



Side-chain sulfonated copolymer cation exchange membranes for electro-driven desalination applications



Benjamin M. Asquith^{a,b}, Jochen Meier-Haack^b, Claus Vogel^b, Wladimir Butwilowski^b, Bradley P. Ladewig^{a,*}

^a Department of Chemical Engineering, Monash University, VIC 3800, Australia

^b Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, 01069 Dresden, Germany

HIGHLIGHTS

- Random and multiblock side-chain sulfonated cation exchange membranes were prepared.
- All membranes yielded relatively low water uptake and good mechanical stability.
- Hydrophilic domains in the polymers enhanced ion exchange capacity and conductivity.
- Membrane conductivity is comparable to commercially available Neosepta CMX.
- Random copolymers exhibited high transport numbers.

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ABSTRACT

Cation exchange membranes prepared from random and multiblock side-chain sulfonated poly(ether sulfone)s have been characterised to evaluate their suitability for electrodialysis and membrane capacitive deionization applications. The side chain sulfonation of the copolymers resulted in membranes with a high degree of sulfonation and ion exchange capacities (IEC) in the range of 1.44–2.05 mmol/g, which is comparable to commercially available membranes. The multiblock copolymer, which can be considered as having a microheterogeneous structure, exhibited a high IEC and water uptake due to large, hydrophilic domains, while the random copolymers had lower swelling rates. Membrane conductivity in the Na⁺ form reached as high as 15.13 mS/cm for the random copolymers and 16.74 mS/cm for the block copolymer. Transport numbers were found to be as high as 0.99 for random copolymers, but as low as 0.84 for the block copolymer. Based on these results, these side-chain sulfonated random copolymers are potential candidates for use in electro-driven desalination systems.

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1. Introduction

Given the rising global demand for water, in addition to other water conservation and reuse strategies, desalination is a key strategy to supplement water supplies. Electrodialysis and MCDI are electro-driven desalination processes that can be used for the highly efficient desalination of brackish water, the production of ultra pure water, water softening and the removal of other charged impurities from water streams [1–11]. The efficiency of these processes relies on the use of ion exchange membranes to remove unwanted charged particles from the feed stream. While many developments in ion exchange membranes have come from research for the chlor-alkali industry and fuel cells [12,13], the development of new materials and further

fundamental research into ion exchange membrane properties and functions will benefit numerous other processes, including electro-driven desalination [14].

Membranes for electrodialysis and MCDI require a high transport number and ion exchange capacity, low resistance and strong mechanical and chemical stability. There is often a trade-off between these properties; for instance, increasing polymer hydrophilicity to improve transport properties typically reduces the mechanical and chemical stability. Thus, polymer design for ion exchange membranes is a challenging task, and there is a need to balance the membrane properties for the desired application. As a way to improve the range of properties that a polymer exhibits, copolymers can be synthesised that combine hydrophobic and hydrophilic monomers. Poly(ether sulfone)s have strong mechanical, thermal and chemical stability and have been successfully used as ion exchange membranes in a wide range of applications [15–21]. State of the art random and multiblock poly(ether sulfone) copolymers have also been developed for pressure-driven desalination membranes [22–26] and for fuel cell applications

* Corresponding author. Tel.: +61 399051995.

E-mail address: bradley.ladewig@monash.edu (B.P. Ladewig).

[27,28], but these materials have yet to be prepared and characterised for ion exchange processes such as electro dialysis and MCDI.

For use as a cation exchange membrane, poly(ether sulfone) must be functionalised to incorporate fixed negatively charged groups. This process plays a large role in determining the properties of the polymer, in particular the electrical resistance and permselectivity [29]. Sulfonation is commonly used over other forms of functionalisation such as carboxylation or phosphonation, as the process is relatively simple and yields membranes with favourable ion transport properties [30]. Post-sulfonation, the direct functionalisation of a polymer with chlorosulfonic acid or concentrated sulfuric acid, allows for less control over the degree of sulfonation and chemical structure of the sulfonated polymer. Nonetheless it is often preferred over pre-sulfonation as it is a simpler and more cost effective process [31]. During the sulfonation process it is often the main chain that becomes sulfonated [32,33], however recent studies have shown that side chain sulfonation may enhance the chemical and mechanical properties of the polymer [28,34–36]. Results from these studies have yielded membranes with excellent properties and have shown good results when applied to fuel cells. However, side-chain sulfonated copolymers are yet to be studied for ion exchange desalination technologies.

In this work, three random and one multiblock side-chain sulfonated poly(ether sulfone)s were prepared and characterised. Correlations between the polymer structure and membrane properties are highlighted, in particular the IEC, water uptake, conductivity and transport number. Membranes are compared to the commercial membrane Neosepta CMX, which is commonly used for desalination via electro dialysis and MCDI, and the potential application of random and block copolymer membranes for these applications is discussed.

2. Experimental

2.1. Materials

4,4'-Difluorodiphenyl sulfone (DFDPhS) was purchased from FuMA-Tech GmbH (Germany) and was purified by vacuum distillation. 4,4'-dihydroxydiphenyl sulfone (DHDPHS) was obtained from Aldrich (Germany). N-methyl-2-pyrrolidone (NMP) was purchased from Merck (Germany) and distilled twice under reduced pressure from CaH₂. Concentrated sulfuric acid (min. 96%) was obtained from Acros (Belgium). 2,5-diphenylhydroquinone (DPhHQ), hydroxy endgroup diphenylated poly(ether sulfone) oligomer (oligo-DP-PES) and decafluorobiphenyl endcapped poly(ether sulfone) oligomer (oligo-PES) were prepared as per the procedure described by Vogel et al. [28].

2.2. Polymer synthesis and sulfonation

Random and multiblock copolymers were synthesised using the silyl-method as per the procedure described by Vogel et al. [28]. For the random copolymers, 10 mmol of DFDPhS, 10-x mmol of bis-TMS-DHDPHS and x mmol of bis-TMS-DPhHQ were weighed into a three-necked flask with 30 mL of anhydrous NMP. After complete dissolution of the monomers a 1:5 mixture of anhydrous potassium carbonate and calcium carbonate was added. The reaction mixture was heated under stirring and argon purging for 24 h to 175 °C and finally for 2 h at 190 °C. The cooled reaction mixture was diluted with NMP and filtered for the removal of insoluble material. The products were precipitated in methanol, then intensively washed with water and methanol. Finally the products were dried in vacuum at 100 °C to constant weight. The molar ratios of DPhHQ and DHDPHS for the random copolymers were 6:4, 5:5 and 4:6 (RCP 1, RCP 2 and RCP 3, respectively).

For the block copolymer, 0.3 mmol of the end-capped oligo-PES and 0.3 mmol of oligo-DP-PES were weighed into a three-necked round-bottomed flask with 50 mL of anhydrous NMP. The block lengths of oligo-PES and oligo-DP-PES were 25 and 39 respectively, where the block length is related to a single diphenylsulfone unit. After complete

dissolution of the precursor oligomers, 2 mmol of anhydrous potassium carbonate was added to the reaction mixture and the temperature was raised to 100 °C under stirring and argon purging for 24 h. The cooled reaction mixture was filtered and the product was coagulated in a 10-fold excess of methanol. The product was isolated by filtration and washed intensively with water and methanol. Finally the product was dried in vacuum at 100 °C to constant weight.

All polymers were sulfonated using concentrated sulfuric acid (96–98%). 30 mL of concentrated sulfuric acid was added to 3 g of polymer in a small flask under stirring for 24 h. The sulfonated polymers were precipitated in water and thoroughly washed with water until the solution obtained a neutral pH. The final products were dried under vacuum at 110 °C to constant weight.

2.3. Membrane preparation

Membranes were prepared by dissolving the sulfonated polymers in NMP. The solutions were cast onto glass and dried under vacuum for 2 h at 60 °C, then for a further 24 h at 80 °C. Membrane samples were removed from the glass using deionised water and thoroughly rinsed with deionised water before soaking for 24 h in 1 M NaCl. The membranes were finally stored in deionised water at room temperature before use.

2.4. Polymer and membrane characterisation

¹H NMR spectra of the polymers were recorded on a Bruker DRX400 spectrometer operating at 400.17 MHz, with DMSO-d₆ used as a solvent and internal chemical shift reference (2.50 ppm). The molecular weights were obtained from GPC measurements on a Knauer GPC equipped with Zorbax PSM Trimodal S columns and a RI detector. A mixture of DMAc with 2 vol.% water and 3 g/L LiCl was used as eluent. Water uptake was measured by first drying membrane pieces at 80 °C under vacuum until constant weight was reached. After soaking the pieces in water at room temperature for 24 h, they were removed, excess water was gently wiped with a tissue and the pieces were immediately weighed. The water uptake (WU) was calculated using the following equation:

$$WU = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \quad (1)$$

where m_{wet} is the weight of the swollen membrane and m_{dry} is the weight of the dry membrane. The ion exchange capacities of the membranes were measured using the titration method. Membrane pieces were first dried at 80 °C under vacuum until constant weight was reached. They were then soaked in 1 M HCl, thoroughly rinsed with deionised water, then soaked in 2 M NaCl for 24 h. The IEC was determined by titrating the NaCl solution with 0.01 M NaOH. The final IEC values were calculated by also taking into account the titration of blank 2 M NaCl solution. In-plane conductivity was determined using electrical impedance spectroscopy with a four point probe. Using a Gamry Reference 600 potentiostat in a frequency range from 1 Hz to 1 MHz, the membrane resistance was taken at the frequency where the phase angle was closest to zero. Membranes were measured in the Na⁺ form at 30 °C and a relative humidity of 99% to prevent them from drying out. As the samples were tested in a humid environment and not submersed in solution, the measured resistance is not influenced by boundary layer effects. Conductivity was calculated based on the measured membrane resistance, R_m (Ω), distance between electrodes, L (cm), and the effective membrane cross section (thickness multiplied by width), A (cm²), such that:

$$\sigma = \frac{L}{R_m A} \quad (2)$$

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