Dielectric Relaxation Studies on Water Absorption of Ethylene Ionomers

Shinichi Yano,* Kenji Tadano,† Nobuaki Nagao, Shoichi Kutsumizu, Hitoshi Tachino,‡ and Eisaku Hirasawa‡

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gigu 501-11, Japan, Gifu College of Medical Technology, Ichihiraga, Seki, Gifu 501-32, Japan, and Technical Center, Du Pont-Mitsui Polychemicals Company, Ltd., Chikusa, Kaigan 6, Ichihara, Chiba 299-01, Japan

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ABSTRACT: Sodium and zinc salts of ethylene–methacrylic acid (5.4 mol %) copolymer were studied by dielectric spectroscopy to clarify how water molecules are absorbed in these ionomers. The samples are denoted EMAA–xNa(or Zn)–$y$$H_2O$, where x and y are degree of neutralization and molar ratio of H_2O to COONa, respectively. The dielectric relaxations of EMAA and EMAA–0.6Zn, whose water absorption is usually small, were scarcely affected by water uptake. On the other hand, the dielectric relaxations of EMAA–xNa, particularly highly neutralized sodium salts, sensitively responded to water uptake. In EMAA–0.90Na–$y$$H_2O$, for example, a water peak appeared near 270 K at 1 kHz in addition to the α and β relaxations and gradually increased with increasing water content (y). Interestingly, the dielectric increment ($\Delta\epsilon$) of this water peak increased more than 100-fold when y was increased from 2 to 3. At $y = 3$, a new peak appeared near 320 K and was independent of measuring frequency. The temperature exhibiting this peak corresponded to the order–disorder transition of ionic clusters. These results indicate that three water molecules per sodium cation form a primary hydration shell and that the excess water molecules are absorbed around that shell. Consequently, we can conclude that the ionic clusters are probably transformed into a structure reminiscent of an inverse micelle upon water absorption.

Introduction

Ionomers are polymers functionalized with ionic groups pendantly attached to the backbone chains. The ionic groups tend to separate from the hydrophobic polymer matrix and form ionic aggregations such as multiplets and ionic clusters. The existence of the ionic aggregations strikingly affects the physical properties of ionomers and furnishes the characteristic functionality to them.[1,2] Water absorption is a key parameter determining the properties of ionomers, because water molecules are known to be preferentially absorbed in the ionic aggregations.[3–12] Perfluorinated ionomers, such as polyfluorosulfonate and -carboxylate, are known to generate their specific functionalities, such as selective ionic transport, upon water absorption. On the other hand, water absorption on ethylene ionomers has been considered to be a disadvantage for the applications to engineering thermoplastics because of the decrease in the strength of ionic interaction. Recently, it was reported that several ethylene isomers show a remarkable increase in electroconductivity upon water uptake.[13,14] These ionomers can be industrially used as antielectrostatic or electroconducting plastics.

In preceding work,[15] we investigated where and how water molecules are absorbed in ethylene ionomers by use of several techniques (IR spectroscopy, DSC, DTA, thermogravimetry, and X-ray diffractometry). It was pointed out that hydrophilic ionic groups in ethylene ionomers are powerful absorption sites of water molecules and that water uptake profoundly affects the properties and structure of ionic aggregates. We reported dielectric relaxation studies of ethylene–methacrylic acid copolymers neutralized with alkali, alkaline earth, and transition metal cations.[16,17] In the study, dielectric relaxations were shown to dramatically change according to whether the ionic groups were clustered or not, since the dielectric relaxations reflect segmental motions of ionomers, which we can detect through the polar ionic groups. Therefore, we anticipate a drastic change in the dielectric relaxations upon uptake of water molecules in the ionic groups. From this viewpoint, the present work aims at clarifying the formation of hydrated ionic clusters in ethylene ionomers from dielectric relaxation studies.

Experimental Section

Sodium or zinc salts of ethylene–methacrylic acid copolymer (hereafter denoted EMAA–xNa or EMAA–xZn) were prepared by a melt reaction of EMAA with a stoichiometric quantity of Na_2CO_3/ZnO_2 in an extruder at 450–530 K. The melt strand from the extruder die was cooled in water and pelletized. The pellet samples were compression-molded into sheets of ca. 0.5-mm thickness at 430 K and cooled to room temperature at a rate of ca. 30 K min^{-1} by circulating cold water outside the press jacket. The EMAA used is ACR-1560 (Du Pont-Mitsui Polychemicals Co., Ltd.), whose MAA content is 5.4 mol %.

Even samples just after the compression-molding contained a small amount of residual water (see Table I), but we denote them as dry samples (EMAA–xNa or EMAA–xZn). The amount of residual water was determined by measuring the weight loss of the dry samples after suction-drying by a rotatory pump at 443–453 K for 40 min. The soaked samples are listed in Table I and are denoted EMAA–xNa–$y$$H_2O$ or EMAA–xZn–$y$$H_2O$. The symbol y means the molar ratio of H_2O to COONa or $(COO)_2Zn$ ($y = [H_2O]/[COONa]$ or $[H_2O]/[(COO)_2Zn]$), and y includes the residual water.

Results

Recently, we proposed an order–disorder transition model of ionic clusters for ethylene ionomers,[18] the inside of the ionic clusters is in an ordered state at room temperature and transformed into a disordered state at T_i (the transition temperature of the ionic clusters). This model well explained dielectric relaxation results of ethylene ionomers neutralized with various metal cations.[17,18] EMAA showed two relaxations, β' near 315 K above T_g and γ near 182 K below T_g at 1 kHz. These relaxations are ascribed, respectively, to a micro-Brownian

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* To whom correspondence should be addressed at Gifu University.

† Gifu College of Medical Technology.

‡ Du Pont-Mitsui Polychemicals Co., Ltd.

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Table I
Sample Lists

sample	water content		method of water uptake^c	T_i^{d}
	wt %	y^b		
EMAA	0.22^a			
EMAA–0.20Na	0.24^a	0.39^a		
EMAA–0.20Na–0.89H_2O	0.55	0.89	RH	
–1.11H_2O	0.69	1.11	IW	
EMAA–0.40Na	0.26^a	0.21^a		321
EMAA–0.40Na–0.76H_2O	0.93	0.76	RH	
–0.80H_2O	0.98	0.80	IW	
–1.10H_2O	1.35	1.10	RH	
EMAA–0.60Na	0.29^a	0.16^a		338
EMAA–0.60Na–0.46H_2O	0.85	0.46	RH	328
–0.86H_2O	1.56	0.86	RH	326
–1.49H_2O	2.73	1.49	IW	325
EMAA–0.90Na	0.43^a	0.16^a		341
EMAA–0.90Na–0.59H_2O	1.61	0.59	RH	329
–1.98H_2O	5.37	1.98	IW	326
–2.36H_2O	6.41	2.36	RH	326
–2.75H_2O	7.46	2.75	IW	327
–3.45H_2O	9.37	3.45	IW	328
EMAA–0.60Zn	0.084^a	0.24^a		
EMAA–0.60Zn–0.40H_2O	0.14	0.40	IW	
EMAA–0.60Zn–0.41H_2O	0.15	0.41	IW	

^{a} Residual water. ^{b} y = $[H_2O]/[COONa]$ or $[H_2O]/[(COO)_2Zn]$, and y includes the residual water. ^{c} RH: stored in 87% relative humidity. IW: immersed in water. ^{d} Transition temperature of ionic cluster.[15,17]

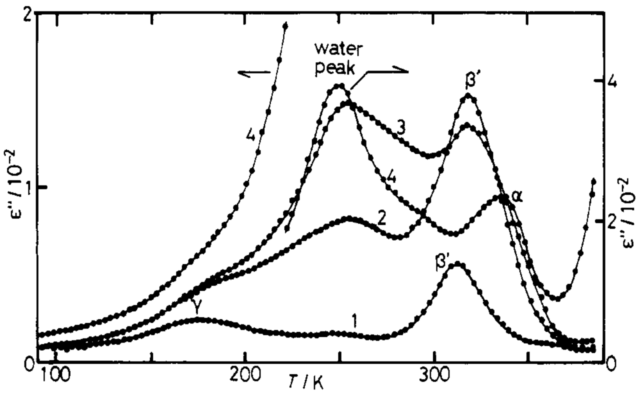

Figure 1. Temperature dependence of dielectric loss (ϵ'') at 1 kHz for EMAA–xNa–yH_2O (x < 0.6): 1, EMAA; 2, EMAA–0.20Na–1.11H_2O; 3, EMAA–0.40Na–1.10H_2O; 4, EMAA–0.60Na–1.49H_2O.

molecular motion of long segments in a rubbery state and to a local molecular motion of short segments in a glassy state. In EMAA–xNa, when x is greater than 0.4, the β' relaxation was replaced by two relaxations, the α relaxation above T_i and the β relaxation below T_i. The α and β relaxations are attributed, respectively, to a micro-Brownian molecular motion of long segments including the ionic groups (COONa) incorporated into the ionic clusters and to a local motion of segments including the isolated COONa groups not incorporated into the ionic clusters. The disordered ionic clusters above T_i are soft enough to produce the α relaxation, while the ordered ionic clusters below T_i act as rigid cross-links, which causes the appearance of the β relaxation. Figure 1 shows the temperature dependence of the dielectric loss, ϵ'', at 1 kHz for EMAA–xNa–yH_2O (x < 0.60). EMAA and EMAA–0.20Na do not form ionic clusters and only show β' and γ relaxations around 315 and 182 K and 326 and 217 K, respectively, at 1 kHz. With absorbing water, the β' relaxation of EMMA–0.20Na gradually shifted to lower temperatures and a new peak developed near 250 K. This peak is located at 255 K for EMAA–0.20Na–1.11H_2O (Figure 1). These observations are not obvious for EMAA, probably because it scarcely absorbs water. The shift of the β' relaxation to lower temperatures may be due to a plasticizing effect of the absorbed water. MacKnight et al.[10] ascribed the peak near 250 K to the water peak, which may be attributed to a reorientation of the hydroxy groups of water molecules absorbed at the ionic groups. Highly neutralized samples, which form ionic clusters, exhibited the α and β relaxations near 333 and 285 K for EMAA–0.40Na and 344 and 294 K for EMAA–0.60Na, respectively, at 1 kHz. With absorbing water, the α relaxation somewhat moved to lower temperatures, while the water peak became larger and shielded the β relaxation (see Figure 1).

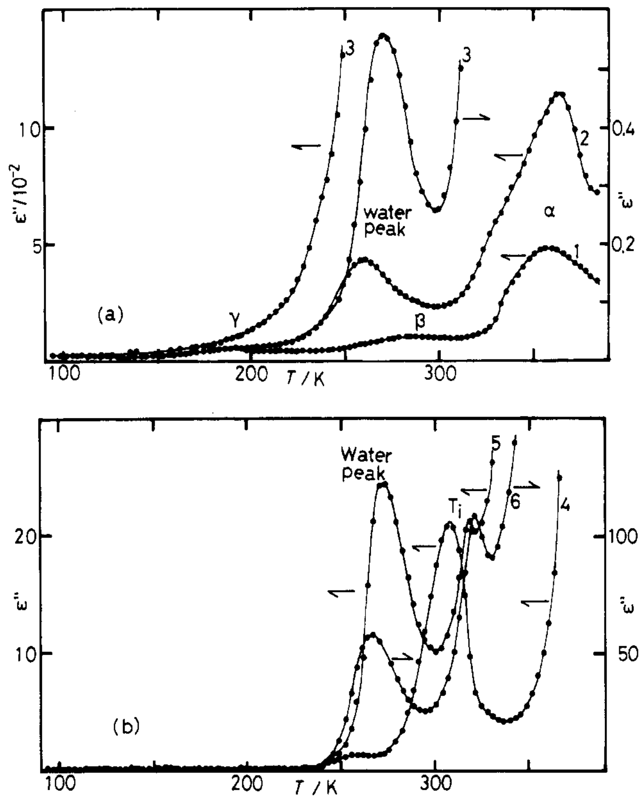

Figure 2. Temperature dependence of dielectric loss (ϵ'' at 1 kHz for EMAA–0.90Na–yH_2O: (a) $y \leq 1.98$; (b) $y \geq 2.36$. 1, EMAA–0.90Na; 2, y = 0.59; 3, y = 1.98; 4, y = 2.36; 5, y = 2.75; 6, y = 3.45.

Figure 2 shows the temperature dependence of ϵ'' for EMAA–0.90Na–yH_2O. When y is less than 2.4 (Figure 2a), both the α relaxation and water peak become larger with increasing y, being similar to those observed in Figure 1. As y becomes larger than 2.75, Figure 2b demonstrates another characteristic peak arising near 320 K in addition to the water peak around 270 K. In addition, a steep increase of ϵ'' is observed with increasing temperature above the 320 K peak, and this increase may be caused by a dc electric conduction increased by the water uptake. The α relaxation is barely observed, because it seems to be buried by the dc conduction. Figure 3 illustrates the temperature dependence of ϵ' and ϵ'' at different frequencies for EMAA–0.90Na–3.45H_2O. In the ϵ''–temperature plots, the 320 K peak becomes larger as frequency decreases, but the temperature exhibiting the peak is apparently independent of frequency. This 320 K peak is seen as an abrupt decrease of ϵ' in the ϵ'–temperature plots. These unusual changes indicate the existence of a transition near 320 K, and this transition may correspond to the order–disorder transition of ionic clusters, since the temperature exhibiting the unusual change corresponds to the order–disorder transition temperature of ionic clusters (T_i) (see Table I).

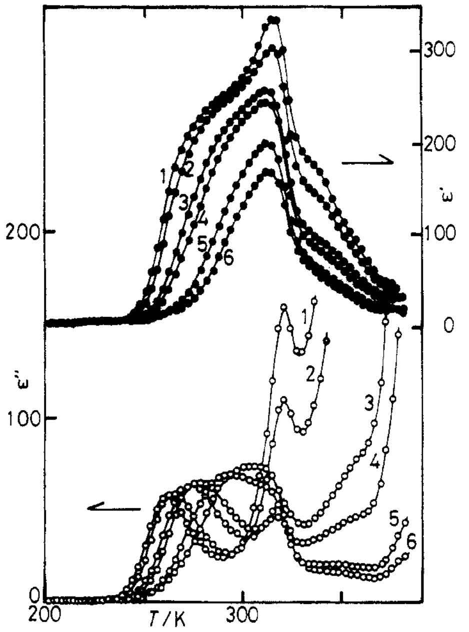

Figure 3. Temperature dependence of (a) dielectric constant (ϵ') and (b) dielectric loss (ϵ'') at different frequencies for EMAA-0.90Na-3.45H_2O: 1, 500 Hz; 2, 1 kHz; 3, 5 kHz; 4, 10 kHz; 5, 50 kHz; 6, 100 kHz.

We attempted to calculate the relaxation temperature (T_{max}) and activation enthalpy change (ΔH) for all the relaxations. The values of ΔH were estimated to be 237 and 367 kJ mol^{-1} for the β' relaxation of dry EMAA and EMAA-0.20Na, respectively, and 330 and 70 kJ mol^{-1} for the α and β relaxations of the other dry EMAA-xNa (x = 0.40-0.90), respectively. The ΔH of the γ relaxation was between 30 and 50 kJ mol^{-1} for all the dry samples. On the other hand, ΔH for the soaked samples (EMAA-xNa-$y$$H_2O$) could not be determined for all the relaxations, because the relaxations sometimes overlapped each other. However, we were able to calculate the value of ΔH only for the water peak in EMAA-0.90Na-$y$$H_2O$, since the water peak was very large. The value of ΔH decreased from 180 to 99 kJ mol^{-1} as y increased from 0.59 to 3.45.

Figure 4 shows the temperature dependence of ϵ'' at 1 kHz for EMAA-0.60Zn-$y$$H_2O$ as a function of water content. The β' and γ relaxations are observed for EMAA-0.60Zn, which is known not to form ionic clusters. The β' relaxation becomes somewhat larger upon water uptake, but the water peak is very small compared with that of the EMAA-xNa-$y$$H_2O$ system. This result can be explained by the fact that the water uptake of the Zn(II) salts is small because of the covalent nature of the Zn-$(COO)_2$ bond (see Table I).

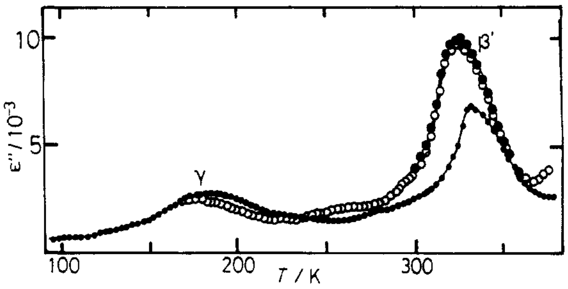

Figure 4. Temperature dependence of dielectric loss (ϵ'') at 1 kHz for EMAA-0.60Zn-$y$$H_2O$: (•) EMAA-0.60Zn; (○) y = 0.40; (●) y = 0.41.

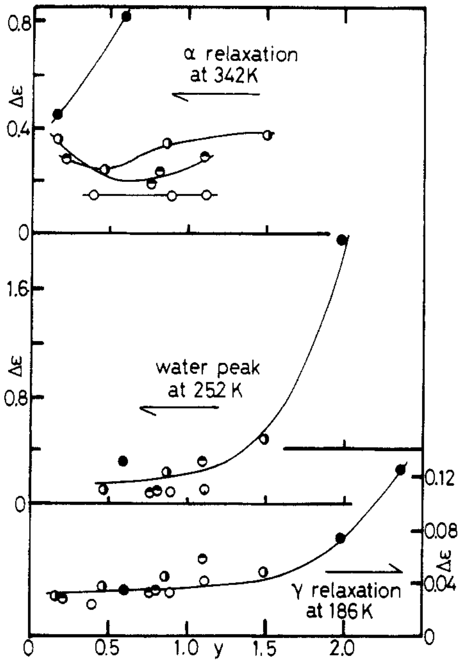

Figure 5. Plots of dielectric increment ($\Delta\epsilon$) versus water content (y) for EMAA-xNa-$y$$H_2O$. The y of EMAA-xNa (the dry samples) in this figure does not indicate zero but the residual water. (○) x = 0.20; (◓) x = 0.40; (◑) x = 0.60; (●) x = 0.90.

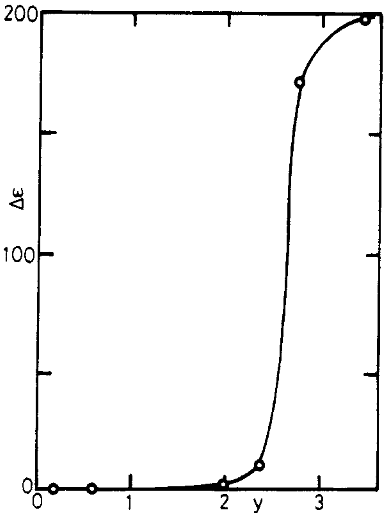

Figure 6. Plots of dielectric increment ($\Delta\epsilon$) at 250 K of water peak versus water content (y) for EMAA-0.90Na-$y$$H_2O$.

Discussion

Figure 5 shows plots of the dielectric increment ($\Delta\epsilon$) in three relaxations—the α relaxation, the water peak, and the γ relaxation—against the amount of water uptake (y). The values of $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ were obtained from Cole-Cole plots,[19] where ϵ_0 and ϵ_∞ are a static dielectric constant and a limiting frequency dielectric constant, respectively. In EMAA-xNa-$y$$H_2O$, the saturated amount of water uptake becomes larger with increasing x (see also Table I). In samples whose neutralization (x) is lower than 0.6, the absorbed water content (y) is below 1.5 and so the values for the three relaxations are scarcely affected by water uptake. However, the value of $\Delta\epsilon$ increases with increasing y in the highly neutralized samples (x = 0.90). Figure 6 shows plots of $\Delta\epsilon$ of the water peak versus y for EMAA-0.90Na-$y$$H_2O$. The value of $\Delta\epsilon$ is lower than 2 (see also Figure 5) at low values of y but abruptly increases around y = 3, where the value of $\Delta\epsilon$ reaches an extremely large value of about 200. This abrupt increase of $\Delta\epsilon$ suggests that the state of H_2O incorporated into the ionomers drastically changes near y = 3. In most ionomers, hydrophilic ionic groups should be powerful absorption sites of water molecules. At the initial stage of water absorption, water molecules may be hydrated at the ions to form primary hydration shells around the ions.[4] From IR and ^{23}Na NMR studies, Mauritz et al.[12] proposed a four-state mode of the hydration–dissociation equilibrium between unbounded and side-chain-associated counterions for the water absorption process of perfluorosulfonate ionomers; at the fully water absorbed state, the primarily hydrated ion pairs are completely dissociated, but as water is removed, their state moves stepwise toward contact ion pairs containing a few water molecules. Generally, the hydration number of a primary shell may depend on the cations and host polymers. Escoubes and Pineri[4] reported that a few carboxylate ethylene-based ionomers absorb 5 ± 1 water molecules per COO^- in the fully hydrated state. In preceding work,[15] we studied water absorption of EMAA–Na systems by use of IR, DSC, and thermogravimetry. The IR spectra of dry EMAA–0.90Na showed 1560- and 1408-cm^{-1} absorptions, which are assigned to antisymmetric (ν_{asym}) and symmetric stretching vibrations (ν_{sym}) of COO^-, respectively. These absorptions are scarcely changed by the hydration when y less than 0.5 but are shifted to lower frequencies as y increases from 0.5, and this shift stops around $y = 3$, where ν_{asym} and ν_{sym} reach 1542 and 1403 cm^{-1}, respectively. The shifts to lower frequencies mean that the state of COO^- groups moves toward an unbounded state. In fact, ν_{asym} and ν_{sym} of sodium *n*-hexanoate are at 1560.6 and 1415.9 cm^{-1}, respectively, in the solid state and at 1544.8 and 1408.3 cm^{-1}, respectively, in aqueous solution.[20] Our IR results, therefore, indicate that about three water molecules may be absorbed in the vicinity of COONa to form a primary hydrated shell and the excess water molecules above three may be absorbed around the primary hydration shells to act as an aqueous solvent. The DSC curves of the EMAA–0.90Na–yH$_2$O system showed endothermic peaks near T_i and T_m.[15] The enthalpy change at T_i (ΔH_i) rapidly decreased with increasing y, but the decrease was saturated near $y = 3$. The magnitude of ΔH_i reflects the degree of orderness of the inside of ionic clusters. The above results clearly indicate that the orderness in the inside of ionic clusters is decreased by water absorption. However, it is noted that ΔH_i remained about 8 mJ/mg even above $y = 3$, which means that an orderness remains even in the fully water absorbed state, although the IR spectral results indicate that the COO^- in this state is as much dissociated as that in the aqueous solution. Therefore, it seems to be true that the remaining orderness originates in an arrangement of short segments of ethylene chains adjacent to COO^- groups. The length of the ordered methylene chains adjacent to COO^- groups was estimated as 1.4 methylene units from the remaining ΔH_i values.[15] In fact, most of the morphological models explaining the structure of ionic clusters suggest that the ionic clusters consist of ionic groups and short segments of backbone chains adjacent to the ionic groups. In the dry state of ethylene ionomers, the ionic clusters may consist of ionic groups and segments of ethylene backbone chains, for example, as Dreyfus's model indicates.[21] When y is less than about 3, water molecules are absorbed near the ionic groups inside the ionic clusters to form the primary hydration shells, while when y is greater than about 3, the excess water molecules are absorbed around the primary hydration shells. As a result, the ionic clusters would have a structure reminiscent of an inverse micelle seen usually in a sodium alkanoate–hydrophobic solvent system. This model well explains the present dielectric relaxation behavior as follows. In the dry ethylene ionomers, the β' relaxation observed in EMAA is replaced by the α and β relaxations, when the ionic groups are clustered by neutralizing with metal cations. The absorption of water molecules leads to an appearance of the water peak. When y is greater than 3, the water peak abruptly increases and its $\Delta\epsilon$ value reaches about 200 at $y = 3$. This abrupt increase of $\Delta\epsilon$ at the critical y value may indicate the onset of an interfacial polarization:[22,23] The ions would move in the aqueous solution inside the inverse micelles toward the applied electric field but the movement would be blocked by the shell of the inverse micelles to accumulate ions at the phase boundaries during half cycles of field alternation. This interfacial polarization may be responsible for the extremely large value of $\Delta\epsilon$ above $y = 3$. In the order–disorder transition model of ionic clusters proposed previously, it was not completely understood why the values of T_i lie around 310–335 K independent of cation species. This dielectric work seems to answer this question as follows: A trigger of the transformation of the ionic clusters from the ordered state to the disordered state might be a melting of the ordered segments of ethylene chains adjacent to ionic groups, although the order–disorder transition of the ionic groups would concur. Further studies are necessary to prove this model.

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Registry No. EMAA–xNa, 25608-26-8; EMAA–xZn, 28516-43-0; EMAA, 25053-53-6; H$_2$O, 7732-18-5.