

Influence of Chemical Structure of Isophthaloyl Dichloride and Aliphatic, Cycloaliphatic, and Aromatic Diamine Compound Polyamides on Their Chlorine Resistance

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ABSTRACT: The influence of the chemical structures of the polyamides on chlorine resistance was studied by measuring their chlorine uptake rates. They were prepared from isophthaloyl dichloride and aliphatic, cycloaliphatic, or aromatic diamines by the solution or interfacial polycondensation method. This study showed that the chlorine resistance was dependent on the chemical structures of the diamine compounds used in the synthesis of the polyamides. We concluded that the polyamides comprising the diamine components with the following chemical structures had higher chlorine resistance: aliphatic or cycloaliphatic diamine compounds with a secondary amino group, aliphatic or cycloaliphatic diamine compounds with a shorter methylene chain length between end amino groups, and aromatic diamine compounds with methyl or chlorine substituents at the ortho position of the amino groups. Chlorine resistance is related to the basicity of the aliphatic and aromatic diamines used. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 201–207, 2000

Key words: chlorination; chlorine resistance; aliphatic polyamide; cycloaliphatic polyamide; aromatic polyamide

INTRODUCTION

Recently, many researchers have been studying new synthetic reverse osmosis (RO) membranes from polyamides, in particular, aromatic polyamides for desalination.

Aromatic polyamide membranes possess superiority in terms of chemical and biological resistances to cellulose acetate membranes. However, it has been pointed out that aromatic polyamides are very sensitive to oxidation by chlorine.

Glater and Zachariah¹ reported the sensitivity of the B-10 membrane [Nomex-type aromatic polyamide, poly(*m*-phenylene-isophthalamide)] to

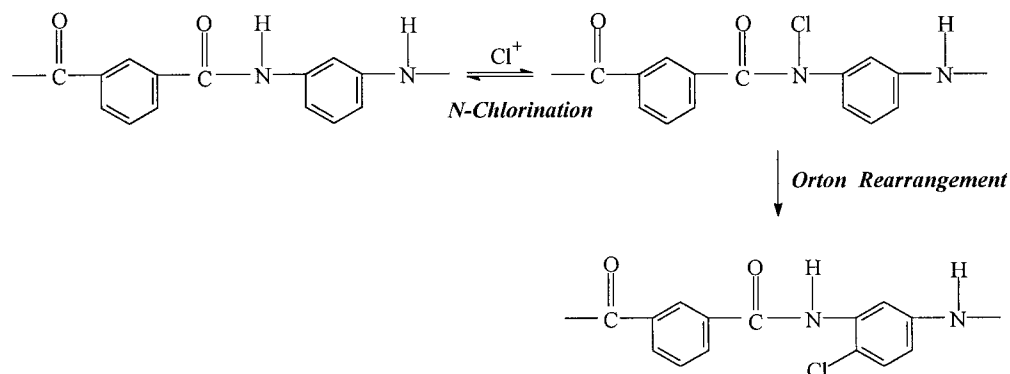
a chlorine disinfectant (active species: Cl⁺), which is commonly used in the field of seawater desalination and food processing, by monitoring the decay of the membrane performance. It was found that the ortho positions of the aromatic diamine compound *m*-phenylenediamine was easily substituted by chlorine (Cl⁺), which caused the decrease of its RO performance (i.e., the flux rate of the product water and salt rejection).

Kawaguchi and Tamura² also reported that chlorine substituted aromatic polyamide is produced under the condition of chlorine infusion.

The Nomex-type aromatic polyamide is supposed to be chlorinated in the manner of an Orton rearrangement³ through N-chlorination as shown in the structure below.

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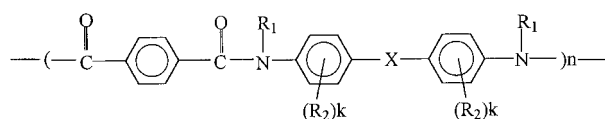
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Credali et al.⁴ and Parrini⁵ studied a class of polymers based on piperazineamide and found that they have high resistance to temperature, pH variation, and chlorine. Novel composite membranes with chlorine resistance were prepared from aliphatic amines such as diethylenetriamine and ethylenediamine and acid chlorides such as isophthaloyl chloride and trimesoyl chloride.⁶ In particular, the membrane from ethylenediamine and trimesoyl chloride is superior in chlorine resistance to the FilmTec FT-30 membrane⁷ that is formed from *m*-phenylenediamine and trimesoyl chloride. As mentioned above, several kinds of chlorine resistant membranes have been developed with the use of aliphatic amine, cycloaliphatic amine and phenylenediamine compounds.

Attention should be paid to the study of the reactivity of aromatic, aliphatic, and cycloaliphatic polyamides with active chlorine to get higher chlorine resistant RO membranes from them.

We previously studied the relationship between the chemical structure of the bis-amino-phenyl compounds in the structure below and their chlorine resistance by measuring the chlorine uptake rate and found out that the efficiency of chlorine resistance is in the order of $\text{---CON(CH}_3\text{)---} > \text{---SO}_2\text{---} > \textit{ortho}\text{-CH}_3$ and is dependent on the number of CH_3 substituents and the position of the $\text{---SO}_2\text{---}$ groups.⁸



($R_1, R_2 = \text{H, CH}_3$, $X = \text{O, CH}_2, \text{SO}_2$, $k = 0, 1, 2$)

However, the difference in chlorine resistance among polyamides prepared from the aliphatic diamine, cycloaliphatic diamine, and phenylenediamine compounds has not been made clear.

This article describes the influence of the chemical structures of the diamine compounds used in aliphatic, cycloaliphatic, and aromatic polyamides on their chlorine resistance, which is their chlorine uptake rate.

EXPERIMENTAL

Preparation of Polyamides

Polyamides were prepared from the commercial grade isophthaloyl dichloride and aliphatic, cycloaliphatic, or aromatic diamine compounds shown in Table I by low temperature solution polymerization or interfacial polymerization as described previously.^{8,9}

Measurement of Reduced Viscosities of Polyamides

The reduced viscosities of the polyamides were measured at 30°C with a polymer concentration of 0.5 g/dL in *N*-methyl-pyrrolidone (NMP).

Measurement of Chlorine Uptake Rates or Amounts of Chlorine Uptake of Polyamides

The polyamides with reduced viscosity of more than 0.5 were used for this study. The polyamides tested were 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 μm or less was added to 500 mL of an aqueous 220 ppm (pH 5) chlorine solution obtained by mixing sodium hypochlorite (chlorine source) and phosphoric acid, potassium dihydrogen phosphate, and dipotassium hydro-

Table I Preparation Results of Polyamides Used in Study

Diacid Chloride	Diamine Compound	Polyamide	Viscosity (dL/g)
Isophthaloyldichloride	Ethylenediamine	C2	1.22
	Hexamethylenediamine	C6	0.66
	<i>iso</i> -Propylenediamine	C3	0.96
	<i>N,N'</i> -Dimethylethylenediamine	C2Me2	1.20
	<i>N,N'</i> -Diphenylethylenediamine	C2Ph2	1.08
	Piperazine	Pi	3.3
	Homopiperazine	HPi	1.16
	<i>trans</i> -2,5-Dimethylpiperazine	PiMe2	2.34
	Dipiperidylpropane	C3Py2	1.11
	<i>para</i> -Phenylenediamine	Ar	1.94
	2-Methyl- <i>p</i> -phenylenediamine	ArMe	0.51
	2,5-Dimethyl- <i>p</i> -phenylenediamine	ArMe2	0.78
	2-Chloro- <i>p</i> -phenylenediamine	ArCl	1.36
	2,5-Dichloro- <i>p</i> -phenylenediamine	ArCl2	0.64

gen 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 uptake rate was obtained by measuring a change in the chlorine concentration with the lapse of time of the solution, the difference of the chlorine uptake rate thus obtained and that of the blank test previously conducted, (i.e., a rate at which the chlorine concentration of the solution containing no polyamide decreases spontaneously) was taken as the chlorine uptake rate of the polyamide itself. The amount of chlorine absorbed during the first hour was expressed in its molar ratio to a monomer unit of polyamide (mol Cl⁺/mol monomer unit). The smaller value of the molar ratio means higher chlorine resistance of the polyamide.

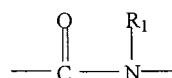
RESULTS AND DISCUSSION

Preparation of Polyamides with Different Chemical Structures

We assumed that the chlorine resistance of aliphatic and aromatic polyamides could be improved by the introduction of a —CONR— tertiary amide bond, substituents at the α -position carbons of the amino group of aliphatic diamine compounds, or substituents at the ortho positions of the benzene nucleus of an aromatic diamine compound as shown below because the inhibitions of N-chlorination and Orton rearrangement due to the masking of active sites or steric hindrance by the substituents R1 are expected to lead to the

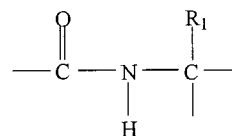
depression of their chlorine uptake as shown in this structure:

Masking of active site N:

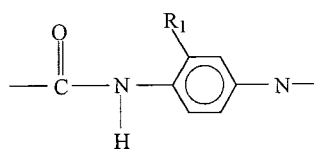


No N-chlorination

Increase of steric hindrance around N:



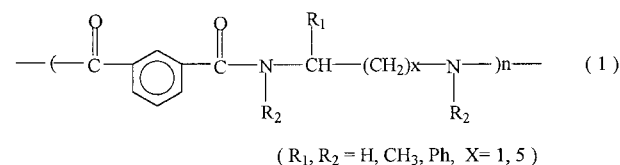
Slow N-chlorination



Slow N-chlorination

Then aliphatic, cycloaliphatic, and aromatic polyamides with different chemical structures represented by the general formulas (1), (2), and (3) shown below were prepared to verify the above assumptions by evaluating their chlorine uptake rates according to the above experimental procedure.

Polyamides(1) prepared with aliphatic diamine compounds:



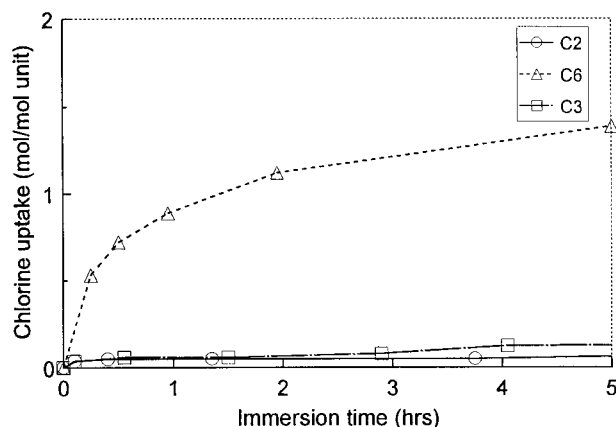
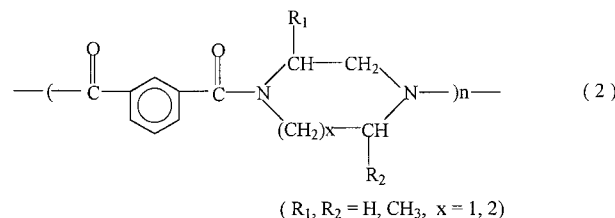
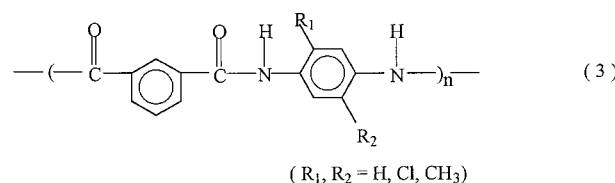


Figure 1 Chlorine uptake curves of aliphatic polyamides with general formula (1).

Polyamides(2) prepared with cycloaliphatic diamine compounds:



Polyamides(3) prepared with aromatic diamine compounds:



The polymerization conditions depended on the diamine components and the results obtained are summarized in Table I.

Relationship between Chemical Structures of Aliphatic and Aromatic Polyamides and Their Chlorine Resistance

Chlorine uptake curves of the aliphatic, cycloaliphatic, and aromatic polyamides with different chemical structures from the above diamine compounds are shown in Figures 1–5. Their chlorine resistance estimated from the chlorine uptake curves are summarized in Table II.

Relationship between Chemical Structures of Aliphatic Polyamides with General Formula (1) and Their Chlorine Resistance

The chlorine uptake curves of polyamides (1) (C2, C3, C6, MeC2, and PhC2) are shown in Figures 1 and 2.

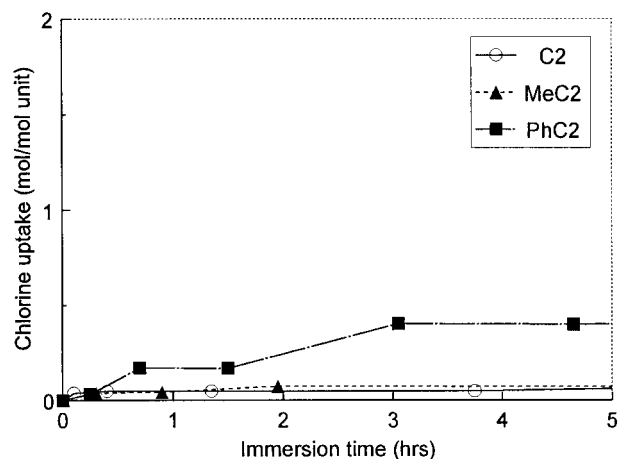


Figure 2 Chlorine uptake curves of aliphatic polyamides with general formula (1).

Figure 1 shows the effects of the $\text{---}(\text{CH}_2)_n\text{---}$ main chain between amino groups and ---CH_3 substituents at the α -position carbons of an amino group in the aliphatic diamine compounds on the chlorine uptake rate. The chlorine uptake rate of C2 is higher than that of C6, which means that the chlorine uptake rates are influenced by the length of the $\text{---}(\text{CH}_2)_n\text{---}$ chain. The base strength increases progressively with the introduction of further methylene groups between the amino groups.

Figure 6 shows the relationship between the $\text{p}K_a$ values of alkylene diamine compounds¹⁰ used in the polyamides (C2, C3, and C6) and their chlorine uptake rates. The basicity of the amide bond of C6 is higher than that of C2, which results in the higher chlorine uptake rate of C6. Although

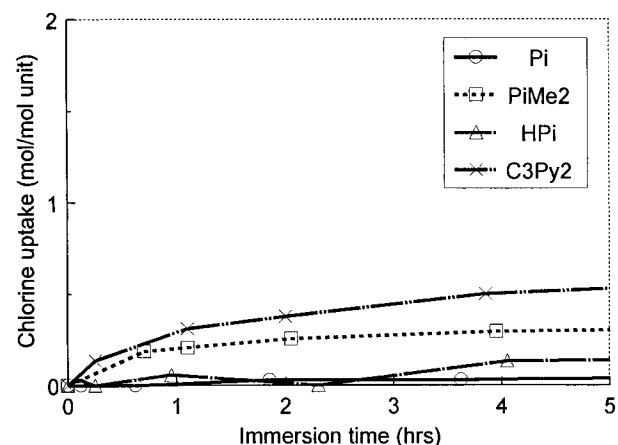


Figure 3 Chlorine uptake curves of cycloaliphatic polyamides with general formula (2).

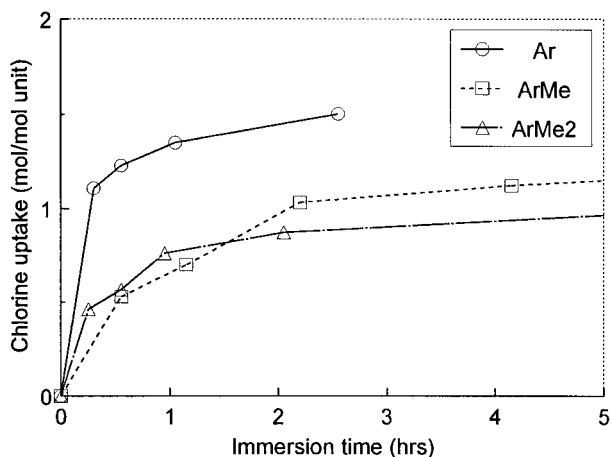


Figure 4 Chlorine uptake curves of aromatic polyamides with general formula (3).

there is some difference in the basicity of C2 and C3, there is no difference in their chlorine uptake rate. We concluded that the methyl substituent at the α -position carbons of propylenediamine has a steric effect on the reduction of chlorine uptake rate.

Figure 2 shows the effect of methyl and phenyl substituents on the amide bond on the chlorine uptake rates. Introduction of a tertiary amide bond like $-\text{CON}(\text{CH}_3)-$ has a large influence on the decrease of chlorine uptake rate, which is due to the inhibition of N-chlorination by the methyl substituent. However, the introduction of a tertiary amide bond like $-\text{CON}(\text{Ph})-$ promotes the chlorine uptake rate. This is probably caused by the weak coordination of chlorine to the $-\text{CON}(\text{Ph})-$ bond, which is stabilized by the phenyl group as shown below.

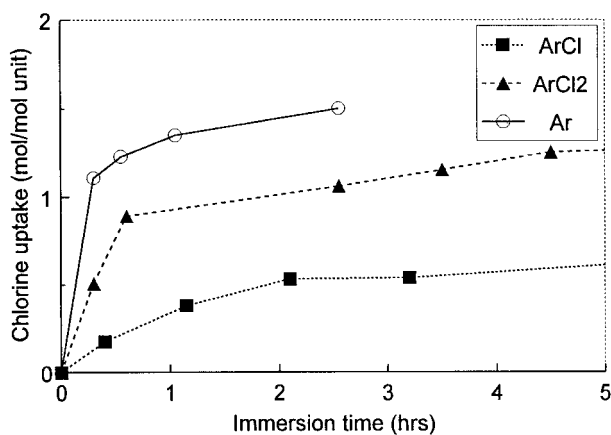


Figure 5 Chlorine uptake curves of aromatic polyamides with general formula (3).

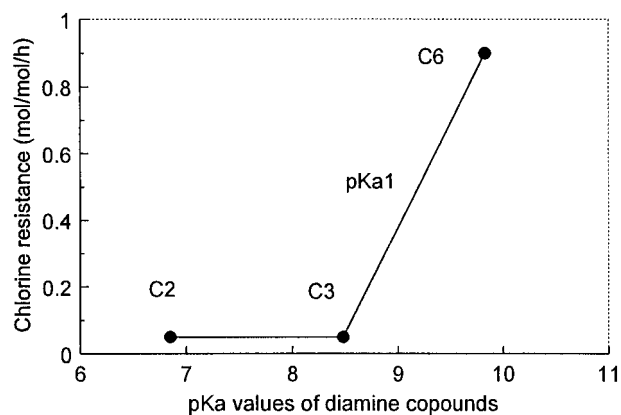
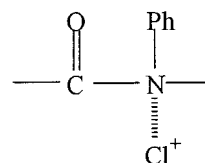


Figure 6 Relationship between $\text{p}K_a$ values of aliphatic diamine and chlorine resistance of polyamides (1).



Relationship between Chemical Structures of Cycloaliphatic Polyamides with General Formula (2) and Their Chlorine Resistance

The chlorine uptake curves of polyamides (2) (Pi, PiMe2, HPi, and C3Py2) are shown in Figure 3. The chlorine uptake curves of Pi and HPi are almost the same. The chlorine uptake rate of PiMe2 with two methyl substituents is higher than that of Pi. The chlorine uptake rate of C3Py2 with further methylene groups between the piperidine ring is a little higher than that of Pi.

The chlorine resistance of the polyamides is ordered as follows.

higher Pi > HPi > PiMe2 > C3Py2 lower

The introduction of a tertiary amide bond is very effective for the suppression of the chlorine uptake rate in the same way as C2Me2 is with the tertiary amide bond $-\text{CON}(\text{CH}_3)-$.

The chlorine uptake rates of polyamides (2) rise with the increase of the number of carbon chains like methylene and methyne groups between end amino groups in a cycloaliphatic diamine component. This effect is ascribed to the difference in the basicity of the amide bond, which increases with the increase of the above carbon

Table II Relationship between Chemical Structures of Polyamides and Their Chlorine Resistance

Polyamides	Chemical Structures of Diamine Compounds Used in Polyamides	n	R1	R2	Chlorine Resistance (mol/mol/hr)
C2		1	H	H	0.05
C3		1	CH ₃	H	0.05
C2Me2		1	H	CH ₃	0.05
C2Ph2		1	H	C ₆ H ₅	0.15
C6		5	H	H	0.9
Pi		1	H	H	0.02
PiMe2		1	CH ₃	CH ₃	0.02
HPi		2	H	H	0.05
C3Py2		—	—	—	0.3
Ar		—	H	H	1.3
ArMe		—	CH ₃	H	0.65
ArMe2		—	CH ₃	CH ₃	0.8
ArCl		—	Cl	H	0.35
ArCl2		—	Cl	Cl	0.8

chain length in a cycloaliphatic diamine component of polyamides (2).

There is a little difference in the chlorine uptake rate between Pi and PiMe2 polyamides, which means methyl substituents at the α -position carbons of *trans*-2,5-dimethylpiperazine have little steric effect on the reduction of chlorine uptake rate.

Relationship between Chemical Structures of Aromatic Polyamides with General Formula (3) and Their Chlorine Resistance

The chlorine uptake curves of aromatic polyamides (3) (Ar, ArMe, ArMe2, ArCl, and ArCl2) are shown in Figures 4 and 5.

Figure 4 and 5 show that the introduction of methyl or chlorine substituents into the ortho positions of *p*-phenylenediamine has a large effect on the decrease of the chlorine uptake rate. In particular, the introduction of a mono chlorine substituent has the largest effect on the decrease of chlorine uptake rate among aromatic polyamides (3). The chlorine uptake rates of ArMe2 and ArCl2 are a little higher than those of ArMe and ArCl.

Their chlorine resistance is ordered as follows:

higher ArCl > ArMe > ArMe2 > ArCl2 > Ar lower

Figure 7 shows the relationship between the chlorine uptake rate of the aromatic polyamides (Ar, ArMe, ArMe2, and ArCl) and the estimated pK_a values of the aromatic diamine components used in the polyamides, which are inferred from the pK_a values of aniline and aniline derivatives (2-methylaniline, 2,5-dimethylaniline, and 2-chloroaniline)¹⁰ that are similar in chemical structure to the aromatic diamine compounds used. The chlorine uptake increases with the increase of the pK_a values, which means the dependence of chlorine uptake on the basicity of the nitrogen atom of

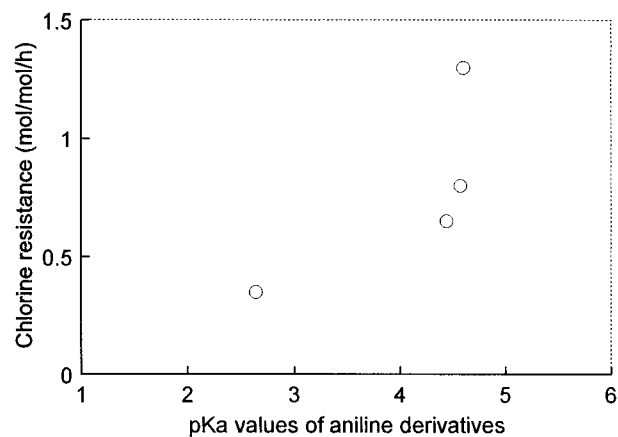
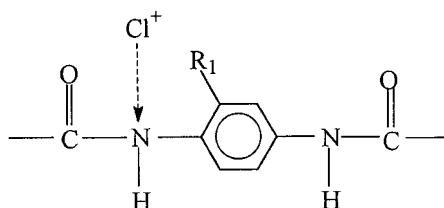


Figure 7 Relationship between pK_a values of aniline derivatives and chlorine resistance of polyamides (3).

the amide bond. The attack of electrophilic chlorine on nitrogen of the amide bond is determined by its basicity.



The reason why the chlorine uptake rate of ArCl₂ is faster than that of ArCl is that one chlorine substituent at the ortho position of the para-phenylenediamine has enough of an electron withdrawing effect to decrease the electron density of the benzene nucleus and nitrogen of the amide bond. However, ArCl₂ with two chlorine substituents at the ortho position on the benzene nucleus of the aromatic diamine component is more easily attacked by active chlorine than ArCl, because ArCl₂ is a higher base than ArCl because of steric hindrance (i.e., inhibition of the coplanarity between the amide bond and the benzene nucleus) by two chlorine substituents in analogy with the ArMe₂.

CONCLUSIONS

The influence of the chemical structures of aliphatic, cycloaliphatic, and aromatic polyamides on chlorine resistance was studied by measuring their chlorine uptake rates. This study showed that the chlorine resistance of the polyamides is dependent on the chemical structures of the diamine components used, and the use of the following diamine compounds are effective for the improvement of chlorine resistance:

1. aliphatic or cycloaliphatic diamine compounds with a secondary amino group,

2. aliphatic or cycloaliphatic diamine compounds with a short methylene chain length between end amino groups, and
3. aromatic diamine compounds with a mono Cl or CH₃ substituent at the ortho position of the amino groups.

Chlorine resistance is related to the basicity of the aliphatic and aromatic diamines used.

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