NEW HYDROCARBON PROTON EXCHANGE MEMBRANES BASED ON SULFONATED STYRENE-ETHYLENE/BUTYLENE-STYRENE TRIBLOCK COPOLYMERS

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Abstract

Commercially available styrene-ethylene/butylene-styrene triblock polymer (Kraton G1650) was partially sulfonated using a SO₃/tributyl phosphate reagent in a dichloroethane/cyclohexane mixed solvent. Films of the product were cast from lower alcohols to give elastic materials with different degrees of sulfonation (ca. 30-60%) as determined by titration. Transmission electron microscopy suggests that the cast films possess cylindrical sulfonated polystyrene domains. The films swell in water, with the extent of swelling being dependent on the sulfonation level. Ionic conductivities as high as 8.5 x 10⁻² S/cm are obtained when fully hydrated, and compare favorably to those exhibited by hydrated, sulfonated fluoropolymers such as Nafion.

Introduction

Polymers with high protonic conductivities are potentially useful as proton exchange membranes (PEM's) in fuel cells. Among the earliest PEM's were sulfonated, crosslinked polystyrenes, and these were employed in fuel cells on the Gemini space missions.¹ More recently, interest has been directed to sulfonated fluorocarbon polymers, of which Nafion has been most extensively studied.²⁻⁷ This material has a high protonic conductivity (ca. 7 x 10⁻² S/cm at 30 °C)⁸ when hydrated and is chemically rather inert. It has been proposed that Nafion possesses an inverted micellar structure, with spherical (ca. 40-50 Å diameter) clusters lined with sulfonic acid groups which are interconnected via ca. 10Å channels.⁹⁻¹¹ We sought to mimic this picture using inexpensive sulfonated, hydrocarbon-based block copolymers. Block copolymers in

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general can exhibit a rich array of microphase-separated morphologies depending on relative block sizes. Such materials provide us with an opportunity to link good ionic (protonic) conductivity through water-swellable microdomains with low material cost and desirable mechanical properties. We note that selected block copolymers have been shown to be useful as alkali metal-based polymer electrolytes, although apparently no efforts have been directed toward obtaining high protonic conductivity based on hydrocarbon block polymers.

We selected Kraton G1650 for our studies as it contains a saturated carbon center block which should be inert to the sulfonation reaction, which in this case employs SO$_3$/triethyl phosphate to achieve high levels of sulfonation without crosslinking. The reaction is summarized in Figure 1. The Kraton used in this study contains 29% by weight styrene and exhibits a microstructure of polystyrene phases intermediate between spheres and cylinders (ca. 150 Å in diameter) in an ethylene/ butylene-rich continuous phase. Sulfonation levels, based on the moles of styrene units sulfonated, ranged from 35-65% as determined by titration. We note that sulfonated, saturated Kratons have been disclosed in a patent, and that Weiss and coworkers have explored in detail the morphology and mechanical properties of lightly sulfonated (up to 12 mol% styrene units) Kraton G1650, the latter representing an interesting new class of ionomers. However, we are unaware of studies directed at highly sulfonated derivatives with the aim of obtaining highly proton conducting films.

**Experimental**

Kraton G1650 was acquired from Shell Chemical; dichloroethane (DCE) and cyclohexane were from Krackeler Scientific; triethyl phosphate (TEP) and sulfur trioxide (SO$_3$) were from Aldrich. All materials were used without further purification. Sulfonation of the styrene-ethylene/butylene-styrene (SEBS) triblock polymer was carried out in a batch mode using SO$_3$/TEP. The reaction vessel was kept slightly below 0°C and reaction times ranged from 60-90 min. After removing most of the cyclohexane and DCE, the residue was taken up into lower alcohols. Films were then cast from these solutions on glass under an IR lamp.

Titrations to determine the sulfonic acid content of the film were carried out using standardized sodium hydroxide solutions. Films were hydrated in deionized water and washed by placing the film in clean deionized water three times for one hour each. About 0.15 g of film was placed in a small vial and approximately 12 ml of sodium chloride solution was added. After immersion for about 2 h, titrations to a phenolphthalein endpoint were carried out. Data are reported as mol% styrene units sulfonated. Samples for transmission electron microscopy (TEM) were first stained for 15 min in the presence of RuO$_4$ vapor and then cryomicrotomed at -100°C using a Reichert-Jung Fc4 microtome. A 2000 FX high resolution transmission electron microscope was employed at a magnification of 275,000x.

Conductivity measurements were made on samples treated to remove any residual sulfuric acid from the sulfonation reaction. Samples were soaked in water for 30 min. and then dried under an IR lamp for 30 min, and this sequence was repeated twice. The conductivity of the membrane was measured by using a pair of pressure-attached high surface area platinum electrodes as described by Zawodinsksi et al. The mounted sample was immersed in distilled, deionized water at room temperature (ca. 24 °C). Once the sample had completely hydrated, measurements were made from 1 Hz to 10KHz using a Solartron 1260 frequency response analyzer. Both real and imaginary...
components of the impedance were measured and the real Z-axis intercept was closely approximated. The cell constant was calculated from the spacing of the electrodes (L), the thickness of the membrane and the area of the platinum electrodes (A). The conductivity (σ) was calculated using the equation

\[ \sigma = \frac{L}{RA}. \]

Results and Discussion

Films of sulfonated triblock polymer are yellow and relatively transparent as well as elastomeric. A transmission electron micrograph of a microtomed and RuO4-stained film (ca. 45% sulfonation) is shown in Figure 2 and reveals what appear to be cylindrical (ca. 150 Å diameter) sulfonated polystyrene domains in an ethylene/butylene matrix. We believe that at this high sulfonation level, relatively homogeneous sulfonated polystyrene domains are present rather than ion clusters of sulfonated styrene repeat units within polystyrene domains as is the case in lightly sulfonated Kratons.16-18

The films swell upon immersion in water, and the extent of swelling is as expected dependent upon the sulfonation level. These hydrogels retain their elastomeric character. We have no information on the organization of the sizes of the sulfonated domains upon hydration, but speculate that these are interconnected upon swelling and perhaps forming bicontinuous phases. X-ray and neutron scattering experiments are planned to address this important issue. The films remain relatively transparent upon hydration, suggesting that the water-swollen domains remain below ca. 400 nm in diameter.

Ionic conductivities of fully hydrated films having various levels of sulfonation are reported in Table 1. Samples having sulfonation levels greater than about 45% have conductivities comparable to Nafion (ca. 7 x 10^{-2} S/cm) under similar conditions.8 The amount of sulfonation within the polystyrene domains is well above the percolation threshold for ionic conduction of ca. 7 mol%, as recently determined by Yeager, Eisenberg and coworkers19 for sulfonated homopolystyrene. The high conductivity we observe indicates that the sulfonated domains are interconnected.

In summary, we have prepared highly proton conducting, elastomeric films by sulfonation of a styrene-ethylene/butylene-styrene triblock polymer. Several applications of these materials are being investigated, including their use as proton exchange membranes in fuel cells.

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Table 1
Conductivities of Sulfonated Block Polymers as a Function of Sulfonation Level

| Percentage Sulfonationa | mmol/gb | Conductivityc (S/cm) |
|-------------------------|---------|---------------------|
| 35                      | 0.96    | 0.068               |
| 43                      | 1.16    | 0.075               |
| 50                      | 1.33    | 0.080               |
| 65                      | 1.72    | 0.089               |

aMole % based on styrene units, determined by titration. Data are averages of triplicate determinations.
bMillimol sulfonic acid per gram of total polymer.
cImmersed in water, room temperature.
Figure 1: Sulfonation of Styrene/Ethylene-Butylene/Styrene Triblock Copolymer

\[ \text{-}(\text{CH}_2\text{CH})_n\{[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]\}_x\{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\}_y\{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\}_m\{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\}_n \]

\[ \text{SO}_3 , \text{TEP} \quad 0^\circ\text{C} \quad \text{DCE}, \quad \text{S} \]

\[ \text{-}(\text{CH}_2\text{CH}^\wedge\text{CH}_2\text{CH})_n\{[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]_x\{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\}_y\{\text{CH}_2\text{CH}^\wedge\text{CH}_2\text{CH}\}_m\{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\}_n \]

\[ \text{SO}_3^\wedge \text{H} \quad \text{SO}_3^\wedge \text{H} \]

Figure 2: Transmission electron micrograph of ca. 45% sulfonated Kraton G-1652 stained with RuO_4. Magnification = 275,000x.