

# Reverse Osmosis Performance and Chlorine Resistance of New Ternary Aromatic Copolyamides Comprising 3,3'-Diaminodiphenylsulfone and a Comonomer with a Carboxyl Group

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**ABSTRACT:** The preparation of asymmetric flat membranes from a series of novel aromatic polyamides comprising 3,3'-diaminodiphenylsulfone and a comonomer with a carboxyl group (&BOND;COOH) were studied and the measurements of reverse osmosis (RO) performance and chlorine resistance were carried out. It was confirmed that the introduction of comonomer with a carboxyl group (MC or  $T_m$ ) to the aromatic polyamides (3I or 3T) comprising 3,3'-diaminodiphenylsulfone was very effective for the improvement of its RO performance. In particular, 3T-MC(30), which was prepared from terephthaloyl dichloride and mixed diamine components of 3,3'-diaminodiphenylsulfone and 3,5-diaminobenzoic acid, exhibited not only some potential for sea water desalination (FR = 159 L/m<sup>2</sup> day, R<sub>j</sub> = 98.3%) but also higher chlorine resistance than conventional Nomex-type aramid [MI-MC(0)]. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 505–513, 2001

**Key words:** low temperature solution polymerization; 3,5-diaminobenzoic acid; aromatic polyamide; diaminodiphenylsulfone; reverse osmosis; chlorine resistance

## INTRODUCTION

Reverse osmosis (RO) membranes have been applied to the desalination for sea water and well water. In these days RO membrane materials are required to have high flux, high salt rejection, and resistance to chlorine and other oxidation agents.<sup>1–6</sup> Resistance to chlorine is especially important since chlorine (Cl<sub>2</sub> giving active species of Cl<sup>+</sup>) is often added to feed water for control of microorganisms and to prevent membrane fouling by microbiological growth in RO systems.

Conventional NOMEX-type aromatic polyamides with the fundamental structure of poly-

(*m*-phenylene isophthalamide) have been used as a membrane forming material, which have good RO performance and mechanical properties, but little resistance to chlorine.<sup>7</sup>

Lots of synthetic polymers have been developed for the purpose of improving chlorine resistance of RO membranes, but none have been put to practical RO desalination use.<sup>8</sup>

The authors<sup>9</sup> reported that the aromatic polyamides (3I and 3T) synthesized from iso- or terephthaloyl chloride and 3,3'-diaminodiphenylsulfone by low temperature solution polycondensation had higher chlorine resistance than conventional NOMEX-type polyamide.

However, the problem is that asymmetric flat RO membranes prepared from 3I or 3T have inferior permeability (flux rate and salt rejection) to the NOMEX type.<sup>10</sup> R. Endo<sup>11</sup> and A. Walch<sup>12</sup>

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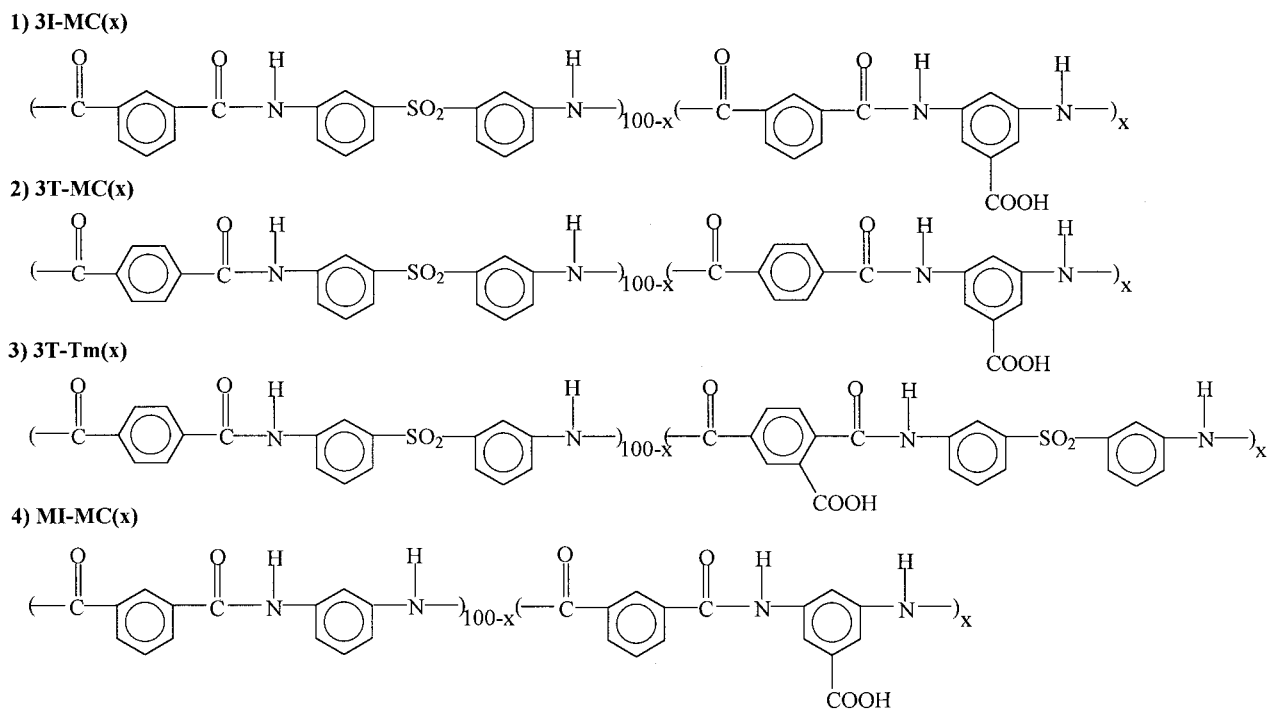


Figure 1 Structural formulas of copolyamides studied.

reported that a higher ratio of hydrophilicity to hydrophobicity in the polymer resulted in an increase in water flux of membranes made from it.

So, the copolymerization of a diamine or an acid component with a carboxyl group, for example 3,5-diaminobenzoic acid or trimellitic anhydride with 3I or 3T, is expected to result in an improvement of their permeability.

In a previous paper<sup>13</sup> the authors reported the preparation of such new copolyamides with a carboxyl group by low temperature solution polycondensation.

In this paper, the authors describe the RO performance and chlorine resistance of the asymmetric flat membranes prepared from new ternary copolyamides with a carboxyl group.

## EXPERIMENTAL

### Materials

Commercially available terephthaloyl (TPC), isophthaloyl (IPC) chlorides, and trimellitic anhydride chloride (Tm) (Mitsubishi Gas Chemical Co. Ltd.) were crushed into small pieces under nitrogen before use. *m*-Phenylenediamine (M) (supplied by Nakarai Chemical Company) was purified by distillation *in vacuo* before use.

3,3'-Diaminodiphenylsulfone (3DDS) was supplied by Wakayama Seika Co. Ltd. and used without purification. 3,5-Diaminobenzoic acid (MC) supplied by Nakarai Chemical Company was recrystallized with pure water before use.

Acid acceptors such as triethylamine (TEA) and pyridine (PY) were dried over calcium hydride overnight and purified by distillation *in vacuo* before use. All the solvents such as *N,N*-dimethylacetamide (DMAC) and *N*-methyl-2-pyrrolidone (NMP) were dried by molecular sieves without further purification.

### Synthesis of Copolyamides

The copolyamides containing a carboxyl group, of which structural formulas were shown in Figure 1, were prepared by low temperature solution polycondensation according to the previous report<sup>9,13</sup> and literature<sup>14</sup> except 3T-Tm(x).

3T-Tm(x) copolyamides were prepared by low temperature solution polycondensation as described below.

Into a 100 mL three-necked round-bottom flask equipped with a thermometer, nitrogen gas inlet, nitrogen gas outlet, and magnetic stirrer were placed 0.1 mol of 3DDS dissolved in 50 mL of DMAC.

The solution was cooled to 2°C and a mixture (0.01 mol) of Tm and TPC was added to it all at once. The polymerization solution was stirred for 0.5 h, during which period temperature was allowed to reach 2°C at which the reaction solution was maintained for 1 h.

The solution was then stirred at 25°C for 5 h. An inlet gas flow was maintained through the system during the course of the reaction. The viscous solution obtained was poured into excess methanol with rapid stirring to precipitate the polymer. The polymer was filtered, washed several times with methanol and water, and dried to give 3T-Tm(x) copolyamides in over 98% yields.

### Characterization of Copolyamides

Reduced viscosities ( $\eta_{sp}/C$ ) of the copolyamides were measured at a concentration of 0.5 g/dL in NMP at 30°C using a suspended-type Ubbelohde viscometer.

### Preparation of Asymmetric Flat Membranes

The casting solution composition is considered one of the most important parameters influencing membrane performance. Lithium chloride and DMAC were used as an additive and solvent respectively to develop the reverse osmosis performance of the membrane.<sup>15,16</sup> The ratio of polyamide/LiCl/DMAC in the casting solution was maintained at 20/4/76 wt % according to the preliminary experimental. Typical procedure of asymmetric flat membranes is as follows:

Flat asymmetric membranes were formed by dissolving the copolyamide into DMAC containing lithium chloride (LiCl) (polymer conc.: 20 wt/v %, LiCl conc.: 5 wt/v %), casting the solution onto a glass plate using a 25-mL doctor knife, evaporating the solvent by heating the cast membrane at 110°C for 10 min, and dipping the plate in a coagulation liquid (ice water). The thickness of the casted film was 150 or 300  $\mu\text{m}$ . The asymmetric flat membranes obtained were dipped in a pure water before the measurement of their RO performance and chlorine resistance.

### Annealing of Asymmetric Flat Membranes

Flat membranes were allowed to float in deionized water for a minimum of a day to achieve complete solvent removal. The solvent-free flat membranes were then annealed in thermostated, deionized water at the temperature of 98°C for 15 min to increase salt rejection. The asymmetric

flat membranes obtained were dipped in a pure water before the measurement of their RO performance.

### Measurement of Water Content

The water content ( $H$ ) of an asymmetric flat membrane was measured and calculated as follows:

An asymmetric flat membrane was put in pure water overnight, and water on its surface was wiped away, followed by the measurement of weight of the wet membrane ( $W_{\text{wet}}$ ). The wet membrane was dried at 105°C for 5 h and its weight ( $W_{\text{dry}}$ ) was measured.

The value of  $H$  was calculated according to the following formula:

$$H(\%) = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{wet}} \times 100$$

### Measurement of RO Performance

A RO performance of an asymmetric membrane is represented by FR (flux rate of product water) and Rj (salt rejection). The former, FR, means an amount of product water ( $\text{L}/\text{m}^2$  day) that permeates through a membrane, when 25°C saline water containing 35,000 ppm of sodium chloride (NaCl) has been supplied to the common continuous pump-type RO apparatus under the pressure of 55  $\text{kg}/\text{cm}^2$ .<sup>17</sup>

The latter, Rj, means a percentage (%) of the difference in sodium chloride concentration between the feed and the permeate to the sodium chloride concentration of the feed.

### Measurement of Chlorine Resistance

Chlorine uptake rates of the copolyamides were measured according to the following new method<sup>18</sup>:

The copolyamide tested was freeze-crushed and dried *in vacuo* at a temperature of 150°C for more than 15 h; 0.5 g of fine powders of 10  $\mu$  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 dihydrogenphosphate, and dipotassium hydrogen phosphate, all of which are a buffer for pH adjustment. The chlorine solution was placed in a constant temperature vessel kept at 40°C, and a chlorine absorption rate was obtained by measuring a change in the chlorine concentration with the lapse of time of the solution. A difference of the chlorine absorption 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 absorption 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.

Chlorine resistance of asymmetric flat membranes was evaluated in the presence of chlorine (Cl<sup>+</sup> conc. = 100 ppm, pH 6 ~ 7), using the common continuous pump-type RO apparatus under the above conditions.

## RESULTS AND DISCUSSION

### RO Performance of Copolyamides with a Carboxyl Group Characteristics of Copolyamides

Reduced viscosities of the copolyamides such as 3I-MC(x), 3T-MC(x), 3T-Tm(x), and MI-MC(x) were summarized in Table I. They were sufficient enough for us to get asymmetric flat membranes suitable for the measurement of their RO performance and chlorine resistance.

### Preparation of Asymmetric Flat Membranes

In order to get asymmetric flat membranes with higher RO performance, the effects of solvent evaporation temperature, evaporation period, composition of coagulation bath, cast film thickness and annealing on the RO performance were examined as follows:

### Effects of Solvent Evaporation Temperature and Period

The effects of solvent evaporation temperature on salt rejection efficiency and water permeability of various membranes have been studied by many researchers.

N. A. Mohamed<sup>16</sup> reported that the salt rejection efficiency of wholly aromatic polyamide-hydrazide membranes increased by increasing the solvent evaporation temperature and that the optimum salt rejection of the membranes was achieved when the solvent evaporation temperature was 120°C and an increase of temperature did not show further improvement of the membrane selectivity. In contrast to the salt rejection power, the water permeability of these membranes reduced by increasing the solvent evapo-

**Table I Properties of Copolyamides with a Carboxyl Group**

| Copolyamides | x (mol %) | $\eta$ sp/C (dL/g) |
|--------------|-----------|--------------------|
| 3I-MC(x)     | 0         | 0.62               |
|              | 10        | 0.97               |
|              | 20        | 0.82               |
|              | 30        | 0.88               |
|              | 50        | 0.65               |
| 3T-MC(x)     | 0         | 0.86               |
|              | 10        | 0.81               |
|              | 20        | 0.91               |
|              | 30        | 0.97               |
|              | 50        | 0.94               |
| 3T-Tm(x)     | 10        | 0.75               |
|              | 20        | 0.64               |
|              | 30        | 0.43               |
|              | 50        | 0.32               |
| MI-MC(x)     | 0         | 1.46               |
|              | 10        | 1.40               |
|              | 20        | 1.30               |
|              | 50        | 1.38               |

ration temperature. Then the solvent evaporation temperature of 110°C was adopted in this work.

Correlations between the solvent evaporation period and salt rejection efficiency as well as water permeability of the membranes prepared in this work are presented in Table II.

The membranes were prepared from different copolyamides, thermally treated at a fixed temperature of 110°C for different intervals between 5 and 10 min. The membranes were coagulated in deionized ice-water at 0°C.

The membranes showed a trend summarized by an increase in R<sub>j</sub> and a reduction in FR as the solvent evaporation period increased, which was described in the previous literature.<sup>16</sup>

Thus it could be concluded that the optimum of evaporation period at 110°C was around 10 min.

### Effect of Composition of Coagulation Bath

The effect of the coagulation bath type on the RO performance of asymmetric flat membranes is shown in Table II.

The membrane coagulated in an ice-water bath (at 0°C), showed higher RO performance (FR: 144 L/m<sup>2</sup> day, R<sub>j</sub>: 97%) than that in 30% DMAC/water bath (FR: 110 L/m<sup>2</sup> day, R<sub>j</sub>: 83%).

In the coagulation procedure, the cast membrane turned white instantly in an ice-water bath, while in the 30% DMAC/water bath its color changed white gradually after being kept trans-

**Table II Effect of Cast Film Thickness, Solvent Evaporation Period, and Coagulation Conditions on RO Performance of 3T-MC(15)**

| Cast Film Thickness ( $\mu\text{m}$ ) | Evaporation Period (min) | Coagulation Bath | Temperature ( $^{\circ}\text{C}$ ) | RO Performance                  |        |
|---------------------------------------|--------------------------|------------------|------------------------------------|---------------------------------|--------|
|                                       |                          |                  |                                    | FR ( $\text{L}/\text{m}^2$ day) | Rj (%) |
| 150                                   | 0                        | Ice water        | 0                                  | 7424                            | 0      |
| 150                                   | 5                        | Ice water        | 0                                  | 347                             | 31     |
| 150                                   | 10                       | Ice water        | 0                                  | 144                             | 97     |
| 300                                   | 10                       | Ice water        | 0                                  | 126                             | 93     |
| 150                                   | 0                        | 30% DMAC/water   | 2                                  | 852                             | 3      |
| 150                                   | 5                        | 30% DMAC/water   | 2                                  | 110                             | 80     |
| 150                                   | 10                       | 30% DMAC/water   | 2                                  | 110                             | 83     |

parent for about 5 min. It was postulated that rapid phase inversion occurred in ice-water to generate bigger pores than in 30% DMAC/water bath, which caused possibly higher RO performance.

So the ice bath with a temperature of  $0^{\circ}\text{C}$  was adopted as a coagulation bath in this study.

#### Effect of Cast Film Thickness

The effect of cast film thickness on the RO performance is shown in Table II.

The 3T-MC(15) asymmetric flat membrane obtained from cast film with a thickness of  $150\ \mu\text{m}$  exhibited FR of  $144\ \text{L}/\text{m}^2$  day and Rj of 97%, while the membrane from cast film with a thickness of  $300\ \mu\text{m}$  exhibited FR of  $126\ \text{L}/\text{m}^2$  day and Rj of 93%. The water permeability and the salt rejection were not substantially influenced by the cast film thickness. So RO performances of the following copolyamide flat membranes were measured by the use of the asymmetric flat membranes obtained from cast film with a thickness of  $150\ \mu\text{m}$ .

#### Effect of Annealing

In general, the RO performance of the membranes is clearly affected by annealing around  $100^{\circ}\text{C}$  with an increase in salt rejection and simultaneous reduction in water permeability.

Table III shows the effect of annealing at  $98^{\circ}\text{C}$  in deionized water on the RO performance of 3I-MC(x) and 3T-MC(x) membranes. The Rj of the 3I-MC(x) and 3T-MC(x) membranes is decreased by the annealing against expectation. Since annealing had no influence on the improvement of the above membranes, the measurements of RO performance and chlorine resistance were carried out with the flat membranes without annealing treatment.

In conclusion, optimum preparation conditions of asymmetric flat membrane is as follows:

Evaporation temperature:  $110^{\circ}\text{C}$ ; evaporation temperature: around 10 min.

Coagulation bath: ice bath with a temperature of  $0^{\circ}\text{C}$ ; cast film thickness:  $150\ \mu\text{m}$ . Treatment: without annealing.

The asymmetric flat membranes obtained are flexible.

#### RO Performance of New Aromatic Copolyamides with a Carboxyl Group

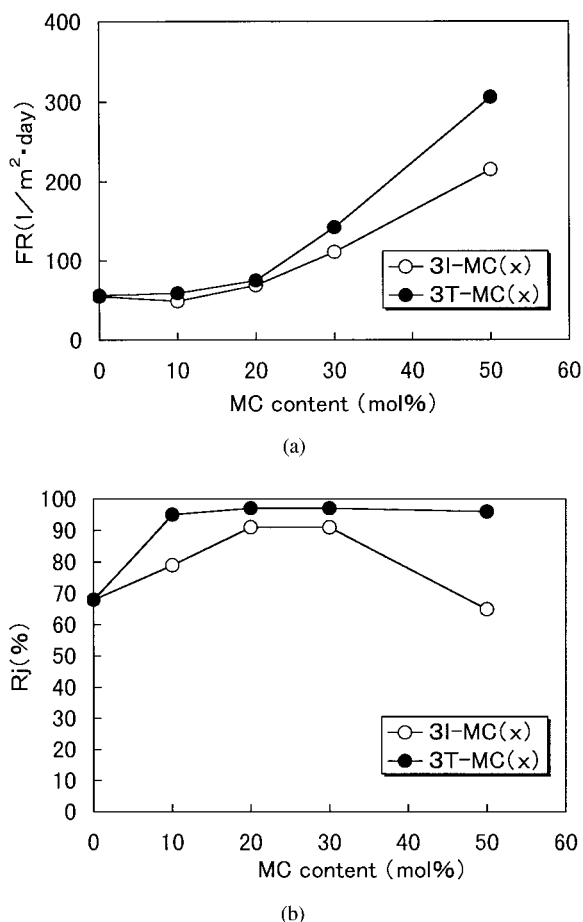
##### RO Performance of 3I-MC(x) and 3T-MC(x) Copolyamides

Figure 2(a) and 2(b) show the RO performance of the asymmetric flat membranes prepared from 3I-MC(x) and 3T-MC(x) copolyamides.

**Table III Effect of Annealing in Water on RO Performance of Asymmetric Flat Membranes<sup>a</sup>**

| Copolyamide Type | RO Performance                  |        |                                 |        |
|------------------|---------------------------------|--------|---------------------------------|--------|
|                  | Nonannealing                    |        | Annealed                        |        |
|                  | FR ( $\text{L}/\text{m}^2$ day) | Rj (%) | FR ( $\text{L}/\text{m}^2$ day) | Rj (%) |
| 3I-MC(10)        | 49                              | 79     | 22                              | 32     |
| 3I-MC(20)        | 69                              | 91     | 41                              | 54     |
| 3I-MC(30)        | 111                             | 91     | 58                              | 41     |
| 3T-MC(10)        | 59                              | 95     | 17                              | 67     |
| 3T-MC(20)        | 75                              | 97     | 24                              | 84     |
| 3T-MC(30)        | 142                             | 97     | 33                              | 82     |

<sup>a</sup> Solution: copolyamide/DMAC/LiCl = 20/76/4 (weight ratio). Cast film thickness:  $300\ \mu\text{m}$ . Evaporation: temp.,  $110^{\circ}\text{C}$ ; period, 10 min. Coagulation conditions: bath, ice water ( $0^{\circ}\text{C}$ ).



**Figure 2** (a) Influence of MC content of FR performance of membrane. (b) Influence of MC content of Rj performance of membrane.

The results showed that *FR* increased with the increase of the comonomer MC and that the maximum of *Rj* was obtained at the molar ratio of MC ranging from 20 to 30 mol %.

In particular, the asymmetric flat membranes from 3T-MC(x) copolyamides exhibited superior *Rj* performance to those from 3I-MC(x) copolyamides. It is concluded that 3T-MC(30) copolyamide is the most favorable RO membrane material for sea water desalination [3T-MC(30): *FR* = 159 L/m<sup>2</sup>/day, *Rj* = 98.3%]. 3T-MC(50) copolyamide is likely to be suitable for brackish water desalination, since it showed high *FR* performance (*FR* = 306 L/m<sup>2</sup>/day and *Rj* = 96.3%).

Such a good RO performance, in particular *Rj*, is possibly due to the higher linearity of 3T-MC(x) copolyamide molecule than 3I-MC(x) one.

Figure 3 shows the water content (*H*) of 3I-MC(x) and 3T-MC(x) copolyamides. The water

content of 3T-MC(x) copolyamide was larger than that of 3I-MC(x) copolyamide. Superior *FR* performance of 3T-MC(x) to 3I-MC(x) is possibly related to higher water content of 3T-MC(x) flat membranes.

### RO Performance of the 3T-Tm(x) Copolyamides

Figure 4(a) and 4(b) show the RO performance of the asymmetric flat membranes prepared from 3T-Tm(x) copolyamides.

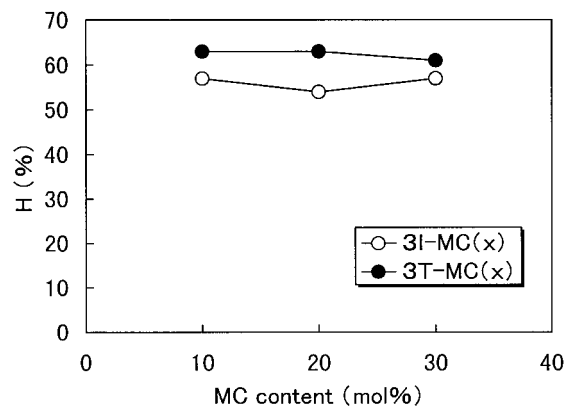
*FR* increased with the increase of the comonomer (Tm), while maximum *Rj* was obtained at the comonomer content of 20 mol % (*FR* = 134 L/m<sup>2</sup> day and *Rj* = 89.1%). Such behavior was observed in the above 3T-MC(x) membranes. In comparison with RO performance of 3T-MC(x) copolyamides, a carboxyl group generated from Tm could not give an effect on the improvement of RO performance more than a carboxyl group of MC.

Judging from the RO performance of asymmetric flat membranes as described above, 3T-MC(x) copolyamides [in particular 3T-MC(30)] are the most promising RO membrane materials for salt desalination.

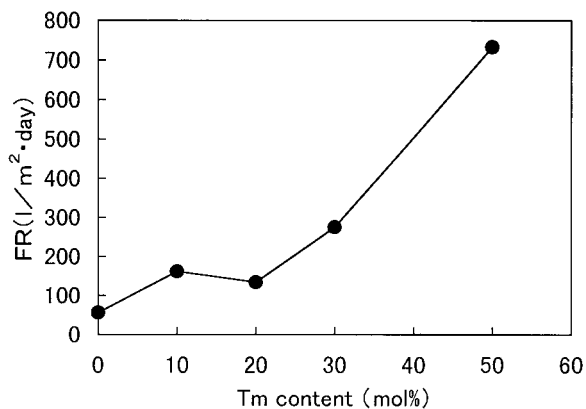
### Difference in RO performance between 3T-MC(x) and MI-MC(x)

Figure 5(a) and (b) show the RO performance of the asymmetric flat membranes prepared from conventional Nomex-type aramid, MI-MC(x).

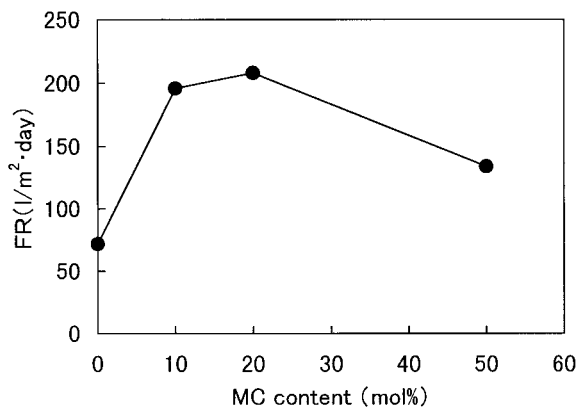
The RO performances of asymmetric flat membranes from 3T-MC(x) were superior to those from MI-MC(x).



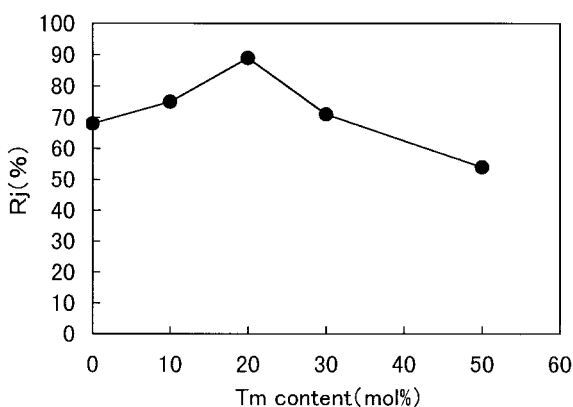
**Figure 3** Influence of MC content on water content (*H*) of membrane.



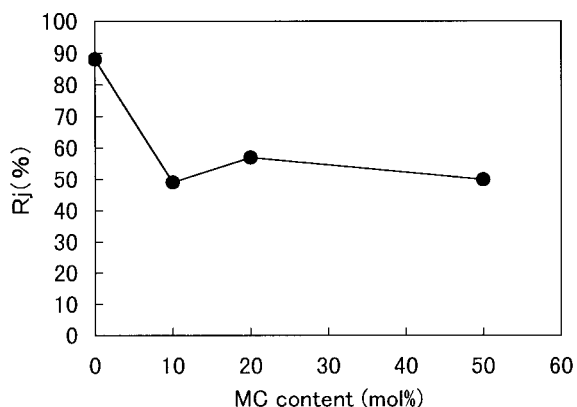
(a)



(a)



(b)



(b)

**Figure 4** (a) Influence of Tm content on FR performance of 3T-Tm(x) membranes. (b) Influence of Tm content on Rj performance on 3T-Tm(x) membranes.

**Figure 5** (a) Influence of MC content on FR performance of MI-MC(x) membranes. (b) Influence of MC content on Rj performance of MI-MC(x) membranes.

In the case of MI-MC(x) membranes, FR increased with the increase of the comonomer and the maximum FR was attained at the comonomer content of 20 mol %. Rj decreased with the increase of MC comonomer, and became constant at the comonomer content of 20 mol %. The carboxyl group of MI-MC(x) did not appear to contribute to the improvement of RO performance of MI-MC(0) copolyamide. This behavior is different from that of 3T-MC(x).

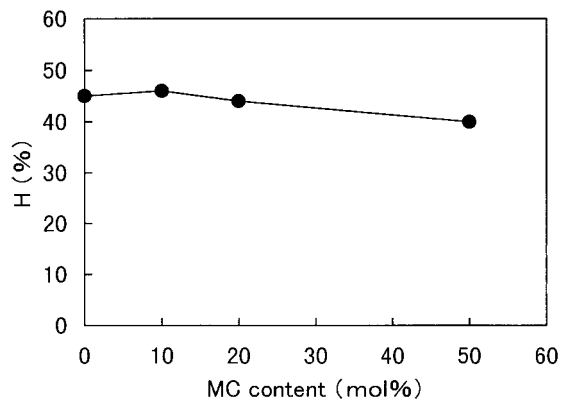
Figure 6 shows the dependence of water content on the comonomer content.

The water content of MI-MC(x) copolyamide was not influenced by the comonomer content and was smaller than that of 3T-MC(x). This result shows that 3T-MC(x) is more hydrophilic than MI-MC(x), which is probably caused by the higher hydrophilicity of diaminodiphenylsulfone unit than that of phenylenediamine unit.

### Chlorine Resistance of Asymmetric 3T-MC(x) Flat Membranes

#### Chlorine Uptake Rate

Figure 7 shows the chlorine uptake curves of powdery 3T-MC(x) copolyamides and conventional



**Figure 6** Influence of MC content on water content (H) of MI-MC(x) membranes.

membrane material Nomex [MI-MC(0)]. As described in our previous report,<sup>19</sup> 3T-MC(0), which had no carboxyl group, showed low chlorine uptake rate, but chlorine uptake of 3T-MC(x) increased with the increase of MC comonomer content. However, their chlorine uptake rate was much smaller than that of Nomex-type aramid, as shown in Figure 7, which suggests that 3T-MC(x) is a membrane material with good chlorine resistance.

### One-Day Chlorine Resistance Test

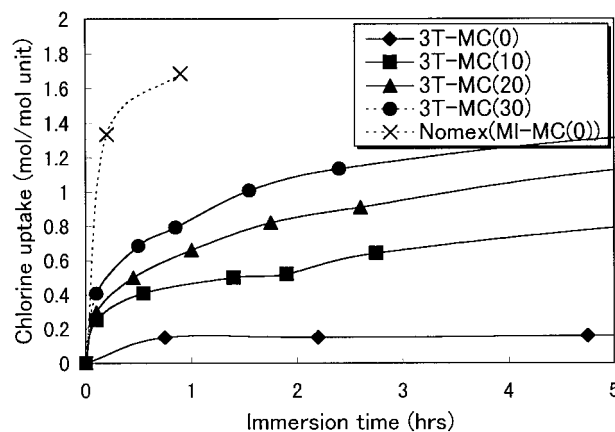
Figure 8 shows the one-day chlorine resistance test result of the asymmetric flat membranes from 3T-MC(10), 3T-MC(30), and 3T-MC(50) under the sea water desalination condition.

The asymmetric flat membrane from 3T-MC(30) proved to indicate the most stable Rj retention for 25 h among them, while the asymmetric flat membrane formed from 3T-MC(50) exhibited less Rj retention than 3T-MC(10) and 3T-MC(30). The trend that the chlorine resistance of 3T-MC(x) flat membrane decreased with the increase of MC comonomer was observed. Such observation is consistent with their chlorine uptake results.

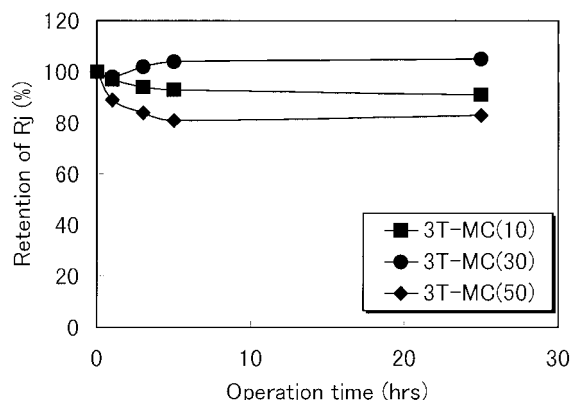
In conclusion, 3T-MC(30) among the new copolyamide is the most promising membrane material with good RO performance and chlorine resistance superior to conventional NOMEX-type aramid.

### CONCLUSIONS

The above results and discussion lead to the following general conclusions:



**Figure 7** Chlorine uptake curves of 3T-MC(x) and NOMEX polyamides. Text conditions:  $\text{Cl}^+$  220, pH 5, 30°C.



**Figure 8** One-day chlorine resistance test of 3T-MC(x) flat membranes. Test conditions: 3.5% NaCl, 55 kg/cm<sup>2</sup>G, 100 ppm  $\text{Cl}^+$ , pH 6–7.

1. High salt rejection capability and flux rate of new aromatic copolyamide [3T-MC(x)] could be achieved after the thermal treatment of the membranes at 110°C for 10 min and the coagulation of the membranes in ice-water, using the casting solution of copolyamide/LiCl/DMAC (20/76/4 wt ratio). Annealing in water at 98°C had no effect on improving RO performance.
2. It was confirmed that the introduction of comonomer with a carboxyl group (MC or Tm) to the aromatic polyamide comprising 3,3'-diaminodiphenylsulfone was very effective for the improvement of its RO performance.
3. 3T-MC(30), which was prepared from terephthaloyl dichloride and mixed diamine components of 3,3'-diaminodiphenylsulfone and 3,5-diaminobenzoic acid, exhibited not only some potential for sea water desalination (FR = 159 L/m<sup>2</sup> day, Rj = 98.3%) but also higher chlorine resistance than conventional Nomex-type aramid [MI-MC(0)].

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