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Sulfonation and characterization of poly(styrene-isobutylene-styrene) triblock copolymers at high ion-exchange capacities

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Abstract

In this study, a triblock copolymer, poly(styrene-isobutylene-styrene), was sulfonated to eight different levels ranging from 0.36 to 2.04 mequiv./g (13 to 82 mol% of styrene; styrene is 19 mol% of the unsulfonated block copolymer). These sulfonated polymers were characterized with elemental analysis and infrared spectroscopy to confirm sulfonation and determine accurate sulfonation levels. Infrared analysis revealed four additional stretching vibrations as a result of sulfonation. Also, a linear relationship between absorbance at 1006 cm^{-1} (stretching of the aromatic ring in styrene caused by the *para*-substituted sulfonic acid) and sulfonation level (measured by elemental analysis) was found. The density and water solubility of all the sulfonated polymers were measured and increased with increasing sulfonation level, as high as 1.31 g/cm^3 and 351 wt%, respectively. In addition, a sulfonated triblock copolymer at 79 mol% sulfonation was neutralized with a cesium cation and revealed an increase in density, but a reduction in water solubility. This study demonstrates the resulting unique properties of sulfonated styrene-based block copolymers at higher ion-exchange capacities than previously reported.

Keywords: Block copolymer; Ionomer; Polyelectrolyte

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1. Introduction

Unique properties arise from incorporating sulfonic acid (anionic group) into polymers via sulfonation, such as increased strength, hydrophilicity, and proton conductivity. These features have led to an exploration of a variety of applications for sulfonated polymers, such as batteries, sensors, displays, and ion-exchange resins. One application in particular, in which sulfonated polymers have made an impact, is fuel cells. For this application, Nafion® (DuPont), a perfluoroether sulfonic acid polymer, is the most frequently used sulfonated polymer. In the fuel cell, the sulfonated polymer or proton exchange membrane (PEM) serves as both a cell separator, separating the anode from the cathode, and an electrolyte, conducting protons from the anode to the cathode. Current research is focused on developing new low-cost, durable PEMs with higher proton conductivities to enhance current fuel cell efficiencies [1–2].

In ion-containing polymers (i.e. ionomers), such as sulfonated polymers, phase segregation occurs on a nanometer scale, in which two phases (ion-rich and ion-poor domains) are formed as a result of the electrostatic interactions among ion pairs or groups. Increasing the sulfonic acid content in the polymer transforms the polymer from an insulator to a conductor, whereby isolated ionic domains become interconnected throughout the polymer. Above this percolation threshold, protons transport across the polymer via hydrolyzed acidic sites through these interconnected ionic pathways. A number of investigations have demonstrated that increasing the sulfonic acid content in the polymer results in increased proton transport and increased water uptake [3–5].

A variety of polymers, such as sulfonated polystyrene [5], sulfonated polyphosphazene [6], sulfonated polyphenylene oxide [7], sulfonated polyarylene ether sulfone [8], and sulfonated polyether ether ketone [9], have been sulfonated and investigated in relation to their application to PEM fuel cells. In addition to these polymers, sulfonated block copolymers are also of interest because they conjoin the concepts of two different materials: block copolymers

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and ionomers, in which only one of the blocks is sulfonated or ionic. In theory, a sulfonated block copolymer should self assemble into a three-phase morphology in the solid state. In this state, different blocks phase segregate as a result of thermodynamic incompatibilities, while phase segregation will occur within the ionic block as a result of electrostatic interactions among ion pairs. A study by Wiess et al. [10], using X-ray scattering on sulfonated poly(styrene-(ethylene-*co*-butylene)-styrene), confirmed this three-phase morphology with a Bragg spacing of 3–4 nm for the ionic domains and 20–30 nm for the polystyrene domains. Sulfonated block copolymers are intriguing materials because of the combination of their different block (ionic and non-ionic) properties and their ordered ionic structures.

Several sulfonated block copolymer studies of interest include sulfonated poly(4-vinylpyridinium-styrene-4-vinylpyridinium) [11], sulfonated poly(styrene-(ethylene-*co*-butylene)-styrene) [12], and sulfonated poly(styrene-isobutylene-styrene) [13]. However, these investigations focused only on the sulfonation and characterization of styrene-based block copolymers at low sulfonation levels or low ion contents (below 20 mol% sulfonation of the styrene block). Recently, several studies have explored the sulfonation and characterization (transport properties) of block copolymers at higher sulfonation levels, as high as 60 mol% sulfonation, and have shown that these sulfonated block coplymers are comparable in performance to Nafion [14–16]. Similarly, our laboratory has investigated the performance of sulfonated poly(styrene-isobutylene-styrene) in regards to fuel cell applications [17–18].

In our laboratory, the sulfonation of block copolymers is of interest for applications to both fuel cells and textiles (protective breathable clothing). Both applications require resistance to organics, while still providing high transport of protons (fuel cells) and water (breathable clothing). The objective of this investigation is to examine the properties of a sulfonated styrene-based block copolymer, poly(styrene-isobutylene-styrene), at higher sulfonation levels (above 80 mol% sulfonation of the styrene block or 2 mequiv./g) than have previously been reported in order to produce materials with increased proton and water transport rates.

2. Experimental

2.1. Materials

Poly(styrene-isobutylene-styrene) (SIBS) triblock copolymer was provided by Kuraray Co., Ltd, Tsukuba research laboratories, (sample name-TS-3000S, lot. no. 990215) with the reported properties: 19.36 mol% (30.84 wt%) styrene, 0.95 specific gravity, $M_w = 71.920$ g/mol, $M_n = 48.850 \times$ g/mol, and PDI = 1.47. Other chemicals used in this study are as follows: toluene (VWR), hexanol (J.T. Baker), methylene chloride (EM Science, HPLC Grade), sulfuric acid (Fisher Scientific, Assay 95.4%), acetic anhydride (Mallinckrodt), methanol (EM Scientific, HPLC Grade), and water (J.T. Baker, HPLC grade).

2.2. Sulfonation

Sulfonation of SIBS was performed in solution with acetyl sulfate as the sulfonating agent. Acetic anhydride reacts with sulfuric acid to form acetyl sulfate (sulfonating agent) and acetic acid (by product) and removes excess water (anhydrous conditions are required for sulfonation) (Fig. 1(a)). The sulfonation reaction produces sulfonic acid substituted to the *para*-position of the aromatic ring in the styrene block of the polymer (Fig. 1(b)).

An example of the sulfonation procedure used in this study is as follows: a 10% (w/v) solution of SIBS (50 g) in methylene chloride (500 ml) was prepared. The solution was stirred and refluxed at approximately 40 °C, while a specified amount of acetyl sulfate in methylene chloride was slowly added to begin the sulfonation reaction. Acetyl sulfate in methylene chloride was prepared prior to this reaction by cooling 150 ml of methylene chloride in an ice bath for approximately 10 min. A specified amount of acetic anhydride and sulfuric acid was then added to the chilled methylene chloride under stirring conditions. Sulfuric acid was added approximately 10 min after the addition of acetic anhydride with acetic anhydride in excess of a 1:1 mole ratio. This solution was then allowed to return to room temperature before addition to the reaction vessel.

After approximately 5 h, the reaction was terminated by slowly adding 100 ml of methanol. The reacted polymer solution was then precipitated with deionized water. The precipitate was washed several times with water and methanol, separately, and then dried in a vacuum oven at 50 °C for 24 h. This washing and drying procedure was repeated until the pH of the wash water was neutral. After this process, the final polymer yield was approximately 98% on average. This sulfonation procedure was repeated with different amounts of acetyl sulfate to produce several sulfonated polymers with various levels of sulfonation or ion-exchange capacities (IECs). Hereafter, the sulfonated triblock copolymers are referred to as S-SIBS-# (S-SIBS represents sulfonated poly(styrene-isobutylene-styrene) and the succeeding number, #, refers to the mol% sulfonation). The mol% sulfonation is defined as:

$$\text{mol\%} = \left(\frac{\text{moles of sulfonic acid}}{\text{moles of styrene}}\right)100 \tag{1}$$

and the IEC is defined as the mille-equivalents of sulfonic acid per gram of polymer (mequiv./g).

After sulfonation and washing of each polymer, the S-SIBS samples were dissolved in a mixed solvent of toluene/hexanol (85/15, w/w) with concentrations ranging from 5 to 2.5% (w/v) and solution cast in open Teflon® Petri dishes for approximately 1 week at ambient conditions. Solvent-cast membranes were then annealed in a vacuum oven at 50 °C for an additional two weeks to remove any

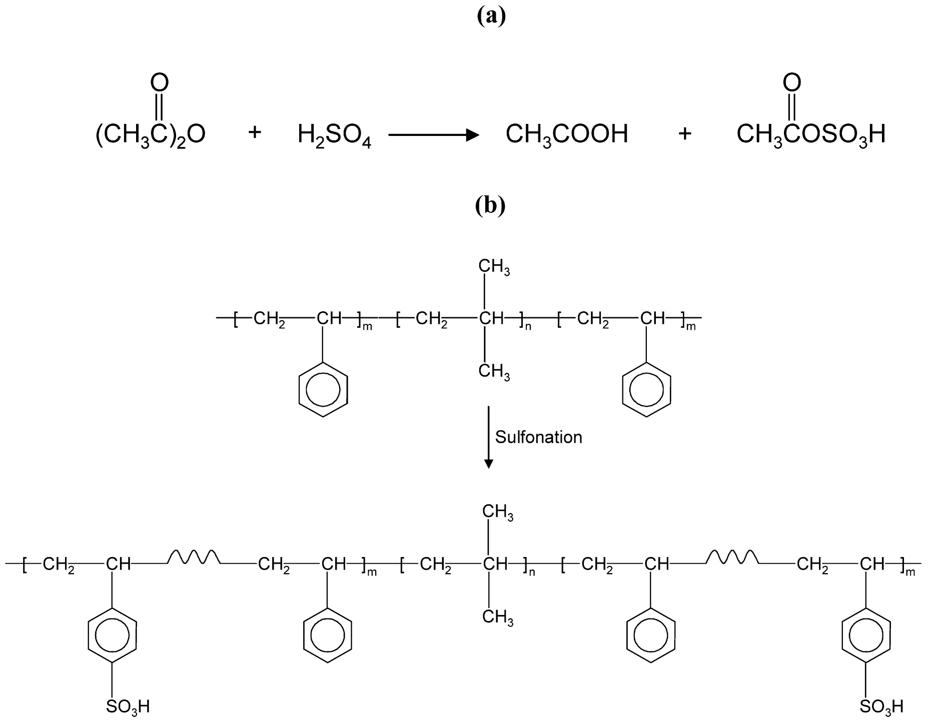

Fig. 1. Sulfonation reactions: (a) preparation of sulfonating agent (acetyl sulfate): acetic anhydride reacts with sulfuric acid to form acetyl sulfate and acetic acid, (b) sulfonation reaction: SIBS reacts with acetyl sulfate to form S-SIBS, where the styrene block is randomly sulfonated (sulfonic acid substituted in the *para*-position of the aromatic rings).

residual solvent. The unsulfonated polymer (S-SIBS-0) was cast similarly, but with pure toluene as the casting solvent. In addition, one sample (S-SIBS-79) was neutralized with a cesium cation (S-SIBS-79-Cs) by submerging the sample into a well-stirred bath of 2.0 M CsCl at 45 °C for 24 h.

2.3. EA

The sulfonation procedure described above was repeated with different amounts of acetyl sulfate to produce several sulfonated polymers with various sulfonic acid concentrations (i.e. ion contents). The amount of sulfuric acid relative to the moles of polystyrene dictates the resulting sulfonation level of the polymer. The IEC of each polymer was determined by elemental analysis (EA). EA was conducted by Atlantic Microlab, Inc. in Norcross, Georgia. All polymers were cryogenically ground to a powder prior to EA.

2.4. Infrared spectroscopy

Infrared spectra of all polymer samples were collected using a FTIR spectrometer (Nicolet Magna 560 Series) equipped with a Thunderdome™ (Spectra-Tech) accessory with a single-reflection ATR crystal (Germanium, refractive index = 4.0). This accessory contains a pressure mechanism for good sample-to-crystal contact. All infrared spectra were collected using 128 scans and 4 cm^{-1} resolution.

2.5. Density

The density of each sample was measured using a helium pycnometer (Quantachrome Ultrapycnometer 1000). This is a non-invasive procedure using purified helium as the displaced medium. After calibration, the specimens were placed in the measurement cell and purged with helium for 5–10 min. At least three experiments were conducted on each sample. The densities and errors reported are the averages and standard deviations of these repeated experiments, respectively.

2.6. Solubility

S-SIBS polymer samples weighing approximately 50 mg were weighed before and after immersion (for a minimum of one week) in deionized water. Water solubility is defined here as:

$$\mathrm{wt\%} = \frac{(\text{wet polymer wt-dry polymer wt})}{\text{dry polymer wt}} 100 \qquad (2)$$

A balance with 0.01 mg accuracy was used. Three experiments were conducted on each sample. The weights and errors reported are the averages and standard deviations of these repeated experiments, respectively.

3. Results and discussion

3.1. Sulfonation analysis

SIBS was sulfonated to eight different sulfonation levels ranging from 0.36 to 2.04 mequiv./g (13 to 82 mol%). The resulting sulfonation amounts, determined from EA, are listed in Table 1. Figs. 2 and 3 show the resulting sulfonation level as a function of moles of sulfuric acid used in each reaction and the reaction efficiency, respectively. Between approximately 0–2 mol of acid/moles of styrene, the sulfonation level increases to 70 mol%, but greater than 2 mol of acid/moles of styrene, the sulfonation level reaches an asymptotic value (see Fig. 2). Between 13 and 54 mol% sulfonation, the reaction efficiency ranges from 60 to 40%. Similarly, a study by Weiss et al. [12] on sulfonated poly(styrene-(ethylene-*co*-butylene)-styrene) finds a constant reaction efficiency of 55% between 0–18 mol% sulfonation.

Above 70 mol% sulfonation, however, the reaction efficiency decreases rapidly from 36 to 12% (see Fig. 3). The significant decrease in efficiency is illustrated more clearly between 79 and 82 mol%, where the amount of acid used in the reaction doubles from 3.5 to 6.8 mol of acid/moles of styrene and the reaction efficiency decreases from 22 to 12%. This sharp decrease in efficiency may be caused by the lack of complete miscibility of the highly sulfonated polymers in methylene chloride. However, it is unclear to what extent, if any, miscibility affects reaction efficiency. In addition, preliminary findings reveal 80–90% reaction completion in the first hour of the sulfonation reaction, so extending reaction time should not significantly alter the sulfonation amount in the polymer. Another study [12] confirms this finding with a sulfonation reaction completion time of approximately 1–2 h.

3.2. Infrared analysis

Fig. 4 shows the infrared spectra of S-SIBS-0 (unsulfonated) and S-SIBS-79 (sulfonated to a high level), where four additional bands appear in S-SIBS-79 that are not present in S-SIBS-0. These four bands in SIBS-79 observed at 1156, 1127, 1034, 1006 cm^{-1} (indicated by the arrows in Fig. 4) are all representative of the stretching vibrations associated with sulfonation [12,19–21]. The in-plane bending vibrations of the aromatic ring (in styrene) *para*-substituted with the sulfonate group and the sulfonate anion attached to the aromatic ring are represented at 1006 and 1127 cm^{-1}, respectively, while the bands at 1034 and 1156 cm^{-1} represent the symmetric and asymmetric stretching vibrations of the sulfonate group, respectively.

The intensity of these four bands increases with increasing sulfonation level. The increase in intensity (which is related to the amount of sulfonation) was quantified and is shown in Fig. 5 as the ratio of absorbances (peak height at 1006 cm^{-1}/1365 cm^{-1}) versus sulfonation level. The band at 1006 cm^{-1} gives an indication of the level of sulfonation in the polymer, while the band at 1365 cm^{-1} represents the symmetric CH_3 deformation in polyisobutylene (a reference band). A linear regression (shown by the solid line) between normalized absorbance

Table 1
Elemental analysis

Sample name[a]	Sulfonation level (mol %)	IEC (mequiv./g)
S-SIBS-0	0	0
S-SIBS-13	12.50	0.36
S-SIBS-29	29.23	0.81
S-SIBS-42	41.95	1.13
S-SIBS-48	48.16	1.28
S-SIBS-54	53.68	1.41
S-SIBS-70	70.14	1.78
S-SIBS-79	79.05	1.97
S-SIBS-82	82.41	2.04

[a] S-SIBS = sulfonated poly(styrene-isobutylene-styrene).

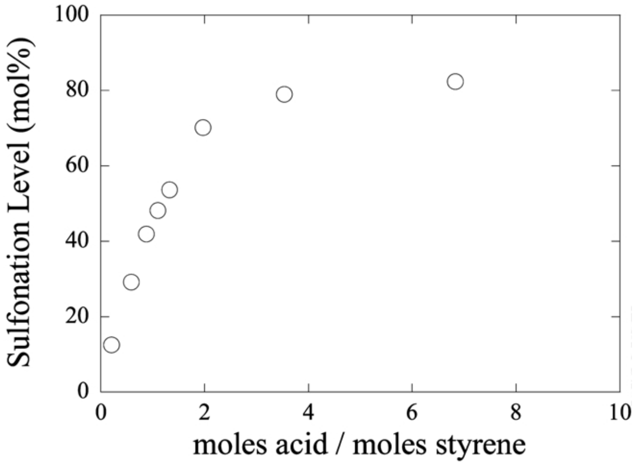

Fig. 2. Moles of sulfuric acid per moles of styrene added to produce a specified sulfonation level (moles of sulfonic acid/moles of styrene) in S-SIBS.

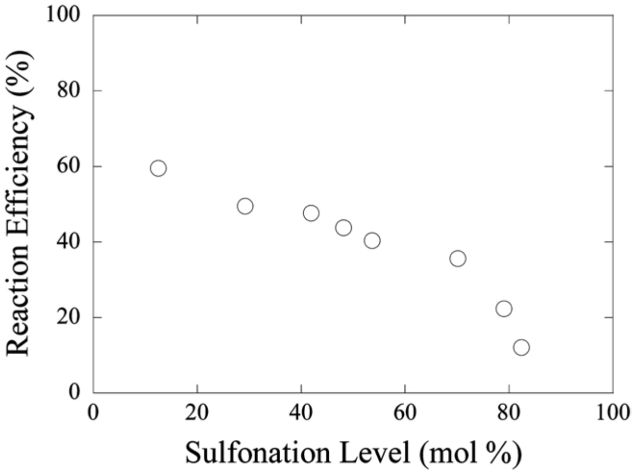

Fig. 3. Reaction efficiency versus sulfonation level in S-SIBS.

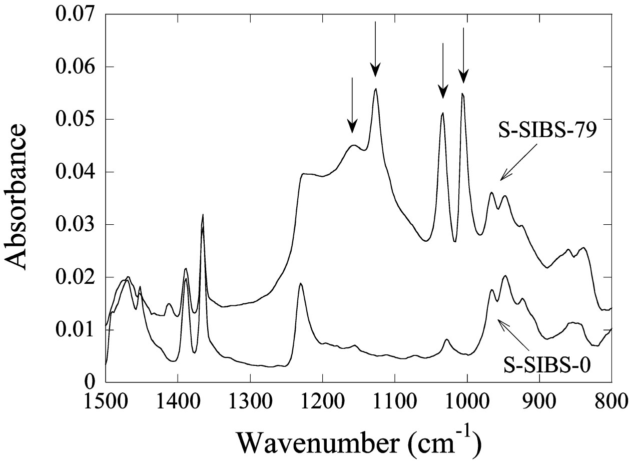

Fig. 4. Infrared spectra for S-SIBS-0 and S-SIBS-79. Four new bands (indicated with arrows) are evident in the sulfonated polymers, 1156, 1127, 1034, 1006 cm^{-1}, representing the stretching vibrations associated sulfonation.

and sulfonation level (determined from EA) in the polymer is shown in Fig. 5.

Additionally, the infrared spectra of S-SIBS at 79 mol% sulfonation in both acid form (S-SIBS-79) and neutralized with a cesium cation (S-SIBS-79-Cs) are shown in Fig. 6. A noticeable difference between the two spectra is a shift (from 1156 to 1183 cm^{-1}) and an increase in intensity of the asymmetric stretching band of the sulfonate group. It is unclear why the asymmetric stretching vibration changes while other stretching modes associated with the sulfonate group remain unaltered. One possible explanation is that the stretching mode at 1156 cm^{-1} does not represent the asymmetric stretch of the sulfonate group, but rather the sulfonate anion attached to the aromatic ring of styrene. If the band assignment between 1127 and 1156 cm^{-1} were reversed, this band shifting due to neutralization may seem more logical. However, there is no literature to support this view.

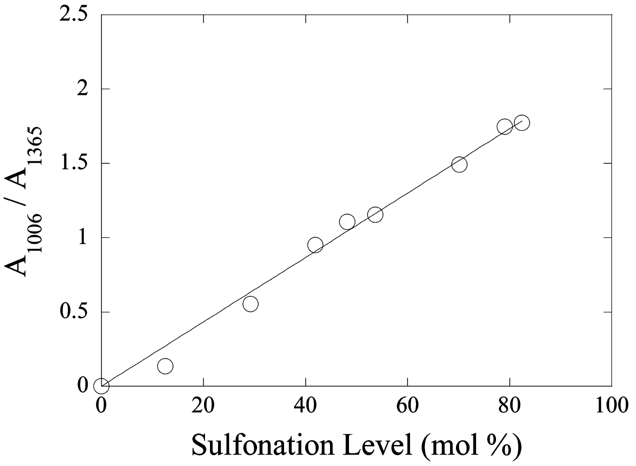

Fig. 5. Absorbance ratio (peak height at 1006/1365 cm^{-1}) versus sulfonation level (determined from EA). 1006 cm^{-1} represents the in-plane ring vibrations of the aromatic ring caused by the *para*-substituted sulfonic acid and 1365 cm^{-1} represents the symmetric deformation of CH_3 in polyisobutylene. The solid line represents a linear regression.

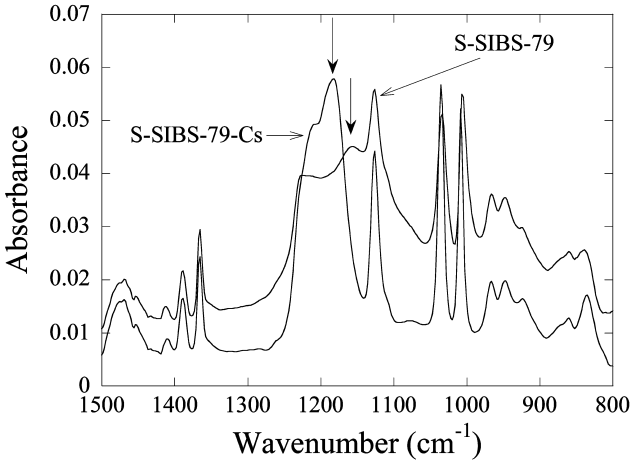

Fig. 6. Infrared spectra for S-SIBS-79 and S-SIBS-79-Cs. A shift in the vibrational band (1156–1183 cm^{-1}) is indicated by the arrows.

Also, a shoulder appears in the S-SIBS-79-Cs infrared spectra around 1210 cm^{-1}, which is also seen in the S-SIBS-79 spectra in the range of 1210–1230 cm^{-1}. Other sources [19–20] have suggested two bands (a doublet) associated with the asymmetric stretching of the sulfonate group, with a second band located around 1200–1230 cm^{-1}. The extra band in these two spectra, shown in Fig. 6, may be associated with a second mode of asymmetric stretching of the sulfonate group, but its exact location is difficult to determine in this study due to a band conflict with the band at 1230 cm^{-1} associated with the unsulfonated polymer (Fig. 4).

3.3. Density

Fig. 7 shows the density of S-SIBS polymers as function of sulfonation level measured with helium pycnometry. The polymer density increases from 0.95 to 1.31 g/cm^3 with increasing sulfonation level. Polymer density increases even

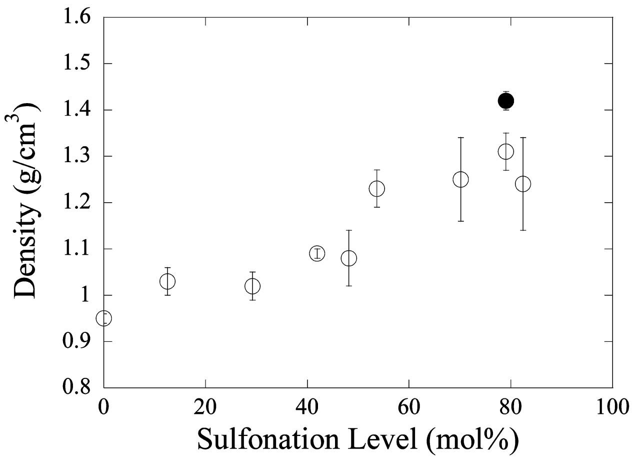

Fig. 7. Density versus sulfonation level in S-SIBS: acid form (○) and neutralized with cesium (●).

further with neutralization with cesium from 1.31 to 1.42 g/cm^3. Adding sulfonic acid and metal cations must increase packing (probably caused by the electrostatic interactions among ion pairs) and produce a denser polymer with less free volume.

3.4. Solubility

The water solubility of each polymer is shown as a function of sulfonation level in Fig. 8. Similar to polymer densities, the water uptake increases up to 351 wt% with increasing sulfonation level. Increasing the amount of polar sulfonic acid in the polymer results in a significant increase in water solubility (greater than 300 wt% water at 2 mequiv./g). From visual observations, the S-SIBS-82 membrane increased approximately 2.5 times its area after immersion in water, but remains completely immiscible in water.

Fig. 8 also reveals a sudden increase from 84 to 229 wt% between 48 and 54 mol% sulfonation. The cause for this sudden increase is unclear. A prior study [5] revealed that the percolation threshold occurs at approximately 0.5 mequiv./g in S-SIBS. It is possible that another structural change occurs between 48 and 54 mol% sulfonation, in which even more ionic groups become accessible to hydration. A recent study in our laboratory on S-SIBS revealed a lamellar morphology in the plane of the membrane, between 0.5 to 1.0 mequiv./g, in which ionic domains are connected within the lamellae block [18]. Future X-ray scattering studies are underway to determine the exact morphology of S-SIBS above 1.0 mequiv./g. Contrary to polymer densities; the water solubility decreases from 308 to 196 wt% as S-SIBS-79 is neutralized with a cesium cation. The cesium cation may act as a mild crosslinker, which results in a decrease in water solubility when compared to its acid form.

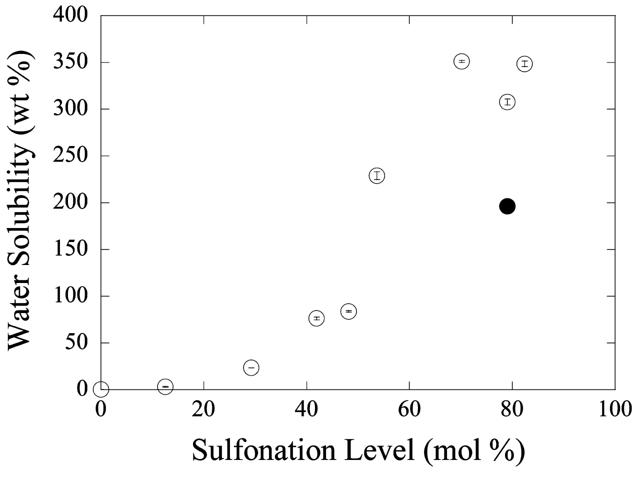

Fig. 8. Water solubility versus sulfonation level in S-SIBS: acid form (○) and neutralized with cesium (●).

4. Conclusions

This study demonstrates the sulfonation of poly(styrene-isobutylene-styrene) to higher sulfonation levels (higher than 2.0 mequiv./g) than previously reported. As sulfonation levels increase, the reaction efficiency decreased considerably. Regardless of reaction efficiency, increased sulfonation levels results in a variety of unique properties, such as increased densities and water solubilities, as well as the generation of an *elastic hydrogel*. Here, the *elastic hydrogel* is composed of ordered blocks; one hydrophobic and elastic, and the other hydrophilic and ionic, in which the polymer swells considerably in water, but maintains complete immiscibility. These new properties in a nanostructured framework may lead to a variety of new materials. Future studies examining the transport properties, structural properties, and fuel cell performance on these new materials are currently underway.

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