

Dynamic mechanical properties and morphology of sulfonated polystyrene ionomers neutralized with mixtures of various cations

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Summary

The effects of the addition of mixed cations to the acid form sulfonated styrene copolymers on their mechanical properties and morphology were investigated. It was found that the matrix T_g does not change with the type of cations. However, the cluster T_g , ionic moduli, and the position of the SAXS peak were affected by the type of cations. The decreasing trends of cluster T_g with increasing the amount of cesium and zinc cations in Na/Cs, Ba/ Cs, and Ba/Zn mixtures, were explained on the basis of the considerations of the size, charge, and type of cations, which alter the degree of clustering as well as ion-hopping mechanism.

Introduction

The ionic interactions between ionic groups in relatively non-polar polymer matrix are known to exhibit significant effects on the properties and morphology of the polymers [1-4]. According to the multiplet/cluster model [5] for random amorphous ionomers, i.e. polymers containing a small amount of ionic groups along the polymer backbone chain, ionic aggregates, i.e. multiplets [6], restrict the mobility of polymer chain segments surrounding them. When ion content increases, the number of multiplet increases. As a result, the size of restricted mobility regions also increases, and the regions start to overlap. At a certain ion content, the reduced mobility regions become large enough to have their own glass transition. The regions are now called clusters [5]. At this point, the ionomer starts to exhibit two glass transitions (T_g s); the T_g at low temperature is due to the matrix (i.e. ion-poor regions) glass transition, while the T_g at high temperature to the cluster (i.e. ion-rich regions) glass transition. Other models have also been proposed to explain the ionomer morphology [7,8].

It has been widely known that, in ionomers having the same polymer matrix, various factors including the size, oxidation state, position and type of ionic groups affect the cluster T_g of ionomers significantly [3,4]. For example, Lefelar and Weiss observed that the “ionic” modulus due to the presence of ionic groups extended to ca. 230 °C for the Zn^{2+} -neutralized sulfonated polystyrene (Zn^{2+} -SPS) ionomer, but for the Na^+ -SPS ionomer it started to drop at lower temperature [9]. In addition, Hara et al. found that the modulus started to drop at ca. 180 °C and 240 °C for the Cs^+ -SPS and K^+ -SPS

ionomers, respectively, and that the Ca^{2+} -SPS ionomer did not show a significant drop in the modulus up to 300 °C [10]. However, the effect of the mixture of cations on the ionomer properties has been left largely unexplored. Thus, in the present work we prepared SPS ionomers neutralized with mixtures of various cations, i.e. Na^+ , Cs^+ , Ba^{2+} , and Zn^{2+} , and investigated their dynamic mechanical properties. In addition, their morphology was also studied by using a small-angle x-ray scattering technique. At this point, it should be mentioned that the above four cations were used because the first two cations are mono-valent cations and alkali metal elements. The third cation is divalent and an alkali-earth metal element; the last is also divalent but a *d*-block transition metal element. In addition to that, we also considered the ionic radii of the four cations; the radii of Na^+ , Cs^+ , Ba^{2+} , and Zn^{2+} cations are ca. 1.1, 1.8, 1.5, and 0.7 Å, respectively [11]. With the results obtained from this study, one is able to deepen one's understanding on the relationship between the type of cations, mechanical properties, and morphology of styrene-based ionomers.

Experimental section

Sample preparation

Polystyrene ($M_w = \text{ca. } 500,000$) was prepared by bulk free-radical polymerization using benzoyl peroxide as the initiator. For homogeneous sulfonation, the method developed by Makowski et al. [12] was used to obtain the poly(styrene-*co*-styrenesulfonic acid) samples. To determine the acid content, the samples were dissolved in a benzene/methanol (9/1 v/v) mixture to make a 5 % (w/v) solution, and titrated with standard methanolic NaOH to the phenolphthalein end point; the acid contents were found to be 5.1 and 4.9 mol%. For both sulfonated polystyrene copolymers, neutralization of the acid groups was performed by the addition of predetermined quantity of methanolic base solution to a 5% (w/v) acid copolymer solution in a benzene/methanol (9/1 v/v) mixture. The bases used to neutralize the acid groups were NaOH, CsOH, $\text{Ba}(\text{OH})_2$, and $\text{Zn}(\text{CH}_3\text{CO}_2)_2$. The pairs of two bases were prepared by mixing them in methanol. The ratios of the two bases were changed to neutralize 0, 30, 50, 70, and 100 % of the acid groups with the one of the two bases. Needless to say, the rest of the acid groups were naturally neutralized with the other base. The solutions were freeze-dried and then dried further under vacuum at 130 °C for 24 h. For the dynamic mechanical experiments, the ionomer samples containing 5.1 mol% of ionic groups were compression-molded at 250 °C under the pressure of 25 MPa. The sample was removed from the mold and annealed under vacuum at 130 °C for 1 day. The dimensions of the molded sample were ca. $2.5 \times 7.0 \times 30$ mm. For the small-angle X-ray experiments, the samples containing 4.9 mol% of ionic groups were also compression-molded. The molded samples in the form of a thin disk have dimensions of ca. 10 mm (diameter) \times 1.0 mm (thickness).

Dynamic mechanical property measurements

A Polymer Laboratories dynamic mechanical thermal analyzer (DMTA, model Mark II) was used for dynamic mechanical property measurements. The experiments were carried out in a dual cantilever bending mode at 5 different frequencies (0.3, 1, 3, 10, and 30 Hz). Storage (E') and loss moduli (E'') values against temperature were

obtained at a heating rate of 1 °C/min. Activation energy values for matrix and cluster T_g s were calculated using an Arrhenius plot of $\log(\text{frequency})$ vs. inverse temperature of the loss modulus curve maximum.

Small-angle x-ray scattering

The small-angle x-ray scattering (SAXS) experiments for the ionomers were conducted at station 4C1 of the PLS synchrotron radiation source (Pohang, Korea). The generated beam energy was 2.8 keV (at 2.5 GeV operation mode). The size of the beam at the sample was smaller than 1 mm². 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. 0.4 to 5 nm⁻¹, where $q = 4\pi\sin\theta/\lambda$, θ is half the scattering angle and λ is the x-ray wavelength. The SAXS data were plotted as relative intensity vs. q after correction for sample absorption and background (The SAXS profile of air was subtracted from that of ionomer samples).

Results and discussion

Figure 1 shows the storage (E') and loss moduli (E'') of the SPS ionomers containing mixtures of sodium and cesium cations. With increasing temperature, the storage modulus curves show a glassy modulus, a modulus drop due to a matrix T_g , a relatively long “ionic” modulus, a relatively slow drop of the modulus due to a cluster T_g , and a very short rubbery modulus, immediately followed by sample flow. It is also observed that with changing the ratio of two cations, the modulus values above the matrix T_g change noticeably. Ionomers containing Ba/Cs and Ba/Zn cations show similar trends (not shown here).

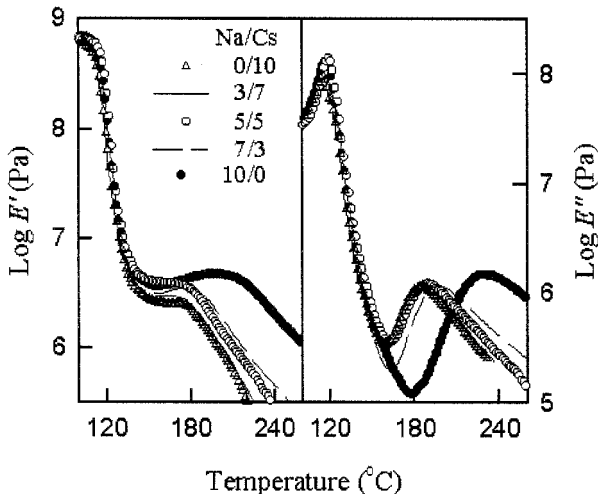


Figure 1. Storage (E') and loss moduli (E'') of the SPS ionomers neutralized with the mixture of Na and Cs cations as a function of temperature, measured at 1 Hz.

As was mentioned before, the presence of ionic aggregates influences the mechanical properties of polymer significantly [1-4]. One of the interesting effects is the appearance of the ionic storage modulus, i.e. the modulus value between the matrix and cluster T_g s [3-5]. Figure 2 shows the ionic storage modulus as a function of the ratio of acid groups neutralized with two different cations. It is seen that for the Na/Cs system the ionic modulus value decreases slightly with increasing Cs⁺ cation content.

However, in the cases of the ionomers containing divalent cations, the maxima in the ionic modulus value are observed. That is, in the cases of the Ba/Cs and Ba/Zn ionomer systems, the ionic modulus increases and then decreases again with increasing the amount of Cs^+ and Zn^{2+} cations, respectively. The ratios of the acid groups neutralized with two cations for the maximum of the ionic modulus are 7/3 and 5/5 for the Ba/Cs and Ba/Zn ionomers, respectively. At this point, it should be pointed out that even though the ionic modulus value changes with the type of cations, the change in the ionic modulus value is not so significant. This implies that the degree of clustering changes slightly with changing the type of cations.

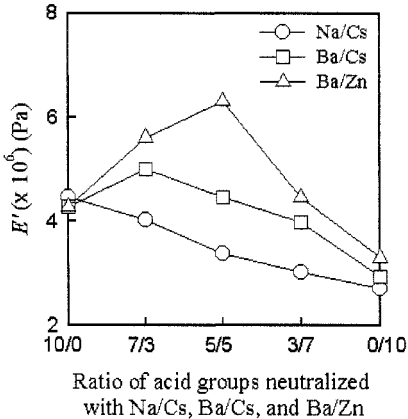


Figure 2. Ionic moduli of the SPS ionomers neutralized with mixtures of two cations of Na/Cs, Ba/Cs, and Ba/Zn, as a function of the ratio of acid groups neutralized with the two different cations, measured at 1 Hz.

Figure 1 also shows the loss modulus (E'') curves for the Na/Cs ionomers as a function of temperature. Two loss modulus peaks are seen for each ionomer sample; one at low temperature is due to the glass transition of the matrix phase, and the other at high temperature is ascribed to the glass transition of the clustered phase [3-5,13,14]. The figure shows that the position of the matrix loss modulus peak does not change much with the ratio of two cations, while that of the cluster loss modulus peak changes significantly. Shown in Figure 3 are the matrix and cluster T_g s of the ionomers as a function of the ratios of acid groups neutralized with two different cations.

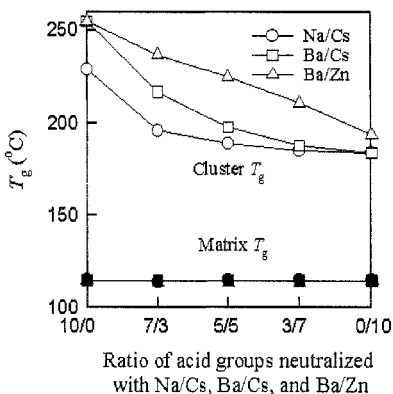


Figure 3. Cluster and matrix glass transition temperatures, obtained from two loss modulus peak maxima of the SPS ionomers neutralized with two different cations, measured at 1 Hz, as a function of the ratio of acid groups neutralized with the mixtures of two cations.

Again, it is clear that the matrix T_g s at ca. 115 °C does not change with the type of neutralizing agents. This implies that the type of cations does not change the nature of

the matrix regions. It is also seen that with increasing the amount of Cs^+ and Zn^{2+} cations, the cluster T_g of the ionomers decreases. In the cases of Na/Cs and Ba/Cs systems, the cluster T_g decreases initially drastically when the Cs^+ cations were added, and then decreases more slowly. However, in the case of the ionomers containing two divalent cations, i.e. Ba/Zn system, the cluster T_g decreases rather linearly with decreasing Ba^{2+} cation content.

At this point, it should be mentioned that the above findings, i.e. the same matrix T_g s and the different cluster T_g s, are naturally reflected in the relaxation mechanisms for glass transitions. One of the methods, which allow us to understand the relaxation behavior of the polymer chains in two different environments, is to investigate the activation energies for the glass transitions. Figure 4 shows the activation energies for the glass transitions of the matrix and cluster regions as a function of the ratio of acid groups neutralized with two different cations. As expected, the activation energies for the matrix T_g remain constant at ca. 550 kJ/mol. However, the activation energies for the cluster T_g change with the type of cations. This implies that the mixtures of two different cations affect ion-hopping mechanism, which is one of the main mechanisms for the cluster glass transitions [3,4,15-22]. Here, the ion-hopping is the migration of ion pairs attached to a particular chain segment from one multiplet to another multiplet as a result of sufficient thermal energy in order to reduce the stress on the polymer chains.

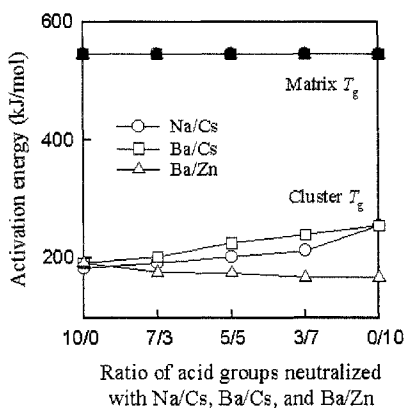


Figure 4. Apparent activation energies for the matrix and cluster glass transitions of the SPS ionomers neutralized with mixtures of two different cations, as a function of the ratio of acid groups neutralized with the two cations.

The small-angle x-ray scattering (SAXS) results for the Na/Cs ionomers are shown in Figure 5. In the figure all the samples show a profound SAXS peak at $q = \text{ca. } 1.8 \text{ nm}^{-1}$ and a significant upturn in a small q range. A small-angle upturn is prominent, but, at this point, we are not able to interpret the upturn data because there is some controversy in the interpretation of the upturn [23-27]. In the figure, it is seen that the intensity of the SAXS peak increases with increasing the ratio of Cs^+ cation in Na/Cs, and this is due to the fact that the electron density of the Cs^+ cation is higher than that of the Na^+ cation. In addition, it should be mentioned that the position of the SAXS peak shifts to slightly lower angle with increasing Cs^+ cation content. The SAXS profiles for the Ba/Cs and Ba/Zn ionomers (not shown here) are shown to be similar to those for the Na/Cs ionomers, and the Bragg distances calculated from the angle for the SAXS peak maximum are shown in Figure 6. The Bragg spacing increases slightly with increasing the amount of Cs^+ cation in Na/Cs ionomers. However, in the cases of the ionomers neutralized with divalent cations, their morphology changes with the

type of cations. For example, for the Ba/Cs ionomers, the Bragg distance increases, that is, the number of multiplets decreases with increasing Cs^+ cation content. For the Ba/Zn ionomers, even though the oxidation states of the Zn^{2+} and Ba^{2+} cations are the same as +2, the number of multiplets decreases initially (meaning the increase in the Bragg distance) and then increases when the content of the Zn^{2+} cation becomes dominant, compared to that of Ba^{2+} cation. However, at this point, it should be mentioned that the neutralization of the acid groups with zinc acetate does not always achieve 100% neutralization, since not all of the zinc acetate molecules dissociate to produce Zn^{2+} cations. Some of the zinc acetate molecules dissociate to be $\text{Zn}(\text{CH}_3\text{COO})^+$ monovalent cations and CH_3COO^- anions. This also affects the mechanical properties of the Ba/Zn system. In fact, it was found that in the present study, when the pre-calculated amount of zinc acetate was added to acid copolymer solution, only ca. 90% of the acid groups were found to be ionized.

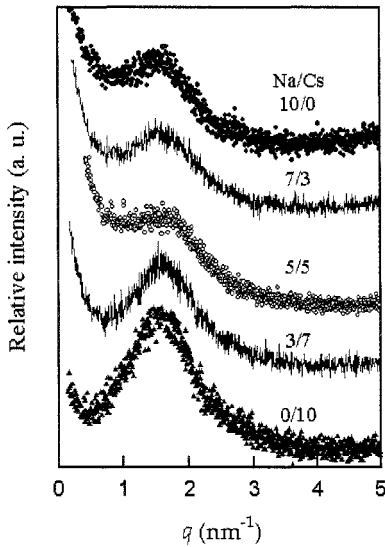


Figure 5. SAXS profiles for the ionomers neutralized with mixtures of sodium and cesium. The ratios of the ionic groups containing sodium and cesium are marked near each curve. Each curve was shifted up by the same magnitude with respect to each other for clarity.

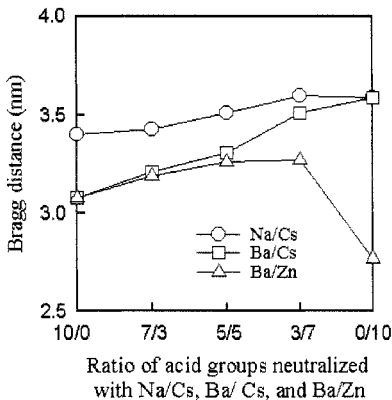


Figure 6. Bragg distances calculated from the maximum of the SAXS peak for the ionomers neutralized with the mixtures of the two different cations, as a function of the ratio of acid groups neutralized with two cations.

Form the above results, we attempt to speculate the nature of multiplets in these three

ionomer systems. In the Na/Cs ionomer system, with increasing the amount of Cs^+ cation, the Cs^+ cations replace the Na^+ cations in the multiplet, resulting in higher intensity of the SAXS peak. The replacement of the Cs^+ cations with the Na^+ cations also induces lower cluster T_g and increasing Bragg distance. This is understandable, since the size of the Cs^+ cation (radius = ca. 1.8 Å) is larger than that of Na^+ cation (radius = ca. 1.1 Å) [11]. Thus, the distance between multiplets becomes slightly longer for the multiplets containing Cs^+ cations than for those containing Na^+ cations, in the case of the numbers of ionic groups per multiplet assuming to be the same for these two ionomer systems. It should also be mentioned that, due to the larger size of the Cs^+ cation, compared to the Na^+ cation, the electrostatic interactions between the ionic groups in the multiplets become weaker for the Cs-sulfonate ionic groups than for the Na-sulfonate ionic groups. In addition, the contact surface area of one ionic group, i.e. surface area on the multiplet occupied by one ionic group, should be considered. It becomes larger for the Cs-sulfonate ionic groups than for the Na-sulfonate groups, when the multiplets contain the same number of ionic groups, since the size of the multiplet is larger for the Cs-sulfonate multiplets than for the Na-sulfonate multiplets. This results in slightly higher mobility of the polymer chains for the Cs case, which, in turn, induces slightly decreasing the degree of clustering. These two factors, i.e. the weak ionic interactions and the slightly low degree of clustering, are probably responsible for the shift of the cluster T_g to lower temperatures and the decrease in the ionic modulus with increasing Cs^+ cation amount.

Now, let us discuss the mechanical and morphological changes in the Ba/Cs system. In the case of the ionomer neutralized with Ba^{2+} cations only, the basic unit of the ionic groups consists of three ionic moieties, i.e. two sulfonate anions and one barium cation. In the case of the Cs ionomer, however, the basic unit of the ionic groups is one sulfonate anion and one cesium cation. This difference in the number of ionic species for the basic ionic unit alters the properties and morphology of the ionomers. As expected, ion hopping of two ionic species is easier than that of three ionic species, which results in the higher cluster T_g for the Ba ionomer than for the Cs ionomer. At this point, it is worth recalling that the Na-neutralized polystyrene ionomers possessing two anionic groups in an ionic repeat unit also show much higher cluster T_g than the corresponding ionomers containing only one anionic group per ionic repeat unit [28,29]. It should also be mentioned that ionomers having two ionic species as the basic ionic unit have less restriction in the formation of relatively large multiplets, compared to ionomers having three ionic species as the basic ionic unit. Thus, the size of the multiplets in the Cs ionomers would be larger than that in the Ba ionomers, which, in turn, implies that the number of the multiplets is larger for the Ba ionomers than for the Cs ionomer. This is reflected in the smaller Bragg distance for the Ba ionomers, compared to the Cs ionomers. At this point, it should be stressed that the ionic modulus is affected by the degree of clustering, which is altered by the type and size of multiplets and contact surface area, persistence length of polymer chains surrounding multiplets. Thus, in this study, the interpretation of the ionic modulus with only a single factor is not possible since the replacement of one cation with the other cation usually changes the various factors mentioned above simultaneously.

In the Ba/Zn ionomer system, the two cations used for the neutralization are divalent cations and the radius of the Ba^{2+} cation (radius = ca. 1.8 Å) is much larger than that of the Zn^{2+} cation (radius = ca. 0.7 Å) [11]. This difference in the cation size should influence the multiplet formation process, leading to difference morphology and mechanical properties. At the same time, as was mentioned before under

neutralization due to the presence of $\text{Zn}(\text{CH}_3\text{COO}^-)^+$ ionic species makes the acid groups reside in multiplets, which weaken the interactions between ionic groups and act as polar plasticizer [20,31]. In this case, the cluster T_g should decrease with increase the amount of zinc acetate added; the very large size of the $\text{Zn}(\text{CH}_3\text{COO}^-)^+$ in the multiplets also a factor for decreasing cluster T_g . This is probably what we observed in the present work.

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