Viscoelastic Behavior of Very Lightly Sulfonated Polystyrene Ionomers

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Received January 17, 2007; Revised Manuscript Received March 19, 2007

ABSTRACT: The linear viscoelastic behavior of sulfonated polystyrene ionomers with as few as one sulfonate group per 1000 styrene repeat units was studied by dynamic mechanical analysis. Interactions of the sulfonate groups shifted the terminal flow region to lower frequency and produced a new low-frequency relaxation that was not present in the unmodified polystyrene. The observation of the low-frequency relaxation at very low sulfonation levels suggests that even for 0.11 mol % sulfonation, ionic clusters form—even though, no SAXS peak has been resolved for ionomers with that low a sulfonation level. The effect of the ionic groups on the viscoelastic properties can be varied for a fixed sulfonation level by weakening the ion-dipole strength of the ion pair. This can be achieved by substituting ammonium (NH_4^+) cations for metal cations such as Na^+.

Introduction

Ionomers, predominantly hydrophobic polymers having small amounts of bonded ionic groups (∼ <15 mol %) are of technological interest because ionic interactions produce large changes in the physical, mechanical, and rheological properties. The changes in the viscoelastic behavior of ionomers are mainly due to the interactions of the sulfonate groups. The effect of ionic group association on the melt rheology of ionomers has been reviewed by Register and Prud'homme.[1] Sulfonated polystyrene ionomers (SPS) have been studied by a variety of research groups as a "model" ionomer.[2] Surprisingly, there have been few studies of the melt rheology of neat SPS.[3−9] The major conclusion of the majority of those studies was that sulfonation produces substantial increases in the melt viscosity, and the choices of the cation and solvent history influence the viscosity.

In an earlier study,[9] we described the viscoelastic behavior of sodium and zinc salts of SPS with sulfonation levels of 1.9−5.8 mol %. Sulfonation increased the glass transition temperature (T_g) of the polymer and produced two new features in the viscoelastic behavior: (1) a rubbery plateau above T_g and (2) a second loss process at elevated temperatures (or at low frequencies). The rubbery plateau was due to the formation of a physical network that persisted over a range of >100 °C. The high-temperature (or low-frequency) relaxation resulted from the formation of an ion-rich nanophase that acted as multifunctional cross-links. The major effect of the nanophase (sometimes referred to as ionic clusters) was to increase the longer time relaxation processes, which increased the viscosity and was responsible for the network-like behavior of ionomers above T_g. In a later paper, Colby et al.[7] measured the diffusion coefficients and the terminal relaxation time for a sodium salt of a deuterated SPS with a sufonation level of 0.85 mol %. There results also showed two separate relaxations in the dynamic mechanical behavior.

Small-angle X-ray scattering (SAXS) evidence for the nanophase separation of ionic clusters (a broad diffuse peak observed in the SAXS data) in SPS has been reported by a number of research groups.[10−17] The characteristic dimension associated with the SAXS peak is ∼2−4 nm, and the clusters for metal neutralized SPS have been observed at sulfonation levels as low as 0.9 mol %.[18] Failure to resolve an X-ray scattering peak below that sulfonation level may be a result of insufficient contrast or lack of formation of ionic clusters.

In this work, we studied the linear viscoelastic behavior of sodium and ammonium salts of SPS with sulfonation levels <1 mol %. The effects of the ionic pair interactions on the rubbery plateau and terminal flow regions are discussed.

Experimental Details

Materials. Atactic polystyrene (Pressure Chemical Inc.; M_n = 400 000 g/mol and polydispersity = 1.06) was randomly sulfonated with acetyl sulfate following the procedure described by Makowski et al.[19] The sulfonation level was determined by titration of the sulfonic acid derivative in toluene with a standard solution of NaOH in methanol. NaSPS and NH_4SPS ionomers were prepared by completely neutralizing the sulfonic acid derivative in toluene with either NaOH or NH_4OH in methanol. The solvent was removed by steam distillation, and the ionomers were dried at 80 °C for 1 day and then dried in a vacuum oven with the temperature raised progressively to 200−220 °C for 1 day to remove any possible solvent residue. The dried samples were hot-pressed into 2 mm thick × 27 mm diameter disks.

Viscoelastic Measurements. Dynamic mechanical analyses of the ionomer melts were performed on a Rheometrics System IV mechanical spectrometer equipped with a 25.4 mm parallel-plate fixture. The expansion of the sample thickness from 130 to 240 °C was measured after equilibrating the samples for ∼45 min, and these values were used to correct the sample thickness during the isothermal measurements of the dynamic shear properties of the ionomer. The samples were first heated to the highest measuring temperature used, and the dynamic shear moduli, G' and G'', were measured at frequencies, ω, from 0.02 to 200 rad/s. The temperature was then lowered by ∼10 °C, and the rheological properties were measured again. This procedure was continued until evidence for slippage of the sample in the shear fixture was observed, at ∼130 °C. Moduli−frequency master curves were constructed by shifting the isothermal moduli curves with respect to a reference temperature of T_r = 140 °C along the frequency axis using computer programs that were developed by Shaw.[20] No vertical corrections were made.

Results and Discussion

The glass transition temperatures (T_g) measured by DSC were similar for all the polymers. For PS, T_g = 101 °C, and the T_g's of the 0.11 and 0.43 mol % salt were the same as that of PS within experimental error. The T_g of the 1.71 mol % salts were

10.1021/ma070136i CCC: $37.00

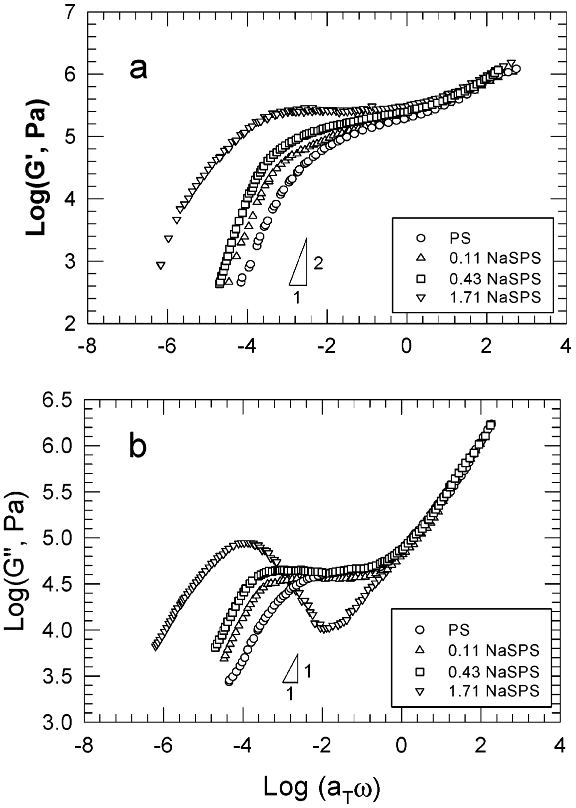

Figure 1. Modulus−frequency mastercurves for PS and NaSPS ionomers at T_r = 140 °C: (a) G' and (b) G''.

a little higher, ∼105 °C, due to the suppression of segmental motion by the interchain association of the ionic groups. However, all of the T_g's were considered similar for the rheology experiments, so that only a single reference temperature (T_r = 140 °C) was used for time (frequency)−temperature superposition (TTS).

The effects of ionic interactions on the viscoelastic behavior of SPS are pronounced, as was demonstrated by the study of Weiss et al.[9] where as few as 1.8 Na sulfonate groups per 100 styrene repeat units suppressed the terminal relaxations by at least 4 orders of magnitude in frequency and produced a new peak in the relaxation spectrum above the transition region. While the T_g of the 1.8-NaSPS was only ∼105 °C, terminal flow behavior was not observed below 240 °C.

Figure 1 shows the G'− and G''−frequency mastercurves for NaSPS ionomers with sulfonation levels of 0.11, 0.43, and 1.71 mol %. TTS worked well for these materials, which is consistent with an earlier finding of the success of TTS for SPS ionomers over as much as 20 decades of frequency.[9] TTS is generally expected to fail for a phase-separated or nanophase-separated material. However, for the SPS ionomers, the two characteristic relaxation processes, i.e., for the ionic and nonionic phases, are widely separated in time such that the individual isothermal measurements, which cover only 2−3 decades of frequency, do not access both processes at a single temperature. As a result, the viscoelastic behavior appears to be rheologically simple.

Even for the 0.11-NaSPS, which has ∼1 sulfonate group per 1000 styrene units, a shift of the terminal region to lower frequency is clear in Figure 1. That sulfonate concentration corresponds to an equivalent weight of ∼104 000 g, or about 4 sulfonate groups per chain on average. The PS, 0.11-NaSPS and 0.43-NaSPS samples exhibited terminal behavior at low frequencies, i.e., $G' \propto \omega^2$ and $G'' \propto \omega$.[21] However, the terminal region was shifted to lower frequency, about $^1/_3$ and $^1/_2$ an order of magnitude for 0.11-NaSPS and 0.43-NaSPS, respectively. The 1.71-NaSPS sample did not reach terminal response for frequencies nearly 3 orders of magnitude lower than that for PS. The rubbery modulus, G'_r, increased with increasing sulfonation level, which is consistent with the idea that the sulfonate groups act as physical cross-links, i.e., classical rubber elasticity predicts an increase in G' following the transition region (i.e., as frequency decreases) as the cross-link density increases.

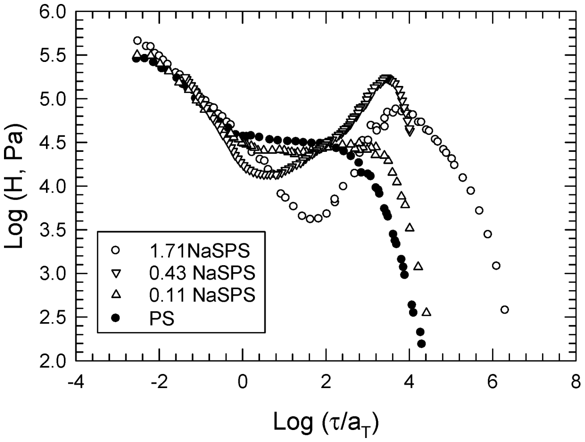

Figure 2. Relaxation time spectra for PS and NaSPS ionomers at T_r = 140 °C.

The shapes of the $G''-\omega$ curves for the 0.11-NaSPS and 0.43-NaSPS are similar to that of the unmodified PS. However, the 1.71-NaSPS exhibited a distinct peak at lower frequency, which is consistent with a second relaxation process. A similar result was observed by Weiss et al.[9] for NaSPS with sulfonation levels between 1.8 and 5.8 mol % and by Colby[7] for 0.85-NaSPS. The low-frequency relaxation was attributed to nanophase separation of ionic clusters. The absence of a clear second relaxation in the $G''-\omega$ curves for the 0.11 and 0.43 mol % ionomers suggests that such clusters are not present in these materials. In that case, the effect of the ionic species on the viscoelastic properties may be due to simple ion-dipole interactions of two or a few ionic groups. No evidence of nanophase separation was found by SAXS for these ionomers, though, as discussed above, that may also be expected if the concentration of clusters is very low; i.e., the electron density contrast is too low to resolve the scattering between the two phases. However, long-lived pairwise ionic associations may also produce a second relaxation process in these materials.

The relaxation time (τ) distributions, $H(\tau)$, for the ionomers were calculated from the master curves of G' and G'' by using the second approximation formula of Tschoegel:[21]

$$H(\tau) = G'\left[\left(\frac{\mathrm{d}\log G'}{\mathrm{d}\log \omega}\right) - \frac{1}{2}\left(\frac{\mathrm{d}\log G'}{\mathrm{d}\log \omega}\right)^2 - \frac{1}{4.606}\left(\frac{\mathrm{d}^2 \log G'}{\mathrm{d}(\log \omega)^2}\right)\right]_{1/\omega=\tau/\sqrt{2}} \quad (1)$$

or

$$H(\tau) = \frac{2}{\pi}\left[G'' + \frac{4}{3}\left(\frac{\mathrm{d}G''}{\mathrm{d}\ln \omega}\right) + \frac{1}{3}\left(\frac{\mathrm{d}^2 G''}{\mathrm{d}(\ln \omega)^2}\right)\right]_{1/\omega=\tau/\sqrt{2}} \quad (2)$$

$H(\tau)$ calculated from eqs 1 and 2 (G' and G'') were in good agreement, and the distributions calculated from G' are shown in Figure 2. The $H(\tau)-\tau$ curve for PS had the general wedge and box shape described by Tobolsky[22] for amorphous polymers,

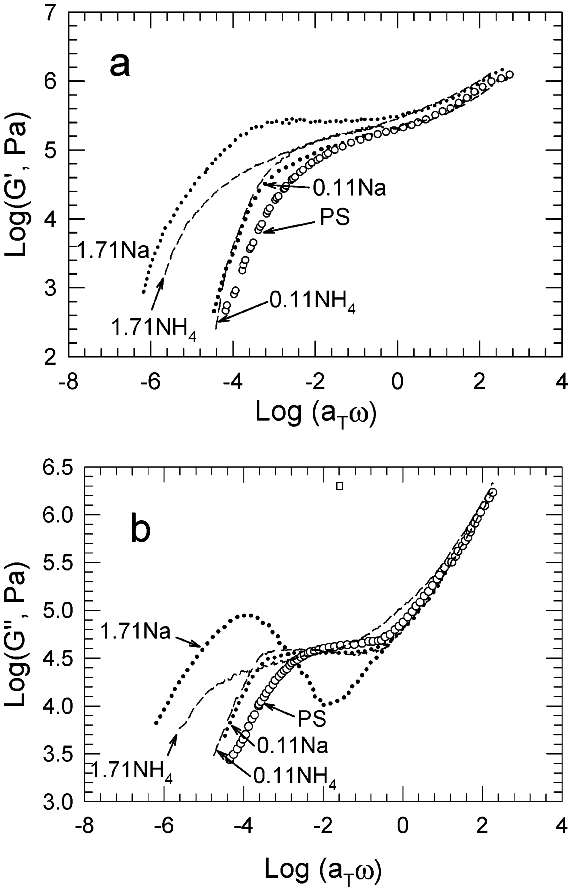

Figure 3. Comparison of modulus−frequency mastercurves for 1.71- and 0.11-NaSPS and NH_4SPS ionomers at $T_r = 140$ °C: (a) G' and (b) G''.

but the ionomers also exhibited a peak at longer times. This is thought to be a consequence of the relaxation of the long-lived ionic interactions, which perturb the rheological behavior even at sulfonation levels as low as 0.11 mol %. The position of the peak maximum moves to higher relaxation time as the sulfonation level increases.

The ammonium (NH_4^+) salts, NH_4SPS, exhibited similar rheological behavior as NaSPS (see Figure 3). Little difference was observed in the G' and G'' behavior for the 0.11-NaSPS and 0.11-NH_4SPS. However, the 1.71-NH_4SPS showed its terminal region at a higher frequency, and its G'_r was lower than those of the NaSPS. That was a consequence of the weaker ion-dipole interaction of the ammonium sulfonate compared with the sodium sulfonate groups. Previously, Stamato[23] showed that the zero shear viscosity of an SPS ionomer with 1.8 mol % sulfonation could be varied over several orders of magnitude by varying the ion-dipole strength by using $NHR_1R_2R_3^+$ salts, where R_1, R_2, and R_3 were C_4H_9 or H. NH_4^+ should provide the strongest ion-dipole interaction among the among $NR_1R_2R_3R_4^+$ salts, but a study by Weiss et al. showed that it was still much weaker than that of metal salts, such as Na^+.[5]

Figure 4 plots the complex viscosity (η^*) vs shear rate for the Na- and NH_4SPS ionomers; η^* was calculated from the dynamic moduli data

$$\eta^* = \sqrt{(G'/\omega)^2 + (G''/\omega)^2} \qquad (3)$$

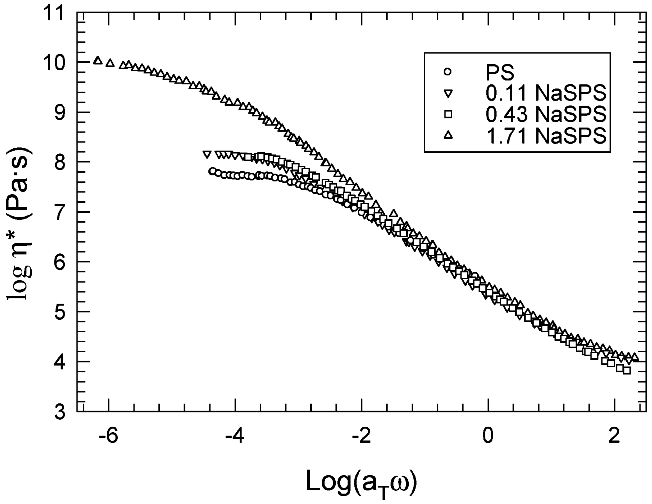

Figure 4. Complex viscosity−frequency mastercurves for PS and NaSPS ionomers at $T_r = 140$ °C.

Table 1. Zero-Shear Rate Viscosities of PS and SPS Ionomer Melts at 140 °C

	Na salt		NH_4 salt	
sample	log(η_0) (Pa•s)	M_{equiv}[a] (10^4 g/mol)	log(η_0) (Pa•s)	M_{equiv}[a] (10^4 g/mol)
PS	7.7	40	7.7	40
0.11-SPS	8.2	56	8.3	60
0.43-SPS	8.5	69		
1.71-SPS	10.0	190	9.5	135

[a] $M_{equiv} = M_{PS}[(\eta_0)_{SPS}/(\eta_0)_{PS}]^{1/3.4}$.

The zero-shear rate viscosity (η_0) was calculated by fitting the Bird−Carreau model[24] to the $\eta^*-\omega$ data and extrapolating to $\omega \rightarrow -\infty$ (from a practical perspective, $\omega = 10^{-10}$ was used). The values of η_0 are given in Table 1. Also given in Table 1 is a calculation of the equivalent molecular weight of polystyrene that would exhibit a similar value of η_0. That was calculated using the experimental value of η_0 for the unmodified polystyrene and assuming a scaling law of $M^{3.4}$ for the zero-shear viscosity.[21] Adding as few as 1 sulfonate group per 1000 styrene units (in this case, ~4 sulfonate groups per chain) acted to increase the PS equivalent molecular weight (M_{equiv}) by nearly a factor of 2. Increasing the sulfonation level to 17 groups per 1000 styrene units increased M_{equiv} by half an order of magnitude.

While it has been well-known for decades that sulfonation can profoundly affect the rheological properties, it is still surprising that such a significant effect can be achieved at the very low sulfonation levels reported herein. In fact, the large increase in viscosity of sulfonated polymers, such as SPS, has previously been seen as a problem in that modest levels of sulfonation (e.g., ~2−5 mol %) increase the viscosity so much that melt processing and even steady shear rheological measurements are difficult, if not impossible, to achieve. The present study suggests that much lower sulfonation levels can be exploited to modify rheological behavior, and presumably some of the more desirable physical property modifications, without greatly sacrificing melt processability. Or, such ionomers may be candidates for compatibilizers without significantly affecting melt processability of polymer blends. Previous work demonstrated that SPS ionomers can be used as compatibilizing agents for a variety of polymer blends.[25]

Conclusions

As few as one sulfonate group per 1000 styrene repeat units can have a profound effect on the viscoelastic behavior of sulfonated polystyrene ionomers. Interactions of the sulfonate groups shift the terminal flow region to lower frequency and produce a new low-frequency relaxation that is not present in the unmodified polystyrene. The low-frequency relaxation is believed to arise from long-lived pairwise ionic associations. No evidence of ionic clusters was found by SAXS analysis. The effect of the ionic groups on the viscoelastic properties can be varied for a fixed sulfonation level by weakening the ion-dipole strength of the ion pair. This can be achieved by substituting ammonium (NH_4^+) cations for metal cations such as Na^+.

Acknowledgment. This work was supported by the Polymer Division of the National Science Foundation (Grant DMR 0304803).

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