

Preparation and characterization of a composite nanofiltration membrane interfacially polymerized from *cis,cis*-1,3,5-triaminocyclohexane and trimesoyl chloride

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ABSTRACT: *cis,cis*-1,3,5-Triaminocyclohexane (TAC) was synthesized and used to prepare composite nanofiltration (NF) membranes by interfacial polymerization with trimesoyl chloride (TMC). The surface elemental composition, morphology, and hydrophilicity of the prepared NF membranes were characterized. The separation performances were examined with various salts and polyethylene glycol (PEG400, PEG600) solutions. The effects of preparation conditions were also systematically studied. The NF membrane was negatively charged and exhibited a salt rejection in the order Na₂SO₄ (98.2%) > MgSO₄ (90.8%) > MgCl₂ (84.5%) > NaCl (54.6%). The water permeability was 1.56 L m⁻² h⁻¹ bar⁻¹, and the molecular weight cutoff was 600 Da. The TAC/TMC membrane exhibited some characteristics that were different from the ones made from common diamines such as *m*-phenylenediamine: (1) the surface was smoother, without a ridge-and-valley structure; (2) there were two kinds of crosslinking points in the polyamide chains; (3) the active layer was formed faster (only 5 seconds was required to reach a Na₂SO₄ rejection of 98%). © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43511.

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INTRODUCTION

Nanofiltration (NF) is an important energy-saving technology nowadays that produces sustainable clean water in a wide variety of fields.^{1,2} The key element of NF is the thin film composite (TFC) membrane, which contains an ultrathin active layer that determines the separation properties and a support layer that provides mechanical strength. There are several methods to form an active layer on a support membrane, such as interfacial polymerization (IP),³ dip-coating,⁴ photografting,⁵ and layer-by-layer assembling.⁶ Among them, IP is a very successful technique that has been widely applied in commercial processes and on which a great deal of research work has been conducted, including many reverse osmosis (RO) membranes as well.

Traditionally, piperazine (PIP) is the most widely used monomer to prepare negatively charged NF membranes with trimesoyl chloride (TMC),⁷ and *m*-phenylenediamine (MPD) is

considered to be the best amine monomer for RO membranes.⁸ However, in order to further improve the separation performance or chlorine resistance of the membrane, several novel monomers have been synthesized to prepare TFC membranes via IP. Li *et al.*^{9,10} synthesized a series of multifunctional biphenyl acid chlorides that were used to prepare TFC membranes with MPD. The membrane made from 3,4',5'-biphenyl triacyl chloride (BTRC) or 3,3',5,5'-biphenyl tetraacyl chloride (mm-BTEC) showed higher NaCl rejection, and the membrane made from 2,2',5,5'-biphenyl tetraacyl chloride (op-BTEC) exhibited better flux than the commercial MPD/TMC membrane. Yu *et al.*¹¹ prepared a TFC membrane with *m*-phenylenediamine-4-methyl (MMPD) and cyclohexane-1,3,5-tricarbonyl chloride (HTC). The methyl group on the aromatic ring could improve the chloride resistance of the membrane, but from the viewpoint of separation performance, it could also reduce the water flux due to its hydrophobicity, so they reduced the

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aromatic ring of TMC to an aliphatic ring (HTC) to offset the influence. Finally, the membrane exhibited a flux comparable to and a slightly lower salt rejection than the MPD/TMC membrane. La *et al.*¹² fabricated a TFC membrane with hexafluoroalcohol (HFA)-substituted diamines and TMC. The membrane exhibited both higher water flux and higher Na₂SO₄ rejection after the chlorine treatment. Some other monomers have also been studied, such as 2,2',4,4',6,6'-biphenyl hexaacyl chloride, 2,4,4',6-biphenyl tetraacyl chloride (BTAC),¹³ and disulfonated bis[4-(3-aminophenoxy)phenyl]sulfone.¹⁴

Up to now, the membranes studied were usually made from diamines, but triamine or multiamine with small molecular weight has not drawn enough attention except for a few attempts. Uemura *et al.*¹⁵ synthesized 1,3,5-triaminobenzene, but they used it in a blending form. Chen *et al.*¹⁶ synthesized cyclen, but they found that the resulting membrane possessed an insufficient rejection of Na₂SO₄; the steric hindrance of the amine group might influence the formation of a dense selective layer. Han *et al.*¹⁷ used melamine to prepare a TFC membrane and found that the low reactivity of melamine affected the interfacial polymerization reaction a lot. So there is still a need to further explore whether triamine or multiamine with small molecular weight could form a denser layer with TMC, which we assume will exhibit a higher salt rejection because a better crosslinking level can be realized with more functional groups. *cis,cis*-1,3,5-Triaminocyclohexane (TAC) contains a rigid aliphatic ring and three amine groups that possess high reactivity and little steric hindrance, and this amine has not yet been reported as being used for a TFC membrane prepared via IP.

To further understand the relationship between the monomer structure and the performance of the membrane, in this work, TAC was synthesized and then used to prepare a TFC membrane with TMC. The separation performance of the membrane was evaluated by solutions of different salts and neutral solutes. Various preparation conditions were also investigated, especially the reaction time, which could reflect the formation rate and crosslinking degree of the active layer. The detailed results and explanation are supplied in the discussion section.

EXPERIMENTAL

Materials

cis,cis-1,3,5-Cyclohexane tricarboxylic acid (98%) was purchased from TCI (Shanghai, China). Diphenyl phosphoryl azide (DPPA, 97%) and HBr/acetic acid solution (33 wt %) were purchased from Accela Reagent Company (Shanghai, China). 1,3,5-Benzenetricarbonyl chloride (TMC, 98+%) was purchased from Alfa Aesar (Shanghai, China). Triethylamine, toluene, and benzyl alcohol were dried with 4 Å molecular sieves. Diethyl ether, polyethylene glycol (PEG400, PEG600), *N*-methyl-2-pyrrolidone (NMP), and dimethylacetamide (DMAC) were obtained commercially and used as received.

Synthesis of *cis,cis*-1,3,5-Triaminocyclohexane

TAC was synthesized in a salt form according to a procedure from the literature.¹⁸ The synthetic route is outlined in Figure 1. *cis,cis*-1,3,5-Cyclohexane tricarboxylic acid (5.0 g, 23 mmol), triethylamine (7.0 g, 69 mmol), and DPPA (19.3 g, 70 mmol)

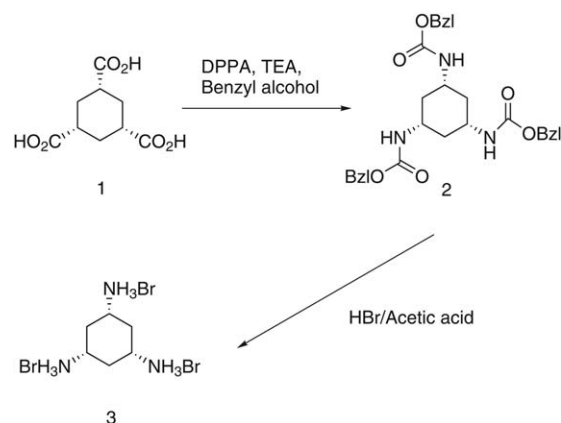


Figure 1. Synthetic route for TAC-3HBr.

were added to toluene (150 mL). The mixture was stirred at room temperature for 30 min and then at 80 °C for 90 min until all solids were dissolved. Benzyl alcohol (10.0 g, 92 mmol) was added, and the solution was refluxed for 24 h. After cooling to ambient temperature, the white precipitate was collected under vacuum filtration and washed with cold toluene, then dried to yield *N,N',N''*-tris(benzylcarbamyl) *cis,cis*-1,3,5-triaminocyclohexane (compound 2) (9.2 g, 17 mmol, 74%).

¹H-NMR (400 MHz, DMSO-d₆, δ): 7.3 (m, 15H; Ar H), 5.0 (s, 6H; CH₂), 3.4 (m, 3H; CH), 1.9 (m, 3H; CH), 1.1 (m, 3H; CH). The spectrum is shown in the Supporting Information as Figure S1.

Compound 2 (9.2 g, 17 mmol) was dissolved in 33% HBr/acetic acid (50 mL). The mixture was stirred for 90 min and then poured into diethyl ether (150 mL). The white precipitate was filtered off and washed with dichloromethane, yielding *cis,cis*-1,3,5-triaminocyclohexane-3HBr (5.8 g, 16 mmol, 91%).

¹H-NMR (400 MHz, D₂O, δ): 3.4 (t, 3H; CH), 2.4 (d, 3H; CH), 1.6 (q, 3H; CH). The spectrum is shown in the Supporting Information as Figure S2.

Preparation of the Polysulfone Support Membrane

A solution of 16 wt % polysulfone (PSF, Udel P3500, Solvay, USA), 10 wt % PEG400, 7 wt % NMP, and 67 wt % DMAC was cast onto a glass plate with a thickness of 150 μm. The plate was immediately immersed in a water bath and stored in deionized water for 12 h before use. The PSF support membrane possessed a pure water flux of 237 L m⁻² h⁻¹ bar⁻¹, and the rejection to bovine serum albumin (BSA) was 99.2%.

Fabrication of TFC Membranes

The TFC membranes were prepared by IP. The monomers used are shown in Figure 2. TAC was directly released from TAC-3HBr by the right amount of NaOH in an aqueous amine solution. Typically, the solution containing 0.2 wt % TAC was prepared at pH 10 adjusted by triethyl amine (TEA) (0.3 wt %) and camphor sulfonic acid. The concentration of acyl chloride in *n*-hexane was 0.15 wt %. First, the aqueous phase was poured onto the surface of the support membrane and kept for 2 min. The excess solution was drained off the surface, which was air-dried until there was no liquid left. Then the organic

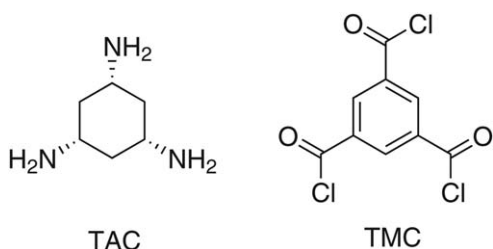


Figure 2. Chemical structures of the monomers used.

solution was used to cover the support membrane for 1 min to form the active layer. After removing the excess organic solution, the membrane was heated at 80 °C for 5 min and then stored in DI water. When examining the effect of a certain preparation condition, all other conditions were kept the same as above.

Characterization

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet iS5, Thermo Fisher Scientific, USA) was used to characterize the functional groups of the NF membrane.

X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, USA) was used to determine the elemental composition of the membrane surface.

Scanning electron microscopy (SEM, SUPER 55, Zeiss, Germany) was used to observe the surface morphology of the NF membrane. The samples were cracked in liquid nitrogen and sputtered with gold before SEM observation.

Atomic force microscopy (AFM, Nanoscope IIIa, Veeco Instrument, USA) was used to measure the surface roughness of the NF membranes. The root mean square (RMS) roughness value in an area of $10 \times 10 \mu\text{m}$ of the membrane was calculated as the membrane surface roughness.

A contact angle meter (JC2000C, Powereach, Shanghai, China) was used to measure the surface water contact angle to evaluate the hydrophilicity of the NF membrane.

All of the membrane samples were dried in vacuum at 35 °C for 24 h before characterization.

Performance Tests

The performance of the TFC membranes was tested at 0.8 MPa at room temperature in a cross-flow cell (18 cm^2) with 1000 ppm each of Na_2SO_4 , MgSO_4 , MgCl_2 , NaCl , PEG400, and PEG600 solutions, and the TFC membranes were prefiltrated for 30 min under these conditions to reach a steady state before testing.

The water permeability (WP) and salt rejection (R) were calculated as follows:

$$\text{WP} = \frac{V}{A \times \Delta t \times \Delta P} \quad (1)$$

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100\% \quad (2)$$

where V (L) is the volume of water permeated in a time Δt (h), A (m^2) is the effective area of the membrane, ΔP is the trans-

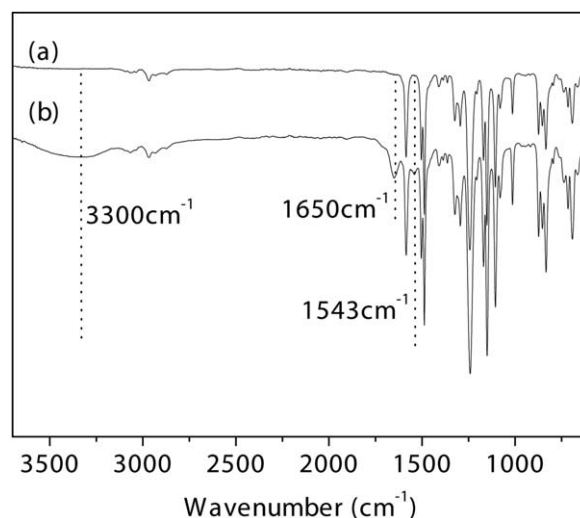


Figure 3. ATR-FTIR spectra of (a) PSF support membrane, (b) TAC/TMC membrane.

membrane pressure drop (bar), and C_P and C_F (g L^{-1}) are the salt concentration of permeate and feed solution, respectively. The concentration of salt was detected by a conductivity meter (DDS-12D, INESA, Shanghai, China). The concentration of PEG was detected with a total organic carbon (TOC) analyzer ($V_{\text{CPH/CPN}}$; Shimadzu, Japan).

RESULTS AND DISCUSSION

ATR-FTIR Spectra and XPS Analysis

The ATR-FTIR analysis of the membrane is shown in Figure 3. It can be seen that several new peaks appeared after IP compared to the neat PSF support layer. The peak at 1650 cm^{-1} corresponds to the stretching vibration of $\text{C}=\text{O}$ in amides, and 1543 cm^{-1} corresponds to $\text{C}-\text{N}$ in amides.⁹ In addition, the broad peak around 3300 cm^{-1} is contributed by the stretching of the $\text{N}-\text{H}$ bond. All of these characteristic absorptions prove the successful formation of a polyamide layer coating the porous support.

The XPS analysis is presented in Figure 4. The surface atomic compositions of the TAC/TMC membrane and four samples for

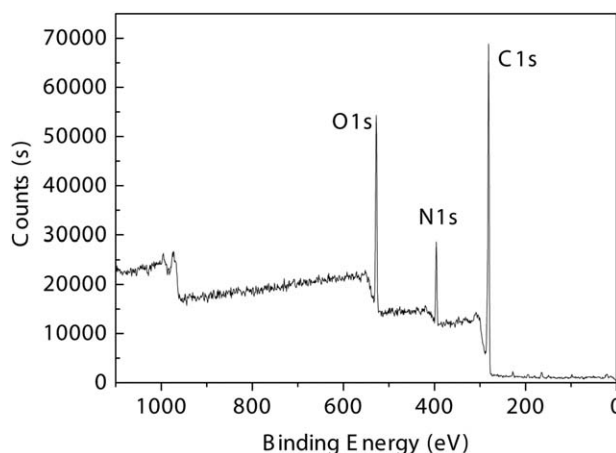


Figure 4. XPS spectra of TAC/TMC membrane surface.

Table I. Surface Atomic Composition of TAC/TMC Membrane and Samples for Comparison

Sample	C%	N%	O%	N/O	Crosslinked portion (%)	Properties of surface charge	Reference
TAC/TMC	73.28	9.78	16.94	0.577	—	Negative	This work
MPD/TMC	74.39	9.39	16.22	0.579	20	Negative	9
MPD/BETC	75.76	8.79	15.45	0.569	—	Negative	9
MPD/BHAC	69.92	7.13	22.95	0.311	—	Negative	13
PIP/BHAC	77.2	12.47	10.33	1.207	—	Positive	19

comparison are listed in Table I. For the MPD/TMC membrane, it is easy to calculate the crosslinking degree of the polymer chain^{9,20} because TMC is the only crosslinking point and the percentage of linear structure and fully crosslinked structure can be figured out by the N/O ratio. But this method does not apply to samples with more complicated chain structures, such as MPD/Biphenyl Tetraacyl Chloride (BETC), MPD/Biphenyl Hexaacyl Chloride (BHAC), and PIP/BHAC. So it was also hard to calculate the crosslinking degree of TAC/TMC according to the XPS analysis because the linear chain of TAC/TMC could be connected not only by TAC, in which situation TMC was the crosslinking point [Figure 5(a)], but also by TMC, in which situation TAC was the crosslinking point [Figure 5(b)]. Nevertheless, we could judge the surface charge to be negative or positive by the N/O ratio, which was applied to all of the samples. For TAC/TMC, the atomic percentage of O was much more than that of N, indicating that there were more carboxylic acid groups hydrolyzed from the acyl chlorides than from the unreacted amine groups. So the TAC/TMC membrane should be negatively charged and prefers to reject SO_4^{2-} .

Morphology Studies

The SEM images of the PSF support membrane and the TAC/TMC membrane are exhibited in Figure 6. The pores on the top surface of the PSF support membrane can be seen in Figure 6(a), mainly distributed in the range of 10–40 nm. According to Figure 6(b), the surface of the TAC/TMC membrane was smooth but dotted by several flat, shallow pits, which was different from the typical ridge-and-valley structure of the MPD/TMC membrane. Usually in the IP process^{21,22} a nascent film is first formed at the aqueous–organic interface, and it possesses a large surface energy and is thermodynamically unstable, resulting in the formation of pinhole defects that could minimize the surface free energy. Thus amine monomers could diffuse

through the defects and continue to react, and the film grows in this way and terminates when it is dense enough to prohibit the diffusion of amines. The formation of this flat surface could be interpreted as follows. First, both TAC and TMC contained three functional groups, so it was faster to form a dense layer, which inhibited the growth of the protruding ridges. Moreover, the nascent film formed by TAC and TMC was more robust, reducing the chance of generating pinhole defects. Second, TAC was more hydrophilic, so it was more difficult to penetrate into the organic phase, which slowed down the growth rate of ridges and minimized the roughness of the surface. From Figure 6(c) it is seen that the active layer was partially embedded into the support layer, and the thickness was around 100 nm.

The surface roughnesses of the PSF support membrane and the TAC/TMC membrane were characterized by AFM (Figure 7). The RMS roughness of the PSF support membrane was 8.093 nm, and that of the TAC/TMC membrane was 9.201 nm, which increased a little and was much smaller than that of most reported NF membranes,^{9,23} indicating that the surface was very smooth, which was in accordance with the SEM analysis. Liu *et al.*²⁴ had proved that the lower surface roughness led to higher fouling resistance because a smooth surface could alleviate the accumulation of colloids on the membrane surface and is easy to clean. Thus the smooth surface of the TAC/TMC membrane should be helpful in enhancing its resistance to fouling.

The surface water contact angle of the TAC/TMC membrane was 40°, which was much lower than the PSF support membrane (75°) and close to the PIP/TMC membrane.²³ It is well known that, when the water contact angle is less than 90°, the rougher the surface is, the smaller the angle. The surface of the PIP/TMC membrane (RMS = 36.7 nm) was much rougher than TAC/TMC,²³ but they had nearly equal water contact angles. So, if they had equal RMS roughness, the water contact angle of TAC/TMC should be lower, which indicated that there were more $-\text{COOH}$ groups on the surface of the TAC/TMC membrane.

Separation Performance of TFC Membranes

The separation performance of the TAC/TMC membrane was examined with six different solutions (Na_2SO_4 , MgSO_4 , MgCl_2 , NaCl , PEG400, PEG600), each with a concentration of 1000 ppm at 0.8 MPa, and the results are presented in Figure 8. The TAC/TMC membrane had a WP around $1.56 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which was lower than the membrane made from the

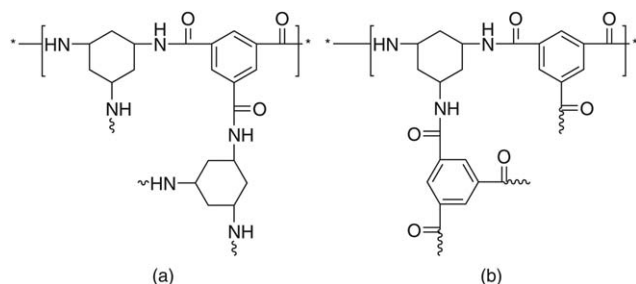


Figure 5. Possible chemical structures of TAC/TMC polymer chains: (a) TMC is the crosslinking point; (b) TAC is the crosslinking point.

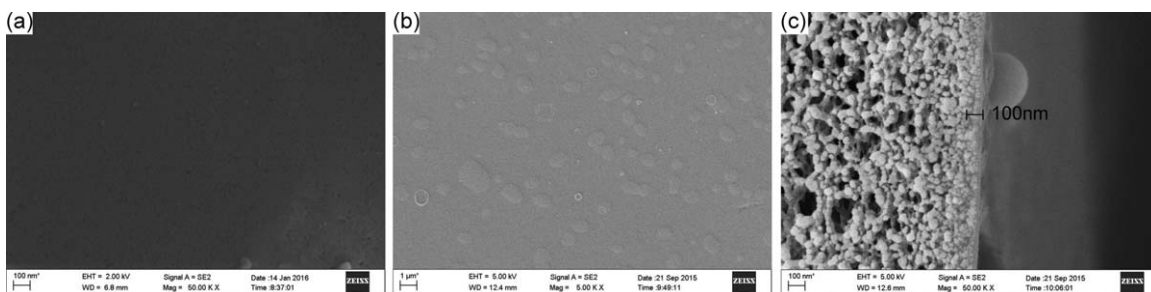


Figure 6. SEM images: (a) top surface of PSF support membrane; (b) top surface of TAC/TMC membrane; (c) cross section of TAC/TMC membrane.

diamine that contained a rigid aliphatic ring. According to general experience, if the structure of diamine is rigid, the polyamide membrane will exhibit a considerable WP ($>4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), whereas if the diamine is soft, the polyamide will exhibit a low WP ($2\text{--}3 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$).^{25,26} This is because the polyamide made from rigid monomers usually contains many permanent pores due to the stiffness of the chain, and the water molecules could pass through quickly. If the chain is soft, the resulting pore will close and open alternately with the thermodynamic movement of the chains, which will hinder the trans-

portation of water molecules. TAC is a rigid monomer, but it possesses three amine groups, so the relatively low WP must result from the high crosslinking degree of the chains. Because the polyamide layer is usually composed of network pores and aggregate pores,²⁷ the higher the crosslinking degree, the more network pores and the less aggregate pores there will be, which can increase the resistance of the membrane.

The salt rejection followed the order Na_2SO_4 (98.2%) $>$ MgSO_4 (90.8%) $>$ MgCl_2 (84.5%) $>$ NaCl (54.6%), and this order is in accordance with the typical characteristics of a negatively charged NF membrane. The negatively charged membranes prefer to reject higher-valence anions, so when the cation was the same, the rejection to SO_4^{2-} was higher than to Cl^- . The larger hydrate ions usually encounter more steric hindrance, and the hydrated radius of Mg^{2+} is 0.428 nm, whereas that of Na^+ is 0.358 nm,²⁸ so the rejection to MgCl_2 was higher than to NaCl . Furthermore, Mg^{2+} is plus-bivalent, which could partly shield the anionic electric field and weaken the effect of Donnan exclusion, which had a great influence on the rejection to SO_4^{2-} . So the rejection to Na_2SO_4 was higher than to MgSO_4 . There are two rejection mechanisms of NF: Donnan exclusion and steric hindrance,²⁹ and they both played important roles in the TAC/TMC membrane.

It is noteworthy that the TAC/TMC membrane could not reject NaCl sufficiently. The membrane made from 1,3-cyclohexane-bis(methylamine) (CHMA) and TMC even possessed a rejection of 78% to NaCl ,³⁰ although the molecular size of CHMA was longer than that of TAC. If the membrane were made from

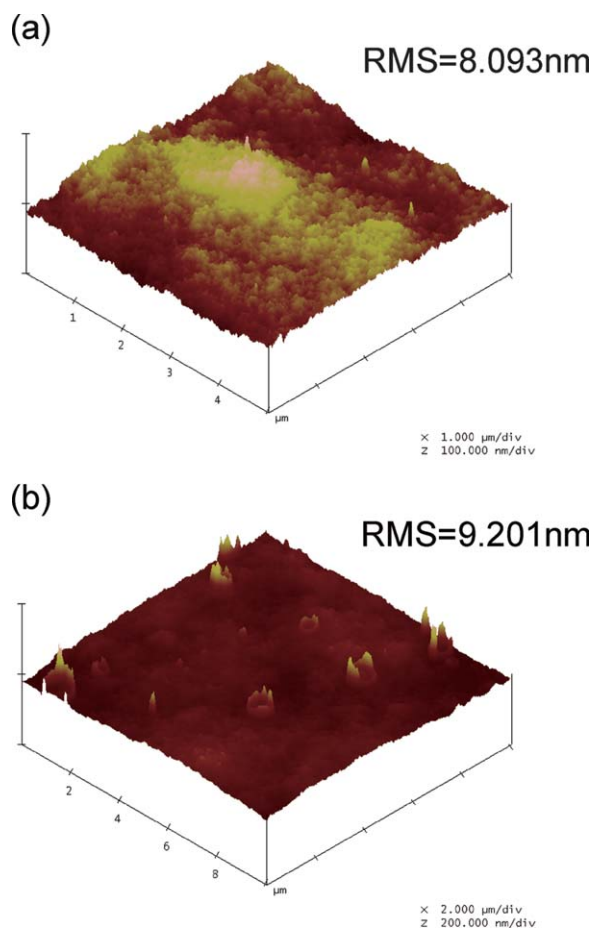


Figure 7. AFM images and roughness analysis results: (a) top surface of PSF support membrane; (b) top surface of TAC/TMC membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

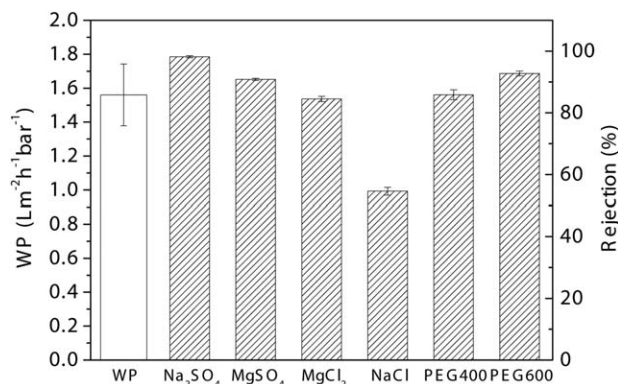


Figure 8. Water permeability of Na_2SO_4 solution and rejection to various salts and organic compounds of TAC/TMC membrane (TAC: 0.2 wt %; TMC: 0.15 wt %; reaction time: 60 s; heat treatment: 80°C for 5 min).

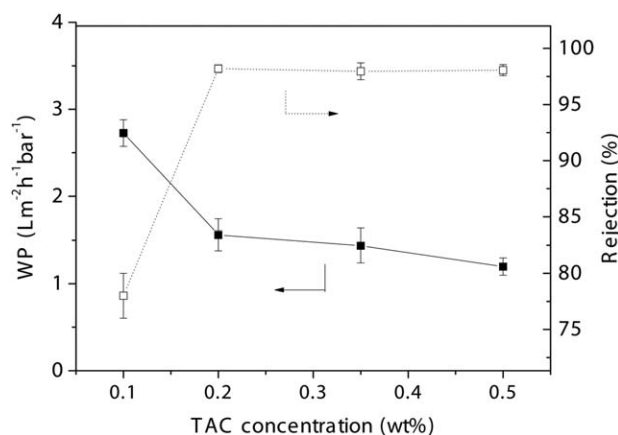


Figure 9. Effect of TAC concentration on the separation performance of TAC/TMC membrane tested by 1000 ppm Na₂SO₄ aqueous solution.

cis,cis-1,3-diaminocyclohexane, it should exhibit a higher NaCl rejection than the CHMA/TMC membrane. So the presence of the third amine group in TAC changed the chain structure a lot because it could also react with TMC, which formed a steric hindrance that destroyed the closed circular structure and enlarged the size of the network pores. The molecular weight cutoff (MWCO) of the membrane was 600 Da since its rejection for PEG600 was higher than 90%, whereas the MWCO of the PIP/TMC membrane was less than 400 Da,⁷ which indicated that there were interconnected, larger pores penetrating across the active layer of the TAC/TMC membrane.

Effects of Preparation Conditions on the Performance of the TAC/TMC Membrane

TAC and TMC Concentration. Figure 9 shows the effect of TAC concentration on the performance of the TAC/TMC membrane. When the concentration was 0.1 wt %, the membrane was not crosslinked well: it presented a low Na₂SO₄ rejection of 78%. When it was 0.2 wt %, the rejection reached the highest level and WP dropped sharply. A further concentration increase did not bring any obvious change to the rejection and WP values. So 0.2 wt % of TAC was good enough to form a dense selective layer, and this concentration is lower than the reported

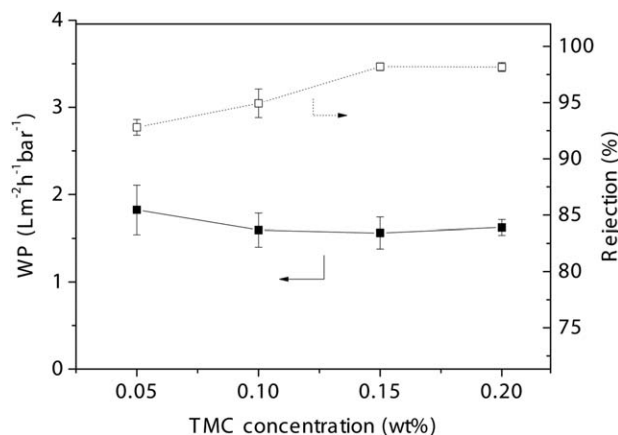


Figure 10. Effect of TMC concentration on the separation performance of TAC/TMC membrane tested by 1000 ppm Na₂SO₄ aqueous solution.

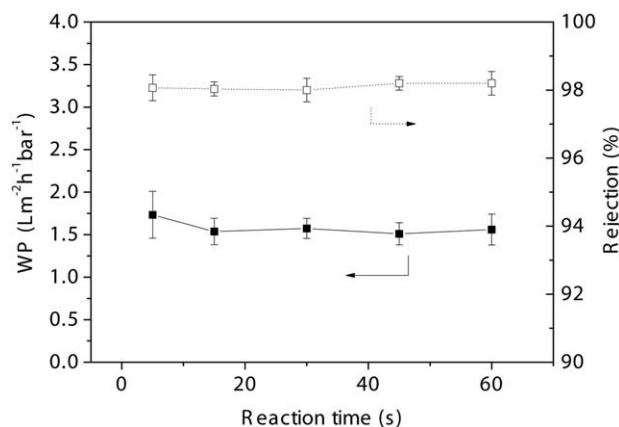


Figure 11. Effect of reaction time on the separation performance of TAC/TMC membrane tested by 1000 ppm Na₂SO₄ aqueous solution.

values of diamines^{7,31,32} as TAC was trifunctional and could provide enough amine groups even at a relatively low concentration.

Figure 10 shows the effect of TMC concentration. The rejection increased and WP decreased slightly with the increase of TMC concentration, and 0.15 wt % was the lowest concentration needed to form a dense selective layer, which was within the range of common values.

Reaction Time. The influence of reaction time on the performance of the membrane was exhibited in Figure 11. It was surprising that the rejection could reach 98% within only 5 s, which was much shorter than the time the other reported amines needed.^{9,16,32} Further increasing the reaction time, the rejection stayed almost constant, and the WP dropped from 1.73 L m⁻² h⁻¹ bar⁻¹ to 1.56 L m⁻² h⁻¹ bar⁻¹, indicating that the active layer formed at 5 s was already dense enough. So the growth rate of the crosslinking chain was very high because there were two kinds of crosslinking points: TAC and TMC. This observation indicated that the active layer was formed very quickly and was highly crosslinked, which support our opinions mentioned in the SEM analysis section and the separation performance analysis section.

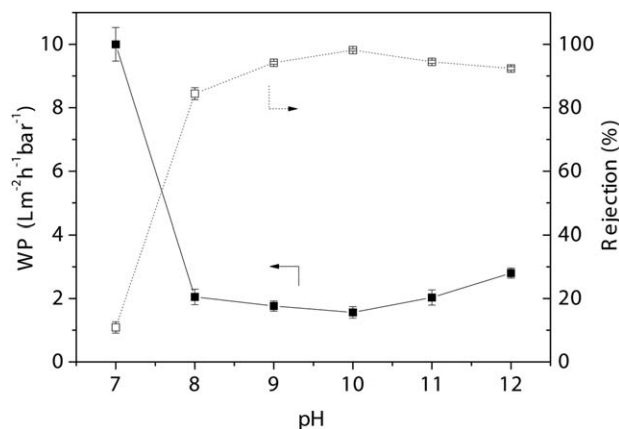


Figure 12. Effect of amine solution pH on the separation performance of TAC/TMC membrane tested by 1000 ppm Na₂SO₄ aqueous solution.

pH of Aqueous Amine Solution. The effect of aqueous solution pH is illustrated in Figure 12. The best rejection of 98.2% was reached at pH = 10, which was consistent with the pH value of common diamine solutions.⁹ It is well known that the reaction of amines and acyl chlorides can produce HCl, which can protonate the amine group. When the pH was 10, the amine groups were well protected by triethylamine from being protonated, and the polymerization could proceed smoothly. When the pH was below 10, there was not enough triethylamine to consume HCl, and the excessive camphorsulfonic acids could also protonate the amine groups of TAC before the polymerization, reducing the degree of crosslinking. When the pH was above 10, there were more acyl chloride groups hydrolyzed to carboxylic acid, producing an active layer with a looser structure, so the WP increased and the rejection decreased.

Curing Temperature. In order to promote the further crosslinking of the unreacted amine and acyl chloride groups, heat curing was required, and the influence of temperature is exhibited in Figure 13. When the membrane was treated at ambient temperature, the rejection of Na₂SO₄ was 95%, whereas when the temperature exceeded 60 °C, the crosslinking reaction was obviously enhanced, and the rejection was improved to nearly 98%, but WP dropped a little because it had already reached a high crosslinking level given that TAC was also a crosslinking point. It is known that an excessively high temperature is harmful to the membrane, and some membranes treated at 100 °C gave a worse separation performance.^{16,17,32} Although it did not happen in our experiments, it seems that 80 °C should be the appropriate choice according to the results.

Operating Pressure. The effect of operating pressure is shown in Figure 14. The flux increased almost linearly with the increase of pressure, and the rejection increased very slightly. This could be explained by the water flux being in proportion to the pressure difference across the membrane, while the salt flux was in proportion to the concentration difference across the membrane, which was little affected by pressure. When the pressure increased, the enhanced flux could dilute the penetrating flow, so the salt concentration decreased and the rejection increased, but at the same time, the concentration polarization

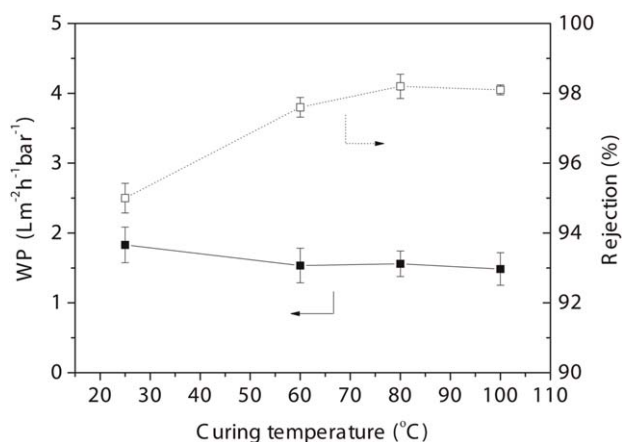


Figure 13. Effect of curing temperature on the separation performance of TAC/TMC membrane tested by 1000 ppm Na₂SO₄ aqueous solution.

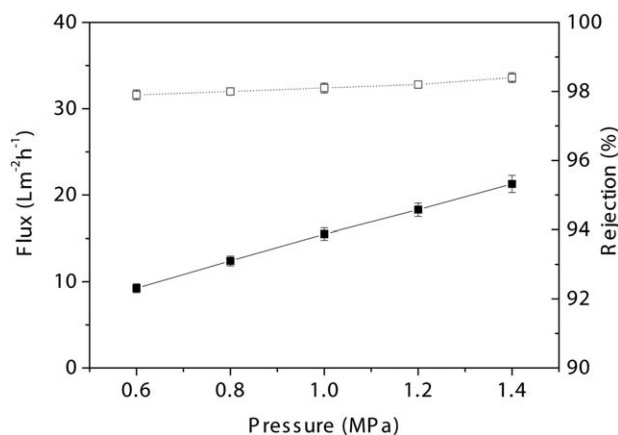


Figure 14. Effect of operating pressure on the separation performance of TAC/TMC membrane tested by 1000 ppm Na₂SO₄ aqueous solution.

became more severe and the concentration difference across the membrane increased, which could enhance the salt flux. Finally, these two mechanisms offset each other and made the rejection change not obvious. Thus the membrane could be operated in a wide range of pressures.

CONCLUSIONS

cis,cis-1,3,5-Triaminocyclohexane was synthesized and used to prepare a composite NF membrane by interfacial polymerization with TMC. TAC/TMC was a negatively charged NF membrane, which rejected salts by both Donnan exclusion and steric hindrance and exhibited a Na₂SO₄ rejection of 98.2%. The water permeability of the membrane was 1.56 L m⁻² h⁻¹ bar⁻¹, and the MWCO was 600 Da. The surface of the TAC/TMC membrane was smooth, which was helpful in enhancing its resistance to fouling. The active layer could be formed much faster than in those made from common diamines, which is very promising for making the industrial production process simpler and faster. The active layer was more highly crosslinked and possessed a potential to accommodate more structure-tailoring molecules that could enhance the WP of the membrane without any serious effects on the salt rejection. We believe the prepared NF membrane possesses great application potential in the field of desalination processes.

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