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Comparison of clustering in various acrylate ionomers

Joon-Seop Kim[a,*], Yeon Hwa Nah[a], Soon-Suck Jarng[b]

[a]*Department of Polymer Science and Engineering, Chosun University, Kwangju 501-600, South Korea*
[b]*Department of Control and Measurement Engineering, Chosun University, Kwangju 501-600, South Korea*

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Abstract

The clustering behavior of three well clustered acrylate ionomers, i.e. poly(ethyl acrylate -*co*-Na acrylate) (PEA), poly(styrene-*co*-Na acrylate) (PS), and poly(vinylcyclohexane-*co*-Na acrylate) (PVCH) ionomers, was compared. It was found that the cluster phase became dominant at ca. 5 mol% for the PEA and PS ionomers but at 9 mol% for the PVCH ionomer. In addition, the temperature differences between the matrix and cluster T_gs were 54, 55 and 49°C for the PEA, PS, and PVCH ionomers, respectively. The very similar values for the PEA and PS ionomers, in spite of their difference in matrix T_gs themselves, led to a postulation that the PEA ionomers have bigger multiplets and longer persistence length than the PS ionomers. © 2001 Published by Elsevier Science Ltd.

Keywords: Ionomer; Cluster; Acrylate

1. Introduction

Polymers of low dielectric constant, containing a relatively small amount of ionic groups, show the characteristic behavior of micro-separated materials [1–5]. This behavior is related to ion aggregation within the relatively non-polar polymer matrix. The ionic aggregates, called multiplets [6], cause the formation of a second phase region, termed clusters [7]. These ionic polymers, known as ionomers, exhibit a dual nature, i.e. ionic and non-ionic natures. This dual nature is responsible for their morphology and physical properties.

In order to explain the morphology and physical properties of ionomers, the Eisenberg–Hird–Moore (EHM) model was proposed in 1990 [7]. According to the model, at very low ion contents only multiplets are formed. The mobility of polymer chains surrounding the multiplet is restricted. As the ion content increases, the regions of restricted mobility start to overlap. Once the dimension of overlapping regions of reduced mobility, i.e. clusters, exceeds ~100 Å, the material shows a second glass transition temperature (T_g) attributed to the regions.

For the acrylate ionomer systems, the Eisenberg group investigated the glass transition temperatures of poly(ethyl acrylate-*co*-metal acrylate) ionomers [8,9]. In addition, the Bazuin group studied the dielectric and mechanical thermal properties of plasticized poly(ethyl acrylate-*co*-sodium acrylate) [P(EA-*co*-ANa)] ionomers containing 5 and 10 mol% of ions [10,11]. They found that the P(EA-*co*-ANa) ionomers, showing a small-angle X-ray scattering (SAXS) peak, were well clustered. Subsequently Kim et al. studied the mechanical properties and morphology of different acrylate ionomers, i.e. poly(styrene-*co*-sodium acrylate) and poly(vinylcyclo-hexane-*co*-sodium acrylate) ionomers, using dynamic mechanical thermal analysis and SAXS techniques, respectively [12].

At this point, it should be noted that the glass transition temperatures of poly(ethyl acrylate), polystyrene, and poly(vinylcyclohexane) are ca. −25, 100 and 120°C, respectively [13]. Therefore, it was thought to be of interest to compare the clustering behavior of the three acrylate ionomers mentioned above. However, since the detailed mechanical property data of P(EA-*co*-ANA) ionomers were largely non-existent, in the present study we first needed to explore the dynamic mechanical properties of the PEA ionomer. With those necessary data in hand, the comparison of the clustering of the three ionomers was made. The findings from the comparison were expected to contribute towards a more thorough understanding of the ionomer behavior.

2. Experimental

2.1. Polymer synthesis

Poly(ethyl acrylate) (PEA) and poly(ethyl acrylate-*co*-acrylic acid) [P(EA-*co*-AA)] samples were prepared by

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* Corresponding author. Tel.: +82-62-230-7211; fax: +82-62-232-2474.
E-mail address: joon@mail.chosun.ac.kr (J.-S. Kim).

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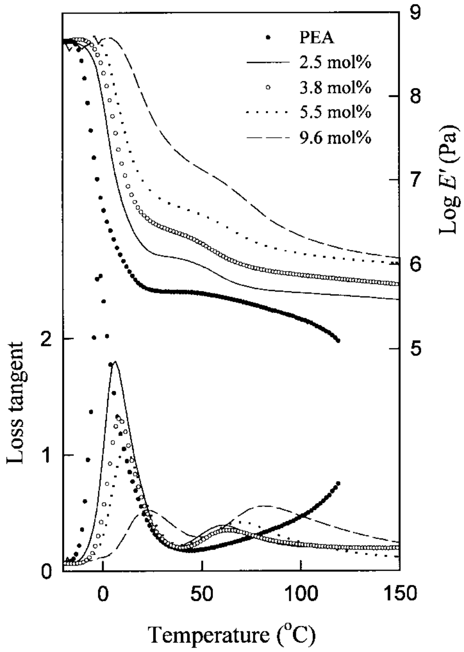

Fig. 1. Storage modulus (E') and loss tangent (tan δ) of poly(ethyl acrylate) homopolymer and poly(ethyl acrylate) ionomers as a function of temperature, measured at 1 Hz.

solution polymerization of purified ethyl acrylate and acrylic acid monomers using benzoyl peroxide as the initiator. The detailed procedure has been described elsewhere [7]. For convenience, only a brief summary of the procedure is given. Dried and distilled benzene was used as the solvent, and the reaction temperature was 60°C. Conversion was less than 10%, yielding a compositional heterogeneity of less than 0.1. The polymer samples were recovered by precipitation into a rapidly stirred excess of hexane. The precipitated polymer was filtered, and dried under vacuum at room temperature for at least 1 day. To determine the acid content, 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 solution to the phenolphthalein end point.

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 NaOH was added to give poly(ethyl acrylate-*co*-sodium acrylate) [P(EA-*co*-ANa)]. The solutions were freeze-dried and then dried further under vacuum at room temperature for at least 1 day.

For the dynamic mechanical thermal analysis (DMTA) experiments, the PEA homopolymer and PEA ionomer samples were compression-molded at 60–70°C, depending on the ion content, under the pressure of 20 MPa. The sample was removed and annealed for 1 day in a vacuum oven at 60°C. The dimensions of the molded sample were ca. $2.5 \times 6.7 \times 28$ mm^3.

2.3. Dynamic mechanical thermal analysis

Dynamic mechanical property measurements were performed on a Polymer Laboratories DMTA Mark II. 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. Activation energy values for matrix and cluster T_gs were calculated using an Arrhenius plot of log(frequency) vs. inverse temperature of the tan δ peak maximum [14].

3. Results and discussion

Fig. 1 shows the storage modulus and loss tangent of poly(ethyl acrylate) (PEA) homopolymer and poly(ethyl acrylate-*co*-sodium acrylate) [P(EA-*co*-ANa)] ionomers as a function of temperature. The storage modulus for the PEA polymer drops rapidly at ca. −5°C; then, the PEA polymer shows a long rubbery plateau. Above 50°C, the sample starts to flow. For the P(EA-*co*-ANa) ionomers, the storage modulus value changes from glassy modulus, to glass transition, to 'ionic' modulus, to glass transition, and to rubbery modulus. The intermediate region between two glass transitions, in which the modulus changes slightly with temperature can be characterized by ionic modulus (E'_{ionic}), i.e. the E' value at the point of minimum slope. This intermediate region reflects ionic cross-linking [14–16]. The figure shows that the temperature at which the storage modulus starts to decrease shifts upward with increasing ion content. It is also seen in the figure that the 'ionic' modulus values increase with ion concentration. For example, the ionic modulus for the P(EA-*co*-ANa) containing 2.5 mol% of ions is ca. 1.3×10^6 Pa (at 35°C), while that for the 9.6 mol% ionomer is 1.4×10^7 Pa (at 50°C).

The loss tangent plots show that there are two tan δ peaks; the one at low temperature is due to the glass transition of the matrix phase, whereas the other at high temperature is due to the glass transition of the cluster phase. The two tan δ peaks, again, shift to higher temperatures with increasing ion content. It is also seen that with increasing ion content the size of the matrix tan δ peak decreases, while that of the cluster tan δ peak increases. Similar trends have been reported for poly(styrene-*co*-sodium acrylate) [P(S-*co*-ANa)] [12], poly(styrene-*co*-sodium methacrylate) [P(S-*co*-MANa)] [16], and poly(vinylcyclohexane-*co*-sodium acrylate) [P(VCH-*co*-ANa)] ionomers [12], which are all well clustered ionomer systems. Therefore, it can be concluded that the PEA ionomers are also well clustered materials, comparable to the PS ionomers.

Shown in Fig. 2 are the ionic modulus (E'_{ionic}) values as a function of ion content of P(EA-*co*-ANa), P(VCH-*co*-ANa)

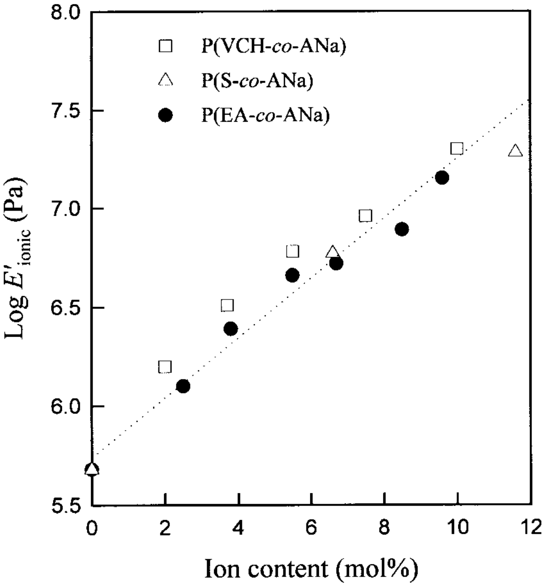

Fig. 2. Ionic modulus for P(EA-*co*-ANa), P(S-*co*-ANa), and P(VCH-*co*-ANa) ionomers as a function of ion content, measured at 1 Hz.

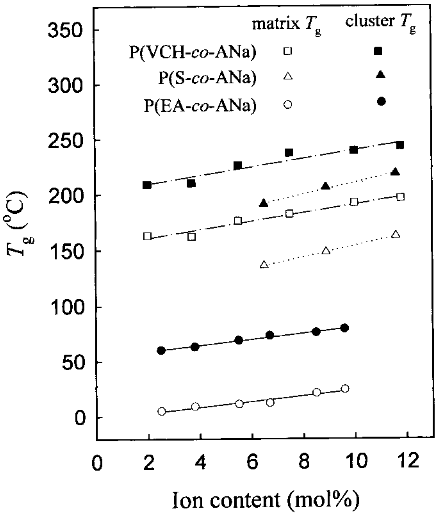

Fig. 3. Matrix and cluster T_gs for P(EA-*co*-ANa), P(S-*co*-ANa), and P(VCH-*co*-ANa) ionomers as a function of ion content, measured at 1 Hz.

[12], and P(S-*co*-ANa) ionomers [12]. As was mentioned before, for the PVCH ionomers the cluster phase became dominant at higher ion content than for the PS ionomers, which means that the PVCH ionomer system is less clustered than the PS ionomer system [12]. In the present study, however, it was found that the ionic modulus values themselves and their rates of increase among three ionomer systems are quite similar. This result shows that for the three ionomer systems small differences in the degree of clustering change ionic modulus significantly. Ionic modulus data as a function of temperature can be fitted with a first order polynomial, and the equation is as follows:

$$\text{Log } E_{\text{ionic}} \text{ (Pa)} = 5.7 + 0.15 \times (\text{mol\% of ion content})$$

The matrix and cluster glass transition temperatures of P(EA-*co*-ANa), P(VCH-*co*-ANa), and P(S-*co*-ANa) ionomers are shown in Fig. 3. The increasing rates of the matrix and cluster T_gs as a function of temperature for the P(EA-*co*-ANa) ionomer system are more or less similar to each other; the similitude is also seen for the P(VCH-*co*-ANa) and P(S-*co*-ANa) ionomers. This is not surprising since the polymer materials, showing their glass transitions, in the matrix and cluster regions are the same. Thus, in amorphous and well clustered ionomers of a certain range of ion content, two T_gs are expected to increase linearly with ion content, despite different polymer matrices.

A second interesting finding in the present study is the value difference between the matrix and cluster T_gs, in spite of their similarity in the rates of increase. In the range of ion content investigated in this study, the temperature difference is 49°C for the P(VCH-*co*-ANa) ionomers, 55°C for the P(S-*co*-ANa) ionomers, and 54°C for the P(EA-*co*-ANa) ionomers. This result tells us that if the ionic unit is the same, i.e. sodium acrylate in the present study, in the well clustered ionomer systems with different polymer matrices, the cluster T_g, including ion-hopping, occurs at ca. 50°C higher than the matrix T_g. However, it should be stressed that if the degrees of clustering in two different ionomer systems differ significantly, the temperature difference between the matrix and cluster T_gs is very large [17]. In addition, in the case of the two ionomer systems, having the same matrix but slightly different ionic units, e.g. acrylate and methacrylate, the cluster T_gs of the ionomers differ significantly due to the difference in contact surface area of the chain as shown in polystyrene ionomer case [12]. The contact surface area for the methacrylate is bigger due to the presence of the methyl group on the polymer main chain than that for the acrylate, and thus the multiplets in the methacrylate ionomers are smaller than those in the acrylate ionomers. Therefore, the cluster T_g for the methacrylate ionomers should be higher than that for the acrylate ionomers.

With a careful look at the data, it is also seen that the temperature divergence between the two T_gs in the PVCH ionomer is somewhat smaller than those in the PEA and PS ionomers. This is owing to the high glass transition temperature of PVCH polymer matrix, as was suggested before [12]. That is to say, the high matrix T_g of the PVC polymer makes fewer multiplets, which, in turn, leads to this ionomer less clustered. However, for the reason why the size of the gap between the matrix and cluster T_gs turns out to be so similar for the PEA and PS ionomers, we do not have any plausible explanation. At this point, it should be mentioned that the glass transition temperatures of ionomers are strongly affected by such factors as the size and stability of multiplets [14], ion content [8,14,16–27], type and size of cation [8,14,18], persistence length [5,7,28,29], and type of polymer matrix [5,19,20,24,27], etc.

Fig. 4 shows the areas under the matrix and cluster loss

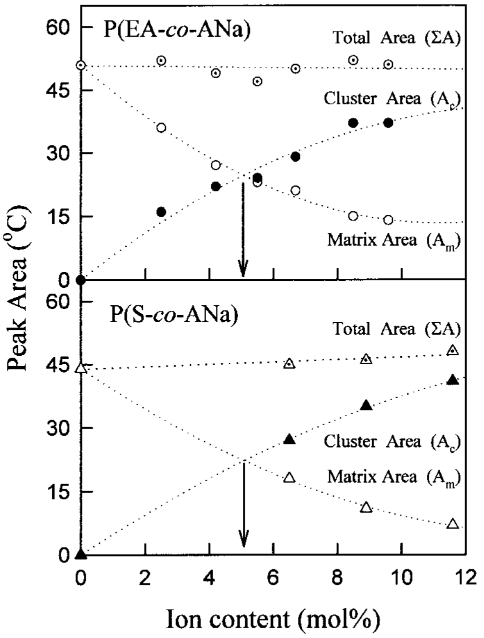

Fig. 4. Areas under matrix (A_m) and cluster (A_c) tan δ peaks and the sum of the areas (ΣA) for P(EA-*co*-ANa) and P(S-*co*-ANa) ionomers as a function of ion content, measured at 1 Hz.

tangent peaks for the PEA and PS ionomers as a function of ion content. It is clearly seen that for the two ionomers the cluster phase becomes dominant at ca. 5 mol%. This result also shows the similarity between the PEA and PS ionomer systems extends to their areas. It is worth recalling that for the poly(styrene-*co*-sodium methacrylate) [P(S-*co*-MANa)] and P(VCH-*co*-ANa) ionomers the cluster phase becomes dominant at ca. 4 mol% and ca. 9 mol%, respectively [12,16]. This means that the P(S-*co*-MANa) ionomer is more clustered than the P(S-*co*-ANa) or P(EA-*co*-ANa) ionomers, while the P(VCH-*co*-ANa) ionomer is least clustered. Thus, the varying degrees of clustering for these four ionomer systems are due to the difference in contact surface area for the first three of them and to the higher glass transition temperature of polymer matrix for the last one.

At this point, it should be recalled that the polarity values of the two relatively non-polar PEA and PS homopolymers are 0.184 and 0.168, respectively [13]. Since the polarity values of PEA and PS polymers are very similar, the balancing factors controlling the degree of clustering could be the persistence length of polymers and the size of multiplets. Since the glass transition temperature of the PEA polymer is lower than that of the PS polymer, the PEA polymer chain moves more easily than the PS polymer chain does. Thus, the PEA ionomer forms bigger multiplets than the PS ionomer does. If this is the case, the number of multiplets is smaller for the PEA ionomers than for the PS ionomers; this, in turn, results in longer inter-multiplet distances. Tong and Bazuin found in the SAXS study that the Bragg distance between multiplets for the P(EA-*co*-ANa) ionomers containing 5 and 10 mol% of ions was ca. 23 Å [11]; Kim et al. found that the Bragg spacing for the P(S-*co*-ANa) ionomer containing 7 mol% of ions was ca. 22 Å [12]. Thus, if the persistence lengths of the PEA and PS ionomers were assumed to be the same, the PEA ionomers would be expected to be less clustered than the PS ionomers. However, our experiment in the present study demonstrated the contrary, i.e. the similitude of clustering for the two ionomer systems. Therefore, we put forward a conjecture that the persistence length of the PEA ionomer might be longer than that of the PS ionomer. Further studies need to be carried out to support or reject this conjecture.

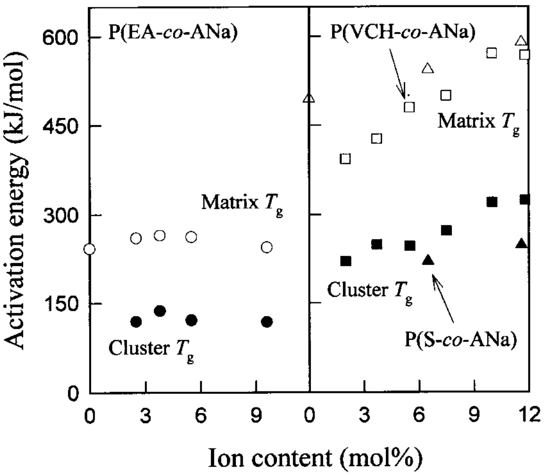

Fig. 5. Activation energies for the matrix glass transition (unfilled) and cluster glass transition (filled) of P(EA-*co*-ANa) (●,○), P(S-*co*-ANa) (▲,△), and P(VCH-*co*-ANa) (■,□) ionomers as a function of ion content.

Shown in Fig. 5 are the activation energy (E_a) values, calculated in the way as indicated in Experimental section, for the matrix and cluster glass transitions of the three ionomer systems. The E_a values for the matrix and cluster glass transitions of the P(EA-*co*-ANa) ionomers do not change significantly with ion content. However, as was found before, the E_a values for the glass transitions of the P(VCH-*co*-ANa) and P(S-*co*-ANa) ionomers seem to increase with increasing ion content [12]. From Fig. 5, it is worth noting that the E_a values for the cluster T_g are approximately a half of those for the matrix T_g. This trend is also evident in the P(S-*co*-MANa) ionomers within the ion content range studied in the present study [16]. It should also be mentioned that the matrix and cluster E_a values for the P(EA-*co*-ANa) are smaller than those for the PS and PVCH ionomers. One possible reason for this trend is the low glass transition temperature of the PEA polymer matrix. Since the PEA has a lower T_g than the PS and PVCH polymers, the PEA needs a lower E_a value for the glass transition. However, this is still inconclusive at this stage since the E_a values are not determined solely by the glass transition temperatures of ionomers, but probably affected by a number of factors such as degree of clustering, the strength between ionic groups, the size of multiplets, the glass transition temperature of polymer matrix, crystallinity, etc. [5].

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