Dielectric Relaxations of Ethylene–Acrylic Acid and Styrene–Methacrylic Acid Copolymers and Their Sodium Salts

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ABSTRACT: Dielectric constant and the loss for ethylene–acrylic acid copolymer (9.3 mol% AA) and its sodium salts with various degrees of neutralization (0–100%) were measured in the temperature range from -130 to 80°C at different frequencies. Two dielectric relaxations were observed, the β' relaxation due to a micro-Brownian motion of segments near 40°C and the γ relaxation due to a local molecular motion of short segments near -100°C . The dielectric increments, $\Delta\epsilon$, for the two relaxations were calculated from Cole–Cole plots, and it was found that the values of $\Delta\epsilon$ increased proportionally to the increase in the degree of neutralization up to 20% and decreased rapidly from about 30%. Therefore, it was concluded that ion-clustering may occur in the copolymers at a higher degree of neutralization above 30%, by postulating that the polar groups for the two relaxations are COONa groups which are not incorporated into the ion-clusters. Furthermore, this conclusion was supported by the change in other relaxation parameters, such as the relaxation temperature and the Arrhenius plots, with the degree of neutralization. Dielectric measurements were also made on styrene–methacrylic acid (4.4 mol% MAA) and the sodium salts which do not form the ion-clusters. The γ relaxation was observed near -25°C and was attributed to a cooperative molecular motion between segments including COOH and those including COONa.

KEY WORDS Ethylene–Acrylic Acid / Styrene–Methacrylic Acid / Sodium Salts / Degree of Neutralization / Dielectric Relaxation / Ion-Cluster /

Recently, the structure and molecular motion of carboxylic acid containing copolymers and their metal salts, typical ionomers, have been studied by many workers,^{1–4} with an interest towards the existence of ion-clustering which may be produced by a phase separation of metal salts in a polymer. Much evidence on the existence of ion-clustering have come mainly from small angle X-ray scattering and mechanical properties, and also from various other methods such as electronmicroscopy, and dielectric measurement. Small-angle X-ray scattering can indicate directly the existence of ion-clusterings, and gives their size and the distance between clusters. From dynamic mechanical measurements, the existence of ion-clustering is

indicated by molecular motion of polymer chains. For example, the β' relaxation due to a micro-Brownian motion above T_g is depressed markedly at a critical concentration of metal salts in polymers and other relaxations, such as the β and α relaxations, appear.^{5–9} These extensive past works support the existence of the ion aggregation of metal salts such as ion-clustering or multiplet.

The dielectric method proves also useful in clarifying the structure and molecular motion of ionomers. Since this method detects molecular motion through the polar groups, carboxylic acid and its metal salts which participate directly in ion-cluster formation, a new interpretation on structure and molecular motion of ionomer can be given by

dielectric measurements. There are, however, only a few papers on dielectric relaxations of metal carboxylate containing copolymers.¹⁰⁻¹² Read, Carter, Connor and MacKnight,¹⁰ and Phillips and MacKnight¹¹ have studied the dielectric relaxations of sodium salts of ethylene-methacrylic acid copolymers (E-MAA), and those of sodium, calcium, and lithium salts of E-MAA, respectively. They observed β' and γ relaxations above and below T_g , respectively. The β' relaxation disappears above a critical concentration of metal salts at which ion-clustering begins to form; the β and α relaxations appear and may be closely related to the structure of ion-clusters. Recently, Hodge and Eisenberg¹² reported dielectric relaxations of styrene-sodium methacrylate copolymers and suggested the existence of ion-clusters at a higher ion concentration.

In this paper, we present the dielectric properties of ethylene-acrylic acid copolymers (E-AA) and styrene-methacrylic acid copolymers (S-MAA), and their sodium salts. Some evidence for the existence of ion-clusters in the sodium salts is proposed on the basis of an examination of molecular motion through dielectric relaxations and an estimation of the number of polar groups responsible for the dielectric relaxations.

EXPERIMENTAL

S-MMA was prepared by bulk copolymerization. Styrene and methacrylic acid (MAA) were dried over barium oxide and calcium sulfate, respectively, and distilled fractionally under reduced pressure in a nitrogen atmosphere just prior to use. Bulk copolymerization was carried out at 80°C, using benzoyl peroxide as the initiator in a pyrex tube in which a mixture of styrene (370 ml) and MAA (10 ml) was sealed under vacuum. The copolymer dissolved in benzene was purified by reprecipitations in methanol at 5°C. The copolymer purified was completely dried in a vacuum desiccator. The amount of MAA in the copolymer was determined to be 4.4 mol% by titrating 2 wt% copolymer in benzene with a standard NaOH in methanol with phenolphthalein indicator. The intrinsic viscosity of S-MAA at 25°C was 1.2×10^2 ml g⁻¹ in benzene, and the apparent molecular weight was estimated to be approximately 4×10^5 .^{13,14} The E-AA's used here are EAA9300 and EAA9500 from Union Carbide Co. The acrylic acid (AA) contents in

Table I. List of samples

Sample	Degree of neutralization	Density at 30°C
	%	g ml ⁻¹
S-MAA ^a	0	1.064
S-MAA-Na10	10	1.063
S-MAA-Na20	20	
S-MAA-Na50	50	
S-MAA-Na100	100	1.064
E-AA9 ^b	0	0.954
E-AA9-Na10	10	0.963
E-AA9-Na20	20	0.975
E-AA9-Na30	30	0.985
E-AA9-Na50	50	
E-AA9-Na100	100	1.006
E-AA8 ^c	0	0.946

^a Styrene-methacrylic acid copolymer (mol% of methacrylic acid is 4.4).

^b Ethylene-acrylic acid polymer (mol% of acrylic acid is 9.3).

^c Ethylene-acrylic acid copolymer (mol% of acrylic acid is 8.2).

EAA9300 and EAA9500 were determined to be 9.3 and 8.2 mol%, respectively, by titrating E-AA in tetrahydrofuran with 0.1 *N* standard NaOH with phenolphthalein indicator. Both S-MAA and E-AA are considered to be random copolymers. The sodium salts of S-MAA were prepared by adding dropwise standard NaOH in benzene-methanol (9:1) to 2 wt% S-MAA in benzene-methanol (9:1). The salts of E-AA were obtained by adding dropwise saturated NaOH in tetrahydrofuran-methanol (1:1) to E-AA in tetrahydrofuran at about 64°C. The degree of neutralization, x , was also confirmed by infrared (IR) spectra.¹⁵⁻¹⁹ The film samples for dielectric measurements were made by compression molding under a pressure of about 50 kg cm⁻² at 150–180°C for the S-MAA samples and at 80–90°C for the E-AA samples, respectively. The sample thickness was approximately 0.5 mm. The samples used are listed in Table I. Neither the E-AA samples¹⁹ nor the S-MAA samples⁴ were crystalline.

Dielectric constant, ϵ' , and the loss, ϵ'' , were measured with a transformer bridge in the frequency range 30 Hz to 30 kHz. The three-terminal electrode system was used as described previously.²⁰ Aluminium was carefully deposited in

vacuo on the surface of the film to ensure electrical contact between electrode and sample. The density at 30°C was measured by a buoyancy method with methanol for the S-MAA samples and with benzene for the E-AA samples.

RESULTS

The temperature dependence of ϵ' and ϵ'' for E-AA9 at different frequencies is shown in Figures 1(a) and (b), respectively. Two dielectric relaxations, β' and γ were observed near 40 and -100°C , respectively. Figure 2 shows the temperature dependence of ϵ'' for E-AA9-Na30 at different frequencies. The two relaxations are also observed, but the β' relaxation occurs in a temperature range higher than that of E-AA9 in Figure 1. Variation of the two relaxations with x is visualized by Figure 3

Figure 1. Temperature dependence of (a) dielectric constant, ϵ' , and (b) the loss, ϵ'' , for E-AA9 at different frequencies.

which illustrates the temperature dependence of ϵ'' at 3 kHz for various samples. In the β' relaxation, the relaxation temperature, $T_{\max}$, does not depend on x below 20%, but the dielectric loss maximum, $\epsilon''_{\max}$, increases with an increase in x . On the other hand, above 30%, $T_{\max}$ increases with increasing x and $\epsilon''_{\max}$ is depressed, and then the β relaxation appears near 10°C . The β' relaxation for E-AA9-Na100 was not observed, since the apparent dielectric loss due to ionic conduction²¹ becomes predominant near -50°C . In the γ relaxation, $T_{\max}$ is independent of x , but $\epsilon''_{\max}$ depends somewhat on x , as shown in detailed in Figure 4. Arrhenius plots for the β' relaxation in

Figure 2. Temperature dependence of dielectric loss, ϵ'' , for E-AA9-Na30 at different frequencies.

Figure 3. Temperature dependence of dielectric loss, ϵ'' , in various sodium salts of the E-AA copolymer at 3 kHz: (○), E-AA9; (◐), E-AA9-Na10; (◑), E-AA9-Na20; (⊖), E-AA9-Na30; (⊕), E-AA9-Na50; (●), E-AA9-Na100; (⊙), E-AA8.

Figure 4. Temperature dependence of dielectric loss, ϵ'' , for γ relaxation in various sodium salts of E-AA9 at 3 kHz: (○), E-AA9; (◐), E-AA9-Na10; (◑), E-AA9-Na20; (⊖), E-AA9-Na30; (⦿), E-AA9-Na50; (◉), E-AA9-Na100.

Figure 5. Plots of logarithm of frequency, $\log f$, against reciprocal of relaxation temperature, $1/T_{\max}$, for β' relaxation in various sodium salts of E-AA9: (○), E-AA9; (◐), E-AA9-Na10; (◑), E-AA9-Na20; (⊖), E-AA9-Na30; (⦿), E-AA9-Na50; (◉), E-AA8.

Table II. Relaxation parameters for β' relaxation in various sodium salts of the E-AA copolymer

Sample	$T_{\max}$ at 3 kHz	ΔH	ΔS	T_0	$B (10)^2$	$\log f_0$	Type of relaxation
	K	kcal mol ⁻¹	eu	K			
E-AA9	318	57	139	260	4.1	11	β' , WLF
E-AA9-Na10	319	55	133	272	2.7	9.3	β' , WLF
E-AA9-Na20	319	61	151	275	2.5	9.2	β' , WLF
E-AA9-Na30	338	81	201				β' , Arrhenius
E-AA9-Na50	295	9	10				β , Arrhenius
E-AA8	311	49	118	245	4.8	11	β' , Arrhenius

various sodium salts of E-AA9 are shown in Figure 5. In the sample with less than 20% of x , the plots exhibit the so-called WLF type,²² but become a straight line above 30%. The relaxation parameters for the β' relaxation are listed in Table II. The following modified Arrhenius equation was used to calculate the activation enthalpy (ΔH) and the enthalpy (ΔS) for the β' relaxations, the Arrhenius plots of which indicate the WLF type.

$$\log f = \log f_0 - B/(T - T_0) \quad (1)$$

Here, T_0 is the temperature at which the β' relaxation freezes, and f_0 and B are constant. T_0 correspond to T_g , although T_0 is usually smaller by several degrees than T_g . The values of T_0 increased with increasing x as shown in Table II, and this is fairly well consistent with the results reported by several authors.^{4,12,18} The Arrhenius plots for the γ

relaxations are shown in Figure 6. The relaxation parameters obtained are listed in Table III. The values of ΔH for the β' relaxation are between 50 and 80 kcal mol⁻¹ and those for the γ relaxation are around 9 kcal mol⁻¹. These values suggest that the β' relaxation is due to the micro-Brownian molecular motion of main chain and that the γ relaxation is caused by the local molecular motion of short segments.

Figures 7 and 8 show the temperature dependence of ϵ'' at various frequencies for S-MAA and S-MAA-Na100, respectively. The γ relaxations are observed between -100 and 0°C for both samples, and a rapid increase in ϵ'' is shown above about 100°C in S-MAA. This increase in ϵ'' at high temperatures is probably related to the β' relaxation shown by Hodge and Eisenberg,¹² but since the sample flowed in a higher temperature region

Figure 6. Plots of logarithm of frequency, $\log f$, against reciprocal of relaxation temperature, $1/T_{\max}$, for γ relaxation in various sodium salts of E-AA copolymer: (○), E-AA9; (◐), E-AA9-Na10; (◑), E-AA9-Na20; (⊖), E-AA9-Na30; (◒), E-AA9-Na50; (⊕), E-AA8.

Table III. Relaxation parameters for γ relaxation in various sodium salts of the E-AA and S-MAA copolymers

Sample	$T_{\max}$ at 3 kHz	ΔH	ΔS
	K	kcal mol ⁻¹	eu
E-AA9	171	8.0	9
E-AA9-Na10	176	8.7	11
E-AA9-Na20	179	8.6	10
E-AA9-Na30	177	9.3	15
E-AA9-Na50	174	9.0	14
E-AA8	178	8.6	11
S-MAA	232	10.5	6
S-MAA-Na10	243	11.2	8
S-MAA-Na20	246	12.5	12
S-MAA-Na50	258	10.9	4
S-MAA-Na100	257	11.1	5

above 100°C, the β' relaxation could not be observed in this experiment. The increase in ϵ'' at high temperatures in S-MAA-Na100 may be due to an ionic conduction, depending on the frequency. Figure 9 shows the temperature dependence of ϵ'' for various sodium salts of S-MAA at 3 kHz. The values of $\epsilon''_{\max}$ decrease gradually with an increase in x up to 20%, but increase considerably above 50%. The values of $T_{\max}$ increase somewhat with increasing x up to 20%, and remain constant above 50%.

Figure 7. Temperature dependence of dielectric loss, ϵ'' , for S-MAA at different frequencies.

Figure 8. Temperature dependence of dielectric loss, ϵ'' , for S-MMA-Na100 at different frequencies.

Figure 9. Temperature dependence of dielectric loss, ϵ'' , for γ relaxation in various sodium salts of S-MAA at 3 kHz: (○), S-MAA; (◐), S-MAA-Na10; (◑), S-MMA-Na20; (⊖), S-MAA-Na50, (⊕), S-MAA-Na100.

Since the sodium salts used here do not form any ion-clusters,^{1,9} the above dielectric results seem to be closely related to the molecular motion of styrene and acrylic acid/sodium acrylate sequences, as will be discussed in the next section. Figure 10 shows the Arrhenius plots for the γ relaxations. The activation parameters obtained are listed in Table III.

Figure 10. Plots of logarithm of frequency, $\log f$, against reciprocal of relaxation temperature, $1/T_{\max}$, for γ relaxation in various sodium salts of S-MAA: (○), S-MAA; (◐), S-MAA-Na10; (●), S-MAA-Na20; (◑), S-MAA-Na50, (◐), S-MAA-Na100.

DISCUSSION

Dielectric Relaxation in Sodium Salt of E-AA Copolymer

The effect of neutralization by sodium on the β' relaxation in the E-AA copolymers is summarized as follows: (a) the values of $T_{\max}$ remained constant up to 20% of x and increased rapidly with an increase in x above 30%; (b) the values of $\epsilon''_{\max}$ increased with increasing x below 20%, but were depressed above 30% with the appearance of the β relaxation; (c) the Arrhenius plots exhibited the WLF type below 20% and gave a straight line above 30%. The results (a) and (b) agree with the mechanical and dielectric results of many workers¹⁻⁴ which have been proposed as evidence for ion-cluster formation. The results (c) also support the existence of ion-clusters above 30%. It has been postulated that the average number of chain carbon atoms in segments related to the micro-Brownian molecular motion is usually about 100–200.²³ Therefore, when the number of chain carbon atoms between ion-clusters is about 100, the cross-linking effect due to ion-clusters might begin to affect the micro-Brownian motion, which gives the straight line in the Arrhenius plots. Since the average number of chain carbon atoms between sodium carboxylates in the copolymer is estimated to be about 70 at 30% of x , the result (c) suggests the existence of ion-clusters in the copolymers with x

Table IV. Values of β , ϵ_0 , ϵ_∞ , $\Delta\epsilon$, and $N\mu^2$ for β' relaxation in various sodium salts of the E-AA copolymer

Sample	T K	β	ϵ_0	ϵ_∞	$\Delta\epsilon$	$N\mu^2$ (10^{-16}) erg
E-AA9	314	0.309	2.7027	2.5778	0.1249	5.47
	318	0.356	2.7100	2.5910	0.1190	5.25
	322	0.336	2.7179	2.5961	0.1218	5.42
E-AA9-Na10	315	0.278	3.251	2.743	0.508	18.39
	319	0.286	3.193	2.713	0.464	18.78
	324	0.289	3.176	2.699	0.477	19.73
E-AA9-Na20	315	0.278	3.585	2.780	0.805	30.45
	319	0.269	3.586	2.760	0.826	31.83
	323	0.269	3.590	2.755	0.835	32.66
E-AA9-Na30	335	0.263	3.226	2.702	0.524	22.28
	338	0.258	3.187	2.684	0.505	21.86
E-AA8	308	0.293	2.6650	2.5520	0.1130	4.91
	311	0.300	2.6710	2.5630	0.1080	4.72
	317	0.304	2.6814	2.5665	0.1149	5.11

above 30%. It has been pointed out that the β relaxation may be caused by the molecular motion of short segments between ion-clusters.¹⁰ In fact, in this work, the β relaxation begins to appear above 30% of x which begins to form the ion-clusters. Furthermore, the value of ΔH is 9 kcal mol⁻¹ which is much smaller than that of the β' relaxation, and the value of $T_{\max}$ is between $T_{\max}$ of the γ relaxation and that of the β' relaxation.

The static dielectric constant, ϵ_0 , the limiting dielectric constant, ϵ_∞ , and the dielectric increment, $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$, for the β' relaxation were calculated by using the Cole-Cole plots.²⁴ Table IV gives the values of ϵ_0 , ϵ_∞ , $\Delta\epsilon$, and $N\mu^2$ for the β' relaxation. Here, β is the Cole-Cole distribution parameter. N and μ are the number of dipolar group per cm³ and the dipole moment of each group, respectively. $N\mu^2$ was calculated by the Onsager equation,²⁵

$$N\mu^2 = (3kT/4\pi)[(3\epsilon_0 + \epsilon_\infty)/3\epsilon_0][3/(\epsilon_\infty + 2)]^2(\epsilon_0 - \epsilon_\infty) \quad (2)$$

The values of ϵ_0 , ϵ_∞ , and $\Delta\epsilon$ were also obtained from both the area under the $\epsilon''-1/T$ plots and the values of ΔH ,¹⁰ and are consistent with those obtained by the Cole-Cole plots within a difference of $\pm 5\%$.

Plots of $\Delta\epsilon$ and $T_{\max}$ versus x are shown in Figure 11. The values of $\Delta\epsilon$ increase proportionally with increasing x up to 20% and then decrease from 30%—0.1190 at 0% (E-AA9) and 0.826 at 20%. Therefore, this polar nature may be due mostly to COONa groups, although COOH groups also contribute to the relaxation. Thus, we can say that the values of $\Delta\epsilon$ are proportional to the number of monomeric COONa groups in a unit volume not included in the ion-clusters. Actually, the COONa groups included in the ion-clusters must be too rigid to contribute to the β' relaxation. Therefore, the above change of $\Delta\epsilon$ against x suggests that the ion-clustering begins to take place from about 30% of x . However, since the value of $\Delta\epsilon$ is 0.505 at 30% of x which is larger than that of E-AA9, it is concluded that not all COONa groups can be incorporated in the ion-clusters. The number of monomeric COONa groups not incorporated into ion-clusters may be governed by the flexibility of the copolymer chain and the solubility of sodium salts toward the copolymer matrix.

In the past work,⁴ the γ relaxation of the ionomer was excluded from the main subject of study, since it

Figure 11. Plots of dielectric increment, $\Delta\epsilon$, and relaxation temperature, $T_{\max}$, against degree of neutralization in β' relaxation of E-AA9 at 3 kHz.

is related to the local molecular motion of short segments between the ion-clusters and is not sensitive to the ion-cluster formation. Indeed, McKenna, Kajiyama, and MacKnight²⁶ indicated mechanically that the magnitude and the relaxation time of the γ relaxation do not undergo any change by either the ionic species (Na, Li, and Ca) or the concentration of metal salts in the S-MAA copolymers. However, we believe that a precise and detailed observation of the γ relaxation by the dielectric method can serve to clarify the structure and molecular motion in ionomers since the magnitude of the relaxation associated with polar COONa groups not included in ion-clusters can be obtained only by the dielectric method. A comparison of the γ relaxation between various sodium salts in the E-AA copolymer is shown in Figure 4. The values of $T_{\max}$ do not change much with x , but the magnitude of the γ relaxation depends apparently on x . Table V gives the values of ϵ_0 , $\Delta\epsilon$, and $N\mu^2$ for the γ relaxation in various sodium salts of E-AA. Plots of $\Delta\epsilon$ and $T_{\max}$ at 3 kHz versus x are shown in Figure 12. The values of $\Delta\epsilon$ increase proportionally with increasing x up to 20% and decrease above 30%. Since the sodium salts do not aggregate at low ion concentrations, the number of polar COONa groups for the γ relaxation increases with an increase in x . But the number of polar group decreases as a result of the formation of ion-clusters at higher ion concentrations. Consequently, we can state, on the basis of the number of polar groups, that the dielectric method provides new evidence for the existence of ion-clusters in ionomers.

Table V. Values of β , ϵ_0 , ϵ_∞ , $\Delta\epsilon$, and $N\mu^2$ for γ relaxation in various sodium salts of the E-AA copolymer

Sample	T	β	ϵ_0	ϵ_∞	$\Delta\epsilon$	$N\mu^2$ (10^{-16})
	K					erg
E-AA9	165	0.294	2.6660	2.6006	0.0654	1.50
	171	0.278	2.6803	2.6070	0.0773	1.74
	181	0.316	2.6980	2.6160	0.0820	2.05
E-AA9-Na10	171	0.300	2.7475	2.6456	0.1019	2.26
	176	0.311	2.7482	2.6428	0.1054	2.41
	185	0.320	2.7488	2.6424	0.1064	2.56
E-AA9-Na20	168	0.273	2.7790	2.6513	0.1277	2.90
	179	0.289	2.7810	2.6526	0.1284	3.10
	186	0.305	2.7832	2.6495	0.1337	3.36
E-AA9-Na30	169	0.256	2.8780	2.7658	0.1122	2.44
	177	0.258	2.8791	2.7610	0.1181	2.70
	186	0.278	2.8805	2.7600	0.1205	2.89
E-AA9-Na50	168	0.263	2.8610	2.7720	0.0890	1.93
	174	0.267	2.8575	2.7660	0.0915	2.07
	182	0.278	2.8556	2.7635	0.0921	2.17
E-AA8	169	0.283	2.6715	2.6082	0.0633	1.48
	176	0.302	2.6800	2.6150	0.0650	1.58
	185	0.316	2.6890	2.6192	0.0698	1.78

Figure 12. Plots of dielectric increment, $\Delta\epsilon$, and relaxation temperature, $T_{\max}$, against degree of neutralization in γ relaxation of E-AA9 and S-MAA at 3 kHz: ($\circ$), plots of the E-AA9 samples; ($\triangle$), plots of the S-MAA samples.

Dielectric Relaxation in Sodium Salts of S-MAA Copolymer

In the sodium salts of S-MAA (4.4 mol% MAA) which produce no ion-cluster, the magnitude and relaxation time for the γ relaxation undergo a clear change with x . Although the value of $\epsilon''_{\max}$ decreases gradually with an increase in x up to 20%, but considerably increases with an increase in x above 50% (see Figure 9), the values of $\Delta\epsilon$ are not very

much dependent on x , as shown in Figure 12. This means that the distribution of the relaxation time becomes wider with an increase in x at the lower degree of neutralization below 50% and narrower at a higher degree of neutralization above 50%. The values of $T_{\max}$ at 3 kHz increase with increasing x up to 50% and become constant above 50%. The interpretation of these results is given as follows: (a) at low degrees of neutralization below 50%, the

model of local molecular motion is probably governed by the molecular motion of the S-MAA sequence which may be perturbed by COONa groups. Therefore, the distribution of the relaxation time becomes wider with increasing x and the value of $T_{\max}$ increases; (b) at high degrees of neutralization above 50%, the γ relaxation is probably dominated only by the molecular motion of sodium salts of S-MAA. This leads to a narrowing of the distribution of the relaxation time. Consequently, the γ relaxation occurs as a cooperative motion between the short segments including MAA and the segments including the sodium salts.

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