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Molecular Weight Dependence of the Viscoelastic Properties of Polystyrene-Based Ionomers

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ABSTRACT: The molecular weight dependence of the viscoelastic properties of polystyrene-based ionomers was examined. To measure the physical properties, a Rheometrics dynamic analyzer (RDA) was utilized for the poly(styrene-*co*-sodium methacrylate) (4 mol %) system, while for the poly(styrene-*co*-sodium styrenesulfonate) samples (5 mol %) the studies were performed on a dynamic mechanical thermal analyzer (DMTA). In the methacrylate samples of high molecular weight (>100 000), the plot of tan δ vs temperature showed two peaks, as in other ionomers. However, for samples of the lowest molecular weight (ca. 21 000), the tan δ plot showed only one peak and a shoulder. Peak deconvolution, however, showed that, even in that sample, there are two peaks and that the deconvoluted peak areas do not change significantly with molecular weight. The flow behavior of the matrix in the low molecular weight samples partially masks the relaxation process of the clusters. In the terminal region, the viscosities of the ionomers are molecular weight dependent in a way similar to that in nonionic polystyrene; above the critical molecular weight for entanglements, compliance values of the ionomers are independent of the molecular weight. In the case of the sulfonates, many trends are similar to those seen in the methacrylates. As the molecular weight increases, the cluster tan δ peak becomes more visible, and slopes of storage modulus curves in the terminal region become less steep. However, there are some differences, which are due to the difference in the strength of the interaction between ionic groups in the multiplets. In the methacrylates, because of weaker interactions, the ionomers start to exhibit appreciable ion-hopping and chain mobility at a relatively low temperature (ca. 170 °C), which is the onset of the glass transition (T_g) of the cluster phase and is only ca. 50 °C higher than the matrix T_g. Above that temperature, the multiplets can no longer act as long-term cross-links, and the ionomers show a strong molecular weight dependent behavior. On the other hand, in the sulfonates, due to the stronger interaction, ion-hopping becomes important only at much higher temperature (ca. 220 °C), which is, again, the beginning of the cluster T_g; above that point these ionomers also start to show appreciable molecular weight dependent behavior. In addition, in the sulfonates, the activation energies for the matrix and cluster transitions and for ion-hopping are independent of the molecular weight. All these results suggest that the stability of multiplets is independent of the molecular weight. The thermal stabilities of the present ionomers are similar to that of polystyrene.

I. Introduction

Since their introduction ca. 30 years ago, the mechanical properties of ionomers in general,[1–8] and melt rheology in particular,[8–20] have received considerable attention. Poly(styrene-*co*-methacrylic acid)[21–31] and/or poly(styrene-*co*-styrenesulfonic acid) systems[29–40] were the subject of extensive studies. The rheological and other mechanical properties of these ionomers are governed by ion association leading to the formation of multiplets and clusters.[41,42] At very low ion contents, only multiplets are formed; as the ion contents increase, clustering of multiplets becomes important. The clusters are composed of multiplets surrounded by overlapping regions of reduced mobility, with total dimensions exceeding ~100 Å. Once clusters form, the material shows a second glass transition attributed to the restricted mobility regions; enhancement of mechanical properties is also observed. This is discussed extensively in a recent publication which deals with the multiplet/cluster model (the EHM model) of random ionomers and also addresses other models of ion aggregation.[42]

The strength of the ionic association depends on the ionic species. For example, it has been reported that ionic sulfonate groups affect the properties of ionomers more strongly than ionic carboxylate groups.[30–32,34,36,43–45] The sulfonate groups form clusters, the effects of which persist to much higher temperatures than those of the carboxylates.

The viscoelastic properties of the ionomers have been investigated in relation to the ion content, nature of the ionic groups, backbone type, etc. Because of the strong ion aggregation, the rheology of the material is affected dramatically by the presence of ions. Thus, in view of the industrial concerns with processability, the viscoelasticity of ionomers has become an area of some interest in its relation to the detailed material compositions. In terms of model studies, polystyrene (PS)-based ionomers have some advantages over other systems, because of their ease of synthesis, ease of control of the molecular weight and polydispersity, absence of crystallinity, ease of functionalization, ease of copolymerization, etc. This is one of the reasons why the styrene ionomers have received considerable attention in the past.

Eisenberg and Navratil performed an early systematic survey of the mechanical properties of poly(styrene-*co*-metal methacrylate) ionomers in the bulk.[23–25] They reported that plots of the relaxation modulus or the loss tangent as a function of temperature showed evidence of the existence of two glass transitions which were attributed to the polystyrene matrix and the cluster regions. In the modulus–time plots two inflection points were also observed. This behavior depended only on the ion contents and types of cation species and was independent of the molecular weight in their experimental range. The molecular weight affected only the length of the rubbery plateau attributed to chain entanglements as well as the

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terminal region. They also showed that time–temperature superposition did not apply to ionomers with an ion content higher than ca. 6 mol %.[23,24] Shohamy and Eisenberg[11] studied the melt rheology of the poly(styrene-*co*-sodium methacrylate) ionomers [P(S-*co*-MANa)] and reported that the terminal region behavior of P(S-*co*-MANa) showed exactly the same shape as that of the nonionic poly(styrene-*co*-methyl methacrylate) of the same molecular weight. It was also shown that dynamic modulus curves in the terminal region can be superimposed on each other by shifting them along the temperature axis, with shifts, ΔT, which depend only on the ion contents.[11]

The melt rheological properties of other ionomers have also been studied, e.g., ethylene–methacrylate ionomers,[7,9,12] sulfonated ethylene–propylene–diene terpolymers,[13,19] propylene–acrylate ionomers,[14] alkyl-substituted ammonium-neutralized sulfonated polystyrene ionomers,[16] poly(ethylene terephthalate)-based ionomers,[20] and α,ω-bis(dimethylamino)polyisoprene telechelic ionomers.[46] Erhardt et al.[10] studied the viscoelastic properties of partially hydrolyzed poly(styrene-*co*-*n*-butyl methacrylate) ionomers. They found that at high molecular weight (>100 000) there are appreciable chain entanglements which affect significantly the limiting viscosity at zero shear rate (η_0) and that the ion pairs play a less important role on η_0. They also found that the rate of the increase in the log(viscosity) with ion content increases with decreasing molecular weights. Bagrodia et al.[17] investigated the effect of molecular weight on the triarm sulfonated polyisobutylene ionomers, i.e., telechelic ionomers which contained one ionic group only at each chain end. They found that the zero-shear viscosity increases with an increase in the molecular weight.

In the sulfonated polystyrene ionomers, the influence of the strong ion aggregation on viscoelasticity has also been investigated. Rigdahl and Eisenberg,[34] Hara et al.,[37,38] Weiss et al.,[39,40] and Hird and Eisenberg[30] have studied the effect of ion content on the viscoelastic properties. Again, two glass transitions are seen: one attributed to the ion-poor phase and the other to the ion-rich phase. As was observed for the methacrylates, the positions of both T_g's increase with increasing ion contents; peak heights related to the glass transition of the matrix phase decrease with increasing ion contents, while those due to the clusters increase.[38] In comparison to the *para*-carboxylated polystyrene ionomers, Lundberg and Makowski[32] reported a higher melt viscosity and Hird and Eisenberg[30] showed a wider rubbery plateau for the sulfonated polystyrene ionomers than for the carboxylated polystyrene ionomers.

As a part of an extensive series of studies of the methacrylate ionomers, it was observed that, under some conditions, no cluster peaks were seen in the loss tangent curve in spite of the fact that the ion content was high enough so that the cluster peak should have been present judging from the previous results. After extensive investigations of the possible reasons for the absence of the cluster peak, it was concluded that a molecular weight effect was responsible for the phenomena. Therefore, since no previous publication has appeared dealing specifically with a study of the molecular weight effect on viscoelastic properties of ionomers, it was believed that such an investigation was timely. This publication is devoted to the description of this study.

In parallel with the rheological study, the thermal stabilities of the styrene ionomers were investigated using a thermogravimetric analyzer (TGA) as a part of the present work. The results showed that the thermal stabilities of unfunctionalized polystyrene and styrene-based ionomers were almost identical, as will be discussed in detail in the discussion section. Thus, above 280 °C, the ionomers start to decompose thermally. Therefore, one cannot perform the experiments on these ionomers at that high a temperature over an extended period of time. As was pointed out before, however, the viscoelastic properties of these ionomers, i.e., the sulfonates and methacrylates, are dominated by the ionic interactions, which are stronger in the sulfonates than in the carboxylates. Thus, the second glass transition temperature in the sulfonate case does not occur until ca. 250–280 °C for ion contents of ca. 5%. It is much higher than that of methacrylate ionomers, in which the second T_g is in the range of ca. 190–210 °C for the same ion contents. Therefore, some thermal decomposition may occur during the measurement on the sulfonates at that high temperature. To circumvent this complication, different instruments were used to study the sulfonates and the methacrylates. These two instruments are the dynamic mechanical thermal analyzer (DMTA) and the Rheometrics dynamic analyzer (RDA-II or rotational melt rheometer, RMR). Measurements on these two instruments are complementary. The DMTA is used primarily for polymers in the solid state, especially in the bending mode, where the moduli of the samples should be higher than ca. 10^5 Pa. An oscillatory shear mode is also available for lower moduli. On the other hand, the RMR is designed for polymers in the molten state, and thus it is difficult to measure the moduli of stiff samples (over 10^7 Pa) with parallel plate geometry. Even though the sensitivity of the RMR is suitable for the study of viscoelasticity from the rubbery region to the terminal region, a high temperature was required for placing the samples between the plates of the rheometer. The RMR measurement also necessitates a long residence time of the sample at high temperature during the measurement. These factors may result in thermal degradation of some polymers. If one tries to use the RMR for the sulfonates, one needs to heat the samples far above 280 °C, which is the cluster T_g and is close to the decomposition temperature. Thus, sulfonated polystyrene would be subject to considerable degradation if the RMR were to be used for the type of study performed here. By contrast, however, the temperature sweeps in the DMTA can be performed reasonably rapidly so that thermal degradation could be minimized in the sulfonates by using the DMTA. Therefore, for the sulfonates, the DMTA was utilized as the experimental technique, while for the methacrylates, the RMR was used.

In the present publication, the first part of the presentation is devoted to a discussion of the melt rheology data obtained on a series of P(S-*co*-MANa) samples of approximately 4 mol % of ions with molecular weights in the range of 21000–270000, using the RMR. The second part deals with the molecular weight effect on mechanical properties of the sulfonated polystyrene ionomers of ca. 5 mol % of ions with molecular weights in the range of 29000–360000, determined using the DMTA. It should be mentioned that for the methacrylates the data obtained from the RMR measurements are comparable to those obtained from DMTA measurements, as will be shown in the results part. Therefore, it is believed that it is not necessary to perform the DMTA measurement on the methacrylates. It is worth noting that previous DMTA measurements on the methacrylates of various ion contents (not various molecular weights) have shown that the results

Table 1. Sample Notations and Molecular Weights of Ionomers

sample notation	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
P(S-3.9-MANa)-21	21	42
P(S-3.7-MANa)-53	53	108
P(S-3.8-MANa)-110	106	227
P(S-3.8-MANa)-220	221	445
P(S-4.0-MANa)-270	273	716
P(S-4.9-SSNa)-29	29	54
P(S-5.7-SSNa)-71	71	145
P(S-5.3-SSNa)-110	105	225
P(S-5.0-SSNa)-260	260	452
P(S-5.5-SSNa)-360	360	580

are comparable to those obtained from the RMR measurements.

II. Experimental Section

A. Polymer Synthesis and Characterization. Except for the sample of M_n = 110 000, all the polystyrene samples were synthesized by bulk free-radical polymerization using benzoyl peroxide as the initiator. The sample of M_n = 110 000 was obtained from Aldrich and was purified by dissolving the polymer in tetrahydrofuran (THF) and precipitating in methanol. The molecular weights and polydispersity indices of all the samples were determined using a Varian 5010 size exclusion chromatograph (SEC) with 10^4, 10^5, and 10^6 Å Ultrastyragel (Waters) SEC columns connected in series, with THF as the solvent. Polystyrene standards (Toyo Soda Manufacturing) were used for calibration of the columns. The method developed by Makowski et al.[47] for homogeneous sulfonation was used to produce the poly(styrene-*co*-styrenesulfonic acid) [P(S-*co*-SSA)] samples, which contained approximately 5 mol % of functionalized repeat units. To determine the ion concentration, samples were dissolved in a benzene/methanol (90/10, v/v) mixture to make a 5% (w/v) solution and titrated with standard methanolic sodium hydroxide to the phenolphthalein end point. Poly(styrene-*co*-methacrylic acid) [P(S-*co*-MAA)] samples were also prepared by bulk free-radical polymerization of styrene and methacrylic acid monomers. The procedure has been described in detail elsewhere.[24] To determine the ion content, the same procedure was used as for the sulfonated samples. Molecular weights and polydispersity indices were determined using a Waters 150 CV SEC with a 1 μm Styragel linear high-temperature column in a THF/acetic acid mixture (95/5, v/v) at 40 °C. Polystyrene standards (Scientific Polymer Products Inc.) were again used for the column calibration.

For both series of polymers, neutralization of the acid groups was performed by addition of a predetermined quantity of methanolic sodium hydroxide to a 5% (w/v) ionomer solution in a benzene/methanol (90/10, v/v) mixture. The solutions were freeze-dried and then dried under vacuum at 160 °C for at least 24 h. For the RMR studies, the samples were dried further in a vacuum oven at around 200 °C for another 24 h. The sample notation used for the ionomers is P(S-*x*-SSNa)-*y* for P(S-*co*-SSNa) samples and P(S-*x*-MANa)-*y* for P(S-*co*-MANa) samples, where *x* is the mole percent of styrenesulfonate or methacrylate and *y* denotes the number-average molecular weight in thousands. Table 1 shows sample notations, number-average molecular weights (M_n), and weight-average molecular weights (M_w) of the ionomers. For the comparison of the results obtained from both instruments and for the TGA study, the 5.2 and 5.4 mol % methacrylate ionomers were used; these ionomers were synthesized as a part of another project; the M_n is estimated to be 300 000.

B. Sample Preparation. For the RMR measurements, the samples were compression molded into disks at temperatures ranging from 180 to 230 °C, depending on the molecular weight. The disks, with dimensions of 25 mm diameter and about 0.7 mm thickness, were then annealed at ca. 200 °C in a vacuum oven for at least 24 h. For the DMTA measurements, the samples were compression molded at ca. 230 °C. The molded samples, with aproximate dimensions of 2.5 × 6.0 × 30.0 mm, were annealed for 24 h in vacuum at 210 °C. For the TGA measurements, the samples of P(S-5.5-SSNa) and P(S-5.4-MANa) were dried at 180 °C for 24 h under vacuum.

C. Thermogravimetric Analysis (TGA). For the studies of thermal stability, a Seiko thermogravimetric/differential thermal analyzer (TG/DTA 220) was used. The experiments were performed as a function of temperature over the range of 50–500 °C at a heating rate of 10 °C/min. For the study of the decomposition rate as a function of time, the samples were heated to 310 °C at a heating rate of 100 °C/min and held at that temperature for 60 min. All experiments were performed under dry nitrogen at a flow rate of 200 mL/min.

D. Rotational Melt Rheometry (RMR). A Rheometrics dynamic analyzer, RDA-II, with parallel plate geometry was used as the rotational melt rheometer (RMR) to measure the dynamic viscoelasticity of the methacrylate ionomers. Temperature sweep measurements were performed at a constant frequency of 1.0 Hz in the temperature range of 100–300 °C. The sweep rate was about 1 °C/min. Frequency sweep measurements were conducted in the frequency range of 0.1–100 rad/s at various temperatures between 120 and 260 °C. At temperatures above 160 °C, the samples were kept in a dry nitrogen atmosphere to prevent oxidation. Strain values were kept within the linear region.

E. Dynamic Mechanical Thermal Analysis (DMTA). The mechanical 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, 3, 10, and 30 Hz and a heating rate of 0.5 °C/min. All experiments were performed under a dry nitrogen atmosphere. For each sample, the storage moduli (E'), loss moduli (E''), and loss tangents (tan δ) were obtained as a function of temperature over the range of 80–350 °C.

F. Differential Scanning Calorimetry (DSC). For the thermal analysis studies, a Perkin-Elmer DSC-7 was utilized. It was calibrated with indium. The sample cells were kept under a purge of dry nitrogen during the measurements. The P(S-*co*-MANa) samples, which were the same as those utilized for the RMR measurements, were scanned at 10 °C/min to above the matrix glass transition temperature. The glass transition temperatures (T_g) were recorded during the first heating run. T_g was taken as the midpoint of the enthalpy change of the exo–endotherms. Repeat runs yielded identical T_g values within experimental error.

III. Results and Discussion

A. Thermal Stability of Materials by TGA. The temperatures of 0.6% (maximum sensitivity of the instrument) and 5% weight loss for the P(S-5.4-MANa) were 280 and 376 °C, respectively. Those for the P(S-5.5-SSNa)-260 were 281 and 378 °C, respectively. It is clear that the thermal stability of these materials is identical. It should be mentioned that the ion contents of both ionomers are similar. Isothermal TGA measurements as a function of time showed that the time of 1% weight loss at 310 °C for the P(S-5.4-MANa) was 11 min, while for the P(S-5.5-SSNa) it was 13 min. Also, after 60 min at 310 °C, the total weight loss of the materials was ca. 5.0% for the methacrylates and ca. 3.7% for the sulfonates. These results agree with previous TGA results from this laboratory, which showed that the temperature at the onset of weight loss of the polystyrene-based ionomers was almost the same as that of pure polystyrene. This similarity in the thermal stability suggests that the small amount of ionic species in the ionomers does not affect the decomposition behavior of the materials significantly at low ion contents.

B. Comparison of DMTA and RMR Data. Since two instruments were used for the measurements of the dynamic viscoelasticity as a function of temperature, it is important to ascertain whether the results obtained from these two instruments yield identical information. The test was performed on the P(S-5.2-MANa) sample using

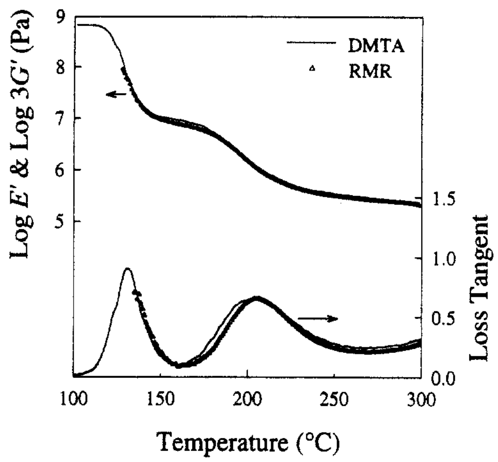

Figure 1. Comparison of the tensile storage modulus (E') and 3 times the shear modulus ($3G'$) as well as of the loss tangent data obtained from DMTA (—) and RMR (Δ) as a function of temperature for the P(S-5.2-MANa)-300 sample. All data were obtained at 1 Hz.

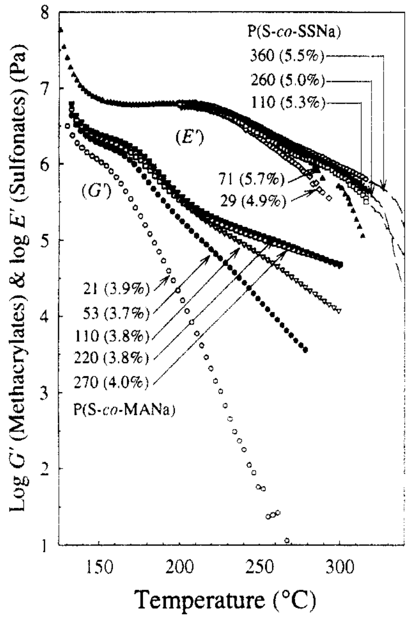

Figure 2. Storage modulus as a function of temperature for the ionomers P(S-*co*-SSNa) (E', upper part) and P(S-*co*-MANa) (G', bottom part) measured at 1 Hz. The molar ion contents and molecular weights are indicated for each sample.

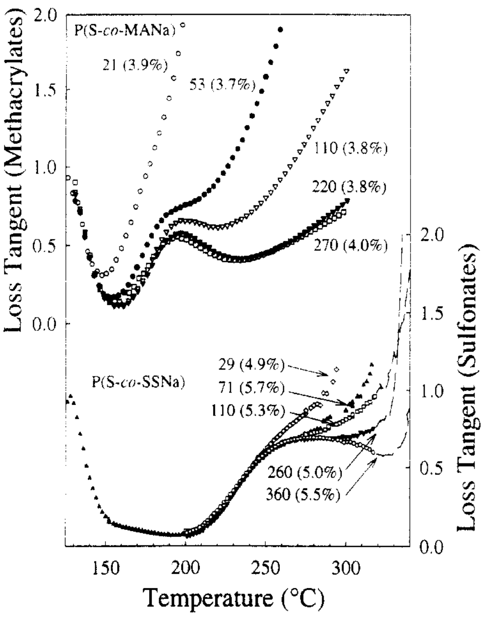

Figure 3. Loss tangent, tan δ, as a function of temperature for the ionomers P(S-*co*-MANa) (upper part) and P(S-*co*-SSNa) (bottom part) measured at 1 Hz. The molar ion content and molecular weight are indicated for each sample.

both the DMTA and the RMR. Figure 1 shows a comparison of the tensile storage modulus, E', obtained from the DMTA measurement, and 3 times the shear storage modulus, $3G'$, obtained from the RMR measurement, as well as the loss tangents, tan δ, measured on both instruments at a frequency of 1.0 Hz. The results are in excellent agreement below a modulus of $E' = 10^8$ Pa.

C. Viscoelastic Properties of the P(S-*co*-MANa) System by RMR. *Dynamic Viscoelasticity as a Function of Temperature.* Figures 2 and 3 show plots of G' and tan δ as a function of temperature for the P(S-*co*-MANa) with 4 mol % of ions for the various molecular weights along with those for the P(S-*co*-SSNa). Data points acquired in the region where the instrument lacks sensitivity in the parallel plate geometry (i.e., for $G' > 10^7$ Pa) have been eliminated. The lowest molecular weight is 21 000, which is lower than the critical molecular weight (M_c)[48] for the entanglement of PS, $2M_e$ (M_e = 18 100 for PS) while the highest is 270 000. In the plot of G' against temperature for the samples with the three higher molecular weights, one can see, with increasing temperature, the end of the transition region for the PS matrix phase (below ~140 °C), the "ionic" plateau (temperature range of 140–160 °C), the drop in modulus accompanying the glass transition of the clusters (temperature range of 160–200 °C), the second inflection (temperature range of 200–270 °C), and, for the sample of lowest molecular weight, the flow region (>200 °C). The value of the "ionic" plateau at low temperatures is related to ionic aggregation, while the inflection at high temperatures should be due to chain entanglements, since its value is comparable to the rubbery plateau modulus of PS. The value of the "ionic" plateau (associated with ion aggregation) for the P(S-3.9-MANa)-21 and the P(S-3.7-MANa)-53 samples decreases slightly with decreasing molecular weight. Its length also decreases. The behavior of the high molecular weight ionomers shows less dependence on the molecular weight. The inflections due to entanglements as well as the region beyond that temperature show a normal molecular weight dependence; it is also seen that the length of the "plateau" associated with entanglements decreases with decreasing molecular weight. The P(S-3.9-MANa)-21 sample does not show any evidence of entanglements.

The tan δ plots (Figure 3) also show the glass transition region associated with the matrix, a peak or shoulder attributed to the glass transition of the cluster regions, and, for the lowest molecular weight sample, the flow region. It should also be mentioned that data points for the matrix tan δ peak on the low-temperature side were scattered due to the sensitivity of the instrument, and thus the data points below 125 °C were eliminated for clarity.

Hird and Eisenberg[28] as well as Kim et al.[49] have estimated the area under the tan δ peak attributed to the glass transition of the cluster regions and reported that the area increased with the ion content. To see the influence of the molecular weight on the tan δ peak more precisely, curve deconvolutions were performed using the Peakfit (Jandel Scientific) computer program. The tan δ curve was taken to be composed of three parts: (1) the end of the glass transition of the matrix phase, (2) the peak due to the glass transition of the cluster phase, and (3) the flow region. In the case of the matrix T_g, only the

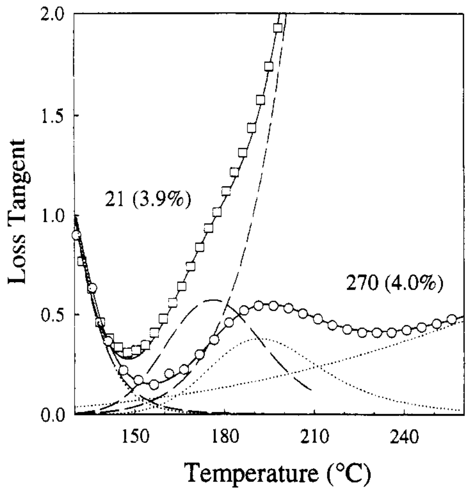

Figure 4. Deconvoluted loss tangent curves as a function of temperature for the P(S-3.9-MANa)-21 and P(S-4.0-MANa)-270 samples measured at 1 Hz.

data for the end of the transition region are available. The Logistic Dose Response function was chosen for that region (1) as the best fit. For the tan δ peak due to the glass transition of the cluster regions (2), the exponentially modified Gaussian function was found to fit very well. For the flow region (3), a modified WLF relation[50] was applied. It must be stressed that there is no single theoretical equation that describes the data and that there is no fundamental scientific meaning to most of parameters of the equations used here, except for the peak positions. As an example, deconvolution results for the lowest and highest molecular weight samples are shown in Figure 4. A cursory inspection of the tan δ plots in Figure 3 shows only an ill-defined feature in the temperature range of the cluster T_g for the P(S-3.9-MANa)-21 sample. However, if one looks at the data and the fitting results in Figure 4, which were obtained by the use of a consistent base-line subtraction procedure, then the existence of shoulder becomes less questionable. In that figure, it is clearly seen that even in the lowest molecular weight sample there is a peak associated with the glass transition of the clusters and that the area under the peak is similar to that for the highest molecular weight sample. The fitting functions are arbitrary, but the consistency of the equations used for this and all the other samples suggests that the features are not artifacts.

From the deconvoluted curves, the area under the peak, temperature at the peak maximum, and the peak width at half-height associated with the glass transition of the cluster regions were obtained. The areas under the peaks are in the range of 20–27 °C and the widths at half-height of the peaks are relatively constant (i.e., ca. 13 °C) for all molecular weights. However, the peak positions shift from ca. 165 to ca. 180 °C as the molecular weight increases from 21 000 to 110 000.

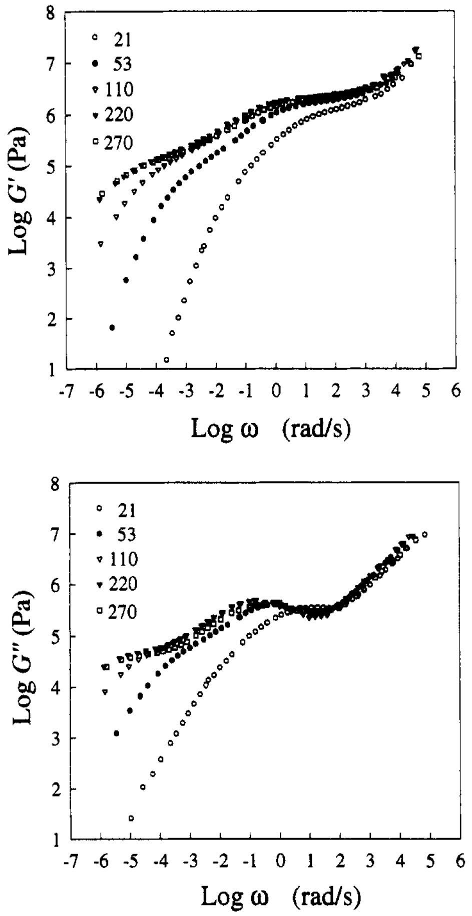

Figure 5. (a, Top) Shear storage modulus, G', and (b, bottom) shear loss modulus, G'', as a function of frequency for the P(S-*co*-MANa) ionomers of various molecular weights. The reference temperature is 160 °C.

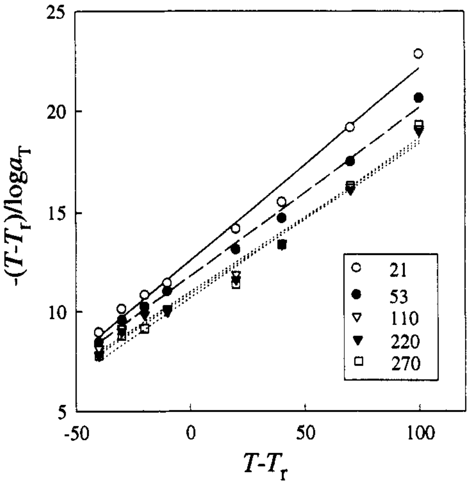

Figure 6. Modified WLF plots for P(S-*co*-MANa) ionomers of various molecular weights.

Dynamic Viscosity as a Function of Frequency. Viscoelastic properties measured as a function of frequency or time frequently show the molecular dynamics more directly than those measured as a function of temperature, because the experimental frequency or time is related directly to the relaxation time. In the case of the P(S-*co*-MANa) system, G' and G'' were measured as a function of frequency. For the P(S-*co*-MANa) system with ion contents lower than 6 mol %, it has been reported that time–temperature superposition is applicable.[24] Parts a and b of Figure 5 show the master curves of G' and G'' for the P(S-*co*-MANa) samples of varying molecular weights. The reference temperature (T_r) was taken as 160 °C. These master curves do not show any deviation from time–temperature superposition. To test the applicability of the WLF relation and to determine the constants c_1 and c_2, a modified WLF plot, i.e., $[-(T-T_r)/\log a_T]$ against $(T-T_r)$, was constructed and is shown in Figure 6. Straight lines are obtained in this plot, which suggests that the WLF relation may, indeed, be appropriate. For random ionomers of a molecular weight higher than 100 000, all a_T values fit on one line; i.e., a_T is independent of molecular weight. By contrast, for the lower molecular weight

Table 2. WLF Parameters[a] and Rheological Characteristics of the P(S-*co*-MANa) Samples

	c_1	c_2	$10^{-6}G_N^0$ ionic (Pa)	$10^{-5}G_N^0$ ent (Pa)	$\omega_{G''_{peak}}$ (rad/s)	η_0 (Pa s)	$10^5 J_e^\circ$ (Pa^{-1})
P(S-3.9-MANa)-21	11	140	2.0		99	3.7×10^6	2.1
P(S-3.7-MANa)-53	12	150	2.1	2.2	8.4	3.5×10^8	5.5
P(S-3.8-MANa)-110	14	150	2.6	2.1	2.1	7.7×10^9	4.5
P(S-3.8-MANa)-220	14	150	2.5	2.2	1.7		
P(S-4.0-MANa)-270	13	140	2.3	2.3	4.3		
PS-71	6.7	120		2.2		1.0×10^5	5.5
PS-360	5.7	110		2.2		5.0×10^6	8.0

[a] The reference temperature is taken as 160 °C for the estimation of WLF parameters c_1 and c_2.

ionomers, deviations from that line are observed. The WLF parameters calculated for these plots are summarized in Table 2. As might be expected from the plot, the WLF parameters are almost the same for ionomers of a molecular weight higher than 100 000, while for the lower molecular weight systems the values are smaller. This molecular weight dependence of WLF parameters cannot be attributed only to the shift of the T_g of the matrix PS. Using supplementary DSC measurements, the T_g values for P(S-3.9-MANa)-21 and P(S-3.8-MANa)-220 were determined to be 107 and 110 °C, respectively. This difference is not large enough to explain the influence of molecular weight on the WLF parameters calculated for these ionomers.

According to the WLF equation,[50] c_1 is inversely proportional to the fractional free volume, f_g, at the glass transition. In the present system, it is seen in Table 2 that the c_1 values for the different molecular weight samples remain constant. From the average value of c_1 of 12.8 for the P(S-*co*-MANa) system, it is calculated that the fractional free volume of the samples at the reference temperature, i.e., 160 °C, is 0.034. It is worth noting that, for the average c_1 for the polystyrene, one obtains ca. 0.070 as the fractional free volume at 160 °C, which is about twice as high as that found for the ionomers. Furthermore, the constant c_2, which equals f_R/β_f, where β_f is the free volume expansion coefficient above T_g, also seems to be independent of the molecular weight for the P(S-*co*-MANa) systems. From the average value of this WLF coefficient, it is found that $\beta_f \approx 2.3 \times 10^{-4}$ °C^{-1}. For polystyrene, one obtains ca. 6.2×10^{-4} °C^{-1} for β_f, which is, again, also almost twice as high as that for the ionomers. It is worth noting that in the present system the reference temperature for the WLF relation is not the glass transition temperature, but 160 °C. From the above, it is concluded that the fractional free volume and the free volume expansion coefficient are smaller than those in polystyrene and are independent of the molecular weight.

G' and G'' plots as a function of frequency show the "ionic" plateaus and peaks at low frequencies attributed to ion aggregation. The values of $G_N^\circ{}_{\text{ionic}}$ as a function of frequency, calculated from dynamic viscoelasticity, are similar to those calculated from dynamic viscoelasticity as a function of temperature. The frequency of the G'' peak for the P(S-3.9-MANa)-21 is about one order of magnitude higher than those for the other samples. A superficial examination of these results may suggest that the low molecular weight ionomers, especially those with a molecular weight lower than the critical molecular weight (M_c) for entanglements, form weaker ionic clusters than those found in high molecular weight ionomers. This is not the case, because the flow behavior of the matrix phase hides the relaxation attributed to ionic clusters. The relaxation due to the cluster phase occurs in a similar time frame to that of the flow behavior. In the high molecular weight ionomers, the time scale difference between the relaxation due to the clusters and the flow region is large enough to show the separate relaxation in the plot of G' vs ω. However, in the low molecular weight samples, the time scale difference is too small for a separate relaxation curve to be seen in the modulus plot. Thus, it is the flow behavior, not ion aggregation, which dominates this obscured relaxation behavior of ionomers with molecular weights lower than 100 000 at that high a temperature.

At this point, it is useful to introduce some characteristic viscoelastic parameters, which are calculated from the shear storage modulus (G') and shear loss modulus (G'') as a function of frequency. The elasticity of the polymer melt can be characterized by the plateau modulus (G_N°). In unfunctionalized polystyrene, G_N° is related to the molecular weight between entanglements (M_e) by

$$G_N^\circ = \frac{\rho RT}{M_e} \tag{1}$$

where ρ is the density of the polymer, T is temperature, and R is the gas constant. The value of G_N° is calculated from the frequency dependence of G'',

$$G_N^\circ = \frac{2}{\pi}\int_{-\infty}^{\infty}(G'' - G''_g)\ \mathrm{d}\ln\omega \tag{2}$$

where G''_g is the shear loss modulus associated with the glass transition. In the terminal region, the viscoelastic flow of the molten polymer is characterized by the limiting viscosity at zero shear rate (η_0) and the steady state shear compliance (J_s°). η_0 represents the fluidity of the polymer and is proportional to the longest relaxation time. J_s° corresponds to the inverse of the permanent elasticity. These values are calculated from the frequency dependence of G' and G'' in the terminal region from the following equations:

$$\eta_0 = \lim_{\omega\to\infty}\left[\frac{G''}{\omega}\right] \tag{3}$$

$$J_s^\circ = \lim_{\omega\to\infty}\left[\frac{G'}{(\eta_0\omega)^2}\right] \tag{4}$$

Plots of G' and G'' as a function of frequency show the matrix transition region, the "ionic" plateau, the cluster transition region, the inflection, and the flow region (or at least the beginning of it); these are also seen in plots of G' and tan δ as a function of temperature. However, G' and G'' as a function of frequency show the terminal region more clearly than G' and tan δ as a function of temperature. From these data, the characteristic viscoelastic values, i.e., G_N°, η_0, and J_s°, were calculated for the P(S-*co*-MANa) systems. These values are also listed in Table 2.

In the case of monodisperse PS, the rubbery plateau appears when the molecular weight exceeds the critical value for the chain entanglement, $2M_e$; above this point, the rubbery modulus (G_N°) is independent of the molecular weight. The limiting viscosity at zero shear rate (η_0) shows a linear molecular weight (MW) dependence for materials of molecular weight lower than $2M_e$; however, for samples of molecular weight higher than $2M_e$, it is proportional to $MW^{3.4}$.[48] The steady state compliance ($J_s°$) also shows a linear molecular weight dependence for systems of molecular weight lower than $4M_e$; however, it becomes constant for systems of molecular weight higher than $4M_e$.[48] On the other hand, η_0 for polydisperse PS samples depends on the weight-average molecular weight (M_w) in the same way as it does in monodisperse PS on the molecular weight. $J_s°$ shows a strong dependence on the polydispersity.[48]

In the present study, except for P(S-3.9-MANa)-21, the P(S-*co*-MANa) samples of high molecular weights show an "ionic" plateau region and an inflection (i.e., the rubbery plateau), as was mentioned above. From Table 2, it is seen that $G_N°_{ionic}$ and $G_N°_{ent}$ are not strongly affected by M_w. The values of the "ionic" or rubbery modulus ($G_N°$) are practically constant as a function of the molecular weight. The values of $G_N°_{ionic}$, the high-frequency or "ionic" plateau, are one order of magnitude higher than those for $G_N°_{ent}$. The $G_N°_{ent}$ value at low frequencies, however, is comparable with that of PS. This low-frequency inflection does not appear for P(S-3.9-MANa)-21, which is the only sample in this system the molecular weight of which is lower than $2M_e$ of PS. By contrast, $G_N°_{ionic}$ for the high-frequency plateau appears even for the P(S-3.9-MANa)-21 sample. This behavior confirms that the viscoelastic behavior at high frequencies is due to ionic aggregation, while the inflection at low frequencies is attributable to chain entanglements. The plot of G'' as a function of frequency (Figure 5b) shows a peak at frequencies between the transition region and the terminal region. This G'' peak is related to the glass transition of the clusters. From Table 2, it is also found that, except for P(S-3.9-MANa)-21, the frequencies at the G'' peak maxima do not change very much with the molecular weight.

It is interesting to compare the characteristic values for viscoelastic flow of the ionomer melts with those for PS. It should be noted that η_0 and $J_s°$ for P(S-3.8-MANa)-220 and P(S-4.0-MANa)-270 cannot be estimated. However, the lower molecular weight ionomers show flow behavior clearly, and thus η_0 and $J_s°$ can be estimated. η_0 represents a characteristic property associated with viscous flow of polymer melts and is proportional to the maximum relaxation time. A plot of η_0 vs M_w (not given here) shows that η_0 is proportional to $M_w^{4.5}$ for the ionomers, while that for PS is proportional to $M_w^{2.8}$ at 160 °C. It should be mentioned that the exponent of 2.8 for the polystyrene is somewhat lower than well-known value of 3.4;[48] however, this may be due to the small number of data points. The value of the exponent suggests that the viscous flow behavior of the polystyrene-based random ionomers shows a similar dependence on M_w as that of the unfunctionalized PS. Naturally, the absolute value of η_0 for the ionomer is much higher than that for PS.

The steady state compliance, $J_S°$, can be thought of as the inverse of the permanent elasticity of the polymer melts. Again, from Table 2, it is seen that $J_s°$ does not change appreciably with M_w; the exception is also P(S-3.9-MANa)-21, which shows a somewhat smaller value of $J_s°$ than those for the other materials. The value of $J_s°$ for the high molecular weight samples is about the same as that for PS. These results suggest that even though the ionic functionalities do affect the terminal behavior of ionomers, the general trend of the behavior of the ionomers in the terminal region is the same as in polystyrene. Thus, it is concluded that the ionic interaction acts as a friction to delay entanglement relaxation but does not affect the compliance in the terminal region.

According to the sticky reptation model for dynamics of entangled networks by Leibler et al.,[51] the terminal relaxation time of the reversible networks, T_d, and the average lifetime of stickers, τ, can be calculated in principle. In the ionomer system, however, the parameters which are needed for the calculation are difficult to determine. In addition, the theory assumes that the chain length between stickers is longer than the entanglement molecular weight, which is not the case here. It is noteworthy that the number of stickers, i.e., ion pairs in the present system, varies for the different chains, and these variations in the number of the stickers per chain depend on the method of preparation of the samples, especially the heterogeneities and molecular weights. Also, the fraction of ion pairs which form multiplets is difficult to determine. In addition, the average lifetime of the multiplets is difficult to determine, because the multiplets are located in large clusters which have various sizes and shapes. However, in spite of this cautionary comment, it is still useful to apply the sticky reptation model qualitatively to the present system. This is discussed below.

In connection with the loss modulus (G'') plot, the authors[51] point out that two peaks should be seen, i.e., high-frequency and low-frequency peaks. A high-frequency peak should be seen at a frequency of $1/\tau$, the position of which is independent of other molecular parameters, such as the number of units and of stickers per chain. The low-frequency peak occurs at a frequency of $1/T_d$ which depends on the chain length and degree of substitution as well as on τ. If this model is applicable to the present system, it can be concluded from Figure 5b that the average lifetime of the stickers, τ, is independent of the molecular weight, while the terminal relaxation time, T_d, does depend on the molecular weight. The T_d's for samples with molecular weights higher than 100 000 seem to be similar, while that for P(S-*co*-MANa)-21 is orders of magnitude lower than those for the high molecular weight ionomers.

D. Dynamic Mechanical Properties of the P(S-*co*-SSNa) System by DMTA. For the P(S-*co*-SSNa) samples, the loss tangent (tan δ) curves as a function of temperature at 1 Hz (not shown here because many examples exist in the literature[30,34,38,52]) show two peaks or one peak and a shoulder. The first peak is due to the matrix glass transition, while the second is attributed to the glass transition of the ionic clusters; a flow region is seen in all plots.

Deconvolution was also used here to explore more quantitatively the molecular weight effect on the loss tangent curves. Because of the differences in the shapes of the tan δ curves between the sulfonates and the methacrylates, different fitting equations were used for the sulfonates. The exponential function was used for the baseline. For the peak of the glass transition of the matrix regions and the peak or shoulder due to the glass transition of the ionic cluster regions, the exponentially modified Gaussian function and the area Gaussian function were utilized, respectively. From these deconvoluted curves, the peak positions, the areas under the peaks, and the peak width at half-height were obtained. The areas under the cluster tan δ peaks increase from 19 to 60 °C with increasing molecular weight; however, it is believed that the dissimilarity of the cluster peak positions and that of the areas under the cluster peak is mainly due to the difference in the baseline subtraction for each sample.

The tan δ curves due to the matrix glass transition change only very slightly as a function of the molecular weight. The slight variations in the peak heights and peak positions are generally related to small variations in the ion contents; i.e., the peak moves to a higher temperature and decreases in height with increasing ion content.[28,49] Areas under the peaks (ca. 21 °C) as well as widths at half-height (ca. 20 °C) remain essentially constant. Figure 3 shows the loss tangent curves as a function of temperature in the range of the cluster glass transition. In the temperature range of 125–200 °C, only the tan δ curve of P(S-5.3-SSNa)-100 is shown for the sake of clarity. It should also be mentioned that the peaks were shifted slightly to obtain overlap in the 200–250 °C range, also for clarity. It should be mentioned that, during the DMTA measurement at a heating rate of 0.5 °C/min, the sulfonate ionomers were also exposed to high temperatures (from 280 to 340 °C) for ca. 2 h. Thus, the detailed results of the data above 320 °C may be not reliable due to some possible decomposition. Therefore the data above 320 °C are shown as dashed lines in Figures 2 and 3. It is, however, believed that the decomposition process does not affect the general trends seen in the flow region at lower temperatures. Figure 3 shows that, as the molecular weight increases, the peak or shoulder due to the glass transition of the ionic cluster region becomes more fully developed; in addition, the temperature of the onset of the flow region increases. When one compares the behavior in the terminal region of the sulfonates and the methacrylates, it is clear that differences in the shape of the curves for the sulfonates are much less pronounced than for the methacrylates; this will be discussed in greater detail below.

Plots of the storage modulus for ionomers (Figure 2) can be divided into five parts: (1) the glassy plateau (not seen here because the plot starts at $T = 125$ °C), (2) the glass transition region of the matrix, (3) the ionic plateau, (4) the glass transition of the ionic clusters, and (5) the rubbery region combined with the flow region. The values of the glassy moduli for the P(S-*co*-SSNa) system (not shown here) remain unchanged for the different molecular weights within experimental error. The behavior of the ionomers in the matrix glass transition region is also independent of the molecular weight, as expected; i.e., the positions, slopes, and ranges of curves in the glass transition region of the matrix are almost identical. In the present system, the values of the ionic moduli as well as the lengths of the plateaus seem to be the same for all the samples.

Molecular weight dependent behavior becomes evident in the cluster T_g and flow regions. The differences for samples of different molecular weights manifest themselves primarily in the log E' vs temperature plots (Figure 2). These curves were also shifted in a manner similar to that described above for the tan δ plots. To avoid crowding, only one log E' curve is shown in the temperature range of 125–200 °C, and the data above 320 °C are shown as dashed lines. Figure 2 shows that the range of the glass transition region becomes wider as the molecular weight increases.

The loss modulus curves (not shown here) contain two peaks. The first peak appears at a low temperature and corresponds to the glass transition of the matrix regions. The positions, widths, and heights of these peaks do not change significantly with molecular weight. The second peak, at high temperature, corresponds to the glass transition of the clusters. The widths of the high-temperature peaks are wider than those for the low-temperature process. However, the positions and widths of the high-temperature peak maxima are also independent of the molecular weight. It should be noted that the widths at half-height of the high-temperature peaks are surprisingly constant, i.e., 65 ± 2.3 °C.

Table 3. Activation Energies for Ion-Hopping, Matrix Transition, and Cluster Transition for the Sulfonate Ionomers

	activation energy (kJ/mol)				
	matrix		cluster		
sample	tan δ peak	E''_{max}	tan δ peak	E''_{max}	ion-hopping
P(S-4.9-SSNa)-29	530	760	260	170	160
P(S-5.7-SSNa)-71	530	790	220	200	240
P(S-5.3-SSNa)-110	550	780	280	210	220
P(S-5.0-SSNa)-260	540	820	240	180	170
P(S-5.5-SSNa)-360	540	770	260	160	140

The activation energies for the matrix and cluster transitions were calculated from an Arrhenius plot of log(frequency) against inverse temperature of the tan δ peak maxima after deconvolution as well as of E'' maxima. In addition, from the modulus data in the ionic plateau region obtained at several frequencies as a function of temperature, ion-hopping activation energies can be calculated. The detailed procedure to calculate these activation energies has been given by Hird and Eisenberg.[30] It involved a linear extrapolation of the ionic plateau and the high-temperature side of each log E' vs temperature curve, to obtain intersection points. The temperatures corresponding to these intersection points were treated using the Arrhenius equation to calculate activation energies. All of the activation energies are listed in Table 3. It should be mentioned that the limits of accuracy in determining peak positions (±0.5 °C) lead to confidence limits in the calculation of the activation energies of ca. ±30 kJ/mol.[28] From Table 3, it is seen that the activation energies are independent of the molecular weight. It is also worth noting that each log E' vs temperature curve shows the onset of the drop in the modulus above the plateau region at essentially the same temperature, i.e., ca. 220 °C. These results suggest that the stabilities or rigidities of the multiplets are independent of the molecular weight.

At this point, it is useful to review some of previous findings on the activation energies for the sulfonates. Kim et al.[52] found that the activation energies of the glass transitions of the matrix and cluster phases for the sulfonates are independent of the ion content and are ca. 510 and ca. 210 kJ/mol, respectively. The values obtained in the present study show good agreement with those values. Hird and Eisenberg[30] also reported that for the sulfonates the activation energies for ion-hopping were independent of ion concentrations. It is noteworthy that for the 3.5 mol % sulfonates, the ion-hopping activation energy obtained by Hird and Eisenberg was 175 ± 1 kJ/mol, which is in the range of the values obtained in this study. The authors[30] also suggested the existence of an interrelation between the ion-hopping process and the glass transition of clusters in the sulfonates.

While, in general, trends in the qualitative temperature dependence of tan δ, log E', or log E'' for the sulfonates are similar to those for the methacrylates, there are significant quantitative differences between the results for the two systems. First, the similarities in the results for the methacrylates and the sulfonates will be discussed.

In the plot of tan δ vs temperature, the shapes of the peaks for the sulfonates are generally similar to those for the methacrylates. The matrix peaks are clearly independent of the molecular weight. At low molecular weight, the cluster peak is not seen. However, as the molecular weight increases, the cluster peak becomes more developed; i.e., the dip in the tan δ curve right above the cluster T_g maximum becomes more pronounced. It is also seen that the slope of curve in the terminal region of the log E' plot decreases with increasing molecular weight.

A discussion on the differences in the results between the methacrylates and the sulfonates is now in order. In the tan δ vs temperature plot for the methacrylates, as has been observed before, the cluster peak positions are seen at a lower temperature than those in the sulfonates.[34] In the studies by Hird and Eisenberg[30] and Fan and Bazuin,[31] it was shown that the ionic plateaus for the P(S-*co*-SSNa) system are longer and more clearly defined than those for the P(S-*co*-MANa) system; this is due to the stronger ionic interactions of the sodium sulfonates. This has been linked to the fact that the ionic interactions in the sodium sulfonates are stronger than those in the sodium carboxylates.[30-32,34,43-45] This results in the fact that the upper T_g of the sulfonate ionomer is higher than that of the carboxylate ionomer of the same ion content and is thus much closer to the temperature of the onset of the flow and decomposition. For example, in present systems, the positions of the cluster peak maxima for the methacrylates are seen at ca. 195 °C, while those for the sulfonates appear at ca. 280 °C. It should be noted that for the methacrylates, the average ion content is ca. 4 mol %, while that for the sulfonates is ca. 5 mol %. It is well known that with increasing ion content both the matrix and cluster T_g's increase; from previous results,[49] one can estimate the cluster T_g for 5 mol % methacrylates to be ca. 200 °C, i.e., 5 °C higher than that in the 4 mol % sample. This temperature is still very much lower than that for the sulfonates.

Also, in the flow region, at a tan δ of 1.2, the temperature difference between P(S-3.9-MANa)-21 and P(S-3.8-MANa)-110 is ca. 95 °C, while that between P(S-4.9-SSNa)-29 and P(S-5.3-SSNa)-110 is only ca. 30 °C. It should be recalled that for the sulfonates the curves were shifted to overlap each other for clarity. However, it is believed that this shift does not make any significant difference in the interpretation of the results. In the plot of the storage modulus (see Figure 2), the difference in the molecular weight effect on both systems can be seen more clearly. For instance, for the sulfonates at 270 °C, the difference in the storage modulus between the highest and lowest molecular weight samples is only ca. $10^{0.2}$, while that for the methacrylates is ca. 10^4. Again, it should be mentioned that, for the methacrylates, if the ion content were increased to 5 mol %, the storage modulus curve will be shifted to a slightly higher temperature and modulus. However, it is believed that it would not change significantly the general shapes of the curves. These differences are due to the difference in the strength of the ionic interactions in the multiplets, which is discussed below in connection with activation energies.

The relation between the stability of multiplets and the molecular weight dependent behavior of ionomers will now be addressed. In the case of the methacrylates, the electrostatic interaction between ion pairs is weaker than that in the sulfonates, and thus the cluster T_g is much closer to the matrix T_g. Above but relatively close to the matrix T_g, as the temperature increases, the chain mobility increases; however, the ion pairs do not yet migrate between multiplets. As the temperature increases further, the chain motion increases and induces ion-hopping; eventually the ionomers go through the cluster glass transition. Above the temperature at which the ion-hopping starts to occur (i.e., the onset of the drop in the log G'), the polymer chain mobility still increases as a function of temperature. Thus, the glass transition of the cluster phase in the methacrylates is influenced by both ion-hopping and chain mobility. It should be recalled that the multiplets in the ionomers act as physical cross-links and thus increase the modulus of the ionomers. However, when ion pairs start to migrate between the multiplets, they can no longer act as long-term physical cross-links, and thus the materials start to show a molecular weight dependent behavior similar to that of the nonionic polymers.

For the sulfonates, the interaction between ion pairs in the multiplets is stronger than that for the methacrylates, and thus the ion-hopping process does not occur until a much higher temperature is reached. Above the glass transition of the matrix phase, as temperature increases, the chain mobility increases. At this point it should be stressed that for the sulfonates the cluster T_g is much higher than the matrix T_g. Thus, just below cluster T_g, the chain mobility is very rapid, but this does not result in the occurrence of the cluster T_g just as yet. As the temperature increases further, ion pairs start to migrate and the material shows the glass transition of the cluster phase. Thus, it seems reasonable to suggest that, in the sulfonates, the ion-hopping process, not the short chain motion, is the limiting step for the cluster T_g. In the present study, for the sulfonates, the activation energies for the ion-hopping are almost the same for all the samples, and thus the contribution of ion-hopping to the cluster glass transition is independent of molecular weight. However, above the onset of the drop in the modulus (see Figure 2), the slope of log E' curves as a function of temperature does become steeper with decreasing molecular weight and the ionomers show a molecular weight dependent behavior in that range.

In addition to the difference in the stability of the multiplets, the difference in the strength of ion interaction also results in a difference in the size of multiplets, which affects significantly the volume fraction of the cluster phase. Therefore, it is not easy to compare the molecular weight dependent behavior of these two ionomer systems directly. However, a qualitative comparison does give an insight into the molecular weight dependence of the mechanical properties of the ionomers. This is given below as a part of the summary.

It should be noted that in the sulfonates, one can shift the tan δ and log E' curves and achieve overlap of curves in the temperature range of ca. 230–340 °C. In the methacrylates, it is also possible to shift the curves along the temperature axis, but only to achieve overlap of the low-temperature side of the cluster tan δ curves (not shown here). Those overlapping curves are somewhat similar to those for the sulfonates. This implies that the molecular weight dependent behavior of these two ionomer systems is similar, with the major difference being only the onset of the temperature at which the ionomers start to show that behavior. In the case of the sulfonates, because of the stronger ionic interaction, the molecular weight dependent behavior is seen at much higher temperatures than in the methacrylates (i.e., 170 vs 220 °C). Also, for the sulfonates, the behavior seems to be less pronounced than in the methacrylates; this is possibly due to the fact that temperature is very high and close to the sample decomposition temperature; thus one cannot obtain the data over a wide range of temperatures.

IV. Conclusions

The dynamic mechanical and melt rheological properties of ionomers are dependent on the molecular weight in the high-temperature or low-frequency region. In the case of the P(S-*co*-MANa) system, the tan δ plots as a function of temperature, for high molecular weight ionomers (M_n > 100 000), show the cluster peaks clearly. However, for the low molecular weight samples, especially those lower than 100 000, the cluster peak becomes less distinct with decreasing molecular weight, and only a shoulder can be seen for the sample of molecular weight 21 000. However, peak deconvolution of the loss tangent peaks suggests that, even in that sample, there are two peaks in the tan δ plot and that the areas under the peaks do not change significantly with molecular weight. Thus, the flow behavior of the matrix phase merely veils the relaxation process of the cluster phase at low molecular weights.

From the values of the rubbery moduli, it is suggested that chain entanglements in the ionomers form in the same way as in pure polystyrene. Also, in the terminal regions, η_0 shows the same molecular weight dependence in the ionomers as in PS. $J_s°$ does not depend on molecular weight, except for the P(S-3.9-MANa)-21 ionomer. The ionic character does affect the flow process of the ionomers and shows a relatively high value of η_0 for the ionomers; ionic interactions thus act as a friction to delay the entanglement relaxation in the terminal region. The ionic interactions in the methacrylates are relatively weak, physical cross-links are less stable, and thus at relatively low temperature (ca. 170 °C) ion-hopping can occur, leading to a decrease in the "ionic" modulus. Therefore, the methacrylates show a pronounced molecular weight dependent behavior at a relatively low temperature.

In the case of the sulfonates, many trends are similar to those found in the methacrylates. In the tan δ plot as a function of temperature, the cluster peak becomes more distinct as the molecular weight increases. In addition, the slope of the storage modulus curve in the flow region become less steep with increasing molecular weight. However, there are some differences in the results between the methacrylates and the sulfonates. The sulfonates show molecular weight dependent behavior at much higher temperatures, i.e., ca. 220 °C, while in the methacrylates, it is seen even below 170 °C. This is due to the difference in the strength of the electrostatic interactions in the multiplets. For the sulfonates the interaction between ion pairs in the multiplets is stronger than that for the methacrylates, and thus the multiplets, i.e., physical cross-links, are intact up to ca. 220 °C. The activation energies for the glass transitions of the matrix and the clusters, as well as for the ion-hopping process, are independent of the molecular weight. These results imply that the rigidity or stability of multiplets does not change with the molecular weight. In the loss modulus plot, it is also seen that the widths at half-height of the peaks and the positions of the peaks, associated with the glass transitions of both the matrix and cluster phases, are independent of the molecular weights. Thus, it can be concluded that the molecular weight does not alter significantly the relaxation mechanism of the ionomers. It is also found that the thermal stabilities of ionomers are similar to that of polystyrene.

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