

Positively Charged Composite Nanofiltration Membrane Prepared by Poly(*N,N*-dimethylaminoethyl methacrylate)/Polysulfone

Runhong Du, Jiasen Zhao

College of Material Science and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300160, China

Received 23 April 2003; accepted 22 July 2003

ABSTRACT: Poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) can be crosslinked by quaternization to develop a positively charged dense network structure. According to this mechanism, PDMAEMA/polysulfone (PSF) positively charged nanofiltration membrane was developed by interfacial crosslinking polymerization using PSF plate microfiltration membrane as support layer, PDMAEMA aqueous solution as coating solution, and *p*-xylylene dichloride/*n*-heptane as crosslinking agent. Technique and condition of developing membrane such as concentration of coating solution, coating time, pH value of coating solution, content of low molecular weight additive in coating solution, concen-

tration of crosslinking agent, crosslinking time, and number of coatings were studied. FTIR, SEM, and X-ray photoelectron spectroscopy were used to characterize the structure of membranes. This membrane had rejection to inorganic salts in water solution, the rejection rate to MgSO₄ (1 g/L water solution at 0.8 MPa and 30°C) was about 90%, and permeation flux was about 10–20 L m⁻² h⁻¹. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2721–2728, 2004

Key words: poly(*N,N*-dimethylaminoethyl methacrylate); polysulfone; nanofiltration; membranes; crosslinking

INTRODUCTION

Nanofiltration (NF) is a novel membrane separation technique developed in the 1980s based on reverse osmosis. It is a pressure-driven membrane process and is applicable for separating dissolved components having a molecular weight cutoff (MWCO) of about 200–1000 and molecular size of about 1 nm. It can also be used to separate inorganic salts with much smaller size than pore size according to electrostatic repulsion.^{1–3} The NF technique may be used in an extensive variety of applications, such as water softening, drinking water purification, wastewater treatment and recycling, dye and antibiotic purification and concentration, and other fields of medicine and chemical engineering.

At present, NF membranes are generally neutral or negatively charged, whether on a commercial or laboratory scale⁴; however, studies on positively charged NF membrane are scarce. Therefore it will be important both theoretically and practically to further investigate the preparation and performance of positively charged NF membranes.

Poly(*N,N*-dimethylaminoethyl methacrylate) PDMAEMA is a cheap polyelectrolyte that can be easily obtained, mainly used as flocculant,⁵ and also can be

used as an ion-exchange resin^{6,7} and mordant.⁸ PDMAEMA is also a water-soluble polymer with very good membrane-forming properties. In the late 1980s, Nakano⁹ was the first to apply PDMAEMA to membrane formation, using a regenerated cellulose membrane as support layer and fixing PDMAEMA as a composite layer by heat crosslinking. This membrane was applied in blood purification. Streicher¹⁰ deposited a PDMAEMA composite layer onto a polysulfone (PSF) or polyacrylonitrile support layer using the same method as above and applied the membrane to separate a mixture of ethyl tertio-butyl ether and ethanol. Bleha¹¹ used a PDMAEMA composite membrane for separating He/N₂ and O₂/N₂ mixtures. Fukutomi¹² made a PDMAEMA mosaic membrane for the separation of an electrolyte and nonelectrolyte for desalination. However, there is no report of which we are aware that applies PDMAEMA to preparation of NF membranes.

PDMAEMA can easily participate in quaternization for a number of tertiary amino groups in side chains. PDMAEMA can be crosslinked if the quaternizing agent is bifunctional. PDMAEMA/PSF composite membrane was first developed by using a PSF microfiltration (MF) membrane as support layer, the prepolymer of PDMAEMA as material for the composite layer, and *p*-xylylene dichloride as quaternizing agent and crosslinking agent. It is a positively charged NF membrane. There are advantages of using quaternization crosslinking instead of heat crosslinking to fix the

Correspondence to: J. Zhao (zjsen@eyou.com).

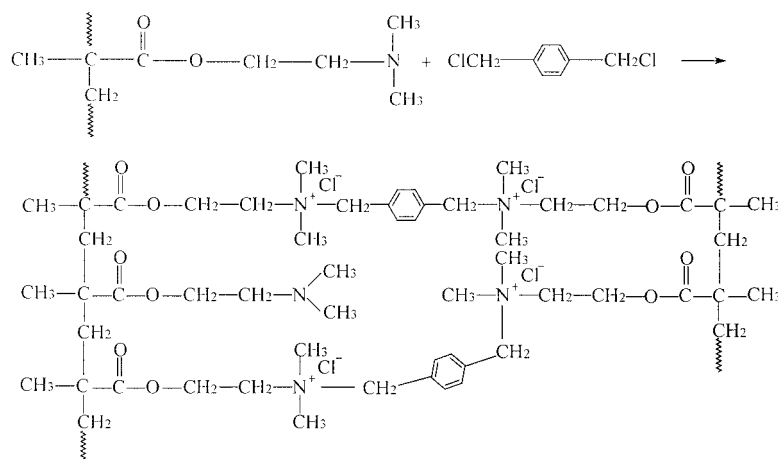


Figure 1 Crosslinking reaction between PDMAEMA and *p*-xylylene dichloride.

PDMAEMA layer onto the support layer. Quaternization crosslinking, which proceeds under room temperature, can not only cause the resulting membrane to be positively charged but also avoid destroying the structure of the support layer by heat. The crosslinking reaction between PDMAEMA and *p*-xylylene dichloride is shown in Figure 1.

EXPERIMENTAL

Materials

Industrial *N,N*-dimethylaminoethyl methacrylate (DMAEMA, obtained from Wuxi Xinyu Chemical Engineering Co., China) was first purified by adsorption using activated charcoal to remove inhibitor *p*-methoxyphenol. PDMAEMA was prepared by bulk polymerization at 50°C for 1 week using 0.004M azobisisobutyronitrile (AIBN) as initiator and cured at 80°C for 4 h in a vacuum oven. The resulting polymer was dissolved in 20–80 g/L water solution followed by prefiltration using G2 glass funnel to remove nonresolvable impurities. Then the polymer solution was charged to a tank and purified by ultrafiltration (UF); the UF membrane was a hollow fiber membrane whose MWCO was 10,000; the operation pressure was

0.06 MPa). The flow diagram of PDMAEMA purification by UF is shown in Figure 2.

Pure water was added to the tank during the UF process and the conductivity of the permeation with small molecules (like DMAEMA and oligomer) was measured regularly using DDS-11A conductometer. Macromolecular PDMAEMA flowed back into the tank as a concentrated solution. As shown in Figure 3, the onset permeation conductivity of a 2.5-L coarse PDMAEMA aqueous solution was 1000 $\mu\text{s}/\text{cm}$. The permeation conductivity was gradually reduced by adding water into the UF system, indicating that small molecular impurities gradually decreased and purification was achieved. When adding 15 L pure water or the total volume of permeation was 6 times as much as that of coarse PDMAEMA solution, the permeation conductivity of 5.4 $\mu\text{s}/\text{cm}$ was near the pure water conductivity of 4 $\mu\text{s}/\text{cm}$ and the PDMAEMA solution could be regarded as having basically no small molecular impurities; only then was the solution in the tank concentrated by UF.

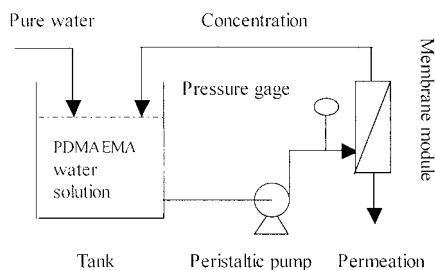


Figure 2 Flow diagram of PDMAEMA purification by UF.

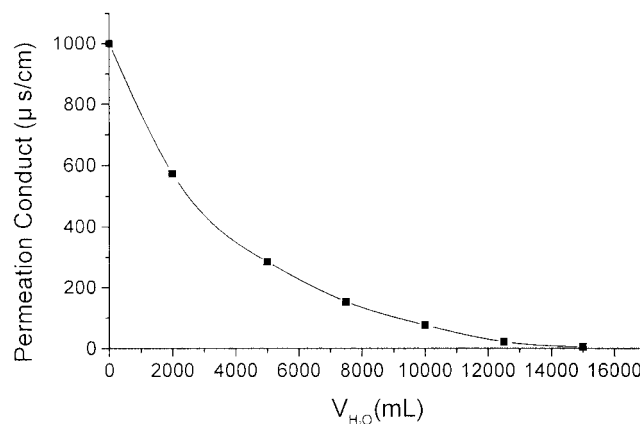


Figure 3 Permeation conductivity as a function of volume of adding pure water.

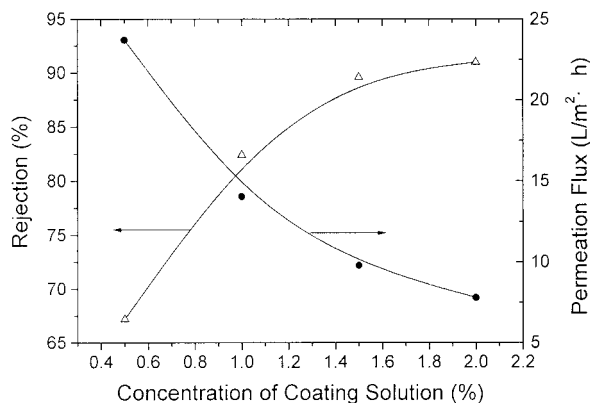


Figure 4 Rejection and permeation flux of NF membrane as functions of concentration of coating solution (coating time: 1 h; concentration of crosslinking agent: 0.5%; crosslinking time: 5 h).

The intrinsic viscosity $[\eta]$ of the purified PDMAEMA was 300 mL/g as determined by a Ubbelohde viscometer (Cannon-Ubbelohde, State College, PA) under 25°C using 0.1 mol/L hydrochloric acid water solution as solvent. The molecular weight and the molecular weight distribution of PDMAEMA can be controlled if the membrane modules with different MWCO are used by series connection in the UF purification process.

The initiator AIBN, crosslinking agent *p*-xylylene dichloride, and solvent *n*-heptane were all graded as analytically pure.

Membrane formation

A pure PDMAEMA membrane was prepared by casting PDMAEMA aqueous solution onto a membrane on a silicon rubber board and tearing off after drying. Crosslinked PDMAEMA uniform membrane was prepared by immersing pure PDMAEMA membrane in 0.5% *p*-xylylene dichloride/heptane crosslinking agent solution for 5 h followed by rinsing three times with pure heptane and drying in the shade.

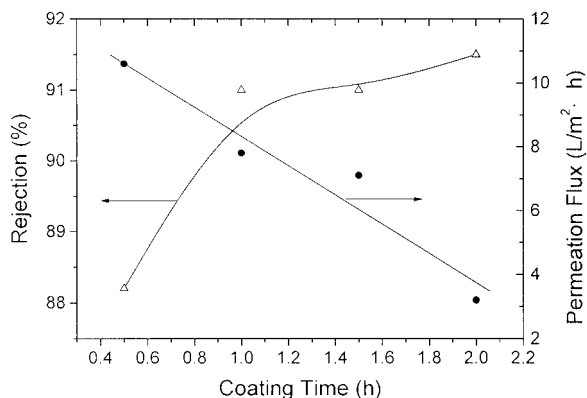


Figure 5 Rejection and permeation flux of NF membrane as functions of coating time (concentration of coating solution: 2%; concentration of crosslinking agent: 0.5%; crosslinking time: 5 h).

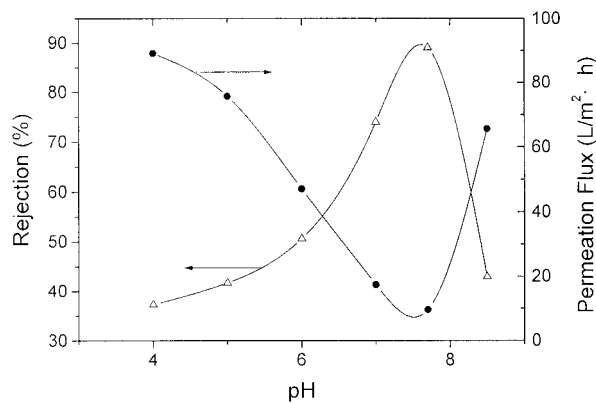


Figure 6 Rejection and permeation flux of NF membrane as functions of pH value of coating solution (concentration of coating solution: 1%; coating time: 1 h; concentration of crosslinking agent: 0.5%; crosslinking time: 5 h).

The support layer of the composite membrane was a PSF plate MF membrane prepared by Loeb–Sourirajan phase inversion (thickness: 0.20 ± 0.01 mm; porosity: 82–84%; average size of pore: $0.053 \mu\text{m}$; pure water flux: $550 \text{ L m}^{-2} \text{ h}^{-1}$ at 0.1 MPa and 30°C). After the PDMAEMA/PSF composite NF membrane was prepared by coating PDMAEMA aqueous solution onto PSF support layer and drying slightly, the above membrane was immersed into *p*-xylylene dichloride/heptane dilute solution to carry on the interfacial crosslinking reaction or interfacial polymerization. The composite membrane was air-dried and immersed in pure water. All processes of membrane formation were carried out at room temperature.

Rejection and permeation flux measurement

The rejection to salts and permeation flux of the NF membrane were measured using 1 g/L MgSO_4 water solution at 0.8 MPa and 30°C.

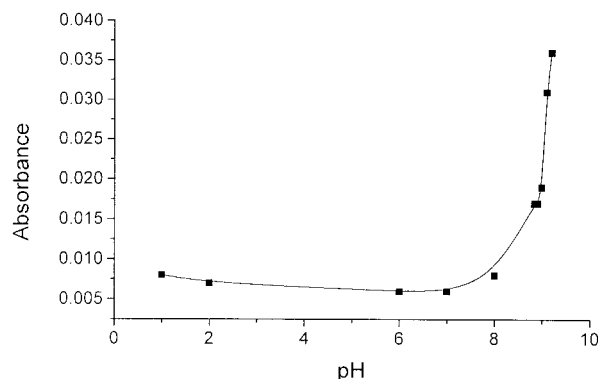


Figure 7 Absorbance as a function of pH value of PDMAEMA aqueous solution.

TABLE I
Effect of Additive Content in Coating Solution on Rejection and Permeation Flux of NF Membrane^a

Content of NaCl (%)	Rejection (%)	Permeation flux ($L m^{-2} h^{-1}$)
0	91	7.8
0.1	75.8	8.9
0.5	57.3	12

^a Conditions: concentration of coating solution: 2%; coating time: 1 h; concentration of crosslinking agent: 0.5%; crosslinking time: 5 h.

FTIR characterization

FTIR spectra were acquired using a Vector 22 FTIR spectrophotometer (Bruker, Germany). The membranes were stored in a desiccator to avoid moisture absorption.

SEM characterization

SEM micrographs were made using an XL 30 ESEM spectrometer (Philips, USA). The composite membranes were dried and broken by quenching in liquid nitrogen and gilded in vacuum before observation.

XPS measurement

X-ray photoelectron spectroscopy (XPS) measurements were made on a PHI 5300 ESCA spectrometer (USA) using an Mg X-ray source; a power of 250 W and pass energy of 35.75 eV were used in the analyzer. The pressure in the analysis chamber was maintained below 10^{-7} Pa during measurements. To compensate for surface charging effects in the insulating samples, all binding energies were corrected with reference to the saturated hydrocarbon C1s peak at 284.8 eV.

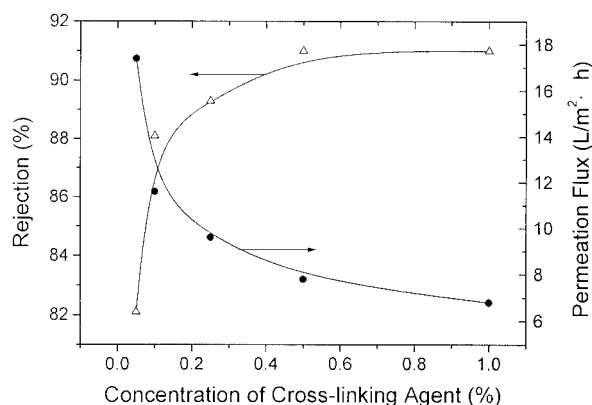


Figure 8 Rejection and permeation flux of NF membrane as functions of concentration of crosslinking agent (concentration of coating solution: 2%; coating time: 1 h; crosslinking time: 5 h).

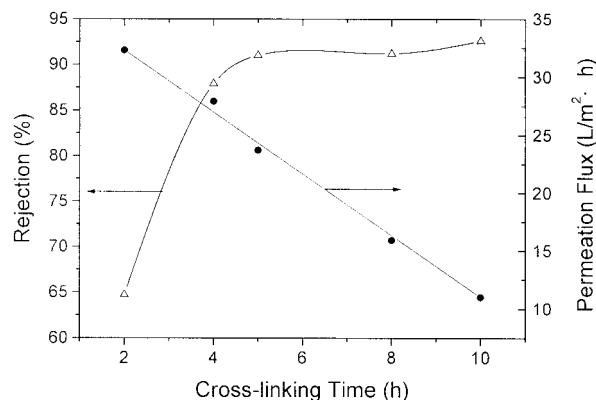


Figure 9 Rejection and permeation flux of NF membrane as functions of crosslinking time (concentration of coating solution: 2%; coating time: 1 h; concentration of crosslinking agent: 0.5%).

RESULTS AND DISCUSSION

Preparation of membrane

Effect of concentration of coating solution on performance of NF membrane

Figure 4 shows that rejection to $MgSO_4$ by the NF membrane improved and permeation flux decreased with increasing concentration of coating solution. The number of tertiary amino groups in the system coupled with the increasing concentration of coating solution caused an increase in crosslinking density. Moreover, the resulting composite layer of the NF membrane was thicker, and consequently the resistance to flow increased.

Effect of coating time on performance of NF membrane

Figure 5 shows that rejection improved and permeation flux decreased with extensions of coating time. The degree of adsorption on the support layer increased with longer adsorption time before reaching equilibrium. Addition of more tertiary amino groups caused an increase in the crosslinking density and, because the composite layer was thicker, the resistance to flow increased. Figure 5 also shows that the range of rejection improvement is negligible after a coating time of more than 1 h, indicating that the effect of crosslinking density and thickness of the composite layer on rejection is not significant after reaching a certain level.

Effect of pH value of coating solution on performance of NF membrane

The pH value of a 1% PDMAEMA aqueous solution is 7.7 and the performance of NF membrane showed a

TABLE II
Effect of Number of Coatings on Rejection and Permeation Flux of NF Membrane

Condition of preparation ^a	Number of coatings	Rejection (%)	Permeation flux (L/m ² · h)
Coating time: 1 h Crosslinking time: 5 h	1	43.4	64.9
Coating time: 20 min Crosslinking time: 100 min	1	41.2	84.7
	2	63.2	32.2
	3	90.9	29.5

^a Concentration of coating solution: 0.5%; concentration of crosslinking agent: 0.05%.

regular change with pH value of coating solution (see Fig. 6).

Figure 6 shows that rejection improved and permeation flux decreased with a change in the coating solution from acid to neutral; rejection achieved the maximum and flux achieved the minimum when the pH value of the coating solution was 7.7; then rejection decreased quickly and flux rapidly increased with constant increases in the pH value.

PDMAEMA aqueous solution shows alkalescence because the combination of the lone electron pair on N and water forms R_3HN^+ and OH^- .

When acid or alkali is added to PDMAEMA aqueous solution, the existent configurations of PDMAEMA molecules are different (see Fig. 7). In water, PDMAEMA is a random-coil molecule with OH^- s distributing around R_3HN^+ s. When acid is added to PDMAEMA aqueous solution, because of neutralization, a portion of tertiary amino groups react with the added acid to form ammonium salts, the concentration of R_3HN^+ s increase, the repulsion among molecular chains is intensified, molecular chains stretch, and the absorbance of this transparent solution is low.

When alkali is added to PDMAEMA aqueous solution, the ionization equilibrium reverses, the concentration of R_3HN^+ s decreases, the repulsion among molecular chains is weakened, the coils of the polymer crimp, the solubility of PDMAEMA decreases (i.e., good solvent gradually turns into poor solvent), and the solution appears turbid and the absorbance increases.

The existent configuration of molecules in the coating solution can influence the degree of the following crosslinking reaction, but the influencing mechanism is different. When acid is added to the coating solution, the amount of reactive tertiary amino groups is less in the following crosslink so crosslinking density is lower. When alkali is added to the coating solution, a portion of the tertiary amino groups are wrapped in the coils and cannot react with the crosslinking agent, thus lowering the crosslinking density.

Effect of additive content in coating solution on performance of NF membrane

The properties of NF membrane changed with the addition of 0.1 and 0.5% small molecular additive NaCl (see Table I).

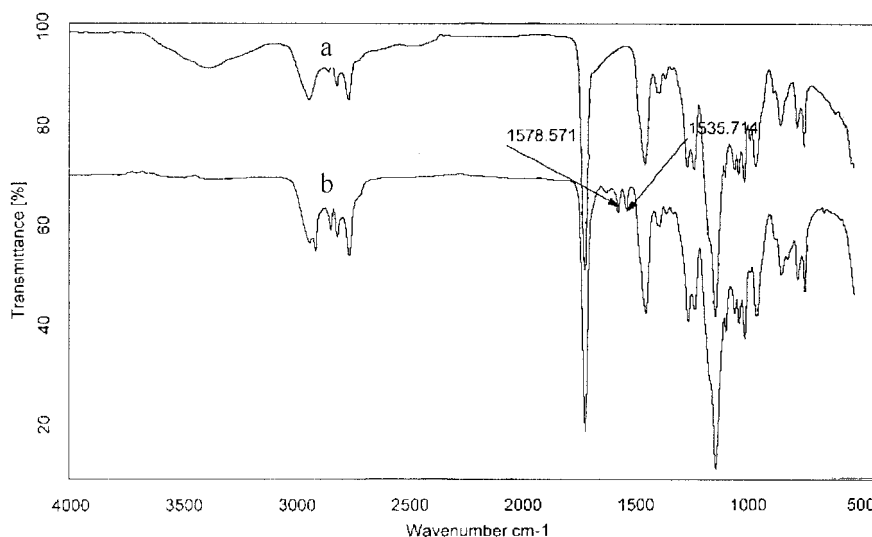


Figure 10 FTIR spectra of (a) pure PDMAEMA and (b) coarse PDMAEMA.

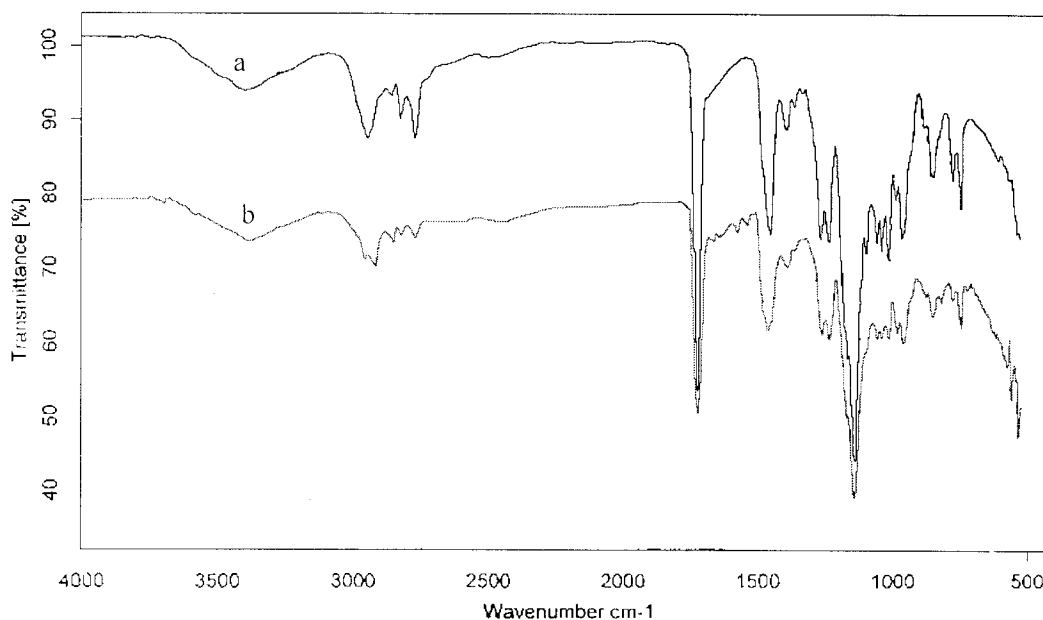


Figure 11 FTIR spectra of (a) pure PDMAEMA and (b) crosslinked PDMAEMA by *p*-xylylene dichloride.

Table I shows that rejection decreased and permeation flux increased when NaCl was added to the coating solution. Small molecules or their hydration ions cannot be crosslinked and the location where they are will cause defects in the resulting membrane so that rejection of membrane reduced. On the other hand, the repulsion among amino ions is weakened because a portion of the Cl^- s permeate into polycations to shield effective charges. The chain crimps with part of tertiary amino groups being wrapped in the chain coils, thus not participating in the crosslinking reaction, so that the crosslinking density is lower.

Effect of concentration of crosslinking agent on performance of NF membrane

Figure 8 shows that rejection improved and permeation flux reduced gradually with increasing concentration of crosslinking agent. The greater the concentration of crosslinking agent, the higher the crosslinking density; moreover, the crosslinking reaction velocity is more rapid so the crosslinking density increases further during the same reaction time. Figure 8 also shows that rejection tends to be constant and the flux decreases slowly after concentration of crosslinking agent achieves a level of 0.5%, indicating that the content of crosslinking agent has been saturated.

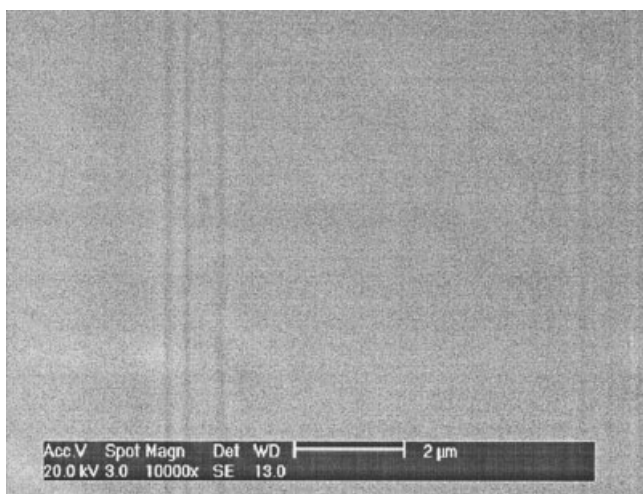
Effect of crosslinking time on performance of NF membrane

Figure 9 shows that rejection improved and permeation flux decreased with prolonged crosslinking time and rejection tended to be constant after 5 h. The

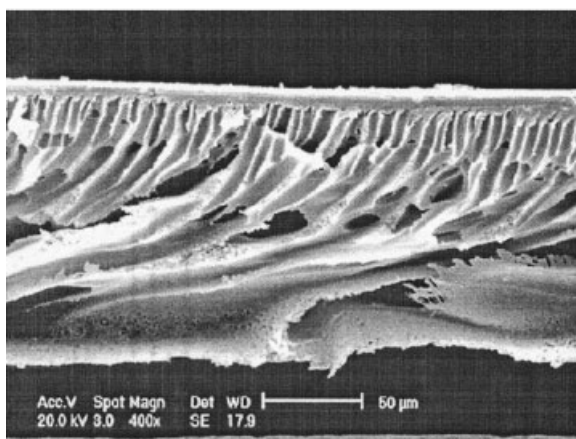
increase in crosslinking density was mainly attributed to the more nearly complete crosslinking reaction with prolonged crosslinking time in some range. Although improvement of rejection is less when the size of surface pores does not significantly change with continually prolonged crosslinking time, permeation flux continued to decrease because the crosslinking reaction proceeds to the inside of the composite layer, which causes lengthening of the passage of network pores and an increase in the number of pores, thus increasing the resistance to permeation.

Effect of number of coatings on performance of NF membrane

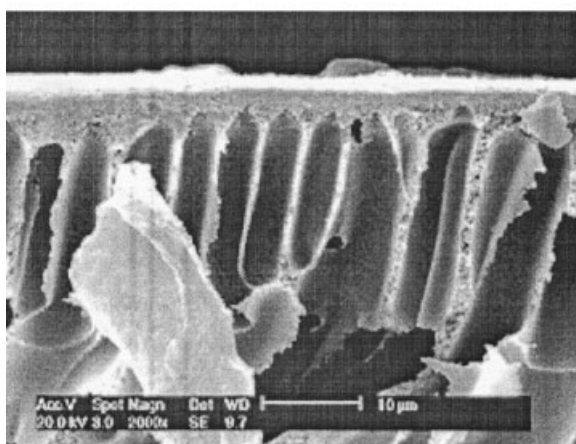
NF membranes with 1 coating, 2 coatings and 3 coatings also were prepared and the results were shown in Table II, which shows that when the concentrations of both coating solution and crosslinking agent were low (0.5 and 0.05%, respectively), regardless of the length of coating time or crosslinking time, rejection of the resulting NF membrane was not high. However, rejection could be improved greatly when the permeation flux was high by increasing the number of coatings. When applying a relatively dilute solution to coat and crosslink in a short time, the resulting crosslinking layer of each application is very thin and the total composite layer by coating and crosslinking several times is still thin, so the permeation flux is high. The several crosslinked thin layers overlap to make a more compact network structure, so rejection is improved.



(a)



(b)



(c)

Figure 12 SEM micrographs of composite NF membrane: (a) surface, (b) section, (c) and enlargement of part of section (concentration of coating solution: 2%; coating time: 1 h; concentration of crosslinking agent: 0.5%; crosslinking time: 5 h).

TABLE III
Content of Each Element in Membranes (%)

Membrane	C1s	O1s	N1s	S2p	Cl2p
PSF support layer	82.13	13.18	2.91	1.78	—
Pure PDMAEMA	73.42	21.53	5.05	—	—
PDMAEMA/PSF NF membrane	74.76	19.13	4.96	0.17	0.98

FTIR characterization

FTIR spectra further show the effect of purification (see Fig. 10). The FTIR spectrum of coarse PDMAEMA has two peaks at 1578.571 and 1535.714 cm^{-1} attributed to C=C stretching, indicating that there are monomer or oligomer. The two peaks disappear in the FTIR spectrum of pure PDMAEMA, indicating that the monomer or oligomer has been removed.

Figure 11 shows that crosslinked PDMAEMA has peaks at 1575.57 and 1537.72 cm^{-1} attributed to C=C stretching, indicating that there are benzene rings in crosslinked PDMAEMA and showing that PDMAEMA reacted with *p*-xylylene dichloride.

SEM characterization

Figure 12 shows that the surface of the resulting composite NF membrane is uniform and dense and the average thickness of the composite layer is about 0.9 μm .

XPS measurements

Table III shows the content of each element in the surface of the PSF support layer, the pure PDMAEMA membrane, and the PDMAEMA/PSF composite NF membrane, respectively. There is N in the support layer because additive polyvinyl-pyrrolidone has not dissolved out completely during the formation of PSF

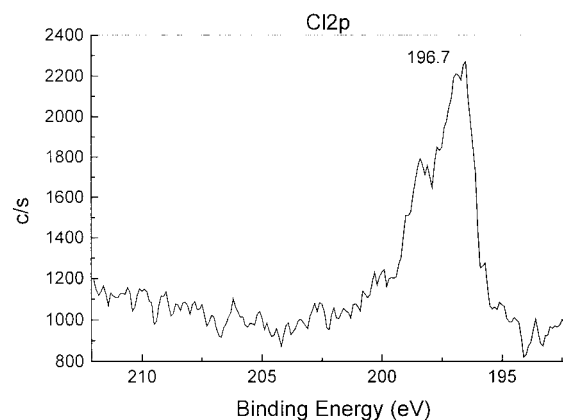


Figure 13 XPS spectrum of Cl2p in PDMAEMA/PSF NF membrane.

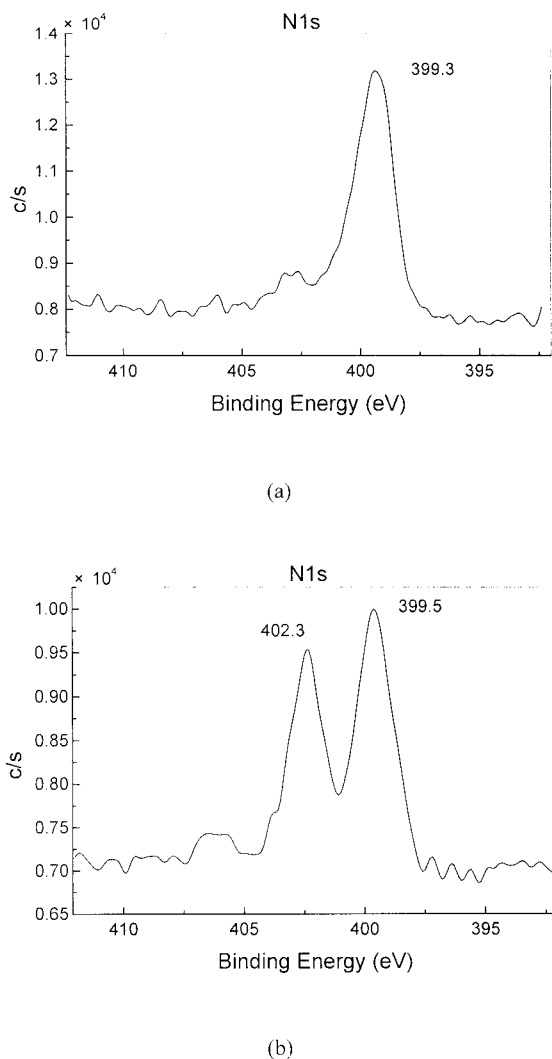


Figure 14 XPS measurement of N1s in (a) pure PDMAEMA membrane and (b) PDMAEMA/PSF NF membrane.

MF membrane. The content of S in the composite membrane is much less than that in the support layer, indicating that the surface of the support layer has been mostly covered by the composite layer. The Cl2p spectrum of the composite membrane features a peak at 196.7 eV (see Fig. 13), indicating that there is Cl in the composite membrane. Two different nitrogen environments can be discerned (see Fig. 14), also showing that there is a crosslinking reaction. The peak of low binding energy N1s at 399.3 eV is characteristic of

tertiary amino groups in pure PDMAEMA, showing a shift to 399.5 eV in the composite membrane, whereas the new peak of the composite membrane at 402.3 eV is characteristic of quaternary ammonium salt by crosslinking reaction of tertiary amino groups. The content of the N1s at 339.5 eV is 55.64% of total nitrogen, demonstrating that a portion of the tertiary amino groups still have not participated in the crosslinking reaction.

CONCLUSIONS

1. The small molecular impurities in PDMAEMA prepared by bulk polymerization can be effectively removed by UF. A PDMAEMA/PSF composite NF membrane can be formed by interfacial crosslinking polymerization at room temperature using a PSF MF membrane as support layer, prepolymer of PDMAEMA as composite layer material, and *p*-xylylene dichloride/heptane as crosslinking agent.
2. The resulting composite layer is uniform and dense and the thickness is around 0.9 μm . The rejection rate to MgSO_4 of 1 g/L water solution at 0.8 MPa and 30°C is about 90% and permeation flux is about 10–20 $\text{L m}^{-2} \text{h}^{-1}$.
3. The factors such as concentration of PDMAEMA coating solution, coating time, pH value of coating solution, low molecular weight additive content of coating solution, concentration of crosslinking agent, crosslinking time, and number of coatings have obvious effects on membrane performance.

References

1. Wang, X. L.; Tsuru, T.; Nakao, S.; Kimura, S. *J Membr Sci* 1995, 103, 117.
2. Bowen, W. R.; Mohammad, A. W.; Hilal, N. *J Membr Sci* 1997, 126, 91.
3. Schaep, J.; Vandecasteele, C. *J Membr Sci* 2001, 188, 129.
4. Raman, L. P.; Cheryan, M.; Rajagopalan, N. *Chem Eng Prog* 1994, 3, 68.
5. Hurlock, J. R. U.S. Pat. 6,025,426, 2000.
6. Cunningham, V.L. U.S. Pat. 4,052,343, 1977.
7. Cunningham, V.L. U.S. Pat. 4,129,534, 1978.
8. Romano, C. E., Jr.; Gallo, E. A. U.S. Pat. 6,224,202, 2001.
9. Nakano, H.; Seita, K.; Imamura, K.; Watanabe, T. U.S. Pat. 4,787,977, 1988.
10. Streicher, C. U.S. Pat. 5,607,557, 1997.
11. Bleha, M.; Schauer, J.; Lokaj, J.; Polockaja, G. A.; Kuznecov, J. P.; Romaskova, K. A. U.S. Pat. 5,059,220, 1991.
12. Fukutomi, T.; Takizawa, M.; Nakamura, M. U.S. Pat. 5,543,045, 1996.