

Preparation and Characterization of Chloromethylated/Quaternized Poly(phthalazinone ether sulfone ketone) for Positively Charged Nanofiltration Membranes

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ABSTRACT: Chloromethylated poly(phthalazinone ether sulfone ketone) (CMPPEK) as a novel membrane material was successfully prepared from poly(phthalazinone ether sulfone ketone), with concentrated sulfuric acid as the solvent and catalyst, and chloromethyl octyl ether with lower toxicity as the chloromethylated reagent. The effects of the reaction conditions on the preparation of CMPPEKs with different degrees of chloromethylation were examined. The quantity of chloromethyl groups per repeated unit (DCM) of CMPPEK was determined by the method of analysis of the chlorine element, and structures were characterized by $^1\text{H-NMR}$ spectroscopy. The introduction of chloromethyl groups into the polymer chains led to a decrease in the decomposition temperature. With increasing DCM, the initial degradation temperature declined. CMPPEK had good solubility and was soluble in *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), and chloroform.

However, quaternized poly(phthalazinone ether sulfone ketone) (QAPPEK) had excellent solvent resistance, was only partly soluble in sulfuric acid (98%), and was swollen in *N,N*-dimethylformamide. QAPPEK nanofiltration (NF) membranes had about 90% rejection for MgCl_2 , and the performance of the NF membrane prepared with DMAc as the solvent was superior to that of the NF membrane prepared with NMP as the solvent. In addition, the rejection to the different salt solutions followed the following sequence: $\text{MgCl}_2 > \text{MgSO}_4 > \text{NaCl} > \text{Na}_2\text{SO}_4$. Furthermore, the thermotolerance of the QAPPEK NF membrane was examined, and the results show that when the solution temperature rose from 11 to 90°C, the water flux increased more than threefold with stable salt rejection. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1809–1816, 2008

Key words: membranes; separation techniques

INTRODUCTION

Nanofiltration (NF) as a separation technology of high efficiency and low energy consumption has been greatly developed in the last decades and widely applied in various industries, such as water softening, drinking-water purification, dye and antibiotic purification and concentration, salt removal, and waste treatment.^{1–4}

As we know, NF membranes can separate or reject ions because they have nanosized pore structures and charges on the surface. At present, most commercial NF membranes are generally neutrally or negatively charged.⁵ Studies on negatively charged

NF membranes have been more numerous than those on positively charged ones because positively charged membrane materials are limited. However, positively charged NF membranes have excellent hydrophilicity and higher rejections for high-valence cations than for low-valence cations and high-valence anions, which is actually needed on some occasions, such as for the retention of multivalent cations and recovery of cathode electrophoresis lacquer.

For the preparation of a positively charged membrane, the most commonly used route is a chloromethylation and quaternization process.^{6–8} Hao et al.⁹ prepared positively charged quaternized polysulfone NF membranes that were applied for the removal of ions in tap water and had 93% salt rejection and a $0.8 \text{ m}^3/\text{m}^2\cdot\text{day}$ product rate. However, methylchloromethyl ether as a chloromethylated reagent in the chloromethylation reaction is a notoriously carcinogenic halomethylether. To avoid the use of methylchloromethyl ether, novel, positively charged composite NF membranes were prepared. Xu and Yang¹⁰ prepared a novel positively charged composite NF membrane from poly(2,6-dimethyl-1,4-phenylene oxide) by *in situ* amine crosslinking. The rejection of MgCl_2 was 32–73%, which was much higher than that of NaCl. Du and Zhao¹¹ prepared poly(*N,N*-dimethyl-

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aminoethyl methacrylate)/polysulfone positively charged NF membranes with interfacial crosslinking polymerization. The membrane, which had a certain resistance to oxidative media and free chlorine, had a rejection 98% for MgCl_2 , and the aqueous flux was $8.3 \text{ L m}^{-2}\cdot\text{h}^{-1}$ at 0.8 MPa. However, the preparation of composite NF membranes are more complicated than that of integrally skinned asymmetric NF membranes. Therefore, it was necessary to further exploit novel membrane materials for integrally skinned, positively charged asymmetric NF membranes with a new method by which long chain and less toxic haloalkyl-ethers, for example, chloromethyl octyl ethers (CMOE), were used as chloromethylated reagents.¹²

A series of poly(phthalazinone ether sulfone ketone) (PPESK) copolymers are known to be outstanding membrane materials with high glass-transition temperatures (263–305°C), superior mechanical strengths, good solubilities, and good chemical resistances.^{13–15} The chemical modification of PPESK, including sulfonation and chloromethylation/quaternization, can lead to important functional membranes. Dai and coworkers^{16–18} synthesized sulfonated PPESKs and prepared negatively charged ultrafiltration and NF membranes. Su et al.¹⁹ successfully prepared positively charged NF membranes with chloromethylated poly(phthalazinone ether sulfone ketone) (CMPPEK; $S/K = 1/1$), which was obtained with concentrated sulfuric acid as a solvent and catalyst, and with chloromethyl butyl ether as a chloromethylated reagent. Quaternized poly(phthalazinone ether sulfone ketone) (QAPPEK; $S/K = 1/1$) NF membranes had perfect results when they were applied to the separation between dyes and NaCl. They had excellent acid resistance, oxide resistance, and could even be rinsed with 5 wt % HCl solution without loss properties. To further exploit PPESK positively charged membrane material on the basis of previous studies, CMPPEK (ratio of sulfone to ketone units (S/K) = 8/2) with high DCM was prepared with longer chain, less volatile, and hazardous CMOE as the chloromethylated reagent.

In this study, CMPPEKs ($S/K = 8/2$) were prepared with concentrated sulfuric acid as the solvent and catalyst and CMOE with lower toxicity as the chloromethylated reagent under a variety of conditions, and a series of CMPPEKs with different DCMs were obtained. The thermal properties, solubility of CMPPEKs, and NF membrane properties of QAPPEKs were also examined.

EXPERIMENTAL

Materials

The PPESK random copolymer used in this study had a sulfone/ketone ratio of 8 : 2 and was supplied by Dalian Polymer New Material Co. CMOE was

prepared in our laboratory. *N*-methyl-2-pyrrolidone (NMP), chloroform, and ethanol were industrial grade. Other chemicals were analytical grade. The chemicals were obtained commercially and were used without further purification. MgCl_2 , MgSO_4 , NaCl, and Na_2SO_4 were used as solutes for membrane characterization.

Synthesis of CMPPEK

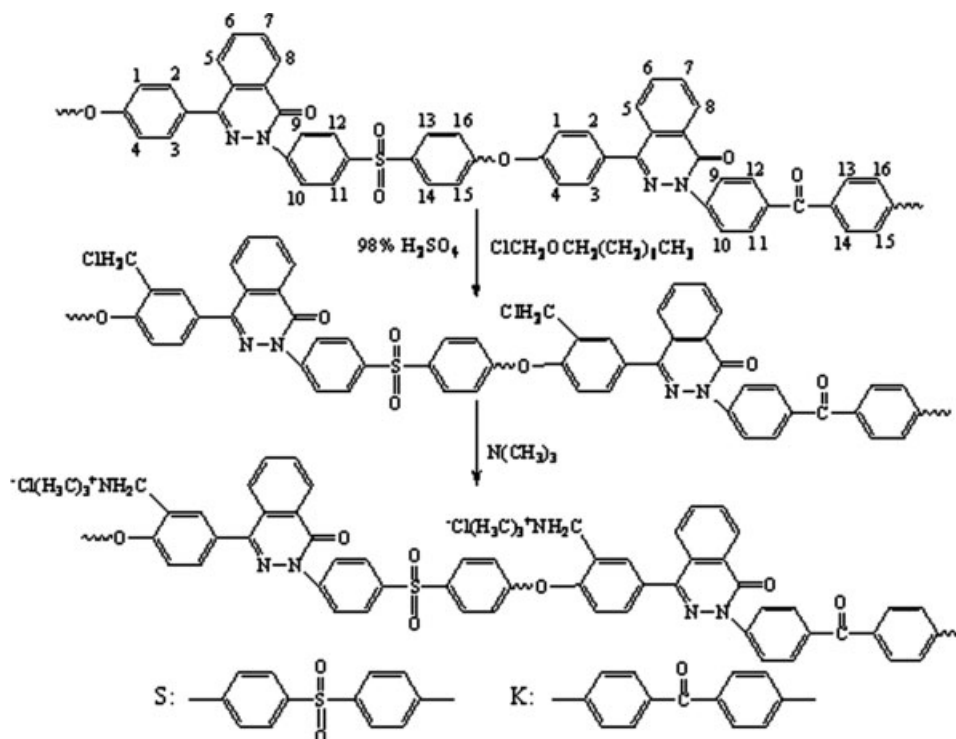
PPESK, dried in a vacuum oven at 100°C for 24 h, and 98% concentrated sulfuric acid were mixed in a three-necked reaction vessel equipped with a mechanical stirrer. After PPESK was completely soluble, CMOE was added dropwise into the polymer solution. CMPPEKs with different DCMs could be obtained at certain reaction temperatures, times, and dosage of CMOE and 98% concentrated sulfuric acid. The prepared polymers were precipitated in ice water, washed with water until the pH was neutral, and then dried. CMPPEKs were purified by redissolution of the polymers in chloroform and reprecipitation of the solutions in ethanol.

Analytical measurements

¹H-NMR spectra were measured on a Varian Unity Inova spectrometer (Varian Co., USA) at 400 MHz with CDCl_3 as solvent. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) of PPESK and CMPPEKs were performed on a Netzsch 209 TGA instrument (Netzsch Co., Germany) in a nitrogen atmosphere at a heating rate of 10°C/min from 50 to 600°C. Membrane separation tests were performed at room temperature with a magnetically stirred dead-end cell module with an effective membrane area of 40 cm² and a feed volume of 850 mL.

DCM was determined by analysis of the chlorine element.²⁰ A sample of precisely weighed CMPPEK (0.3 g) covered with sodium carbonate (2 g) was put into a crucible and was then placed in a muffle furnace at 600°C for 4 h. After cooling, the residuum was dissolved in 10 mL of deionized water. Then, the solution, including washing crucible water, was shifted to a 100-mL conical flask. The solution was acidified with 5 mol/L nitric acid boiled for 10 min, added to 15 mL 0.1 mol/L AgNO_3 solution and 1 mL of saturated $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ solution as an indicator, and then titrated with 0.05 mol/L KSCN to the pink; that was the end point. The blank experiment was also done by the same process. DCM was calculated with the following equation:

$$\text{DCM} = \frac{(V'_{\text{KSCN}} - V_{\text{KSCN}}) C_{\text{KSCN}}}{m_{\text{CMPPEK}}} \quad (1)$$



Scheme 1 Chloromethylation/quaternization reaction of PPESK (S/K = 8/2). The ratio of sulfone to ketone units was 8 : 2.

where V_{KSCN} is the volume of KSCN in the blank experiment, V_{KSCN} is the volume of KSCN in the solution, C_{KSCN} is the concentration of KSCN, and m_{CMPPEK} is the mass of CMPPEK.

The ion exchange capacity (IEC) was determined by the Mohr method. Dry QAPPEK membranes were immersed in 1.0 mol/L NaNO_3 solution for 48 h; thus, the chloride form was converted into the nitrate form. The chloride ions released from the membranes were determined by the titration of a 0.1M AgNO_3 solution with K_2CrO_4 as an indicator, and IECs were calculated from the released chloride ions and given as millimoles per gram of dry material (in Cl^- form).

Membrane preparation

Asymmetric CMPPEK membranes were prepared according to the dry/wet phase separation process. Casting solutions generally consisted of 20 wt % CMPPEK (DCM = 1.80 mmol/g), 10 wt % ethylene-glycol monomethylether, and solvent. CMPPEK membranes were cast on glass plates at a temperature of 70°C and kept for some time in air. The casting solutions were precipitated by immersion into a water bath at less than 5°C until the CMPPEK membranes formed and came off the glass plates, and then, the membranes were moved into another water bath at ambient temperature and kept for a further 36 h. CMPPEK membranes were further immersed into a 5.0 mol/L trimethylamine solution

for 5 h at 30°C and were then put into a 5 wt % HCl solution for 1 h. Finally, QAPPEK NF membranes were obtained with the group of $-\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$.

Membrane characterization

The membranes were characterized in the dead-end membrane module after they were pretreated under a pressure of 0.5 MPa for 30 min. The pure water flux (PWF) and the rejections of 1000 ppm MgCl_2 , MgSO_4 , Na_2SO_4 , and NaCl solutions were measured under a pressure of 0.4 MPa (the pressure was adopted in all of the experiments except for the extra label) at ambient temperature.

The permeation flux (F) was calculated as follows:

$$F = \frac{W}{At} \quad (2)$$

where W is the total weight of the pure water or solution permeated during the experiment, A is the membrane area, and t is the operation time. Rejection (R) was calculated as follows:

$$R = 1 - \frac{C_p}{C_f} \quad (3)$$

where C_p and C_f are the concentrations of the permeate and the feed, respectively.

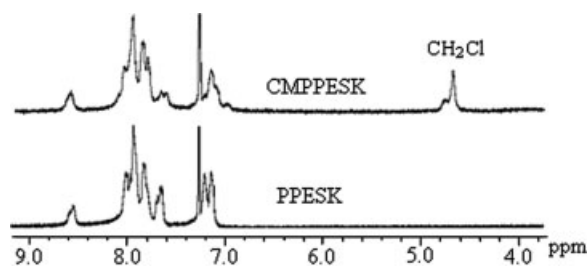


Figure 1 $^1\text{H-NMR}$ spectra of PPEsk/CMPPEsk.

RESULTS AND DISCUSSION

Structural characterization of CMPPEsk

As depicted in Scheme 1, CMPPEsk with a DCM of 1.80 mmol/g was prepared from PPEsk with concentrated sulfuric acid as the solvent and catalyst and CMOE as the chloromethylated reagent. The introduction of the $-\text{CH}_2\text{Cl}$ groups was evidenced by the presence of the $-\text{CH}_2\text{Cl}$ signal at $\delta = 4.68$ ppm and $\delta = 4.75$ ppm (Fig. 1) in the $^1\text{H-NMR}$ spectra. Compared with the $^1\text{H-NMR}$ spectrum of PPEsk, the area of the proton peak at $\delta = 7.20$ ppm (H1/H4) decreased, and the peak at $\delta = 7.66$ ppm (H2/H3) was gradually displaced downfield in the $^1\text{H-NMR}$ spectrum of CMPPEsk. The reason was that H1/H4 was substituted by the $-\text{CH}_2\text{Cl}$ group, and H2/H3, which was shielded by the $-\text{CH}_2\text{Cl}$ group, was displaced downfield.

Chloromethylation reaction conditions for CMPPEsk

DCM of CMPPEsk depended on several factors, including reaction temperature, reaction time, and contents of CMOE and H_2SO_4 . In this experiment, 1 g of PPEsk was used to react in 15 mL of H_2SO_4 at 25°C for 9 h, and the effect of CMOE content on

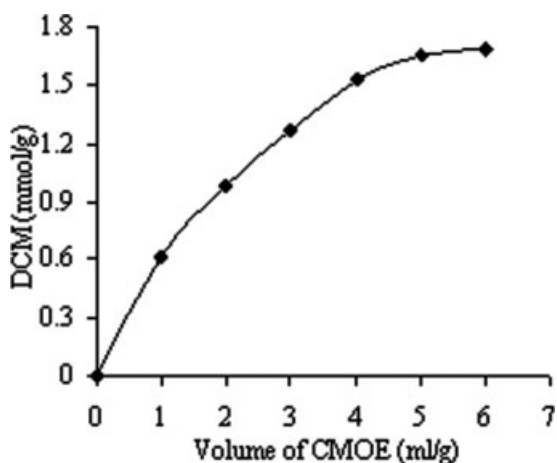


Figure 2 Effect of CMOE content on DCM (PPEsk : $\text{H}_2\text{SO}_4 = 1 \text{ g} : 5 \text{ mL}$; temperature = 25°C ; time = 9 h).

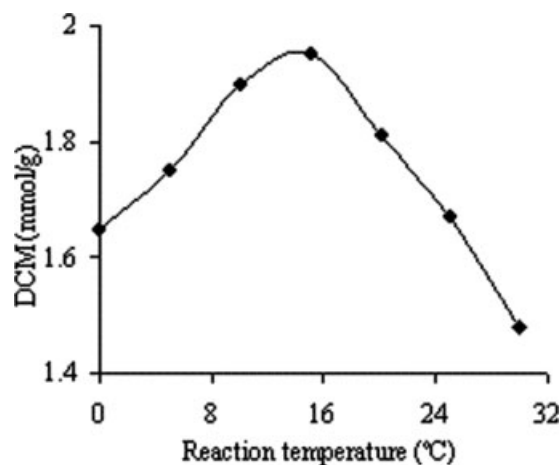


Figure 3 Effect of the reaction temperature on DCM (PPEsk : H_2SO_4 : CMOE = 1 g : 15 mL : 5 mL; time = 9 h).

DCM was examined, as shown in Figure 2. DCM increased with the content of CMOE. When the ratio of CMOE/PPEsk was more than 5 mL/1 g, the tendency leveled off.

In this experiment, 1 g of PPEsk reacted with 5 mL of CMOE in 15 mL of H_2SO_4 for 9 h, and the effect of reaction temperature on DCM was investigated, as shown in Figure 3. As the reaction temperature increased from 0 to 30°C , DCM of CMPPEsk increased gradually, reached a maximum of 1.95 mmol/g at 15°C , and then declined as the temperature increased further.

In this experiment, 15 g of PPEsk reacted with 75 mL of CMOE in 225 mL of H_2SO_4 , and the effect of reaction time on DCM was studied at 0, 15, and 25°C , respectively. The results are shown in Figure 4. DCM increased slowly with the reaction time at 12 h and 0°C . However, DCM increased much rapidly at the beginning of 4 h and then was maintained nearly

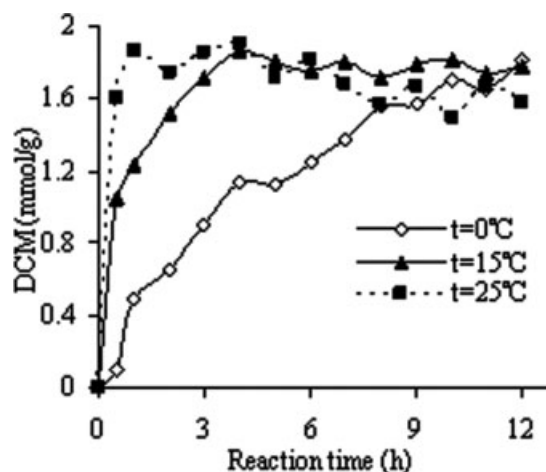


Figure 4 Effect of the reaction time on DCM (PPEsk : H_2SO_4 : CMOE = 1 g : 15 mL : 5 mL).

TABLE I
Effect of the Content of H₂SO₄ on DCM

Volume of H ₂ SO ₄ (mL/g)	10	13	15	17	20
DCM (mmol/g)	1.99	1.87	1.82	1.77	1.61

PPESK : CMOE = 1 g : 5 mL; temperature = 15°C; time = 9 h.

invariably at 15°C. When the reaction temperature was 25°C, DCM increased more rapidly in the first 1 h and began to decrease after 4 h. The reason was that a higher reaction temperature was advantageous for speeding up the reaction, but a much higher reaction temperature may have resulted in a side reaction, and DCM decreased.

H₂SO₄ acted not only as the solvent but also as the catalyst in the chloromethylation of PPESK. In this experiment, 1 g of PPESK reacted with 5 mL of CMOE at 15°C for 9 h, and the effect of the content of H₂SO₄ on the DCM was studied. The results are shown in Table I. As shown in Table I, DCM decreased as the volume of H₂SO₄ increased. This may have been due the declination of PPESK concentration, which was disadvantageous to this reaction.

CMPPEK characterization

Thermal properties of PPESK and CMPPEKs

The thermal stabilities of PPESK and CMPPEKs with different DCM were evaluated by TGA. Temperatures for the maximum weight loss rate in nitrogen were also measured by DTG of PPESK and CMPPEKs. TGA and DTG curves of representative PPESK and CMPPEKs, respectively, are shown in Figure 5.

As shown in the TGA curves, the 5% weight loss temperatures of PPESK, CMPPEK (DCM = 1.19 mmol/g), and CMPPEK (DCM = 1.97 mmol/g) were 491, 423, and 380°C, respectively. PPESK had only one sharp weight loss, which was ascribed to the decomposition of the polymer main chain. From the TGA curves, we found that the introduction of chloromethyl groups into the polymer chains led to a decrease in the decomposition temperature. With increasing DCM, the initial degradation temperature declined. For CMPPEKs with different DCMs, the weight loss between 280 and 420°C was ascribed to the decomposition of the chloromethyl groups. Theoretically speaking, in the range of 200–600°C, the weight loss of CMPPEK (DCM = 1.97 mmol/g) was more than that of CMPPEK (DCM = 1.19 mmol/g). However, as shown in the TGA curves of CMPPEKs, the weight loss of CMPPEK (DCM =

1.97 mmol/g) was less than that of CMPPEK (DCM = 1.19 mmol/g) when the temperature increased above 530°C. The possible reason was that there were different decomposition mechanisms for CMPPEK with different DCMs. The decomposition of CMPPEK may have occurred by both the elimination of chloromethyl functional groups and a crosslinking reaction. Thus, some products that were difficult to degrade were obtained because of a crosslinking reaction. This phenomenon could be further explained by the DTG curves. For CMPPEKs with different DCMs, as clear from the DTG curves, there were different weight loss rates. CMPPEK (DCM = 1.19 mmol/g) had two peaks of weight loss rate, which occurred at 353 and 524°C, respectively. CMPPEK (DCM = 1.97 mmol/g) had three peaks of weight loss rate in the DTG curves, which occurred at 335, 389, and 516°C. When the DCM was lower, the crosslinking reaction occurred

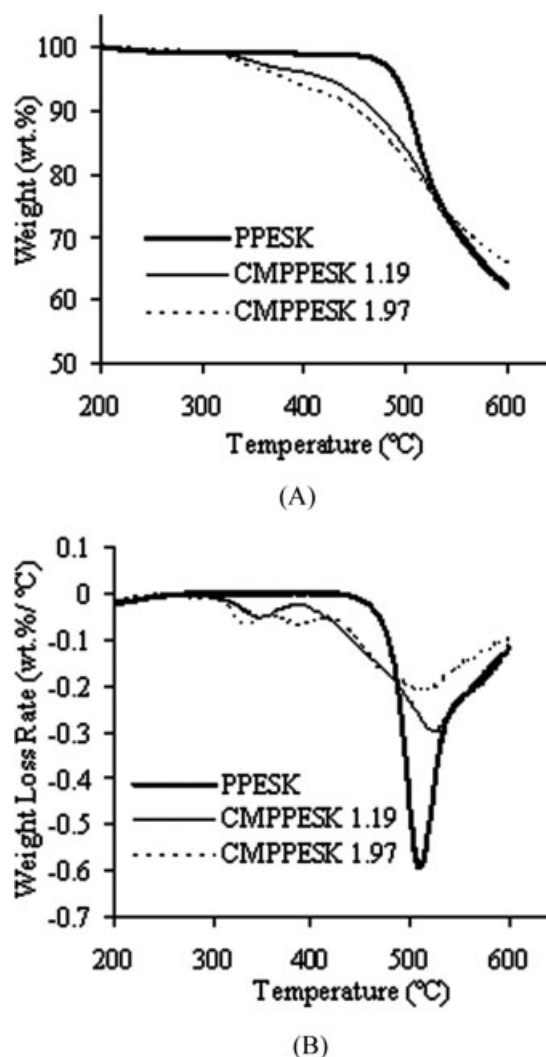


Figure 5 (A) TGA and (B) DTG curves of PPESK and CMPPEKs in nitrogen at a heating rate of 10°C/min.

TABLE II
Solubility of PPESK/CMPPEK/QAPPEK

Solvent	PPESK	CMPPEK	QAPPEK
NMP	+	+	-
DMAc	+	+	-
DMF	±	±	sw
Toluene	-	-	-
Pyridine	+	+	-
Acetone	-	-	-
Methylene dichloride	+	+	-
Chloroform	+	+	-
Carbon tetrachloride	-	-	-
Tetrahydrofuran	-	-	-
Ethylene glycol monomethylether	-	-	-
Hexane	-	-	-
Cyclohexane	-	-	-
Dioxane	-	-	-
Aether	-	-	-
Sulfuric acid(98%)	+	+	±
Butanone	-	-	-
Benzene	-	-	-
Ethanol	-	-	-

Solubility: + = soluble at room temperature; ± = partly soluble; - = insoluble; sw = swollen.

with difficulty. So the decomposition of the chloromethyl groups occurred at temperatures lower than 353°C. When the DCM was higher, the crosslinking reaction occurred easily, and many more products with different degrees of crosslinking might have been obtained. The products with lower degrees of crosslinking might have been able to degrade at the higher temperature. So, in the DTG curve of CMPPEK (DCM = 1.97 mmol/g) appeared the second peak of weight loss rate at 389°C. However, the products with higher degrees of crosslinking were much more difficult to degrade even at the higher temperature. So the residual quantity of CMPPEK (DCM = 1.97 mmol/g) was more than that of CMPPEK (DCM = 1.19 mmol/g) above 530°C. The decomposition of chloromethylated polysulfones also exhibited similar results.²¹

Polymer solubility

The solubilities of PPESK, CMPPEK, and QAPPEK were determined by the dissolution of 0.05 g of each polymer in 1 mL of solvent at room temperature. As shown in Table II, CMPPEK had the same good solubility as PPESK, which was soluble in selected polar aprotic solvents and chlorinated solvents. However, QAPPEK had excellent solvent resistance, was only partly soluble in sulfuric acid (98%), and was swollen in *N,N*-dimethylformamide (DMF). Therefore, the positively charged QAPPEK NF membrane could not be directly prepared from QAPPEK but could be obtained through the following two steps: (1) the preparation of CMPPEK membrane by a phase-inversion method and (2) the quaternization of the CMPPEK membrane. In this step, the CMPPEK membrane was immersed in an aqueous trimethylamine solution to induct positively charged quaternary nitrogen groups into the membrane, as shown in Scheme 1.

Properties of QAPPEK NF membranes

The separation properties of the membranes prepared with different solvents are given in Table III. CMPPEK membranes without charge had no rejection for MgCl₂ and lower PWFs than QAPPEK membranes with positive charges. The IEC values of QAPPEK NF membranes were all 1.4 mmol/g. QAPPEK NF membranes prepared with *N,N*-dimethylacetamide (DMAc) as the solvent had a MgCl₂ rejection of 84–90%, whereas those prepared with NMP as solvent had a MgCl₂ rejection of 71–76%. With increasing evaporation time, the rejection of QAPPEK NF membranes prepared with DMAc as the solvent had an increase in solute rejection but showed a sixfold decrease in PWF at the same time. The reason was that the longer evaporation time led to a denser skin layer. The QAPPEK NF membrane prepared with DMAc and NMP as solvents had MgCl₂ rejections of 84 and 71% and PWFs of 47 and 43 L/m²·h, respectively. However, the evaporation

TABLE III
Effect of Solvent in the Casting Solution on the Membrane Performance

Membrane number	Solvent system	Evaporation time (min)	CMPPEK membranes		QAPPEK membranes	
			R (%)	PWF (L m ⁻² ·h ⁻¹)	R (%)	PWF (L m ⁻² ·h ⁻¹)
M1	NMP	10	0	34	71	43
M2	NMP + CHCl ₃ ^a	10	0	16	76	27
M3 ^b	DMAc	10	—	—	90	8
M4	DMAc	5	0	9	84	47
M5	DMAc + CHCl ₃ ^a	5	0	5	85	31

Test conditions: 0.4 MPa, 14°C, 1000 ppm MgCl₂ aqueous solution. R, rejection for MgCl₂.

^a Content of CHCl₃ = 10 wt %.

^b Operation pressure = 1.0 MPa.

TABLE IV
Performance of the QAPPESK NF Membranes in Different Salt Feed Solutions

	<i>R</i> (%)	<i>F</i> (L m ⁻² ·h ⁻¹)
MgCl ₂	84	49
MgSO ₄	41	53
NaCl	31	54
Na ₂ SO ₄	16	51

Test conditions: 0.4 MPa, 18°C, 1000 ppm salt aqueous solution. *R*, rejection for different salts; *F*, solution flux.

time with DMAc as the solvent was only 5 min, which was less than that of preparation with NMP as the solvent. A possible reason was that DMAc was more volatile than NMP at 70°C, and the skin layer became much dense in a short time. When QAPPESK NF membranes were prepared by the addition of CHCl₃ to NMP or DMAc, the rejection increased, and PWF decreased modestly. This was because the volatility of CHCl₃ was higher than that of DMAc or NMP. As shown by the previous results, the properties of QAPPESK NF membranes were close to those of positively charged NF membranes investigated by Xu and Yang.¹⁰ The technique and conditions of the development of QAPPESK NF membranes still need further optimization. The properties of QAPPESK NF membranes can be improved.

The separation properties to different salt aqueous solutions of M4 membranes are shown in Table IV. As shown in Table IV, the separation properties of the membranes to various salts were different, and the rejections for the different salts decreased in the following order: MgCl₂ > MgSO₄ > NaCl > Na₂SO₄, whereas the negatively charged NF membrane prepared by Zhang et al.²² was the opposite. The results demonstrate that the rejection to salts by the NF membranes not only was related to the pore size of the membrane but also largely depended on the static electric action between the membrane and ions in solution.²³ Therefore, the charge character of the membrane surface was the main influencing factor on the separation properties of the NF membranes. The permeate fluxes of the four salt solutions were almost the same in the range 52 ± 2 L m⁻²·h⁻¹. The deviation of 4% was reasonable in the range of experimental error.

To examine the thermal stability of QAPPESK NF membranes, the QAPPESK NF membrane prepared with DMAc as the solvent was studied at different operating temperatures after the QAPPESK NF membrane was pretreated under a pressure of 0.4 MPa at 90°C for 30 min. The results are shown in Figure 6. As shown in the figure, the MgCl₂ rejection increased from 77 to 80% when the solution temper-

ature rose from 11 to 53°C and then declined from 80 to 73% when temperature rose from 53 to 90°C. When the temperature dropped back to 11°C, the salt rejection and water flux resumed to the original values. This indicated that the QAPPESK NF membranes had excellent thermostability.

CONCLUSIONS

CMPPEKs (*S/K* = 8/2) as membrane materials were successfully prepared from PPEK with concentrated sulfuric acid as the solvent and catalyst and CMOE as the chloromethylated reagent. Furthermore, the reaction conditions were mild and controllable. CMPPEK with higher DCMs were obtained at 15°C for more than 4 h when the ratio of PPEK/H₂SO₄/CMOE was 1 g : 10 mL : 5 mL. The introduction of chloromethyl groups into the polymer chains led to a decrease in the decomposition temperature, and with increasing DCM, the initial degradation temperature declined. CMPPEKs had good solubilities and were soluble in NMP, DMAc, and CHCl₃. However, the resultant QAPPESK derived from CMPPEK had excellent solvent resistance, was only partly soluble in sulfuric acid (98%), and was swollen in DMF. QAPPESK NF membranes prepared with DMAc as the solvent had a higher rejection for MgCl₂ than those prepared with NMP as the solvent. The QAPPESK NF membrane had higher rejections for high-valence cations than both low-valence cations and high-valence anions, and the order of rejection for the different salts was MgCl₂ > MgSO₄ > NaCl > Na₂SO₄. Furthermore, QAPPESK NF membranes exhibited excellent thermal stabilities in the operation temperature range of 11–90°C.

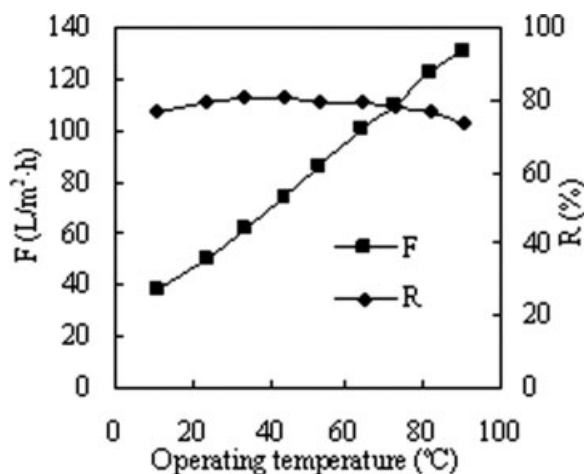


Figure 6 Effect of the operating temperature on QAPPESK NF membrane performance (test conditions: 0.4 MPa, 1000 ppm MgCl₂ aqueous solution; *R*, rejection for MgCl₂; *F*, solution flux).

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