Rheological behavior of oligomeric ionomers

R. A. Weiss

Polymer Program and Chemical Engineering Department, University of Connecticut, Storrs, Connecticut 06269

Hongying Zhao

Polymer Program, University of Connecticut, Storrs, Connecticut 06269

(Received 17 March 2008; final revision received 30 September 2008)

Synopsis

The rheological behavior of the alkali metal salts of oligomeric sulfonated polystyrene (PS) ionomers was characterized using dynamic and steady shear measurements. The starting PS had a weight average molecular weight of 4000 g/mol and a narrow molecular weight distribution (1.06). Two sulfonation levels were examined, 2.5 and 4.8 mol %, which corresponded, respectively, to one and two sulfonate groups per chain on average. The ionomers exhibited nanophase separation of an ion-rich phase, and as a consequence, time-temperature superposition failed for all samples. Sulfonation increased the melt viscosity of the ionomers, as much as seven orders of magnitude. The zero shear viscosity scaled as \( \frac{c q}{a} \), where \( c \) was the concentration of the ionic groups, \( q \) was the charge of the cation, and \( a \) was the cation radius, and although the molecular weight of the parent polystyrene was much lower than the entanglement molecular weight, the ionomer melts exhibited strong elastic behavior. The flow activation energy of the ionomers was similar to that of high molecular weight PS and the calculated molecular weight between “entanglements” of the ionomers was the same as for PS. © 2009 The Society of Rheology. [DOI: 10.1122/1.3003570]

I. INTRODUCTION

Ionomers, predominantly hydrophobic polymers having small amounts of bonded ionic groups, are of technological interest because ionic interactions produce large changes in the physical, mechanical, and rheological properties. Studies of ionomers have included carboxylated, sulfonated and phosphonated polymers [Jérôme and Mazurek (1997)]. Interchain interactions of the ionic species generally increase the glass transition temperature \( T_g \), change the solubility behavior, improve the stiffness and/or the toughness and strength of the polymer, and increase the solution and melt viscosities. Although a definitive elucidation of the microstructure of these polymers (i.e., the spatial arrangement of the ion pairs) has eluded scientists for over 40 years, it is generally believed that the unique properties of ionomers arise from nanophase separation of ion-rich aggregates with a characteristic dimension of \( \sim 1–5 \) nm. Various conceptual models for this nanostructure have been proposed [Mauritz (1997)], though none has been definitively con-

\(^{a)} \) Author to whom correspondence should be addressed; electronic mail: rweiss@ims.uconn.edu

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firmed experimentally. The literature on ionomers is predominantly concerned with two general classes of materials: random ionomers, where the ionic groups are randomly located along the chain, and telechelic ionomers, where the ionic groups are located only at the chain ends. In this paper, only random ionomers are discussed.

The melt rheology of ionomers has been reviewed by Register and Prud'homme (1997). At relatively low temperatures, the ionic aggregates act as physical crosslinks. These crosslinks persist to elevated temperature, but "ion hopping" [Cooper (1958)] of ion pairs from one aggregate to another allows for melt flow. The viscosities of the ionomer melts, however, are usually very high due to the relatively long relaxation times of the ionic associations [Weiss et al. (1991)].

The characterization of the rheological behavior of ionomers is complicated by the long relaxation times required to achieve steady state in a steady shear experiment. For anionomers, the choice of the bonded anion and the mobile cation significantly affect the rheology. Carboxylate ionomers tend to exhibit much weaker intermolecular interactions compared to sulfonate ionomers with the same backbone [Lundberg and Makowski (1980)], and the viscosity of an ionomer is sensitive to the choice of the counterion. Because of the poor melt flow properties of ionomers, most studies of their rheology have involved dynamic characterization. Steady-shear behavior has been characterized for poly[ethylene-ran-(meth)acrylic acid] [Earnest and MacKnight (1978); Bonotto and Bonner (1968); Sakamoto et al. (1970)], poly(propylene-ran-acrylic acid) [Weiss and Agarwal (1980)], and poly(styrene-ran-butyl methacrylate-ran-potassium methacrylate) [Erhardt et al. (1974)] ionomers, but there is very little literature on the steady-shear properties of sulfonated ionomers. Lundberg and Phillips (1984) reported steady state melt viscosities of the sodium salt of a sulfonated polystyrene ionomer (SPS) with low sulfonation (1.7 mol %), and Weiss et al. (1984) and Weiss and Stamato (1989) studied the viscosity behavior of alkyl-ammonium salts of SPS. Both of those groups used capillary viscometry in their investigations, so no information on elasticity of the melt was obtained.

In addition to the high viscosity and poor flow characteristics of ionomers, characterization of the effect of the ionic interactions on the rheology is complicated by the difficulty in separating effects due to molecular entanglements and the ionic interactions. Although, one might expect the latter to dominate the behavior in most melt flow situations, the entanglement effects, and especially trapped entanglements, also play a significant role in the melt rheology. This is demonstrated by the fact that rubber-elasticity models that treat the ionic interactions as simple molecular crosslinks tend to underestimate the crosslink density of an ionomer melt, and the calculated contribution of trapped entanglements due to dipole-dipole associations to the dynamic storage modulus has been reported to be similar to that of the ionic crosslinks [Weiss et al. (1991)].

In this paper, low molecular weight (DP ~ 39) SPS was used to study the dynamic and steady shear rheology of SPS ionomers, including salts formed from alkali metals. The motivation of this work was to isolate the effect of the ionic interactions on the melt rheology. The approach was predicated on the fact that the polymer chain length used was far below the entanglement molecular weight of polystyrene. Thus, there should be no influence of molecular entanglements on the flow properties. Chain entanglements arising from an effective lengthening of the polymer chains due to interchain ionic associations, however, may be important.
II. EXPERIMENTAL

A. Materials

Low molecular weight polystyrene (PS), $M_w=4000\;\text{g/mol}$, with a polydispersity index, PDI=1.06, was obtained from Pressure Chemical Co. This was sulfonated in dichloroethane (DCE) using acetyl sulfate, following the procedure of Makowski et al. (1975) that produces random sulfonation primarily at the para-position of the phenyl ring. The acetyl sulfate was prepared by slowly adding concentrated sulfuric acid to a 60% excess of acetic anhydride in 1,2-dichloroethane at $0\;\text{°C}$. The freshly prepared acetyl sulfate was added to a stirred 10% solution of PS in DCE at $\sim50\;\text{°C}$. The reaction was terminated after 1 h by the addition of 2-propanol. The SPS was isolated by steam distillation of the solvent, washed three times with boiling water, dried in air at $70\;\text{°C}$ for 1 day, and finally dried at $120\;\text{°C}$ in a vacuum oven for 1 week. The sulfonation level was determined by elemental sulfur analysis (Galbraith Laboratories, Inc.) and $^1$H NMR using the procedure described by Baigl et al. (2002). Two different SPS were prepared, with degrees of sulfonation (DS) of 2.5 and 4.8 mol %, where DS is defined as the average number of sulfonate groups in 100 styrene repeat units. The DS values reported in this paper are based on the elemental analysis. The values calculated from nuclear magnetic resonance agreed within 10%. The DS values for the ionomers used correspond to about one and two sulfonate groups per chain, respectively, for the low molecular weight SPS, though it should be noted that since sulfonation proceeds randomly, the product will include a distribution of chains with varying sulfonation.

Alkali metal salts of SPS were prepared by adding a 50% excess of the appropriate metal hydroxide or acetate to the SPS acid derivative in a 90/10 (v/v) mixture of toluene and methanol. The neutralizing base was dissolved in methanol or methanol with a small amount of water and added drop-wise to an agitated 15% (w/v) solution of the polymer. After 30 min the neutralized SPS was recovered by steam distillation and washed and dried as described above for the SPS. The sample notation used for the ionomers is MSPSx.y, where M denotes the cation ($\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{Rb}^+$, $\text{Cs}^+$) and x.y is the DS.

B. Materials characterization

The glass transition temperatures ($T_g$) of the starting PS and the ionomers were measured by differential scanning calorimetry using a Perkin Elmer model DSC-7 and a heating rate of $20\;\text{°C/min}$. A nitrogen atmosphere was used. The microstructure of the ionomers was characterized by small angle x-ray scattering (SAXS) using a Bruker–Anton–Paar small-angle scattering instrument with a Rigaku Ru-300 rotating anode generator (Cu $K\alpha$ radiation) and a Bruker HiStar two-dimensional detector. The SAXS samples were the dried powders recovered from the sulfonation reactions described above, which were placed in a 5 mm hole in a 1 mm thick aluminum plate and sealed with polyimide film. The data shown in this paper were for unannealed samples, but annealing at elevated temperatures had little effect on the SAXS curves.

SAXS measurements were also made on samples undergoing simple shear flow. These were performed at Brookhaven National Laboratory on beamline X-27C using a Linkam CSS-450 high temperature shear stage that consists of parallel plates in which the top plate rotates at a fixed speed. A MAR charge coupled device x-ray detector was used. The specimens were prepared by compression molding at 210–250 °C under vacuum using a custom-designed press, composed of four steel springs to apply a compressing force to parallel steel plates, that fit inside a temperature-controlled vacuum oven. The shear rates used varied from 0 to 20 s$^{-1}$. 

OLIGOMERIC IONOMERS
**C. Rheology**

Dynamic and steady-shear measurements were made with a TA Instruments advanced rheometric expansion system, a strain-controlled rheometer. Cooling was achieved with liquid nitrogen. A 25 mm parallel plate fixture was used for dynamic shear testing and a 25 mm cone-and-plate fixture was used for steady-state shear experiments. The specimens were prepared by compression molding at 210–250 °C under vacuum.

Frequency sweep tests at temperatures from 120 to 260 °C were performed covering a frequency range of 0.01–100 Hz. All measurements were made within the linear viscoelastic limit, which was determined from strain sweep experiments. Time-temperature-superposition (TTS) master curves of $G'$ and $G''$ were constructed at reference temperatures of $T_r=T_g+45$ °C. Vertical corrections were made by multiplying the moduli by $\beta=T_g/T$ to compensate for the temperature dependence of the modulus. Steady-shear experiments were run from 150 to 280 °C using step shear experiments and shear rates from 0.001 to 25 s$^{-1}$. As the sample temperature was changed, the cone-and-plate gap was adjusted to account for thermal expansion of the fixture and maintain a constant separation. The samples were sheared prior to the measurements until a constant stress was achieved at each shear rate, usually within 5 min, and the rheology measurements were made and averaged over a period of 5 min.

**III. RESULTS AND DISCUSSION**

Sulfonation increased the $T_g$ of the PS by about 2 °C/mol % sulfonation, see Table I, which is due to the suppression of chain mobility due to intermolecular hydrogen bonding for the acid derivative and dipole-dipole interactions for the salts. This value is lower than other reports of the effect of sulfonation on rate of change of $T_g$ of PS [Weiss et al. (1991); Mattera and Risen (1986); Hara et al. (1991)]. That may be due to the lack of entanglements in the oligomeric ionomers. The properties of ionomers, such as $T_g$, often scale with $q/a$, where $q$ is the charge of the counter-ion and $a$ is the separation of the charges in the ion pair (essentially the ionic radius) [Eisenberg (1971)]. The quantity $q/a$ is a measure of the ionization potential, or Coulomb energy, of the ion pair. The $T_g$s of the oligomeric SPS ionomers, however, were independent of $q/a$, which is consistent with the earlier findings for higher molecular weight SPS by Mattera and Risen (1986).

SAXS data for the SPS2.5 and SPS4.8 ionomers are shown in Fig. 1. The salts exhibited a broad, diffuse scattering maximum between $q=0.5$ and 3.0 nm$^{-1}$ ($q = 4\pi \sin \theta/\lambda$ where $\lambda$=the x-ray wavelength (0.154 nm for Cu $K\alpha$) and $2\theta$=the scatter-
ing angle), which is consistent with that observed in most ionomers [Grady and Cooper (1997)]. Although it is not possible to unambiguously delineate the microstructure of the ionomer from a single, broad scattering peak, it is generally agreed that the peak arises from a correlation length, \( d = 2\pi / q \), attributable to nanophase separation of the ionic groups. That is supported by the fact that the peak intensity increases as DS and/or the electron density of the cation increases; see Fig. 1. The latter effect increases the electron density contrast between the ionic and nonionic phases. The one exception was a lower scattering intensity observed for the Cs salts, which has the highest electron density. That anomaly is due to strong absorption of the x-ray radiation by Cs\(^+\). Note that although the samples were exposed with radiation for the same amount of time, quantitative compari-
sons between the curves in Fig. 1 cannot easily be made. As was described in the Sec. II, the samples were powders and although the nominal sample volume (5 mm diameter × 1 mm thick) was the same in each case, the powder particle size(s) were not exactly the same, so that the amount of material being exposed to x rays varied.

In general, the scattering peak moved to higher $q$ and $d$ decreased from $\sim 5.3$ to $\sim 4.2$ nm when the DS increased from 2.5 to 4.8 mol %. The scattering curves could be fit with a the liquid-like, hard sphere model of Yarusso and Cooper (1983) that attributes the correlation length to interparticle interference of ionic domains, called ionic clusters. Based on that model, the decrease in $d$ corresponds to a decrease in the distance of closest approach of the clusters, or a decrease in the size of the clusters. The corresponding higher scattering intensity for the ionomers with higher DS indicates a higher concentration of smaller clusters for the higher sulfonation. The strong upturn in the scattering intensity as $q \rightarrow 0$, see Fig. 1, is also a characteristic of ionomers, which has been attributed to an inhomogeneous distribution of isolated ion pairs [Grady and Cooper (1997)].

Neither PS, nor the HSPS samples exhibited a scattering peak. The lack of a scattering peak for PS is expected, since there is no phase separation in the homopolymer, but the lack of the scattering peak in HSPS may be due either to the absence of nanophase separation of the acid derivative or to the poor electron density contrast between a sulfonic acid rich phase and the hydrocarbon continuous phase. The viscoelastic behavior discussed below indicates that those materials were not nanophase separated.

A. Dynamic rheology

Frequency-temperature mastercurves for PS and the SPS ionomers are compared in Figs. 2 and 3. Whereas time TTS was successful for the PS and H-SPS ionomers, TTS failed for the metal salt ionomers. This is more easily seen in Fig. 4, which shows the attempted superposition of the data at different temperatures for the Na-SPS2.5. The superposition failed for $G'$ and $G''$ in the midrange of reduced frequencies, though the failure is more apparent in the $G''$ data in Fig. 4. This result is in contrast to earlier results for high molecular weight SPS ionomers, where TTS worked well [Weiss et al. (1991)]. In that case, the explanation for the success of TTS was that even though the materials were nanophase separated, the relaxation times for the two phases were so far apart that only one mechanism was accessed in a single experiment. The slopes of the high frequency region of $G'$ and $G''$ versus $\omega$ in Fig. 4 were between 0.6 and 0.7, which agree better with a Zimm model (slope=2/3) than a Rouse model (slope=1/2), which is not surprising, since hydrodynamic interactions are likely to be important in the melt.

A comparison of Figs. 2 and 3 indicates that the plateau modulus of the ionomers, $G_N$, increased as DS increased, which is consistent with the theory of rubber elasticity that predicts that $G_N$ is proportional to the cross-link density. As the sulfonation level increased, the number of ionic interactions per chain also increased, which produces a higher $G_N$. Except for the Li salts, $G_N$ was relatively independent of the cation used, which indicates that the structure of the networks formed by the different metal sulfonates are similar, though the relaxation of the networks strongly depended on the cation, i.e., $q/a$. The reason for the anomalous behavior of the LiSPS described here and elsewhere in the discussion that follows is not known, but the divergence of the behavior of the Li salt from other metal salts of ionomers has been noted for a variety of properties by various research groups. Lithium is the smallest cation possible and that may be the origin of its anomalous behavior, but at the present time, this remains an unanswered question.

All of the ionomers exhibited terminal behavior of $G''$ data, with a limiting slope of
The $G'$ data also appeared to reach terminal behavior at low frequencies, though the limiting slopes for the ionomers was $\lim_{\omega \to 0} (\log G'/\log \omega) \sim 1.7$, which is smaller than the terminal slope of 2.0 expected (i.e., $G' \propto \omega^2$) [Ferry (1980)]. The PS and HSPS samples behaved as Rouse chains [Ferry (1980)]. $G'' \propto \omega$ over the entire range of frequencies studied, and $(\log G'/\log \omega) = 1.9$, which was close to the theoretical value of 2. The Rouse-like behavior was expected for the unentangled PS oligomer, but it was somewhat surprising for the H-SPS2.5, since hydrogen bonding is strong enough in that material to raise the $T_g$ about 5 °C. It would appear, however, that the hydrogen bonding was sufficiently weakened at elevated temperatures so as not to greatly influence the rheological behavior. The deviation of the $G'$ data from $G' \propto \omega^2$ at low frequency for the H-SPS sample may indicate the onset of solid-like behavior at the lowest frequencies, where the applied stresses may have been insufficient to disrupt the physical network, or it may be due to instrument error—specifically, a small error in the tuning of the phase angle ($\delta$) [Velankar and Giles (2007)].

The zero-shear rate viscosities ($\eta_0$) and first normal stress coefficients ($\psi_{1,0}$) for the PS

**FIG. 2.** $G'$ and $G''$ master curves for PS and MSPS2.5 ionomers. Reference temperatures are $T_g + 45$ °C.
oligomer and the ionomers were calculated from Eqs. (1) and (2) [Ferry (1980)], where $J_e^0$ is the recoverable compliance. $\eta_0$, $\psi_{1,0}$, and $J_e^0$ are listed in Table II and $\eta_0$, $\psi_{1,0}$ are plotted against $cq/a$ in Fig. 5 (c is the mol % sulfonation)

$$\eta_0 = \lim_{\omega \to 0} (G''/\omega),$$  \hspace{1cm} (1)

$$\psi_{1,0} = 2J_e^0\eta_0^2 = 2 \lim_{\omega \to 0} (G'/\omega^2).$$  \hspace{1cm} (2)

The values of $\eta_0$ and $\psi_{1,0}$ for the H-SPS and PS were comparable and significantly lower by orders of magnitude than the values for the metal salt ionomers, which indicates that hydrogen bonding of the sulfonic acid groups had, at most, a minor perturbation on the rheological properties of the PS. The small, but finite, values of $\psi_{1,0}$ for the PS oligomer and the sulfonic acid derivative of SPS were consistent with the Rouse theory predictions of $J_e^0 = 5 \times 10^{-7}$ Pa$^{-1}$ [Ferry (1980)]; see Table II.

The $\eta_0$ and $\psi_{1,0}$ values for the metal salts scaled linearly with $cq/a$, with the exception of the Li ionomers. The values for $\eta_0$ were orders of magnitude greater than those of PS and the H-SPS derivative. Table II lists the calculated PS-equivalent molecular weights

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**FIG. 3.** $G'$ and $G''$ master curves for PS and MSPS4.8 ionomers. Reference temperatures are $T_g + 45^\circ$C.
that correspond to the $\eta_0$ values. These calculations were based on the scaling laws, $\eta_0 \propto M$ when $M \leq M_e$ and $\eta_0 \propto M^{3.4}$ when $M > M_e$, where $M_e$ is the entanglement molecular weight, of PS, 16 600 g/mol [Graessley (2004)]. There were also small differences in the temperatures for the $\eta_0$ values of the different ionomers, but compared with the large changes in $M_{\text{equiv}}$, the temperature effect is likely to be insignificant. These effective molecular weights, as high as 1 400 000 g/mol for the Na-SPS4.8, are remarkable when one considers that they result simply from dipole-dipole associations of a 4000 g/mol SPS. The values for $\eta_0$ and the effective molecular weight were very sensitive to the choice of the counter-ion, even though the $G_N$ results described above seemed to indicate that the crosslink density was independent of the counter-ion. The reason is due to differences in the strength of the dipole-dipole interactions, i.e., $q/a$, which, as discussed below, control the terminal relaxation time of the ionomer melt.

**TABLE II.** Material properties and PS-equivalent molecular weights of SPS ionomers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{ref}}$ (°C)</th>
<th>$\eta_0$ (Pa s)</th>
<th>$\psi_{\text{1.0}}$ (Pa s$^2$)</th>
<th>$f_e^0$ (Pa$^{-1}$)</th>
<th>$\tau$ (s)</th>
<th>$M_{\text{equiv}}^{a}$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>125</td>
<td>$6.3 \times 10^2$</td>
<td>$1.3 \times 10^{-4}$</td>
<td>$1.6 \times 10^{-7}$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$4.0 \times 10^3$</td>
</tr>
<tr>
<td>H-SPS2.5</td>
<td>130</td>
<td>$1.3 \times 10^1$</td>
<td>$4.0 \times 10^{-4}$</td>
<td>$1.2 \times 10^{-7}$</td>
<td>$1.6 \times 10^{-4}$</td>
<td>$8.3 \times 10^3$</td>
</tr>
<tr>
<td>Li-SPS2.5</td>
<td>131</td>
<td>$1.3 \times 10^4$</td>
<td>$3.2 \times 10^7$</td>
<td>$9.5 \times 10^{-4}$</td>
<td>$1.2 \times 10^2$</td>
<td>$5.2 \times 10^4$</td>
</tr>
<tr>
<td>Na-SPS2.5</td>
<td>131</td>
<td>$1.3 \times 10^6$</td>
<td>$6.3 \times 10^8$</td>
<td>$1.9 \times 10^{-4}$</td>
<td>$2.5 \times 10^5$</td>
<td>$1.0 \times 10^5$</td>
</tr>
<tr>
<td>K-SPS2.5</td>
<td>131</td>
<td>$3.2 \times 10^3$</td>
<td>$1.6 \times 10^7$</td>
<td>$7.8 \times 10^{-5}$</td>
<td>$2.5 \times 10^7$</td>
<td>$6.86 \times 10^4$</td>
</tr>
<tr>
<td>Rb-SPS2.5</td>
<td>130</td>
<td>$1.6 \times 10^8$</td>
<td>$5.0 \times 10^{10}$</td>
<td>$9.8 \times 10^{-5}$</td>
<td>$1.6 \times 10^7$</td>
<td>$5.6 \times 10^4$</td>
</tr>
<tr>
<td>Cs-SPS2.5</td>
<td>131</td>
<td>$5.0 \times 10^6$</td>
<td>$2.5 \times 10^8$</td>
<td>$5.0 \times 10^{-5}$</td>
<td>$2.5 \times 10^9$</td>
<td>$4.0 \times 10^4$</td>
</tr>
<tr>
<td>H-SPS4.8</td>
<td>135</td>
<td>$7.9 \times 10^2$</td>
<td>$3.1 \times 10^{-4}$</td>
<td>$2.5 \times 10^{-7}$</td>
<td>$2.0 \times 10^{-4}$</td>
<td>$5.0 \times 10^3$</td>
</tr>
<tr>
<td>Li-SPS4.8</td>
<td>136</td>
<td>$1.6 \times 10^9$</td>
<td>$7.9 \times 10^{13}$</td>
<td>$1.5 \times 10^{-5}$</td>
<td>$2.4 \times 10^4$</td>
<td>$8.4 \times 10^4$</td>
</tr>
<tr>
<td>Na-SPS4.8</td>
<td>135</td>
<td>$1.0 \times 10^{10}$</td>
<td>$7.9 \times 10^{14}$</td>
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<td>$4.0 \times 10^4$</td>
<td>$1.4 \times 10^6$</td>
</tr>
<tr>
<td>K-SPS4.8</td>
<td>136</td>
<td>$2.0 \times 10^6$</td>
<td>$2.0 \times 10^{11}$</td>
<td>$2.5 \times 10^{-6}$</td>
<td>$5.0 \times 10^5$</td>
<td>$4.5 \times 10^5$</td>
</tr>
<tr>
<td>Rb-SPS4.8</td>
<td>135</td>
<td>$4.0 \times 10^2$</td>
<td>$7.9 \times 10^9$</td>
<td>$2.5 \times 10^{-6}$</td>
<td>$1.0 \times 10^2$</td>
<td>$2.8 \times 10^5$</td>
</tr>
<tr>
<td>Cs-SPS4.8</td>
<td>136</td>
<td>$1.0 \times 10^7$</td>
<td>$7.9 \times 10^8$</td>
<td>$4.0 \times 10^{-6}$</td>
<td>$4.0 \times 10^1$</td>
<td>$1.9 \times 10^5$</td>
</tr>
</tbody>
</table>

$^a$For $\eta_0 \leq 2600$ Pa s (corresponding to $M_e=16 600$ g/mol), $M_{\text{equiv}}=16 600 \eta_0/2600$ for $\eta_0 > 2600$ Pa s, $M_{\text{equiv}}=16 600(\eta_0/2600)^{1.34}$.
The increase of \( J_e^0 \), by as much as three orders of magnitude upon conversion of the sulfonic acid groups to metal sulfonate groups, is consistent with the conclusion that the dipole-dipole interactions persist into the terminal region. Substantial increases in \( J_e^0 \) are usually observed in neutral polymers as a result of increases in the polydispersity of molecular weight and/or chain-branching. For the ionomers, the long-lived physical crosslinks essentially provide similar branching, which explains the increases in \( J_e^0 \) [Tierney and Register (2003)]. For a fixed DS, \( J_e^0 \) was relatively insensitive to the choice of the cation, with the exception of the Li salt, for which \( J_e^0 \) was about 4–5 times greater than for the other alkali salts. However, within the uncertainty of the calculation of \( J_e^0 \), recoverable compliances for each ionomer appeared to be independent of the counter-ion used. That conclusion is consistent with the observations of Register and co-workers that \( J_e^0 \) of partially neutralized poly(ethylene-r-methacrylic acid) ionomers depended only upon the molecular structure of the polymer, not on the cation type or neutralization level [Tierney and Register (2002); Vanhoorne and Register (1996)]. \( J_e^0 \) for the SPS ionomers did, however, decrease nearly two orders of magnitude when DS increased from 2.5 to 4.8 mol %. The remarkable aspect of these data is that these ionomers, which are far below the entanglement molecular weight of the parent polymer, exhibit a high level of elasticity in the melt. The origin of the elasticity is the ionic associations, which clearly persist into the terminal flow region.

The terminal relaxation time \( \tau \) was calculated from Eq. (3), and the values are listed in Table II. \( \tau \) increased by many orders of magnitude from \( \sim 10^{-4} \) s for PS to \( \sim 10^0 \cdots 10^4 \) s for the metal salt ionomers. The \( \tau \) data are plotted against \( cq/a \) in Fig. 6 and the relationship, \( \tau \propto [\log (cq/a)]^{3.1} \), fits the data reasonably well and demonstrates the strong dependence of the relaxation behavior of these ionomers on the strength of the ion pair. In general, \( \tau \) increased with increasing \( cq/a \), i.e., with increasing sulfonation level and with decreasing ionic radius of the cation—except for the Li salt, which exhibited a relaxation time intermediate between those of the Na and K salts. The increase in the

**FIG. 5.** Zero shear viscosity (open symbols) and zero shear first normal stress difference (filled symbols) calculated from dynamic shear data \((T = T_g + 45 \degree C)\) as a function of \( cq/a \): PS (○), H-SPS (∆), Li-SPS (□), Na-SPS (◇), K-SPS (◇), Rb-SPS (+), Cs-SPS (*). Note that the temperatures range from \( \sim 130 \) to \( 136 \degree C \).
relaxation time is a consequence of the ionic interactions and the accepted mechanism of flow of ionomers, namely ion hopping, where the rate dependent step is the release of one intermolecular association and the jump to another intermolecular association for a given ion pair [Hara et al. (1986); Leibler et al. (1991); Colby et al. (1998)].

\[ \tau = f(0) \eta_0. \]  

The \( G'' \) pseudomastercurves of the SPS4.8 ionomers exhibited a weak maximum in the plateau region, which is shown in Fig. 7(a) for the LiSPS4.8, for which the relaxation within the plateau region (marked by the arrow) was most distinct. The shape of the viscoelastic pseudomastercurve shown in Fig. 7 is qualitatively similar to the experimental results and theory reported by Daniels et al. (2001) for “H-polymers,” which are shown schematically in Fig. 7(b). Two distinct relaxation times are exhibited by separate relaxation modes of the arms and crossbars shown in Fig. 7(b). A schematic of the associated ionomer structure that resembles the structure of a H-polymer is shown in Fig. 7(c). This aspect of the viscoelastic behavior of these polymers was not pursued in this study, but deserves attention in future work.

**B. Steady-shear rheology**

Steady-shear data for the SPS2.5 ionomers at 160 °C are shown in Fig. 8. The parent PS oligomer and the H-SPS2.5 exhibited Newtonian behavior, constant viscosity, \( \eta = \eta_0 \), and zero first normal stress coefficient, \( \psi_1 \), over the entire shear rate range studied. The viscosity of the H-SPS2.5 was about 60% higher than that of the PS, due to hydrogen bonding between the sulfonic acid groups. The Cs-SPS2.5 ionomers exhibited Newtonian viscosity behavior, but a finite, constant \( \psi_1 \). The appearance of elasticity effects was remarkable in that the polymer chain had a degree of polymerization of only 39. This clearly demonstrates the profound influence dipole-dipole associations have on polymer material properties and the persistence of these associations to temperatures of 160 °C or,
The viscosity of the Cs-SPS2.5 was two orders of magnitude greater than that of PS, due to intermolecular dipole-dipole associations of the Cs-sulfonate groups. When smaller cations, i.e., Rb, K, Na, and Li, were used, the viscosity generally increased with increasing $q/a$ and reached values as much as four orders of magnitude greater than PS for the Na-SPS2.5. Shear-thinning behavior of the viscosity was observed at the higher shear rates and the onset of shear thinning increased as $q/a$ increased. The exception to those trends was the Li salt, which showed departure from the general dependence of the material properties on $q/a$. Similarly, $\psi_1$ increased with increasing $q/a$ and, again, the Li salt was the exception to this trend. The first normal stress coefficient of the Na salt was more than four orders of magnitude greater than that of the Cs salt. As frequency was lowered, the $\psi_1$ data for the Na and K salts reached a relatively constant value, but the data for the Li and Rb salts continued to increase. The reason for that is not clear, but may simply be due to a large experimental error in measuring the normal stresses for the highly elastic samples. Although the data were limited, it did appear that the nonlinear behavior in $\psi_1$ occurred at a lower shear rate than the nonlinearity in $\eta$ and the decrease in $\psi_1$ was greater than that for $\eta$, as is usually the case for viscoelastic fluids [Bird et al. (1987)].

Figure 9 shows the temperature dependence of $\eta$ and $\psi_1$ versus shear rate for Na-SPS2.5, for 160–230 °C. As expected, both quantities decrease with increasing temperature, but even at 230 °C, the viscosity of the ionomer was nearly four times that of the PS oligomer at 160 °C. Similarly, $\psi_1$ was still measurable at 140 °C above $T_g$. At all temperatures, the onset of shear thinning occurred at an earlier shear rate for $\psi_1$ than for $\eta$ and the decrease in $\psi_1$ with increasing shear rate was greater than for $\eta$.

Steady-shear data for the SPS4.8 ionomers were more difficult to obtain because of the much higher viscosities of these ionomers compared with the SPS2.5 materials. Data for
these ionomers at 240 °C are shown in Fig. 10. At this temperature, the viscosity behavior was Newtonian for all the salts, though the viscosity varied by about two orders of magnitude as the counter-ion was changed from Cs⁺ to Na⁺. Only limited $\psi_1$ versus shear rate data for the SPS4.8 ionomers were obtained at 240 °C, see Fig. 10(b), and these showed that $\psi_1$ was relatively constant over the shear rates studied.

With the notable exception of the Li salt, the zero-shear viscosities of the ionomers at
a fixed temperature scaled linearly with \(\frac{cq}{a}\); see Fig. 11. Figure 12 plots the first normal stress coefficient against \(\frac{cq}{a}\) at two different temperatures. The \(\psi_1\) data were limited and the uncertainty in the normal force difference measurements was much greater than that in the shear stress measurement. The data in Fig. 12 show considerable scatter, but do appear to correlate roughly with \(\frac{cq}{a}\). Arrhenius plots of the temperature dependence of the zero shear viscosity of the SPS2.5 ionomers are shown in Fig. 13. The linearity of the plots indicates an activated process for the flow of the ionomers, and the calculated constants for the equation, \(\eta_0 = A \exp\left(\frac{E_p}{RT}\right)\), i.e., the prefactor, \(A\), and the flow activation energies, \(E_p\), are summarized in Table III. The activation energy was constant for each ionomer over the range of temperatures studied.
For each sulfonation level, $E_\eta$ was relatively independent of the cation used, see Table III, though $E_\eta$ appeared to be a little higher for the SPS4.8 ionomers than the SPS2.5 ionomers. For the two sets of ionomers, the average values of $E_\eta$ were $142 \pm 11$ kJ/mol K and $150 \pm 6$ kJ/mol K for the SPS2.5 and SPS4.8 ionomers, respectively. Those results are consistent with the results by Weiss et al. (1991) for high molecular weight SPS ionomers, for which the activation energy was independent of cation, but increased with increasing sulfonation level. The difference between $E_\eta$ for the SPS2.5 and SPS4.8 ionomers, however, was not much greater than the experimental error in $E_\eta$ for either ionomer.

The independence of the activation energy on the cation was surprising in that $E_\eta$ is a

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**FIG. 10.** Steady-shear properties of MSPS4.8 ionomers at 240 °C: (a) viscosity and (b) first normal stress coefficient.
measure of the potential barrier to translation of the monomer segments. The ionomers include styrene and sulfonated styrene segments, and one might reasonably expect based on the rheology data reported herein, that the sulfonated segments should dominate the flow process. One might reasonably expect, therefore, that $E_\theta$ would depend on the nature of the cation, specifically the size and the strength of the ion pair, which controls the release of the dipole-dipole associations during flow. The values of $E_\theta$ listed in Table III, however, are similar to the flow activation energy for high molecular weight polystyrene, $\sim 150$ kJ/mole K [Siline and Leonov (2002)].

FIG. 11. Zero shear viscosity of MSPS2.5 (open symbols) and MSPS4.8 (filled symbols) ionomers at 160 and 220 °C as a function of $cq/a$: Li-SPS (□), Na-SPS (◇), K-SPS (◇), Rb-SPS (+), Cs-SPS (●).

FIG. 12. Zero shear first normal stress coefficient of SPS2.5 (open symbols) and SPS4.8 (filled symbols) ionomers at 160 and 200 °C as a function of $cq/a$: Li-SPS (□), Na-SPS (◇), K-SPS (◇), Rb-SPS (+), Cs-SPS (●).
That the flow activation energy for the ionomers is similar to that of polystyrene suggests that the relaxation time of the dipole-dipole associations is sufficiently long compared to the experimental time frame of the zero shear viscosity determination so that

**FIG. 13.** Arrhenius plot of the zero shear viscosity of SPS2.5 ionomers vs reciprocal temperature: steady state shear (open symbols); dynamic shear (filled symbols). To improve clarity of the figure, the linear fits are only shown for the NaSPS2.5 and CsSPS2.5 ionomers. The steady shear data for the other salts were also linear, and the regression coefficient ($r^2$) for each of the linear fits was greater than 0.95. The data for dynamic shear deviated from the linear fit of the steady shear data.

**TABLE III.** Activation energies for flow of SPS2.5 and SPS4.8 ionomers: Arrhenius equation parameters $\eta_0 = A \exp(E_\eta/RT)$ for the zero shear viscosity and $E_r$, calculated from the terminal behavior determined from the dynamic experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M$</th>
<th>$\eta_0$ ($10^{-14}$ Pa s)</th>
<th>$E_\eta$ (kJ/mol K)</th>
<th>$E_r$ (kJ/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>240</td>
<td>...</td>
<td>240</td>
<td></td>
</tr>
<tr>
<td>HSPS2.5</td>
<td>...</td>
<td>...</td>
<td>227</td>
<td></td>
</tr>
<tr>
<td>HSPS 4.8</td>
<td>...</td>
<td>...</td>
<td>234</td>
<td></td>
</tr>
<tr>
<td>MSPS2.5</td>
<td>Li</td>
<td>5.3</td>
<td>137</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>0.092</td>
<td>159</td>
<td>177</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>9.7</td>
<td>134</td>
<td>189</td>
</tr>
<tr>
<td></td>
<td>Rb</td>
<td>0.32</td>
<td>146</td>
<td>205</td>
</tr>
<tr>
<td></td>
<td>Cs</td>
<td>4.2</td>
<td>132</td>
<td>210</td>
</tr>
<tr>
<td>MSPS4.8</td>
<td>Li</td>
<td>...</td>
<td>...</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>690</td>
<td>148</td>
<td>285</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>5.1</td>
<td>156</td>
<td>218</td>
</tr>
<tr>
<td></td>
<td>Rb</td>
<td>3.4</td>
<td>154</td>
<td>228</td>
</tr>
<tr>
<td></td>
<td>Cs</td>
<td>0.22</td>
<td>142</td>
<td>237</td>
</tr>
</tbody>
</table>
the ionic associations behave as if they were permanent in that time frame such that the flow is of branched polymer involving multiple chains linked by ion-pair associations. The ionic nanostructure also persists under shear at temperatures and shear rates well within the “Newtonian” viscosity region; see Fig. 14. As a result, the ionomer flow behavior is essentially that of a high molecular weight, entangled polystyrene melt. For an entangled polymer melt, the molecular weight between entanglements, \( M_e \), is related to \( G_N \) by Eq. (4),

\[
M_e = \frac{\rho RT}{G_N},
\]

where \( \rho \) is the density of the melt, \( T \) is the absolute temperature, and \( R \) is the Universal Gas constant. The values of \( G_N \) calculated from the \( G' \) data for the 4.8SPS ionomers, see Fig. 3, yield a value of \( M_e = 1.7 \times 10^5 \) g/mol (corrected to 140 °C) which is identical to the value for polystyrene given by Rubinstein and Colby (2003). However, for the 2.5SPS ionomer data shown in Fig. 2, \( M_e \) is \( \sim 10^5 \) g/mol, an order of magnitude greater than expected for polystyrene.

One explanation for the high value of \( M_e \) for the 2.5SPS ionomers is that while the chains contain on the average one sulfonate group, some chains may contain no sulfonate groups. For a random sulfonation, the probability, \( P(x) \), that any chain will contain \( x \) sulfonate groups is shown by the binomial distribution in Fig. 15. The distribution for the 2.5SPS ionomers indicates that close to 70% of the chains are either unsulfonated or have only one sulfonate group, and for the polystyrene molecular weight used in this study (4000 g/mol), those chains will be unentangled. The high value of \( M_e \) (or, actually, the low value of \( G_N \)) for these ionomers may arise because the unsulfonated and monosulfonated chains are mechanically inactive in the physical network formed by the ionic interactions and do not contribute to the elastic behavior. The 4.8SPS ionomers have about half that concentration of inactive chains, so their elastic response is expected to be closer to that of an entangled polystyrene melt. However, based simply on the number of potential active chains, i.e., where \( n \geq 2 \), the measured \( G_N \) is too high (\( M_e \) too low), the reason for which is not yet known.

**FIG. 14.** SAXS of Rb-SPS2.5 undergoing shear flow at 190 °C as a function of shear rate.
Figure 13 also plots the zero shear viscosities of the SPS2.5 ionomers at \( \sim 131 \, ^\circ C \), calculated from the dynamic experiments described earlier in this paper. The \( \eta_0 \)'s calculated from the dynamic data were systematically higher than the steady shear values, but the agreement was reasonable considering the errors in the measurements and calculations for the two different experiments.

Activation energies calculated for the terminal region measured by the dynamic experiments are also listed in Table III. One must use caution with these values, since time-temperature superposition was not valid for the dynamic data. However, superposition in the terminal region was relatively good, so these values may be considered reasonable approximations of the activation energy. However, clearly these values do not agree, either in magnitude or with the effect of the cation, with the flow activation energies calculated from the viscosity data or the terminal relaxation times calculated from the dynamic experiments; cf. Tables II and III. These calculations raise the question as to whether the terminal relaxation, one might expect to be ion hopping, actually occurred in the steady shear viscosity measurements. And, while the viscosity data suggest that the nature of the flow unit is a branched chain, the role of the cation is still not completely clear with regard to the dynamics of these fluids.

C. Shear thickening behavior

Shear thickening behavior has been previously been reported in ionomer solutions [Peiffer et al. (1986); Broze et al. (1983); Lundberg and Duvdevani (1991); Maus et al. (1995); Shao et al. (1995); Bhargava and Cooper (1998); Li et al. (2006)]. Witten and Cohen (1985) proposed a mechanism for the shear thickening phenomena—that shear flow elongates the polymer chains in solutions, which results in an increasing number of interchain associations at the expense of intrachain associations. Thus, larger complexes are formed at higher shear rates, and they yield higher viscosities. When the shear rate is larger than the polymer chain relaxation rate, shear-thinning behavior occurs.

Figure 16 shows the shear rate dependence of the melt viscosity of the Na and Li salts of SPS2.5 at 160–180 \( ^\circ C \). These data show shear-thickening behavior over a narrow
shear rate range, and the shear-thickening region is followed by shear thinning. Note that the viscosity is plotted on a linear scale to more clearly see the shear thickening, which is not substantial. Shear thickening for those ionomers was not observed at higher temperatures, nor was shear thickening observed for any of the other alkali metal salts. The Na and Li salts exhibited the strongest dipole-dipole interactions, as was discussed earlier in this paper, and the effects of those interactions are greatest at the lower temperatures. Although the data here are limited, it would appear that the strength of the intermolecular interactions, which are influenced by the choice of the cation and by the melt temperature, is the key variable responsible for shear-thickening behavior. Even though the backbone molecular weight of these polymers was low, the melt viscosities were extremely high, which distinguishes the shear-thickening behavior in these systems from the previous reports for ionomer solutions. The shear-thickening mechanism, however, is probably the same mechanism proposed by Witten and Cohen (1985) for ionomer solutions.

IV. CONCLUSIONS

Light sulfonation of a PS oligomer produced ionomers whose melt rheology behavior was comparable to high molecular weight, entangled polymer. Zero-shear viscosities, $\eta_0$, consistent with PS with molecular weights of 10–103 kg/mol were achieved by the alkali metal salts of a sulfonated PS with $M_w=4000 \text{ g/mol}$ and containing on the average one or two sulfonate groups per chain. Even though the parent polymer molecular weight was far below the entanglement molecular weight of PS, the sulfonated ionomers also exhibited elastic behavior with finite values of the zero-shear first normal stress coefficient, $\psi_{1,0}$, $\eta_0$ and $\psi_{1,0}$ increased with increasing sulfonation and decreasing cation size, and the values scaled with the quantity $cq/a$, where $c$ is the concentration of sulfonate groups, and $q$ and $a$ are the charge and radius of the cation, respectively. The origin of the viscosity increase was intermolecular dipole-dipole associations of the ionic groups and the formation of nanophase separated ion-rich aggregates. Dipole-dipole interactions increased the terminal relaxation time of the melts as much as much as seven orders of magnitude greater than the unentangled PS melt.

The complex compliance $\mathcal{J}_0^0$ and plateau modulus, $G_N$, of the ionomers was relatively independent on the choice of the cation, though $\mathcal{J}_e^0$ decreased and $G_N$ increased with
increasing sulfonation level. The entanglement molecular weight of the ionomers, calculated from $G_N$, containing $\sim 2$ sulfonate groups per chain was similar to the value for high molecular weight PS and the flow activation energies were also similar. That indicated that the elastic effect of the ionomer is mainly due to chain extension as a result of the ionic associations. However, since the sulfonation reaction was random, it produced a statistical distribution of sulfonate group concentrations per chain. As a result, some chains contained no sulfonate groups, and that was particularly important for the ionomers with an average of one sulfonate group per chain. In that case, nearly 40% of the chains had no sulfonation and were ineffective at contributing to the melt elasticity.

These low molecular weight ionomer melts also exhibited shear-thickening behavior up to some critical shear rate, after which shear thinning behavior was observed. The shear thickening is believed to be due to the mechanism proposed by Witten and Cohen (1985) that interchain association of the chains increase as they are deformed in the shear flow. That theory, however, also predicts that the shear-thinning behavior should begin when the shear rate exceeds the chain relaxation rate, but for these ionomers, the shear thinning was observed at about 1–2 orders of magnitude higher shear rate.

**ACKNOWLEDGMENTS**

This work was supported by the Polymer Program of the National Science Foundation (Grant No. DMR-0304803). The authors thank Professor Andrey Dobrynin, Professor Montgomery Shaw, and Professor Ralph Colby for helpful discussions and Professor Benjamin Hsiao for help with the shear-SAXS measurements.

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