

Preparation and Characterization of Positively Charged Composite Nanofiltration Membranes by Coating Poly(ether ether ketone) Containing Quaternary Ammonium Groups on Polysulfone Ultrafiltration Membranes

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ABSTRACT: The novel positively charged poly(ether ether ketone)s (PEEKs) with pendant quaternary ammonium groups were synthesized by copolymerization of 3, 3'-dimethylaminemethylene-4,4'-biphenol (DABP), 3,3',4,4'-tetramethylbiphenol, and 4,4'-bisfluorobenzophenone followed by reaction with iodomethane. The resulting copolymers were used to prepare thin film composite (TFC) nanofiltration (NF) membranes via the dip-coating method. The effects of different parameters such as copolymer concentration and curing time on the membrane performance (flux and rejection of inorganic salts) were investigated. The optimum parameters were that 1.5 wt % quaternary ammonium PEEK containing 1.8 quaternary ammonium groups per unit with 0.5 wt % DMSO coated on the polysulfone (PSf) support membrane and cured at 100°C. The results of the performance testing showed that the trend for rejection was $R_{\text{MgCl}_2} > R_{\text{CaCl}_2} > R_{\text{NaCl}} > R_{\text{Na}_2\text{SO}_4}$ (R = rejection), which was a typical positively charged membrane. The best performance of these composite nanofiltration membranes was 91.3% rejection for 500 ppm MgCl_2 and 62.5 L/m² h water permeability at 0.4 MPa. The MWCO of the membrane was 800 Da. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: nanofiltration; dip-coating; positively charged; selectivity

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INTRODUCTION

Nanofiltration (NF) is a relatively new pressure-driven technology developed during the 1970s and 1980s, which takes in the upper end (in separation size terms) of reverse osmosis and the lower end of ultrafiltration, covering MWCO values of 100 to 1000 Daltons.¹ The key feature of nanofiltration is that it retains divalent salts, whereas it allows monovalent salts (such as sodium chloride) to pass, due to its nanometer-sized pores (0.5–2 nm in diameter) and electrical charges on the surface. Nanofiltration is a promising technology for water softening, separation of dye-salt, and waste water reclamation.^{2–4}

Most NF membranes are composites with a selective layer on the top of a substrate. The predominant method of preparing a composite NF membrane is interfacial polymerization.⁵ An aqueous phase containing diamine and an organic phase containing acyl halide are reacted with each other on a porous sup-

port to form a thin selective layer.⁶ This method improves TFC NF membranes with respect to both solute rejection and water permeability. However, interface polymerization limits the chemical composition of the active layers to polyamides for most commercial NF membranes.

Dip-coating, coating a dilute polymer solution on a support, is a simple method to prepare the separating layer of composite membranes.⁵ The advantage of this method is that the type of the dilute polymer solution can be tailored to the specific application of interest.⁷ McGrath and Freeman successfully prepared highly chlorine-tolerant desalination membranes by using sulfonated polysulfone in a dip-coating method. These membranes showed high tolerance to chlorine over a wide pH range compared with commercial available Polyamide membranes (SW30HR, Dow FilmTec).⁸ Ba et al. designed a near neutral charged NF membrane developed by coating negatively charged

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sulfonated polyketone onto the surface of a positively charged NF membrane. The neutrally charged membrane exhibited much better resistance to fouling than both the positively charged and the negatively charged NTR-7450 membranes.⁹ Other sulfonated polymers such as sulfonated PPO¹⁰ and sulfonated PPESK¹¹ were also used to prepare NF membranes using the dip-coating method. Although these membranes provided a variety of separation capabilities, they are generally negatively charged and reject multivalent anions more effectively than monovalent anions. Therefore, it is necessary to develop positively charged NF membranes that have a better capacity to reject multivalent cations.¹² To prepare positively charged NF membranes, a polymer containing cationic groups such as quaternary ammonium groups along the backbone is required. Unfortunately, due to their limited variety and poor solubility positively charged aromatic polymers are not suitable for preparation of composite NF membranes by the dip-coating method.

In this article, we develop a soluble poly(ether ether sulfone) (PEEK) ionomer with pendant quaternary ammonium groups (QAPEEK). The copolymers described herein are synthesized by direct polymerization of 3, 3'-dimethylaminemethylene-4,4'-biphenol (DABP), 3,3',4,4'-tetramethylbiphenol, and 4,4'-bis-fluorobenzophenone followed by reaction with iodomethane. To study the use of QAPEEKs as the active layer of nanofiltration composite membranes, fundamental transport properties, as well as the mechanical and thermal stability of the QAPEEK dense membranes were investigated in details. Then the thin film composite (TFC) membranes with poly(ether ether sulfone) (PEEK) ionomer with pendant quaternary ammonium groups (QAPEEK) as the top layer coated on polysulfone ultrafiltration (UF) membranes were prepared under different preparation conditions including the polymer concentration and drying temperature. Membrane performances for nanofiltration that separated electrolytes such as MgCl₂ and NaCl from aqueous solution were investigated using the composite membranes thus prepared.

EXPERIMENTAL

Materials

3,3'-Bimethylaminemethylene-4,4'-biphenol(DABP) was synthesized as we reported before.¹³ 2,2',6,6'-Tetramethyl-4,4'-biphenol(TMBP) and 4,4'-bisfluorodiphenylacetone(BFDPA) were purchased from Aldrich. Formaldehyde solution (37%), dimethylamine solution (33%), dimethyl sulfoxide (DMSO), glycerol, and polyethylene glycol (PEG) were purchased from Sinopharm Group Chemical Reagent. Cs₂CO₃ was purchased from Hubei Baijierui Advanced Material. *N,N*-Dimethylacetamide (DMAc) was stirred over CaH₂ for 24 h, then distilled under reduced pressure, and stored over molecular sieves. Polysulfone ultrafiltration membranes were supplied by AMFOR, with a cut-off molecular weight of 30,000 Da. Its pore size is 26 nm and the pore contribution of the surface area is 72.2%. The pure water flux of the substrate membrane was 132 L/m² h at 25°C at a transmembrane pressure of 0.1 MPa. These values are given by given by the manufacturer. All other reagents were obtained from commercial sources and used as received.

Preparation of Polymer

Poly(Arylene Ether Ketone) Bearing Pendant Tertiary Amine Groups (TAPEEK-x). The number of tertiary amine groups/repeat unit was controlled by adjusting the molar ratio of DABP to TMBP. A typical synthesis procedure of TAPEEK-90, where 90 refers to the feed percent of DABP, was as follows. DABP (2.7036 g, 9 mmol), TMBP (0.2423 g, 1 mmol), BFDPA (2.1820 g, 10 mmol), Cs₂CO₃ (6.84 g, 21 mmol) and dry DMAc (50 mL, 10% solids) were added to a flame-dried 100 mL three-necked flask, which was equipped with a nitrogen inlet and overhead stirrer. The mixture was heated at 120°C for 16 h. After cooling to room temperature, an additional 30 mL of DMAc was added so as to dilute the highly viscous solution, after which the solution was filtered and dropped into stirred deionized water. The precipitate was filtered off and washed with hot water three times prior to being dried under vacuum to produce the final product. Yield: 98%.

Poly(Arylene Ether Ketone) Bearing Pendant Quaternary Ammonium Groups (QAPEEK-x). The following represents a typical procedure for the synthesis of quaternary ammonium of QAPEEK-x. QAPEEK-90 was prepared by dissolving 1 g TAPEEK-90 in 20 mL of dimethylsulfoxide (DMSO) and then 0.6 g iodomethane was added. The reaction mixture was stirred at 30°C for 12 h in the dark and then poured into ethanol. The precipitate was filtered off, washed with distilled water thoroughly, and dried in vacuum oven for 24 h at 100°C.

Preparation of Dense Membranes

The dense membranes were prepared by casting 8.0 wt % QAPEEK-x DMSO solution onto a clean glass substrate, followed by drying at 80°C for 12 h and vacuum-dried at 100°C for 24 h. Then the membrane was immersed into deionized water and peeled off. The nominal thickness of all films was approximately 40–50 μm.

Preparation of the Composite Membrane

First, Polysulfone ultrafiltration membranes were modified by immersing them in 10% glycerol/H₂O solution for 5 min. The modified PSf ultrafiltration membranes were taken out, wiped with tissue paper and were mounted on a glass plates. Then a mixture solution of QAPEEK-90 with different concentrations (0.5, 1.0, 1.5, and 2 wt %) and 0.5 wt % DMSO in HCOOH was poured on PSf ultrafiltration membranes and kept in contact for 3 min. Excess polymer solution was drained off by leaving the membrane vertically. Then the membranes were dried in the oven for 10 min at different temperature (80, 100, and 120°C).

Measurements

¹H-NMR spectra were measured at 300 MHz on an AV300 spectrometer. Thermogravimetric analysis (TGA) was conducted in nitrogen with a PerkinElmer TGA-2 thermogravimetric analyzer at a heating rate of 10°C/min in N₂. Molecular weights were also determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, coupled with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector operating at a wavelength of 260 nm. DMF was used as eluent. The mechanical properties of membranes were measured by means of tensile test in dry state at room

temperature, 30% humidity using an Instron-1211 mechanical testing instrument at a speed of 2 mm/min. Membranes were cut into a rectangular shape with dimensions 50 mm × 5 mm. At least five specimens from each sample were tested. Totally, 0.02 g dry polymer was immersed in 1 mL different solvent at room temperature for 48 h to investigate the solubility of the polymer.

Water uptake (%) was calculated using the following equation:

$$\text{water uptake(\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

where W_d and W_w are the measured masses of dry and fully hydrated film samples, respectively. Each sample, $\sim 4 \times 4 \text{ cm}^2$, was dried in a vacuum oven at 110°C for 24 h before measuring W_d and immersed in deionized water at 25°C for 24 h before measuring W_w .

The morphology and thickness of the active layers of the composite membranes were characterized with XL 30 ESEM FEG from the FEI Company. The cross-section was obtained by fracturing the membranes in liquid nitrogen. All the samples were sputtered with gold prior to SEM measurement. The solution conductivity was measured at Elmeiron conductivity meter CC-501, Poland. The concentrations of NaCl and MgCl₂ mixture solution were analyzed by atomic absorption. Total organic carbon was characterized with Shimadzu TOC-5050A.

Performance Testing

The water permeability (P_w) and salt rejection (R) of dense membrane were evaluated at 25°C using a cross-flow filtration apparatus (Figure 1). The feed solution of measuring P_w was deionized water; the feed solution of measuring R was an aqueous feed solution containing 2000 ppm NaCl at pH 6.5–7.5; the applied feed pressure was 2 MPa; and the permeate pressure was atmospheric.

P_w was calculated from the volume of water V permeated through a membrane of area A and thickness l divided by the pressure difference ΔP at time t [eq. (2)].

$$P_w = \frac{V \cdot l}{A \cdot t \cdot \Delta P} \quad (2)$$

Salt rejection (R) was calculated as follows:

$$R (\%) = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (3)$$

Here, C_f and C_p are the NaCl concentrations in the feed and permeate, respectively. Salt concentration was measured by electrical conductivity.

The composite nanofiltration membranes were characterized by measuring the water flux and salt rejection. The nanofiltration experiments were conducted using a laboratory-scale cross-flow filtration cell as shown in Figure 1. The effective area of the membranes was 13.4 cm². The membranes were pre-treated with pure water at 0.4 MPa for 4 h. Then, the salt solution flux was evaluated at 0.4 MPa and room temperature (around 25°C).

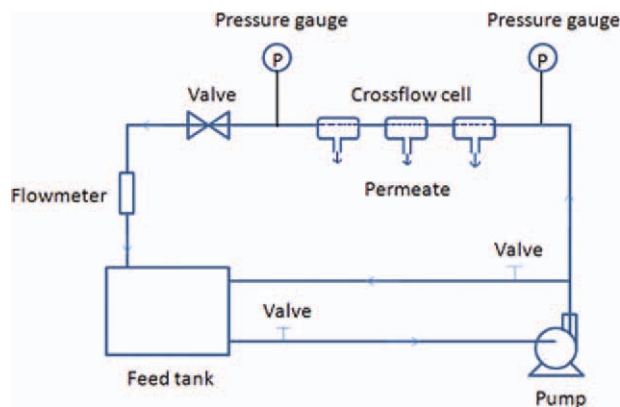


Figure 1. Cross-flow filtration system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The flux was calculated by the equation

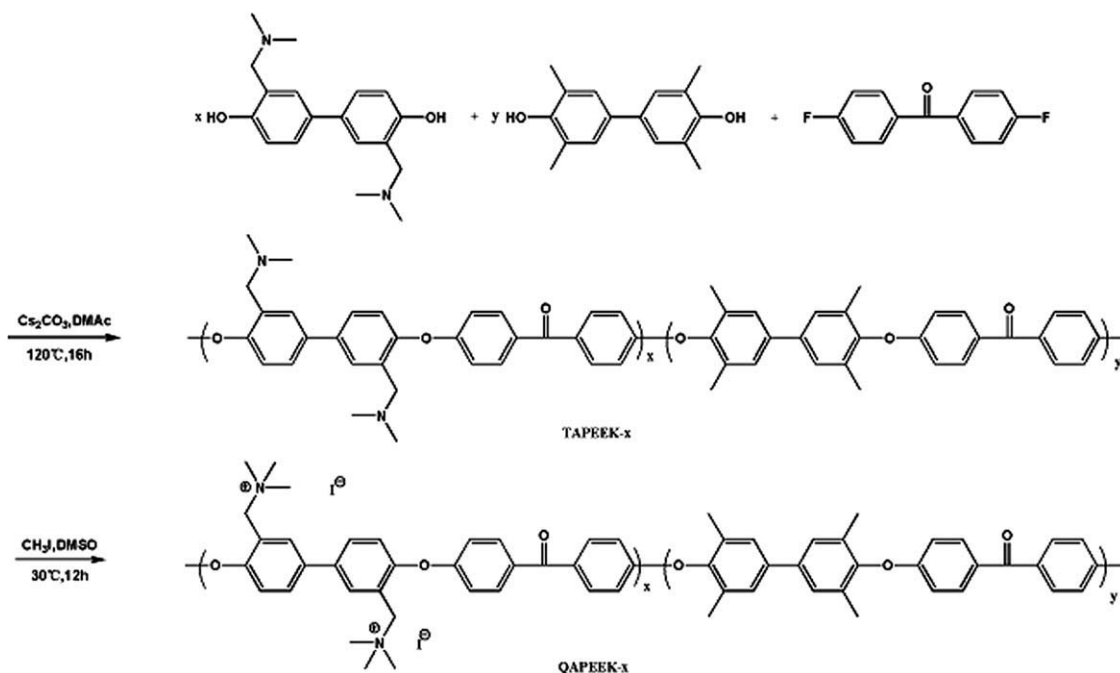
$$F = \frac{V}{At} \quad (4)$$

where V (L) is the volume of permeate collected under transmembrane pressure during time period t (h) and A is the effective area of the membrane (m²). Salt rejection (R) was calculated by using eq. (3). The concentration of single salt solution was measured by electrical conductivity. The concentration of mixed salt was determined by atomic absorption spectrometry. Before atomic absorption test, both concentration of feed and permeate are diluted to the magnitude of 10⁻⁶. The concentrations of PEG were analyzed by total organic carbon (TOC). The presented data for permeability and salt rejections of membranes in this study are the average of three measurements.

RESULTS AND DISCUSSION

Polymer Preparation

The random TAPEEK- x copolymers were synthesized by direct polymerization of tertiary amine biphenol monomer (3,3'-dimethylaminemethylene-4,4'-biphenol (DABP)), 2,2',6,6'-tetramethyl-4,4'-biphenol (TMBP) and 4,4'-bisfluorobenzophenone as indicated in Scheme 1. High-molecular-weight polymers were obtained, as shown by inherent viscosities and GPC in Table I. Typical number-average molecular weights and polydispersities ranged from 69,000 to 74,000 and 2.1 to 2.3, respectively. The chemical structure of the synthesized polymers was confirmed by ¹H NMR spectroscopy with CDCl₃ as the solvent. Figure 2(a) shows the spectra of the protons for the TAPEEK-100. The peaks at δ 3.3 ppm and δ 2.1 ppm are the chemical shifts of protons on methylene and methyl groups, respectively. The intensity ratio of H (—CH₂—) to H (—CH₃) is close to 1 : 3, as expected for the composition of the tertiary amine groups on TAPEEK-100. The peaks at δ 7.1 ppm and δ 7.69 ppm were attributed to the hydrogen atom of the 4,4'-bisfluorobenzophenone unit. The thermal stability of TAPEEK-100 was evaluated by thermogravimetric analysis. TAPEEK-100 exhibited two thermogravimetric steps. The first weight loss occurred at about 290°C that was associated with the degradation of tertiary



Scheme 1. Effect of feed concentration on QAPEEK-90 composite NF membranes at 0.4 MPa.

amine groups of the polymer main chains. The weight loss of this step was about 30%, matching the weight percent of quaternary amine groups in the polymer main chains. The second weight loss at about 500°C was assigned to the degradation of the polymer main chains.

The TAPEEK-x was converted to the quaternized poly(arylene ether ketone)s (QAPEEK-x) by reaction with iodomethane. The mole ratio of iodomethane to tertiary amine groups was set to be 2.1 : 1 to ensure complete conversion of the tertiary amine units into the quaternary ammonium moieties. The corresponding ^1H NMR spectrum of QAPEEK-90 is shown in Figure 2(b). The signal at δ 2.4 ppm, δ 3.1 ppm and δ 4.7 ppm could be assigned to H_a , H_b , and H_c , respectively.

Chemical and Physical Properties of QAPEEK

The chemical and physical properties of QAPEEK copolymers are shown in Table II. QAPEEK showed excellent solubility in polar aprotic solvents such as DMSO, DMAc, and HCOOH. These membranes had tensile stresses at maximum load of 31.5–38.7 MPa, Young's moduli of 516–602 MPa, and elongation at break of 25.3–35.3%.

The thermal stability of QAPEEK-90 was evaluated by thermogravimetric analysis. QAPEEK-90 exhibited three thermogravimetric steps. The first slight weight loss occurred before 210°C, corresponding to the evaporation of absorbed water that the strong hydrophilic quaternary ammonium group attracted from the atmosphere. The weight loss of this step was about 4%. The second weight loss occurred at about 240°C that was associated with the degradation of quaternary ammonium groups of the polymer main chains. The weight loss of this step was about 45%, matching the weight percent of quaternary ammonium groups in the polymer main chains. The third weight loss at

about 400°C was assigned to the degradation of the polymer main chains.

The above results show that the prepared poly(ether ether ketone)s (PEEKs) containing quaternary ammonium groups not only retained the excellent high mechanical strength and good thermal properties of conventional PEEKs, but also exhibited enhanced solubility.

Fundamental Transport Properties of the Dense QAPEEK Membranes

The fundamental transport properties of the dense polymer membranes are shown in Table III. Both water uptake and water permeability of QAPEEK-x membranes were dependent upon the number of quaternary ammonium salt groups on the polymer chain (or IEC values). With IEC increasing from 1.92 to 2.62, the water uptake of QAPEEK-x films increased from 14.6 to 98.5% and the water permeability increased from 0.71 to 7.58 L $\mu\text{m}/\text{m}^2$ h bar. There was a sharp increase in water permeability from IEC 1.92 to IEC 2.30, perhaps because continuous hydrophilic micro-domains were formed at high IEC values.¹⁴ A tradeoff between good water permeability and salt

Table I. Inherent Viscosity, Molecular Weight of TAPEEKs

Sample	η_{inh}^a (dL g ⁻¹)	M_n ($\times 10^4$ g mol ⁻¹)	M_w ($\times 10^4$ g mol ⁻¹)	PD ^b
TAPEEK-60	0.43	7.2	16.6	2.3
TAPEEK-80	0.40	7.6	16.7	2.2
TAPEEK-90	0.41	6.9	15.8	2.3
TAPEEK-100	0.42	7.4	15.5	2.1

^aInherent viscosity measured at a concentration of 0.5 dL g⁻¹ in DMAc at 30°C, ^bPolydispersity.

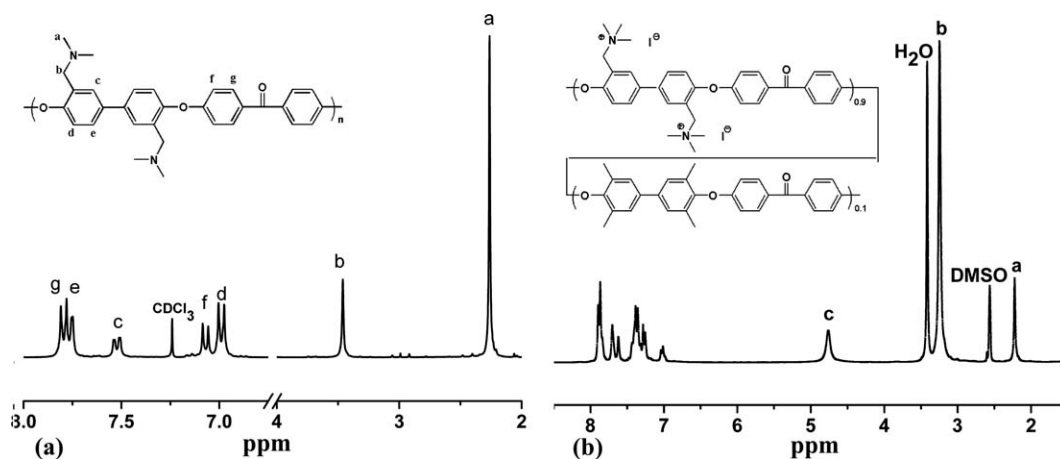


Figure 2. The $^1\text{H-NMR}$ spectra of polymers (a) TAPEEK-100 and (b) QAPEEK-90.

Table II. The Solubility and Mechanical Properties of TAPEEK-100 and QAPEEK-x

	Solubility					Mechanical properties		
	H ₂ O	CHCl ₃	DMSO	DMAc	HCOOH	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
TAPEEK-100	–	+	+	+	+	39.2	951	7.7
QAPEEK-100	±	–	+	+	+	31.5	516	35.3
QAPEEK-90	–	–	+	+	+	33.8	556	29.0
QAPEEK-80	–	–	+	+	+	36.5	595	27.8
QAPEEK-60	–	–	+	+	+	38.7	602	25.3

±, Partially soluble when heating; –, insoluble; +, soluble; DMAc, *N,N*-dimethylacetamide; and DMSO, dimethyl sulfoxide.

rejection was observed. For example, QAPEEK-100 showed higher water permeability than QAPEEK-60 (7.58–0.71 L $\mu\text{m}^2/\text{m}^2$ h bar), but lower salt rejection than QAPEEK-60 (70.72–94.22%). This flux-rejection trade-off relationship was also found for a series of sulfonated films.¹⁵ This is because dense membranes prepared from high IEC polymers have a higher degree of swelling in water. Polymeric chains moved farther apart in water solution, and the films became more open. This resulted in lower rejections and higher water permeability.

Optimization of the Coating Procedure

Coating Solution Preparation. PSf ultrafiltration membrane with a molecular weight cut-off of 30,000 Da was used as a

support membrane. Before coating, the substrate membrane was immersed in a 10% glycerol/H₂O solution. This pretreatment was to prevent the collapse of substrate membrane pores during the curing process.^{16,17} On the basis of the performance test of the dense films, films with high IEC show higher water permeability and lower salt rejection. This is due to the highly swelling of high IEC polymer in water. While a composite membrane is prepared through dip-coating method, the swelling of the polymer is constrained by the pores of the support membrane. When QAPEEK-90 is chosen as the coating polymer, it may not only keep high water permeability but also be with enhanced salt rejection for swelling constraint. Because the membranes prepared by QAPEEK-100 are partly soluble in

Table III. Fundamental Transport Properties of QAPEEK

	IEC		Water uptake (%)	Water permeability ^b (L $\mu\text{m}^2/\text{m}^2$ h bar)	NaCl rejection ^c (%)
	Theoretical	Experimental ^a			
QAPEEK-100	2.62	2.59	98.5	7.58	70.72
QAPEEK-90	2.47	2.43	81.7	5.76	77.25
QAPEEK-80	2.30	2.30	39.2	3.80	87.15
QAPEEK-60	1.92	1.90	14.6	0.71	94.22

^aIECs calculated from NM spectra, ^bMeasured at 25°C using cross-flow filtration (feed pressure 2.0 MPa), ^cMeasured at 25°C using cross-flow filtration (feed pressure 2.0 MPa, feed concentration 2000 ppm NaCl).

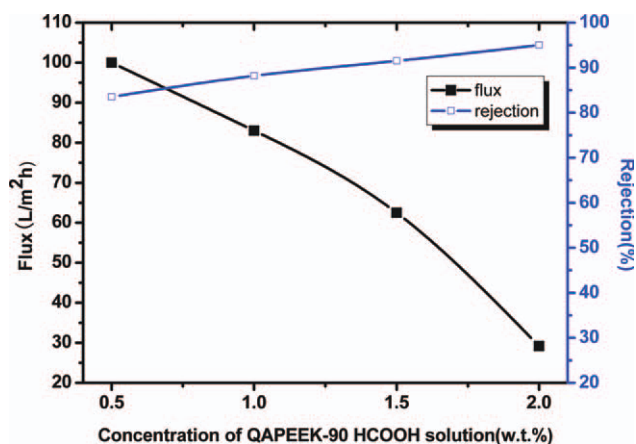


Figure 3. Effect of QAPEEK-90 concentration on TFC membrane performances for a 500 mg/L MgCl₂ solution at 0.4 MPa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

water, it can not be chosen to prepare composite membrane. Considering the solubility of QAPEEKs, HCOOH was chosen as a solvent for the coating solution because it can dissolve the polymer but does not dissolve the PSf support membrane. A small amount of aprotic solvent DMSO (0.5%) was added to the casting solution to decrease the interfacial tension and increase the swelling of the support, thereby making it more compatible with the surface coating solution.¹⁸

Influence of the Coating Solution Concentration of QAPEEK-90 on the Performance of the NF Membrane. The substrate membranes were coated with QAPEEK-90 solutions of various concentrations, and the TFC membranes were prepared and dried at 100°C. Figure 3 shows the effect of the QAPEEK-90 concentration in the coating solution on the water flux and MgCl₂ rejection of the TFC membranes. The increase of QAPEEK-90 concentration from 0.5 to 2% resulted in an enhancement of MgCl₂ rejection from 83.5 to 92.7% and a decrease of the flux from 100 L/m² h to 27.5 L/m² h. This was expected because the increase in QAPEEK-90 concentration results in a thicker skin layer. SEM (Figure 4) was used to char-

Table IV. Influence of Curing Temperature on the QAPEEK-90 Composite Membrane Performance

T (°C)	F (L/m ² h)	R _{MgCl₂} (%)
80	71.7	85.95
100	62.5	91.42
120	37.1	92.77

acterize the morphology of the membrane surface and its cross-section. The surface of the composite membrane was smooth and no visible pores were observed on the surface of the composite membrane when visualized using 40,000 magnification. It was easy to distinguish the thin-active layer from the support layer, and the thickness of the active layer was about 500 nm.

Influence of Drying Temperature. Studies of TFC membranes have indicated that curing is a necessary step for imparting stability to the thin film and increasing the salt rejection.^{19,20} Table IV shows the influence of curing temperature on the QAPEEK-90 composite membrane performance and indicates that the performance of the TFC membrane changed with the curing temperature. The rejection increased with an increase in curing temperature and simultaneously the water flux decreased under 0.4 MPa for 500 mg L⁻¹ MgCl₂ solution. Probably, as both formic acid and dimethylsulfoxide are the solvents with high boiling points, drying at 80°C for 10 min is not enough to remove all the solvent. Some traces of solvents remain in the membrane (and swell it very little) and when the membrane gets in contact with water, the solvents are extracted and microporosity appears (a phase inversion process at a very small scale), which leads to the lower rejection and higher flux compared with those at elevated temperatures.

Conditions for obtaining good composite NF membranes include coating conditions of 1.5% QAPEEKs, HCOOH solutions containing 0.5% DMSO, and 100°C curing temperature.

Nanofiltration Performance of QAPEEK-90 Composite Membranes

The TFC NF membrane was prepared using the optimal parameters described above, and the performance of QAPEEK-90

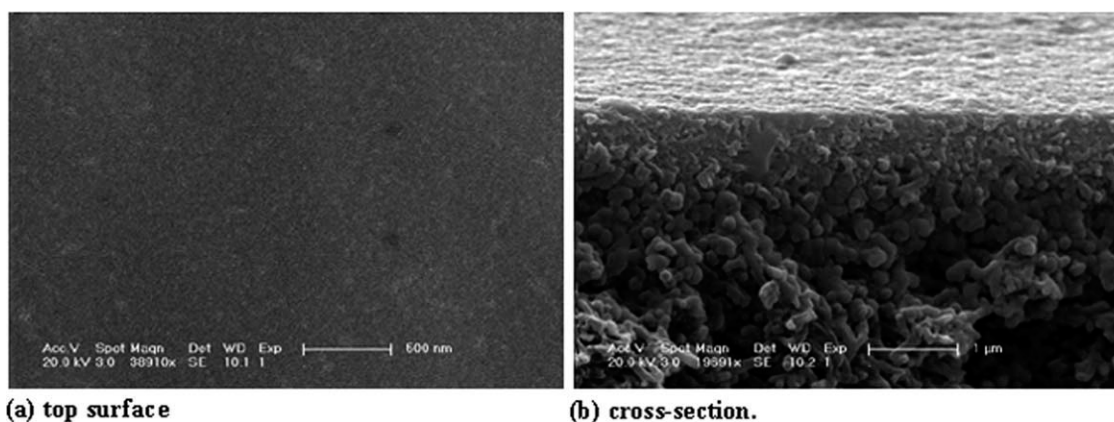


Figure 4. SEM images of the composite membrane: (a) top surface and (b) cross-section. (coating solution: 2.0 wt % QAPEEK-90 solution).

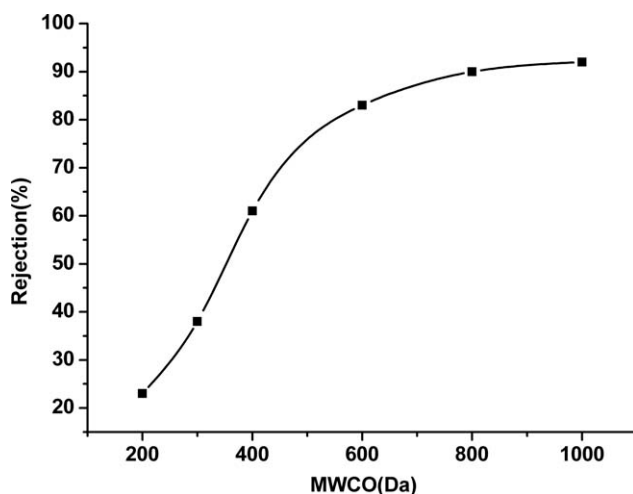


Figure 5. PEG retention of QAPEEK-90 composite membrane for 1000 ppm PEG solutions at 0.4 MPa.

composite membranes was measured. The molecular weight cut off is a fundamental method to characterize membrane pore size and refers to the MW of a neutral solute with a rejection value greater than 90%. Herein, MWCO was based on the rejection of PEG and the measurements for determining MWCO of QAPEEK-90 composite membranes are plotted in Figure 5. The MWCO was about 800Da (diameter of PEG 800 Da is about 2.5 nm),²¹ which is in the range necessary for nanofiltration.

Membrane performance was tested using different solutes and the results presented in Table V showed that the salt rejection of the membrane occurred with $\text{MgCl}_2 \approx \text{CaCl}_2 > \text{NaCl} > \text{Na}_2\text{SO}_4$, which is a result that is typical of a positively charged membrane that can be explained by electrostatic effects.²² The flux variation for each salt may be related to the osmotic pressure. The water flux of the NF membrane prepared in this paper was higher than that of our previously reported positively charged NF membrane and the MgCl_2 and NaCl rejection of the NF membrane prepared in this article was lower than our previously reported positively charged NF membrane.²³ The feed concentration effect experiments were carried out at 0.4 MPa operating pressure with increasing the NaCl concentration from 0.5 to 2.0 g/L as shown in Figure 6. Both rejection and flux decrease with an increase of NaCl concentration. This result can be explained by Donnan exclusion. As the feed concentration increases, the electrostatic interaction between anions in

Table V. Membrane Performance for Removal of Metal Ions

Inorganic salt	Flux ($\text{L}/\text{m}^2 \text{ h}$)	Rejection (%)
MgCl_2	65.0	91.3
CaCl_2	60.4	89.5
NaCl	57.9	52.6
Na_2SO_4	46.7	23.7
MgCl_2^{23}	50.3	94.9
NaCl^{23}	56.6	58.0

Operating conditions: 500 mg/L salt solution, 0.4 MPa.

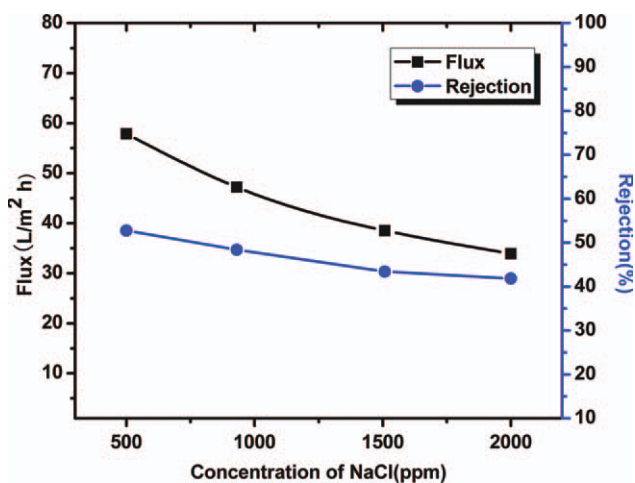


Figure 6. Effect of feed concentration on QAPEEK-90 composite NF membranes at 0.4 MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the solution and the positively charged membrane surface becomes progressively stronger. This result leads to the decrease of the electrostatic repulsion effect of the electrolytic membrane on the cations, resulting a decrease in rejection. Besides, the flux also decreases with the increase of the ionic concentration, which may be due to the presence of the polarization layer next to the membrane surface.

Because these membranes show better rejection of high valence cations than low valence cations, it is of interest to consider the separation efficiency in a mixture of ions with different valences. A salt solution containing NaCl and MgCl_2 was used as a feed solution, and as shown in Table VI, the rejection of Mg^{2+} ions was not affected by the presence of Na^+ ions. However, the rejection of monovalent Na^+ ion was reduced in the presence of Mg^{2+} . With large amounts of NaCl and MgCl_2 (each salt concentration was about 500 ppm in the mixed salt solution), the high concentration of the Cl^- counter-ion may have resulted in efficient shielding of membrane charge. Although the less charged membrane may have decreased rejection to all the cations, there is a stronger influence on the monovalent cation (Na^+) than on the divalent ions (Mg^{2+}) because of the Donnan effect. The lower rejection for monovalent salt is the main characteristic of nanofiltration membranes with numerous applications including pretreatment before reverse osmosis processes. In general, the prepared thin-film composite membrane provides the capability for water softening.

Table VI. Rejection of Ionic Species in a Solution Containing Mixtures of Salts

MgCl ₂ and NaCl			
Feed Mg ²⁺	Feed Na ⁺	Rejection of Mg ²⁺ (%) ^a	Rejection of Na ⁺ (%) ^a
1.069 μg/mL	4.290 μg/mL	85.5	20.2

^aTest pressure: 0.4 MPa; permeate concentrations were measured by atomic absorption.

CONCLUSIONS

In conclusion, the novel positively charged poly(ether ether ketone)s (PEEK) with pendant quaternary ammonium groups were prepared using 2,2'-dimethylaminemethylene-4,4'-biphenol, 2,2',6,6'-tetramethyl-4,4'-biphenol and 4,4'-bisfluorodiphenylacetone. Because the quaternary ammonium copolymers obtained exhibited excellent solubility in HCOOH, QA-PEEK-90 was used to prepare the active layer of the thin film composite (TFC) nanofiltration (NF) membrane using the dip-coating method. The optimum parameters were 1.5 wt % QA-PEEK-90 copolymer with 0.5 wt % DMSO coated on the PSf support membrane and cured at 100°C. The order of rejection to different salts decreased in the order of MgCl₂, CaCl₂, NaCl, and Na₂SO₄, that reflected the positively charged characteristics of the NF membranes. QAPEEK-90 composite NF membrane showed 91.3% MgCl₂ rejection and 62.5 L/m² h of flux at a concentration of 500 mg/L at 0.4 MPa.

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