

Development of a Chlorine-Resistant Polyamide Nanofiltration Membrane and Its Field-Test Results

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ABSTRACT: For the development of chlorine-resistant nanofiltration membranes, a thin-film-composite membrane was prepared by the interfacial polymerization of *N*-phenylethylenediamine and 1,3,5-benzenetricarbonyl trichloride on a microporous polysulfone support substrate. The polymerization on the substrate surface was confirmed by Fourier transform infrared measurements, and membrane surface properties such as the roughness and ζ potential were characterized. Rejections of NaCl and isopropyl alcohol of the prepared membrane were 95 and 50%, respectively. The membrane showed much higher chlorine resistance than a commercial

polyamide membrane when the membranes were immersed in an aqueous NaOCl solution. A field test was carried out with a spiral-type membrane module. Tap water was treated by this module for more than 70 days under the condition of continuous NaOCl injection. The prepared membrane module was quite stable, and no distinguished change in the rejection and flux was recognized. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4174–4179, 2007

Key words: membranes; polyamides; nanofiltration membrane; chlorine resistance

INTRODUCTION

Nanofiltration (NF) membranes have attracted attention because NF is more suitable for producing drinking water without remineralization.¹ One way of preparing NF membranes is interfacial polymerization on a substrate. Typically, an active polyamide layer is formed on a microporous substrate of polysulfone (PSf). This type of membrane is called a thin-film composite (TFC). Another procedure is the modification of a reverse-osmosis (RO) membrane. A polyamide RO membrane and a cellulose acetate RO membrane can be modified for the use of NF.² NF membranes can also be prepared from ultrafiltration membranes with different polymers.³

Membrane fouling has been a serious problem for membrane technology. The fouling phenomenon increases operation and maintenance costs and shortens membrane life. Biofouling often occurs in RO and NF processes.⁴ Microorganisms adsorb onto the membrane surface and form a biofouling layer. Chlorine disinfectant is commonly used in water desalination to reduce biofouling. However, the aromatic polyamide active layer in RO and NF TFC membranes is very sensitive to such chlorine treatment.

In our previous study,⁵ various polyamides were synthesized from 17 kinds of diamines and 2 kinds of acid chlorides to screen polyamides with high resistance to chlorine. The membrane prepared from *N,N'*-dimethyl-*m*-phenylenediamine (*N,N'*-DMMPD) and 1,3,5-benzenetricarbonyl trichloride (TMC) showed much higher chlorine resistance than commercial polyamide and cellulose acetate RO membranes. In our previous work, the retention ratio of the molecular weight after immersion in a chlorine solution and the retention ratio of the polymer weight after immersion in a chlorine solution were used for the evaluation of chlorine resistance, and these values were measured for various polyamides. The obtained data for polyamides synthesized from three kinds of diamines are shown in Figure 1. An RO membrane is often prepared from *m*-phenylenediamine (MPD) and TMC.⁶ Compared with this polyamide, the polyamide synthesized from *N,N'*-DMMPD showed much higher chlorine resistance.⁵ The polyamide synthesized from *N*-phenylethylenediamine (*N*-PED) had lower chlorine resistance than that from *N,N'*-DMMPD. However, it still had high chlorine resistance. The membrane prepared from *N*-PED had properties suitable for NF applications. Thus, in this work, a chlorine-resistant polyamide NF membrane was developed from *N*-PED and TMC. In addition to clarification of the membrane's basic performance, a field test was carried out for the obtained membrane module.

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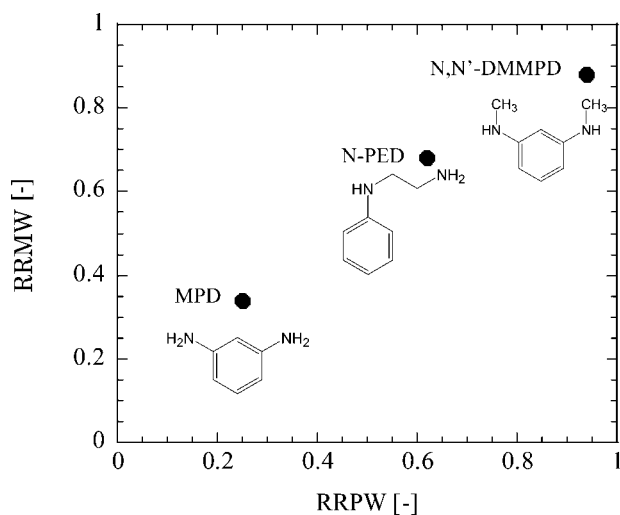


Figure 1 Relation between the retention ratio of the polymer weight after immersion in a chlorine solution (RRPW) and the retention ratio of the molecular weight after immersion in a chlorine solution (RRMW) for three polyamides.

EXPERIMENTAL

Materials

Polyamides were prepared from *N*-PED and TMC. *N*-PED and TMC were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). PSf (Udel P-3500), used for the preparation of a porous support substrate, was purchased from Solvay Advanced Polymers Co. (Georgia, USA).

Membrane preparation

A porous support substrate was first prepared for the TFC membranes. The support membrane was prepared by the same method used in the previous work.⁵ A solution of 18 wt % PSf in *N,N*-dimethylformamide was cast onto a glass plate with an applicator with a 254- μ m gap. The glass plate was immediately immersed in a water bath at room

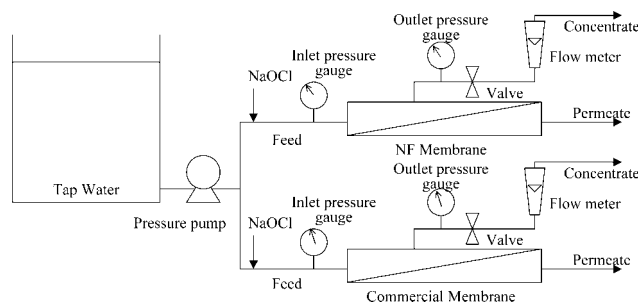


Figure 2 Schematic diagram of the water-treatment apparatus for the field test.

temperature. The PSf membrane was rinsed with water and stored in deionized water. The pore size was about 0.03 μ m.

The active polyamide layer on the top surface was prepared from *N*-PED and TMC. The aqueous diamine solution used for the interfacial reaction was a solution of *N*-PED (2 wt %), sodium lauryl sulfate (0.15 wt %), triethylamine (2 wt %), and camphorsulfonic acid (4 wt %). The organic solution was isooctane containing TMC (0.15 wt %). The PSf support membrane was immersed in an aqueous diamine solution for 30 s and pulled up slowly. Excess of the diamine solution was removed from the surface of the PSf support membrane. The PSf substrate was then covered with a solution of TMC for 10 s to deposit a thin polymeric layer on the substrate by the interfacial reaction. The resulting TFC membrane was dried at 120°C for 5 min. Hereafter, this membrane is called the NF membrane.

Flat membrane performances

Membrane performances were measured with a method similar to that used in the previous work.⁵ Salt rejection and water permeability were measured under the condition of pH = 6.5–7 at 25°C with a common continuous pump-type RO apparatus under an applied pressure of 1.0 MPa. The solutes used for the rejection tests were NaCl (weight-average molecular weight = 58), Na₂SO₄ (142), MgCl₂ (94), MgSO₄ (120), NH₄SO₃ (80), ethanol (46), and isopropyl alcohol (60). Each solute concentration was 1500 ppm, and the rejection test was carried out in the single-solute-component system.

For the measurement of the chlorine resistance, the membrane was immersed in an aqueous sodium hypochlorite solution (200 ppm) including calcium

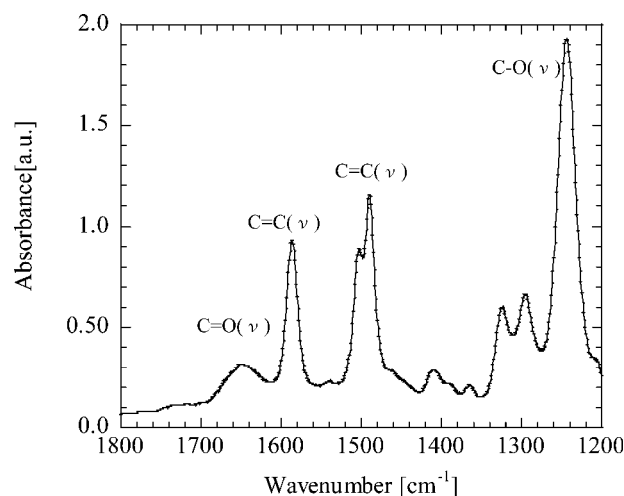


Figure 3 FTIR spectrum of the prepared NF membrane.

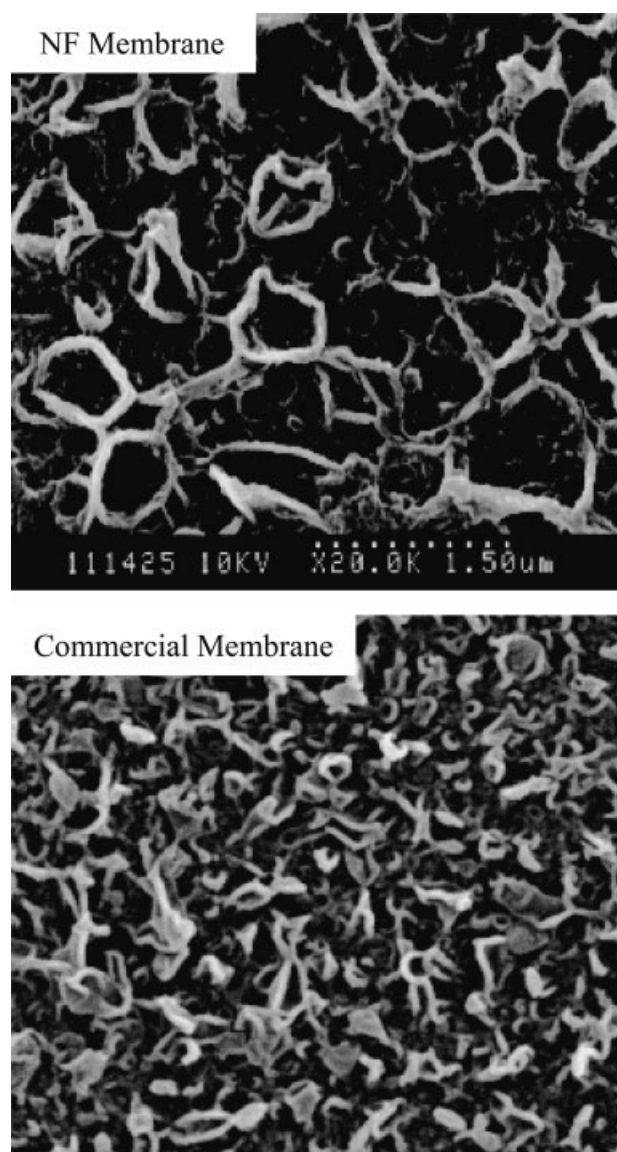


Figure 4 SEM results of the membrane surfaces.

chloride (500 ppm) as an oxidation accelerator⁷ at pH = 7.0 for 240 h. Experimental temperatures were changed from 8 to 40°C.

For comparison, a commercial polyamide membrane (NTR-759HR, Nitto Denko Co., Osaka, Japan) was also used for the membrane performance measurements in addition to the prepared membrane. The commercial polyamide membrane was prepared from MPD and a mixture of TMC and isophthaloyl dichloride. The membrane performances were compared at 40°C.

Analysis of the NF membrane surface

For the confirmation of interfacial polymerization, an attenuated total reflection/Fourier transform infrared (FTIR) analysis (FT/IR-470, Jasco, Tokyo, Japan) was

carried out for the membrane surfaces. In addition, the membrane surfaces were examined with a scanning electron microscope (Semedx type N, Hitachi Co., Tokyo, Japan). Furthermore, the ζ potentials of the membrane surfaces were measured with an electrophoretic light scattering spectrophotometer (ELS-8000, Otsuka Electronics Co., Hirakata, Japan) in the pH range of 3.0–9.0 at 25°C.

Field test

For application to more realistic water treatment, a 4-in. spiral-type membrane module with a membrane area of 6.5 m² was prepared. The tap water in the Shiga prefecture was treated with this membrane module under the condition of a continuous injection of NaOCl of 20 ppm. The electric conductivity and pH of the tap water were about 120 μ S/cm and 8.5, respectively. The water temperature ranged from 16 to 21°C. The membranes were the NF membrane and commercial polyamide membrane. To obtain the same water permeability of 0.48 (m³/m²/d), the applied pressures were controlled for two membrane modules. That is, the applied pressure for the NF membrane module was 0.5 MPa, whereas that for the commercial membrane module was 0.75 MPa. The water recovery was about 25%. A schematic diagram of the water-treatment apparatus for the field test is shown in Figure 2.

RESULTS AND DISCUSSION

Figure 3 shows FTIR spectra of the prepared NF membrane. The peak of C=O stretching appears at 1650 cm⁻¹ and indicates the existence of an amide group formed by the interfacial polymerization. The peaks at 1490 and 1590 cm⁻¹ are attributable to C=C stretching of the benzene ring in the polyamide

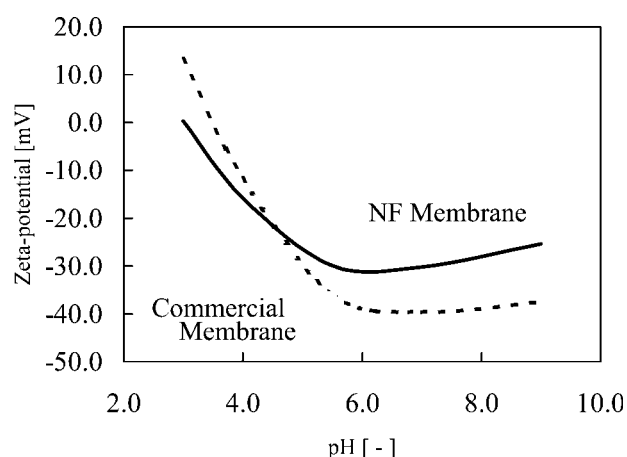


Figure 5 ζ potential of the membrane surfaces.

TABLE I
Solute Rejection Data for the Prepared Membrane and Commercial Polyamide Membrane

Solute	Molecular weight	Rejection (%)	
		Membrane obtained in this work	Commercial polyamide membrane
NaCl	58	95	99.6
Na ₂ SO ₄	142	99.5	99.9
MgCl ₂	94	93	99.5
MgSO ₄	120	99.2	99.6
NH ₄ NO ₃	80	85	98
Ethyl alcohol	46	20	44
Isopropyl alcohol	60	50	94

membrane. The peak at 1245 cm^{-1} is attributable to C—O stretching of the PSf support.

Figure 4 shows scanning electron microscopy (SEM) results for the membrane surface. The SEM results for the commercial polyamide membrane (NTR-759HR) are also shown in this figure. The membrane prepared in this work (the NF mem-

brane) had a rough surface, and many prominent structures were formed on the surface. The roughness was more pronounced than that of the commercial polyamide membrane.

The ζ potential of the membrane surface is shown in Figure 5. In the wide pH range, the obtained membrane showed a negative charge. This is attributable to the carboxyl group originated from unreacting site —COCl of TMC. The ζ potential of the prepared membrane (NF membrane) was similar to that of the commercial membrane.

The solute rejection result for each solute is summarized in Table I. The rejections of NaCl and Na₂SO₄ were 95% and 99.5%, respectively. The neutral solutes showed lower rejection because of the lack of electrical repulsion. For example, the rejection of isopropyl alcohol with a molecular weight similar to NaCl was only 50%. These data show that the prepared membrane was a typical NF membrane. The rejections of the commercial polyamide RO membrane are included in this table. This membrane had higher rejection and RO membrane performance.

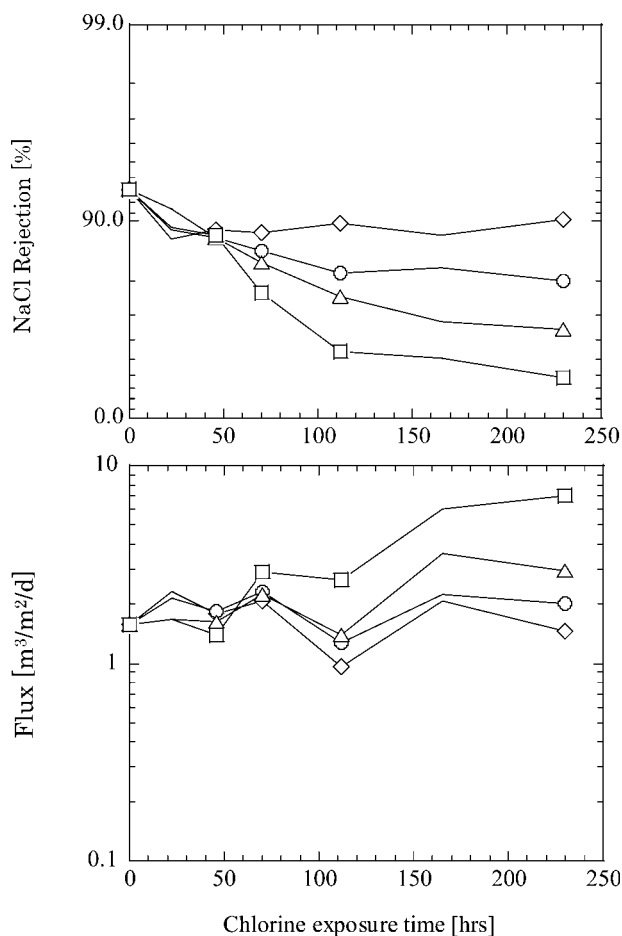


Figure 6 Effect of the immersion time in a chlorine solution on NaCl rejection and membrane flux at various temperatures: (\diamond) 8, (\circ) 20, (\triangle) 30, and (\square) 40°C.

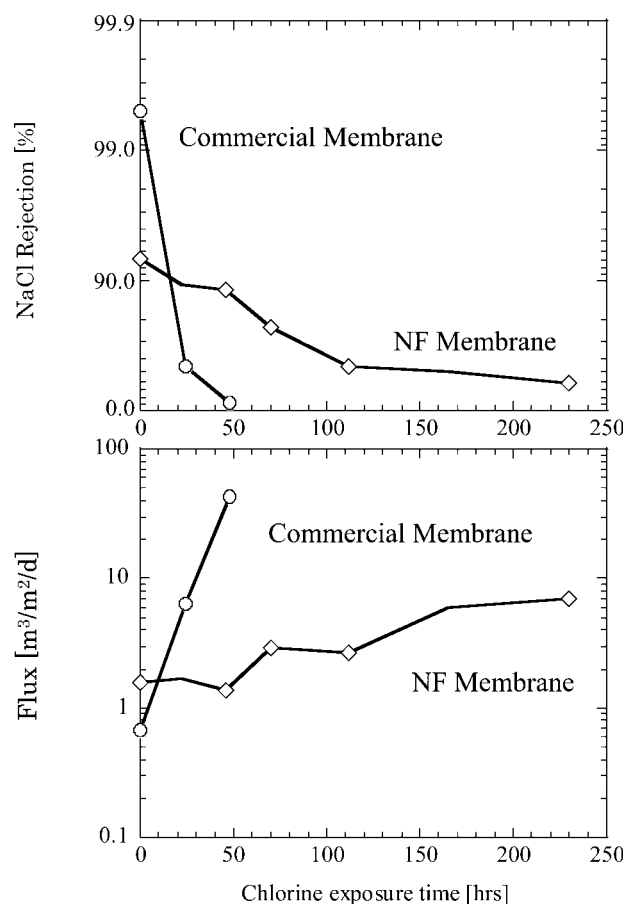


Figure 7 Comparison of chlorine tolerance for the prepared NF membrane and commercial membrane at 40°C.

Figure 6 shows the effect of immersion time in a chlorine solution on the NaCl rejection and membrane flux of the NF membrane. At the experimental temperature of 8°C, the rejection and flux hardly changed after 240 h of immersion in a chlorine solution, and this indicated that the prepared NF membrane had high chlorine resistance. As the experimental temperature increased, the rejection gradually decreased with the increased flux. This was due to the accelerated decomposition of the polymer material by chlorine at a higher temperature. Thus, the chlorine tolerance was more pronounced at a higher temperature, and therefore the chlorine tolerances were compared at 40°C for the prepared membrane and commercial membrane.

A comparison of the chlorine tolerances is shown in Figure 7. The commercial membrane showed higher initial solute rejection because the membrane had not NF but rather RO performance. However, the rejection abruptly decreased during chlorine immersion and reached almost zero after 50 h. In contrast to this quite low chlorine tolerance, the membrane prepared in this work had higher tolerance. That is, both the rejection decrease and the flux increase were clearly suppressed.

The spiral-type membrane module with the NF membrane was applied to the field test of the tap-water treatment. The obtained average solute analysis data in the feed, permeate, and concentrate are summarized in Table II. The cations, anions, and

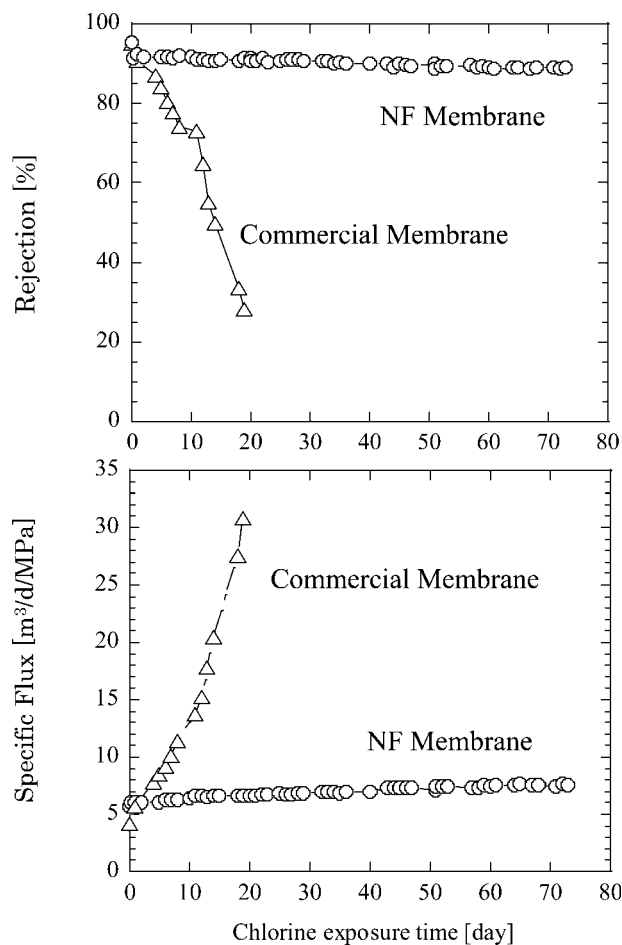


Figure 8 Long-term stability results of the field tests.

TABLE II
Average Solute Analysis Data for the Feed, Permeate,
and Concentrate in the Case of the Field Test

	Feed	Permeate	Concentrate	Rejection (%)
pH	7.3	6.4	7.4	—
Electric conductivity ($\mu\text{s}/\text{cm}$)	120.3	14.7	172.1	89.9
Cation				
Na (mg/L)	11.0	2.09	19.2	86.2
K (mg/L)	1.91	0.30	2.41	86.1
Ca (mg/L)	7.50	0.57	11.3	93.9
Mg (mg/L)	1.90	0.23	2.49	89.5
Total (mg/L)	22.3	3.19	35.4	88.9
Anion				
Cl (mg/L)	17.9	1.9	23.8	90.9
HCO ₃ (mg/L)	34.3	4.4	43.6	88.7
NO ₃ (mg/L)	0.14	0.06	0.22	66.7
SO ₄ (mg/L)	11.3	— ^a	15.2	>84.9
Total (mg/L)	63.6	6.35	82.8	—
SiO ₂ (mg/L)	1.8	1.1	2.0	42.1
Total dissolved solids (mg/L)	88	10.6	120	89.8
Total organic carbon (mg/L)	2.31	0.63	2.88	75.7

^a Not determined (<2.0).

organic solutes were highly rejected by this membrane module.

Figure 8 shows the long-term stability results. The total solute rejection was evaluated by the electric conductivity, and the specific flux plotted in this figure is the flux per unit of pressure difference across the membrane. The prepared NF membrane module showed quite stable performance for more than 70 days. On the other hand, for the commercial membrane, the rejection decreased drastically, and this was accompanied by an abrupt increase in the flux.

CONCLUSIONS

An NF membrane with chlorine resistance was prepared by the interfacial polymerization of *N*-PED and TMC on a porous PSf support substrate. The membrane had a rough membrane surface and negative charge in a wide pH range. The NF performance was confirmed by rejection results of several kinds of ions and neutral species.

For the measurement of the chlorine resistance, the membrane was immersed in an aqueous NaOCl solution. The membrane prepared in this work showed much higher chlorine resistance than a commercial polyamide RO membrane. For application to a field test, a 4-in. spiral-type membrane module was prepared. A tap-water treatment was carried out under the condition of a continuous injection of NaOCl of 20 ppm for more than 70 days. The solute rejection and flux hardly changed for the prepared membrane module, and this indicated that the membrane module had high chlorine tolerance.

References

1. Nunes, S. P.; Peinemann, K.-V. In *Membrane Technology*; Nunes, S. P.; Peinemann, K.-V., Eds.; Wiley-VCH: Weinheim, 2001; Chapter 4.
2. Mickols, W. E. U.S. Pat. 5,755,964 (1998).
3. Sforca, M. L.; Peinemann, K.-V. *J Membr Sci* 1995, 106, 49.
4. Ivnitsky, H.; Katz, I.; Minz, D.; Shimoni, E.; Chen, Y.; Tarchizky, J.; Semiat, R.; Dosoretz, C. G. *Desalination* 2005, 185, 255.
5. Shintani, T.; Matsuyama, H.; Kurata, N. *Desalination* 2007, 207, 340.
6. Petersen, R. J. *J Membr Sci* 1993, 83, 81.
7. Gabelich, C. J.; Frankin, J. C.; Gerringer, F. W.; Ishida, K. P.; Suttet, I. H. *J Membr Sci* 2005, 258, 64.