Positively Charged Hollow-Fiber Composite Nanofiltration Membrane Prepared by Quaternization Crosslinking

Zhichao Zhang, Wei Wang

State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, Tianjin 300160, China
Correspondence to: W. Wang (E-mail: wangwei7126@126.com)

ABSTRACT: Poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) can be crosslinked by interfacial polymerization to develop a positively charged dense network structure. According to this mechanism, a positively charged hollow-fiber composite nanofiltration (NF) membrane was prepared by quaternization to achieve a crosslinked PDMAEMA gel layer on the outer surface of polysulfone hollow-fiber ultrafiltration (UF) membranes with a PDMAEMA aqueous solution as a coating solution and p-xylylene dichloride as an agent. The preparation conditions, including the PDMAEMA concentration, content of additive in the coating solution, catalyzer, alkali, crosslinking temperature, and hollow-fiber substrate membrane, were studied. Fourier transform infrared spectroscopy and scanning electron microscopy were used to characterize the structure of the membranes. This membrane had a rejection to inorganic salts in aqueous solution. The rejection of MgSO$_4$ (2 g/L aqueous solution at 0.7 MPa and 25°C) was above 98%, and the flux was about 19.5 L m^{-2} h^{-1}. Moreover, the composite NF membranes showed good stability in the water-phase filtration process. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2806–2812, 2013

INTRODUCTION

Nanofiltration (NF) is a novel membrane separation technique developed in the 1980s and based on reverse osmosis.[1] It has been gaining increasing attention for many separation and water treatment processes because of its low energy consumption, high rejection rate, and water flux (J_v) at low pressure,[2] and it has become a hot spot in the study of separation membranes.[3] It is a pressure-driven membrane process used to separate multivalent ions or dissolved components with molecular weights ranging from 200 to 1000,[4] and it can be used as an alternative to reverse osmosis in water softening, color removal, chemical oxygen demand reduction, and the recovery of valuable pharmaceutical products.[5]

NF membranes usually consist of a thin top-barrier layer supported by a reinforced porous UF membrane.[6] The physical and chemical characters and structures of the ultrathin top-barrier layer determine the separation and permeation properties of the NF membrane, whereas the porous sublayer only acts as a mechanical support.[7] Various approaches for active top-layer preparation, such as interfacial polymerization,[8,9] chemical crosslinking,[10] UV photografting,[11] and low-temperature plasma grafting,[12] have been developed. Interfacial polymerization, however, is still a common method for producing NF membranes. There are advantages in using interfacial polymerization

to fix the poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) layer onto the support layer. Interfacial polymerization, which proceeds at room temperature, can not only cause the resulting membrane to be positively charged but also prevent the destruction of the structure of the support layer by other methods.[13] The reason for that the PDMAEMA layer was selected as the thin top-barrier layer was that PDMAEMA is a cheap polyelectrolyte that can be easily obtained, and it is also a water-soluble polymer with very good membrane-forming properties. Also, the crosslinked PDMAEMA layer was fixed onto the surface of the polysulfone (PSF) hollow fibers by physical adhesion; this made the process more simple and ensured its strength.

In the salt-transport process, the electric properties of an NF membrane have a great effect on the ion permeation.[1,14] At present, because of commercial interests, NF membranes are generally neutral or negatively charged, whether on a commercial or laboratory scale,[13] because most NF applications are focused on the retention of low-molecular-weight molecules and multivalent anions. However, on some occasions, such as for the retention of multivalent cations and the recovery of a cathode electrophoresis lacquer, a positively charged NF membrane is actually needed.[15] To date, most commercial NF membrane modules have been spiral-wound and tubular

modules. Spiral-wound modules are extremely susceptible to floating matter, have high energy losses caused by friction in the spacers, and cannot be backwashed.[16] Tubular modules are expensive because of their lower packing density.[17] A hollow-fiber module would give a high packing density and would allow a less demanding pretreatment and maintenance. A hollow-fiber module would provide a much larger membrane area per unit of membrane module volume, self-mechanical support, and ease of handling during module fabrication and system operation. This kind of module would be a good solution for the treatment of low-quality surface water by direct capillary NF.[18] However, studies of positively charged hollow-fiber NF membranes have been scarce. Therefore, it was of great theoretical and practical significance to further investigate the preparation and performance of positively charged hollow-fiber NF membranes.

In this article, we report a novel method for preparing positively charged hollow-fiber composite NF membranes; these were prepared by quaternization to achieve a crosslinked PDMAEMA gel layer on the outer surface of the PSF hollow-fiber UF membranes with a PDMAEMA aqueous solution as the coating solution and *p*-xylylene dichloride as the agent. This approach showed at least three advantages: (1) first, the ultrathin active layer achieved a combination of high selectivity and larger flux to get a more perfect, more practical NF;[19] (2) second, the composite NF membrane highlighted the features of hollow-fiber membrane in which a compact module with a very high membrane surface area could be formed; and (3) last, the composite NF reflected the characteristics of the functional material PDMAEMA, such as positive electricity, temperature, and pH response.[13] In the domain of the removal of multivalent cations,[20,21] the reuse of wastewater from spinning and dyestuff,[6] the desalination and concentration of positively charged dyestuff, and the separation and purification of positively charged amino acid,[15] the positively charged PDMAEMA hollow-fiber composite NF membrane displayed excellent separation characteristics.

EXPERIMENTAL

Chemicals and Instruments

A PSF hollow-fiber UF membrane used as a support membrane was kindly offered by Tianjin Motian Membrane Engineering and Technology Co., Ltd. (Tianjin city, China). *N,N*-Dimethylaminoethyl methacrylate (DMAEMA) was obtained from Wuxi Xinyu Chemical Engineering Co., Ltd. (Wuxi city, Jiangsu Province, China), and was purified by adsorption with activated charcoal to remove the inhibitor *p*-methoxyphenol. PDMAEMA was prepared by bulk polymerization at 50°C for 1 week with 0.004M azobisisobutyronitrile as an initiator and was cured at 80°C for 4 h in a vacuum oven. The resultant was dissolved into a 20–60 g/L aqueous solution and then prefiltered with a G2 glass funnel to remove nonresolvable impurities. Then, the polymer solution was put into a tank and purified by UF (the UF membrane was a hollow-fiber membrane with a molecular weight cutoff (MWCO) of 10,000. The operating pressure was 0.1 MPa. Small molecules (e.g., DMAEMA and oligomer) could easily permeate through the UF membranes and were removed continuously. The macromolecular PDMAEMA was recycled to

the tank as the concentrate. Pure water was added until the permeate conductivity was close to that of the added pure water. In the end, the concentrate in the tank was pure PDMAEMA. *P*-Xylene dichloride (chemical grade) was purchased from Wuhan Youji Industrial Co., Ltd. (Wuhan, Hubei Province, China), and was recrystallized twice with *n*-heptane. An MC226 conductivity meter was obtained from Mettler-Toledo, Inc. (Switzerland). The NF evaluation system was homemade. The initiator azobisisobutyronitrile, solvent *n*-heptane, $MgSO_4$, $NaHCO_3$, and absolute ethyl alcohol were analytically pure grade and were purchased from commercial sources.

Membrane Formation

We prepared the composite NF membrane by casting the PDMAEMA aqueous solution onto the outward surface of the PSF hollow-fiber UF membranes. The support membrane was a PSF hollow-fiber UF membrane prepared by phase inversion with a 120 L m^{-2} h^{-1} pure J_v at 0.1 MPa and 25°C. The composite NF membrane was first prepared by the coating of the PDMAEMA aqueous solution onto the outward surface of the PSF support membranes for 1 h and by vertical drying for 20 min. Second, the mentioned membrane was immersed into 1% *p*-xylylene dichloride/*n*-heptane solution to react for 4–5 h to carry on the interfacial crosslinking reaction. After the quaternization crosslinking was completed, the prepared NF was rinsed with *n*-heptane and immersed in glycerin for 12 h; this was followed by air drying for later use. We prepared the membrane module by casting one of the bundles including 40 fibers with epoxy resin and plugging the other end with polysiloxane rubber. Before testing, the glycerin was washed away with pure water, and we conducted leak detection with blowing air to ensure that the module was without defect.

Membrane Characteristics

Determination of the Porosity (ε) of the Hollow-Fiber Substrate Membrane. The apparent density (ρ_m) of the PSF hollow-fiber membrane was assayed precisely and compared with the true density of the PSF hollow-fiber membrane, which was PSF's density (ρ_{PSF}). The ε value of the PSF hollow-fiber membrane was calculated according to eq. (1):
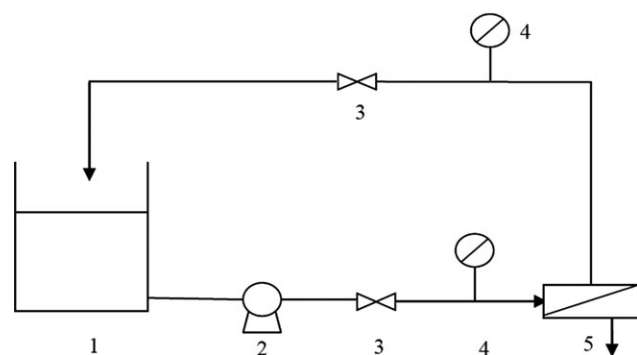
$$\varepsilon(\%) = (1 - \rho_m/\rho_{PSF}) \times 100\% \qquad (1)$$

Rejection and Permeation Flux Measurements. The salt rejection (R) and permeate flux (F) of the NF membranes were measured by a 2 g/L $MgSO_4$ aqueous solution at 0.7 MPa and 25°C after pretreatment for 30 min. The average data were determined from three pieces of tested membrane. The flow diagram for the testing performances of the composite NF membrane is shown in Figure 1.

F and rejection (R) were measured as follows. F was calculated by eq. (2):

$$F = \frac{V}{At} \qquad (2)$$

where F is the permeate flux of the $MgSO_4$ aqueous solution (L m^{-2} h^{-1}), V the volume of permeate solution at time t (L), A the effective area of the membrane (m^2), and t is the time (h).

The rejection was calculated by the changing ratio of conductivity with eq. (3):

$$R = \frac{\tau - \tau_1}{\tau} \times 100\% \qquad (3)$$

where τ is the feed conductivity (μS/cm) and τ_1 is the permeate conductivity (μS/cm).

Fourier Transform Infrared (FTIR) Characterization. FTIR–attenuated total reflectance spectroscopy was used to investigate the surface chemical composition changes of the PSF membrane before and after modification. We collected the spectra with wave numbers ranging from 4000 to 500 cm^{-1} by accumulating 32 scans at a resolution of 2 cm^{-1} with a Bruker Vector 22 FTIR spectrophotometer (Karlsruhe, Germany).

Testing Stability of the Composite Membrane. A long-term test was conducted at operating pressure of 0.7 MPa with a 2 wt % MgSO₄ solution to investigate the performance stability of the composite membrane. Periodic measurements were carried out to check the permeability and R values of the membrane.

RESULTS AND DISCUSSION

Effect of the Hollow-Fiber Substrate Membrane
We used the PSF hollow-fiber UF membrane as the substrate membrane, with MWCOs of 6000 and 20,000 and determined ε and the performances of the prepared NF membrane in a 2 g/L MgSO₄ solution (Table I). As shown in Table I, the substrate membrane with a MWCO of 6000 had a comparatively lower ε, and the flux and the rejection of the prepared NF membrane was not high.

Table I. Rejection Rate and Flux Values of the NF Membranes

| MWCO[a]	ε (%)[a]	R (%)[b]	J_v (L m^{-2} h^{-1})[b]
6,000	49.62	60.2	10.2
20,000	86.10	98.0	17.4

[a]Substrate membranes.
[b]NF membranes.

Effect of the Concentration of PDMAEMA
A series of PDMAEMA solutions with various concentrations (when the ethanol content of the ethanol/water solution as solvent was 7.5% v/v) were prepared, and the composite membrane was made with the method mentioned previously. Figure 2 shows that the rejection to MgSO₄ improved, and the flux decreased with increasing concentration of PDMAEMA. When the concentration of PDMAEMA was very low, the formative network was comparatively thin and had defects, so it was not able to cover the surface of the support membrane completely. Therefore, the flux was large, and the rejection was low. The process of diffusion was the key part of the interfacial polymerization, so the overall rate was determined by the diffusion rate. The high concentration of PDMAEMA made the PDMAEMA layer thicker and resisted the monomer diffusion to the reaction site. As a result, the number of the crosslinking points decreased. At the same time, the Marogoni effect made the concave–convex phenomenon on the surface of the membrane severe. Therefore, the density of the network hole was nonuniform at the end of the reaction, and the binding force with the support membrane was weak, and this caused the reduction of the flux and the rejection.

Effect of the Concentration of Ethanol
The performance of the hollow-fiber NF membrane, which was prepared by 0.75% PDMAEMA aqueous solution with different concentrations of ethanol, is demonstrated in Figure 3. The addition of ethanol improved the rejection to some extent and raised the flux a lot. This could be explained as follows: (1) the use of ethanol as solvent increased the nucleophilic activity of tertiary amine and helped the reaction to go toward the products direction and accelerated the rate of substitution reaction. (2) After ethanol was added into the PDMAEMA aqueous solution, the molecular chain of PDMAEMA stretched, which macroscopically reflected the increase in the viscosity of the solution; consequently, the PDMAEMA solution could cover the hills and pores on the surface of the supporting membrane efficiently at a low concentration. Therefore, the PDMAEMA layer left after drying had a loose structure and an even thickness; this benefited the effusion of the small molecules in the
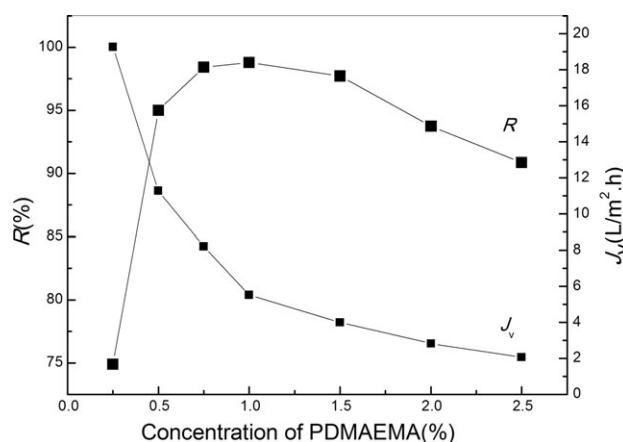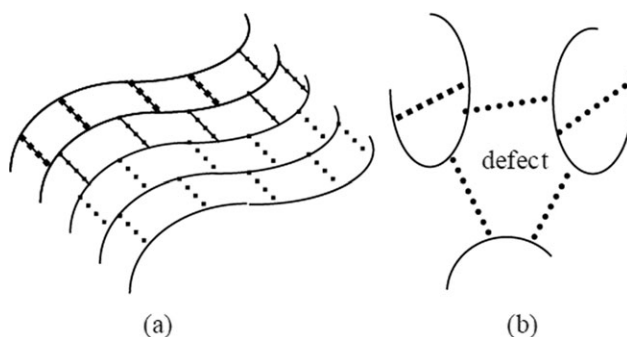

Figure 2. Rejection and permeation flux of the NF membrane as functions of the PDMAEMA concentration.
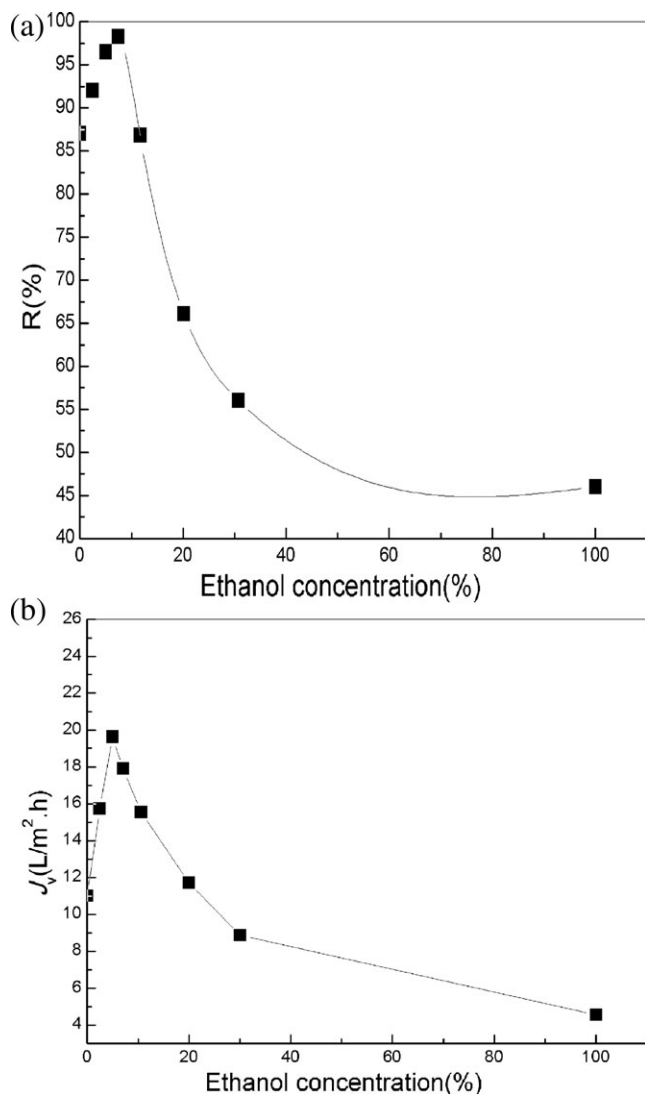
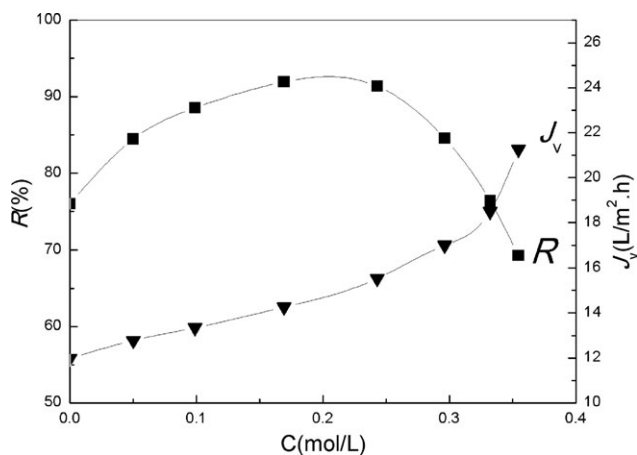Figure 3. (a) Rejection and (b) permeation flux of the NF membrane as functions of the ethanol contents.

Figure 4. Schematic diagrams of the crosslinking network formed by the stretched PDMAEMA molecule and the network defect formed in the crosslinking process of the curled PDMAEMA molecule.

We prepared the NF membrane by dipping the outward surface of the hollow fiber into a 0.75% PDMAEMA aqueous solution that contained a fixed proportion of $NaHCO_3$. The effect of the $NaHCO_3$ concentration on the rejection performance of NF is shown in Figure 5. A certain concentration of $NaHCO_3$ improved both the rejection and flux of NF efficiently. The rejection rate of NF was at a maximum when the concentration of $NaHCO_3$ was 0.243 mol/L (the concentration was about 2% tertiary amine). The advantages of adding $NaHCO_3$ were as follows: (1) the buffering alkali made the tertiary amine exposed through a salting-out effect and entered into the organic phase to conduct the crosslinking reaction, and (2) the change in the pH value was balanced when the polyelectrolyte solution was concentrated on the surface of the porous membrane so that the stretching and curling degree of the high-molecular chain was made consistent and the distribution of tertiary amine was made even, so as to form a polymer network with a flat crosslinking density.
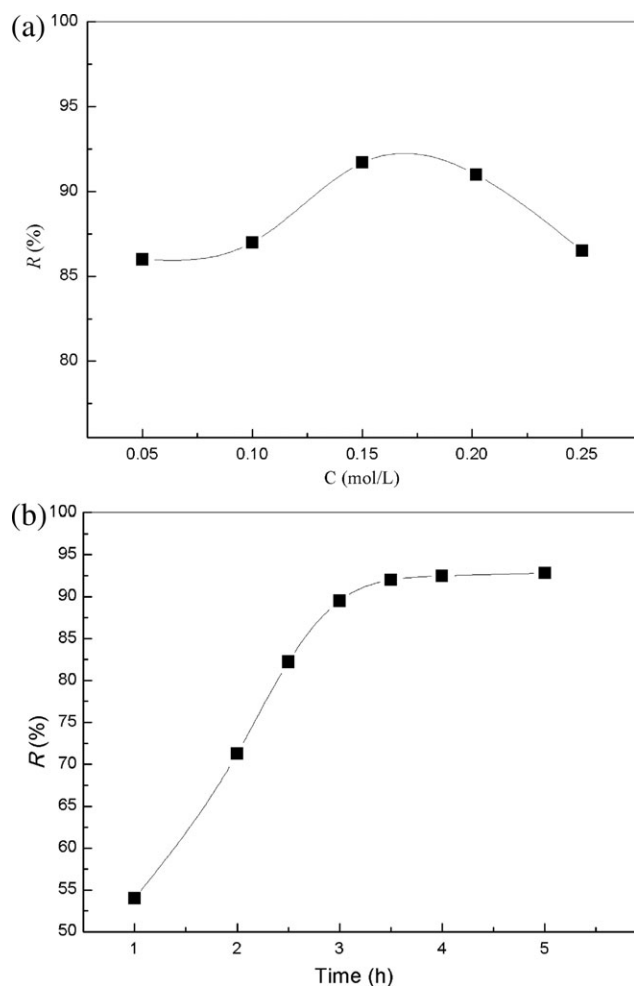
Effect of the Addition of Potassium Iodide (KI)

The reaction between the tertiary amine and p-xylene dichloride belonged to the typical SN_2 bimolecular nucleophilic substitution process. The steric space hindrance between the groups was very strong, and the contact between the attacking agent

crosslinking agent solution and made the distribution of the crosslinking network pores more uniform. (3) When the quaternization with p-xylene dichloride was in progress, the stretched molecular chain of PDMAEMA increased the crosslinking between the molecules, decreased the crosslinking in the same molecule efficiently, made the configuration of the space-network more orderly, and decreased the minimum pore formed by crosslinking in the same molecules and the defect caused by disorder; this is shown in Figure 4. (4) The swelling performance of ethanol toward the support membrane also promoted the bridging of cuticle pores, reduced the macropore, and prevented the pore-effusion phenomenon efficiently. (5) The surface tension of the PDMAEMA solution was reduced, and the spreading coefficient on the surface of the support membrane was increased. However, when the content of ethanol was above 10% v/v, the support membrane swelled excessively, and the pore was spaced out; this reflected the distortion of the membrane, the rapid reduction of the flux, and the rejection rate of the composite NF.

Figure 5. Influence of the $NaHCO_3$ content (C) on the entrapping performance of NF membrane.

Figure 6. Influences of the (a) KI content (C) and (b) crosslinking time on the rejection of the hollow-fiber NF membrane.

$[-CH_2N(CH_3)_2]$ and the carbon atom of which the C—X bond took part in the positron center was comparatively difficult, so the reaction rate was very slow. Therefore, how to improve the reaction rate became the key to the reaction. In addition to the effect of the solvent, the difficulty level of the breaking the C—X bond in p-xylene dichloride also affected the rate of this substitution reaction. The higher the polarizability of the C—X bond was, the easier the X⁻ split and the more smooth the reaction progressed, so we could make use of the characteristic of I⁻ in that it could replace Cl⁻ in the bond of C—Cl and be added in moderate potassium iodide as a catalyst to shorten the reaction time efficiently. Figure 6(a) shows that the optimal concentration of KI was 0.172 mol/L. Figure 6(b) shows the relations between the crosslinking time and the rejection rate after the support membrane was dipped in 0.75% PDMAEMA solution (of which the KI content was 0.172 mol/L), and the determined crosslinking time was 3.5 h.

Effect of the Temperature
Because the interfacial polymerization in this experiment was the substitution reaction of SN$_2$ bimolecular and the activity of the employed monomer was great, in the reaction process, the effect of temperature toward the chain growth rate was not the main problem. T_g of the employed PDMAEMA was 43°C. So, from Figure 7(a,b), we observed that when the temperature was below T_g, the shrinking of the support membrane caused the flux to decrease and the rejection to improve slightly. Although the temperature was above T_g, the flux of NF increased rapidly. At the same time, the rejection of the NF to the salt was lost [shown in Figure 7(b)]; this indicated that inner stress existed in the frozen molecular chain in the process of drying in the shade. When the crosslinking temperature was above T_g, high elastic deformation occurred in the molecular chain, and the compound layer was torn. Scanning electron micrographs are shown in Figure 8. As shown in the figure, under high temperatures (50°C, 10 min), the extra-contracting of the PDMAEMA gel membrane formed stress cracks in the membrane.

FTIR Characterization
The pure PDMAEMA and PDMAEMA crosslinked by p-xylylene dichloride were characterized by FTIR spectroscopy to confirm the reaction of PDMAEMA and p-xylylene dichloride. Figure 9 shows that the crosslinked PDMAEMA had peaks at 1575.83 and 1537.26 cm^{-1} attributed to C=C stretching; this indicated
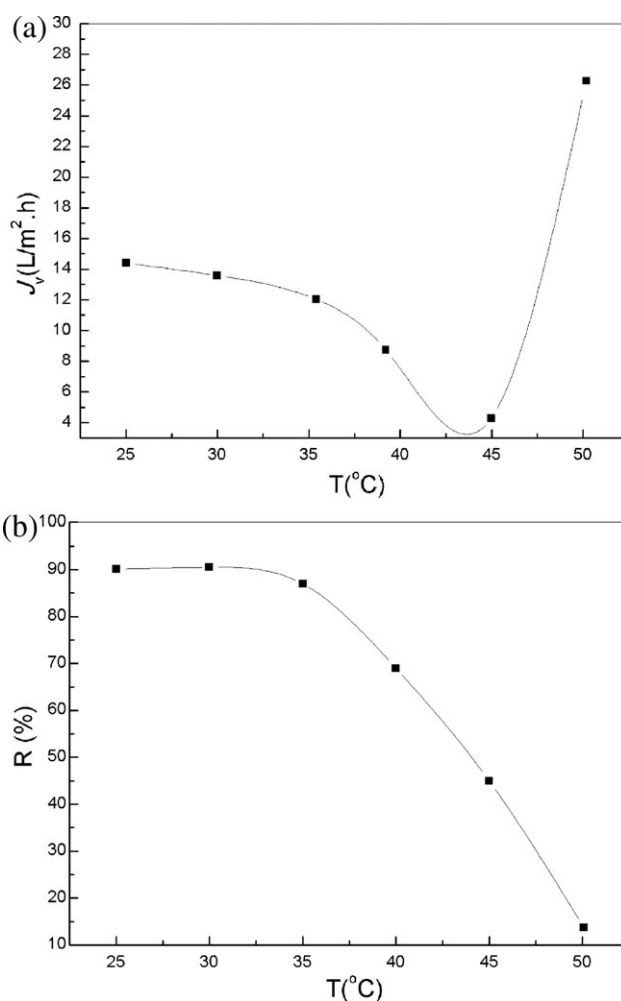
Figure 7. (a) Rejection and (b) permeation flux of the NF membrane as functions of the crosslinking temperature.
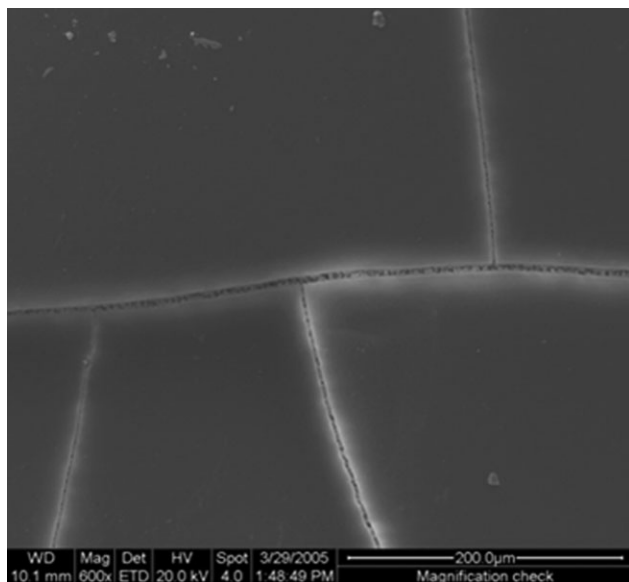
Figure 8. Scanning electron micrographs of crack formation when the NF membrane was heat-treated at 50°C for 10 min.

that there were benzene rings in the crosslinked PDMAEMA and showed that PDMAEMA reacted with *p*-xylylene dichloride.

Stability and Durability of the Membranes

The composite membranes maybe had weak adhesion between the selective layer and the support membrane surface. We measured the stability of the mentioned composite NF membranes by testing the rejection and permeation flux for different time spans. The membrane was preserved in a 0.5% sodium bisulfite solution to protect the membrane surface from bacteria to prevent contamination or destruction. As shown in Figure 10, the *F* value of the NF membrane decreased less slightly and the rejection of the NF membrane did not change greatly when the time was prolonged; this suggested that the hollow-fiber com-
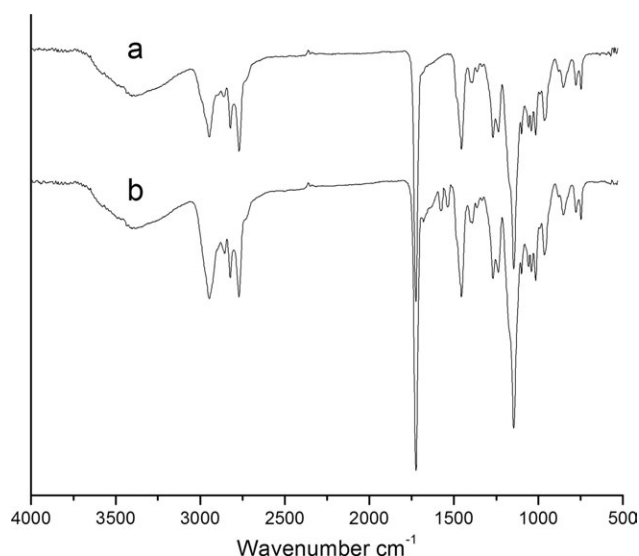
Figure 9. FTIR spectra of the (a) pure PDMAEMA and (b) crosslinked PDMAEMA by *p*-xylylene dichloride.
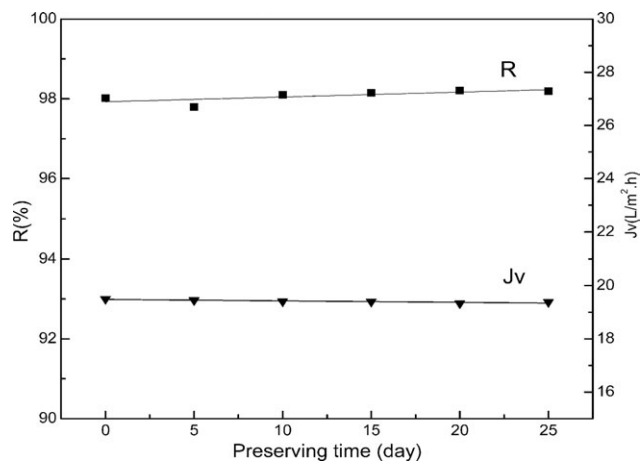
Figure 10. Variation of R and J_v of the hollow-fiber composite NF membrane with testing time (feed: 2 g/L $MgSO_4$ aqueous solution at 0.7 MPa and 25°C).

posite NF membranes had a very good stability at long times and good durability for the filtration process.

CONCLUSIONS

The preparation requirements of the hollow-fiber composite NF were examined in this study. The preparation technology of the hollow-fiber composite NF membrane was very strict; this means that the temperature and humidity in the environment had to be constant, the fiber dipped in the PDMAEMA solution could not take drops and cohere and had to avoid cohering in the process of crosslinking; otherwise, it would have influenced the test data.

Some of our experimental conclusions are as follows:

1. The asymmetric hollow-fiber PSF UF membrane (MWCO = 20,000 and ε = 86.1%) could be used as a supporting membrane for hollow-fiber external composite NF membranes.
2. The optimum concentration of the coating PDMAEMA solution was 0.75–1 wt %.
3. The reaction could be improved efficiently by the addition of 0.243 mol/L $NaHCO_3$ to the PDMAEMA aqueous solution. It could also maintain the PDMAEMA molecular conformation, raise the rejection of the NF membrane to bivalent salt (>95%), and contribute little to the increase of flux.
4. After the organic solvent ethanol was added to the PDMAEMA aqueous solution, the rejection of the NF was above 98%, and the flux increased to 19.5 L m^{-2} h^{-1}.
5. The reaction time was shortened to 3.5 h with the addition of the catalyst KI to the system. From experiments 2, 3, and 4, we observed that the performance of the composite layer in the NF membrane was not simply determined by the crosslinking reaction when we prepared the composite NF membrane with the polyelectrolyte as the interfacial polymerizing monomer. The factors that affected the conformation of the polyelectrolyte molecular, such as the ionic strength and the polarity of the solvent,

influenced the polyion's stretching state, the density of distribution, the depth of pore effusing, and the thickness of the absorbed layer on the surface of the support membrane, and then, they influenced the space-network ε, distribution of pores, thickness and evenness, and attaching fastness of the composite layer after crosslinking on the surface of the support membrane. Therefore, we could prepare NF membranes with some certain rejection performance from the point of adjusting the polyelectrolyte conformation and the aggregate structure.

6. The composite NF membranes showed good stability in the water-phase filtration process.

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