Roles of mono- and di-functional organic salts as plasticizer and/or filler in styrene-based ionomers

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Abstract

The plasticization and/or filler effects of sodium salts of hexanoate (Na6), adipate (Na6Na), dodecanedioate (Na12Na), and dodecylbenzenesulfonate (Na12) on the dynamic mechanical properties of styrene-based ionomers were investigated. When a small amount of Na6, having one carboxylate ionic group at one end of alkyl chain, was added to a styrene-methacrylate ionomer, the salt acted as a very effective plasticizer for the ionomer cluster regions. With increasing salt contents, however, the salts became phase-separated and formed bilayer crystalline domains that acted as filler. In the case of the Na12Na and Na6Na salts, containing two carboxylate ionic groups, one at each end of alkyl chain, they formed phase-separated domains, acting as filler, in the methacrylate ionomers. Na12, possessing one sulfonate ionic group at only one end of a long alkyl chain, acted as a plasticizer in a sulfonated polystyrene ionomer. However, an excess amount of Na12 salt also formed phase-separated domains. It was also found that Na12 showed a filler effect only at much higher salt contents in comparison with Na6.
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1. Introduction

The polymers having a small amount of ionic groups in a polymer matrix of low polarity, called ionomers, first appeared in the market in 1965. Since then, the physical properties and morphologies of various ionomers have been studied extensively [1–3]. The electrostatic interactions between ionic groups make the ionic groups in a relatively non-polar polymer matrix form ionic aggregates, called multiplets [4]. According to the multiplet/cluster model, so called EHM model, the multiplets reduce the mobility of polymer chains in their immediate viscinity [5]. When an ion concentration increases, more multiplets form, and eventually the restricted mobility regions surrounding the multiplets start overlapping, resulting in large continuous regions. These large restricted mobility regions, called clusters, show their own glass transition temperature (T_g), which is higher than the T_g of the ion-poor matrix regions of the ionomer [5].

Since the ionomers have the ion-rich cluster and ion-poor matrix regions, the ionomers can be plasticized selectively by the addition of materials of various polarities [6–26]. For example, Lundberg et al. found that a material of low polarity acted as a plasticizer for the hydrocarbon phase (i.e. both matrix and cluster regions) of sodium sulfonated polystyrene (NaSPS) ionomers, and that a material of high polarity behaved like a plasticizer for the ionic aggregates [7]. Later, the group of Weiss studied the viscoelastic behavior of the plasticized NaSPS system more thoroughly [10,12,13]. They found that the addition of dioctyl phthalate, a non-polar plasticizer, to the NaSPS ionomer decreased the matrix T_g of the

ionomer, without changing the relaxation-time spectrum of the glass transition of cluster regions. On the other hand, glycerol, a polar plasticizer, affected the long-time relaxation of the cluster regions of the NaSPS ionomer significantly, without changing the viscoelastic response of a non-polar polymer backbone phase. In the case of poly(styrene-*co*-sodium methacrylate) (PSMANa) ionomers, Bazuin and Eisenberg observed that the addition of glycerol to the PSMANa ionomer decreased the matrix T_g of the ionomer slightly and caused the complete disappearance of an ionic plateau in a modulus-−temperature plot, suggesting that the formation of cluster regions had diminished effectively [11]. When the ionomer was plasticized with non-polar diethylbenzene, the slope of the modulus−temperature curve for a primary glass transition became less steep with increasing plasticizer contents. Furthermore, the loss tangent peaks for the matrix and cluster glass transitions shifted to lower temperatures, and the temperature difference between the matrix and the cluster T_gs increased with the plasticizer content [11].

The low molecular weight compounds of linear saturated aliphatic hydrocarbon containing an ionic group at the end of the alkyl chain can also be used as plasticizers for ionomers. Agarwal et al. studied the mechanical properties of Zn-sulfonated ethylene-*co*-propylene-*co*-ethylidene norbornene terpolymer (Zn-EPDM) containing a Zn stearate amphiphile [8]. It was found that the phase-separated, crystalline zinc stearate acted as filler and, thus, raised the T_g of the ionomer. On the other hand, the zinc stearate also acted as a ''multiplet'' plasticizer because some carboxylate ionic groups of the zinc stearate possibly incorporated with the multiplets consisting of sodium sulfonate ionic groups. This lowered the onset temperature of the ion-hopping of the ionic groups in the multiplets. In addition, at high temperatures, the crystalline regions of the zinc stearate melted, which also weakened the strength of electrostatic interactions between ionic groups [8]. Later, Jackson et al. studied the morphology of the same system using a small-angle X-ray scattering (SAXS) technique and proposed that the Zn stearate in the Zn-EPDM ionomers formed a bilayer structure [23]. Recently, Wakabayashi and Register studied the effects of metal soaps on the mechanical properties and morphology of ethylene-*co*-meth(acrylic) acid ionomers [26]. It was found that the properties of the ionomers depended on both the neutralizing cation and on the crystallizability of the long alkyl chain of the metal soaps. In the case of the poly(ethyl acrylate-*co*-sodium acrylate) ionomers containing mono-functional sodium hexadecanoate, Tong and Bazuin found that sodium hexadecanoate acted as phase-separated, crystalline filler and not as a plasticizer [15]. Kim et al. reported that the addition of sodium dodecylbenzenesulfonate (Na12) to the NaSPS ionomer decreased the cluster T_g of the NaSPS ionomer significantly, with only a minor change in the matrix T_g [17]. Thus, they suggested that Na12 acted mainly as a preferential plasticizer for the cluster regions. Plante et al. discovered that both the matrix and the cluster regions of *p*-carboxylated polystyrene ionomers could be plasticized with mono-functional styrene oligomers [18,19]. Nah et al. investigated the effects of sodium *p*-toluate and sodium
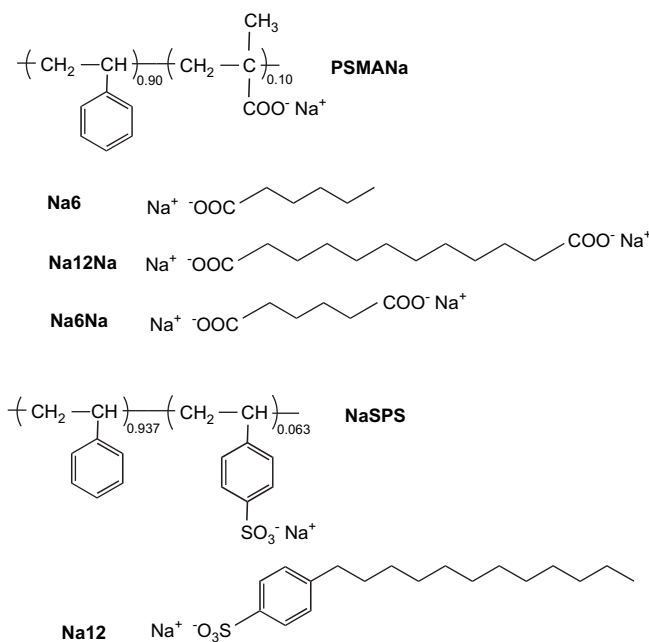
Scheme 1.

p-toluenesulfonate salts on the mechanical properties of styrene-based ionomers and found that the organic salt acted both as the filler and as the plasticizer [24].

Recently, we found that, with increasing aliphatic diacid salt contents, the ionic modulus and the cluster T_g of the PSMANa ionomer decreased and, thus, suggested that the diacid salts might act as plasticizers [25]. Shortly after, we came to know that the samples were partly and not fully, neutralized, which might cause a plasticization effect on the ionomer properties. A recent study (will be published in near future) indicated that the modulus of the diacid salt-containing PS-based ionomers indeed increased, while the matrix and cluster T_gs remained more or less constant. Thus, we decided to investigate the dynamic mechanical properties and morphology of the fully neutralized PSMANa ionomers containing acid salts of saturated aliphatic hydrocarbon. Furthermore, in the course of the investigation, the following question arose; what would be the effects of the number of ionic groups per organic acid salts, the length of the alkyl chain, and the type of ionic groups of the organic salts on the properties and morphology of polystyrene (PS)-based ionomers? Certainly, the understanding of these effects would be important to predict possible roles of various acid salts in amorphous random ionomers. Thus, this work was designed to analyze the mechanical properties of acid salts-containing PSMANa ionomers and also to give an answer to the question mentioned above. In this study, we chose four organic salts; sodium hexanoate (Na6), sodium adipate (Na6Na), sodium dodecanedioate (Na12Na) and sodium dodecylbenzenesulfonate (Na12) (see Scheme 1). Na12 was selected because some of the mechanical and morphological data of the styrene ionomers containing the Na12 salt were already available, as was mentioned before [17], and the comparison of the results obtained from Na6- and Na12-containing PS-based ionomers would be useful to understand the roles of

mono-functional amphiphiles in the PS-based ionomers. The similarity and differences in the four acid salts are as follows. Na6 and Na12Na have the same type of ionic groups, $-COO^-$ Na^+, but Na6 has one ion pair at only one end of the alkyl chain, in comparison with total two ion pairs with one ionic group at each end of the alkyl chain of Na12Na. In addition, the alkyl chain length of Na6 is just half to that of Na12Na. Thus, the comparison of Na6 and Na12Na organic salts is useful to understand the effects of both the number of ion pairs per molecule and the length of alkyl chains of the organic salts on the properties of PS-based ionomers. In the case of Na6Na, the number of carbon atoms is the same as that of Na6, but Na6Na has two ion pairs per molecule instead of one in Na6. Therefore, if we made a comparison of the mechanical data of the ionomers containing either the Na6 or the Na6Na salt, we could understand the effect of the number of ion pairs per molecule on the mechanical properties of the PS-based ionomers. In the case of the mono-functional Na12, it has a relatively long alkyl chain and a benzene ring with a sulfonate ionic group at its *para* position; the strength of the ionic interactions between Na-sulfonate ionic groups is more than that between Na-carboxylate ionic groups [26,27]. Therefore, it is worth comparing the dynamic mechanical data of the PS-based ionomers containing the Na6 and Na12 organic salts to obtain the information on the effects of both the alkyl chain length and the strength of ionic interactions on the ionomer properties.

2. Experimental

2.1. Materials

Poly(styrene-*co*-methacrylic acid) copolymer containing 10.0 mol% of methacrylic acid units was prepared using the free-radical bulk copolymerization method [28]. To obtain ionomer samples containing various amounts of organic salts, the acid copolymer and organic acids were mixed together in a benzene/methanol (90/10, v/v) mixture, and the acid groups were fully neutralized with methanolic NaOH. The organic acids used were adipic acid (Aldrich Chemical Company, 99%, m.p. = 151–154 °C), hexanoic acid (Aldrich Chemical Company, 99.5+%, m.p. = −3 °C), and dodecanedioic acid (Aldrich Chemical Company, 99%, m.p. = 128–130 °C). The solution was freeze-dried and dried further under a vacuum at ca. 130 °C for 1 day. To prepare Na6Na and Na12Na-containing PSMANa ionomers, a similar method described above was used. To prepare the Na12-containing NaSPS ionomer for the X-ray and thermal studies, poly(styrene-*co*-styrenesulfonic acid) (6.3 mol% of acid content), prepared for another study [25], was mixed with sodium dodecylbenzenesulfonate (Aldrich Chemical Company, technical grade), and the acid groups were fully neutralized with NaOH. Subsequently, the samples were freeze-dried and dried further under a vacuum at ca. 130 °C for 1 day. To prepare non-ionic polystyrene (PS) samples containing organic salts, the same amount of salt, which was needed to prepare an ionomer containing a desired amount of the salt, was added to PS.

2.2. Dynamic mechanical thermal analysis

For the mechanical property measurements, the samples were compression-molded at ca. 250 °C under a pressure of ca. 25 MPa. The molded samples with approximate dimensions of $2.5 \times 7.0 \times 30.0$ mm were annealed under a vacuum at 130 °C for 1 day. To measure the dynamic mechanical properties of ionomers, a TA dynamic mechanical analyzer (DMA) (Q 800) was employed. The dual cantilever bending mode at frequencies of 0.3, 1, 3, 10 and 30 Hz was applied, and the heating rate was 1 °C/min. For each ionomer sample, storage moduli (E') and loss tangents were obtained as a function of temperature. Even though the dynamic mechanical measurements of each sample were conducted at five different frequencies, a detailed data analysis was performed only on 1 Hz data.

2.3. Differential scanning calorimetry

For the thermal analysis studies, a TA differential scanning calorimeter (DSC 3000) was used. The DSC was calibrated with indium. The sample cell containing ca. 8 mg of a sample was stored under the nitrogen atmosphere. The samples were scanned from 70 °C to 280 °C to span the temperature range of the matrix and cluster T_gs of the ionomers. The DSC data were obtained from a second heating scan.

2.4. X-ray experiments

For the X-ray experiments, the samples were also compression-molded at ca. 250 °C under a pressure of ca. 25 MPa. The approximate dimensions of the molded samples were 0.5 (thickness) × 10.0 (diameter) mm. The X-ray diffraction (XRD) patterns of ionomers were recorded using a PANalytical X-ray diffractometer (X'pert PRO MPD) with a PW 3015/20 X' celerator detector. The Cu radiation ($\lambda = 0.1542$ nm) was utilized, and the power of the X-ray generator was 40 kV and 30 mA. The scanning speed was 1°/min, and the sampling width was 0.05°. The small-angle X-ray scattering (SAXS) experiments were performed at Station 4C1 of the Pohang Synchrotron Radiation Source (Pohang, Korea). The detailed experimental conditions have been described elsewhere [29,30]. The type of light source was a bending magnet, and the generated critical beam ($\lambda = 1.608$ Å) 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 300 mm, which allowed SAXS data to be obtained in the q range from ca. 0.16 to 5.91 nm^{-1}, where $q = 4\pi \sin \theta/\lambda$, θ is half the scattering angle and λ is the X-ray wavelength.

3. Results and discussion

Shown in Fig. 1 are the plots of a series of storage modulus (E') and loss tangent curves as a function of temperature for PSMANa ionomers containing various amounts of Na6, Na12Na and Na6Na. In the modulus plots, with increasing temperature, one sees the glassy region, the matrix glass transition
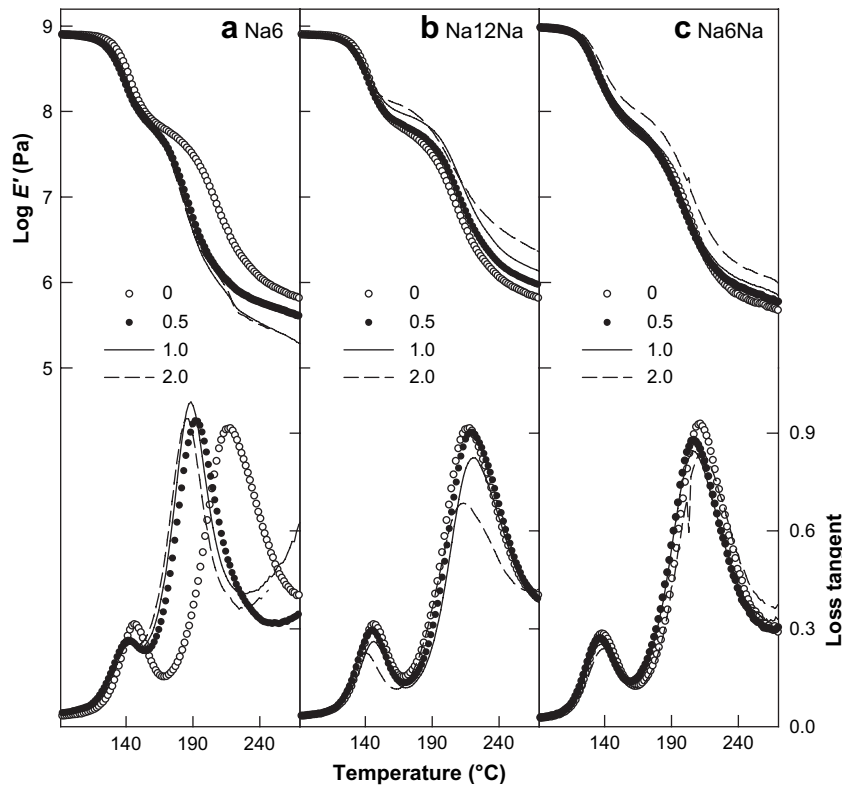
Fig. 1. Storage moduli and loss tangents of the PSMANa ionomer and its blends with (a) sodium hexanoate (Na6); (b) sodium dodecanedioate (Na12Na) and (c) sodium adipate (Na6Na) as functions of temperature. All data were measured at 1 Hz. The number indicates the mole ratio of ionic groups of the organic salts to that of the ionomer.

(T_g), the ionic plateau (i.e. the segment of moduli curve between two T_gs), the cluster T_g and the rubbery plateau. In the case of Na6-containing ionomers, it is seen that with increasing Na6 contents the ionic plateau shifts to lower temperatures and to higher modulus values. In addition, the modulus value at ca. 270 °C, i.e. rubbery modulus, decreases slowly as Na6 content increases. In the case of the Na12Na- and Na6Na-containing ionomers, however, the ionic and rubbery plateaus shift to higher modulus with increasing organic salt contents. A matrix loss tangent peak at low temperatures and a cluster peak at high temperatures are also seen in the same figure. As the amount of Na6 increases, the matrix and cluster peaks shift to lower temperatures noticeably and then marginally. In the case of peak height, the height of the cluster peak does not change much with the amount of Na6, and that of the matrix peak decreases slightly and then remains more or less constant. Upon the addition of Na12Na and Na6Na to the ionomers, the heights of the matrix and cluster loss tangent peaks decrease without changing the peak positions significantly. These findings are different from what we observed in the Na6-containing ionomer system. This difference will be discussed later in more detail.

The ionic modulus (E'_{ionic}) measured as the value of E' at the point of a minimum slope of an ionic plateau is related to the rigidity of clustered regions and the degree of clustering [5,27,28]. Fig. 2(a) shows the E'_{ionic} values of the ionomers containing Na6, Na12Na and Na6Na as a function of the mole ratio of ionic groups of the amphiphilic organic salts to those of the ionomer. In addition, the E'_{ionic} values of

sulfonated polystyrene (8.4 mol% of ions) containing Na12 are also seen in the same figure (data were obtained from Ref. [17]). It is seen that the E'_{ionic} values of the three PSMANa ionomer systems increase linearly with increasing mole ratio of ionic groups of the organic salts to those of the ionomer, and that the increasing rates of the E'_{ionic} of the Na6- and Na6Na-containing ionomers, which are similar to each other, are lower than that of the Na12Na-containing ionomer. The E'_{ionic} data can be fitted with a first order polynomial, and
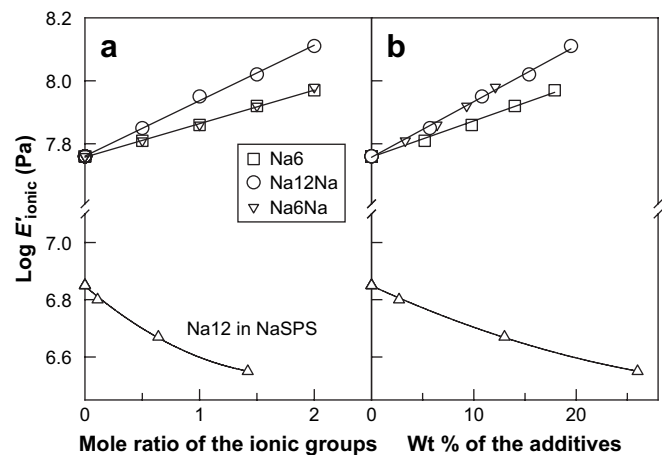

Fig. 2. Ionic modulus of the PSMANa ionomer and ionomers containing Na6, Na12Na, Na6Na and Na12 salts as a function of (a) the mole ratio of ionic groups of the salts to that of the ionomer and (b) wt% of the salts in the ionomer, measured at 1 Hz.

the equations are as follows (r^2 is linear least-squares correlation coefficient).

For Na6- and Na6Na-containing PSMANa ionomer systems

$$\log E'_{\text{ionic}}(\text{Pa}) = 7.76 + 0.11$$
$$\times \text{(mole ratio of the ionic groups)}\,(r^2 = 0.9962),$$

for Na12Na-containing PSMANa ionomer system

$$\log E'_{\text{ionic}}(\text{Pa}) = 7.76 + 0.18$$
$$\times \text{(mole ratio of the ionic groups)}\,(r^2 = 0.9986).$$

These two equations imply that the increasing rates of the E'_{ionic} of the organic salt-containing PSMANa systems are related to the number of carbon atoms of the organic salts (i.e. six vs. twelve) and not to the number of the ionic groups per salt (i.e. one vs. two). However, when the E'_{ionic} values are presented as a function of the weight percentage of the organic salts, instead of the mole ratio of ionic groups of the salts to that of the ionomer, the increasing rates of E'_{ionic} of the ionomer systems containing di-functional organic salts are found to be similar to each other (Fig. 2(b)). The data can also be fitted with the first order polynomial, and the equations are as follows.

For Na12Na- and Na6Na-containing ionomer systems

$$\log E'_{\text{ionic}}(\text{Pa}) = 7.76 + 0.02$$
$$\times \text{(wt\% of the organic salts)}\,(r^2 = 0.9972),$$

for Na6-containing ionomer system

$$\log E'_{\text{ionic}}(\text{Pa}) = 7.76 + 0.01$$
$$\times \text{(wt\% of the organic salts)}\,(r^2 = 0.9955).$$

This indicates that when the amphiphilic organic salts are added to an ionomer by their weight, the number of ionic groups of the salt becomes more important to control the ionic modulus of the ionomers, in comparison with the chain length of the salts. In the case of Na12 in the NaSPS ionomer, the E'_{ionic} decreases with increasing Na12 amounts. The E'_{ionic} data can be fitted with a second order polynomial; the equations are as follows:

$$\log E'_{\text{ionic}}(\text{Pa}) = 6.85 - 0.34 \times \text{(mole ratio of the ionic groups)}$$
$$+ 0.094 \times \text{(mole ratio of the ionic groups)}^2$$
$$\times \,(r^2 = 0.9982),$$

$$\log E'_{\text{ionic}}(\text{Pa}) = 6.85 - 0.016 \times \text{(wt\% of the organic salts)} + 1.89$$
$$\times \text{(wt\% of the organic salts)}^2\,(r^2 = 0.9995).$$

At this point, it should be mentioned that the E'_{ionic} of the unblended NaSPS ionomer is lower than that of the unblended PSMANa ionomer. This is attributed to two factors: first, the ion content of the former system is lower than that of the latter one (i.e. 8.4 mol% vs. 10.0 mol%), which naturally leads to the lower degree of clustering for the NaSPS ionomer. Thus,
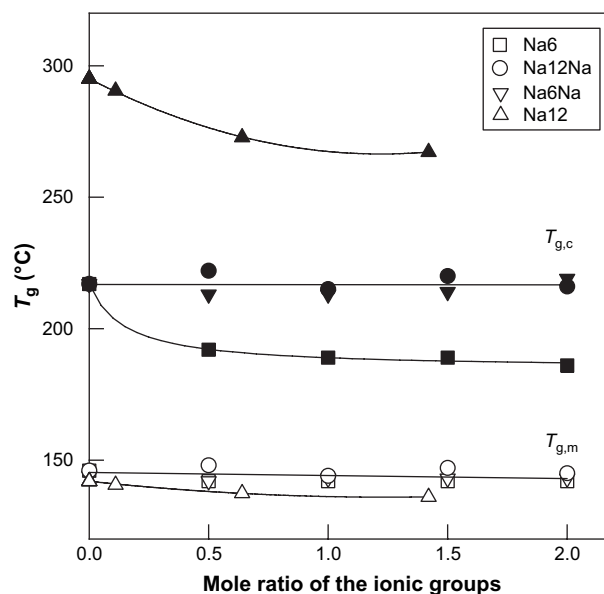

Fig. 3. Glass transition temperatures of the PS-based ionomers and their blends with Na6, Na12Na, Na6Na and Na12 salts as a function of the mole ratio of ionic groups of the salts to that of the ionomer, measured at 1 Hz.

the E'_{ionic}, related to the degree of clustering is lower for the NaSPS ionomer in comparison with the PSMANa ionomer [5,27,28]. Second, even at similar ion contents, the amount of clustered material of the NaSPS system is known to be smaller than that of the PSMANa system; the discussion on this topic is beyond the scope of this paper, and, thus, the interested readers are referred to Ref. [3]. According to the factors mentioned above, the ionic modulus is lower for the NaSPS ionomer, compared to the PSMA ionomer, at comparable ion contents.

The glass transition temperatures of the matrix and cluster regions of the ionomers containing organic salts, obtained from the loss tangent peak maxima, are shown in Fig. 3 as a function of the mole ratio of ionic groups of the salts to that of the ionomer. It is seen that, with increasing salt contents in PSMANa ionomer, the cluster T_g ($T_{g,c}$) decreases strongly and then very gently, while the matrix T_g ($T_{g,m}$) changes only slightly. This implies that Na6 might act as a very effective plasticizer for the cluster regions, even only a small amount of the salt is added to the ionomer. Further addition of the salt does not show a strong plasticization effect. In the case of the Na12–NaSPS system, the $T_{g,c}$ also decreases noticeably and then gently, but the $T_{g,m}$ does not change with salt contents. As was suggested earlier in the Na12-containing NaSPS system [17], the plasticization mechanism might be as follows. The Na-carboxylate ion pairs of the Na6 salt incorporate with a number of the Na-carboxylate ionic groups of the ionomer to form multiplets. Then, the alkyl chains of Na6 reside in the restricted mobility region surrounding the multiplet, since the low polarity of the alkyl chains prevent the chains from being found in the ionic multiplet. In this case, the alkyl chains emanating from the multiplet introduce free volume into the regions of polymer chains of restricted mobility. This naturally results in the decrease of the cluster T_g of the ionomer. A small amount of the ionic groups of the ionomer, not forming ionic aggregates, possibly exist in the matrix region,

and the ionic groups of Na6 can also incorporate with them. Thus, only a minor change in the matrix T_g is observed.

Now, the decreasing trends of $T_{g,c}$ of the Na6-containing PSMANa ionomer and the Na12-containing NaSPS ionomer as a function of salt content could be further explained as follows. The average number of ionic groups per multiplet is dependent on various factors including thermodynamic parameters; i.e. enthalpy and entropy. In view of the energy balance (enthalpy vs. entropy), the average size of the multiplet should have its upper limit (i.e. the limit of the number of ionic groups that can possibly get together to form multiplets). First, the ionic groups of the salt molecules incorporate with the ionic groups of the ionomers to form multiplets, and, thus, the salt acts as a plasticizer for the ionomer cluster regions. Above a certain concentration of salt, however, the ionic groups of the salt molecules would no longer participate in the formation of ionic aggregates with the ionic groups of the ionomers, and the salt molecules now become phase-separated. The phase-separated salt molecules then rearrange themselves to minimize an enthalpy penalty owing to repulsion between the non-polar alkyl chains and the ionic groups, and, thus, act as filler. With increasing salt contents further, both the plasticization and the filler effects become stronger, but the filler effect appears to be more prominent than the plasticization effect due to the upper limit of the multiplet size. This indicates that the increasing salt content sets off the one effect against the other effect, at least to some extent. Thus, the decreasing rates of $T_{g,c}$ become lower with increasing salt contents. In the figure, it is seen that the initial decreasing rate of the $T_{g,c}$ of the Na6 system is higher than that of the Na12 system. This might suggest that the preferential plasticization effect of Na6 is very strong at the beginning and then the other effect, i.e. filler effect, becomes more applicable with increasing salt contents. In the case of Na12, the salt also shows both the plasticization and the filler effects. However, the plasticization of Na12 becomes more effective in a relatively wide range of salt contents. Thus, the filler effect becomes meaningful only at high salt contents. At this point, it should also be noted that the relative areas under the loss tangent peaks are thought to represent the relative amount of matrix and cluster regions. Thus, the fact that the areas under the matrix and cluster loss tangent peaks of the ionomer do not change strongly with the addition of the salt suggests that the added salt induces the change in the mobility of the polymer chains in the cluster regions and not the relative amount of cluster regions significantly. In the case of the matrix and cluster T_g of the Na12Na- and Na6Na-containing ionomers, they do not change strongly with salt contents. This finding and the increasing E'_{ionic} value with increasing salt contents imply that Na12Na and Na6Na act mainly as fillers and not as plasticizers. This will be discussed later in more detail.

The activation energies (E_as) for the glass transitions of the ionomers were calculated using Arrhenius plots of log frequency vs. inverse temperature (confidence limits $<\pm30$ kJ/mol). Fig. 4 shows plots of the E_as for the glass transitions of the matrix and cluster regions of three PSMANa ionomer systems vs. the mole ratio of ionic groups of the organic salt to those of the ionomer.
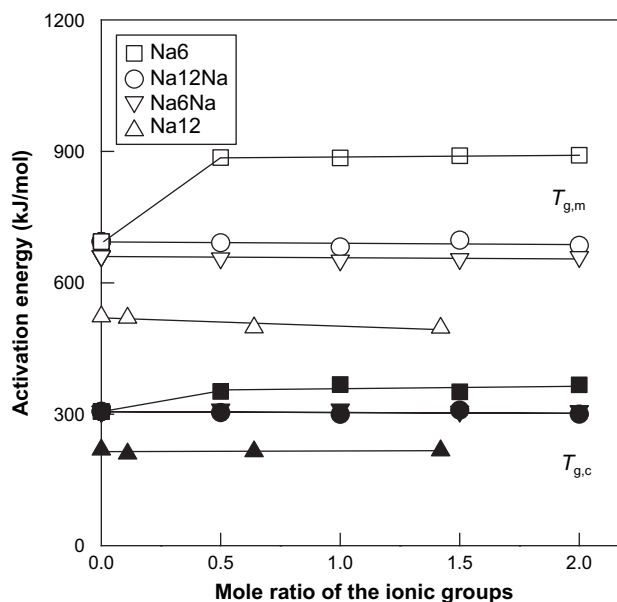

Fig. 4. Activation energies for the matrix and cluster glass transitions of the Na6-, Na12Na-, Na6Na- and Na12-containing ionomers as a function of the mole ratio of ionic groups of the salts to that of the ionomer.

The figure also includes the E_a data of the Na12–NaSPS system, obtained from Ref. [17]. The E_a for the matrix T_g of Na6-containing ionomer increases noticeably and then marginally, and that for the cluster T_g also changes slightly and then again marginally with increasing salt contents. However, in the case of the Na12Na-, Na6Na- and Na12-containing PS-based ionomers, the E_as for the matrix and cluster T_gs do not change with the amounts of the salt. These findings could be understood. Since the Na12Na and Na6Na organic salts become phase-separated in the PSMANa ionomer matrix, and, thus, act as filler, they do not affect the glass transition mechanisms of both ion-poor matrix regions and ion-rich cluster regions of the ionomer. In the case of the Na6 system, however, at low salt contents, the ionic groups of the organic salts incorporate with the ionic groups of the ionomers to form multiplets, and, thus, the organic salts behave like plasticizers. This definitely affects the characteristic nature of multiplets in the cluster regions and ionic groups residing singly or in the form of small aggregates in the matrix regions. On further increasing the content of Na6 in the ionomer, the excess amount of the Na6 molecules now becomes phase-separated, acting as filler. In this case, no change in the E_as for the glass transitions is expected. In the case of the Na12–NaSPS system, where Na12 acts as a preferential plasticizer for the cluster regions, the E_a's do not change with the amount of organic salt, implying that the plasticization does not induce any changes in the multiplet formation [17].

Shown in Fig. 5 are the DSC thermograms of polystyrene (PS) homopolymer and PSMANa ionomers containing Na6, Na6Na and Na12Na, and NaSPS ionomers containing Na12. It is clear that the Na6-containing PS homopolymer and PSMANa ionomers show a matrix glass transition at ca. 100 °C and 120 °C, respectively, and an endothermic peak at ca. 230 °C. The presence of the sharp endothermic peak indicates that there are phase-separated crystalline domains in the Na6-containing
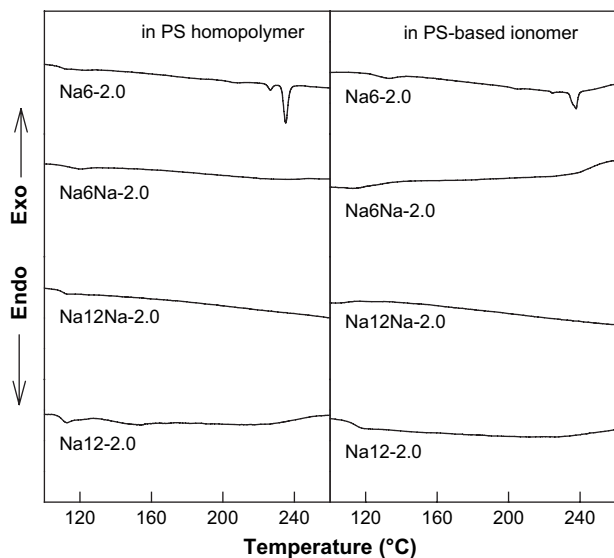
Fig. 5. DSC thermograms of the PS homopolymers and the PSMANa ionomers containing organic salts at a molar ratio of 2.0. Each curve was shifted up by the same magnitude with respect to each other for clarity.
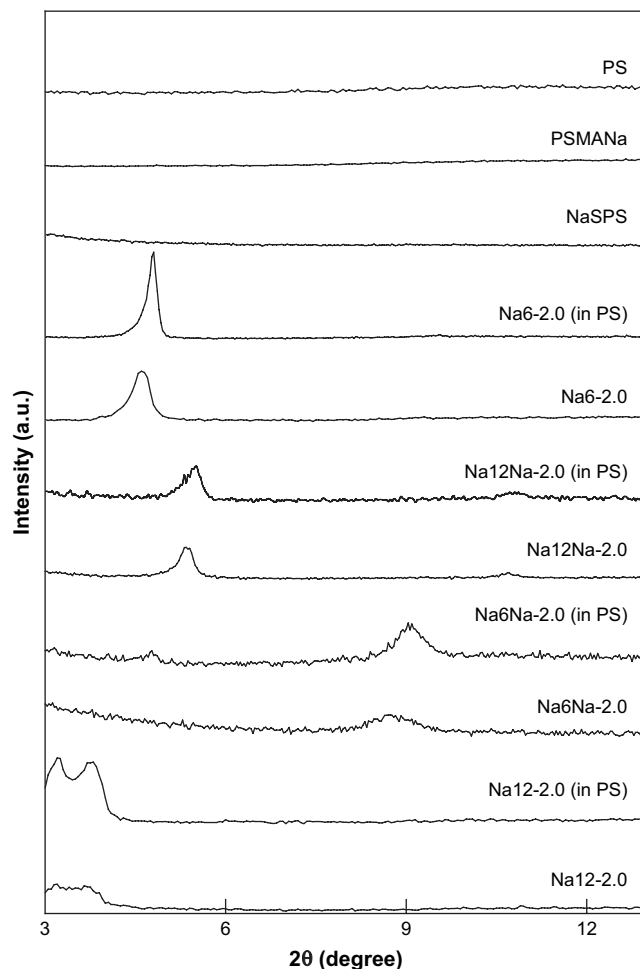

Fig. 6. XRD profiles for the PS and the PSMANa ionomers containing Na6, Na12Na, Na6Na and Na12 salts. The number indicates the mole ratio of ionic groups of the salts to that of the ionomer. Each curve was shifted up by the same magnitude with respect to each other for clarity.

ionomer. However, the Na6Na-, Na12Na- and Na12-containing PS ionomer systems show only the glass transition of the ionomers and not the endothermic peaks due to the presence of crystalline domains. Three explanations are possible for this absence of the endothermic peak. First, the DSC is sensitive only to domain sizes of the order of 30 nm [31]. If the size of the phase-separated domains of the salts, if any, were smaller than 30 nm, the thermal transition of the phase-separated domains would not be detected by a DSC method. Second, if the degree of crystallinity of the phase-separated salts in the ionomer were very low, the DSC thermogram would not show a well-developed endothermic peak. Third, we run the DSC only up to 280 °C because the ionomer started decomposing thermally above that temperature. Thus, if the melting temperatures of the phase-separated crystalline domains of the salts were higher than 300 °C, we could not observe any endothermic peaks. To find out an appropriate explanation, we used a DSC to study thermal transitions of pure Na12Na and Na6Na samples. It was observed that the thermal decomposition of Na12Na started at 308 °C, and that an endothermic peak appeared to be at 337 °C (not shown here). In the case of Na6Na, the thermal decomposition started at 320 °C, without a DSC endothermic peak for the crystalline domains up to 400 °C. In the case of Na12, it does not show an endothermic peak below 300 °C. This information makes the third explanation quite possible as an answer to the absence of the DSC endothermic peak for the Na12Na-, Na6Na- and Na12-containing samples. It would be worth reminding that the rubbery modulus in PSMANa ionomers containing Na6 decreases slowly with increasing Na6 contents. It may be due to the melting of Na6 at ca. 230 °C, which causes the relatively free movement of the polymer chains. However, for the PSMANa ionomers containing Na12Na and Na6Na, the modulus increases with increasing salt contents throughout the temperature studied. Since the observed melting/decomposition temperatures of Na12Na and Na6Na from DSC are much higher than the highest temperature studied,

the increasing trends of the modulus in these systems can be understood by the possible filler effects of the these salts.

In addition to the mechanical and thermal studies, X-ray diffraction (XRD) experiments were also performed to investigate the crystallinity of the domains of the organic salts phase-separated in PS homopolymer and PS-based ionomers. The XRD profiles are shown as a function of diffraction angle (2θ) in Fig. 6. It is seen that, below 13°, PS homopolymer and unblended PSMANa and NaSPS ionomers show no XRD peak. Upon the addition of Na6 to PS and PS-based ionomer, an XRD peak is seen at $2\theta = 4.6°$ ca., which corresponds to a Bragg spacing of ca. 1.9 nm. This spacing is more or less a double length of a fully extended Na6 molecule. It is also seen that the peak intensity of Na6 in the ionomer is lower than that in PS. At this point, it should be mentioned that the ionomer containing Na6-0.5 did not show a strong XRD peak (not shown here), implying that Na6 was not phase-separated to a great extent. Similar XRD results are seen for the Na12Na- and Na6Na-containing systems. However, the Bragg distance calculated from the angle of the peak maximum for PSMANa–Na12Na-2.0 ($2\theta = 5.3°$ ca.) is 1.7 nm that is slightly shorter than that of PSMANa–Na6-2.0; the Bragg

distance calculated from $2\theta = 8.9°$ ca. for the PSMANa–Na6Na-2.0 ionomer is 0.99 nm. These Bragg distances of the Na12Na- and Na6Na-containing ionomer systems coincide with the distances between the ionic groups placed at each end of the fully extended alkyl chains of Na12Na and Na6Na. Thus, the above XRD and DSC results and possible filler effects indicate a possibility of the bilayer crystalline structure of Na6 and the monolayer crystalline structure of the Na12Na and Na6Na molecules in the PS homopolymer and the PSMANa ionomer, similar to that of the phase-separated zinc stearate in Zn–EPDM ionomers [23]. At this point, it should be mentioned that some of the bi-functional salts might act as possible cross-linkers between the multiplets because the ionic groups of both ends of the salt can interact with the multiplets of the ionomer, resembling a bridge between the two multiplets. In this case, the position of the XRD peak due to the presence of multiplets should be proportional to the fully extended chain length of the salts. However, it should be noted that this type of the salt molecules would not show filler behavior strongly. The XRD peaks for Na12-containing non-ionic PS are also shown at $2\theta = 3–4°$ ca., and that the peaks decrease in their intensity for the NaSPS–Na12-2.0 system. This indicates that Na12 also becomes phase-separated above a certain salt content. However, the intensity of the peaks of Na12 in NaSPS sample is much lower than that of Na12 in PS sample, compared to the peak intensity of Na6 in PSMANa vs. that of Na6 in PS. This indicates that the phase-separation of Na6 in PSMANa ionomer is as almost effective as that in PS, but that the phase-separation of Na12 in NaSPS ionomer is not much effective, compared to that of Na12 in PS. In addition, it should be mentioned that the pure PSMANa ionomer is known to show a very broad and weak ionomer peak at $2\theta = 3.9°$ ca. [27,28]. However, the relatively weak contrast of the electron densities of the matrix and scattering centers, i.e. multiplets of the PSMANa ionomers, causes the difficulty in the detection of the ionomer peak using the XRD technique applied in the present work. Thus, in the XRD profile, one cannot find an ionomer peak. To complete a morphological study, the SAXS experiments were also conducted, and similar X-ray scattering results obtained from the XRD study were observed. Thus, we do not discuss the SAXS data any further.

Finally, the roles of the Na6, Na12Na, Na6Na and Na12 organic salts in changing the mechanical properties of PS-based ionomers are discussed below. Na6 is mono-functional, and, thus, its ionic groups can easily aggregate with the ionic groups of both the PSMANa ionomer and the Na6 salt. Thus, Na6 acts both as a plasticizer and as a filler, respectively. The Na6 salts participating in the multiplet formation introduce more free volume to the cluster regions (e.g. cluster T_g), but does not affect the relative amount of cluster regions of the ionomer. Once its amount exceeds a certain concentration for the formation of multiplets of maximum size, Na6 starts forming phase-separated domains that act as filler. In the case of the di-functional Na6Na and Na12Na in the ionomer, they become phase-separated and stack on each other with fully extended chain inside and ionic groups outside. These phase-separated domains can act as filler, leading to higher modulus but no change in the matrix and cluster T_g's of the

ionomers. In the case of the mono-functional Na12 in the NaSPS ionomer, Na12 can also act as a preferential plasticizer for the cluster regions. However, the length of alkyl chain of Na12 is much longer than that of Na6, and Na12 and introduce more free volume to the cluster regions, compared to Na6. Thus, the strong plasticization effect of Na12 becomes much more operative and suppresses the filler effect, caused by the presence of phase-separated salt domains, effectively in comparison with that of Na6. Therefore, the E'_{ionic} value of the NaSPS–Na12 system decreases with increasing salt contents, compared to the increasing E'_{ionic} value of the PSMANa–Na6 system.

Acknowledgements

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