Effect of Organic Amine Type on the Structure and Properties of the Complex Zn(II) Salts of Ethylene–Methacrylic Acid Copolymer with Organic Amines

EISAKU HIRASAWA,[1]* HIROHIDE HAMAZAKI,[1] KENJI TADANO,[2] and SHINICHI YANO[3]

[1]Technical Center, Du Pont-Mitsui Polychemicals Co. Ltd., Chigusa Kaigan 6, Ichihara, Chiba, 299-01 Japan, [2]Gifu College of Medical Technology, Ichihirage Seki, Gifu 501-32 Japan, and [3]Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido Gifu 501-11, Japan

SYNOPSIS

The complex Zn(II) salts of ethylene–methacrylic acid copolymer (EMAA) were synthesized by using various organic amines from monoamines to polyamines, from primary amines to tertiary amines, and from molecular amines to polymer amines. Thermal analyses by differential scanning calorimetry (DSC), and the measurement of stiffness, melt flow rate (MFR), and dielectric properties were employed for the complex salts. It was found that the valence, strength of base, rigidity and flexibility, and bulkiness of the organic amines affect the degree of crystalline order of the ionic crystallites, which governs the stiffness of the complex ion ionomers. The stiffness is higher for the complex salts which form the higher orderliness in the ionic aggregates. The organic amines with two or more primary aliphatic amino groups and higher boiling temperatures form more rigid ionic crystallites in the complex ion ionomers leading to the enhanced modulus. Monoamines or polyamines with amino groups attached to flexible chains such as polyether and polysiloxane scarcely develop ionic crystallites and preferentially solvate the amorphous region including ionic groups leading to the decreased modulus. These results provide us with the fundamental information to control the modulus of ionomers.

INTRODUCTION

Ionomers are defined as polymers containing hydrophobic backbone chains and a small amount of ionic groups attached on the backbones. It is generally accepted for ionomers that the polar salt groups form ionic aggregations such as multiplets and clusters in the hydrophobic polymer matrix.[1–5] The ionic aggregation results in a dramatic increase in mechanical properties such as modulus, tensile strength, impact resistance, and, in particular, stiffness (bending modulus).[6–9]

We have developed a new type of ethylene ionomers in which the ionic groups are the complex Zn(II) salt of ethylene methacrylic acid copolymer (EMAA) with organic amines, in order to obtain high-performance or functional ionomers. It was found that the complex Zn(II) salt with some specified diamines such as 1,3-bis(aminomethyl) cyclohexane (BAC) show enhanced modulus (stiffness) compared with conventional metal salt type ethylene ionomers while some complex Zn(II) salts which differed in amine species showed decreased modulus.[10,11] In our preceding studies[12,13] on the Zn(II) salts and the complex Zn(II) salts with BAC of EMAA, we obtained the following new and interesting results: The ionic clusters consist of ordered assemblies of ionic groups (ionic crystallites) in the solid state. The ionic clusters undergo an order–disorder transition of the first order at the transition temperature (T_i) near 330 K. The ionic clusters are in a disordered state inside above T_i. The ionic crystallites are not formed at T_i during the cooling from melt, but originate and develop gradually on aging at temperatures below T_i. The origin of the enhanced stiffness upon neutralization is the formation of the
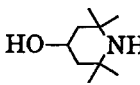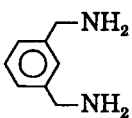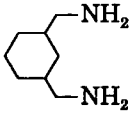
---
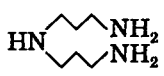
ionic crystallites. The stiffness of ionomer is closely connected with the degree of crystallinity of the ionic crystallites (heat of fusion of the ionic crystallites), and the increase in stiffness differs by the type of cation species.

Following the preceding works, this paper deals with the difference in the structure and properties of the complex Zn(II) salts of EMAA with various organic amines depending on the organic amine species. The modulus of the complex Zn(II) salts differed so much depending on the organic amine species, we wanted to know what makes the difference in the modulus so significant. To make clear the cause, thermal analyses by DSC, dynamic di-

Table I   Type of Amine Used in this Work

Type and Name of Amine	Abbr.	Molecular Structure	Molecular Weight	Melting Point (°C)	Boiling Point (°C)
Molecular amine: n-hexylamine	nHA	n-$C_6H_{13}NH_2$	101		128–130
Hexamethylene-tetramine	HMT		140	285	
2,2,6,6,*tetra*-methyl-4, *hydroxy*-piperizine	TAAM		157	100	
Ethylene-diamine	EDA	H_2N—$(CH_2)_2$—NH_2	60	8.5	117
Hexamethylene-diamine	HMDA	H_2N—$(CH_2)_6$—NH_2	116	42	190
Methaxylene-diamine	MXDA		136	14–15	247
1,3,bis(amino methyl) cyclohexane	BAC		142	–70	220
Piperazine		HN◯NH·$6H_2O$	194	44	125–130
Imino-*bis*-propylamine	IBPA		131		241
Methylimino-bispropylamine	MIBPA		145		234
Polymeric amine: Silicone diamine			1680	Liquid at R.T.	
Polyether-diamine	PEDA			Liquid at R.T.	
Polyamide oligomer	PAO		2000	215	

electric analyses, and measurements of stiffness (bending modulus) and melt flow rate (MFR) were employed for the complex salts.

EXPERIMENTAL

Materials and Sample Preparation

The complex Zn(II) salts of EMAA with organic amines are represented as EMAA-xZn-y · Amine: x is the degree of neutralization by Zn, y is the equivalent ratio of amino group of the amine to the carboxyl group of EMAA and Amine is the amine species represented by chemical name or its abbreviation. The EMAA is ACR-1560 of Du Pont-Mitsui Polychemicals, where methacrylic acid content is 5.4 mol %. The organic amines used in this work are listed in Table I. The organic amines: n-hexylamine, hexamethylene-tetramine, 2,2,6,6-tetramethyl-4-hydroxypiperizine, ethylenediamine, piperazine, iminobis-propylamine, methyliminobis-propylamine, are the products of Koei Chemicals Co. Methaxylenediamine and 1,3-bis(aminomethyl) cyclohexane are the products of Mitsubishi Gas Chemicals Co., silicone diamine is a product of Shinitsu Chemicals Co., polyether diamine is a product of Mitsui Petrochemical Industry, polyamide oligomer is a product of Toray Co., and hexamethylenediamine is a reagent grade of Wako Chemicals Co. The Zn(II) salt was prepared by means of a melt reaction of EMAA and zinc oxide in an extruder at 200–280°C. The complex Zn(II) salts with organic amines were prepared by a melt reaction of the mixture of the Zn(II) salts and organic amines in an extruder at 150–230°C. The pellet samples of the complex Zn(II) salts with organic amines were formed into 3 mm thick sheets by compression molding at 5 MPa and 160°C. These sheet samples were then cooled to room temperature for 5 min at 5 MPa and a cooling rate of about 30°C/min. The formation of the complex Zn(II) salts with organic amines were confirmed by IR spectra. As the complex Zn(II) salts with amine were formed, the absorption of 1583 cm^{-1}, which is attributable to the asymmetric stretching vibration of —COO$^-$ group in the zinc carboxylate, was replaced by absorption at 1510–1565 cm^{-1} (depending on the amine species), which indicates the formation of the complex Zn(II) salts with amines.

Measurements

Differential scanning calorimetric measurements (DSC) were conducted on 10 mg specimens at a heating/cooling rate of 10°C/min using a Du Pont DSC-990 calorimeter. The assignments of the endo/exothermic peaks of the DSC thermograms of ionomer, which were attributed to in our preceding works,[12,13] are shown in Figure 1. The melting temperatures of both polyethylene (T_m) and ionic crystallites (T_i) were determined as the temperature exhibiting the maximum of the endothermic peaks on DSC thermograms. The crystallization temperature of the polyethylene region (T_c) was obtained from the peak temperature of the exothermic peak in the cooling process. The heat of fusion for polyethylene crystallites (ΔH_m) and that for ionic crystallites (ΔH_i) were calculated from the peak area of the endothermic peak. Indium was used as a calibration standard. Here, the values of ΔH_m and ΔH_i refer to the melting enthalpy per 1 mg of sample. Measurements of DSC were made for the pellet samples at various aging durations in moisture barrier bags, which are shown in each table or figure.

Melt flow rate (MFR) was measured as weight of flow in grams per 10 min from a melt indexer at 190°C and under 2160g load.

Stiffness (bending modulus) was measured at 23°C for a slab (20 mm wide × 100 mm long × 3 mm thick) stamped out from compression-molded sheets, according to ASTM D-747. Stiffness was measured for the sheets aged for 9 days in moisture barrier bags at room temperature after molding because the stiffness of ionomer increases with physical aging.[13]
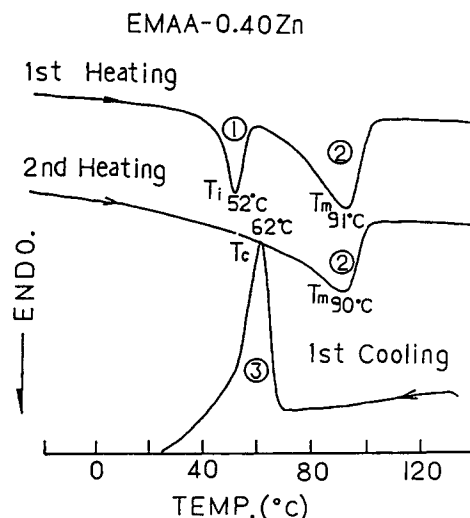
Figure 1 Typical DSC thermograms of ethylene ionomer. ①: endothermic peak caused by the melting of ionic crystallites; ②: endothermic peak caused by the melting of polyethylene crystallites; and ③: exothermic peak caused by the crystallization in polyethylene region.

Dielectric measurements were carried out by means of a multi-frequency LCR meter (Yokokawa-Hewlett Packard, Type 4274A) equipped with a personal computer in a temperature range of $-195°C$ to $100°C$ at 1 kHz of frequency.
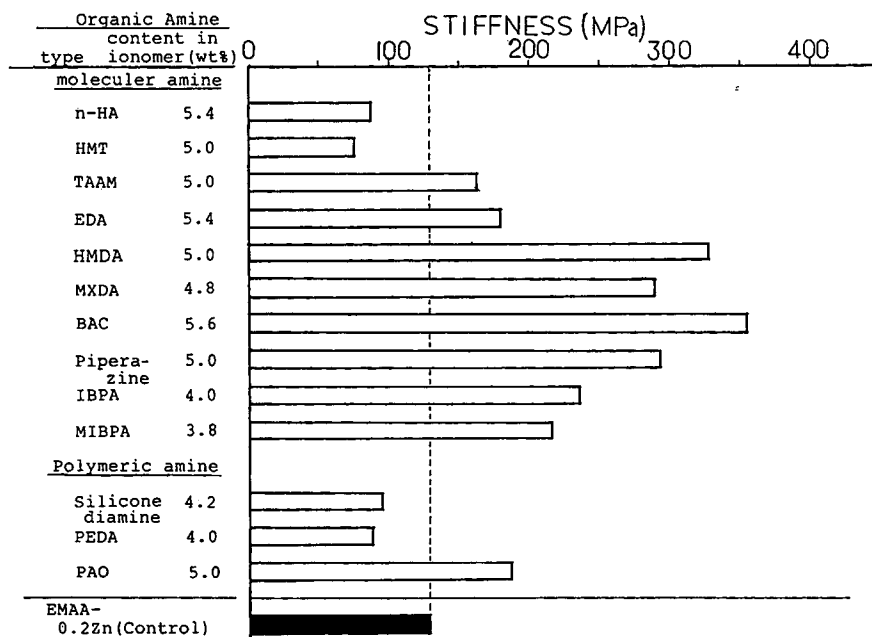
RESULTS AND DISCUSSION

Figure 2 illustrates a comparison of the stiffness in the complex Zn(II) salts of EMAA with various organic amines. Each complex salt consists of about 5 wt % of organic amine and 95 wt % of EMAA-0.2Zn (control ionomer). The stiffness of each complex salt differs greatly depending on the organic amine species. Some complex salts show the stiffness several times higher than that of the control ionomer—and some complex salts show decreased stiffness. Among molecular amines, the polyamines with primary or secondary aliphatic amino groups and higher boiling points show higher stiffness, but monoamines and tertiary amines do not. Among polymeric amines, crystalline amine (PAO) increases stiffness, while amorphous liquid amines (silicone diamine and polyether diamine) decrease stiffness.

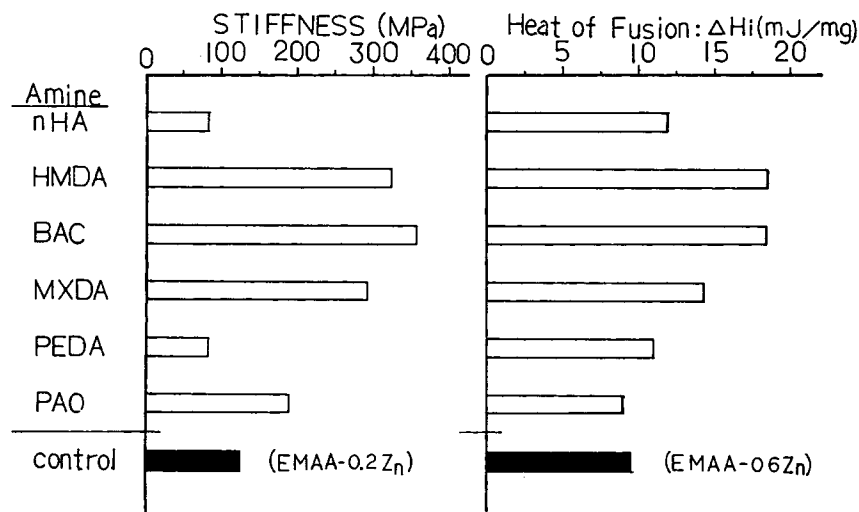Figure 3 shows the correlation between the stiffness and the heat of fusion of ionic crystallites (ΔH_i)

in the complex salts for each organic amine. The figure indicates that the stiffness of the complex Zn salts with amines except PAO strongly correlates with ΔH_i. The stiffness is higher for the amine species which show larger ΔH_i value in the complex Zn salt. This result clearly indicates that the stiffness of the complex Zn salts with organic amines is governed by the degree of crystalline order in the ionic crystallites, being consistent with the results of our preceding work.[13]

Based on the above results the amine species that make ionomers stiffer possess the following characteristics: (i) two or more amine groups in a molecule (polyamine), (ii) amine groups having primary or secondary aliphatic amines, (iii) a higher boiling point, and (iv) a rigid or bulky molecular structure (does not include flexible chain structure).

These imply that (i) crosslinking effect, (ii) strength of base, (iii) low molecular motion, and (iv) rigidness are the important factors of the organic amines for the higher stiffness in the complex ion ionomers. PAO is a monoamine and does not satisfy the item (i), however, its stiffness increases considerably. PAO is a rigid and crystalline amine with a high melting point (215°C) and forms a microphase-separated crystalline PAO phase in the complex Zn salts with PAO.[11] The crystalline PAO microdomains are bonded to ionic aggregates of zinc carboxylate through coordination ionic bonds. This

Figure 2 Comparison of the stiffness of the complex Zn(II) salts of EMAA with various organic amines. Each complex salt consist of about 5 wt % of organic amine and about 95 wt % of EMAA-0.2Zn.

STIFFNESS (MPa)   Heat of Fusion: ΔHi (mJ/mg)

0   100 200 300 400   0   5   10   15   20

Amine

nHA

HMDA

BAC

MXDA

PEDA

PAO

control   (EMAA-0.2Zn)   (EMAA-0.6Zn)

Figure 3   Correlation of the stiffness and the heat of fusion of ionic crystallites (ΔH_i) for each organic amine in the complex Zn salts. Each complex salt sample contains about 5 wt % of organic amine. Samples for stiffness measurement—EMAA-0.2Zn + 5 wt % amine. Samples for ΔHi measurement—EMAA-0.6Zn + 5 wt % amine.

rigid PAO crystallite and its interactions with ionic aggregates as crosslinking segment, are probably the cause of the increased stiffness of the complex salts.

Table II lists the change of MFR, DSC thermal data, and stiffness with amount of amines for the EMAA-0.2Zn-y · amine systems, where amine is BAC, nHA, PEDA, and PAO. In the EMAA-0.2Zn-y · PAO system, y means the weight fraction of PAO in the system. In the other systems y means the equivalent ratio of amino group to the carboxyl group of EMAA. The changes of MFR, T_i, ΔH_i, ΔH_m, T_c, and stiffness with amount of amines differ by species. MFR increases with increasing y in BAC, nHA, and PEDA, but decreases in PAO. T_i and ΔH_i increase in BAC, but do not change in nHA, PEDA, and PAO. T_c and ΔH_m decrease in BAC, but do not change in nHA, PEDA, and PAO. Stiffness increases in BAC and PAO but decreases in nHA and PEDA.

Figure 4(a) and (b) illustrate the plots of ΔH_i, ΔH_m and stiffness vs. y for EMAA-0.27Zn-y · BAC, EMAA-0.2Zn-y · nHA, and EMAA-0.2Zn-y · PEDA, respectively. In the EMAA-0.2Zn-y · BAC system, where stiffness increases with amount of amine, ΔH_i increases and ΔH_m decreases along with the increase in stiffness. For this complex salt, the increase of stiffness is caused by the development of ionic crystallites in ionic aggregates (the increase of ΔH_i), which decreases ΔH_m by the increased ionic interaction of BAC with zinc carboxylates.[13] In the EMAA-0.2Zn-y · nHA and EMAA-0.2Zn-y · PEDA systems, where stiffness decreases with amount of

amines, both H_i and ΔH_m are almost unchanged. This result suggests that the two organic amines do not develop ionic crystallites in the complex Zn salts. The values of ΔH_i for these two complex salts may be attributed to the ionic crystallites of zinc carboxylate. Both weak coordination bonds to Zn and flexible chains of nHA and PEDA probably restrict the development of the ionic crystallites for these two complex Zn salts. No remarkable changes in ΔH_m and T_c with amount of amines in these two complex Zn salts imply weakness in the coordination bond of nHA and PEDA to zinc carboxylate. In the solid state, the two organic amines would exist in the amorphous phase surrounding the ionic crystallites of the zinc salt, which reduces the crosslinking effect of the ionic crystallites of Zn salt by a plasticizing effect, leading to the decreased stiffness in the two complex salts.

Figure 5 represents the temperature dependence of dielectric loss (ϵ'') for the Zn(II) salt and the complex Zn(II) salts with various organic amines. In the Zn(II) salt, two relaxations are observed near 45°C (β') and −95°C (γ), which are ascribed to a micro-Brownian molecular motion of long segment related to a glass–rubber transition in the amorphous region including ionic groups and to a local molecular motion of ethylene chains in the amorphous region below T_g, respectively.[14,15] This implies that no distinct microphase separation of ionic aggregate are formed in the Zn(II) salt. The addition of BAC to the Zn(II) salt changes the dielectric properties drastically. Though the γ remains at the same tem-

Table II   MFR, DSC Thermal Data, and Stiffness of the Complex Zn Salt of EMAA With Various Organic Amines

| Sample	MFR (dg/min)	T_i (°C)	ΔH_i (mJ/mg)	T_m (°C)	ΔH_m (mJ/mg)	T_c (°C)	Stiffness (MPa)
		DSC Thermal Data					
	(190°C)						
[a]EMAA-0.2Zn	14	44	5.0	91	60	64	124
[a]EMAA-0.2Zn							
−0.16BAC	12	47	8.7	91	52		245
−0.40BAC	16	48	9.3	90	45	55	379
−0.97BAC	22	54	13.5	90	26	44	407
−1.21BAC	32	53	12.9	89	21	44	378
[b]EMAA-0.2Zn	14	51	12.6	92	60	64	124
[b]EMAA-0.2Zn							
−0.14nHA	30	53	14.5	92	56	64	110
−0.52nHA	48	53	13.9	92	59	63	75
−0.94nHA	53	53	13.8	93	52	60	62
[b]EMAA-0.2Zn							
−0.14PEDA	24	52	14.1	92	59	65	89
−0.34PEDA	37	53	13.6	92	55	65	60
−0.52PEDA	52	52	11.8	92	56	65	43
	(230°C)						
[b]EMAA-0.2Zn	81	51	12.6	92	60	64	124
[b]EMAA-0.2Zn							
−0.05PAO	35	52	14.4	91	58	65	186
−0.10PAO	15	55	13.8	92	57	63	212
−0.15PAO	9.6	54	13.5	91	52	67	234

[a] DSC thermal data were measured at 9 days of aging after molding.

[b] DSC thermal data were measured at 2–3 months of aging after molding.

perature, the β' relaxation is replaced by two new relaxations: α relaxation near 75°C and β relaxation near 0°C. The α peak, which is related to a glass–rubber transition of microphase-separated ionic clusters,[16,17] is much bigger and shifts to a higher temperature compared with the β' peak of the Zn(II) salt. The β peak is assigned to a relaxation in the amorphous branched polyethylene phase from which most of the ionic materials have been excluded.[16] These findings indicate that the addition of BAC to the Zn(II) salt promotes the development and the microphase-separation of ionic clusters.[17] On the other hand, the additions of nHA, PEDA, and PAO to the Zn(II) salt only make the β' peak bigger. This suggests that these amines neither develop the microphase separation of ionic clusters nor promote the formation of ionic crystallites in ionic aggregates.

Consequently, the difference in stiffness of the complex Zn(II) salts with organic amines comes from differences in both the structure of ionic aggregates and the crystalline order of the ionic crystallites, depending on the type of amine species.
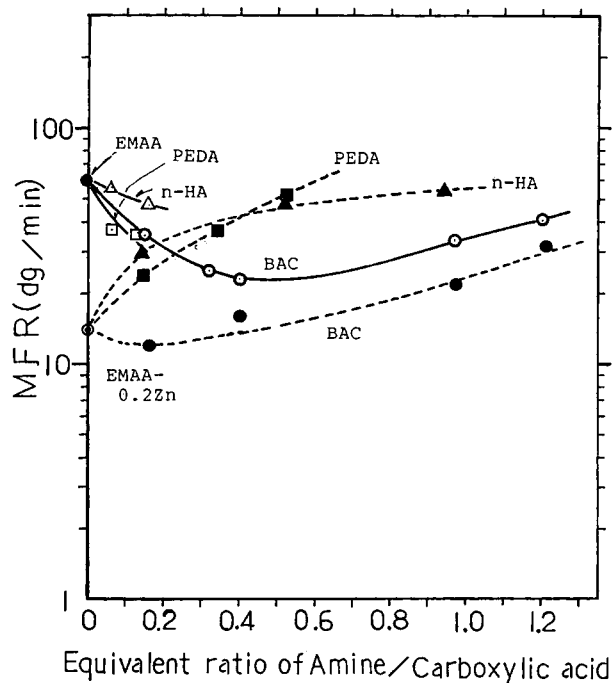
Figure 6 shows the change of MFR with amount of amines in EMAA-y · amine systems (ammonium salt) and EMAA-0.2Zn-y · amine systems (complex salts). In the EMAA-y · amine systems, MFR decreases with increasing amount of amine (degree of neutralization by amines) at low amine contents for all species. This means that all amines in the figure act as cations and increase melt viscosity by ionic interactions. However, MFR increases with amine amount for the EMAA-0.2Zn-y · nHA and EMAA-0.2Zn-y · PEDA systems. This means that the ionic interactions in these two complex salt systems are weak at molten state (190°C) and nHA and PEDA prefer to act as a plasticizer. On the other hand, MFR decreases slightly at first then increases with BAC content for the EMAA-0.2Zn-y · BAC system. This indicates that the ionic interactions in the complex Zn(II) salt with BAC are higher than that in the complex Zn(II) salts with nHA and PEDA. The difference in the change of ΔH_m with amount of amine between Figure 4(a) and (b) supports the above interpretation.
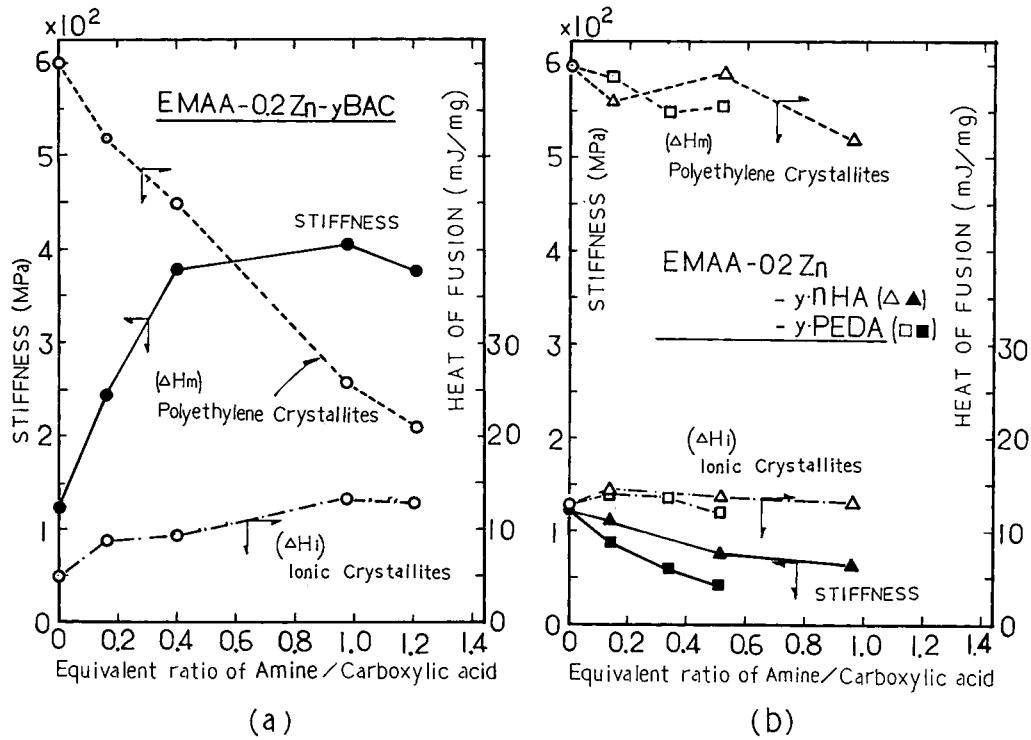
Figure 4   Stiffness and heat of fusion of ionic crystallites (ΔH_i) and heat of fusion of polyethylene crystallites (ΔH_m), vs. amount of amine. The values of ΔH_i and ΔH_m, were measured for the pellet samples aged for 2-3 months at room temperature in moisture barrier bags. (a)—EMAA-0.2Zn-y · BAC; and (b)—EMAA-0.2Zn-y· nHA, EMAA-0.2Zn-y· PEDA.
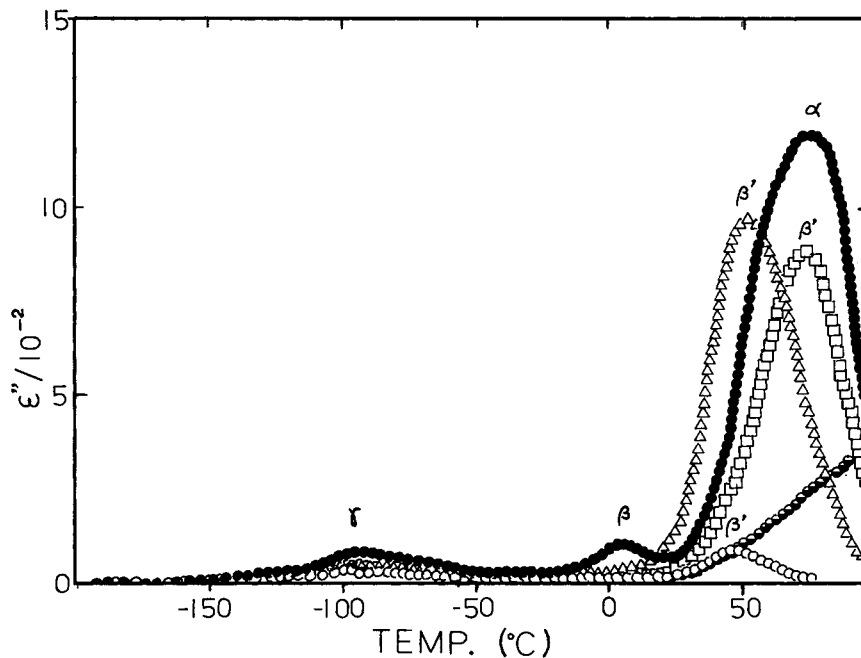
Figure 5   Temperature dependence of dielectric loss ϵ'' at 1 kHz for EMAA-0.2Zn (O); EMAA-0.2Zn-0.40BAC (●); EMAA-0.4Zn-0.23nHA (□); EMAA-0.2Zn-0.52PEDA (△); and EMAA-0.2Zn-0.10PAO (◒).

Figure 6 Change of MFR with amount of amine for various organic amines. EMAA-y·amine ($\triangle$, $\bigcirc$, $\square$); EMAA-0.2Zn-y·amine ($\blacktriangle$, $\bullet$, $\blacksquare$).
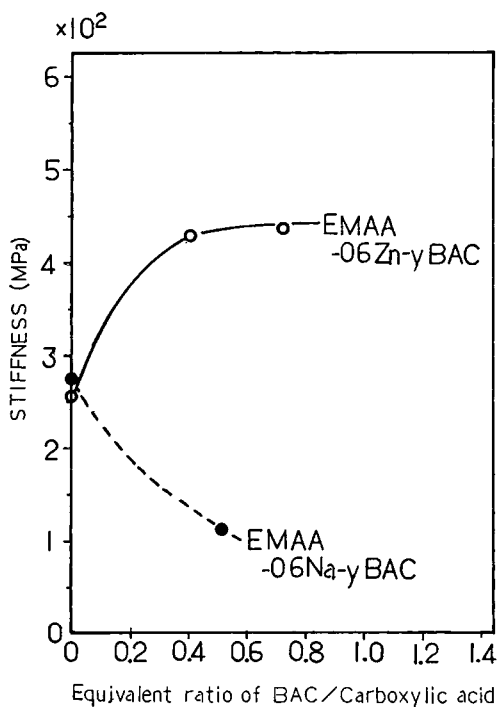
Figure 7 Change of stiffness with BAC in EMAA between EMAA-0.6Zn-y·BAC and EMAA-0.6Na-y·BAC.

Figure 7 shows the change of stiffness by addition of BAC in EMAA-0.6Zn-y·BAC and EMAA-0.6Na-y·BAC. Stiffness increases drastically for the Zn

salt, but drastically decreases inversely for the Na salt. Since the Na salt does not form complex salt with amine, BAC acts as a plasticizer in the EMAA-0.6Na-y·BAC. Bleeding of BAC was observed on the surface of the EMAA-0.6Na-y·BAC sheet, which supports the above explanation.

In conclusion, the valence (number of amino groups), strength of base, rigidity and flexibility, and bulkiness of the organic amines affect the structure of ionic aggregation and the degree of crystalline order of the ionic crystallites in the complex Zn (II) salts, governing the stiffness of the complex ionomers. These results provide us with the fundamental information to control the modulus of ionomers.

REFERENCES

1. *Ionic Polymer*, L. Holliday, Ed., Applied Science, London, 1975.
2. *Ion-Containing Polymers, Polymer Physics*, A. Eisenberg and M. King, Eds., Academic, New York, 1977, Vol. 2.
3. W. J. Macknight and T. R. Earnest, *J. Polym. Sci. Macromol. Rev.*, **16**, 41 (1981).
4. R. Longworth, *Development in Ionic Polymers—1*, D. Wilson and H. Proser, Eds., Applied Science, London, 1983.
5. *Structure and Properties of Ionomers*, M. Pineri and E. Eisenberg Eds., NATO ASI series, Reidel, Dordrecht, 1987.
6. R. W. Rees and D. J. Vaugham, *ACS Polym. Preprints*, **6**, 287 (1965).
7. R. W. Rees and D. J. Vaugham, *ACS Polym. Preprints*, **6**, 296 (1965).
8. U. S. Pat. 3,264,272 (1963) (to E. I. DuPont Co. Inc.).
9. S. Bonner and E. F. Bonner, *Macromolecules*, **1**, 510 (1968).
10. Jpn. Pat. Tokkaisho 61-9403, Tokkaisho 61-281154, 1473952 (Registered), Tokkaisho 62-22481, to DuPont-Mitsui Polychemicals Co. Ltd.
11. E. Hirasawa and H. Hamazaki, *J. Soc. of Rheology, Jpn.*, **14**, 113 (1986).
12. K. Tadano, E. Hirasawa, H. Yamamoto, and S. Yano, *Macromolecules*, **22**, 226 (1989).
13. E. Hirasawa, Y. Yamamoto, K. Tadano, and S. Yano, *Macromolecules*, **22**, 2276 (1989).
14. B. E. Read, E. A. Carter, T. M. Connor, and W. J. Macknight, *Br. Polym. J.*, **1**, 123 (1969).
15. W. J. Macknight and F. A. Emerson, *Dielectric Properties of Polymers*, F. E. Karaz, Ed., Plenum, New York, 1972, p 237.
16. P. J. Phillipes and W. J. Macknight, *J. Polym. Sci. Pt. A-2*, **8**, 727 (1970).
17. S. Yano, H. Yamamoto, K. Tadano, Y. Yamamoto, and E. Hirasawa, *Polymer*, **28**, 1965 (1987).