



Mechanical properties and ionic conductivity of electrospun quaternary ammonium ionomers

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ARTICLE INFO

Article history:

Received 18 June 2011

Received in revised form 2 November 2011

Accepted 4 November 2011

Available online 11 November 2011

Keywords:

Ionomers

Electrospinning

Anion-exchange membranes

Polysulfone

ABSTRACT

Solution processable cationic ionomers are receiving widespread attention for their promising roles as anionic exchange membranes, antimicrobial coatings, and dialysis membranes. The ion conductivity can be improved by increasing the material's ion-exchange capacity; however this often results in poor mechanical properties. Here we report the synthesis of solution processable polysulfone ionomers with a tunable density of quaternary ammonium functional groups. Electrospinning is explored to create fibrous mats that can be solvent welded and filled with a second material to modulate membrane properties. The tradeoff between hydroxide anion conductivity and mechanical properties in solution cast and electrospun mats is assessed, and electrospinning is shown to improve mechanical properties of the fiber phase with relatively small losses in ion conductivity.

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1. Introduction

Poly(aryl ether) sulfones are engineering thermoplastics that contain linear aryl, ether, and sulfone repeat units in the polymer backbone. The rigid backbone imparts good mechanical properties, thermal stability, and chemical resistance. Polysulfones are affordable and biocompatible materials that have found industrial and medical applications as advanced membranes [1]. Polysulfone ionomers combine the mechanical, chemical, and thermal stability of the aryl ether sulfone backbone with the hydrophilicity and ion-exchange ability of a charged backbone [2,3]. Quaternized ammonium polysulfones (QAPS's), for example, can be obtained using the well established and recently popularized chloromethylation method [4]. QAPS membranes are conductive toward hydroxide and carbonate ions and are being developed as solution processable polymer electrolyte membranes for alkaline fuel cells [5–11]. Unlike fuel cells based on the proton exchange membrane, alkaline fuel cells do not require expensive Pt-based catalysts. However, alkaline fuel cell development is limited primarily by the lack of durable anion-exchange membranes with sufficient hydroxide conductivity. Recently, Pan et al. measured the ionic conductivity of solution processable QAPS and reported conductivities on the order of 0.01 S/cm [6]. Increasing the concentration of ion-exchange groups further improves the ionic

conductivity of QAPS at the expense of mechanical properties [11,12].

Here, we investigate electrospinning of QAPS ionomers as an approach to overcome the engineering tradeoff between ion conductivity and mechanical properties. Electrospun mats consist of a network of submicron fibers that span macroscopic dimensions. Fibers are created by electric field assisted extrusion of a polymer solution from a spinneret, followed by rapid solvent removal. Below a critical fiber diameter, individual fibers can exhibit significantly higher tensile modulus than in the bulk; and this is attributed to confinement of supramolecular structures within polymer nanofibers during solvent removal [13]. Ion conductivity is influenced by other factors including ion content, the degree of swelling, the mobile ion type, and the spatial arrangement of hydrophilic (ion rich) and hydrophobic domains [14]. We hypothesize that electrospinning of QAPS ionomers will have a larger effect on tensile modulus than on ion conductivity, offering a way to overcome the tradeoff. Our study is further motivated from a membrane processing standpoint. The interstitial spaces between electrospun fibers form continuous pathways in three dimensions and can be used to transport fluids through the network of fibers. Liquid permeability is needed for liquid separation membranes, and the interstitial spaces could be used to introduce an epoxy or thermoset support for electrospun fibers.

In this study, quaternary ammonium polysulfones were synthesized with varying ionic content and processed into membranes by both solvent-casting and electrospinning techniques. To our knowledge, this is the first systematic study of electrospinning

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of cation-containing polysulfones. The solution viscosity of the neutral polysulfone and the quaternized polysulfones were studied to understand how chain entanglements and ion clusters affect fiber formation. Tensile testing and ion conductivity measurements were performed on solvent-cast and on electrospun membranes under identical conditions to assess the tradeoff between mechanical and ion transport properties. Finally, to further improve mechanical properties, composite membranes were fabricated by imbining electrospun mats with a curable siloxane elastomer.

2. Experimental

2.1. Materials

Polysulfone (PSU, Udel P-1700) was kindly provided by Solvay Advanced Polymers, average molecular weight (M_w) is 67,000–72,000 g/mol. Chloromethyl methyl ether (CMME) and trifluoroacetic acid (TFA, 99+%) were purchased from Sigma–Aldrich; trimethylamine (TMA, 45 wt.% in water) from Alfa Aesar; zinc powder, 1,2-dichloroethane, and sodium hydroxide (NaOH) from J.T. Baker; dimethyl formamide (DMF) from EMD; hydrochloric acid (HCl, 36.5–38%) from Mallinckrodt Chemicals; methanol from BDH. All chemicals were used without further purification.

2.2. Synthesis

Solvent-cast quaternary amine alkaline polysulfone (**QAPS-OH**) membranes were prepared following Fig. 1. Chloromethylated polysulfone (**CMPS**) was prepared according to Lu et al. [5] In a typical procedure, 10 g of polysulfone (Udel P-1700) was dissolved in 200 ml of 1,2-dichloromethane. Then, 0.75 g of zinc powder, 3 ml of trifluoroacetic acid (TFA), and 7.5 ml of chloromethyl methyl ether (CMME) were added. The reaction mixture was stirred at 30 °C for 1–6 h to vary the degree of chloromethyl substitution, and the product was precipitated in methanol and dried at room temperature overnight. $^1\text{H NMR}$ (DMSO, 400 MHz): $\delta = 1.66$ (s, 6H), 4.64 (s, 2H), 7.0 (d, 4H), 7.2–7.5 (multiple d, 6H), 7.55 (s, 1H), 7.9 (d, 4H). Drying the product at high temperature was avoided since heating can result in lower solubility due to thermal crosslinking between reactive chloromethyl groups [7].

To obtain quaternary ammonium chloride polysulfone (**QAPS-Cl**), nitrogen gas containing trimethylamine was bubbled through a DMF solution of chloromethylated polysulfone (10%, w/v) for 2 h to ensure complete reaction between chloromethyl groups and TMA. The resulting solution was cast into a film and dried at 50 °C under vacuum overnight to obtain a thin polymer membrane with thickness $\sim 100 \mu\text{m}$. Chloride counter ions were then exchanged with hydroxyl ions by immersing cast films into 1 M NaOH for 48 h, followed by washing several times with deionized water. The resulting transparent films (**QAPS-OH**) were dried at 50 °C in vacuum oven for 72 h. $^1\text{H NMR}$ (DMSO, 400 MHz): $\delta = 1.66$ (s, 6H), 3.1 (d, 9H), 4.6 (s, 2H), 5.95 (s, 1H), 7.0 (d, 4H), 7.2–7.5 (multiple d, 6H), 7.55 (s, 1H), 7.9 (d, 4H).

2.3. Electrospinning

A DMF solution containing 18 wt.% **QAPS-Cl** was prepared and injected at a rate of 1.0–1.5 ml/h through a blunt end syringe needle (gauge 22) using a syringe pump (Cole-Parmer, IL, USA). The stainless steel syringe needle was connected to a high voltage power supply (Gamma high voltage research, Inc., FL, USA) and maintained at a potential of 20–27 kV relative to ground. A negative bias potential of 1.5–3 kV was applied to a rectangular aluminum collector positioned 15 cm away from the syringe tip.

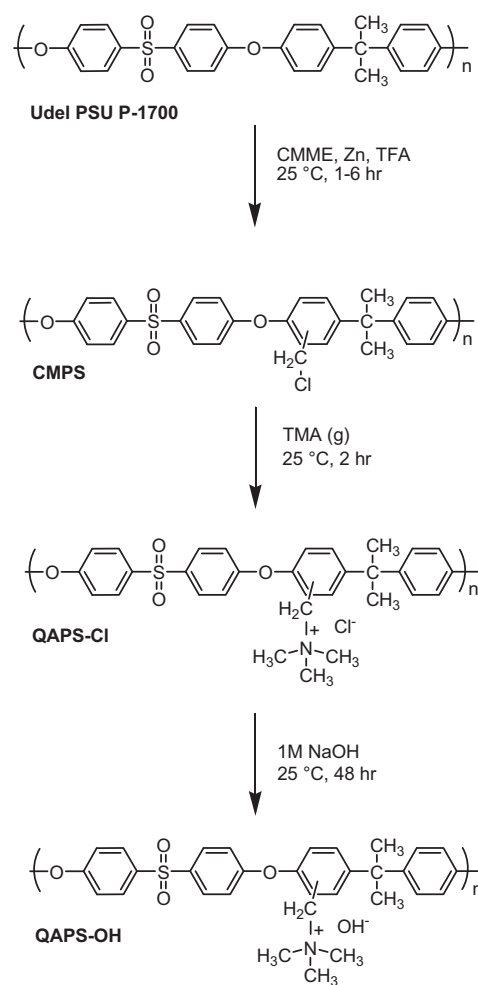


Fig. 1. Synthesis scheme of quaternary ammonium alkaline polysulfones (**QAPS-OH**).

Electrospun **QAPS-Cl** membranes were ion-exchanged with hydroxyl anions by immersion in 0.1 M NaOH for 48 h followed by washing with deionized water. Compared to ion-exchange of solvent-cast films, a weaker NaOH solution was used because the nano-fibrous membranes are more readily ionic exchanged due to their high surface area. Ion-exchange using high NaOH concentrations was found to induce stress-damage to the fibers.

2.4. Characterization

Product chemical structures were confirmed using $^1\text{H NMR}$ (Bruker 400 MHz NMR) with *d*-DMSO as a solvent. Steady-shear viscosity measurements of polymer solutions (1–15 wt.%) were made using a Brookfield viscometer operating at 40 °C in a cone-in-plate geometry with a cone radius of 2.4 cm. Measurements determined the specific viscosity, defined as $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$, where η_0 is the polymer solution viscosity and η_s is the pure solvent viscosity. The morphology of the electrospun fibrous membranes was investigated by field effect scanning electron microscope (FESEM, Zeiss Supra 40VP).

Ion-exchange capacities (IEC) were measured by soaking the alkaline exchange membranes in weakly acidic aqueous solutions (0.001 M HCl) and measuring the resulting pH change. The pH of the exchange solution increased as hydroxyl groups were released, partially neutralizing the acid solution. Films were exposed to the acidic solution for about 72 h, or until the pH ceased to change.

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