Comparisons of Styrene Ionomers Prepared by Sulfonating Polystyrene and Copolymerizing Styrene with Styrene Sulfonate


Synopsis

As part of a continuing study of ion-containing polymers, a comparison has been made on styrene-based sulfonate ionomers obtained by two different processes. Copolymers of styrene with sodium styrene sulfonate (SSS) have been compared with corresponding polymers obtained by the sulfonation/neutralization of preformed polystyrene (S-PS). The former system covered a range of sulfonate level from 1 to 30 mol %, while the latter ranged from about 1 to 7 mol %. The characterization of these materials has been conducted using solubility behavior, dilute solution viscometry, thermal mechanical analysis, density measurements, and water adsorption studies. At low (ca. 1%) levels the solubility behavior of the SSS copolymers and the sulfonated polystyrenes were similar. However, at higher sulfonate levels the solubility behavior in different solvents and the dilute solution viscometry were significantly different for the two systems. Similarly, thermal analysis studies (DSC) showed that the glass transition of the sulfonated polystyrene increased linearly with sulfonate level, while the $T_g$ for the SSS copolymer increased modestly, up to about 7 mol % sulfonate content, and then remained constant. Significant differences in the softening behavior and water absorption characteristics were also observed for these two classes of ionomers. Although molecular weights and molecular weight distributions are not now available for these ionomers, the differences in their behavior does not appear to be due simply to differences in molecular weight. It is postulated that the differences in the copolymer and the S-PS ionomers may originate with differences in sulfonate distribution. It is suggested that the SSS monomer units are incorporated as blocks in the copolymer as opposed to a more random distribution in the S-PS ionomer. Indirect evidence in support of his argument is found, for example, in the case of the copolymer in the solubility behavior, the relative independence of $T_g$ on sulfonate concentration and the apparent existence of a second, high temperature transition tentatively attributable to an ion-rich phase. Additional studies are required to confirm this hypothesis.

INTRODUCTION

The incorporation of small amounts of ionic functionality into a predominantly hydrocarbon polymer provides a unique method for controlling polymer properties. These materials, ionomers, have received considerable attention in recent years, as evidenced by several monographs1-3 and review articles.4,5 While any acid functionality can be used to prepare ionomers, carboxylic acid derivatives comprise the majority of ionomers. Over the past several years there has been considerable interest in sulfonate-containing ionomers, and systems based on polystyrene,6-16 EPDM,7-23 polysulfone,24

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polypentenamer, and fluorinated hydrocarbons (Nations) have been described. These materials are prepared by sulfonating the preformed polymer.

More recently, several laboratories have prepared sulfonate ionomers by copolymerizing a sulfonated monomer and either a vinyl or diene hydrocarbon monomer. The chemistry by which these copolymers have been prepared is complicated and was recently described by Turner, Weiss, and Lundberg, and it has been demonstrated that these materials exhibit many of the properties associated with ionomers. In this article we describe the similarities and differences between styrene ionomers prepared by copolymerization of styrene and sodium styrene sulfonate and the chemically equivalent material prepared by sulfonation of polystyrene.

EXPERIMENTAL

Materials

Styrene monomer was freshly distilled at 145°C prior to use. The remainder of the reactants, sodium styrene sulfonate (SSS), sodium lauryl sulfate (emulsifier), diisopropylbenzene hydroperoxide (initiator), triethylenetetramine (reducing agent), sodium pyrophosphate (buffer), and 1-dodecanethiol (chain transfer agent) were used as received. Water was distilled and boiled prior to use.

Polymerizations

Free-radical emulsion copolymerizations were carried out in beverage bottles at room temperature. The reactions were terminated by the addition of hydroquinone and the polymers were stabilized with 2,2'-methylene-bis(4-methyl-6-t-butyl phenol). Whenever possible, the polymers were recovered either by precipitation in methanol or by the addition of NaCl to the latex.

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Styrene (g)</th>
<th>SSS (g)</th>
<th>Reaction temperature (°C)</th>
<th>Reaction time (h)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1.6</td>
<td>106.4</td>
<td>3.5</td>
<td>23</td>
<td>21</td>
<td>94</td>
</tr>
<tr>
<td>C2.9</td>
<td>106.4</td>
<td>6.9</td>
<td>23</td>
<td>21</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>C4.1</td>
<td>106.4</td>
<td>13.8</td>
<td>23</td>
<td>16</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>C8.1</td>
<td>106.4</td>
<td>26.6</td>
<td>23</td>
<td>16</td>
<td>80</td>
</tr>
<tr>
<td>C9.3</td>
<td>106.4</td>
<td>39.9</td>
<td>23</td>
<td>16</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>C11.9</td>
<td>106.4</td>
<td>53.2</td>
<td>23</td>
<td>16</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>C17.7</td>
<td>53.2</td>
<td>33.7</td>
<td>22</td>
<td>ca. 18</td>
<td></td>
</tr>
<tr>
<td>C31.2</td>
<td>26.6</td>
<td>33.7</td>
<td>22</td>
<td>ca. 18</td>
<td></td>
</tr>
</tbody>
</table>

* Standard recipe: 2.65 g of diisopropylbenzene hydroperoxide, 2.65 g of triethylenetetramine, 12.2 g of sodium lauryl sulfate, 0.74 g of dodecanethiol, 1.6 g of sodium pyrophosphate, 266 g of water.

* Based on styrene charge.

* Used one-half the standard recipe, except for water (266 g).

* Used one-quarter the standard recipe, except for water (266 g).
In those cases where the latex displayed unusually high stability, e.g., at the higher concentrations of SSS, the copolymer was recovered by evaporating the latex to dryness. Each copolymer was subsequently dissolved or swelled in a suitable solvent, reprecipitated in methanol, and dried under vacuum. A summary of the reactions is given in Table I.

Polystyrene (PS) was polymerized by the same procedures used in the copolymerizations. Sulfonated polystyrene (SPS) was prepared in 1,2-dichloroethane solution at 50°C using acetyl sulfate as the sulfonating agent.\textsuperscript{34} The sulfonic acid derivative was converted to the sodium salt by titrating with excess sodium acetate.

**Polymer Characterization**

Sulfur content was determined by Dietert sulfur analysis\textsuperscript{35} and was used to calculate the copolymer composition. Wherever the thiol chain transfer agent was used, the sulfur due to the thiol was subtracted from the total sulfur when determining the sulfonate concentration. Sodium concentrations were determined by emission spectroscopy.

Glass transition temperatures $T_g$ were measured with a Perkin-Elmer differential scanning calorimeter (DSC) model 2 using a scanning rate of 20°/min and a nitrogen atmosphere. $T_g$ was taken as the temperature at which the change in the heat capacity associated with the transition reached one-half of its ultimate value. Softening behavior was measured under a helium atmosphere with a Perkin-Elmer TMS-2 thermomechanical analyzer (TMA) using a quartz compression probe with a hemispherical tip (1.52-mm radius) and a heating rate of 10°C/min.

The molecular weights and molecular weight distributions of the polystyrene homopolymers were determined by high-speed gel permeation chromatography. Dilute solution viscosities were determined in various solvents using a Ubbelohde capillary viscometer for which the kinetic energy correction was negligible. The Huggins equation

$$\eta_p/c = [\eta] + k'[\eta]c$$

was used to calculate the intrinsic viscosity $[\eta]$ and the Huggins constant $k'$.

**RESULTS AND DISCUSSION**

The styrene–SSS copolymers and the sulfonated polystyrenes (SPS) described in this article are summarized in Table II. Some of the sulfur in these materials originates with the thiol chain-transfer agent and must be accounted for if the sulfur analysis is to be used to calculate the sodium sulfonate concentration. If all of the charged thiol reacted, it will account for 0.11% sulfur in the product. This is in fair agreement with the sulfur analysis (0.16%) of the PS homopolymer, prepared from the same recipe. The excess sulfur due to unremoved emulsifier is believed to be negligible, an assumption supported by the sodium analysis of the PS sample (0.01%). As a consequence, the sulfonate concentrations and the sulfur/sodium ratios given in Table I were calculated after subtracting 0.11% S from the original sulfur analyses in column 2.
A plot of the sulfur analysis versus the feed composition for the copolymerization experiments is given in Figure 1. The data fall on a straight line with an intercept at zero SSS charge of 0.29% sulfur. This corresponds to a slightly higher value of residual sulfur than can be accounted for by the thiol concentration, which suggests that some emulsifier may remain in these polymers. In any event, it is estimated that the experimental uncertainty in the sulfonate concentration corresponds to the difference between this extrapolated residual sulfur result and the sulfur due to thiol—i.e., 0.18% sulfur or 0.6 mol % sulfonate.

The sulfonated polystyrenes were prepared from a styrene homopolymer synthesized using the identical formulation employed in the copolymerization experiments, but without the SSS comonomer. This homopolymer, PS, had an intrinsic viscosity of 0.33 dL/g in 90% toluene/10% methanol.

![Figure 1. Sulfur content of copolymers versus sodium styrene sulfonate monomer concentration in the copolymerization charge.](image-url)
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at 25°C, which corresponds to a viscosity average molecular weight of 79,000. Gel permeation chromatography yielded the following molecular weights: $M_n = 23,000$, $M_w = 91,000$, $M_t = 233,000$, and $M_{t+1} = 498,000$.

Molecular weights and molecular weight distributions of ion-containing polymers are difficult to determine because of the strong ionic associations which prevail even in dilute solution. Therefore, the traditional methods for characterizing polymer molecular weights, such as intrinsic viscosity, yield at best apparent molecular weights and are likely to be strongly dependent on the solvent used. On the basis of intrinsic viscosity measurements under conditions which minimize ionic associations, Lundberg and Makowski concluded that the sulfonation/neutralization process has no significant effect on the backbone molecular weight of the polymer at sulfonate contents as high as 5 mol %. GPC studies on SPS by Siebourg, Lundberg, and Lenz suggest, however, that some molecular weight degradation may occur during these processes. This conflict arises primarily because of the difficulties in interpreting experimental data which may be affected by hydrodynamic volume perturbations resulting from intramolecular interactions. The molecular weights of the copolymers are even more difficult to determine, because in this case there is no preformed non-ionic polymer to use as a reference.

In the discussion that follows comparisons are made of the styrene-SSS copolymers and SPS polymers. It is assumed that these materials have similar molecular weights and that the effects of differences in molecular weight and molecular weight distribution are minor. In order to demonstrate to some degree what effect molecular weight has on the properties of SPS, some data are presented for SPSs prepared from a polymer of higher molecular weight ($M_n = 106,000$ and $M_w = 288,000$). In light of the difficulties in obtaining reliable GPC measurements of sulfonated polymers as pointed out in Ref. 12, no attempts were made to measure the molecular weights of either the copolymers or the SPS by GPC. Instead all discussion of molecular weight is based either on the molecular weight of the starting PS in the case of SPS or inferred from dilute solution viscosity in the case of the copolymers.

**Solubility Behavior**

Ionomers, particularly sulfonate-containing ionomers, exhibit such strong ionic associations that dissolution in solvents of low polarity is difficult. Depending upon the concentration of ionic groups, and to some degree upon the polymer concentration, attempts to dissolve a sulfonate ionomer in a hydrocarbon solvent, such as toluene, results in either an extremely viscous solution or insolvency.

The addition of a small amount of a polar cosolvent such as an alcohol, which selectively solvates the ionic species, weakens the ionic association and permits dissolution of the ionomer. Lundberg has explained this behavior as an equilibrium between a solvated species and an aggregated species of multiple ion-pairs.

An alternative to the mixed solvent approach is to use a solvent of higher polarity, i.e., higher dielectric constant $\epsilon$ than a hydrocarbon solvent. It has recently been demonstrated that SPS is soluble in many single solvents,
TABLE III
Solubility of Styrene-SSS Copolymers and Sodium-Sulfonated Polystyrene

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mol % SO₃⁻Na⁺</th>
<th>Toluene</th>
<th>90% Toluene</th>
<th>10% Methanol</th>
<th>DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1.6</td>
<td>1.6</td>
<td>97</td>
<td>96</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>C2.9</td>
<td>2.9</td>
<td>97</td>
<td>96</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>C4.1</td>
<td>4.1</td>
<td>32</td>
<td>97</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>C8.1</td>
<td>8.1</td>
<td>9</td>
<td>56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C9.3</td>
<td>9.3</td>
<td>8</td>
<td>50</td>
<td>74</td>
<td></td>
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<tr>
<td>C11.9</td>
<td>11.9</td>
<td>14</td>
<td>44</td>
<td>78</td>
<td></td>
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<tr>
<td>C17.7</td>
<td>17.7</td>
<td></td>
<td>—</td>
<td>55</td>
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<tr>
<td>C31.2</td>
<td>31.2</td>
<td></td>
<td>—</td>
<td>41</td>
<td></td>
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<tr>
<td>SPS-1.0</td>
<td>1.0</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
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<td>SPS-1.5</td>
<td>1.5</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
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<td>SPS-4.1</td>
<td>4.1</td>
<td>80</td>
<td>100</td>
<td>100</td>
<td></td>
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<tr>
<td>SPS-5.7</td>
<td>5.7</td>
<td>36</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>SPS-7.2</td>
<td>7.2</td>
<td>22</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

such as dioxane (ε = 2.2), tetrahydrofuran (ε = 7.6), 2-methoxy-ethanol (ε = 16.9), cyclohexanone (ε = 18.2), dimethylformamide (ε = 36.7), and dimethylsulfoxide (ε = 46.7). Solubility in these solvents is, of course, dependent on the sulfonate level, and, in general, the higher the dielectric constant, the better the solvent is for the more highly sulfonated polystyrenes. For example, whereas sulfonated polystyrene with 6 mol % sodium sulfonate is insoluble in tetrahydrofuran (THF), it is soluble in dimethylformamide (DMF).

The solubility of the copolymers and SPS in several solvent systems are given in Table III, and the results are consistent with the above discussion. Up to a sulfonate concentration of about 3 mol %, the copolymers are soluble in toluene alone. Above this concentration, the addition of 10% methanol as a cosolvent improves the solubility, but above about 4 mol % the copolymers are not completely soluble in the mixed solvent. The solubility is improved with DMF, but for the higher sulfonated materials complete solubility is still not attained.

The solubility characteristics of the SPSs are somewhat different. Above 1.5 mol % sodium sulfonate these materials, too, are insoluble, in toluene; however, over the entire range studied, 1–7 mol %, the SPSs are completely soluble in 90% toluene/10% methanol and in DMF. These differences in the solubility behaviors of the copolymers and SPS may be a result of differences in sulfonate group distribution as will be discussed later in this article. Data will be presented later in this paper that suggest that the SSS is incorporated in the copolymers in a blocky manner.

Density

In a recent discussion of clustering in ionomers, Eisenberg showed that a plot of the density of styrene–sodium methacrylate copolymers as a function of carboxylate concentration exhibits an appreciable change in slope
at ca. 6 mol % which he attributed to the onset of clustering in these materials. He then calculated the fraction of ions in the clusters from the integrated intensities of the two dielectric peaks observed in the glass transition region\textsuperscript{40} and showed that the density varied linearly with this variable. From this and other results presented in that paper, Eisenberg concluded that the clusters dominate the properties of ionomers.

The densities of the styrene–SSS copolymers and the SPS’s were measured with a pychnometer and are plotted against sulfonate concentration in Figure 2. The data for both materials fall on a straight line, and contrary to Eisenberg’s results for styrene–sodium methacrylate copolymers, neither of the two sulfonate ionomer systems exhibits a change in the slope of the density–concentration curve. This result may be a consequence of differences in the ion association between sulfonate and carboxylate ionomers as demonstrated by the thermomechanical analysis, melt rheology, and dilute solution behavior reported by Lundberg and Makowski\textsuperscript{7} for polystyrene ionomers. If indeed, as suggested by Eisenberg, the density of an ionomer is extremely sensitive to the morphology of the ionic aggregation, one is tempted to conclude from Figure 2 that the morphologies of the copolymers and SPS are similar. This conclusion is somewhat puzzling in light of the differences in the thermal behavior and water uptake of the two systems as will be discussed later in this article.

**Solution Behavior**

The viscosity of ionomers in dilute solutions can provide important information concerning the interactions of the ionic species as well as delineate differences between materials. Whereas the behavior of polyelectrolytes in dilute solution has received considerable attention, (cf. Ref. 1), very few studies have considered the behavior of ionomers in solution. In this regard, the work of Lundberg et al.\textsuperscript{37,38} probably represents the most definitive investigation of ionomers using solution techniques.

Lundberg and Phillips\textsuperscript{38} have shown that the solution behavior of SPS can vary from classical polyelectrolyte behavior to that characteristic of
ion-pair interactions depending upon the solvent polarity. In solvents of low polarity, ion-pair interactions predominate. At polymer concentrations greater than ca. 0.5% the solution viscosity exceeds that of an unfunctionalized polymer because of intermolecular associations, while at lower polymer concentrations the viscosity can be lower than that of the corresponding unfunctionalized polymer as a result of intramolecular interactions.

In more polar solvents, the charges are effectively separated. In dilute solution the fully ionized anions repel each other resulting in an expansion of the polymer coil and a marked increase in the solution viscosity. This "polyelectrolyte effect" which is well known for highly functionalized polymers such as poly(sodium acrylate) or fully sulfonated polystyrene can be eliminated by the addition of simple salts which associate with the anions and, as a consequence, shield them from each other. In principle, this is what happens in solvents of low polarity where the ion pair is not fully ionized.

The dilute solution behavior of SPS is shown for two different solvents, 90% toluene/10% methanol and DMF, in Figures 3 and 4. In the mixed solvent the intrinsic viscosity decreases with increasing sulfonate concent-

Fig. 3. Reduced viscosity versus polymer concentration for sulfonated polystyrenes in toluene/methanol (90/10): (○) 0.5 mol % sodium sulfonate, (□) 1.0%, (△) 1.5%, (●) 4.1%, (■) 5.7%, (▲) 7.2%.

Fig. 4. Reduced viscosity versus polymer concentration for sulfonated polystyrenes in DMF: (○) 0.5 mol % sodium sulfonate, (□) 1.0%, (△) 1.5%, (●) 4.1%, (■) 5.7%, (▲) 7.2%.
TABLE IV
Intrinsic Viscosity and Huggin's Constant of SPS and Styrene–SSS Copolymers in 90% Toluene/10% Methanol at 25°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mol % SO₃⁻ Na⁺ (dL/g)</th>
<th>[η] (dL/g)</th>
<th>k'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1.6</td>
<td>1.6</td>
<td>0.30</td>
<td>0.48</td>
</tr>
<tr>
<td>C2.9</td>
<td>2.9</td>
<td>0.33</td>
<td>0.59</td>
</tr>
<tr>
<td>C4.1</td>
<td>4.1</td>
<td>0.36</td>
<td>1.34</td>
</tr>
<tr>
<td>C8.1a</td>
<td>8.1</td>
<td>0.42</td>
<td>1.29</td>
</tr>
<tr>
<td>C9.3a</td>
<td>9.3</td>
<td>0.50</td>
<td>1.40</td>
</tr>
<tr>
<td>C11.9a</td>
<td>11.9</td>
<td>0.50</td>
<td>1.02</td>
</tr>
<tr>
<td>SPS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>0</td>
<td>0.32</td>
<td>0.35</td>
</tr>
<tr>
<td>SPS-1.0</td>
<td>1.0</td>
<td>0.30</td>
<td>0.52</td>
</tr>
<tr>
<td>SPS-1.5</td>
<td>1.5</td>
<td>0.29</td>
<td>0.60</td>
</tr>
<tr>
<td>SPS-4.1</td>
<td>4.1</td>
<td>0.27</td>
<td>0.69</td>
</tr>
<tr>
<td>SPS-5.7</td>
<td>5.7</td>
<td>0.20</td>
<td>1.55</td>
</tr>
<tr>
<td>SPS-7.2</td>
<td>7.2</td>
<td>0.14</td>
<td>3.97</td>
</tr>
</tbody>
</table>

*Soluble fraction.

tration (cf. Table IV) and this result is thought to be a consequence of increasing intramolecular ionic associations and not of decreasing molecular weight. The linear relationship between the reduced viscosity and concentration persists up to a polymer concentration of 2%. The effect of the polystyrene molecular weight on the dilute solution viscosity of SPS is demonstrated in Figure 5 by reduced solution viscosity for an SPS sample described in this paper and a sample with comparable sulfonate concentration, but based on a polymer with a number average molecular weight of about five times that of the PS used in this study. The data have been normalized with the intrinsic viscosities of the starting polystyrenes. It is clear that the effects of sulfonation are more pronounced in the higher-molecular-weight material, and this may be a consequence of the greater

Fig. 5. Reduced viscosity of sulfonated polystyrenes containing about 6 mol % sodium sulfonate normalized with respect to the intrinsic viscosity of the parent polystyrene versus polymer concentration in toluene/methanol (90/10): (◯) Mₙ (PS) = 23,000, (●) Mₙ (PS) = 106,000.
number of ionic species per chain in these materials. While the viscosity-concentration curves for the lower-molecular-weight polymers are linear over the entire concentration range studied, the curve for the higher sulfonated, higher-molecular-weight material becomes nonlinear above ca. 0.6% polymer concentration. This upswing in the curve is indicative of strong intermolecular interactions that increase the apparent polymer molecular weight.

The effect of the reduced viscosity on polymer concentration in DMF solutions is shown in Figure 4 for the SPS samples. Polymers containing greater than 1.5 mol % sodium sulfonate groups clearly exhibit a polyelectrolyte effect below polymer concentrations of ca. 2%. These results are consistent with those of Lundberg and Phillips and indicate that DMF effectively ionizes the sulfonate species.

The reduced viscosity-concentration curves for the system SSS copolymers in 90% toluene/10% methanol are given in Figure 6. The interpretation of these data is complicated by the fact that unlike the SPS these materials do not originate from the same polymer and the molecular weights of these materials are not known. Up to a polymer concentration of 1%, the viscosity-concentration curves of all the copolymers are linear, and the intrinsic viscosity and the slope of the curves increase with increasing sulfonate concentration. The reason for the increase in the intrinsic viscosity is not known for certain, but may be due to an increase in the molecular weight of the copolymers as the formulation is varied in order to incorporate more SSS. This result would not be surprising since high sulfonate contents are achieved by increasing the SSS concentration in the feed, and our previous study has suggested that the SSS comonomer leads to a Tromsdorff effect in the growing particle that would lead to an increase in molecular weight. This effect was enhanced as the SSS concentration was increased.

Differences in the molecular weights of the copolymers complicate any comparisons of these materials, though the range of intrinsic viscosities, 0.3–0.6 dL/g is bracketed by the intrinsic viscosities of the two different

Fig. 6. Reduced viscosity versus polymer concentration for styrene-co-sodium styrene sulfonate copolymers in toluene/methanol (90/10): (●) 1.6 mol % sodium styrene sulfonate, (○) 2.9%, (■) 4.3%, (□) 8.1%, (▲) 10.1%, (△) 13.1%.
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1.2, I

0.0 0.5 1.0 1.5 2.0 2.5
CONC. (g/dl)

Fig. 7. Reduced viscosity versus polymer concentration for styrene-co-sodium styrene sulfonate copolymers in DMF: (●) 1.6 mol % sodium styrene sulfonate, (○) 2.9%, (□) 4.1%, (▲) 10.1%, (△) 13.1%.

PS's used to prepare the SPSs. Therefore, as a first approximation the effects of molecular weight on the properties of the copolymers can be estimated from the differences in the two series of SPS.

Although quantitative comparisons cannot be made between the reduced viscosity–concentration data for the copolymers and the SPSs because of differences in molecular weight, one consistent point is found in the curves in Figures 3 and 6. The Huggins constant $k'$ increases with increasing sulfonate concentration (cf. Table IV); the high values of $k'$ are indicative of strong polymer–polymer interactions and suggest aggregation of the polymers in solution. These results compliment the viscometric study by Misra, Banthia, and Mandid,41 of polystyrenes containing sulfonate end groups in which they showed that in nonpolar solvents such as toluene aggregation occurred, while in more polar THF, polymer association appeared to be absent.

In DMF, the copolymer solution behavior is similar to that of SPS (c.f. Fig. 7). Above the sulfonate concentration of 2.9 mol %, polyelectrolyte behavior is evident, while at a sulfonate concentration of 1.7 mol % the reduced viscosity–concentration curve is linear over the entire concentration range studied.

The solution behavior of the styrene–SSS copolymers and SPS are qualitatively similar. On the basis of the data given here it would appear that the major differences in the two types of sulfonate ionomers is molecular weight. The discussion that follows, however, will demonstrate that there are some significant differences between these materials, even though these differences do not appear to be manifested in their solution behavior.

Thermal Analysis

Eisenberg1 has reviewed the effect of pendant ionic groups on the glass transition temperatures of carboxylate ionomers. In general, $T_g$ increases with increasing ionic group concentration, and the effects of different counterions can be superimposed if the cation charge and the distance between

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Footnotes:
centers of charge are considered. Studies of the effect of sulfonation on the 
$T_g$ of polysulfone, polypentenamer, Nafion, polystyrene, and EPDM yielded similar results. The increase in $T_g$ is a consequence of the reduction in chain mobility that occurs as a result of the ionic interactions.

The $T_g$ of the styrene-SSS copolymers and SPS determined by DSC are plotted versus sulfonate concentration in Figure 8, along with DSC data for a higher-molecular-weight Zn-SPS and the torsion pendulum data of Rigdahl and Eisenberg for Na-SPS prepared from a $M_w = 30,000$ PS. In the latter study $T_g$ was defined as the maximum in tan δ. The DSC data for the two SPS increase linearly with sulfonate concentration, and although two different molecular weights and counterions were used, the data fall on a single line. The difference between the $T_g$'s determined by torsion pendulum and by DSC is about 8$^\circ$ which is attributed to differences in the experimental time scales of the two techniques.

While the $T_g$ data for SPS are consistent with the results of other ionomer systems, the $T_g$-sulfonate concentration data for the styrene-SSS copolymers are not. In this case, an increase in $T_g$ is observed up to a sulfonate concentration of ca. 8 mol %, but above this concentration $T_g$ remains unchanged. In contrast to SPS, the increase in $T_g$ below 8 mol % is not linear. In fact, below ca. 3 mol % Na-sulfonate, $T_g$ is actually lower than the $T_g$ of a PS of comparable intrinsic viscosity. These data suggest that either there is a genuine decline in the $T_g$ as a consequence of the first few mol % comonomer incorporation or that the molecular weights of the copolymers are substantially lower than would be expected on the basis of their intrinsic viscosities. The latter possibility is inconsistent with the reduced viscosity data presented earlier which suggest that, if anything, the copolymers were of higher molecular weight than the PS made by the same procedure.

The alternative explanation that low degrees of SSS incorporation result in a lowering of $T_g$ is not without precedent. For example, in their studies of the chlorination of polyethylene, Schneider and Wolf found that as chlorination increases, the dynamic mechanical β-loss maximum initially
COMPARISONS OF STYRENE IONOMER

Fig. 9. DSC thermogram of a styrene-co-sodium styrene sulfonate copolymer containing 17.7 mol % sodium styrene sulfonate (20°C/min heating rate).

decreases in temperature, but above a concentration of ca. 4.4 chlorine groups per 100 carbon atoms the trend reverses and $T_g$ increases with increasing chlorination. Similarly, for phosphonated polyethylene, Weiss, Lenz and MacKnight\textsuperscript{43} observed a decline in $T_g$ below a degree of substitution of 0.1 phosphonate groups per 100 carbon atoms and an increase in $T_g$ above this concentration. These authors attributed their results to competing influences of the pendant group. At low concentrations a steric effect increases the free volume and lowers $T_g$, while at higher concentrations dipolar interactions dominate to raise $T_g$. One might expect a similar result where a sulfonate pendant group is involved, and the copolymer data in Figure 8 are consistent with this explanation.

The constancy of $T_g$ with composition above 8 mol % SSS suggests phase separation—i.e., a two-phase material consisting of a styrene-rich phase and a SSS-rich phase. Evidence for this can be seen in Figure 9 which is the DSC thermogram of sample C17.7, a copolymer containing 17.7 mol % SSS. The two $T_g$'s observed here, at 108°C and 257°C, indicate two separate phases; the lower $T_g$ corresponds rather closely to that of polystyrene and the higher $T_g$ is most likely due to a SSS-rich phase.

Phase separation of an ion-rich phase has been proposed to explain many of the peculiar characteristics of ion-containing polymers (c.f. Ref. 1) and experimental evidence such as small-angle x-ray and neutron scattering, electron microscopy, and viscoelastic data support this hypothesis. In no previous study, however, have multiple $T_g$'s been observed by DSC, though several researchers have attributed high-temperature dispersion regions in dynamic mechanical or dielectric relaxation experiments to an ion-rich phase. In this aspect, these copolymers represent unique materials, different in their thermal behavior from not only previously studied carboxylate-containing copolymers, but also different from sulfonated polystyrene. The latter point is important, because chemically there is no difference between a sulfonated polystyrene and a styrene–SSS copolymer. Therefore, any differences in the microstructure of the two materials must arise from some material characteristic other than composition.

It is believed that the distinction between the two ionomers originates in the distribution of the ionic species along the ionomer chain. Sulfonation of polystyrene is believed to proceed more or less randomly, and the sulfonate groups are homogeneously distributed on the polymer chain. On the other hand, because of the large differences in the polarity and solubility
of the two monomers, styrene and SSS, one might expect a random copolymerization to be improbable. Recent results\textsuperscript{32} that show a dramatic change in sulfonate concentration with conversion support a nonrandom copolymerization reaction. Thus, a copolymer consisting of blocky SSS regions could be expected, and the occurrence of two separate $T_g$'s in such a material would be considered classical behavior for a block system. Unfortunately, because of the chemical similarities of the two systems, it has not been possible to confirm this hypothesis by such techniques as infrared spectroscopy or $^{13}$C- or $^1$H-NMR.

**Thermomechanical Analysis**

Intermolecular physical interactions such as occur between ionic species can have profound effects on the mechanical and rheological behavior of a polymer, especially at temperatures above the $T_g$ where the normal relaxation rates for linear polymers are relatively rapid. For example, Rigdahl and Eisenberg\textsuperscript{10} showed that the stress relaxation rate of SPS decreases with increasing ion concentration. For a SPS containing 9.7 mol % sodium sulfonate the 10-s relaxation modulus at 150°C is more than two orders of magnitude greater than that of polystyrene, and at 200°C where polystyrene is well into the viscous flow regime, the SPS is still a rubbery solid with a 10-s relaxation modulus of the order of $10^8$ dyne/cm$^2$. These authors attributed this behavior and the failure of time–temperature superposition for the higher sulfonated materials to ionic cluster formation, and they postulated a multiple relaxation mechanism involving diffusion of the ion-poor matrix in the transition region and a secondary process of a purely viscous nature involving yielding of the ion-rich clusters.

![Thermal mechanical analysis penetration thermograms for sulfonated polystyrene](image)

**Fig. 10.** Thermal mechanical analysis penetration thermograms for sulfonated polystyrene: 20 g load (40 g load for 7.2 mol % sample), 10°C/min heating rate. The numbers in parentheses represent the mol % sulfonates.
Lundberg and Makowski\textsuperscript{7} compared the thermomechanical and rheological behavior of polystyrene and the sodium salts of carboxylated and sulfonated polystyrene. Like Rigidahl and Eisenberg, they found that interactions between ionic groups increased the softening point and the melt viscosity. An important result of their study was that sulfonate and carboxylate ionomers were different in several respects; the ionic associations of the sulfonate groups appeared to be much stronger and persisted to higher temperatures than in the case of the carboxylate groups.

The TMA penetration curves for the various SPS and styrene–SSS copolymers discussed in this report are given in Figures 10 and 11. The behavior of the two types of materials is similar; the major difference is in the $T_g$ which is consistent with the findings from the DSC. The high-temperature transition characterizing the onset of viscous flow increases in temperature with increasing sulfonate content for both materials, and with the exception of the lower sulfonate-containing polymers, the softening behavior at elevated temperatures of the SPS and copolymers are similar. At the lower sulfonate concentrations (e.g., 1–2 mol \%) the copolymer exhibits a small but distinct rubbery plateau which persists to ca. 140°C, while the SPS shows only a single transition region. Although strictly qualitative, this result suggests a subtle difference in the polymer microstructure. The high-temperature transition region results from the intermolecular associations of the ionic groups, and the location of this transition is a function of the sulfonate concentration and the counterion. Where differences in the sulfonate distribution exist, one might expect phase separation to occur more readily with a blocky distribution than with a random distribution. If such were the case, ionic crosslinking should be more prominent at a lower sulfonate concentration in the blocky material. At higher sulfonate
concentrations, there would be sufficient interactions in both systems that the TMA responses would be indistinguishable. Other experiments, however, such as quantitative dynamic mechanical analysis or volume swelling might discriminate between such different microstructures.

**Water Sorption**

Several authors\textsuperscript{44-47} have attempted to correlate the results of water sorption and diffusion experiments with the morphology of ion-containing polymers, specifically the nature of the ionic aggregation. Eisenberg and Navratil\textsuperscript{44} observed that the number of water molecules absorbed per sodium ion in a styrene–sodium methacrylate copolymer varied substantially above and below a salt concentration of ca. 6 mol %. Below this concentration, equilibrium was attained after ca. 300 h and the water sorption corresponded to ca. one water molecule per sodium ion, while above 6 mol % salt the water content increased significantly and equilibrium was not reached in some cases even after 4000 h. The authors attributed these results to the presence of predominantly dispersed ion pairs or multiple ion pairs (multiplets) below 6 mol % of the ionic species, with the onset of ionic cluster formation occurring at ca. 6 mol % salt.

Other authors\textsuperscript{45-47} considered the water sorption and transport phenomenon in perfluorosulfonated (Nafion) membranes based on polytetrafluoroethylene. Mauritz, Hora, and Hopfinger\textsuperscript{46} developed a thermodynamical model to predict phase separation in ionomers and correlated this model with experimental water absorption data for sodium Nafion membranes. Cutler\textsuperscript{46} studied the transport properties of Nafion membranes at high current densities and found that in the hydrated state, large hydrated ionic clusters were thermodynamically favored. Takamatsu, Hashiyoma, and

![Fig. 12. Water sorption isotherms for sulfonated polystyrenes: (○) 1.0 mol % sodium sulfonate, (□) 1.5%, (△) 4.1%, (■) 5.7%, (●) 7.2%. \(M_0\) = dry polymer mass, \(M_t\) = mass at time of measurement.](image-url)
Eisenberg\textsuperscript{47} observed a secondary absorption process in Nafion films with a low degree of neutralization (ca. 10–60%) that was absent in the higher neutralized and the unneutralized materials. This, they suggest, might be due to a structural rearrangement. These authors also observed that, whereas the diffusion of water in samples of low neutralization was Fickian, indicating that segmental mobility of the chains was relatively high, the sorption for samples with a high degree of neutralization becomes non-Fickian, suggesting that segmental mobility was more restricted, probably because of strong intermolecular interactions.

Water sorption experiments are described below for films of SPS and styrene–SSS copolymers. Dried compression molded films were immersed in water at 25°C and were removed periodically, patted dried with a tissue, and weighed on an analytical balance. While this study was not exhaustive, several interesting trends and differences were observed for the two types of polymers. The water sorption isotherms for various SPS and styrene–SSS copolymers are given in Figures 12 and 13, respectively. The results are qualitatively consistent with those of Eisenberg and Navratil for styrene–methacrylate copolymers.\textsuperscript{44} At low sulfonate concentration water sorption is relatively low and equilibrium is reached fairly rapidly, while at higher sulfonate concentrations the hydration is higher and the approach to equilibrium is much slower. For the sulfonate ionomers the change in hydration behavior occurs between 1–2 mol % ionic groups, as opposed to 6 mol % as observed by Eisenberg and Navratil for the carboxylate ionomers. This result is consistent with recent small-angle x-ray scattering results of Peiffer, Weiss, and Lundberg\textsuperscript{15} that indicate that ionic clusters exist in SPS at sulfonate concentrations as low as 2%.

![Fig. 13. Water sorption isotherms for styrene-co-sodium styrene sulfonate copolymers: (○) 1.6 mol % sodium styrene sulfonate, (□) 2.9%, (△) 4.1%. $M_0$ and $M_t$ are defined in Fig. 12.](image-url)
Fig. 14. Water sorption isotherms for (○) sulfonated polystyrenes and (●) styrene-co-sodium styrene sulfonate copolymers. The numbers in parentheses represent the mol % sulfonate. $M_c$ and $M_t$ are defined in Fig. 12.

In addition to differences between the sulfonate and carboxylate ionomers, the hydration characteristics of the two sulfonate ionomer systems are different. This is seen in Figure 14 in which the sorption isotherms of SPS and the copolymers are compared at two different sulfonate concentrations, ca. 1.5 and 4.1 mol %. At the lower ion concentration, the SPS has a much higher equilibrium hydration and a slower approach to equilibrium. In fact, whereas it takes ca. 100 h to achieve equilibrium in the SPS sample, equilibrium occurs within the first 2 h for the copolymer. At higher sulfonate concentrations, e.g., 4.1 mol %, the hydration of the copolymer was higher than that of the SPS and the rate of hydration was much faster. However, above a sulfonate concentration of 3 mol %, equilibrium was not reached in the time frame of the experiment, ca. 859 h. The copolymer containing 1.5 mol % and the SPS containing 1.6 mol % had equilibrium hydrations corresponding to ca. one water molecule per sodium ion which agrees with Navratil and Eisenberg’s result for styrene–sodium methacrylate copolymers. Above these sulfonate concentrations, however, the number of water molecules per salt group increased significantly.

Although it would be premature to attempt to attribute the hydration behavior of these materials to a particular morphology on the basis of these limited results, two points are clear: First, the sulfonate-containing styrene ionomers are different from the carboxylate-containing styrene ionomers described by Eisenberg and Navratil. This result supports the conclusion reached by Lundberg and Makowskï regarding the differences between sulfonate and carboxylate ionomers. Second, the differences between the hydration behaviors of SPS and the styrene–SSS copolymers support the hypothesis that the morphologies of these materials are substantially different. Again, this is thought to be a consequence of differences in sulfonate group distribution in the two materials.

**CONCLUSIONS**

It has been shown that there are some significant differences between sulfonated polystyrene ionomers prepared by copolymerization of styrene
and sodium styrene sulfonate and by the sulfonation/neutralization of poly-
styrene. Specific differences include the solubility behavior, the effect of sulfonate concentration on the $T_g$, and the equilibrium hydration and sorp-
tion kinetics. Although the molecular weights and molecular weight distri-
butions of these ionomers are not well-characterized, the differences in their behavior do not appear to be a consequence simply of differences in molecular weight.

The differences in the copolymer and SPS ionomers may originate with differences in the sulfonate distribution, though additional characteriza-
tions are needed in order to confirm this. The solubility behavior, the rel-
ative independence of the $T_g$ on sulfonate concentration, and the observation of a second, high temperature glass transition for the copolymers suggest the existence of a two-phase structure which most likely consists of ion-
rich and ion-poor regions. Although, phase separation of ion-rich clusters also occurs in SPS, the phenomenon appears to be more apparent in the copolymers. This and the fact that the copolymerization shows a significant change in sulfonate composition with conversion suggest that the SSS mon-
omer units are incorporated as blocks in the copolymers as opposed to a more random distribution of the sulfonate group in SPS. Other results, such as the sorption/hydration experiments appear to be consistent with this conclusion.

Additional characterizations of these polymers are warranted in order to assess the hypothesis concerning the sulfonate distributions. Such studies as excimer fluorescence, dynamic mechanical analysis, dielectric analysis, small-angle x-ray scattering, and volume swelling, may provide useful in-
formation concerning differences in the polymer microstructure. Studies of the solid-state mechanical properties and melt rheology may provide ad-
ditional information concerning differences between these chemically equiv-
alent materials.

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