Sulfonated Polystyrene Ionomers Prepared by Emulsion Copolymerization of Styrene and Sodium Styrene Sulfonate


Synopsis

Sulfonated polystyrene (S-PS), which is of considerable scientific and technological interest, has been traditionally prepared by the sulfonation of preformed polystyrene. This report describes the preparation and properties of S-PS prepared by emulsion copolymerization of styrene and sodium styrene sulfonate. S-PS prepared by copolymerization gave solubility, solution behavior and thermal characteristics that are consistent with an ionomeric structure. The solubility characteristics indicated some chain-to-chain sulfonate heterogeneity. Thermal analysis studies indicated that the glass transition does not increase with increasing sulfonate content. This is contrary to what has been observed for S-PS prepared by sulfonation and suggests that the S-PS prepared by copolymerization is fundamentally different in structure than S-PS prepared by sulfonation of polystyrene.

INTRODUCTION

Metal sulfonate-containing ionomers have generated considerable scientific as well as technological interest because of the unique properties that result from the associations of the ionic sulfonate groups.¹ The nature of this sulfonate aggregation in a variety of polymers, e.g., EPDM, butyl rubber, and polystyrene has received considerable attention.²⁻⁵ Comparisons of the degree of aggregation of carboxylate and sulfonate ionomers indicate stronger aggregation of the more polarizable sulfonate species.⁶ Exploitation of these stronger interactions has been duly reported, for example, thermoplastic elastomers,⁷ stable foams,⁸ and solution properties.⁹

Until recently most sulfonate ionomers have been prepared by sulfonation of a preformed polymer backbone, e.g., EPDM¹⁰ and polystyrene.¹¹ Some recent reports have shown that sulfonate ionomers can be prepared by direct emulsion copolymerization of a hydrocarbon monomer and a metal sulfonate-containing monomer. For example, the copolymerization of isoprene and sodium styrene sulfonate¹² and butadiene and sodium styrene sulfonate¹³ have been shown to yield elastomeric sulfonate ion containing copolymers that exhibit ionomeric characteristics. Lightly sulfonated polystyrene (S-PS) has been one of the most thoroughly studied of the metal sulfonate ionomers. Studies concerned with the solution behavior,⁹ viscoelastic properties,¹⁴ EXAFS analyses,² fluorescence mea-
measurements, \textsuperscript{3} thermal analysis, \textsuperscript{15} small-angle x-ray scattering \textsuperscript{4,5} and electron spin resonance \textsuperscript{5} have recently been reported. The S-PS used in the above studies was prepared by the sulfonation of preformed polystyrene. We report here that S-PS can be prepared by the emulsion copolymerization of styrene and sodium styrene sulfonate. Our studies show that while S-PS prepared by this copolymerization possesses ionomeric properties, these properties significantly differ from S-PS prepared by polymer sulfonation. A concurrent publication \textsuperscript{16} describes the copolymerization reaction in more detail.

EXPERIMENTAL

Typical Copolymerization Procedure

All copolymerizations were carried out with freshly distilled styrene (St). Sodium styrene sulfonate (NaSS) was used as received from Air Products, Inc. (Allentown, PA). Distilled water was deaerated before use by boiling and then cooled in a nitrogen atmosphere. Sodium dodecyl sulfonate (SDS), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), and $n$-dodecylthiol ($\text{C}_{12}\text{SH}$) were used as received.

A small glass pressure bottle (250 mL) was charged with a small magnetic stir bar to enhance agitation, 25 g of St (0.24 mol), 1.0 g of NaSS (0.0048 mol), 60 mL of $\text{H}_2\text{O}$, 0.1 g of $\text{C}_{12}\text{SH}$, 1.6 g of SDS, and 0.1 g of $\text{K}_2\text{S}_2\text{O}_8$. The flask was purged with nitrogen and capped with a two-hole crown cap containing a rubber septum. The bottle was placed into a safety screen in a thermostatted Erback water shaker bath at 50°C and was agitated for a 6-h polymerization time. The bottle was removed and ca. 3 mL of a hydroquinone "shortstop" solution was added via a syringe. The bottle was shaken for an additional 10 min, cooled, and opened. This polymer was coagulated by addition of ca. 250 mL of methanol with some NaCl added. The very fine precipitate was difficult to filter, thus the slurry was centrifuged at ca. 2000 rpm for about 45 min. The solid polymer was washed two to three times with distilled water and brought down by centrifugation each time. About 15 g (after drying under vacuum at 40°C) of white powder were obtained by this procedure. This represented about 58% conversion. Evaporation of the washes yielded the remainder of the expected product. These washes, of course, were contaminated with surfactant and the NaCl used to assist in coagulating the emulsion. Elemental analysis of the coagulated portion was 0.71% S. A control without NaSS present gave a S analysis of 0.21%. Therefore, the polymer actually contained 0.50% S, which is equivalent to 1.57 mol % NaSS incorporation. The evaporated fraction was found to contain 1.21% S.

Similar results were obtained when the redox couple initiator triethylenetetramine and diisopropylbenzene hydroperoxide was used at room temperature.

Alternative Workup

In some cases, especially at high sulfonate charges, the copolymer was isolated by evaporation of the water, dissolution in an appropriate solvent and reprecipitation into methanol.
Polymer Characterization

Sulfur content was determined by Dietert sulfur analysis and was used to calculate the copolymer composition. Thiol and persulfate contributions to total sulfur were determined on for polystyrene samples polymerized by the same procedure and subtracted in order to obtain accurate sulfonate contents.

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 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°/min.

Dilute solution viscosities were determined in a Ubbelohde capillary viscometer for which the kinetic energy correction was negligible.

RESULTS AND DISCUSSION

Copolymer Preparation

Previous studies of the emulsion copolymerization of styrene and sodium styrene sulfonate were concerned with the preparation of stable lattices at

![Graph](https://via.placeholder.com/150)

Fig. 1. NaSS content in the copolymer versus NaSS content in the copolymerization feed for the precipitated fractions: (—) diisopropyl benzene hydroperoxide/triethylenetetramine; (——) potassium persulfate-initiated copolymerization.
Fig. 2. NaSS content in the copolymer versus NaSS content in the copolymerization feed for the dispersed fractions: (—) diisopropyl benzene hydroperoxide/triethylenetetramine; (—) potassium persulfate-initiated copolymerization.

low NaSS levels in the absence of surfactants. The resulting copolymers were not isolated and consequently the properties of these copolymers were not reported. In this study higher levels of NaSS were utilized, up to about 40 mol % NaSS, and the copolymerizations were conducted in the presence of sodium dodecyl sulfate (SDS). Polymers were isolated by coagulation into methanol with the addition of sodium chloride. The coagulated polymers were extremely difficult to filter, thus centrifugation was used to effect the isolation with some solid remaining dispersed. The precipitate was washed three times with water. The washes were combined with the dispersed solids from the coagulation and evaporated. Thus two fractions of copolymer and copolymer contaminated with surfactant and salt were obtained. The sulfonate content of these fractions was dependent on the NaSS charge and was always lower than the initial charge of NaSS. The nondispersed or precipitated fraction, which was normally 60–70% of the product, contained lower sulfonate levels than the dispersed fraction (Figs. 1 and 2).
This behavior appeared to be almost independent of the initiator, whether it was a water soluble persulfate or a two-component redox system with one component present in the hydrocarbon phase and the other in the aqueous phase. These results contrast sharply with those that have been previously reported for the isoprene/NaSS copolymerization where the redox system was claimed to be necessary for the copolymerization to occur.¹² We will discuss the copolymerization reaction of styrene and sodium styrene sulfonate in more detail in a subsequent publication.

**Copolymer Properties**

*Solubility Behavior*

Ionomers, in general, and 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 insolubility. In some cases, the system may form a highly swollen gel.

The addition of a small amount of a polar cosolvent such as an alcohol, which selectively solvates the ionic species, weakens the ionic associations and permits dissolution of the ionomer. Lundberg and Markowski¹¹ have explained this behavior as a equilibrium between a solvated species and an aggregated species of multiple ion pairs.

The solubility behavior of the copolymers prepared in this study indicate strong association of the metal sulfonate groups. Under 3 mol % sulfonate level the copolymers were soluble in toluene alone. Above this concentration they were insoluble in toluene, but the addition of 10% methanol as cosolvent improves the solubility. The addition of methanol also results in a visible reduction in viscosity of the soluble copolymers. The solubility could be further improved by using a solvent with a relatively high dielectric constant such as dimethylformamide (DMF). These solubility data versus sulfonate level content are summarized in Table I.

<table>
<thead>
<tr>
<th>% Soluble copolymer</th>
<th>Toluene</th>
<th>90/10 toluene/methanol</th>
<th>DMF</th>
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<tr>
<td>1.6</td>
<td>97</td>
<td>96</td>
<td>100</td>
</tr>
<tr>
<td>2.9</td>
<td>97</td>
<td>96</td>
<td>100</td>
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<td>8</td>
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<td>&lt;1</td>
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</tr>
<tr>
<td>31.2</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>41</td>
</tr>
</tbody>
</table>

*Prepared with redox initiator.
Fig. 3. Reduced viscosity versus concentration of 4.3 mol % S-PS from copolymerization in 90/10 (v/v) toluene/methanol and dimethylformamide.

Fig. 4. Glass transition temperature versus sulfonate level for S-PS from sulfonation of polystyrene and S-PS from copolymerization.
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Solution Behavior

Lundberg and Phillips\textsuperscript{19} have demonstrated that the solution properties of sulfonated ionomers can vary from classical polyelectrolyte behavior to behavior characteristic of strong ion pair interactions. In nonpolar media the ion pair interactions predominate, while in more polar solvents there is sufficient ionization to exhibit a significant polyelectrolyte effect. This behavior is exhibited in Figure 3 for a copolymer containing 4.3 mol % NaSS in 90/10 toluene/methanol (nonpolar solvent) and in dimethylformamide (DMF).

Thermal Analysis

Eisenberg\textsuperscript{20} has reviewed the effect of pendant ionic groups on the glass transition temperature of carboxylate ionomers. In general, $T_g$ increases with increasing ionic group concentration, and the effects of different counternions can be superimposed if the cation charge and the distance between centers of charge are considered. Studies of the effect of sulfonation on the $T_g$ of polysulfone\textsuperscript{22} polypentenamer,\textsuperscript{23,24} Nafion,\textsuperscript{14} polystyrene,\textsuperscript{25} and EPDM\textsuperscript{26} yielded similar results.

The increase in the $T_g$ with increasing ionic group concentration may be due to either a copolymer effect—i.e., the $T_g$ of the copolymer is between the $T_g$'s of the homopolymers prepared from the two comonomer units—or it may be a result of the decrease in free volume produced by the formation of ionic crosslinks. Arguments have been made for both explanations; however, there is no universal agreement as to which mechanism prevails.

The $T_g$'s of the styrene–NaSS copolymers and sulfonated polystyrene determined by DSC are plotted versus sulfonate concentration in Figure 4. The $T_g$ data for the S–PS by copolymerization are inconsistent with previous

![Fig. 5. TMA penetration curves for S–PS from copolymerization.](image-url)
observations of an increase in $T_g$ with increased ionic group content. These results suggest phase separation and may be indicative of a nonrandom distribution of sulfonate groups along the polymer chain.

**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. The ionic groups decrease the rate of stress relaxation processes. This results in increased softening points and increased melt viscosities. Such results have been observed by Rigdahl and Eisenberg\(^\text{14}\) for sulfonated polystyrene and by Lundberg and Makowski\(^\text{26}\) for the sodium salts of sulfonated and carboxylated polystyrene. Thermomechanical analyses (TMA) of the NaSS styrene copolymers prepared in this study show a significant increase in the rubbery plateau region with increasing ionic content as has been observed for sulfonated and carboxylated prepolymers as described above. These results are shown in Figure 5.

**CONCLUSIONS**

The results presented in this study clearly show that ionomeric sulfonated polystyrene can be synthesized by emulsion copolymerization of styrene and sodium styrene sulfonate. Polymer properties such as solubility, solution behavior, $T_p$, and viscoelastic behavior exhibited ionomeric characteristics. The results also suggest, especially $T_g$ data, that the S–PS prepared by copolymerization is fundamentally different from S–PS prepared by sulfonation of preformed polystyrene. This topic will be covered in detail in a subsequent paper.\(^\text{27}\) In another paper,\(^\text{16}\) we report on the unusual copolymerization chemistry of styrene and NaSS.

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**References**

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