Dielectric properties of complex salts of Zn(II) salts of ethylene–methacrylic acid copolymer with 1,3-bisaminomethylcyclohexane

Shinichi Yano and Hitoshi Yamamoto
Department of Synthetic Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11, Japan

Kenji Tadano
Gifu College of Medical Technology, Ichihiraga, Seki, Gifu 501-32, Japan

Yasufumi Yamamoto and Eisaku Hirasawa
Research and Technical Service Laboratory, Du Pont-Mitsui Polychemicals Co. Ltd, Chikusa Kaigan 6, Ichihara, Chiba 299-01, Japan

(*Received 6 January 1987; revised 18 February 1987; accepted 5 March 1987*)

Dielectric relaxations in complex salts of Zn(II) salts of ethylene–methacrylic acid copolymer (E-MAA), MAA content 5.4 mol%, with 1,3-bisaminomethylcyclohexane (BAC) were studied in detail. In E-MAA and the Zn(II) salts, β' and γ relaxations were observed around 320 and 190 K at 1 kHz, which are attributed to micro-Brownian molecular motion of long segments and local molecular motion of short segments. When BAC is added to the two polymers, the β' relaxation was replaced by α and β relaxations. The α and β relaxations were related to a glass–rubber transition of ionic clusters and to molecular motion of isolated salts and carboxylic acid not incorporated into the ionic clusters, respectively. From the above results, it was concluded that BAC strongly promotes the formation of ionic clusters.

(Keywords: complex salts; zinc ionomer; 1,3-bisaminomethylcyclohexane; dielectric relaxation; ionic clusters)

INTRODUCTION

Ionomers are polymers that are functionalized with ionic groups attached to polymeric backbones, and so the ionic groups exert a profound influence on the physical properties of the polymers. Our knowledge of the structure and properties and of the applications of ionomers has been advanced with the development of various ion-containing polymers[1–4]. On this standpoint, the recently revived interest in ionomers is due to the exploitation of new backbone polymers (for example, Nafion) and of ionomers neutralized by various metals (for example, transition metals such as Cu, Mn and Fe)[4]. However, to our knowledge, little attention has been paid to ionomers neutralized by organic amines.

Organic amine derivatives can be counterions to form ionomers of various characters, since they can form different quaternary organic amine salts with ionomers. The properties of organic amines, themselves (for example, valence and strength of base, polarizability, bulkiness and flexibility), depend on chemical structure. Therefore, we can design a characteristic ionomer by choosing an appropriate amine as the counterion. Furthermore, this study should be one way to obtain more detailed and sometimes new information on the structure and properties of ionomers. Very recently we reported preliminary dielectric and small-angle X-ray scattering (SAXS) work on several complex salts of Zn(II) salts of ethylene–methacrylic acid copolymer (E-MAA) with 1,3-bisaminomethylcyclohexane, $H_2N–CH_2$–cyclohexyl–$CH_2–NH_2$ (*meta*) (BAC)[5].

This paper reports more detailed work on the structure and molecular motion of complex salts of the Zn(II) salts of E-MAA with BAC by dielectric measurements. The mechanism of formation of ionic clusters by BAC is discussed.

EXPERIMENTAL

The samples used here are listed in *Table 1*. The E-MAA is ACR-1560 of Du Pont-Mitsui Polychemicals Co. Ltd, the MAA content of which is 5.4 mol%. The Zn(II) and BAC salts were prepared by a melt reaction of E-MAA and zinc oxide/BAC in an extruder at 410–490 K. The pellet samples obtained were re-formed into sheets by compression moulding at about 430 K, and cooled rapidly to room temperature by circulating cold water outside of the sheet container. The complex salts of Zn(II) salts with BAC were prepared by the melt reaction of a mixture of zinc ionomer and BAC by the same procedure as described above. The thickness of all sheets was about 0.5 mm. The melting point T_m and the heat of fusion were measured by a differential scanning calorimeter (Du Pont, type DSC-990) at a heating/cooling rate of 10 K min^{-1}. The degrees of crystallinity were estimated

0032-3861/87/111965-06$03.00

Table 1 List of samples

Samples[a]	Degree of neutralization by Zn (%)	Equivalent ratio of BAC to carboxylic acid	Melting point, T_m (K)	Degree of crystallinity X_c	*MFR*[c] (dg min^{-1})	Size of ionic clusters[b]	
						Cluster radius (Å)	Short-range order distance (Å)
E-MAA	0	0	364	0.266	60	5.8	35
0.04BAC	0	0.04	364	0.260	51		
0.08BAC	0	0.08	364	0.255	45		
0.16BAC	0	0.16	365	0.244	35		
0.24BAC	0	0.24	365	0.234	29		
0.32BAC	0	0.32	365	0.224	25		
0.40BAC	0	0.40	366	0.215	23		
0.87BAC	0	0.87	363	0.070		6.2	31
0.97BAC	0	0.97	364	0.076	34		
1.21BAC	0	1.21	364	0.079	41		
0.20Zn	20	0	366	0.246	14	5.4	36
0.20Zn–0.04BAC	20	0.04	365	0.238	13		
0.20Zn–0.08BAC	20	0.08	364	0.231	12		
0.20Zn–0.16BAC	20	0.16	365	0.218	12		
0.20Zn–0.24BAC	20	0.24	365	0.205	14		
0.20Zn–0.32BAC	20	0.32	364	0.193	15		
0.20Zn–0.40BAC	20	0.40	365	0.182	16	5.8	30
0.20Zn–0.73BAC	20	0.73	364	0.070		6.3	32
0.20Zn–0.97BAC	20	0.97	364	0.084	22		
0.20Zn–1.21BAC	20	1.21	363	0.069	32		
0.40Zn	40	0	365	0.217	3.1		
0.40Zn–0.04BAC	40	0.04	365	0.215	3.9		
0.40Zn–0.08BAC	40	0.08	365	0.189	4.4		
0.40Zn–0.16BAC	40	0.16	365	0.180	5.0		
0.40Zn–0.24BAC	40	0.24	365	0.176	5.4		
0.40Zn–0.32BAC	40	0.32	365	0.158	5.8		
0.40Zn–0.40BAC	40	0.40	365	0.147	6.2		
0.40Zn–0.97BAC	40	0.97	363	0.073	12		
0.40Zn–1.21BAC	40	1.21	363	0.059	16		
0.60Zn	60	0	363	0.205	0.7	4.7	31
0.60Zn–0.04BAC	60	0.04	363	0.190	1.0		
0.60Zn–0.08BAC	60	0.08	363	0.180	1.3		
0.60Zn–0.16BAC	60	0.16	364	0.160	1.5		
0.60Zn–0.24BAC	60	0.24	363	0.142	1.7		
0.60Zn–0.32BAC	60	0.32	364	0.121	1.9		
0.60Zn–0.40BAC	60	0.40	364	0.095	2.4	5.8	31
0.60Zn–0.97BAC	60	0.97	362	0.068	4.7		
0.60Zn–1.21BAC	60	1.21	363	0.068	7.3		

[a] E-MAA is ethylene–methacrylic acid copolymer (MAA content is 5.4 mol%). In *x*Zn–*y*BAC, *x* is degree of neutralization by Zn for MAA, and *y* is equivalent ratio to carboxylic acid, where BAC is divalent

[b] Ref. 5

[c] Melt flow rates under 2160 g load at 463 K

from the heat of fusion by assuming that the heat of fusion of polyethylene is 290.4 J g^{-1}. The melt flow rates (*MFR*) were obtained at 463 K and under 2160 g load. Sizes of ionic clusters were calculated from the small-angle X-ray scattering (SAXS) data according to the MacKnight–Taggart–Stein model, where the SAXS data were measured in a position sensitive proportional counter (PSPC) system using monochromatic Cu Kα radiation generated by a Rigaku Denki RU-200 generator[5].

Dielectric measurements were carried out with a Multi-Frequency LCR meter (Yokokawa-Hewlett Packard, type 4274A) equipped with a personal computer in a temperature range of 85 to 390 K at several frequencies between 100 Hz and 100 kHz. The details of the electrode system have been described previously[6].

RESULTS AND DISCUSSION

As is well known, E-MAA copolymers generally have two dielectric relaxations, β' and γ, which are ascribed to micro-Brownian molecular motion of long segments related to a glass–rubber transition and to local molecular motion of ethylene chains in the amorphous region below T_g, respectively[7,8]. For the present E-MAA, the β' and γ relaxations were seen near 315 and 182 K at 1 kHz, respectively.

Figure 1 shows the temperature dependence of dielectric loss ε'' for 40% neutralized zinc ionomer (0.40 Zn) at several frequencies. Two relaxations are observed near 328 and 196 K at 1 kHz. Change of the two relaxations with x, the degree of neutralization by Zn, is shown in *Figure 2*. Clearly, the two relaxations are similar to the β' and γ relaxations of E-MAA, which indicates that the two relaxations are attributable to β' and γ relaxations, respectively. In the β' relaxation, the peak gradually shifts to higher temperatures with increasing x and the peak height exhibits a maximum around $x = 0.40$. These phenomena have also been seen previously in Cu(II), Mn(II) and Ni(II) salts[9–11]. In E-MAA and their salts, the polar groups responsible for the β' relaxations

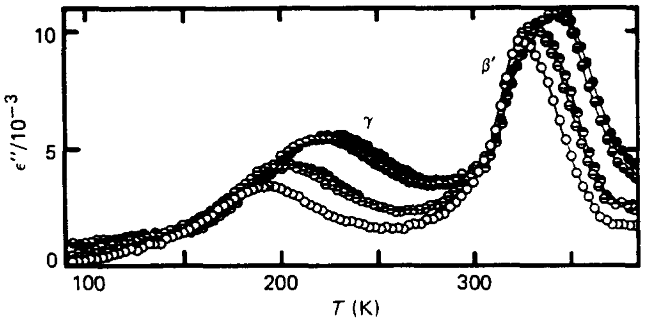

Figure 1 Temperature dependence of dielectric loss ε'' for 0.40Zn at several frequencies: ○, 1 kHz; ⊖, 5 kHz; ◓, 10 kHz; ◒, 50 kHz; ●, 100 kHz

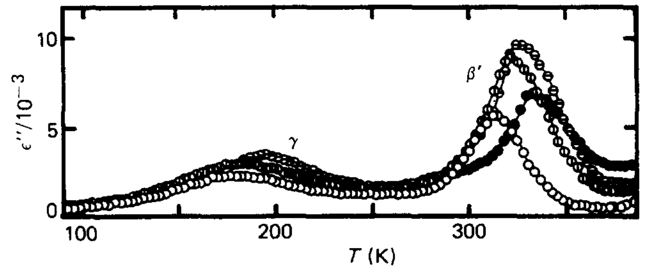

Figure 2 Temperature dependence of dielectric loss ε'' for xZn at 1 kHz: ○, $x=0$; ⦶, $x=0.20$; ⊖, $x=0.40$; ●, $x=0.60$

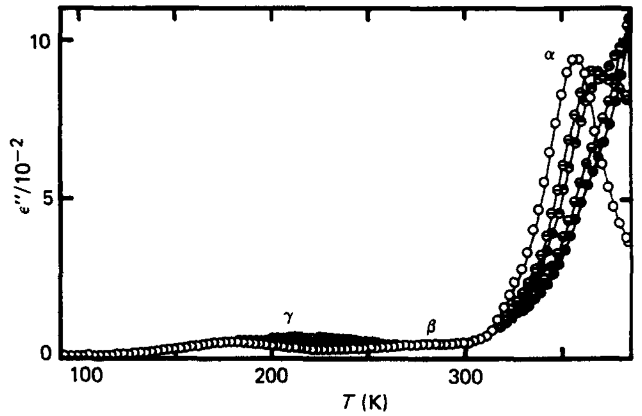

Figure 3 Temperature dependence of dielectric loss ε'' for 0.40Zn–0.40BAC at several frequencies: ○, 1 kHz; ⊖, 5 kHz; ◓, 10 kHz; ◒, 50 kHz; ●, 100 kHz

come only from isolated ionic groups, because the aggregated ionic groups may be dielectrically inactive. Therefore the decrease of peak height for the 60% neutralized zinc ionomer suggests the decrease of isolated ionic groups in the polymer matrix by the aggregation.

The addition of BAC to zinc ionomers changes the dielectric properties drastically as shown in *Figure 3*, which gives the temperature dependence of ε'' in 0.40 Zn–0.40 BAC. Although the γ relaxation remains at the same temperature near 183 K at 1 kHz, the β' relaxation is replaced by two new relaxations, an α relaxation near 359 K at 1 kHz and a β relaxation near 285 K. The α peak is much bigger and shifts to higher temperatures compared with the β' peak of the Zn(II) salts. Typical changes in the ε''–temperature plots with BAC content are shown in *Figures 4a* and *4b* for 0.20Zn–yBAC and *Figures 5a* and *5b* for 0.60Zn–yBAC. Apparently, the α and β

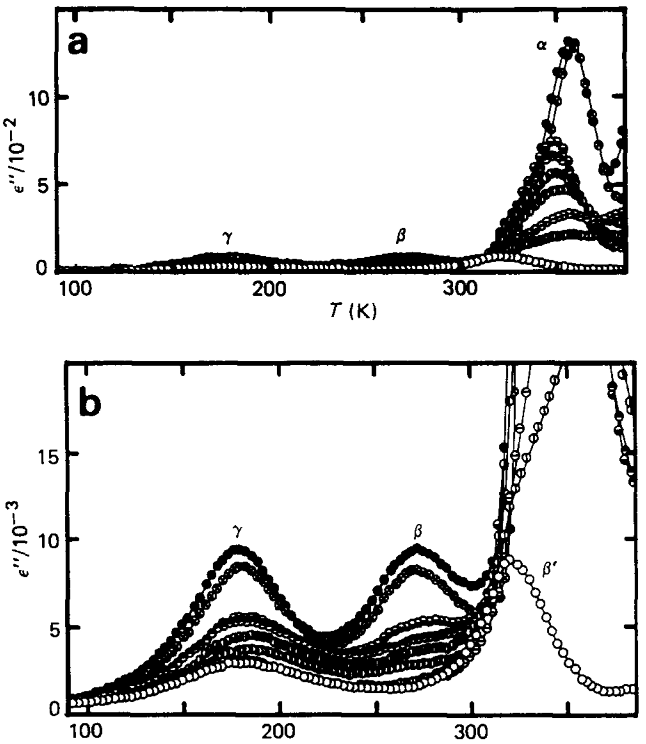

Figure 4 (a) and (b) Temperature dependence of dielectric loss ε'' for 0.20Zn–yBAC at 1 kHz: ○, $y=0$; ⦶, $y=0.04$; ⊖, $y=0.08$; ◐, $y=0.16$; ◑, $y=0.24$; ◓, $y=0.32$; ◒, $y=0.40$; ⊗, $y=0.97$; ●, $y=1.21$

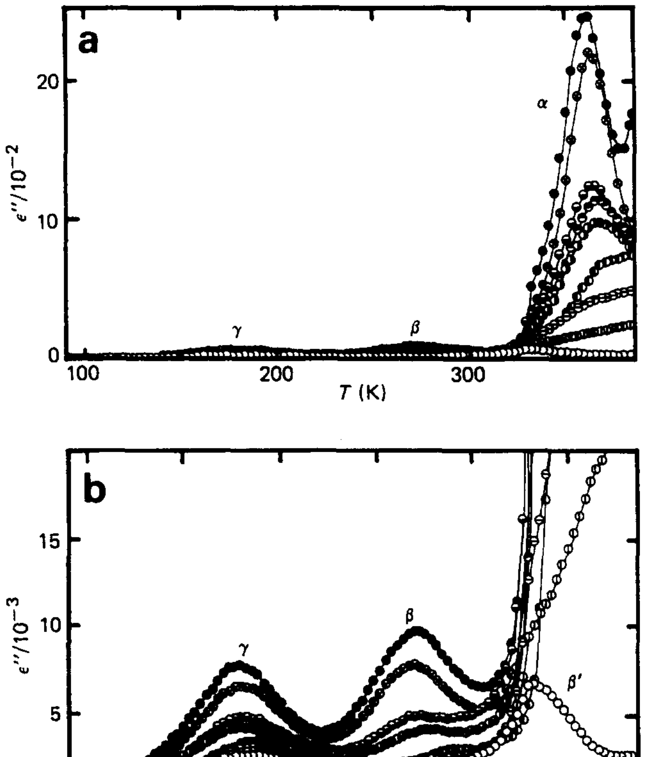

Figure 5 (a) and (b) Temperature dependence of dielectric loss ε'' for 0.60Zn–yBAC at 1 kHz: ○, $y=0$; ⦶, $y=0.04$; ⊖, $y=0.08$; ◐, $y=0.16$; ◑, $y=0.24$; ◓, $y=0.32$; ◒, $y=0.40$; $y=0.97$; ●, $y=1.21$

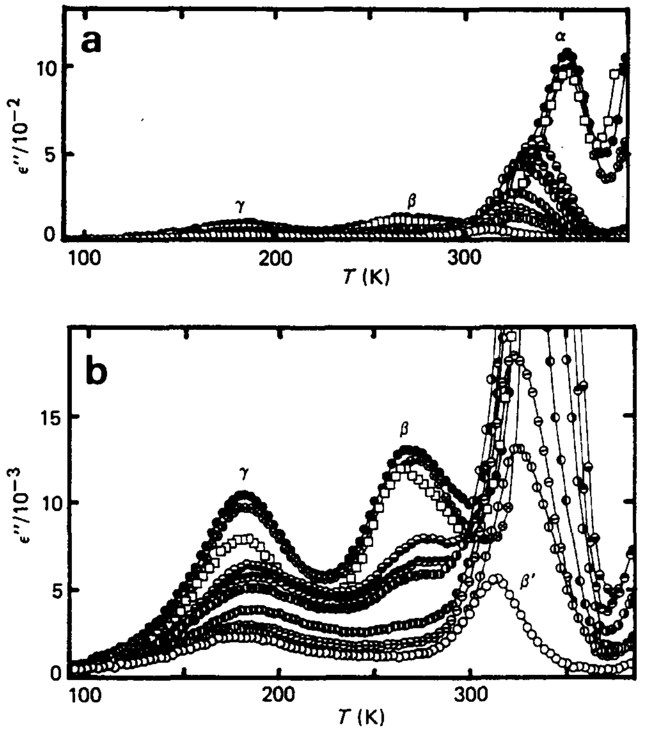

Figure 6 (a) and (b) Temperature dependence of dielectric loss ε'' for yBAC at 1 kHz: ○, $y=0$; ⦶, $y=0.04$; ⊖, $y=0.08$; ◐, $y=0.16$; ◑, $y=0.24$; ⬘, $y=0.32$; ⬙, $y=0.40$; □, $y=0.87$; ⊗, $y=0.97$; ●, $y=1.21$

relaxations are shown above 250 K and the β' relaxation seems to be veiled by the α relaxation. For low contents of BAC, the α peak is diffuse, but it is clearer and drastically bigger as more BAC is added. *Figures 6a* and *6b* show the temperature dependence of ε'' in all the BAC salts. For lower BAC contents below $y=0.40$, the α peak gradually shifts to higher temperatures and rapidly increases in height with increasing BAC content; and above $y=0.87$, the α peak is located around 355 K at 1 kHz.

Typical Arrhenius plots of logarithms of frequency, $\ln f$, *versus* reciprocal of relaxation temperature, $1/T_{max}$, for all the relaxations are shown in *Figures 7* and *8*. The relaxation parameters obtained from the plots are listed in *Table 2*. The α relaxation may be attributed to molecular motion related to a glass–rubber transition of ionic clusters, from the following facts. (1) The previous SAXS results indicated that the formation of ionic clusters is promoted by adding BAC[5]. (2) By adding BAC, the α relaxation appears at much higher temperatures than the β' relaxations of E-MAA and the Zn(II) salts. (3) The dielectric increments $\Delta\varepsilon$ are much larger than that for the β' relaxation (see *Figure 10*). This large value of $\Delta\varepsilon$ cannot be explained by the polar isolated salts, which are not incorporated in the ionic clusters, and so may come from the polar ionic groups of the ionic clusters themselves. (4) The activation enthalpies ΔH have large values of 180–330 kJ mol^{-1}. The β relaxation may be associated with molecular motion of isolated salts and carboxylic acid not incorporated into the ionic clusters, by analogy with the β relaxation of low-density polyethylene, which is due to molecular motion of branching segments in the amorphous region[12].

Figure 9 shows plots of relaxation temperature T_{max} *versus* BAC concentration for all the relaxations. In the β and γ relaxations, T_{max} remains constant, regardless of BAC content. In the α relaxation, T_{max} for the BAC salts gradually increases as y increases, but rather surprisingly T_{max} for the Zn(II)–BAC system suddenly jumps on adding a small amount of BAC. The dielectric increment $\Delta\varepsilon$ for all the relaxations was obtained from Cole–Cole plots. The values of $\Delta\varepsilon/(1-X_c)$ are plotted against BAC concentration in *Figure 10*. Here, X_c is the degree of crystallinity. When BAC is added, values of $\Delta\varepsilon$ for the α relaxation increase and reach a saturated value at the highest concentration of BAC. The increase of $\Delta\varepsilon$ on BAC addition is more pronounced when the Zn content is large. On the other hand, the values of $\Delta\varepsilon$ for β and γ relaxations increase very slightly on adding BAC, and the increase is smaller when the Zn content is large. These results suggest that BAC promotes the formation of ionic clusters. Our previous SAXS results[5] indicated that both ionic cluster radius R and concentration of ionic clusters increase with increasing BAC content. The formation of ionic clusters was negligible in the Zn(II) salts. The complex salts of Zn(II) salts with BAC may be more ionized than the Zn(II) salts, that is the RCOO–Zn(II) bonds may be mostly covalent, whereas the RCOO–Zn(BAC)$_n$ bond may be more ionic. We measured i.r. spectra of ionomers in order to clarify the structure of complex salts. In E-MAA, two i.r. absorption peaks were observed around 1700 and 1740 cm^{-1} which are attributed to the stretching vibrations of COOH groups. In the Zn(II) salts, the two peaks decreased in magnitude with increasing degree of neutralization by Zn, and one absorption peak near 1583 cm^{-1} appeared, which is

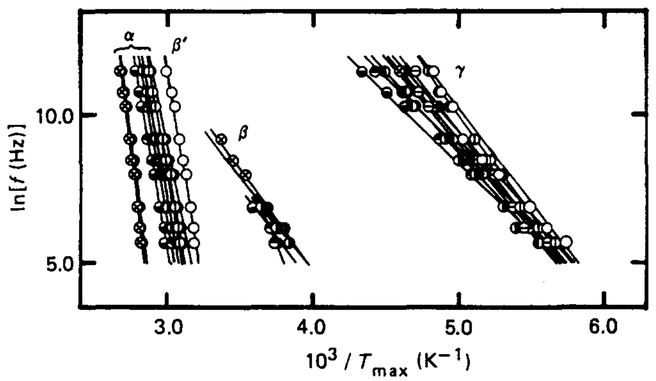

Figure 7 Arrhenius plots for all the relaxations in yBAC: ○, $y=0$; ⦶, $y=0.04$; ⊖, $y=0.08$; ◐, $y=0.16$; ◑, $y=0.24$; ⬘, $y=0.32$; ⬙, $y=0.40$; ⊗, $y=0.97$; ●, $y=1.21$

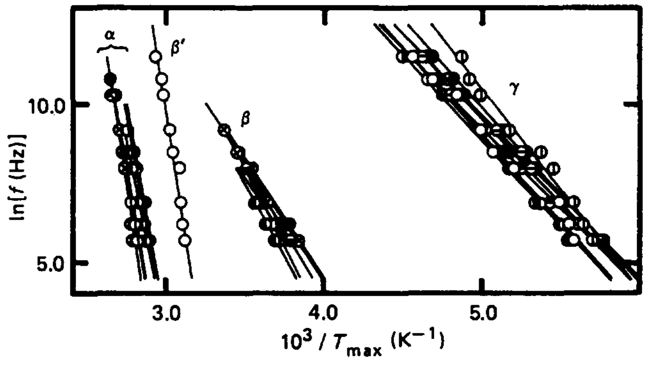

Figure 8 Arrhenius plots for all the relaxations in 0.20Zn-yBAC: ○, $y=0$; ⦶, $y=0.04$; ⊖, $y=0.08$; ◐, $y=0.16$; ◑, $y=0.24$; ⬘, $y=0.32$; ⬙, $y=0.40$; ⊗, $y=0.97$; ●, $y=1.21$

Table 2 Values of relaxation temperature T_{max} and activation enthalpies ΔH for four relaxations

	α relaxation		β' relaxation		β relaxation		γ relaxation	
Sample	T_{max} (K)	ΔH (kJ mol^{-1})	T_{max} (K)	ΔH (kJ mol^{-1})	T_{max} (K)	ΔH (kJ mol^{-1})	T_{max} (K)	ΔH (kJ mol^{-1})
E-MAA			315	251			182	51
0.04BAC	326	218					184	54
0.08BAC	324	197					186	50
0.16BAC	327	228					187	44
0.24BAC	331	225			273	53	188	46
0.32BAC	334	211			275	85	188	42
0.40BAC	338	241			278	53	186	38
0.97BAC	356	333			272	61	183	46
1.21BAC	354	317			270	57	182	45
0.20Zn			323	261			182	44
0.20Zn–0.04BAC	360	206					179	51
0.20Zn–0.08BAC	358	206					181	41
0.20Zn–0.16BAC	353	195			280	73	186	46
0.20Zn–0.24BAC	351	203			277	59	187	44
0.20Zn–0.32BAC	349	208			278	70	184	40
0.20Zn–0.40BAC	349	232			276	64	184	42
0.20Zn–0.97BAC	360	266			274	61	182	43
0.20Zn–1.21BAC	358	263			274	60	180	43
0.40Zn			328	232			196	48
0.40Zn–0.04BAC							184	43
0.40Zn–0.08BAC	364	210			273		181	41
0.40Zn–0.16BAC	374	182			270		185	38
0.40Zn–0.24BAC	363	210			282		183	41
0.40Zn–0.32BAC	360	234			280		181	43
0.40Zn–0.40BAC	359	224			285		183	42
0.40Zn–0.97BAC	363	214			278	62	182	45
0.40Zn–1.21BAC	363	256			282	61	180	44
0.60Zn			336	304			186	50
0.60Zn–0.04BAC							183	50
0.60Zn–0.08BAC					280	92	185	56
0.60Zn–0.16BAC					285	69	188	52
0.60Zn–0.24BAC	368	215			280	64	185	48
0.60Zn–0.32BAC	368	215			279	71	183	52
0.60Zn–0.40BAC	365	195			273	57	181	47
0.60Zn–0.97BAC	364	253			270	62	183	46
0.60Zn–1.21BAC	362	228			270	60	180	47

assigned to asymmetric stretching vibrations of COO groups in $(\text{–COO})_2\mathrm{Zn}$ groups[9,13]. In the Zn–BAC systems, the peak at 1583 cm^{-1} was replaced by one peak near 1564 cm^{-1}, which suggests the formation of complex quaternary amine salts with Zn. The values of *MFR* shown in *Table 1* may be associated with the number and nature of interchain crosslinks by the BAC salts/complex salts, since they were measured at 463 K, a temperature that may be high enough to ignore any crosslinking effect by the ionic clusters. In the Zn(II) salts, the values of *MFR* decrease with increasing content of Zn due to the crosslinking effect of the Zn(II) salts. In the 0.40Zn–BAC and 0.60Zn–BAC systems, the values of *MFR* increase with increasing BAC content. This result suggests that the quaternary BAC salts with Zn would act as a kind of plasticizer in these highly neutralized zinc ionomers. In the BAC and 0.20Zn–BAC systems, however, the *MFR* values decrease with increasing BAC content at lower concentrations of BAC due to the crosslinking effect, whereas they gradually increase at higher concentrations of BAC due to the plasticizing effect of BAC. The above *MFR* results may also suggest the formation of complex salts of Zn with BAC. In the course of preparation of various complex salts of zinc ionomer with organic amine, in fact, we found that organic amines decomposed very rapidly in the polymer matrix at 463 K when they did not react with zinc ionomers, and that the Zn–BAC ionomers were chemically stable at 463 K. The reaction of zinc ionomers with BAC can be tentatively written as follows:

$$(\mathrm{COO})_2\text{–}\mathrm{Zn} + n\mathrm{BAC} \rightarrow (\mathrm{COO})_2^{2-}[\mathrm{Zn(BAC)}_n]^{2+} \qquad (n = 1\text{–}4)$$

The solubility of more ionized salts in the polymer matrix may be lower than that of covalently bonded salts. This may lead to the formation of ionic clusters on adding BAC. Consequently, the ionized complex salts by BAC form ionic clusters in the polymer matrix. The $\Delta\varepsilon$ for the α relaxation rapidly increases with increasing BAC and the increase is larger at higher contents of Zn, since the amount of complex salts coordinated by BAC is larger in ionomers of higher Zn content. Conversely, the increase of $\Delta\varepsilon$ by BAC for the β and γ relaxations is somewhat weakened when the content of Zn is smaller, since the polar isolated salt groups responsible for the two relaxations may be decreased due to the more enhanced formation of ionic clusters by BAC.

Dielectric properties of several alkali-metal ionomers have been studied by several workers[11,14,15]. In various alkali-metal salts of E-MAA, Phillips and MacKnight[14] found α and β relaxations which do not exist in E-MAA itself at all. The α relaxation shifted to higher

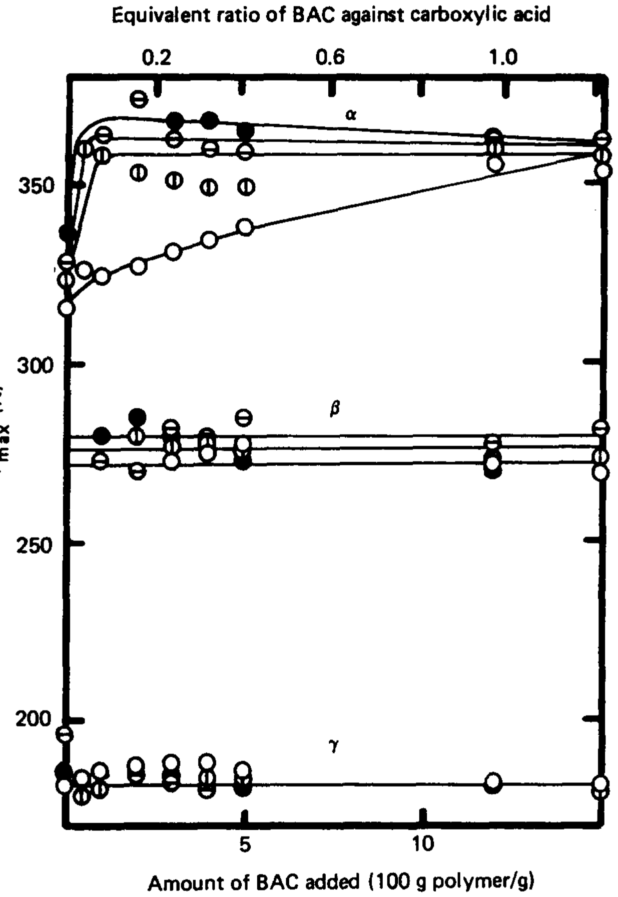

Figure 9 Plots of relaxation temperature T_{max} against BAC concentration: ○, $x=0$; ⦶, $x=0.20$; ⊖, $x=0.40$; ●, $x=0.60$

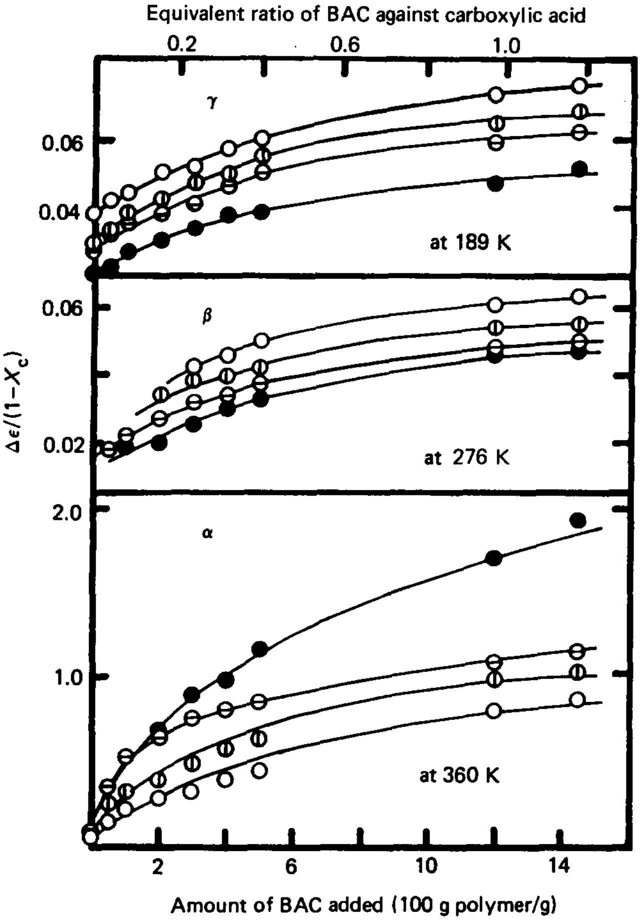

Figure 10 Plots of dielectric increment $\Delta\varepsilon/(1-X_c)$ against BAC concentration: ○, $x=0$; ⦶, $x=0.20$; ⊖, $x=0.40$; ●, $x=0.60$

temperatures above 370 K and increased in magnitude with increasing degree of neutralization. The activation enthalpies ΔH were 340–540 kJ mol^{-1}, larger than the ~210 kJ mol^{-1} of E-MAA. They identified the α relaxation to be related to a glass–rubber transition of ionic clusters.

In the Zn–BAC system, T_{max} is located between 349 and 374 K at 1 kHz, being lower than that of the alkali-metal salts. It is, however, noted that T_{max} for the BAC salts gradually increases on adding BAC and approaches T_{max} for the Zn–BAC systems at higher contents of BAC. These phenomena suggest that the value of T_{max} reflects the temperature at which the glass–rubber transition of ionic clusters begins to occur. The BAC salts might construct a structurally loose ionic cluster at low concentrations, and a more rigid one at higher concentrations. Previously, several workers[16] suggested from modulus measurements that some structure is formed in the ionic clusters. Very recently, we found from an e.s.r. study on the Mn(II) salts of ethylene–acrylic acid copolymers that Mn interacts closely with the other Mn in the ionic aggregates (the distance of the $(COO)_2Mn---Mn(COO)_2$ bond was estimated to be around 5 Å)[9,17]. These results suggest that the ionic clusters would be structural assemblies of ionic groups. It is a topic for further discussion to clarify how the ionic groups are constructed in the ionic clusters.

REFERENCES

1 Holiday, L. 'Ionic Polymers', Applied Science, London, 1975
2 Eisenberg, A. and King, M. 'Ion-Containing Polymers', Polymer Physics, Vol. 2, Academic Press, New York, 1977
3 Longworth, R. 'Developments in Ionic Polymers—1', (Eds. A. D. Wilson and H. J. Prosser), Applied Science, London, 1983, Ch. 3
4 Pineri, M. and Eisenberg, A. (Eds) 'Structure and Properties of Ionomers', NATO ASI Series, D. Reidel, Dordrecht, 1987
5 Yano, S., Tadano, K., Suigiura, T. and Hirasawa, E. *ibid.*, p. 481
6 Koizumi, N. and Yano, S. *Bull. Inst. Chem. Res., Kyoto Univ.* 1969, **47**, 320
7 Read, B. E., Carter, E. A., Connor, T. M. and MacKnight, W. J. *Br. Polym. J.* 1969, **1**, 123
8 MacKnight, W. J. and Emerson, F. A. 'Dielectric Properties of Polymers', (Ed. F. E. Karasz), Plenum Press, New York, 1972, p. 237
9 Yano, S., Yamashita, H., Matsushita, M., Aoki, K. and Yamauchi, J. *Colloid Polym. Sci.* 1981, **259**, 514
10 Pineri, M., Meyer, C., Levelut, A. M. and Lambert, M. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 115
11 Arai, K. and Eisenberg, A. *J. Macromol. Sci.-Phys.* 1980, **B17**, 803
12 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, New York, 1967, Ch. 10
13 Edward, D. A. and Hayward, R. N. *Can. J. Chem.* 1968, **46**, 3433
14 Phillips, P. J. and MacKnight, W. J. *J. Polym. Sci. (A-2)* 1970, **8**, 727
15 Hodge, I. M. and Eisenberg, A. *Macromolecules* 1978, **11**, 289
16 Rees, R. W. and Vaughan, D. J. *ACS Polym. Prepr.* 1965, **6**, 296; Bonotto, S. and Bonner, E. F. *Macromolecules* 1968, **1**, 510; Wilson, F. C., Longworth, R. and Vaughan, D. J. *ACS Polym. Prepr.* 1968, **9**, 505; Hirasawa, E. and Ishimoto, R. *J. Adhes. Soc., Jap.* 1983, **19**, 95
17 Yamauchi, J. and Yano, S. *Macromolecules* 1982, **15**, 210