

## Dynamic Mechanical and Morphological Studies of Styrene-*co*-Methacrylate and Sulfonated Polystyrene Ionomers Containing Aliphatic Dicarboxylate Salts

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**Abstract:** This study examined the effects of the sodium salts of aliphatic dicarboxylic acids (DCAs) on the dynamic mechanical properties and morphology of two sets of poly(styrene-*co*-sodium methacrylate) (MNa) and poly(styrene-*co*-sodium styrenesulfonate) (SNa) ionomers. When the DCA content was relatively low, the ionic moduli of the MNa and SNa ionomers increased but the matrix and cluster glass transition temperature ( $T_g$ ) did not change significantly. The increasing ionic modulus was almost independent of the type of the ionic groups of the ionomer, and the chain length of DCAs. When a large amount of the sodium succinate (DCA4) was added to the MNa and SNa ionomers, the ionic moduli of the two ionomers increased strongly but the matrix and cluster  $T_g$ 's increased slightly and significantly, respectively. In the case of sodium hexadecanedioate (DCA16), DCA16 increased the ionic moduli of the two ionomers. The addition of DCA16 changed the matrix and cluster  $T_g$ 's of the MNa ionomer slightly, but decreased the cluster  $T_g$  of the SNa ionomer significantly with no change in the matrix  $T_g$ . In addition, the DCA-containing ionomers showed an X-ray diffraction peak indicating the presence of ordered domains of DCAs in the ionomers. Hence, DCA4 acts mainly as a reinforcing filler in MNa and SNa systems. In the case of DCA16, it initially behaved like a filler but also functioned as a preferential plasticizer for the clusters at high content.

**Keywords:** ionomers, aliphatic dicarboxylic acids, phase-separation, fillers, plasticization.

### Introduction

Ionomers are polymeric materials containing a small amount of ionic groups (< 15 mol%) embedded in a relatively non-polar polymer matrix.<sup>1</sup> The presence of the ionic groups in the polymer matrix generally causes ion aggregation. The interpretation of the mechanical properties and morphology of random ionomers can possibly be done with the help of the multiplet-cluster or so-called Eisenberg-Hird-Moore (EHM) model.<sup>2</sup> The ionic aggregates, i.e. multiplets, cause the restriction of the mobility of the polymer chains emanating from the multiplets. As the ion content increases, the partially restricted mobility regions begin to overlap. Eventually, the restricted mobility regions form sufficiently large domains, the so-called "clusters". At this point, the ionomer starts to show characteristics of phase-separated materials such as a second glass transition at much higher temperatures, compared to the glass transition temperature

( $T_g$ ) of the matrix regions. As the ion content increases further, the ionomer undergoes a transition from a matrix-dominant material to a cluster-dominant material. Since 1970s, the mechanical properties and morphology of ionomers have been studied extensively by varying a number of factors, including the type, size, position of ionic units, the degree of neutralization, and the type of plasticizers, additives and neutralizing agents.<sup>1</sup>

Plante *et al.* performed dynamic mechanical studies on matrix-dominant and cluster-dominant carboxylated polystyrene (PS) ionomers blended with chemically identical mono- and bi-functional styrene oligomers.<sup>3</sup> The mono-functional oligomers were found to plasticize both the matrix and cluster regions of the ionomers. In the case of the bi-functional oligomers, however, the oligomers in the matrix-dominant ionomers showed anti-plasticization behavior at low oligomer contents. However, in the cluster-dominant system, the oligomers were phase-separated because of the insufficient amounts of non-ionic polymer matrix. In a subsequent study, Plante and Bazuin investigated the effects of

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the addition of mono-dispersed, tertiary amine-terminated styrene oligomers on the properties of lightly Na-sulfonated PS (SNa) ionomers.<sup>4</sup> The mono-functional styrene oligomers also plasticized the SNa, but much less than the mono-functional alkyl oligomers did, due to the bulkiness and stiffness of the styrene segments of the oligomer. The bi-functional oligomers showed a very weak plasticization effect and, at their higher concentrations, became phase-separated despite extensive inter-component interactions. Jeon *et al.* investigated the effects of various carboxylated benzene salts on the morphology and mechanical properties of poly(styrene-*co*-sodium methacrylate) (MNa) ionomers.<sup>5</sup> They found that the additives became phase-separated in the range of 5 and 46 wt% of benzene salts and, hence, acted mainly as reinforcing filler. Wakabayashi and Register studied the effects of few fatty acid salts (C<sub>16</sub>-C<sub>22</sub> in chain lengths) on the morphology and mechanical properties of ethylene/(meth)acrylic acid (EMNa) ionomers.<sup>6</sup> They observed that the structural and property modifications of the ionomers by the addition of the additives were complex, and depended on both the type of neutralizing cations and the degree of the crystallinity of the polymer chains and the hydrocarbon tails of the fatty acid salts. Recently, our group investigated the dynamic mechanical properties and morphology of the MNa ionomers containing sodium salts of aliphatic dicarboxylic acids (DCA's). It was found that the DCA's disrupted the formation of the multiplets of the ionomer.<sup>7</sup> However, later on, the authors came to know that the disruption of the multiplets was partly due to the inadvertent under-neutralization of the acid groups.<sup>8</sup> In a very recent paper, we reported that the mono-functional organic salts in PS-based ionomers acted as both plasticizer and filler, and that the bi-functional organic salts behaved only like filler.<sup>8</sup> Few other groups had also studied the effects of the organic acids (salts) on various properties of ionomers, and readers are referred to the original articles.<sup>9-12</sup>

Despite extensive studies on the behavior of mono- to multi-functional oligomers and aliphatic or aromatic compounds with or without functional groups and alkyl chains, only a few studies on the effects of aliphatic dicarboxylic acids (salts) on the properties of amorphous PS-based random ionomers have been performed, as mentioned above. Now we know that the bi-functional organic salts (adipate and dodecanedioate) become phase-separated and act as filler in the MNa ionomers.<sup>8</sup> However, the effects of the chain lengths of DCA's on the mechanical properties of the MNa ionomers are still not known. In addition, the roles of DCA's in carboxylated and sulfonated ionomers have not been explored yet. Thus, in the present study, we attempted to investigate the effects of various DCA's and the amounts of the DCA's on the dynamic mechanical properties and morphology of the MNa and SNa ionomers. As the DCA's, we used sodium succinate [NaOOC-(CH<sub>2</sub>)<sub>2</sub>-COONa] (DCA4), adipate [NaOOC-(CH<sub>2</sub>)<sub>4</sub>-COONa] (DCA6), dodecanedioate [NaOOC-(CH<sub>2</sub>)<sub>10</sub>-COONa]

(DCA12), and hexadecanedioate [NaOOC-(CH<sub>2</sub>)<sub>14</sub>-COONa] (DCA16).

## Experimental

**Sample Preparation.** PS homopolymer (molecular weight (MW) = ca. 500,000) and poly(styrene-*co*-methacrylic acid) (PSMAA) copolymer (MW = ca. 500,000) were synthesized by the method described elsewhere.<sup>13</sup> To prepare poly(styrene-*co*-styrenesulfonic acid) (PSSA) copolymer, the sulfonation reported by Makowski *et al.* was used.<sup>14</sup> To determine the acid contents, the copolymer samples were dissolved in a benzene/methanol (9/1, v/v) mixture to make a 5% (w/v) solution and titrated with methanolic NaOH solution to the phenolphthalein end point. The acid contents were 3.8 and 7.1 mol% for the PSMAA copolymers, and 4.5 mol% for PSSA copolymer. To prepare the ionomers containing DCA's, the acid forms of the DCA's and PSMAA or PSSA copolymers were dissolved in a benzene/methanol (9/1, v/v) mixture, and neutralized with methanolic NaOH fully. In this study, we prepared two sets of samples. In the first set of samples, the mole ratios of the ionic groups of the DCA's to those of the ionomers were kept at 1:1. Since the molecular weight of the DCA's increased with increasing number of the carbon atoms of the DCA's, the amount of the DCA's in the samples increased with the number of the carbon atoms of the DCA's to maintain the mole ratios of the ionic groups at 1:1 (Table I). Thus, the changes in the properties of the ionomers by the addition of the DCA's might be due to the variations in both the number of the carbon atoms of the DCA's and the amounts of the DCA's in the ionomers. Therefore, it would be helpful to study only the effect of the amounts of the DCA's on the ionomer properties. To do so, we prepared the second set of samples; the ionomers containing varying amounts of the DCA's of lowest and highest numbers of carbon atoms, i.e. DCA4 (sodium succinate) and DCA16 (sodium hexadecanedioate). The samples were freeze-dried and dried further in a vacuum oven at ca. 150 °C for 24 h. For the dynamic mechanical property measurements, the samples were compression-molded at ca. 240 and 260 °C for the methacrylate and sulfonated ionomers, respectively, at a pressure of ca. 25 MPa. The molded sam-

**Table I. The Amounts of DCA's in Ionomers\***

Dicarboxylates	Notation	Amount of DCA's (wt%)	
		7.1-MNa	4.5-SNa
Sodium succinate	DCA4	3.94	2.44
Sodium adipate	DCA6	4.83	2.96
Sodium dodecanedioate	DCA12	7.40	4.60
Sodium hexadecanedioate	DCA16	9.01	5.64

\*The mole ratios of the ionic groups of the DCA's to those of the ionomers were kept at 1:1.

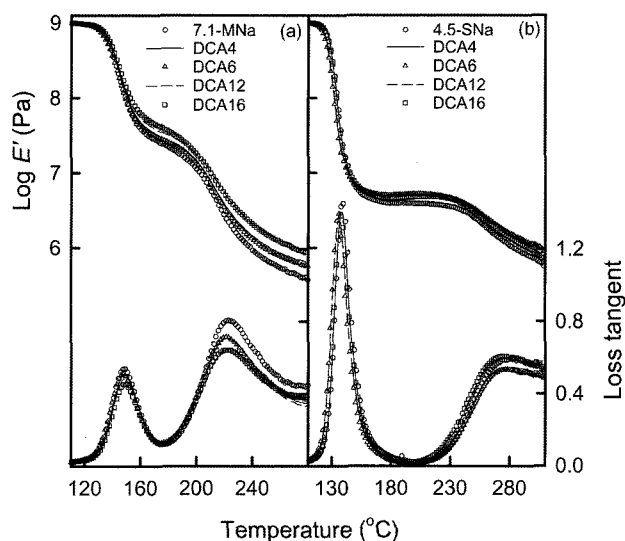
ples were annealed *in vacuo* at 150 °C for 24 h. The notation for the ionomers is x-MNa and x-SNa, where x is the ion content in mol%, and MNa and SNa are sodium-neutralized PSMAA and PSSA, respectively.

**Dynamic Mechanical and Thermal Property Measurements.** A TA Q 800 dynamic mechanical analyzer (TA Instruments, New Castle, DE) was used to measure the storage modulus and loss tangent of each sample as a function of temperature in a dual cantilever-bending mode at five different frequencies. The heating rate was 1 °C/min. To analyze the loss tangent plots, curve de-convolutions were performed using a Peakfit program (SPSS Inc.). The best fits were obtained using an exponential equation as the baseline and fitting the matrix and cluster loss tangent peaks with Gaussian functions. For a thermal property study, a TA DSC 2010 differential scanning calorimeter (TA Instruments, New Castle, DE) was used. The samples were scanned using the DSC from 30 to 300 °C, with a heating rate of 10 °C/min.

**X-ray Experiments.** The small-angle X-ray scattering (SAXS) experiments were conducted at Station 4C1 of the Pohang Light Source synchrotron radiation source (Pohang, Korea).<sup>15</sup> The generated critical beam energy was 5.5 keV (at 2.5 GeV operation modes), and the size of the beam at the sample was smaller than 1 mm<sup>2</sup>. The position-sensitive two-dimensional CCD X-ray detector was used. The SAXS data were plotted as relative intensity vs.  $q$  after correction for the sample absorption and a background, where  $q=4\pi \sin \theta/\lambda$ ;  $\theta$  is half the scattering angle, and  $\lambda$  is the X-ray wavelength ( $\lambda=0.1608$  nm). A PANalytical X'pert PRO MPD X-ray diffractometer (Almelo, the Netherlands) was used to obtain the X-ray diffraction (XRD) patterns. The scanning speed and sampling width were 0.3°/min and 0.018°, respectively.

## Results and Discussion

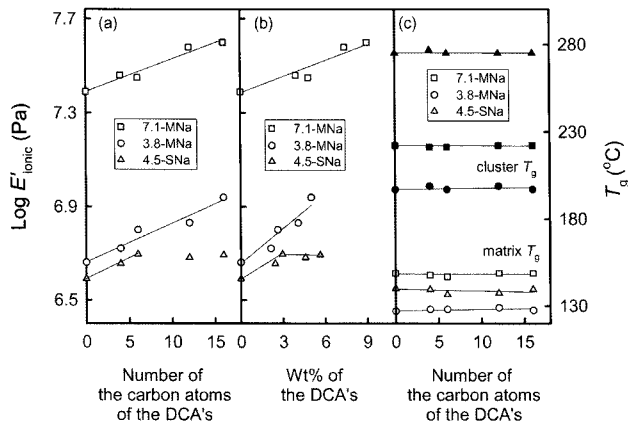
The storage moduli ( $E'$ ) as a function of temperature of 7.1-MNa and 4.5-SNa ionomers and the ionomers containing DCA's are shown in Figures 1(a) and 1(b), respectively. In these ionomers, the mole ratios of the ionic groups of the DCA's to those of the ionomers are 1:1. It is seen that with increasing temperature the modulus curve changes its shape from a plateau (i.e. glassy plateau), through a first drop (i.e. matrix glass transition), through a first descending plateau, so-called ionic plateau, through a second drop (i.e. cluster glass transition), to a second descending plateau (i.e. rubbery and flow regions). It is observed that below ca. 135 °C there is almost no difference in the modulus plots for all the samples including the pure ionomers. Above 135 °C, however, the heights of modulus plot of both 7.1-MNa and 4.5-SNa ionomers containing DCA's increase with increasing number of the carbon atoms of DCA's. It is also seen that the widths of the ionic plateaus do not change strongly with the number of the carbon atoms of the DCA's. At this point,



**Figure 1.** Storage moduli and loss tangents as a function of temperature of (a) 7.1-MNa and (b) 4.5-SNa ionomers containing various DCA's, measured at 1 Hz. The mole ratio of the ionic groups of the DCA's to those of the ionomers was kept at 1:1.

it should be mentioned that the width of the ionic plateau is related to the strength of interactions between the ionic groups of the ionomers in the multiplets.<sup>1</sup> Thus, the similar widths of the ionic plateaus imply that the addition of the DCA's, having the  $-\text{COO}^-\text{Na}^+$  ionic group, affects negligibly the formation of the multiplets of the 7.1-MNa and 4.5-SNa ionomer systems, having  $-\text{COO}^-\text{Na}^+$  and  $-\text{SO}_3^-\text{Na}^+$  ionic groups, respectively. Also, shown in Figures 1(a) and 1(b) are the loss tangent plots of the ionomers as a function of temperature. Each ionomer shows two loss tangent peaks; one at low temperatures is related to the glass transition of ion-poor regions (i.e. matrix regions) and the other at high temperatures to the glass transition of ion-rich regions (i.e. cluster regions).<sup>1,2,13,16</sup> It is seen that the addition of DCA's does not change the position, shape and width of the matrix and cluster loss tangent peaks significantly. Only the heights of the two peaks seem to decrease with increasing number of the carbon atoms of the DCA's. At this point, it should be mentioned that in some of filled systems including chloride-filled polyurethanes,<sup>17</sup> glass-fiber reinforced methacrylate polymers,<sup>18</sup> silica-filled ethylene-propylene-diene terpolymer (EPDM) rubbers,<sup>19</sup> and wood-fiber reinforced styrene-maleic anhydride polymers,<sup>20</sup> the  $T_g$ 's of the materials were independent of the filler content and/or filler size. From this, it can be suggested that the DCA's-containing MNa and SNa ionomer systems, showing similar  $T_g$ 's, might resemble the filled material.

The modulus at the point of the minimum slope of an ionic plateau is termed ionic modulus ( $E'_{\text{ionic}}$ ).<sup>1,2,13</sup> Figures 2(a) and 2(b) show the plots of the  $E'_{\text{ionic}}$  as a function of the number of the carbon atoms of the DCA's and the amounts of the DCA's in the ionomer systems. It is seen that the  $E'_{\text{ionic}}$



**Figure 2.** Ionic moduli and glass transition temperatures of 7.1-MNa, 3.8-MNa, and 4.5-SNa ionomers containing various DCA's, measured at 1 Hz.

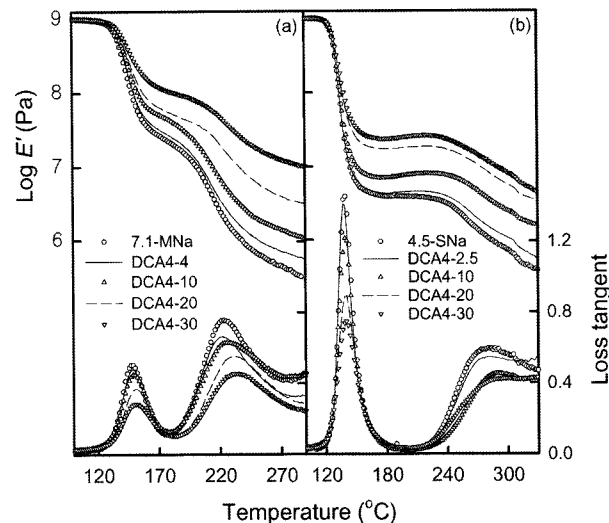
values of 7.1-MNa ionomer system increase considerably and linearly with increasing number of the carbon atoms of the DCA's and with increasing amounts of the DCA's. The  $E'_{ionic}$  data can be fitted with a first order polynomial equation; the best fitting results are as follows:

$\text{Log } E'_{ionic} \text{ (Pa)} = 7.4 + 0.014 \times (\text{the number of the carbon atoms of the DCA's})$  ( $r^2 = 0.9730$ ) and

$\text{Log } E'_{ionic} \text{ (Pa)} = 7.4 + 0.023 \times (\text{the weight percentage of the DCA's})$  ( $r^2 = 0.9449$ ).

Here,  $r^2$  is a linear least-squares correlation coefficient. In the case of the 4.5-SNa system, upon increasing number of the carbon atoms of the DCA's from 0 to 6, there is an increase in the  $E'_{ionic}$ . On a further increase in the number of the carbon atoms, the  $E'_{ionic}$  remains more or less constant. It is observed that the initial slope of the  $E'_{ionic}$  as a function of the carbon atom number of the DCA's of the 4.5-SNa ionomer is not much different from that of the 7.1-MNa ionomer (i.e. 0.017 for the 4.5-SNa vs. 0.014 for the 7.1-MNa). This indicates that the initial rates of the increasing  $E'_{ionic}$  might be independent of the type of the ionomer systems (i.e. methacrylate vs. sulfonate). When the  $E'_{ionic}$  values of the 4.5-SNa ionomer are plotted as a function of the weight percentage of the DCA's, however, it is seen that the initial slope appears to be somewhat higher than that of the 7.1-MNa ionomer (0.032 for the SNa vs. 0.023 for the MNa). At this point, it should be mentioned that we also studied the mechanical properties of the 3.8-MNa ionomer containing DCA's to investigate the effect of ion content on the mechanical properties of the DCA's-containing ionomers. Figure 2 also includes the  $E'_{ionic}$  values of 3.8-MNa ionomers. It is seen that the increasing rate of  $\log E'_{ionic}$  of the 3.8-MNa is slightly higher than that of the 7.1-MNa when the  $\log E'_{ionic}$  values are plotted as a function of the number of the carbon atoms of the DCA's. However, it is much higher in the plots of  $\log E'_{ionic}$  vs. the weight % of the DCA's as follows:

$\text{Log } E'_{ionic} \text{ (Pa)} = 6.7 + 0.017 \times (\text{the number of the carbon$



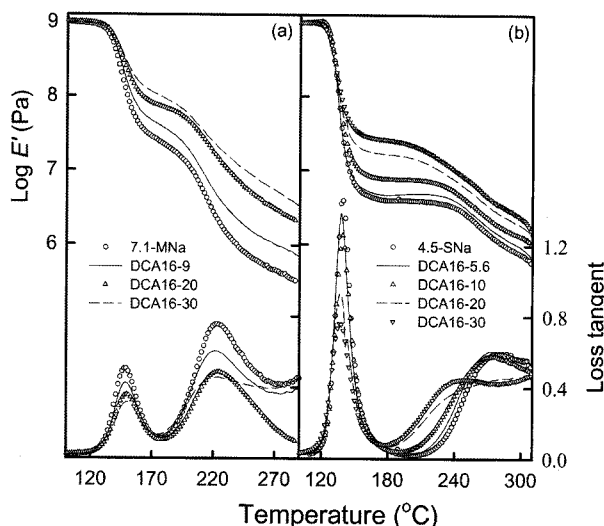
**Figure 3.** Storage moduli and loss tangents as a function of temperature of (a) 7.1-MNa and (b) 4.5-SNa ionomers containing varying amounts of DCA4, measured at 1 Hz.

atoms of the DCA's) ( $r^2 = 0.9695$ ) and

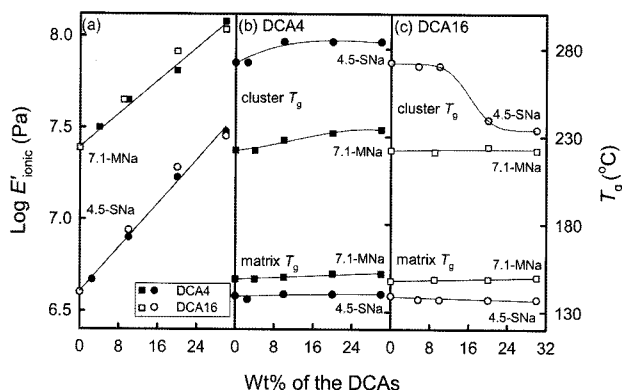
$\text{Log } E'_{ionic} \text{ (Pa)} = 6.7 + 0.050 \times (\text{the weight percentage of the DCA's})$  ( $r^2 = 0.9513$ ).

This indicates that, as expected, the effect of the addition of DCA's on the increasing  $E'_{ionic}$  is stronger for the ionomers of low ion contents, i.e. matrix-dominant ionomers, compared to the ionomers of high ion contents, i.e. cluster dominant materials.

The maximum weight percentage of the DCA's in the first set of samples was less than 10% (Table I), which is not sufficient to draw a conclusion of the effect of the amount of DCA's on the properties of the ionomers. Figures 3(a) and 3(b) show the storage modulus and loss tangent plots of the 7.1-MNa and 4.5-SNa ionomer systems containing varying amounts of DCA4 as a function of temperature. Above ca. 135 °C, the heights of the ionic plateau increase significantly with increasing amount of the DCA4. In the loss tangent plots, the matrix peak does not change its position strongly, but the cluster peak shifts to slightly high temperatures with increasing amount of the DCA4. However, the heights of the two loss tangent peaks decrease significantly. The storage modulus and loss tangent plots of the ionomers containing different amounts of DCA16 are also shown in Figures 4(a) and 4(b). In the storage modulus plots, again, the heights of the ionic plateau increase considerably with increasing amount of the DCA16. In the loss tangent plots of the 7.1-MNa system, it is observed that the positions of the peaks seem to remain more or less constant with increasing amount of the DCA16. However, in the case of the 4.5-SNa ionomer, the matrix peak shifts slightly to lower temperatures, and the cluster peak moves slowly and then significantly to lower temperatures with increasing amount of the DCA16. This will be discussed later in more detail.



**Figure 4.** Storage moduli and loss tangents as a function of temperature of (a) 7.1-MNa and (b) 4.5-SNa ionomers containing varying amounts of DCA16, measured at 1 Hz.



**Figure 5.** (a) Ionic moduli and (b and c) glass transition temperatures of 7.1-MNa and 4.5-SNa ionomers containing varying amounts of DCA4 and DCA16, measured at 1 Hz.

Shown in Figure 5(a) are the  $E'_{ionic}$  plots as a function of the amount of DCA's in the ionomers. As shown in Figure 2, it is observed that with increasing amount of the DCA's, the  $E'_{ionic}$  increases almost linearly. It should be noted that for a particular ionomer system, the plots of the  $E'_{ionic}$  of the ionomers containing DCA4 and DCA16 could be superimposed. This implies that the  $E'_{ionic}$  depends not on the type of the DCA's but on their amount in the ionomers. The  $E'_{ionic}$  values can also be fitted with a first order polynomial equation as follows:

For 7.1-MNa system,

$$\text{Log } E'_{ionic} \text{ (Pa)} = 7.4 + 0.022 \times (\text{weight percentage of DCA4}) \quad (r^2 = 0.9947),$$

$$\text{Log } E'_{ionic} \text{ (Pa)} = 7.4 + 0.023 \times (\text{weight percentage of DCA16}) \quad (r^2 = 0.9834),$$

and for 4.5-SNa system,

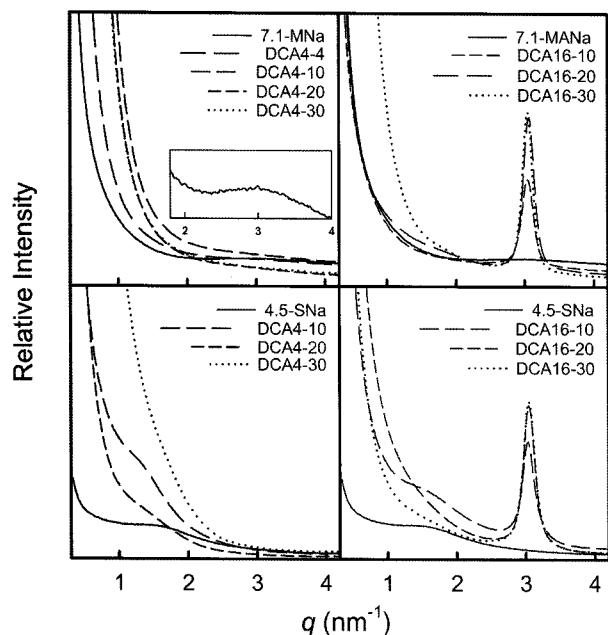
$$\text{Log } E'_{ionic} \text{ (Pa)} = 6.6 + 0.030 \times (\text{weight percentage of DCA4})$$

$$(r^2 = 0.9985),$$

$$\text{Log } E'_{ionic} \text{ (Pa)} = 6.6 + 0.030 \times (\text{weight percentage of DCA16}) \quad (r^2 = 0.9894).$$

The similarity in the slopes of the plots of the 7.1-MNa and 4.5-SNa systems indicates again that the increasing rates of  $E'_{ionic}$  depend only on the amount of DCA salts. Figures 5(b) and 5(c) show the  $T_g$ 's of the ionomers as a function of the amount of the DCA4 and DCA16, respectively. It is seen that the addition of the salts does not change the matrix  $T_g$ 's significantly. In the case of the cluster  $T_g$ 's of the DCA4 system, the  $T_g$  increases slightly. The similarity in the trends of the cluster  $T_g$ 's of the 7.1-MNa and 4.5-SNa systems indicates that the role of the DCA4 in both ionomer systems might be the same. In the case of the DCA16 systems, with increasing amounts of the organic salt, a negligible change in the cluster  $T_g$ 's of the 7.1-MNa ionomers is observed. However, the cluster  $T_g$  of the 4.5-SNa ionomers decreases drastically, implying that the role of the DCA16 in the ionomers is different from that of the DCA4.

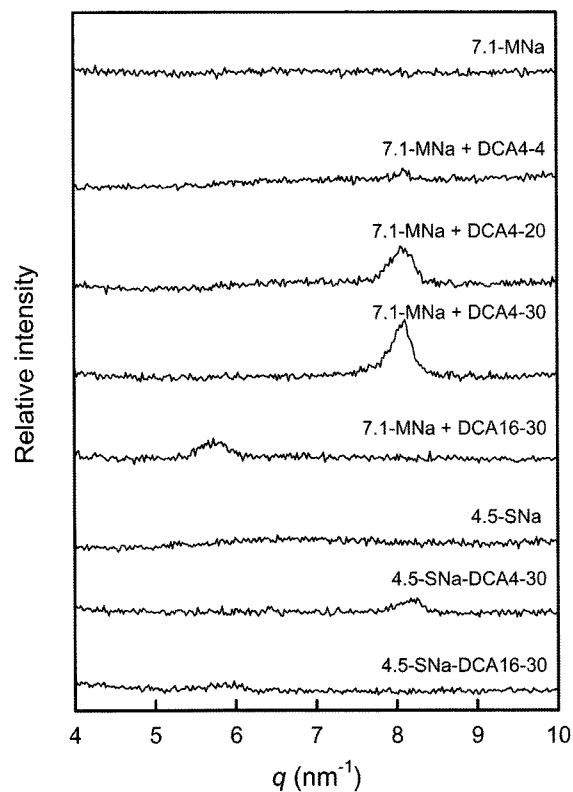
At this point, it should be mentioned that all the samples, except for the pure ionomers, were opaque. Since the phase-separated polymer blends are known to be opaque, we investigated the possible phase-separation of the DCA's in the ionomers using differential scanning calorimetry (DSC) and X-ray methods. In the DSC thermograms (not shown here), no melting peak of ordered domains was observed for all the systems below the decomposition temperature of the ionomers, i.e. ca. 280 °C.<sup>21</sup> This is not surprising because the thermal decomposition of DCA6 and DCA12 are expected to start well above 280 °C,<sup>7</sup> suggesting that, using the DSC, we could not detect the thermal transition of the ordered domains of DCA's. The small-angle X-ray scattering (SAXS) profiles of the ionomers containing DCA4 and DCA16 are shown in Figure 6. For the 7.1-MNa system, small angle upturns (SAUT's), probably representing the compositional heterogeneity of the ionomers,<sup>22-25</sup> are shown at very low angles. The position of the SAUT shifts to higher angles for the ionomers containing DCA's. This indicates that the heterogeneity of the systems increases upon the addition of the DCA's. A very broad and weak SAXS peak (see the inset of Figure 6), attributed to the inter-multiplet distances,<sup>26,27</sup> appears for the pure 7.1-MNa ionomer at  $q$  (scattering vector) = 3.0 nm<sup>-1</sup>, corresponding to a  $D_{Bragg}$  (Bragg distance) of ca. 2.1 nm. The position of the broad ionomer SAXS peak for the pure ionomer is in good agreement with the results reported in previous studies.<sup>3,14,27,28</sup> In the case of the DCA-containing 7.1-MNa ionomers, a sharp peak for the DCA16 systems is seen at  $q = 3.0 \text{ nm}^{-1}$ , but no well-developed peak for the DCA4 system is observed. It should also be noted that the position of the sharp peak of the DCA16 system is coincided with that of the broad ionomer SAXS peak. For pure 4.5-SNa ionomer, the SAUT and ionomer peak at  $q = 1.5 \text{ nm}^{-1}$  are observed. The ionomer peak position is, again, in good accordance with the results reported before.<sup>24,28-36</sup> In the case



**Figure 6.** SAXS profiles of the ionomers containing varying amounts of DCA4 and DCA16. The x in DCA's-x indicates the wt% of DCA's in the ionomer. The inset shows a SAXS profile of the 7.1-MN ionomer (the range of the y axis was adjusted to see a SAXS peak clearly).

of the DCA16 system, an additional sharp peak is seen at  $q=3.0 \text{ nm}^{-1}$ , but no additional peak is seen for the DCA4 system. The intensities of the sharp X-ray peaks for the MNa and SNa systems increase strongly and then slightly with increasing amount of the DCA16. In addition to the above findings, it is also seen that the addition of the DCA's does not change the position of the broad ionomer peak considerably. This suggests that the multiplet formation is not affected by the addition of DCA's.

The absence of a sharp SAXS peak for DCA4-containing systems leads us to the wide-angle X-ray study on the ionomers to see a possible phase-separation of the DCA4. The X-ray diffraction (XRD) patterns are shown in Figure 7. At this point, it should be mentioned that Figure 7 exhibits XRD data in the  $q$  range that the SAXS could not cover. The pure MNa and SNa ionomers do not show a sharp XRD peak for the ordered domains. In the case of the DCA4 systems, a sharp XRD peak is observed at  $q \approx 8.0 \text{ nm}^{-1}$  ( $D_{\text{Bragg}} \approx 0.79 \text{ nm}$ ), indicating the presence of the ordered domains of the DCA4 in the MNa and SNa ionomers. In the case of DCA16-containing ionomers, only a very weak peak at  $q \approx 5.5 \text{ nm}^{-1}$  is observed, which is related with the strong SAXS peak at  $q \approx 3.0 \text{ nm}^{-1}$ . It should be noted that the  $D_{\text{Bragg}}$ 's of ca. 0.79 nm for the DCA4 system and 2.1 nm for the DCA16 system, obtained from the SAXS study, are similar to the distances between the ionic groups of the fully extended DCA4 and DCA16, respectively. This suggests that the DCA's are phase-separated and form ordered



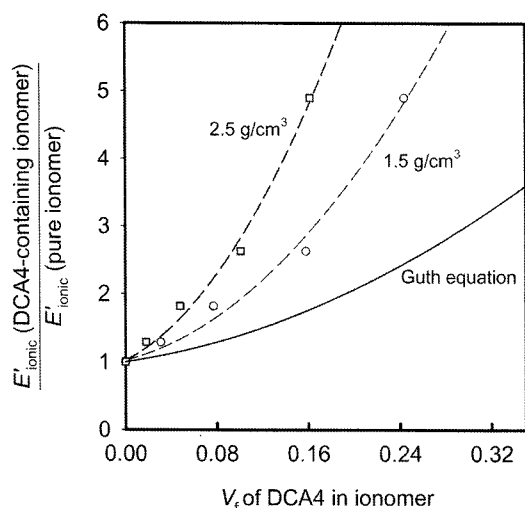
**Figure 7.** XRD patterns of the ionomers containing varying amounts of DCA4 and DCA16. The x in DCA's-x indicates the wt% of DCA's in the ionomer.

domains in the ionomers.

Since the addition of the filler increases the polymer modulus,<sup>37,38</sup> the phase-separated and ordered domains of DCA's in the present system can be thought as filler. Thus, an attempt was made to fit the experimental  $E'_{\text{ionic}}$  data with the Guth equation that can be used to calculate the modulus of composites having rigid spheres. It should be mentioned that this equation is applicable to the systems having the non-elastic, spherical filler particles up to ca. 30 vol% of the fillers in the sample.<sup>39</sup> The Guth equation shows the relationships between the Young's moduli of the filled/unfilled polymers and the volume fraction of the filler as follows:

$$E^*/E = 1 + 2.5V_f + 14.1V_f^2$$

where  $E^*$  and  $E$  are the Young's moduli of the filled and unfilled polymer, respectively, and  $V_f$  is the volume fraction of the filler in the composite. In the present work, the  $E'_{\text{ionic}}$  of the ionomer systems having DCA's was taken as  $E^*$ , and that of the pure ionomer as  $E$ . To calculate the  $V_f$  of the DCA's, we needed the densities ( $d$ ) of the ionomers and the DCA's. The density of the pure MNa ionomer was ca. 1.13  $\text{g}/\text{cm}^3$ , measured using a pycnometer, but the density data of the DCA's were not available. Thus, we used an indirect method to estimate the density of, for example, DCA4 by analyzing the densities of some of the organic acids and



**Figure 8.** The ratio of the ionic modulus of the ionomers containing DCA4 to that of the pure ionomer as a function of volume fraction of the DCA4 in the ionomers.

their salt forms, whose chemical structure resembling that of the DCA4. The organic acids and salts were formic acid ( $d=1.22 \text{ g/cm}^3$ )/sodium formate ( $d=1.92 \text{ g/cm}^3$ ), acetic acid ( $d=1.049 \text{ g/cm}^3$ )/sodium acetate ( $d=1.53 \text{ g/cm}^3$ ), and oxalic acid ( $d=1.65 \text{ g/cm}^3$ )/sodium oxalate ( $d=2.34 \text{ g/cm}^3$ ).<sup>40</sup> From these data, we assumed that the density of sodium salt of the succinic acid (DCA4) would be in the range of 1.5 and 2.5  $\text{g/cm}^3$ . With the estimated density and weight fractions of DCA4, it was possible to calculate the volume fractions of the DCA4 in the ionomers; all of the DCA4 molecules were assumed to act as filler particles. In Figure 8, the experimental data and calculated data using the Guth equation are present. It is seen that the experimental values are significantly higher than those obtained from the Guth equation. This implies that the increasing  $E'_{ionic}$  is not only due to the filler effect of DCA's but also possibly due to the formation of more multiplets, leading to higher degree of clustering. The latter induces naturally a higher  $E'_{ionic}$  and a higher cluster  $T_g$  of the ionomer that are indeed what we observed in Figures 5(a) and 5(b). In the case of DCA16, it was not easy to estimate the  $V_f$  of the phase-separated DCA16 using the method mentioned above because of the lack of relevant data. Thus, we could not apply the Guth approach to the DCA16 system.

In the section dealing with the  $T_g$ 's, we have shown that the addition of the DCA's does not change the matrix  $T_g$ 's of the 7.1-MNa and 4.5-SNa ionomers strongly. However, the cluster  $T_g$ 's increase slowly upon the addition of DCA4. In the case of the DCA16, it does not affect the cluster  $T_g$  of the 7.1-MNa. However, the addition of DCA16 decreases the cluster  $T_g$  of the 4.5-SNa ionomer. The possible reasons for the different trends in the cluster  $T_g$ 's upon the addition of the DCA4 and DCA16 are given below. At this point, it is

worth recalling that at low ion contents, some of the ion pairs of the ionomers, which are beyond the loop-back distances for ion aggregation, are not able to take part in a multiplet formation.<sup>1,2</sup> As the DCA's are phase-separated and reside in the matrix of the ionomers, the isolated ion pairs of the ionomers might have more chances to come close to each other, leading to the formation of more multiplets. If this were the case, the cluster  $T_g$  should increase, at least to a certain extent. When a large amount of the DCA16 is added to the ionomers, some of the DCA16 molecules are not fully phase-separated and might exist singly or as imperfectly ordered domains in the matrix of the ionomers. It should also be noted that the DCA16, being much less polar compounds than the DCA4 naturally prefer to reside in the relatively non-polar regions of the ionomers, i.e. the bulk matrix regions and restricted mobility regions of clusters. Initially, the DCA16 molecules would prefer to be phase-separated in the bulk matrix regions; then, the DCA16 acts as filler. Upon further increasing amount of the DCA16, some of the DCA16 start to reside in the restricted mobility regions; now, the DCA16 behaves like a plasticizer for the cluster regions as well, leading to a decreasing cluster  $T_g$ . It should be reminded that the ion pairs of DCA16 (i.e.  $-\text{COO}^- \text{Na}^+$ ) and SNa ionomer ( $-\text{SO}_3^- \text{Na}^+$ ) are different. Thus, at high DCA16 contents, the ion pairs of some of the DCA16 molecules are expected to interact with the ion pairs in the multiplets of the ionomer. If this were the case, the  $-\text{COO}^- \text{Na}^+$  ion pairs of the DCA16 would weaken the interactions between  $-\text{SO}_3^- \text{Na}^+$  ion pairs in the multiplets of the 4.5-SNa ionomer. This leads to the strong decrease in the cluster  $T_g$  of the 4.5-SNa ionomer. Agarwal *et al.* observed similar results in the zinc sulfonate EPDM system containing the zinc stearate that acted as "multiplet plasticizers".<sup>41</sup>

## Conclusions

When the amounts of the DCA's in the MNa and SNa ionomers were relatively small, the DCA's acted mainly as filler. The filler effect depended only on the amount of the DCA's, and the type of ionic groups of the ionomers and the chain lengths of the DCA's did not influence the filler effect significantly. However, in the case of the ionomers containing relatively large amounts of DCA's, the DCA4, the chain length of which was too short to show a strong plasticization effect, acted, again, primarily as a reinforcing additive and increased the modulus of both the MNa and SNa systems. On the other hand, the DCA16, the chain length of which was long enough to exhibit a possible plasticization effect, played a role, again, as filler and, thus, increased  $E'_{ionic}$ . At high DCA16 content, the salt behaved both as filler and as plasticizer. Furthermore, in the SNa ionomer, the DCA16 even functioned as a multiplet plasticizer, causing a drastic decrease in the cluster  $T_g$ .

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