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EFFECTS OF CHEMICAL CONSTITUENTS ON CRYSTALLINE PROPERTIES OF ETHYLENE IONOMERS

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Abstract

The effect of % methacrylic acid (%MAA), % neutralization (%N) and ion type (Na^+ or Zn^{++}) on the crystalline properties of neutralized ethylene-methacrylic acid copolymers (ionomers) were studied using differential scanning calorimetry (DSC). Two endothermic melting peaks were observed for all the nine ionomers studied, the lower melting point (LMP) due to ordered ionic clusters and the higher melting point (HMP) due to polyethylene crystallites. Effects of %MAA, %N and ion type on LMP and HMP for as-received, aged and annealed samples are compared. Effect of types of pretreatments on LMP and HMP of ionomers at high and low %MAA contents for both ion types are discussed. Most of these results are explained from the point of view of crystalline morphology of ionomers.

Keywords: crystalline properties, ethylene ionomers

Introduction

Ionomers are polymeric materials consisting of hydrophobic organic backbone chains and a small amount of ionic groups introduced by copolymerization with an acid and subsequent neutralization of the acidic groups with suitable bases. It is generally accepted that the polar salt groups form ionic aggregates such as multiplets and clusters in the hydrophobic polymer matrix. The presence of ionic clusters has been evidenced by means of various techniques such as electron microscopy, small-angle X-ray scattering (SAXS), mechanical and dielectric measurements, etc. [1–4]. The formation of ionic clusters profoundly influences physical properties of ionomers, as evidenced by a dramatic increase in the mechanical properties, such as modulus, tensile strength, impact resistance and stiffness [5–8]. Ionomers have been widely used in commercial applications by taking advantage of their characteristic properties originating in the ionic interactions. Ethylene ionomers consist of three phases: ionic clusters, polyethylene crystallite region, and amorphous region. Figure 1 depicts the interrelationship between these three phases and the effect of temperature on the

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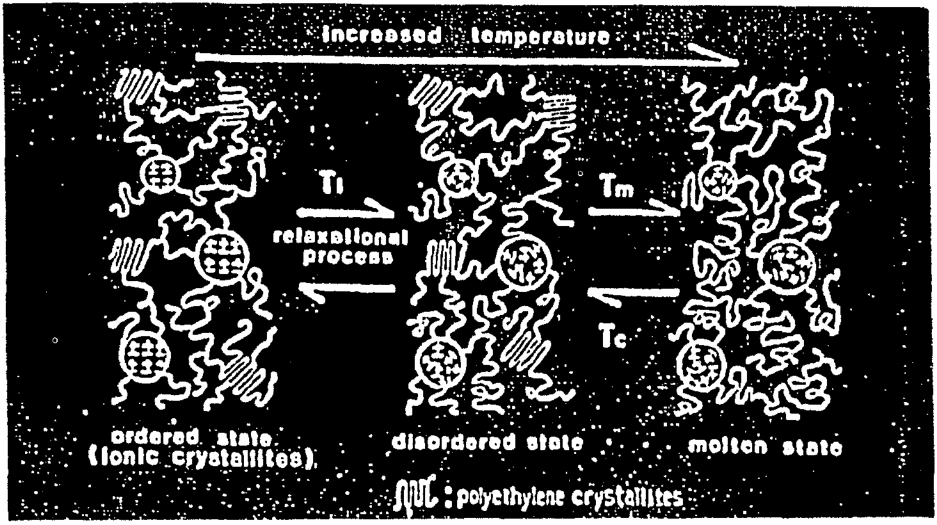

Fig. 1 Adapted with permission from E. Hirosawa *et al.*, Macromolecules, 22 (1989) 2777

ionic clusters and polyethylene crystallites. In this work, the effect of chemical constituents (%MAA, %neutralization and ion type) on the crystalline properties of polyethylene ionomers were investigated using DSC.

Experimental

Materials

Nine polyethylene ionomers used in this study were Surlyn® ionomers manufactured by DuPont Co. These are ethylene-methacrylic acid copolymers neutralized by bases to incorporate either Na^+ or Zn^{++} ions. The sample designation, %MAA, %N and ion type were supplied by the appropriate DuPont research laboratory and are listed in Table 1.

Samples of the above Surlyn® ionomers were labelled as A, B, C, D, E, F, G, H, and I in order to maintain the confidentiality of these products. These samples were taken from polymer batches which were extruded about the same time and stored in foil-lined bags, heat-sealed to prevent contact with moisture. The Surlyn® samples were packed in heavy Ziplock polyethylene bags, double-sealed by reinforced nylon adhesive tapes and mailed by overnight mail to the author. The sealed samples were then stored in desiccators prior to use.

Thermal analysis

DSC measurements were carried out using TA Instrument's computerized DSC 10 system including the DSC module, TA 2000 thermal controller and

Table 1 Chemical constituents of Surlyn® ionomers

Sample designation	Methacrylic acid/wt%	Acid neutralized/%*	Ion type
A	10	54	Na^+
B	10	36	Na^+
C	10	25	Na^+
D	15	54	Na^+
E	15	25	Na^+
F	15	25	Zn^{++}
G	15	54	Zn^{++}
H	10	71	Zn^{++}
I	10	54	Zn^{++}

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* average

data analyzer. A heating rate of 10°C min^{-1} was used with nitrogen purge gas flow rate of 100 ml min^{-1}. The sample weights were 9 to 11 mg with indium as the reference material. Each sample was cooled to near 0°C using a special cooling accessory with crushed ice as the coolant before subjecting it to programmed heating. Annealing at a temperature higher than room temperature was done by cooling the sample which has been heated to 140°C, using the special cooling accessory filled with ice and computer-controlled isothermalization at desired level for a specific time.

These as-received samples contained in closed plastic bags were stored in desiccator for about two years before being used for this study. The lower and higher melting points correspond to the respective melting peaks of the endotherms for each DSC curve.

Results and discussion

Thermal analysis of as-received, aged samples

The first heat DSC curves of as-received and aged Surlyn® samples are shown in Figs 2 to 5. The DSC curves are cross-plotted together as shown in order to demonstrate the effects on %MAA, %N and ion type on the crystalline properties. At first heating, two endothermic peaks are observed, one between 50 and 70°C and the other between 90 and 100°C for all the nine samples. The higher temperature peak corresponds to the melting of the polyethylene crystalline region in the polymer matrix and designated as high melting point (HMP). The lower temperature peak is attributed to the order-disorder transition of a first order in ionic clusters (melting of ionic crystallites) and designated as low melting point (LMP). The model explaining the order-disorder transition of

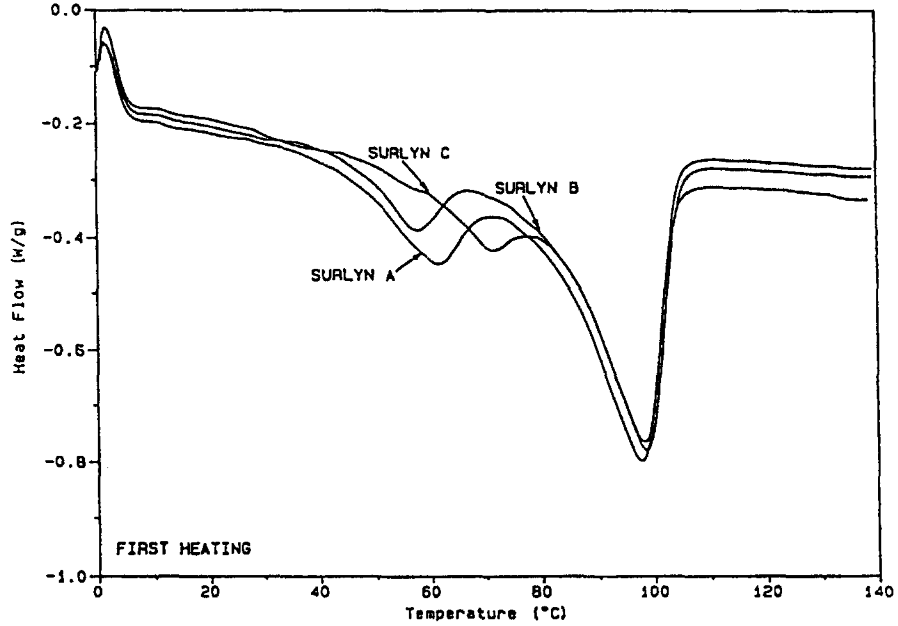

Fig. 2 DSC curves of as-received, aged Surlyn A (10%MA, 54%N), Surlyn B (10%MA, 36%N) & Surlyn C (10%MA, 25%N), all with Na$^+$ ions

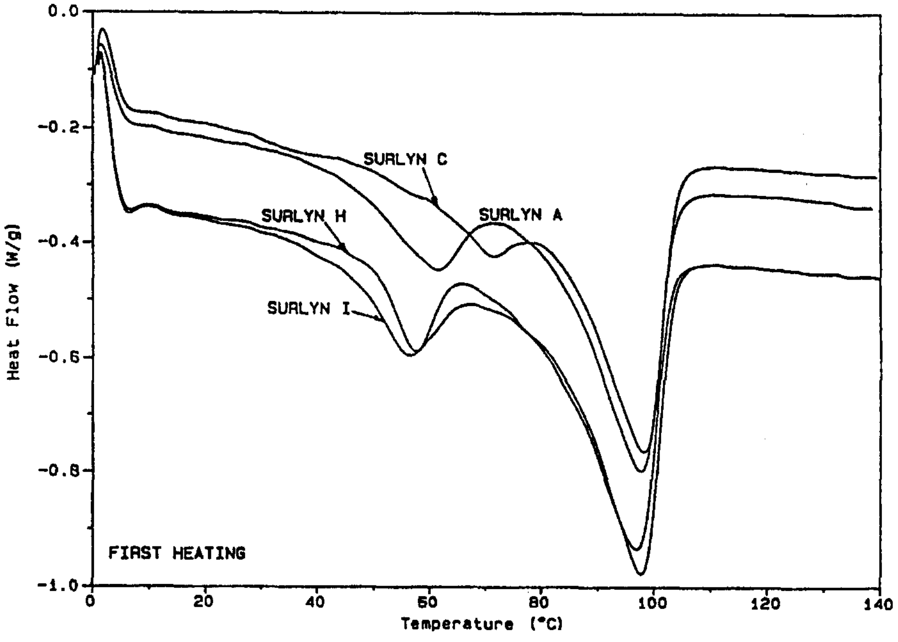

Fig. 3 DSC curves of as-received, aged Surlyn A (10%MA, 54%N, Na$^+$), Surlyn C (10%MA, 20%N, Na$^+$), Surlyn H (10%MA, 71%N, Zn^{++}) & Surlyn I (10%MA, 54%N, Zn^{++})

ionic clusters is shown in Fig. 1. When the temperature is increased from room temperature, the crystalline order inside the ionic clusters is destroyed at LMP giving disordered state; and on further increasing the temperature, the polyethylene crystallites melt at HMP, but the disordered ionic clusters still exist [9].

The existence of LMP can also be caused by melting of crystallites composed of short segments, as proposed by Marx and Cooper [10]. Their DSC work involving low-density polyethylene (LDPE), ethylene–MAA copolymer and ethylene–MAA ionomers showed that, annealing these polymers at room temperature for a period of one month gave additional transition/endotherm at lower temperature (LMP). The sharpness of these transition/endotherm increased slightly with copolymerization and dramatically with ionization. They proposed that the low temperature of this transaction was caused by melting of crystallites composed of short polyethylene chain segments. Further detailed research using additional sensitive characterization tools will be required to test the relative validity of these two theories explaining the existence of LMP in polyethylene ionomers.

The more recent theory of order-disorder transition of ionic clusters will be used to explain the effects of chemical constituents on LMP.

Figure 2 shows the first heating samples of Surlyn® A, Surlyn® B and Surlyn® C, all at 10% methacrylic acid (%MAA) with Na^+ ion type, but different in % neutralization (%N). Percent N affects the LMP without showing a specific trend and has very little effect on the HMP. At 10% MAA with Zn^{++} ion

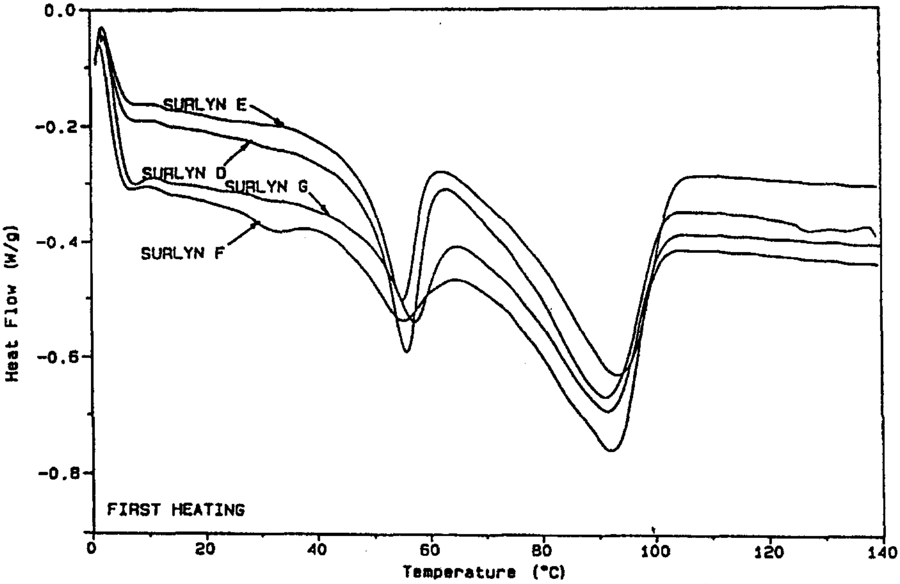

Fig. 4 DSC curves of as-received, aged Surlyn D (15%MA, 54%N, Na^+), Surlyn E (15%MA, 25%N, Na^+), Surlyn F (15%MA, 25%N, Zn^{++}) & Surlyn G (15%MA, 54%N, Zn^{++})

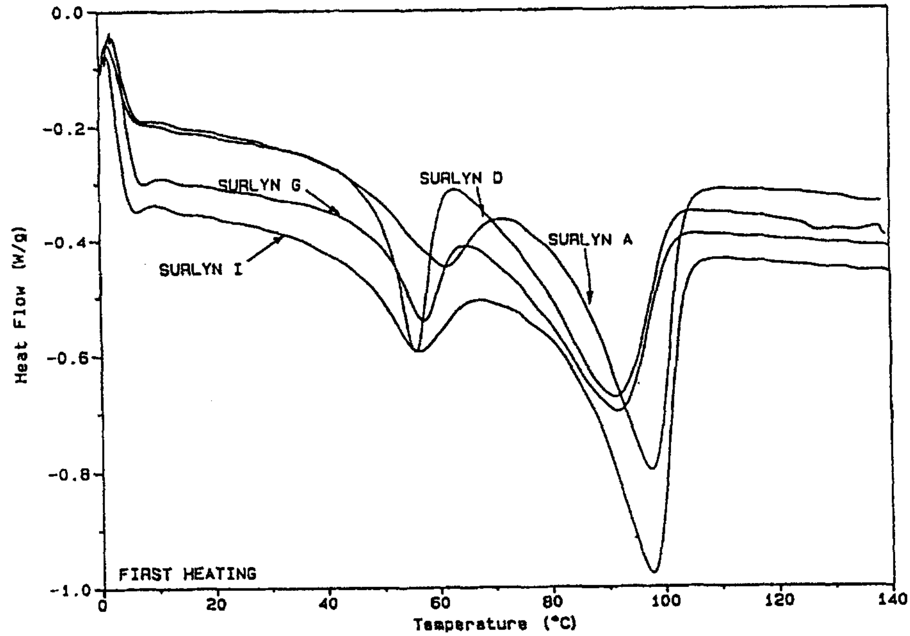

Fig. 5 DSC curves of as-received, aged Surlyn A (10%MA, 54%N, Na^+), Surlyn D (15%MA, 54%N, Na^+), Surlyn G (15%MA, 54%N, Zn^{++}) & Surlyn I (10%MA, 54%N, Zn^{++})

type, %N has very little effect both on LMP and HMP (curves H *vs.* I, Fig. 3), whereas change of ion types from Na^+ to Zn^{++} lowers LMP without affecting HMP (curves A *vs.* I, Fig. 3). At the 15% MAA level, %N or ion type has practically no effect on LMP or HMP (curves D *vs.* E and F *vs.* G, Fig. 4). At 15% MAA, a change of ion type from Na^+ to Zn^{++} has very little effect on LMP or HMP (curves D *vs.* G, Fig. 5). Increase of %MAA from 10 to 15% at 25% N level lowers LMP and HMP for Na^+ ion type (curves C *vs.* E, Figs 3 and 4). An increase of %MAA at 54% N level lowers both LMP and HMP for both ion types (curves A *vs.* D and G *vs.* I, Fig. 5).

Above-mentioned results can be explained on the basis of morphological entities of ethylene ionomers as follows: at a higher level of %MAA, the ionomer has more ions to be able to aggregate together to form bundle-like crystals (clusters) and less polyethylene chains to form chain-folded lamellae. This combination seems to make crystalline order and size of ionic clusters and dimensions of polyethylene chain-folded lamellae independent of level of %N and ion type (Na^+ and Zn^{++}). Since the LMP and HMP are related to the crystalline order and dimensions of these crystals [11], these are rather independent of %N and ion type. At a lower level of %MAA, less ions are available to form ionic clusters and more polyethylene chains to form chain-folded lamellae. But only the LMP is affected due to %N or ion type, signifying changes in order and dimen-

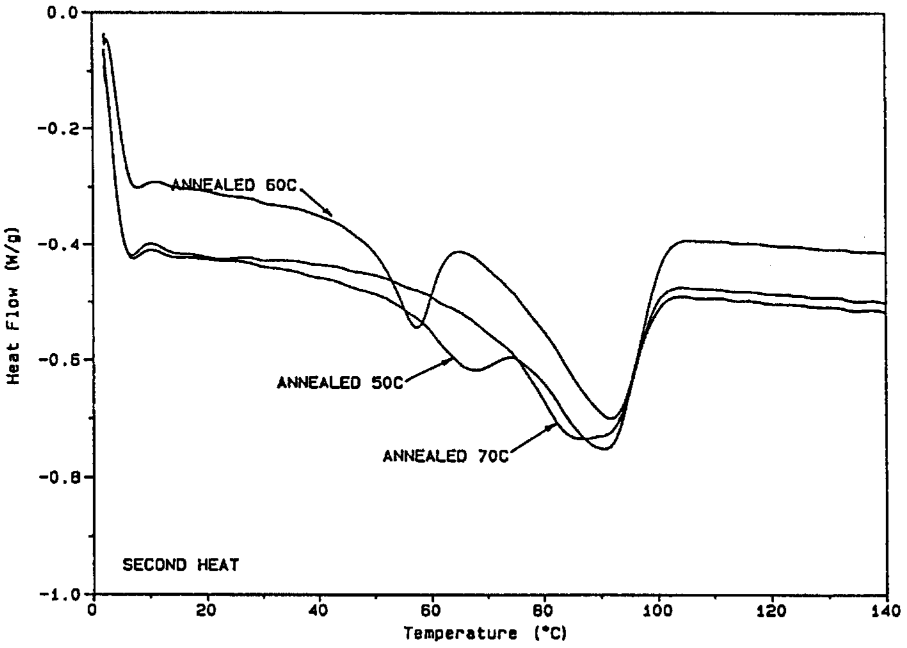

Fig. 6 Effect of annealing temperature on the high & low melting points of Surlyn G (annealing time 30 min)

sions of ionic crystallites (clusters). When %MAA is increased to from 10% to 15% at 54% for either Na^+ or Zn^{++} ion type, there is an increase in the number of ions to form clusters, but a decrease in the number of polyethylene chains to form chain-folded lamellae. At this high level of %MAA and %N, ions seem to hinder formation of highly ordered clusters leading to lowering of melting of these (LMP). The lower concentration of polyethylene chains leads to smaller and thinner crystalline lamellae and, hence, lowering of HMP. These reasonings are in line with the reasonings expressed by Kinoshita *et al.* in their research studies on crystallization and formation of cluster of ethylene ionomer [11, 12]. Further work using other characterizing techniques is needed to confirm these explanations.

Thermal analysis of annealed samples

Quenching (ice) of the first heated samples, referred to in the previous section, and reheating (second heating) led to only one endothermic peak due to melting of polyethylene crystallites (curves labelled '3rd heat, quenched,' Figs 11 and 12). The quick-quenching did not allow enough thermal energy and time for the crystallization of the ions to form ordered ionic clusters. However, using proper annealing conditions (temperature and time) should cause crystallization to occur in order to form ordered ionic clusters. This should yield the

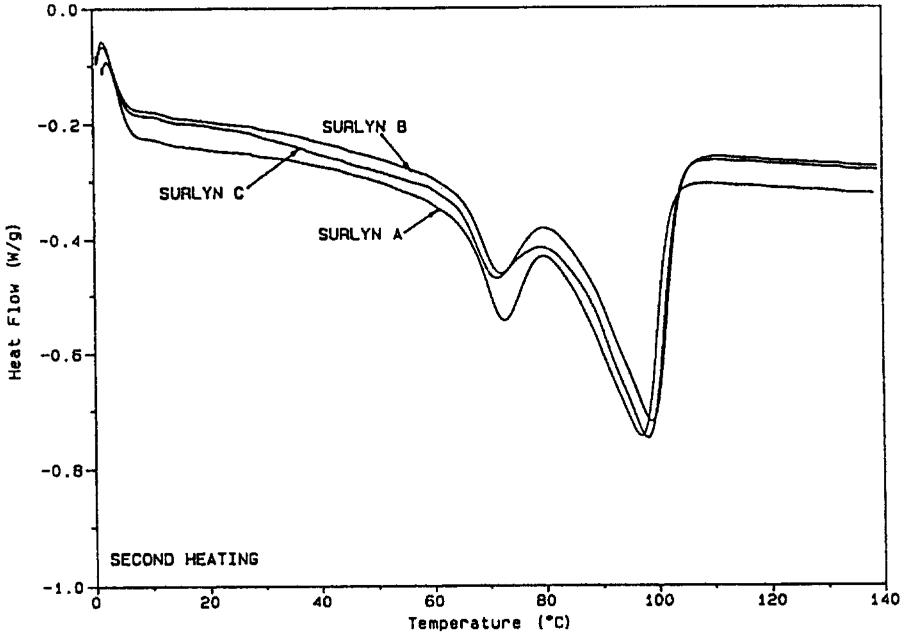

Fig. 7 DSC curves of Surlyn A (54%N), Surlyn B (35%N) & Surlyn C (25%N) annealed at 60°C for 30 min, showing effects of % neutralization on lower melting point at 10%MA, Na^+ levels

two typical melting endotherms as indicated on Figs 2–5. Figure 6 shows the effect of annealing on the LMP and HMP of ethylene ionomer (Surlyn® G). The range of temperature (50–70°C) and annealing time of 30 minutes were chosen based on the research work of Tsujita *et al.* [11]. Annealing at 60°C gave good separation between the two endotherms, with poor separation at 50°C and no separation at 70°C. Hence, all the subsequent annealing was done at 60°C for 30 min with some exceptions which will be discussed later on. Figures 7–10 show the effects of %MAA, %N and ion type on LMP and HMP. At the 10% MAA level, %N has negligible effect on LMP or HMP both for Na^+ and Zn^{++} ion types (curves A *vs.* C and H *vs.* I, Fig. 8). The effect of ion type also has negligible effect on LMP or HMP at 10% MAA and 54% N (curves A and I, Fig. 10). At the 15% MAA level, ion type (Na^+ or Zn^{++}) has no effect on LMP or HMP (curves G *vs.* D and E *vs.* F, Fig. 9), but an increase in %N gives slightly higher LMP with practically little effect on HMP (curves D *vs.* E and F *vs.* G, Fig. 9). An increase in %MAA (10% to 15%) increases LMP with a decrease in HMP for both Na^+ and Zn^{++} ion type (curves A *vs.* D and G *vs.* I, Fig. 10).

The main difference between the DSC curves of as-received, aged and annealed samples, is that at 10% MAA level, %N and ion type have moderate

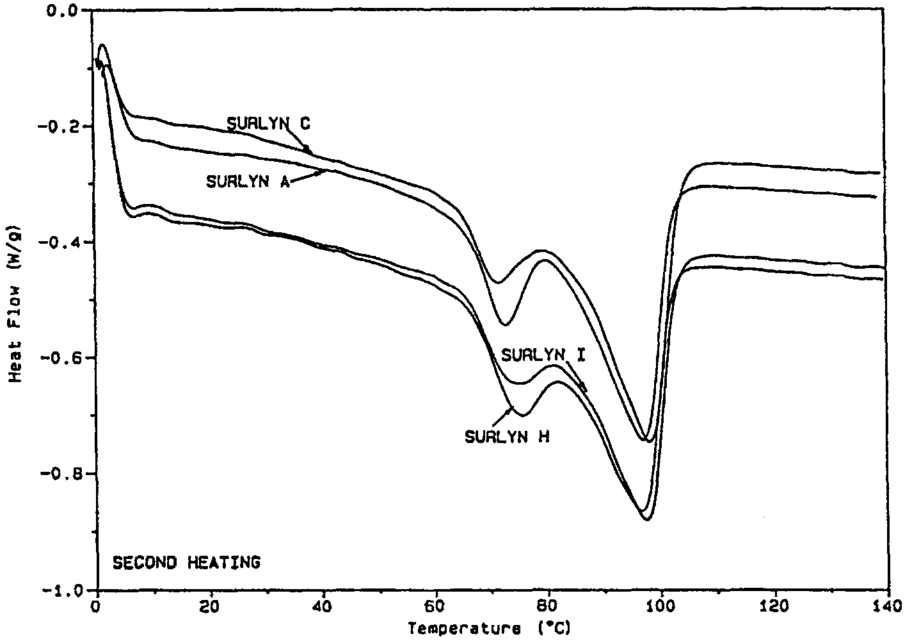

Fig. 8 DSC curves of Surlyn A (10%MA, 54%N, Na^+), Surlyn C (10%MA, 20%N, Na^+), Surlyn H (10%MA, 71%N, Zn^{++}) & Surlyn I (10%MA, 54%N, Zn^{++}) annealed at 60°C for 30 min

effect on LMP for the former, but no effect on LMP or HMP for the latter. At 15% MAA level, %N or ion type has practically no effect on LMP or HMP for either type of sample. An increase of %MAA at fixed %N causes lowering of HMP for both types of samples with opposite effects on LMP. The differences stated above is most plausibly due to formation of smaller ionic clusters (lower LMP) for as-received, (room temperature) aged samples compared to first-heated sample annealed at 60°C as evidenced by the comparison of the LMP's of the samples annealed at 60°C for 30 min and 20°C for 20 h discussed in the following section. Hence, for the as-received, aged sample, an increase in %N or changing ion type should lead to further changes in dimensions of ionic clusters and, hence, LMP.

Thermal analysis of multiple heated samples

The effect of different types of annealing on the LMP and HMP was studied using four types of conditioning of the first heated samples referred to in the earlier section: annealing at 60°C for 30 and 5 min, quenching with ice and annealing at 20°C for 20 h. The results of this study is typified by Figs 11 and 12, which represent the multiple heating of Surlyn® A (10% MAA, 54%N, Na^+) and Surlyn® D (15% MAA, 54%N, Na^+). Both at 10% and 15% MAA levels,

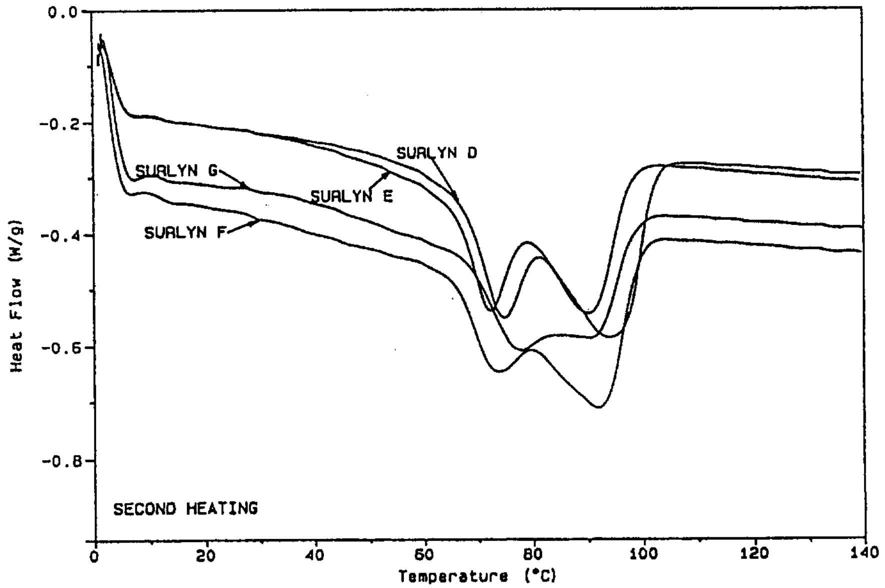

Fig. 9 DSC curves of Surlyn D (15%MA, 54%N, Na^+), Surlyn E (15%MA, 25%N, Na^+), Surlyn F (15%MA, 25%N, Zn^{++}) & Surlyn G (15%MA, 54%N, Zn^{++}) annealed at 60°C for 30 min

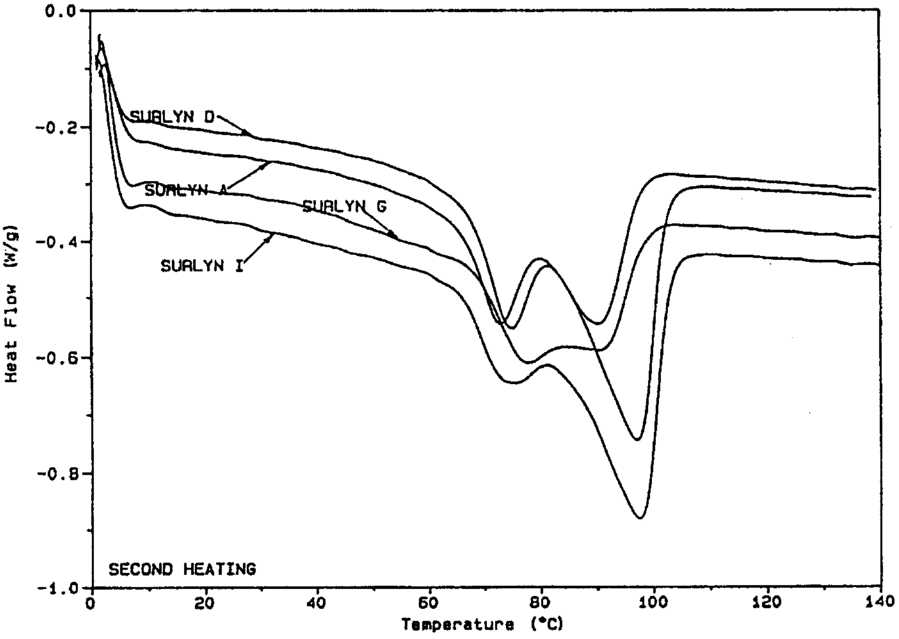

Fig. 10 DSC curves of Surlyn A (10%MA, 54%N, Na^+), Surlyn D (15%MA, 54%N, Na^+), Surlyn G (15%MA, 54%N, Zn^{++}) & Surlyn I (10%MA, 54%N, Zn^{++}) annealed at 60°C for 30 min

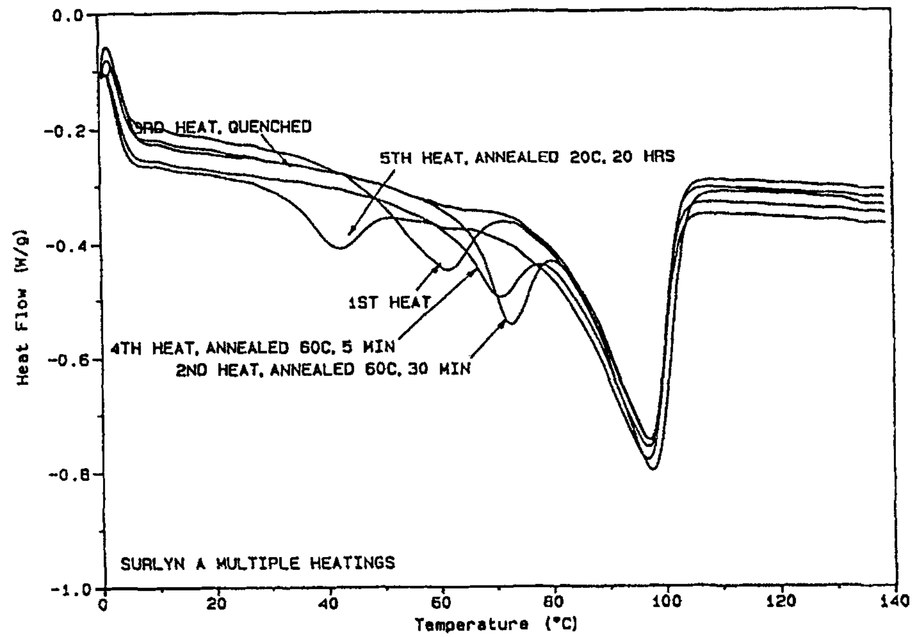

Fig. 11 DSC curves of Surlyn A (10%MA, 54%N, Na^+) treated at different conditions prior to heating

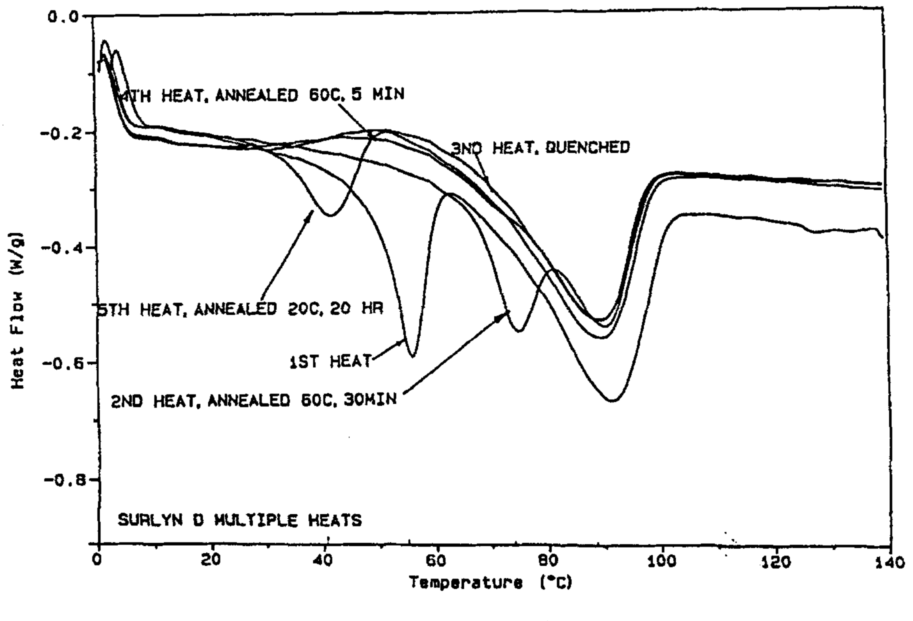

Fig. 12 DSC curves of Surlyn D (15%MA, 54%N, Na^+) treated at different conditions prior to heating

annealing at 60°C for 30 min causes an appreciable increase in LMP (15–20°C), whereas annealing at 20°C for 20 h leads to an appreciable decrease (15–20°C) in LMP with very little effect on HMP. Shortening the annealing time from 60 to 5 min at 60°C leads to less increase in LMP than that for samples annealed for 30 min at 60°C at 10% MAA level. At 15% MAA level, the shorter annealing time at 60°C leads to only one endotherm due to chain-folded polyethylene crystallites. Annealing at 60°C for 30 min gives the highest LMP, signifying formation of larger and thicker clusters, whereas annealing at 20°C for 20 h gives lowest LMP signifying formation of smaller and thinner clusters. Types of annealing has no appreciable effect on HMP, both at 10 and 15% MAA levels. An increase of %MAA from 10 to 15% causes practically no difference in LMP for samples annealed at 60° for 30 min at 20°C for 20 h, but causes lowering of HMP. The increase in %MAA leads to a decrease in the number of polyethylene chains, requiring lower energy of melting and thus yielding lower melting temperature (HMP). Similar results are derived for samples having 10 and 15% MAA at 54% N with Zn^{++} ion type (Surlyn® G and I). The results are not included to prevent redundancy.

Conclusions

1. Two endotherms, due to ionic clusters and polyethylene crystallites, are manifested for all the nine as-received, aged ionomers on heating.
2. Type of annealing of the once-heated sample has a strong effect on LMP, with samples annealed at 60°C, 30 min giving much higher LMP than samples annealed at 20°C for 20 h on heating.
3. For as-received, aged samples, at 10% MAA level, %N and ion type have a moderate effect on LMP, but no appreciable effect at 15% MAA level on heating. An increase of %MAA (10 to 15%) at fixed %N causes moderate lowering of both LMP and HMP.
4. Annealing once-heated samples at 60°C for 30 min gives somewhat different results than these given above, on heating. At the 10% MAA level, %N and ion type have practically no effect on LMP and HMP. At the 15% MAA level, %N affects LMP with little effect on HMP for both ion types. An increase in %MAA (10 to 15%) at fixed %N causes moderate lowering of LMP and HMP, similar to these recorded above for as-received, aged samples.

These results can be explained from the viewpoint of effects of the chemical constituents on the more recently proposed crystalline morphology of the polyethylene ionomers studied.

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