Far-Infrared Study on the Zinc(II) Complex Salts of Ethylene–Methacrylic Acid Copolymer with 1,3-Bis(aminomethyl)cyclohexane

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Received December 19, 1990; Revised Manuscript Received June 17, 1991

ABSTRACT: Far-infrared spectra have been measured for ethylene–methacrylic acid copolymers partially neutralized with Zn(II) and 1,3-bis(aminomethyl)cyclohexane [1,3-$(H_2NCH_2)_2C_6H_{10}$] to clarify the structure and transition of the ionic clusters ($T_i \approx 60$ °C). It was found that the broad well-defined band near 250 cm^{-1}, which is attributable to Zn(II)–O vibrations within the ionic clusters, shifts to lower frequency with increasing temperature above T_i. This observation is satisfactorily explained by a structural transition of the ionic clusters, which was proposed in our previous publications.

Introduction

Ionomers are polymers having ionic side groups attached to hydrophobic organic backbones. The hydrophilic ionic groups frequently separate from the hydrophobic polymer matrix to form ionic aggregates.[1] The presence of ionic aggregates has been verified by small-angle X-ray scattering (SAXS), extended X-ray absorption fine structure (EXAFS), and electron spin resonance (ESR) analysis.[2–4] The formation of ionic aggregates strongly influences the polymer properties, and as a result extensive studies have been done by many investigators for various types of ionomers to clarify the formation and structure of ionic aggregates and their effects on polymer properties. Several structural models for the ionic aggregates have been proposed.[2–4] One widely accepted model is the multiplet–cluster model proposed by Eisenberg,[1] where "ionic multiplets" refers to ionic aggregates containing at most several ion pairs and the aggregates of the ionic multiplets are denoted as "ionic clusters". However, the colloidal size of the ionic aggregates has prevented the elucidation of their structure and nature in ionomers, despite much research by many workers.

To date, several far-infrared spectroscopic studies of ionomers have been reported.[5–8] Far-infrared spectroscopy is a powerful technique for investigating the structure of ionic aggregates because cation vibrations are sensitive to the local environment around the cations. Risen and coworkers[5,7,8] observed the low-frequency bands, which are cation-dependent, in the region of 100–300 cm^{-1} for various ionomers and assigned them to the cation vibrations incorporated in the ionic aggregates. In this paper we have studied the far-infrared spectra of ethylene–methacrylic acid copolymers (EMAA) partially neutralized with Zn(II) and/or an organic amine, 1,3-bis(aminomethyl)cyclohexane [1,3-$(NH_2CH_2)_2C_6H_{10}$] (BAC). We abbreviate the present ionomer system as EMAA–xZn–yBAC, where x is the degree of neutralization by Zn(II) and y is the molar equivalent ratio of BAC to carboxylic acid (where BAC is divalent). Our recent studies[9] on this ionomer system by differential scanning calorimetric (DSC) and thermal expansion techniques revealed the existence of a first-order transition near 60 °C (T_i), below the melting point of the polyethylene crystallites ($T_m \approx 90$ °C). In conjunction with the dielectric,[10] conductivity,[11] and mechanical[12] results, we intepreted this transition as an order–disorder transition within the ionic cluster; the inside of the ionic cluster is in an ordered state at room temperature and is transformed into a disordered one above T_i. The purpose of this study is to clarify the structural changes in ionic groups incorporated in the ionic clusters upon the transition by investigating spectral changes at T_i.

Experimental Section

EMAA is ACR-1560 of Du Pont–Mitsui Polychemicals Co. Ltd., the MAA content of which is 5.4 mol %. EMAA–xZn–yBAC copolymers were prepared by the melt reaction procedure described previously.[12] The formation of the Zn(II) salts and their BAC complexes was confirmed by the infrared spectra.[10] As EMAA was neutralized with a Zn(II) cation, the hydrogen-bonded carbonyl stretching band at 1700 cm^{-1} in EMAA was suppressed, and the 1583-cm^{-1} band, which is attributable to the asymmetric stretching vibrations of the COO^- groups in the Zn(II) carboxylates,[13,14] appeared and increased in intensity. With addition of BAC to the Zn(II) salts this asymmetric stretching band shifted from 1583 cm^{-1} to 1564 cm^{-1}, which indicates a coordination of BAC to the Zn(II) ion.

The far-infrared spectra were measured for 0.05–0.2-mm-thick films of the EMAA–Zn–BAC ionomers with a Bruker IFS-113V spectrometer. Each trace represents the average of 256 scans at 2-cm^{-1} resolution. Spectra at elevated temperatures were obtained by using a Hitachi high-temperature cell modified for our spectrometer. Temperatures were measured with an alumel–chromel thermocouple.

Results and Discussion

Figure 1 shows the far-infrared spectra at room temperature in the region 50–700 cm^{-1} for (a) EMAA, (b) EMAA–0.6Zn, (c) EMAA–0.6Zn–0.4BAC, and (d) EMAA–0.6Zn–0.97BAC. Table I summarizes the frequencies of the bands observed and their assignments based on those of Tsatsas et al.[5] Our spectral results of EMAA are entirely consistent with those of Tsatsas et al.[5]

Spectral changes due to introduction of Zn(II) and/or BAC to EMAA are evident; the most prominent feature is that the broad well-defined bands which are absent in the spectra of the base polymer (EMAA) (Figure 1a) are

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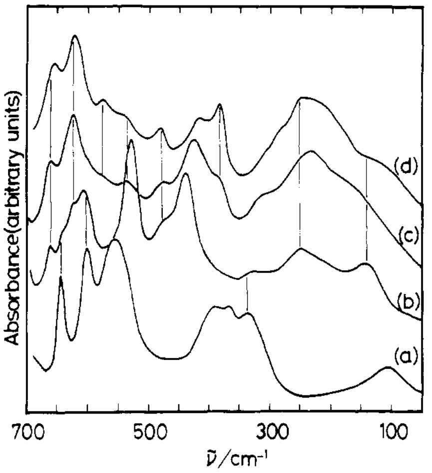

Figure 1. Far-infrared spectra at room temperature for (a) EMAA, (b) EMAA–0.6Zn, (c) EMAA–0.6Zn–0.4BAC, and (d) EMAA–0.6Zn–0.97BAC.

Table I
Observed IR Frequencies (cm^{-1}) of the EMAA–Zn–BAC Ionomers

EMAA	EMMA–0.6Zn	EMMA–0.6Zn–0.4BAC	EMAA–0.6Zn–0.97BAC	assignment
	660	659	654	COO wagging
642	643			
	623	623	620	CCC bending
600	606			
		sh[a]	574	CCC wagging
554				
	529	535	539	CCC skeleton vib (?)
	479	475	481	
	439	424	416	
390				CCC bending
366				CCC twisting
333	328	315		$(COOH)_2$ out-of-plane def
		383	382	?
	248			Zn–O in multiplets
		233	248	Zn–O in clusters
	140	160 (sh)	120 (sh)	Zn–O (isolated)

[a] sh = shoulder.

observed in the region below 300 cm^{-1} for EMAA–0.6Zn, EMAA–0.6Zn–0.4BAC, and EMAA–0.6Zn–0.97BAC (Figure 1b–d). The far-infrared spectroscopic study on $Zn(CH_3COO)_2$[13] indicates that the bands attributable to the COO^- vibrations appear in the region above 600 cm^{-1} while those related to Zn(II)–O vibrations are observed in the region below 300 cm^{-1}. Therefore, the bands below 300 cm^{-1} observed in the Zn(II) salt and its BAC complexes can be assigned to the Zn(II)–O vibrations. The large bandwidth of the Zn(II)–O bands (their values are ca. 100 cm^{-1}) suggests that the Zn(II) cations are present in various environments. On the other hand, the previous dielectric[12] and thermal expansion[9] studies indicated that ionic clusters are hardly formed in EMAA and EMAA–0.6Zn but are formed in EMAA–0.6Zn–*y*BAC. Consequently, in EMAA–0.6Zn–0.4BAC and EMAA–0.6Zn–0.97BAC, the bands below 300 cm^{-1} are mainly attributable to Zn(II)–O vibrations within the ionic clusters, while in EMAA–0.6Zn they may be ascribed to those associated with ionic multiplets and/or isolated ion pairs (i.e. $Zn(II)(COO^-)_2$).

These assignments are also supported by the following facts. EMAA–0.6Zn contains two well-defined bands near 250 and 140 cm^{-1}. The addition of BAC to EMAA–0.6Zn increases both the intensity and the bandwith of the 250-cm^{-1} band. Inferring from the fact that the addition of BAC to EMAA–0.6Zn promotes the formation and development of the ionic clusters,[9,12] the 250-cm^{-1} band can be assigned to the cluster mode. However, the 250-cm^{-1} band for EMAA–0.6Zn should be assigned not to the cluster mode but to the vibrational mode of less clustering aggregates, i.e., ionic multiplets, since EMAA–0.6Zn hardly forms ionic clusters.[9,12] On the other hand, the 140-cm^{-1} band is probably due to vibrations of cations not incorporated in the ionic aggregates because it is present and dominant in EMAA–0.6Zn but it is obscured in EMAA–0.6Zn–0.4BAC and EMAA–0.6Zn–0.97BAC in which most of the COO^- groups are incorporated in the ionic clusters.[10] Our interpretation, however, disagrees with that of Rouse et al.[7]; among the three bands observed between 150 and 300 cm^{-1} in poly(styrene-*co*-methacrylic acid) ionomers, the lowest band near 170 cm^{-1} can be assigned to the cluster mode, the highest band near 250 cm^{-1} to the multiplet mode, and the middle of the three bands, which is observed near 220 cm^{-1} as a shoulder, to an internal mode of the polymer backbone. At present, it is uncertain whether this disagreement is due to the difference in the base polymers of both ionomer systems.

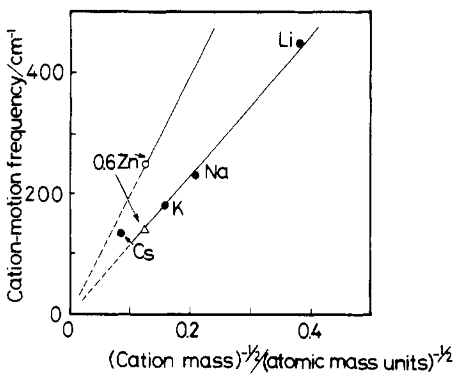

Figure 2. Plots of the cation vibration frequency vs (cation mass)$^{-1/2}$ for EMAA-Li, -Na, -K, -Cs, and -0.6Zn films. For EMAA–0.6Zn, the open circle denotes the 250-cm^{-1} band and the open triangle denotes the 140-cm^{-1} band. (●) data abstracted from ref 5.

Another piece of evidence for the cluster mode is obtained from the relationship of the vibrational frequency vs (cation mass)$^{-1/2}$. In poly(styrene-*co*-sulfonic acid) ionomers,[8] the plots of cation vibration frequency vs (cation mass)$^{-1/2}$ for both monovalent and divalent cations show linear relations, but the slope (which gives the force constant of a given vibrational mode) for the divalent ions is almost twice as large as that for the monovalent ions. In Figure 2 data points of the present EMAA ionomer (EMAA–0.6Zn) are plotted together with those of Tsatsas et al.[5] The slope for the 250-cm^{-1} band of EMAA–0.6Zn is nearly twice as large as that for the monovalent ions by Tsatsas et al.,[5] while the slope for the 140-cm^{-1} band is almost equal to it. Hence, considering that Zn(II) ion is a divalent cation, it is reasonable to assign the 250-cm^{-1} band of EMAA–0.6Zn–*y*BAC to the cluster mode and the 250-cm^{-1} band of EMAA–0.6Zn to the multiplet mode.

In the above identification of the cluster/multiplet modes, the formation of so-called acid salts should be considered in EMAA–0.6Zn, since this ionomer is the partially neutralized ionomer. However, the presence of the acid salts in EMAA–0.6Zn seems unlikely for the following two reasons: (1) The two types of the acid salts isolated have been reported in the alkali/alkaline earth metal acetate–acetic acid systems, but no acid salt has been found in the Zn(II) acetate–acetic acid system.[15] (2) Infrared spectral studies for the EMAA–Zn(II) ionomers by us[16] and Han et al.[17] have indicated that the 1583-cm^{-1} band, attributable to the COO^- asymmetric stretching vibrations, is invariant over the whole range of the degree of neutralization, including complete neutralization, which suggests that the carboxylate structure does not change in EMAA–Zn(II) ionomers under variations in the degree of neutralization. Therefore, the carboxylate structure in a partially neutralized Zn(II) ionomer is almost the same as that of the completely neutralized ionomer. Of course, the above assumption that the acid salts are not formed in EMAA–Zn(II) ionomers remains speculative and needs more detailed investigation.

We now focus our attention on the shift of the frequency of the Zn(II)–O band with addition of BAC; the peak position of the Zn(II)–O band shifts from 248 cm^{-1} in EMAA–0.6Zn to 233 cm^{-1} in EMAA–0.6Zn–0.4BAC to 248 cm^{-1} in EMAA–0.6Zn–0.97BAC, as seen in Figure 1. These shifts may reflect the coordination of BAC to $Zn(COO)_2$, which makes the Zn(II)–O bonds more ionic because the decrease in covalency of the bond should shift the frequency to lower values. This shift, therefore, supports our interpretation that the addition of BAC to EMAA–0.6Zn makes the Zn(II)–O bonds more ionic to promote formation of the ionic clusters in the EMAA–Zn–BAC system.[10,18] Of course, the broad band of Zn(II)–O vibrations indicates the presence of many Zn(II)–O modes corresponding to the aggregates of COO$^-$ groups such as ionic multiplets or clusters, and, strictly speaking, this shift of the peak position means that the number of COO$^-$ groups incorporated in the ionic clusters increases with addition of BAC to EMAA–0.6Zn. In addition, this band shifts from 233 cm^{-1} (EMAA–0.6Zn–0.4BAC) to 248 cm^{-1} (EMAA–0.6Zn–0.97BAC) with increase of the BAC content. This higher energy shift suggests that the ionic clusters become more rigid or, in other words, more clustering to form more ordered aggregates due to the completion of the coordination of one BAC to one $Zn(COO)_2$ site. In fact, the stiffness increases with increasing BAC content, y, and its increase levels off near $y = 1$.[12]

Effects of the formation of ionic clusters also appear in the COO$^-$ vibrational and CCC skeletal deformation modes. Although the correspondence of the vibrational modes in EMAA with those in the Zn(II) salt and its BAC complexes is not completely clear, the COO wagging mode (642 cm^{-1}) and CCC bending mode (600 cm^{-1}) in EMAA shift to ca. 660 and ca. 620 cm^{-1}, respectively, in the Zn(II) salt and its BAC complexes. These higher energy shifts seem to be related to a crosslinking effect of the ionic aggregates.

The temperature dependences of the far-infrared spectra of (a) EMAA, (b) EMAA–0.6Zn, (c) EMAA–0.6Zn–0.4BAC, and (d) EMAA–0.6Zn–0.97BAC are shown in Figure 3. Several features are noteworthy.

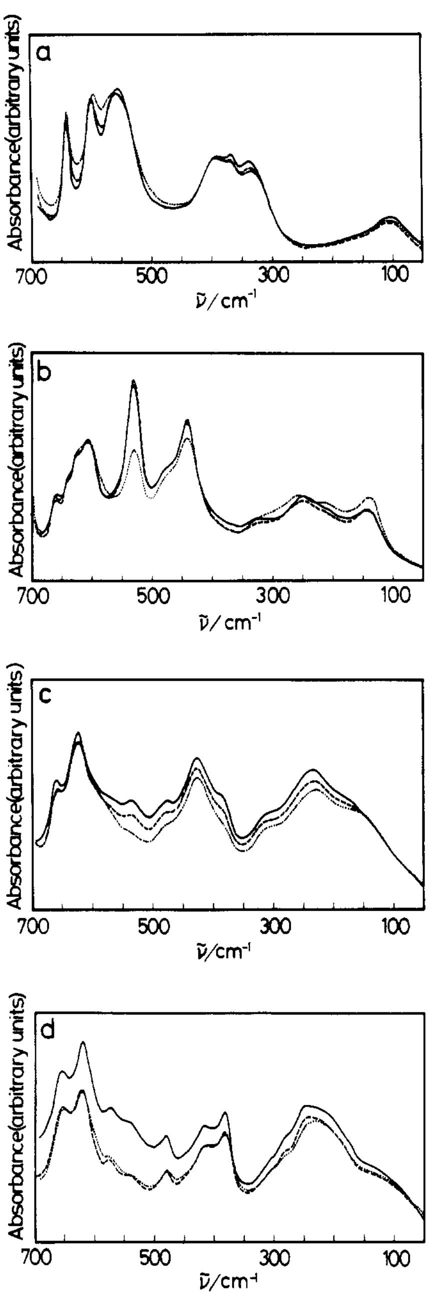

Figure 3. Temperature-dependence of far-infrared spectra for (a) EMAA, (b) EMAA–0.6Zn, (c) EMAA–0.6Zn–0.4BAC, and (d) EMAA–0.6Zn–0.97BAC: (—) room temperature (24 °C); (- - -) 50 °C; (···) 80 °C.

Roughly speaking, changes of the vibrational intensity in the 300–700-cm^{-1} region between temperatures below and above T_i for these four samples are in the order EMAA–0.6Zn–0.97BAC > EMAA–0.6Zn–0.4BAC > EMAA–0.6Zn > EMAA. Dielectric[10] and other measurements[9,11,12,18] showed that ionic clusters are formed in both EMAA–0.6Zn–0.4BAC and EMAA–0.6Zn–0.97BAC but not in EMAA–0.6Zn or EMAA. Moreover, DSC analyses[9,12] revealed that the heat of transition of the ionic clusters (ΔH_i) are also in the same order: EMAA–0.6Zn–0.97BAC (ca. 18 mJ/mg) ~ EMAA–0.6Zn–0.4BAC > EMAA–0.6Zn (ca. 10 mJ/mg) > EMAA (ca. 4 mJ/mg). Generally, the value of ΔH_i is believed to be proportional to the degree of order in the ionic aggregates. Therefore, these changes in intensity of the spectra between temperatures below and above T_i for the EMAA–Zn–BAC system appear to arise primarily from the structural change of the ionic aggregates at T_i; the more ordered ionic aggregates restrict more effectively the motions of the polyethylene backbone, changing the infrared-inactive modes to active ones because the bands in the region of 300–700 cm^{-1} are attributable either to the vibrations of the COO$^-$ groups or to those of the polymer backbones. In contrast with the above results, increasing temperature hardly changes the vibrational frequencies over the same frequency region, which suggests that the polymer backbones do not directly participate in the transition of the ionic clusters at T_i.

It should be noted that the cluster modes of the Zn(II)–O vibrations in the EMAA–Zn–BAC system change appreciably with the order–disorder transition of the ionic clusters. In EMAA–0.6Zn–yBAC, both the frequency and the intensity of the cluster mode decrease with increasing temperatures above T_i. Since the change in frequency is connected with a change in the nature of the Zn(II)–O bonds, these results may evidence the existence of a structural transition within the ionic clusters at T_i.[9] This

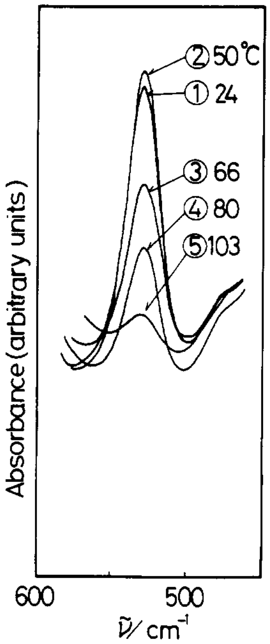

Figure 4. Infrared spectra in the region 450–600 cm^{-1} for EMAA–0.6Zn plotted as a function of temperature.

mechanism can be explained as follows: At temperatures above T_i, the ordered ionic clusters are transformed into the disordered ones. In the disordered ionic clusters, the ions are more loosely packed than in the ordered ones, which causes the frequency of the Zn(II)–O vibrations to be lower. At the same time, the surroundings of the Zn(II) ions become more centrosymmetric upon disordering the ionic groups within the ionic clusters above T_i, and this disordering results in a decrease in the intensity of the Zn(II)–O vibrations. On the other hand, in EMAA–0.6Zn, both the frequency and the intensity of the band near 250 cm^{-1} hardly change with increasing temperature above T_i. The vibrational frequency of the lower frequency band (ca. 140 cm^{-1}) also does not change but the intensity increases slightly with increasing temperature. These results suggest that the ionic aggregations of $Zn(COO)_2$ occurs only to a small extent in EMAA–0.6Zn and that the Zn(II)–O bonds are relatively rigid compared with those in its BAC complexes.

Another interesting observation is a distinct change in the intensity of the 530-cm^{-1} band in EMAA–0.6Zn with temperature, which is shown in Figure 4. This intense absorption band is independent of temperature below T_i, but above T_i, it begins to decrease dramatically and almost disappears at 103 °C. Although the assignment of this band is not clear at this stage, a plausible explanation could be that the appearance of this band is associated with a deformation of the polymer backbones; the destruction of the ordered structure in the ionic aggregates above T_i could lead this band to be infrared-inactive. However, this explanation contradicts the fact that no similar temperature-dependent modes are observed in the corresponding BAC complexes. Another possible explanation is based on hydrogen-bonding effects; the dimers of the pendent COOH groups also act as cross-links. Nevertheless, the corresponding mode is not observed in EMAA. To clarify this observation, further investigations are needed.

Summary and Conclusions

Our far-infrared study of the EMAA–Zn–BAC system has led us to the following results:

(i) Two broad well-defined bands, which are absent in the spectra of EMAA, are observed near 250 and 140 cm^{-1} for the EMAA–Zn–BAC ionomers. We assign the band near 250 cm^{-1} to Zn(II)–O vibrations within the ionic aggregates, which may be either ionic multiplets or clusters. The addition of BAC to EMAA–0.6Zn increases both the intensity and the bandwidth, which can be explained by the formation and development of ionic clusters. The 140-cm^{-1} band in EMAA–0.6Zn is assigned to a Zn(II)–O vibration not incorporated in the ionic aggregates, which is obscured in its BAC complexes.

(ii) The cluster mode near 250 cm^{-1} in the Zn–BAC complexes shifts to lower frequency with increasing temperature above T_i; this result may provide direct evidence for the order–disorder transition of the ionic clusters because the Zn(II)–O vibrational motions within the ionic clusters change near T_i.

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

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Registry No. EMAA–*x*Zn–*y*BAC (copolymer), 135952-68-0.