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Dynamic mechanical properties of weakly clustered poly(styrene-*co*-sodium citraconate) ionomers

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Summary

The properties of poly(styrene-*co*-citraconate) ionomers were investigated dynamic mechanically. It was found that the loss tangent peak for the matrix glass transition decreased with increasing content of ionic units, while the loss tangent peak for the cluster glass transition was barely detectable. However, the ionic modulus values of the citraconate ionomers as a function of the amount of ionic units were comparable to those of well-clustered methacrylate ionomers. Thus, it was postulated that the ionic modulus was affected by both clustering due to the overlapping of regions of restricted mobility and strong physical cross-links originated from the ionic association of ca. 4 ion pairs.

Introduction

Ionomers are polymers containing ionic groups, which form ionic aggregates through ionic bonds. The presence of the small amount of ionic group (up to ca. 20 mol%) in relatively non-polar polymers such as polystyrene can give rise to drastic increase in glass transition temperature and conductivity, water uptake, and anomalous viscoelastic behavior [1-4]. It is generally accepted that ionic aggregates, so called multiplets [5], are surrounded by regions of restricted mobility of polymer chains [6]. When an ion content is low, only multiplets are present, and only a matrix glass transition temperature (T_g) is observed. However, when the ion content is high, the restricted mobility regions overlap to form large contiguous regions, which are now called clusters [6]. When the dimensions of clustered regions exceed ca. 100 Å, the ionomer exhibits a second T_g associated with the glass transition of the clustered regions.

A number of studies have been carried out to explore the effect of parameters on the formation of multiplets and clusters in ionomers. The parameters are the ion concentration as well as type, size, and position of ionic groups, etc [4]. However, most of the studies have been devoted to ionomers containing a single ion pair in the ionic repeat unit. Thus, against this lack of studies on polymers containing more than two ion pairs per ionic repeat unit, we investigated in the present study the properties of poly(styrene-*co*-sodium citraconate) ionomers, which contain two adjacent ion pairs in the same ionic repeat unit of the polymer chain. The presence of the two ionic of poly(styrene-*co*-sodium citraconate) ionomers, which contain two adjacent ion pairs in the same ionic repeat unit of the polymer chain. The presence of the two ionic pairs in the same ionic repeat unit was assumed to affect significantly the formation of multiplets and furthermore the clustering of the ionomers.

Experimental

Sample preparation

Poly(styrene-*co*-citraconic anhydride) (MW = ca. 300,000) was synthesized by bulk free-radical polymerization using benzoyl peroxide as the initiator [7]. The anhydride was hydrolized with NaOH in methanol/water to make poly(styrene-*co*-sodium citraconate) [P(S-*co*-CitraNa)] ionomers. The solutions were freeze-dried and then dried under vacuum at 130 °C for at least 24 h. To determine the ion concentration, a cation exchange between Na^+ and H^+ was conducted. To do so, the ionomer was dissolved in THF/methanol, and then a few drops of hydrochloric acid were added to the solution. The acid form sample was dissolved in a benzene/methanol (90/10, v/v) mixture to make a 5% (w/v) solution, and titrated with standard methanolic NaOH to the phenolphthalein end point.

For the DMTA measurements, the samples were compression-molded at ca. 270 °C with a pressure of ca. 20 MPa. The molded samples, with approximate dimensions of 2.5 x 6.0 x 30.0 mm, were annealed for 24 h in a vacuum oven at 130 °C.

Dynamic mechanical thermal analysis

In order to measure dynamic mechanical properties of ionomers, we employed the Dynamic Mechanical Thermal Analyzer (DMTA, model Mark II), developed by Polymer Laboratories. The measurements were performed in a dual cantilever bending mode at frequencies of 0.3, 1, 3, 10 and 30 Hz, and the heating rate was 1 °C/min. For each sample the storage moduli (E') and loss tangents (tan δ) were obtained as a function of temperature over the range of 80—320 °C.

Results and discussion

Shown in Figure 1 are the storage modulus and loss tangent curves of P(S-*co*-CitraNa) ionomer samples as a function of temperature. The modulus values change with increasing temperature from a glassy modulus, through a matrix glass transition, and to a long plateau, the modulus of which is denoted as "ionic modulus"; at high temperature the sample started to flow. It is clear that the ionic modulus values for the ionic plateau increase with increasing content of ionic repeat units. The matrix loss tangent peak shifts to high temperature, and the size of the peak decreases as the ion content increases.

Enlarged loss tangent curves in the temperature range for the cluster glass transition of the P(S-*co*-CitraNa) ionomers containing 4.5 and 7.1 mol% of ionic repeat unit are shown in Figure 2. A very weak but discernible shoulder on the loss tangent curve due to the cluster T_g is observed, and the temperature of the shoulder

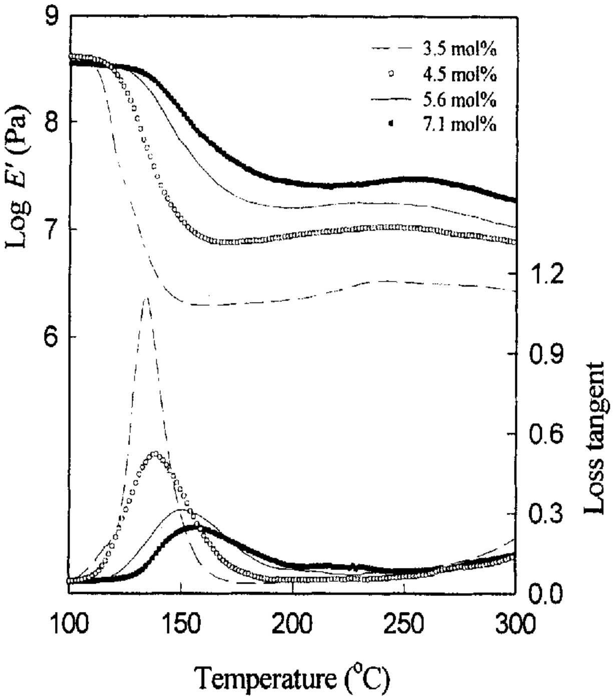

Figure 1. Storage modulus (E') and loss tangent as a function of temperature for P(S-*co*-CitraNa) ionomers. All data were obtained at 1 Hz.

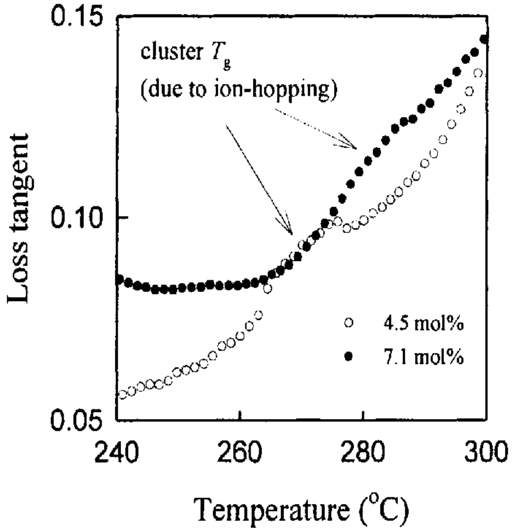

Figure 2. Enlarged loss tangent curves of P(S-*co*-CitraNa) ionomers containing 4.5 and 7.1 mol% of ionic repeat units.

maximum rises with increasing mol% of the ionic repeat units. However, the size of the shoulder seems to remain constant. A very weak loss tangent curve similar to the one observed in the present study was also seen in other weakly clustered ionomer systems, e.g. plasticized poly(methyl methacrylate-*co*-cesium methacrylate) ionomers [8,9], and *p*-hydroxystyrene ionomers [10, 11]. Thus, it can be deduced that the clustering in this poly(styrene-*co*-sodium citraconate) ionomer is also very weak.

Figure 3 shows the matrix and cluster T_gs as a function of content of ionic repeat units. The rate of increase in matrix T_g is 117 °C + 5.6 °C x (mol% of ionic repeat units), while for the cluster T_g it is 255 °C + 3.3 °C x (mol% of ionic repeat units). It should be noted that these increasing rates are quite different from those obtained from poly(styrene-*co*-sodium methacrylate) [P(S-*co*-MANa)] ionomers [12]; where the increasing rates of T_gs are ca. 3.3 and 5.5 °C/(ion content) for the matrix and cluster T_gs, respectively. Although the reason for this difference is not clear at present, it should be remembered that, for the P(S-*co*-CitraNa) ionomers, the number of data is too small to give sufficiently reliable values for the increasing rate of T_g. It is also clear that the divergence between the matrix and cluster T_gs shows differently in these two ionomer systems. At ca. 6 mol% of ionic (or ionic repeat) units, the P(S-*co*-MANa) ionomer system shows ca. 70 °C of divergence, while the P(S-*co*-CitraNa) ionomer system shows ca. 125 °C. This result can be explained by ion-hopping [13-20]. At cluster T_gs, it is believed that three ionic moieties, i.e. two Na^+ cations and one citraconate anion, have to hop at the same time, which is naturally more difficult than the hopping of two ionic groups (e.g. one Na^+ cation and one methacrylate anion). Thus, the cluster T_g is much higher for the citraconate ionomers than for the methacrylate ionomer.

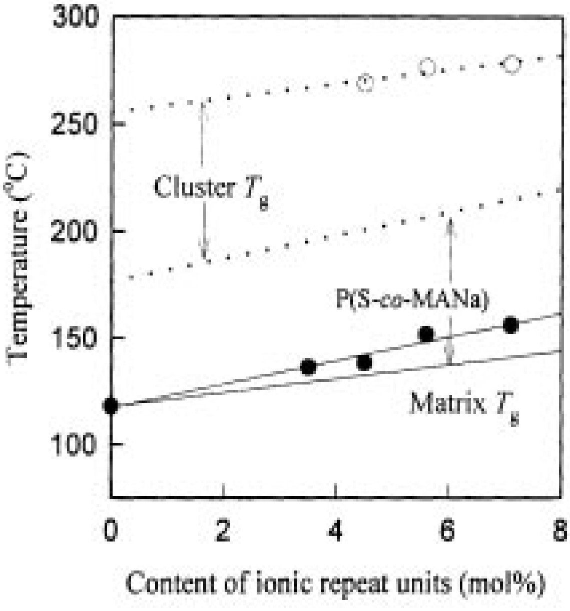

Figure 3. Matrix and cluster T_gs of P(S-*co*-CitraNa) and P(S-*co*-MANa) ionomers as a function of mol% of ionic repeat units.

In Figure 4, the ionic storage modulus values of the P(S-*co*-CitraNa) and P(S-*co*-MANa) systems are shown as a function of mol% of ionic repeat units. Surprisingly, the ionic modulus values for the two ionomer systems are not much different at similar mol% of ionic repeat units. To understand the result, it is useful to look at the loss tangent data carefully. When the loss tangent peak for the matrix glass transition was deconvoluted with an exponential function for a baseline and a Gaussian Area function for the matrix tan δ peak [12], peak-fitting results were obtained as follows:

Table 1. Peakfit results for P(S-*co*-CitraNa) ionomers

Content of ionic repeat units (mol%)	3.5	4.5	5.6	7.1
Center of the matrix tan δ peak (°C)	135	139	152	156
Width of the matrix tan δ peak at half-height (°C)	7.90	13.2	15.6	16.2
Area of the matrix tan δ peak (°C)	19.2	15.5	10.3	6.9

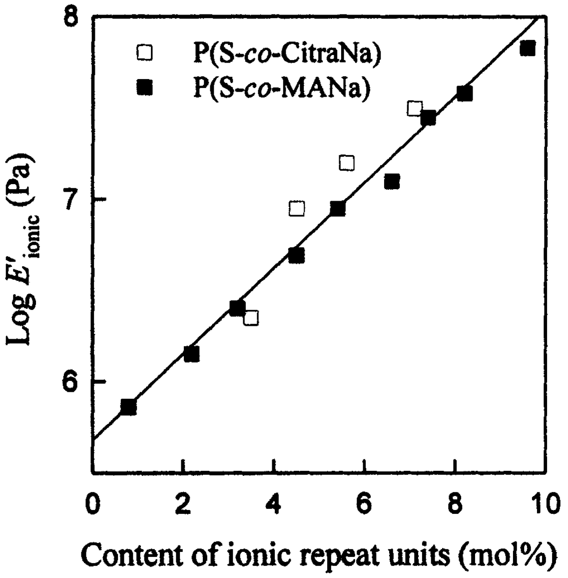

Figure 4. Storage ionic modulus of P(S-*co*-CitraNa) and P(S-*co*-MANa) ionomers as a function of ionic repeat units, measured at 1 Hz.

It should be stressed that there is no fundamental scientific significance in the functions used for the peak fitting, except for the center of a peak, the peak width at half-height, and the area of the peak. The peak width at half-height increases with ion content. This implies that the matrix phase becomes more heterogeneous with increasing ion content. It is also found that with increasing ionic unit content, the area under the matrix tan δ peak decreases significantly, which represents that the amount of the matrix phase decreases drastically. However, it should be stressed that, as mentioned before, the loss tangent peak for the cluster glass transition did not change significantly. Thus, Table 1 and Figure 4 together show that the ionic modulus of the citraconate ionomer increases with increasing content of ionic repeat units not only due to clustering, which is the main reason for the P(S-*co*-MANa) ionomers [12,21], but also due to the relatively more frequent physical cross-links by the presence of citraconate ionic groups in the P(S-*co*-CitraNa) ionomers. Therefore, it can be concluded that the increase in the number of physical cross-links of this type induces the enlargement of the area of restricted mobility in the ionomer. At this point, it should be noted that the nature of the restricted mobility regions is different from that found in the methacrylate ionomer. In the latter case, polymer chains surrounding the multiplets are less mobile due to the crowding. However, in the former case, with increasing ion content more physical cross-links appear, which reduce the mobility of the chains surrounding the ionic aggregates.

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