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Disruption of the multiplets in poly(styrene-*co*-methacrylate) ionomers by the addition of aliphatic diacid salts

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Abstract

Dynamic mechanical properties and morphology of poly(styrene-*co*-sodium methacrylate) ionomers containing disodium salts of aliphatic diacid were investigated. It was found that upon the addition of diacid salts to the ionomers, the position of the matrix loss tangent peak remained constant, but the cluster loss tangent peak shifted to lower temperatures; the size of the matrix loss tangent peak increased, but that of the cluster peak decreased. In addition, the ionomers containing diacid salts showed X-ray diffraction patterns at relatively wide angles but no DSC melting peak. Thus, it was postulated that the organic salts prohibit the ionic groups of the ionomer from forming multiplets, and that the ionic groups of the ionomer, not forming the multiplets, participate in the formation of ionic aggregates with the ionic groups of the diacid salts.

Keywords: Ionomer; Multiplet; Plasticization

1. Introduction

Ionomers have a small number of ionic groups in a polymer matrix of low dielectric constant and frequently show two-phase behavior. This two-phase nature is due to the formation of polar ion aggregates within the non-polar matrix. These ionic aggregates, called multiplets [1], lead to the reduction in mobility of the polymer chain segments surrounding them [2]. When the ion content is low, only a few of multiplets with the restricted mobility layer are existed. When the ion content increases, overlapping of the restricted mobility regions occurs to form larger continuous regions, called clusters, which show their own glass transition temperature (T_g) [2]. Thus, in a certain range of ion content some of amorphous ionomers, e.g. styrene ionomers and ethyl acrylate ionomers, show two T_gs. The T_g at low temperatures is ascribed to the glass transition of the unclustered (i.e. matrix) regions and the T_g at high temperatures to the glass transition of the clustered regions [2].

Since polystyrene ionomers have relatively non-polar hydrocarbon matrix regions and relatively polar multiplets, it is possible to plasticize selectively either multiples or matrix regions, or both, depending on the type of plasticizers used [3–14]. For example, Kim et al. found that the addition of mono-functional surfactant, sodium dodecylbenzenesulfonate (SDBS), to sodium sulfonated polystyrene (NaSPS) ionomers decreased the cluster T_g of the ionomer significantly [10]. However, the matrix T_g of the ionomer changed only slightly upon the addition of the plasticizer. Subsequently, Orler and Moore studied the dynamic mechanical properties of NaSPS ionomers containing sodium benzenesulfonate (SBS), and found that the addition of the SBS to the NaSPS ionomer decreased the cluster T_g of the ionomer slightly, without changing the matrix T_g [11]. Recently, Nah et al. investigated the effects of organic salts, i.e. sodium *p*-toluate and sodium *p*-toluenesulfonate, on the mechanical properties of styrene ionomers [12]. Plante et al. studied the plasticization of *p*-carboxylated polystyrene ionomers by the addition of oligomeric styrene amphiphiles (M_w = ca. 800) [13]. It was found that, upon the addition of the amphiphiles, the cluster T_g of the Cs^+-neutralized system dropped more significantly than that of the Ba^{2+}-neutralized system. In those two systems, the matrix T_g decreased nearly in parallel. In a

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subsequent study by the same authors [14], it was observed that in the matrix-dominated ionomer the bi-functional oligomeric amphiphiles, i.e. α,ω-dicarboxystyrene (M_w = ca. 4400) showed anti-plasticization effects at low amphiphile contents. In the cluster-dominated ionomer, however, it was found that the amphiphiles formed a separated phase due to its very low ion content, compared to the ionomer.

Even though the effects of the bi-functional oligomeric styrene amphiphiles, which were prepared by anionic polymerization, were studied by Plante et al, the effects of bi-functional aliphatic amphiphiles of low molecular weight, which can be obtained much more easily, have not been investigated. Thus, in the present study, we explored the effects of the addition of aliphatic diacid salts on the dynamic mechanical properties of styrene-*co*-sodium methacrylate ionomers. As the aliphatic diacid salts, we chose three sodium neutralized organic diacid compounds, which have various lengths of alkyl chain, such as disodium salts of succinic acid [$Na^+ \ ^-OOC{-}(CH_2)_2{-}COO^- \ ^+Na$], adipic acid [$Na^+ \ ^-OOC{-}(CH_2)_4{-}COO^- \ ^+Na$], and dodecanedioic acid [$Na^+ \ ^-OOC{-}(CH_2)_{10}{-}COO^- \ ^+Na$]. These three salts have ionic groups at both ends of the alkyl chain; the ionic groups at both ends of the alkyl chain were thought to reside either in the same multiplet or in two different multiplets, depending on the chain length, or exist in another form. Thus, the results obtained in this study would give us the information on the effect of the diacid salt additives on the mechanical properties and morphology of the ionomers.

2. Experimental

2.1. Materials

Poly(styrene-*co*-methacrylic acid) random copolymer (molecular weight = ca. 300,000) was prepared by free-radical polymerization of purified styrene and methacrylic acid. For convenience, only a brief summary of the procedure is given here. The bulk polymerization was carried out at 60 °C using benzoyl peroxide as the initiator. After the pre-calculated polymerization time to give the conversion of ca. 4% for a compositional heterogeneity of ca. 0.1, the reaction mixture was cooled and diluted with tetrahydrofuran. The acid copolymer was recovered by the precipitation of the reaction mixture into excess methanol and by the subsequent filtration. The acid copolymer sample was then dried under vacuum at 120 °C for 12 h. To determine the acid content, the copolymer sample was dissolved in a benzene/methanol (9/1 v/v) mixture to make a 5% (w/v) solution and titrated with standard NaOH in methanol to the phenolphthalein end point; the acid content was 9.4 mol%. In order to prepare the ionomers containing disodium salts of aliphatic diacids, the diacid compounds (i.e. succinic acid (SD), adipic acid (AD), and dodecanedioic acid (DD)) (purchased from Aldrich) were added to a benzene/methanol (9/1 v/v) mixture containing the acid form copolymer. The ratios of (the mole of the acid groups of the aliphatic diacid compounds)/(the mole of the acid groups of the acid form copolymer) were 0/1, 0.5/1, 1/1, and 2/1. A predetermined amount of methanolic NaOH was added to the solution to neutralize the acid groups of both the acid form copolymer and the aliphatic diacid compounds. The solution was freeze-dried and dried further under vacuum at ca. 130 °C for 24 h. The notation used for these samples is M–*y*, where M is the type of sodium neutralized diacid compound, i.e. NaSD, NaAD, and NaDD, and *y* denotes the ratio of ionic groups in (aliphatic diacid salts/ionomer), i.e. 0, 0.5, 1, and 2.

For the dynamic mechanical property measurements, the samples were compression-molded at ca. 240–260 °C, depending on the amount of the aliphatic diacid salt, and a pressure of ca. 25 MPa. The molded samples, with approximate dimensions of $2.5 \times 7.0 \times 30.0\ mm^3$, were annealed for 24 h in a vacuum oven at 130 °C. For the small-angle X-ray scattering (SAXS) and X-ray diffraction (XRD) studies, the cesium and sodium neutralized samples were compression-molded, respectively. At this point, it should be mentioned that CsOH was used as the neutralizing agent instead of NaOH for the investigation of the morphology of ionomers by the SAXS technique, since the former scatters more than the latter. The molded samples in the form of a disk with dimensions of 12 mm (diameter) × 0.5 mm (thickness) were stored under vacuum at 100 °C for 24 h.

2.2. Dynamic mechanical thermal analysis

To measure the dynamic mechanical properties of ionomers, a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA, Mark II model) was used. The dual cantilever bending mode, at frequencies of 0.3, 1, 3, 10 and 30 Hz, was utilized. The heating rate was 1 °C/min. For each sample, the storage moduli (E') and loss tangents were obtained as a function of temperature. Even though dynamic mechanical measurements for each sample were conducted at five different frequencies, detailed analysis was performed only on 1 Hz data. Curve de-convolutions were performed on the loss tangent data using the Peakfit (SPSS Inc.) software. The best fits were obtained by using the exponential equation as a background and fitting the matrix and cluster loss tangent peaks with two Gaussian area functions.

2.3. X-ray experiments

The SAXS experiments for the cesium neutralized samples were conducted at Station 4C1 of the PLS synchrotron radiation source (Pohang, Korea) [15]. The generated critical beam energy was 2.8 keV (at 2.5 GeV operation mode). The size of the beam at the sample was smaller than 1 mm^2. The position-sensitive one-dimensional

Si diode-array detector was used. The sample-to-detector distance was 400 mm, which allowed SAXS data to be obtained in the q range from ca. 0.4 to 5.7 nm^{-1}, where $q = 4\pi \sin \theta/\lambda$, θ is half the scattering angle, and λ is the X-ray wavelength ($\lambda = 0.1608$ nm). The SAXS data were plotted as relative intensity vs. q after correction for sample absorption and a background. The XRD patterns for sodium neutralized samples were recorded by using an X-ray diffractometer (Rigaku Co., D/MAX-3C model). The Cu radiation ($\lambda = 0.15418$ nm) was utilized, and the power of the X-ray generator was 35 kV and 15 mA. The scanning speed was 1°/min, and the sampling width was 0.01°.

2.4. Differential scanning calorimetry

For the thermal analysis studies, a TA differential scanning calorimeter (DSC 3000) was used. It was calibrated with indium. The sample cell containing ca. 8 mg of sample was stored under a nitrogen atmosphere. The samples were scanned from 70 °C to ca. 240–260 °C to span the range of the two glass transition temperatures of the ionomer and the melting temperature of the phase-separated and crystallized diacid salts.

3. Results and discussion

The storage moduli (E') as a function of temperature for the poly(styrene-*co*-sodium methacrylate) ionomer containing 9.4 mol% of ionic groups [P(S-9.4-MANa)] and ionomers containing disodium salts of dodecanedioic acid (NaDD) are shown in Fig. 1(a). With increasing temperature, the modulus value changes from the glassy modulus, through the glass transition of the matrix phase, through the 'ionic modulus', through the glass transition of the cluster phase (180–230 °C), through the rubbery modulus, to modulus for sample flow. It is seen that above ca. 130 °C the moduli of the pure ionomer are higher than those of the ionomers containing the aliphatic diacid salts. Especially, it is shown that at ca. 170 °C the pure ionomer shows its 'ionic' modulus, i.e. the modulus between the matrix and cluster T_gs, and that with increasing diacid salt content the modulus value at 170 °C decreases significantly. In addition, it is also shown that the modulus value at ca. 270 °C, which is the rubbery modulus of the pure ionomer, decreases slightly with increasing amount of the aliphatic diacid salts. In the case of the ionomers containing sodium succinate (NaSD) and sodium adipate (NaAD), the plots of modulus value as a function of the amount of aliphatic diacid salts show similar trends (not shown here). Fig. 1(b) shows the storage modulus values of the P(S-9.4-MANa) ionomer and ionomers containing three different diacid salts. At this time, the ratio of the number of the ionic groups of the diacid salts to that of the ionomer is set to be 1/1. Again, above the matrix T_g, the moduli of the ionomers containing the three different diacid salts are lower than that of the pure ionomer. It is also shown that the shapes of the modulus curve for the ionomer samples containing three different aliphatic diacid salts are very similar to each other. This result implies that the degree of clustering of the ionomer is affected not by the type of the salts but by the amount of the salts.

Fig. 2 shows the modulus values at 170 and 270 °C of the ionomers containing NaSD, NaAD, and NaDD diacid salts as a function of the amount of the diacid salts. In the figure, as was mentioned above, it is clear that with increasing diacid salt content, the modulus values at 170 and 270 °C decrease. This result suggests that the diacid salts may not act as filler, since the addition of filler to polymers usually results in the increase of the modulus value [16]. As was mentioned above, with increasing diacid salt content the decrease of the modulus at 170 °C is more profound than that of modulus at 270 °C. For example, upon the addition of diacid salts, the modulus at 170 °C decreases from ca. $10^{7.6}$ Pa for the pure ionomer to ca. $10^{6.4}$ Pa for the NaAD-2

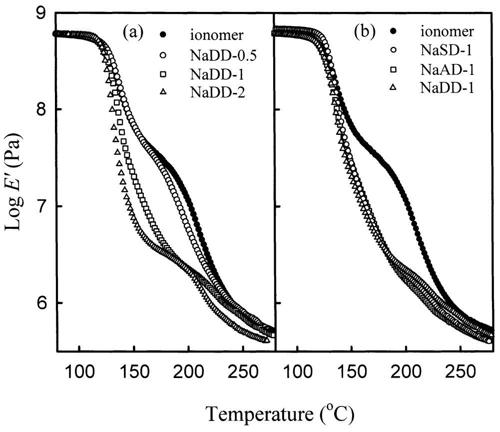

Fig. 1. Storage moduli as a function of temperature for (a) the P(S-*co*-MANa) ionomer containing 9.4 mol% of ions, and the ionomers containing various amounts of sodium dodecanedioate and for (b) the ionomers containing various sodium salts. All data were measured at 1 Hz.

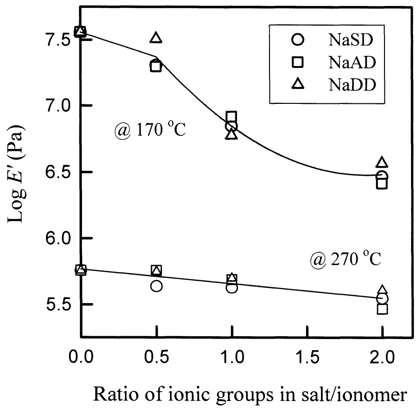

Fig. 2. Storage moduli at 170 °C (top) and at 270 °C (bottom) as a function of the ratio of ionic groups in (salt/ionomer), for the P(S-*co*-MANa) ionomer and ionomers containing disodium salts of adipic acid (NaAD), succinic acid (NaSD), and dodecanedioic acid (NaDD). All data were measured at 1 Hz.

sample. In the case of the modulus at 270 °C, it decreases from ca. $10^{5.8}$ Pa for the pure ionomer to ca. $10^{5.5}$ Pa for the NaAD-2 sample. At this point, it should be mentioned that the ion aggregation and chain entanglement are responsible for the ionic and rubbery moduli, respectively [3]. Thus, the above findings indicate that the addition of the aliphatic diacid salts to the ionomer affects the mechanical properties of ionomers attributed to ion aggregation more strongly, compared to those attributed to the chain entanglements. In the figure, it is, again, seen that the type of aliphatic diacid salts does not affect the ionic modulus value strongly.

Shown in Fig. 3(a) are the loss tangent values as a function of temperature for the P(S-9.4-MANa) ionomer and ionomers containing disodium salts of dodecanedioic acid. It is seen that the loss tangent peak at lower temperature, i.e. the matrix loss tangent peak, remains at similar temperatures with increasing diacid salt content, but the area under the peak increases significantly. In the case of the cluster loss tangent peak, however, the peak shifts to lower temperatures with increasing diacid salt content, and the area under the peak decreases; the cluster peak of the NaDD-2 sample seems to merge into the matrix peak. This figure also shows a shoulder-like peak for the ionomers containing diacid salts in the temperature range for the cluster T_g of the pure ionomer. This shoulder-like peak is also observed in other ionomer systems containing NaAD and NaSD salts. The presence of this shoulder-like peak implies that there are phase-separated cluster regions, unaffected by the addition of the diacid salts. At this point, it should be mentioned that the determination of the position of a shoulder-like loss tangent peak was very difficult due to the obscure shape of the peak, and, thus, we did not attempt to analyze the shoulder-like peak in detail using the Peakfit program.

Fig. 3(b) shows the loss tangent values of the pure P(S-9.4-MANa) ionomer and ionomers containing three different aliphatic diacid salts. As in Fig. 1(b), the ratio of the ionic groups is set as 1/1. In the figure, it is seen that there are minor differences in the shape and position of the peaks. In the case of the NaAD-containing ionomer, the cluster T_g is slightly higher than those of the other two ionomers containing NaDD and NaSD. In addition, the height of the matrix loss tangent peak for the NaAD-1 ionomer is somewhat lower than those for the NaSD-1 and NaDD-1 ionomers. It is also shown that, as was mentioned above, the shoulder-like peak is present for all of the ionomers containing aliphatic diacid salts in the temperature range for the cluster T_g of the pure ionomer.

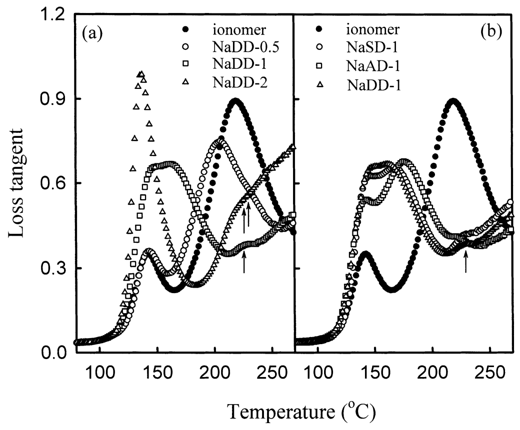

Fig. 3. Loss tangent curves as a function of temperature for (a) the P(S-*co*-MANa) ionomer containing 9.4 mol% of ions and the ionomers containing various amounts of sodium dodecanedioate, and for (b) the ionomer containing various sodium salts. The ratio of the ionic groups was fixed as 1:1. All data were measured at 1 Hz.

In Fig. 4, the glass transition temperatures of the ionomer and ionomers containing the diacid salts are shown as a function of the ratio of ionic groups. The matrix T_gs seem to remain constant, while the cluster T_gs decrease significantly with increasing diacid salt content. When the ratio of the ionic groups is 1/1, the cluster T_g decreases by ca. 40–60 °C. When the ratio becomes 2/1, the cluster T_g decreases even further by ca. 75 °C, leading to the cluster T_g almost merging into the matrix T_g. At this point, it should be noted that the type of the diacid salts, in other words, the length of the alkyl chains in the diacid salt molecules, does not change the decreasing rates of the cluster T_g noticeably with increasing diacid salt content.

Shown in Fig. 5(a) are the areas under the loss tangent peaks for the matrix and cluster T_gs and the sum of the areas as a function of the ratio of ionic groups. Fig. 5(b) shows the relationship between the areas and the wt% of the ionomeric materials in the ionomer containing organic salts. The two figures show a similar trend. As was mentioned before, it is clear that the area under the cluster loss tangent peak (A_c) decreases strongly, while the area under the matrix loss tangent peak (A_m) increases drastically with increasing diacid salt content (i.e. with decreasing wt% of the ionomer in the sample). It is also noted that the total area ($\sum A$) decreases more or less linearly with decreasing wt% of the ionomer in the sample. Since the relative area under the peak is thought to represent the relative amount of a corresponding material in the sample containing filler,

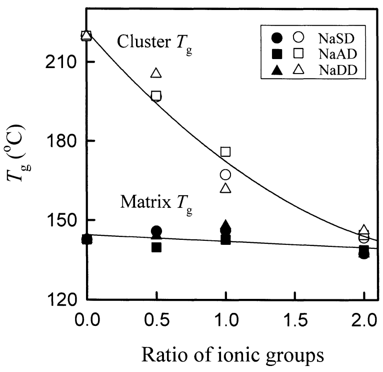

Fig. 4. Glass transition temperatures of the matrix and cluster regions for the ionomers containing sodium succinate (NaSD), adipate (NaAD), and dodecanedioate (NaDD) as a function of the ratio of ionic groups, measured at 1 Hz.

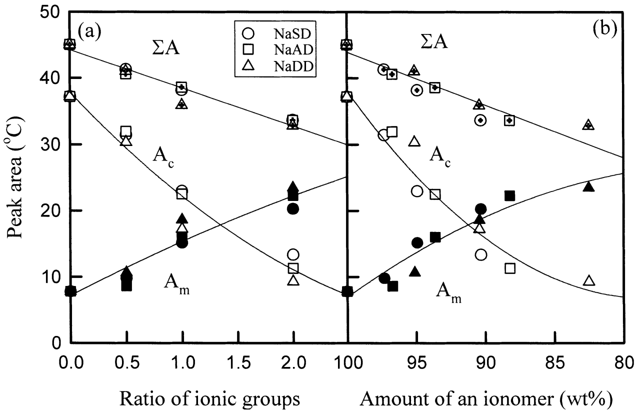

Fig. 5. Areas under matrix tan δ peak (A_m) and cluster tan δ peak (A_c), and the sum of the areas ($\sum A$) as a function of both (a) the ratio of ionic groups and (b) the wt% of ionomer in the sample, measured at 1 Hz. The sum of the areas is also shown.

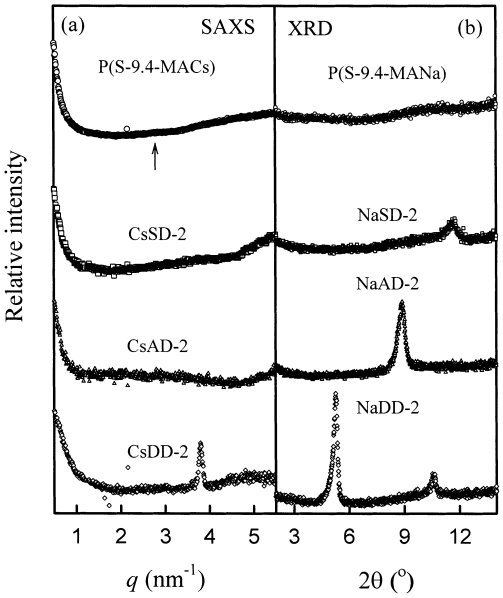

Fig. 6. (a) SAXS data for the Cs-neutralized ionomer, CsSD-2, CsAD-2, and CsDD-2 samples and (b) XRD data for Na-neutralized samples. Each curve was shifted up by the same magnitude with respect to each other for clarity.

additives, or other polymers [12,17–20], in the present study the decreasing trend in the total area with decreasing ionomer content can be understood.

The addition of either polar or preferential plasticizers usually decreases only the cluster T_g of ionomers [3–10, 20–23]. Thus, at the first glance, the results obtained in this study can be thought to imply that the organic diacid salts may act either as polar plasticizers or as preferential plasticizers. If polar plasticizers were added to ionomers, the plasticizers would reside in the multiplets and weaken the strength of the ionic interactions between the ionic groups in the multiplets, resulting in the decreasing cluster T_g [3–9, 20–23]. However, this may not be the case here; because the non-polar alkyl chains of the organic salts probably reside in the non-polar matrix regions surrounding the polar multiplets [10,11], the diacid salts cannot be considered as a polar plasticizer in the present work. It should also be mentioned that since the ionic groups of the ionomer and the organic salt are the same, i.e. sodium carboxylate, the possibility of the plasticization of multiplets by incorporating different types of ionic groups into the same multiplet is also ruled out. The example of such plasticization is Zn-sulfonate EPDM system containing Zn-stearate [24], in that the introduction of carboxylate ionic groups to the sulfonate multiplets weakens the strength of ionic interactions between Zn-sulfonate ionic groups.

Shown in Fig. 6(a) are the results of SAXS experiments. It is seen that the pure cesium neutralized ionomer shows a very weak SAXS peak at $q =$ ca. 3.0 nm^{-1} (the Bragg distance of ca. 2.0 nm) as well as a small angle upturn (SAUT). The SAXS peak is ascribed to the distance between ionic aggregates [2,26], and the SAUT is associated with the polydispersity and irregularity of the structure of scattering entities [27]. In the figure, it is interesting to note that in the case of the CsDD-2 sample, a sharp X-ray peak is seen at $q =$ ca. 3.8 nm^{-1}, which corresponds to $2\theta =$ ca. 5.3°. The pure ionomer, CsSD and CsAD-containing samples, however, do not show a sharp X-ray peak. Thus, we performed XRD experiments to detect a wide-angle X-ray peak, if there were any. It should be mentioned that for the XRD study we used Na-neutralized ionomer systems, which were the identical samples used for the DMTA experiments. Fig. 6(b) shows the XRD results; a sharp peak is seen at $2\theta = 11.7°$, 8.9°, and 5.3° for the NaSD-2, NaAD-2, and NaDD-2 ionomers, respectively. These angle values correspond to the Bragg distances of ca. 0.76, 0.99, and 1.68 nm, respectively, which are similar to the distances between ionic groups of the fully extended diacid salts; that is, the distances between the two ionic end groups for SD, AD, and DD molecules are assumed to be ca. 0.8, 1.1, and 1.6 nm, respectively.

In order to study the possible phase-separation and crystallization of added diacid salts, we used a DSC technique. Fig. 7 shows the DSC thermograms of ionomer-diacid salt blends and polystyrene samples containing a comparable amount of various diacid salts. In the figure, no DSC melting peak is observed for the ionomer and its diacid salt blends as well as PS-NaSD-2 sample, while the peak is seen at ca. 153 and 176 °C for the PS-NaAD-2 and PS-NaDD-2 samples, respectively. This result reveals that in the PS homopolymer matrix the NaAD and NaDD salts are phase-separated, well ordered, and thus crystallized. In the case of the PS-NaSD sample, the alkyl chain of NaSD salts in the PS homopolymer might not be long enough to form crystalline regions. From the above results, it can be suggested that the presence of the X-ray peak and no DSC melting peak for the ionomers containing diacid salts implicate that the diacid salt molecules in the ionomer samples exist either singly in the matrix or in the form of

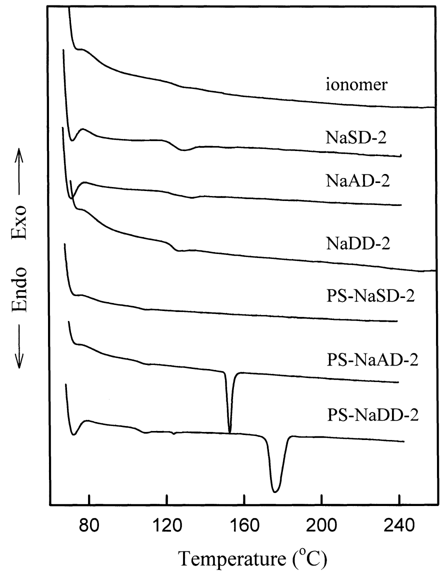

Fig. 7. DSC thermograms of the Na-neutralized ionomers and polystyrene samples containing the comparable amount of diacid salts. Each curve was shifted up by the same magnitude with respect to each other for clarity.

phase-separated and ordered entities that are, however, too small to be detected by a DSC technique, or probably both.

Now, let us discuss the possibility of the preferential plasticization. At this point, the preferential plasticization in the SDBS-NaSPS system is worth recalling [10]. In that system, the alkyl chain of the SDBS surfactant molecule resides mainly in the restricted mobility layer surrounding the multiplet of the NaSPS ionomer. Thus, the cluster T_g decreases not by disruption of the multiplets but by the plasticization of the restricted mobility regions. It should also be mentioned that in the case of the preferential plasticization, the position and size of the matrix loss tangent peak were found to remain more or less constant, and only the position of the cluster peak shifted to lower temperature [10]. In the present study, however, the size of the matrix loss tangent peak increases significantly with increasing amount of diacid salts, and, thus, it might be suggested that the aliphatic diacid salts in the present system do not mainly act as preferential plasticizer, but possibly in part. At this point, the possibility of the presence of looping-back alkyl chains of the NaDD in the restricted mobility regions is worth mentioning. In the case of the NaDD-containing ionomers, the two terminal ionic groups of the NaDD salt could be placed in the same multiplet, leading to the alkyl chains of the diacid salt folding-back to make a loop. Then, the looping-back alkyl chains introduce a significant amount of free volume to the restricted mobility regions, and, thus, the clustering due to the chain crowding should be reduced drastically, resulting in a lower cluster T_g. However, in the present study this is not the main mechanism because in another study from our group the mono-functional sodium hexanoate-containing ionomers, resembling the ionomer containing looping-back dodecandioate chains, show different dynamic mechanical results (not shown here), compared to the results obtained in this study [25]. The detailed results on the hexanoate-containing ionomer system will be discussed later in a separate paper.

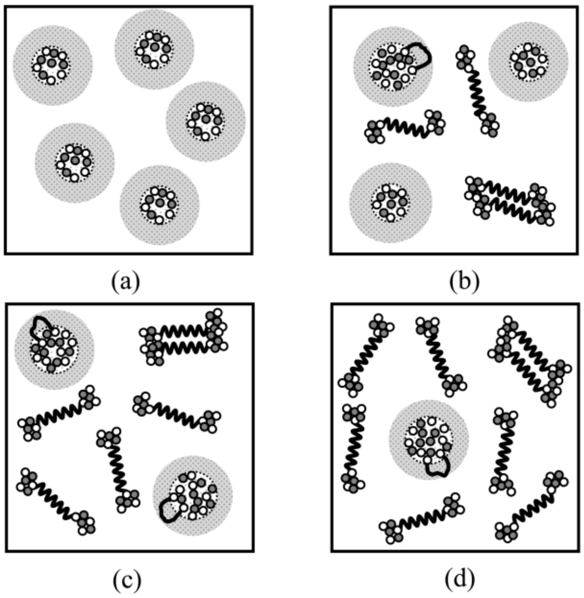
(a) (b)
(c) (d)

Fig. 8. Schematic representation of the morphologies of ionomers containing a various amount of NaDD salts; (a) pure ionomer; (b) low diacid salt concentration; (c) intermediate diacid salt concentration; (d) high diacid salt concentration. Shaded area represents restricted mobility regions, and the white and black circles represent ionic groups. The zigzag line indicates a fully extended alkyl chain of NaDD, and curved lines represent the looping-back alkyl chains of the diacid salts.

Therefore, at this point, we propose a new type of plasticization. When organic salts, e.g. NaDD salts, are added to the ionomer, the NaDD salts may be distributed in the ionomer matrix either singly or in the form of small-sized aggregates consisting of a few diacid salt molecules, or both. Then, the ionic groups at both ends of the diacid salts participate in the formation of ionic aggregates with ionic groups of ionomers (see Fig. 8(b)). This process results in the disruption of some of multiplets. When more NaDD salts are added to the ionomer, more multiplets break up, and the ionic groups from the burst multiplets form ionic aggregates with the ionic groups of the organic salts (see Fig. 8(c) and (d)). At this point, it should be mentioned that the alkyl chains of the diacid salts are fully extended because the full extension of the chain is favorable for the stacking of the diacid salts to form small-sized aggregates. In addition, at this point, it is worth recalling that when the ionic groups of styrene ionomers form multiplets, they probably give rise to a most prevalent spacing [2]. Thus, under those circumstances when one adds the diacid salts to ionomers, one could expect that the full extension of the alkyl chain of the diacid salt, existing singly or/and in the form of stacking of a few salt molecules in the ionomer matrix, is energetically desirable for the formation of new ionic aggregates with the ionic groups of the diacid salts and ionomer. If this proposed plasticization mechanism were acceptable, the amount of matrix regions should increase substantially with the amount of the diacid salts, and the properties of the ionomers should not be changed with the type of the diacid salts; they are changed with the amount of the salts. In addition, the sharp X-ray peak should arise from the presence of ionic terminal groups of diacid salt molecules, alkyl chains of which are fully extended. This might be what we observed in the present work.

At this point, it should be mentioned that the results obtained above are different from those obtained from the PS ionomers containing bi-functional oligomeric styrene amphiphiles investigated by Plante et al. [14]. This is, however, not surprising since at least three factors are different in these two systems; the amount of salts added and the natures of the oligomeric materials. First of all, Plante et al. prepared ionomer blends containing up to 60 wt% oligomer, compared to the present system which contains up to 17 wt% oligimer. Secondly, Plante et al. added styrene oligomer molecules to the styrene ionomers, and, thus, they did not have any problem in mixing. Thirdly, the styrene oligomer is amorphous, compared to the crystalline diacid oligomeric materials used in the present work. Naturally, the plasticization effects on the properties of PS ionomers depend strongly on the three factors mentioned above. It should also be mentioned that the results obtained in this work are different from those obtained in the NaSPS–SDBS system studied by Kim et al. [10]. However, this can also be understood. As was mentioned in the section in which we compared the effect of di-functional NaDD salt to that of mono-functional sodium hexanoate, it was found that the functionality of oligomeric salts changes the ionomer properties significantly. In addition, the ionic groups in NaSPS–SDBS are sodium sulfonate, while those in this study are sodium carboxylate. This difference in the types of ionic groups definitely has influence on the ionomer properties and morphology sufficiently [3]; the changes include the size of multiplets, the strength of ionic interactions between the ionic groups in multiplets, the degree of clustering, and cluster T_gs.

Finally, the activation energies (E_as) for the glass transitions of diacid salt-containing ionomers are calculated using Arrhenius plots of log frequency vs. inverse temperature. Even though there are limitations in accuracy in determining the temperature of peak maximum and the deviations from linearity in the Arrhenius plots, the E_a values can be calculated with confidence limits of ± 40 kJ/mol. Fig. 9 shows the activation energies for the glass transitions of the matrix and cluster regions. It is seen that the activation energies for the cluster T_g are ca. 230 kJ/mol, and those for the matrix T_g are ca. 560 kJ/mol; the activation energies do not change significantly with the amount of the diacid salts. This result is understandable. Since the ionic groups of the organic salt and ionomer are the same and the glass transition mechanisms for the matrix and cluster phases should be similar for all the ionomers containing diacid salts, the activation energies are expected to be similar. The similar trend was also observed in the NaSPS–SDBS system [10], in that the activation energies did not change with the amount of SDBS surfactants.

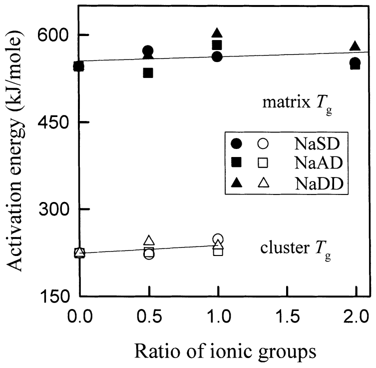

Fig. 9. Activation energies of the matrix and cluster glass transitions of ionomers containing various Na-neutralized diacid salts, as a function of the ratio of ionic groups.

4. Conclusions

The effect of the addition of disodium salts of aliphatic diacids to the poly(styrene-*co*-methacrylate) ionomer on the properties of the resulting ionomer samples was investigated dynamic mechanically. On one hand, with increasing aliphatic diacid salt content, the loss tangent peak for the cluster T_g was found to shift to lower temperatures and its size decreased. On the other hand, the loss tangent peak for the matrix T_g remained at similar temperatures, but its size increased. In addition, it was observed that the ionic modulus increased with increasing amount of the diacid salts. However, the effect of the type of the diacid salts on the dynamic mechanical properties of the ionomers was not evidenced. In the X-ray studies, a sharp peak at relatively wide angle was observed for the ionomers containing salts; the Bragg distance calculated from the angle of the peak maximum was found to be similar to the fully extended chain length of the aliphatic diacid salt. However, a DSC study showed no evidence of phase-separation of diacid salts in the ionomer system. Thus, it was postulated that the addition of the aliphatic diacid salts to the present ionomer system causes the disruption of the multiplets, leading to the formation of new ionic aggregates consisting of both the ionic groups of diacid salts and those of the ionomer.

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