Polymer 51 (2010) 5352–5358

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

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

Brent C. Norris [a], Wen Li [b], Eungje Lee [b], Arumugam Manthiram [b], Christopher W. Bielawski [a,*]

[a] Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station, A5300, Austin, TX 78712, USA
[b] Materials Science and Engineering Program, The University of Texas at Austin, Austin, TX 78712, USA

ARTICLE INFO

Article history:
Received 28 June 2010
Received in revised form
12 September 2010
Accepted 15 September 2010
Available online 8 October 2010

Keywords:
Polysulfone
Fuel cells
Click chemistry

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].

* Corresponding author.
E-mail address: bielawski@cm.utexas.edu (C.W. Bielawski).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.09.041

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