

Dynamic Mechanical Properties of Polystyrene-co-Styrenesulfonic Acid Copolymers Neutralized with Aliphatic Diamines

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ABSTRACT: In this article, we reported the effects of the addition of various aliphatic diamines (ADAs) on the dynamic mechanical properties of poly(styrene-co-styrenesulfonic acid) copolymers. It was found that the ionic modulus decreased with increasing chain length of ADAs but increased for the ADA12-containing ionomers. Upon the neutralization of the copolymers with ADAs, a minor change in the size and position of the matrix loss tangent peak was observed. However, the position of the cluster loss tangent peaks shifted to lower temperatures, and the shift rate depended on the chain length of ADAs. Thus, it was suggested that the ADAs acted mainly as preferential plasticizer for the cluster regions. In addition, the effect of the amount of ADA on the difference between the matrix and cluster temperatures of the ionomers was strongest than that of the type of ADA or ion content. The X-ray peak of ADA12 suggested that the ADA12 acted both as plasticizer and as filler. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Ionomers have a small amount of ionic groups along relatively nonpolar polymer chains.^{1–4} Because of the attractive electrostatic interactions between the ion pairs of the ionomer and the high degree of incompatibility between the ionic groups and the relatively nonpolar hydrocarbon polymer matrix, the ionic groups tend to aggregate themselves. These ionic aggregates, called “multiplets,”⁵ lead to the reduction of the mobility of the polymer chain segments surrounding them.⁶ At very low ion contents, only a small amount of multiplets exists. At this stage, the ionomers show behavior that is similar to that of a nonionic polymer, that is, only one glass transition (T_g) for nonionic amorphous matrix regions. With increasing ion contents, the number and size of the multiplets increase, and, hence, the restricted mobility regions surrounding the multiplets start overlapping, making large continuous regions.⁶ When the restricted mobility regions exceed about 10 nm in their size, they exhibit their own T_g at higher temperatures than that for the nonionic matrix regions. At this point, the restricted mobility regions along with the multiplets are termed “clusters,” and the ionomer

behaves like a biphasic material, showing two T_g s, that is, matrix and cluster T_g s.⁶ It should be mentioned that at the cluster T_g , in addition to the relaxation of polymer chains in the restricted mobility regions, the hopping of ionic groups from one multiplet to another also becomes operative.⁷

It is well known that the mechanical properties and morphology of ionomer systems are influenced by various factors such as ion contents, type of counter-ions, type and position of ionic groups attached to polymer chains, and type of backbone chains.^{3,6} For example, Weiss et al. investigated the mechanical and rheological properties of sulfonated polystyrene (SPS) ionomers neutralized with mono-, di-, and trisubstituted alkyl amines.⁸ The authors demonstrated that the properties of the ionomers were affected by the chain lengths of the alkyl amines and the number of the substituents. Later, Smith and Eisenberg investigated the effects of neutralization of SPS ionomers with either flexible or rigid monofunctional amines on the mechanical properties of the ionomers.⁹ They found that the flexible aliphatic monofunctional amines (AMAs) acted as plasticizer and, thus, decreased the T_g of the ionomers, proportional to the

number of carbon atoms of amines (C_n). Fan and Bazuin studied the mechanical properties of SPS ionomer neutralized with 1,6-hexamethylene diamine.¹⁰ They found that this ionomer also behaved like SPS ionomers neutralized with metal ions. A number of other groups have also studied the various properties of the ionomers containing amine derivatives.^{11–31}

Although the effects of the organic diamines on the properties of crystalline ethylene-based ionomers had been studied, little attempts have been made to explore the effects of aliphatic diamines (ADAs), having one amine group at both ends of the alkyl chain, on the dynamic mechanical properties of the amorphous polystyrene (PS)-based ionomers.^{10,18,19} In addition, very recently we studied the effects of aliphatic dicarboxylate (DCA) salts, having varying length of alkyl chains, on the mechanical properties of PS-based ionomers³²; in this case, the DCAs are additives, not neutralizing agents. We found that the DCA salts acted mainly as filler. The above two facts lead us to the study on the effects of the neutralizing agent ADAs on the properties of PS-based ionomers. Thus, in the present work, SPS ionomers containing four ADAs were prepared: the length of alkyl chain of ADAs varies from C_2 (ethylene) to C_{12} (dodecamethylene). The copolymers of low, medium, and high acid contents were also prepared to explore the effects of the ion contents on the mechanical properties of the ionomers containing ADAs. This study will make us to gain an insight of the effects of small ionizable organic molecules on the properties of amorphous ionomers.

EXPERIMENTAL

Polymer Synthesis

Polystyrene (PS) homopolymer (MW = ca. 500,000) was synthesized by the free radical polymerization of purified styrene at 60°C using benzoyl peroxide as the initiator. The sulfonation method reported by Makowski et al. was used to prepare poly(styrene-*co*-styrenesulfonic acid) SPS random copolymers.³³ The contents of acidic repeat units of the copolymers were 4.1, 7.3, and 11.5 mol %.

Sample Preparation

As suggested by Smith and Eisenberg in their AMA-neutralized SPS ionomers,⁹ to neutralize the acid groups of the copolymers with ADAs, the copolymer and the ADAs were dissolved in a benzene/methanol (9/1, v/v) mixture to make a 5% (w/v) solution. The ratio of the moles of the acid groups of the copolymers to those of the amine groups of the ADAs was kept at 1/1. The copolymer solutions were freeze-dried and dried further under a vacuum at about 130°C for 24 h. The Fourier transform infrared results indicated that ADA-SPS ionomers are fully neutralized like the Na-SPS ionomer. We also prepared SPS ionomers neutralized with NaOH to compare the mechanical data of the ADA-neutralized SPS ionomers with those of the Na-neutralized SPS ionomers. The sample notation used for these samples is x -ADAY or x -Na, where “ x ” indicates the mol % of the ionic repeat units of the SPS ionomers neutralized with either ADAs or sodium, and “ y ” is the number of the carbon atoms (C_n) of a particular ADA molecule; i.e., 2 for 1,2-ethylene diamine (m.p. = 8.5°C),³⁴ 6 for 1,6-hexamethylene diamine (m.p. = 42°C),³⁴ 10 for 1,10-decamethylene diamine (m.p. = 59–61°C),³⁴ and 12 for 1,12-dodecamethylene diamine (m.p. =

67–69°C).³⁴ For the dynamic mechanical property measurements, the samples were compression molded at about 150–250°C and at a pressure of about 25 MPa. All the molded samples with approximate dimensions of $2.5 \times 7.0 \times 30.0$ mm³ were transparent and annealed under a vacuum at 130–150°C for 24 h. For the small-angle X-ray scattering (SAXS) measurements, the samples were compression-molded at about 150–250°C. A pressure of about 25 MPa was applied for 5 min, and then slowly released, and the mold was allowed to cool to below the matrix T_g . The dimensions of the molded samples were about 0.5 mm (thickness) \times 10 mm (diameter).

Dynamic Mechanical Analysis

To measure the dynamic mechanical properties of the ionomers, a Q-800 dynamic mechanical analyzer (DMA) (TA Instruments, DE) was used. The dual cantilever bending mode at frequencies of 0.3, 1, 3, 10, and 30 Hz was utilized, but the detailed data analysis was performed only on 1 Hz data. The heating rate was 1°C min⁻¹. For each sample, the storage moduli (E') and loss tangents were obtained as a function of temperature.

X-Ray Experiments

The small angle X-ray scattering (SAXS) experiments were conducted at Station 4C1 of Pohang Light Source (PLS) synchrotron radiation source (Pohang, Korea). The sample-to-detector distance was 400 mm, which allowed SAXS data to be obtained in the q (scattering vector) ranging from about 0.2 to 4.2 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). A PANalytical X'pert PRO MPD X-ray diffractometer was used to obtain the X-ray diffraction (XRD) patterns.

RESULTS AND DISCUSSION

Figure 1 shows the storage moduli (E') as a function of temperature for the SPS ionomers containing either 4.1 or 11.5 mol % of ionic repeat units, neutralized with either NaOH or ADAs. With increasing temperature, the ionomers show a plateau for glassy moduli, a steep slope for a matrix T_g , a narrow ionic plateau, a gentle slope for a cluster T_g , and a descending plateau-like feature for rubbery moduli and sample flow. The width of ionic plateau (i.e., the moduli between the matrix and cluster T_g s) extends to about 260°C for the 4.1-Na ionomer. However, it becomes narrower for the 4.1-ADA ionomers and extends only to about 170–200°C, depending on the chain length of ADAs. At this point, it should be mentioned that the width of the ionic plateau is treated as a symbol of the strength of the interactions between the ion pairs in the multiplets; the narrower the ionic plateau is, the weaker the interactions between the ion pairs are.^{3,7,35} This is due to the fact that the electrostatic force F_{el} between the charges is inversely proportional to the square of the distance (x) between two charges: i.e., $F_{el} \propto q_a q_c / x^2$, where q_a and q_c are the anion and cation charges, respectively.³⁶ Thus, if the size of cation is smaller, the distance between two charges is shorter and the cluster T_g , at which ion-hopping occurs and is related to the F_{el} , becomes higher. Because the size of Na⁺ is smaller than that of quaternary ammonium cation (e.g., the ionic radius of Na⁺ is 0.95 Å, but that of NH₄⁺ is 1.43 Å),³⁷ the ionic plateau is wider for the Na ionomer, compared to the ADA

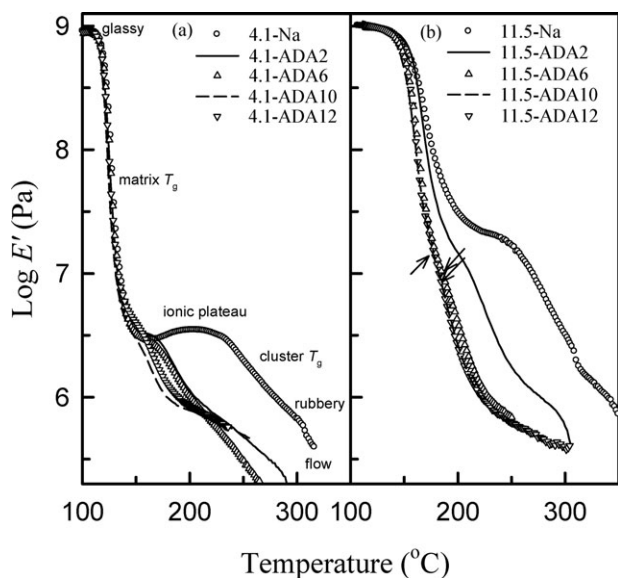


Figure 1. Storage moduli of SPS ionomers neutralized with either Na or ADAs as a function of temperature (1 Hz data). The ion contents of ionomers are (a) 4.1 mol % and (b) 11.5 mol %. For clarity, arrows indicate the ionic moduli of 11.5-ADA6, ADA10, and ADA12 ionomers.

ionomer, at a particular ion content; this will be discussed later in connection with cluster T_g .

It is worth mentioning that the height of the ionic plateau in the plots of E' vs. temperature generally reflects the amount of the clustered regions (i.e., the degree of clustering).^{3,6,35} The height of ionic plateau of 4.1-ADA ionomers is lower, compared to that of 4.1-Na ionomer, and decreases further as the chain length of the ADAs increases. However, the ionic plateau of 4.1-ADA12 ionomer moves to higher moduli in comparison with that of 4.1-ADA10 ionomer. The ionic plateau of 11.5-Na ionomer is higher than that of 4.1-Na ionomer and the ionic plateau also shifts to lower modulus values upon the neutralization with ADAs, and moves further down to lower moduli with increasing chain length of ADAs. Again, the position of the ionic plateau of 11.5-ADA12 ionomer is higher than that of 11.5-ADA10 ionomer. It is also seen that the segment of the modulus curve for the cluster T_g becomes steeper and shifts to lower temperatures upon the neutralization with ADA and with increasing chain length of ADAs. The 7.3 mol % ionomers show a similar trend (not shown here).

Because the position of the ionic plateau is related with the degree of clustering, we tried to analyze it more quantitatively. The modulus values at the point of a minimum slope of the ionic plateau in $\log E'$ vs. temperature plots, so-called ionic modulus (E'_{ionic}), are shown in Figure 2(a) as a function of the number of carbon atoms of ADAs. It is seen that the E'_{ionic} decreases smoothly with increasing chain length up to C_{10} (i.e., ADA10), and that the decreasing rate seems to increase with ion content. It is also shown that the E'_{ionic} values of the three ionomers neutralized with ADA12 are higher than those of the ionomers neutralized with ADA10. This implies that the role of ADA12 might be different from that of the rest of ADAs, at least to some extent. Figure 2(a) also includes the E'_{ionic} data of

4.5-Na ionomers containing aliphatic dicarboxylates (DCAs) that act mainly as reinforcing filler,²² the ion content of which is slightly higher than that of 4.1-ADA ionomers. It is seen that the E'_{ionic} of 4.5-DCA ionomer increases initially and remains more or less constant as the chain length of DCA increases from C_6 to C_{12} .³² The difference in the trends of E'_{ionic} values 4.5-DCA and 4.1-ADA ionomers indicates that the roles of DCA and ADA in SPS ionomer are not the same. Interestingly, the E'_{ionic} value of 4.1-ADA12 is in the middle of those of 4.5-DCA12 and 4.1-ADA10 ionomers. This suggests that the ADA12 molecules might act as filler in part. At this point, it should be mentioned that the increasing chain length of ADAs results in the increase in the weight percentage (wt %) of ADA in the ADA-neutralized ionomers. Thus, in Figure 2(b) we plotted the E'_{ionic} data as a function of wt % of ADAs in the ionomers. It is seen that the E'_{ionic} values, except for that of ADA12, decrease regularly with increasing wt % of ADAs. Figure 2(c) shows the E'_{ionic} data as a function of the ion content of ionomers. It is clear that the E'_{ionic} s of ADA-neutralized ionomers increase with increasing ion content, similar to those of Na-neutralized PS-based ionomers.^{3,35} This indicates that the diamines act also as neutralizing agents for the sulfonic acid groups effectively, to some extent.^{9,10,18,19} It is observed that at a certain ion content, the E'_{ionic} value is the highest for Na-ionomer and decreases with increasing chain length of ADAs, except for the ADA12. This means that the ADA2, ADA6, and ADA10 act as effective plasticizer to make the ionomer relatively softer at the temperatures where the ionomer show its ionic modulus, while the ADA12 behaves differently.

Shown in Figure 3 are the loss tangents as a function of temperature for the Na and ADA ionomers having either 4.1 or 11.5 mol % of ionic repeat units. It is clear that these ionomers represent biphasic behavior by showing two loss tangent peaks; one

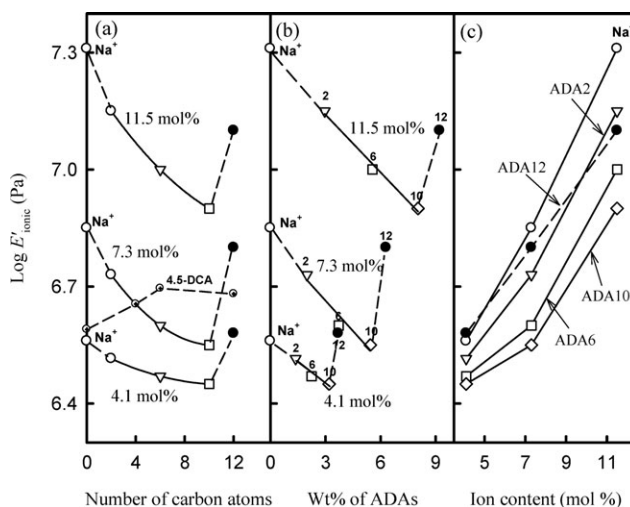


Figure 2. Ionic moduli (E'_{ionic}) of SPS ionomers neutralized with either Na or ADAs as functions of (a) number of carbon atoms of ADAs, (b) wt % of ADAs (the numbers near the symbols indicate the number of carbon atoms of the ADAs) and (c) ion contents of ionomers (1 Hz data). The ionic modulus values of DCA-containing SPS ionomers (ion content = 4.5 mol %) (data were obtained from Ref. 32) are also included in (a).

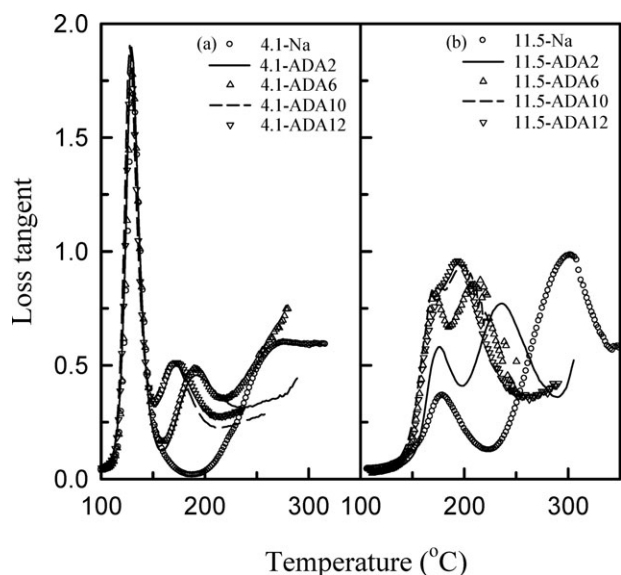


Figure 3. Loss tangents of (a) SPS ionomers neutralized with either Na or ADAs as a function of temperature (1 Hz data). The ion contents of ionomers are (a) 4.1 mol % and (b) 11.5 mol %.

at low temperatures for the glass transition of matrix regions and the other at high temperatures for that of cluster regions. It should be mentioned that, at first glance, the shapes of the matrix and cluster peaks of the 4.1-ADA and 11.5-ADA ionomers look different from each other. However, if one considers the deconvolutions of the peaks with baseline subtraction,³⁵ one may find not much different shapes and sizes of the matrix and cluster peaks for each ionomer. In Figure 3, it is clear that the addition of ADAs does not change the positions of the matrix loss tangent peaks of the 4.1 and 11.5 mol % ionomers noticeably. On the other hand, upon the neutralization with the ADAs, the cluster peak position moves to low temperatures progressively. For example, the cluster peak of the 4.1-Na ionomer at about 265°C shifts to about 200°C for the 4.1-ADA2 ionomer and further down to about 170°C for the 4.1-ADA12 ionomer. In the case of the 11.5-Na ionomer, the matrix and cluster peaks are smaller and larger, respectively, than those of the 4.1-Na ionomer because of the higher degree of clustering.³⁵ When the ionomer is neutralized with ADA, the cluster peak of the 11.5-Na ionomer at about 300°C shifts to about 235°C for the 11.5-ADA2 ionomer and further down to about 195°C for the 11.5-ADA12 ionomer.

Figure 4(a) is the plots of T_g s vs. the number of carbon atoms of ADAs (or DCAs or AMAs). As expected, with increasing ion content from 4.1 to 11.5 mol %, the matrix T_g ($T_{g,m}$) and cluster T_g ($T_{g,c}$) of the Na- and ADA-ionomers increase significantly. The increasing $T_{g,m}$ is due to both the copolymerization effect and the increasing degree of clustering and the increasing $T_{g,c}$ is due mainly to the increasing degree of clustering with increasing ion content.^{3,4,6,35} Now, let us look at the T_g s as a function of the number of carbon atoms of ADAs. It is evident that the matrix T_g changes only slightly as the number of carbon atoms of ADAs increases; however, the cluster T_g drops significantly. As mentioned before, at the $T_{g,c}$ two mechanisms are operative simultaneously; the relaxation of the polymer

chains in clustered regions and the hopping of the ionic groups between multiplets.^{3,7} Thus, stronger interactions between ionic groups require higher temperatures for ions to hop from one multiplet to another multiplet. Therefore, the type of cations affects a cluster T_g strongly, with only a marginal effect on a matrix T_g .³⁸ In the present work, since the size of Na⁺ cation is smaller than that of a monosubstituted ammonium cation, the cluster T_g of Na ionomer is higher than that of the ADA ionomers. Furthermore, the cluster T_g of the ionomer decreases with increasing chain length of ADAs. At this point, it should be recalled that the type of ion pairs in ADA ionomers is similar to each other, i.e. $-\text{SO}_3^- + \text{H}_3\text{N}-\text{C}_n-\text{NH}_3^+ - \text{O}_3\text{S}-$. Thus, the electrostatic forces between $-\text{NH}_3^+ - \text{O}_3\text{S}-$ ion pair and other $-\text{NH}_3^+ - \text{O}_3\text{S}-$ ion pairs in the multiplet are similar for all of the ADA ionomers, if the alkyl chain did not participate in the multiplet formation. However, this idea may not be fully applicable here, since the cluster T_g decreases with increasing chain length of ADAs. This implies that the alkyl chains of ADA may participate in the preferential plasticization of the cluster regions of the ionomer, to some extent, by residing in the multiplets and/or in the regions of restricted mobility. At this point, it can be mentioned that the alkyl chains in the vicinity of multiplets would reduce the number of polymer chains emanating from the multiplets, to some extent, and provide more room for the polymer chains to move, leading to the decrease in cluster T_g . On the other hand, if the thickness of restricted mobility regions surrounding the multiplet decreased, the amount of cluster region should decrease, leading to the decreasing size of cluster loss tangent peak; this is not observed here. Thus, the

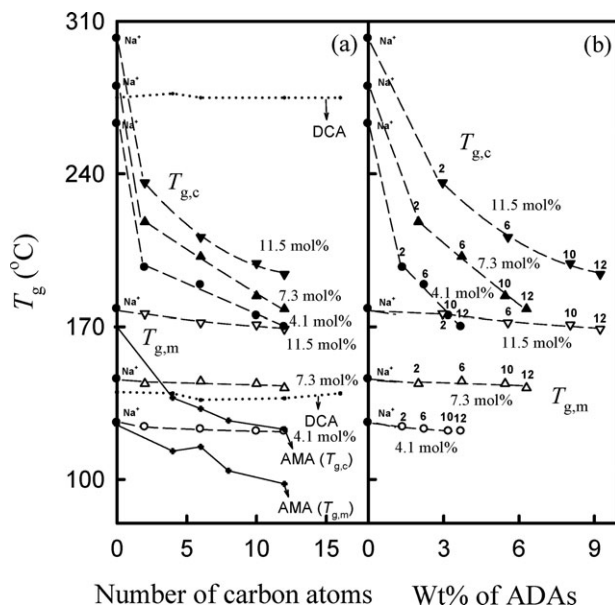


Figure 4. Glass transition temperatures of matrix ($T_{g,m}$) and cluster ($T_{g,c}$) regions of SPS ionomers neutralized with either Na or ADAs (dashed lines) as functions of (a) number of carbon atoms of ADAs and (b) wt % of ADAs (1 Hz data) (the numbers near the symbols indicate the number of carbon atoms of the ADAs). The $T_{g,m}$ and $T_{g,c}$ of SPS ionomers (ion content = 4.5 mol %) containing DCA (dotted lines, data were obtained from Ref. 32) and those of SPS ionomers (ion content = 8.1 mol %) neutralized with AMA (data were obtained from Ref. 22) are also included in (a).

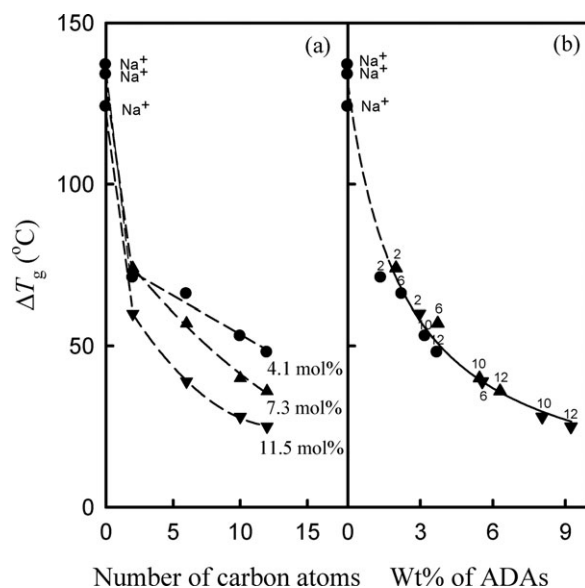


Figure 5. Temperature difference (ΔT_g) between cluster T_g and matrix T_g of SPS ionomers neutralized with either Na or ADAs as functions of (a) number of carbon atoms of ADAs and (b) wt % of ADAs (1 Hz data) (the numbers near the symbols indicate the number of carbon atoms of the ADAs).

possibility of the decrease in the thickness of restricted mobility regions by the introduction of ADAs can be ruled out. The T_g s of 4.5-DCA ionomers are also presented in Figure 4(a) (data were obtained from Ref. 32). Because the DCA acts mainly as filler, the matrix and cluster T_g s remain constant with increasing chain length of DCAs. In the same figure, the T_g s of monofunctional amine, AMA-neutralized SPS ionomers (8.1 mol % of ion content), are also shown (data were obtained from Ref. 22). It is seen that the matrix and cluster T_g s of AMA-ionomers decrease with increasing AMA chain length, and that the T_g s can be fitted to a linear function for the matrix T_g s and a quadratic function for the cluster T_g s. These results are quite different from what we observed here, that is, no significant change in the matrix T_g for ADA ionomers vs. a strong decrease in the matrix T_g for 8.1-AMA ionomer. This can be understood: The AMAs, being monofunctional amines and having relatively freely movable alkyl chains, act as normal “internal” plasticizers for both the matrix and cluster regions. However, the ADAs, being difunctional amines, behave like “cluster” plasticizers that decrease only a cluster T_g . This is due to the fact that the alkyl chain of ADA, unlike that of AMA, would reside inside the multiplet and/or outside but only in close proximity to the multiplet because most of the ion pairs of both ends of the ADA chain would form ionic aggregates; sometimes, two ion pairs of one ADA may reside in the same multiplet, making the alkyl chain stay outside the multiplet. In this case, the alkyl chains of ADA are too short to reside in matrix regions and, thus, stay in the regions of restricted mobility; therefore, the ADA acts as cluster plasticizer. Now, let us consider the effect of the amount of ADA on the T_g s of the ionomer. Because the amount of ADAs in the ionomers changes with the ion content of the ionomers and the chain length of the ADAs, the T_g s are also shown as a function of wt % of ADAs in Figure 4(b). It is seen that the cluster T_g seems to decrease more smoothly as a

function of wt % of ADAs in comparison with that shown in Figure 4(a), and the decreasing rates depend on the ion content of ionomers. This indicates that the dynamic mechanical properties of ADA ionomers are affected by the ion content of ionomers but more strongly by the amount of ADAs.

Figure 5(a) exhibits temperature differences between the cluster T_g and matrix T_g (ΔT_g) as a function of the chain length of ADAs. First of all, as expected, the ΔT_g decreases with increasing chain length of ADAs. As mentioned before, this is possibly due to the preferential plasticization of the cluster regions by the alkyl chains of ADAs, which becomes more effective with increasing chain length of ADAs. Second, the ΔT_g becomes smaller with increasing ion contents of the ADA ionomers. This means that the preferential cluster plasticization effect becomes more profound for the ionomers of higher ion content, which have more clustered regions. Because the cluster T_g changes more smoothly as a function of wt % of ADAs, we also obtained ΔT_g as a function of wt % of ADAs [see Figure 5(b)]. Interestingly enough, the ΔT_g data seem to be fitted to a single equation. This implies that the ΔT_g depends more strongly on the amount of ADAs, which, in turn, depends directly on both the type of ADAs and the ion content of ionomers, simultaneously.

The morphological details of the ionomers were examined by SAXS experiments. Shown in Figure 6 are the SAXS profiles of 4.1-Na and 4.1-ADA ionomers. A well-developed peak is seen at q (scattering vector) = ca. 1.7 nm^{-1} for the 4.1-Na ionomer, which corresponds to a Bragg spacing (d_{Bragg}) of about 3.7 nm. This Bragg spacing, ascribed to an intermultiplet distance, is almost the same as the results obtained elsewhere.^{22,39–43} In the present work, the increase of ADA chain length from C_2 to C_{12} induces a shift of SAXS peak position from $q = \text{ca. } 1.8 \text{ nm}^{-1}$ to $q = \text{ca. } 1.5 \text{ nm}^{-1}$ with decreasing its intensity. The shift of the peak to smaller q values indicates that the distance between scattering centers increases, which, in turn, means that the

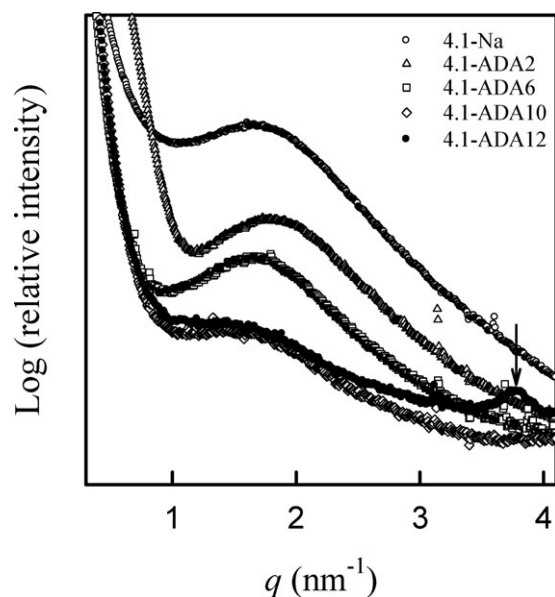


Figure 6. SAXS profiles of SPS ionomers (ion content = 4.1 mol %) neutralized with either Na or ADAs.

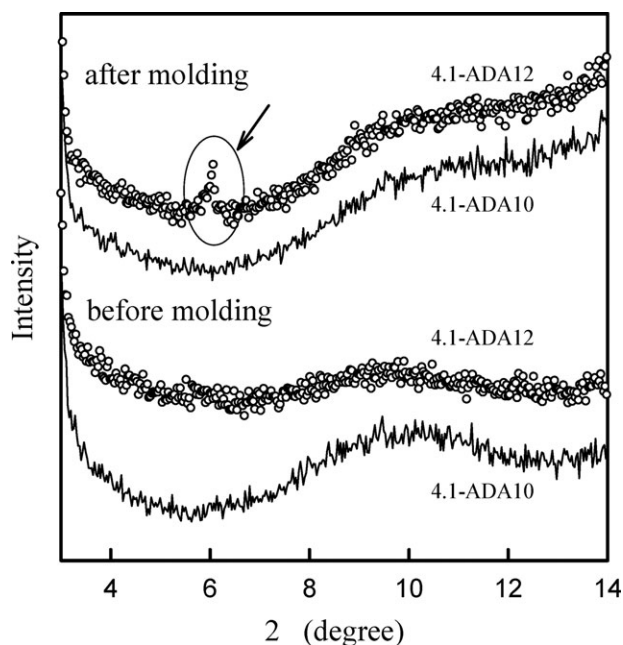


Figure 7. XRD patterns of SPS ionomers (ion content = 4.1 mol %) neutralized with ADA10 and ADA12.

number of scattering centers decreases since the number of scattering centers is inversely proportional to the distance between scattering centers. In addition, the decreasing intensity can be caused by the following two factors: the number of the scattering centers (i.e., multiplets) at prevalent distances decreases with increasing chain length, and the electron density contrast of the scattering centers decreases. It should be noted that the ADA molecules with long chains lead to the reduction of the short range order in multiplets arrangement in the cluster regions. Thus, for ADA10 and ADA12 ionomers, only a small number of multiplets of relatively low electron density may exist. Therefore, the size of the SAXS peak decreases drastically, and the peak position shifts to lower q value. In the present work, if some of the alkyl chains of the ADAs reside in multiplets, the sizes of the multiplets will increase as the chain length of ADAs increases. Then, the enlargement of multiplet sizes increases the distance between multiplets, to some extent, and decreases the effective electron density of multiplets, which, in turn, lowers the SAXS peak intensity. In addition, 4.1-ADA12 ionomer shows an additional small SAXS peak at $q = \text{ca. } 3.8 \text{ nm}^{-1}$ ($d_{\text{Bragg}} = \text{ca. } 1.7 \text{ nm}$). This morphological difference suggests that the role of ADA12 may not be the same as that of the rest of ADAs. The XRD profile of the 4.1-ADA12 ionomer shows a small sharp peak at $2\theta = \text{ca. } 6^\circ$ ($d_{\text{Bragg}} = \text{ca. } 1.5 \text{ nm}$) and a very broad peak at larger angles, associated with the amorphous phase of the polymers (see Figure 7). The rest of ionomers show only a very broad peak (only XRD pattern of ADA10 is shown here for comparison). At this time, it should be mentioned that the freeze-dried ADA12 ionomer in a powder form does not show the small peak, but the sample molded and annealed at high temperatures exhibits the peak. This indicates that the small XRD peak is originated from the thermal treatment of ADA12 ionomer. Interestingly enough, the Bragg spacing values calculated from

the positions of the small SAXS and XRD peaks are similar to the length of fully extended ADA12 molecules (i.e., ca. 1.6 nm). Thus, it can be suggested that the small peaks in the SAXS and XRD profiles are due to the presence of phase-separated quaternary ADA12 salts. This phase-separated ADA12 salt might act as filler that increases ionic modulus strongly; however, it does not affect the cluster T_g since the cluster T_g is related with both the strength of ionic interaction and the amount of cluster regions. At this point, it should be noted that the melting temperature of 1-dodecylamine is 28–30°C, but that of its quaternary form, 1-dodecylamine hydrochloride, is 186–188°C; the melting temperatures of 1,2-diaminoethane and 1,4-diaminobutane are 8–11°C and 25–28°C, respectively, but those of their quaternary form 1,2-diaminoethane dihydrochloride and 1,4-diaminobutane dihydrochloride are over 300°C and 279–281°C, respectively.³⁴ Thus, in the present work, with consideration of the melting temperature of pure ADA12 of 67–69°C, one can expect that the melting temperature of the quaternary ADA12 would be very high. This implies that the phase-separated quaternary ADA12 molecules can act as filler above matrix T_g . However, it should be mentioned that at this moment we do not have a clear explanation for the reason why the rest of ADAs are not phase-separated.

Let us discuss the possible reasons for the change in the properties of the SPS ionomers by the incorporation of the ADA. First of all, the addition of small organic molecules containing amine groups to copolymers containing sulfonic acid groups creates ion pairs by proton-transfer from the acid groups to the basic amine groups. Because the ADAs are bifunctional, one ADA molecule can form two ion pairs with two acid groups of the copolymers, resulting in physical crosslinks. In this case, the alkyl chains of the ADAs may reside both inside and outside the multiplets. The alkyl chains remaining inside the multiplet lead to the increase in the size of the multiplets. This prevents ammonium-sulfonate ion pairs from approaching closely each other. As a result, the strength of interactions between adjacent ion pairs becomes weak, and it becomes weaker with increasing chain length of ADAs. The decrease in the temperature range of the ionic plateau and the shift rate of the cluster loss tangent peak to lower temperatures with increasing chain length of ADAs are in accordance with this expectation. Furthermore, if the size of the multiplet increases upon the neutralization with ADA but the average number of anionic groups per multiplet is the same, the crowdedness of polymer chains emanating from the multiplet will be reduced due to the larger contact surface area of the multiplet per emanating polymer chain. This, in turn, makes the clustered regions relatively less crowded, compared to that of the Na ionomers, without changing the relative amount of clustered regions in the ionomer. If this is the case, the ionic modulus of ADA ionomer will decrease not by the decreases in the amount of clustered region but by the less crowdedness of the clustered region. In addition, the alkyl chains of ADAs can also reside in the regions of restricted mobility, which induces more free volume in the cluster regions. This also decreases the cluster T_g . In this case, one can expect the similar sizes of the deconvoluted matrix and cluster loss tangent peaks and the decreasing ionic modulus with increasing chain length of ADAs, which were what we observed here. If ADAs act as plasticizer for the multiplets

and clustered regions, the amount of the ADAs must affect the T_g ^{44,45}; the T_g data, indeed, show direct relation with the amount of ADAs, indicating the plasticization by ADAs. In the case of ADA12 molecules, some of them may be phase-separated and act as filler that increases ionic modulus, and the ADA12-neutralized ionomer shows a second SAXS peak and an XRD peak for the phase-separated regions.

CONCLUSIONS

It was found that the ionic modulus decreased with increasing chain length of ADAs, except for the ADA12, indicating that the addition of ADAs induced more flexibility in the polymer chains in the restricted mobility regions surrounding multiplets. Upon the neutralization of the SPS with ADAs, only a small change in the shape, size and position of the matrix loss tangent peaks of the ionomers was observed. However, the position of the cluster loss tangent peaks, with similar sizes, shifted drastically to low temperatures. Thus, it was suggested that the alkyl chains of ADAs could reside both in multiplets and cluster regions and acted mainly as cluster plasticizer. In the case of ADA12 molecules, however, some of them might be phase-separated, acted as filler particles.

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