Effects of the Addition of LiCl and CsCl Salts on the Mechanical Properties and Morphology of Poly(styrene-*co*-methacrylate) Ionomers

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ABSTRACT: The effects of the addition of LiCl and CsCl salts to Li- and Cs-neutralized styrene-*co*-methacrylate ionomers, respectively, on the mechanical properties and morphology of the ionomers were studied. It was observed that with increasing inorganic salt contents, the ionic modulus increased, and this indicated that the inorganic salts in the ionomers acted as fillers. However, the type of salt did not affect the increase in the ionic modulus. It was also found that the addition of the inorganic salts did not change the matrix glass-transition temperatures of the ionomers strongly but reduced the cluster glass-transition temperature significantly and slowly for the LiCl- and CsCl-containing ionomers, respectively. In addition, with increasing salt contents, a small-angle X-ray scattering peak shifted to slightly lower angles. These findings suggested that some of the inorganic salts resided in the multiplet with the ionic groups of the ionomers, acting as plasticizers. The presence of an X-ray diffraction peak for the polymers containing a relatively large amount of CsCl indicated that the CsCl salt formed phase-separated domains at sufficiently high salt contents. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 633–639, 2008

Key words: fillers; ionomers; mechanical properties

INTRODUCTION

Ionomers are polymers that have a small number of ionic groups. They usually exhibit the characteristics of two-phase materials because of the presence of ion aggregation within a matrix of low polarity.[1,2] According to the Eisenberg-Hird-Moore (EHM) model for amorphous random ionomers, the ionic aggregates, termed *multiplets*, lead to a reduction in the mobility of polymer chains surrounding them.[3] When the ion concentration increases, the regions of polymer chains of restricted mobility start to overlap and become large, continuous regions called *clusters*.[7] Now, the cluster regions have their own glass-transition temperature (T_g), that is, the cluster glass-transition temperature ($T_{g,c}$), which is higher than T_g of the polymer chains in ion-poor regions, that is, the matrix glass-transition temperature ($T_{g,m}$).

The mechanical properties of poly(styrene-*co*-metal methacrylate) and poly(styrene-*co*-metal styrenesulfonate) ionomer systems have been the subject of extensive studies.[4–16] In particular, Kim et al.[13] investigated the mechanical properties of poly(styrene-*co*-methacrylate) (PSMA) ionomers thoroughly and found that the ionic modulus (E'_{ionic}) increased with increasing ion contents. This behavior of the PSMA ionomers was thought to resemble that of a polymer system containing a filler. Furthermore, the authors suggested that clusters, not ionic aggregates, acted as fillers. In common filled polymeric systems, inorganic materials are usually used as fillers. Thus, in the PSMA ionomer system, it had been expected that the ionic aggregates, organic salts, would act as fillers. Therefore, the suggestion by Kim et al. was unexpected. From that study, one question arose: if we added inorganic salts to PSMA ionomers, what would be the roles of the inorganic salts? Thus, in this study, we explored the effects of the presence of inorganic salts, that is, LiCl and CsCl, on the dynamic mechanical properties and morphology of lithium- and cesium-neutralized PSMA ionomers, respectively. Here, we chose the lithium- and cesium-containing systems because the radius of the lithium ion is much smaller than that of the cesium ion (0.076 vs 0.174 nm).[17] In addition, $T_{g,c}$ of the Cs-neutralized ionomer is lower than that of the Li-neutralized ionomer.[1,2] Therefore, we could understand the size effect of cations of inorganic salts on the mechanical properties and morphology of PSMA ionomers having different $T_{g,c}$ values.

TABLE I
Weight Percentages of Salts in Samples and E'_{ionic}, $T_{g,m}$, $T_{g,c}$, $E_{a,m}$, and $E_{a,c}$ Values for
PSMALi and PSMACs Ionomers Containing LiCl and CsCl Salts, Respectively

| Ionomer | Amount of salt | | E'_{ionic} ($\times 10^7$ Pa) | $T_{g,m}$ (°C) | $T_{g,c}$ (°C) | $E_{a,m}$ (kJ/mol) | $E_{a,c}$ (kJ/mol) |
	wt %	vol %					
PSMALi	0	0.0	2.9	150	222	546	213
Li-LiCl-1	3.8	2.0	3.5	147	204	533	214
Li-LiCl-3	10.9	6.0	4.3	145	203	528	210
Li-LiCl-5	16.9	9.6	5.0	144	200	533	224
Li-CsCl-5	45.1	18.3	7.6	146	203	537	221
PSMACs	0	0.0	3.2	140	184	536	250
Cs-CsCl-1	14.2	4.3	3.9	140	181	532	244
Cs-CsCl-3	33.0	11.8	6.5	140	181	544	248
Cs-CsCl-5	45.1	18.3	10.0	139	181	531	260
Cs-LiCl-5	17.0	9.7	6.8	141	219	533	257

$E_{a,m}$ = matrix activation energy; $E_{a,c}$ = cluster activation energy.

EXPERIMENTAL

Sample preparation

Poly(styrene-*co*-methacrylic acid) (PSMAA; molecular weight $\approx$ 300,000) containing 10.0 mol % acid units was synthesized by a free-radical bulk polymerization method. The detailed procedure has been described elsewhere.[13] To obtain ionomers containing LiCl and CsCl salts, the salts were added to a benzene/methanol (9/1 v/v) mixture containing the PSMAA copolymer. In the case of the system containing a relatively large amount of CsCl, because of the relatively low solubility of the salt, a small amount of distilled water was added to the solution to make the solution homogeneous. The amounts of the salts added were changed to make the ratios of the moles of inorganic salt molecules to the moles of the ionic groups of an ionomer 1/1, 3/1, and 5/1. Subsequently, to neutralize the acid groups of the PSMAA copolymer, a predetermined quantity of either methanolic LiOH or CsOH was added to the acid polymer solution containing LiCl or CsCl salts, respectively. The solution was freeze-dried and then dried further in a vacuum oven at 180°C for 24 h. The amounts of the salts added are listed in Table I. Here, the sample denotation is *x-y-z*, where *x* is the type of cation of the neutralizing agent, *y* is the type of inorganic salt, and *z* is the ratio of the moles of salt molecules to the moles of the ionic groups of the ionomer.

Dynamic mechanical property measurements

For mechanical property measurements, the samples were compression-molded at about 250°C and a pressure of 25 MPa. The molded sample (2.7 $\times$ 7.0 $\times$ 30 mm) was annealed *in vacuo* at 130°C for 24 h. To determine the dynamic mechanical properties of the ionomers, a TA Q-800 dynamic mechanical analyzer was used (TA Instruments, New Castle, DE). The experiments were carried out in a dual-cantilever bending mode at frequencies of 0.3, 1, 3, 10, and 30 Hz. The storage modulus (E') and loss tangent values were obtained as a function of temperature at a heating rate of 1°C/min. For a detailed loss tangent data analysis using Peakfit software (SPSS, Inc.), only 1-Hz data were used.

X-ray experiments

The small-angle X-ray scattering (SAXS) experiments were conducted at Station 4C1 of the Pohang Light Source synchrotron radiation source (Pohang, Korea). The detailed conditions for the experiments have been given elsewhere.[18] The X-ray diffraction (XRD) patterns of the samples were recorded with a PANalytical X'pert PRO MPD X-ray diffractometer (Almelo, the Netherlands). Cu radiation (λ = 0.1542 nm) was used, 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°.

RESULTS AND DISCUSSION

Figure 1 shows the E' and loss tangent values of the poly(styrene-*co*-lithium methacrylate) (PSMALi) ionomer and ionomers containing LiCl salt molecules as a function of temperature. With increasing temperature, the modulus changes from a glassy modulus to a matrix glass transition to an ionic plateau to a cluster glass transition to a very weak rubbery plateau accompanied by sample flow. Here, the ionic plateau is the segment of the modulus curve in the intermediate region in which the modulus decreases slightly with temperature. In Figure 1, it is evident that the shapes of the modulus curves above $T_{g,m}$ are affected by the addition of the LiCl salt. With increasing LiCl
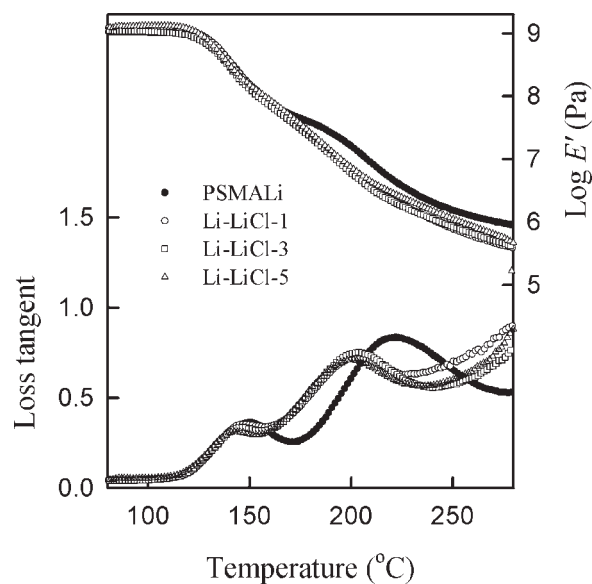
Figure 1 E' and loss tangent values as a function of temperature for PSMALi ionomers containing various amounts of LiCl salt (measured at 1 Hz).

salt contents, the ionic plateau shifts to lower temperatures but moves to slightly higher modulus values; E'_{ionic}, the value of E' at the point of the minimum slope of the ionic plateau, is listed in Table I. Upon the addition of LiCl to the ionomer, E'_{ionic} increases, and this suggests that a filler effect is operative in this system. In the case of the loss tangent curves, two loss tangent peaks can be seen, that is, a matrix loss tangent peak at lower temperatures and a cluster loss tangent peak at higher temperatures. It is observed that upon the addition of the LiCl salt, the matrix and cluster loss tangent peaks shift to slightly and significantly lower temperatures, respectively. The $T_{g,m}$ and $T_{g,c}$ values obtained from the loss tangent peak maxima are also listed in Table I. It is clear that, with increasing LiCl contents, $T_{g,m}$ decreases slowly from 150°C for the unblended PSMALi ionomer to 144°C for the Li-LiCl-5 ionomer. However, $T_{g,c}$ drops significantly from 222°C for the unblended PSMALi ionomer to 204°C for the Li-LiCl-1 ionomer and then decreases gently to 200°C for the Li-LiCl-5 ionomer. At this point, it should be mentioned that polar plasticization and preferential plasticization induce the drop of $T_{g,c}$ of ionomers.[1,2,7,11,19–21] Thus, the drastic decrease in $T_{g,c}$ upon the addition of the LiCl salt implies that the salts might act as a plasticizer to some extent. This will be discussed later in more detail.

Shown in Figure 2 are the E' and loss tangent values of the poly(styrene-*co*-cesium methacrylate) (PSMACs) ionomer and ionomers containing CsCl salt molecules as a function of temperature. Similar trends observed in Figure 1 are also found in this figure. However, there is certainly a divergence

between the Li-neutralized system and the Cs-neutralized system, that is, in the $T_{g,c}$ values and the decreasing rates of $T_{g,m}$ and $T_{g,c}$. This might be due to the different strengths of the ionic interactions. The strength of interaction between a cation and an anion is inversely related to the size of the ionic species and is directly related to $T_{g,c}$, at which the ions start to hop.[22–25] Now, it should be recalled that the size of Cs^+ is much larger than that of Li^+, and so the strength of interactions between $Li^+/—COO^-$ ion pairs is much stronger than that between $Cs^+/—COO^-$ ion pairs, leading to much higher $T_{g,c}$ for the PSMALi ionomer ($T_{g,c}$ = 222°C) in comparison with that for the PSMACs ionomer ($T_{g,c}$ = 184°C). It can also be seen that the matrix and cluster loss tangent peaks of the ionomer system containing CsCl salt do not change significantly in their positions, but the peak heights decrease with increasing salt contents. The $T_{g,m}$ and $T_{g,c}$ values of the Cs ionomers are also listed in Table I. It is clear that, upon the addition of CsCl, the $T_{g,m}$ values seem to remain constant at about 140°C, and $T_{g,c}$ decreases slightly from 184 to 181°C and remains unchanged.

Figure 3 illustrates the temperature differences between the T_g values of the unblended ionomers and those of the ionomers containing salts as a function of the amounts of the salts in the ionomers. As mentioned previously, whereas $T_{g,c}$ of the Li-LiCl-5 ionomer decreases by about 22°C, that of the Cs-CsCl-5 ionomer drops by only about 3°C in comparison with the $T_{g,c}$ values of the unblended Li-neutralized and Cs-neutralized ionomers, respectively. In the case of the $T_{g,m}$ values, they decrease by about 6°C and by about 1°C for the Li-LiCl-5 and Cs-CsCl-5
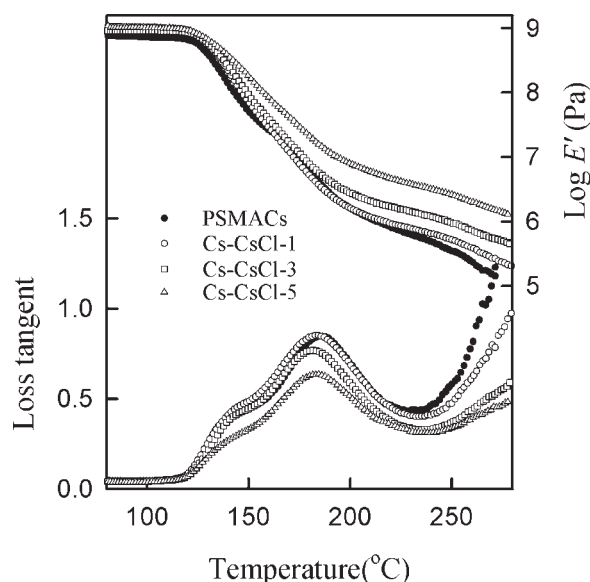

Figure 2 E' and loss tangent values as a function of temperature for PSMACs ionomers containing various amounts of CsCl salt (measured at 1 Hz).
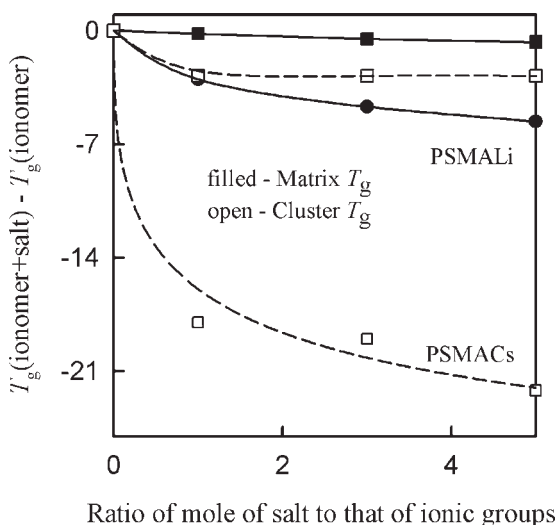
Figure 3 Effects of added inorganic salts on the $T_{g,m}$ and $T_{g,c}$ values for the ionomers containing various amounts of inorganic salts.

ionomers compared to those of the unblended ionomers, respectively.

The activation energy (E_a) values for the glass transitions of the ionomers were calculated with Arrhenius plots of the logarithm of the frequency versus the inverse temperature with confidence limits of ±30 kJ/mol. The E_a values are listed in Table I. As expected, the E_a values for $T_{g,m}$ of the PSMALi and PSMACs ionomer systems and for $T_{g,c}$ of the PSMALi ionomer system remain relatively constant at about 535 and 250 kJ/mol because the T_g values change only slightly with increasing salt contents. In the case of the E_a values for $T_{g,c}$ of the PSMALi ionomer, they also change only slightly, even though the $T_{g,c}$ values decrease noticeably. This result indicates that the mechanism for the cluster glass transitions of the PSMALi ionomer system is not changed by the addition of the LiCl salts.

Now, let us look at the E'_{ionic} data in Table I again. As mentioned before, E'_{ionic} increases with salt contents. Because the modulus value of the material increases upon the addition of the filler,[26] the increase in E'_{ionic} with the addition of inorganic salts might be due to a filler effect of the salts. Thus, to interpret the data on the basis of a filler concept, the salt molecules are thought to form phase-separated domains that act as filler particles. Figure 4 shows the E'_{ionic} data versus the weight percentage of LiCl and CsCl salts in ionomer samples. In the same figure, the rubbery modulus ($E'_{rubbery}$) values of polystyrene (PS) homopolymers containing comparable amounts of LiCl and CsCl salts are also shown. Interestingly, E'_{ionic} increases with the salt contents, and the increasing rates of E'_{ionic} seem to be independent of the types of salts. Because the PS homo-

polymer is not an ionic material, the majority of inorganic salts in the PS homopolymer can be assumed to be phase-separated, acting as a filler. The increasing rates of the modulus as a function of the amount of salt can be obtained from the fitting of the E'_{ionic} and $E'_{rubbery}$ data with a first-order polynomial, and the equations are as follows (r^2 is the linear least-squares correlation coefficient):

$$\log E'_{ionic}(\text{Pa}) = 7.5 + 0.011$$
$$\times (\text{wt \% of salts in the ionomer})(r^2 = 0.9643)$$

$$\log E'_{rubbery}(\text{Pa}) = 5.9 + 0.014$$
$$\times (\text{wt \% of salts in PS})(r^2 = 0.9919)$$

It is clear that the increasing rate of E'_{ionic} is smaller than that of $E'_{rubbery}$, and this indicates that the filler effect becomes more effective for increasing $E'_{rubbery}$ of the homopolymer than for increasing E'_{ionic} of the ionomer. This suggests that when a small amount of inorganic salt is added to the PSMA ionomer, the inorganic salt molecules in the ionomer system act not only as a filler but also as a plasticizer, in contrast to those in the PS system, in which the inorganic salts probably act only as fillers.

One of the equations known earlier for the calculation of Young's modulus as a function of the concentration of the filler was set up by Guth[27]: $E* = E(1 + 2.5V_f + 14.1V_f^2)$. Here, $E*$ is Young's modulus of the filled material, E is Young's modulus of the material without a filler, and V_f is the volume fraction of the filler. For spherical particles, the Guth equation is applicable up to $V_f \approx 0.3$. In this study, one can take
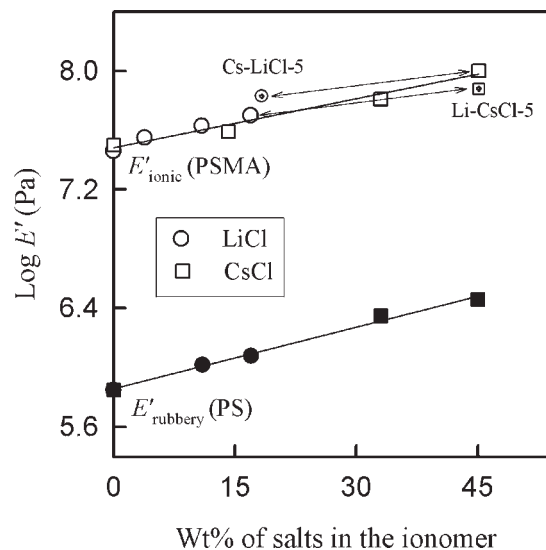

Figure 4 E'_{ionic} of the inorganic salt containing PSMA ionomers and $E'_{rubbery}$ of the inorganic salt containing PS homopolymers as a function of the weight percentage of the salts in the samples (measured at 1 Hz).

E'_{ionic} of the ionomer-containing salts as E^*; E'_{ionic} of the unblended ionomer as E, and the volume fraction of salts as V_f. At this point, it should be mentioned that to calculate the volume percentage of the salts, the densities of the salts (2.07 g/cm^3 for LiCl and 3.99 g/cm^3 for CsCl), PS (1.036 g/cm^3), and poly(styrene-*co*-sodium methacrylate (PSMANa) ionomer (1.086 g/cm^3) were used.[28,29] $E'_{rubbery}$ of PS homopolymers containing salts can also be treated in the same manner. Figure 5 shows the experimental data points and the Guth equation. It is seen that, with increasing salt contents, E^*/E of E'_{ionic} increases. The figure also shows gradual deviations between the experimental data of E'_{ionic} and the values calculated with the Guth equation. This implies that the inorganic salts in the ionomers form phase-separated domains of various sizes and shapes rather than spherical filler particles. We also attempted to fit the data points with a modified Guth equation. To do so, the second term was varied, the first term of 2.5 being kept constant. The modified equation for E'_{ionic}, $E^*/E = 1 + 2.5V_f + 48.1V_f{}^2$ ($r^2 = 0.9622$), is also shown in Figure 5 as the short-dash line. In the figure, E^*/E of $E'_{rubbery}$ of the PS containing inorganic salts is also shown. At a comparable volume percentage of the salts, E^*/E for $E'_{rubbery}$ is higher than that for E'_{ionic}. Again, this indicates that in the ionomers some of the salts act as plasticizers, and, so the molar percentage of the salts forming phase-separated filler particles is lower than that in the non-ionic PS homopolymer.
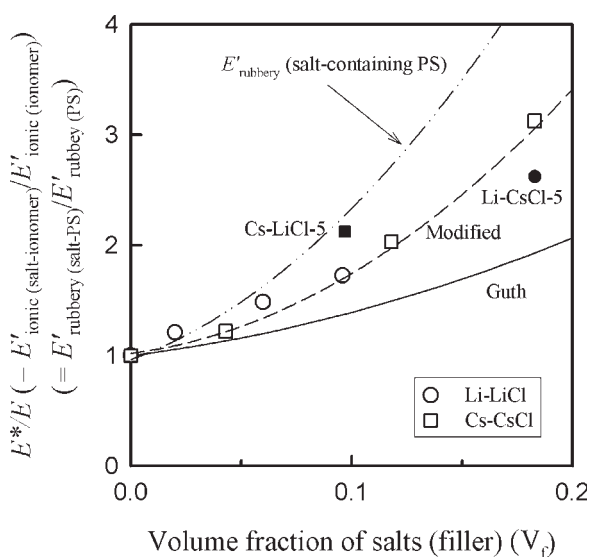

Figure 5 Ratios of E'_{ionic} and $E'_{rubbery}$ versus the volume fraction of salts in the ionomers and PS homopolymers, respectively. The solid line represents the Guth equation, and the medium-dash line shows the modified Guth equation. The dot–dash line is for the ratios of $E'_{rubbery}$ of PS containing salts.
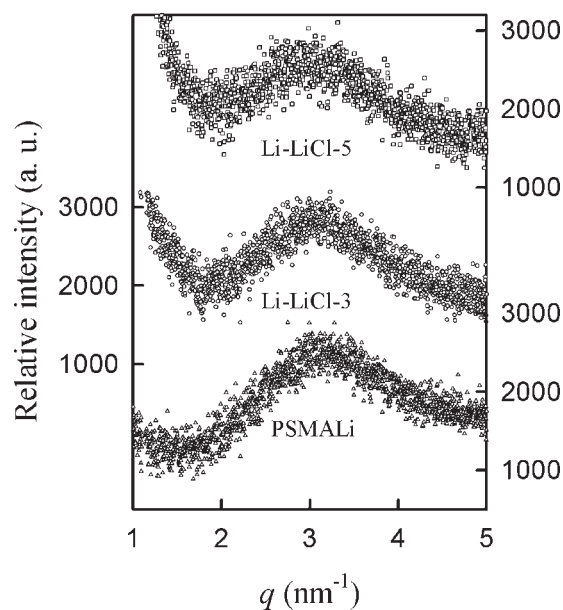

Figure 6 SAXS profiles for the PSMALi ionomer and ionomers containing various amounts of LiCl salts.

In Figure 6, the SAXS peaks for the PSMALi, Li-LiCl-1, and Li-LiCl-5 ionomers can be seen at q (scattering vector) ≈ 3.0 nm^{-1}. From the q value for the PSMALi ionomer, one can calculate the Bragg distance between scattering centers, that is, multiplets, which is about 21 Å and similar to the Bragg distance obtained in other studies for PSMA ionomers.[3,12,13] With increasing salt contents, the SAXS peak shifts to slightly lower angles, and so the Bragg distance becomes slightly larger. From this result, it can be speculated that, as mentioned before, some of the inorganic salts reside in the multiplets with ionic groups of the ionomer, which enlarges the size of the multiplets. This, in turn, would increase the distance between multiplets. At this point, it should be mentioned that if the multiplets contain the same number of ionic groups and increase their size, the contact surface area of the multiplet occupied by one anionic group should increase. Therefore, the degree of restriction in the mobility of the chains surrounding multiplets decreases with the increasing size of the multiplets. As a result, the salts in the multiplets may act as plasticizers for cluster regions, resulting in the decrease in $T_{g,c}$. The Cs ionomer system shows similar results (not shown here).

In addition to the dynamic mechanical thermal analysis and SAXS experiments, we also performed XRD measurements to investigate the possible formation of phase-separated regions consisting of salts and acting as fillers. The XRD patterns for the PSMA ionomers and PS homopolymers containing LiCl and CsCl salts are shown in Figure 7. In the figure, there is a diffraction peak due to the presence of crystalline regions of the CsCl-containing PS and PSMA
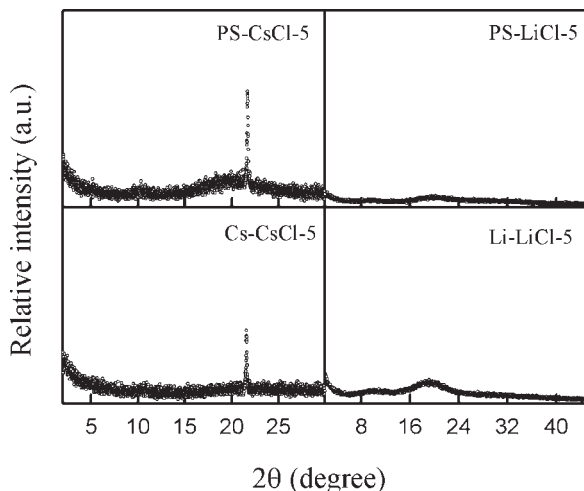
Figure 7 XRD patterns for the salt-containing PSMA ionomers and PS homopolymers.

ionomer samples at $2\theta \approx 21.5°$, which are due to a (100) plane diffraction of CsCl.[30] In addition, the peak intensity of the salt in PS is somewhat higher than that of the salt in the Cs-CsCl-5 ionomer. This indicates that some of the salts in the ionomers are phase-separated and form crystalline regions, and the rest of the salts reside in the multiplets with the ionic groups of ionomers, acting as plasticizers for the cluster regions. In the case of pure LiCl, the salt shows XRD peaks at 2θ values of approximately 23, 30, 33 (highest intensity), and 35° (not shown here). However, the LiCl-containing PS and Li-LiCl-5 ionomer do not show a peak in the range of $2\theta = 2$–45°. This indicates that, unlike the CsCl salt, the LiCl salt molecules do not form phase-separated crystalline domains, the presence of which can be detected by the XRD method. At this point, we do not have any clear explanation for the difference in XRD results in the LiCl- and CsCl-containing polymer materials. However, it should be noted that the weight percentage of LiCl in the Li-LiCl-5 ionomer is lower than that of CsCl in the Cs-CsCl-5 ionomer (i.e., 17 vs 45 wt %). In addition, because the plasticization effect of LiCl on decreasing $T_{g,c}$ is found to be stronger than that of CsCl, the ratio of the salt molecules acting as fillers to those behaving as plasticizers might be lower for the LiCl salt than for the CsCl salt. If this were applicable here, the XRD peak intensity of the LiCl salt should decrease, at least to some extent. Also, it should be recalled that to dissolve the CsCl salt in a benzene/methanol mixture completely, we had to add a small amount of water to the solution. This suggests that some of the CsCl salt may not be dissolved completely in the mixed solvent. Then, there might be (sub)micrometer-sized crystallites of CsCl in the materials, which act as fillers and show an XRD peak. In the case of LiCl salt, the salt, well dissolved in a mixed solvent without water, might

be well distributed in the polymer matrix. If the sizes of the well-distributed particles are very small, the salt in the polymer matrix might not show a well-developed XRD peak.

At last, it would be interesting to compare the results obtained from the samples of PSMALi (or PSMACs) ionomers containing CsCl (or LiCl) salts, that is, Li-CsCl (or Cs-LiCl), to those obtained from the Li-LiCl (or Cs-CsCl) sample. Shown in Figure 8 are the E' and loss tangent values of the ionomers containing LiCl and CsCl salts as a function of temperature. When the LiCl and CsCl salts are added to the PSMALi ionomer, $T_{g,m}$ and $T_{g,c}$ of the unblended ionomer decrease. It is also found that the types of cations do not affect the decreasing rates of the T_g's significantly. In the case of the PSMACs system, however, different trends are observed. When the LiCl salt is added to the PSMACs ionomer, $T_{g,c}$ increases significantly by about 40°C, and this means that the LiCl salts act not as plasticizers but as antiplasticizers. It can also be seen that the addition of either LiCl salts or CsCl salts to the PSMALi ionomers increases E'_{ionic} and that the types of cations seem to change E'_{ionic} marginally. These results imply that once the PSMAA copolymer is neutralized with LiOH, the interactions between Li^+/ $-COO^-$ ionic groups are strong enough to hold the ionic groups in the multiplet tight, and so the Li^+ cations cannot be replaced with the Cs^+ cations; some of the excess amounts of LiCl and CsCl salts reside in multiplets, acting as plasticizers. Thus, the Li-CsCl-5 ionomer shows a $T_{g,c}$ value similar to $T_{g,c}$ of the Li-LiCl ionomers and a higher E'_{ionic} value because of the filler behavior of phase-separated CsCl salts. On the other hand, the strength of interactions between Cs^+/$-COO^-$ ionic groups are not strong enough to hold the ion pairs tight because of
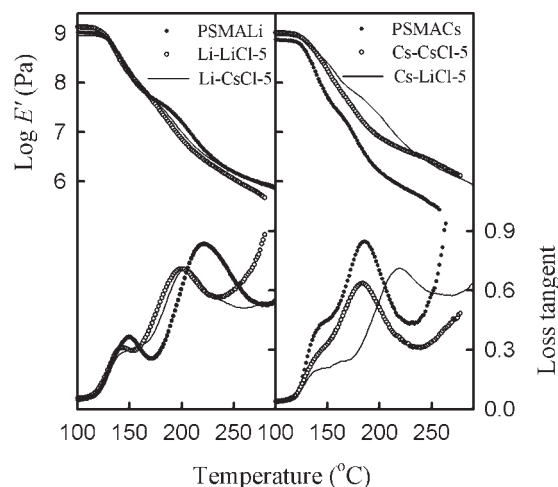

Figure 8 E' and loss tangent values as a function of temperature for PSMALi and PSMACs ionomers and ionomers containing LiCl and CsCl salts (measured at 1 Hz).

the large size of the Cs^+ cation compared to Li^+ cation. Thus, upon the addition of LiCl salts to the Cs ionomer, the cation-exchange process for $Cs^+ \leftrightarrow Li^+$ can take place. This process converts PSMACs to the PSMALi ionomer gradually, and the CsCl salts start to form phase-separated domains, behaving like fillers. Thus, the Cs-LiCl-5 ionomer shows a high $T_{g,c}$, closer to that of the PSMALi ionomer, and the phase-separated CsCl and LiCl salt domains act as fillers, increasing E'_{ionic}, which is between the E'_{ionic} values of CsCl- and LiCl-containing ionomers.

CONCLUSIONS

E'_{ionic} of ionomers containing inorganic salts was found to increase with the amount of the salts. This suggests that the inorganic salts act as fillers. However, it was also observed that the types of salts did not affect the increasing rates of E'_{ionic}. The addition of the inorganic salts to the ionomers changed the $T_{g,m}$ values of the ionomers only slightly but reduced $T_{g,c}$ strongly and slowly for the LiCl- and CsCl-containing ionomers, respectively. SAXS suggested that some of the inorganic salts might reside in the multiplet with the ionic groups of the ionomers, acting as plasticizers. The XRD investigation of the ionomers containing a relatively large amount of CsCl indicated that the CsCl salts were phase-separated in the polymer matrix.

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