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Polymer 46 (2005) 12393–12400

polymer

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Effects of compositional inhomogeneity on the mechanical properties and morphology of styrene-*co*-methacrylate random ionomer mixtures

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Received 20 July 2005; received in revised form 18 October 2005; accepted 23 October 2005
Available online 10 November 2005

Abstract

A series of poly(styrene-sodium methacrylate) SMANa ionomers of varying ion contents was synthesized, and mixtures of the ionomers were made to artificially broaden the compositional inhomogeneity of the SMANa ionomers at a constant ion content of 7.3 mol%. The mechanical properties of the unblended SMANa ionomer containing 7.3 mol% of ions and the ionomer mixtures were compared. It was found that the ionic moduli of the unblended ionomer and ionomer mixtures were very similar to each other, indicating that the mixing process did not change the degree of clustering. However, the slope of ionic plateau became steeper as the difference in the ion contents of two ionomers in the ionomer mixture increased, suggesting that the inhomogeneity of the matrix and cluster phases increased. It was also observed that the difference between the matrix and cluster T_gs increased as the divergence of the ion contents of two ionomers in the ionomer mixture became wider. In addition, it was found that when the difference of the two ion contents exceeded over 6 mol%, the ionomer mixture started to show a trace of phase-separation. At ca. 9 mol% of ion content difference, the ionomer mixture exhibited a third loss tangent peak, possibly due to the presence of the phase-separated matrix regions. The SAXS study showed that, even though the three-dimensional arrangement of multiplets in an ionomer matrix was not changed upon mixing two ionomers, the matrix phase became inhomogeneous.

Keywords: Ionomers; Bends; Compositional inhomogeneity

1. Introduction

When one introduces a small amount of ionic groups to a non-ionic polymer as pendent groups, one finds that this ion-containing polymer, i.e. an ionomer, shows two-phase behavior [1–3]. This is due to the formation of ionic aggregates, called multiplets [4]. According to the EHM model that was proposed to explain both the mechanical and morphological data of amorphous random ionomers [5], the polymer chains surrounding multiplets experience reduction in their mobility. At low ion contents, only a few multiplets exist in a matrix phase. When the ion content of the ionomer increases, the regions of reduced mobility overlap. When the dimension of the reduced mobility regions (the so-called 'clusters') exceeds over ca. 10 nm, the ionomer begins to show a second glass transition (T_g) at much higher temperatures than that of the ion-poor matrix phase. At this point, it should be mentioned that at the second T_g (i.e. cluster T_g) both the hopping of ionic groups from one multiplet to another [6–15] and the relaxation of the polymer chains in reduced mobility regions [5,6,15] are operative significantly. When the ion content increases further, the nature of the ionomer changes from a matrix-dominant material to a cluster-dominant material [5,15].

The dynamic mechanical properties of styrene-based ionomers have been investigated extensively [6,15–35]. It is now well known that two peaks are seen in the plots of loss tangent of styrene-based ionomers vs. temperature; one peak at low temperatures is due to the T_g of an ion-poor matrix phase, whereas the other peak at high temperatures is due to the T_g of an ion-rich cluster phase. As the ion content increases, the two loss tangent peaks shift to higher temperatures. In addition, with increasing ion content, the size and height of the matrix loss tangent peak decrease, whereas those of the cluster loss tangent peak increase. In the case of the storage modulus, the 'ionic' plateau (i.e. moduli in a temperature range between the matrix and cluster T_gs), related to the degree of clustering, shifts to higher values with increasing ion concentration [5,6,15,26,31].

When one wants an ionomer with a certain ion content, there must be times to wonder what would happen if one mixes two

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doi:10.1016/j.polymer.2005.10.124

ionomers of different ion contents and takes the average ion content level of the two? Could the average be treated as the same as one ion content level? They should be the same if considered only arithmetically. Yet, one cannot be sure of the possibility of mixing effects unless one actually looks into the dynamic mechanical properties of the ionomer mixtures. For instance, are the mechanical properties of a 6 mol% ionomer equivalent to those of a 50/50 blend of 3 and 9 mol% ionomers? This is a very important and practical question, which is to be answered. Therefore, in the present study, we prepared ionomer mixtures containing ca. 7 mol% of ionic groups, when averaged, and compared their dynamic mechanical data with those of a reference ionomer containing the same amount of ions. At this point, it should be mentioned that we chose the 7 mol% SMANa ionomer as the reference, on the ground that, at ca. 7 mol% of ions, the SMANa ionomer, a well clustered ionomer, shows the matrix and cluster loss tangent peaks of comparable size [15,26]. Thus, it is rather easy to detect any changes occurred in the two loss tangent peaks upon mixing two ionomers.

2. Experimental

2.1. Polymer preparation

Poly(styrene-*co*-methacrylic acid) (SMAA) (MW = ca. 300,000) random copolymers were prepared by bulk polymerization of purified styrene and methacrylic acid monomers. Detailed procedures have been described elsewhere [15,16]. In order to keep the compositional heterogeneity less than 0.1, the conversion was less than 4%. The contents of methacrylic acid were found to be 2.5, 3.7, 5.6, 7.3, 9.1, 10.3, and 11.6 mol%; we chose the 7.3 mol% ionomer as the reference ionomer. To prepare ionomer mixtures containing 7.3 mol% of ions, when averaged, two SMAA copolymers of different acid contents were dissolved in a benzene/methanol (9/1 v/v) mixture to make a 5% (w/v) solution. To neutralize the acid groups of the SMAA copolymer mixtures, a predetermined amount of methanolic NaOH was added. The solutions were freeze–dried. Subsequently, the powder form samples were dried further under vacuum at 130 °C for 24 h. The sample notations used for the unblended ionomers and ionomer mixtures are x mol% and $7.3(y+z)$ mol%, respectively, where x, y, and z are the mol percentage of sodium methacrylate units in the ionomer. The weight fractions of two ionomers in ionomer mixtures are listed in Table 1.

2.2. Mechanical property measurements

For the dynamic mechanical thermal analysis (DMTA) experiments, the unblended ionomers and ionomer mixtures were compression-molded at 250 °C and a pressure of 25 MPa. The transparent samples were removed from the mold and annealed under vacuum at 130 °C for at least 12 h. The dimensions of the molded samples were ca. 2.7×7.0×30 mm. For the mechanical property measurements, we used a Polymer Laboratories DMTA (Mark II). The experiments were carried out in a dual cantilever bending mode at frequencies of 0.3, 1, 3, 10, and 30 Hz; a heating rate was 1 °C/min. From the experiments, we obtained storage moduli (E') and loss tangents (tan δ's) as a function of temperature.

Table 1

Weight fractions and ion content differences of two ionomers, Δ(ion contents), in ionomer mixture

Ionomers (mol%)	Wt. fraction of the former polymer	Wt. fraction of the latter polymer	Δ(ion contents) (mol%)
7.3(3.7 + 10.3)	0.455	0.545	6.6
7.3(5.6 + 9.1)	0.500	0.500	3.5
7.3(3.7 + 9.1)	0.333	0.667	5.4
7.3(5.6 + 10.3)	0.638	0.362	4.7
7.3(2.5 + 11.6)	0.473	0.527	9.1
7.3(3.7 + 11.6)	0.544	0.456	7.9
7.3(5.6 + 11.6)	0.705	0.295	6.0

2.3. Small-angle X-ray scattering experiments

The small-angle X-ray scattering (SAXS) experiments for the unblended ionomers and ionomer mixtures were conducted at Station 4C1 of the PLS synchrotron radiation source (Pohang, Korea). The detailed condition for the experiments has been given elsewhere [36,37]. The wavelength of light was 0.1608 nm, and the generated beam energy was 3.1 keV (at 2.7 GeV operation mode). The two-dimensional gas-filled detector was used. The sample-to-detector distance was 150 cm, which allowed SAXS data to be obtained in a q range from ca. 0.1 to 3.5 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).

3. Results and discussion

Before the discussion on the mechanical properties of SMAA ionomer blends, it would be useful to have some idea on those of the unblended ionomers used in the present study. A series of representative storage modulus (E') and loss tangent curves for unblended SMAA ionomers of various ion contents vs. temperature is seen in Fig. 1. There are three plateaus and two transition regions. The first plateau at ca. 100 °C is described as the glassy modulus. The first transition corresponds to the glass transition of the matrix. The intermediate region, in which the modulus changes slightly with temperature, is called ‘ionic’ plateau. This region reflects ionic cross-linking. This plateau is followed by a more rapid decrease in the slope and is associated with the glass transition of the clustered regions. The last plateau at high temperatures is characterized by a gentle decrease in slope and is denoted as the rubbery plateau. With increasing ion content, the position of ionic plateau shifts to higher modulus. It is also seen that the matrix and cluster loss tangent peaks shift to higher temperatures with increasing ion content. The size of

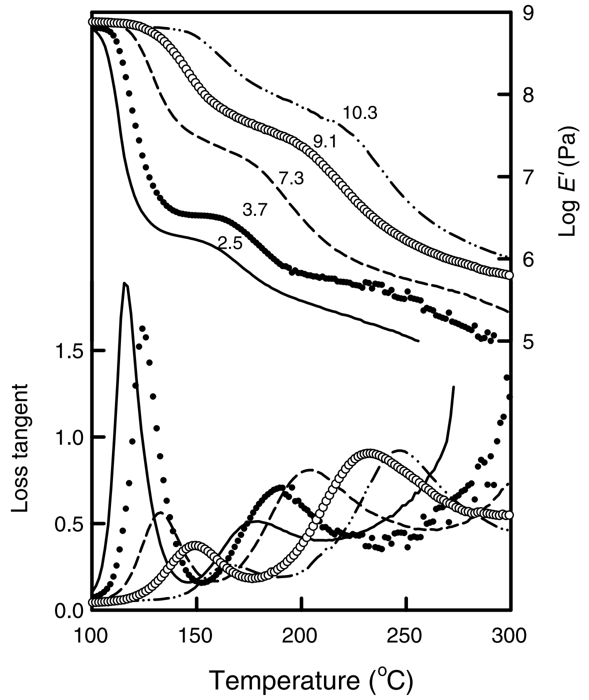

Fig. 1. Storage modulus and loss tangent data measured as a function of temperature at 1 Hz for some of SMAA ionomers with ion contents marked near each modulus plot.

the matrix peak decreases, while that of the cluster peak increases with increasing ion content.

The storage moduli and loss tangents of 3.7 and 10.3 mol% ionomers, and their ionomer mixture (i.e. 7.3(3.7 + 10.3) mol% ionomer) are shown in Fig. 2 as a function of temperature. With increasing ion content, the position of ionic plateau shifts to higher modulus. It is also seen that above ca. 120 °C the modulus curve of the 7.3(3.7 + 10.3) mol% ionomer is placed in between those of the two unblended ionomers. In addition, the slopes of the ionic plateau of the 7.3(3.7 + 10.3) mol% and 10.3 mol% ionomers are steeper than that of the 3.7 mol% ionomer. This result indicates that, with increasing ion content, the matrix and cluster regions become more inhomogeneous; this aspect will be discussed in more detail later. At this point, it should be mentioned that very weak shoulder-like features on the modulus curve of the 7.3(3.7 + 10.3) mol% ionomer are observed at ca. 140 and 200 °C. This indicates that very small phase-separated regions might exist in the 7.3(3.7 + 10.3) mol% ionomer.

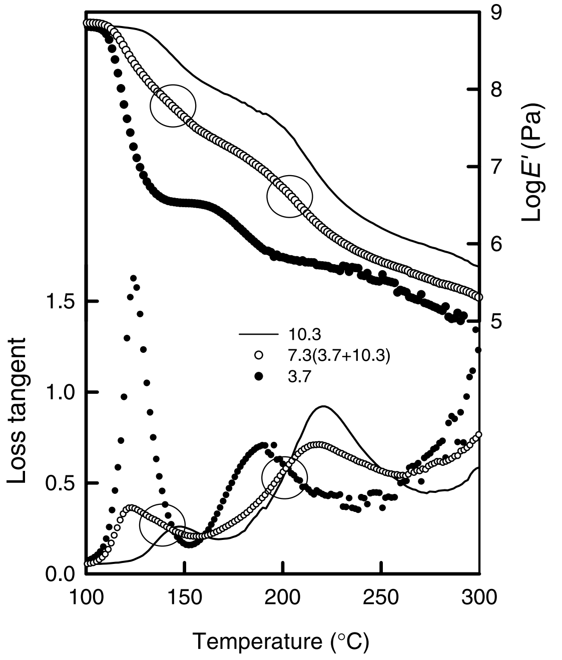

Fig. 2. Storage moduli and loss tangents of 3.7, 10.3, and 7.3(3.7 + 10.3) mol% ionomers as a function of temperature, measured at 1 Hz. Shoulder-like features are marked with round circles.

In Fig. 2, the matrix and cluster loss tangent peaks of the 3.7 and 10.3 mol% ionomers, and their ionomer mixture are also seen. Again, the sizes and positions of the peaks of the 7.3(3.7 + 10.3) ionomer lie in between those of the two unblended ionomers. However, it should be noted that the position of the matrix peak of the 7.3(3.7 + 10.3) mol% ionomer is closer to that of the 3.7 mol% ionomer than that of the 10.3 mol% ionomer. On the other hand, the position of the cluster peak of the 7.3(3.7 + 10.3) mol% ionomer is closer to that of the 10.3 mol% ionomer than that of the 3.7 mol% ionomer. This aspect will be discussed in more detail in the section dealing with the glass transition temperatures vs. ion content and ion content difference (Fig. 7). Again, the shoulder-like features on the loss tangent curve are seen at ca. 140 and 200 °C, implying the possibility of the presence of a very low degree of phase-separation in this ionomer mixture. In the case of 5.6 and 9.1 mol% ionomers, and their mixture (i.e. 7.3(5.6 + 9.1) mol% ionomer), similar trends seen in Fig. 2 are also observed (not shown here) except that the differences in the storage moduli and the loss tangent peaks are relatively small. However, the shoulder-like features found in the 7.3(3.7 + 10.3) mol% ionomer are not observed in this 7.3(5.6 + 9.1) mol% ionomer. This might be due to the fact that the difference in ion contents [⊿(ion contents)] is only 3.5 mol% for the 7.3(5.6 + 9.1) mol% ionomer, compared to 6.6 mol% for the 7.3(3.7 + 10.3) mol% ionomer.

Fig. 3 shows the storage moduli and loss tangents of the unblended 7.3 mol% ionomer and various ionomer mixtures as a function of temperature; again, all the ionomers contain the same amount of ionic groups (i.e. 7.3 mol% of ions). It is seen that storage modulus and loss tangent curves for the 7.3, 7.3(3.7 + 10.3), and 7.3(5.6 + 9.1) mol% ionomers look similar to each other; the detailed analysis of the data is given later. For the sake of completeness, we prepared two different series of ionomer mixtures. Since the weight fractions of the two ionomers in the ionomer mixtures mentioned above are similar to each other, we prepared the first series of ionomer mixtures in which the weight fractions of the two ionomers are quite different; they are 7.3(3.7 + 9.1) and 7.3(5.6 + 10.3) mol% ionomers (Table 1). The storage moduli and loss tangents of these two ionomer mixtures are also shown in Fig. 3. Again, the shapes of the modulus and loss tangent curves resemble those of the unblended 7.3 mol% ionomer. Only the size

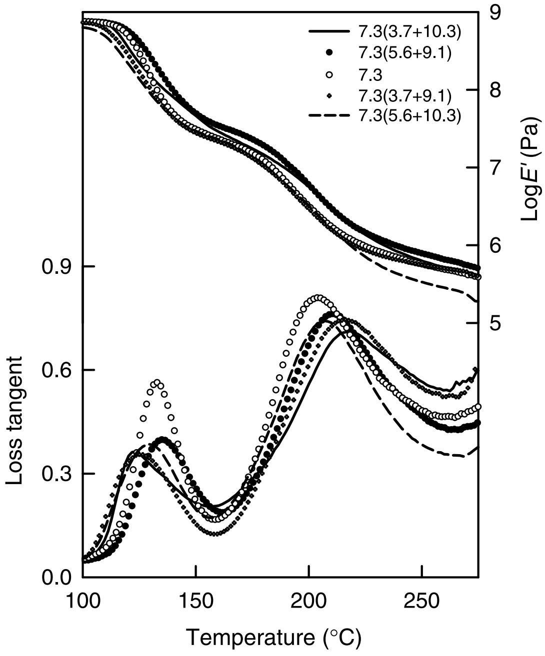

Fig. 3. Storage moduli and loss tangents of 7.3 mol% ionomer and ionomer mixtures containing 7.3 mol% of ions as a function of temperature, measured at 1 Hz.

and positions of the loss tangent peaks and rubbery plateaus are different.

The second series of ionomer mixtures includes 11.6 mol% ionomers mixed with ionomers having 2.5, 3.7, and 5.6 mol% of ionic groups. The Δ(ion contents) of the two ionomers in the ionomer mixtures increases from 6.0 to 9.1 mol% points. Fig. 4 shows the storage moduli and loss tangents of the ionomer mixtures. It is seen that when the Δ(ion contents) is 6.0 mol% (i.e. 7.3(5.6 + 11.6) mol% ionomer), only two loss tangent peaks and a relatively long, high rubbery modulus curve are seen. In the case of the 7.3(3.7 + 11.6) mol% ionomer, the Δ(ion contents) being 7.9 mol%, however, a hint of phase-separation is observed as shoulders on the loss tangent curve at ca. 140 and 180 °C. For the 7.3(2.5 + 11.6) mol% ionomer (the Δ(ion contents) = 9.1 mol%), three loss tangent peaks are seen. As expected, on one hand, the position of the loss tangent peak at ca. 115 °C (1st peak) is close to that of the matrix peak of the 2.5 mol% ionomer (not shown here). On the other hand, the position of the peak at ca. 230 °C (3rd peak) is close to that of the cluster peak of the 11.6 mol% ionomer, and the position of the peak in the middle (2nd peak) is close to that of the matrix peak of the 11.6 mol% ionomer (not shown here). Thus, it can be speculated that the first and second loss tangent peaks might be related with the glass transitions of polymer chains in phase-separated matrix regions in two different conditions.

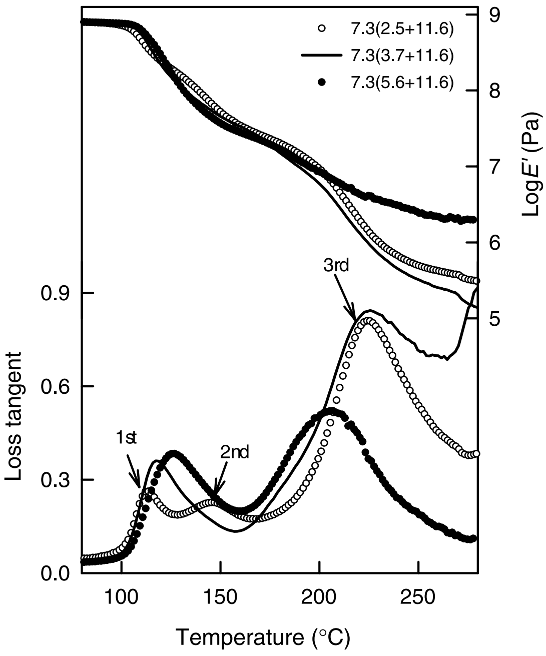

Fig. 4. Storage moduli and loss tangents of 11.6 mol% ionomers mixed with 2.5, 3.7, and 5.6 mol% ionomers as a function of temperature, measured at 1 Hz. The resulting ionomer mixtures contain 7.3 mol% of ions.

Fig. 5 shows the number of loss tangent (tan δ) peaks for all the ionomer samples studied in the present work as a function of the Δ(ion contents). It is seen that when the Δ(ion contents) is below ca. 6 mol%, the ionomer mixtures show only two loss tangent peaks. However, above 9 mol%, the ionomer mixture exhibits three loss tangent peaks, suggesting that a certain degree of phase-separation occurs in the ionomer mixture. Between 6 and 9 mol%, the ionomer mixtures show weak shoulder-like features, indicating a very low degree of phase-separation. At this point, we could not explain clearly why, at 6 mol% of Δ(ion contents), the ionomer mixture starts to show phase-separation. However, it should be noted that the 6 mol% of Δ(ion contents) coincides accidentally with the 6 mol% of ion content of the SMANa ionomer for the percolative clustering [15]. That is, at 6 mol% of ion content, the SMANa ionomer system changes its nature from a matrix-dominant system to a cluster-dominant system. In addition, at 6 mol% of ions, another discotinuities or maxima in physical

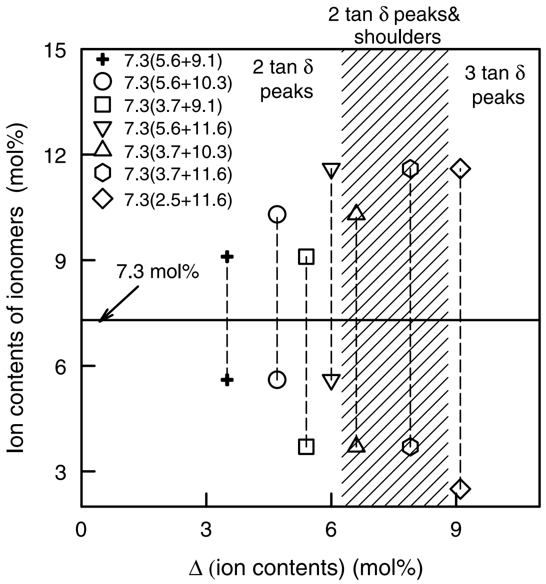

Fig. 5. Number of loss tangent (tan δ) peaks as a function of the difference in ion contents of two ionomers in an ionomer mixture.

properties have also been observed, but the discussion on this topic is beyond the scope of this paper, and, thus, the interested readers are referred to the original paper, i.e. Ref. [15].

A characteristic feature in the modulus plots is an ionic plateau, which is related with the presence of ionic groups in the ionomer, and the degree of clustering is responsible for the height of ionic plateau. For example, the increasing ion content results in the increase in the clustering. This, in turn, leads to the shift of ionic plateau to higher values. The ionic modulus can be measured as the value of storage modulus E' at the point of minimum slope of the ionic plateau. The ionic moduli of all the ionomers are illustrated in Fig. 6(a) as a function of ion content. It is seen that the ionic modulus (E'_{ionic}) of seven unblended ionomers increases with increasing ion content, and that the 7.3 mol% ionomer and all ionomer mixtures show very similar ionic moduli. This similarity in the ionic moduli implies that if the ion contents of the ionomer and ionomer mixtures, when averaged, were the same, the mixing process could not change the degree of clustering significantly. However, it is also shown that for the 7.3(2.5 + 11.6) mol% ionomer, there are two ionic plateaus, instead of one ionic plateau for the rest of the ionomer mixtures. The one at lower temperatures is probably related with the presence of the matrix regions phase-separated from the matrix regions originated from a low ion content ionomer, while the other at higher temperatures is related with the presence of cluster regions. It should be noted that the second ionic modulus value (i.e. E' between second and third T_gs) is very similar to the ionic moduli of the unblended 7.3 mol% ionomer and the rest ionomer mixtures.

If the matrix and cluster phases were relatively homogeneous, and the difference between the matrix and cluster T_gs were relatively large enough to show two well-separated T_gs, the gradient of the ionic plateau would be nearly negligible. At low ion contents, the matrix regions of the ionomer are dominant, and the cluster regions exist only as impurity. In this case, the slope of ionic plateau is very low. When an ion content increases, however, the amount of cluster regions increases, and at the same time, the size distribution of the clusters becomes wider, as well. As a result, the matrix regions as well as the cluster regions become inhomogeneous. This, in turn, leads to the ion-hopping [6–15] and the relaxation of chains in cluster regions [5,6,15], being the main mechanisms for the cluster T_g, to occur in a relatively wider range of temperature. If this were the case, the slope of the ionic plateau would become steeper with increasing ion content [15]. In Figs. 2 and 3, the ionic plateau exhibits a slightly downward slope. The slopes ($-\mathrm{d}E'_{\text{ionic}}/\mathrm{d}T$) are plotted in Fig. 6(b). It is seen that the slope of ionic plateau of the ionomer mixture becomes steeper with increasing Δ(ion contents). This can be understood. When the Δ(ion contents) increases, one of the materials becomes more matrix-dominant and the other more cluster-dominant. Therefore, the two ionomers might tend to be phase-separated and exhibit their own properties, at least to some extent. Furthermore, the increasing ion content leads to the chemical composition of one copolymer quite different from that of the other copolymer. If this copolymerization effect were operative here, the two ionomers of very different ion contents would become less miscible, even though the majority of repeat units in the copolymer is the same as styrene. In the figure, it is also seen that there is a discontinuity at ca. 6 mol% of ions in the plot of slopes vs. ion content. This is possibly due to the inversion of the nature of ionomers from a matrix-dominant material to a cluster-dominant material, occurring at ca. 6 mol% of ions for the SMANa ionomer system [5,15,26].

In Figs. 2 and 3, it is seen that the heights and positions of the matrix and cluster peaks change upon mixing two ionomers. To interpret the dynamic mechanical data more quantitatively, we performed curve deconvolutions on 1 Hz data using the Peakfit (SPSS Inc.) program. The best fits were achieved assuming an exponential background and fitting the matrix and cluster peaks with Gaussian area functions. Fig. 7(a) shows the positions of the peaks, i.e. T_gs, of unblended ionomers and ionomer mixtures as a function of ion content. It is clear that the matrix and cluster T_gs of unblended ionomers increase gradually with increasing ion content. In the case of the ionomer mixtures, the matrix and cluster T_gs deviate from those of the unblended 7.3 mol%

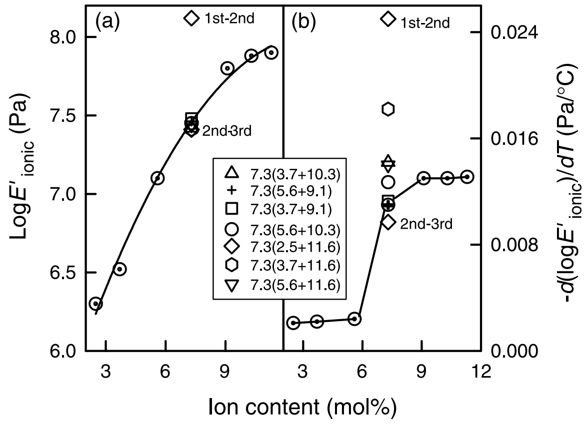

Fig. 6. (a) Ionic moduli and (b) the slopes of an ionic plateau of unblended SMANa ionomers and ionomer mixtures as a function of ion content (1 Hz data).

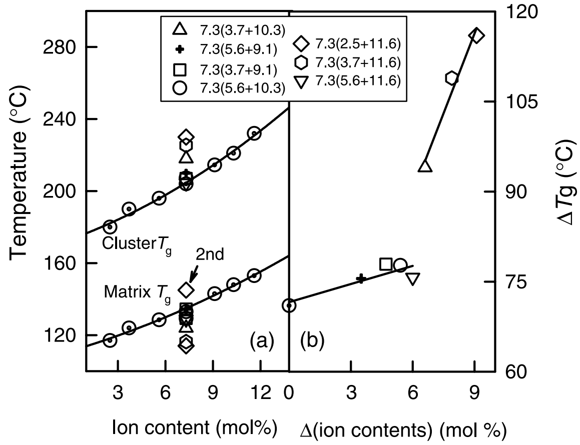

Fig. 7. (a) Glass transition temperatures of unblended SMANa ionomers of various ion contents and ionomer mixtures that contain 7.3 mol% of ions as a function of ion contents (1 Hz data) and (b) the difference in the matrix and cluster T_gs (ΔT_g) vs. the divergence in ion contents of the two ionomers in the ionomer mixture [Δ(ion contents)].

ionomer. As was mentioned before, it is seen that the cluster T_g of the ionomer mixture is closer to that of the higher ion content ionomer, compared to those of the lower ion content ionomer. On the other hand, the matrix T_g of the ionomer mixture is closer to that of the lower ion content ionomer. If one considers the temperature dependence of the ionomer properties, the above result can be interpreted as follows: on one hand, in a low temperature range, the ionomer mixture tends to behave like the ionomers of low ion contents rather than the ionomers of high ion contents. On the other hand, in a high temperature range, the ionomer mixture is apt to behave like the ionomers of high ion contents rather than the ionomers of low ion contents. Shown in Fig. 7(b) is the divergence between the two T_gs (ΔT_g) as a function of Δ(ion contents). It is seen that up to 6 mol% of Δ(ion contents) the ΔT_g increases gently; however, above that ion content, the ΔT_g increases drastically, meaning again that above 6 mol% of Δ(ion contents), the ionomer matrix phases start forming separated regions.

Now let us examine the inhomogeneities of the matrix and cluster phases. Fig. 8 shows the width at the half height of loss tangent peak as a function of ion content. Needless to say, the peak width represents the homogeneity of a phase; when the phase becomes more homogeneous, the peak width becomes narrower. At low ion contents, the glass transition of the matrix regions of the unblended ionomers takes place in a relatively narrow temperature range, and the temperature range for the glass transition (i.e. peak width) increases slowly with increasing ion content. This implies that the matrix phase becomes more inhomogeneous. In the case of the cluster peak of the unblended ionomers, the peak width decreases much slowly with increasing ion content, indicating that the cluster phase becomes more homogeneous. It is also seen that the width of the matrix peak is narrower than that of the cluster peak at a given ion content. This can be understood since the cluster phase, containing multiplets of different sizes, cannot become as homogeneous as the ion-poor matrix phase. At this point, two mechanisms for cluster T_g (i.e. a bond interchange process through ion-hopping [6–15] and a chain mobility process [5,6,15]) should be taken into account. The mobility of the chains in the cluster regions varies with the size of cluster regions, the location of the chain segments, and the type of ionic groups, etc. Therefore, the width of the cluster loss tangent peak is wider than that of the matrix peak. In the case of the ionomer mixtures, the wider widths of the matrix and cluster peaks, compared to those of the unblended ionomer, indicate that the matrix and cluster phases become more inhomogeneous as the ion content difference increases.

The total areas under the loss tangent peaks are found to remain relatively constant (not shown here), regardless of the ion contents and weight ratios of two ionomers. In the case of unblended ionomers, the cluster peak area increases, while the matrix peak area decreases with increasing ion content. At this point, it should be mentioned that the relative area of the SMANa ionomers might represent the relative amount of the materials in the matrix and cluster regions [15,26,34]. Thus, the above result suggests that with increasing ion content the nature of the material changes smoothly from matrix phase-dominant materials to cluster phase-dominant materials. In the case of the ionomer mixtures, it should be noted that the areas under the loss tangent peaks seem to remain constant even though the matrix and cluster T_gs change noticeably upon mixing (in the case of the 7.3(2.5 + 11.6) mol% ionomer, the first and second peaks were regarded as matrix peaks, while the third one as the cluster peak). This manifests itself that the total amount of clustered materials does not change significantly upon mixing two styrene-based ionomers, but that only the mechanical characteristics of the matrix and cluster phases change.

Activation energies of the matrix and cluster T_gs were calculated using an Arrhenius plot of log(frequency) vs. inverse temperature. Fig. 9 shows the apparent activation

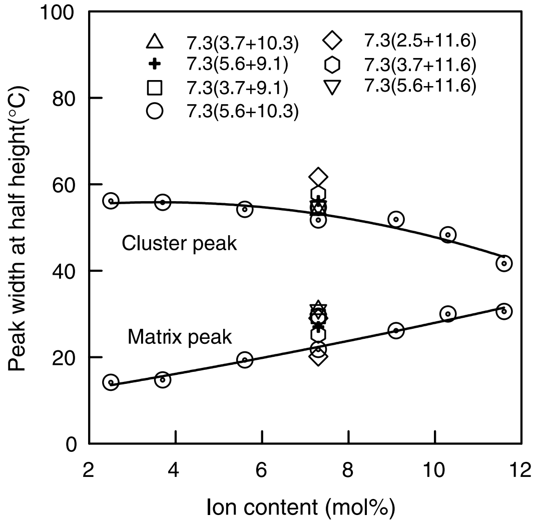

Fig. 8. Width at half height of the loss tangent peaks of unblended SMANa ionomers of various ion contents and ionomer mixtures that contain 7.3 mol% of ions as a function of ion contents as a function of ion contents, measured at 1 Hz.

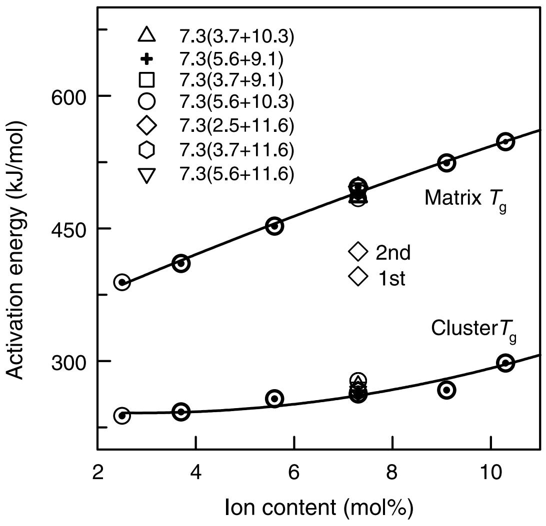

Fig. 9. Activation energies of unblended SMANa ionomers of various ion contents and ionomer mixtures that contain 7.3 mol% of ions as a function of ion contents as a function of ion contents.

energies of the glass transitions of the cluster and matrix phases vs. ion content. It is seen that with increasing ion content, the activation energy increases smoothly; this is similar to what Kim et al. observed in the study of the mechanical properties of SMANa ionomers of various ion contents [15]. It is also found that the activation energies for the matrix and cluster T_gs of the SMANa ionomer and ionomer mixtures containing 7.3 mol% of ions are similar. This implies that the main mechanisms of the matrix and cluster glass transitions do not change upon mixing. This is understandable since the materials in the matrix and cluster regions are mainly polystyrene. In addition, the phase-separation in the ionomer mixtures is relatively weak, and, thus, the activation energies for the matrix and cluster T_gs do not change significantly upon mixing two ionomers. In the case of 7.3(2.5 + 11.6) mol% ionomer, however, due to the presence of two matrix loss tangent peaks, two activation energies for the matrix T_gs were obtained. The presence of the two activation energies indicates that the mechanical responses of the two matrix regions are somewhat different from that of the rest ionomer samples. Interestingly enough, the first activation energy value for the matrix T_g of the 7.3(2.5 + 11.6) mol% ionomer is comparable to that of the 2.5 mol% ionomer, implying that the nature of the matrix regions responsible for the first T_g is similar to that of the 2.5 mol% ionomer. At this point, it is also worth noting that the activation energies of the cluster T_gs are approximately a half of those of the matrix T_gs, which is also evident in the various styrene ionomers [15,26]. This is due to the fact that the activation energies are determined not only by the glass transition temperatures of ionomers, but influenced also by a number of factors including the degree of clustering, the strength of ionic interactions, the size of multiplets, and the matrix T_g [3].

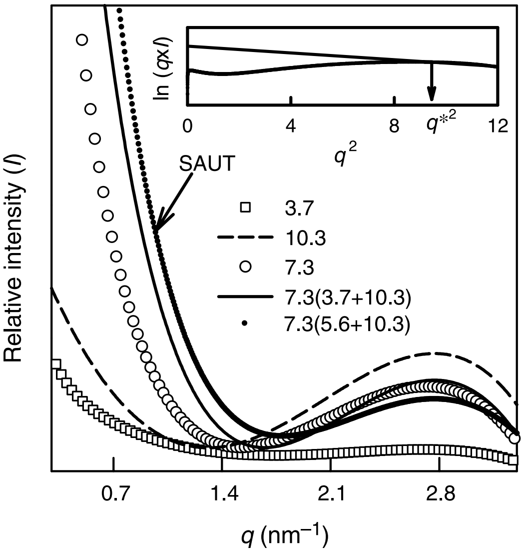

Fig. 10. SAXS data for unblended SMANa ionomers containing 3.7, 7.3, and 10.3 mol% of ions and ionomer mixtures containing 7.3 mol% of ions. The inset shows a plot of ln(Iq) vs. q^2 for the 7.3(3.7 + 10.3) mol% ionomer.

In order to investigate the morphology of this ionomer system, small-angle X-ray scattering (SAXS) experiments were performed. Fig. 10 shows the smoothed SAXS data for the unblended 7.3, 7.3(3.7 + 10.3), and 7.3(5.6 + 10.3) mol% ionomers. First of all, the small-angle upturn (SAUT) and small-angle ionomer peak are seen for all the samples. Secondly, it is observed that the SAXS peak remains more or less constant at $q_{\max}$ = ca. 2.8 nm^{-1}. This $q_{\max}$ value corresponds to the Bragg spacing (D_{Bragg}) between scattering centers of ca. 2.3 nm (Table 2), and this Bragg spacing is in good accordance with the inter-multiplet distances for the SMANa ionomers reported previously by a number of authors [5,6,15,31]. Third, as expected, the SAXS peak intensity increases with increasing ion content. The increasing intensity illustrates that the number of scattering centers at the most prevalent inter-multiplet distance increases. In Fig. 10, it is also seen that the peak intensities of 7.3 mol% ionomer and ionomer mixtures containing 7.3 mol% of ions are not much different. These results indicate that the morphology of ionomer is not altered noticeably by the mixing of two ionomers. In other words, the compositional inhomogeneity in styrene-based ionomers does not affect the three-dimensional arrangement of ionic aggregates in polymer matrix strongly. However, at this point, it is worth recalling that the majority of the SAUT would be caused by a number of factors; e.g. the compositional inhomogeneity of the ionomers, the inhomogeneous distribution of multiplets, the presence of the neutralizing cations in the matrix, the nonrandom distribution of ionic groups present singly in the matrix, and the concentration variation of metal cations in a long range [38–43]. Thus, in the present study, the increasing SAUT upon mixing two ionomers indicates that the phases of the ionomer mixtures are more inhomogeneous, compared to those of the unblended ionomers. It was also reported that the persistence length of ionenes was related to 2.87/q^*, where q^* was the angle at which the X-ray scattering data begin to deviate from the linear extrapolation line in the plot of log[scattering intensity (I)×q] vs. q^2 [44]. Therefore, we also evaluated the persistence lengths of the five ionomers and ionomer mixtures from the SAXS data. The inset in Fig. 10 shows the plot for the 7.3(3.7 + 10.3) mol% ionomer. The extrapolated line starts to deviate from the smoothed SAXS data at q^* = ca. 3.12 nm^{-1}, which corresponds to a persistence length of ca. 0.90 nm. The persistence lengths calculated from the q^* values for another ionomers are also listed in Table 2; the average persistence length is ca. 0.89 nm. These results imply again that the morphology of the ionomer mixtures does not change upon mixing two ionomers, but only the inhomogeneities of the matrix and cluster phases change.

Table 2
SAXS data for the unblended ionomers and their ionomer mixtures

Ionomers (mol%)	$q_{\max}$ (nm^{-1})	D_{Bragg} (nm)	Persistence length (nm)
3.7	2.73	2.30	0.90
7.3	2.76	2.28	0.89
10.3	2.76	2.28	0.89
7.3(3.7 + 10.3)	2.76	2.28	0.90
7.3(5.6 + 9.1)	2.77	2.27	0.88

4. Conclusions

The properties of unblended SMANa ionomer and SMANa ionomer blends, both of which contain 7.3 mol% of ions, were investigated dynamic mechanically. The ionic moduli of the SMANa ionomers and ionomer mixtures were found to be very similar to each other. This result revealed that the degree of clustering was not changed significantly upon mixing two ionomers of different ion contents. The gradient of the ionic plateau increased with increasing the difference in the ion contents of two ionomers in the ionomer mixture. From this result, it was speculated that the inhomogeneity of the matrix and cluster phases increased. In the case of the loss tangent peaks, the difference in the positions of the matrix and cluster peaks became larger as the divergence of the ion contents increased. Furthermore, when the difference in the ion contents of the two SMANa ionomers exceeded over 6 mol%, the SMANa ionomer mixture started showing a hint of phase-separation, and above 9 mol% the ionomer mixture clearly exhibited two matrix T_gs as well as one cluster T_g. Thus, it was suggested that, with increasing the difference of ion contents, the inhomogeneity of the matrix phase increased, to some extent. The morphological study also indicated that upon blending the inhomogeneity of the phases increased, but the arrangement of the ionic aggregates did not change much.

Acknowledgements

This work was supported by the Korea Research Foundation (Grant number: KRF-2003-D20163). W-G. Kim would like to thank Konkuk University for a financial support (2003). The SAXS experiments at PLS were supported in part by the Ministry of Science and Technology and Pohang Steel Company.

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