Polyamide interfacial composite membranes prepared from m-phenylene diamine, trimesoyl chloride and a new disulfonated diamine

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\textbf{A R T I C L E   I N F O}

Article history:
Received 19 December 2011
Received in revised form 17 February 2012
Accepted 20 February 2012
Available online 3 March 2012

Keywords:
Interfacial polymerization
Aromatic polyamide thin-film composite
Post-polymerization thermal treatment
Sulfone diamine
Chlorine tolerance

\textbf{A B S T R A C T}

The influence of synthesis conditions (e.g., monomer concentration and membrane preparation protocol) on transport properties of polyamide thin-film composite (TFC) membranes prepared using m-phenylenediamine (MPD) and trimesoyl chloride (TMC) via interfacial polymerization is reported. For example, at 25 °C, NaCl rejection and permeate flux combinations of 99.6 ± 0.1% and 42 ± 3 L/(m\textsuperscript{2} h), respectively, were achieved in crossflow filtration using a 2000 ppm aqueous solution of NaCl and a transmembrane pressure difference of 225 psi (15.5 bar). Additionally, a sulfone diamine, disulfonated bis[4-(3-aminophenoxy)phenyl]sulfone (S-RAPS), was used in place of MPD to prepare TFC membranes. The resulting membranes had low NaCl rejection but somewhat higher permeate flux than MPD/TMC membranes. These membranes had reduced chlorine tolerance compared to those prepared using MPD as the diamine.

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1. Introduction

Interest in polymer membranes for desalination dates back more than 50 years [1,2]. Many modern commercial desalination membranes, such as reverse osmosis (RO) and nanofiltration (NF) membranes, are prepared as thin film composites (TFC)s that have a thin, i.e., ~100 nm, crosslinked polyamide barrier layer synthesized from m-phenylenediamine (MPD) and trimesoyl chloride (TMC); these membranes are prepared in a similar fashion to those reported by Cadotte in the early 1980s [3–6]. Research to optimize these membranes has focused, for example, on alternative amine and acyl halogen monomers [7–12] and treatment techniques (e.g., exposure of the TFC membranes to oxidants) [13–15].

There are many literature reports regarding the performance of interfacially polymerized, aromatic polyamide TFC desalination membranes based on MPD and TMC [16–22]. However, as shown in Table 1, the performance of these membranes is often different from that of commercially available desalination membranes [23–25]. For example, most of the literature studies in Table 1 report TFC membranes with less than 90% NaCl rejection, while the rejection of commercial brackish water desalination membranes in Table 1 is greater than 99.5%. Some of this variability is undoubtedly due to different experimental operating conditions (e.g., transmembrane pressure difference (TMP), feed salt concentration, pH, etc.), and some of the differences in properties may be due to additives or processing steps in the commercial membranes that are not widely reported. However, at the same TMP and feed salt concentration (e.g., 225 psi and 2000 ppm NaCl), there are wide variations in reported properties. For example, Kim et al. [18] report TFC membranes with a flux of 25.8 L/(m\textsuperscript{2} h) (LMH) and a salt rejection of 96.4%, while the manufacturer’s specifications report fluxes of 40 LMH or more and NaCl rejections of at least 99.5%.

In seeking to understand the effect of a different diamine on the properties of TFC membranes in this study, it was important to have a stable baseline of data on membranes prepared using MPD and TMC. Therefore, we studied (and report) the effect of several interfacial polymerization parameters (e.g., MPD and TMC concentration, support membrane wetting protocol, etc.) on water and salt transport properties.

Chlorine is a widely used economical disinfectant in desalination processes [26]. However, MPD/TMC desalination membranes have limited chemical resistance to oxidizing agents such as chlorine [27,28]. Alternative monomers, which are less sensitive to chlorination, have been explored to increase the chlorine tolerance of desalination membranes [11,12,29,30]. Disulfonated polysulfone-based polymers have been reported to be more tolerant to aqueous chlorine than polyamide-based polymers [28,31–33]. In this study, sulfonated diamine monomers are incorporated into TFC membranes via interfacial polymerization, and

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doi:10.1016/j.memsci.2012.02.038
Table 1

<table>
<thead>
<tr>
<th>Membrane Manufacturer</th>
<th>Transmembrane pressure difference (psi)</th>
<th>NaCl feed concentration (ppm)</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Permeate flux (L/m² h)</th>
<th>Apparent NaCl rejection (%)</th>
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<tr>
<td>Hydranautics LFCI [23]</td>
<td>225</td>
<td>1500</td>
<td>6.5–7</td>
<td>25</td>
<td>47</td>
<td>99.5</td>
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<tr>
<td>Hydranautics LFC [23]</td>
<td>225</td>
<td>1500</td>
<td>6.5–7</td>
<td>25</td>
<td>40</td>
<td>99.6</td>
</tr>
</tbody>
</table>

**Table 1**

Performance of polyamide thin-film composite membranes.

the chlorine tolerance, as well as flux and rejection, of the resulting membranes was characterized.

2. Experimental

2.1. Materials and reagents

Asymmetric polysulfone (PSf) ultrafiltration (UF) support membrane cast on polyester non-woven fabric was kindly supplied by Dow Water & Process Solutions (Edina, MN). The following reagents and solvents were received from Sigma–Aldrich (St. Louis, MO): m-phenylenediamine (MPD, ≥99%, cat. #P23954), trimesoyl chloride (TMC, 98%, cat. #147532), potassium carbonate (K₂CO₃, ≥99%, cat. #209619), n-dodecane (anhdydrous, ≥99%, cat. #297879), and n-hexane (mixture of isomers, anhydrous, ≥99%, cat. #227064). The following chemicals were purchased from Fisher Scientific (Hampton, NH): sodium hydroxide solution (0.1 M NaOH, cat. #1310-73-2), and hydrochloric acid solution (0.1 M HCl, cat. #7647-01-0). All chemicals and solvents were used as received, unless otherwise noted. 3,3′-Disulfonated-4,4′-dichlorodiphenylsulfone (SCDPS) was purchased from Akron Polymer Systems (Akron, OH) and dried in vacuo at 160°C for 24 h prior to use. 3-Aminophenol (m-AP, 98%, cat. #100242) was purchased from Sigma–Aldrich (St. Louis, MO) and purified via sublimation in vacuo before use. N,N-Dimethylacetamide (DMAc, ≥ 99%, cat. #D5511) and toluene (anhdydrous, 99.8%, cat. #244511) were purchased from Sigma–Aldrich and vacuum distilled before use. Deionized (DI) water was generated by a Milli-Q Advantage A10 water purification system (Millipore, Billerica, MA).

Acrylic plastic plates (8 in × 11 in × 0.24 in) were purchased from Interstate Plastics (Austin, TX). They were used to support the UF membrane during TFC membrane preparation. Additionally, plastic frames (inner size: 6 in × 9 in) were cut from these plates. Rubber gaskets having the same size of the plastic frames were purchased from Advanced Gasket & Supply (Fort Worth, TX). Soft rubber rollers (cat. #R1275) were purchased from Sigma–Aldrich Co. (St. Louis, MO).

2.2. Synthesis and characterization of disulfonated bis[4-(3-aminophenoxo)phenyl]sulfone (S-BAPS)

Disulfonated bis[4-(3-aminophenoxo)phenyl]sulfone (S-BAPS) was synthesized via nucleophilic aromatic substitution between SDCPS and m-AP as shown in Fig. 1. A typical S-BAPS synthesis was: 24.5618 g (50.0 mmol) SDCPS, 12.0043 g (110.0 mmol) m-AP and 7.6016 g (55.0 mmol) K₂CO₃ were added to a 250 mL three-neck flask equipped with a condenser, Dean Stark trap, nitrogen inlet, and mechanical stirrer. Distilled DMAc (120 mL) and toluene (60 mL) were added to the flask, and the reaction mixture was stirred and heated to 145°C. The solution was allowed to reflux at 145°C while the toluene azeotropically removed moisture from the system. After 4 h, the toluene had been removed from the reaction mixture, and the reaction temperature was slowly (over approximately an hour) increased to the reaction mixture’s reflux temperature. The reaction mixture remained at reflux under nitrogen purge for at least 48 h. Finally, the reaction mixture was cooled to room temperature and filtered. The product was precipitated in IPA. The precipitant was filtered and vacuum dried at 110°C for 24 h. Synthesis of S-BAPS was confirmed by 1H NMR (Fig. 1) using a Varian Unity 400 NMR spectrometer (Varian Analytical Instruments, Walnut Creek, CA) at a resonance frequency of 400 MHz. Spectra were obtained at room temperature using a 10% solution (w/v) of S-BAPS in DMSO-d₆.

2.3. Preparation of thin-film composite (TFC) membranes

Several key steps of the interfacial polymerization membrane preparation process used in this study are illustrated in Fig. 2. This process is believed to be similar to that reported by Mitchell et al. [34]. A PSf support membrane was immersed in DI water overnight (Fig. 2a), then removed from the water and positioned on a plastic plate. A rubber gasket and a plastic frame were placed on top of the support membrane, and binder clips were used to hold the plate–membrane-gasket-frame stack together (see Fig. 2b). 100 mL of 1.5% (w/v, i.e., g MPD/100 mL water) MPD solution were poured into the frame (Fig. 2b) and allowed to contact the PSf membrane for at least 5 min before draining the excess MPD solution. This residence time allowed MPD to at least partially penetrate into the pores of the porous support. The frame and gasket were disassembled, and residual solution between the plate and the PSf membrane was removed using paper towels. Residual droplets of solution on the top surface of the PSf membrane were removed by rolling a rubber roller across the membrane surface one time (Fig. 2c). Consistent with previous literature reports, the rubber roller was firmly pressed against the membrane surface to ensure that no visible aqueous droplets, which could form defects if left on the membrane, remained following the rolling process [4,35,36]. Afterwards, the frame and gasket were reassembled on top of the PSf membrane, and 80 mL of 0.05% (w/v) TMC/n-dodecane solution were poured into the frame (Fig. 2d). N-dodecane was selected as the organic solvent because of its lower volatility and flammability than, for example, n-hexane. After 1 min, the TMC/n-dodecane solution was drained from the frame, and the frame and gasket were disassembled. The membrane surface was rinsed using n-hexane (100 mL) to
wash away residual reagents (Fig. 2e), and the membrane was dried in air at ambient conditions for 1 min. Finally, the entire membrane was immersed in DI water until use (Fig. 2f). No base was added as a catalyst in this process.

Thermal treatment of MPD/TMC membranes involved placing fresh polyamide TFC membranes in an oven at 80 °C in air at ambient pressure for 10 min. Thermal treatment in water involved contacting the top surface, i.e., the side of the membrane with the polyamide active layer, with boiling water for 10 min using the plate, frame and gasket setup shown in Fig. 2h. The boiling water was replaced every 2 min to keep the water temperature close to 100 °C.

2.4. Characterization of TFC membranes

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize the chemical structure of the polyamide TFC membranes. A Thermo Nicolet Nexus 470 FTIR with an Avatar Smart Miracle ATR accessory and a ZnSe crystal (Thermo Fisher Scientific Inc., Waltham, MA) was used. Spectra were collected in air, in the mid-infrared region (600–4000 cm$^{-1}$), using 256 scans at resolution 4 (1.928 cm$^{-1}$ spacing). After each measurement, a background spectrum was obtained and subtracted from that of the membrane to remove any atmospheric absorbance peaks.

The TFC membrane’s polyamide surface and cross-sectional morphology was characterized by scanning electron microscopy (SEM, Zeiss Supra 40 VP, Carl Zeiss NTS, Peabody, MA). High voltage ETH mode was used and the voltage was set to 5 kV. An InLens detector was selected, and the working distance was between 5 and 7 mm. Samples were prepared by peeling away the polyester backing fabric and fracturing the remaining polysulfone and polyamide layers after immersion in liquid nitrogen. A Cressington 208 Benchtop Sputter Coater (Cressington Scientific Instruments Ltd., Watford, England), having a Pt/Pd metal target (#91115, Ted Pella Inc., Redding, CA) was used to coat the resulting samples. The coating thickness was set to 8–9 nm to ensure adequate sample surface conductivity.

Permeate flux and salt rejection were measured using crossflow filtration as described previously [37]. The 25 °C aqueous feed contained 2000 ppm (0.034 M) NaCl, and the pH was adjusted using 0.1 M NaOH or HCl to be between 6 and 7. The feed flow rate was 0.7 gallons per minute (gpm) (2.7 L/min), and the average crossflow velocity was 40 cm/s, which corresponded to a Reynolds number of 2200. The transmembrane pressure difference was 225 psi (1.55 MPa or 15.5 bar), and the permeate pressure was essentially atmospheric. An inline particulate/carbon filter (KX CTO/2 carbon block carbon/5 μm particle filter, Big Brand Water Filter, Chatsworth, CA) was connected upstream of the membranes to continuously remove particulate matter (e.g., dust) or organic

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Fig. 1. Synthesis of S-BAPS and its $^1$H NMR spectrum (as synthesized).
molecules that might be present in the feed. All flux and rejection measurements were made 30 min after starting the crossflow experiment to ensure that the filtration process had reached steady state. Because most of the membranes exhibited high salt rejection (i.e., the concentration of salt in the permeate was low), the permeate flux was essentially equal to the flux of water through the membrane. The steady state permeate flux \( J_W \) through a film of area \( A \), was calculated as the volume of permeate \( \Delta V \) collected during a time period \( \Delta t \):

\[
J_W = \frac{\Delta V}{A \cdot \Delta t}
\]  

The definition of the apparent salt passage, \( \text{Pass} \), is:

\[
\text{Pass} (\%) = 100 - R(\%) = \frac{C_P}{C_F} \times 100
\]  

The influence of salt concentration polarization on apparent rejection was estimated as described previously [37]. Several representative membranes were tested to measure the effect of concentration polarization on apparent NaCl rejection, and the results are shown in the Supporting Material. A typical membrane having a permeate flux of 43.5 L/(m² h) and 99.37% apparent NaCl rejection had a true rejection value of 99.46%, which corresponds to a concentration polarization modulus [38] of 1.17. The largest difference between apparent rejection (99.24%) and true rejection (99.53%) was 0.29%, which corresponds to a concentration polarization modulus of 1.62 at a permeate flux of 59.5 L/(m² h). To be consistent with data published in the literature, apparent (or nominal) rejection values were reported in this study without correcting for concentration polarization unless noted otherwise. However, the most significant effect of concentration polarization in this study was an 0.3% increase in the salt rejection of the membranes exhibiting the highest permeate flux.
2.5. Evaluation of chlorine tolerance

Chlorine tolerance was evaluated by comparing the permeate flux and NaCl rejection of membranes before and after exposure to aqueous chlorine solutions in a manner similar to that of other studies [27,28]. Membrane samples were immersed for 8 h in an aqueous solution of approximately 2000 ppm available chlorine prepared from a stock aqueous sodium hypochlorite solution (10–15% available chlorine, cat. #425044, Sigma–Aldrich Co. (St. Louis, MO)). 16 mL of this concentrated sodium hypochlorite solution was added to a volumetric flask and diluted to obtain 1 L of ~2000 ppm aqueous sodium hypochlorite solution with DI water. The solution’s pH was then adjusted to 11 using NaOH, and the membrane sample’s total chlorine exposure was approximately 16,000 ppm-h. Following chlorine exposure, membrane samples were rinsed with DI water for 3 min before characterization. The permeate flux and NaCl rejection of these chlorine–exposed membranes were compared to those of control membranes that had not been exposed to chlorine.

3. Results and discussion

3.1. Synthesis and characterization of disulfonated diamine monomer (S-BAPS)

Synthesis of S-BAPS, performed in DMAc with potassium carbonate and toluene as the dehydrating agents, proceeded without significant side reactions (see Fig. 1). Although using a different set of reagents required a longer reaction time (>48 h) than previously reported (24 h) [39], a high yield (>95%) of very pure S-BAPS was obtained. The 1H NMR spectrum in Fig. 1 confirms the purity of as synthesized S-BAPS without any further purification.

3.2. Optimum conditions for membrane fabrication

Properties of polyamide membranes prepared via interfacial polymerization are sensitive to preparation protocol [40]. Interfacial polymerization is initiated when the top surface of a PSF UF membrane, whose porous structure contains an aqueous MPD solution, is contacted with a TMC organic solution [3,4]. Based on the classic view of interfacial polymerization described by Morgan, the low solubility of TMC in water and somewhat higher solubility of MPD in the organic phase results in MPD diffusion from the aqueous phase into the organic phase to react with TMC and grow an interfacial polyamide from the organic/water interface into the organic phase [41]. Initially, the polyamide layer is quite thin, but MPD diffuses through the polyamide layer into the TMC-rich organic phase where it reacts with TMC and thereby increases the polyamide layer thickness. The growth of the polyamide layer essentially stops when the mass transfer resistance of the polyamide layer becomes great enough to decrease MPD transport into the organic phase to very low rates [41]. TMC acid chloride groups are readily hydrolyzed by water [41]. Therefore, water diffusion into the organic layer can reduce the number of TMC reactive sites, which acts as a further limitation on the thickness and crosslink density of the polyamide layer. Due to the rapid condensation polymerization between MPD and TMC, the self-limited formation of the polyamide dense layer can be completed over time scales of the order of seconds, beyond which the growth of dense layer may still occur at a very low rate but with little effect on membrane performance [4].

Initially, polyamide TFC membranes were prepared from MPD (3% w/v in water) and TMC (0.13% w/v in n-dodecane) following conventional protocols described by Cadotte [4]. Fig. 2b–f presents photographs of these steps. To minimize the effect of residual reagents on the performance of TFC membranes, n-hexane was used to rinse the top membrane surface immediately following the polymerization step. N-hexane is highly volatile, so it rapidly evaporated from the membrane surface.

However, the salt passage of membranes prepared using this original protocol was highly variable, ranging from 0.5 to 4.5% (i.e., salt rejection ranged from 95.5 to 99.5%). This large variability, which included some rather high values of salt passage, was likely due to the formation of pinhole defects during the membrane fabrication process. If any PSF support membrane pores were not adequately wetted during contact with the aqueous MPD solution, these regions of low or negligible MPD concentration could become pinhole defects in the resulting interfacial composite membrane.

The membrane fabrication protocol was revised by adding the water soaking step shown in Fig. 2a to decrease the possibility that pinholes would form during interfacial polymerization. Membranes prepared using a protocol that included soaking the PSF UF membrane in DI water for 1 h, 2 h, or 4 h yielded low salt rejection, i.e., 95.0–99.0%. Alternatively, membranes prepared using a protocol that included soaking the PSF UF membrane in DI water for >12 h yielded membranes with greater than 99.0% salt rejection; presumably due to more complete wetting of the support and, subsequently, more complete coverage of the MPD solution in the porous membrane support. In addition, it was crucial to apply sufficient force to the roller (Fig. 2c) to remove water droplets; if the roller pressure was low, water droplets remained on the surface of the PSF membrane, and these droplets could become pinhole defects during interfacial polymerization.

The salt passage and permeate flux of membranes prepared using this revised protocol are shown as filled circles in Fig. 3a. Using this protocol, the resulting membranes consistently had salt passage values less than 1% (i.e., salt rejection >99%). Some scatter exists because the TFC membranes are made by hand, which inherently leads to some sample-to-sample variability. For comparison, the permeate flux and NaCl rejection of a number of commercial membranes, tested at identical feed pressure, pH and salt concentration are shown in Fig. 3a [23–25]. While the salt passage of the membranes prepared in this study was similar to that of these particular commercial membranes, the permeate flux was lower. Permeate flux and NaCl rejection data of MPD/TMC composite membranes reported in the literature (and shown in Table 1) are also included in Fig. 3a for comparison.

The permeate flux of RO membranes is reported to be influenced by the hydrophilicity, thickness and density of the polyamide barrier layer [40,41]. Correlations between membrane performance and both film thickness and structure have been studied experimentally and simulated using mathematical models [42–45]. Generally, interfacial polymerization of MPD and TMC is believed to involve an incipient fast stage that forms a dense core barrier layer followed by a slow growth stage that is monomer diffusion limited [42,44]. The fast reaction upon contact of both monomers at the oil-water interface in the incipient stage provides the dense core layer that is significantly thinner than the extended loose layer formed later as monomer diffuses through the dense core layer [45]. Fresger [44] suggested that the thickness of the dense core layer decreases as the concentration of either monomer increases. However, the overall polyamide layer thickness may respond differently to increases in monomer concentration because increased MPD concentration may increase the driving force for diffusion of MPD into the organic phase, thereby increasing the polyamide thickness during the slow growth stage. For example, Chai and Krantz [42] observed increased film thickness with increased amine concentration, and permeate flux would typically decrease as polyamide layer thickness increased and vice versa.

On the other hand, permeate flux and NaCl rejection also depend on the polyamide layer density, which is influenced by, for example, crosslink density [43]. The polymer density across the
barrier layer is not uniform [34]. The core layer (near the original MPD/TMC interface) is the most dense region, and the polymer density decreases gradually as the polymer grows further into the organic phase [44,46]. In many applications of interfacial polymerization using MPD and TMC, the initial amine concentration is much higher than the acyl chloride concentration. Either decreasing the amine concentration or increasing the acyl chloride concentration (thereby bringing the molar ratio of amine to acid chloride groups closer to unity) results in a more dense polyamide layer compared to those prepared using higher amine/acid chloride molar ratios [47]. Increases in either the density or thickness of the MPD/TMC barrier layer should increase the mass transfer resistance of the resulting membrane, thereby reducing permeate flux. Thus, varying the initial concentration of monomers can influence the membrane’s water and salt transport properties.

Polyamide TFC membranes were prepared by varying the concentration of MPD and TMC and MPD residence time, respectively. MPD residence times ranging from 5 to 60 min had no measurable effect on permeate flux or NaCl rejection, so the MPD residence time was set to 10 min for all membranes reported hereafter. The influence of MPD and TMC concentrations on permeate flux and salt passage is presented in Fig. 4. To assist in the discussion below, the molar ratio of amine groups on the MPD to the acid chloride (i.e., acyl chloride) groups on the TMC, based on the concentrations of MPD and TMC used in the polymerization process, is reported in these figures as well. All membranes exhibited salt passage values of less than 0.5% (i.e., rejection >99.5%), but permeate flux varied significantly.

Fig. 4a illustrates the influence of MPD concentration on permeate flux and salt passage. Salt passage was relatively insensitive to MPD concentration over the range of concentrations considered, suggesting the formation of defect-free (or at least nearly defect-free) membranes in all cases. Permeate flux exhibited a maximum near 1.5% (w/v) MPD. As MPD concentration increases, the driving force for MPD diffusion into the organic phase increases; increased MPD concentration could, therefore, increase the barrier layer thickness and, thus, lower permeate flux. As MPD concentration decreases, layer thickness is expected to decrease, which would tend to increase flux, but the resulting layer is expected to become more dense as the molar ratio of amine/acyl chloride becomes closer to unity, which would lower flux [44,48]. Based on what is potentially a complex interplay between these phenomena, a maximum in permeate flux was observed.

Fig. 4b presents the influence of TMC concentration in the organic phase on permeate flux and salt passage when the MPD concentration in the aqueous phase was held constant at 1.5% (w/v), which is near the optimum value observed in Fig. 4a. Since interfacial polymerization is typically MPD-diffusion controlled during growth of the polyamide layer, variations in TMC concentration would affect the layer density by varying the amine/acyl chloride molar ratio [44,48]. As TMC concentration increases, the amine/acyl chloride molar ratio decreases, which is expected to increase flux density, resulting in lower permeate flux [44,48]. However, a decrease in permeate flux was also observed at the lowest TMC concentration considered. At low TMC concentration (<0.01%), the interfacial polymerization reaction is reported to be TMC diffusion limited [42]. A low concentration of acyl chloride groups in the reaction zone may allow the polyamide film to grow thicker, which would decrease flux [43]. Perhaps at 0.025%, with a rather high amine/acyl chloride molar ratio (98), the interfacial polymerization process was influenced by both MPD diffusion in the polyamide layer and TMC diffusion in the organic layer.

At the optimum conditions (1.5% MPD, 0.05% TMC), polyamide TFC membranes were prepared as described in Section 2, and their performance is presented as the filled diamonds in Fig. 3b. NaCl passage was 0.4 ± 0.1% (i.e., NaCl rejection was 99.6 ± 0.1%), and the permeate flux was 42 ± 3 L/(m² h). The transport properties of these membranes were comparable to those of the commercial membranes reported in Fig. 3b.

3.3. Post-polymerization heat treatment

Post-polymerization heat treatment has been used in several studies to modify the water and salt transport properties of polyamide TFC membranes synthesized from MPD and TMC [17–22] and those synthesized from alternative amine [19,49–52] and acyl chloride [50,51,53,54] monomers. In those studies, thermally cured polyamide TFC membranes usually exhibited higher salt rejection than untreated analogs, presumably because the polymerization process continued at high temperature. Typically, when
salt rejection was reported to improve with heat treatment, the membranes before heat treatment had rejection values significantly lower than those of commercial membranes, suggesting that the polyamide layer formed during polymerization contained defects potentially due to, but not limited to, lack of thorough wetting of the ultrafiltration support membrane, residual aqueous amine droplets on the support membrane before contact with acyl chloride solution, or sub-optimal monomer concentration and amine/acyl chloride molar ratio [18,21,22]. In such cases, the post-polymerization curing process had a positive effect on salt rejection [20]. However, permeate flux did not increase as salt passage decreased [20]. For example, Ghosh et al. found that MPD/TMC membranes treated at 90 °C for 10 min exhibited almost the same permeate flux but lower salt passage (3%) than those treated at only 45 °C for 10 min (salt passage = 4%) [20].

The effect of thermal treatment on water and salt transport properties of the TFC membranes prepared using the optimized protocol was examined, and the results are recorded in Table 2. One thermal treatment temperature was selected to be below 90 °C because pore shrinkage may occur in the support membrane at higher temperatures [20]. Relative to the control membranes, which were not heat treated, the thermally treated membranes had similar permeate flux and salt rejection (with somewhat higher variability), so heat treatment did not improve salt rejection.

Inspired by previous studies on the effect of boiling disulfonated polysulfone films on water and salt transport properties [55], the influence of boiling water on polyamide TFC membrane performance was studied by rinsing the membranes with boiling water for 10 min as described in Section 2. Only the polyamide layer of the TFC membrane was exposed to the boiling water to minimize any changes to the support membrane. The free volume of linear disulfonated polysulfone films increases upon boiling films in water, which increases water and salt transport properties [31,32,55]. As shown in Table 2, neither the permeate flux nor salt passage of the polyamide TFC membranes was strongly influenced by exposure to hot water.

Representative membrane surface and cross-section SEM images are presented in Fig. 5. Unlike the smooth, porous PSf surface, the polyamide TFC surface was rough, having a layer of tightly packed globules and scattered ear-shaped polyamide ridges, presumably generated on top of PSf areas having surface pores so that sufficient MPD could diffuse into the organic phase to form these microporotherabes [56]. The observed surface morphology is consistent with the so-called ridge-and-valley structure that is characteristic of MPD/TMC polyamide TFC membranes [16,20]. The PSf support cross-section illustrates the UF membrane’s asymmetric structure; the porosity of the membrane gradually increases throughout the membrane’s thickness as shown in Fig. 5c. The polyamide TFC membrane cross-sections allowed for estimation of the thickness of the polyamide layer (Fig. 5d); this layer was estimated to be about 100–150 nm thick.

### 3.4. Membranes prepared from disulfonated sulfone diamine

The disulfonated sulfone diamine monomer, S-BAPS, was used instead of MPD to synthesize polyamide TFC membranes. The chemical structure of S-BAPS based polyamide TFCs was characterized by ATR-FTIR, and its infrared spectrum was compared to that of MPD based polyamide TFCs (i.e., control membranes) in Fig. 6. Because the depth of ATR-FTIR penetration was about 0.4–0.5 μm in the wavelength region of interest [17], the IR spectra shown in Fig. 6 reflect a combination of the polyamide barrier layer (0.1–0.15 μm) and the PSf substrate. Peaks at 1660 cm−1 and 1548 cm−1 correspond to N=C=O and C=N–H vibrations, respectively, and the peak at 1608 cm−1 is associated with the hydrogen bonded carbonyl of the amide linkage [57]. All three peaks correspond to the amide linkages in the polyamide barrier layer, and these peaks are weaker

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeate flux (L/(m² h))</th>
<th>Apparent NaCl rejection (%)</th>
<th>NaCl passage (%)</th>
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<tr>
<td>Control PA TFC (no thermal treatment)</td>
<td>42 ± 3</td>
<td>99.6 ± 0.1</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>PA TFC in 80 °C oven for 10 min</td>
<td>45 ± 2</td>
<td>99.2 ± 0.6</td>
<td>0.8 ± 0.6</td>
</tr>
<tr>
<td>PA TFC rinsed with 100 °C water for 10 min</td>
<td>38 ± 2</td>
<td>99.5 ± 0.3</td>
<td>0.5 ± 0.3</td>
</tr>
</tbody>
</table>

Note: At least 3 membranes were prepared and tested for each set of experiments, and the standard deviation was used to estimate the uncertainty of these measurements.

![Fig. 4. Dependence of polyamide TFC membrane performance on: (a) MPD concentration in aqueous solution (TMC concentration = 0.13% (w/v)), and (b) TMC concentration in n-dodecane solution (MPD concentration = 1.5% (w/v)). The ratio of moles of amine groups in the MPD to moles of acid chloride groups in the TMC, based on their concentrations in the water and n-dodecane solutions, respectively, used to prepare the TFCs, is also reported on the secondary x-axis.](image-url)
for the S-BAPS based polyamide than for the MPD based polyamide. The peaks at 1029 cm\(^{-1}\) and 1077 cm\(^{-1}\) are characteristic of the symmetric stretch of the S-BAPS sulfonate groups [58].

TFC membranes prepared from S-BAPS and TMC were evaluated, and the results are shown in Fig. 7. The S-BAPS concentration was either 2\% or 5\% (w/v), and the TMC concentration varied from 0.1\% to 2\% (w/v). Membranes prepared using S-BAPS and low TMC concentration (0.1\%) exhibited high salt passage (>66\%). When the TMC concentration was increased to 0.5\%, salt passage decreased to 22\%, but further increases in TMC concentration did not further decrease salt passage. Salt passage of membranes prepared using 2\% S-BAPS decreased steadily from 32\% to 12\% as TMC concentration increased.

S-BAPS has a much higher molecular weight (669 g/mol) than MPD (108 g/mol), and S-BAPS may be more hydrophilic (because of the highly hydrophilic sulfonate groups) than MPD. Therefore, transport of S-BAPS into the organic phase may have been slower than that of MPD. Thus, the crosslink density of S-BAPS/TMC membranes may have been much lower than that of the MPD/TMC membranes, which would be consistent with high salt passage [44]. The permeate flux of S-BAPS/TMC TFCs is shown in Fig. 7b. S-BAPS/TMC membranes exhibited a tradeoff relationship between salt passage and permeate flux, with membranes having high permeate flux also having high salt passage and vice versa. Such a tradeoff is typically observed in desalination membranes [59].

The membrane chlorine tolerance was examined for MPD-based (i.e., control membranes) and S-BAPS based polyamide TFC membranes, respectively. The results shown in Table 3 imply that the S-BAPS based membranes had lower chlorine tolerance than the control membranes because, following exposure to aqueous chlorine, permeate flux increased more and salt rejection decreased much more than in the MPD/TMC control membranes. A proposed chlorination mechanism for aromatic polyamides [60] suggests that free chlorine can attack the amide nitrogen and replace the hydrogen in the amide linkage with chlorine. Next, an Orton rearrangement of the chlorine to the N-H bonded aromatic ring occurs, and the polymer undergoes chain scission [60]. One
result of extensive chlorine-induced chain scission is decreased membrane separation performance. Polyamide TFC membranes prepared using S-BAPS are susceptible to chlorine degradation via the mechanism described above. The S-BAPS-based membranes showed larger changes in permeate flux and NaCl rejection upon contact with aqueous chlorine than the MPD/TMC membranes. This difference may be a result of lower S-BAPS polyamide crosslink density compared to its MPD analog due to the higher S-BAPS molar mass; therefore, the impact of chlorine degradation could be more severe in membranes prepared using S-BAPS as compared to the control membranes. It has been suggested that having the amine units connected directly to the aromatic rings may increase the membrane’s susceptibility to chlorine attack [61]. Thus, one potential direction for future research in this area would be to synthesize analogs of S-BAPS that have spacer groups, such as aliphatic linkages (e.g., CH2 groups) between the aromatic rings and the amine linkages, and use such diamines to prepare TFC membranes.

4. Conclusions

Polyamide thin-film composite membranes were prepared from m-phenylenediamine and trimethyl chloride via interfacial polymerization. By optimizing the preparation conditions, desalination membranes were prepared having 0.4 ± 0.1% apparent NaCl passage and permeate flux of 42 ± 3 L/(m² h). The effect of postpolymerization thermal treatment on membrane performance was studied, and thermal treatment did not improve salt rejection or permeate flux. Polyamide TFC membranes were synthesized from S-BAPS, a disulfonated sulfone diamine and TMC. Generally, the salt passage of these TFCs was much higher and permeate flux was somewhat higher than those of MPD/TMC TFCs. For example, a membrane having a NaCl passage of 12% and a permeate flux of 55 L/(m² h) was prepared from a 2% (w/v) S-BAPS aqueous solution and a 2% (w/v) TMC n-dodecane solution. TFC membranes prepared using S-BAPS had lower chlorine tolerance than those prepared using MPD.

Acknowledgements

This work was partially supported by the NSF’s Partnerships for Innovation (PFI) Program (Grant IIP-0917971), the NSF Division of Chemical, Bioengineering, Environmental, and Transport Systems (Grants 0932781/0931761) and the NSF Center for Layered Polymeric Systems (Grant DMR-0423914). The authors gratefully acknowledge Dr. Bill Mickols for demonstrating the preparation of interfacially polymerized thin film composite membranes to our laboratory group.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.memsci.2012.02.038.

References
