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Formation of Ionic Crystallites and Its Effect on the Modulus of Ethylene Ionomers

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ABSTRACT: Modulus (stiffness), thermal properties by DSC, and dynamic mechanical properties were studied for Zn(II) salts, complex Zn(II) salts with 1,3-bis(aminomethyl)cyclohexane (BAC), and BAC salts of ethylene–methacrylic acid copolymer (EMAA). Modulus outstandingly increased as the degree of neutralization increased, and especially it was observed that the modulus for the mold sample cooled down from melt gradually increases with aging at room temperature. The increase of modulus with aging was explained well by the formation and development of ionic crystallites in ionic clusters in a relaxation process. The present work found that the dramatic increase of modulus on ionomerization originates in the rigidity and cross-linking effect of the ionic crystallites and the formation and nature of the ionic crystallites depending on the type of salts predominantly governing the stiffness of ethylene ionomers.

Introduction

Ionomers are polymers containing ionic salt groups attached pendantly to hydrophobic organic backbone chains. It is widely recognized that introduction of small amounts of ionic groups onto hydrocarbon backbone chains results in substantial changes in physical properties such as modulus and hardness, in particular.[1,2] These changes result, to a great extent, from the formation of microphase-separated ionic domains (ionic clusters) in the polymer matrix. The presence of ionic clusters have been evidenced by various techniques such as small-angle X-ray scattering (SAXS), mechanical and dielectric measurements, electron microscopy, etc. Several structural models for ionic clusters have been proposed.[1-5] However, despite much research effort on the morphological nature of ionic clusters, not one convincing conclusion has yet been drawn. Also, not yet fully elucidated is the mechanism underlying the above-mentioned property changes associated with ionomerization.

Recently, a new type of ionomer in which the ionic group is the complex Zn(II) salts of ethylene–methacrylic acid copolymer (EMAA) with 1,3-bis(aminomethyl)cyclohexane [1,3-$(H_2NCH_2)_2C_6H_{10}$] (BAC) has been developed in our laboratory. Dielectric and SAXS analyses of the complex Zn(II) salts showed that the addition of BAC to the Zn(II) salt promotes the formation of ionic clusters.[6,7] Furthermore, our thermal expansion, wide-angle X-ray scattering, and differential scanning calorimetric studies of the ionomers indicated the existence of an order–disorder transition inside the ionic clusters (melting of ionic crystallites) near 50 °C, below the melting point of the polyethylene crystalline region (T_m = 90 °C). The transition inside the ionic cluster showed a thermal hysteresis, which was explained by a relaxation process from the ordered state to the disordered state, as shown in Figure 1.[8,9] Formation of ionic crystallites (order–disorder transition) should faithfully influence various physical properties of ionomers.

The purpose of the present work is to clarify how the formation and development of the ionic crystallites affect the modulus of ionomers. The chemical structures of the samples used here are listed in Table I.

Experimental Section

Materials. The samples used are represented hereafter as EMAA-*x*Zn-*y*BAC, where EMAA is ethylene–methacrylic acid copolymer, *x* is the degree of neutralization by Zn, and *y* is the equivalent molar ratio of BAC to carboxylic acid (the degree of neutralization by BAC) on the basis that BAC is divalent. EMAA is ACR-1560 of Du Pont–Mitsui Polychemicals Co. Ltd., where the methacrylic acid content is 5.4 mol %. BAC was purchased from Mitsubishi Gas Chemicals Co. Ltd., where the melting point is below −70 °C and boiling point is 220 °C. The Zn(II) and BAC salts of EMAA were prepared by means of a melt reaction of EMAA and zinc oxide/BAC in an extruder at 150–280 °C. The complex Zn(II) salts with BAC were synthesized from the mixture of the Zn(II) salts and BAC under melt by the same procedure described above. The pellet samples obtained were re-formed into 3 mm thick sheets by compression molding at 5 MPa and 160 °C and cooled to room temperature at a cooling rate of about 30 °C/min by circulation of chilled water in the mold jacket.

The sheet samples were stored at 23 °C in dry nitrogen atmosphere or in air with 50% relative humidity. The measurements were made for the samples at certain aging durations. The aging durations were 0, 1, 3, 9, and 38 days after molding. Aging for 0 day means 3–5 h of aging after molding.

Measurements. Differential scanning calorimetric measurements (DSC) were conducted on 5-mg specimens at a heating/cooling rate of 10 °C/min using a Du Pont DSC-990 calorimeter. The melting temperatures of both polyethylene crystallites (T_m) and ionic crystallites (T_i) were determined as the temperature exhibiting the maximum of the endothermic peaks on the DSC thermograms. The heats of fusion for polyethylene crystallites (ΔH_m) and that for ionic crystallites (ΔH_i) were calculated from the peak area of the endothermic peak. Indium was used as a calibration standard. Here, the values of ΔH_m and ΔH_i mean the melting enthalpy per 1 mg of sample. Stiffness (bending modulus) was measured at 23 °C for a slab 20 mm wide × 100 mm long × 3 mm thick, according to ASTM D-747. Dynamic mechanical properties were measured at a heating rate of 1 °C/min using a Du Pont 982 DMA. Here, the oscillation mode produced by dynamic stress imposed on a 3 mm thick sheet retains a constant amplitude of 0.2 mm. Frequency varies between 2 and 20 Hz depending on the modulus. Moisture content in the polymer was determined by using Mitsubishi Chemical Moisture Analyzing System Model CA-01 and VA-01.

Results and Discussion

Typical DSC thermograms of ethylene ionomer stored for 3 months at room temperature are shown in Figure 2 for EMAA-0.40Zn. At the first heating, an endothermic peak is observed at 52 and 91 °C, respectively. The higher temperature peak (the peak temperature is denoted by T_m) clearly corresponds to the melting of the polyethylene

Table I
Chemical Structure of the Samples Used in This Work

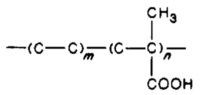
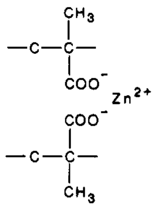
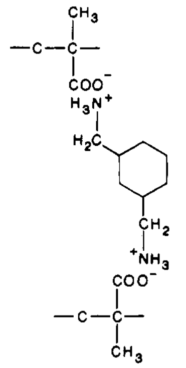
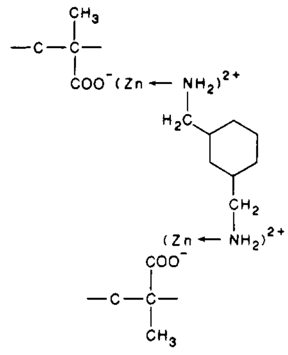
EMAA	ionomer		
	Zn salt	BAC salt	complex Zn with BAC salt
			

Table II
Change of DSC Thermal Data during Aging at 23 °C after Compression Molding

aging atm	aging time, day	heat of fusion[a] and melting peak temp[b] in DSC thermograms															
		EMAA				EMAA-0.20Zn-0.97BAC				EMAA-0.60Zn				EMAA-0.60Zn-0.40BAC			
		T_i[c]	T_m[d]	ΔH_i[e]	ΔH_m[f]	T_i	T_m	ΔH_i	ΔH_m	T_i	T_m	ΔH_i	ΔH_m	T_i	T_m	ΔH_i	ΔH_m
23 °C	0	35	90	3.0	49	43	89	7.0	32	41	87	4.7	38	42	89	6.7	34
dry N_2	1	36	90	3.3	53	47	89	9.9	24	45	87	7.2	34	47	89	8.7	32
	3	39	91	3.2	47	49	89	10.9	24	47	89	8.0	34	48	89	8.4	30
	9	41	91	4.3	52	54	90	13.5	26	50	88	8.3	32	52	90	14.2	29
	38	42	91	4.0	49	57	89	17.8	26	52	87	12.1	38	55	89	17.6	32
			(220 ppm H_2O)				(460 ppm H_2O)				(390 ppm H_2O)				(470 ppm H_2O)		
23 °C, 50% RH, air	38	41	90	5.3	56	53	89	18.1	31	51	88	12.3	31	53	89	15.7	36
			(250 ppm H_2O)				(3050 ppm H_2O)				(760 ppm H_2O)				(2010 ppm H_2O)		

[a] Heat of fusion is calculated from endothermic peak area in DSC thermogram. [b] Melting peak temperature denotes peak top temperature of endothermic peak in DSC thermogram. [c] T_i = melting peak temperature of ionic crystallites in °C. [d] T_m = melting peak temperature of polyethylene crystallites in °C. [e] ΔH_i = heat of fusion of ionic crystallites based on the entire sample weight in mJ/mg. [f] ΔH_m = heat of fusion of polyethylene crystallites based on the entire sample weight in mJ/mg.

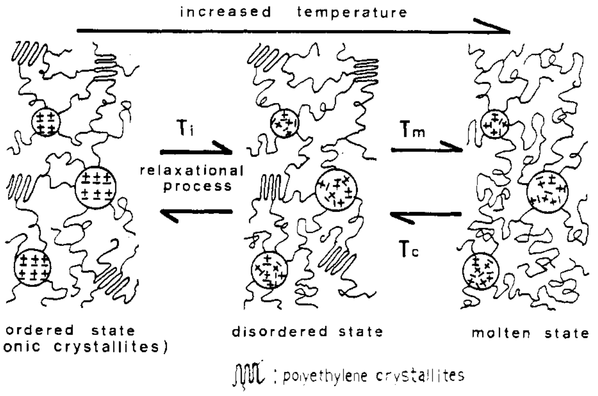


Figure 1. Model for order–disorder transition of ionic clusters (melting–crystallizing ionic crystallites).

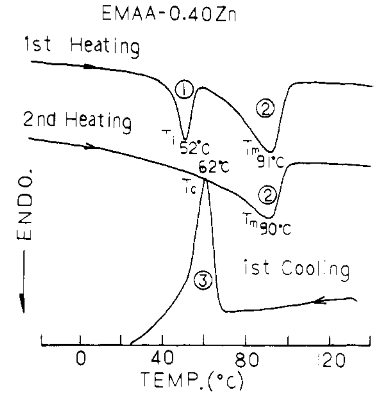


Figure 2. DSC thermograms of ethylene ionomer. ①, endothermic peak caused by the melting of ionic crystallites. ②, endothermic peak caused by the melting of polyethylene crystallites. ③, exothermic peak caused by the crystallization in polyethylene region.

region in the polymer matrix.

From our preceding work,[8,9] the lower temperature peak (the peak temperature is denoted by T_i) is attributed to the order–disorder transition of a first-order in ionic clusters (melting of ionic crystallites). In the cooling process, one exothermic peak (the peak temperature is denoted by T_c) is observed at 62 °C. This peak corresponds to the crystallization in the polyethylene region. At the second heating soon after the cooling, only one endothermic peak is observed at 90 °C, indicating the melting of polyethylene crystallites. These DSC thermograms obviously indicate that the lower temperature peak in the first heating undergoes thermal hysteresis: the peak is depressed both at the cooling and at the second heating processes. DSC thermograms similar to this were observed for all samples used in this work.

In the following sections, it is discussed that the order–disorder transition and its thermal hysteresis are closely connected with the magnitude in stiffness of ionomers.

Changes of Stiffness (Modulus) during Physical Aging. Figure 3 shows how DSC thermograms in the first heating vary with aging at room temperature for EMAA, EMAA-0.60Zn, and EMAA-0.60Zn-0.40BAC. Changes with respect to the melting peak temperatures and the heat of fusion in the first heating, in DSC thermograms during

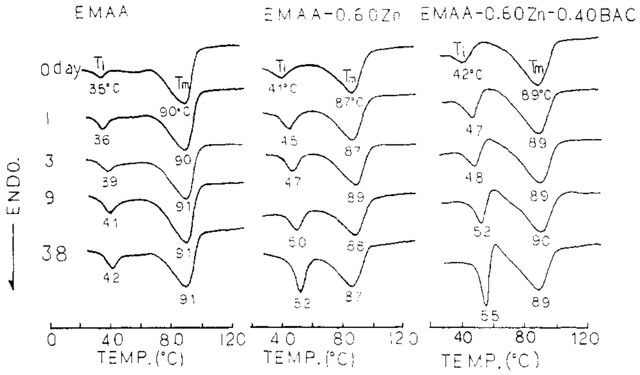


Figure 3. Change of DSC thermograms in the first heating for EMAA, EMAA-0.60Zn, and EMAA-0.60Zn-0.40BAC during aging at 23 °C in nitrogen.

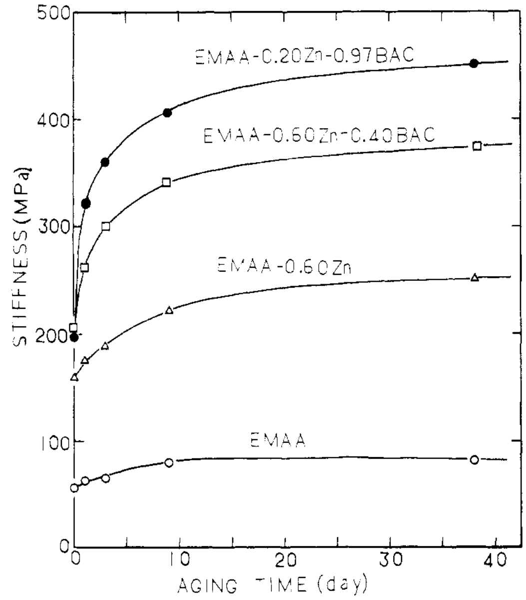


Figure 4. Change of stiffness of the compression molding sheets during aging at 23 °C in nitrogen.

physical aging at 23 °C, are shown for EMAA, EMAA-0.20Zn-0.97BAC, EMAA-0.60Zn, and EMAA-0.60Zn-0.40BAC in Table II. Two endothermic peaks were observed for all samples. We hereafter denote the peak temperature and peak area (heat of fusion) as T_m and ΔH_m for the higher temperature peak and as T_i and ΔH_i for the lower temperature peak, respectively.

The values of T_m and ΔH_m are almost unchanged with aging time for all samples. This indicates that the polyethylene crystalline regions are mostly formed in the cooling process from melt and not by aging at room temperature. On the other hand, the values of T_i and ΔH_i increase with aging time for all samples. The value of ΔH_i is very small for a short aging time but becomes considerably larger after 38 days of aging time. These results indicate that the ionic crystallites are scarcely formed in the process of cooling from molding at 160 °C but begin to form and build up gradually at room temperature in a relaxation process with a very long relaxation time (see Figure 1). It is noted that both T_i and ΔH_i at 38 days of aging are higher for higher degrees of neutralization by Zn and higher amounts of BAC. Unexpectedly, a small lower temperature peak and its slow buildup are seen in EMAA, which seems to mean that some weakly ordered structure would be formed due to hydrogen bonds of carboxyl groups in the hydrocarbon chain. In this work, we treat tentatively this weakly ordered structure in EMAA as ionic crystallites.

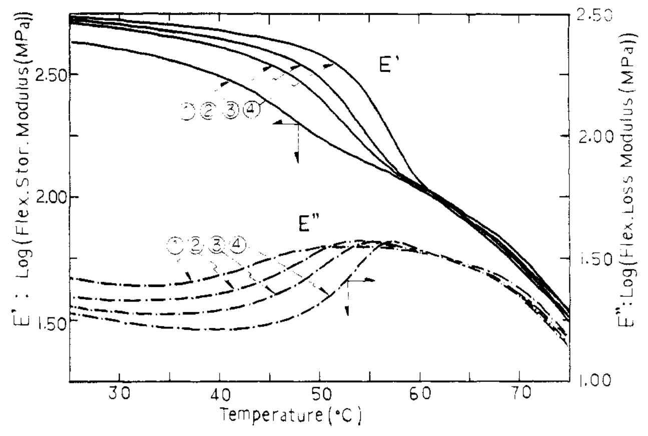


Figure 5. Temperature dependence of dynamic modulus (E') and the loss (E'') for the sheet of EMMA-0.60Zn-0.40BAC aged at 23 °C in nitrogen. ①, aged for 0 day (3-5 h) after molding. ②, aged for 3 days after molding. ③, aged for 9 days after molding. ④, aged for 38 days after molding.

Figure 4 shows the plots of stiffness versus aging time for the samples aged in dry nitrogen. Stiffness increases with aging time for all samples. The magnitude of increase depends on the type and the concentration of cations; the increase is small for EMAA, fairly large for EMAA-0.60Zn, and very large for EMAA-0.60Zn-0.40BAC and EMAA-0.20Zn-0.97BAC. The differences in the increase of stiffness among the four samples are very similar to those in the increase of ΔH_i shown in Table II. Therefore, these results indicate that the stiffness is closely connected with the degree of the formation of ionic crystallites.

Figure 5 shows the temperature dependence of the dynamic modulus (E') and the loss (E'') for EMAA-0.60Zn-0.40BAC aged for different aging times at room temperature. The value of E' below 60 °C increases with aging time and the bending point on E'-temperature curve shifts to higher temperatures with aging time. Above 60 °C, the E'-temperature curve is almost unchanged by aging. In the E''-temperature curve, one peak is observed, corresponding to the bending point on the E' curve. This peak shifts to higher temperatures with aging time, commensurate with the change of the bending point on the E' curve. This peak may be caused by the melting of ionic crystallites. The shift of the bending point in E' and the peak in E'' to higher temperatures with aging indicate that T_i increases with aging, which may correspond with the buildup of the ionic crystallites. The buildup of ionic crystallites causes the increase of E' below 60 °C with aging. Indeed the peak temperature of E'' and the change with aging time are fairly consistent with the results of T_i determined by DSC curves in Figure 3. The value of E' above 60 °C does not apparently changed with aging, since the ionic crystallites melt above 60 °C.

Kohzaki et al.[10] reported an increase in the modulus and in the lower temperature endothermic peak with aging time at 25 °C, for EMAA and its ionomers neutralized by sodium and zinc. They concluded that the increase in the lower temperature endothermic peak originates in the thickening of polyethylene lamellar crystal, which increases the modulus. However, on the wide-angle X-ray diffraction pattern, we have not observed any increase in the crystallinity of polyethylene region by physical aging at room temperature as was observed by Longworth and Wilson.[11]

In conclusion, the present results indicate that the increase of stiffness with aging at room temperature is caused by the formation and buildup of the ionic crystallites.

Stiffness versus Amount of BAC and Degree of Neutralization by Zn. It is widely recognized that the

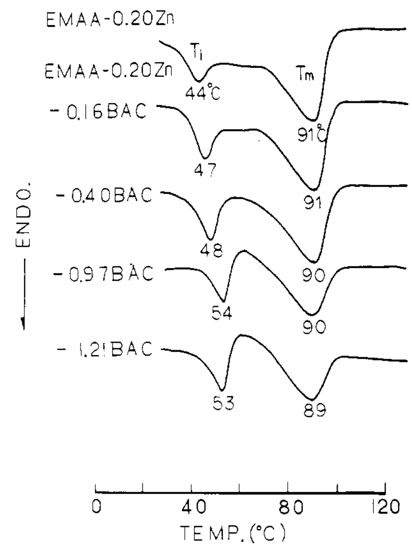


Figure 6. DSC thermograms in the first heating versus amount of BAC for EMAA–0.20Zn–*y*BAC aged for 9 days at 23 °C in nitrogen after molding.

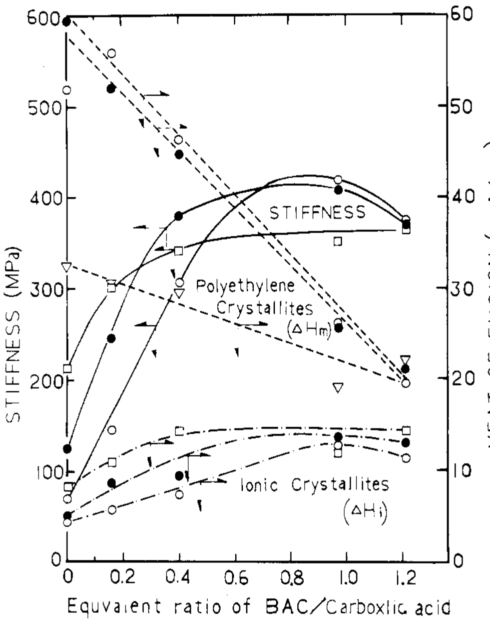


Figure 7. Stiffness and heats of fusion of ionic and polyethylene crystallites versus amount of BAC. Measurements were done for the samples aged for 9 days at 23 °C in nitrogen. ○, EMAA–*y*BAC; ●, EMAA–0.20Zn–*y*BAC; □, ▽, EMAA–0.60Zn–*y*BAC.

stiffness (modulus) of ionomer increases considerably with the degree of neutralization by metal cations, and this increase is explained by the cross-linking effect due to ionic interactions.[12,13] However, the structural mechanism for the increase in stiffness has not been fully clarified yet.

Figure 6 shows DSC thermograms of several EMAA–0.20Zn–*y*BAC samples aged for 9 days. The value of T_m is almost independent of the amount of BAC, but the peak area (ΔH_m) decreases with increasing amount of BAC. On the other hand, both the value of T_i and the peak area increase with the amount of BAC and reach a maximum near the BAC amount at 1.00. Results similar to the above are obtained for EMAA–*y*BAC and EMAA–0.60Zn–*y*BAC.

The values of ΔH_m and ΔH_i obtained from the peak areas are plotted in Figure 7 against BAC content with the value of stiffness. We can easily understand that the increases in stiffness with the amount of BAC (the degree of neutralization by BAC) are closely connected with ΔH_i but not with ΔH_m. Above 1.0 BAC content, both stiffness and ΔH_i go slightly down. Those decreases probably result from a plasticizing effect owing to the excess of BAC over the equivalent amount of carboxylic acid.

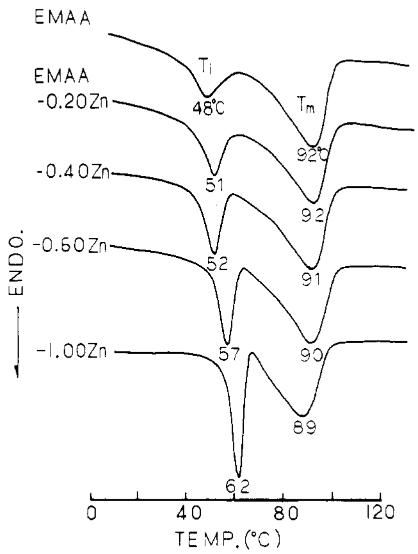


Figure 8. DSC thermograms in the first heating for Zn ionomers aged for 2 months at room temperature.

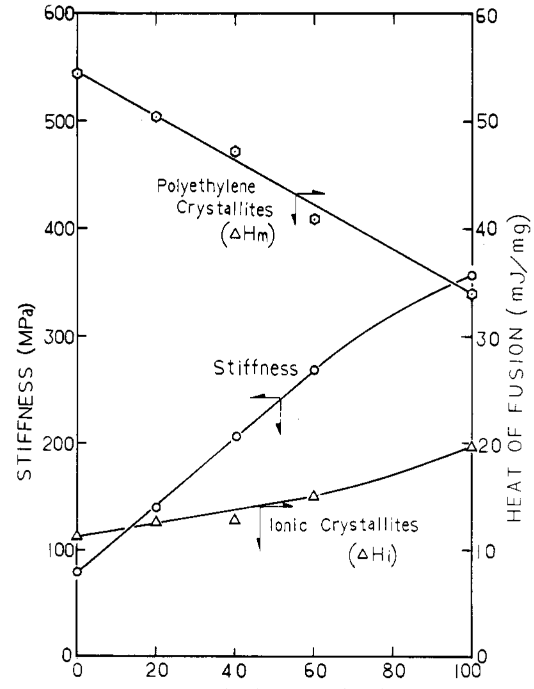


Figure 9. Stiffness and heats of fusion of ionic and polyethylene crystallites versus percent neutralization for Zn ionomers.

Trends similar to the above are found in the change of DSC diagrams with degree of neutralization for zinc ionomer as shown in Figure 8. The endothermic peak of ionic crystallites increases and shifts to higher temperatures as the degree of neutralization by Zn increases. On the other hand, the peak area of polyethylene crystallites decreases gradually and the peak temperature slightly changes with the degree of neutralization.

Figure 9 shows the plots of the stiffness, ΔH_m, and ΔH_i versus the degree of neutralization for the ionomers shown in Figure 8. The stiffness and ΔH_i increase with increasing the degree of neutralization, and ΔH_m decreases inversely. Consequently, the stiffness seems to be closely connected with ΔH_i but not with ΔH_m.

The Relation between Stiffness and ΔH_i. Figure 10 represents the plots of stiffness versus ΔH_i for all samples. The stiffness apparently increases monotonously with ΔH_i

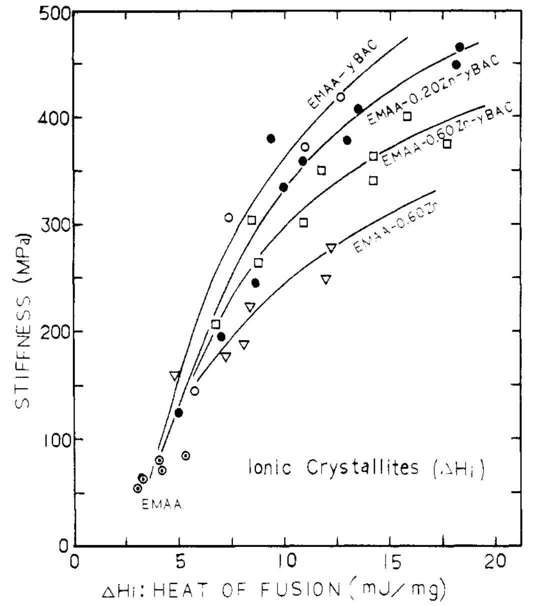


Figure 10. Stiffness versus heat of fusion of ionic crystallites for all samples. ⊙, EMAA; ○, EMAA-*y*BAC; ●, EMAA-0.20Zn-*y*BAC; □, EMAA-0.60Zn-*y*BAC; ▽, EMAA-0.60Zn.

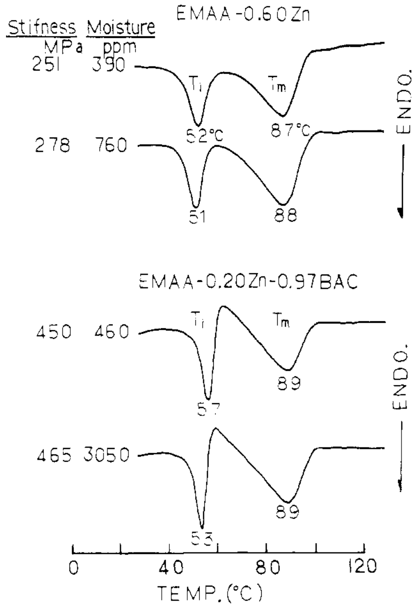


Figure 11. Effect of moisture in ionomer on DSC thermograms (first heating) and stiffness. Samples were aged at 23 °C for 38 days in dry nitrogen or in air with 50% relative humidity.

in all samples, regardless of aging time and the degree of neutralization by Zn/BAC. Thus, we conclude that the changes and enhancement of the ionomer moduli originate in the formation and development of ionic crystallites.

The stiffness increases with the increase of ΔH_i, but the magnitude of increase differs according to the type of salts. The order of the magnitude is as follows: EMAA < EMAA-0.60Zn < EMAA-0.60Zn-*y*BAC < EMAA-0.20Zn-*y*BAC < EMAA-*y*BAC. This suggests that the structure and nature of ionic crystallites differ according to the type of salts. The rigid, bulky, and divalent structure of BAC may lead to the rigid and bulky ionic crystallites, which makes the ionomers containing BAC stiffer.

From the above result, it is concluded that the formation and nature of ionic crystallites predominantly govern the stiffness of ethylene ionomers.

The Effect of Moisture. Figure 11 shows the effect of moisture pickup on stiffness as well as the DSC thermal data for EMAA-0.60Zn and EMAA-0.20Zn-0.97BAC. In both ionomers, the stiffness is almost uncharged by the moisture level. However, T_i is lower for the ionomer with the higher moisture level. This may suggest that the water absorbed in the ionomer at room temperature is incorporated into ionic crystallites as a coordinated water and scarcely affects the stiffness. By many researchers, it has been reported that water absorbed in ionomers decreases the stiffness.[1,2] Longworth[14] showed that water decreased the stiffness owing to a plasticizing effect on ionic clusters. His experiments on absorption of moisture were conducted under 80% relative humidity and at 70 °C. Since the softening (disordering) of ioinic crystallites should occur at 70 °C, the decrease in stiffness seems not to be due to the absorption of water. The present results indicate that a small amount of water absorption scarcely affects the stiffness of ionomers.

Registry No. EMAA·*x*Zn, 28516-43-0; EMAA·*x*BAC, 108338-54-1.

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