Synthesis of Ternary Copolyamides from Aromatic Diamine (m-Phenylenediamine, Diaminodiphenylsulfone), Aromatic Diamine with Carboxyl or Sulfonic Group (3,5-Diaminobenzoic Acid, 2,4-Diaminobenzenesulfonic Acid), and Iso- or Terephthaloyl Chloride

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ABSTRACT: The copolymerization of iso- or terephthaloyl chloride, m-phenylenediamine or diaminodiphenylsulfone, and 3,5-diaminobenzoic acid or 2,4-diaminobenzene sulfonic acid (or sulfonate) was studied. Copolymers with high reduced viscosity could be obtained by low temperature solution polymerization, but not by interfacial polymerization. The reduced viscosity of the copolyamides obtained was dependent upon the species of the aromatic diamine compounds and the acid acceptors used. Low temperature solution copolymerization with the comonomer 3,5-diaminobenzoic acid should be done without acid acceptors, because acid acceptors cause gelation. With 2,4-diaminobenzenesulfonic acid or 2,4-diaminobenzenesulfonate, pyridine or triethylamine as acid acceptors give polymers with higher reduced viscosity. The flat asymmetric membranes of the copolyamides prepared from terephthaloyl dichloride and mixed diamine components of 3,3′-diaminodiphenylsulfone and 3,5-diaminobenzoic acid showed not only good reverse osmosis performance, but also high chlorine resistance. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 913–920, 2000

Key words: low temperature solution polymerization; 3,5-diaminobenzoic acid; 2,4-diaminobenzene sulfonic acid (or sulfonate); copolymer

INTRODUCTION

Recently, many researchers have proposed new ideal synthetic reverse osmosis (RO) membranes for desalination from polyamides with the following properties[1–6]: (1) high flux, (2) high salt rejection, (3) resistance to chlorine and other oxidation agents, (4) capability 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.

NOMEX-type aromatic polyamides with the structure of poly(m-phenylene isophthalamide) have been used as a membrane-forming material, which has good RO performance and mechanical properties, but lower resistance to chlorine.[7] In RO systems, chlorine may be added to feedwater for control of microorganisms and to prevent membrane fouling by microbiological growth.

Several kinds of synthetic polymers have been developed for the purpose of improving chlorine resistance, but none have been put to practical use as a RO membrane material.[8]

The authors[9] have been studying the relationship between the chemical structure of polyamides and their chlorine resistance, and have

made it clear that the aromatic polyamides synthesized with the use of 3,3'- or 4,4'-diaminodiphenylsulfone as a diamine compound have higher chlorine resistance than NOMEX-type polyamides, because such compounds have an electron withdrawing group ($-SO_2-$).
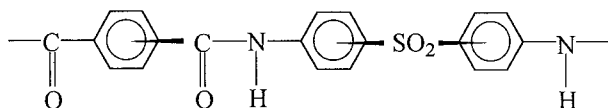
However, the problem is that RO membranes from such aromatic polyamides have permeability inferior to the NOMEX-type ones.[10] R. Endo[11] and A. Walch[12] reported that a higher ratio of hydrophilicity to hydrophobicity in the polymer resulted in an increase in water flux of membranes from it.

So, the copolymerization of the aromatic diamines with a hydrophilic group, for example 3,5-diaminobenzoic acid and 2,4-diaminobenzenesulfonic acid, with the above monomers is expected to result in an improvement of permeability.

In this paper, we describe the synthesis of ternary copolyamides from aromatic diamines with a hydrophilic group such as 3,5-diaminobenzoic acid and 2,4-diaminosulfonic acid, 3,3'- or 4,4'-diaminodiphenylsulfone and iso- or terephthaloyl chloride, and the RO performance and chlorine resistance of the flat asymmetric membranes prepared from them.

EXPERIMENTAL

Materials

Commercially available terephthaloyl and isophthaloyl (IPC) chlorides (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) and 4,4'-diaminodiphenylsulfone (4DDS) were supplied by Wakayama Seika Co., Ltd., and used without purification.

3,5-Diaminobenzoic acid (MC) and 2,4-diaminobenzenesulfonic acid (MS), which were commercially supplied by Nakarai Chemical Company, were recrystalized with pure water before use. 2,4-Diaminobenzenesulfonate sodium salt (MSNa) was prepared by the reaction of 2,4-dia-

minobenzenesulfonic acid with sodium hydroxide in water and purified by recrystalization in water. An aqueous solution of tetramethylammonium hydroxide was purchased from Nakarai Chemical Company. 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 the Copolyamides

The synthesis of copolyamides containing carboxyl or sulfonic groups, whose structural formulas are shown in Figure 1, were studied by interfacial or low temperature solution polymerization of iso- or terephthaloyl chlorides with m-phenylenediamine or 3,3'- (or 4,4')-diaminodiphenylsulfone and 3,5-diaminobenzoic acid or 2,4-diaminobenzenesulfonic acid using acid acceptors.

All the copolyamides were prepared according to the previous report[9] and literature.[13]

A typical procedure for the synthesis of the 3T-MC(x) copolyamides is described as follows:

Copolymerization was carried out in a 500 mL round-bottomed flask attached to a thermometer, a reagent funnel, a nitrogen bubbler, and a stirrer.

A mixture (0.200 mol) of 3,3'-diaminodiphenylsulfone and 3,5-diaminobenzoic acid was dissolved in NMP (250 mL) and the solution was cooled below 5°C. And powdery terephthaloyl chloride (0.198 mol) was added portionwise into the precooled solution under rapid stirring within a few minutes. At that time the reaction temperature rose to about 65°C. The resulting mass was stirred at 0°C for 30 min and at room temperature for 1 h. The reaction mixture was poured into methanol in a home blender to precipitate the polymer. The polymer was washed with pure water repeatedly to remove the free acid HCl and dried at 100°C for a day *in vacuo*. The yield is over 90% of the theoretical value.

Characterization of the Copolyamides

Reduced viscosities (η sp/C) 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 infrared spectrometer.

^{13}C- and H-NMR spectra were measured at 50°C by the use of Varian XL-300 (300 MHz NMR spectrum) in d6-dimethylsufoxide (DMSO).

1) MI-MC(x)

2) MI-MS(x)

3) 3(or 4) I(or T)-MC(x)
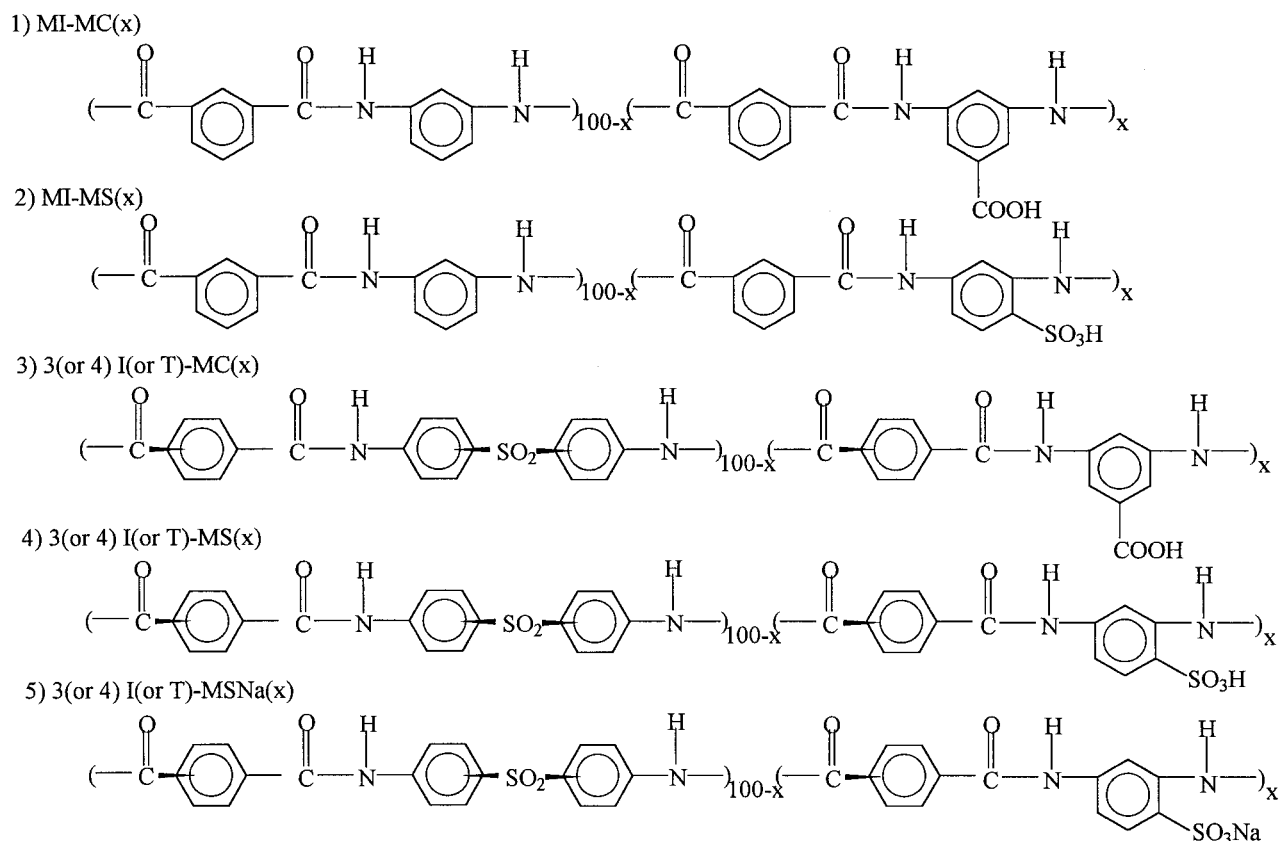
4) 3(or 4) I(or T)-MS(x)

5) 3(or 4) I(or T)-MSNa(x)

Figure 1 Structural formulas of copolyamides obtained.

The copolymerization ratio of an aromatic diamine compound with carboxyl or sulfonic group was determined by the use of the above ^{13}C-NMR or H-NMR spectrum according to the following procedure:

3,5-Diaminobenzoic acid in the copolyamide was determined from the ^{13}C-NMR spectra in d6-DMSO at 50°C.

2,4-Diaminobenzene sulfonic acid in the copolyamide was determined from the H-NMR spectra of its tetramethyl ammonium salt $[-SO_3{}^-N^+(CH_3)_4]$ in d6-DMSO at 50°C, which was obtained according to the following procedure:

The copolyamide was dissolved in NMP, and an excess amount of 10% aqueous solution of tetramethylammonium hydroxide was added slowly to the solution with stirring, in order to convert sulfonic acid groups into the ammonium salts. After the solution was vigorously stirred for 1 h at room temperature, the solution was poured into methanol to give a precipitate. The precipitate was washed with methanol several times and dried *in vacuo* at 60°C.

Formation of Flat Asymmetric Membranes

Flat asymmetric membranes were formed by dissolving the polyamide into DMAC containing lithium chloride (LiCl) (polymer concentration: 20 wt/v %, LiCl concentration: 5 wt/v %), casting the solution onto a glass plate, 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 μm. The flat asymmetric membranes obtained were dipped in pure water before the measurement of RO performance and chlorine resistance.

Measurement of RO Performance and Chlorine Resistance

RO Performance

Flux rate of product water (FR) and Salt rejection (Rj) represent a RO performance of an asymmetric membrane.

FR means an amount of product water (L/m^2 day) that permeates through a membrane, when

Table I   Synthesis of Ternary Copolyamides [MI-MC(x) and MI-MS(x)] with Low Temperature Solution Polymerization Method

Copolyamides	x (mol %) (Calcd.)	Acid Acceptor	Reaction Product	x (mol %) (Found)	η sp/C (dl/g)
MI-MC(x)	0	None			1.46
	10	None		7.0	1.40
		PY	Gelation	—	a
	20	None		—	1.30
		PY	Gelation	—	a
	30	None		—	1.38
	50	None		—	1.38
MI-MS(x)	10	None		—	0.54
		PY		8.3	0.98
	20	PY		17.7	0.92
		TEA		—	0.63
	30	PY		—	0.81
	40	PY		—	0.77
	50	PY		46.1	0.75

a Measurement was impossible.

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^2.[14]

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.

Chlorine Resistance Test

Chlorine resistance of flat asymmetric membranes was evaluated in the presence of chlorine (Cl$^+$ conc. = 50 ppm, pH 6), using the common continuous pump-type RO apparatus under the above conditions.

RESULTS AND DISCUSSION

Preparation of Copolyamides with Carboxyl or Sulfonic Groups

Copolymerization of MI-MC(x) Copolyamides

The results for the preparation of the copolyamides from isophthaloyl chloride, m-phenylenediamine, and 3,5-diaminobenzoic acid by low temperature solution polymerization are summarized in Table I.

Copolyamides with high degrees of polymerization could not be obtained by interfacial polycon-

densation, but they could be by low temperature polymerization, as shown in Table I.

The polymerization degree of the copolyamides was influenced by the molar ratio of added 3,5-diaminobenzoic acid and experimental conditions—in particular, species of acid acceptors.

The use of pyridine as an acid acceptor resulted in the formation of a gelatinized polymer, which was insoluble and swelled in NMP and DMAC.

However, no use of acid acceptors produced a copolyamide with high reduced viscosity, which was soluble in NMP and DMAC. There is some possibility that the copolyamide prepared with the use of an acid acceptor was crosslinked according to the following scheme:

(crosslinked structure)
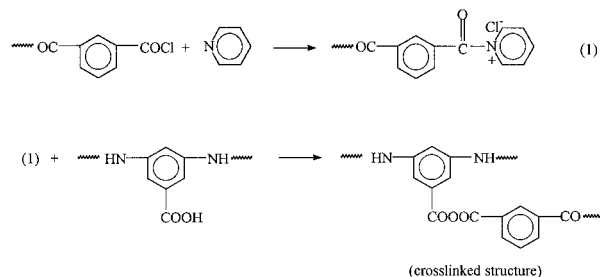
The activation of acid chlorides by pyridine might be followed by the formation of an acid anhydride.

Preparation of the MI-MS(x) Copolyamides

The results for the preparation of the copoly-amides from isophthaloyl chloride, m-phenylene-diamine, and 2,4-diaminobenzenesulfonic acid by low temperature solution polymerization are summarized in Table I.

The reduced viscosities of the copolyamides are dependent upon the acid acceptors used and the molar ratio of 2,4-diaminobenzenesulfonic acid.

The addition of pyridine and triethylamine (TEA) as an acid acceptor to the reaction mixture has a large effect on the production of the copoly-amide with higher reduced viscosity.

Moreover, the control of the reaction temperature could influence the polymerization degree of the copolyamide. Rapid addition of IPC in the presence of TEA as an acid acceptor raised the reaction temperature, which resulted in the decrease of the polymerization degree of the product, probably because a part of the acid chloride decomposed at a higher reaction temperature. On the other hand, gradual addition of IPC could produce a copolyamide with higher reduced viscosity, even if in the presence of TEA as an acid acceptor. The presence of an acid acceptor and its gradual addition are quite effective for the production of the copolyamide MI-MS(x) with high reduced viscosity.

The reason why the addition of acid acceptors such as pyridine and TEA was so effective for the copolymerization of MI-MS(x) was studied as follows:

The MI-MS(x) copolyamides obtained with the use of pyridine or TEA as an acid acceptor were very easily dissolved in DMAC and NMP.

Their ^{13}C-NMR spectra exhibited peaks at the intermediate value between the chemical shifts of pyridine and pyridinium cation,[15,16] which implied the existence of pyridinium cation in the copolyamide as shown in Table II. IR spectrum of MI-MS(x) copolyamide also revealed a strong peak at 1020 cm^{-1}, which was assigned to sulfonate group ($-SO_3^-$).[17] These results implied that MI-MS(x) copolyamide remained as the pyridinium salt as shown below:
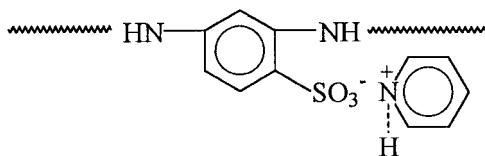
When the copolyamides were treated with a dilute aqueous HCl solution, peaks attributable

Table II ^{13}C-NMR Spectrum Data of Pyridine Left in MI-MS(x) Products

Products and Reference	Carbon Positions of Pyridine		
	C-2	C-3	C-4
MI-MS(10) product	147.2	124.9	139.1
MI-MS(50) product	145.2	125.9	142.0
a	149.8	123.6	135.7
	142.5	129.0	148.4

^{a} Refs. 14 and 15.

to pyridine and pyridinium disappeared and the copolyamides turned out to be insoluble in DMAC and NMP. Then the pyridinium sulfonate $[-SO_3^-H^+$(pyridine) salt] was surely changed to sulfonic group ($-SO_3H$). This result means that MI-MS(x) copolyamides with a sulfonic group ($-SO_3H$) are insoluble in DMAc and NMP. Since the MI-MS(x) copolyamide prepared without pyridine as an acid acceptor does not have the pyridinium sulfonate group but the sulfonic acid group ($-SO_3H$), it is so easily precipitated that it cannot grow longer during solution polymerization to exhibit low reduced viscosity.

Synthesis of the Copolyamides from Iso- or Terephthaloyl Chloride, 3,3'- or 4,4'-Diaminodiphenylsulfone, and Aromatic Diamine Compounds with a Hydrophilic Group such as 3,5-Diaminobenzoic Acid and 2,4-Diaminobenzenesulfonic Acid (Sulfonate)

Synthesis of Copolyamides Comprising 3,5-Diaminobenzoic Acid Moiety

Synthesis of the copolyamides from iso- or terephthaloyl chloride, 3,3'- or 4,4'-diaminodiphenylsulfone, and 3,5-diaminobenzoic acid were carried out without acid acceptors in analogy with the MI-MC(x) series as mentioned above. The results are summarized in Table III.

The polymer composition measured by ^{13}C-NMR was almost the same as the monomer composition for the 3I-MC(x) copolyamides. The 3I-MC(x) copolyamides showed slightly lower re-

Table III   Synthesis of Ternary Copolyamides Comprising 3,5-Diaminobenzoic Acid and Diaminodiphenylsulfone with Low Temperature Solution Polymerization Method

Copolyamide	x (mol %) (Calcd.)	Acid Acceptor	x (mol %) (Found)	η sp/C (dL/g)
3I-MC(x)	10	None	12	0.97
	20	None	24	0.82
	30	None	28	0.88
	50	None	50	0.65
3T-MC(x)	10	None	—	0.81
	20	None	—	0.91
	30	None	—	0.97
	50	None	39	0.94
4T-MC(x)	15	None	—	2.66
	30	None	—	3.07
	50	None	—	2.06

duced viscosity values than MI-MC(x), which were attributable to the lower reactivity (lower basicity) of 3,3′-diaminodiphenylsulfone to isophthaloyl chloride than m-phenylenediamine. The reduced viscosity of 4T-MC(x) series is much higher than that of 3T-MC(x), which means that 4,4′-diaminodiphenylsulfone has higher reactivity to terephthaloyl chloride than 3,3′-diaminodiphenylsulfone.

Synthesis of Copolyamides Comprising 2,4-Diaminobenzenesulfonic Acid (Sulfonate) Moiety

Synthesis of the copolyamides from iso- or terephthaloyl chloride, 3,3′- or 4,4′-diaminodiphenylsulfone, and 2,4-diaminobenzenesulfonic acid were carried out with the use of acid acceptors such as pyridine or TEA in analogy with MI-MS(x) series.

The copolyamides with high reduced viscosity could not be obtained, even if acid acceptors such as pyridine or TEA could be added, as shown in Table IV.

Such results were attributable to the lower reactivity (lower basicity) of diaminodiphenylsulfone to isophthaloyl chloride than m-phenylenediamine.

However, the use of 2,4-diaminobenzenesulfonate sodium salt instead of 2,4-diaminobenzenesulfonic acid as a comonomer gave copolyamides with higher reduced viscosity as shown in Table V. The Hammett constant of the sulfonic group [σ p(SO$_3$H) = 0.50] is more positive than that of the sulfonate group [σ p(SO$_3$) = 0.05),[17] which means

Table IV   Synthesis of Ternary Copolyamides Comprising 2,4-Diaminobenzene Sulfonic Acid with Low Temperature Solution Polymerization Method

Copolyamide	x (mol %) (Calcd.)	Acid Acceptor	η sp/C (dL/g)
3I-MS(x)	10	None	No product
3T-MS(x)	10	None	No product
		PY	0.43
	30	None	0.17
		PY	0.29
		TEA	0.26

that the basicity of the amino group in 2,4-diaminobenzenesulfonate sodium is larger than that of the amino group in 2,4-diaminobenzenesulfonic acid. So, 2,4-diaminobenzenesulfonate sodium is expected to be more reactive to isophthaloyl chloride than 2,4-diaminobenzenesulfonic acid, which resulted in the formation of the 3I-MSNa(x) copolyamide with high reduced viscosity.

The species of acid acceptors also gave an influence on the copolymerization, and TEA was the most suitable acid acceptor for the preparation of the copolyamide comprising 2,4-diaminobenzenesulfonate sodium as shown in Table VI.

RO Performance and Chlorine Resistance of Flat Asymmetric Membranes Prepared from the Copolyamide 3T-MC(x)

The RO performance of the flat asymmetric membranes prepared from 3T-MC(x) and NOMEX is

Table V   Synthesis of Ternary Copolyamides Comprising 2,4-Diaminobenzene Sulfonate with Low Temperature Solution Polymerization Method

Copolyamide	x (mol %) (Calcd.)	Acid Acceptor	η sp/C (dL/g)
3I-MSNa(x)	10	None	0.39
		PY	0.55
		TEA	0.66
	20	TEA	0.66
	30	TEA	0.60
3T-MSNa(x)	10	None	0.34
		PY	0.26
		TEA	0.72
	20	TEA	0.73
	30	TEA	1.06
4T-MSNa(x)	10	TEA	1.03
	20	TEA	0.88
	30	TEA	0.99

Table VI   Favorable Acid Acceptors for the Low Temperature Solution Polymerization of Phthaloyl Dichloride, Diaminodiphenylsulfone, and Aromatic Diamines with a Hydrophilic Group

Diacid	Diamine 1	Diamine 2		
		MC	MS	MSNa
IPC	M	None	PY	
	3DDS	None	—	TEA
TPC	3DDS	None	PY	TEA
	4DDS	None	—	TEA

Table VII   RO Performance of Flat Asymmetric Membranes from the New Copolyamides [3T-MC(x)]

Copolyamide Species	FR (L/m^2/day)	Rj (%)
3T-MC(10)	59	94.5
3T-MC(30)	142	97.3
3T-MC(0)	55	68.0
NOMEX	84	61.5

summarized in Table VII. The new copolyamides, 3T-MC(10) and 3T-MC(30), exhibited superior RO performance to the polyamides without carboxyl group. The RO performance of the polyamide was improved by the copolymerization of a diamine compound with a hydrophilic group, 3,5-diaminobenzoic acid.

Figure 2 shows the result of the chlorine resistance test for the flat asymmetric membranes from 3T-MC(30) and NOMEX-type aromatic polyamides.

Rj and FR retention of the flat asymmetric membrane from 3T-MC(30) were very stable, while those of the flat asymmetric membrane from NOMEX-type aromatic polyamide decreased rapidly in the early time. It was confirmed that the new copolyamides have superior chlorine resistance to NOMEX-type aromatic polyamides.

CONCLUSIONS

The copolymerization of iso- or terephthaloyl chloride, m-phenylenediamine or diaminodiphenylsulfone, and aromatic diamine compounds with carboxylic or sulfonic group was studied. Copolymers with high reduced viscosity values could not be obtained by interfacial polymerization, but could be by low temperature solution polymerization. The reduced viscosity of the copolyamides obtained was dependent upon the species of aromatic diamine compounds with a hydrophilic group and the species of the acid acceptors used. The relationship between the species of aromatic diamine compounds and favorable acid acceptors was summarized in Table VI.

Low temperature solution copolymerization with the use of 3,5-diaminobenzoic acid as a comonomer should be done without acid acceptors, because the addition of acid acceptors accelerates gelation of the product polymer.
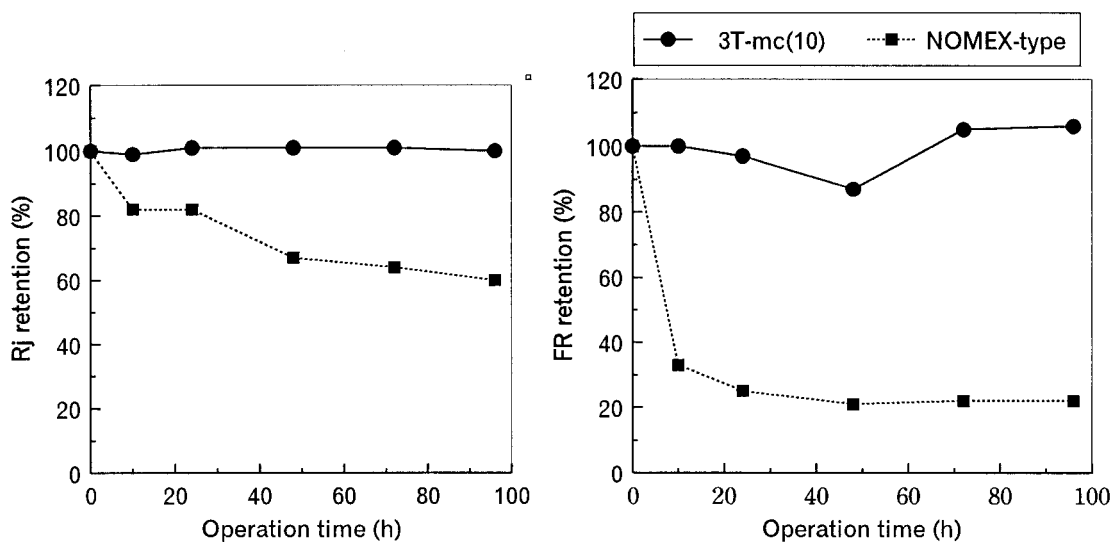
Figure 2 Chlorine resistance of flat asymmetric membranes of 3T-mc(10) and NOMEX type.

In the case of copolymerization using 2,4-diaminobenzenesulfonic acid, pyridine as an acid acceptor, which forms sulfonate salt, contributes to the increase of solubility of the product in the reaction solvent; therefore, pyridine should be added to the reaction mixture. However, in the case of the copolymerization for 2,4-diaminobenzenesulfonate moiety, triethylamine as an acid acceptor should be added.

The flat asymmetric membranes of the copolyamides [3T-MC(x) series] prepared from terephthaloyl dichloride and mixed diamine components of 3,3′-diaminodiphenylsulfone and 3,5-diaminobenzoic acid showed not only good RO performance, but also high chlorine resistance.

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