1870 *Macromolecules* **2003,** *36,* 1870−1875

Effects of Low Matrix Glass Transition Temperature on the Cluster Formation of Ionomers Having Two Ion Pairs per Ionic Repeat Unit

Su-Hwan Kim and Joon-Seop Kim*

Department of Polymer Science & Engineering, Chosun University, Gwangju 501-759, Korea

Received September 17, 2002

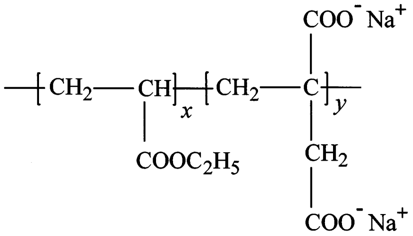
ABSTRACT: The dynamic mechanical properties and morphology of novel ethyl acrylate ionomers, poly(ethyl acrylate-*co*-itaconate) [P(EA-*co*-ITA)], were investigated. It was found that the P(EA-*co*-ITA) ionomers showed a well-developed cluster loss tangent peak, which was not seen in poly(styrene-*co*-itaconate) ionomers. This is probably due to the low matrix T_g of the PEA ionomers, which allows ITA units to form a significant number of multiplets, leading to high clustering. The large difference in the matrix and cluster T_g's was also observed; this is mainly due to two factors. First, the presence of two ion pairs in an ionic repeat unit makes ion-hopping difficult, resulting in higher cluster T_g. Second, the clustering induced by the low matrix T_g naturally increases the cluster T_g. It was also found that the clustering degree was weaker for the itaconate ionomers than for the acrylate ionomers, which is probably due to the fact that the presence of two ion pairs in one ITA unit is more effective in stiffening polymer chains compared to the case of acrylate ionomers. In an SAXS study, an ionomer peak was observed, and the position of the peak shifted to slightly higher angle with increasing ion content, implying that more multiplets form with increasing ion content.

1. Introduction

Ionomers are polymers containing a small amount of ionic groups in a matrix of relatively low dielectric constant. It has been well-known that the ionic groups in the ionomers tend to form ionic aggregates, so-called multiplets.[1] It is also widely accepted that the mobility of chains surrounding the multiplet is reduced.[2] When the multiplets are sufficiently dense so that the regions of restricted mobility surrounding each multiplet overlap and thereby form larger regions of restricted mobility, so-called clusters, the cluster regions show their own glass transition temperature (T_g), i.e., cluster T_g, which is higher than the T_g of the matrix phase.[2]

In the case of ethyl acrylate ionomer systems, the group of Eisenberg studied the glass transitions of poly(ethyl acrylate-*co*-acrylate) ionomers neutralized with various cations.[3,4] It was found that sigmoid curves were observed in the T_g, measured by a differential scanning calorimeter, against ion content plot for ionomers containing any cations.[3] In the study of viscoelastic properties of poly(ethyl acrylate-*co*-vinylpyridinium) ionomers plasticized with dimethyl malonate, the dielectric constant of which is similar to that of the ethyl acrylate matrix, Duchesne and Eisenberg suggested that a lowering of the matrix T_g is an important factor for the cluster formation in that ionomer system.[5] The group of Bazuin also investigated the dielectric, thermal, and mechanical properties of plasticized poly(ethyl acrylate-*co*-sodium acrylate) [P(EA-*co*-ANa)] ionomers.[6,7] It was found that the P(EA-*co*-ANa) ionomers, showing a small-angle X-ray scattering (SAXS) peak, are highly clustered materials. Very recently, Kim et al. studied the mechanical properties of the ethyl acrylate ionomers using a dynamic mechanical thermal analysis technique.[8] They found that the clustering in the P(EA-*co*-ANa) ionomers is comparable to that in highly clustered poly(styrene-*co*-sodium acrylate) [P(S-*co*-ANa)] ionomers.

Scheme 1



$$\left[\mathrm{CH_2{-}CH(COOC_2H_5)}\right]_x\left[\mathrm{CH_2{-}C(COO^-\,Na^+)(CH_2COO^-\,Na^+)}\right]_y$$

Recently, Kim et al. investigated the dynamic mechanical properties of poly(styrene-*co*-itaconate)[9] and poly(styrene-*co*-citraconate)[10] ionomers, both of which have two ion pairs in one ionic repeat unit. They found that the two ionomer systems show only very weak clustering and suggested that the polymer chains, where ionic groups are attached, experience steric hindrance when the ionic groups form multiplets and, thus, form only a few multiplets, leading to weak clustering. Now, one question arises: can we make highly clustered ionomers that contain itaconate units? One of the answers can be found from the study by Duchesne and Eisenberg,[5] i.e., the lowering of the ionomer matrix T_g. Thus, in the present study, we studied the properties and morphology of the poly(ethyl acrylate-*co*-itaconate) ionomer system (see Scheme 1), the matrix T_g of which is ca. 125 °C lower than that of polystyrene-based ionomer system.[11] The results obtained in the present study will give us useful information on the relationships between chemical structure−mechanical property−morphology of ionomers.

2. Experimental Section

2.1. Polymer Synthesis. Poly(ethyl acrylate-*co*-itaconic acid) [P(EA-*co*-ITA)] copolymers were prepared by solution polymerization of ethyl acrylate and itaconic acid monomers. For the polymerization, we modified a procedure that was described elsewhere.[3] For convenience, only a brief summary

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* Corresponding author: e-mail joon@mail.chosun.ac.kr; Ph +82-62-230-7211; Fax +82-62-232-2474.

10.1021/ma021502v CCC: $25.00

Table 1. Polymerization Conditions for the P(EA-*co*-ITA) Copolymers

carboxylic acid content (mol %)	ITA in monomer feed[a] mol %/mass (g)	benzoyl peroxide (g)	reaction time	reaction temp (°C)	actual yield (%)
7.4	2.98/0.77	0.0135	11 h 50 min	61	71
8.8	4.11/1.05	0.0137	12 h 20 min	62	68
10.4	3.69/0.95	0.0139	12 h 10 min	63	62
13.4	6.49/1.65	0.0135	12 h 40 min	63	76
16.4	4.99/1.28	0.0136	12 h 40 min	62	67
19.0	9.01/2.28	0.0134	12 h 20 min	61	70
20.4	6.99/1.78	0.0140	12 h 30 min	63	73
24.8	9.99/2.52	0.0134	13 h 10 min	60	72

[a] Total monomer mass in all case was 20 g, and the reactivity ratios of main monomer and comonomer were assumed to be the same as 1.0.

of the procedure is given. The monomers were purified by distillation under reduced pressure. Since the reactivity ratios of the monomers have not been reported, we deduced the ratios from the reactivity ratios of styrene/itaconic acid (0.26/0.12), styrene/acrylic acid (0.25/0.15), and ethyl acrylate/acrylic acid (1.02/0.91) pairs;[12] the reactivity ratios of the ethyl acrylate/itaconic acid were assumed to be ca. 1.0/1.0. The monomers were dissolved in dried 1,4-dioxane, and the initiator, benzoyl peroxide, was added to the solution. Detailed reaction conditions are listed in Table 1. At this point, it should be mentioned that even though theoretical conversion for compositional heterogeneity of less than 0.1 was 100%, the polymerization was terminated when the conversion became ca. 70% to make reaction time relatively short. The reaction solution was diluted with tetrahydrofuran, and the polymer samples were recovered by precipitation into a rapidly stirred excess of methanol. The precipitated polymer was filtered and dried under vacuum at 60 °C for at least 1 day. To determine the content of itaconic acid units, the acid form 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 solution to the phenolphthalein end point. The itaconic acid contents were found to be 3.7, 4.4, 5.2, 6.7, 8.2, 9.5, 10.2, and 12.4 mol %. In other words, the carboxylic acid contents were 7.4, 8.8, 10.4, 13.4, 16.4, 19.0, 20.4, and 24.8 mol %, respectively. The acid 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 to the solution to give poly(ethyl acrylate-*co*-sodium itaconate) [P(EA-*co*-ITANa)] ionomers. The solutions were freeze-dried and then dried further under vacuum at 60 °C for at least 1 day.

2.2. Sample Preparation. For the dynamic mechanical thermal analysis (DMTA) experiments, the PEA ionomer samples were compression-molded at 120−170 °C, depending on the ion content, under a pressure of 25 MPa. The sample was removed from the mold and annealed under vacuum at 60 °C for 1 day. The dimensions of the molded sample were ca. 2.5 × 7.0 × 30 mm. For the small-angle X-ray scattering (SAXS) experiments, the samples were also compression-molded. The molded samples in the form of a thin disk have dimensions of ca. 10 mm (diameter) × 1.0 mm (thickness).

2.3. Dynamic Mechanical Property Measurements. A Polymer Laboratories dynamic mechanical thermal analyzer (DMTA Mark II) was used for dynamic mechanical property measurements. The experiments were carried out in a dual cantilever bending mode at five different frequencies (0.3, 1, 3, 10, and 30 Hz). Storage modulus (E') and loss tangent (tan δ) 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(frequency) vs inverse temperature of the tan δ peak maximum. Even though the dynamic mechanical measurements for each sample were conducted at five different frequencies, detailed analysis was done only on 1 Hz data. Deconvolutions of the loss tangent peaks were performed on the loss tangent data using the Peakfit (SPSS Inc.) software. The best fits were obtained by using an exponential equation as a background to fit the terminal flow region and fitting the matrix and cluster loss tangent peaks with two Gaussian area functions.

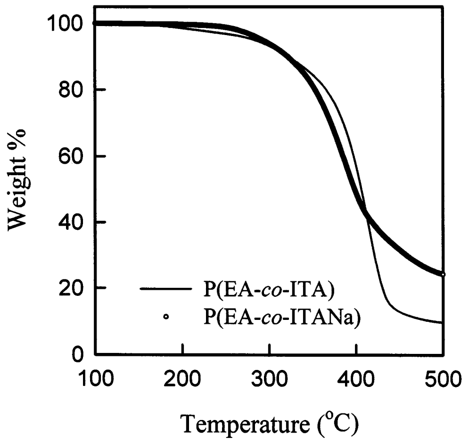

Figure 1. TGA thermograms for P(EA-*co*-ITA) acid copolymer and its sodium ionomer containing 20.4 mol % functional groups.

2.4. Thermogravimetric Analysis. For the studies of the thermal stability of ionomers, a TA Instruments thermogravimetric analyzer (TGA 2050) was used. The experiments were performed from room temperature to 600 °C at a heating rate of 20 °C under a nitrogen atmosphere.

2.5. 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 detailed condition for the experiments has been given elsewhere.[13] The wavelength of light was 0.1608 nm, and 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 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. 0.4 to 2.6 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

Figure 1 shows the weight loss of P(EA-*co*-ITA) acid copolymer containing 20.4 mol % of carboxylic acid units and its sodium salt form as a function of temperature. The temperatures of 5% weight loss for the acid form copolymer and the sodium ionomer are ca. 283 and 292 °C, respectively. Thus, in the present study, the maximum temperature of ca. 250 °C is suitable for the measurement of the dynamic mechanical properties of these ionomers because the exposure time of the samples to that high temperature was relatively short.

Shown in Figure 2 are the storage modulus (E') and loss tangent values of some of P(EA-*co*-ITANa) ionomers as a function of temperature. In the case of the modulus curves, with increasing temperature, the modulus

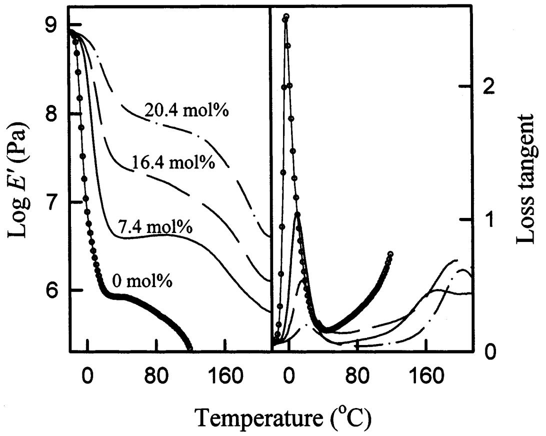

Figure 2. Storage modulus (E') and loss tangent values as a function of temperature for some of the P(EA-*co*-ITANa) ionomers measured at 1 Hz.

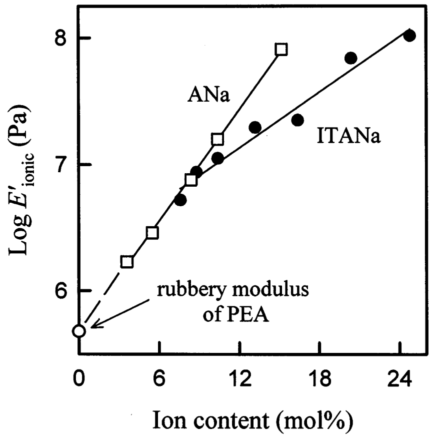

Figure 3. Ionic moduli (E'_{ionic}) as a function of ion content for the P(EA-*co*-ITANa) and P(EA-*co*-ANa) ionomers measured at 1 Hz.

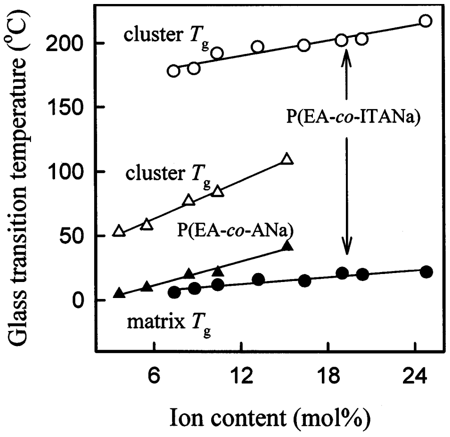

Figure 4. Matrix and cluster glass transition temperatures as a function of ion content for the P(EA-*co*-ITANa) and P(EA-*co*-ANa) ionomers measured at 1 Hz.

changes from the glassy modulus, through the modulus for a matrix glass transition, through the "ionic" modulus (E'_{ionic}), through the modulus for a cluster glass transition, to a rubbery modulus. It is clear that with increasing ion content the ionic modulus (i.e., the value of E' at the point of minimum slope in the temperature between the matrix and cluster T_g's) increases. Figure 3 shows the ionic moduli of the P(EA-*co*-ITANa) and poly(ethyl acrylate-*co*-sodium acrylate) [P(EA-*co*-ANa)] ionomers, which were obtained from another study,[14] as a function of ion content. It is clear that above ca. 6 mol % of ionic groups the increasing rate of the ionic modulus as a function of ion content might become slower for the sodium itaconate (ITANa) ionomer system compared to the sodium acrylate (ANa) ionomer system. This means that the effect of the incorporation of the ionic groups on the mechanical properties of the PEA polymer is relatively weaker for the ITANa ionomer system than for the ANa ionomer system. In addition, at a comparable ion content, the ionic modulus of the ITANa ionomer is relatively lower than that of the ANa ionomer. This suggests that the former system is less clustered than the latter. This will be discussed later.

In Figure 2, it is also seen that as ion content increases, the matrix loss tangent peak at lower temperature shifts to higher temperatures, but its size decreases. The cluster loss tangent peak at higher temperature also shifts to higher temperatures, but the peak size increases with increasing ion content. A similar trend was also observed in various highly clustered ionomer systems, including polystyrene-based[15−18] and PEA-based[8] ionomers that contain one ion pair in one ionic repeat unit. Therefore, the P(EA-*co*-ITANa) ionomers, even though they have two ion pairs in one ionic repeat unit, are also thought to be highly clustered polymers. At this point, it should be stressed that the presence of a well-developed cluster peak in the P(EA-*co*-ITANa) system is quite different from what we observed in poly(styrene-*co*-sodium itaconate) [P(S-*co*-ITANa)] ionomers, in which the cluster loss tangent peak appeared as a very small shoulder. As expected, this difference is due to the divergence in the matrix T_g's of poly(ethyl acrylate) and polystyrene. In the case of both ITANa ionomer systems, the presence of two ion pairs in one repeat unit causes steric hindrance for the ionic groups and polymer chains when the ionic groups form multiplets with another ionic groups. Thus, in the case of the P(S-*co*-ITANa) ionomers, having a relatively high matrix T_g, ionic groups form only a few multiplets. However, in the P(EA-*co*-ITANa) ionomer case, since the matrix T_g is ca. 125 °C lower than that of the styrene ionomer, ionic groups in itaconate units might be able to form a significant number of multiplets against the steric hindrance, leading to sufficient clustering. The formation of a number of multiplets will be discussed later in connection with the results obtained from X-ray experiments.

Shown in Figure 4 are the matrix and cluster T_g's of the P(EA-*co*-ITANa) ionomers vs ion content. For comparison, two sets of T_g's of the P(EA-*co*-ANa) ionomers[14] are also shown in the same figure. The first-order polynomial equations for fitting the data are as follows: For the cluster T_g of the ITANa system, T_g (°C) $= 166 + 2.0 \times$ (ion content) ($r^2 = 0.9205$); for the matrix T_g of the ITANa system, T_g (°C) $= 2 + 0.9 \times$ (ion content) ($r^2 = 0.9002$); for the cluster T_g of the ANa system, T_g (°C) $= 34 + 4.9 \times$ (ion content) ($r^2 = 0.9925$); and for the matrix T_g of the ANa system, T_g (°C) $= -7 + 3.1 \times$ (ion content) ($r^2 = 0.9794$). It is clear that the difference between the matrix and cluster T_g's is much larger for the ITANa ionomers than for the ANa ionomers. At this point, it should be mentioned that for the glass transition of clustered regions the hopping of ionic groups should occur.[16,19−23] Thus, in the ITANa system, at a cluster T_g three moieties, i.e., two Na^+ cations and one itaconate anion (i.e., two carboxylate anions), should hop simultaneously, while in the ANa system only two

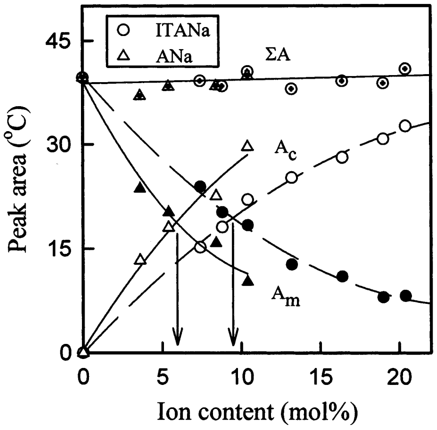

Figure 5. Areas under matrix and cluster loss tangent peaks, A_m and A_c, respectively, and the sum of the areas (ΣA) as a function of ion content for the P(EA-*co*-ITANa) and P(EA-*co*-ANa) ionomers measured at 1 Hz.

moieties, i.e., one Na^+ cation and one acrylate anion (i.e., carboxylate anion), need to hop concurrently. This means that the cluster T_g of the ITANa system would be much higher than that of the ANa system. Now, it is worth recalling that, in the case of ionomers containing one acid group per ionic repeat unit, the neutralization of acid groups with divalent cations also increases the cluster T_g of ionomer to higher temperatures compared to the neutralization with monovalent cations.[24,25] For example, the cluster T_g of Ca^{2+}-neutralized sulfonated polystyrene ionomer is higher than that of Cs^+-neutralized ionomer.[25] In that system, at the cluster T_g three ionic moieties, i.e., $-SO_3^-...Ca^{2+}...^-O_3S-$, for the Ca ionomers instead of two ionic moieties, i.e., $-SO_3^-...Cs^+$, for the Cs ionomer have to move from one multiplet to the other multiplet synchronously. In addition, it is note worthy that the difference between the matrix and cluster T_g's for the P(EA-*co*-ITANa), i.e., 170−180 °C, is larger than that for the very weakly clustered poly(styrene-*co*-sodium itaconate) [P(S-*co*-ITANa)] ionomers, i.e., 130 °C.[9] This result can be understood since the degree of clustering increases the cluster T_g significantly,[2] and because of their low matrix T_g, the P(EA-*co*-ITANa) ionomers are highly clustered (judging from the presence of the well-developed cluster loss tangent peak) compared to the P(S-*co*-ITANa) ionomers. In the figure, it is also seen that the increasing rates of cluster T_g's as a function of ion content are different between the two ionomer systems. The rates for the ITANa ionomers are lower than those for the ANa ionomers. This implies, again, that the effect of ionization of the polymer on the mechanical properties of ionomers is weaker for the former ionomer system than for the latter ionomer system.

In Figure 5, the areas under the loss tangent peaks for the matrix and cluster T_g's and the sum of the areas for the P(EA-*co*-ITANa) and P(EA-*co*-ANa) systems[14] are shown as a function of ion content. At this point, it should be mentioned that the areas under the matrix and cluster loss tangent peaks are assumed to represent the relative amounts of the matrix and cluster regions in ionomers, respectively.[2,8,15,18] As expected, with increasing ion content, the matrix peak area decreases, while the cluster peak area increases. It is also seen that the cluster peak area becomes dominant at ca. 9.5 and 6 mol % for the ITANa and ANa systems, respectively. This, again, indicates that at the same ion content the ITANa system is less clustered than the ANa system.

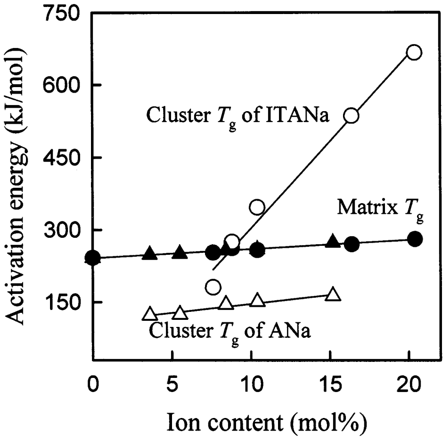

Figure 6. Activation energies for the matrix and cluster glass transitions of the P(EA-*co*-ITANa) and P(EA-*co*-ANa) ionomers.

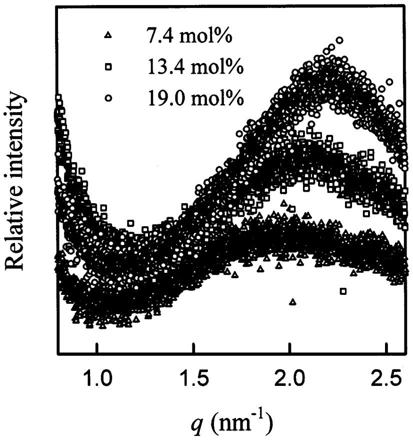

Figure 7. SAXS data for P(EA-*co*-ITANa) ionomers containing 7.4, 13.4, and 19.0 mol % ionic groups.

Table 2. SAXS Data for the P(EA-*co*-ITANa) Ionomers

carboxylate content (mol %)	q_{max} (nm^{-1})	D_{Bragg} (nm)
7.4	2.02	3.10
13.4	2.11	2.98
19.0	2.20	2.85

Figure 6 shows the activation energies for the matrix and cluster glass transitions of the ITANa and ANa ionomer systems. It is seen that the activation energies for the matrix T_g's of both the ITANa and ANa systems are similar. However, the activation energies for the cluster T_g are different between the two ionomer systems. This reveals that the types of clustering in these two systems may be different. These data and the data shown in Figures 3−5 imply that the types of multiplets and/or clustered regions in these two ionomer systems are not similar.

To investigate the morphology of this ionomer system, small-angle X-ray scattering (SAXS) experiments were performed. Figure 7 shows the SAXS data for some of the P(EA-*co*-ITANa) ionomers. For the 7.4 mol % ionomer, an SAXS peak is seen at q_{max} = ca. 2.0 nm^{-1}, which corresponds to the Bragg distance between scattering centers (D_{Bragg}) of ca. 3.1 nm. It is also seen that, with increasing ion content, the SAXS peak shifts to higher q values. The SAXS data are listed in Table 2. The decreasing Bragg distance indicates that, with increasing ion content, more scattering centers appear, as expected. At this point, it would be interesting to compare the SAXS data of P(EA-*co*-ITA) ionomers with

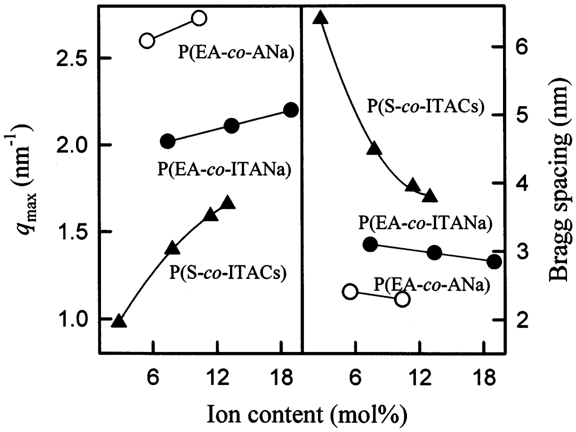

Figure 8. Values of q for the SAXS peak maximum ($q_{\max}$) and Bragg distance calculated from $q_{\max}$ as a function of ion content for the P(EA-*co*-ITANa), P(EA-*co*-ANa), and P(S-*co*-ITACs) ionomers.

those of P(EA-*co*-A)[14] and P(S-*co*-ITA) ionomers.[9] The available SAXS data for these three ionomer systems are shown in Figure 8. It is seen that the Bragg distance between scattering centers is longest for the P(S-*co*-ITA) ionomer system and shortest for the P(EA-*co*-A) ionomer system at a comparable ion content; the Bragg distance for the P(EA-*co*-ITA) ionomer system is in the middle. This result means that the number of multiplets is largest for the P(EA-*co*-A) ionomer system, then the P(EA-*co*-ITA) ionomer system, and smallest for the P(S-*co*-ITA) ionomer system.

From the above mechanical and morphological data, it can be concluded that the degree of clustering is clearly following order: P(EA-*co*-ANa) > P(EA-*co*-ITANa) > P(S-*co*-ITANa). In the case of the two ITANa ionomer systems, the presence of two ion pairs in one ionic repeat unit is more effective in decreasing chain mobility compared to one ion pair in the ANa ionomer system. Thus, when the ionic groups tend to form multiplets, the polymer chains experience steric hindrance (i.e., reduced chain movement), resulting in only a few multiplets even at relatively high ion content. Especially, for the P(S-*co*-ITANa) ionomer system, the large aggregates consisting of small and loosely bound ionic aggregates govern the mechanical properties of the P(S-*co*-ITANa) ionomers. However, in the P(EA-*co*-ITANa) system, the ionic modulus and cluster T_g are affected not only by the large aggregates consisting of small and loosely bound multiplets caused by the restrained chain mobility but also by the clustering caused by the low matrix T_g. In the case of P(EA-*co*-ANa) system, which has one ion pair per ionic repeat unit, it is not expected that the polymer chains undergo severe mobility restriction when the ionic groups start forming multiplet. Thus, the degree of clustering is highest for the P(EA-*co*-ANa) ionomer system.

At last, one simple additional question arises: when 50% of the carboxylic acid groups of P(EA-*co*-ITA) copolymer are neutralized, does the resulting ionomer behave like P(EA-*co*-ANa) ionomers or does it behave like an ionomer, whose property lies in between those of the 100% neutralized ITANa and ANa ionomers? To give an answer, we neutralized 50% of the acid groups of P(EA-*co*-ITA) copolymer containing 20.4 mol % of carboxylic acid groups and compared its dynamic mechanical data with those of the 100% neutralized P(EA-*co*-ANa) ionomer containing 10.4 mol % of ANa units.

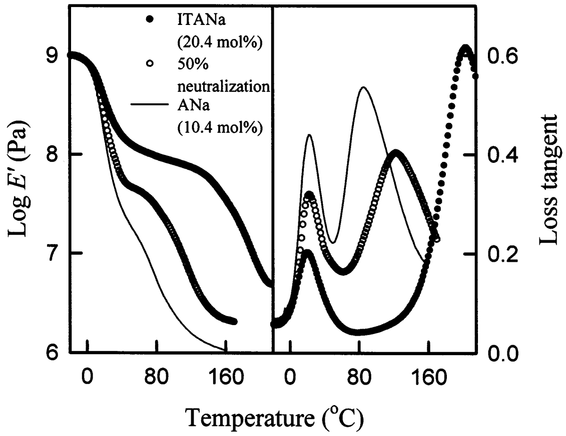

Figure 9. Storage modulus (E') and loss tangent values as a function of temperature for 50% and 100% neutralized P(EA-*co*-ITANa) ionomers containing 20.4 mol % functional groups and 100% neutralized P(EA-*co*-ANa) ionomer containing 10.4 mol % ionic groups. All data were measured at 1 Hz.

Figure 9 shows the storage modulus and loss tangent values of the ionomers as a function of temperature. It is seen clearly that above the matrix T_g the modulus curve for the 50% neutralized ITANa ionomer lies in between those for the 100% neutralized ITANa and ANa ionomers. In addition, the cluster loss tangent peak of the 50% neutralized ITANa ionomer is found to be located in between those of the 100% neutralized ITANa and ANa ionomers. This implies that the 50% neutralization process of the ITA units induces, naturally, the neutralization of two acid groups of ITA units as well as that of only one acid group of ITA units. This result suggests that we are able to prepare the ionomers, whose properties are in between those of the 100% neutralized ANa and ITANa ionomers, just by changing the degree of neutralization.

Acknowledgment. This work was supported by the Korea Science & Engineering Foundation (Grant R01-1999-00285), and the SAXS experiments at PLS were supported in part by the Ministry of Science & Technology and Pohang Steel Co. The authors also thank one of the reviewers for the valuable comments and suggestions.

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MA021502V