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Effects of Two Ionic Groups in an Ionic Repeat Unit on the Properties of Styrene Ionomers

Joon-Seop Kim,*,† Min-Chul Hong,† and Yeon Hwa Nah‡

Department of Polymer Science & Engineering, Chosun University, 375 Seosuk-Dong, Dong-Gu, Kwangju 501-759, Korea, and Insulating Materials T/G Research Lab., LG Cable Ltd., Anyang-Shi, Kyungki-Do 431-080, Korea

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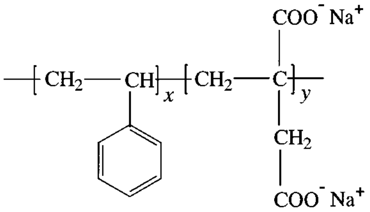
ABSTRACT: The properties of poly(styrene-*co*-itaconate) ionomers were studied dynamic mechanically. It was observed that ionic moduli increased as ion content increased and that the increased ionic modulus values were comparable to those of well-clustered polystyrene ionomers. It was also found that only a very weak cluster loss tangent peak was present and that the shoulder-like peak shifted to higher temperatures with increasing ion content. This implies that the itaconate ionomers are weakly clustered materials. Also, the cluster T_g of the itaconate ionomers was found to be much higher than that of the well-clustered poly(styrene-*co*-methacrylate) ionomers. From these results, it was postulated that in the present ionomer system the ion hopping of the ion pairs in multiplets played an important role in determining the mechanical properties of the ionomers. The SAXS study showed that as ion content increased more ionic groups formed not at the prevalent distances, but very randomly, inferring that the multiplets in the present system were not in line with those in the EHM model. In addition, it was discovered that nonpolar plasticization was effective for the formation of more clustering, while upon polar plasticization, interaction between ionic groups became weaker, and thus a more distinct cluster loss tangent peak due to ion hopping was observed at lower temperature.

1. Introduction

Ionomers are ion-containing polymers that have a relatively small amount of ionic groups along polymer backbone chains. Since their first appearance ca. 35 years ago, ionomers have been studied extensively because they exhibit unique physical properties owing to the ionic interaction.[1−10] According to the multiplet/cluster (or EHM) model[11] for random amorphous ionomers, ionic aggregates, so-called multiplets, restrict the mobility of polymer chain segments surrounding them.[11−19] When ion concentration increases, the number of multiplet increases. Consequently, the size of regions of restricted mobility also increases, and the regions start to overlap. At a certain ion content, the overlapping regions of reduced mobility become large enough to have their own glass transition; the regions are now called clusters.[11] 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 glass transition, while the T_g at high temperature to the cluster glass transition. Other models, e.g., the core−shell model[20] and the hard-sphere model,[21] have also been proposed to explain the ionomer morphology.

It has been extensively researched that in ionomers, with the same polymer matrix, such factors as the size, oxidation state, position, and type of ionic groups affect the cluster T_g of ionomers significantly.[10] Yet, the effect of the number of ion pairs in an ionic repeat unit on the ionomer properties has been left largely unexplored.[22] To fill the lacuna, in the present work we prepared poly(styrene-*co*-sodium itaconate) ionomers that have two ion pairs in the same ionic repeat unit (see Scheme 1) and investigated their properties dynamic mechanically. In addition, their morphology was studied. Furthermore, since the ionomer has two ion pairs in the same ionic unit, we attempted to compare the data obtained from this system with those of the ionomers containing a single ion pair in an ionic unit, which were probed previously by one of the authors.[23] Finally, the effect of plasticization on the dynamic mechanical properties of ionomers was investigated.

Scheme 1



2. Experimental Section

2.1. Polymer Synthesis. Poly(styrene-*co*-itaconic acid) [P(S-*co*-Ita)] samples were prepared by solution polymerization of purified styrene monomer and itaconic acid monomer dissolved in a small amount of dioxane using benzoyl peroxide as the initiator (MW = ca. 300 000). The reaction temperature was ca. 60 °C, and conversion was less than 6%, yielding a compositional heterogeneity of less than 0.1. The specific reaction conditions are listed in Table 1. The polymer samples were recovered by precipitation into a rapidly stirred excess of methanol. The precipitated polymer was filtered and dried in a vacuum oven at 120 °C for 24 h. To determine the acid concentration, acid 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 itaconic acid contents were found to be 1.4, 3.9, 5.7, 6.5, 8.2, and 10.0 mol %.

2.2. Sample Preparation. The P(S-*co*-Ita) samples were dissolved in a benzene/methanol (9/1 v/v) mixture to give a 5% (w/v) solution. To neutralize the acid groups, a predetermined quantity of methanolic NaOH was added and resulted

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† Chosun University.
‡ LG Cable Ltd.
* Corresponding author: telephone +82-62-230-7211; Fax +82-62-232-2474; e-mail joon@mail.chosun.ac.kr.

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Table 1. Polymerization Conditions and Percentage of Conversion for the P(S-*co*-Ita) Copolymers

content of ionic repeat units (mol %)	Ita in monomer feed: mol %[a]/mass (g)	benzoyl peroxide (g)	reaction time[b]	reaction temp (°C)	conv (%)
1.4	1.10/0.55	0.0373	3 h, 10 min	60	2.80
3.9	2.30/1.15	0.0369	4 h, 40 min	59	4.40
5.7	3.26/1.63	0.0365	5 h, 10 min	58	4.75
6.5	3.60/1.80	0.0364	5 h, 50 min	59	5.41
8.2	4.05/2.03	0.0362	5 h, 50 min	60	5.43
10.0	6.60/3.30	0.0356	6 h, 00 min	58	5.50

[a] Total monomer mass in all case was 50 g, and the reactivity ratios of main monomer and comonomer were 0.26 and 0.12, respectively.[24]
[b] Reaction time was calculated to obtain a conversion of ca. 3−5.5%, depending on the content of ionic repeat units.

in poly(styrene-*co*-sodium itaconate) [P(S-*co*-ItaNa)]. For the morphology study by using an X-ray scattering technique, since the Cs is more scattered than Na owing to the higher electron density of the former, methanolic CsOH was added to neutralize the acid groups. The solutions were freeze-dried and then dried further in a vacuum oven at 160 °C for 24 h.

Plasticized ionomers were obtained by dissolving fully neutralized ionomers containing 6.5 mol % of ionic repeat units in a mixed solvent of benzene/methanol (9/1 v/v) and subsequently by adding dioctyl phthalate (DOP) and glycerol (Gly) to the ionomer solution. The plasticized ionomers were then freeze-dried and further dried under vacuum at 90 °C for 24 h.

For the dynamic mechanical thermal analysis (DMTA) experiments, the P(S-*co*-ItaNa) ionomer samples were compression-molded at 250−280 °C, depending on the ion content, under the pressure of 25 MPa. The sample was removed and annealed under vacuum at 170 °C for 12 h. For the study of plasticization effect, ionomers were molded at ca. 250 °C and annealed at 90 °C for 24 h. The dimensions of the molded sample were ca. 2.7 × 7.0 × 30 mm.

For the small-angle X-ray scattering studies, the cesium-neutralized samples were compression-molded. The molded samples in the form of a thin disk with dimensions of 12 mm (diameter) × 0.5 mm (thickness) were stored under vacuum at 100 °C for 24 h.

2.3. Dynamic Mechanical Thermal Analysis (DMTA). A Polymer Laboratories DMTA Mark II was used to determine dynamic mechanical properties of ionomers. The experiments were carried out in a dual cantilever bending mode at frequencies of 0.3, 1, 3, 10, and 30 Hz. Storage moduli (E') and loss tangents (tan δ) were obtained as a function of temperature at a heating rate of 1 °C /min.

2.4. Small-Angle X-ray Scattering. The small-angle X-ray scattering experiments were conducted at Station 4C1 of the PLS synchrotron radiation source (Pohang, Korea). The type of light source was bending magnet, and the generated critical beam energy was 2.8 keV (at 2.5 GeV operation mode). The size of the beam at the sample was smaller than 1 mm^2. The position-sensitive one-dimensional Si diode-array detector was used. The sample-to-detector distance was 840 mm, which allowed SAXS data to be obtained in the q range from ca. 0.54 to 2.4 nm^{-1}, where $q = 4\pi \sin \theta/\lambda$, θ is half the scattering angle, and λ is the X-ray wavelength ($\lambda = 1.608$ Å). The SAXS data were plotted as relative intensity vs q after correction for sample absorption and background. (The SAXS profile of pure polystyrene was subtracted from that of ionomer samples.)

2.5. Thermogravimetric Analysis. For the studies of the thermal stability of the ionomer, a Polymer Laboratories thermogravimetric analyzer was utilized. The experiments were carried out over the range of 100−600 °C, at a heating rate of 10 °C/min in air.

2.6. Data Analysis. For each sample, dynamic mechanical property measurements were performed at five different frequencies; however, a detailed analysis was performed only on the 1 Hz data. Curve deconvolutions were performed on tan δ data using the PeakFitä (SPSS Inc.) program. The best fits were achieved by fitting the matrix and cluster peaks with exponentially modified Gaussian or Gaussian area equations with an exponential background. The equations for fitting are described elsewhere.[23]

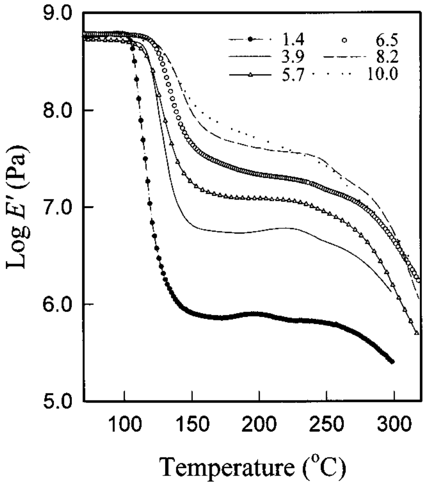

Figure 1. Storage moduli (E'), measured as a function of temperature at 1 Hz, for P(S-*co*-ItaNa) ionomers. The content of ionic repeat units is indicated for each sample.

3. Results and Discussion

Upon heating, the thermal stability of polystyrene, of P(S-*co*-Ita), and of P(S-*co*-ItaNa) ionomer containing 6.5 mol % of ionic repeat units was found to be similar; all the three samples started to show their weight loss above ca. 320 °C. Thus, in the present study, the maximum temperature of 300 °C is suitable for the dynamic mechanical measurement, considering that sample residence times are relatively short.

Shown in Figure 1 are the plots of the storage modulus curve as a function of temperature for P(S-*co*-ItaNa) ionomers. With increasing temperature, the modulus value changes from the glassy modulus, through the glass transition of the matrix phase, through the "ionic modulus", through the glass transition region of the cluster phase (200−270 °C, depending on the content of ionic repeat units), through the rubbery modulus, to the modulus for sample flow. It should be noted that even the 1.4 mol % sample shows a long ionic plateau. It is also seen that the ionic modulus increases with increasing ion content. For example, the modulus value at 200 °C increases from 7.9×10^5 Pa for the 1.4 mol % ionomer to 5.1×10^7 Pa for the 10.0 mol % ionomer. This drastic increase in the ionic modulus implies that, as expected, ionic aggregation affects the polymer modulus significantly.

In Figure 2, the "ionic" storage modulus values of P(S-*co*-ItaNa) ionomers, chosen as the modulus at the intermediate temperature of the two glass transition temperatures of the ionomers, are shown as a function of the content of ionic repeat units along with those of well-clustered poly(styrene-*co*-sodium methacrylate) [P(S-*co*-MANa)] ionomers, whose latter data were produced from a previous study by one of the authors.[23] It is clear

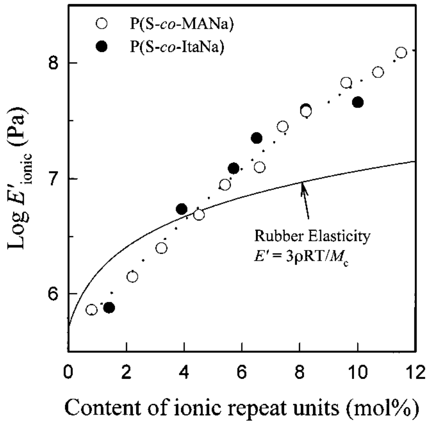

Figure 2. Log of the ionic modulus E' as a function of the content of ionic repeat units at 1 Hz for the P(S-*co*-ItaNa) and P(S-*co*-MANa) ionomers of various ion contents. The solid line represents modulus values calculated by using a rubber elasticity approach.

that the ionic modulus values of the P(S-*co*-ItaNa) ionomers are similar to those of the P(S-*co*-MANa) ionomers. This finding shall be discussed later. In the figure, one also observes that the log E' value of the two ionomer systems increases from ca. 5.7 to ca. 8.2 with increasing ion content from 0.8 to 11.5 mol %. At low ion contents, a linear relation is evident in the data, while above ca. 7 mol % a slight curvature is observed. We attempted to relate the ionic modulus values to the calculated modulus values of polymers cross-linked by the ionic groups. In doing so, we used the equation from rubbery elasticity theory, $G = \rho RT/M_c$, where G $(=E'/3)$ is the shear storage modulus, ρ the density of polystyrene, R the gas constant, T absolute temperature, and M_c the average molecular weight between cross-links.[25] In the present study, the M_c is the molecular weight of chain segments between two ionic aggregates. For the simple calculation, the ionic groups are considered to be located at a regular interval in the polymer chain, and the distance between the ionic groups is inversely related to the ion content. It should also be mentioned that for the calculation of the M_c we took into consideration the cross-links from chain entanglements in addition to those from ionic aggregates. In the figure, it is seen that up to ca. 5 mol % of ionic repeat units, the calculated values seem to be higher than the experimental data. This implies that below ca. 5 mol % of ionic repeat units all the ionic groups do not form aggregates. However, above ca. 5 mol %, the experimental data become higher than the calculated modulus values. Thus, it can be postulated that above ca. 5 mol % ion aggregation determines the mechanical properties of ionomer strongly and makes the ionomer behave like composite materials. As a result, the rubber elasticity theory is not operative here.

In Figure 3, one sees a tan δ peak at lower temperatures and a shoulder at higher temperatures, which are due to the glass transitions of the matrix and cluster phases, respectively. These aspects have been discussed elsewhere.[23,26] With increasing ion content, the tan δ peak for the matrix T_g shifts to higher temperatures, but its height decreases. As for the shoulder due to the cluster T_g, its size increases and its position also shifts to higher temperatures with increasing ion content. However, it is not easy to determine the exact temperature of the shoulder maximum.

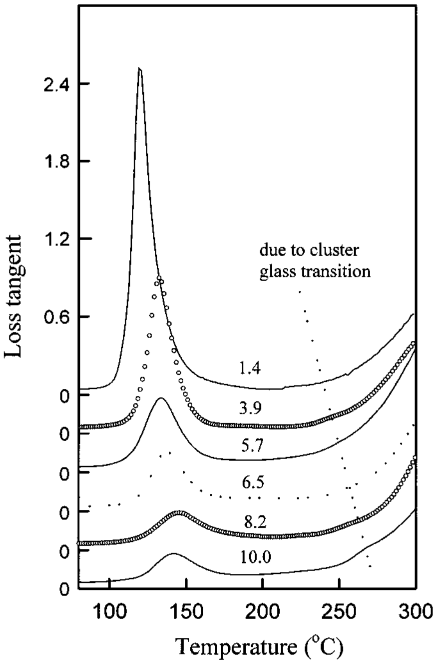

Figure 3. Loss tangent plots, measured as a function of temperature at 1 Hz, for P(S-*co*-ItaNa) ionomers. The content of ionic repeat units is indicated for each sample. Each curve is shifted up by the same magnitude with respect to each other for clarity.

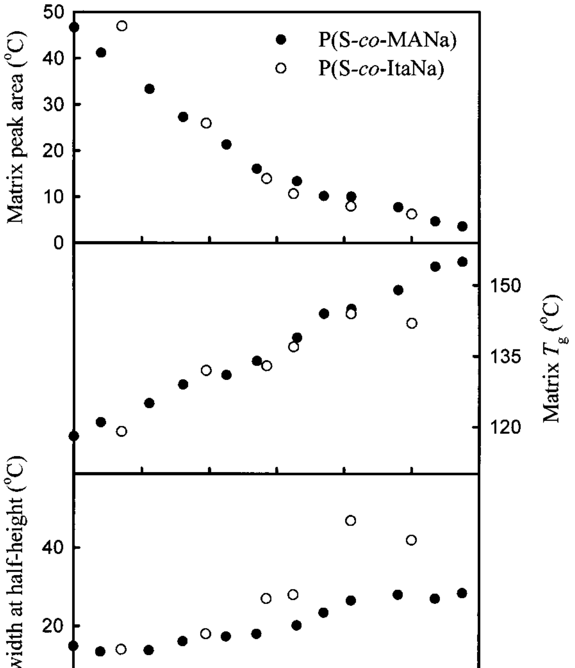

Figure 4. Area under the matrix tan δ peak, matrix T_g, and width of the peak at half-height for the P(S-*co*-ItaNa) and the P(S-*co*-MANa) ionomers as a function of the content of ionic repeat units, measured at 1 Hz.

Figure 4 shows the areas under the matrix tan δ peak, the matrix T_g's (measured as the center of a tan δ peak), and the widths of the peak at half-height for the P(S-*co*-ItaNa) and P(S-*co*-MANa) ionomers[23] as a function of the content of ionic repeat units. In the figure, it is seen that the areas under the matrix peak and the matrix T_g's for the two ionomer systems at the same content of ionic units are similar. However, with increasing ion content, the matrix tan δ peak width for the itaconate ionomer becomes larger than that for the methacrylate ionomer. These results imply that the amounts of matrix regions as a function of the content of ionic repeat units are similar in the two systems, although the matrix regions of the itaconate ionomers become more heterogeneous than those of the methacrylate ionomers. At this point, the trends of peak areas in the P(S-*co*-MANa) ionomer system should be mentioned.[23] With increasing ion content, the area under the matrix tan δ peak decreases, while the area under the cluster tan δ peak increases; however, the total area under the two peaks does not change much with varying ion content. At ca. 5 mol % of ions, the matrix tan δ peak area becomes smaller than the cluster tan δ peak area: i.e., the cluster phase becomes dominant. Yet, in the P(S-*co*-ItaNa) system, even though the ionic modulus and the tan δ shoulder curve for the cluster T_g appeared, it was difficult to measure the area under the tan δ shoulder for the cluster T_g. Thus, a crossing point of phase dominance as a function of ion contents could not be determined. It should be stressed that the two ionomers have the same polymer matrix (i.e., polystyrene) and the same ionic group (i.e., sodium carboxylate). The difference in the chemical structures of the two ionomers is that the P(S-*co*-ItaNa) ionomer has two ion pairs in an ionic repeat unit, while the P(S-*co*-MANa) ionomer has a single ion pair. At this stage, it should be noted that in Figure 3 the total area under the matrix and cluster tan δ peaks for the P(S-*co*-ItaNa) ionomers appears to decrease with increasing ion content, while that for the P(S-*co*-MANa) ionomers is more or less constant,[23] as was mentioned above. It should be recalled that Ma et al. found a decreasing trend in the total area under the tan δ peaks for poly(methyl methacrylate) (PMMA) ionomers with increasing ion content.[27] They suggested that at high temperatures a chemical reaction such as cross-linking occurred and that the PMMA ionomers showed a hint of a composite system, i.e., the longer modulus plateau and the decrease in the area under the tan δ peak. However, this is not the case here, since the P(S-*co*-ItaNa) ionomer sample used for the DMTA measurement at ca. 300 °C can still be redissolved in a benzene/methanol solvent. At present, we do not have any clear explanation for the reason why the total area for the itaconate ionomers decreased. However, it can be postulated that the ion aggregation of the P(S-*co*-ItaNa) ionomer is different from that in the P(S-*co*-MANa) ionomer, which will be discussed below, and that this might be responsible for our results.

In the present system, the cluster T_g is much higher than the usual expectation based on the study of the mechanical properties of the P(S-*co*-MANa) system.[23] A plausible explanation is that for the cluster T_g, at which ion hopping of ionic groups from one multiplet to another occurs,[28-32] two ion pairs at the same ionic repeat unit have to hop simultaneously in the present system. Naturally, this is more difficult than a single ion pair hopping, requiring higher temperature. This is indeed what was observed in the present study.

The small-angle X-ray data for some of the P(S-*co*-ItaCs) ionomers are shown in Figure 5. The position of peak maximum shifts to a higher angle with increasing ion content. For example, a shoulder-like peak for the 1.4 mol % ionomer is seen at a lower angle (q = ca. 0.98 nm^{-1}, $d_{\mathrm{Bragg}} = 6.4$ nm), while for the 3.9 mol % ionomer a relatively strong SAXS peak is seen at q = ca. 1.4 nm^{-1} ($d_{\mathrm{Bragg}} = 4.5$ nm). With increasing ion content further, the SAXS peak shifts to a higher q, but the peak becomes less acute (not shown here). SAXS data are listed in Table 2. With the data of ion content, of the Bragg distance, and of the densities measured by using a pycnometer, we calculated the average number of ionic repeat units per scattering moiety. For the simple calculation, we used a simple space-filling approach for a simple cubic lattice. The average numbers are also listed in Table 2. It is interesting to note that the average numbers of ionic repeat units per scattering center are very much similar to each other at 28.1 ± 0.3.

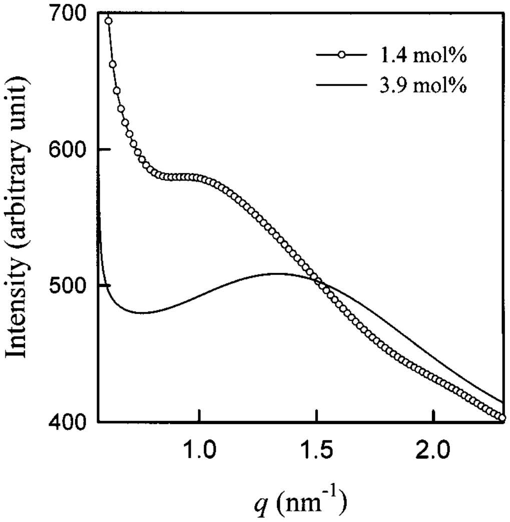

Figure 5. Smoothed SAXS data for P(S-*co*-ItaCs) ionomers.

Table 2. SAXS Data, Density, and the Number of Ion Pairs per Scattering Moiety for the P(S-*co*-ItaCs) Ionomers

content of ionic repeat units (mol %)	$q_{\max}$ (nm^{-1})	d_{Bragg} (nm)	density (g/cm^3)[a]	av no. of ionic repeat units per scattering moiety[b]
1.4	0.98	6.41	1.36	28.2
3.9	1.40	4.49	1.44	27.6
5.7	1.59	3.95	1.51	28.1
6.5	1.66	3.79	1.53	28.3

[a] Density was measured by using a pycnometer. [b] Calculated from simple space-filling argument for a simple cubic lattice.

At this point, it should be considered that in the P(S-*co*-ItaNa) ionomers the two ion pairs in a repeat unit experience the severe angle strain during the formation of multiplets. Probably, one ion pair in an ionic repeat unit forms an ionic aggregate by linking itself with a corresponding ion pair in another ionic repeat unit. Consequently, most ionic aggregates (i.e., multiplets) are probably formed in only ca. two ion pairs. If ion content is enhanced, an ion pair starts to aggregate with its nearest ion pair, producing randomly distributed ionic aggregates. However, all the ion pairs are not able to aggregate because already existing aggregates restrict the mobility of chains surrounding them and make it more difficult for the rest, especially for the ionic groups on the same carbon atom in the polymer chain, to form aggregates at prevalent intermultiplet distances. If the ion content increases further, more ionic aggregates are formed, resulting in large aggregates, incorporating

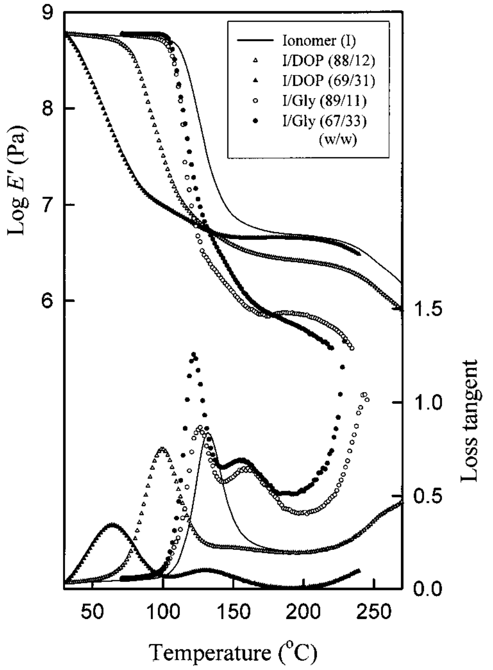

Figure 6. Storage modulus (E') and loss tangent values vs temperature for P(S-*co*-ItaNa) ionomers containing 6.5 mol % of ions, plasticized with dioctyl phthalate (DOP) and glycerol (Gly), measured at 1 Hz.

small ionic aggregates, not at a prevalent distance but at a random interval. With still further increasing ion content, this process advances. Thus, the intensity of SAXS peak increases, and the SAXS peak due to the scattering from large aggregates shifts to higher q values, but the peak becomes less acute. From this morphological picture, it can be suggested that the P(S-*co*-ItaNa) ionomers would not show clustering by chain crowding proposed in the EHM model and that it is instead the large aggregates consisting of small ionic aggregates that determine the mechanical properties of the P(S-*co*-ItaNa) ionomers.

Figure 6 shows the effect of plasticization on the mechanical properties of the P(S-*co*-ItaNa) ionomers. In the case of ionomers mixed with a nonpolar plasticizer dioctyl phthalate (DOP), the modulus curve does not change much in terms of its shape but merely shifts to lower temperatures upon the addition of DOP. It is also seen that with increasing the amount of the DOP the matrix tan δ peak shifts to lower temperatures and that the cluster tan δ peak becomes better developed. From the observation, we suggest that the nonpolar plasticizer remains in polymer matrix regions, resulting in a drop of matrix T_g, which induces clustering. Thus, when the DOP was added to the ionomer up to 31 wt %, the ionomer showed a profound cluster loss tangent peak. In the case of the addition of a polar plasticizer glycerol (Gly), above the matrix T_g the modulus value for the plasticized ionomer decreases more drastically than that for the unplasticized ionomer upon the addition of the plasticizer. It is also seen that the position of the matrix loss tangent peak remains more or less constant but that well-developed cluster peak appears and shifts to lower temperatures with increasing the plasticizer amount. Thus, it is suggested that the polar plasticizer resides in multiplets and weakens ion interactions, causing the decrease in cluster T_g. Therefore, for the ionomer containing 11 wt % Gly [i.e., I/Gly(89/11)], the strong cluster T_g peak due to ion hopping appears, and with increasing plasticizer content further, the matrix T_g peak becomes larger while the cluster T_g peak shifts to lower temperature. These results imply that upon plasticization even the ionomers, whose ionic groups experience steric hindrance during multiplet formation, are able to form more multiplets and, in turn, induce more clustering.

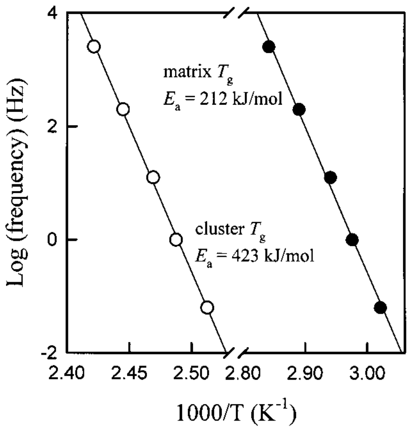

Figure 7. Arrhenius plots for the matrix and cluster glass transitions in the P(S-*co*-ItaNa) ionomer, containing 6.5 mol % of ionic repeat units, plasticized with 31% of DOP.

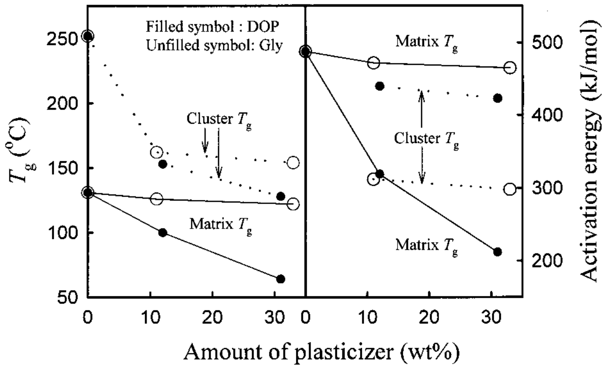

Figure 8. Glass transition temperatures and activation energies for the glass transitions of plasticized ionomers as a function of the amount of plasticizer.

The activation energies (E_a's) for the glass transitions of plasticized ionomers were calculated using Arrhenius plots of log frequency vs inverse temperature. Figure 7 shows the Arrhenius plots for the matrix and cluster glass transitions in the 6.5 mol % ionomer containing 31 wt % of DOP. Even though there are limitations in accuracy in determining the temperature of peak maximum and the deviations from linearity in the Arrhenius plots, the E_a values can be calculated with confidence limits of less than ±30 kJ/mol. The glass transition temperatures and the activation energies for the glass transitions of the plasticized ionomers are shown in Figure 8. In the figure, it is observed that when increasing the amount of plasticizer, the matrix and cluster T_g's decrease, where the latter decreases more rapidly than the former. Also observed is that the activation energies (E_a's) for the matrix and cluster T_g's of the Gly plasticized ionomers and for the cluster T_g of the DOP-plasticized ionomers remain almost unchanged regardless of the difference in the amount of plasticizers. In the case of the Gly plasticized ionomers, the E_a values for the cluster T_g are smaller than those for the matrix T_g. This is due to the fact that when the polar plasticizer resides in the multiplet and weakens ionic interactions, ion hopping requires less energy. This result also suggests that once the ionic aggregates have been plasticized with polar glycerol enough for the ion pair to hop, the further addition of the plasticizer would not affect the E_a for the T_g's. In the case of the DOP plasticized ionomers, the DOP molecules exist in the polymer matrix, and thus they do not affect the ion-hopping process; therefore, the E_a values for the cluster T_g remain constant, but the E_a values for the matrix T_g decrease.

4. Conclusions

In the present study, a strong matrix tan δ peak and a shoulder-like cluster peak for poly(styrene-*co*-itaconate) ionomers were observed. This suggests that the itaconate ionomers are weak-clustered materials. It was also found that the cluster T_g of the itaconate ionomers was much higher than that of the methacrylate ionomers. From this result, it is postulated that simultaneous hopping of two ion pairs is much more difficult than hopping of one ion pair, which makes the cluster T_g shift to higher temperature. The ionic modulus was found to increase with ion content, and the modulus values were comparable to those of well-clustered poly(styrene-*co*-methacrylate) ionomers. In the morphology study, a SAXS peak was observed at very low angle and then shifted to higher angle with increasing ion content. However, a further increase in ion content resulted in a less acute peak. Thus, it is suggested that this ionomer system might not be able to make clusters from chain crowding proposed in the EHM model, which is usually found in other random amorphous ionomers. It was also discerned that upon nonpolar plasticization more clusters were formed and also that polar plasticization caused weaker interaction between ionic groups, which led to a more distinct cluster loss tangent peak due to ion hopping at lower temperature.

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