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'Click'-functionalization of poly(sulfone)s and a study of their utilities as proton conductive membranes in direct methanol fuel cells

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ABSTRACT

Using the copper-catalyzed 1,3-dipolar "click" cycloaddition reaction, poly(sulfone)s containing pendant azide moieties were functionalized with various quantities of sodium 3-(prop-2-ynyloxy)propane-1-sulfonate and crosslinked with 1,7-octadiyne. The degrees of sulfonation and crosslinking were systematically varied by changing the ratios of the aforementioned reagents. The polymers were cast into membranes, acidified, and then tested for proton conductivity, methanol permeability, and membrane-electrode assembly (MEA) performance. The membranes showed a reduction in methanol permeability with increasing concentration of crosslinker and exhibited performance on par with direct methanol fuel cells containing Nafion-based membranes.

1. Introduction

Direct methanol fuel cells (DMFC) provide a convenient source of power because they do not require recharging with an electrical outlet and, unlike hydrogen fuel cells, they use a relatively less volatile liquid fuel that is easy to store and transport [1,2]. Unfortunately, current DMFC technology is hampered by the sluggish methanol oxidation kinetics and the crossover of methanol fuel from the anode to the cathode through the membrane, which leads to fuel loss, cathode catalyst poisoning, and cell voltage drop [3].

The most common electrolyte used in fuel cells, including DMFCs, is a sulfonated fluoropolymer called Nafion. This polymer is known to exhibit high proton conductivities (100–150 mS/cm; typical operating conditions: 65 °C, 100% relative humidity), but is expensive and suffers from high methanol permeability (1.2×10^{-6} cm^2/s) [4]. Sulfonation of commercially-available polyaromatic materials, such as poly(sulfones) [5–7] and poly(ether ether ketones) [8–11], has been demonstrated to afford proton conductive membranes that exhibit reduced methanol permeability relative to Nafion ($1–9 \times 10^{-7}$ cm^2/s). One drawback, however, is that these sulfonated membranes are hindered by relatively low proton conductivities (11–17 mS/cm), particularly under low humidity conditions [10] where there is insufficient water present to act as a proton carrier.

To enhance conductivity, various N-heterocycles, such as imidazole or triazole, may be added to the aforementioned membranes [12]. The N-heterocycles are believed to function as proton carriers and have been shown to improve the conductivities of membranes which contain them under a range of humidities [13]. However, the added N-heterocycles often leach from the polymer membrane when they are operated at temperatures less than 100 °C, where liquid water is present, and some of them also poison the cathode catalyst [14]. To alleviate this issue, various nitrogen-containing bases have been covalently linked to polymer chains within the membrane [15]; however, such approaches often entail complicated syntheses and/or require multiple post-polymerization modifications.

Another strategy to reduce methanol permeability while maintaining high proton conductivities has been to crosslink the polymer chains in the membrane [16]. It is believed that the crosslinks formed limit membrane swelling and decrease the size of the proton conducting channels in the hydrated state. Smaller channels slow the diffusion of methanol and ultimately lower methanol crossover. However, the post-polymerization crosslinking reaction is practically challenging because it must be performed during or after membrane casting. One successful strategy for increasing the proton conductivity while decreasing the methanol permeability is through the synthesis of membranes comprised of block copolymers [17]. In particular, block copolymers with hydrophilic and hydrophobic segments that are capable of phase separation often generate organized highly proton conductive hydrophilic regions [17j].

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Herein we describe a method that overcomes many of the aforementioned challenges and enables simultaneous installation of tethered N-heterocycles (to enhance proton transfer) and covalent crosslinking (to reduce swelling and methanol crossover) [18,19]. The procedure utilizes the copper-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuCAAC) reaction between poly(sulfone)s containing pendant azides with alkyne additives. This "click" reaction [20,21] was selected because it not only proceeds to high conversions, but also is highly selective, tolerant to many functional groups and generates Brønsted basic 1,2,3-triazoles (pK_B: 0–1) [22], which were envisioned to serve as the N-heterocycles [13,23] in the proton shuttling processes described above.

2. Experimental

2.1. General considerations

N,N-Dimethylacetamide (DMAc) was purchased from Fisher Scientific, 1,3-propanesultone was purchased from MP Biomedicals LLC, and propargyl alcohol and 1,7-octadiyne were purchased from Acros Organics. Udel® P-1700 was purchased from Solvay Advanced Polymers. Nafion® 117 was purchased from DuPont. All reagents were used as received. Membranes were cast from solution in a 10 cm diameter custom-made flat-bottom sealed vessel under an atmosphere of nitrogen. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum BX FTIR spectrophotometer. High resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E instrument (CI). NMR spectra were recorded on Varian UNITY+ 300, Varian Mercury 400, and Varian INOVA 500 spectrometers. Chemical shifts (δ) are given in ppm and are referenced downfield from residual solvent (^{1}H: DMSO-d_6, 2.49 ppm; ^{13}C: DMSO-d_6, 39.5 ppm). Molecular weights were determined by gel permeation chromatography (GPC) using a Waters HPLC system consisting of three Viscotek I-series columns (2 × GMHHRH and 1 × G3000HHR) arranged in series, a 1515 pump, and a 2414 RI detector and are reported relative to polystyrene standards in DMF (0.1 M LiBr) at 40 °C (column temperature). Melting points were obtained using a Mel-Temp apparatus and are uncorrected. Thermogravimetric analyses were performed on a Mettler Toledo TGA/SDTA851e and differential scanning calorimetry analyses were performed on a Mettler Toledo DSC 823e. The IEC (ion exchange capacity) was measured by drying the polymer in a vacuum oven at 70 °C and then stirring in a 2 M NaCl solution for 1 h. The resulting polymers were then titrated with an 8 mM solution of NaOH using phenolphthalein as an endpoint indicator [24]. Proton conductivity values of the membranes were obtained from the impedance data, which were collected with a computer interfaced Solartron SI 1260 Impedance Gain Phase Analyzer coupled to a SI 1287 Electrochemical Interface. Samples were measured in the frequency range of 5 Hz–13 MHz with an applied voltage of 10 mV. The impedance measurement was carried out using a home-made two-electrode setup and stainless steel foil was used as the electrodes. The impedance was measured in the plane of the membrane sample and the cell size used was of the following dimensions: 1 cm (width) × 1 cm (length) × 50–200 μm (thickness). The selectivities were calculated by determining the quotient of a membrane's conductivity over permeability, as described previously [25]. The relative selectivities were calculated by determining the quotient of the selectivities of the new membranes described below over that measured for Nafion 117. Liquid uptake and swelling were measured by drying the membranes in a vacuum oven for 12 h before measuring their dry weight and thickness. After soaking the membranes in water or 1 M methanol for various amounts of time, they were removed from the aforementioned solutions and their surfaces were gently wiped with a paper towel to remove the residual liquid present on the surface. The membranes were then weighed and measured. This process was repeated until the weight of the membrane reached a constant value. The percent uptake was calculated using the following equation: % uptake = 100 × (wet weight − dry weight)/dry weight. The percent swelling was calculated using the following equation: % swelling = 100 × (wet length − dry length)/wet length.

2.2. Methanol permeability measurements

Methanol permeability measurements were conducted in a glass cell consisting of two chambers, each with a total volume of 100 mL [26]. Magnetic stir bars were added to each chamber. The membrane was sandwiched between two rubber circular gaskets (internal diameter of 3 cm) and then tightly clamped together. One side of the cell was filled with 80 mL of 1 M methanol (aq.) and ethanol ($[\text{ethanol}]_0 = 0.01$ M) as an internal standard. The other side (analyte) was filled with 80 mL of 0.01 M ethanol (aq.) The chambers were then sealed with septa and each side was stirred with a magnetic stir bar. The concentration of methanol in the analyte side was measured by gas chromatography and integrated against the ethanol internal standard over time. The methanol permeability was calculated according to equation (1), where C_a and C_b refer to the methanol concentration in the feed and the permeate, respectively, V_b refers to the solution volume of permeate, and L, A, and t refer, respectively, to the membrane thickness, membrane area, and time [27].

$$P = \frac{C_b V_b L}{A C_a t} \tag{1}$$

2.3. Syntheses

2.3.1. Sodium 3-(prop-2-ynyloxy)propane-1-sulfonate (**1**)

A 200 mL round bottom flask was charged with a magnetic stir bar, sodium hydride (95%; 1.03 g, 40.9 mmol) and *N,N*-dimethylformamide (DMF) (30 mL). The flask was cooled in an ice bath and a solution of propargyl alcohol (2.39 mL, 40.9 mmol) in DMF (30 mL) was slowly added under continuous stirring over 10 min. A solution of 1,3-propanesultone (5.00 g, 40.9 mmol) in DMF (30 mL) was then added slowly. The resulting mixture was stirred on ice for 10 min, warmed to 60 °C and then stirred for an additional 2 h. The reaction was then concentrated under reduced pressure (with the aid of a rotary evaporator) at 60 °C and diethyl ether (500 mL) was added which caused the product to precipitate. The desired product (7.9 g, 97% yield) was collected via filtration as a white powder. Note: in the solid state, **1** was found to develop a reddish color and became insoluble over time. However, the material was found to be stable under ambient conditions when dissolved in *N,N*-dimethylacetamide (DMAc) ($[\mathbf{1}]_0 = 0.503$ M). m.p. 120–150 °C (the material turned from white to dark red). ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.05 (d, $J = 2.4$ Hz, 2H), 3.4 (t, 2H, overlaps with H_2O), 3.35 (t, $J = 2.4$ Hz, 1H), 2.47 (2H, m, overlaps with DMSO), 1.78 (2H, m). ^{13}C NMR (100 MHz, D_2O; referenced to an internal methanol standard, 49.5 ppm): δ 80.1, 76.5, 69.0, 58.2, 48.5, 24.8. HRMS [M^-] calcd. for $C_6H_9O_4S$, 177.02215; found 177.02282. IR (KBr): ν = 3478 (broad), 3290, 2945, 2870, 2112, 1638, 1199, 1066, 630 cm^{-1}.

2.3.2. Polysulfone containing pendant azides (**2**)

The azide-functionalized poly(sulfone) **2** was synthesized using a modified literature procedure [28]. A 1 L flask was charged with poly(sulfone) (Udel® P-1700) (6.0 g, 13.5 mmol based on its repeat unit, $M_w = 45.6$ kDa, PDI = 2.01), a Teflon coated magnetic stir bar and THF (400 mL) under nitrogen. After cooling the reaction mixture to −78 °C, *n*-butyl lithium (2.5 M; 2 equiv, 10.8 mL, 27.0 mmol) was added dropwise over a period of 2 h. In a separate

flask, a solution of *p*-toluensulfonyl azide (7.99 g, 40.5 mmol) in THF (20 mL) was cooled to −40 °C and then added to the aforementioned polymer solution which caused solids to precipitate. The reaction mixture was then slowly warmed to −30 °C at which point it became homogeneous. A 4:3 v/v mixture of water : ethanol (800 mL) was then added. The precipitated solids were collected by filtration to afford the desired polymer (6.7 g, 95% yield) as a white powder. Spectroscopic data were consistent with literature values [28]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8.9 Hz, 4H), 6.98 (d, J = 8.5 Hz, 4H), 6.76 (dd, J = 8.9, 2.3 Hz, 2H), 6.71 (d, J = 2.3 Hz, 2H), 1.71 (s, 6H). GPC (DMF with 0.1 M LiBr, 40 °C): M_w = 56.9 kDa, PDI = 2.14. IR (KBr): υ_{N3} = 2119 cm^{-1}.

*2.3.3. Synthesis of sulfonated polymer **3** (not crosslinked)*

A 25 mL flask was charged with polymer **2** (500 mg, 0.954 mmol based on the molecular weight of its repeat unit), DMAc (5 mL), and a magnetic stir bar. The solution was stirred until the polymer was completely dissolved. After adding a DMAc solution of **1** ([**1**]$_0$ = 0.756 M; 2.52 mL, 1.908 mmol), the reaction vessel was sealed with a septum. After degassing the vessel under reduced pressure, CuI (38.3 mg, 200 μmol) was added. The resulting mixture was stirred for 30 min at ambient temperature and then heated at 60 °C in an oil bath for 12 h. The residual solvent was removed on a rotary evaporator at 60 °C. The resulting polymer was then acidified by heating at 80 °C for 2 h in the presence of H_2SO_4 (2 M, 100 mL). Finally, the polymer was heated in 100 mL of de-ionized water at 80 °C for 2 h and then dried in a vacuum oven at 70 °C for 12 h to yield 716 mg (86% yield) of **3**. T_g = 67 °C. T_d (onset) = 170 °C. On account of stoichiometry of the starting materials employed, the membranes contained residual azides, as determined by IR spectroscopy (υ_{N3} = 2120 cm^{-1}; KBr). Both the crude polymer **3Na**$^+$ (sodium sulfonate salt) as well as its acidified derivative **3** were analyzed by GPC. GPC of **3Na**$^+$ (DMF with 0.1 M LiBr, 40 °C): M_w = 59.1 kDa; PDI = 2.99. GPC of **3** (DMF with 0.1 M LiBr, 40 °C): M_w = 27.5 kDa; PDI = 1.43. ^{1}H NMR of **3** (300 MHz, DMSO-d_6): 8.12 (s, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.4 Hz, 4H), 7.1–7.2 (m, 8H), 4.48 (s, 4H), 3.52 (t, J = 6.0 Hz), 1.83 (s, 4H), 1.69 (s, 6H). ^{13}C NMR of **3** (100 MHz, DMSO-d_6) 161.8, 152.0, 147.2, 143.8, 135.9, 131.56, 129.6, 128.7, 127.3, 119.7, 118.7, 118.1, 69.1, 62.9, 48.3, 42.11, 30.5, 25.7.

*2.3.4. Representative crosslinked poly(sulfone) membrane cast procedure used to prepare **3f***

A 25 mL flask was charged with polymer **2** (700 mg, 1.29 mmol based on the molecular weight of its repeat unit), DMAc (5 mL), and a magnetic stir bar. The solution was stirred until the polymer was completely dissolved. After adding a DMAc solution of **1** ([**1**]$_0$ = 0.503 M; 2.44 mL, 1.23 mmol), the reaction vessel was sealed with a septum. The vessel was then degassed under reduced pressure, and CuI (38.3 mg, 200 μmol) and 1,7-octadiyne (51.0 μL, 0.387 mmol) were added. The resulting mixture was stirred for 30 min at ambient temperature and then filtered through a cotton plug into a custom-built, air-free Petri dish as it was continuously purged with nitrogen. The purging was stopped upon completion of the transfer. The chamber was then sealed and heated at 60 °C in an oven for 12 h. The chamber was then removed from the oven and allowed to cool to ambient temperature. To allow the residual solvent to evaporate, the top of the chamber was removed and the chamber was heated at 60 °C in the oven for an additional 6 h followed by heating at 80 °C for 12 h. The membrane was released from the cell by adding 100 mL of H_2SO_4 (2 M; 100 mL). Upon removal of the membrane, it was acidified by heating at 80 °C for 2 h in the presence of H_2SO_4 (2 M, 400 mL) in a 1 L Erlenmeyer flask. Finally, the membrane was heated in 400 mL of de-ionized water at 80 °C for 2 h and then dried in a vacuum oven at 70 °C for 12 h (815 mg, 84% yield).

*2.3.5. Representative crosslinked poly(sulfone) copolymer membrane casting procedure used to prepare **5b***

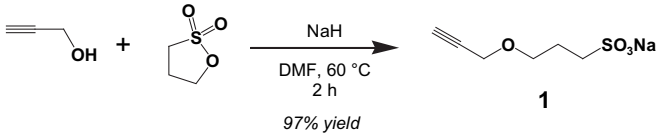
A 50 mL flask was charged with a magnetic stir bar, polymer **2** (550 mg, 1.05 mmol based on the molecular weight of the repeat unit), and DMAc (5 mL). The polymer was allowed to completely dissolve before adding a solution of **1** in DMAc (([**1**]$_0$ = 0.503 M; 2.49 mL, 1.25 mmol), and CuI (23 mg, 0.121 mmol). The flask was then sealed with a septum, degassed under reduced pressure for 10 min and then backfilled with nitrogen. The resulting reaction mixture was stirred at ambient temperature for 8 h to generate polymer **4**. In a separate vial, polymer **2** (200 mg, 0.452 mmol based on the molecular weight of the repeat unit) was dissolved in DMAc (3 mL) and added to the reaction vessel containing **4** followed by a solution of DMAc (1 mL) containing 1,7-octadiyne (56 μL, 0.43 mmol). The resulting mixture was degassed for 10 min under reduced pressure, backfilled with nitrogen, and then filtered through a cotton plug into a custom-built, air-free chamber as it was purged with nitrogen. After the purging was ceased, the chamber was sealed and heated at 60 °C in an oven for 12 h. The chamber was then removed from the oven and allowed to cool to ambient temperature. To allow the residual solvent to evaporate, the top of the chamber was removed and the chamber was reheated at 60 °C for 6 h with the aid of small circulation fan to facilitate drying. The membrane was then dried at 80 °C for 12 h and released from the cell by adding 100 mL of H_2SO_4 (2 M; 100 mL). Upon removal of the membrane, it was acidified by heating at 80 °C for 2 h in the presence of H_2SO_4 (2 M, 400 mL) in a 1 L Erlenmeyer flask. Finally, the membrane was heated in 400 mL of de-ionized water at 80 °C for 2 h and then dried in a vacuum oven at 70 °C for 12 h (812 mg, 70% yield).

3. Results and discussion

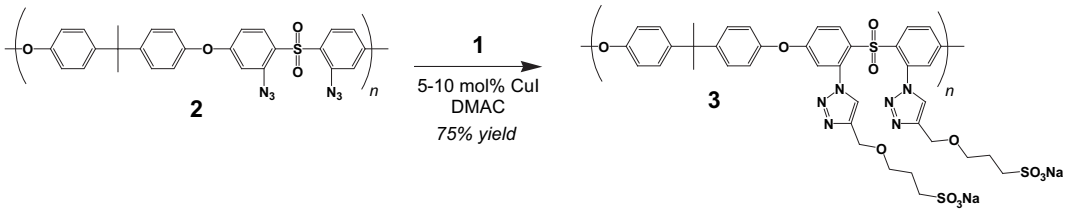
3.1. Sulfonation of poly(sulfone)s containing pendant azides via click chemistry

As a potentially suitable reagent to modify poly(sulfone)s containing pendant azides, alkyne sulfonate **1** features a flexible alkyl chain that was envisioned to distance the sulfonic acid from the main chain of the polymer to which it may be attached. Hence, the hydrophobic regions of the resulting polymer backbone may be effectively separated from the hydrophilic regions and result in better swelling properties [29]. As shown in Scheme 1, **1** was synthesized by the nucleophilic ring-opening of 1,3-propanesultone with sodium propargylate under mild conditions and isolated in high yield (97%) following precipitation and collection via filtration. Although **1** was found to decompose over a period of days, forming an insoluble red powder, a solution of this compound in *N*,*N*-dimethylacetamide (DMAc) was found to be stable under ambient conditions for extended periods of time.

Upon the synthesis of **1**, efforts shifted toward exploring the utility of this compound to modify azide-functionalized poly (sulfone)s. As shown in Scheme 2, polysulfone **2** (M_w = 45.6 kDa; PDI = 2.01; prepared as described by Guiver [28]) was treated with **1** (2.0 equiv per repeat unit of **2**) under Cu-catalyzed cycloaddition conditions in DMAc. The progress of the reaction was monitored by



Scheme 1. Synthesis of alkyne sulfonate **1** via the ring-opening of 1,3-propanesultone with propargyl alcohol under basic conditions.



Scheme 2. Synthesis of poly(sulfone) **3** via Cu-catalyzed 1,3-dipolar cycloaddition of alkyne sulfonate **1** with an azide modified polysulfone (**2**).

the disappearance of the distinct IR absorption of the aryl azide (υ_{N3} = 2119 cm^{-1} in a KBr matrix; see Fig. 1) as well as the appearance of a singlet at δ = 8.1 ppm (DMSO-d_6), diagnostic of a triazole C–H proton, in the ^{1}H NMR spectrum (see Fig. 2). Characterization of this crude reaction mixture (which contained the sodium sulfonate salt **3Na**$^+$) by GPC showed a small increase in molecular weight (M_w = 59.1 kDa) and polydisperisty (PDI = 2.99) compared to its starting material (**2**) (M_w = 56.9 kDa, PDI = 2.14) (see ESI). The acidified poly(sulfone) **3** was isolated in 75% by removal of the solvent under reduced pressure at 60 °C followed by washing with excess water and methanol and finally treatment with 2 M H_2SO_4 (aq.) Analysis of **3** by GPC revealed a relatively low molecular weight polymer (M_w = 27.5 kDa) of lower polydispersity (PDI = 1.43). This change in molecular weight as well as the decreased PDI was attributed to selective fractionation of the polymer during the aforementioned purification and isolation procedures. Regardless, the IEC (ion exchange capacity) of **3** (2.1 meq/g) corresponded well with the theoretical value (2.2 meq/g). The thermal properties of **3** were also analyzed: the polymer exhibited a glass transition temperature (T_g) at 67 °C which was not present in any of the crosslinked systems (see below), as determined by differential scanning calorimetry, and was stable until 170 °C, as determined by thermogravimetric analysis (TGA) (see ESI).

3.2. Synthesis and study of crosslinked poly(sulfone) membranes

Once it was demonstrated that polymer **2** was successfully modified with **1** using the aforementioned cycloaddition chemistry, efforts shifted toward the synthesis of crosslinked polymers using a similar approach. Poly(sulfone) **2** was dissolved in DMAc followed by the addition of various quantities of alkyne sulfonate **1**, 1,7-octadiyne as a crosslinker, and copper catalyst (10 mol%); see Table 1. Each of these solutions were independently degassed and then heated at 60 °C for 12 h in a Petri dish under nitrogen. The solvent was then evaporated at 60 °C to produce polymeric membranes that were released from the dish by addition of 2 M H_2SO_4 (aq.) The crosslinked polymeric materials obtained from these reactions were insoluble; hence, they could not be analyzed via NMR spectroscopy. However, as summarized in Table 1, a close correlation between the theoretical and the measured IECs was observed. In addition, the methanol permeabilities and proton conductivities of these membranes were measured at 25 °C and 65 °C, with all membranes showing significant improvements in conductivity at the later temperature. Low levels of sulfonation resulted in membranes that exhibited low methanol permeabilities and modest conductivities. For example membrane **3f** (which contained 30% crosslinker and an IEC of 1.3) displayed a 10-fold reduction in methanol crossover (1.03×10^{-7} cm^2/s) but exhibited a reduction in proton conductivity from 120 to 40 mS/cm versus Nafion 117 (120 mS/cm). Utilization of larger quantities of **1** as a means to increase the IEC of the material even further resulted in membranes that were too mechanically unstable for further testing, unfortunately. As summarized in Table 1, the relative selectivities of the membranes, which were determined by comparing the conductivity/permeability ratio of the membrane versus the same ratio measured for Nafion 117, were also calculated and ranged from 0.02 to 5.21. In general, the membranes that exhibited low methanol permeabilities exhibited the highest relative selectivities.

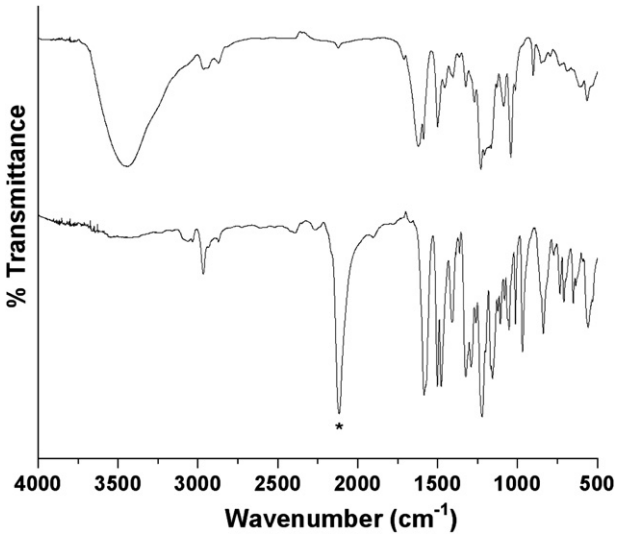


Fig. 1. FT-IR spectrum (KBr) of poly(sulfone)s **2** (bottom) and **3** (top). The asterisk denotes an azide stretching frequency.

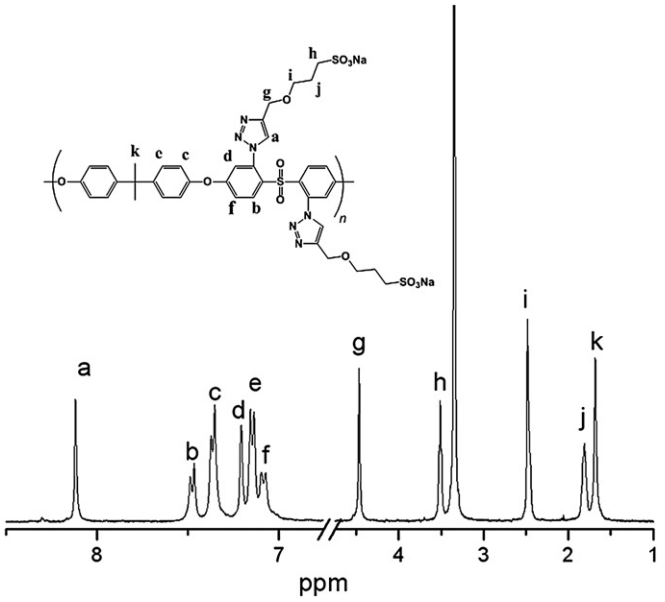


Fig. 2. ^{1}H NMR spectrum (DMSO-d_6) of poly(sulfone) **3**. The diagnostic chemical shifts are labeled.

Table 1
Selected methanol permeability and proton conductivity (σ) data.

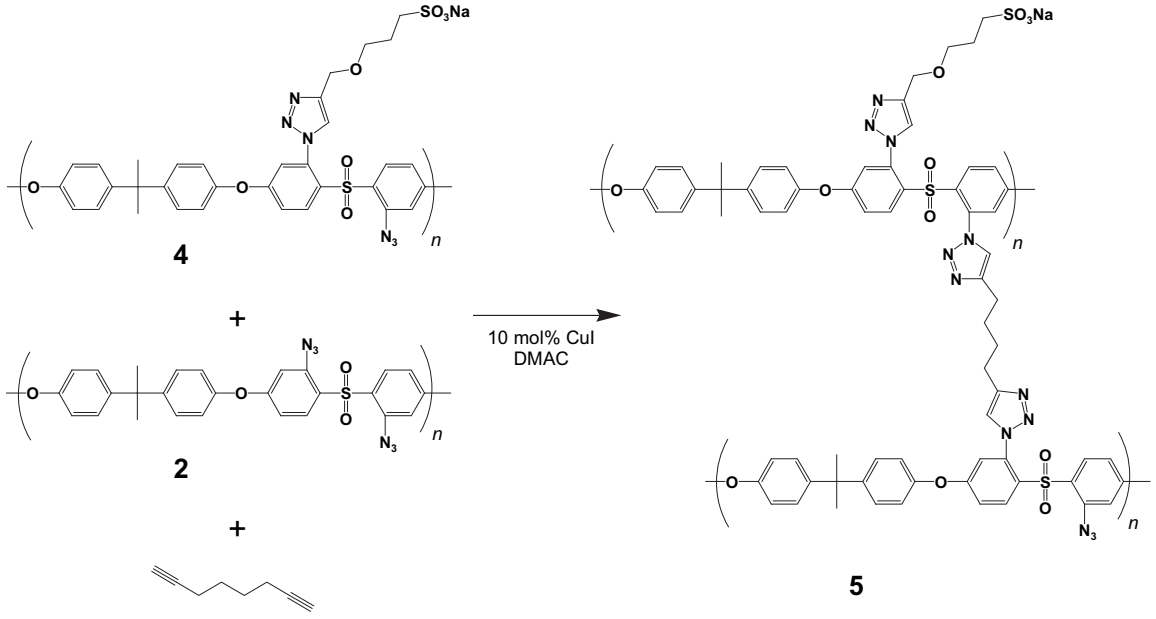
Polymer	IEC (theory), meq/g [a]	IEC (exp) meq/g [b]	mol % 1,7-octadiyne	MeOH perm (cm^2/s) [c]	relative selectivity (25 °C) [d]	σ (mS/cm) (25 °C) [e]	σ (mS/cm) (65 °C) [e]
3a	0.82	0.74	0	1.44×10^{-8}	5.21	5.7	9.1
3b	0.82	0.81	10	2.45×10^{-8}	1.56	2.9	4.3
3c	0.82	0.79	20	8.44×10^{-9}	3.74	2.4	2.9
3d	1.3	1.2	0	6.85×10^{-7}	0.44	23	60
3e	1.3	1.3	20	3.10×10^{-7}	1.70	40	74
3f	1.3	1.3	30	1.03×10^{-7}	1.02	8.0	40
3g[f]	1.6	1.5	30	4.11×10^{-5}	0.02	72	111
3h[f]	1.8	1.8	0	[g]	[g]	[g]	[g]
3i[f]	1.8	1.7	20	3.90×10^{-6}	0.17	50	53
3j[f]	1.8	1.7	25	4.83×10^{-6}	0.13	49	50
117[h]	0.91	0.91	0	1.25×10^{-6}	–	95	120

[a] The theoretical IEC was determined by the quotient of the total amount of sulfonate added in mmol over the total theoretical mass of the membrane in g.
[b] The experimental IEC was determined by the quotient of the acid content of a representative sample, measured by titration, over the mass of the sample.
[c] The methanol (MeOH) permeability data was acquired by measuring the diffusion of a 1 M solution of methanol through a membrane (area = 7.1 cm^2) at 25 °C.
[d] The relative selectivity was determined by the quotient of membrane selectivity over the selectivity of Nafion 117.
[e] The impedance measurements were performed at 100% relative humidity.
[f] These membranes formed mechanically weak gels upon acidification and were too fragile to incorporate into viable MEAs.
[g] These membranes proved to be too weak for further testing.
[h] Nafion 117 was tested for comparison.

3.3. Synthesis and study of crosslinked poly(sulfone) copolymer membranes

To enhance the mechanical properties of the aforementioned materials and to further separate the hydrophilic regions from the hydrophobic regions as described in the Introduction, a series of crosslinked copolymers comprised of polymer **2**, a partially-sulfonated polysulfone with varying degrees of sulfonation (**4**), and a crosslinker (1,7-octadiyne) were synthesized as shown in Scheme 3. As summarized in Table 3, this protocol afforded copolymers **5** that formed mechanically robust membranes, and exhibited lower methanol permeabilities and similar conductivities as Nafion 117. Unfortunately, further sulfonation of the hydrophilic block led to films that were visually hazy or opaque. The phase separation in this material is most likely due to the incompatibility of the sulfonated polymer with the unsulfonated polymer [30]. In addition, these membranes showed poor mechanical and conductive properties, and therefore were not investigated further [31].

In general, we have observed that increasing either the degree of sulfonation or the crosslink concentration resulted in more brittle membranes. To balance these two factors, a new copolymer membrane **5a**, which has a more moderate IEC and only 10% crosslinker, was synthesized and tested. Qualitatively, this membrane exhibited improved mechanical properties in the dry state when compared to the other membranes reported herein. The thermal stability of these membranes was probed by thermogravimetric analysis, and found to exhibit a decomposition temperature of 170 °C, which is similar to that of the poly (sulfone) **3** (not crosslinked) described above. The proton conductivities of membranes **5** were measured at 25 and 65 °C. Consistent with literature reports, higher conductivities were observed at the elevated temperature. As summarized in Table 3, the relative selectivities of these membranes were also calculated and ranged from 0.55 to 1.85. In general, higher selectivities were observed in membranes that exhibited relatively lower proton conductivities.



Scheme 3. Copolymer formation via crosslinking of two different polymer chains.

Table 2
Selected liquid uptake and swelling data.[a]

% Liquid Uptake				% Swelling		
Polymer	H_2O @ 25 °C	MeOH (1 M) @ 25 °C	MeOH (1 M) @ 65 °C	H_2O @ 25 °C	MeOH (1 M) @ 25 °C	MeOH (1 M) @ 65 °C
3a	14.7	18.7	19.7	5.4	6.8	8.1
3b	14.4	15.9	17.5	3.9	3.9	5.9
3c	12.8	15.3	18.3	2.2	3.3	5.5
3d	40.1	42.0	77.1	11.7	13.3	20.0
3e	31.7	38.9	50.7	9.2	11.7	15.8
3f	19.8	21.1	30.7	4.5	7.1	10.7
3g	124	146	276	28.6	38.1	47.6
3i	486	572	1589	124	129	[b]
3j	528	535	581	62.5	62.5	75.0
5a	16	18	24	5.7	5.7	5.7
5b	31.2	34.3	38.3	7.0	9.3	14.0
5c	129.3	138.0	174.4	28.3	30.4	43.5

[a] The percent liquid uptake was calculated using the following equation: 100 × (wet mass − dry mass)/dry mass. The percent swelling was calculated using the following equation: 100 × (wet length − dry length)/dry length.
[b] This membrane formed a gel that proved to be too fragile to evaluate further.

3.4. Liquid uptake and swelling

Membranes with high liquid uptake often exhibit high methanol crossover. As summarized in Table 2, the membranes described herein were measured for their abilities to uptake water at 25 °C as well as methanol at 25 and 65 °C. The uptake for these membranes ranged from 14.4% to 1600% with larger uptakes observed at higher methanol concentrations and elevated temperatures. Moreover, liquid uptake appeared to be proportional with the acid content of the membrane tested and inversely proportional with the concentration of the crosslinker employed for membrane synthesis. Membrane swelling is another critical parameter that should be considered for proper function of proton exchange membranes in fuel cells since swelling can have detrimental effects on fuel cell performance. The swelling properties of the membranes described herein were measured and the trends observed were similar to that of the uptake (range: 2.2% to greater than 129%); see Table 2.

3.5. Membrane-Electrode Assembly (MEA): fabrication and testing

Upon synthesis, MEAs containing copolymers **5a** and **5b** as the electrolyte were independently fabricated and tested. The MEAs were fabricated by placing the membrane between two carbon cloth electrodes coated in Pt (cathode) and Pt/Ru (anode) and a Nafion ionomer. Both catalyst loadings were 5 mg/cm^2 and the active cell area was measured at 5 cm^2. The electrodes were then pressed onto the membrane using a Carver hot press at varying temperatures (25–150 °C) under 1500 psi of pressure for 2.5 min. For comparison, a MEA containing Nafion 117 was also fabricated as previously described, and assembled by hot pressing at 120 °C under otherwise identical conditions as described above [15]. The electrochemical performances of the MEAs were evaluated using a computer controlled fuel cell testing setup (Scribner 840) at 65 °C with 1 M methanol cycled through the anode at rate of 2.5 mL/min and oxygen fed to the cathode at rate of 200 mL/min. As summarized in Fig. 3, the performance of the fuel cell containing **5b** was found to be highly dependent on MEA fabrication conditions. Assembly at 150 °C (designated **5b 150C**) afforded a membrane that became brittle when drying during the hot pressing procedure and was difficult to manipulate. In addition, delamination of the membranes pressed under these conditions was also observed, which may be due to the swelling properties of the membrane. We believe that the hot pressed membrane bonded to the electrode in the dry state and then wrinkled upon wetting which resulted in higher interface resistance between electrode and membrane [32], and ultimately resulted in cell voltage loss. However, assembly of the MEA containing **5b** at ambient temperature (designated **5b 25C**) afforded a membrane that remained hydrated and flexible, which resulted in a better contact between the electrode and membrane interface. Moreover, as shown in Fig. 3, improved performance compared to the MEA fabricated at higher temperature was observed. The MEA containing **5b** (pressed at 25 °C) also showed a relatively high maximum power density (130 mW/cm^2), comparable to that measured for the MEA containing Nafion 117 (150 mW/cm^2) under the same conditions.

Although the membrane comprised of **5b** was measured to be thinner than the Nafion 117 membrane (110 μm vs. 175 μm, respectively), the former showed slightly lower performance due to its relatively low proton conductivity as well as the incompatibility between the aromatic polymer membrane and Nafion ionomer coated on the electrodes. However, the open circuit voltage (OCV)

Table 3
Selected methanol permeability and conductivity data.

Polymer	Degree of sulfonation [a]	sulfonated/ unsulfonated wt/wt [b]	IEC (theory), meq/g [c]	IEC (exp) meq/g [d]	mol % 1,7-octadiyne	MeOH perm (cm^2/s) [e]	Relative Selectivity [f]	σ (mS/cm) [g] 25 °C	σ (mS/cm) [g] 65 °C
5a	1.0	2.0	0.93	0.86	10	5.55×10^{-8}	1.85	7.8	14.2
5b	1.2	4.0	1.3	1.2	30	3.57×10^{-7}	1.33	36	86
5c	1.6	3.8	1.5	1.4	30	1.87×10^{-6}	0.55	78	111

[a] Equivalents of acid per repeat unit of the sulfonated polymer.
[b] This ratio refers to the relative amounts of sulfonated and unsulfonated polymers added to the reaction mixture.
[c] The theoretical IEC was determined by the quotient of the total amount of sulfonate added in mmol over the total theoretical mass of the membrane in g.
[d] The experimental IEC was determined by the quotient of the acid content of a representative sample, measured by titration, over the mass of the sample.
[e] The methanol permeability data was acquired at 25 °C.
[f] Relative selectivity was determined by the quotient of membrane selectivity over the selectivity of Nafion 117.
[g] The impedance measurements were performed at 100% relative humidity.

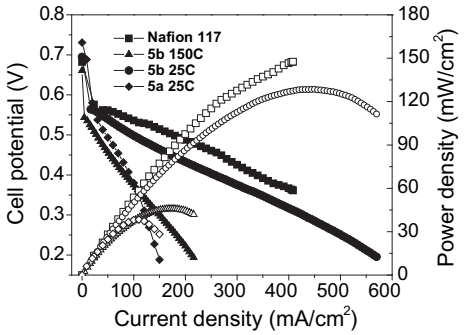


Fig. 3. MEA tests of **5a**, **5b** and Nafion 117. Filled shapes represent the polarization curve; open shapes represent the power density curve. A Pt-black catalyst was used at the cathode and a Pt:Ru black catalyst was used at the anode (the loading of each was 5 mg/cm^2). The active cell area was 5 cm^2. Sample **5b 150C** refers to a MEA containing **5b** that was assembled via hot pressing at 150 °C. Sample **5b 25C** refers to a MEA containing **5b** that was assembled via pressing at ambient temperature. **5a 25C** was also assembled at 25 °C.

of **5b** was measured to be higher than that of Nafion 117, which was attributed to the lower methanol permeability of the former and the consequent smaller voltage loss at the cathode side.

For comparison membrane **5a** was also tested in a fuel cell. This membrane had a smaller IEC and crosslink density which made it much less brittle in the dry state but also reduced its conductivity relative to **5b**. The fuel cell showed a slightly higher OCV but a steeper polarization curve which is typically associated with less conductive electrolytes. However, the lower methanol permeability of these membranes may not only help to lower the Pt catalyst loading at the cathode but also lead to an improved long-term stability and performance in the respective DMFC; such studies are underway.

4. Conclusions

A modular method for modifying poly(sulfone)s containing pendant azides is reported. Using copper-catalyzed, 1,3-dipolar cycloaddition chemistry, Brønsted basic 1,2,3-triazoles and crosslinks were successfully formed in a single step which was found to significantly decrease the methanol permeability while maintaining relatively high proton conductivity in the resulting membranes. In addition, the fuel cell performances of MEAs containing these materials were comparable to those containing Nafion-based membranes, and exhibited a maximum power output of 130 mW/cm^2. On a broader level, the strategy described herein effectively establishes a new and versatile route to functionalization of aromatic polymers and extension of this methodology to other proton conductive materials is currently underway.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.polymer.2010.09.041.

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