Chlorine-Resistant Membrane for Reverse Osmosis. II. Preparation of Chlorine-Resistant Polyamide Composite Membranes

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Synopsis

Polyethylenetrimesamide (PET), poly(trimesoyl piperazine) (PTP), and poly(*m*-phenylene-trimesamide) (PMT) were fabricated into thin film composite to evaluate the membrane performance and resistance to oxidative chlorine. The salt rejection of these membrane increased in the following order: PTP < PET < PMT. The degree of performance deterioration of the membrane after the exposure to aq hypochlorous acid was in the following order: PMT > PET > PTP. The reaction behavior of these polyamide membranes with hypochlorous acid could be properly predicted by that of corresponding polyamide powder. Thus, polyethylenetrimesamide has proved to be one of the potential chlorine-resistant reverse osmosis membrane possessing excellent rejection to monosaccharides, amino acids, phenolics, and other solutes having a molar volume larger than 80 cm³/mol.

INTRODUCTION

In the preceding paper,[1] we described the correlation between chemical structures and chlorine resistance of polyamides. Three types of reactions of polyamides with hypochlorous acids were found: no reaction in the case of tertiary polyamide, reversible *N*-chlorination in the case of secondary polyamide from aliphatic primary diamines, and irreversible chlorination in the case of polyamides from aromatic primary diamines and aralkylene primary diamines.

In this paper we describe the preparation of novel chlorine-resistant polyamide membranes and their membrane performances. Correspondence of the chlorine resistance of the membrane with that of polyamide powder is also discussed.

EXPERIMENTAL

Fabrication of Thin Film Composite

Microporous polysulfone membrane of which average surface porosity and pore diameter measured by scanning electron microscope is 21% and 210 Å, respectively, was dipped in an aq diamine solution (0.3–0.5 wt %) for 5 min. Then the membrane was drained off for 10 min in the ambient atmosphere. The membrane was then interfacially reacted with 0.1 wt % (or 0.3 wt %) of acid chloride in *n*-hexane (or CCl₄) solution for 30 (or 5) s followed by air drying for 30 min.

Dynamic Membrane Performance Measurement

Reverse osmosis tests were performed under the following conditions: operating pressure = 4.30 MPa (42.5 kg/cm²), temp = 25°C, feed solution 0.5% NaCl aq. The membrane performance was measured for 2 h after 15 h preconditioning operation under the above conditions. Membrane performances are defined as follows:

water flux = amount of liquid permeate through membrane per hour
$$(m^{-2} \cdot h^{-1})$$

$$\text{salt rejection} = \left(1 - \frac{\text{salt concn in permeate}}{\text{salt concn in feed solution}}\right) \times 100 \ (\%)$$

Evaluation of Membrane Chlorine Resistance

Immersion Test. The membrane was immersed in a hypochlorous solution (500 ppm, pH 6.0), at 23°C for a predetermined period of time. After the immersion test, the membrane properties were examined by reverse osmosis test for 2 h, followed by washing with sodium hydrosulfite under the same pressurized conditions for 30 min to confirm the rate of water flux restoration of the membrane.

Dynamic Test. The following test cycles were repeated until the membrane performance deteriorated:

$$
\begin{array}{ccc}
A & \rightarrow & B \\
\uparrow & & \downarrow \\
D & \leftarrow & C
\end{array}
$$

where A = treatment with hypochlorous acid (100 ppm, pH 5.0, 25°C), B = membrane washing with dechlorinated water, C = treatment with sodium hyposulfite aq. solution (300 ppm, 25°C), and D = membrane washing with dechlorinated water. Each procedure was performed under the pressure of 4.30 MPa (42.5 kg/cm²), at 25°C for 30 min and the change of the membrane performance was measured periodically after procedure D for 1 h.

Evaluation of Chemical Resistance

Chemical resistance of the membrane was evaluated by immersion tests under the prescribed conditions, and the change of the membrane performance before and after the immersion was examined.

RESULTS AND DISCUSSION

Preparation and Separation Properties of Polyamide Thin Films

We have chosen polyethyleneisophthalamide (PEI), poly(isophthaloyl piperazine) (PIP), and poly(m-phenyleneisophthalamide) (PMI) as the representatives of three types of polyamides categorized by the reaction behaviors with hypochlorous acid in the preceding paper to examine the separation properties.

TABLE I
Reverse Osmosis Properties of Dense Polyamide Films

	PIP[a]	PMI[b]	PEI[c]	CA[d]
Membrane thickness (μm)	10.2	6.8	—[g]	5.3
Membrane performance				
WF$_1$[e]	0.57	0.04	—	0.40
WF$_2$[f]	5.77×10^{-10}	0.27×10^{-10}	—	2.13×10^{-10}
SR (%)	97.5	94.2	—	98.7

[a] Poly(isophthaloyl piperazine) thin film composite.
[b] Polymetaphenyleneisophthalamide thin film composite.
[c] Polyethyleneisophthalamide thin film composite.
[d] Cellulose diacetate.
[e] Membrane water flux $(g \cdot m^{-2} \cdot h^{-1})$.
[f] Water permeability per unit thickness (cm) of the membrane $(g \cdot cm^{-1} \cdot s^{-1} \cdot atm^{-1})$.
[g] Membrane was too fragile to measure the performance.

Table I shows the separation performance of the dense thin films prepared by complete evaporation of solvent from the cast solution. Among these polyamides, PEI is not so tough as to stand the reverse osmosis test at 4.3 MPa. The water flux of the thin film of PIP and PMI was 5.77×10^{-10} and 0.27×10^{-10} $g \cdot cm^{-1} \cdot s^{-1} \cdot atm^{-1}$, respectively. Cellulose diacetate membrane prepared by the similar method as a reference, showed the water permeability of 2.13×10^{-10} $g \cdot cm^{-1} \cdot s^{-1} \cdot atm^{-1}$. The NaCl rejection of these membrane, PIP, PMI, and CA was 97.5%, 64.2%, and 98.7%, respectively. These results suggest that the polyamide PIP and PMI would be of practical utility if the membrane thickness could be reduced to less than 0.1 μm.

Riley and Milstead[2] reported that the empirical lower limit of the membrane thickness of a thin film prepared by spreading a polymer solution onto water surface was around 0.035 μm. However, the film often contained many pinholes or defects. This prompted us to examine an interfacial polycondensation instead of spreading a thin film onto a water surface to get a pinhole-free polyamide thin-film composite. Table II shows the properties of polyamide thin film composite thus obtained: polyethyleneisophthalamide (PEI), poly(m-phenyleneisophthalamide) (PMI) and poly(isophthaloyl piperazine) (PIP). However, none of these films withstood high pressure of 4.30 MPa in the reverse osmosis test.

Then we examined interfacial crosslinking reaction in order to get a membrane with enough mechanical strength. We used trifunctional tri-

TABLE II
Reverse Osmosis Properties of Interfacially Formed Noncrosslinked Polyamide
Thin Film Composite

	PIP[a]	PMI[b]	PEI[c]
WF ($m^{-2} \cdot h^{-1}$)	70–100	100–180	500
SR (%)	50–70	40–65	15–27

[a] Poly(isophthaloyl piperazine) thin film composite.
[b] Polymetaphenyleneisophthalamide thin film composite.
[c] Polyethyleneisophthalamide thin film composite.

TABLE III
Reverse Osmosis Properties of Interfacially Crosslinked Polyamide Thin Film Composite

	PTP[a]	PMT[b]	PET[c]
Thickness of the skin layer (Å)	780	1580	555
Membrane performance			
WF $(m^{-2} \cdot h^{-1})$	77	65	54
WF $(g \cdot cm^{-1} \cdot s^{-1} \cdot atm^{-1})$	4.32×10^{-10}	7.41×10^{-10}	2.16×10^{-10}
SR (%)	78	99.3	95

[a] Poly(trimesoyl piperazine).
[b] Polymetaphenylenetrimesamide.
[c] Polyethylenetrimesamide.
[d] Thickness of the membrane skin layer was measured by transmission electron micrography.

mesoyl chloride in place of isophthaloyl chloride to introduce crosslinks. Table III shows the results of the interfacial crosslinking of ethylenediamine, m-phenylenediamine, and piperazine. All the resulting membranes, polyethylenetrimesamide (PET), poly(trimesoyl piperazine) (PTP), and poly(m-phenylenetrimesamide) (PMT) were tough enough to withstand the reverse osmosis test.

In order to compare the water permeability of these membranes with each other, the water flux of the membranes was normalized to a unit thickness which was measured by transmission electron micrograph. The membranes of PTP, PET, and PMT showed the water permeability of 4.32 $\times 10^{-10}$, 2.16 $\times 10^{-10}$, and 7.41 $\times 10^{-10}$ g $\cdot$ cm^{-1} $\cdot$ s^{-1} $\cdot$ atm^{-1}, respectively. The salt rejection of the membranes, on the other hand, was 78%, 95%, and 99.30%, respectively. The difference in the salt rejection might be
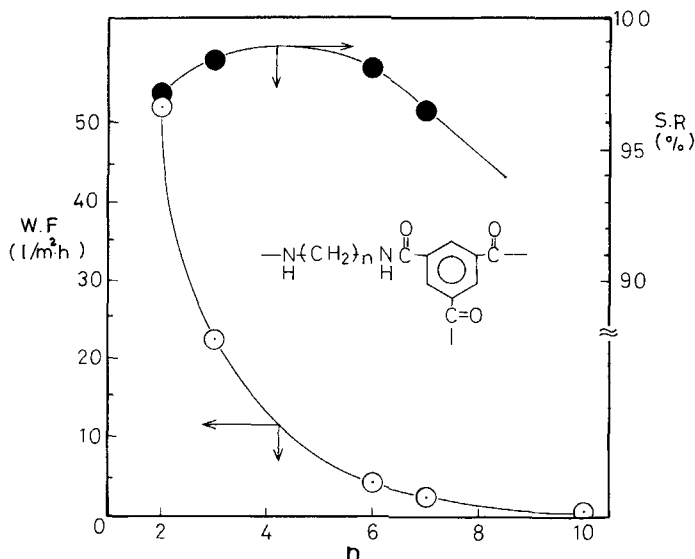

Fig. 1.   Separation properties of polyalkylenetrimesamide thin film composite at 4.30 MPa and 25°C.

caused by the degree of crosslinking because the membrane of poly(trimesoyl piperazine) (PTP) was found quite porous compared with the other membrane of PET and PMT by scanning electron micrograph.

Judging from these results, poly(m-phenylenetrimesamide) showed the best performance, followed by polyethylenetrimesamide. However, as was revealed in the preceding paper, polyamides with an aromatic primary diamine component was least resistant to oxidative hypochlorous acid, suggesting the superiority of polyethylenetrimesamide to poly(m-phenylene-trimesamide) as a chlorine-resistant membrane.

In order to get the most potential membrane, we then examined various aliphatic diamine components such as polymethylene diamine: H_2N—$(CH_2)_m$—NH_2 (I) and oligomeric polyethyleneimine: H_2N—$(CH_2CH_2NH)_{m'}$—H (II) as an amine component of the polyamide thin film composite. Figures 1 and 2 gives the performance of these polyamide membrane. When [I] was used as a diamine component, the membrane water flux decreased markedly with increase of m. In case of [II], on the other hand, the membrane flux
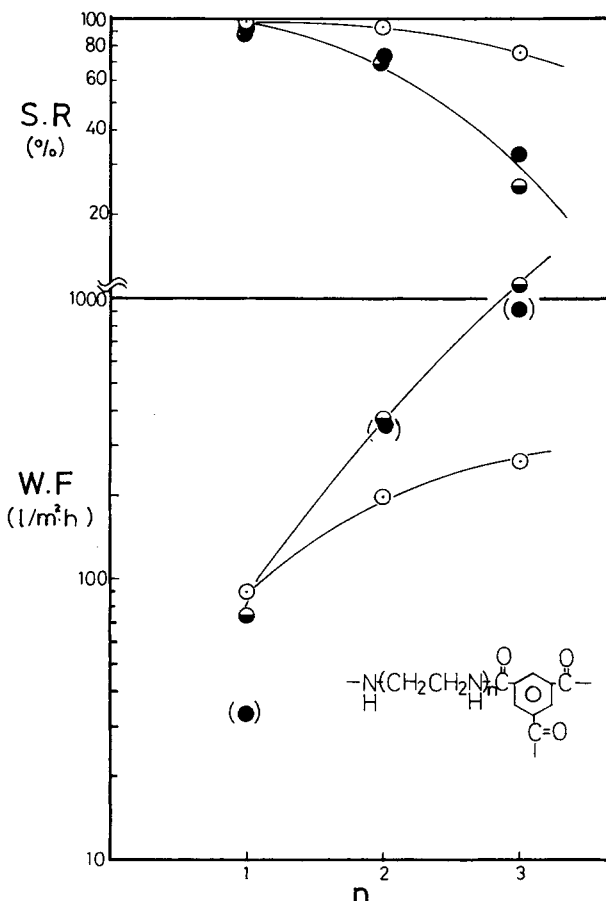

Fig. 2. Separation properties of polyiminoethylenetrimesamide thin film composite and their chlorine resistance: (○) initial performance; (●) after hypochlorous acid immersion; (◖) treatment with $Na_2S_2O_4$ after hypochlorous acid immersion.
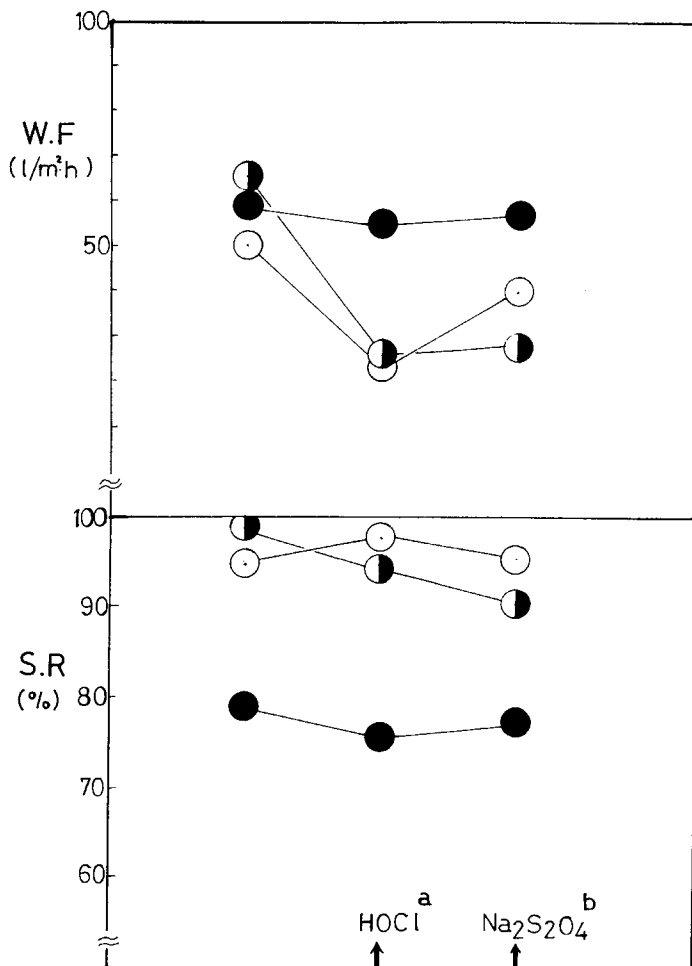
Fig. 3. Chlorine resistance of polyamide membranes by an immersion test: (a) 500 ppm of hypochlorous acid at 23°C for 15 h; (b) 300 ppm of sodium hydrosulfite added; (○) polyethylenetrimesamide; (◑) poly(m-phenylenetrimesamide); (●) poly(trimesoyl piperazine).

increased two- to threefold with an increase of m', but at the sacrifice of the salt rejection, especially after chlorine exposure. This is presumably caused by the cleavage of the free imino group, $+$CH$_2$CH$_2$NH$+$, which may remain unreacted in the main chain of the polymer. These results recommend the selection of ethylene diamine as an amine component of the polyalkylenetrimesamide.

Chlorine Resistance of Polyamide Membranes

Figure 3 shows comparative membrane performance of polyethylenetrimesamide, poly(m-phenylenetrimesamide), and poly(trimesoyl piperazine) thin film composite. The test was performed by immersing them in an aq hypochlorous acid solution (500 ppm, pH 6.0) for 15 h. The results were summarized a follows:

(1) Poly(ethylenetrimesamide) membrane suffered from the loss of water flux, one third to one fourth of the initial water flux, upon contact with
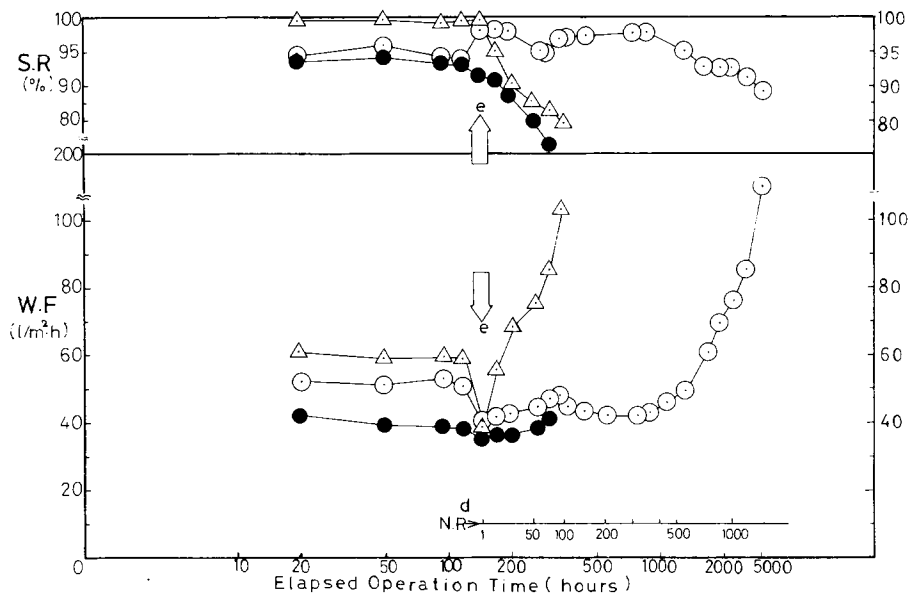
Fig. 4.   Life test of the polyamide thin film composites: (○) polyethylenetrimesamide; (△) poly(m-phenylenetrimesamide) (●) cellulose acetate (Eastman 398-3). (d) The number of recycled sterilizing test (see Experimental); (e) sterilizing test started.

hypochlorous acid, but the flux was recovered to the level of 80–90% of the initial value by the treatment with 300 ppm of aq sodium hydrosulfite for 30 min.

(2) Poly(m-phenylenetrimesamide) also suffered from the loss of water flux, one third of the initial flux, which could not be recovered by the treatment with reducing agents such as sodium hydrosulfite, sodium bisulfite, or sodium hyposulfite. The salt rejection of this membrane was decreased from 99.40% to 90.2% after the test, indicating a kind of membrane deterioration.

(3) Poly(trimesoyl piperazine) showed little change both in water flux and salt rejection, but the initial salt rejection was as low as 78%.

These results were compared with the chemical behavior observed in the reaction of powdered polyamides with hypochlorous acid, as was discussed in the preceding paper. In case of polyethylenetrimesamide, the loss of water flux might be caused by N-chlorination, which renders the membrane hydrophobic and the restoration of the membrane water flux can be explained by the dechlorination of the membrane after the treatment with sodium hydrosulfite. In case of poly(m-pheny-lenetrimesamide), irreversible chlorination of the membrane might be a plausible explanation for both the loss of water flux and salt rejection of the membrane after the immersion test.

Figure 4 shows the results of continuous dynamic reverse osmosis operation for the evaluation of chlorine resistance of polyethylenetrimesamide, poly(m-phenylenetrimesamide) thin film composites, and an asymmetric cellulose diacetate membrane as a control. Poly(trimesoyl piperazine) was omitted as a candidate membrane in the recycle test because of its low salt rejection (70–80%).

TABLE IV
Organic Substrate Rejection

	PET composite membrane[b] (%)	CA[c] (%)
Amino acid		
Leucine	99.5	98.0
Aspartic acid	99.6	97.1
Glutamic acid	99.4	97.5
Carboxylic acid		
Acetic acid	73.8	4.8
Lactic acid	98.8	84.2
Alcohol		
Methanol	42.1	5.2
Ethanol	82.1	12.3
Ethylene glycol	83.3	41.4
Glycerol	95.4	86.3
Saccharise		
Glucose	99.9	98.3
Sucrose	99.9	99.1
Lactose	99.9	99.0
Other Solute		
Urea	74.1	23.3
Phenol	85.2	−3.5
DMF	95.8	48.7
NMP	99.4	75.5
Sodium chloride	95.9	75.5

[a] RO conditions: 1% concn, 42.5 kg/cm², 25°C.

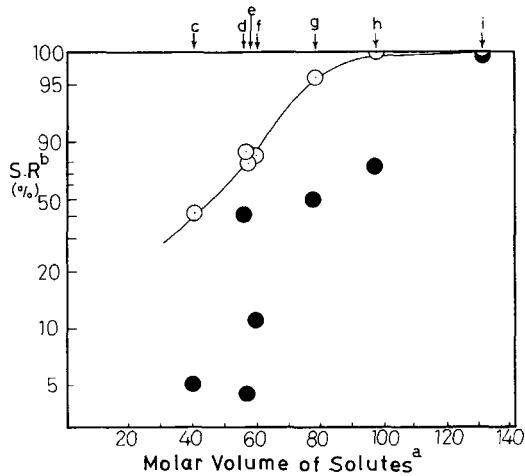[b] Polyethylenetrimesamide.

[c] Cellulose diacetate (Eastman 398-3).

Fig. 5. Correlation between molar volume of solutes and solute rejection of membranes: (a) Sv is a molar volume of a solute; (b) SR is a solute rejection of the membranes; (c) CH_3OH; (d) C_2H_5OH; (e) H_2NCONH_2; (f) CH_3COOH; (g) $(CH_3)_2NCHO$; (h) N-methylpyrrolidone; (i) glucose; (○) polyethylenetrimesamide thin film composite; (●) cellulose diacetate anisotropic membrane (Eastman 398-3). Concentration of the solute-1.0 wt %; reverse osmosis test conditions: 4.30 MPa (42.5 kg/cm² · G); 25°C, 1% aq solution of the organic solutes.

TABLE V
Chemical Resistance of the Membrane[a]

Chemicals	Concn (%)	Immersion time (h)	Water flux retention (%)	SR change (%)
Formalin	3.7	91		+2.0
Phenol	0.2	16		+1.0
Hydrogen peroxide	2.0	20		+1.0
Benzalconium chloride	0.2	20		−2.5
Iodophor	5.0	20		+4.0
PEG-600	5.0	67		+3.1
Sodium lauryl sulfate	0.5	16		+0.9
Sodium dodecyl benzene sulfonate	0.5	16		+2.5
Nonyl phenyl ether	0.2	24		+0.5
Methyl acetate	5.0	16		−0.9
Methyl ethyl keton	5.0	16		+0.2
Acetic acid	5.0	67		+2.3
	10	16		+2.0
Anilin	0.1	16		+1.9
NMP	5.0	67		+2.4
Ethanol	100	16		+0.9
Ethylene glycol	1.0	67		+3.0
Aspartic acid	1.0	24		+5.0
Bovine serum albumin	1.0	24		+0.4

[a] Immersion test: 25°C; performance test: 42.5 kg/cm², 0.5% NaCl; salt rejection after immersion test—initial salt rejection.

The dynamic reverse osmosis test consists of four cyclical steps as explained in Experimental. In the initial stage of this cycle test, the water flux of polyethylenetrimesamide decreased to the level of 80% of the initial value, but gradually recovered. Poly(m-phenylenetrimesamide) and CA membrane deteriorated rapidly after the contact with hypochlorous acid. Polyethylenetrimesamide thin film composite, on the other hand, retained NaCl rejection higher than 90% for 2300 h of elapsed operation time in which the real contact time of the membrane with hypochlorous acid was 575 h. This may imply the membrane life to be 575 days if it is sterilized with 100 ppm of hypochlorus acid once a day for 1 h. The membrane deterioration after 2300 h seems to be attributed to a mechanophysical damage such as peeling off of the skin layer by concentrated and accumulated physical stress during the long period of operation.

Other Properties of Polyethylenetrimesamide Thin Film Composite

Table IV shows the rejection of this membrane to organic solutes. This membrane rejects amino acids, saccharides, N-methylpyrrolidone, and phenolics almost perfectly. Figure 5 elucidates the correlation between solute rejection of the membrane and molar volume of the solute. These correlation does not seem to exist in a CA membrane, indicating that the mechanism of solute rejection of the crosslinked thin film composite is different from that of an ordinary membrane.

Table V gives the chemical resistance of the polyethylenetrimesamide composite membrane. The change of membrane properties after the immersion test was shown by retention of the initial value. Generally speaking, this membrane showed an excellent chemical resistance against aq. solution of acetic acid, ethanol, methyl ethyl ketone, formalin, phenolics, anionic, and nonionic surfactants. Methyl acetate and benzalconium chloride causes a slight decrease in the membrane rejection.

Among these chemical resistance, antifouling properties against nonionic surfactants are characteristic in the polyethylenetrimesamide membrane. Table VI discloses the results of the fouling test. In this experiment, mixture of polypropyleneglycol and a nonionic surfactant was used to examine the change of the membrane properties. Among the membranes tested, polye-

TABLE VI
Resistance of RO Membranes to Nonionic Surfactant[a]

Membrane performance[b]	PET[c]		PMT[d]		CA[e]	
	Initial	After immersion[f]	I[g]	A[h]	I[g]	A[h]
Water flux (m^{-2} · h^{-1})	67.7	64.8	63.2	18.0	90.4	51.4
Salt rejection (%)	95.9	97.6	99.3	98.0	91.5	82.3

[a] Polypropylene glycol/nonionic surfactant: 17.0 wt %.
[b] RO conditions: 43.0 × 10^5 Pa, 25°C, 0.5% NaCl aq.
[c] Polyethylenetrimesamide thin film composite.
[d] Polymetaphenylenetrimesamide thin film composite.
[e] Cellulose diacetate anisotropic membrane (Eastman 398-3).
[f] Immersion test conditions: 70 h, 25°C.
[g] Initial performance.
[h] After immersion test.

thylenetrimesamide showed quite satisfactory resistance to the fouling by a nonionic surfactant.

CONCLUSIONS

Polyethylenetrimesamide has proved to be an interesting candidate material for reverse osmosis membrane with high chlorine resistance and quantitative rejection to lactose, amino acids, and other solutes with a molar volume higher than 80 cm^3/mol. Moreover, the membrane is resistant to fouling by nonionic surfactants.

These properties of the membrane are to be put into practical uses such as concentration or recovery of lactose from cheese whey under sufficient sterilizing conditions with hypochlorous acid, or the treatment of process effulent containing nonionic surfactants.

References

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2. R. J. Riley and J. Milstead, O.S.W. Report No. 851, 1973.