Thermal Properties of Ethylene Ionomers

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Synopsis

The annealing effect of ethylene ionomers annealed at various temperatures and for various periods was studied by differential scanning calorimetry. Two endothermic melting peaks were observed for all the ethylene ionomers annealed. The melting peak at the lower temperature, which was assigned to bundlelike crystal owing to a Hoffman-Weeks relationship, shifted to a higher temperature with the annealing temperature and period, indicative of recrystallization. There is physical cross-linking consisting of ionic aggregates, such as multiplets and clusters in ethylene ionomers. The crystallization kinetics of ethylene ionomers was fundamentally similar, but different from that of low-density polyethylene. Crystallization and recrystallization suggested a mobile ethylene chain in both amorphous regions and ionic aggregates even in the presence of cross-linking.

INTRODUCTION

Salt groups, such as Na or Zn, in ethylene ionomers are well known to form microstructural ionic aggregates separated from hydrophobic hydrocarbon phases.[1-4] Ethylene ionomer with fewer than about 1 mol% salt groups consists of a multiplet composed of a few ion pairs. Ionomer with more than 1 mol% consist of a cluster composed of more ion pairs. Although many models[5-8] of ionic aggregates of clusters are proposed, there are no discriminative structural models. The MacKnight-Taggart-Stein model[8] is likely to be acceptable at the present time. This consists of a core structure of densely packed ions and surrounding matrix ions separated by a shell of ethylene chain units.

Ethylene ionomers have also crystalline and amorphous phases of ethylene chain units. It is a three-phase structure, with crystalline, amorphous, and ionic aggregate phases. The cluster in ethylene ionomers causes an apparent physical cross-linking that exhibits a rubbery plateau region in a molten state and also affects recrystallization of the crystalline phase below the melting temperature of crystallites. Tsujita et al.[9] reported the annealing effect of ethylene ionomers. A study on a longitudinal acoustic mode by low-frequency Raman spectroscopy provided the information that the lamellar thickness of crystallites increases gradually with increasing annealing temperature, irrespective of the presence of the cluster.[9] Furthermore, Coleman and Painter et al. reported the Fourier transform infrared spectroscopic studies of fully neutralized ethylene ionomers, indicative of the mutual role of the three

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phases in the formation of ionic aggregates and crystalline phases.[10,11] Thus, information about the relation of the cluster phase to the crystalline phase may provide an intuitive interpretation of physical properties of ionomers.

In this article, we study the annealing effect of the melting behavior of a crystalline phase coexisting with the multiplet and cluster phases as a function of annealing temperature and annealing period, and in addition we examine the crystallization of ethylene ionomers from the molten state in the presence of multiplet and cluster phases.

EXPERIMENTAL

Copolymer of ethylene (E) and methacrylic acid (MAA) or its salt, such as Na or Zn, whose acid content is 5.4 mol% and degree of neutralization 60% Na, 60% Zn, and 90% Zn, was designated E-0.054MAA, E-0.054MAA-0.60Na, E-0.054MAA-0.60Zn, and E-0.054MAA-0.90Zn, respectively. High-pressure polyethylene (YUKALON YF-30, Mitsubishi Petrochemical Co.) was also used as a reference sample.

Melting behavior, melting temperature T_m, heat of fusion, and crystallization were measured at the sensitivity of $2 \sim 0.5$ mcal/s by a differential scanning calorimeter (DSC) manufactured by Seiko Denshi Kogyo KK (SSC/560-S). Ethylene ionomers were annealed at temperature from 40 to 80°C during 60, 600, and 1500 min, and thereafter DSC measurement was carried out at the heating rate of 10°C/min. The melting temperature was determined as a peak temperature in an endothermic peak.

Isothermal crystallization was studied by measurement of heat flow by DSC, which was performed by quenching from the molten state at 30°C higher than the melting temperature of crystalline phase to crystallization temperature T_c. The reciprocal of a period when an exothermic peak due to isothermal crystallization reaches maximum was regarded as the rate of crystallization.[12]

RESULTS AND DISCUSSION

Typical DSC thermograms of annealed E-0.054MAA-0.60Na are shown in Figure 1. There appear to be two fundamental endothermic peaks at lower and higher melting temperatures. The peak at lower melting temperature shifts to a high temperature and becomes sharp as the annealing temperature increases and the annealing period is prolonged. This means the recrystallization of bundlelike crystal by annealing (described later), irrespective of the presence of the physical cross-linking that consists of ionic aggregates, such as the multiplet and cluster. The peak at the higher melting temperature shifts slightly to high temperature by annealing, meaning a slight thickening of crystalline lamellae with higher melting temperatures. Such an annealing effect corresponds to the lamellar thickening studied on longitudinal acoustic mode by low-frequency Raman spectroscopy.[9] The heat of fusion of both peaks also increases slightly and levels off with the annealing temperature and period: crystallinity evaluated from the heat of fusion reached about 21% for E-0.054MAA-0.60Na. Furthermore, such an annealing effect is a trend very similar to the annealing effect on wide-angle x-ray scattering studied by MacKnight et al.[13] The amorphous ethylene chain is able to be incorporated
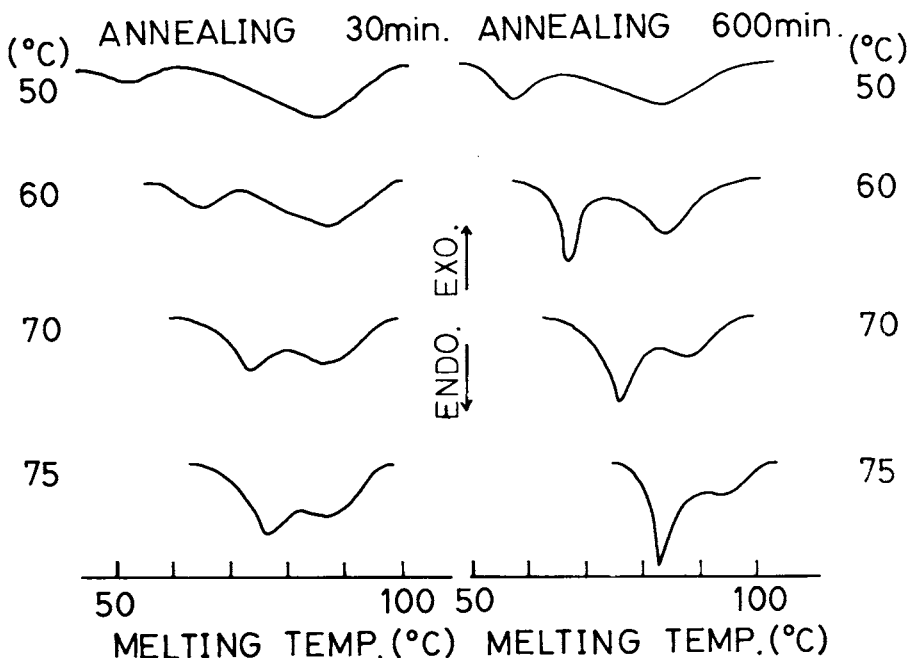
Fig. 1.   DSC thermograms of E-0.054MAA-0.60Na annealed at 50, 60, 70, and 75°C for 30 and 600 min.
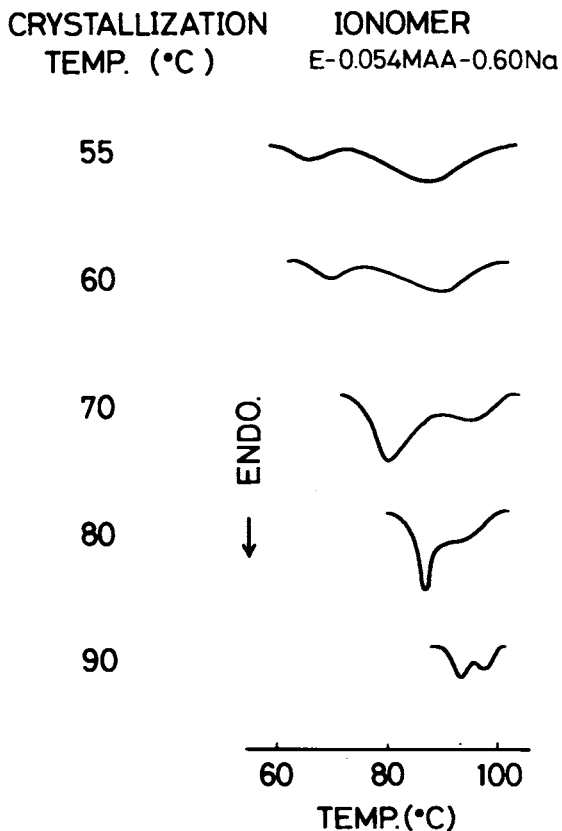

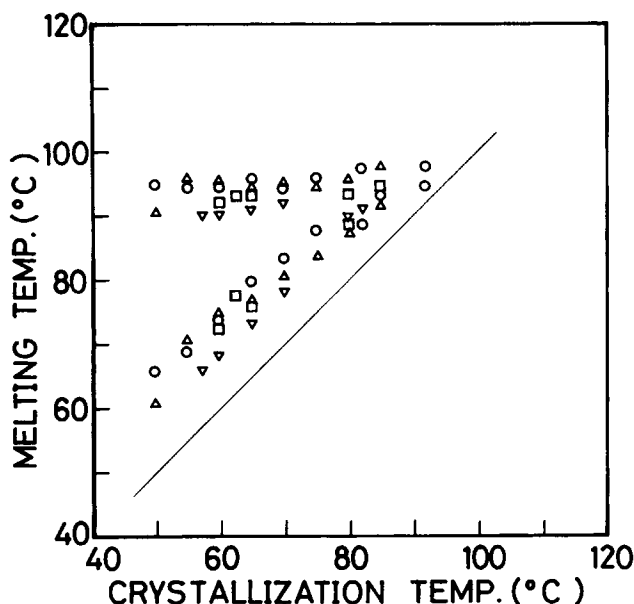Fig. 2.   DSC thermograms of E-0.054MAA-0.60Na crystallized at 55, 60, 70, 80, and 90°C.

Fig. 3. The plot of melting temperature (lower melting temperature T_l and higher melting temperature T_h) of ethylene ionomers melt crystallized against crystallization temperature: E-0.054MAA ($\triangle$), E-0.054MAA-0.60Na ($\circ$), E-0.054MAA-0.60Zn ($\square$), and E-0.054MAA-0.90Zn ($\triangledown$).

into ethylene crystallites by annealing, irrespective of the reduced molecular motion of the ionic aggregates composed of multiplet and cluster. This might indicate a mobile ethylene chain in ionic aggregates.

Figure 2 shows typical DSC thermograms of E-0.054MAA-0.60Na melt crystallized at various temperatures. Two endothermic melting peaks are observed and a shift to high temperatures is similar to the annealing effect as the crystallization temperature rises. This also indicates the segmental molecular motion of ethylene chain in the presence of the ionic aggregates that are believed to play the role of physical cross-linking at high temperatures above the melting temperature of the crystalline phase of ethylene ionomers.

The melting temperature (lower melting temperature T_l and higher melting temperature T_h) of ethylene ionomers crystallized at various temperatures for 1500 min was plotted against T_c, as shown in Figure 3. The slope of T_m versus T_c (Hoffman-Weeks relationship) may provide information on the such crystalline types as chain-folded lamellae and bundlelike crystals. The T_c dependence of T_m was almost the same for all ethylene ionomers studied. The slope

TABLE I
Equilibrium Melting Temperature T_m^0 of E-0.054MAA, E-0.054MAA-0.60Na,
E-0.054MAA-0.60Zn, and E-0.054MAA-0.90Zn

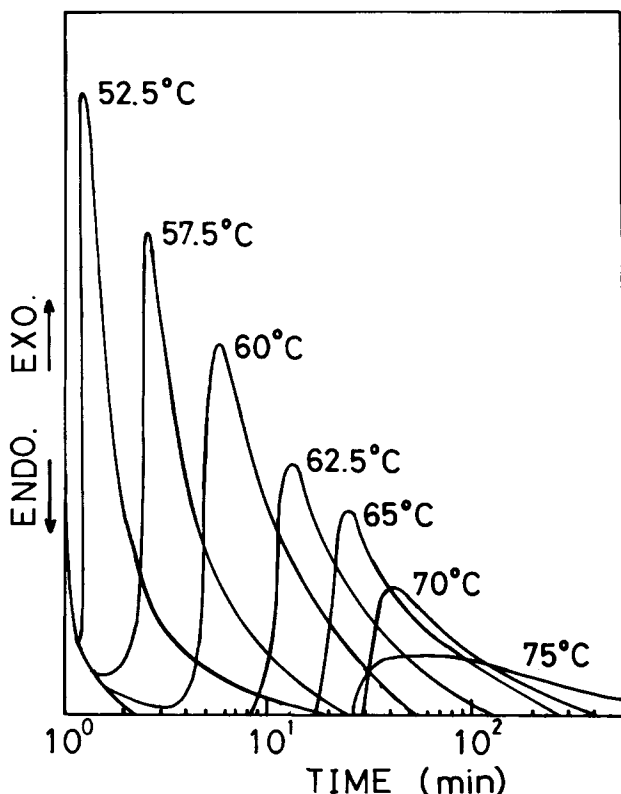| Sample	T_m^0 ($^\circ$C)
E-0.054MAA	97.5
E-0.054MAA-0.60Na	96.0
E-0.054MAA-0.60Zn	96.0
E-0.054MAA-0.90Zn	91.5

Fig. 4. The exothermic DSC thermograms of E-0.054MAA-0.60Na crystallized at various crystallization temperatures.

for T_l and T_h was approximately 1.0 and 0.12. Hoffman and Weeks[14] reported that the theoretical slope must be 0.5 for chain-folded lamella. Furthermore, the slope for the bundlelike crystal is proposed to be 1.0 by Matsumoto et al.[15] These experimental results suggest the probable assignment of the bundlelike crystal and folded lamella to the lower and higher melting temperatures, respectively, although a slope of 0.12 is very small compared with the 0.5 expected for a folded lamellar crystal. The equilibrium melting temperature T_m^0 was also obtained by extraporating the melting temperature observed to the $T_m = T_c$ line. The equilibrium melting temperature is tabulated in Table I. The equilibrium melting temperature is lowered as the degree of neutralization increases, although it is considered almost constant.

Isothermal crystallization of ethylene ionomers was studied by the DSC method. The variation in the exothermic DSC thermograms of E-0.054MAA-0.60Na is demonstrated in Figure 4. Isothermal crystallization ends rapidly as the T_c is lowered. The rate of crystallization was conventionally determined as the reciprocal of time required to reach the maximum of the exothermic peak as described above.[12] The rate of crystallization of ethylene ionomers, including low density polyethylene (LDPE), was plotted in Figure 5. It can be seen that the rate of crystallization is larger for LDPE and decreases with the degree of neutralization at a certain T_c. This indicates the interference in crystallization by ionic aggregates.
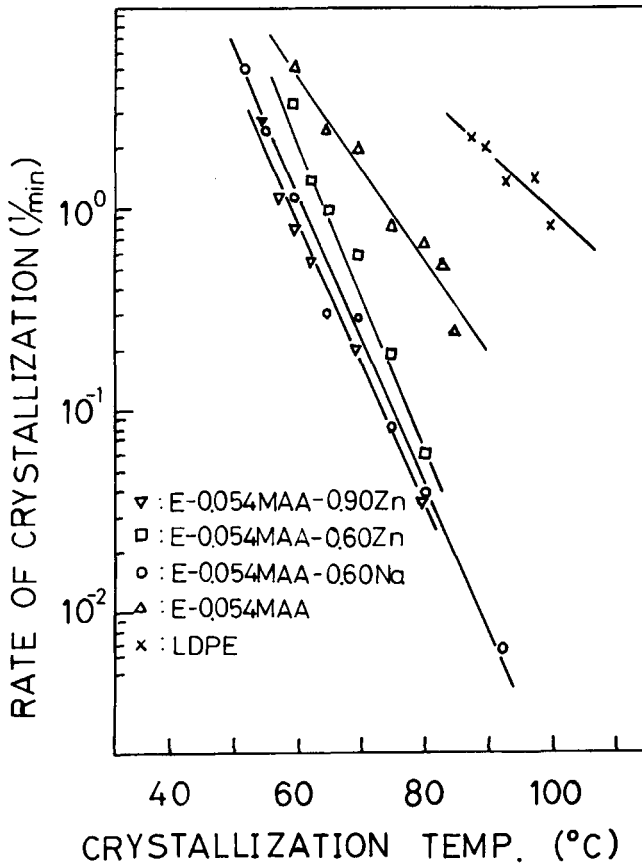
Fig. 5. The rate of crystallization of low-density polyethylene (×), E-0.054MAA (△), E-0.054MAA-0.60Na (○), E-0.054MAA-0.60Zn (□), and E-0.054MAA-0.90Zn (▽) against the crystallization temperature.

The rate of crystallization G in the vicinity of the melting temperature was described by the equation[16]

$$\log G = \text{const} - \frac{CT_m^0}{RT_c\left(T_m^0 - T_c\right)}$$

where C is the term containing the interfacial energy and heat of fusion and $\log G$ should be directly proportional to $1/T_c(T_m^0 - T_c)$. A plot of $\log G$ versus $T_m^0/T_c(T_m^0 - T_c)$ is shown in Figure 6. A linear relation was reasonably obtained for all the ethylene ionomers, including LDPE. The slopes of ethylene ionomer and LDPE in the $\log G$ versus $T_m^0/T_c(T_m^0 - T_c)$ plot were remarkably different. The former slope was very large compared with the latter slope. The term C of ethylene ionomers is considerably greater than LDPE, and there was no remarkable difference in C between ethylene ionomers with different degrees of neutralization. This means that the difference in the interfacial energy and heat of fusion between ethylene ionomers is not remarkable, but there was considerable difference between ethylene ionomer and LDPE. At present one cannot discriminate which terms are the main
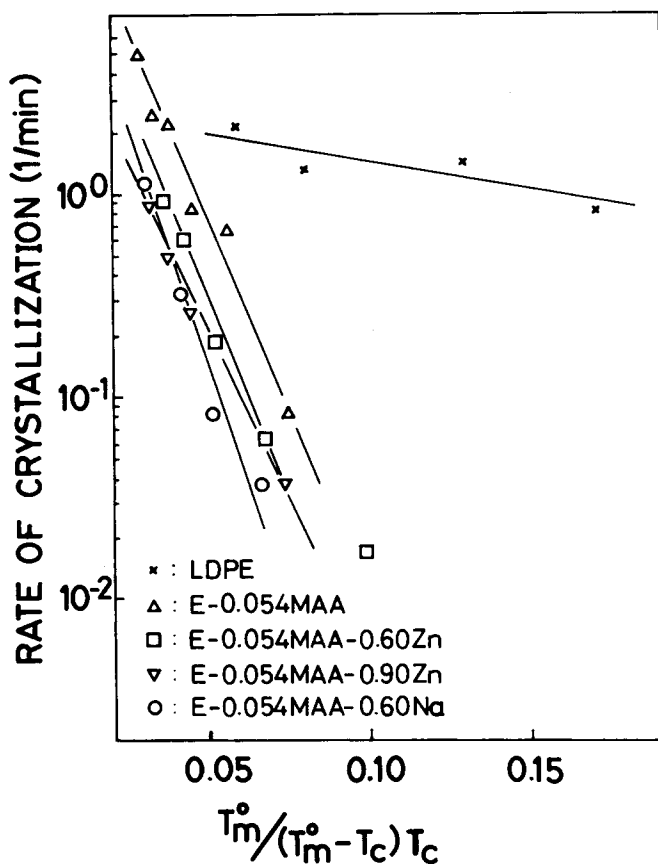
Fig. 6. The plot of log G against $T_m^0/T_c(T_m^0 - T_c)$ for low-density polyethylene ($\times$), E-0.054MAA ($\triangle$), E-0.054MAA-0.60Na ($\circ$), E-0.054MAA-0.60Zn ($\square$), and E-0.054MAA-0.90Zn ($\triangledown$).

contribution, the interfacial energy at lamellar side, or the interfacial energy at lamellar surface.

SUMMARY

The characteristic melting behavior of ethylene ionomers is fundamentally understood by the melting of two types of crystal: chain-folded lamellae and bundlelike crystals, which melt at higher and lower temperature, respectively. The lower melting temperature is shifted to a high temperature with increasing the annealing temperature and period even in the presence of the ionic aggregates, such as multiplets and clusters. On the other hand, the higher melting temperature was raised slightly by annealing. These shifts in the melting temperature indicate the growth of the folded lamellae or bundlelike crystal by annealing. Although the crystallites of ethylene ionomer are known to be the chain-folded lamellae, we suggest the formation of the bundlelike crystal as well as folded lamellae. Crystallization of ethylene ionomers is able to proceed even in the presence of physical cross-linking in multiplets and clusters. The crystallization kinetics of ethylene ionomers was basically similar, irrespective of the degree of neutralization, indicating almost the same

TSUJITA ET AL.

interfacial energy for ethylene ionomers. It was found that the role of interfacial energy was remarkable for ethylene ionomers compared with low-density polyethylene. Crystallization and recrystallization in ethylene ionomers suggest that molecular motion of the polymer chain in the ionic aggregates is possible and that the polymer chain in the ionic aggregate is not fixed by the physical cross-linking.

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