Relationships between the Glass Transition Temperatures and the Type of Cations in Poly(ethyl acrylate) Ionomers

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ABSTRACT: Glass transition temperatures of poly(ethyl acrylate) ionomers neutralized with various cations were studied dynamic mechanically in terms of ion content and the type of cations. On one hand, it was found that with increasing ion content the matrix T_gs increased linearly and identically regardless of the variety of cations. Thus, it is inferred that the type of cations did not affect the matrix T_gs. On the other hand, in the plots of the cluster T_gs vs (ion content × charge)/(distance between charges), it was observed that the cluster T_gs were superimposed on the straight line. This result implies that the cluster T_g involving ion hopping is affected by the type of cations. It was also found that the ionic modulus did not change with the type of cations significantly. In addition, the small-angle X-ray study showed that with increasing the radius of a cation the distance between scattering centers increased. Thus, it was postulated that the restricted mobility layer became thicker slightly with the increasing size of a cation.

1. Introduction

Ionic groups within the relatively nonpolar polymer matrix form ionic aggregates, called multiplets,[1] which, in turn, induce the formation of a second phase, i.e., the ion-rich phase. These ionic polymers, i.e., ionomers, exhibit the characteristic behavior of materials of two phases: ion-poor (i.e., matrix) phase and ion-rich (i.e., cluster) phase.[2−5] This two-phase nature is responsible for the morphology and physical properties of ionomers. To explain these two aspects, Eisenberg et al. proposed the multiplet/cluster model for random amorphous ionomers.[6] According to the model, the polymer chains in the vicinity of the multiplet are restricted in mobility. At low ion contents, only a few multiplets are formed. With increasing ion content, the regions of restricted mobility overlap forming clusters; if their size exceeds a certain minimum dimension (e.g., ∼100 Å), the ionomer shows a second glass transition (T_g) due to the combined effect of relaxation of the polymer chains in cluster regions and the hopping of ionic groups in multiplets. Other morphological models of ionomers have also been offered.[7,8]

The glass transition temperatures of various ionomer systems (e.g., silicates, phosphonate, acrylate, ethylene ionomers, and styrene ionomers) were studied extensively.[9−26] Especially, the glass transition temperatures of ethyl acrylate ionomers as a function of ion content were investigated by Matsuura and Eisenberg.[14] Using a differential scanning calorimetry (DSC) technique, they found sigmoid curves in the T_g vs ion content plots. They also found that when the T_gs were plotted as a function of cq/a (where c is the ion content, q the charge of the cation, and a the distance between charges), all the curves were superimposed on one sigmoid curve. Thus, they concluded that the sigmoid curves in T_gs vs cq/a plots might arise in heterogeneous polymers.

Later, however, the sensitivity of the DSC technique was questioned on the basis of its inability to detect the existence of smaller regions. Now it is widely agreed that a dynamic mechanical thermal analysis (DMTA) technique is more sensitive than a DSC technique in determining the thermal transitions of the materials of small size. Thus, in this paper, we explored the effect of the type of cation on the T_gs, especially the cluster T_gs of poly(ethyl acrylate) ionomers neutralized with various cations by using the DMTA technique. With the necessary data in hand, we reexamined the cq/a effects found in the PEA ionomers. In addition, other DMTA data, i.e., peak area, ionic modulus, and activation energy for the glass transitions, were discussed. The morphology of the ethyl acrylate ionomers containing various cations was also investigated by using a small-angle X-ray scattering (SAXS) technique. The findings were expected to contribute toward a more thorough understanding of the nature of the cluster T_g of ionomers.

2. Experimental Section

2.1. Polymer Synthesis. Poly(ethyl acrylate-*co*-acrylic acid) [P(EA-*co*-AA)] samples were prepared by solution polymerization of purified ethyl acrylate and acrylic acid monomers using benzoyl peroxide as the initiator. Dried benzene was used as the solvent, and the reaction temperature was kept at 60 °C. Conversion, with reactivity ratios of $r_1 = 1.02$ and $r_2 = 0.91$,[27] was over 50%, yielding a compositional heterogeneity of less than 0.1. The polymer samples were precipitated into a rapidly stirred excess of hexane, filtered, and dried under vacuum at room temperature for at least 1 day. The acid contents were found to be 3.6, 5.5, 8.4, 10.4, and 15.2 mol % by titration.

2.2. Sample Preparation. The P(EA-*co*-AA) 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 lithium hydroxide, sodium hydroxide, potassium hydroxide, cesium hydroxide, barium hydroxide, and calcium acetate was added to give Li^+-, Na^+-, K^+-, Cs^+-, Ba^{2+}-, and Ca^{2+}-neutralized poly(ethyl acrylate-*co*-acrylate) ionomers, respectively. The solutions were freeze-dried and then dried further under vacuum at 40 °C for at least 2 days. For the dynamic mechanical thermal analysis (DMTA) experiments, the PEA ionomer samples were compression-molded at ca. 65 °C and a pressure of 25 MPa. The samples were annealed for 1 day under vacuum at 60 °C. The dimensions of the molded samples were ca. 2.5 × 7.0 × 28 mm.

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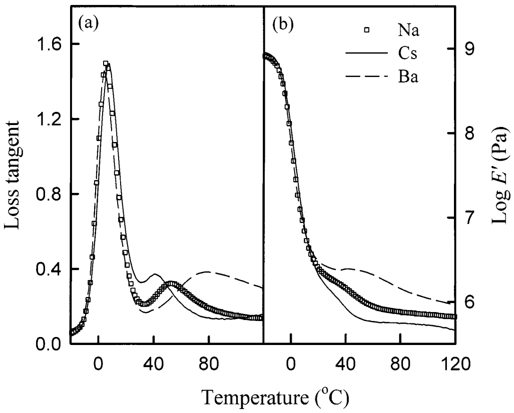

Figure 1. (a) Loss tangent (at 1 Hz) and (b) storage modulus (E') values as a function of temperature for Na^+-, Cs^+-, and Ba^{2+}-neutralized PEA ionomers containing 3.6 mol % of ionic groups.

2.3. Dynamic Mechanical Thermal Analysis and Small-Angle X-ray Scattering. Dynamic mechanical property measurements were performed on a Polymer Laboratories DMTA (Mark II model). The experiments were carried out in a dual cantilever bending mode at frequencies ranging from 0.3 to 5 Hz. Storage moduli (E') and loss tangents (tan δ) were obtained as a function of temperature at a heating rate of 1 °C /min. Detailed data analysis was performed only on 1 Hz data using the Peakfit (SPSS Inc.) computer program for curve deconvolutions of loss tangent data. The best fits were obtained by using an exponential equation as a background and by fitting the matrix and cluster peaks with Gaussian area functions. Small-angle X-ray scattering (SAXS) experiments were conducted at Station 4C1 of the PLS synchrotron radiation source (Pohang, Korea), and the detailed condition for the experiments was described elsewhere.[28]

3. Results and Discussion

Shown in Figure 1a are a series of representative loss tangent curves as a function of temperature, recorded at 1 Hz, of Na^+-, Cs^+-, and Ba^{2+}-neutralized PEA ionomers containing 3.6 mol % of ionic groups. As with poly(styrene-*co*-methacrylate) ionomers,[4–6,29–31] two loss tangent peaks are seen. The peak at low temperature is due to the matrix T_g, while that at high temperature is due to the cluster T_g. It is seen that the matrix T_gs of the three ionomers are similar to each other, while their cluster T_gs are all different. The order of cluster T_g of the three ionomers is as follows: Ba^{2+}-ionomer > Na^+-ionomer > Cs^+-ionomer. This order can be easily understood if the charge and size of the cations are taken into consideration. This will be discussed later. It should also be mentioned that, with increasing ion content, the two loss tangent peaks shift to higher temperatures (not shown here). In addition, with increasing ion content, the size of the matrix loss tangent peak decreases, whereas that of the cluster loss tangent peak increases. Since this behavior has all been observed in well-clustered polystyrene (PS) ionomer systems,[4–6,29–31] we can suggest that the PEA ionomers are also well clustered.[32]

Figure 2a shows the T_gs of PEA ionomers neutralized with various cations as a function of ion content. It is shown that, with increasing ion content, the matrix T_g increases relatively slowly, while cluster T_g increases rapidly. In the figure, it is also seen that the matrix T_g increases linearly, unaffected by the type of the cation.

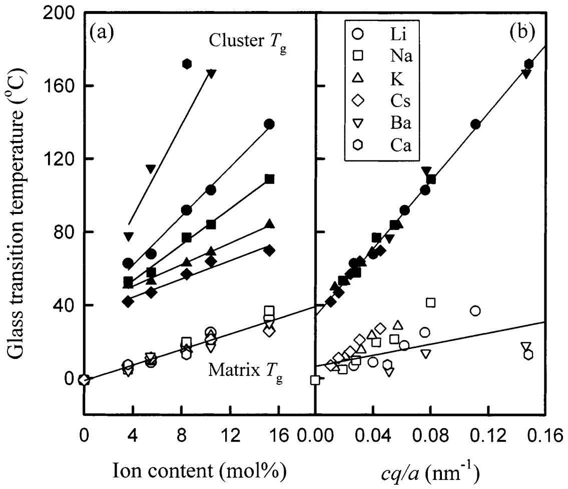

Figure 2. Glass transition temperatures (at 1 Hz) of PEA ionomers containing various cations as functions of (a) ion content and (b) cq/a.

The equation for the line fitting the matrix T_g data is the following:

$$\text{matrix } T_g\ (°\text{C}) = -1.3 + 2.1 \times (\text{ion content}) \quad (r^2 = 0.9521)$$

where r^2 is the linear least-squares correlation coefficient. From Figure 2a, it is clear that the increase in the cluster T_gs as a function of ion content becomes slower with increasing size of cation. For example, at 3.6 mol % of ion content, the divergence in the cluster T_gs of lithium and cesium neutralized ionomers is ca. 21 °C, while at 10.4 mol % it is ca. 39 °C.

Now, let us consider the relationship between the T_g and the electrostatic work necessary to remove an anion at some constant rate from the spheres of ionic aggregates consisting of cations and anions, i.e., ion hopping, which is one of the major mechanisms for the cluster T_g.[30,33–40] The electrostatic work is proportional to the electric force (F_{el}) integrated over the distance from the distance of closest approach to infinity.[41] The F_{el} is inversely proportional to the square of the distance (x) between two charges; i.e., $F_{el} \propto q_a q_c/x^2$, where q_a and q_c are the anion charge and the cation charge, respectively. This leads to $T_g \propto \int q_a q_c/x^2\,dx \propto q_a q_c/x$. Thus, if the size of cation is smaller, the cluster T_g involving ion hopping should be higher. In the PEA ionomer system, like many other ionomer systems, ion hopping is one of the two contributive factors to the cluster glass transition, the other being the relaxation of polymer chains in cluster regions. Thus, the cluster T_gs of the PEA ionomers should show a relationship with the strength of the ionic interactions, such as a q/a effect, where a is the distance between cation and anion. Therefore, as Matsuura and Eisenberg had done,[14] we presented our T_g data as a function of cq/a. Figure 2b shows the T_gs of the PEA ionomers as a function of cq/a. It is seen that there is a linear relationship in the cluster T_g data. The equation fitting the data for the cluster T_g is as follows:

$$\text{cluster } T_g\ (°\text{C}) = 34 + 930 \times cq/a \quad (r^2 = 0.9923)$$

From this result, it is clear that a cq/a effect on the cluster T_g is operative, judging from the r^2 of 0.9923.

The straight line is, however, different from the one found by Matsuura and Eisenberg, i.e., a sigmoid curve.[14] As was mentioned before, this dissimilarity reflects the difference in the sensitivity of the respective instruments used, i.e., DSC and DMTA. Using the less sensitive DSC, Matsuura and Eisenberg probably measured only the matrix T_g for the ionomers of low ion contents and only the cluster T_g for the ionomers of high ion contents. In the intermediate ion contents, it was probably the average of the two T_gs that was obtained. In other words, the matrix T_g for high ion content ionomers and the cluster T_g for low ion content ionomers were both absent in their data. With this restriction of data, only a sigmoid curve of the T_g against cq/a could be constructed. Now, employing the more sensitive DMTA technique, the present study obtained two separate sets of data as functions of ion content and constructed the first-order expression for the cluster T_g vs cq/a. Thus, we are able to conclude that, in the PEA ionomers, a linear relationship between T_g and cq/a is indeed operative. However, it should be stressed that the cq/a effect is more applicable to the cluster T_g than the matrix T_g because the ion-hopping mechanism governed by the strength of ionic interaction is directly involved in the cluster T_g. As for the matrix T_g, the strength of ionic interactions is not directly related. For example, the equation fitting the matrix T_g data in Figure 2b is as follows:

$$\text{matrix } T_g\ (^\circ\text{C}) = 9.9 + 128.3 \times cq/a \quad (r^2 = 0.2328)$$

The low r^2 value of 0.2328 clearly illustrates that the matrix T_g is not directly related with cq/a, but only with ion content.

Let us shift our discussion to another data set obtained from the loss tangent curves, i.e., the areas under the two loss tangent peaks for the matrix and cluster T_gs. In the figure of the area vs ion content (not shown here), it is seen that, with the increase of ion content, the area under the matrix loss tangent peak decreases, while that under the cluster loss tangent peak increases; the total area seems to remain constant. Similar trends were reported by Hird and Eisenberg and Kim et al. for PS ionomers[29,31] and by Kim et al. for PEA ionomers.[32] It is also seen that the ratio of a cluster peak area, which is known to be directly related with the degree of clustering,[4−6,29,31] stays unchanged against the various types of cations.

Shown in Figure 1b are the storage moduli as a function of temperature of Na^+-, Cs^+-, and Ba^{2+}-neutralized PEA ionomers containing 3.6 mol % of ionic groups. It is seen that with increasing temperature the modulus value changes from a glassy modulus, through a matrix glass transition, through a plateau, denoted as “ionic modulus”, through a cluster glass transition, to a long rubbery plateau. The ionic modulus value, i.e., the value of E' at the point of minimum slope in the temperature between the matrix and cluster T_gs, is thought to be related to the degree of clustering[4−6,30,31] and is shown in Figure 3 as a function of ion content. It is clear that the ionic modulus of alkali metal neutralized ionomers increases almost linearly with increasing ion content, regardless of the type of cations. It is also seen that the ionic modulus of alkali earth metal neutralized ionomers slightly deviates from the linearity. In the case of the ionomers neutralized with alkali metal cations, the type of the cations changes the modulus only slightly, and the first-order expression fitting the data is as follows:

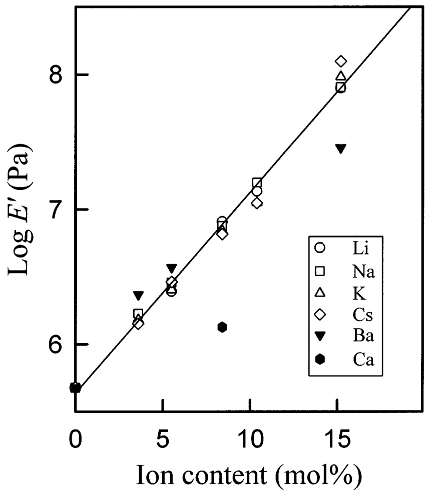

Figure 3. Ionic modulus values for the PEA ionomers as functions of ion content, measured at 1 Hz.

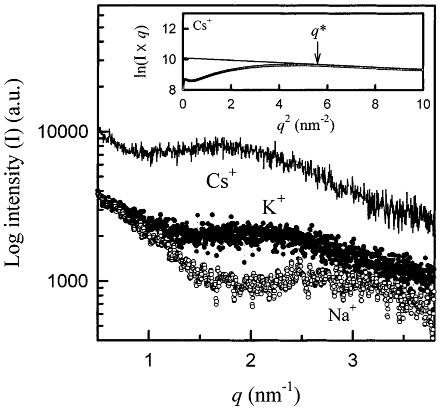

Figure 4. SAXS data for the PEA ionomers containing 5.5 mol % of ionic groups. The inset shows a plot of ln(Iq) vs q^2 for the Cs^+-neutralized ionomer. The meaning of the arrow is described in the text.

$$\log E'\ (\text{Pa}) = 5.6 + 0.15 \times (\text{ion content}) \quad (r^2 = 0.9914)$$

The linearity in the modulus vs ion content plot clearly shows that within the range of ion contents as chosun for the present study the degree of clustering increases linearly with increasing ion content, regardless of the type of cations. At this point, it is worth noting that the increase in ionic modulus with increasing ion content is comparable with that of the well-clustered poly(styrene-*co*-sodium methacrylate) ionomers.[30] This implies that, as was suggested in a precedent paper,[32] the PEA ionomers are as well-clustered as the PS ionomers.

Figure 4 shows the SAXS data for 5.5 mol % PEA ionomers containing Na^+, K^+, and Cs^+ cations. An SAXS peak and a small-angle upturn in the small q range are observed. In the case of Li^+-neutralized ionomer, no well-developed peak is seen, owing to the low electron density of the lithium cation (not shown here). The small-angle upturn might represent the polydispersity of the size of scattering moieties and the irregularity of their structure.[42] It is observed that the position of peak maximum, i.e., q_{max}, being ascribed to intermultiplet spacing,[6,8] shifts to a lower angle with increasing size of the cation. SAXS data are listed in Table 1. For an

Table 1. SAXS Data, Density, and Calculated Morphological Parameters for the PEA Ionomers Containing 5.5 mol % of Ionic Groups Neutralized with Various Alkali Metal Cations

	type of cation		
	Na^+	K^+	Cs^+
q_{max} (nm^{-1})	2.6	2.2	1.8
D_{Bragg} (nm)	2.4	2.9	3.5
density[a] (g/cm^3)	1.147	1.177	1.223
no. of ionic groups per multiplet	5.2	9.4	16.2
no. of multiplets per 1 cm^3 of a sample	7.2×10^{19}	4.2×10^{19}	2.3×10^{19}
radius of a multiplet (Å)	3.6	4.6	5.9
surface area of a multiplet (Å^2)	163	267	442
surface area per an ionic group (Å^2)	31	29	27
vol % of multiplets	1.4	1.7	2.0
% area of cluster loss tangent peak	48	49	49
thickness of restricted mobility layer (Å)	8.1	9.5	11.0
average persistence length calculated from SAXS data (Å)	9.7 ± 0.1	10.8 ± 0.1	12.3 ± 0.2

[a] Density values were measured by using a pycnometer.

illustrative purpose, with the data of the Bragg distance ($d_{Bragg} = 2\pi/q_{max}$) and the density of the three ionomers, we calculated the average number of ionic groups/scattering moiety (i.e., multiplet). For the simple calculation, we assumed that all ionic groups were in multiplets and used a simple space-filling approach for a simple cubic lattice. The average numbers are also listed in Table 1. The number of ionic groups per multiplet increases with increasing cation size, which, in turn, results in the decrease in the number of multiplets per a comparable volume of a sample. According to the multiplet/cluster model by Eisenberg et al.,[6] the decreasing number of multiplets induces less overlapping regions of restricted mobility, i.e., a lower degree of clustering. [At this point, it should be mentioned that a considerable amount of supportive evidence of the presence of the restricted mobility layer surrounding ionic aggregates has been collected by using nuclear magnetic resonance (NMR), electron spin resonance (ESR) spectroscopy, and dynamic mechanical techniques.[43-50]] Thus, the above results imply that with increasing ionic radius the degree of clustering should decrease. However, this is not the case here; i.e., at a certain ion content the degree of clustering is independent of the type of cations (see Figure 3). To interpret this result, we should consider the change of the thickness of restricted mobility layer surrounding a multiplet, as the degree of restriction in the mobility of polymer chains surrounding multiplets should increase when the number of ionic groups per one multiplet increases with increasing ionic radius. The persistence length of the polymer chains surrounding the multiplet, which is directly related to the thickness of the reduced mobility layer, should increase; that is, the restricted mobility layer should become thicker.

To back up the above interpretation, we also calculated the thickness of restricted mobility layer. Again, it should be stressed that the calculation was made on the purpose of simple comparison only. For the simple calculation, the size of carboxylate group ($-COO^-$) was assumed 33.9 Å^3 (i.e., 3×11.3 Å^3),[31] and the size of the cation was taken from the *Handbook of Physics and Chemistry*.[51] Having calculated the radius and surface area of a multiplet in the simple cubic lattice, we, subsequently, calculated the surface area occupied by one ionic group, the volume percentage of the multiplets, and the thickness of the restricted mobility layer surrounding a multiplet assuming that the area percentage of the cluster loss tangent peak could represent the volume percentage of cluster regions. The calculated values are also listed in Table 1. If our line of reasoning proved to be correct, it might be noteworthy that the thickness of the restricted mobility layer increases from 8.1 to 11.0 Å with increasing radius of multiplet from 3.6 to 5.9 Å.

In addition, we also evaluated the persistence lengths of the three ionomers from small-angle X-ray scattering data. Yamazaki et al. reported that the persistence length of ionenes in methanol was related to $2.87/q^*$, where q^* was the coil-to-rod transition point at which the SAXS data start to deviate from the linear extrapolation line in the plot of log[scattering intensity $(I) \times q$] vs q^2.[52] The inset in Figure 4 shows the plot for the Cs^+-neutralized ionomer. The extrapolated line starts to deviate from the smoothed SAXS data from q^* value of ca. 2.34 nm^{-1} (indicated by using an arrow in the figure), which corresponds to a persistence length of ca. 12.3 Å. The persistence lengths calculated from q^* values for the other two ionomers are also listed in Table 1. Again, it is seen that, with increasing size of cation, the calculated persistence length also increases from ca. 9.7 to 12.3 Å and that the values are not much different from those calculated above using simple space-filling arguments. The increasing persistence length with ion size is understandable; the smallest surface area per one ionic group of Cs^+-ionomer, i.e., 27 Å^2, smaller than 31 Å^2 for the Na^+-ionomer (see Table 1), implies that the polymer chains emanating from the multiplet of Cs^+-ionomer have relatively more restricted mobility compared to those in the Na^+-ionomer. This naturally induces the longer persistence length. If this argument proved to be correct, the degree of clustering might not be changed with the size of cation.

4. Conclusions

In the present study, the relationship between T_gs and cq/a of poly(ethyl acrylate) ionomers neutralized with various cations was explored. It was found that the matrix T_gs of the ionomers increased relatively linearly with increasing ion content and that they were superimposed on the same line. It was also observed that the cluster T_gs were superimposed on a straight line, when they were plotted as a function of cq/a. From these results, it was concluded that the matrix T_g is directly related only to the ion content, leaving more complex and indirect its relationship with the strength of the ionic interactions between ionic groups in multiplets. On the other hand, the cluster T_g related with ion hopping was affected by the type of cations strongly (i.e., the cq/a concept was effective). It was also found that the ionic modulus values of the ionomers increased with increasing ion content regardless of the type of cations. These results implied that the type of cations did not affect the degree of clustering. In addition, the SAXS profile showed that with increasing radius of cation the distance between scattering centers increased, leading to a formation of fewer multiplets. From these findings, it was postulated that the increase of cation size might induce a slight increase of the thickness of the restricted mobility layer surrounding a multiplet.

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