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Cross-Linking Disulfonated Poly(arylene ether sulfone) Telechelic Oligomers. 1. Synthesis, Characterization, and Membrane Preparation

Benjamin J. Sundell,[†] Kwan-soo Lee,[†] Ali Nebipasagil,[†] Andrew Shaver,[†] Joseph R. Cook,[‡] Eui-Soung Jang,[‡] Benny D. Freeman,[‡] and James E. McGrath^{*,†}

[†]Macromolecules and Interfaces Institute, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, United States

[‡]Department of Chemical Engineering, Center for Energy and Environmental Resources, The University of Texas at Austin, Austin, Texas 78758, United States

ABSTRACT: *meta*-Aminophenol was used during nucleophilic step copolymerization to end-cap partially disulfonated bisphenol A based random copolymers with controlled oligomeric molecular weights. The amine end groups were thermally reacted with a tetrafunctional epoxy reagent to produce networks. Very high gel fractions, up to 99%, and ductile film formation were achieved. The oligomer was further functionalized with acryloyl chloride, phenylethynyl phthalic anhydride, and maleic anhydride to obtain several novel free radically cross-linkable oligomers. The structure and molecular weights (M_n) were established with ¹H NMR spectroscopy of the oligomers and end groups. TGA analysis demonstrated the high thermal stability of these oligomers; DSC investigations showed that the oligomers had curing exotherms from 140 to 330 °C and that residual casting solvent during cross-linking was necessary to avoid vitrification during membrane formation. In addition to the thermally cross-linkable systems, photocross-linking was demonstrated with the telechelic acrylamide functionalized oligomers. Two compositions were identified as potential candidates for further development. Cross-linking disulfonated poly(arylene ether sulfone) copolymers limits the high water sorption and swelling of these hydrophilic materials, which enhances several properties for membrane applications. Initial transport results indicate that cross-linking greatly reduces salt permeability while modestly decreasing water permeability, resulting in improved water/NaCl selectivity.

■ INTRODUCTION

More than two billion people live with inadequate freshwater resources as a result of either physical or economic water scarcity.^{1,2} This problem will be further exacerbated by rising population levels, which will necessitate the production of potable drinking water from alternative sources. Seawater accounts for 97% of the water on Earth and can be desalinated by methods such as multistage flash distillation and reverse osmosis (RO). The energy required for RO is now approaching theoretical minimums, resulting in its dominance for seawater desalination.^{3,4}

The most critical component of the RO process is the polymeric membrane, often fabricated into thin asymmetric films.² These membranes have high salt rejection, high water flux, chemical resistance, and satisfy many other requirements.^{5–7} The state-of-the-art material for RO is a highly cross-linked aromatic polyamide, initially reported in 1980.^{7–9} A major shortcoming of this polymer is susceptibility to degradation by chlorinated disinfectants, which attack the amide bond and degrade the membrane by various mechanisms.^{10–13} The seawater feed must be treated with disinfectant to reduce biofouling, and the freshwater permeate should also contain chlorine to act as a biocide.^{14,15} Somewhat more chlorine resistant cellulosic membranes have been demonstrated, but they exhibit significantly lower salt rejection than the state-of-the-art cross-linked aromatic polyamides.¹⁶ Thus, it is an important goal to identify a desalination

membrane with high chlorine tolerance while maintaining state-of-the-art transport properties.

Poly(arylene ether sulfone)s demonstrate both high chemical inertness and suitable mechanical properties for RO.^{17,18} Sulfonation imparts hydrophilicity to these otherwise hydrophobic polymers.^{19,20} The first sulfonation routes were postpolymerization reactions that resulted in side reactions and difficulties in controlling the extent of sulfonation.^{21,22} McGrath et al. and Ueda et al. synthesized linear sulfonated polysulfones directly from a disulfonated monomer²³ and demonstrated high molecular weights.^{24,25} The sulfonated copolymers showed high chlorine resistance in accelerated tests with modest levels of salt rejection and high water flux.²⁶ Recent fundamental studies of these linear copolymers have investigated the trade-off between salt rejection and permeability,^{27–29} effect of free volume on transport properties,³⁰ influence of processing history, and the ability to fabricate these materials into thin-film composite membranes.^{31,32} Polymers with higher levels of sulfonation were more hydrophilic and had higher water flux. However, the ionic regions swelled significantly in water, leading to increased salt diffusion and lower salt rejection.

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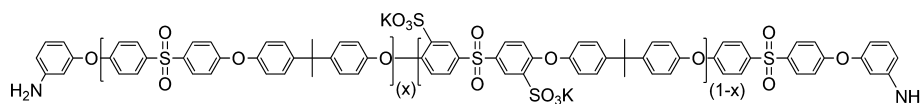


Figure 1. Structure of amine-end-capped bisphenol A based 50% disulfonated polysulfone copolymer.

Cross-linked networks limits the swelling associated with increased levels of sulfonation.³³ Electrostatic physical cross-linking of polysulfones can be accomplished by incorporating complementary acidic and basic units in the polymer backbone.^{34–37} However, covalent cross-links are less environmentally sensitive^{38,39} and are more stable in an RO environment. Polysulfones have also been covalently cross-linked along the backbone of the polymer chain. Early work involved activation with diimidazole,⁴⁰ disproportionation of acid,⁴¹ or S-alkylation of sulfinate groups,^{42,43} all of which consumed sulfonate groups. More recently, main chain cross-linking was accomplished by reacting pendant hydroxyl groups with dihaloalkanes,⁴⁴ sulfonic acid groups with poly(vinyl alcohol),⁴⁵ and thermally curable allylic groups.⁴⁶ An alternative method to produce covalently cross-linked polysulfones synthesized oligomers with telechelic end groups and then linked together chain ends into a network. One advantage of this approach is that oligomeric materials are more soluble and easily processed than their high molecular weight counterparts.⁴⁷ Several oligomers have been synthesized including thermally curable ethynyl,^{47,48} allyl,⁴⁹ and propargyl⁴⁹ end groups but with varying backbone structures and acidified forms for investigation as fuel cell materials. The first desalination studies with telechelic oligomers involved the cross-linking of phenoxide end groups with a tetrafunctional epoxide.³³ Gel fractions up to 85% were obtained, and the reduced swelling drastically improved the desalination properties of these materials.

The present investigation has developed the synthesis of a novel sulfonated polysulfone oligomer with telechelic amine end groups. In addition, this amine terminated oligomer was used to synthesize acrylamide, 4-phenylethynyl phthalimide, and maleimide termination with a constant polymer backbone structure. The properties of these materials as a function of cross-linking conditions and film fabrication were investigated and reported in this paper. The need for residual casting solvent during oligomeric cross-linking to reduce the T_g of these polymeric glasses was affirmed. Two oligomers capable of large-scale ductile film formation were identified for further development. The acrylamide terminated oligomers were also photochemically initiated to afford cross-linking at room temperature, a first for sulfonated polysulfone oligomers. The amine terminated oligomers were cross-linked to over a 99% gel fraction. This value is the highest reported value for such sulfonated polysulfone oligomers. Initial transport results demonstrate that water/NaCl selectivity is drastically improved as a function of cross-linking, especially at high gel fractions. This paper, part I, focuses on the synthesis, characterization, and fabrication of these cross-linkable materials; part II is investigating the influence of cross-linking, degree of sulfonation, and oligomer backbone structure on water transport properties and will be reported later.

EXPERIMENTAL SECTION

Materials. 4,4'-(Propane-2,2-diyl)diphenol (BisA) and 4,4'-dichlorodiphenylsulfone (DCDPS, 99%) were kindly provided by Solvay and recrystallized from toluene before use. The 3-

aminophenol (*m*-AP, 99%) monomer and *N,N*-dimethylacetamide (DMAc, 99%) were purchased from Acros Organics. The DMAc reaction solvent was dried with calcium hydride (CaH_2), distilled under reduced pressure, and stored under molecular sieves before use. Calcium hydride (90–95%) was purchased from Alfa Aesar. *N,N*-Dimethylformamide (DMF) was purchased from Spectrum. Akron Polymer Systems (Akron, OH) kindly provided 4-phenylethynylphthalic anhydride (4-PEPA) and 3,3-disulfonated-4,4'-dichlorodiphenylsulfone (SDCDPS, 98%) prepared using procedures developed earlier.^{50,51} 1,2-Dichlorobenzene (*o*-DCB, anhydrous), 2-propanoyl chloride (acryloyl chloride, 96%), triethylamine (TEA, 99.5%), potassium carbonate (K_2CO_3 , 99%), maleic anhydride (99%), 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%), pentaerythritol tetraacrylate (PETA), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), triphenylphosphine (TPP, 99%), and tetraglycidyl bis(p-aminophenyl)methane (TGBAM, 92%³³) were purchased from Aldrich. Toluene, cyclohexane, 2-propanol (IPA), 1-methyl-2-pyrrolidone (NMP), and bis(1-methyl-1-phenylethyl) peroxide (DCP, 99%) were purchased from Fisher Scientific.

Synthesis. *Synthesis of a Controlled 5,000 Molecular Weight (M_n) Amine-End-Capped Bisphenol A Based 50% Disulfonated Polysulfone Copolymer (am-BisAS50).* The precursor oligomer (Figure 1) was produced by nucleophilic aromatic substitution step polymerization,^{52,53} which directly incorporated the sulfonated monomer into the backbone.

Prior to the reaction, it was necessary to dry the hydroscopic SDCDPS for 72 h at 160 °C under vacuum to ensure removal of moisture. SDCDPS contains some NaCl impurities remaining from monomer synthesis, which were quantified using UV–visible light spectroscopy.⁵¹ BisA (43.6 mmol, 9.9534 g), DCDPS (25 mmol, 7.1790 g), SDCDPS (25 mmol, 12.6611 g), *m*-AP (12.7 mmol, 1.3999 g), and DMAc (130 mL) were added to a 250-mL three-necked flask. The reaction flask was equipped with a mechanical stirrer, nitrogen inlet, and Dean–Stark trap filled with toluene. A stirring, thermocouple regulated, oil bath was used to heat the reaction mixture to 155 °C. After the bath temperature reached 155 °C, K_2CO_3 (78.48 mmol, 10.8467 g) was added with toluene (65 mL). The reaction was stirred at 155 °C until all water was azeotropically removed with toluene. The temperature was then increased to 175 °C, and water and toluene were drained. After 48 h, the amber opaque solution was cooled to room temperature and filtered. The resulting transparent solution was precipitated in isopropyl alcohol (IPA) as a white solid. The copolymer was filtered, washed with IPA, and dried in a vacuum oven at 120 °C for one day.

Conversion of Amine-End-Capped Oligomers to Acrylamide-End-Capped Oligomers (AA-BisAS50). Am-BisAS50 (0.517 mmol, 3.000 g) was dissolved in DMAc (45 mL) in a 100-mL round-bottom flask. The flask was sealed with a septum and flushed with nitrogen and placed in an ice bath. Triethylamine (TEA, 10 mmol, 0.5856 g) was added via syringe as an acid scavenger. An excess of acryloyl chloride (3.47 mmol, 0.3143 g) dissolved in DMAc (5 mL) was added slowly via syringe, resulting in an opaque solution. The reaction

was allowed to proceed for 4 h. Polymer isolation and drying was the same as described earlier.

Conversion of Amine-End-Capped Oligomers to 4-Phenylethynyl Phthalic Anhydride-End-Capped Oligomers (PEPA-BisASSO). 4-PEPA terminated oligomers were synthesized via a two-step amic-acid route previously reported for the synthesis of polyetherimides.⁵⁴ The am-BisASSO (2.08 mmol, 10.000 g) was dissolved in DMAc (67 mL) in a 250-mL three-necked flask. The reaction flask was equipped with a mechanical stirrer, nitrogen inlet, and Dean–Stark trap. The solution was heated to 130 °C, and cyclohexane (22 mL) was added and refluxed for 4 h. The trap was drained, and the flask was cooled to room temperature. 4-PEPA (4.38 mmol, 1.086 g) was added and stirred for 3 h, resulting in a pale yellow solution. For cyclodehydration, the trap was filled with *o*-DCB, and additional *o*-DCB (15 mL) was added directly to the flask. The temperature was increased to 150 °C for 30 min and then to 180 °C for 24 h. Polymer isolation and drying was the same as described earlier.

Conversion of Amine-End-Capped Oligomers to Maleic Anhydride-End-Capped Oligomers (MA-BisASSO). Reactions to afford maleimide terminated oligomers involved a two-step amic-acid route, previously reported.⁵⁵ The reaction conditions and apparatus were similar to those used for the synthesis of PEPA-BisASSO. The am-BisASSO (1 mmol, 5 g) was dissolved in DMAc (50 mL), and then maleic anhydride (3 mmol, 0.2942 g) was added and stirred for 6 h. The reaction was heated to 130 °C, the final reflux temperature and cyclodehydrated at 130 °C with *o*-DCB (10 mL) overnight. Product isolation and drying was the same as described earlier.

Film Casting and Curing. Amine Terminated Oligomers. A mixture of am-BisASSO (0.1633 mmol, 0.8 g), TGBAM (0.4083 mmol, 0.1917 g), and TPP (0.0187 mmol, 0.0049 g) were dissolved in DMAc (12 mL) and stirred until a homogeneous solution was obtained. The solution was syringe filtered through a 0.45 μm PTFE filter. It was cast on a clean glass plate on a level surface inside a vacuum oven and dried under vacuum for 2 h at 100 °C. Vacuum was released, and the oven was heated to the cross-linking temperature (150–160 °C) for 90 min.

4-Phenylethynyl Phthalimide Terminated Oligomers. The PEPA-BisASSO (0.36 mmol, 1.8 g) was dissolved in NMP (15 mL) and stirred until a homogeneous solution was obtained. The solution was syringe filtered through a 0.45 μm PTFE and sonicated for two 60 min cycles to facilitate removal of dissolved gas. A glass plate was wrapped with aluminum foil to reduce adhesion of the cured membrane to the glass surface. The oligomeric solution was cast on this surface, placed on a level hot plate, and covered with a glass dish that contained a nitrogen inlet and outlet. A nitrogen flow was applied, and the plate was heated to 180 °C. The hot plate was held at this temperature until the solution could no longer flow. The hot plate was then slowly heated to a temperature of 360 °C where it was cured for one hour.

Maleimide Terminated Oligomers. MA-BisASSO (0.16 mmol, 0.8 g) was dissolved in DMAc (12 mL) and stirred until a homogeneous solution was obtained. The solution was syringe filtered through a 0.45 μm PTFE and sonicated for two 60 min cycles to facilitate removal of dissolved gas, cast on a clean glass plate, and dried under an infrared lamp until it could no longer flow. The membrane was then inserted into a forced air oven (Type 47900 Furnace, Thermolyne) at 300 °C under a

nitrogen atmosphere. The film was cured for 1 h at this temperature.

Acrylamide Terminated Oligomers. The AA-BisASSO (0.2 mmol, 1.000 g), PETA (0.1 mmol, 0.035 g), and DMF (2 mL) were stirred thoroughly to form a homogeneous mixture. DMPA UV initiator (2 wt % of total mass, 15–20 mg) was added into the mixture and stirred thoroughly. The solution was cast on a 5 \times 7.5 cm glass slide and placed in a Spectronics Corp. model XL-1000 UV cross-linker three times for 360 s to achieve photocross-linking. The typical intensity of the UV irradiation was between 3,500 and 4,500 $\mu\text{W cm}^{-2}$.

Polymer Characterization. Nuclear Magnetic Resonance Spectroscopy (NMR). ¹H NMR analysis of the oligomers was performed on a Varian Unity Plus spectrometer and a Varian Inova spectrometer, both operating at 400 MHz. The spectra of the oligomers were obtained from a 15% (w/v) 1 mL solution in DMSO-*d*₆.

Thermogravimetric Analysis (TGA). Thermal stability of the polymers in the range of their curing temperatures was probed using a TGA Q500 (TA Instruments). The samples were heated to at least 150 °C, held isothermally for 10 min to remove any ambient water, and then heated to 500 °C at 10 °C min^{−1} under nitrogen.

Differential Scanning Calorimetry (DSC). The glass transition temperatures (*T*_g) and curing exotherms of the oligomers were obtained with a DSC Q200 (TA Instruments). The effect of solvent plasticization of the curing temperature was investigated with oligomers that were solution cast, dried until the material would not flow, and collected into high volume pans capable of withstanding high pressures (TA Instruments). The solvent plasticized oligomers were heated at 10 °C min^{−1} to 300 °C. Baseline corrections were applied to the heating curves obtained for the solvent plasticized oligomers, and thus the first derivative of the heating curve was used to quantify *T*_g's and cure temperatures.

Water Uptake. Films were dried at 120 °C under vacuum overnight, then removed, and weighed to obtain the dry weight (*W*_{dry}). Next, they were immersed in DI water for at least 48 h. The films were removed, quickly blotted dry to remove any water droplets, and weighed to obtain the wet weight (*W*_{wet}). Water uptake values were calculated by eq 1.

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

Gel Fractions. Gel fractions were performed to estimate the extent of cross-linking. Cross-linked films were dried at 120 °C under vacuum overnight. Then 0.1–0.2 g of initial sample was placed in a 20 mL scintillation vial filled with DMAc and stirred at 100 °C overnight. The remaining solid was filtered, transferred to a preweighed vial, and dried at 120 °C under vacuum overnight. The final weight was taken the next day. Gel fraction values were calculated by eq 2.

$$\text{Gel Fraction (\%)} = \frac{W_{\text{initial}} - W_{\text{final}}}{W_{\text{final}}} \times 100 \quad (2)$$

Initial Investigations of Water Transport Properties. The water permeability (L $\mu\text{m m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ or $\text{cm}^2 \text{s}^{-1}$), salt permeability ($\text{cm}^2 \text{s}^{-1}$), salt rejection (%), and water/NaCl selectivity were determined at 25 °C in a previously described cross-flow filtration system using stainless steel crossflow cells machined at the University of Texas at Austin.⁵⁶ The pressure difference across the membrane (15.1 cm^2) is listed in Table 1.

Table 1. Effect of Cross-Linking on Water Permeability, NaCl Rejection and Permeability, and Water/NaCl Selectivity for BisAS60 Films^a

sample	gel fraction (%)	water uptake (%)	pressure (psi)	water permeability (L $\mu\text{m}/\text{m}^2$ h bar)	NaCl rejection (%)	water permeability ($\times 10^{-6}$, cm^2/s)	NaCl permeability ($\times 10^{-9}$, cm^2/s)	water/NaCl selectivity
BisAS60	0	48	400	4.2 ± 0.6	88.1 ± 1.5	15.9 ± 2.3	43.5 ± 10.5	366
5k-am-BisAS60	45.1	26.8	200	1.2	91.8	4.4	7.7	580
5k-am-BisAS60	93.0	26.6	400	0.8 ± 0.1	97.1 ± 0.2	3.2 ± 0.2	1.9 ± 0.3	1700
SW30HR-380	-	-	800	0.05^b	99.7^b	-	-	-

^aThree samples were used to obtain these average values, except for the mechanically weak 45% gel fraction material which yielded one measurement. ^bCommercial aromatic polyamide membrane,⁶⁹ test conditions: 32,000 mg L^{-1} , 25 °C. Value is usually listed as 0.5 (L/ m^2 h bar) and was converted to 0.05 (L $\mu\text{m}/\text{m}^2$ h bar) by assuming a thickness of 0.1 μm

The aqueous feed contained 2000 ppm NaCl, and the feed solution was circulated past the samples at a continuous flow rate of 3.8 (L min^{-1}). The feed pH was adjusted to a range between 6.5 and 7.5 using a 10 g/L sodium bicarbonate solution. NaCl concentrations in the feedwater and permeate were measured with an Oakton 100 digital conductivity meter.

RESULTS AND DISCUSSION

Oligomer Synthesis. The bisphenol monomer used was BisA instead of 4,4'-biphenol (Figure 2). BisA is more

**Figure 2.** Bisphenol A (left) and 4,4'-biphenol (right).

chemically reactive than 4,4'-biphenol and contains the 2,2'-isopropylidene moiety in the middle of the molecule. This tetrahedral bond linkage leads to a lower density copolymer compared to a copolymer containing the less flexible 4,4'-biphenol. For example, the density of BisA polysulfone (Udel) is lower than that of 4,4'-biphenol based polysulfone (Radel). Initial unreported work in our group supports that this phenomenon remains true for the sulfonated copolymers. The lower density of BisA copolymers should lead to higher fractional free volume and thus more volume available for water transport.³⁰ The fractional free volume has been related mathematically to diffusion and permeability coefficients.⁵

The synthesis of am-BisAS50 shown in Figure 3 was performed using nucleophilic aromatic substitution with a weak base.⁵² A monofunctional amine *m*-AP was added in amounts calculated by the modified Carothers equation⁵⁷ to target a number average molecular weight of 5,000 g mol^{-1} and to provide functional aromatic amine end groups. Previous telechelic oligomers were synthesized by adding an excess of the diol, which produces a relatively unstable *p*-phenoxide terminated species. Thus, the *m*-AP end group greatly extends the shelf life of these oligomers.

Toluene was used as the azeotropic solvent, removing any water sorbed by the monomers during weighing and also water formed by K_2CO_3 decomposition products. The water/toluene azeotrope appeared as a cloudy layer in the condenser of the Dean–Stark trap. Refluxing was continued until no more water was observed in the distillate. During the azeotropic period of the reaction, it was important to periodically use a heat gun to dry the joints connecting the three-necked flask to the Dean–Stark trap. The temperature was raised slowly to the final

reaction temperature by heating the oil bath to 175 °C, and then toluene was slowly removed until the initial charged volume was collected. The reaction appeared unchanged in viscosity after 24 h and slightly more viscous after 48 h. Since the molecular weight of these copolymers was targeted at 5,000 g mol^{-1} , no drastic change in viscosity was anticipated or observed. The solution appeared off-white or wheat colored near the reactions end, compared to BisA phenoxide end groups that impart a dark green color to the solution.

The nucleophilic substitution reaction that converted am-BisAS50 to AA-BisAS50 (Figure 3) occurred very rapidly; thus, the reaction flask was cooled to 0 °C before addition of TEA and acryloyl chloride. The am-BisAS50 was dried overnight under vacuum to remove ambient water sorption, as water could also react with the acryloyl chloride.

The synthesis of the high temperature curing oligomers PEPA-BisAS50 and MA-BisAS50 is also shown in Figure 3. The anhydride was added at lower temperatures because the ring-opening reaction and formation of the amic-acid intermediate does not require elevated temperatures. ¹H NMR was used to monitor the ring-opening reactions by taking hourly aliquots of the reaction solution. The appearance of amic-acid peaks at 10.5 ppm indicated formation of the intermediate species, and the disappearance of the amine end groups were used to judge sufficient reaction time for the first step. Similarly, sufficient time for cyclodehydration was found by monitoring the disappearance of the amic-acid intermediate.

Oligomer Characterization. The am-BisAS50 oligomer was characterized for degree of sulfonation (D.S.), M_n , and purity by ¹H NMR. The ¹H NMR spectrum of the am-BisAS50 oligomer is shown in Figure 4. The solid sample completely dissolved in DMSO- d_6 , and the spectrum showed no side products, residual monomer, or solvent. The D.S. was calculated by eq 3. The measured D.S. was 49%, compared to the targeted D.S. of 50%.

$$\text{D.S.} = \frac{[(H_a + H_B + H_c)/3]/2}{[(H_a + H_B + H_c)/3]/2 + [(H_f + H_g)/2]/4} \quad (3)$$

The chemical shifts of the *m*-AP end groups differ depending on whether they are linked to DCDPS or SDCDPS. The *m*-AP end groups adjacent to DCDPS occur at a slightly more downfield position compared to the SDCDPS linkage, and these closely related singlets (i) give the appearance of a doublet. The M_n calculated by ¹H NMR was 4,800 g mol^{-1} , determined by comparing the integration values of the amine end groups (i) to the aromatic BisA peaks in the oligomer

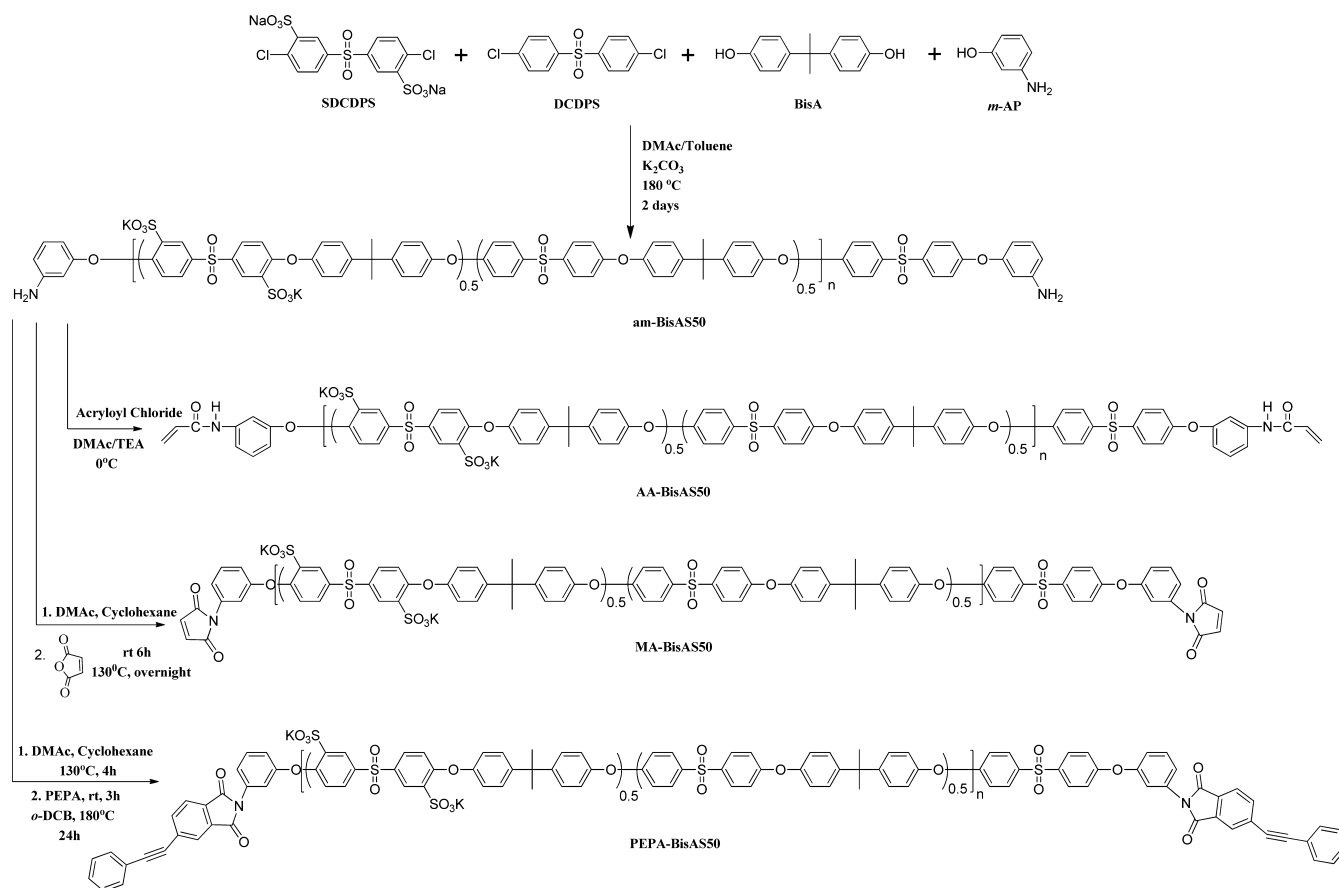


Figure 3. Synthetic schemes for am-BisAS50, AA-BisAS50, MA-BisAS50, and PEPA-BisAS50.

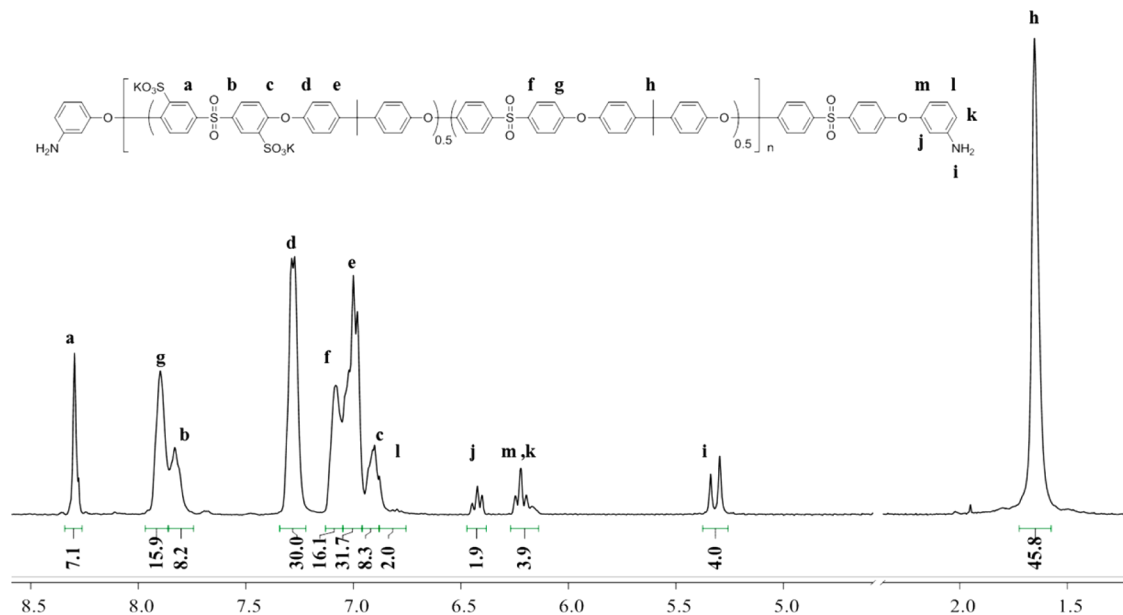


Figure 4. 1H NMR of am-BisAS50.

backbone (d+e). Calculation of M_n by this method assumes that there is no other end group species in the oligomer, the only other candidate being BisA end groups. This assumption was considered reasonable, since the 1H NMR spectrum of a control reaction to produce $5,000\text{ g mol}^{-1}$ BisA terminated oligomer had strong end group peaks at 6.64 ppm, which are not observed in this spectrum.

The end group characterization for the further functionalized oligomers was also accomplished with 1H NMR. The aromatic regions in Figure 5 are expanded to highlight the differences in end group structure. The complete disappearance of the amine peak was observed in AA-BisAS50, MA-BisAS50, and PEPA-BisAS50. This indicated complete end group conversion for AA-BisAS50. The absence of amic-acid intermediate peaks at

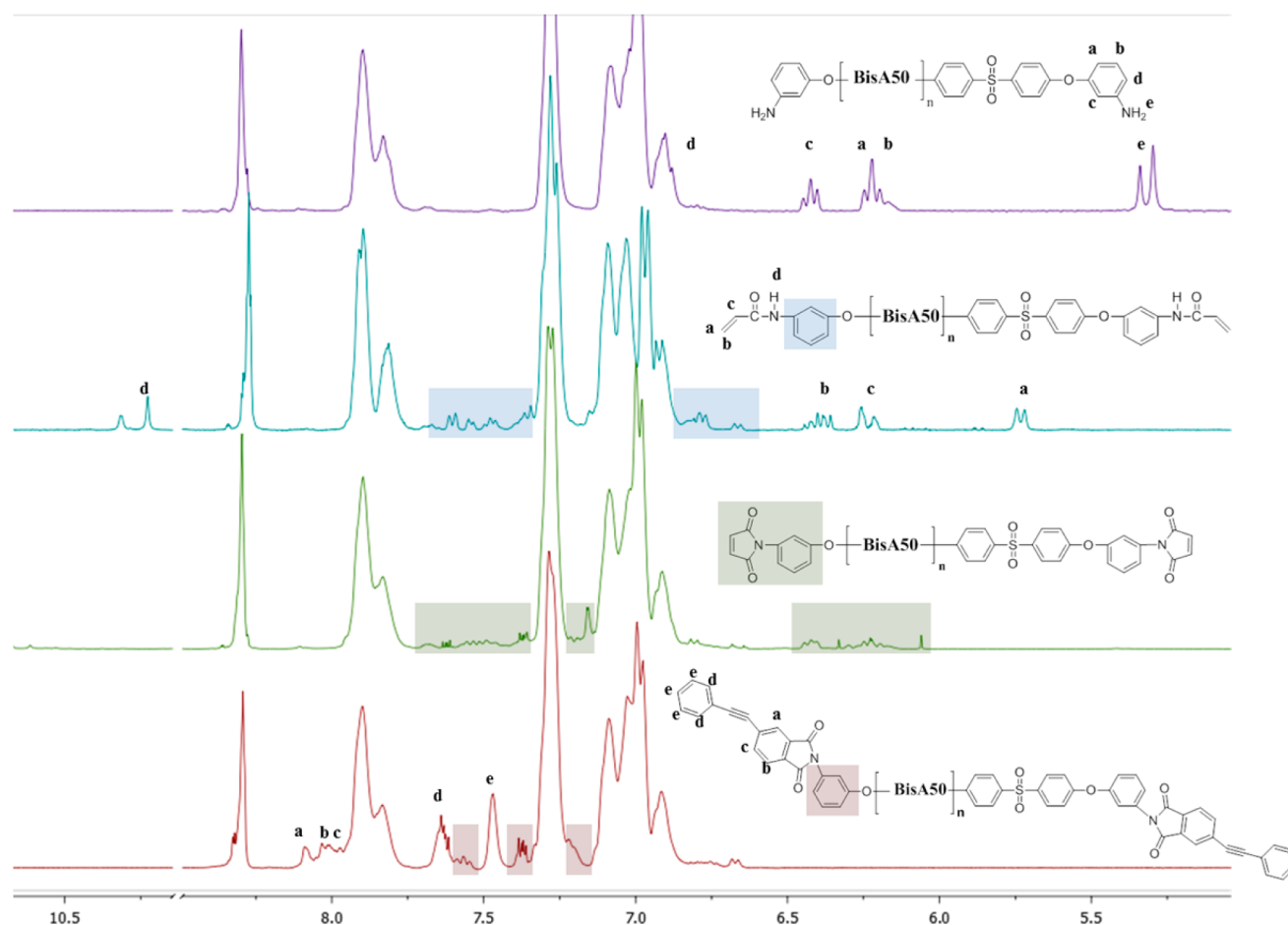


Figure 5. ^1H NMR comparison of am-BisAS50 starting oligomer shows complete conversion to further functionalized end groups.

10.5 ppm indicated complete end group conversion and successful cyclodehydration for MA-BisAS50 and PEPA-BisAS50. Comparison of the final spectra to reagent ^1H NMR showed no residual starting material left. The end group peak assignment of AA-BisAS50 and PEPA-BisAS50 was well-defined and integrated out to appropriate values when compared to the starting oligomer. The end group peak assignment of MA-BisAS50 was more difficult, because the maleic anhydride end groups overlap with backbone peaks in the aromatic region.⁵⁵

Thermal Stability of the Oligomers. TGA studies were performed under N_2 at $10\text{ }^\circ\text{C}/\text{min}$ to ensure that the oligomers were stable at high temperatures. This step is particularly important for ruling out oligomer degradation as a cause for exotherms observed in DSC heating curves. Figure 6 shows that all of the oligomers had less than 1% weight loss in the range of 200 to 375 $^\circ\text{C}$. The oligomers showed similar thermal behavior to high molecular weight BisAS50, denoted as BisAS50 Control in Figure 6. The degradation temperature for this series was taken at values of 10% weight loss: 480 $^\circ\text{C}$ for the BisAS50 control, 470 $^\circ\text{C}$ for PEPA-BisAS50, 460 $^\circ\text{C}$ for am-BisAS50, and 440 $^\circ\text{C}$ for MA-BisAS50. These weight losses occur in the range expected for desulfonation, the primary mechanism for initial sulfonated polysulfone degradation.²³ All of these degradations occurred well above the curing temperatures investigated.

Investigation of Oligomer Cross-Linking Temperature. The determination of T_g for ionomers such as

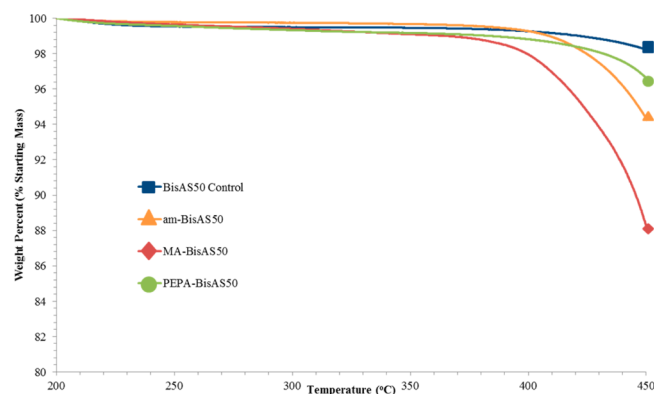


Figure 6. TGA shows that the oligomers are thermally stable in nitrogen at the curing conditions.

sulfonated polysulfones is not trivial. At high levels of sulfonation, the glass transition temperature becomes hard to distinguish from the baseline.⁵⁸ Because of the aforementioned phenomenon, the first derivative of the heating curve was used, and the T_g 's were reported as the endothermic maxima. Previous work established the importance of cross-linking these high T_g copolymers in the presence of water and/or a high boiling point solvent. The T_g of a $5,000\text{ g mol}^{-1}$ 4,4'-biphenol based 50% sulfonated polysulfone (ph-BPSS0) was lowered by over $100\text{ }^\circ\text{C}$ in the presence of NMP, enabling cross-linking at $150\text{ }^\circ\text{C}$.³³ The oligomers in this study are well below the entanglement molecular weight and cannot produce free-

standing films without cross-link formation. The formation of these materials into a coherent ductile film is necessary for use as separation membranes. DSC studies were performed in pressurized pans on oligomers with a significant amount of DMAc left to plasticize their T_g 's and afford cross-linking. The heating curves of the solvent plasticized oligomers are shown in Figure 7.

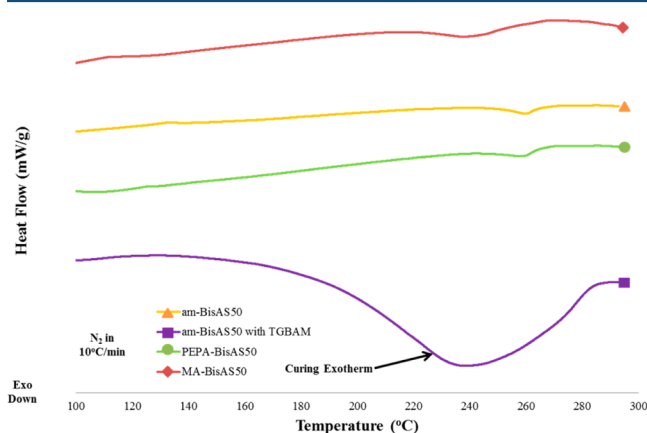


Figure 7. DSC thermogram comparison of solvent plasticized oligomers demonstrates that the epoxy cured system cross-links at a much lower temperature than MA-BisAS50 and PEPA-BisAS50.

The only oligomer to show strong evidence for cross-linking behavior was the am-BisAS50 with tetra-epoxide (TGBAM). Cross-linking in this system began at 140 °C and had a maximum rate at 208 °C. This curing behavior was not observed in the am-BisAS50 spectrum without TGBAM, as expected. The am-BisAS50 spectrum displayed a small

endothermic maximum at 125 °C, possibly a solvent plasticized T_g . The am-BisAS50 spectrum did have large endothermic maxima at 261 and 283 °C; no exotherm was observed after these T_g 's. PEPA-BisAS50 showed a solitary T_g at 260 °C and gave no indication of an exotherm afterward. MA-BisAS50 showed a solitary T_g at 247 °C with some indication of an exotherm occurring after 270 °C.

The results from the solvent plasticized oligomer heating curves prove that curing am-BisAS50 with TGBAM occurs at much more facile conditions than MA-BisAS50 and PEPA-BisAS50. The T_g of the am-BisAS50 cured with TGBAM was raised 15 °C, as cross-links formed and restricted oligomer chain mobility. The cessation of the cross-linking reaction between 210 and 240 °C may be a result of a complete loss of the solvent DMAc, which has a boiling point of 165 °C.

Cross-Linking and Film Fabrication of am-BisAS50.

The cross-linking reaction between am-BisAS50 and TGBAM (Figure 8) was optimized to produce large ductile films with high extents of cross-linking. Small-scale films were prepared with varying molar ratios of TGBAM to determine which stoichiometry gave the highest gel fraction. These results are compared with the previous ph-BPS50 curing in Figure 9.³³

The phenoxide terminated oligomers produced a maximum gel fraction at 2.1 mol equiv of TGBAM. The amine terminated oligomers did not have a distinct maximum and continued to trend upward with increasing epoxy concentration. This is possibly because the functionality of ph-BPS50 toward epoxy is 2 and for am-BisAS50 it is 4. The reactions of amines with glycidyl ethers are primary amine addition (**1**), secondary amine addition (**2**), and etherification (**3**),⁵⁹ all shown in Figure 8. The kinetics of these competing reactions has been modeled in the literature.⁵⁹ Primary amine addition occurs 2–10 times as quickly as secondary amine addition. Etherification has the

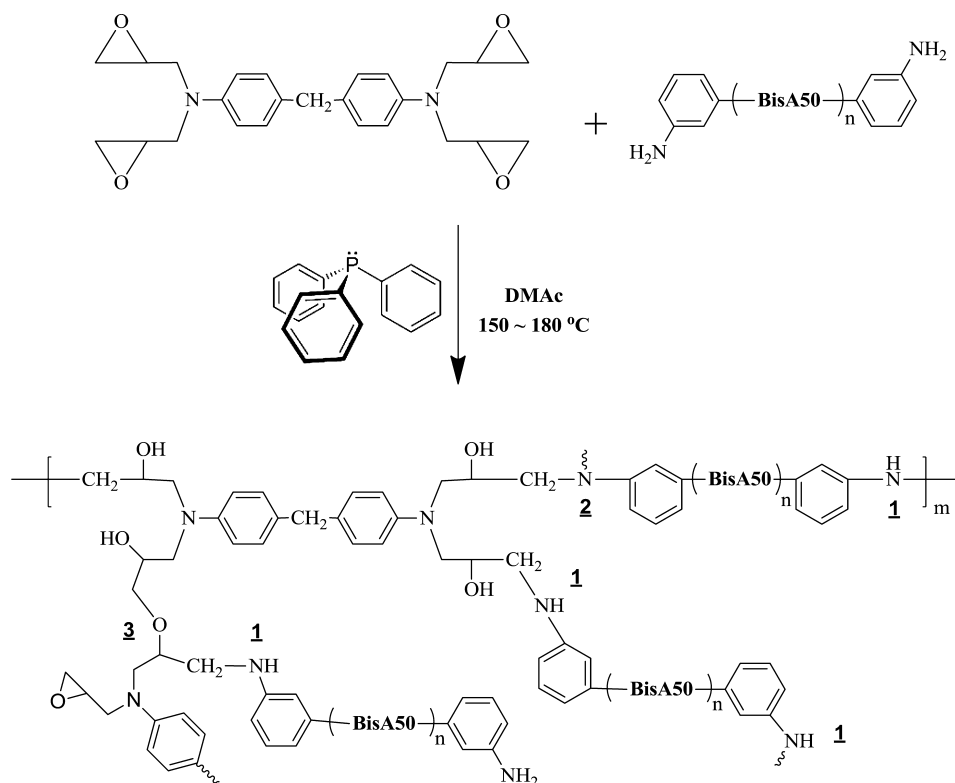


Figure 8. Schematic for cross-linking am-BisAS50 with TGBAM in the presence of TPP results in various linkages and some unreacted end groups.

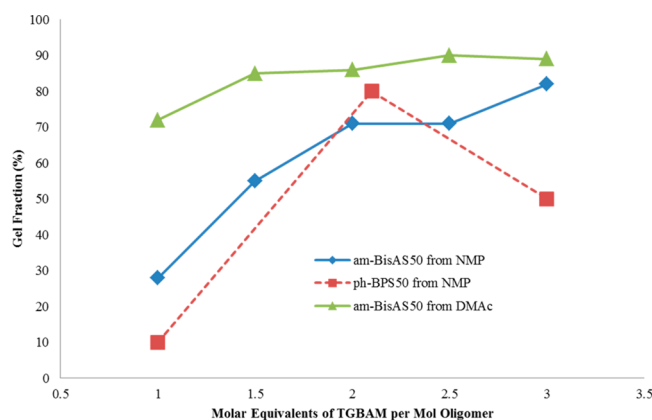


Figure 9. Optimal stoichiometry of TGBAM varies for phenoxide and amine terminated 5,000 Mn oligomers.³³

lowest reaction rates and only occurs when the primary amines have all reacted. The soluble filtrates from gel fraction tests were also analyzed by ^1H NMR to determine remaining unreacted material. The sample prepared from a 3 mol equiv of TGBAM contained excess epoxy, thus the optimal molar equivalency of TGBAM was taken to be 2.5. Figure 9 shows that the 2.5 molar equivalency sample had a gel fraction of 90%, and gel fractions up to 99% were obtained when the films were increased in size for transport testing. These are the highest reported gel fractions for sulfonated polysulfone oligomers to our knowledge.

Several other variables were investigated to determine effect on final gel fractions. Both DMAc and NMP have been utilized as solvents for this curing reaction and produced similar results, though films from DMAc had higher gel fractions. TPP was added in catalytic amounts to lower the onset of the curing exotherm. The kinetics of this reaction has been studied for epoxies and phenolic resins where it lowered cure temperatures by over 40 °C.⁶⁰ Varying the weight percent of TPP (relative to g TGBAM) from 0 to 2.5 to 5% had no impact on gel fraction. Increasing both the curing time and temperature improved gel fractions, and 90 min at 150–160 °C was sufficient to obtain a high extent of cross-linking.

Removal of the cross-linked film from the glass substrate was not trivial. It is hypothesized that epoxy reacts with both the glass surface and the oligomer. Silanation of the glass surface decreases the reaction of epoxy with glass but caused the film to shrink as it dried. This problem was circumvented by soaking the cross-linked film and glass plate in a stirring solution of dilute K_2CO_3 dissolved in DI water. The weak base conditions had no effect on resulting gel fraction. After several days, the bonds between the film and glass plates were reduced and allowed for easy removal.

Cross-Linking and Film Fabrication of PEPA-BisAS50.

High gel fractions were consistently obtained with PEPA-BisAS50, though large film fabrication was unsuccessful. The resulting deep brown membrane had several bubbles that disrupted the otherwise smooth surface. In addition to the procedure outlined in the Experimental Section, films were cast on glass substrates and cured in a Type 47900 Furnace or melt press. The final cure temperatures were in the range of 330–380 °C, producing blackened brittle materials that adhered to the casting surface and had gel fractions of over 90%. The best films obtained required a careful stepwise heating regimen using a hot plate. These films also had gel fractions over 90%,

but bubble formation occurred between 200 and 300 °C and disrupted the otherwise smooth surface area of the film. These results are consistent with the DSC heating curves, which indicated that the cure temperature was not sufficiently depressed and that solvent rapidly evaporated from the films while heating to the cure temperature. In other literature studies, the cure temperature of PEPA terminated polyetherimides was in the range of 345–360 °C despite a T_g of 200 °C, much lower than these sulfonated polysulfones.^{54,61,62} Additionally, the curing of polyetherimides occurred above their melt temperature, whereas the PEPA terminated sulfonated poly(arylene ether sulfone) copolymers cure before any melt behavior is observed. Kinetic and mechanistic studies of the phenylethynyl curing reaction reported a minimum cure temperature of 318 °C, and the reaction proceeded slowly under these conditions.⁶³

Cross-Linking and Film Fabrication of MA-BisAS50.

The cross-linking results of MA-BisAS50 were similar to those of PEPA-BisAS50; high gel fractions were obtained, and ductile film formations were not. The membrane produced from curing at 300 °C in the forced air oven was free-standing but very brittle. This material was wholly soluble in the casting solvent. The membrane was further cross-linked for 30 min by melt press at 330 and 380 °C. The 330 °C cured membrane was partly soluble in gel fraction studies. The 380 °C cured membrane was completely insoluble but broke into many pieces when removed from the glass plate. Even if large cross-linked membranes of this oligomer could be fabricated, their inherent brittleness would prohibit use in high pressure water purification operations.

Cross-Linking and Film Fabrication of AA-BisAS50.

The thermal cross-linking of AA-BisAS50 without initiator was attempted, resulting in cracked membranes with $11.5 \pm 1.5\%$ gel fraction. The curing of the AA-BisAS50 oligomer was also attempted via thermally initiated free radical polymerization. AIBN was charged to polymer solutions in 0.5, 3, 5, 10, and 20 wt % relative to AA-BisAS50. The membranes were dried and cured at 100 °C for 12 h, resulting in extremely brittle membrane formation with no gel fraction. DCP was charged to polymer solutions in 1, 3, and 5 wt % relative to AA-BisAS50. This system was cured at 140 °C, 160 °C, and 200 °C for several hours in a systematic series of experiments, all of which resulted in no membrane formation.

The successful cross-linking of AA-BisAS50 was photochemical, opposed to the thermal curing of the other oligomers. DMPA is a well-known initiator for photochemical reactions, and its efficiency and mechanism have been elucidated.^{64,65} Benzophenone initiators readily react with acrylates^{66,67} and successfully cross-linked AA-BisAS50 with PETA. The resulting transparent films were free-standing and ductile. The role of PETA equivalency was studied in a comparative test to am-BisAS50 and TGBAM. The molar equivalents of PETA to AA-BisAS50 ranged from 0.5 to 2.5, and gel fractions of up to 58% were obtained. However, no logical trend in cross-linker concentration to gel fraction was observed. We determined that the UV cross-linker used did not have sufficient intensity to penetrate the 30–40 μm thick films. Future research into this oligomers photochemical cross-linking is planned with a higher intensity UV cross-linker that can sufficiently penetrate the films thickness.

Effect of Gel Fraction on Water Uptake. The ultimate importance of cross-linking these oligomeric materials are to reduce the high degree of membrane swelling and sorption.

The effect of cross-linking on water uptake was studied by curing am-BisAS50 oligomer with 2.5 mol equiv of TGBAM. The oligomer was cured for 0, 10, 20, 45, 60, and 90 min at 150 °C. The samples cured for 0 and 10 min did not give free-standing films because of the low extent of cross-linking. The water uptake of the samples was measured before the gel fractions, with data plotted in Figure 10.

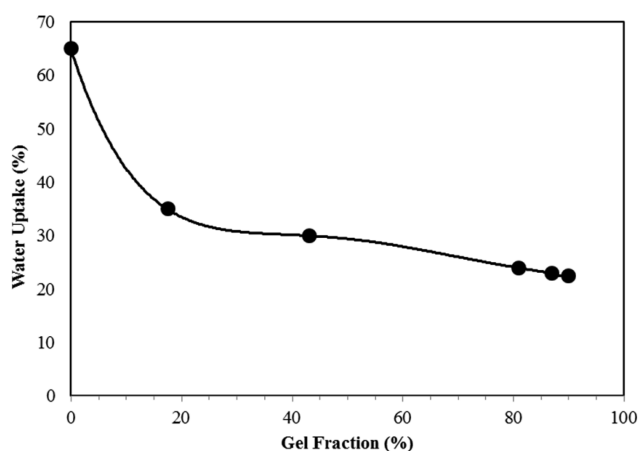


Figure 10. Water uptake of am-BisAS50 decreases rapidly and then plateaus as a function of increasing cross-linking with TGBAM.

The water uptake of the films quickly dropped during the initial stages of cross-linking, which was similarly observed in the previous studies with ph-BPS50.³³ After the initial drop, water uptake plateaus, decreasing slowly to 90% gel fraction. The water uptake for the un-cross-linked am-BisAS50 was much higher than the BisAS50 control (35%), possibly because of the additional hydrophilic amine end groups on the oligomer. The water uptake can be taken as proportional to the free volume of the polymer and by extension related to water partition and permeability coefficients.⁶⁸ The loss in water permeability corresponds to an increase in water/NaCl selectivity, in accordance with fundamental trade-off relationships.²⁹

Initial Transport Results. The effect of cross-linking on the trade-off relationship between water permeability and water/NaCl selectivity was investigated with preliminary cross-flow filtration experiments. The amine terminated oligomers were synthesized with a 60% degree of sulfonation to produce a material more hydrophilic than am-BisAS50. This oligomer (5k-am-BisAS60) was fabricated into large scale membranes at 45 and 93% extents of cross-linking. These cross-linked oligomers are listed with a high molecular weight linear control at the same level of sulfonation (BisAS60) and the state-of-the-art polyamide (SW30HR-380) material in Table 1. It is germane to note that water permeability standardizes these films for thickness when reported in ($L \mu m/m^2 h bar$) but that the state-of-the-art material has a submicrometer film thickness while the dense cross-linked materials are in the range of 40–50 μm . The fabrication of sulfonated poly(arylene ether sulfone)s into films with a submicrometer thickness is currently being investigated.

The results clearly demonstrate that the water/NaCl selectivity greatly increases as the material becomes highly cross-linked and, in accordance with trade-off relationships, that the water permeability decreases. The cross-linked membrane with a 45% gel fraction was much less ductile than the

membrane with a 93% gel fraction. Thus, the 45% gel fraction membrane was run at a reduced trans-membrane pressure during cross-flow experiments compared to the linear control and highly cross-linked material. The NaCl rejection is not comparable for membranes tested at different pressures. Increasing the pressure will increase the water flux but will not substantially influence the salt flux, thus higher pressures will increase the NaCl rejection.⁷⁰ However, the water permeability and salt permeability ($cm^2 s^{-1}$) and water/NaCl selectivity are intrinsic membrane properties and are comparable across varying pressures. The conversion of hydraulic water permeability ($L \mu m m^{-2} h^{-1} bar^{-1}$) to diffusive permeability ($cm^2 s^{-1}$) has been detailed in previous studies.²⁹

The results across the intrinsic membrane properties vary greatly between the linear, modestly cross-linked (45% gel fraction) and highly cross-linked (93% gel fraction) samples. Notably, the modestly cross-linked sample has nearly twice as high selectivity compared to the linear control but at the expense of a greatly reduced permeability. However, the highly cross-linked sample has a selectivity almost three times as high as the modestly cross-linked sample with only a minor decrease in water permeability. The water uptake was higher for the linear control (48%) but nearly identical for both the moderately and highly cross-linked materials (27%). It is surprising that the moderately and highly cross-linked membranes had nearly identical water uptake values despite very different transport properties. Part 2 of this paper will investigate this result in more depth. It appears that in this regime of high cross-linking that salt diffusion is increasingly limited despite only minor differences in water permeability.

A very high extent of cross-linking is necessary for the high selectivity that the state-of-the-art aromatic polyamides demonstrate.^{13,71} It may follow that a high extent of cross-linking is necessary to achieve high selectivity and high water permeability for sulfonated polysulfones, and the amine terminated oligomers with epoxy can achieve this high extent of cross-linking while producing ductile films. Cross-linking certainly has a profound influence on the transport properties of these sulfonated poly(arylene ether sulfone) oligomers. Part 2 of this paper will compare the transport properties across a range of degree of sulfonation levels, cross-linking, and oligomer backbone structure to further develop the influence that cross-linking has on permeability and selectivity relationships for water purification.

CONCLUSIONS

In this paper, four novel cross-linkable oligomers were synthesized for use as water purification membranes, and their structures were validated by 1H NMR. These oligomers have the same backbone structure with different telechelic functionalities, and the effects of end group structure on extent of cross-linking and film fabrication were investigated. The oligomers were all thermally stable to over 400 °C. The cross-linking reactions of the oligomers were very different mechanistically and occurred at varying temperatures and conditions. Oligomers end-capped with maleimide and phenylethynyl phthalimide produced networks with over 90% gel fraction at high temperatures, but cross-link formation occurred after a majority of the casting solvent evaporated. The necessity of residual casting solvent during cross-linking was demonstrated, and the aforementioned oligomers produced brittle discontinuous films. Acrylamide terminated BisAS50 oligomers were photochemically cross-linked to modest gel fractions with

a multifunctional acrylate at low temperatures, resulting in ductile film formation. Amine terminated BisASSO was reacted with a multifunctional epoxy to produce gel fractions of 99%, and large-scale ductile films were fabricated. The water uptake of these polymers decreases drastically with initial network formation and then plateaus at higher extents of cross-linking. This upper regime with a high extent of cross-linking may be significant for developing these materials as water purification membranes.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jmcgrath@vt.edu.

Notes

The authors declare no competing financial interest.

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