethylene crystalline region, respectively. Their intensities decrease with increasing x and almost disappear at $x = 0.6$. These results are well consistent with the DSC results which will be presented later in Figure 8. At $x \geq 0.4$, another peak appears near $2\theta = 5^\circ$. This result indicates that ionic aggregation occurs at $x \geq 0.4$ because the 5° peak is assigned to a so-called *ionomer peak*. The Bragg spacings (d_{Bragg}) of the ionomer peak in the Nd(III) ionomers are 17–20 Å, being almost equal to those in

Figure 1. X-Ray scattering patterns of EMAA- $x\text{Nd}$.

Figure 2. Visible spectra in the region of 550–620 nm for EMAA- $x\text{Nd}$.

the Zn(II) ionomers^{42,43} ($d_{\text{Bragg}} = 17\text{--}19 \text{ Å}$) but slightly smaller than those in the Na ionomers^{3,43} ($d_{\text{Bragg}} = 19\text{--}27 \text{ Å}$). Assuming that the d_{Bragg} value roughly corresponds to the inter-aggregate distance and that all the neutralized side groups are incorporated into ionic aggregates,⁴⁴ the larger d_{Bragg} means the larger size of ionic aggregates, and hence, it is concluded that the size of ionic aggregates in the Nd(III) ionomers is almost equal to that in the Zn(II) ionomers but smaller than that in the Na ionomers.

Visible Spectra

Figure 2 shows visible spectra in the region of 550–620 nm for EMAA- $x\text{Nd}$. All the samples exhibit a broad absorption band near 585 nm, which is assigned to the Nd(III) $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$, $^4\text{G}_{7/2}$ transition. According to Karraker,⁴⁵ the band shape of this transition is sensitive to the coordination number and ligand geometry on Nd(III) ions. The band shapes observed for all the EMAA- $x\text{Nd}$ samples are fairly similar to that for the 8-coordinated Nd(III) ion in $\text{Nd}(\text{CF}_3\text{COCHCOCF}_3)_4$.⁴⁵ Therefore, we concluded that the averaged coordination number of Nd(III) ions is 8 in EMAA- $x\text{Nd}$, independent of x .

Figure 3 shows plots of the peak absorbance of Nd(III) $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$, $^4\text{G}_{7/2}$ band versus x in EMAA- $x\text{Nd}$, where the peak absorbance is normalized to the same thickness of 1 mm. The plots appear to be composed of two straight lines and the slope above $x = 0.5$ is about one-fourth of that below $x = 0.5$. The deviation of Beer's

Figure 3. Plots of the peak absorbance of the Nd(III) $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^4G_{7/2}$ band versus the degree of neutralization (x). Linear least-squares fits are also shown as solid lines.

law above $x=0.5$ indicates the existence of Nd(III)–Nd(III) interactions above $x=0.5$, and, in other words, that the local environment of Nd(III) ions changes around $x=0.5$ with increasing x . These results support the X-ray scattering results that ionic aggregation occurs at $x > 0.4$ (see Figure 1).

IR Spectra

Figure 4 shows IR spectra in the region of 1100–1800 cm^{-1} for EMAA- x Nd. Spectral intensities are normalized by the intensity of the CH_2 bending peak at 1467 cm^{-1} , where it is assumed that the intensity of the 1467- cm^{-1} band is unchanged with x .⁴⁶ In this figure, two peaks near 1698 and 1270 cm^{-1} are assigned to hydrogen-bonded carbonyl stretching bands $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$, respectively, and two peaks in the region of 1600–1500 cm^{-1} and at 1406 cm^{-1} are assigned to the asymmetric ($\nu_{\text{as}}(\text{COO}^-)$) and symmetric ($\nu_{\text{s}}(\text{COO}^-)$) carboxylate stretching bands, respectively.^{2,30,31} The intensities of these peaks depend on x , but their frequencies are almost independent of x . As x increases, the intensity of the 1698- cm^{-1} band decreases and then another new peak appears near 1669 cm^{-1} . Figure 5 plots the intensities of the 1698- and 1669- cm^{-1} bands and the sum of these two intensities against x . The intensity of the 1698- cm^{-1} band monotonously decreases as x increases from 0 to 1.0. On the other hand, the intensity of the 1669- cm^{-1} band increases when x increases from 0 to 0.5, but begins to decrease above $x=0.5$. Since the sum of these two intensities gives a straight line with zero at $x=1.0$, it can be considered that the 1669- cm^{-1} band is also associated with the unneutralized COOH groups. Han and Williams⁴⁶ reported that $\nu(\text{C}=\text{O})$ bands in several metal salts of EMAA shift to lower frequencies with increasing x and suggested that this is due to the formation of acid-base complexes between metal cations (acting as a Lewis acid) and unneutralized COOH groups. Therefore, we assigned the 1669- cm^{-1} band to the stretching vibration of hydrogen-bonded carbonyl groups that are weakly coordinated to the Nd(III) carboxylates.

In the region of 1500–1600 cm^{-1} , three COO^- asymmetric stretching bands ($\nu_{\text{as}}(\text{COO}^-)$) are observed at 1584, 1541, 1518 cm^{-1} , suggesting that the COO^- groups in EMAA- x Nd are at least in three different

Figure 4. IR spectra in the region of 1100–1800 cm^{-1} for EMAA- x Nd.

Figure 5. Plots of the peak absorbances of the 1698- and 1669- cm^{-1} bands and the sum of these two bands versus x . First- and second-order polynomial fits are also shown as solid and dashed lines, respectively.

Figure 6. Neutralization (x) dependence of the peak intensities of the 1584-, 1541-, 1518-, and 1406- cm^{-1} bands. First- (— and ----) and second-order (— · —) polynomial fits are also shown.

environments. Figure 6 shows neutralization dependence of the intensities for these three bands, along with the data for the COO^- symmetric stretching band ($\nu_{\text{s}}(\text{COO}^-)$) at 1406 cm^{-1} . The $\nu_{\text{s}}(\text{COO}^-)$ band is superposed on the C–O–H in-plane bending band ($\delta(\text{COH})$) at 1407 cm^{-1} , but the intensity of the latter band is considered to be almost independent of x . In the range $x=0$ –0.4, only two $\nu_{\text{as}}(\text{COO}^-)$ bands at 1584 and 1541 cm^{-1} are present (see also Figure 4), and their intensities increase with increasing x . Above $x=0.5$, the band at 1518 cm^{-1}

appears, and its intensity steeply increases with increasing x , while the intensities of the 1584- and 1541-cm⁻¹ bands gradually decrease. The sum of the intensities of these three bands increases in proportion to x and this relation seems to hold for $\nu_s(\text{COO}^-)$ band. Nakamoto⁴⁷ argued that the higher symmetry of COO^- groups on the coordination to metal ions may give the smaller difference between $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ frequencies. Since the frequency difference in EMAA- x Nd decreases from 133 to 106 cm⁻¹ with increasing x from 0.1 to 0.8, the average mode of coordination of the COO^- groups is considered to become more spherically symmetric. The frequencies of the 1584- and 1541-cm⁻¹ bands almost agree with those of Nd(III) acetates⁴⁵ ($\nu_{as}(\text{COO}^-)=1550\text{--}1535\text{ cm}^{-1}$), and therefore, these two bands are associated with isolated Nd(III) carboxylates. The 1518-cm⁻¹ band, which is present only in highly neutralized EMAA- x Nd, is probably associated with aggregated Nd(III) carboxylates. From these assignments, we can depict the following picture: From the law of electric neutrality, three COO^- groups coordinate to one Nd(III) ion. The 8-coordination, which was deduced by the visible spectra, should require another two oxygens, assuming that the COO^- groups act as a bidentate ligand. Such oxygens can be offered from the carbonyl groups of unneutralized COOH groups exhibiting the 1669-cm⁻¹ $\nu(\text{C}=\text{O})$ band. As mentioned above, ionic aggregation takes place above $x=0.5$, and in ionic aggregate regions, one oxygen of COO^- groups may be shared with two adjacent Nd(III) ions, giving rise to corner-sharing, edge-sharing, or face-sharing of two NdO_8 octahedra. This would lower the electron density of $\text{O}=\text{C}=\text{O}^-$ bond and hence lower the frequency of the $\nu_{as}(\text{COO}^-)$ band, resulting in the appearance of the 1518-cm⁻¹ band. Such sharings, on the other hand, would reduce the number of COOH carbonyl groups required to the 8-coordination, resulting in the decrease of the intensity of the 1669-cm⁻¹ $\nu(\text{C}=\text{O})$ band, as observed. It is concluded that the local environment of the Nd(III) ions substantially changes near $x=0.5$, and this change reflects the formation of ionic aggregates, indicated by the X-ray scattering results mentioned above.

DSC Data

Figure 7 shows DSC curves for EMAA-0.6Nd aged at room temperature for 30 days. In the first heating, EMAA-0.6Nd exhibits two endothermic peaks near 324 and 359 K. Clearly, the 359-K peak originates from the melting of the polyethylene crystalline regions (T_m). The subsequent cooling shows an exothermic peak at 321 K, which is assigned to the recrystallization of polyethylene segments (T_c). In the second heating, only the T_m peak is seen near 358 K, and the lower temperature peak (T_i) disappears. The T_i peak reappeared by aging at room temperature after the second heating. The DSC curves for other EMAA- x Nd ionomers were essentially the same as those for EMAA-0.6Nd described above, and the thermal parameters obtained for all the Nd(III) ionomers are summarized in Table II. Although the thermal hysteresis found on DSC is a general feature of EMAA ionomers, a final answer has not been obtained yet for the assignment of T_i peak. On the basis of our

Figure 7. DSC curves for EMAA-0.6Nd: 1H, 1st heating; 1C, 1st cooling; 2H, 2nd heating.

Table II. DSC parameters of EMAA- x Nd

Sample	1st heating				1st cooling		2nd heating	
	T_i	ΔH_i	T_m	ΔH_m	T_c	ΔH_c	T_m	ΔH_m
	K	J g ⁻¹	K	J g ⁻¹	K	J g ⁻¹	K	J g ⁻¹
EMAA	324	8	364	62	332	71	364	64
EMAA-0.1Nd	315	9	363	63	344	69	362	64
EMAA-0.2Nd	318	10	363	59	342	66	362	59
EMAA-0.3Nd	319	11	362	53	338	62	363	53
EMAA-0.4Nd	322	11	362	45	329	51	362	45
EMAA-0.5Nd	323	12	360	41	324	43	360	41
EMAA-0.6Nd	324	12	359	32	321	31	358	28
EMAA-0.8Nd	325	11	357	21	318	21	355	15
EMAA-1.0Nd	328	11	354	13	315	12	353	7

Figure 8. Plots of the degree of crystallinity (X_c) versus the degree of neutralization (x) for the Nd, Na, Mg, and Zn ionomers.

proposed model,³⁸⁻⁴⁰ we assign the T_i peak to an order-disorder transition of ionic aggregate regions⁴⁸; the thermal hysteresis appears as a result of a slow reorganization of ionic aggregate regions below T_i .

Figure 8 shows plots of the weight fraction of crystallinity (X_c) versus x for EMAA- x Nd, where the curves for EMAA- x Na, EMAA- x Mg, and EMAA- x Zn are also included. The increase of x decreases the X_c values for these four ionomer systems. This is probably because ionic interactions prevent their crystallization.⁴⁹ The decrease of ΔH_m with increasing x in EMAA- x Nd is larger than that in EMAA- x Zn, being comparable to those in EMAA- x Na and EMAA- x Mg. This result

suggests that the strength of ionic interactions in EMAA- x Nd is comparable to those in EMAA- x Na and EMAA- x Mg. This interpretation is also supported by MFR data which will be discussed later.

Dilatometry

Figure 9 shows plots of the specific volume (V) versus temperature (T) for EMAA, EMAA-0.4Nd, and EMAA-0.8Nd. EMAA shows two anomalies near 323 K and 369 K in the V - T plot. The latter anomaly is also seen in EMAA-0.4Nd and EMAA-0.8Nd, and corresponds to the melting of polyethylene crystallites (T_m). The former anomaly, on the other hand, depends on the degree of neutralization, and is observed near 317 K for EMAA-0.4Nd, and as a broad peak near 325 K for EMAA-0.8Nd, respectively. From the DSC results mentioned above, the former anomaly near 320 K is clearly related to the DSC T_i peak. The thermal expansion coefficient, α , below 313 K changed from 7.7×10^{-4} for EMAA to 6.9×10^{-4} for EMAA-0.4Nd, and to $5.6 \times 10^{-4} \text{ K}^{-1}$ for EMAA-0.8Nd. It is considered that the decrease of α with the increase of x may result from the formation of a cross-linked network.

Dynamic Mechanical Results

Figure 10 shows temperature dependence of dynamic loss modulus (E'') at 10 Hz for EMAA- x Nd. EMAA shows two relaxations in the temperature range of 123–393 K. Previous investigations^{21,23,24} have shown that the relaxation near 140 K, denoted as γ , is ascribed to a local molecular motion of the short chain segments and the relaxation at 292 K, denoted as β' , to a micro-Brownian motion of the long chain segments in the amorphous region. The E'' curve of EMAA-0.3Nd is similar to that of EMAA, indicating that when $x \leq 0.3$, the Nd(III) carboxylate side groups are not aggregated. When x reaches 0.5 or higher, the β' relaxation is replaced by two relaxations at 315–335 K and near 263 K. The former shifts to higher temperatures with increasing x while the latter stays at almost the same temperature independent of x . Such splitting is commonly seen for other EMAA ionomers^{21,23,24}; the higher temperature relaxation, usually denoted as α , is generally associated with a glass-rubber transition of the ionic cluster phase, and the lower temperature relaxation, denoted as β , is ascribed to a micro-Brownian motion of the long chain segments in the amorphous polyethylene phase. The appearance of the two relaxations implies that the phase separation between the ionic cluster and polymer matrix phases occurs around $x=0.5$. The X-ray results indicated that the formation of ionic aggregates occurs at $x \geq 0.4$. Therefore, by combining the dynamic mechanical data with the X-ray scattering results, it is concluded that at $\sim 50\%$ neutralization, the Nd(III) ionomer begins to form ionic aggregates which, at the same time, construct regions of microphase-separated ionic cluster. This result is contrast to that for other transition-metal(II) salts of EMAA; for example, the X-ray scattering results^{42,43} indicated that the Zn(II) salt forms ionic aggregates above $\sim 40\%$ neutralization, while the dynamic mechanical results²⁴ of this salt showed that microphase separation occurs above 80% neutralization.

Figure 9. Plots of the specific volume (V) versus temperature (T) for EMAA, EMAA-0.4Nd, and EMAA-0.8Nd.

Figure 10. Temperature dependence of the dynamic loss modulus (E'') at 10 Hz for EMAA- x Nd.

Dielectric Relaxational Results

Figures 11 and 12 show temperature dependence of dielectric loss (ϵ'') at 1 kHz for EMAA- x Nd. The results were essentially identical to those from the dynamic mechanical measurements mentioned above; at $x=0.6$ or higher, the β' relaxation is replaced into α and β relaxations, indicating the formation of ionic cluster phase. In this case, the dielectric β relaxation arises primarily from a motion of polar isolated Nd(III) salt groups dispersed in the amorphous polyethylene phase. In EMAA-0.6Nd and EMAA-0.8Nd, a high ionic conduction occurring above T_m tends to veil the α relaxation at lower frequencies, as seen in Figure 12, but at higher frequencies such as 50 or 100 kHz, the α relaxation is clearly visible (see the inset of Figure 12).

Table III summarizes the relaxation parameters of EMAA- x Nd from both mechanical and dielectric measurements, where the activation enthalpies (ΔH) were calculated from the Arrhenius plots of the relaxation temperatures versus frequencies. The ΔH of the mechanical β' relaxation is almost equal to that of the dielectric β' relaxation for $x=0$ and 0.1, but shows a slightly smaller value than the dielectric β' relaxation for $x=0.2$ and 0.3. The ΔH of the β relaxation for $x=0.8$ gives a good agreement between the two measurements. For $x=0.4$ –0.6, the dielectric β relaxation peak was weak and showed a severe overlap with the low tem-

Figure 11. Temperature dependence of the dielectric loss (ϵ'') at 1 kHz for EMAA- x Nd ($x = 0$ – 0.3).

Figure 12. Temperature dependence of the dielectric loss (ϵ'') at 1 kHz for EMAA- x Nd ($x = 0.4$ – 0.8). The inset shows the ϵ'' - T curves at higher frequencies for EMAA- 0.8 Nd.

Table III. Relaxation parameters of EMAA- x Nd

Sample	Mechanical						Dielectric							
	α		β'		β		α		β'		β		γ	
	$T_{\max}^a$	ΔH	$T_{\max}$	ΔH	$T_{\max}$	ΔH	$T_{\max}^a$	ΔH	$T_{\max}$	ΔH	$T_{\max}$	ΔH	$T_{\max}$	ΔH
	K	kJ mol^{-1}	K	kJ mol^{-1}	K	kJ mol^{-1}	K	kJ mol^{-1}	K	kJ mol^{-1}	K	kJ mol^{-1}	K	kJ mol^{-1}
EMAA			292 ^b	246 ^b					318	243 (5) ^c			187	46 (1)
EMAA-0.1Nd			296	271 (0)					322	270 (10)			193	48 (1)
EMAA-0.2Nd			298	252 (6)					322	290 (10)			192	52 (1)
EMAA-0.3Nd			302	252 (6)					328	330 (10)			190	46 (2)
EMAA-0.4Nd	318	420 (20)			~260	— ^d	347	270 (10)			—	—	196	41 (1)
EMAA-0.5Nd	326	380 (0)			261	160 (10)	356	295 (10)			~295 ^e	—	197	42 (2)
EMAA-0.6Nd	323	420 (20)			268	160 (20)	363 ^f	380 (20)			~295 ^e	—	198	36 (1)
EMAA-0.8Nd	333	340 (40)			260	190 (0)	362 ^f	340 (20)			300	197 (4)	192	50 (2)
EMAA-1.0Nd	329	750 (60)			263	180 (0)								

^a Temperatures of the mechanical and dielectric relaxations were measured at 10 Hz and 1 kHz, respectively. ^b Taken from ref 24. ^c Parentheses indicate the standard deviation from the least-squares fit. ^d —, not determined. ^e Seen as a shoulder at 300 Hz. ^f Extrapolated values at 1 kHz in the Arrhenius plots (see the text).

perature side of the α relaxation peak, which makes it difficult to estimate their ΔH 's accurately. In EMAA-0.6Nd and EMAA-0.8Nd, the ΔH of the dielectric α relaxation fairly agrees with that of the mechanical α relaxation; the ΔH 's are between 340 and 420 kJ mol^{-1} , and are as large as those of the Na salts of EMAA.^{26,28}

In conclusion, the dielectric relaxation studies indicated that the Nd(III) ionomers form the ionic cluster phase above $\sim 50\%$ neutralization, being well consistent with the dynamic mechanical results. Here it is noted that the neutralization, at which the ionic cluster phase begin to form, is dependent on the species of metal cation; the neutralization is known to be $\sim 30\%$ for the Na ionomer^{3,21,23–26,28} and $\sim 80\%$ for the Zn(II) ionomer.^{24,27}

Resentry, Eisenberg *et al.*¹¹ proposed an ionic cluster phase model for ionic aggregations; when the ion content increases, the isolated ions begin to form multiplets, which are surrounded with a region restricting the chain mobility. When the ion content increases more, the region of restricted mobility overlaps each other to form an ionic cluster phase which is phase-separated from the polymer matrix. One important point of this model is that the construction of ionic cluster phase does not necessarily accompanied with the formation of larger

ionic aggregates. Actually, as already described in the X-ray scattering section, the size of ionic aggregation was about 17–20 Å, in the Nd(III) ionomers above 40% neutralization, comparable to that of Zn(II) ionomer (17–19 Å) and somewhat smaller than that of Na ionomer (19–27 Å). Moreover the IR $\nu_{\text{as}}(\text{COO}^-)$ band splitted into the three peaks near 1584, 1541 and 1518 cm^{-1} , where the former two peaks come from the isolated COO^- groups and the latter peak, from the COO^- group incorporated into the ionic aggregates (see Figure 6). The fraction of Nd(III) ions incorporated into the ionic aggregates was estimated to be about 25% at 50% neutralization, assuming the same absorption coefficient for the three $\nu_{\text{as}}(\text{COO}^-)$ peaks. (This assumption seems to be reasonable, because the sum of the three absorbance intensities was proportional to x in Figure 6.) The ion content in an ionomer neutralized partially by metal cation is estimated as $(px/n)q$, where p , x , n , and q are MAA content in EMAA, degree of neutralization, valence of metal cation, and fraction of ions incorporated into ionic aggregates, respectively. The ion content was calculated to be about 0.2 mol% for the Nd(III) ionomers at 50% neutralization, since $p = 5.4$ mol%, $x = 0.5$, $n = 3$, and $q = 0.25$. The minimal ion content causing ionic cluster phase separation in the

Nd(III) ionomer (~ 0.2 mol%) is about one-fifth of that in the Na ionomer (~ 1.3 mol%) and much less than in the Zn(II) ionomer (~ 2.4 mol%).

MFR Data

Figure 13 shows plots of the melt flow rate (MFR) versus x for EMAA- x Nd. The MFR curves for alkali-metal, alkaline-earth-metal, and transition-metal salts of EMAA are cited from ref 21. The logarithms of MFR of all the EMAA ionomers decrease almost linearly with increasing x . MFR value is usually used as an index of molecular weight of polymers, and in the cross-linked polymers such as ionomers, this value is also affected by the degree of cross-linking.^{20,21} All the EMAA ionomers in Figure 13 were produced from the same starting polymer, EMAA with a specified MFR value of 60. MFR was measured at 463 K far above T_m and so the polyethylene crystallites, which may act as cross-links at room temperature, were completely melted. Therefore, the MFR value simply reflects the cross-linking effect of the neutralizing cations. Consequently, the observed decrease in MFR with the increase of x suggests the neutralization promotes the formation of ionic aggregates, which act as physical cross-links even in the molten state.

The Nd(III) ionomers show the largest decrease of MFR with neutralization among the EMAA ionomers studied here; the degree of the decrease is in the order of: the Nd(III) ionomers > the alkaline-earth-metal ionomers > the alkali-metal ionomers > the transition-metal(II) ionomers. In ionomers, two types of neutralizing cations, (a) isolated ions and (b) aggregated ions, may act as cross-links. The cross-linking effect of aggregated ions is closely connected with the average number of salt groups included in one ionic aggregate. Preliminary X-ray scattering results⁴³ showed that the size of the ionic aggregates is largest for the alkali-metal (Na) ionomers and no marked difference is observed among the transition-metal(II), alkaline-earth-metal, and Nd(III) ionomers. The cross-linking effect of the alkali-metal salt groups only comes from the ionic aggregation because they are one-connectivity (monovalent) units. On the other hand, the Nd(III) salt groups should act as three-connectivity units such as $(-\text{COO})_3\text{Nd(III)}$, and the salt groups of the alkaline-earth-metal and transition-

Figure 13. Plots of the melt flow rate versus the degree of neutralization (x) for various types of EMAA ionomers. Cation type: (○) Na^+ ; (■) K^+ ; (□) Mg^{2+} ; (▲) Mn(II) ; (△) Co(II) ; (◇) Cu(II) ; (◆) Zn(II) ; (●) Nd(III) . Linear least-squares fits are also shown.

metal(II) ions act as two-connectivity units. Therefore, in the Nd(III) ionomers, both (a) isolated ions and (b) aggregated ions may act as cross-links. The ionic aggregates in the Nd(III) ionomers have a similar size to those of the transition-metal(II) and alkaline-earth-metal ionomers, whereas the Nd(III) ionomers show the largest decrease of MFR with increasing x among the EMAA ionomers neutralized by various metal cations. Therefore, the isolated Nd(III) ions are considered to contribute to the largest decrease of MFR with x . This conclusion reveals one feature of the Nd(III) ionomers that the number of salt groups incorporated into one ionic aggregate is comparatively small, compared with that in the alkali-metal salts, but the density of ionic cross-links formed by both isolated and aggregated ions in the polymer matrix is conversely high. This feature also gives one answer to why the minimal ion content causing the microphase separation is so small in the Nd(III) ionomers compared with the corresponding values of the Na and Zn(II) ionomers.

Stiffness

Figure 14 shows how the stiffness changes with x for EMAA- x Nd, $-x\text{Na}$, $-x\text{Mg}$, and $-x\text{Zn}$, where the data curves of the latter three ionomer systems are cited from ref 21. The stiffness curves of all the ionomer systems show a maximum at a degree of neutralization (x), *i.e.*, ~ 0.5 for EMAA- x Nd and ~ 0.4 for EMAA- $x\text{Na}$ and $-x\text{Mg}$, and ~ 0.8 for EMAA- $x\text{Zn}$, respectively. In the Na, Mg and Zn ionomer systems, these degrees of neutralization were reported to correspond with the minimal degrees of neutralization causing microphase separation of ionic aggregates from the polymer matrix.^{21,24} Apparently, this result holds in the Nd(III) ionomer system; the dynamic mechanical and dielectric relaxational results indicated that the microphase separation of ionic aggregates begins to occur near $x = 0.5$ in the Nd(III) ionomer system. The stiffness data also show that the Nd(III) ionomer system exhibit the largest maximum value among the four ionomer systems, which reflects the densely cross-linked structure of this ionomer system, as described above. Table IV summarizes a few mechanical properties of the Nd(III) ionomers. The Nd(III) ionomers show no marked difference in tensile strength and elongation at break, compared with other EMAA ionomers.²¹

Figure 14. Plots of the stiffness versus the degree of neutralization (x) for EMAA- x Nd, EMAA- x Na, EMAA- x Mg, and EMAA- x Zn.

Table IV. Mechanical data of EMAA-*x*Nd

Sample	Stiffness	Tensile properties	
		Tensile strength	Elongation at break
	MPa	MPa	%
EMAA	47	24	542
EMAA-0.1Nd	149	19	370
EMAA-0.2Nd	183	20	300
EMAA-0.3Nd	219	26	372
EMAA-0.4Nd	341	28	340
EMAA-0.5Nd	383	28	244
EMAA-0.6Nd	348	27	212
EMAA-0.8Nd	340	27	120
EMAA-1.0Nd	352	23	40
EMAA-0.6Na ^a	256	32	295
EMAA-0.6Mg ^a	254	29	299
EMAA-0.6Zn ^a	255	28	375

^a Taken from ref 21.

CONCLUSIONS

The Nd(III) salts of EMAA with various degrees of neutralization were synthesized as the first examples of well-characterized EMAA ionomers containing a trivalent neutralizing cation, and the structure and physico-chemical properties were studied for these materials. The X-ray scattering patterns showed an ionomer peak near $2\theta = 5^\circ$, when $x \geq 0.4$, and the increase of x decreased the degree of crystallinity of polyethylene segments. In the visible spectra, there was observed a broad absorption peak near 585 nm which are assigned to $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^4G_{7/2}$ transition for the octahedral coordinated Nd(III) ions. The plot of absorption intensity versus x bent near $x = 0.5$ and this bend indicated the existence of Nd(III)-Nd(III) interactions at $x \geq 0.5$. The IR results suggested that local environments around Nd(III) ions significantly change at $x \sim 0.5$: The 1698-cm^{-1} peak, assigned to the hydrogen-bonded carbonyl stretching vibration, monotonously decreased with increasing x , while the 1669-cm^{-1} peak, assigned to the stretching vibration of the hydrogen-bonded carbonyl groups weakly coordinated to the Nd(III) carboxylates, increased with increasing x from 0 to 0.5 but decreased above $x = 0.5$. The COO^- asymmetric stretching bands ($\nu_{\text{as}}(\text{COO}^-)$) were observed near 1584 and 1541-cm^{-1} , and these intensities initially increased with increasing x but reversely decreased above $x = 0.5$. On the other hand, another peak appeared near 1518-cm^{-1} around $x = 0.4$ and steeply increased with increasing x above $x = 0.5$. The 1518-cm^{-1} peak was assigned to the asymmetric stretching vibration of COO^- coordinated to aggregated Nd(III) ions. The IR spectral result suggests that when $x \geq 0.5$ a part of Nd(III) ions is incorporated in the ionic aggregates. From the present X-ray scattering, visible and IR spectral studies, it was concluded that ionic aggregation begins to occur near $x = 0.5$ for the Nd(III) salts of EMAA.

In dynamic mechanical and dielectric relaxational results, the β' relaxation, assigned to a micro-Brownian molecular motion of long chain segments, was replaced by α and β relaxations, which were assigned, respectively,

to a glass-rubber transition of the ionic cluster phase and a micro-Brownian molecular motion of long chain segments in the amorphous polyethylene phase. Therefore, we concluded that a microphase separation of ionic aggregates from the polymer matrix, *i.e.*, the formation of ionic cluster phase, occurs above $x \sim 0.5$. The activation energy for the α relaxation is large ($340\text{--}420\text{ kJ mol}^{-1}$), which suggests that the backbone chain segments incorporated into the ionic cluster phase are densely cross-linked and largely entangled, and thus their segmental mobility is significantly reduced. This picture supports Eisenberg's new cluster model.¹¹ The minimal ion content causing the microphase separation was roughly estimated to be 0.2 mol%, being only about one-fifth of the case of the Na ionomers. The MFR data also support the formation of a densely cross-linked network, especially above $x \sim 0.5$. The highly cross linked Nd(III) ionomers provided the highest stiffness maximum among the EMAA ionomer systems neutralized with various metal cations.

In conclusion, the Nd(III) salts of EMAA start associating near 50% neutralization to form ionic aggregates, and almost simultaneously with the ionic aggregation, noteworthy, a microphase separation of ionic aggregates from the polymer matrix begins to occur and construct an ionic cluster phase. As a result, the structure becomes a densely cross-linked state.

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REFERENCES AND NOTES

1. R. W. Rees and D. J. Vaughan, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **6**, 287 (1965).
2. R. W. Rees and D. J. Vaughan, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **6**, 296 (1965).
3. L. Holliday, Ed., "Ionic Polymers," Applied Sciences, London, 1975.
4. A. Eisenberg and M. King, "Ion-Containing Polymers: Physical Properties and Structure," *Polymer Physics Vol. 2*, Academic Press, New York, N. Y., 1977.
5. M. Pineri and A. Eisenberg, Ed., "Structure and Properties of Ionomers," NATO ASI Series C: Mathematical and Physical Sciences Vol. 198, D. Reidel Co., Dordrecht, The Netherlands, 1987.
6. L. A. Utracki and R. A. Weiss, Ed., "Multiphase Polymers: Blends and Ionomers," ACS Symposium Series 395, American Chemical Society, Washington, D.C., 1989.
7. A. Eisenberg, *Macromolecules*, **3**, 147 (1970).
8. W. J. MacKnight, W. P. Taggart, and R. S. Stein, *J. Polym. Sci., Polym. Symp.*, **45**, 113 (1974).
9. A. Moudden, A. M. Levelut, and M. Pineri, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1707 (1977).
10. D. J. Yarusso and S. L. Cooper, *Macromolecules*, **16**, 1871 (1983).
11. A. Eisenberg, B. Hird, and R. B. Moore, *Macromolecules*, **23**, 4098 (1990).

12. J. A. Lefelar and R. A. Weiss, *Macromolecules*, **17**, 1145 (1984).
13. Y. S. Ding, R. A. Register, C. Yang, and S. L. Cooper, *Polymer*, **30**, 1204 (1989).
14. Y. S. Ding, R. A. Register, C. Yang, and S. L. Cooper, *Polymer*, **30**, 1213 (1989).
15. Y. S. Ding, R. A. Register, C. Yang, and S. L. Cooper, *Polymer*, **30**, 1221 (1989).
16. M. R. Tant, J. H. Song, G. L. Wilkes, J. Horrion, and R. Jérôme, *Polymer*, **27**, 1815 (1986).
17. M. R. Tant, L. N. M. Venkateshwaran, J. H. Song, R. Subramanian, G. L. Wilkes, P. Charlier, and R. Jérôme, *Polymer*, **33**, 1347 (1992).
18. R. A. Register, M. Foucart, R. Jérôme, Y. S. Ding, and S. L. Cooper, *Macromolecules*, **21**, 1009 (1988).
19. S. Yang, K. Sun, and W. M. Risen, Jr., *J. Polym. Sci., Polym. Phys.*, **28**, 1685 (1990).
20. S. Bonotto and E. F. Bonner, *Macromolecules*, **1**, 510 (1968).
21. E. Hirasawa, Y. Yamamoto, K. Tadano, and S. Yano, *J. Appl. Polym. Sci.*, **42**, 351 (1991).
22. H. Tachino, H. Hara, E. Hirasawa, S. Kutsumizu, and S. Yano, *Macromolecules*, **27**, 372 (1994).
23. W. J. MacKnight, L. W. McKenna, and B. E. Read, *J. Appl. Phys.*, **38**, 4208 (1967).
24. H. Tachino, H. Hara, E. Hirasawa, S. Kutsumizu, K. Tadano, and S. Yano, *Macromolecules*, **26**, 752 (1993).
25. B. E. Read, E. A. Carter, T. M. Connor, and W. J. MacKnight, *Br. Polym. J.*, **1**, 123 (1969).
26. P. J. Phillips and W. J. MacKnight, *J. Polym. Sci., Polym. Phys. Ed.*, **8**, 727 (1970).
27. S. Yano, H. Yamamoto, K. Tadano, Y. Yamamoto, and E. Hirasawa, *Polymer*, **28**, 1965 (1987).
28. S. Yano, N. Nagao, M. Hattori, E. Hirasawa, and K. Tadano, *Macromolecules*, **25**, 368 (1992).
29. H. W. Straus, U. S. Patent 4 716 202 (1987).
30. Y. Li, G. Liu, and G. Yu, *J. Macromol. Sci.-Chem.*, **A26**, 405 (1989).
31. G. Yu, Y. Li, Y. Qu, and X. Li, *Macromolecules*, **42**, 6702 (1993).
32. E. Hirasawa, H. Hamazaki, K. Tadano, and S. Yano, *J. Appl. Polym. Sci.*, **42**, 621 (1991).
33. Abstracts of Papers, International Symposium on Organo-Metallic Chemistry and Catalysis, Hohhot, China, August, 1994, p. 17.
34. E. Hirasawa, K. Tadano, and S. Yano, *J. Polym. Sci., Polym. Phys. Ed.*, **29**, 753 (1991).
35. J. J. Fitzgerald, D. Kim, and R. A. Weiss, *J. Polym. Sci., Polym. Lett.*, **24**, 263 (1986).
36. S. Kutsumizu, N. Nagano, K. Tadano, H. Tachino, E. Hirasawa, and S. Yano, *Macromolecules*, **25**, 6829 (1992).
37. H. Tachino, H. Hara, E. Hirasawa, S. Kutsumizu, and S. Yano, *J. Appl. Polym. Sci.*, **55**, 131 (1995).
38. K. Tadano, E. Hirasawa, Y. Yamamoto, H. Yamamoto, and S. Yano, *Jpn. J. Appl. Phys.*, **26**, L1440 (1987).
39. K. Tadano, E. Hirasawa, H. Yamamoto, and S. Yano, *Macromolecules*, **22**, 226 (1989).
40. E. Hirasawa, Y. Yamamoto, K. Tadano, and S. Yano, *Macromolecules*, **22**, 2776 (1989).
41. N. Koizumi and S. Yano, *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 320 (1969).
42. D. J. Yarusso and S. L. Cooper, *Polymer*, **26**, 371 (1985).
43. S. Kutsumizu, unpublished results.
44. R. B. Moore, D. Bittencourt, M. Gauthier, C. E. Williams, and A. Eisenberg, *Macromolecules*, **24**, 1376 (1991).
45. D. G. Karraker, *J. Inorg. Nucl. Chem.*, **31**, 2815 (1969).
46. K. Han and H. L. Williams, *J. Appl. Polym. Sci.*, **38**, 73 (1989).
47. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed, John Wiley & Sons, New York, N. Y., 1978.
48. In EMAA, some weakly ordered structure would be formed via hydrogen bonding of carboxylic acid groups.
49. Y. Tsujita, K. Shibayama, A. Takizawa, T. Kinoshita, and I. Uematsu, *J. Appl. Polym. Sci.*, **33**, 1307 (1987).
50. K. Tadano, unpublished results.