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Effects of contact surface area of chains on the mechanical properties of poly(methyl methacrylate-*co*-acrylate) ionomers

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Summary

The dynamic mechanical properties of a new ionomer system, poly(methyl methacrylate-*co*-sodium acrylate), were studied. In addition, to investigate the effect of the chemical structure of ionic group on the mechanical properties, the data obtained from the sodium acrylate ionomers were compared to those obtained from sodium methacrylate ionomers. The matrix and cluster T_gs for the methacrylates were found to be higher than those for the acrylates. It was argued that the difference in the T_gs might be explained with the concept of contact surface area of the chain.

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. It is generally accepted that ionic groups aggregate to form multiplets.[11] Eisenberg et al. proposed that restricted mobility regions of polymer chains surround the multiplets.[11] At low ion content, only a few multiplets are present. With increasing ion content, the restricted mobility regions start to overlap; as a result, large contiguous regions of reduction in mobility, called clusters, form.[11] Dimensions of the clusters exceed ca. 100 Å. In this state, ionomers show a second glass transition (T_g), which is associated with the T_g of the cluster regions.

Recently, a series of poly(methyl methacrylate) (PMMA) ionomers were studied.[12-18] Ma et al. found that in a poly(methyl methacrylate-*co*-sodium methacrylate) ionomer system, two glass transitions were observed, for both of which the temperatures increased with ion content.[12] It was also found that total area under tan δ peaks decreased with increasing ion content. However, Gronowski et al. found that in the case of cesium neutralized PMMA ionomers, only one T_g was observed; it was suggested that it might be due to the difference in ionic strength.[15]

Kim et al. studied the effect of a chemical structure of copolymers on the

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mechanical properties of polystyrene ionomers.[19] It was found that the general trends of dynamic mechanical data of styrene-*co*-acrylate ionomers were similar to those of styrene-*co*-methacrylate ionomers. Yet, at the same time, there were some differences shown in these two systems; the higher cluster T_g of the methacrylates than that of the acrylates at the same ion content was a case in point. Kim et al. proposed that this difference was due to the bigger contact surface area of the chain for the methacrylates, which has a methyl group on a α-carbon of an ionic unit, than that for the acrylates.[19]

In the present study, we prepared a new polar ionomer system, i.e. poly(methyl methacrylate-*co*-sodium acrylate) and studied its mechanical properties. To investigate the effects of a contact surface area on the properties of the acrylate ionomer system, we also prepared poly(methyl methacrylate-*co*-sodium methacrylate) ionomers and compared the mechanical data of these two systems.

Experimental

Polymer synthesis

Poly(methyl methacrylate) (PMMA), poly(methyl methacrylate-*co*-acrylic acid), and poly(methyl methacrylate-*co*-methacrylic acid) copolymers were prepared by free-radical solution polymerization using benzoyl peroxide as the initiator and tetrahydrofuran as the solvent. The similar synthesis procedure has been described elsewhere.[20] To determine the acid content, acid copolymers were dissolved in a benzene/methanol (9/1 v/v) mixture and titrated with 0.050N sodium hydroxide solution in methanol to the phenolphthalein end point.

Sample preparation

The acid form sample was neutralized by adding a predetermined amount of methanolic sodium hydroxide to a polymer solution in a benzene/methanol mixture. The solution was freeze-dried and further dried at 150 °C for 1 day under vacuum. The sample notation used for the ionomer is P(MMA-*x*-ANa) for poly(methyl methacrylate-*co*-sodium acrylate) samples and P(MMA-*x*-MANa) for poly(methyl methacrylate-*co*-sodium methacrylate) samples, where *x* is the mol% of sodium acrylate or sodium methacrylate.

For the mechanical study, the samples were compression-molded in a mold at 230-250 °C; a pressure of ca. 25 MPa was applied for 5 min and was slowly released. The mold was allowed to cool to below the matrix T_g. The molded samples, with dimensions of ca. 2.5 x 7.0 x 30 mm, were annealed at 160 °C for 1 day under vacuum.

Dynamic mechanical measurements

The mechanical property measurements were performed using a Polymer Laboratories Mark II dynamic mechanical thermal analyzer (DMTA) in the dual cantilever bending mode, at frequencies of 0.3, 1, 10, and 30 Hz. The heating rate was 1 °C/min. For each sample, the storage moduli (E') and loss tangent (tan δ) were obtained as a function of temperature.

Data analysis

For each sample, a detailed analysis of tan δ peak was carried out on the 1 Hz data only. Peak deconvolutions of tan δ curve were performed using the PeakFit (Jandel Scientific) computer program. The best fits were achieved taking an exponential function as a baseline and fitting matrix and cluster peaks with Gaussian area functions.

Results and discussion

Storage modulus and loss tangent values as a function of temperature for PMMA and poly(methyl methacrylate-*co*-sodium acrylate) [P(MMA-*co*-ANa)] ionomers of various ion contents are shown in Figure 1. With increasing temperature, pure PMMA homopolymer undergoes glass transition at ca. 135 °C and shows rubbery modulus above 150 °C. In the case of P(MMA-*co*-ANa) ionomers, the drops in the modulus curves due to the glass transition shift to higher temperatures with ion contents, and rubbery modulus values become higher. For example, at 230 °C the modulus value for the 3.1 mol% sample is ca. 1.5 x 10^6 Pa, while that for the 12.4 mol% sample ca. 3.2 x 10^7 Pa. It is interesting to note that above ca. 4.5 mol% of ions acrylate ionomers do not show profound flow behavior. As was suggested in the mechanical study of P(MMA-*co*-MANa) system by Ma et al.[12], this absence of the flow behavior in the present study may also be due to the formation of chemical crosslinking at high temperatures.

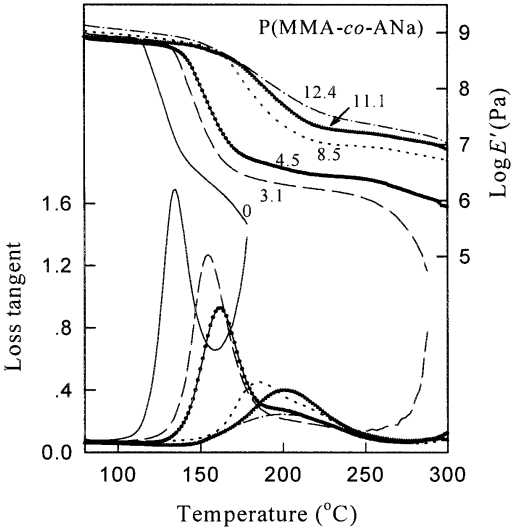

Figure 1.
Storage modulus and loss tangent as a function of temperature for the P(MMA-*co*-ANa) system with ion contents marked near each plot. All data obtained at 1 Hz.

In the figure, the PMMA and the 3.1 mol% ionomer samples show only one matrix tan δ peak at 135 and 155 °C, respectively. For the ionomer containing 4.5 mol% of ions, a matrix peak is shown at 162 °C and a weak cluster peak is shown at 200 °C. In the case of the 8.5 mol% ionomer, the matrix and cluster peaks are shown at 183 and 215 °C, respectively. However, the 11.1 mol% and the 12.4 mol% ionomers show only one tan δ peak. The results of the peak deconvolutions of the tan δ peaks are listed in Table 1. In the table it is seen that areas under matrix and cluster peaks decrease with increasing ion contents; thus, total area (A_{total}) also decreases. From Table 1 and Figure 1, it could be thought that for the ionomers containing ions > 8.5 mol% the cluster tan δ peak would be very small. Therefore, the peak deconvolutions to separate a cluster tan δ peak were not performed for the samples containing ions > 8.5 mol%.

Figure 2 shows modulus and tan δ curves as a function of temperature for

P(MMA-*co*-MANa) ionomers, the trends of which are similar to those of acrylate ionomers. The rubbery modulus is seen to increase with ion contents, and tan δ peaks shift to higher temperatures. In the case of ionomers containing 2.5, 4.7, and 7.1 mol% of ions, the matrix tan δ peak centers at 154, 165, 187 °C, and the weak cluster peak at 196, 208, and 218 °C, respectively. However, for the 9.7 and 12.4 mol% samples, only one tan δ peak is observed at 212 and 227 °C, respectively. Total area under tan δ peaks also decreases with increasing ion contents. The results of curve deconvolutions are also listed in Table 1.

Table 1. Sample notations, glass transition temperatures and tan δ peak areas

Sample	$T_{g,m}$[1] (°C)	$T_{g,c}$[2] (°C)	A_m[3] (°C)	A_c[4] (°C)	A_{total}[5] (°C)
PMMA	135		29.5	--	29.5
P(MMA-3.1-ANa)	155		30.7	--	30.7
P(MMA-4.5-ANa)	162	200	23.7	7.0	30.1
P(MMA-8.5-ANa)	183	215	11.4	9.4	20.8
P(MMA-11.1-ANa)	195	--	18.7	--	18.7
P(MMA-12.4-ANa)	200	--	13.0	--	13.0
P(MMA-2.5-MANa)	154	196	27.9	3.8	31.7
P(MMA-4.7-MANa)	165	208	20.7	6.2	26.9
P(MMA-7.1-MANa)	187	218	15.5	6.6	22.1
P(MMA-9.7-MANa)	212	--	16.6	--	16.6
P(MMA-12.4-MANa)	227	--	--8.6	--	8.6

[1] center of the matrix tan δ peak

[2] center of the cluster tan δ peak

[3] area under the matrix tan δ peak

[4] area under the cluster tan δ peak

[5] $A_m + A_c$

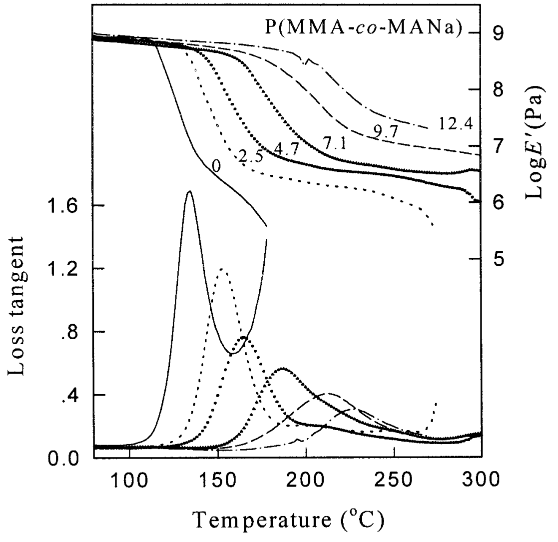

Figure 2.
Storage modulus and loss tangent as a function of temperature for the P(MMA-*co*-MANa) system with ion contents marked near each plot. All data obtained at 1 Hz.

Figure 3 represents A_{total} values as a function of ion content. The A_{total} value decreases with increasing ion content. It should be mentioned that Chang et al. found that tan δ peak area decreased with increasing crosslinking density of PMMA polymer.[21] The same reason might be operative here. In addition, as was suggested by Eisenberg and Kim, methyl methacrylate ionomer more or less behaves like a composite material than a classical ionomer.[10] Thus, in the composite regions, the ionic groups do not form classical multiplet but regions in which ionic groups are coordinated to several carboxylate groups of nonionic PMMA units, with which they interact strongly. Thus, with increasing ion content, the area under the matrix tan δ peak becomes smaller, rubbery modulus increases, and rubbery plateau extends to higher temperatures.

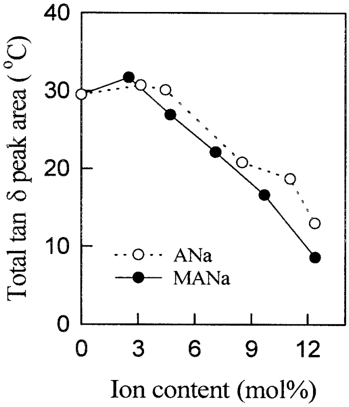

Figure 3.
Total area under tan δ peaks (A_{total}) as a function of ion content for P(MMA-*co*-MANa) and P(MMA-*co*-ANa) ionomers.

Figure 4 shows the matrix and cluster T_g values of the two systems as a function of ion content. The matrix T_g increases at a rate of 5.2 and 7.6 °C/(mol% of ions) for acrylate and methacrylate ionomers, respectively. The rates of increase in the cluster T_gs are 3.7 and 4.8 °C/(mol% of ions) for acrylate and methacrylate ionomers, respectively. It should be mentioned that in the Ma et al.'s study the rate of increase in matrix T_g of P(MMA-*co*-MANa) ionomers was ca. 5.5 °C/(mol% of ions),[12] which does not much differ from the value obtained in the present study. The glass transition temperatures of random copolymers can be calculated using the Fox equation,[22] with which the T_gs of PMMA ionomers were calculated in the present study. To calculate the T_gs, we chose 135, 335, and 255 °C for the T_gs of PMMA, poly(sodium methacrylate), and poly(sodium acrylate) polymers.[23] The calculated data are also shown in Figure 4. From the figure, it is clear that the calculated T_gs are very dissimilar from the experimental data for the matrix and cluster T_gs of the ionomers. This implies that increase in matrix T_gs of two ionomer systems is not simply due to copolymerization effect. It is the formation of multiplets and clusters that probably cause the increase in the T_gs.

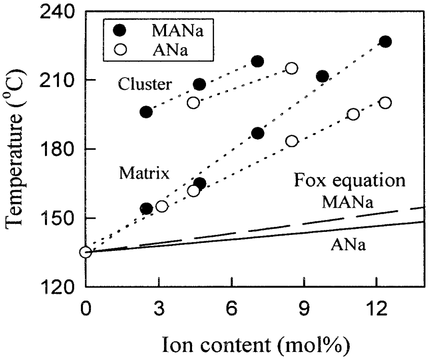

Figure 4.
Matrix and cluster Glass transition temperatures as a function of ion content for the P(MMA-co-MANa) and P(MMA-co-ANa) ionomers. Calculated glass transition temperatures from the Fox equation are also shown.

From Figure 4, it is worth noting that at the same ion content the matrix and cluster T_gs of the methacrylate ionomers are higher than those of the acrylate ionomers. In addition, the increase rates of the T_gs for the methacrylate ionomers are also higher than those for the acrylate ionomers. It should also be pointed out that in the methacrylates even 2.5 mol% ionomer showed a cluster T_g, while in the acrylates the 3.1 mol% sample no cluster T_g was observed. At this stage, let us ask why the differences in the T_gs and mechanical properties are observed in these two systems; to answer this question is one of main objectives in this study. The only difference in the chemical structures of these two systems lies in the nature of the ionic repeat units, i.e. acrylate vs. methacrylate. The difference between the two ionic units is the presence of a methyl group on the α-carbon of an ionic unit. This methyl group affects the contact surface area of a chain, i.e. the area of chain segments which are connected to the pendant ion and which cannot get out of the way in the formation of the multiplet. Because the ion pairs are identical, i.e. sodium carboxylate, the radius of the multiplet is inversely related to the contact surface area of the chain. Based on the concept of the contact surface area of a chain, one can suggest that the number of ion pairs per multiplet in the acrylate ionomer would be somewhat larger than that in the methacrylate system. Therefore, the size of multiplets for the acrylates is slightly larger than for the methacrylates. As a result, there are fewer multiplets in the acrylates, which means less clustering; this results in lower T_gs in the acrylates than in the methacrylates.[24,25] This is, indeed, found to be the case in the present study.

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