



Structure-property relationships of crosslinked disulfonated poly(arylene ether sulfone) membranes for desalination of water



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ABSTRACT

Controlled molecular weight poly(arylene ether sulfone) oligomers with aromatic amine end groups and systematically varied degrees of disulfonation were synthesized by direct polymerization of disulfonated and non-sulfonated 4,4'-dichlorodiphenylsulfone. The oligomers were crosslinked with a tetrafunctional epoxy curing agent in the membrane casting process. Water uptake and IEC were investigated to understand how the structure and ion content affected the fixed charge concentrations (moles of ions/L of sorbed water). The hydrated mechanical properties of these copolymer networks were also studied in light of their ion contents and water uptake. At similar IECs, membranes with shorter ~5000 Da oligomers absorbed less water than those with ~10,000 Da blocks. The salt permeabilities correlated with water uptake and fixed charge density. Among the crosslinked membranes, the one with the 10,000 Da oligomer and with 50% disulfonation (*m*B5-10) had an excellent combination of water uptake, hydrated mechanical properties, fixed charge density, and low salt permeability.

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1. Introduction

The scarcity of pure water is a global challenge that needs to be addressed immediately [1,2]. Technologies such as reverse osmosis (RO) [3] and electrodialysis (ED) [4–11] use dense, non-porous membranes for water purification [7,12–14]. The principles of these methods differ but both rely on the molecular and topological structures of polymeric membranes to control water and ion transport.

RO is currently the most used process for desalination of water. It utilizes an applied hydrostatic pressure on the upstream brine side of the membrane that opposes the osmotic pressure to drive the water flux downstream. The most prominent separation membranes for RO are very thin (~100 nm) crosslinked polyamides atop a porous polymer that supplies the necessary mechanical support [3,12,13].

The main components of ED are anion exchange membranes (AEM) and cation exchange membranes (CEM) [4–11,15]. These are

placed alternately in stacks between cathodic and anodic electrodes. Brine is pumped into the system between each AEM and CEM and a current is applied to drive the ions in opposite directions toward the respective electrodes. The role of the AEMs and CEMs is to promote counterion permeation through the membrane while repelling co-ion transport. The ED process leaves purified water in the diluate compartments [15]. The ability of ED membranes to transport counterions to the fixed membrane charges and to block co-ion transport depends highly on the polymer structure, charge concentration in the membrane and water uptake [9,16]. Commercial CEMs for ED are highly crosslinked polymers such as sulfonated poly(styrene-co-divinylbenzene) with inherently poor mechanical properties in the hydrated state. To improve the mechanical properties, these crosslinked polymers are prepared with a non-ionic porous or fabric support. Having the non-ionic support membrane results in lower ion permeability and ion conductivity, and higher electrical resistance [17–22]. Thus, a goal of our work is to develop unsupported or reinforced active membrane materials with high fixed ion concentration and mechanical properties suitable for the ED process.

It is quite common to characterize charged polymers, such as ion

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exchange membranes (IEMs), in terms of their ion exchange capacity (IEC), which is the millimoles of fixed charge groups on the polymer backbone per gram of dry polymer. However, based on the Donnan model [12], the ability of RO membranes to reject salt based on electrostatic effects and for ED membranes to inhibit transport of co-ions across an ED membrane depends on the fixed charge concentration (FCC), which is the moles of fixed charge groups per unit volume of water in the polymer matrix. That is, the effective concentration of fixed charged groups experienced by ions being transported through membranes under either a concentration gradient or electric field gradient is the FCC, not the IEC, and these two properties are not always proportional to one another. For example, as additional fixed charge groups are added to a polymer backbone to increase IEC, these highly hydrophilic charged groups also tend to increase the equilibrium water uptake in the membrane. Whether FCC increases or decreases with increasing IEC depends on the delicate balance between the increase in the number of fixed charge groups in the membrane (i.e., increasing IEC) and the increase in water content coming along with the increase in the number of fixed charge groups, which tends to reduce FCC.

When linear ionic copolymers sorb water, they swell significantly, while crosslinked membranes with similar IECs sorb less water [23–25]. Our group has studied the salt rejection properties of crosslinked disulfonated poly(arylene ether sulfone)s with fairly low IECs (maximum of 1.84 (meq/g)) [23]. Under reverse osmosis conditions, these copolymers showed reasonable water flux and NaCl rejection. The properties of such crosslinked copolymers with higher IECs, however, are not well understood. Moreover, as IEC is increased, the hydrated mechanical properties of the crosslinked membranes becomes an important issue. Our hypothesis is that engineering polymers such as the poly(arylene ether)s that are crosslinked only at the termini of controlled molecular weight oligomers can be designed to have superior hydrated mechanical properties to the IEMs that are synthesized by conventional free radical copolymerization.

This paper describes the membrane properties and performance of unsupported membranes of disulfonated poly(arylene ether sulfone) oligomers that were crosslinked at their termini with epoxy reagents. Effects of the degree of disulfonation and molecular weight of precursor oligomers were investigated with respect to water uptake, IEC and fixed ion concentration, then these properties were related to their salt permeabilities and hydrated mechanical properties.

2. Experimental

2.1. Materials

Toluene was purchased from Sigma-Aldrich and used as received. 4,4'-Biphenol (BP) was provided by Eastman Chemical Company. 4,4'-Dichlorodiphenylsulfone (DCDPS) was provided by Solvay Advanced Polymers and was recrystallized from toluene and dried under vacuum at 120 °C prior to use. 3-Aminophenol (*m*-AP, 99%) was purchased from Acros Organics and used as received. 3,3'-Disulfonated-4,4'-dichlorodiphenylsulfone (SDCDPS, >99%) was purchased from Akron Polymer Systems and dried under vacuum at 180 °C for 72 h before use. Potassium carbonate was purchased from Sigma-Aldrich and dried under vacuum at 180 °C for 72 h before use. Calcium hydride (90–95%) was purchased from Alfa Aesar. Triphenylphosphine (TPP, 99%), and tetraglycidyl bis(*p*-aminophenyl)methane (TGBAM, 92%) were purchased from Sigma-Aldrich. Toluene and 2-propanol were purchased from Fisher Scientific. *N,N*-Dimethylacetamide (DMAc) was purchased from Sigma-Aldrich, distilled from calcium hydride and stored over

molecular sieves before use.

2.2. Synthesis of *m*-AP terminated oligomers

Aromatic nucleophilic substitution step copolymerization was used to synthesize the terminally-reactive oligomers with *m*-aminophenol end groups. The nomenclature used in this manuscript is BiPhenyl Sulfone (*m*Bx-*y*) in which “x” and “y” represent 10% of the actual degree of disulfonation value and 0.1% of the oligomer molecular weight, respectively. A typical disulfonated *m*-Aminophenol terminated BiPhenyl Sulfone 60 with a molecular weight of 10,000 Da expressed in the abbreviated form of *m*B6-10 was synthesized as follows. BP (0.47 mmol, 8.752 g), DCDPS (20 mmol, 5.743 g), SDCDPS (30.0 mmol, 14.767 g), *m*-AP (6 mmol, 0.639 g) and DMAc (100 mL) were charged into a 250-mL three neck round bottom flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and Dean-Stark trap filled with toluene. The mixture was stirred in an oil bath at 150 °C until the monomers completely dissolved. K₂CO₃ (51 mmol, 8.44 g), and toluene (50 mL) were added into the flask. The reaction was refluxed for 4 h to azeotropically remove water from the system. Toluene was drained from the Dean-Stark trap, and the oil bath temperature was raised to 180 °C to remove residual toluene from the reaction. The reaction solution was stirred for 48 h to complete polymerization, then allowed to cool to room temperature. After dilution of the resulting solution with DMAc (100 mL), it was filtered to remove the salt. The transparent solution was precipitated by addition into isopropanol with stirring. The polymer was filtered and dried at 120 °C under reduced pressure in a vacuum oven. Yield 96% copolymer.

2.3. Nuclear magnetic resonance spectroscopy (NMR)

¹H NMR analysis of the statistical copolymers was conducted on a Varian Unity Plus spectrometer operating at 400 MHz. The spectra of the copolymers were obtained from a 10% (w/v) solution in DMSO-*d*₆ with 256 scans.

2.4. Size exclusion chromatography (SEC)

Molecular weights and polydispersities of the polymers were measured using SEC. The mobile phase was DMAc distilled from CaH₂ containing dry LiCl (0.1 M). The column set consisted of 3 Agilent PLgel 10-mm Mixed B-LS columns 300 × 7.5 mm (polystyrene/divinylbenzene) connected in series with a guard column having the same stationary phase. The columns and detectors were maintained at 50 °C. An isocratic pump (Agilent 1260 Infinity, Agilent Technologies) with an online degasser (Agilent 1260), autosampler and column oven were used for mobile phase delivery and sample injection. A system of multiple detectors connected in series was used for the analyses. A multi-angle laser light scattering detector (DAWN-HELEOS II, Wyatt Technology Corp.), operating at a wavelength of 658 nm and a refractive index detector operating at a wavelength of 658 nm (Optilab T-rEX, Wyatt Technology Corp.) provided online results. The system was corrected for interdetector delay and band broadening using a 21,000 Da polystyrene standard. Data acquisition and analysis were conducted using Astra 6 software from Wyatt Technology Corp. Validation of the system was performed by monitoring the molar mass of a known molecular weight polystyrene sample by light scattering. The accepted variance of the 21,000 Da polystyrene standard was defined as 2 standard deviations (11.5% for M_n and 9% for M_w) derived from a set of 34 runs. Specific refractive index values were calculated based on the assumption of 100% recovery.

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