

Chlorine-Resistant Membrane for Reverse Osmosis.

I. Correlation between Chemical Structures and Chlorine Resistance of Polyamides

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Synopsis

Correlation between the chemical structure of polyamides and the reactivity to hypochlorous acid was investigated to evaluate their chlorine resistance as a membrane material for reverse osmosis. Modes of interaction of polyamides with hypochlorous acid were classified into three; no reaction, reversible chlorination at the amide nitrogen, and irreversible chlorination at the aromatic nucleus. These modes of interaction were dependent upon the amine component of polyamide. Secondary amines such as piperazine and *N*-methylaniline gave amides which were quite stable against hypochlorous acid. Thus, poly(isophthaloyl piperazine) was most stable among the polyamides investigated in this study. Polyamide derived from aliphatic primary diamines such as polyethyleneisophthalamide gave an *N*-chlorinated amide, which could be reversibly dechlorinated by the treatment with a reducing agent such as sodium hydrosulfite. Polyamides comprised of aromatic primary diamines such as poly(*m*-phenyleneisophthalamide), on the other hand, gave a product with chlorinated *m*-phenylene nucleus which could not be dechlorinated by a reducing agent.

INTRODUCTION

Blais¹ has reported the correlation between chemical structure and membrane performance of polyamides which are one of the most representative membrane materials for reverse osmosis²⁻⁷ possessing superior chemical resistance to cellulose acetate membranes.⁸ It has been pointed out, however, that polyamides are sensitive to oxidation, but few studies have been done to investigate the correlation between chemical structure of polyamides and their oxidation resistance.

Glator et al.⁹ have recently reported the sensitivity of polyamide reverse osmosis membranes to halogen disinfectants by monitoring the decay of the membrane performance. The polyamides they examined were, however, restricted to commercially available aramids, and the mode of the chemical reaction of various polyamides with active chlorine still remains undisclosed.

In order to get a chlorine-resistant reverse osmosis membrane, we intended to investigate the reactivity of polyamides with hypochlorous acid, which is a common sterilizing agent used in the field of seawater desalination and food processing. This paper describes the correlation between chemical structures and chlorine resistance of polyamides.

TABLE I
 Polyamides^a Used in This Study

Structure of polyamide	η_{sp}/c (dL/g) ^b	Solvent ^c
$\text{---} \underset{\text{H}}{\text{N}} \text{CH}_2 \text{CH}_2 \underset{\text{H}}{\text{N}} \text{---} \text{C}(=\text{O}) \text{---} \text{C}_6\text{H}_4 \text{---} \text{C}(=\text{O}) \text{---}$	0.39	CHCl ₃
$\text{---} \underset{\text{H}}{\text{N}} \text{CH}_2 \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_2 \underset{\text{H}}{\text{N}} \text{---} \text{C}(=\text{O}) \text{---} \text{C}_6\text{H}_4 \text{---} \text{C}(=\text{O}) \text{---}$	0.21	NMP ^d
$\text{---} \text{N} \text{---} \text{C}_6\text{H}_{10} \text{---} \text{N} \text{---} \text{C}(=\text{O}) \text{---} \text{C}_6\text{H}_4 \text{---} \text{C}(=\text{O}) \text{---}$	0.49	CHCl ₃
$\text{---} \text{N} \text{---} \text{C}_6\text{H}_{10} \text{---} \text{N} \text{---} \text{C}(=\text{O}) \text{---} (\text{CH}_2)_8 \text{---} \text{C}(=\text{O}) \text{---}$	0.19	CHCl ₃
$\text{---} \underset{\text{H}}{\text{N}} \text{---} \text{C}_6\text{H}_4 \text{---} \underset{\text{H}}{\text{N}} \text{---} \text{C}(=\text{O}) \text{---} (\text{CH}_2)_8 \text{---} \text{C}(=\text{O}) \text{---}$	0.12	HCOOH
$\text{---} \underset{\text{H}}{\text{N}} (\text{CH}_2)_6 \underset{\text{H}}{\text{N}} \text{---} \text{C}(=\text{O}) \text{---} \text{e}$	0.89	HCOOH
$\text{---} \underset{\text{H}}{\text{N}} \text{---} \text{C}_6\text{H}_4 \text{---} \underset{\text{H}}{\text{N}} \text{---} \text{C}(=\text{O}) \text{---} \text{C}_6\text{H}_4 \text{---} \text{C}(=\text{O}) \text{---} \text{f}$	1.02	NMP ^d

^a All the polyamides except e and f were prepared by interfacial polycondensation using CHCl₃ as an organic layer solvent.

^b Measured at 30°C with a polymer concentration of 0.5 g/dL.

^c Solvent used for reduced viscosity measurement.

^d *N*-methylpyrrolidone

^e Staple fiber of 6-nylon (Teijin)

^f Powdered sample of Teijin conex.

EXPERIMENTAL

Materials

All polyamides otherwise noticed were prepared by the interfacial polycondensation developed by Morgan.¹⁰ The concentration of diamine, acid chloride, and NaOH (acid acceptor) is 0.10, 0.10, and 0.22 mol/L, respectively and the solvent for acid chloride was CHCl₃. The polyamides thus prepared were shown in Table I. These polyamides were ground to a fine powder with particle size of less than 10 μm for the evaluation of their chlorine resistance.

Evaluation of Chlorine Resistance of Powdered Polyamides

A suspension of dry polymer (0.30 g) in an aq hypochlorous acid (70 mL) with 500 ppm of active chlorine concentration at pH 6.0 was stirred at 23°C for 15 h. The active chlorine concn in the solution phase was measured by titration with 0.1*N* sodium thiosulfite. The active chlorine concns (ppm) thus observed will be denoted as follows: C_0 (ppm) for the initial hypochlorous acid solution (70 mL), C_1 (ppm) for the supernatant layer (10 mL) of the polymer suspension after 15 h mixing, and C_2 (ppm) for the residual polymer suspension (60 mL).

The amount of chlorine consumed, C_i^* (eq/polymer unit), and that absorbed by polymer, C_r^* (eq/polymer unit), were determined as follows using C_0 , C_1 , and C_2 :

$$C_i^* = \frac{C_0 \times 70 - (C_2 \times 60 + C_1 \times 10) \times 0.30}{35.5 \times 10^6} \bigg/ \frac{1}{M_0}$$

$$C_r^* = \frac{(C_2 - C_1) \times 60 \times 0.30}{35.5 \times 10^6} \bigg/ \frac{1}{M_0}$$

where M_0 stands for the molecular weight of the polymer repeating unit.

NMR Measurement

^1H NMR measurement was performed using 60 MHz Varian's NMR spectrometer at 25°C. The solvent for the polymer sample was HCOOH in the case of poly(ethyleneisophthalamide) and *N*-methylpyrrolidone in the case of poly(*m*-phenyleneisophthalamide). The polymer sample treated with hypochlorous acid was carefully dried (50°C for 20 h *in vacuo*) because of the possibility of thermal dechlorination of the polymer.

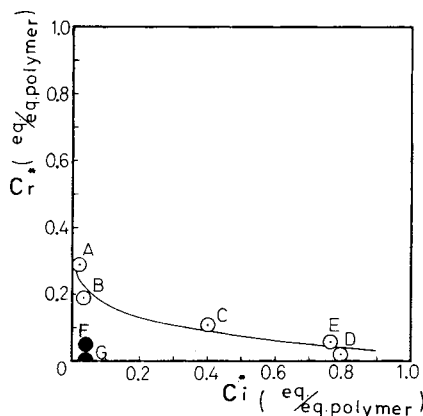


Fig. 1. The reaction of polyamides with hypochlorous acid. (a) C_i : the amount of chlorine irreversibly reacted with polyamides; (b) C_r : the amount of chlorine adsorbed reversibly on polyamides. (A) poly(ϵ -capramide); (B) poly(ethyleneisophthalamide); (C) poly(*p*-xylyleneterephthalamide); (D) poly(*m*-phenyleneisophthalamide); (E) poly(*m*-phenyleneadipamide); (F) poly(isophthaloyl piperazine); (G) poly(sebacoyl piperazine).

Analysis for the Amount of Chlorine in Polyamides

The amount of chlorine atoms in the polyamide before and after the treatment with hypochlorous acid was determined by oxidative microtitration method.¹¹

RESULTS AND DISCUSSION

Reaction of Powdered Polyamides with the Hypochlorous Acid

We examined the chlorine resistance of polyamides using powdered samples as described in the Experimental section. The polyamides examined were classified into three groups: secondary polyamides with aliphatic amine component, e.g., 6-nylon (A), poly(ethyleneisophthalamide) (B); secondary polyamide with aromatic amine component, e.g., poly(*m*-phenyleneisophthalamide) (D); poly(*m*-phenyleneadipamide) (E) and tertiary polyamides such as poly(isophthaloyl piperazine) (F) and poly(sebacoyl piperazine) (G).

Figure 1 shows the relationship between the amount of chlorine reversibility adsorbed (C_r^*) and irreversibly consumed (C_i^*) by the polyamides. C_r^* and C_i^* in Figure 1 are the parameters already defined in Experimental. The results obtained in this examination were summarized as follows: (1) The values of C_i^* and C_r^* are dependent on the amine component rather than on the acid component of polyamide. (2) Polyamides derived from aromatic primary diamine, (D) and (E) show 15–20 times as large C_i^* value and one half to one tenth as small C_r^* value as those of polyamides from aliphatic diamines. (3) Tertiary polyamides such as piperazine polyamides, (F) and (G), show smallest C_r^* and C_i^* values, indicating the highest stability among the polyamides examined. (4) Polyamides from aliphatic primary diamines, (A) and (B) have a larger C_r^* value than that of the other type of polyamides.

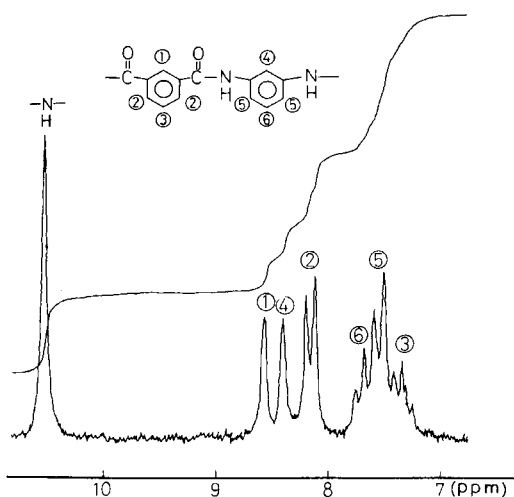


Fig. 2(a). ^1H NMR spectrum of poly(*m*-phenyleneisophthalamide) in *N*-methylpyrrolidone at 25°C.

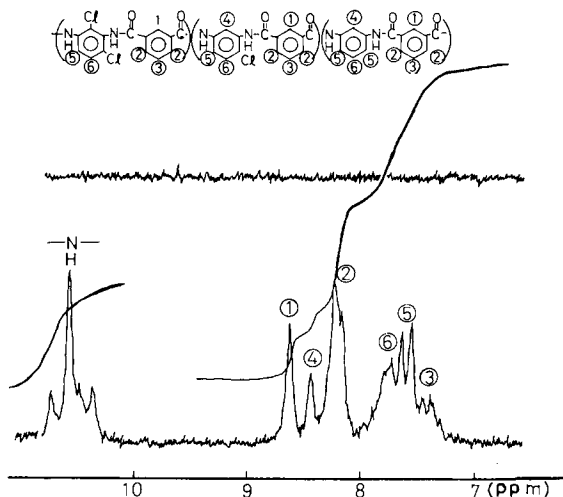


Fig. 2(b). ¹H NMR spectrum of poly(*m*-phenyleneisophthalamide) in *N*-methylpyrrolidone after the reaction with hypochlorous acid.

Larger Ci^* value implies irreversible chlorination or deterioration of polyamide and such polyamides are not suitable as a chlorine resistant membrane material for reverse osmosis. Larger Cr^* value, on the other hand, reflects the reactivity of active chlorine to polyamide, but the reacted chlorine still retains its oxidation capability and is easily dechlorinated by a reducing agent. This implies that the polyamide with higher Cr^* value may give a chlorine sterilizable membrane if the dechlorinating agent does not alter the chemical structure of the polymer.

Figures 2 and 3 show the ¹H NMR of the reaction products of poly(*m*-phenyleneisophthalamide) and poly(ethyleneisophthalamide) with hypochlorous acid. Table II gives the chlorine content of the polymer before and after the hypochlorous acid treatment. Remarkable change of ¹H NMR

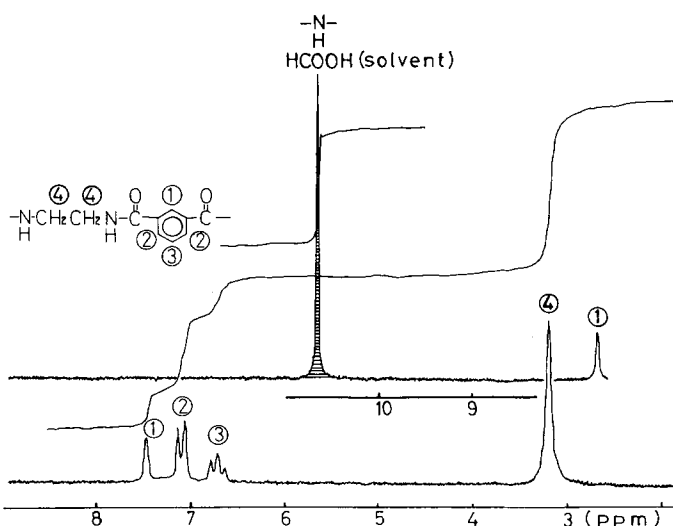


Fig. 3(a). ¹H NMR spectrum of poly(ethyleneisophthalamide) in HCOOH at 25°C.

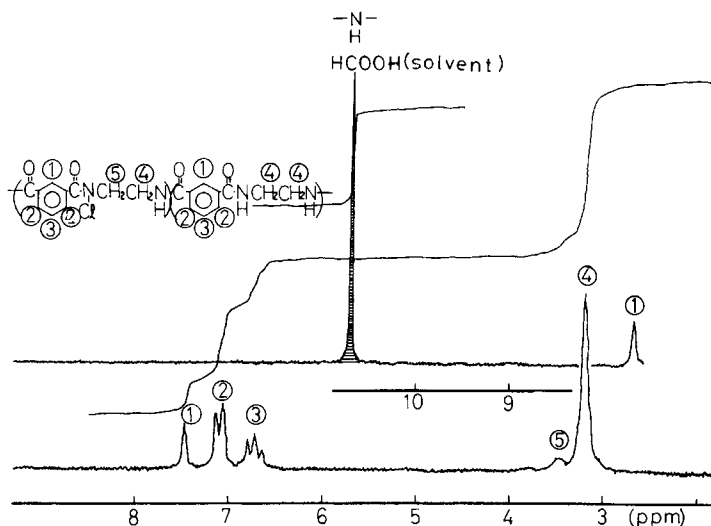
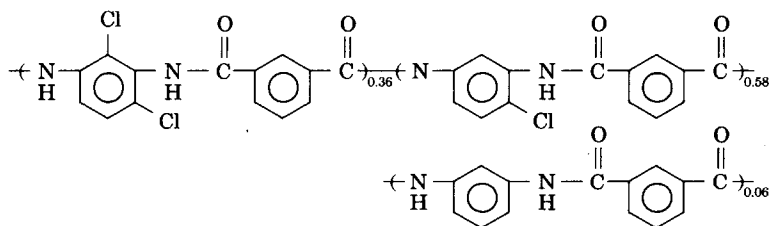


Fig. 3(b). ^1H NMR spectrum of poly(ethyleneisophthalamide) in HCOOH at 25°C after the reaction with hypochlorous acid.

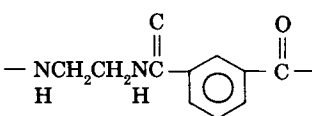
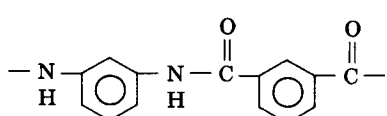
signal of poly(*m*-phenyleneisophthalamide) was observed after the hypochlorous acid treatment. The peak of amide proton at 10.52 ppm splits into three (10.36, 10.57, 10.72 ppm) after the treatment indicating the formation of three types of amide segment. The proton chemical shift of poly(*m*-phenyleneisophthalamide) before the treatment was assigned and is shown in Figure 2(a).

It should be noted that the ratio of nucleus protons (1, 2, 4, 3+5+6) changes from 1:2:1:4 to 1:2.1:0.64:2.9 after the hypochlorous acid treatment, and especially the change in the signal intensity of the protons 4 and 5 was significant. In addition to this proof of the changed structure of the polymer by ^1H NMR, the content of chlorine atom in the polymer was examined before and after the treatment with hypochlorous acid. Table II shows chlorine content of the polyamides (D) and (B) before and after the treatment. The polyamide (D) gave 15.80% of chlorine content. Thus, we estimated the structure of the polymer as follows:



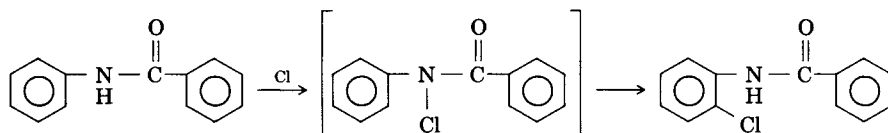
The chlorinated polyamide (II) could not be dechlorinated by a reducing agent, indicating that the above reaction is irreversible. Similar reaction of an aromatic amide with an active chlorine has been reported by Orton¹² on the chlorination of benzamide. The reaction scheme was postulated as follows:

TABLE II
Chlorine Content of Polyamides after Hypochlorous Acid Treatment^a

		
Initial	0.01%	0.03%
After the treatment	3.57% (0.97 meq/g) ^b	15.80% (0.70 meq/g) ^b

^a Active chlorine concentration: 500 ppm; immersion time (h); pH 6.0

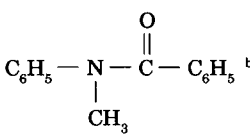
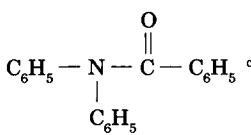
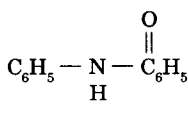
^b meq chlorine/polymer.



In order to investigate whether poly(*m*-phenyleneisophthalamide) was chlorinated directly at the aromatic nucleus or via *N*-chlorination, we performed the chlorine resistance test of *N*-methylbenzanilide, *N*-phenylbenzanilide, and benzanilide. Table III gives the results of the test. Benzanilide gave the reaction product which is chlorinated at aromatic nucleus, but the amides from secondary amines, on the other hand, gave no reaction product. This may suggest that the direct chlorination at an aromatic nucleus is much less feasible and "via *N*-chlorination scheme" seems to be more practical in the nucleus chlorination of polyamides from aromatic primary diamines. Thus, poly(*m*-phenyleneisophthalamide) was supposed to be chlorinated in the similar manner to Orton rearrangement through *N*-chlorination.

Figure 3 shows the ¹H NMR spectra of poly(ethyleneisophthalamide) (III) before and after the hypochlorous acid treatment. Judging from the relative intensity of methylene protons (3.30 and 3.20 ppm) observed after hypochlorous acid treatment [Fig. 3(b), the proton 4:5 = 8.5:1] and the chlorine content in the polymer (3.57%; see Table II), the structure of the reaction product was assumed as follows:

TABLE III
Chlorine Resistance of Aromatic Amides from Secondary and Primary Aromatic Amine^a

			
Cl ^d	0.02 eq/mol	0.01 eq/mol	0.71 eq/mol
Cr ^e	0.03	0.02	0.03

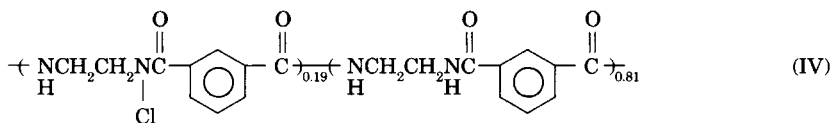
^a The test conditions: HOCl conc., 500 ppm, PH 6.0, temp 23°C, the reaction time 15 h.

^b Prepared by solution condensation of *N*-methylaniline with benzoyl chloride.

^c Prepared by solution condensation of *N,N*-diphenylamine with benzoyl chloride.

^d The amount of chlorine irreversibly reacted with amide.

^e The amount of chlorine adsorbed reversibly on amide.

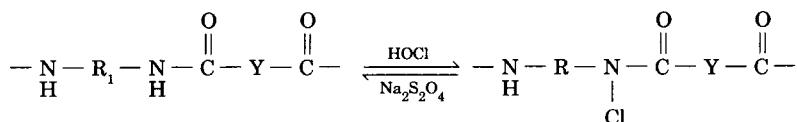


Schultz¹³ reported the similar reaction of 6-nylon with chlorine monoxide (Cl_2O) in carbon tetrachloride leading to the formation of *N*-chlorinated products. Treatment of (IV) with an aq sodium hydrosulfite and subsequent ¹H NMR measurement gave the same chart as that of (III), showing reversible dechlorination of (IV) to (III).

Tertiary amides such as poly(isophthaloyl piperazine) and *N*-methylbenzanilide did not interact with hypochlorous acid, presumably because of the absence of an amide proton.

Figure 4 shows the change of reduced viscosity of representative polyamides before and after the hypochlorous acid treatment. No change in the viscosity of the polyamide was observed. Consequently, any type of polyamides did not undergo bond cleavage upon the treatment with hypochlorous acid.

As a consequence, the modes of interaction of polyamides with hypochlorous acid are classified into three: (1) no reaction in case of tertiary polyamides; (2) reversible chlorination at amide nitrogen,



where R_1 is an aliphatic radical and Y is an aliphatic or aromatic radical; and (3) irreversible chlorination



where R_2 is an aromatic radical.

CONCLUSION

Diamine components play an important role in determining the reactivity of polyamides to oxidative chlorine. Aromatic primary diamines give polyamides which are susceptible to oxidative chlorination resulting in irreversible reaction at the aromatic nucleus. Aliphatic primary diamines, on the other hand, give polyamides which react at the amide nitrogen to yield *N*-chlorinated amide. The *N*-chlorinated amide can be reversibly regenerated to the initial amide by the treatment with reducing agent. Tertiary polyamides are inactive towards to oxidative chlorine.

On the basis of these results, the tertiary polyamides are the preferred candidates for a chlorine-resistant membranes and the aliphatic secondary polyamides are the next best. The polyamides from aromatic primary diamines seem to be least favorable for a chlorine-resistant membrane because

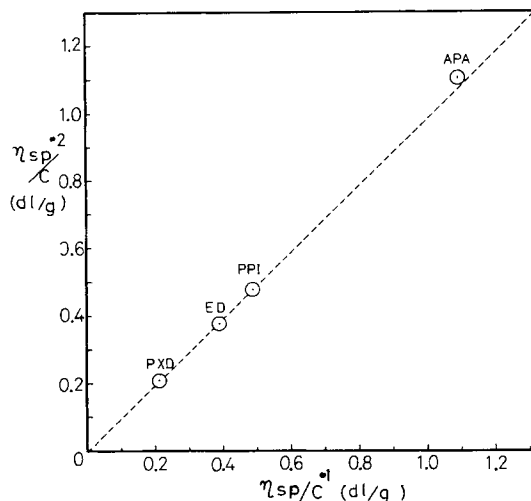


Fig. 4. The reduced specific viscosity of polyamides before and after the reaction with hypochlorous acid: (APA) poly(*m*-phenyleneisophthalamide); (PPI) poly(isophthaloyl piperazine); (ED) Poly(ethyleneisophthalamide); (PXD) poly(*p*-xylyleneterephthalamide).

they are susceptible to active chlorine resulting in nucleus chlorination, which may enhance membrane hydrophobicity.

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