

# New Reverse Osmosis Membrane Materials with Higher Resistance to Chlorine

S. KONAGAYA, H. KUZUMOTO, O. WATANABE

Toyobo Research Center, 1-1 Katata 2-Chome, Ohtsu, Shiga, 520-0292 Japan

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**ABSTRACT:** Copolyamides were prepared from mixed diamine components of 3,3'- or 4,4'-diaminodiphenylsulfone, piperazine, and dichlorides such as isophthaloyl or terephthaloyl. The obtained copolyamides are random copolymers, which have good solubilities in organic solvents and good mechanical properties, even in water. The asymmetric membranes prepared from the copolyamides [ex: 4I-PIP(20)] not only have more excellent reverse osmosis performance, but also higher chlorine resistance than NOMEX-type aromatic polyamide. New membrane materials with excellent reverse osmosis performance and higher chlorine resistance than the NOMEX-type aromatic polyamide could be demonstrated successfully. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1357–1364, 2000

**Key words:** membrane; polyamide; diaminodiphenylsulfone; piperazine; chlorine resistance

## INTRODUCTION

Recently, many researchers have proposed new ideal synthetic reverse osmosis (RO) membranes for desalination from polyamides with the following properties: (1) high flux; (2) high salt rejection; (3) resistance to chlorine and other oxidation agents; (4) capable of withstanding higher temperatures; (5) good mechanical stability; (6) no need for preservation while standing idle; and (7) excellent performance under a variety of acid/alkaline conditions.<sup>1</sup>

Polyamides with piperazine (PIP) moiety such as poly(isophthaloyl piperazineamide) and poly(terephthaloyl piperazineamide) have superior permeability and high chlorine resistance, but poor mechanical stability and poor solubility in aprotic solvents such as *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAC), and therefore they have not been applied to practical use.

Several kinds of polyamides containing PIP moiety have been synthesized for the purpose of

improving their physical properties, solubility in aprotic solvents, and mechanical properties, but have not been put to practical use as RO membrane materials for desalination.<sup>2–6</sup>

We have reported previously<sup>7–9</sup> that the aromatic polyamides prepared from an aromatic diamine compound with an electron withdrawing group such as 3,3'- or 4,4'-diaminodiphenylsulfone have higher chlorine resistance, higher solubility in aprotic solvents, and better physical properties than PIP polyamides. The polysulfonamides have higher solubility in aprotic solvents and better physical properties, but poorer RO performance than PIP polyamides.

In this report, we describe the formation of membrane materials with high chlorine resistance, excellent mechanical properties in water, solubilities in aprotic solvents (NMP and DMAC) and RO performance by the modification of PIP polyamide with 3,3'- or 4,4'-diaminodiphenylsulfone.

## EXPERIMENT

### Materials

Commercially available terephthaloyl dichlorides and isophthaloyl dichlorides (both obtained

Correspondence to: S. Konagaya.

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from Mitsubishi Gas Chemical Co., Inc.) were crushed into small pieces under nitrogen before use. 3,3'-Diaminodiphenylsulfone (Konishi Chemical Ind. Co., Ltd.) or 4,4'-diaminodiphenylsulfone (Wakayama seika Kougyo Co., Ltd.) and PIP (Tohso Co., Ltd.) were used without any further purification. Acid acceptors such as *N,N*-dimethylaniline, *N,N*-diethylaniline (Nakarai Chemical Co., Ltd.) and pyridine (Kohei Chemical Co., Ltd.) were dried over calcium hydride overnight and purified by distillation in vacuo before use. All the solvents such as DMAC (Mitsubishi Gas Chemical Co., Inc.) and NMP (Nitto Kagaku Co., Ltd.) were used after dried by molecular sieves without any further purification.

### Preparation of Copolyamides

All of the copolyamides were prepared according to the previously reported method.<sup>10</sup> A typical procedure for the preparation of the copolyamides containing PIP moiety is as follows. A mixture of 3,3'- or 4,4'-diaminodiphenylsulfone and PIP, and acid acceptors such as *N,N*-dimethylaniline, *N,N*-diethylaniline, and pyridine were dissolved in DMAC and the solution was cooled below 5°C. Also, powdery iso- or tere-phthaloyl dichloride was added into the solution with stirring within a few minutes. At that time, the reaction solution climbed to approximately 65°C. After the reaction flask was kept in the ice bath for 30 min and at room temperature for 1 h, the reaction mixture was poured into methanol to precipitate the polymer with crushing with a home mixer. The isolated polymer was filtered off, washed with pure water and methanol, and dried at 100°C for a day in vacuo.

### Preparation of Dense Films from the Copolyamides

The powdery copolyamide was dissolved in NMP at 80°C (polymer conc.: 20 wt/v %) and the solution was spread out on a hot Pyrex glass plate (50 ≈ 60°C). After the solvent (NMP) was perfectly removed with an infrared (IR) heating lamp at 80°C and with a vacuum dryer at 200°C, the glass plate was put in pure water at room temperature to strip a dense film off of it. The transparent dense film obtained was dried at 150°C overnight in vacuo.

### Formation of Flat Asymmetric Membranes

Flat asymmetric membranes were formed by dissolving the polyamide into DMAC containing lithium chloride (polymer conc.: 20 wt/v %, lithium

chloride conc.: 5 wt/v %), casting the solution onto a glass plate, evaporating the solvent by heating the cast membrane at 110°C for 20 min and dipping the plate in a coagulation liquid (ice water). The flat asymmetric membranes obtained were dipped in pure water before use.

### Characterization of the Copolyamides

Reduced viscosities of the copolyamides were measured at a concentration of 0.5 g/dl in NMP at 30°C. IR absorption spectra were measured by the KBr method using a Hitachi 270 IR spectrometer. Nuclear magnetic resonance (NMR) spectra were measured at 50°C by the use of a Varian XL-300 (300 MHz H-NMR spectrum) in the *d*<sub>6</sub>-dimethylsulfoxide. The differential scanning calorimetry (DSC) measurement of polymer (10 mg) was performed at a heating rate of 20°C/min in nitrogen with a Perkin-Elmer differential scanning calorimeter (DSC-7). Number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) were determined at 55°C by means of gel permeation chromatography (GPC) on the basis of a polystyrene calibration on a Waters Associate's High Speed Liquid Chromatography (4 columns: Shodex GPC AD 802/S+802/S+803/S+80M/S) with RI detector, using *N,N*-dimethylformamide—0.01*N* LiBr as an eluent (0.9 mL/min).

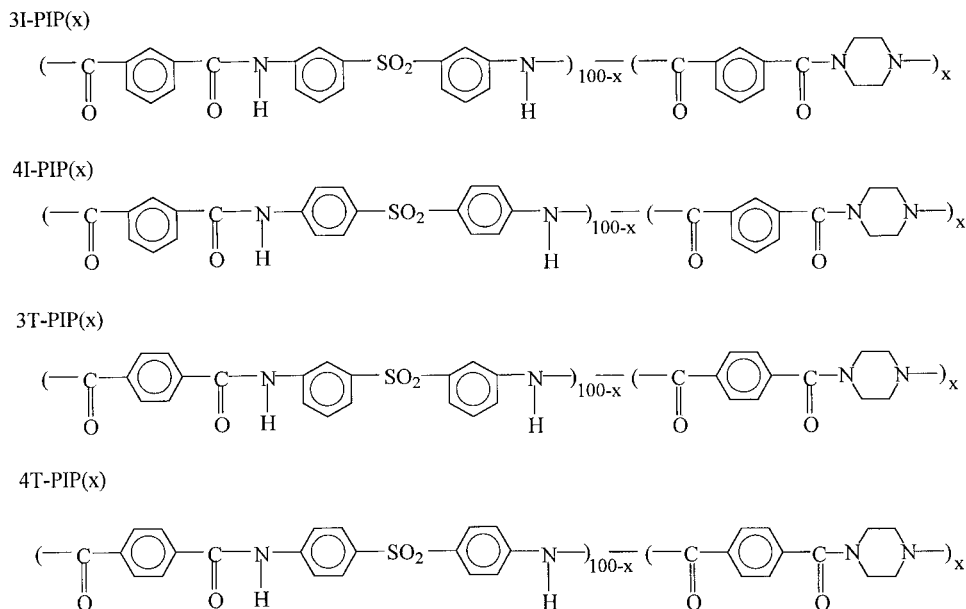
### Measurements of Physical Properties

Solubility of copolyamides was evaluated at a concentration of 20 wt % in NMP and DMAC at 30°C, and classified into the following groups: ++, soluble at room temperature; +, soluble at heating; ±, partially soluble; -, insoluble at room temperature. Viscoelasticity of dense film (10 μ) in water was measured at 35 Hz with a heating rate of 2°C/min using Rheology's DVE-V4 FT-RHEO SPECTOLER with a water tank at a temperature range from 25 to 95°C. Tensile strength in the water-containing state was measured as follows. Dumbbell-shaped dense films (≈10 μm) prepared from the copolyamides were soaked at room temperature in pure water overnight. After the wipe of water on the film surface with a filter paper, tensile strength was measured, using Shimadzu's Tensilon.

### Measurement of Chlorine Resistance and RO Performance

#### Chlorine Resistance

The copolyamides were freeze-crushed and dried at 150°C for more than 15 h in vacuo; 0.5 g of fine



**Figure 1** Structural formula of copolyamides studied.

powders of 10 microns or less was added to 500 cc of an aqueous 220 ppm (pH = 5) chlorine solution obtained by mixing sodium hypochlorite (chlorine source) and phosphoric acid, potassium dihydrogen phosphate, and dipotassium hydrogen phosphate, all of which are a buffer for pH adjustment; the chlorine solution was placed in a constant temperature vessel maintained at 40°C, and a chlorine uptake rate was monitored by measuring a change in the chlorine concentration with the lapse of time of the solution. A difference of the chlorine uptake rate thus obtained and that of the blank test previously conducted, i.e., a rate at which the chlorine concentration of the solution containing no polyamide decreases spontaneously, was taken as the chlorine uptake rate of the polyamide itself and the amount of chlorine absorbed during the first hour was expressed in its molar ratio to a monomer unit of polyamide (mol Cl<sup>+</sup>/mol monomer unit). The smaller value of the molar ratio means the higher chlorine resistance of the polyamide.

#### RO Performance

“Flux rate of product water” (FR) and “salt rejection” (R<sub>j</sub>) represent an RO performance of an asymmetric membrane. The former FR means an amount of product water (L/m<sup>2</sup> day) which permeates through a membrane, when 25°C saline water containing 35,000 ppm of sodium chloride has been supplied to the common continuous pump-type RO apparatus under the pressure of

55 kg/cm<sup>2</sup>. The latter R<sub>j</sub> means a percentage (%) of the difference in sodium chloride concentration between the feed and the permeate to the sodium chloride concentration of the feed.

#### Long-Term Chlorine Resistance Test of Flat Asymmetric Membrane

Chlorine resistance of a flat asymmetric membrane formed from one of the newly developed copolyamides, 4I-PIP(20), was evaluated in the presence of chlorine (Cl<sup>+</sup> conc. = 50 ppm, pH = 5), using the common continuous pump-type RO apparatus under the above conditions.

## RESULTS AND DISCUSSION

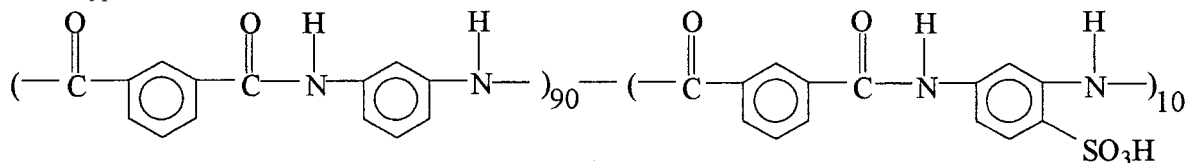
#### Preparation of Copolyamides with PIP Moiety

Copolyamides containing PIP moiety, of which structural formulas were shown in Figure 1, were synthesized by low-temperature solution polycondensation of aromatic dicarboxylic acid dichlorides with diaminodiphenylsulfone and PIP using acid acceptors. The conditions and results of the copolymerization are summarized in Table I. The transparency of the reaction solution became lower with the increase of copolymerization ratio of PIP, probably because of the increase of poly-piperazineamide unit with lower solubility to NMP.

**Table I** Synthesis and Properties of Copolyamides

Copolyamide		Properties				
Polymer Species	x (mol %)	$\eta_{sp}/C$ (dL/g)	Solubility		$T_g$ ( $^{\circ}\text{C}$ )	Chlorine Uptake Rate (Cl <sup>+</sup> mol/mol/h)
			NMP	DMAC		
4T-PIP(x)	0		++	+		0.52
	10	1.18	++	+	362	
	20	1.35	++	++	356	
	30	1.10	++	++	349	
	40	0.99	+	+	345	
	60	0.60	±	±	327	
3T-PIP(x)	0		++	++		0.24
	20	0.79	++	++	277	
	30	0.86	++	++	281	
	50	0.77	+	+	286	
	100		—	—	295	
4I-PIP(x)	0					0.33
	10	0.75	++	++	317	
	20	0.77	++	++	308	
	30	0.75	++	++	303	
	40	0.87	++	++		
	60	0.80	+	+	289	
3I-PIP(x)	0					0.15
	20	0.72	++	++	258	
	30	0.85	++	++	260	
	100	1.53	—	—	239	
NOMEX-type			+	+		7.2

NOMEX-type:

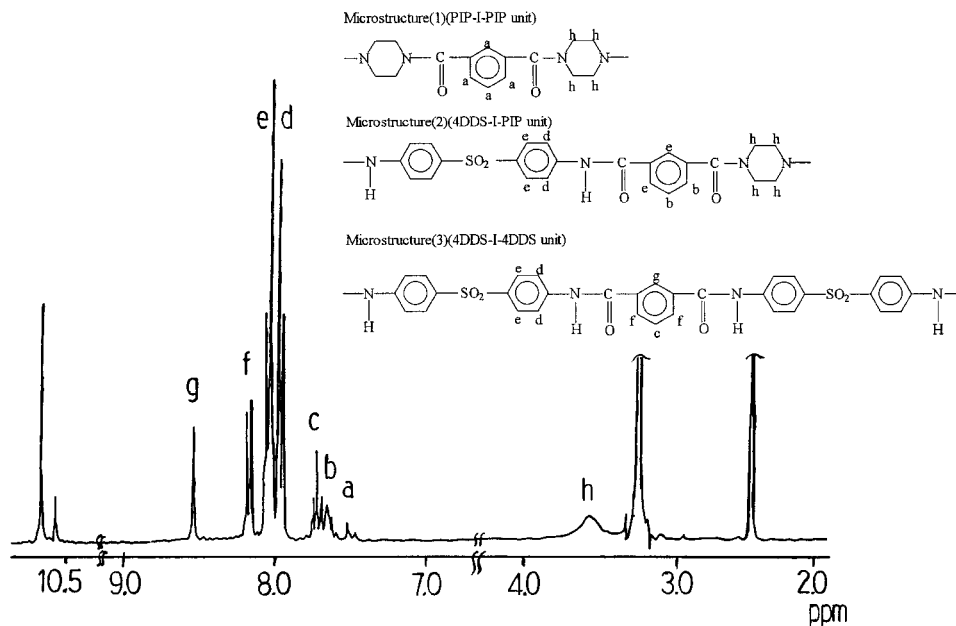


As shown in Table I, the reduced viscosities of the copolyamides were in the range 0.60–1.35 dL/g. However, the reduced viscosity of the copolyamides decreased with the increase of PIP content, in particular, in the 4T-PIP(x) series, probably because of the lower solubility of the copolyamides to the reaction solvents such as NMP and DMAC.

#### Characterization of the Copolyamides

In the IR spectrum of 4I-PIP(20), typical absorptions were observed at  $1675\text{ cm}^{-1}$  and  $1615\text{ cm}^{-1}$  (shoulder peak), which might be ascribed to  $\nu$  C=O stretching vibrations of 4I-PIP(0) [poly(isophthaloyl 4,4'-diaminodiphenylsulfone)] and 4I-PIP(100) [poly(isophthaloyl piperazine)]. The

absorption at  $1615\text{ cm}^{-1}$  increased with the copolymerization content of PIP. The C—H stretching vibration of the PIP ring at  $2860\text{ cm}^{-1}$  also increased with the increase of PIP content. Figure 2 shows the 300 MHz H-NMR spectra of the copolyamide 4I-PIP(20) in dimethylsulfoxide- $d_6$  at  $50^{\circ}\text{C}$ . The broad absorptions observed at 3.55 ppm could be assigned to the protons of the PIP ring. The content of PIP to the total diamine components in the copolyamide was 19 mol %, which was evaluated from the spectrum. The observed value was in good agreement with the calculated one (20 mol %). The content of three components and the random character in the copolyamide were estimated from the spectra data, and their results are shown in Table II. The copolyamide was proved to be a



**Figure 2** H-NMR spectrum of 4I-PIP(20). Measurement conditions: 300 MHz in d6-dimethylsulfoxide at 50°C.

random polymer by NMR spectrum.<sup>11–15</sup> Figure 3 shows the GPC curve of the copolyamide 4I-PIP(20). The single peak may mean that the polymer is not composed of the homopolymers [4I-PIP(0), 4I-PIP(100)] but copolymer.

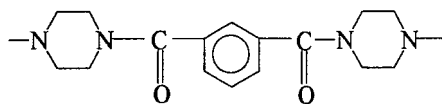
### Chemical and Mechanical Properties of the Copolyamides

Solubility of the copolyamides in organic solvents was evaluated at a concentration of 20 wt % in

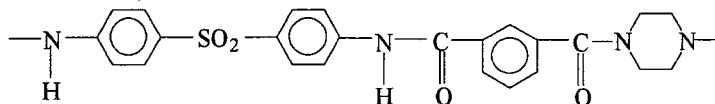
**Table II** Analysis of Microstructures of 4I-PIP(20) by H-NMR

Ratio of Microstructures (mol %)			Average Chain Length		Block Copolymerization Ratio
(1) <sup>a</sup>	(2) <sup>b</sup>	(3) <sup>c</sup>	Ln(I-4) <sup>d</sup>	Ln(I-P) <sup>e</sup>	1/Ln(I-4) + 1/Ln(I-P)
5.9	26.6	67.5	6.07	1.44	0.86

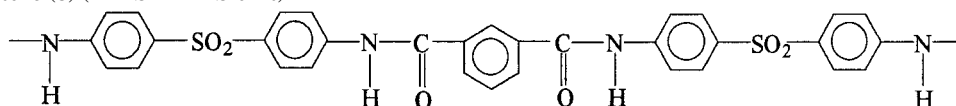
<sup>a</sup> Microstructure (1) (PIP-I-PIP unit)



<sup>b</sup> Microstructure (2) (4DDS-I-PIP unit)



<sup>c</sup> Microstructure (3) (4DDS-I-4DDS unit)



<sup>d</sup> I-4: Iso-phthaloyl 4,4'-diaminodiphenylsulfoneamide unit

<sup>e</sup> I-P: iso-phthaloyl piperazineamide unit

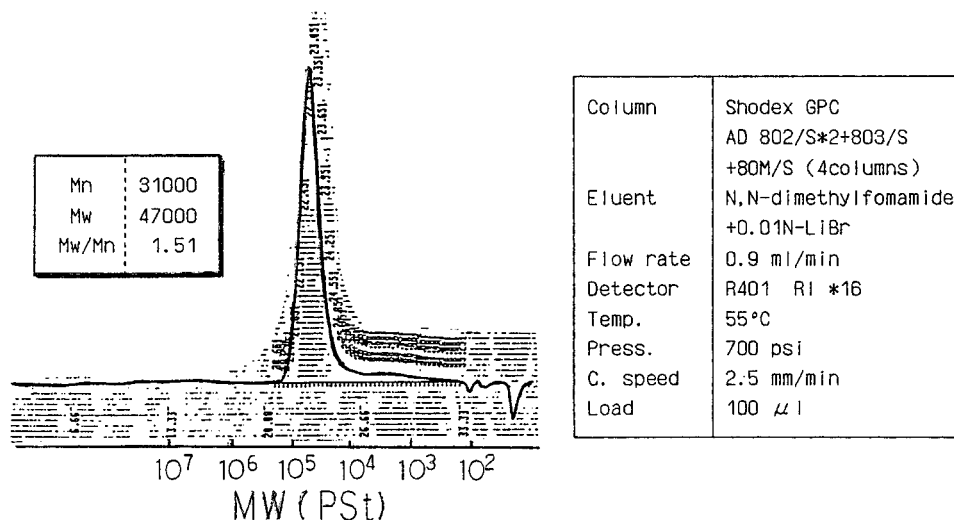


Figure 3 Gel permeation chromatogram of 4I-PIP(20).

NMP and DMAC in the state of the powdery samples and the results are listed in Table I. The homopolymer 4T-PIP(0) exhibited lower solubility to DMAC, but 4T-PIP(20) containing PIP moiety had good solubility in DMAC. That is, the solubility of poly(terephthaloyl diaminodiphenylsulfone) could be remarkably improved by copolymerization of PIP. However, much incorporation of PIP content (more than 50 molar ratio) de-

creased the solubility in NMP and DMAC, as shown in Table I. Thermal stability of the copolyamides was evaluated by DSC under nitrogen atmosphere. DSC data ( $T_g$ ) of the copolyamides are summarized in Table I. The  $T_g$  value of the copolyamide such as 4I-PIP(x) was almost equal to the mean  $T_g$  values of constituent homopolymers [4I-PIP(0),4I-PIP(100)]. Figure 4 shows the dynamic viscoelasticity in water at 35 Hz as a

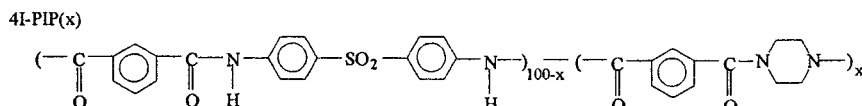
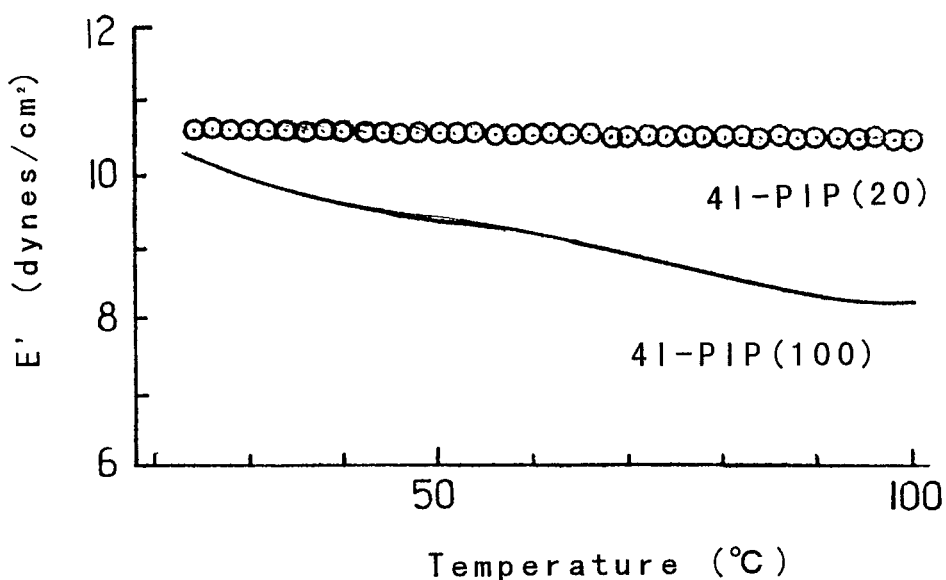
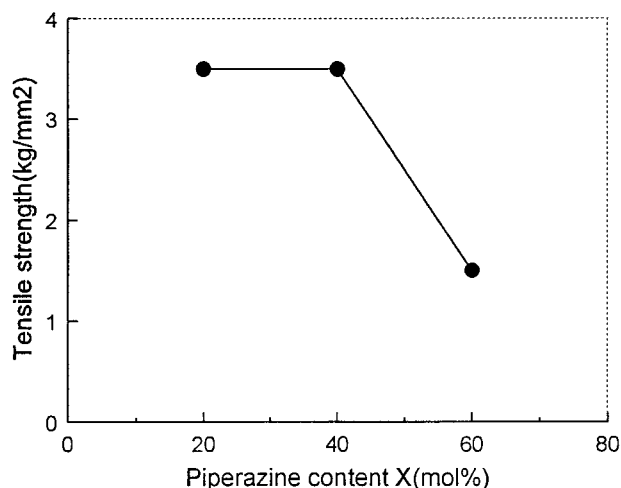


Figure 4 Modulus-temperature relation of 4I-PIP(x) in water.



**Figure 5** Tensile strength of 4I-PIP(x) copolyamides in the water-containing state.

function of temperature for samples of 4I-PIP(20) and 4I-PIP(100). Storage elastic modulus ( $E'$ ) of the dense film of the copolyamide did not change up to 95°C whereas a rapid decrease of  $E'$  was observed in the PIP polyamide. Such phenomena were observed in all of the 4I-PIP(x) ( $x = 0-60$ ).

These results show that the PIP polyamides such as 4I-PIP(100) are easily plasticized by water, probably because they do not have intermolecular hydrogen bonding, but only secondary amide-bond ( $>N-CO$ ). This is the reason why the RO membrane prepared from PIP polyamide has poor mechanical property. On the other hand, the other copolyamides containing diaminodiphenylsulfone moiety have such strong intermolecular hydrogen bonding that they are not plasticized easily by water. Figure 5 shows the tensile strength of the water-containing copolyamide [4I-PIP(x)]. There was no change of tensile strength up to the PIP copolymerization content of 40 mol %. This result shows that the copolyamides are not so easily plasticized by water, probably because of the intermolecular hydrogen bonding by NHCO groups.

#### RO Performance and Chlorine Resistance of the Copolyamides

Judging from the solubilities in organic solvents (NMP and DMAC) and the film-forming abilities of the copolyamides, they might be expected to be suitable for RO membrane materials. Therefore, the chlorine resistance and RO performance of the copolyamides, which were prepared from iso- or terephthaloyl dichlorides and mixed diamine

components of 3,3'- or 4,4'-diaminodiphenylsulfone and PIP are summarized in Tables I and III. All of the copolyamides could demonstrate higher chlorine resistance, and there was little difference in chlorine resistance among them. Especially, the copolyamides prepared from 3,3'-diaminodiphenylsulfone gave a little higher chlorine resistance to those from 4,4'-diaminodiphenylsulfone. Their chlorine resistance increased as the PIP content increased.

The RO performance was dependent on the components of diaminodiphenylsulfone compounds and phthaloyl moieties. The copolyamides composed of 4,4'-diaminodiphenylsulfone were superior to those composed of 3,3'-diaminodiphenylsulfone in RO performance. Moreover, the terephthaloyl component gave a slightly superior RO performance to the isophthaloyl component. The RO performance was also dependent on the PIP content, as shown in Table III. FR increased as PIP content increased, and the highest value of  $R_j$  was obtained at 20% of it.

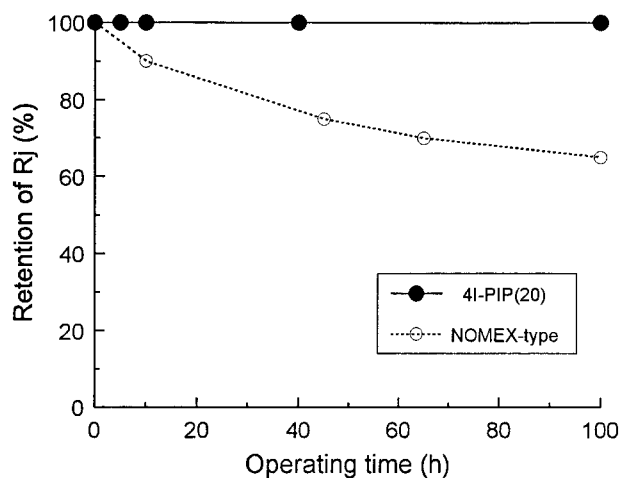
It was consequently proved that the copolyamides prepared from iso- or terephthaloyl dichloride and mixed diamine components of 4,4'-diaminodiphenylsulfone and PIP showed not only high chlorine resistance, but also excellent RO performance.

#### Long-Term Chlorine Resistance of a Flat Asymmetric Membrane Prepared from 4I-PIP(20)

The result of the test of chlorine resistance is shown in Figure 6.  $R_j$  of the flat asymmetric membrane from 4I-PIP(20) were very stable, whereas

**Table III** RO Performance of the Copolyamides

Copolyamide	$x$ (mol %)	RO Performance	
		$R_j$ (%)	FR (L/m <sup>2</sup> × day)
3I-PIP(x)	0	68.0	60
	20	40.0	147
	30	50.4	281
4I-PIP(x)	0	67.5	62
	10	97.3	58
	20	99.3	65
	30	98.9	98
	100	4.9	13,399
3T-PIP(x)	0	69.0	60
	20	80.8	148
	30	60.6	205
4T-PIP(x)	0	71.5	51
	20	98.6	73



**Figure 6** Long-term chlorine resistance test of flat asymmetric membrane.

that of the flat asymmetric membrane from NOMEX-type aromatic polyamide decreased rapidly in the early time. It was confirmed that new copolyamides have superior chlorine resistance to NOMEX-type aromatic polyamides.

## CONCLUSIONS

To develop RO membrane materials with high chlorine resistance, copolyamides containing both 3,3'- or 4,4'-diaminodiphenylsulfone and PIP as diamine components were prepared. The copolyamides prepared from iso- or terephthaloyl dichloride and mixed diamine components of 4,4'-diaminodiphenylsulfone and PIP are random copolymers, which had good solubilities in organic solvents and good mechanical properties, even in water. Furthermore, the asymmetric membranes prepared from the copolyamides had not only excellent RO performance, but also high chlorine resistance. Moreover, a long-term test of chlorine resistance showed that  $R_j$  and  $FR$  of the membrane prepared from 4I-PIP(20) was very stable longer than 100 h, but those of the membrane from NOMEX-type aromatic polyamide decreased rapidly in early time ( $Cl^+$  conc. = 50 ppm, pH

= 5). New membrane materials with excellent RO performance and higher chlorine resistance than the NOMEX-type aromatic polyamide have been demonstrated successfully.

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