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Cross-linking of sulfonated styrene–ethylene/butylene–styrene triblock polymer via sulfonamide linkages

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Abstract

Sulfonated styrene–butadiene–styrene (SSBS) triblock copolymer was cross-linked through condensation of sulfonic acid groups with bis(4-aminophenyl)sulfone to form sulfonamide linkages using a coupling agent (carbonyldiimidazole). Intact and clear light brown membranes were obtained when cast from solution, and cross-linking was established by measuring percent water uptake, determined gravimetrically and by near-IR (NIR) spectroscopy, and percent sulfonation by titration. The cross-linked SSBS membranes were found to absorb less water, showed higher resistance to thermal degradation and, when not highly cross-linked, showed better membrane integrity when immersed in water for extended periods. The percent sulfonation of the cross-linked SSBS membranes was found to be 2–10% lower than the non-cross-linked membranes. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Sulfonated styrene–butadiene–styrene triblock copolymer; Cross-linking; Percent water uptake

1. Introduction

Polymer electrolyte membranes (PEM) for fuel cells have been known since the 1960s, having being employed in spacecrafts and submarines [1]. In the past decade, there has been considerable effort in academia and industry to bring the technology of fuel cells closer to the consumer, specifically to power cars and everyday electrical appliances. From a materials standpoint, the perfluorinated PEM (for example DuPont's Nafion® and Dow's material) are considered among the best candidates because these are chemically stable, show good mechanical properties and exhibit high ionic conductivities [2–4]. However, there are some drawbacks that prevent the use of these materials on a large scale. They are difficult to process, still too expensive for commercialization and, with respect to properties, the fluorinated PEMs suffer from lower ionic conductivities at high temperatures and at low humidity. In the recent past, there has been a lot of interest in developing more cost-effective membranes that come close to the properties of Nafion®, and attention has focused on hydrocarbon based PEM [5,6]. One such example is the DAIS material, sulfonated styrene–ethylene/butylene–styrene triblock polymer (SSBS), that is obtained by sulfonation of the hydrogenated styrene–ethylene/butylene–styrene (Kraton® G-1652) using sulfur trioxide to give highly sulfonated SBS materials, in the range 35–68 mol% of the styrene block [7–10]. SSBS is currently available from Aldrich Chemical Co.

The SSBS membrane is believed to have a microphase-separated morphology where cylindrical sulfonated polystyrene domains (polar regions) are found in a non-polar ethylene/butylene matrix [7]. Like Nafion®, the SSBS membrane swells upon hydration and shows high ionic conductivity of 0.09–0.10 S/cm. It was observed that SSBS films left soaking in water for long periods became cloudy (opaque) and began to frail in water after about two to 3 months. The loss in membrane integrity may be associated with an increase in pressure with continual uptake of water when immersed in water for long periods, causing the membrane to rupture eventually. There are other possible changes with prolonged hydration of the SSBS membrane, for example morphological changes associated with further phase separation or desulfonation. Overall, any method that improves the membrane integrity of SSBS would be highly desirable because SSBS membrane could be usable over longer periods or, possibly, even at higher temperatures. One approach to achieve this objective is to lightly cross-link

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the SSBS membrane, with the idea that this would strengthen the membrane [11] and also result in slightly reduced water uptake.

Nolte et al. [12] has previously reported the cross-linking of a polyelectrolyte membrane to reduce water swelling of the membrane without impairing other membrane properties, such as protonic conductivity. The focus of this project was to attempt cross-linking of SSBS via the sulfonic acid groups, by forming bis sulfonamide linkages using bis(4-aminophenyl)sulfone and carbonyldiimidazole as the coupling agent.

2. Experimental

2.1. Materials and instrumentation

The SSBS polymer was provided by DAIS Corporation as a 10 wt% solution in *n*-propanol/dichloroethane (50/50). Additionally, a 5 wt% SSBS solution in *n*-propanol/dichloroethane was obtained from Aldrich Chemical Co. Sodium chloride, 1,2-dichloroethane (DCE), phosphorus pentoxide (P_2O_5), propanol, bis(4-aminophenyl)sulfone and 1,1′-carbonyldiimidazole (CDI) were purchased from Aldrich Chemical Co. and used as received. ^1H and ^{13}C NMR spectra were collected on a Bruker 300 MHz NMR spectrophotomer using deuterated acetone as solvent; all chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonances. Mass spectra were obtained on a Hewlett–Packard GC/MS 5973 (GC 6890).

2.2. Cross-linking reaction

The cross-linking procedure was adapted from Nolte et al. [12]. CDI (0.013 g, 0.25 mol equiv. with respect to sulfonic acids groups of SSBS) was added to 5 g of a 5 wt% polymer solution (or 2.5 g if a 10 wt% polymer solution was used). The solution was warmed slightly (45–50 °C) to dissolve CDI and some gas evolution was observed (mostly likely CO_2). The reaction mixture was stirred for 1 h, followed by the addition of 0.0099 g (0.12 mol equiv.) of bis(4-aminophenyl) sulfone (Note: if dissolution was not achieved, ~2 ml of NMP were added and warmed again). After stirring for 3 h at room temperature, the reaction mixture was poured into a glass petri dish (3 in. in diameter) and allowed to evaporate slowly for 2 days at room temperature and, if NMP was used, followed by vacuum evaporation overnight at 45 °C. An intact film was generally obtained that was rinsed in distilled water for 3 days (water changed everyday). The film was then dried in vacuum overnight at room temperature, followed by heating it under an IR lamp for 10 min. A film thickness of 0.3 mm was obtained. For comparison, a non-cross-linked film was also obtained by casting 5 g of the polymer solution.

2.3. Control reaction

CDI (0.1038 g) and 5 ml of 50/50 (v/v) 1,2-dichloroethane/*n*-propanol solution were placed in a flask, stopped with a rubber septum and flushed with nitrogen for 2 min. The reaction mixture was heated to 45 °C and allowed to stir overnight. A white precipitate was observed that was filtered and dried under vacuum over P_2O_5. This turned out to be imidazole, as determined by ^1H NMR spectroscopy. Solvent was removed from the filtrate by rotary evaporation to yield a white solid. This product was analyzed without further purification and a mixture of products were identified. *Imidazole* {GC/MS: *m/e* 68; ^1H NMR, ppm [10.25 (s, 1H); 7.55 (s, 1H), 7.15 (s, 2H)]; ^{13}C NMR, ppm (135.5, 122.0)}. 1-imidazole-propylmethanoate (product **A**) {GC/MS: *m/e* 154 (M +), 95 (imidazole–C=O), 68 (imidazole), 43 ($CH_2CH_2CH_3$); ^1H NMR, ppm [8.2 (s, 1H); 7.8 (s, 2H); 4.4 (t, 2H); 1.80 (sextet, 2H); 1.05 (t, 3H)]. ^{13}C NMR, ppm [149.0 (C=O), 137.5, 131.0, 117.7, 70.0, 22.0, 10.0)]. *Dipropylcarbonate* (product **B**) {GC/MS: *m/e* 59 ($OCH_2CH_2CH_3$), 43 ($CH_2CH_2CH_3$); ^1H NMR, ppm [4.05 (t, 2H); 1.65 (sextet, 2H); 0.9 (t, 3H); 7.15 (s, 2H)]; ^{13}C NMR, ppm [149.0 (C=O), 69.0, 22.3, 10.3]}.

2.4. Percent sulfonation by titration

This was carried out on ~0.20 g film samples. A sample was immersed in 0.5 M NaCl solution overnight under nitrogen gas flow to convert $-SO_3H$ to $-SO_3Na$. The solution with the membrane was then titrated with 0.0527 M NaOH (standardarized against potassium hexaphosphate) with phenolphthalein as the indicator. Percent of styrene units sulfonated are reported.

2.5. Percent water uptake

The weight gained by dried cross-linked and non-cross-linked membranes was monitored over a period 400 min in a humid environment (enclosed glass chamber with distilled water on the base and maintained at 30 °C). Near IR (NIR) spectra were also obtained to monitor D_2O uptake using a Perkin–Elmer Lambda 900 UV–VIS/NIR spectrophotomer. The peaks associated with D_2O were found at 1550 and 1950 nm; water uptake was reported as a ratio of the absorbance at 1937 nm relative to 1730 nm; the latter remained unchanged during hydration and was attributed to the SSBS polymer itself.

3. Results and discussion

The SSBS polymer was cross-linked by reacting sulfonic acid groups on the styrene units with bis(4-aminophenyl)-sulfone using a coupling agent (CDI) to obtain intermolecular sulfonamides linkages. The SSBS polymer is insoluble in the solid form and, therefore, the cross-linking

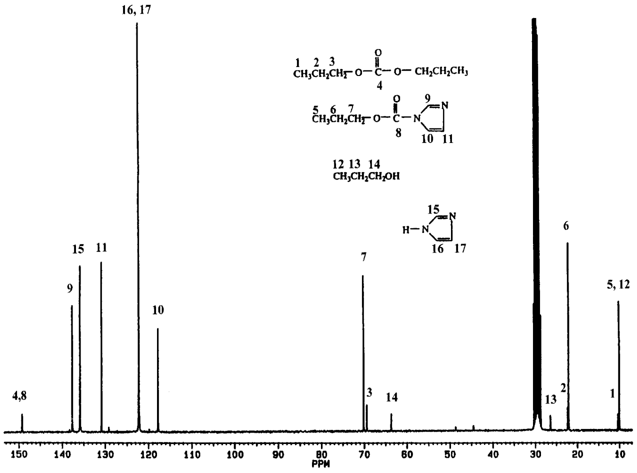
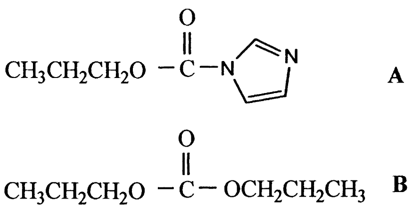


Fig. 1. ^{13}C NMR spectrum of products from control reaction.

reaction was carried on solutions of SSBS in DCE/propanol (50/50 v/v) as received. This in itself posed a problem because *n*-propanol could react with the CDI coupling agent; a control reaction was run to follow the possible side reactions and several products were identified when CDI was stirred in 50/50 DCE/propanol, as determined by GC/MS, ^{1}H and ^{13}C NMR spectroscopy. Fig. 1 shows the ^{13}C NMR spectrum of the products from the control reaction, and these included condensation products **A** and **B** (Scheme 1), along with imidazole and *n*-propanol (residual solvent).

Despite the aforementioned side reaction, the cross-linking reaction of SSBS was still deemed feasible because, first, sulfonic acids are likely to be more reactive than propanol with CDI and, secondly, even if the reaction gave a low yield of the sulfonamides linkages in the polymer, this could still have the desired impact on the SSBS membrane. Light cross-linking has the potential to strengthen the membrane, lower the continual uptake of water and possibly reduce phase separation, if the latter is an issue.

The cross-linked SSBS membrane was insoluble in ordinary laboratory solvents, including all apolar protic solvents, which made characterization difficult. Thus, the presence of cross-linking reaction was determined by measuring percent water uptake, changes in percent sulfonation, and looking for differences between the cross-linked and non-cross-linked membranes when immersed in water.



Scheme 1.

3.1. Physical state of non-cross-linked and cross-linked SSBS membranes

The cross-linked membrane (XL) was clear and light brown in color, similar in appearance to the uncross-linked membrane (NXL). To probe if there were any differences between the two membranes, thermal stability and appearance in water upon prolonged immersion in water were evaluated. Heating the two membranes with an IR lamp for 24 h gave drastically different results. The NXL membrane was black, shriveled and cracked into many tiny pieces while the XL membrane, on the other hand, was slightly tanned, opaque but remained intact. The results indicate that the NXL degraded far more than the XL membrane, an indication that the XL membrane is likely to be more resistant to degradation than the NXL membrane.

Both NXL and XL were also evaluated after being soaked in water for an extended period of time. Fig. 2 is a photograph of the two membranes after 4 months in water. This is probably the most conclusive evidence that the XL membrane is changed for the better. The XL membrane remained clear, intact, retaining the original light brown color and was less expanded in the hydrated state as compared to the NXL that was clearly opaque and expanded to a larger size (the same initial membrane dimensions were used in this study). The results clearly demonstrate that the cross-linking reaction had the effect of improving the membrane.

3.2. Percent water uptake studies

The insolubility of the XL SSBS membranes made it difficult to determine if cross-linking was present by ^{1}H and ^{13}C NMR spectroscopy. Instead, water uptake by the NXL and XL membranes was measured by gravimetric and spectroscopic methods because cross-linking in polymers is generally accompanied by lower water uptake. Both NXL

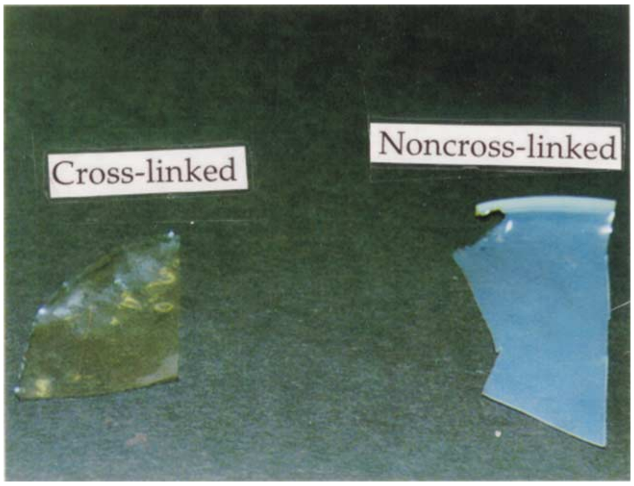


Fig. 2. Appearance of SSBS membranes after immersion in water for 4 months.

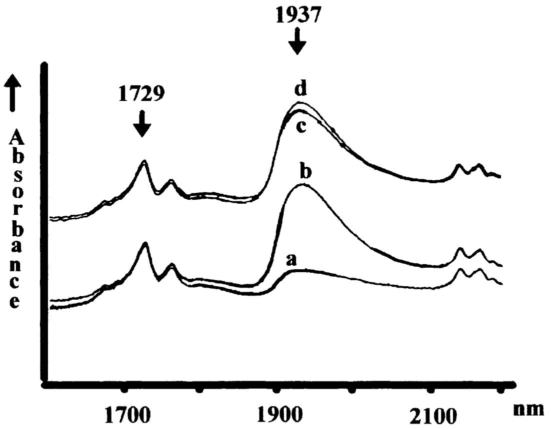


Fig. 3. NIR spectra of cross-linked membrane upon hydration in a 100% D_2O humid environment at 30 °C: (a) 0 min (membrane dried under vacuum over P_2O_5), (b) 30 min, (c) 60 min, (d) 270 h, and (e) 600 h.

and XL were dried in vacuum at room temperature overnight, followed by drying for 10 min under an IR lamp. Upon suspension in a humid environment at 30 °C for 400 min, the percent weight gained associated with hydration was 14% and 8–10.5% for the NXL and XL membranes, respectively. The lower percent uptake of water in the XL membrane is strong evidence that cross-linking in the SSBS membrane was achieved.

A second method was also used to evaluate the hydration profile of NXL and XL membranes. The membranes were either vacuum dried or vacuum dried over P_2O_5, the latter usually being more efficient in drying the membranes. The dried membranes were suspended in a D_2O humidified environment at 30 °C and analyzed by NIR spectroscopy over a period of about 40 h. The D_2O absorption bands were observed at 1550 and 1937 nm; the 1937 nm peak was selected to monitor the uptake of D_2O in the membranes because it was relatively free from overlapping peaks from the SSBS polymer. Fig. 3 shows the NIR spectrum of the XL membrane when dry, at 30, 60, 270 and 600 min. There is a dramatic increase in the 1937 nm absorption peak by the end of 60 min that indicates significant hydration over this period. Fig. 4 shows the change in the hydration profile for the NXL and XL membranes. The amount of D_2O absorbed by the membranes is reported in terms of peak height ratio, which is defined here as the ratio of the absorbance of the 1937 nm relative to 1730 nm peak absorbance, the latter chosen because it was unchanged during the hydration period and attributed to the copolymer itself. Both membranes absorb water rapidly in the first hour, with a slightly higher amount of absorption by the NXL membrane at the end of first hour. Beyond this point, the NXL continues to be hydrated further while the XL membrane only increases very slightly. The data shows that the XL membrane does not significantly change in hydration after the initial rapid phase of hydration, and is less hydrated than the NXL membranes. These findings are consistent with the preceding gravimetric analysis.

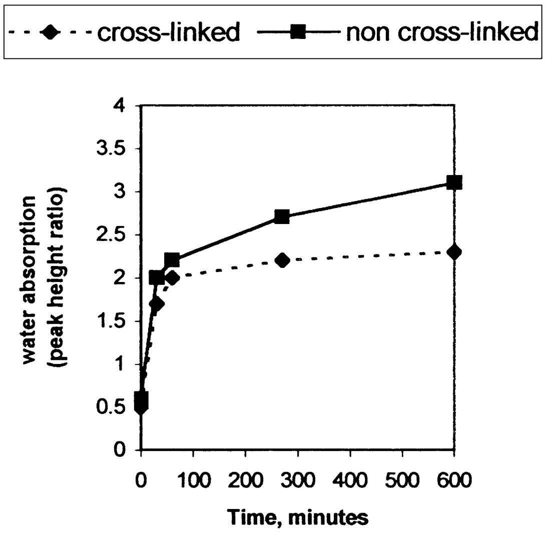


Fig. 4. Water uptake of cross-linked (XL) and non-cross-linked (NXL) SSBS membranes, reported in terms of peak height ratio (absorbance of D_2O peak at 1937 nm/absorbance of polymer peak at 1720 nm).

3.3. Percent sulfonation

Another approach to follow the cross-linking reaction of SSBS was percent sulfonation by titration. It was expected that percent sulfonation would decrease with cross-linking, as the styrene sulfonic acid groups were converted to sulfonamide groups. Although there were some variations in the percent sulfonation of SSBS samples from batch to batch, percent sulfonation in general was found to decrease by 2–10% upon cross-linking relative to the NXL membranes. The SSBS membrane that showed a decrease of 10% sulfonation upon cross-linking became brittle when immersed in water, indicating excessive levels of cross-linking. The XL SSBS membranes that showed lower decreases in percent sulfonation, 2–5%, remained clear and intact when immersed in water.

4. Conclusions

The cross-linking of SSBS triblock copolymer via sulfonamide linkages was carried out in solution, despite the presence of side reactions between the coupling agent and *n*-propanol in the reaction mixture. The cross-linked SSBS membranes absorbed less water and showed greater thermal resistance. For the cross-linked SSBS membranes that were not too highly cross-linked, the membranes showed better film qualities when immersed in water for extended periods (remained clear and intact). It can be concluded from the preceding that light cross-linking can be used to improve the quality of the SSBS membranes.

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