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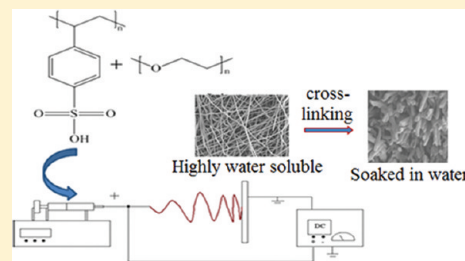
Chemical Cross-Linking of Highly Sulfonated Polystyrene Electrospun Fibers

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ABSTRACT: Electrospun nanofibers of highly sulfonated polystyrene (IEC \sim 4.8 mequiv/g) might be good candidates for use in ion exchange applications because of their ability to form continuous, highly conducting pathways for cation transport. However, such fibers suffer in terms of dimensional stability due to high water uptake at elevated humidity. To improve the stability of the electrospun nanofiber mats in water, the polyelectrolyte was coelectrospun in the presence of a high molecular weight poly(ethylene oxide) (PEO). Addition of PEO to the spinning dope helped improve the spinnability of the polyelectrolyte and subsequent heat treatment improved the stability of the fiber mats in water. Increasing PEO concentration in the fiber mats reduced the solubility of the heat-treated fiber mats in water; suggesting that the fibers were cross-linked by or in the presence of the PEO. To understand the chemistry of this apparent cross-linking reaction, the electrospun fiber mats were heated in a solid state ^1H NMR rotor and changes in the spectrum were monitored as the reaction progressed. The hypothesis is that at higher temperatures, the two polymers react with each other to form sulfonic acid esters that form water-resistant cross-links. An alternative hypothesis of a free-radical cross-linking reaction was not supported by the observations.



1. INTRODUCTION

Perfluorinated ionic membranes such as Nafion are the dominant transport media used for proton exchange membrane (PEM) fuel cells, primarily because of their high proton conductivity and exceptional oxidative stability.¹ Nafion is a random copolymer composed of a hydrophobic backbone with acid-containing side groups. One limitation of the random-copolymer PEM is that the transport and mechanical properties are coupled, so that optimizing one usually degrades the other. Hence, there has been a renewed effort to develop new PEM materials, especially composite materials that allow separation of the transport and mechanical properties. Some of the approaches that have been investigated are block copolymers,² nanofiber-based networks³ and filled systems using particles of high ion exchange capacity (IEC).⁴

Sulfonated polystyrene (SPS), either as a pure polymer or in blends, has been explored for PEM fuel cells. One limitation with using sulfonated polymeric membranes is to strike a balance between proton conductivity and dimensional stability in water at high sulfonation levels. A high degree of sulfonation helps attain high proton conductivity; but, at the same time, high sulfonation levels lead to water solubility. Hence the membranes swell excessively and have poor dimensional stability. In the past, researchers have investigated different cross-linking methods, particularly ionic and covalent cross-linking, to improve the mechanical stability of sulfonated polymeric membranes.

Mikhailenko et al.⁵ successfully cross-linked sulfonated poly(ether ether ketone) (SPEEK) with polyatomic alcohols via a condensation reaction between the sulfonic acid groups.

Helmer-Metzmann et al.⁶ cross-linked SPEEK by reacting the sulfonic acid groups with aromatic or aliphatic amines. Gu et al.⁷ covalently cross-linked sulfonated poly(phthalazinone ether sulfone ketone) with poly(vinyl alcohol) by heat treating the films at 120 °C. The hypothesis was that cross-linking involved sulfonic acid ester groups generated by condensation of $-\text{OH}$ and $-\text{SO}_3\text{H}$ from the two polymers. Kerres et al.⁸ have described covalent cross-linking of ionomeric membranes by alkylation of sulfinate groups with α,ω -dihalogenoalkanes. These cross-linked membranes exhibited good thermal stability but became brittle on drying. A review paper by Kerres et al.⁹ describes both covalently and ionically cross-linked ionomeric membranes and their advantages. Ionic cross-linking was demonstrated by Gasa et al.,¹⁰ who used barium cations to form water-resistant ionic clusters in sulfonated poly(ether ketone ketone). The membranes could be cross-linked to varying degrees by varying the sulfonation level and/or the extent of neutralization with Ba^{2+} .

Specific interactions, e.g., hydrogen bonding, have been used to improve miscibility in polymeric blends. However, Lee et al.¹¹ observed that binary blends of poly(ethylene oxide), PEO, and SPS were miscible only at the lower PEO concentrations (10 wt % PEO at 3 mol % sulfonation of SPS). The composition range at which the blends were miscible increased with increasing sulfonation of the SPS (20 wt % PEO at 8.8 mol % sulfonation of SPS). Addition of PEO to SPS also reduced

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the intensity of the SAXS peak due to ionic clusters, indicating that the PEO suppressed microphase separation of the ionic species in the ionomer due to interaction of highly polar ether linkages present in PEO with the ionic domains groups. Cross-linked polystyrenesulfonic acid (SXLPS) particles have been used to improve the compatibility of polystyrene and PEO.⁴ According to Hong et al.⁴ in the SPS + PEO + PS system, SXLPS particles physically cross-link with PEO and the polystyrene chains entangle in this cross-linked network formed thus inhibiting the phase separation. Yamanis et al.¹² reported that Amberlyst 15, a cation-exchange resin used as a catalyst for the reaction of ethylene oxide with ethanol, lost its catalytic activity in a short period. They showed that ethylene oxide reacts with sulfonic acid groups to form esters. This process in turn decreases catalytic activity simply due to the drop in the number of active protons.

Robertson et al. reported that there was strong interaction of amidic solvents like dimethylformamide (DMF) and dimethylacetamide (DMAc) with sulfonated polymers. The interaction adversely influences the PEM performance of membranes cast from those solvents. They showed that the amide group of DMF forms strong hydrogen bonds with the sulfonic acid groups of the polymer at about 60 °C. Researchers have shown in the past that conversion of sulfonic acid to sulfonamides was possible by dissolution of highly acidic polyelectrolytes in amidic solvents such as formamide.^{14,15}

In this work, we cross-linked electrospun fiber mats of fully sulfonated polystyrene using low- and high-molecular-weight glycols. Addition of high-molecular-weight PEO improved the electrospinnability of the polyelectrolyte, and subsequent heat treatment of the fiber mats improved the stability in water. In view of the latter observation, we have attempted to understand the chemistry of this apparent cross-linking reaction.

2. EXPERIMENTAL SECTION

2.1. Materials. Poly(ethylene oxide) (PEO) with $M_w = 100\,000$ g/mol was obtained from Polysciences Inc. and used as received. The sodium salt of sulfonated polystyrene with $M_w = 500\,000$ g/mol (Na-SPS-500) was obtained from Scientific Polymer Products. *N,N*-dimethylformamide (DMF) was obtained from Acros Organics and used as received.

2.2. SPS-PEO Blend Electrospinning. The Na-SPS was first converted to the acid form by passing a 5 wt % solution of the polymer in distilled water through an ion-exchange column of Dowex Marathon C. The ion exchange capacity of resulting polystyrenesulfonic acid (SPS) was 4.8 mequiv/g as determined by titration with 0.01 N NaOH.

The electrospinning solutions were prepared by dissolving SPS and PEO in varying ratios in DMF while stirring at room temperature and then heating at ~40 °C for 30 min. Blends of SPS-PEO were electrospun at room temperature using the setup shown schematically in Figure 1. The electrospinning system used a 1-mL Norm-Ject syringe with the tip of the syringe needle (20 Gauge, 12.7 mm length) connected to the positive terminal of a high-voltage DC source (Gamma High Voltage Research, Inc., ES 30R/DDPM). The flow rate at which the solution was dispensed from the syringe was controlled using a syringe pump (KD Scientific, model number 780212). The electrospun web was collected onto a grounded collector (Figure 1) and stored in a desiccator. The collector was a grounded drum; but, to generate sufficiently thick mats, the drum was not rotated.

The spinning distance between the needle and collector was 12 cm, the flow rate at which the polymer solution was dispensed from the syringe was 0.35 mL/h and the applied voltage was 23.5 kV. The solution used for spinning had a polymer concentration of 20 wt %. The relative humidity in the spinning chamber was decreased and held

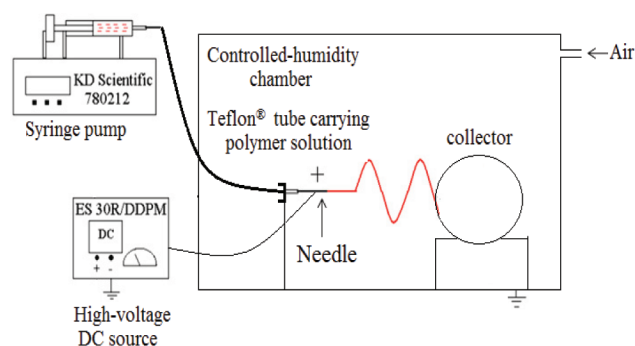


Figure 1. Schematic of the electrospinning setup.

at ~20% because highly sulfonated PS is extremely sensitive to humidity.

2.3. Curing of SPS-PEO Fiber Mats. The electrospun fiber mat was dried in a vacuum oven at 50 °C overnight to remove most of the solvent. For the heat treatment, the temperature in the vacuum oven was gradually raised over an 8-h period to the 130 °C, and the fiber mat was then heated under vacuum for ~12 h. To avoid shrinkage during drying and heat treatment, the fiber mat was fixed to an aluminum plate by clips on all four sides.

2.4. NMR Analysis of the Curing Process. To investigate the cross-linking reaction, ~0.1 g of electrospun mat was heated in the rotor of a solid state NMR, and changes of the spectrum with temperature were monitored. Solid-state magic angle spinning (MAS) ¹H NMR spectra were acquired using a 4-mm double-resonance MAS probe with a Bruker DMX 300 NMR spectrometer operating at 300 MHz. The samples were packed in a zirconia rotor with a polyimide (Vespel) cap and spun at 9 kHz at room temperature. Lorentzian line broadening of 10 Hz was applied to all the NMR data. ¹H MAS NMR spectra were acquired with a 90° pulse width of 4.0 μs, a delay time of 5 s and 100 kHz of spectral width. The ¹H chemical shifts were calibrated by using tetrakis(trimethylsilyl)silane (TTMS) as an external reference.

The electrospun fiber mats were dried overnight in the vacuum oven at room temperature and packed in the rotor. The temperature was increased from 25 to 130 °C in steps of 20 °C and held isothermally at each intermediate temperature for 15 min to equilibrate. At the final temperature of 130 °C, the sample was held for 2 h and then cooled back to room temperature in a similar manner as it was heated. The spectra shown represent an average of 64 scans.

2.5. Gas Chromatography–Mass Spectrometer (GC–MS). The electrospun fiber mats were analyzed by GC–MS (HP 6890 GC and HP 5972 MS) to measure the amount of residual solvent in the dried mats. The reason for this is that DMF may interfere with the curing process, details of which will be covered in the Results and Discussion section. The GC column used was a Restek Rxi-1 ms with a 30-m length, 0.25-mm inside diameter and 1-μm film thickness. The injection port was set to 150 °C. The GC column was held isothermally at 35 °C for 2 min and then ramped to 300 °C at a rate of 15 °C/min. Both the as-spun fiber mat and fiber mat heated in the vacuum oven overnight at ~50 °C were analyzed. A small section of the mat was then heated to 150 °C for 5 min and the volatiles were trapped using liquid nitrogen. Known concentrations (0.01, 0.05, 0.1, 0.5, 1 wt %) of DMF in acetone were run in a similar fashion to calibrate the solvent measurements.

2.6. Characterization of Electrospun Mats. **2.6.1. Microscopy.** Small sections of the electrospun fiber mat before and after curing were analyzed using a field-emission scanning electron microscope (JEOL JSM-6335F) to determine the fiber size and morphology. The samples were first sputter coated with gold for 1 min.

In a separate test, heat-treated fiber mats were exposed to distilled water and analyzed by FESEM to determine if the fiber structure was retained on exposure to water. For this test, a ~0.5-mg sample of the heat-treated fiber mat was immersed in 3 mL distilled water for 15 h.

The fiber mat was then dried in the vacuum oven and mounted onto a stub to be analyzed using FESEM. The diameters of the fibers were determined using Image J software.

2.6.2. Ion Exchange Capacity (IEC). The IEC of electrospun fiber mats was determined by titration. Approximately 0.5 mg of the dried fiber mat was treated with 5 mL of 20% NaCl solution for 1 day to exchange the H^+ with Na^+ . The HCl formed as a result of the ion exchange was titrated against 0.005 N NaOH using phenolphthalein as an indicator.

2.6.3. X-ray Diffraction. X-ray diffraction patterns of the as-spun and heat treated electrospun fiber mats were collected using an Oxford diffraction, XCalibur PX Ultra with an Onyx areal detector. The diffraction patterns were obtained using Cu $K\alpha$ X-ray radiation with 1.5418 Å wavelength. The samples were held at room temperature.

3. RESULTS AND DISCUSSION

3.1. Electrospinning of SPS-PEO Fiber Mats. Previously, we reported the successful electrospinning of highly sulfonated polystyrene (IEC ~ 4.5 mequiv/g) nanofibers from solution.¹⁶ Although the high sulfonation level is advantageous in achieving high ion exchange capacity, the as-spun fiber mats dissolved when exposed to water. That problem can be resolved by chemically cross-linking the nanofibers, which was achieved in the present work by adding a second polymer, PEO, to the spinning dope (Table 1). PEO has been added to the spinning

Table 1. Stoichiometry of Sulfonic Acid Groups from SPS to Ethylene Oxide Units of PEO in the Spinning Solution

SPS:PEO (w/w)	moles (SO_3H)/moles (CH_2CH_2O)
80:20	0.84
70:30	0.49
60:40	0.31

dope in the past to spin polyelectrolyte like Nafion that has a very low solution viscosity to sufficiently entangle and form continuous fibers.^{16,17} In our experiments too, the addition of PEO to the SPS–DMF solution improved the spinnability of the polyelectrolyte and reduced the polymer concentration needed to generate bead-free fiber mats. With increase in concentration of PEO the morphology changed from beads to bead-on-string and finally bead-free fiber mats.

Subjecting the electrospun SPS-PEO fiber mats to heat treatment, as described in the Experimental Section, improved the dimensional stability of the fiber mats when immersed in water. Whereas, neat SPS fiber mats exhibited no shrinkage upon heating, the SPS-PEO fiber mats shrunk when heated due to the melting of the PEO at $\sim 60^\circ C$. However, the heating also produced cross-linking of the mat, which was evident from the retention of the fiber structure upon exposure to water following the heat treatment. Figure 2 shows how the addition of PEO and heating and soaking in water affected the morphology of the fiber mats. While most of the fiber structure in the neat SPS mat disappeared when exposed to water, the fibrous structure in the SPS-PEO mats is still evident in the films after immersion in water. The heat-treated neat SPS fiber mats swelled considerably in water at room temperature to form a hydrogel. As a result of the swelling, a homogeneous film formed and the fibrous structure was destroyed; see Figure 2(e).

Heating the SPS-PEO fiber mats to the curing temperature ($130^\circ C$) melted the PEO component of the fibers. For samples with ≤ 30 wt % PEO, the integrity of the fibers was retained through the curing process. However, for the 60–40 w/w

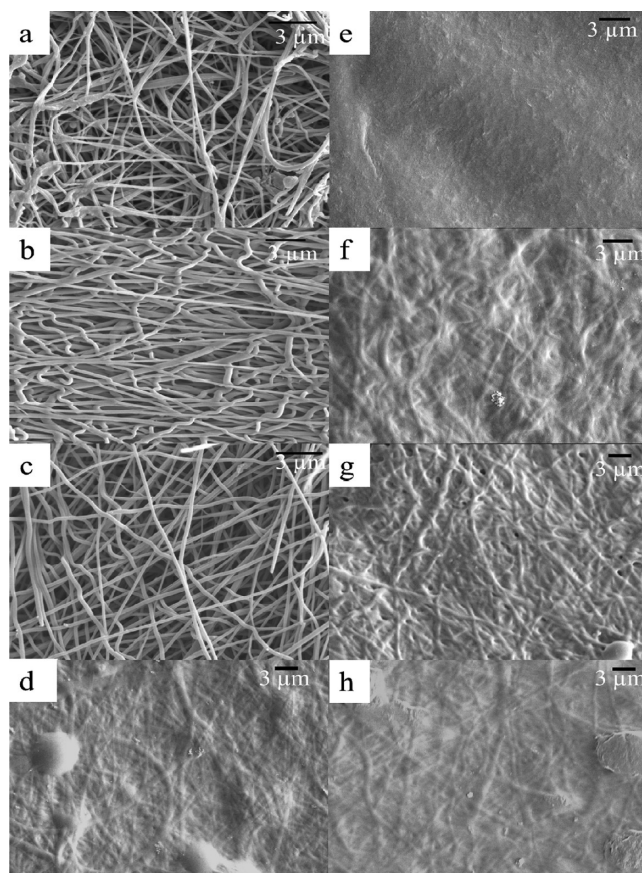


Figure 2. Electrospun fiber mats (a) SPS (b) SPS-PEO 80–20 w/w (c) SPS-PEO 70–30 w/w (d) SPS-PEO 60–40 w/w, all the samples (a–d) were heat treated at $130^\circ C$. Images on the right (e–h) correspond to fibers mats (a–d), respectively, after soaking in water and drying.

SPS-PEO mats, the fibers fused upon heating and formed a nearly void-free film, although a fibrous component of the film was still evident; see Figure 2d. Note also that some of the fibers coalesced into large ($>3 \mu m$) globules, a morphology that was not observed in the other samples. Although the phase structure of the fibers was not evaluated in this study, the results for the 60–40 w/w SPS-PEO sample suggest that a phase inversion may have occurred at this composition, where the PEO became either a cocontinuous or continuous phase in the fibers. This would account for the morphology change of the fibers upon melting the PEO component.

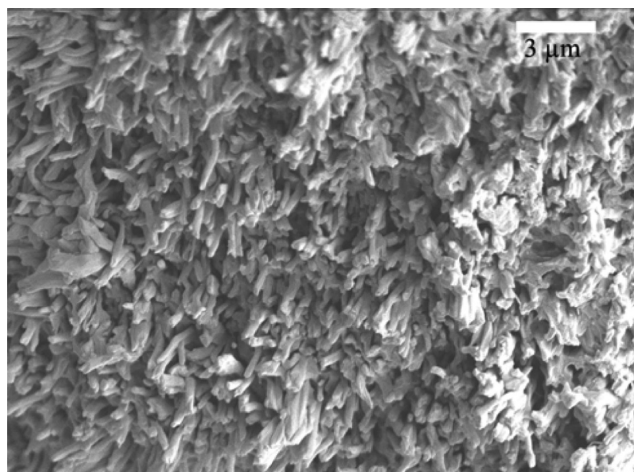
In the case of fiber mats containing less than 30% or less PEO, the heating step did not substantially change the fiber structure of the mat, as shown in Figure 2b,c. Exposure of these heat-treated fiber mats to water, however, did fuse the fibers into a film, though part of the individual fibers can still be observed in Figure 2f–h. The diameter statistics for the fibers are reported in Table 2. These are based on 50 measurements made on random sections of the fiber mat.

Unlike the unexposed fiber mats, the fiber boundaries in the case of heat-treated fiber mats exposed to water were not very distinct. Hence the fiber diameters were not compared because picking fibers with sharper boundaries for the measurements would undoubtedly bias the result. In the presence of PEO, the fiber structure was retained in the heat-treated fiber mats, even after long exposure to water, as shown in Figure 3.

Table 2. Fiber Diameters of As-Spun and Heat-Treated Fiber Mats

sample SPS-PEO (w/w)	IEC of SPS-PEO fibers ^a , meq/g	average diameter of as-spun fibers, nm	average diameter of heat treated fibers, nm	evidence of fiber structure retained after exposure to water
100–0	4.1 ± 0.5 ^b	150 ± 28 ^c	175 ± 60	no
80–20	2.2 ± 0.3	271 ± 48	322 ± 86	yes
70–30	2.6 ± 0.07	245 ± 40	228 ± 42	yes
60–40	2.4 ± 0.2	306 ± 68	550 ± 159	yes

^aOn the basis of mass of the blend. ^bStandard deviation of the mean based on three determinations. ^cStandard deviation of the mean based on 50 measurements.

**Figure 3.** FESEM image of a break surface of heat-treated SPS-PEO (70/30 w/w) fiber mat after soaking in water and drying.

3.2. NMR Analysis of the Fiber Mats. 3.2.1. ¹H NMR

Analysis of As-Spun and Heat-Treated SPS-PEO Fiber Mat. Solution ¹H NMR spectra were obtained for the as-spun and heat-treated SPS-PEO fiber mats in D₂O, in which the as-spun fiber mat readily dissolved. Not surprisingly, the liquid-state ¹H NMR showed the standard resonances for polystyrenesulfonic acid [broad band at 0.8–2 ppm from aliphatic chain protons (3 H's), 6.5 and 7.5 ppm from the aromatic protons (4 H's) from positions 3,4 as shown in the schematic in Figure 4a],¹⁸ water (4.7 ppm) and PEO (3.6 ppm from the methylene groups, 4 H's).¹⁹ Relative area of aromatic proton (labeled as 3 in Figure 4a) to the aliphatic broad band at 0.8–2 ppm of SPS was 0.69. This value is similar to that reported by Baigl et al., who observed a ratio of 2/3 at all sulfonation levels investigated by these authors.¹⁸ Composition of the two polymers was calculated by comparing areas of the aromatic protons closest to the sulfonic acid groups at 7.39 ppm (2 H's) to protons from the methylene groups of PEO (4 H's). The molar ratio of as-spun SPS/PEO fibers by NMR was calculated to be 0.29 and was close to the molar ratio of SPS/PEO in the spinning dope (0.34); the variability may be due to error during weighing the polymer, since SPS is very sensitive to humidity.

Residual DMF shows up in the ¹H NMR spectrum at 2.8 and 2.9 ppm¹³ and a singlet at 2.54 ppm. For the hydrogen bonded DMF, the aldehyde proton appears at ~8 ppm.¹³ Robertson et al.¹³ have reported similar resonances for sulfonated poly(ether ether ketone) films cast from DMF and DMAc. The different chemical environments around two CH₃ groups in DMF results in two different peaks at 2.8 and 2.9 ppm for the free DMF.

According to Robertson et al.¹³ when the sulfonic acid groups from the polymer hydrogen bonds with the electron pair of the nitrogen, free rotation about the C–N bond becomes possible. Hence, the methyl groups average out to give a single resonance at 2.54 ppm.¹³

In the case of the heat-treated fibers (SPS:PEO 80:20, 70:30, 60:40 w/w), the mats swelled to form hydrogels instead of dissolving. The gel fraction and sol fraction after exposing the heat-treated fiber mat in D₂O for 48 h were separated and analyzed by solid-state and liquid-state ¹H NMR respectively. The insoluble (gel) fraction showed sulfonation peaks (Figure 4b), while the solution containing the extracted polymer did not (Figure 4c). This result indicates that the water-soluble fraction was PEO and that was substantially free of DMF. The swollen, insoluble fraction was analyzed by solid state ¹H NMR (Figure 4b). The insoluble fraction showed all the resonances for SPS, including a resonance at 3.6 ppm corresponding to the methylene protons and sharp peaks at ~2.6 ppm from the residual DMF in the system.²⁰ The suppression of solubility of SPS component in the heat-treated fibers indicates that cross-linking had occurred.

3.2.2. Interaction of Sulfonic Acid Groups with DMF.

Although the heat-treated SPS fibers did not retain their fibrous structure on exposure to water, the fiber mats swelled to form gels. A hypothesis to explain this behavior is that the fibers reacted with residual DMF to form weak cross-links. To further confirm the interaction of SPS with DMF, the polymer was reacted with excess DMF, similar to the procedure reported by Robertson et al.¹³ for SPEEK. The reaction was attempted on Dowex Marathon C (cross-linked sulfonated polystyrene resin). Since the resin beads were cross-linked, it was easy to separate them from the liquid after the reaction. The resin was first washed to remove free acids. After drying, the resin was exposed to excess DMF (20 wt % of resin in DMF) at two different temperatures, for 6 h at room temperature and at 60 °C. The resin was then washed repeatedly to remove unreacted DMF. The IEC of the resin was determined by titration against 0.01 N NaOH. The IEC of the resin (treated with DMF at 60 °C) dropped from 4.6 mequiv/g (untreated resin and resin treated with DMF at room temperature) to 0.4 mequiv/g, which suggests that the sulfonic acid groups from SPS were reacting with DMF at higher temperatures. To confirm that the drop in IEC was not due to desulfonation, the resin was analyzed by TGA. Desulfonation did not occur until 200 °C, much higher than our reaction temperatures. Dragan et al.²⁴ have reported amidation of poly(2-acrylamido-2-methylpropanesulfonic acid) using DMF. The sharp drop in IEC could be due to reaction of SPS and DMF to form sulfonamides, as shown in Figure 5.

By way of discussion of the DMF interaction or reaction with –SO₃H, Dragan et al.²⁴ have reported amidation of sulfonic acid groups of poly(2-acrylamido-2-methylpropanesulfonic acid) to sulfonamides on reacting the polymer with DMF and DMAc. They also reported that higher temperatures were avoided because partial gelation of the products occurred at 70 °C with longer reaction times. Above 100 °C slight cross-linking was observed, although the cross-linking mechanism was not reported. Thus, the poorly soluble electrospun mats of SPS may be due to the mild cross-linking as reported by Dragan et al.²⁴ Although a reaction mechanism to form chemical cross-links is hard to imagine, it is possible that the sulfonamides, if sufficiently plentiful, could microphase separate and physically cross-link the polymer.

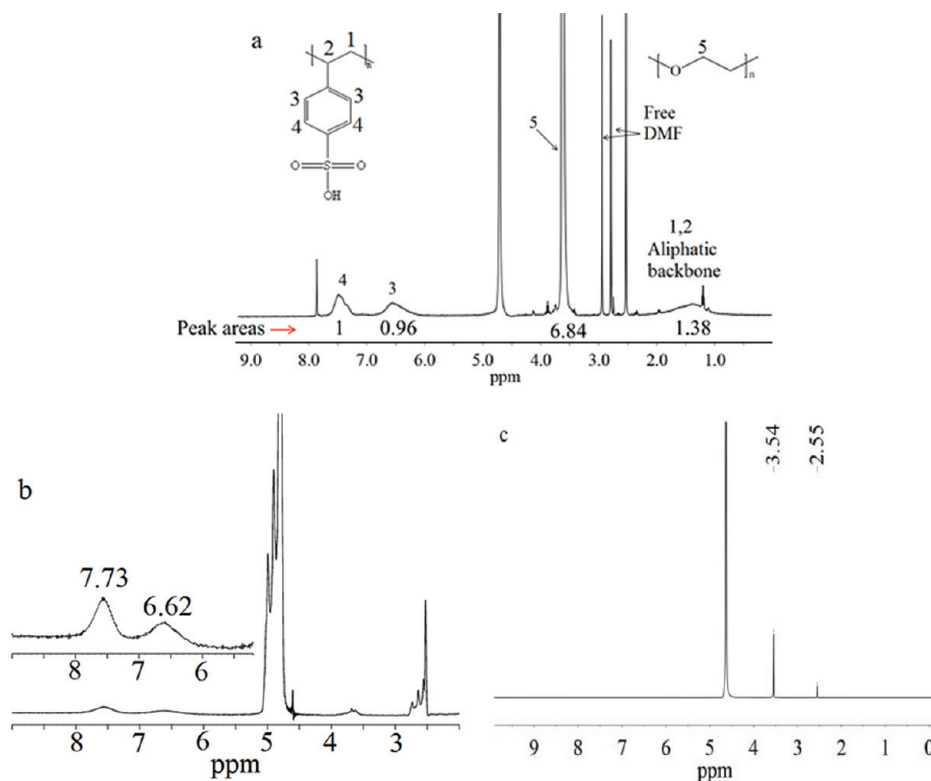


Figure 4. ^1H NMR spectra of SPS-PEO (70–30 w/w) in D_2O : (a) dissolved as-spun fibers; (b) insoluble fraction of heat-treated fibers; (c) water-soluble fraction of heat-treated fibers.

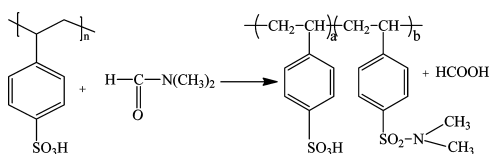


Figure 5. Reaction mechanism for formation of sulfonamides.

From these experiments, it is clear that DMF indeed can interact with the sulfonic acid groups of the polymer, although, it must be noted that this experiment was done in excess DMF; hence, the influence would be much more pronounced than for the real system. Thus, as an additional check, the fiber mats were analyzed by GC–MS to determine the residual solvent present in the fiber mats before cross-linking. As shown in Table 3, the DMF content of the fiber mats was low (molar

Table 3. GC–MS Analysis of Electrospun Fiber Mats for DMF

sample	DMF content (wt %)
as-spun neat SPS	4.5 ± 5.2^a
neat SPS heated at 50°C overnight	1.5 ± 0.8
as-spun SPS-PEO (70–30 w/w)	1.6 ± 1.7
SPS-PEO 70–30 heated at 50°C overnight	0.02 ± 0.02

^aEstimated standard deviation based on three observations.

ratio of $\text{DMF}/\text{SO}_3\text{H} = \sim 0.15$). The residual DMF present in the fiber mats heated overnight at 50°C in the vacuum oven was even lower than in the as-spun fiber mats, an expected result since the sulfonic acid groups from SPS will have a

tendency to hydrogen bond to DMF and retain the solvent in the fiber mat. Hence, before cross-linking, all the electrospun fiber mats were left overnight in the vacuum oven at 50°C to remove the majority of the residual DMF, thus avoiding or substantially reducing DMF-related reactions during the final heat treatment.

3.2.3. Heat-Treatment of Electrospun Fiber Mats in Solid-State ^1H NMR Rotor. To understand the chemistry of the cross-linking reaction between the two polymers, the as-spun fiber mats were subjected to the heating cycle in the solid-state NMR rotor to monitor the progressive changes in spectrum. Čanovas et al.²⁰ showed that solid-state NMR spectrum of anhydrous polystyrenesulfonic acid features a resonance at ~ 10 ppm corresponding to the acid OH from sulfonic acid groups. Solid-state NMR spectra of dry sulfonated polymers like SPEEK and Nafion have been reported in the past.^{21,22} Ye et al.²¹ observed that the proton mobility depends both on the temperature and water content; a broad peak at ~ 9.7 ppm corresponds to protons from sulfonic acid in dry acidified Nafion. Heating Nafion to temperatures as high as 170°C shifts the peak to ~ 13 ppm.²²

The neat SPS fiber mats from this study showed a peak at 10.7 ppm corresponding to sulfonic acid groups, Figure 6. The two broad peaks at ~ 8.3 and 2.9 ppm^{13,23} in the NMR spectrum can be assigned to residual solvent (DMF) present in the fiber mats. On heating the fiber mat in the rotor, the sulfonic acid peak shifted upfield to 9.2 ppm. This shift could possibly be due to the interaction of sulfonic acid from the polymer with amide groups of the residual DMF present in the fiber mats²⁴ and/or due to increased mobility of the protons in sulfonic acid groups at higher temperatures. As the temperature increases, segmental mobility also increases, leading to faster

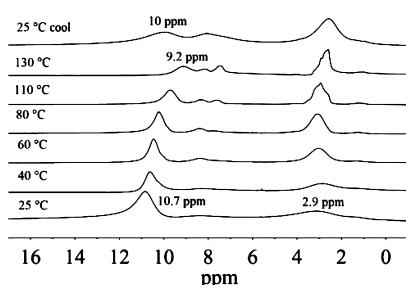


Figure 6. Temperature-resolved solid-state NMR of SPS fibers heated in the rotor.

exchange of protons from sulfonic acid groups. As a result, variations in chemical shifts of these protons are observed.

On cooling after a 2-h hold at 130 °C, the sulfonic acid peak shifted back downfield to ~10 ppm, as shown in Figure 6. In short, changes observed in the NMR spectrum on heating were reversed on cooling, suggesting there were no permanent changes in the chemical environment. The resonances from aromatic and aliphatic protons were clearly resolved for higher number of scans (512), but the number of scans for the temperature-resolved experiments was set lower to control the total time of exposure of the polymer to high temperatures. Also, since the resonances from residual DMF are broad in the solid state NMR spectrum, the peaks overlap and the signals for other protons resonating in the affected region do not resolve distinctly.

The neat PEO fiber mats showed a broad peak at 3.6 ppm corresponding to the methylene groups (Figure 7). At the

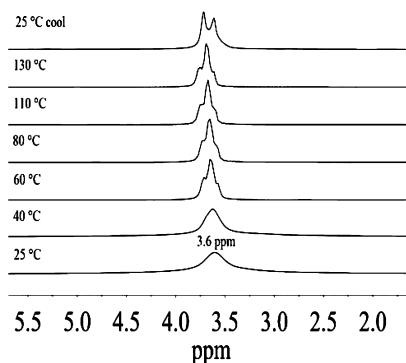


Figure 7. Temperature-resolved solid-state NMR of PEO fibers heated in the rotor.

melting temperature of the polymer, the resonance splits. Above the melting temperature of the polymer, there will be conformational changes which can cause the resonance to split.^{25,26}

On heating SPS-PEO fiber mats, the sulfonic acid peak shifted upfield from 9 to 8.4 ppm. This shift was most pronounced above 60 °C, corresponding to the melting temperature of PEO. Additionally the peaks at ~3.5 ppm due to the CH₂ groups of PEO split above 60 °C, as observed for neat PEO, due to the polymer chains gaining mobility on melting. In contrast to neat fiber mats, the sulfonic acid peak from SPS-PEO fibers did not shift back downfield on cooling, and splitting of methylene peaks from PEO was not reversible. Both of these observations are consistent with permanent changes in the chemical environment (Figure 8), i.e., a reaction

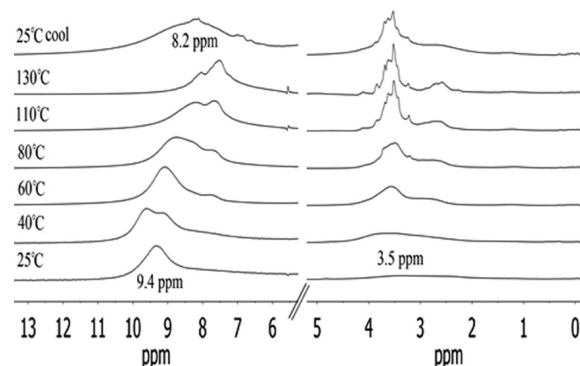


Figure 8. Temperature-resolved solid-state ¹H NMR of SPS-PEO 70–30 w/w fibers curing in the rotor.

between PEO and SPS. Splitting of resonances has been reported for the PEO–*p*-nitrophenol complex.²⁷ According to Spevacek et al.²⁷ the most probable explanation for the splitting is a conformational change in PEO in a complex. The hypothesis is that the two polymers react at higher temperatures to form sulfonic acid esters, as described in Figure 10.

Another possible route for cross-linking could be due to the free radicals generated at higher temperatures due to the oxidation of PEO. To test this hypothesis, a number of classical experiments were conducted that are known to influence the rate of free-radical reactions. In one, the SPS-PEO fiber mats were heated in a DSC pan to 130 °C in an inert atmosphere of N₂. The experiment was repeated with an O₂ atmosphere. In both the cases the fibers cross-linked, as confirmed by checking the solubility of heat treated fibers in water. Solutions of SPS-PEO in water with varying concentrations of ascorbic acid (a free-radical inhibitor) were cast into films and these films were dried in the vacuum oven followed by heat treatment. Even in the presence of a radical inhibitor, the films cross-linked. In a third trial, cross-linking was attempted using Na-SPS and PEO films. If oxidative cross-linking were active, some cross-linking would be expected; however, the heat-treated films did not exhibit cross-linking. These trials favor the hypothesis of ionic reactions to form sulfonic acid esters, wherein the acid form of the polymer is essential for the cross-linking reaction to take place.

3.3. WAXS of As-Spun and Heat Treated Fiber Mats.

WAXD patterns of the as-spun and heat-treated electrospun fiber mats are shown in Figure 9. In the as-spun and heat-treated mats, a broad peak appears at ~17–18° which corresponds to the amorphous polymer (SPS). When the weight fraction of PEO in the fiber mats was ≥30 wt %, the as-spun fiber mats showed two sharp crystalline peaks at 19 and 23° corresponding to PEO, in addition to the broad amorphous peak from SPS. This is in-line with what has been reported in the literature for electrospun PEO fibers.²⁸ Unlike the as-spun fiber mats, heat-treated SPS-PEO fiber mats did not show any signs of crystallinity over the investigated concentration range (Figure 9a–d). Although the heat-treated, neat PEO electrospun fiber mat (control) lost its fiber morphology completely on heating, the crystalline peaks in the WAXD pattern were not lost.

3.4. Gas Chromatography–Mass Spectrometer (GC–MS). In addition to the DMF peak discussed earlier, SPS-PEO mats showed a distinct peak for dioxane, which was practically absent for both neat SPS and PEO. Dioxane is undoubtedly a PEO degradation product (Table 4).²⁹

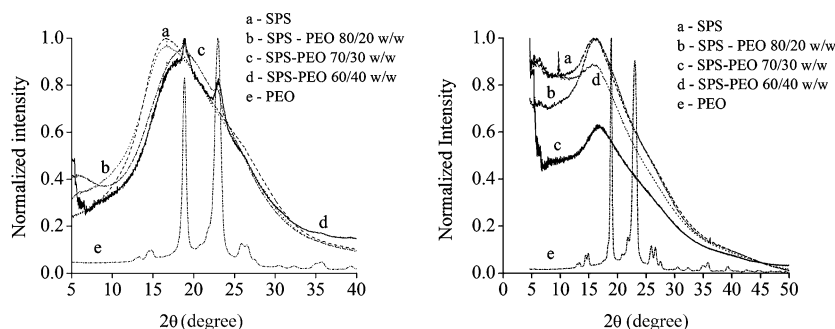


Figure 9. WAXD of as-spun (L) and heat-treated at 130 °C (R) fiber mats.

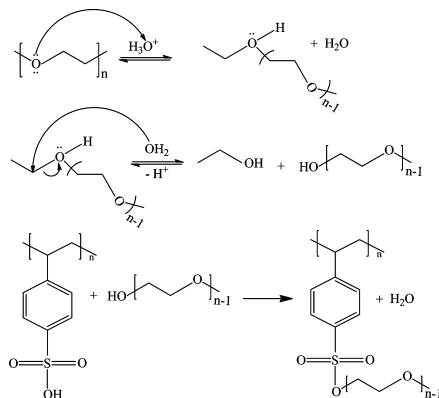


Figure 10. Hypothesized reaction mechanism for formation of sulfonic acid esters.

Table 4. GC–MS Analysis of Electrospun Fiber Mats for Dioxane Content^a

sample	dioxane content (%)
neat SPS	0
SPS-PEO (80–20 w/w)	0.009
SPS-PEO (70–30 w/w)	0.047
SPS-PEO (60–40 w/w)	1.37
neat PEO	0

^aFiber mats were heated overnight at 50 °C in a vacuum oven before analysis.

Choi et al.²⁹ have reported that PEO can undergo degradation in an acidic environment to form dioxane; a volatile compound. In fact, dioxane has been synthesized by acid-catalyzed dehydration of poly(ethylene glycol) in the presence of cation exchange resin as catalyst.³⁰ Yamanis et al.¹² observed that in the reaction of ethylene oxide with ethanol catalyzed by cation exchange resin, the high activity of the cation-exchange resin disappeared quickly due to formation of sulfonic acid esters. Their paper explains in detail the various reactions occurring at high temperatures, and one of the byproducts formed was dioxane. They reported that dioxane is formed by a backbiting mechanism after esters of sulfonic acid are formed, which is in-line with what we observed for SPS-PEO fiber mats. In the presence of a strong acid, the ether linkages can be cleaved.³¹ The oxygen in the ether can be protonated to form corresponding glycols. These glycols in turn can react with the sulfonic acid of the SPS to form sulfonic acid esters.

On the basis of all the observations, the most probable hypothesis for the cross-linking reaction mechanism in our system is depicted in Figure 10.

4. CONCLUSIONS

At high sulfonation levels (IEC ~ 4.8 mequiv/g), sulfonated PS fibers can be electrospun, but the fibers are very moisture sensitive and tend to lose their structure when exposed to water or even humid air. To overcome this problem, a method was sought to chemically cross-link the polymer to improve stability of the electrospun mats in water. It was found that addition of PEO to the spinning dope not only helped to improve spinnability of the polyelectrolyte; but, also, with subsequent heat-treatment, the PEO improved the stability of fiber mats in water. As-spun SPS-PEO mats readily dissolved in water and ¹H NMR spectrum of the as-spun SPS-PEO fiber mats in D₂O showed sulfonic acid peaks. With increase in PEO concentration in the fiber mats, the heat-treated fiber mats swelled less on exposure to water, suggesting that the fibers were cross-linking in the presence of PEO. ¹H NMR spectra of the sol and gel portion of the cross-linked fiber mats showed sulfonic acid peaks in the gel portion but not in solution containing the extracted polymer (sol). The ¹H NMR spectra of the sol fraction confirmed that the extracted material was PEO. These results strongly suggest that the PEO is cross-linking the SPS. To further understand this cross-linking reaction, the electrospun fiber mats were heated in a solid state NMR rotor to track changes in the spectrum as the reaction progressed. The hypothesis resulting from the observations is that the PEO is hydrolyzed at higher temperatures to form PEO oligomers with hydroxyl end groups. In turn, these react with the sulfonic acid groups to form esters. Multiple reactions lead to cross-linking, which reduces the solubility of the fiber mats in water.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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