Dynamic Mechanical Relaxations of Ethylene Ionomers

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ABSTRACT: Dynamic mechanical properties were measured for metal salts (Li, Mg, Na, and Zn) of poly(ethylene-*co*-methacrylic acid) (EMAA) using a dynamic viscoelastometer. The study reproduced the previous observation that the mechanical relaxation behavior clearly responded to ionic cluster formation and its phase separation from the hydrocarbon matrix—the Li, Mg, and Na ionomers formed ionic clusters at a neutralization of ~35% or higher, and the Zn ionomer did not form ionic clusters at neutralization up to 60%. However, this work has revealed clear evidence that even the Zn ionomer forms regions of microphase-separated ionic clusters at a neutralization of 80% or higher. A peak, designated as the α' peak, appeared at ~325 K on the loss modulus curve of all EMAA ionomers that form ionic clusters, and the temperature exhibiting this peak proved to be independent of frequency. The order–disorder transition temperature (T_i) of the ionic clusters of EMAA ionomers, measured by differential scanning calorimetry, agreed with the α' peak temperature. From the frequency independence of this α' peak temperature, it is proposed that the α' peak is regarded as a first-order transition at T_i and represents the existence of the order–disorder transition in the ionic clusters.

Introduction

Ethylene ionomer, in which ionic groups are pendantly attached to the backbone chains, tends to form ionic aggregates in the hydrophobic polymer matrix.[1-6] Mechanical,[7-10] dielectric,[11-14] electron spin resonance (ESR),[15-17] and small-angle X-ray scattering (SAXS)[4,6,18] studies revealed that these aggregates are multiplets (several ion pairs) at lower ionic content and develop into ionic clusters upon increasing neutralization. An updated picture of the morphological model for ionic aggregation of random ionomers was recently presented by Eisenberg et al.,[19] where the model indicates that the ionic clusters, exhibiting phase-separated behavior, consist of large contiguous regions that are formed by the restricted mobility of surrounding multiplets. The dynamic mechanical relaxations of ethylene ionomers neutralized with alkali and alkaline earth metal cations show that ionic cluster formation leads to the depression of a β' relaxation and the corresponding appearance of two relaxations (α and β) when neutralization reaches ~35% or higher.[8,20] The β' relaxation, usually seen in un-ionized acid copolymers, is ascribed to a micro-Brownian molecular motion of long segments in the amorphous region, where carboxylic acid dimers act as cross-links and restrict that motion.[8,20] The α relaxation is generally attributed to a glass–rubber transition of the ionic clusters, and the β relaxation is ascribed to motion of long segments in the amorphous branched-polyethylene phase, from which most ionic groups are excluded.[8,13] The two relaxations above and below the β' relaxation should individually reflect molecular motions in the ionic cluster and polyethylene phases. Therefore, the appearance of the two relaxations is thought to be an indication of phase separation between the two phases. We reported similar relaxation changes in the dielectric studies for ethylene ionomers neutralized with various metal cations and for complexes of transition metal cations with 1,3-bis(aminomethyl)cyclohexane.[14,21-24]

Recently we proposed that the order–disorder transition exists in the ionic clusters.[25,26] This transition is considered to be the melting of ionic crystallites. In this paper, we will extend our ionomer relaxation study to understanding the effects of ionic cluster formation and its order–disorder transition on their segmental molecular motions.

Experimental Section

The starting poly(ethylene-*co*-methacrylic acid) (EMAA) was from Du Pont-Mitsui Polychemicals Co., Ltd., whose methacrylic acid unit is 5.4 mol %. The metal salts of EMAA used in this study were prepared by a melt reaction of EMAA with a stoichiometric quantity of cation sources such as metal hydroxides, metal carbonates, and metal oxides. The melt reaction was carried out on an extruder at 450–530 K, and the products out of the extruder die were cut into pellets. These pellet samples were compression-molded into a 1-mm-thick sheet at 450 K and cooled to room temperature at a cooling rate of ~30 K/min. All of the compression-molded sheets were clear and transparent and showed no signs of unreacted metal salts, which indicated that the reaction proceeded stoichiometrically. If the reaction was incomplete, the sheets were opaque or translucent. The formation of metal carboxylate was also confirmed by the infrared spectra. We delineated our samples in this paper as EMAA-xM, where x and M mean neutralization degree and metal cation, respectively.

A Rheospectoler Model DVE-V4 (Rheology Co., Ltd.) attached to a NEC PC9801EX computer was used to measure dynamic mechanical properties. A compression-molded sheet was cut into a specimen of approximately 20-mm length, 6-mm width, and 1-mm thickness and then aged at 23 °C and 50% relative humidity for 2–3 weeks before the measurement. All of the specimens were analyzed in the tensile mode at a constant tension, at a heating rate of 3 K/min from 123 to 393 K and with frequencies of 1, 10, and 100 Hz.

Order–disorder transition temperatures of ionic clusters (T_i) was determined by a differential scanning calorimeter (Du Pont DSC-990) at a heating and cooling rate of 10 K/min. A 10-mg specimen used for the measurement was cut from the compression-molded sheets, which were aged at 23 °C and 50% relative humidity for 2 months. At the first heating, two endothermic peaks were observed near 325 and 365 K. The lower temperature peak was assigned to the order–disorder transition in the ionic clusters,[25,26] and the higher one corresponded to the melting of the polyethylene crystallites.[25,26]

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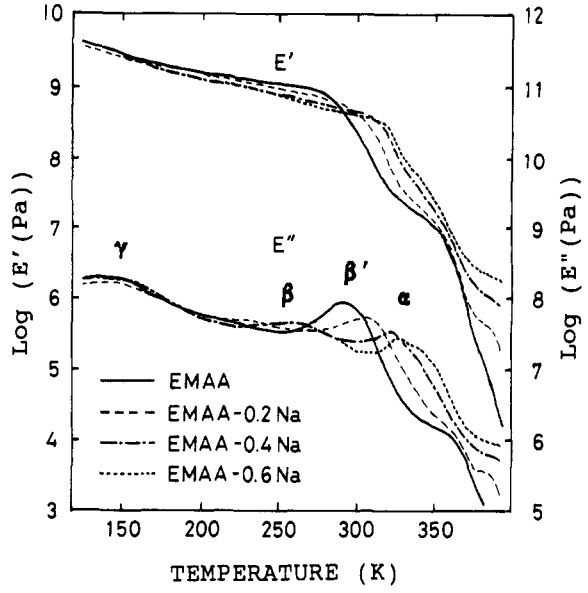

Figure 1. Temperature dependence of dynamic storage modulus (E') and loss modulus (E'') at 10 Hz for sodium salts of EMAA ionomers.

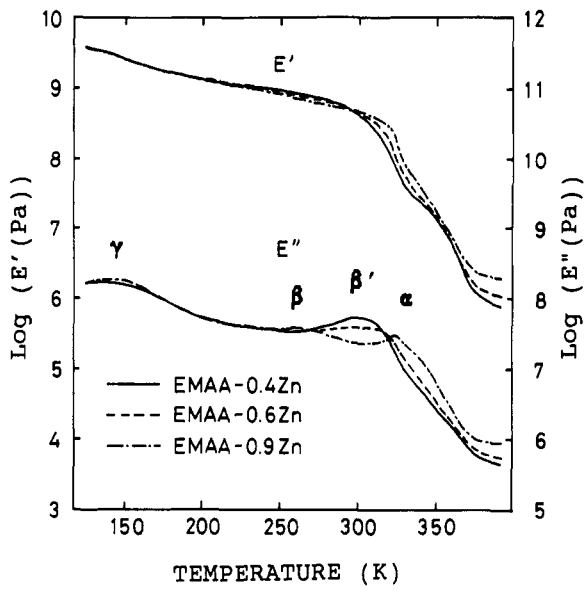

Figure 2. Temperature dependence of dynamic storage modulus (E') and loss modulus (E'') at 10 Hz for zinc salts of EMAA ionomers.

Results and Discussion

Figure 1 shows the temperature dependence of the dynamic mechanical properties for EMAA and its Na ionomers at 10 Hz. We used the loss modulus (E'') as the basis of this relaxation study. EMAA exhibited two relaxations in the investigated temperature range: β' relaxation at 291 K and γ relaxation at 143 K. The β' relaxation is assigned to a micro-Brownian segmental motion in the amorphous region. The γ relaxation is ascribed to a local molecular motion of the short segments in the amorphous phases.[8,20] The E'' of EMAA-0.2Na showed similar relaxations to EMAA, but the β' relaxation shifted to higher temperature. When the neutralization was increased to 40% or higher, the α and β relaxations appeared and replaced the β' relaxation. The α relaxation, generally associated with a glass–rubber transition of the ionic clusters, shifted to higher temperatures while the β relaxation stayed at almost the same temperature (~258 K) with increasing neutralization. These results apparently agree with those observed in our previous mechanical relaxation study.[20] MacKnight et al.[8] explained that β relaxation in the ionomers arises from the amorphous hydrocarbon phase and is identical to the β relaxation in a branched polyethylene. Therefore, the appearance of α and β relaxations is regarded to indicate the phase separation of ionic aggregates from the hydrocarbon matrix and the formation of the ionic clusters.

Figure 2 shows the temperature dependence of dynamic mechanical properties for Zn ionomers at 10 Hz. In contrast to the Na ionomers, even a 60% neutralized Zn ionomer exhibited β' relaxation, and the α and β relaxations appeared only on the E'' of EMAA-0.9Zn. We did not include the E'' of EMAA-0.8Zn in Figure 2, but it also exhibited signs of the existence of α and β relaxations. In previous works,[20,24,27] distinct β relaxations were not observed on the E'' of (1) the Cu, Mn, and Ni salts of poly(ethylene-*co*-acrylic acid) up to 70% neutralization, (2) the Co, Cu, and Mn salts of EMAA at 60% neutralization, and (3) the Zn salt of EMAA at 80% neutralization. Consequently, this work has revealed clear evidence that even Zn ionomers can form regions of microphase-separated ionic clusters at a neutralization of 80% or higher. This finding also allows us to predict that, at much higher neutralization degrees, other transition metal ionomers probably form an ionic cluster phase that is separated from the hydrocarbon matrix.

In previous work[20,28,29] on physical property changes for EMAA ionomers, K, Mg, and Na ionomers showed maximum stiffness near 33% neutralization and Zn ionomer reached a stiffness plateau at ~70% neutralization. Because these neutralization degress coincide with those showing the appearance of α and β relaxations, our mechanical relaxation results suggest that ionic cluster formation along with its phase separation apparently influences the physical properties of EMAA ionomers. More interestingly, from the neutralization degrees causing the phase separation, we can assume that both Na and Zn ions form ordered structures with three carboxyl groups per cation, namely, 33% neutralization for Na ion ($(COO^-)Na(COOH)_2$) and 67% neutralization for Zn ion ($(COO^-)_2Zn(COOH)$).

Figure 3 shows the frequency dependence of the E'' of EMAA, EMAA-0.6Zn, and EMAA-0.9Zn. In this study, we used frequencies of 1, 10, and 100 Hz. The β' relaxation temperature of EMAA and EMAA-0.6Zn increased with increasing frequency. The α and β relaxation temperatures of EMAA-0.9Zn also showed frequency dependence. However, it should be emphasized that a peak superposed on the α relaxation of EMAA-0.9Zn was almost independent of frequency. We designate it as the α' peak. Figure 4 demonstrates the same frequency independence of the α' peak of EMAA-0.6Na, EMAA-0.6Li, and EMAA-0.6Mg, which is also superposed on their α relaxations. This frequency-independent peak appeared at ~325 K upon ionic cluster formation for all EMAA ionomers studied. Table I summarizes the α' peak temperature as a function of the frequency. This frequency independence strongly supports the α' peak as a first-order transition. We confirmed by the Rheospectoler that a transition temperature corresponding to a melting point of polyethylene crystallites of a branched polyethylene showed a frequency independence similar to that of the α' peak.

We recently proposed that the ionic clusters form an ordered structure at room temperature and are transformed into a disordered structure above an order–disorder transition temperature (T_i).[25,26] Table II lists the T_i of EMAA ionomers and the mechanical and dielectric relaxation temperatures including the α' peak temperature,

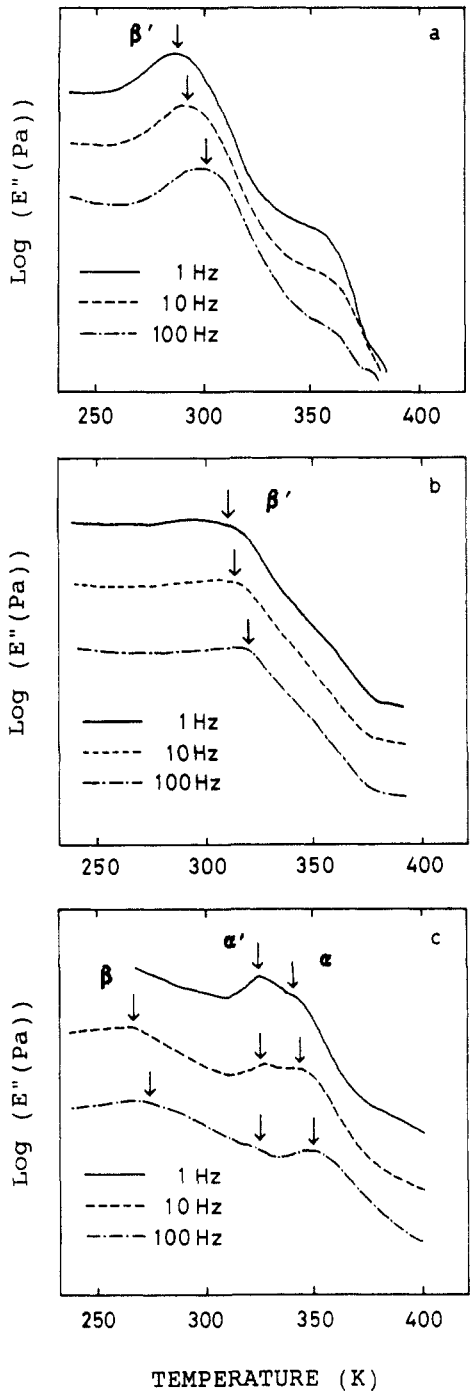

Figure 3. Temperature dependence of dynamic loss modulus (E'') at a few frequencies for (a) EMAA, (b) EMAA-0.6Zn, and (c) EMAA-0.9Zn.

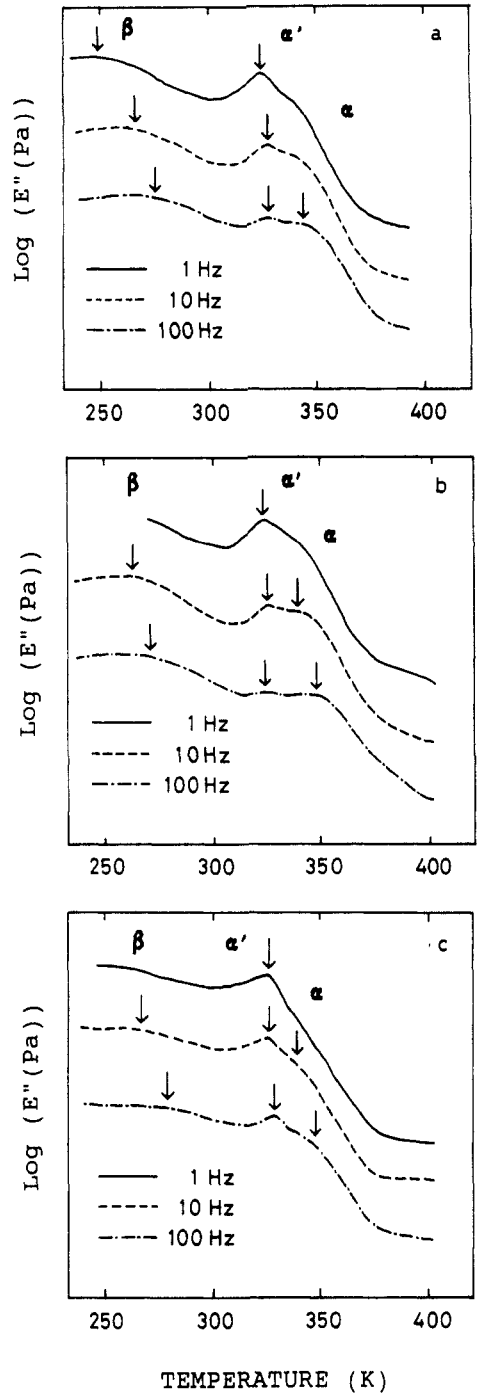

Figure 4. Temperature dependence of dynamic loss modulus (E'') at a few frequencies for (a) EMAA-0.6Na, (b) EMAA-0.6Li, and (c) EMAA-0.6Mg.

where T_i was obtained by differential scanning calorimetry (DSC) as described in the Experimental Section. You can see that the T_i of all the EMAA ionomers agree with this α' peak temperature. This study has revealed that the α' peak represents a first-order transition. Therefore, it is proposed the observation of the α' peak should be clear evidence that the order–disorder transition exists in the ionic clusters. There is controversy about the assignment of the DSC T_i peak and the existence of the order–disorder transition. It is known that even polyethylene exhibits a second crystallization upon annealing at elevated temperatures.[30,31] However, our assignment seems to be more reasonable from the following experiments: No observable increase in the polyethylene crystallinity of an Na salt of the ethylene ionomer was detected by the X-ray diffraction study during aging.[2] A water-absorbed EMAA-0.9Na showed significant decreases in the peak area and

Table I
α' Peak Temperature of the Loss Modulus (E'') for EMAA Ionomers as a Function of the Frequency

ionomer description	α' peak temp (K)		
	1 Hz	10 Hz	100 Hz
EMAA-0.4Na	318	321	322
EMAA-0.6Na	324	326	327
EMAA-0.8Na	330	330	333
EMAA-0.9Zn	325	325	326
EMAA-0.6Li	323	324	324
EMAA-0.6Mg	325	326	326

peak temperature of T_i, but minimal changes for T_m.[32] Moreover, changes in the environment of neutralizing cations at T_i were evidenced by the UV[33] and IR[34] studies on EMAA-0.6Co, the far-IR study[35] on the complex of EMAA-0.6Zn with bis(aminomethyl)cyclohexane, and the

Table II
Order–Disorder Transition Temperatures of the Ionic Clusters (T_i) and the Mechanical and Dielectric Relaxation Temperatures[a] (T_{max}), Including the Mechanical α' Peak Temperature

ionomer description	DSC T_i (K)	mechanical T_{max} (K)				dielectric T_{max} (K)		
		α	α'	β'	β	α	β'	β
EMAA	–[b]	–	–	292	–	–	315	–
EMAA-0.2Na	318	–	–	308	–	–	326	–
EMAA-0.4Na	321	–	321	–	261	333	–	285
EMAA-0.6Na	323	–	326	–	265	344	–	294
EMAA-0.8Na	323	342	330	–	262	353	–	282
EMAA-0.9Na	327	343	329	–	263	360	–	285
EMAA-0.4Zn	321	–	–	298	–	–	328	–
EMAA-0.6Zn	323	–	–	313	–	–	336	–
EMAA-0.8Zn	325	–	322	–	261			
EMAA-0.9Zn	326	–	325	–	264			
EMAA-0.6Li		337	324	–	263			
EMAA-0.6Mg	330	345	326	–	263	366	–	306

[a] Temperatures of the mechanical and dielectric relaxations were measured at 10 Hz and 1 kHz, respectively. [b] –, not determined.

Table III
Activation Enthalpy (ΔH) of the Mechanical and Dielectric Relaxations of EMAA Ionomers

ionomer description	mechanical ΔH (kJ/mol)				dielectric ΔH (kJ/mol)			
	α	β'	β	γ	α	β'	β	γ
EMAA	–[a]	246	–		–	251	–	
EMAA-0.2Na	–	272	–		–	348	–	
EMAA-0.4Na	–	–	115	35	396	–	67	40
EMAA-0.6Na	–	–	101	51	301	–	66	42
EMAA-0.8Na	327	–	144	32	328	–	85	42
EMAA-0.4Zn	–	319	–	39	–	232	–	48
EMAA-0.6Zn	–	704	–	41	–	304	–	50
EMAA-0.9Zn	–	–	113	48				
EMAA-0.6Li	274	–	137	42				
EMAA-0.6Mg	364	–	171	40	163	–	105	40

[a] –, not determined.

ESR study[17] on EMAA-0.99Mn. We can also refer to the SAXS[36] and extended X-ray absorption fine structure (EXAFS)[37,38] studies, which predict that there exists a fairly well-ordered structure within the ionic clusters.

In our dielectric relaxation study,[14] highly neutralized Na ionomers exhibited abrupt changes at ~330 K in dielectric constant (ϵ') and the loss (ϵ''). These abrupt changes were frequency-independent, and the temperature exhibiting these changes coincided with the T_i determined by DSC. In Figure 4, the highly neutralized EMAA ionomers exhibiting the α' peak showed another relaxation at ~10 K higher than the α' peak temperature. We assign it to the α relaxation because extrapolation of its Arrhenius plot (relaxation temperatures versus frequencies) agrees with the Arrhenius plot of the dielectric α relaxation. This α relaxation is ascribed to a micro-Brownian molecular motion of long hydrocarbon chains attached to the ionic clusters. At room temperature, this motion should be hindered by the ordered ionic clusters acting as rigid cross-links, and above T_i, the disordered ionic clusters should become soft enough to participate in this motion. The E'' curves indicate that increasing frequency tends to depress the α' peak and to increase the α relaxation peak. The dielectric measurement usually uses higher frequencies over the mechanical measurement. Therefore, we assume that, in the dielectric measurement, the α' peak corresponding to the order–disorder transition may be completely depressed and observed as an abrupt change due to high frequencies.

It is interesting to speculate on why only the phase-separated EMAA ionomers presented a first-order transition as the α' peak. A plausible explanation is as follows. DSC analysis on EMAA ionomers shows an endothermic peak, assigned to T_i, regardless of the degree of neutralization (Table II and refs 20, 25, and 26). Perhaps this indicates ordered structure exists in ionic aggregates even when the neutralization is low. Increasing neutralization is known to increase the number of associated or interacted cations, reported in the ESR studies for Mn(II) ionomers of EMAA.[15-17] This probably means that increasing neutralization increases the number and size of the ionic aggregates. At high levels of neutralization, the ionic aggregates should be well-developed and a first-order transition of such ionic aggregates should become clear enough to be observed by the dynamic mechanical measurement. In addition, microphase separation of the ionic cluster phase may help to distinguish the first-order transition from the molecular motions in the polymer matrix phase.

Table III summarizes the activation enthalpy (ΔH) of the mechanical and dielectric relaxations for EMAA ionomers, calculated from the Arrhenius plots of the relaxation temperatures versus frequencies. In regard to EMAA ionomers exhibiting α relaxation (EMAA-0.6Li, EMAA-0.6Mg, EMAA-0.4Na, EMAA-0.6Na, EMAA-0.8Na, EMAA-0.9Zn), the ΔH of the mechanical α relaxation was between 270 and 370 kJ/mol, which was almost identical with that of the dielectric α relaxation (160–400 kJ/mol). This result is compatible with our speculation that the mechanical α relaxation corresponds to the dielectric α relaxation, as already discussed. The ΔH of the mechanical β relaxation was always 1.5–1.7 times as large as that of the dielectric β relaxation. The ΔH of the mechanical β' relaxation was also 1.4–2.5 times as large as that of the dielectric β' relaxation for EMAA-0.4Zn and EMAA-0.6Zn, but the ΔH of the β' relaxation for EMAA showed good agreement between the two measurements. The reason for this discrepancy is uncertain at the present time. It might originate from different frequencies employed by each measurement or different measurement

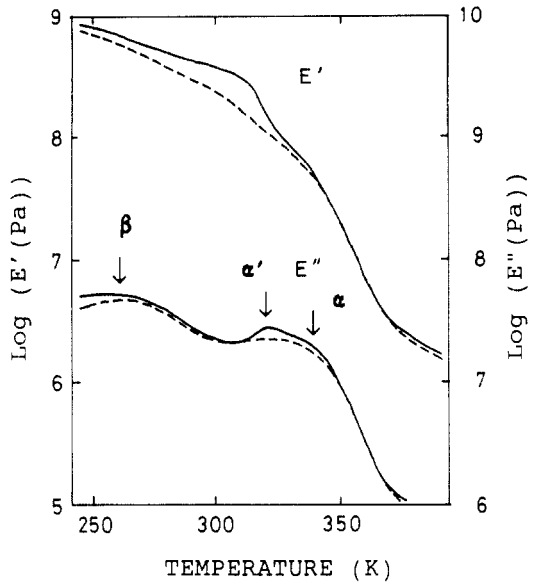

Figure 5. Temperature dependence of dynamic storage modulus (E') and loss modulus (E'') at 10 Hz for EMAA-0.6Na aged at +23 (—) and −5 °C (- - -) for 3 days.

methods. The ΔH of the γ relaxation was between 30 and 50 kJ/mol and was apparently independent of the type of metal cations, neutralization degrees, and measurement methods. This strongly suggests that the ionic aggregates or the carboxylic acid dimers do not affect a local molecular motion of the short segments in the amorphous phases.

In order to examine the effects of aging and temperature on the relaxation behavior of ethylene ionomers, EMAA-0.6Na was compression-molded, quenched, and aged at different temperatures (23 and −5 °C) for 3 days. The E' and E'' curves for these samples are shown in Figure 5. Both samples exhibited α and β relaxations, indicating that microphase separation of the ionic cluster phase and the matrix phase occurs regardless of the aging temperatures. However, the α' peak, representing the order–disorder transition, is seen only for the sample aged at 23 °C. This indicates that the ionic cluster phase can gradually form some ordered structure during aging at 23 °C, but they should stay disordered when they are aged at low temperatures, and therefore, the mobility of long-chain segments attached to the ionic clusters is restricted. Weiss et al.[39] found in their ESR study that the aggregation of ionic groups of sulfonated polystyrene ionomers begins above the T_g of the polymer matrix. This finding also supports not only the formation of ionic aggregates but also that rearrangement of their inside structure requires segmental motions of backbone chains. Generally, the T_g of the polymer matrix of ethylene ionomers is about −30 to −5 °C and that of sulfonated polystyrene ionomers is near 100 °C. This difference may be one of the reasons why an order–disorder transition of the ionic clusters is obvious for aged ethylene ionomers. Other factors that influence the formation of some ordered structure within the ionic clusters might include (a) steric hindrance of short-chain branches and (b) polarity difference between ionic groups and backbone chains. Studies on the polarity effects are in progress on the present ethylene ionomer system, and results will be reported elsewhere in the near future.

Conclusions

Our dynamic mechanical relaxation study of EMAA ionomers furnishes the following new findings:

(1) It is revealed that the Zn ionomer forms regions of microphase-separated ionic clusters at a neutralization of 80% or higher. This finding also allows us to predict that, at much higher neutralization degrees, other transition metal ionomers probably form an ionic cluster phase that is separated from the hydrocarbon matrix.

(2) The α' peak appears around 325 K with the ionic cluster formation, and the temperature exhibiting this peak proves to be independent of frequency. Order–disorder transition temperatures of ionic clusters of EMAA ionomers agreed with this α' peak temperature. Therefore, it is proposed that the α' peak is regarded as a first-order transition and represents the existence of the order–disorder transition in the ionic clusters.

(3) The highly neutralized EMAA ionomers shows the α relaxation at ~10 K higher than the α' peak temperature. This relaxation is assigned to a micro-Brownian molecular motion of long hydrocarbon chains attached to the ionic clusters. This motion begins above T_i, where the disordered ionic clusters become soft enough to participate in this motion.

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