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Clustering in poly(methyl acrylate) ionomers

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Abstract

Dynamic mechanical properties of poly(methyl acrylate-*co*-sodium acrylate) ionomers were studied. It was found that the 'ionic' modulus of the poly(methyl acrylate) (PMA) ionomers was lower than that for the poly(styrene-*co*-sodium methacrylate) (PS) ionomers at the same ion content. This implies that the PMA ionomer is less clustered than the PS ionomer, which is explained in terms of the differences in the glass transition temperature and polarity of the polymer matrix. It was also found that the increasing rates in the matrix and cluster T_gs of the PMA ionomers were similar to those of the PS ionomers. However, the difference in the matrix and cluster T_gs was higher for the PS ionomer than for the PMA system because of the lower clustering of the PMA ionomers.

Keywords: Poly(methyl acrylate); Ionomer; Cluster

1. Introduction

Since their introduction ca. 35 years ago, the properties of ionomers have received substantial attention [1–10]. Due to ionic interactions, these polymers have unique physical properties, which make them interesting from both industrial and academic points of view. According to the multiplet/cluster (or EHM) model [11], ionic aggregates, i.e. multiplets, restrict the mobility of ionomer segments surrounding them. With increasing ion content, the number and size of regions of restricted mobility increase and the regions start to overlap. At a certain ion content, the overlapping regions of reduced mobility become large enough to exhibit their own glass transition; these regions are called clusters [11]. Now, this material starts to show two glass transitions (T_gs); the one at the lower temperature is the T_g of the matrix regions, and the other at the higher temperature is the T_g of the cluster regions. A few other models have also been proposed [12,13].

Recently, the morphology and mechanical properties of a series of poly(methyl methacrylate) (PMMA) ionomers were investigated [14–21]. In poly(methyl methacrylate-*co*-sodium methacrylate) [14] and poly(methyl methacrylate-*co*-sodium acrylate) [21] ionomer systems, two glass transitions were observed. The positions of the two T_gs shifted to higher temperatures with ion content. The total area under tan δ peaks was also seen to decrease with ion content. From the above studies, it was also found that these two ionomer systems show only weak clustering. This weak clustering is attributed to the high T_g and relatively high polarity of PMMA matrix, which reduce the formation of multiplets, resulting in weak clustering.

In the present study, we prepared new ionomers, poly(methyl acrylate-*co*-sodium acrylate), and investigated their dynamic mechanical properties. We also compared the mechanical properties of this ionomer system to those of poly(styrene-*co*-sodium methacrylate) and of poly(methyl methacrylate-*co*-sodium methacrylate) ionomers. These three ionomer systems have the same ionic moiety, i.e. sodium methacrylate. The ionic modulus, glass transition temperatures, and activation energies for the glass transitions of the three ionomer systems were studied, and the results were discussed on the basis of the T_gs and polarity values of the polymer matrix.

2. Experimental

2.1. Polymer synthesis

Poly(methyl acrylate) (PMA) and poly(methyl acrylate-*co*-methacrylic acid) [P(MA-*co*-MAA)] samples

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($MW = \text{ca. } 300{,}000$) were prepared by solution polymerization of purified methyl acrylate and methacrylic acid monomers using benzoyl peroxide as the initiator. Dried and distilled tetrahydrofuran was used as the solvent, and the reaction temperature was 60°C. The conversion was less than ca. 10%, yielding a compositional heterogeneity of less than 0.1. The polymer samples were recovered by precipitation into a rapidly stirred excess of methanol. The precipitated polymer was filtered, and dried under vacuum at 70°C 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 ca. 5% (w/v) solution and titrated with standard NaOH solution in methanol to the phenolphthalein end point.

2.2. Sample preparation

The P(MA-*co*-MAA) samples were dissolved in a benzene/methanol (9/1 v/v) mixture to give a ca. 5% (w/v) solution. To neutralize the acid groups, a predetermined quantity of methanolic NaOH was added to give poly (methyl acrylate-*co*-sodium methacrylate) [P(MA-*co*-MANa)]. The solutions were freeze-dried and then dried under vacuum at 70°C for at least 1 day.

For the dynamic mechanical thermal analysis (DMTA) experiments, P(MA-*co*-MANa) ionomer samples were compression-molded at 50–70°C, depending on the ion contents, under the pressure of ca. 20 MPa. The sample was removed and annealed for 1 day in a vacuum oven at 70°C, which proved to be sufficient for the ionomers to have a stable structure [22–24]. The PMA homopolymer was molded and annealed at ca. 50°C. The dimensions of the molded sample were ca. 2.5 × 7.0 × 30 mm.

2.3. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical property measurements were performed on a Polymer Laboratories DMTA Mark II. The experiments were carried out in the dual cantilever bending mode at frequencies ranging from 0.3 to 5 Hz. The storage moduli (E') and loss tangents (tan δ) were obtained as functions of temperature at a heating rate of 1°C/min. Activation energies for the matrix and cluster T_gs were calculated using an Arrhenius plot of log(frequency) vs inverse temperature.

3. Results and discussion

Shown in Fig. 1 are the storage moduli (E') and loss tangents as functions of temperature at 1 Hz for PMA homopolymer and [P(MA-*co*-MANa)] ionomers. The E' value for the PMA polymer starts to drop rapidly from ca. 15°C; above 50°C, the sample starts to flow. For the P(MA-*co*-MANa) ionomers, the storage modulus value changes from glassy modulus, to glass transition, to 'ionic' modulus, to glass transition, and to rubbery modulus. As expected, the temperature at which the storage modulus starts to decrease shifts to a higher temperature with increasing ion content. It is also seen that the 'ionic' modulus values increase as ion concentration increases. For example, the ionic modulus for the P(MA-*co*-MANa) containing 3.3 mol% of ions is ca. 2.5×10^6 Pa (at 57°C), while that for the 9.4 mol% ionomer is 4.0×10^7 Pa (at 71°C).

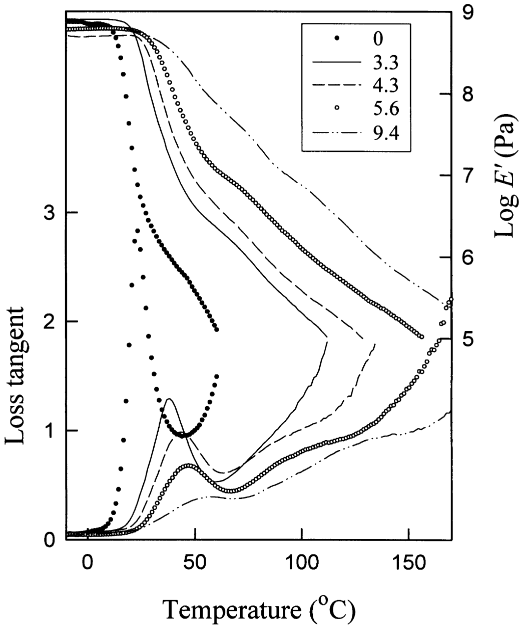

Fig. 1. Storage moduli (E') and loss tangents, measured as functions of temperature at 1 Hz, for PMA and several P(MA-*co*-MANa) ionomers. The molar ion content is indicated for each sample.

In Fig. 1, two loss tangent peaks for each ionomer sample are seen; one peak at lower temperatures is due to matrix glass transition, while the other at higher temperatures is due to cluster glass transition [11]. It is seen that a matrix loss tangent peak shifts to higher temperatures, whereas the size of the peak decreases with increasing ion contents. A cluster loss tangent peak shown as a shoulder or a broad peak in the temperature range of ca. 70–150°C shifts to higher temperatures with increasing ion concentration.

Shown in Fig. 2 are the ionic moduli of poly(methyl methacrylate-*co*-sodium methacrylate) [P(MMA-*co*-MANa)] and poly(styrene-*co*-sodium methacrylate) [P(S-*co*-MANa)] ionomers vs ion content along with those of P(MA-*co*-MANa) ionomers. As mentioned above, it should be noted that these three ionomer systems have the same ionic group, i.e. sodium methacrylate (MANa). What is also common to the three ionomer systems is their annealing condition; all the ionomers were annealed at a temperature ca. 50°C higher than their respective matrix T_gs. Thus, the sharing of the same ionic group and annealing condition provides a sound basis for the comparison among the three ionomer systems. The differences between these three systems are the glass transition temperatures and polarities of the polymer matrix. The T_gs of PS, PMMA, and

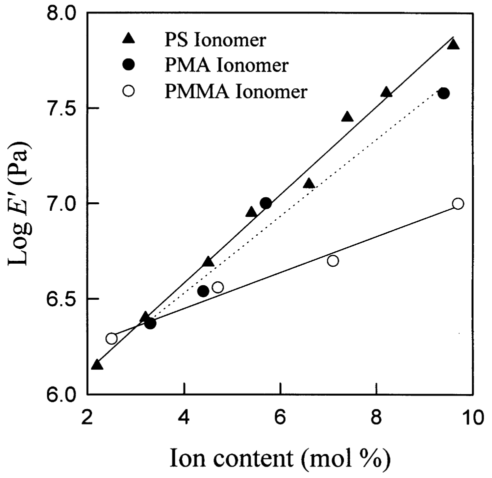

Fig. 2. Log(ionic modulus) as a function of ion content at1 Hz for the P(S-*co*-MANa), P(MA-*co*-MANa), and P(MMA-*co*-MANa) ionomers.

PMA are ca. 100, 105 and 10°C, and the polarities of those homopolymers are 0.168, 0.282 and 0.248, respectively [25]. Thus, if one compares the clustering in P(S-*co*-MANa) ionomers with that in P(MMA-*co*-MANa) ionomers, one will expect that more clusters form for the P(S-*co*-MANa) ionomers [14,19,21]. This is due to the fact that the polar PMMA backbone will dissolve ionic aggregates, thus resulting in weaker or fewer multiplets [19,21]. However, if one compares the clustering in the P(MA-*co*-MANa) ionomers with that in P(MMA-*co*-MANa) ionomers, one will expect more clustering in the PMA-based ionomers; since the T_g and polarity of the PMA are lower than those of the PMMA, it is easier for the P(MA-*co*-MANa) ionomers than for the P(MMA-*co*-MANa) ionomers to form multiplets. In the figure, it is seen that at ca. 8 mol% of ions, the ionic modulus is higher for the PS-based ionomer, and it is lower for the PMMA-based ionomer. This finding implies that the order of the degree of clustering is as follows: P(S-*co*-MANa) ionomers > P(MA-*co*-MANa) ionomers > P(MMA-*co*-MANa) ionomers. From the comparison between the PS-based ionomers and the PMA-based ionomers, it should be stressed that the decrease of T_g by as much as 90°C does not lead to the formation of sufficient clustering, unless the former is accompanied by a substantial decrease of polarity.

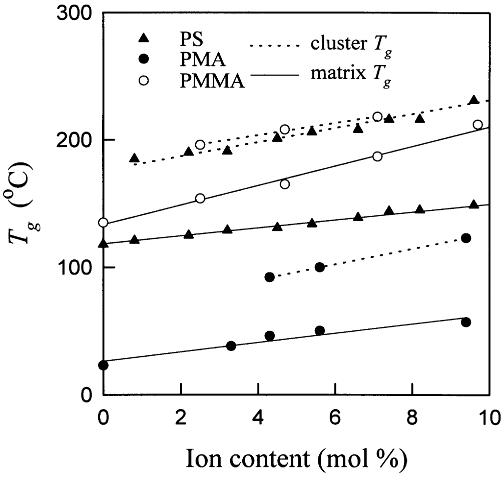

Fig. 3. Glass transition temperatures of matrix and cluster regions, as functions of ion content, measured at 1 Hz, for the P(MMA-*co*-MANa), P(S-*co*-MANa), and P(MA-*co*-MANa) ionomers.

In Fig. 3, the glass transition temperatures of the matrix and cluster regions are shown for the above three ionomer systems as a function of ion content. As was discussed before, the matrix and cluster T_gs progressively increase with increasing ion content. However, the increasing rates of the T_gs and the size of divergence between the matrix and cluster T_gs are different for each ionomer system. Data can be fitted with a first order polynomial. The equations for the matrix and cluster T_gs are as follows:

For the P(MMA-*co*-MANa) ionomers [21],

Matrix $T_g = 133°C + 7.8°C \times$ (mol% of ion content) ($r^2 = 0.989$),

Cluster $T_g = 185°C + 4.8°C \times$ (mol% of ion content) ($r^2 = 0.994$),

for the P(S-*co*-MANa) ionomers [26],

Matrix $T_g = 118°C + 3.3°C \times$ (mol% of ion content) ($r^2 = 0.997$),

Cluster $T_g = 173°C + 6.1°C \times$ (mol% of ion content) ($r^2 = 0.998$),

for the P(MA-*co*-MANa) ionomers,

Matrix $T_g = 26°C + 3.7°C \times$ (mol% of ion content) ($r^2 = 0.925$),

Cluster $T_g = 66°C + 6.0°C \times$ (mol% of ion content) ($r^2 = 0.999$),

where r^2 is the linear least-squares correlation coefficient. The above findings tell us that the increasing rates of the matrix and cluster T_gs of the P(S-*co*-MANa) ionomers as functions of ion content are similar to those of the P(MA-*co*-MANa) ionomers. This may suggest that the degree and nature of clustering in the P(MA-*co*-MANa) ionomers are not very different from those in the P(S-*co*-MANa) system. It should be noted that the increasing rates of the T_gs for the PMMA-based ionomer system differ from those for the PS- and PMA-based ionomer systems. This is not surprising if one considers that the PMMA-based ionomers are very weakly clustered materials unlike the other two ionomer systems [14,19,21]. The fitting results also show that differences in the matrix and cluster T_gs are ca. 55 and 40°C for the PS- and PMA-based ionomers, respectively. At this point, it is worth recalling that Kim et al. [27] found that the difference in the matrix and cluster T_gs depends on the nature of ionic groups and the size of multiplets. As ionic interactions between ionic groups become stronger and as the size of multiplets becomes smaller, resulting in more clusters, the difference in the two T_gs widens. The present study shows that the P(MA-*co*-MANa) ionomers are less clustered than the P(S-*co*-MANa) ionomers, and thus the

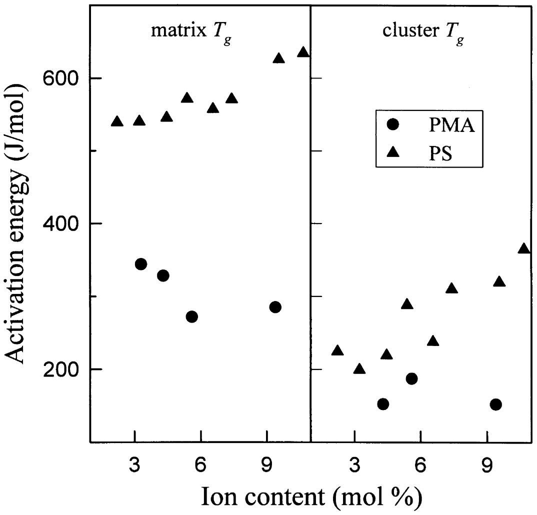

Fig. 4. Activation energies for the matrix and cluster transitions of the P(S-*co*-MANa) and P(MA-*co*-MANa) ionomers as functions of ion content.

difference between the two T_gs should be smaller for the P(MA-*co*-MANa) ionomer system than for the P(S-*co*-MANa) ionomer system, which is indeed the case here. This trend can also be expected on the basis of the EHM model [11] and the work of Hird and Eisenberg on the size and stability of multiplets [28].

The activation energies (E_as) for the matrix and cluster T_gs of two clustered ionomers, i.e. PMA- and PS-based ionomers [26], are shown in Fig. 4 as functions of ion content. The E_as for the matrix T_g of the P(S-*co*-MANa) ionomers increases from ca. 550 to 650 kJ/mol [26], while that for the P(MA-*co*-MANa) ionomers decreases from ca 350 to 270 kJ/mol with increasing ion content. The E_a for the cluster T_g of the P(S-*co*-MANa) ionomers increases from ca. 200 to 350 kJ/mol [26], while that of the P(MA-*co*-MANa) system is not changed significantly with increasing ion content. It is worth noting that the E_a values for two T_gs of the PMA-based ionomer system are lower than those for the PS-based ionomer system, i.e. the PMA-based ionomers need smaller activation energies for glass transitions. This is reasonable because the PMA-based ionomers have less clustering and lower matrix T_gs than the PS-based ionomers, which require lower energies for the transition. At this point, it should be remembered that one is to be careful when dealing with activation energies for the T_gs in ionomers. To discuss the E_as for the glass transitions in ionomers, one has to consider the T_g of the matrix, the strength of ionic interaction, and the degree of clustering, etc. simultaneously [26].

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