New Chlorine-Resistant Polyamide Reverse Osmosis Membrane with Hollow Fiber Configuration

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ABSTRACT: New asymmetric hollow fiber reverse osmosis (RO) membrane was developed from a new chlorine-resistant copolyamide [4T-PIP(30)] with a piperazine moiety by a conventional phase-separation method. The new 4T-PIP(30) hollow fiber membrane has the same low-pressure RO performance as cellulose triacetate hollow fiber membrane (FR = 205 L/m^2 day, Rj = 99.6%) and superior chlorine resistance as well as pH resistance to conventional aramid RO membranes. Structural analysis and viscoelastic study revealed that the new hollow fiber consisted of a top skin, dense layer, and microporous layer, and that it began to decrease its elasticity at 80°C in water, which is possibly related to its good and stable RO performance around room temperature. Several kinds of RO modules were made from the new hollow fiber membranes, for which RO performances were stable for 2 years in chlorinated feed water desalination (the free residual chlorine ranged from 0.l to 1.1 mg/L). © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 517–527, 2001

Key words: reverse osmosis; hollow fiber membrane; chlorine resistance; polyamide; piperazine; diaminodiphenylsulfone

INTRODUCTION

Reverse osmosis (RO) membranes have been applied to the desalination of seawater and well water. In particular, materials for such RO membranes are required to have high flux, high salt rejection, and resistance to chlorine and other oxidation agents[1] because chlorine may be added to feed water for control of micro-organisms and to prevent membrane fouling by microbiological growth and potential microbiological degradation of membrane polymer in RO systems.

Major membrane materials for RO membrane are cellulose triacetate (CTA),[2] and Nomex-type aromatic polyamide (aramid)[3]. Aramid RO membrane is more stable against chemicals and microbial attack than cellulose acetate RO membrane, but it has quite poor chlorine resistance. It is well known that chlorine attack on aramid RO membrane causes a decline of salt rejection and an increase of water flux.[4–9] Therefore, in the desalination process with the use of aramid RO membrane, dechlorination pretreatment is necessary when chlorine exists in feed water. (Sodium bisulfite or activated carbon is usually used to dechlorinate feed water.) Several kinds of synthetic polymers have been developed for the purpose of improving chlorine resistance of synthetic RO membranes, but none has been put to practical use as an RO membrane material.

The authors[10,11] studied the correlation between chemical structure and chlorine resistance of polyamides by measuring their chlorine uptake rate and concluded that flat asymmetric membranes of the ternary copolyamide synthesized
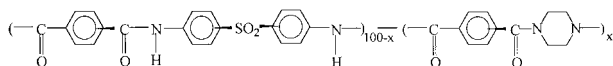
Structure 1   Formula of new copolyamides.

from iso- or terephthaloyl chloride, diaminodiphenylsulfone, and piperazine had not only good RO performance but also higher chlorine resistance than conventional aramid membranes.

Among several membrane types, hollow fibers have been selectively used in industry because of their economical efficiency.[12] Therefore, the authors have been trying to develop an asymmetric hollow fiber membrane from one of the new copolyamides with a piperazine moiety.

In this report, the authors describe the characteristics, RO performance and resistance to chemicals (pH resistance and chlorine resistance) of the asymmetric hollow fiber membranes prepared from one of the new ternary copolyamides, and chlorine resistance of a module applied for brackish water desalination.[13–16]

EXPERIMENTAL

Materials

Commercially available terephthaloyl chloride (Mitsubishi Gas Chemical Co. Ltd., Tokyo, Japan) was crushed into small pieces under nitrogen before use. 4,4′-Diaminodiphenylsulfone (4DDS) and piperazine (PIP) were supplied by Wakayama Seika Co. Ltd. (Wakayama, Japan) and Koei Chemistry Co. Ltd. (Osaka, Japan), respectively, and were used without purification.

Pyridine, as an acid acceptor, was dried over calcium hydride overnight and purified by distillation *in vacuo* before use. *N,N*-dimethylacetamide and *N*-methyl-2-pyrolidone (NMP) were dried by molecular sieves and used without further purification.

Analytical grade inorganic compounds such as LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, NH_4Cl, NaBr, $NaHCO_3$, $Na_2C_2O_4$, Na_2SO_3, Na_2SO_4, $NaNO_3$, and $(NH_4)_2SO_4$, were purchased from Nakarai Tec Co. Ltd. and used without further purification.

Membrane Materials

Synthesis of Copolyamide

The copolyamide used in this study, 4T-PIP(30), of which the structural formula is shown in Figure 1, was prepared from terephthaloyl chloride,

4DDS, and PIP with pyridine as an acid acceptor by low temperature solution polymerization according to the previous report and the literature.[17]

Dense Film Formation

The obtained 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 completely removed with an infrared heating lamp around 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 from it. The transparent dense film was dried at 150°C *in vacuo* overnight.

Characterization

Reduced viscosity (ηsp/C) of 4T-PIP(30) was measured at a concentration of 0.5 g/dL in NMP at 30°C using a suspended type Ubbelohde viscometer. NMR spectrum of 4T-PIP(30) was measured at 50°C with a Varian XL-300 (300 MHz ^{1}H-NMR spectrum) in d[6]-dimethylsulfoxide and its microstructure was identified according to previous reports[17] and the literature.[18–22]

Viscoelasticity of a dense film with the thickness of 10 μm was measured at 35 Hz in an N_2 atmosphere and in pure water with a heating rate of 2°C/min using Rheology's DVE-V4 FT-Rheospectror with a water tank.

Tensile strength of a dense film in the water-containing state was measured as follows: dumbbell-shaped dense films (10-μm thickness) were soaked at room temperature in pure water overnight. After wiping off water on the film surface with a filter paper, tensile strength was measured by using Shimadzu's Tensilon.

Asymmetric Hollow Fiber Membrane

Preparation

Asymmetric hollow fiber membranes with an outer diameter of 170 μ and an inner diameter of 70 μ were formed by spinning a dope solution of 4T-PIP(30)/*N,N*-dimethylacetamide/nonsolvent,
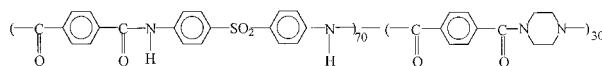

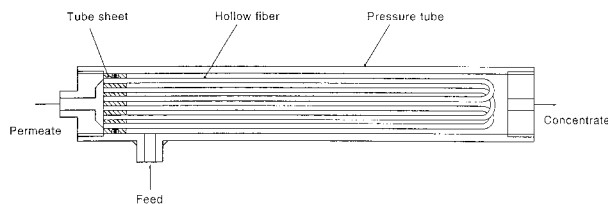**Figure 1**   Structural formula of 4T-PIP(30).

Figure 2   Illustration of mini-fiber module.

followed by soaking in coagulation bath (ice water) and washing with pure water. The hollow fibers obtained were dipped in pure water before use.

Characterization

Observation of cross-section. After a hollow fiber membrane was soaked in liquid N_2, it was broken into two pieces to open out its cross-section. The cross-section was coated with Au-Pd and observed with a scanning electron microscope S-800 (Hitachi Seisakusyo Co. Ltd.) under the following conditions: accelerating voltage, 10 kV; WD, 15 mm; tilt, 0°; magnification, ×500 and ×10,000.

Wide angle X-ray diffraction. A hollow fiber sample was dried at room temperature overnight and its crystallinity was measured by the wide angle X-ray diffraction apparatus (Rigaku X-ray generator Ru-200 + Data system RAD-γA) under the following conditions: target, Cu; power, 40 kV × 100 mA.

Viscoelasticity. Viscoelasticity of a hollow fiber was measured in water at 35 Hz with a heating rate of 2°C/min by using Rheology's DVE-V4 FT-Rheospectror with a water tank over the temperature range from 25 to 95°C.

Tensile strength. Tensile strength of a hollow fiber was measured in pure water at temperatures ranging from 25 to 80°C with an Instron tension meter equipped with a water tank.

RO Performance

A mini-fiber module was made for the RO performance evaluation of an asymmetric hollow fiber membrane according to the following procedure: several hundred hollow fibers, with an outer diameter and length of 170 μm and 0.95 m, respectively, were bundled with the shape of a U as shown in Figure 2. Both ends of the bundles were potted with an epoxy resin. The mini-fiber module was constructed by installing the U-shaped bun-
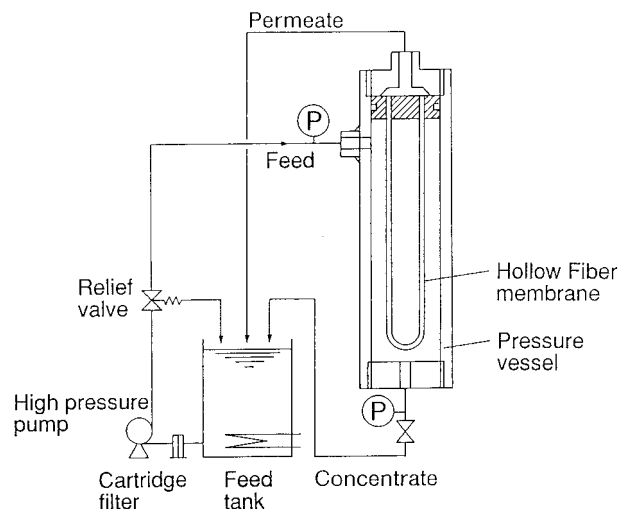

Figure 3   Schematic flow diagram of mini-fiber module RO experimental apparatus.

dle in a 1-in. diameter stainless pressure vessel. RO performance of a mini-fiber module was measured by the apparatus shown in Figure 3.

The water flux (FR) and salt rejection (Rj) of the hollow fiber membranes under an operating pressure of 10 kg/cm^2 were determined by using feed water containing 0.15% salt (ex. NaCl) at 25°C and at the recovery ratio of less than 1%, after an elapsed time of 2 h. The former FR means an amount of product water (L/m^2 day) which permeates through a membrane. The latter Rj means a percentage (%) of the difference in salt concentration between the feed and the permeate to salt concentration of the feed.

Resistance to Chemicals

pH resistance. Certain amounts of mini-fiber modules were soaked in the solutions with pH values of 1 and 11 without stirring at 25°C. The pH was adjusted with hydrogen chloride and sodium hydroxide. One of them was taken out from the solution and its tensile strength and elonga-
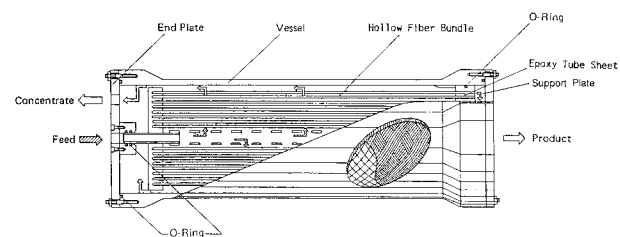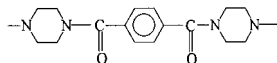

Figure 4   Structure of an HS-series module.

Table I   Reduced Viscosity and Microstructure of 4T-PIP(30) Copolyamide

$\eta sp/C$ (dL/g)	Molar Ratio of PIP/4DDS (mol/mol) Found (Calcd)	Molar Ratio of Microstructure (mol %)			Average Chain Length		Block Copolymerization Ratio 1/Ln(TS) + 1/Ln(TP)
		$(1)^a$	$(2)^b$	$(3)^c$	$Ln(TS)^d$	$Ln(TP)^e$	
0.75	70.6/29.4 (30/70)	10.3	38.2	51.5	3.70	1.54	0.92

[a]Microstructure (1) (PIP-T-PIP unit)

[b]Microstructure (2) (4DDS-T-PIP unit)
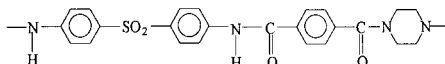
[c]Microstructure (3) (4DDS-T-4DDS unit)
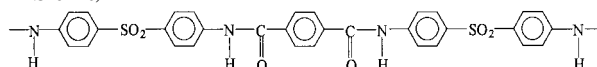
[d]TS, tere-phthaloyl 4,4′-diaminodiphenylsulfoneamide unit.
[e]TP, tere-phthaloyl piperazineamide unit.

tion in pure water of room temperature were measured with the Instron tension meter.

Chlorine resistance. Chlorine resistance of the mini-fiber module was evaluated by the continuous RO operation of tap water containing chlorine of 0.1 to 1.4 ppm as a feed at our laboratory according to the above procedure.

Module

Preparation

Several kinds of modules with different sizes for actual use were prepared as follows: hollow fibers, with an outer diameter of 170 μm, were cross-wound around a porous core tube. Both ends of the cross-wound cylindrical fiber bundle were pot-
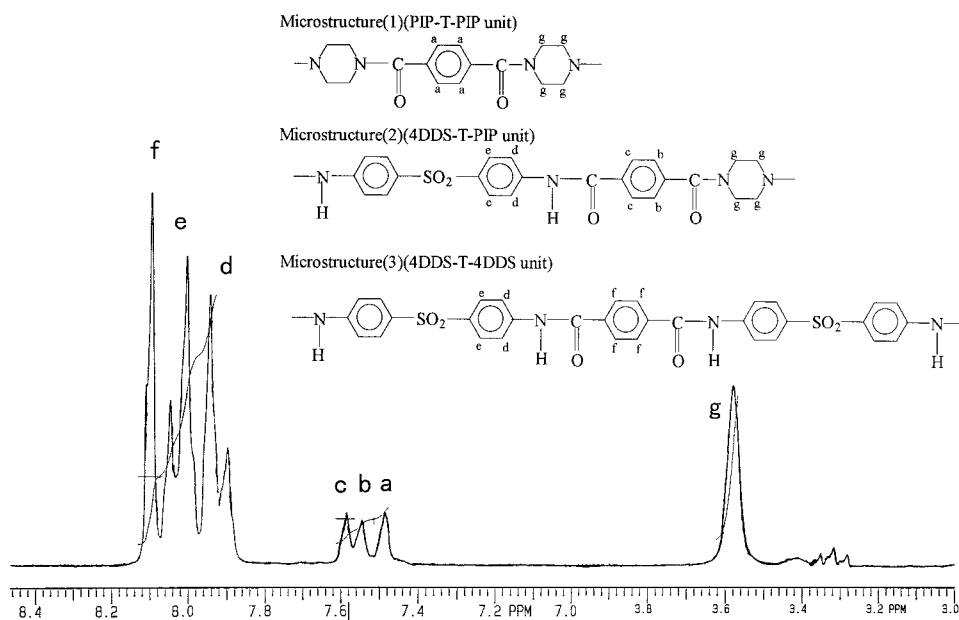

Figure 5   H-NMR spectrum of 4T-PIP(30) copolyamide. Measurement conditions: 300 MHz in d6-dimethylsulfoxide at 50°C.
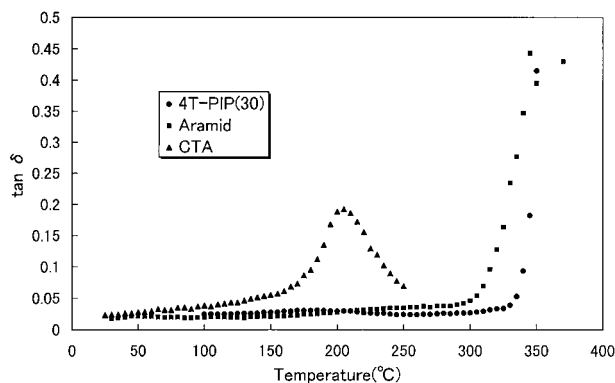
Figure 6 Dynamic viscoelasticity of membrane materials.

Figure 7 Dynamic viscoelasticity of membrane materials in water.

ted with an epoxy resin, and one side was then vertically sliced to give open hollow fibers. The permeate solution flows through the fiber bore to the openings. The bundle was finally installed into a pressure vessel and sealed as shown in Figure 4. Such modules were named TOYOBO's Hollosep HS-series.

RO Performance

RO performance of the module was measured according to the following procedure: as shown in Figure 4, a feed solution was pumped to the porous core tube and distributed radially through the fiber bundle toward the outer shell. The feed solution was then separated into a permeated solution and a concentrated solution, which flowed respectively in the fibers to the production side through the fiber openings and in the annular path between the bundle and the pressure vessel to the concentrated side. RO performance was represented by FR and Rj.

Chlorine Resistance

Chlorine resistance of the module was evaluated by continuous RO operation using tap water containing chlorine of 0.1 ppm to 1.1 ppm as a feed and at several conditions according to the above procedure.

RESULTS AND DISCUSSIONS

Membrane Materials

Synthesis and Characteristics of 4T-PIP(30) Copolyamide

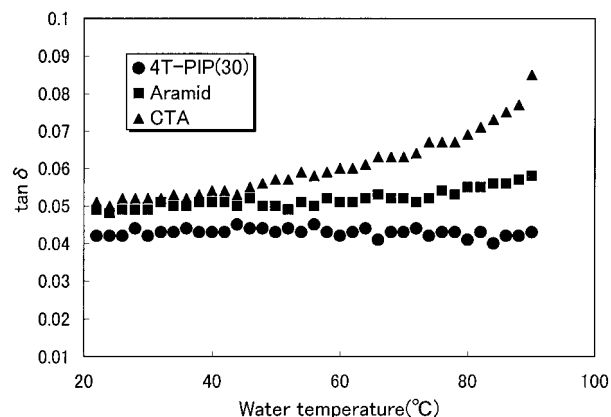Table I shows the reduced viscosity and microstructure of the membrane material, 4T-PIP(30)

copolyamide. Figure 5 shows the NMR spectrum of 4T-PIP(30) copolyamide. The NMR spectrum showed that the copolyamide composition was almost the same as the monomer composition. The microstructure of 4T-PIP(30) copolyamide was analyzed according to the previous report[17] and the literature.[18–22] Because its block copolymerization ratio was 0.92 (B $\fallingdotseq$ 1), as shown in Table I, its microstructure was proved to be a random copolymer with a glass transition temperature of 349°C.[17]

Figure 6 shows the dynamic viscoelasticity in nitrogen atmosphere at 35 Hz as a function of temperature for the dense films of 4T-PIP(30), CTA, and aramid. Tan δ of 4T-PIP(30) film did not change up to 325°C, whereas a rapid increase of

Table II   Characteristics of 4T-PIP(30) Hollow Fiber Membrane

Characteristics	
Hollow fiber dimension	
Outer diameter	170 μ
Inner diameter	70 μ
Mechanical properties in tension	
Yield strength	22 g/yarn
Elongation	4%
Tensile strength	39 g/yarn
Elongation	95%
RO performance[a]	
FR	205 L/m² day
Rj	99.6%

[a]Test conditions: feed solution, 1500 ppm NaCl/water; pressure, 30 kg/cm²; temperature, 25°C; recovery, <5%.

(a)

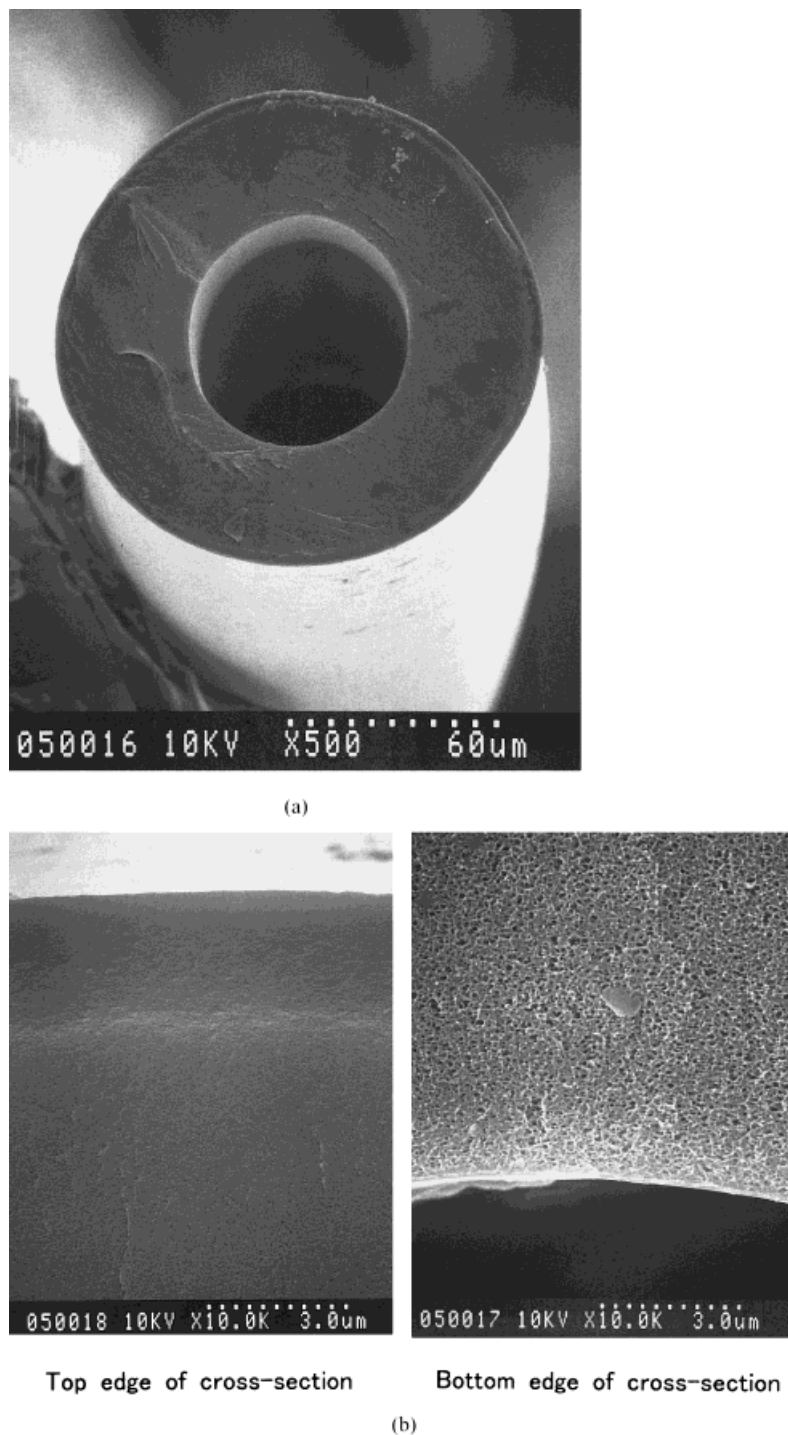Top edge of cross-section   Bottom edge of cross-section

(b)

Figure 8 (a) Scanning electron micrograph of the cross section of a 4T-PIP(30) hollow fiber membrane. (b) Scanning electron micrographs of the fracture sections of a 4T-PIP(30) hollow fiber membrane.

tan δ was observed in CTA and aramid at the temperatures of 160 and 300°C, respectively. This result is compatible with the measurement result of glass transition temperature. 4T-PIP(30)

proved to have higher heat resistance than CTA and conventional aramid.

Figure 7 shows their dynamic viscoelasticity in water at 35 Hz as a function of temperature. Tan
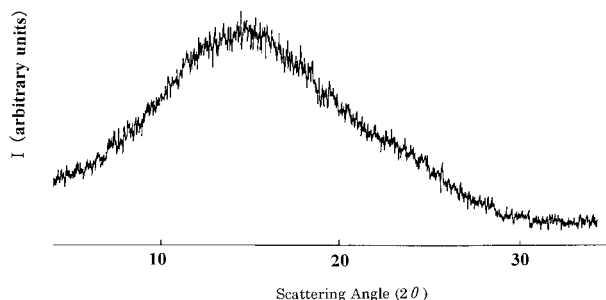
Figure 9 Wide-angle X-ray diffractogram of 4T-PIP(30) hollow fiber membrane.

Figure 11 Dynamic viscoelasticity of 4T-PIP(30) hollow fiber membrane in water.

δ of 4T-PIP(30) does not change up to 95°C, whereas the slight increase of tan δ was observed in CTA and aramid at the temperatures of 45 and 75°C, respectively.

These results show that 4T-PIP(30) are less plasticized by water than CTA and aramid and keep good mechanical properties even under high-temperature conditions. Such behavior in water is based on the difference of glass transition temperature in the dry states.

Asymmetric Hollow Fiber Membrane

Structural Features of the Cross-Section

Fundamental characteristics of a 4T-PIP(30) hollow fiber membrane are summarized in Table II. Typical outer and inner diameters of a hollow fiber are 170 and 70 μm, respectively. The tensile strength of the 4T-PIP(30) hollow fiber is stronger than that of conventional aramid hollow fiber membrane.
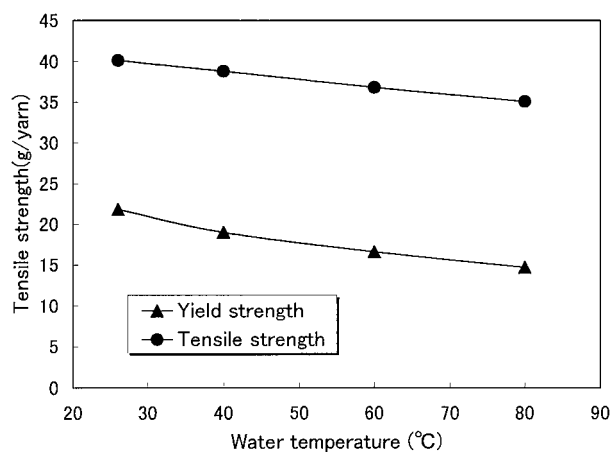

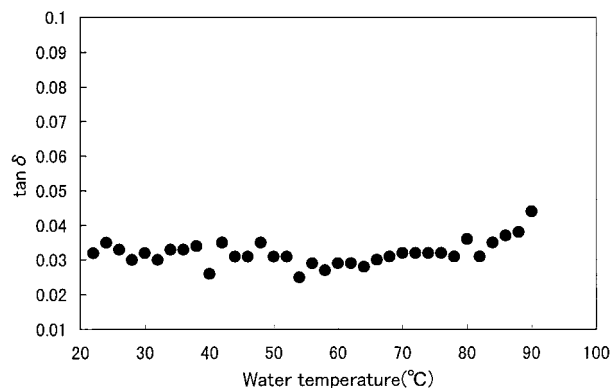**Figure 10** Yield and tensile strength of a 4T-PIP(30) hollow fiber in water.

Figure 8(a) shows the scanning electron photomicrograph of the typical structure in cross-section of the asymmetric hollow fiber RO membrane. The hollow fiber mainly consists of three layers, which are what we call top skin, dense layer with a thickness of about 2 μm, and microporous layer with a thickness of 5 to 10 μm, as shown in Figure 8(b). This structure is very similar to that of conventional aramid membrane.[23] High FR and Rj of 4T-PIP(30) hollow fiber membrane are ascribed to have such a typical structure with a top skin and porosity.

Figure 9 shows the wide-angle X-ray diffractogram of 4T-PIP(30) hollow fiber membrane. The X-ray diffractogram exhibited low crystallinity, and with little orientation present in the membrane, which is possibly related to high FR value (high water permeability).

Figure 10 shows the yield and tensile strength of 4T-PIP(30) hollow fiber membrane in hot water. There was a gradual decrease of yield and tensile strength with the increase of water temperature up to 80°C. However, there was no change of tan δ up to 80°C, as shown in Figure 11. This result showed that 4T-PIP(30) hollow fiber membrane, which was plasticized by hot water, began to decrease its elasticity at 80°C. Then the RO performance of the 4T-PIP(30) hollow fiber membrane is likely to change quickly at the water temperature of 80°C, probably because of the loss of the intermolecular hydrogen bonding by NHCO groups.

RO Performance

RO performance of 4T-PIP(30) hollow fiber is shown in Tables II and III. The NaCl desalination test with a mini-fiber module showed good RO

Table III   Influence of Cation and Anion Species of the Salts, on the Salt Rejection Power of 4T-PIP(30) Hollow Fiber Membrane

Cation	Anion						
	Cl^-	Br^-	HCO_3^-	NO_3^-	$C_2O_4^{2-}$	SO_3^{2-}	SO_4^{2-}
Li^+	99.31	—	—	—	—	—	—
Na^+	99.25	99.09	99.54	97.86	99.82	99.94	99.92
K^+	99.24	—	—	—	—	—	—
Mg^{2+}	99.55	—	—	—	—	—	—
Ca^{2+}	99.53	—	—	—	—	—	—
NH_4^+	98.54	—	—	—	—	—	99.46

Test conditions: feed solution, 1500 ppm salt/water; pressure, 30 kg/cm^2; temperature, 25°C; recovery, <5%.

performance of high FR and Rj, respectively, 205 L/m^2/day, 99.6%, which is almost equal to the RO performance of CTA hollow fiber membrane.

Salt rejection power of the 4T-PIP(30) hollow fiber membrane against ammonium salt, alkaline metal, and alkaline earth metal salts such as LiCl, NaCl, KCl, MgCl$_2$, CaCl$_2$, NH$_4$Cl, NaBr, NaHCO$_3$, Na$_2$C$_2$O$_4$, Na$_2$SO$_3$, Na$_2$SO$_4$, NaNO$_3$, and (NH$_4$)$_2$SO$_4$, are summarized in Table III. The new 4T-PIP(30) hollow fiber membrane exhibited high rejection of all the salts shown above, which were dependent on the cation and anion species of the salts. Rejection to cations and anions are ordered as follows. Cation species: Mg^{2+}, Ca^{2+} > Li^+, Na^+, K^+ > $NH4^+$; and anion species: SO_4^{2-}, SO_3^{2-}, C_2O4^{2-}, HCO_3^- > Cl^-, Br^- > NO_3^-.

The 4T-PIP(30) hollow fiber membrane showed a high rejection to cation and anion species with higher electrical charge and with higher molecular weight, but poorer rejection against NH_4^+ and NO_3^-. Its poor rejection to such N-containing ionic species is probably caused by the good solubility of such nitrogen species to the 4T-PIP(30) membrane material in analogy with PSA, PBIL, and CA membrane materials.[24,25]

pH Resistance

Figure 12(a,b) shows the pH resistance of 4T-PIP(30) and conventional aramid hollow fibers. 4T-PIP(30) hollow fiber showed the same pH resistance to alkaline (pH = 11) as aramid hollow fiber and superior resistance to strong acid (pH = 1) to it.

The amide bond of 4T-PIP(30) copolyamide is less attacked by proton (H$^+$) because the bond is inactivated by the electron withdrawing group (—SO$_2$—), as shown in Figure 1.[26,27]

Chlorine Resistance

Chlorine resistance of the 4T-PIP(30) hollow fiber membrane was also evaluated in tap water desalination (the free residual chlorine ranged from
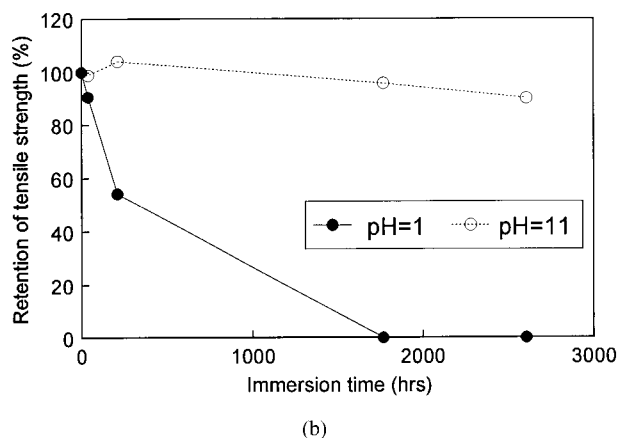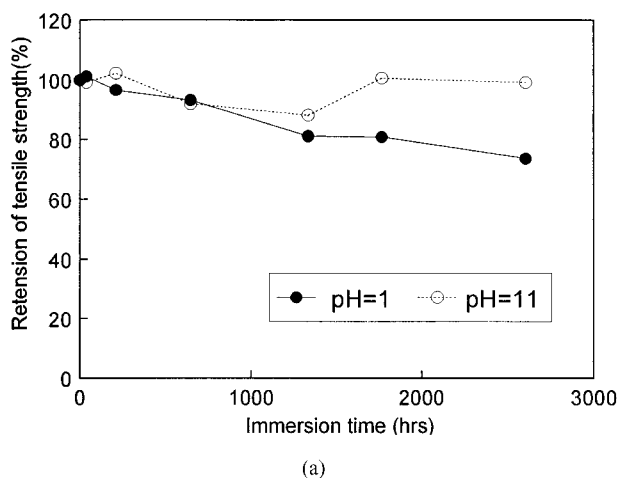

(a)

(b)

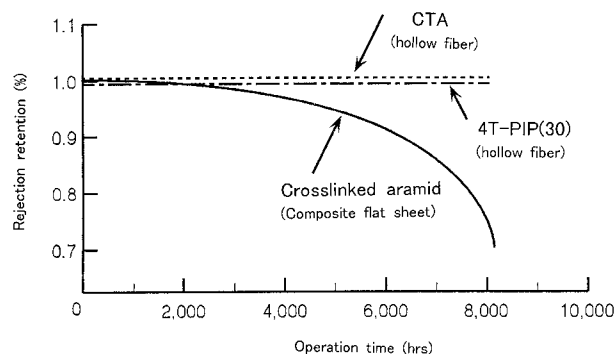**Figure 12**   (a) pH resistance of 4T-PIP(30) hollow fiber; (b) pH resistance of aramid hollow fiber.

Figure 13 Long-term characteristics of RO membranes in tap water desalination. Test conditions: feed tap water, press. 10 kg/cm^2, temp. 25°C, Cl$^+$ conc. 0.1 ~ 0.4 mg/L, recovery ratio less than 5%.

Table V   Rejection Properties of Module (HS 3110) in the Case of Tap Water Desalination

Total Hardness (CaCO$_3$ Converted)	Feed (mg/L)	Product (mg/L)	Rj (%)
	35.4	0.33	98
Ca	11.2	0.10	98
Mg	2.1	0.02	99
Sr	0.05	<0.01	>80
Na	8.4	0.15	92
K	1.7	0.03	92
Fe	0.04	0.001	97
Cu	<0.001	<0.001	—
Zn	0.06	<0.01	83
Mn	0.004	<0.001	>75
SiO$_2$	0.51	0.18	65

0.1 to 0.4 mg/L). Figure 13 shows the test results and comparative RO performance of CTA hollow fiber membrane (HOLLOSEP HA series) and conventional crosslinked aramid composite flat sheet membrane.

The 4T-PIP(30) hollow fiber membrane was tolerable to chlorine over test periods of up to 8000 h as well as CTA hollow fiber RO membrane. However, the crosslinked aramid composite flat sheet RO membrane lost rejection power around 4000 h. These results agree with the chlorine uptake rate of membrane materials described in our previous report.[27]

In conclusion, 4T-PIP(30) hollow fiber membrane not only has the same RO performance and chlorine resistance as CTA hollow fiber membrane, but also superior pH resistance and chlorine resistance to aramid membrane.

Module

RO Performance

Table IV shows the features of HOLLOSEP (HS-series) module loaded with 4T-PIP(30) asymmetric hollow fiber membrane. The module showed stable R0 performance against the solution of pH values ranging from 4 to 10 and the same low-pressure RO performance as CTA module (Hollosep HA type).[27]

Table V shows the tap water desalination results (composition of feed waiter and product water, and the rejection properties). The module showed rejection of more than 90% to Ca, Mg, Fe, Na, and K, which was equal to CaCO$_3$ rejection of more than 98%. It was confirmed that the module

Table IV   Specification of New HS-Series Modules

	Low Pressure		Middle Pressure	
Type Module Model	HS-3110	HS-5110	HS-5230	HS-5330
Size				
Diameter (mm)	90	140	150	150
Length (mm)	420	420	840	1240
FR (m^3/day)	>0.6	>2.0	>11	>20
Rj (%)	≥92	≥92	≥92	≥92
Conditions				
Feed water (ppm NaCl)	500	500	1500	1500
Pressure (kg/cm^2)	10	10	30	30
Temperature (°C)	25	25	25	25
Recovery (%)	30	30	75	75

Table VI   Rejection Properties of HS-Series Module

Organic Compound	Molecular Weight	Rj (%)
Methanol	32	15
Ethanol	46	45
Iso-propanol	75	85
Acetic acid	60	40

Experimental conditions: module, HS 3110; feed conc., 100 mg/L; press., 30 kg/cm^2; temp., 25°C; recovery, 20%.

had good rejection properties to inorganic compounds.

Table VI shows the rejection characteristics of the module to organic compounds such as alcohols and acetic acid. The module exhibited higher rejection to alcohols with an increase of their molecular weight but poor rejection to acetic acid. The module showed a little poorer rejection to organic solutes than inorganic solutes, which was ascribed to the good solubility of organic compounds to the 4T-PIP(30) membrane material.

Chlorine Resistance

Figure 14 shows the result of the long-term chlorine-resistance test in tap water desalination (the free residual chlorine ranging from 0.l to 0.4 mg/L) with a small-size module. It was confirmed that the R0 performance of the modules was quite stable and chlorine resistance was also sufficient enough for a period of up to 1 year. Figure 15 shows the results of long-term desalination of tap water containing residual chlorine ranging from
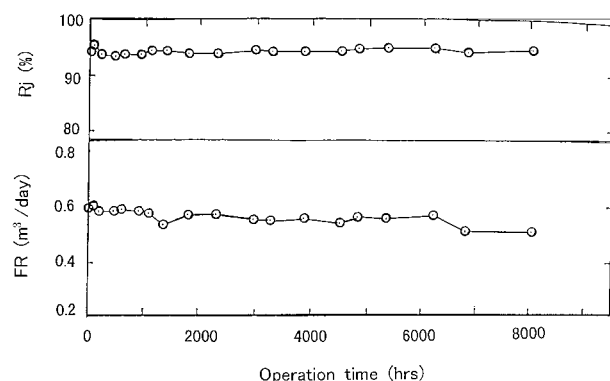

Figure 14 Long-term characteristics of HS-series module in tap water desalination. Test conditions: module type HS3110, feed tap water, press. 10 kg/cm^2, temp. 25°C, Cl$^+$ conc. 0.1 ~ 0.4 mg/L, recovery ratio 30%.
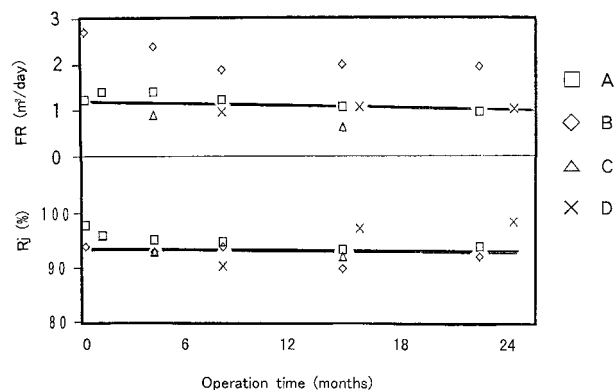

Figure 15 Long-term characteristics of the module RO performance. Test conditions: module type HS5110, feed tap water (130 μ S/cm), press. 10 kg/cm^2, temp. 25°C, Cl$^+$ conc. 0.1 ~ 1.1 mg/L, recovery ratio 30%.

0.1 to 1.1 mg/L, which were performed in four places (A, B, C, and D).

Despite the existence of residual chlorine in these applications, the module R0 performance had been stable for a period of up to 24 months, as shown in Figure 15. In this way, the modules prepared from the new membrane material, 4T-PIP(30), proved to show excellent RO performance and higher chlorine resistance than conventional aramid.

CONCLUSIONS

1. New asymmetric hollow fiber RO membrane was developed from 4T-PIP(30) copolyamide by a conventional phase-separation method, of which RO performance is the same as that of CTA hollow fiber membrane (FR = 205 L/m^2 day, Rj = 99.6%). It has superior chlorine resistance as well as pH resistance to conventional aramid RO membranes.

2. Structural analysis and viscoelastic study disclosed that the new hollow fiber consisted of top skin, dense layer, and microporous layer, and that it began to decrease its elasticity at 80°C in water, which is possibly related to its good and stable RO performance around room temperature.

3. RO performance of the modules prepared from the new hollow fiber membranes were stable for 2 years in chlorinated feed water desalination (the free residual chlorine ranged from 0.l to 1.1 mg/L).

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