Oxidative Degradation of Polyamide Reverse Osmosis Membranes: Studies of Molecular Model Compounds and Selected Membranes

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ABSTRACT: Selected aromatic amides were used to model the chemical reactivity of aromatic polyamides found in thin-film composite reverse osmosis (RO) membranes. Chlorination and possible amide bond cleavage of aromatic amides upon exposure to aqueous chlorine, which can lead to membrane failure, were investigated. Correlations are made of the available chlorine concentration, pH, and exposure time with chemical changes in the model compounds. From the observed reactivity trends, insights are obtained into the mechanism of RO membrane performance loss upon chlorine exposure. Two chemical pathways for degradation are shown, one at constant pH and another that is pH-history dependent. An alternative strategy is presented for the design of chlorine-resistant RO membranes, and an initial performance study of RO membranes incorporating this strategy is reported. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1173–1184, 2003

Key words: polyamides; reverse osmosis; membranes; chlorination; degradation

INTRODUCTION

Thin-film composite membranes that use aromatic polyamides as the barrier layer are widely employed in the purification of water.[1] It is well documented that the performance of such membranes declines[1,2] [i.e. flux increases and salt rejection drops below reverse osmosis (RO) specifications] after exposure to an oxidizing environment (e.g., 500–2000 ppm·hr of chlorine exposure),[3–7] usually from sodium hypochlorite that is used to clean the membrane module or found in residual amounts as a disinfecting agent. Because this situation raises both basic and practical questions, it has been of interest to understand the mechanism of membrane degradation and find ways to increase the lifetime membrane materials by making them resistant to oxidizing agents.[1]

The polyamide membrane degradation effect is known to be pH dependent[8]; several groups have studied the mechanism and sought ways to prevent the degradation.[9–17] Glater et al.[2] published a review of previous efforts in 1994. In particular, there are several cases where insights into a polymer's chemical behavior have been generated from model compounds. Lowell et al.[18] found they could predict the chlorine sensitivity of several types of interfacially polymerized materials by analyzing the extent of chlorination in analogous model systems. Khanna and coworkers[19] showed that the mechanism of thermal decomposition in aromatic polyamides could be determined using amide model compounds. Finally, Kawaguchi and Tamura[17] reported that two chemical processes occur in polyamides and amide molecular model compounds upon chlorine exposure, a reversible N[sbond[H bond chlorination and an irreversible aromatic ring chlorination (Fig. 1). Some also believe these two processes precede cleavage of the polymer chain and interchain crosslinks, most likely at the amide linkage.[10,16]

The previous model compound studies have sparked efforts to modify the polyamides used as barrier layers, to increase chlorine resistance. Strategies have involved both the removal of the N—H functionality and adding electron-withdrawing groups to the amino aromatic rings. Singh[9] reported that membranes soaked in nitric acid showed improved chlorine resistance, presumably because of the addition of nitro groups to aromatic rings in the polyamide. These electron-withdrawing groups deactivate the aromatic ring to electrophilic chlorine addition. Unfortunately, along with increased chlorine resis-

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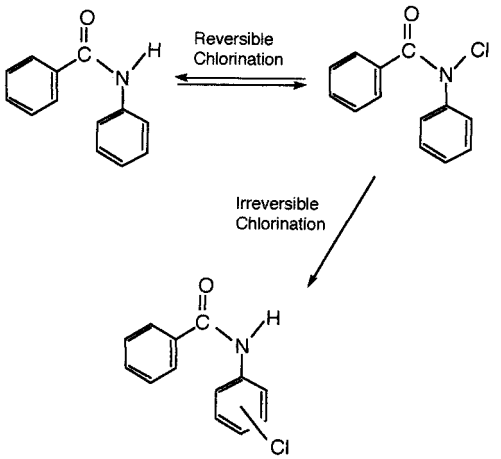


Figure 1 Proposed mechanism of chlorination in polyamides.

tance, these modified membranes suffered significant losses in salt rejection, making them ineffective RO membranes. Another effective strategy for increasing the chlorine resistance is the removal of the N—H functionality from the polyamide. This can be accomplished by substitution of piperazine, a secondary amine, for aromatic primary diamines during membrane formation.[20–22] The resulting membranes show increased chlorine resistance (e.g., exposures up to about 24,000 ppm·hr), but salt rejections were lower than that of aromatic diamine-based membranes. These examples illustrate the compromise that occurs between salt rejection and chlorine resistance that hinders the development of RO membranes with improved chlorine resistance.

One reason salt rejection and chlorine resistance have not been optimized simultaneously may be attributed to the lack of information correlating the chemical mechanism of chlorine degradation with loss of salt rejection. Several chemical changes can occur in the polyamide as a result of chlorine exposure, but it is unknown which is primarily responsible for the loss of salt rejection. Some investigators propose a three-step process in which N—H and aromatic ring chlorination precedes depolymerization, which ultimately renders the membrane useless. There is debate whether polyamide chain cleavage causes membrane failure and, if it does, whether it occurs by oxidation or hydrolysis of the polyamide.[2] One goal of the study reported herein is to correlate the chlorine exposure at a given pH to chemical and/or morphological changes, in an attempt to develop a better understanding of the mechanism of membrane failure. Furthermore, if the chemical changes important to the loss in salt rejection can be better understood, improved strategies to prevent this process might be devised. Our studies are described below.

EXPERIMENTAL

Materials

meta-Phenylene diamine (MPD), 2,4-dichloroaniline, 3-aminobenzyl alcohol, 4-fluoroaniline, 4-(thiomethyl)aniline, benzoyl chloride, acetic anhydride, 3-amino-α-methylbenzyl alcohol, 3,5-diaminobenzylalcohol hydrochloride, 3-nitroaniline, phenyl acetate, phosphate buffers (pH = 4, 7, and 10), diethyl ether, iron (powder), sodium hydroxide, hydrochloric acid, sodium phosphate, borax, benzyl alcohol, chloroform, methylene chloride, acetone-d_6, D_2O, benzene-d_6 and chloroform-d_1, absolute ethanol, and methanol (Aldrich, Milwaukee, WI) were used as received. Acetanilide (**1**, Aldrich), *N*-ethylacetanilide (**5**, Eastman Kodak, Rochester, NY), 2-chloroacetanilide (Eastman Kodak), and 4-nitroacetanilide (**10**, Eastman Kodak) were recrystallized from water/ethanol mixtures. Aniline (Aldrich) and trimesoyl chloride (Aldrich) were distilled before use. Buffers for pH 8.5 (borax, HCl) and pH 12 (Na_2HPO_4, NaOH) were prepared according to published procedures.[23] Sodium hypochlorite solutions, >4%, available chlorine (Aldrich) were calibrated before use, using iodometric titration.[24]

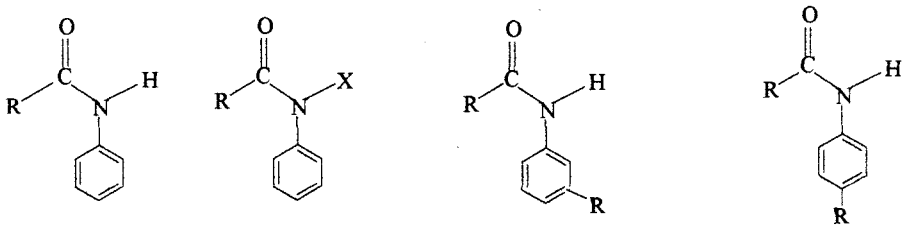
Synthesis of model compounds

Dichloroacetanilide, benzanilide (**2**), 4-thiomethylacetanilide (**12**), 4-flurobenzanilide (**11**), *N*-benzoyl-*m*-phenylenediamine (**9**), 3*N*-acetylaminobenzyl alcohol (**6**), 3*N*-aectylamino-α-methylbenzyl alcohol (**7**), *N,N*-dibenzoyl-*m*-phenylenediamine)[25] (**8**), *t*-butyl hypochlorite,[26] and *N*-chlorobenzanilide[27] (**4**) were synthesized using previously published techniques.[28,29] Compounds were characterized and purity was determined using NMR, GC/MS, and IR spectral analysis.

N-Chlorinated acetanilide (**3**) was synthesized with a modification of the procedure published by Dietze and Underwood.[30] Acetanilide (2–3 g), dissolved in methanol or ethanol, was added to a base solution (NaOH or $NaHCO_3$) that contained 33 mL of >4% available chlorine, NaOCl solution. The reaction was stirred for 10 min and the resulting solid product was filtered and dried *in vacuo*.

Characterization of model compounds

^{1}H-NMR spectra were acquired using a Bruker AM-400 spectrometer (Bruker Instruments, Billerica, MA) referenced to an external TMS standard (δ = 0 ppm). NMR data were transferred and analyzed using Varian software (Varian Associates, Palo Alto, CA). IR spectra were recorded on a Nicolet Impact 410 IR spectrometer (Nicolet Analytical Instruments, Madison, WI), using Omnic 3.1a software. UV-vis spectral data were collected using an HP 8452 diode array spectrophotometer (Hewlett–Packard, Palo Alto, CA),



1, R = Me
2, R = Ph

3, R = Me, X = Cl
4, R = Ph, X = Cl
5, R = Me, X = CH_2CH_3

6, R = Me, R' = CH_2OH
7, R = Me, R' = $CH(OH)CH_3$
8, R = Ph, R' = $N(H)COC_6H_5$
9, R = Ph, R' = NH_2

10, R = Me, R' = NO_2
11, R = Me, R' = F
12, R = Me, R' = SCH_3

Figure 2 Model compounds used in this study. Me = CH_3, Ph = C_6H_5. Not shown are 2-chloroacetanilide, 2,4-dichoroacetanilide, 2,4-dichlorobenzanilide, aniline, diphenylsulfone [$(C_6H_5)_2SO_2$], and phenylacetate [$MeC(O)OC_6H_5$].

fitted with 1-cm quartz cells. GC/MS data were acquired with an HP 5988A system using an HP-5 fused silica capillary column (5% crosslinked phenyl methyl silicone). The parameters used for the GC program were: starting oven temperatures ranged from 80 to 200°C, the injector port temperature was 250°C, the source temperature was 200°C, and the quadrupole detector was maintained at 80°C. The oven was equilibrated for 30 s before each run and the temperature was increased at 6°C/min. Masses were scanned from 30 to 400 amu.

Reactions of model compounds with chlorine

Model compounds (Fig. 2) were subjected to aqueous chlorinating solutions ranging from 1000 to about 1.5 million ppm·hr (0.04 to ~ 20 mol ratios of available chlorine[31] to model compound) and with pH controlled using buffers. To simplify the analysis of our data we classified the chlorine exposure into three categories: high, intermediate, and low. High chlorine exposure is 5000 to 24,000 ppm available chlorine for up to 65 h (molar ratio of chlorine to model compound **8** to about 20). Intermediate chlorine exposures are 1000 ppm from 1 to 46 h (molar ratio ~ 2). A low chlorine exposure is defined as 20 to 75 ppm for 1 to 46 h (molar ratio = 0.04). Adjustments in pH were done by the addition of NaOH. A Corning 430 pH meter (Corning, Corning, NY) was used along with pH paper to monitor the pH before, during, and after chlorine exposure. Reactions were carried out in 20-mL glass vials placed on a shaker for the duration of the chlorine exposure and during the extraction process. Compounds were extracted from the reaction mixture with diethyl ether and methylene chloride. The organic solvents were removed by rotary evaporation, and the solids redissolved in methanol. Two (2.0) microliter samples were injected into an HP 5988A GC/MS system. In all cases, controls were run using identical conditions, but without chlorine, to determine the amount of competing acid/base catalyzed hydrolysis. In selected cases, or if ambiguously defined mass spectra were obtained, additional analysis was done using NMR, IR, and UV-vis spectral analysis to confirm our characterization.

GC/MS calibration for model compounds

Detection limits were established by making aqueous solutions containing 1, 10, and 25 mol % 2-chloroacetanilide relative to the remaining molar percentages (99, 90, 75 mol %) of acetanilide. This calibration showed that by using our extraction method we could easily detect 1% ring chlorination, which for the purposes of this study were quantified as a "minor" degree of chlorination. Detection in our system of "trace" amounts of chlorination corresponds to product amounts lower than 1%. Results reported as "major" chlorination correspond to GC peaks for chlorinated products of relative intensities greater than 25%, as had been determined in calibration studies with 2-chloroacetanilide.

Example GC/MS data for model compounds

In a typical reaction, the amide model compound was allowed to react with aqueous chlorine for several days under constant agitation. After extraction of the aqueous layer with an organic solvent, the samples were prepared for GC/MS analysis. An example data analysis of a GC/MS experiment is as follows: { } = relative GC peak height, ( ) = relative counts at a given mass.

Benzanilide ($C_{13}H_{11}NO$), 0.04 g (2.0×10^{-4} mol) was allowed to react for 62 h with 24,000 ppm available chlorine (~ 1.5 million ppm·hr, reactant molar ratio of ~ 20). Analysis by GC/MS showed GC peaks at retention times 23.0, 23.5, and 26.6 min. The peak at 23.0 min {250} contained masses at *m/z*: 197 (3), M^+; 105 (10), loss of C_6H_6N to give $C_7H_5O^+$; 77 (5), for $C_6H_5^+$. This GC peak correlates to the starting material. The peak with retention time 23.5 min {500} contained

masses, *m/z*: 231 (10) M^+, for $C_{13}H_{10}NOCl$; 105 (200), loss of C_6H_6N to give $C_7H_5O^+$; 77 (100), for $C_6H_5^+$; attributed to one chlorinated isomer, based on retention times for similar compounds, and taken to be the *ortho*-chlorinated isomer. The peak at 26.6 min {400} contained masses at *m/z*: 231 (30) M^+, for $C_{13}H_{10}NOCl$; 105 (85), loss of C_6H_6N to give $C_7H_5O^+$; 77 (40), for $C_6H_5^+$; assigned to a second chlorinated isomer, based on retention times for similar compounds, and taken to be the *para*-chlorinated isomer.

Based on the above analysis, benzanilide exposure to chlorine at pH 7 (1.5 million ppm·hr) results in ring chlorination as a "major" product. The fragmentation pattern shows that there are three separate compounds, two possessing chlorine and one without. The production of $C_7H_5O^+$ and $C_6H_5^+$ is typical for benzanilides,[32] and the presence of these fragments adds credibility to the molecular assignment.

Similar analyses were performed on all GC/MS samples run in this study. It is important to note that the GC/MS experiment was run up to 20 min after the last peak had eluted to ensure that the analysis was complete for other products. Based on the intensity of GC/MS peaks for solvent stabilizers (BHT), it was concluded that all species present in solution were identified at a concentration limit above about 1 ppm.

Hand-cast membranes

Sample Cadotte type (MPD/TMC) membranes were hand-cast onto polysulfone/polyester nonwoven fabric supports provided by Koch/Fluid Systems. The support (8 × 15 cm) was placed in a 2% MPD/water solution for 30 s. Excess MPD solution was removed with a flow of nitrogen gas. The support was then fixed to a glass plate (with tape) so that only the polysulfone surface was exposed. This was dipped into a 0.1% TMC/heptane solution for 15 s and then air dried for 90 s. The resulting membrane was soaked in distilled water for 2–3 min and tested for the presence of a complete polyamide coating using a dye provided by Koch/Fluid Systems. Samples were then shipped to Fluid Systems in distilled water, where salt rejection and flux measurements were made on two membranes of each composition at 220 psig, and with 2000 ppm NaCl for 8 h.

RESULTS AND DISCUSSION

Our model compound studies are described in two parts: examination of (1) the mechanism of membrane degradation caused by chlorine exposure, and (2) model compounds that provide a strategy for formation of oxidatively resistant RO membranes.

Mechanistic studies

The results of model compound chlorination studies are summarized in Tables I, III, and IV. Acetanilide (**1**) and benzanilide (**2**) and derivatives were mainly used as models for the chemistry of aromatic polyamides (Fig. 2). Benzanilide had been shown to be a good model in previous studies[2]; previously, and by us, chlorination of the benzoyl aromatic ring was never observed. Because this aromatic ring does not participate in reactions with chlorine, acetanilide—in which a methyl group replaces the phenyl ring in **2**—is expected to be an equally good model for the chemistry of aromatic polyamides. This assumption is further justified by studies of the Orton rearrangement, in which **1** and **2** were shown to undergo similar chlorinations.[33] Therefore, acetanilide was used extensively in this study because of its higher water solubility and easier elution in the GC/MS experiments.

Because these amide model compounds possess differing degrees of solubility in water as a function of pH and the GC/MS data were taken on subsequent organic solvent extracts, quantification of the data is difficult. However, we have attempted to quantify our results by calibrating the degree of chlorination seen in known mixtures. For purposes of this report we group the extent of ring chlorination into four categories, where aromatic ring chlorination is: (1) a major component of reaction mixture (>25%), (2) a minor component (<25 to 1%), (3) a trace component (<1%), or (4) none (not a detectable component). It would be inappropriate to quantify the chlorination to a greater degree based on GC peaks because these areas are affected by subtle solubility differences of the extracted products. Furthermore, in almost every model compound experiment, even at extremely high chlorine concentrations, some unreacted starting material was found. We believe this is attributed to the time scale and heterogeneous nature of our experiments. Attempts to perform the chlorine exposures under homogeneous conditions provided additional complications described later. It is also important to recognize that crosslinked aromatic polyamides have essentially no solubility in water, a situation that our model systems mimic to some degree.

Several trends are shown in Table I related to aromatic amide chlorination. The first is the dependency of aromatic ring chlorination on pH. At pH 4, an intermediate concentration of available chlorine is enough to cause major aromatic ring chlorination. In contrast, the same amount of available chlorine at pH 7 yields ring-chlorinated amides as minor reaction products. Chlorination of the aromatic ring was never observed at pH 10, even at high chlorine exposures. These results are consistent with observed changes in the equilibrium species found in hypochlorite solutions upon variation of pH. Aqueous chlorine solutions contain three species in equilibrium . At very low pH (e.g., pH = 1) Cl_2 can be as high as 79%.[34] At pH 7 the solution is approximately 80% HOCl and 20% $[OCl]^-$ with trace amounts of Cl_2. At pH values above

TABLE I
pH Dependency of Model Compound Chlorination

Model compound	[NaOCl]	pH	Amount of chlorination product	Number of isomers
1	low	4	minor	1
	low	7	none	0
	inter[a]	4	major	2
	inter	7	minor	1
	inter	10	none	0
	high	7	major	2
	high	10	none	0
2	inter	4	major	2
	inter	7	minor	2
	inter	7	minor	2
	high	12	none	0
	high	7	major	2
	high	10	none	0
8	inter	7	major	1
	inter	10	none	0
5	high	7	minor	2
11	high	7	none	NA[b]
12	inter	7	trace	1
Phenyl Acetate	inter	7	none	NA
Diphenyl Sulfone	inter	7	none	NA

[a] inter, intermediate chlorine concentration.
[b] NA, not applicable.

7 the equilibrium shifts such that the major species becomes $[OCl]^-$; at pH 10, HOCl accounts for less than 1% of the species in solution (Table II). The established "chlorinating strength" (based on oxidation/reduction potentials) of these species is $Cl_2 \sim HOCl > [OCl]^-$,[34] which is consistent with our results showing no ring chlorination when $[OCl]^-$ is the major chlorinating species in solution.

The data in Table I also show the importance of the amide N—H functionality to aromatic ring chlorination. *N*-Ethyl acetanilide (**5**) and phenyl acetate, two model compounds with no N—H functionality, show little or no chlorination (Table I). This is consistent with the previous findings of Kawaguchi and Tamura.[17] Aromatic ring chlorination by the Orton rearrangement depends on the presence of a N—H functionality in the molecule[28] (Fig. 3). However, this is not the only pathway for the addition of chlorine to the aromatic ring. Depending on the pH of the solution and the chlorine concentration, direct chlorination of the aromatic ring by Cl_2 is possible. This is shown experimentally by the minor amount of ring chlorination of **5** that occurs at high chlorine exposures. However, the harsh nature of this chlorinating condition is usually not found in RO membrane applications. Therefore, the Orton rearrangement is taken to be the dominant mode of aromatic ring chlorination in the system under RO operating conditions.

Experiments at extremely high chlorine exposures were conducted to further probe the question of amide bond cleavage. Kawaguchi and others[13,17,35] found no evidence for polyamide chain cleavage in their studies, although there are conflicting reports[10,14,16] of the cleavage of polymer chains under chlorinating conditions. Our GC/MS study shows only one example of possible minor cleavage, and then under only the harshest chlorinating conditions and at constant pH. In this experiment, the amide model compound 2,4-dichloroacetanilide was subjected to conditions far beyond those needed to cause membrane failure.

It is possible that the cleavage products, aromatic amines, further react with chlorine to form higher molecular weight or charged materials that may be harder to detect by GC/MS than their parent amide compound.[36,37] In the measurement of chlorine concentrations colorimetrically, a diamine is often used as an indicator to react with available chlorine.[38] Thus, we reacted aniline with concentrations of chlorine identical to those in our amide model compounds to detect the formation of unextractable cleavage products. The UV-vis absorbancy for these solutions at 1, 10, and 100 dilution factors was taken and used to represent 100, 10, and 1% amide bond cleavage. A representative UV-visible spectrum for 10 dilutions is shown in Figure 4. The shoulders at 320 and 400 nm are consistent with the oxidation products of aromatic amines.[39] These spectra were then compared with UV-vis spectral data from both the initial pH buffer/chlorine solutions and the organic extracts of the amide compounds of interest. Figure 5 shows the UV-vis spectrum for 2,4-dichloroacetanilide exposed to 50,000 ppm·hr. Clearly, there is no absorbancy attributed to the presence of aniline/aqueous chlorine oxidation products. The results of these experiments for all the model compounds in this study are summarized in the top half of Table III. In no cases were absorbancies attributed to aniline oxidation products found in concentrations greater than 1%. This suggests that amide bond cleavage does not occur readily under these chlorinating conditions.

Of the model compounds we studied, only 2,4-dichloroanilide showed possible cleavage products at

TABLE II
Distribution of Species in Aqueous Chlorine Solutions[a]

pH	NaOCl (ppm)	T (°C)	Cl_2 (%)	HClO (%)	ClO^- (%)
4	500	15	0.26	99.72	~ 0
4	1500	15	0.77	99.20	~ 0
4	3500	15	1.76	98.16	~ 0
7	5000	15	0.0017	79.10	20.89
7	7000	15	0.0024	79.10	20.89
7	10,000	15	0.0034	79.10	20.89
7	A[b]	20	0	79.29	20.71
8.5	A	20	0	10.80	89.20
10	A	20	0	0.38	99.62

[a] Compiled from data in The Handbook of Chlorination.[34]
[b] A, calculated value based of equilibrium constant for HOCl dissociation.

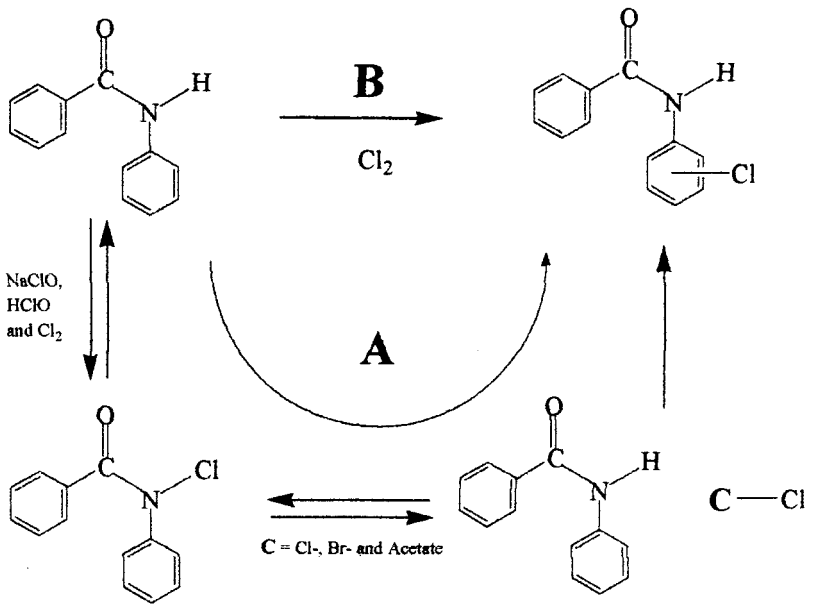


Figure 3 Possible chlorination pathways: (A) the Orton rearrangement; (B) direct ring chlorination by aqueous chlorine gas.

constant pH. However, we believe the chlorinating conditions used in these experiments far exceed those known to cause loss of membrane performance. Therefore, polymer chain cleavage appears not to be the major cause of the decline of performance associated with chlorine exposure of RO membranes at constant pH.

There are indications that exposure of membranes to chlorine under certain conditions improves performance.[40] However, it also is clear that RO membranes are affected by chlorine at basic pH values and will eventually fail after continuous exposure.[8] In our study, we found no evidence for ring chlorination at high pH. Therefore, to understand what chemical changes influence polymer performance at high pH we performed two sets of experiments involving: (1) the analysis of the effect of pH on N—Cl formation and (2) examination of the relative reactivity of free and terminal amino groups with aqueous chlorine. The synthesis of N—Cl amides is well developed,[27,30] and involves reactions of the parent amide with aqueous chlorine and sodium bicarbonate, conditions that afford a pH around 8. We attempted to synthesize *N*-chloroacetanilide (**3**) at pH 8 and pH 12, by substituting sodium hydroxide for sodium bicarbonate. Under strongly basic conditions (pH 12), where $[ClO]^-$ is the major chlorinating species, we found no evidence for N—Cl formation. This implies that $[ClO]^-$ does not react readily to form N—Cl species. This is consistent with our data that show no aromatic ring chlorination occurs at pH 10, a process that we believe proceeds primarily through N—Cl formation.

Our second set of experiments to determine chlorination effects at high pH involves testing the relative reactivity of aromatic amino groups. In the interfacial polymerization reaction used to synthesize polyamide membranes the diamine is usually in high excess.[41] It is likely that under these conditions polymeric chains are terminated with aromatic amino groups and also that the resulting polymer contains free diamine.

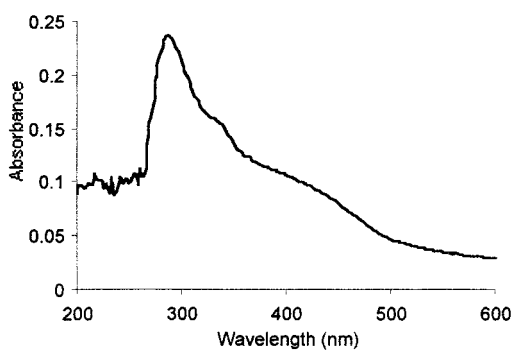


Figure 4 UV-vis data for aniline (diluted by factor of 10) exposed to 50,000 ppm·hr available chlorine at pH 7.

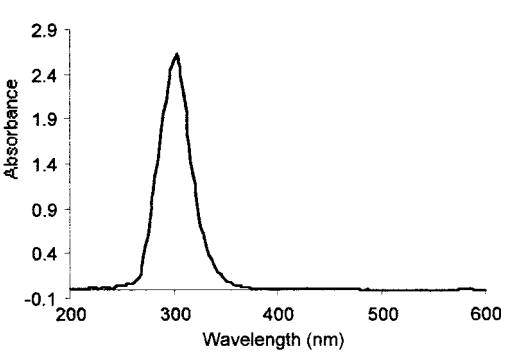


Figure 5 UV-vis data for 2,4-dichloroacetanilide exposed to 50,000 ppm·hr available chlorine at pH 7.

TABLE III
UV-Visible Data for Amide Model Systems

Model compound	[NaOCl]	pH	λ_{max}	Absorbance	Cleavage products
1	inter[a]	7	314	2.75	No
	inter	10	278, 330	0.87, 0.14	No
2	inter	7	288, 336	0.62, 0.23	No
	inter	10	284, 310	0.13, 0.04	No
2,4-Dichloroacetanilide	inter	7	300	2.6	No
	inter	10	294, 330	1.9, 0.14	No
2,4-Dichlorobenzanilide	none	12	320	2.9	No
Aniline	inter	7	298, sh@ 325, 400[c]	0.25, 0.15, 0.1	NA[b]
	inter	12	292, 572	1.4, 0.65	NA
3	none	8.5	300	2.4	No
	none	12	320, sh@ 340, 400	3.1, 2.0, 1.2	Yes
4	none	12	320, sh@ 400	3.0, 1.0	Yes
3 and aniline	none	7	324, 456	3.7, 1.4	NA
9	inter	7	330, sh@ 360	3.1, 2.8	NA
4 and aniline	none	7	320, sh@ 414	3.2, 0.51	NA

[a] inter, intermediate chlorine concentration.
[b] NA, not applicable.
[c] sh, shoulder.

These amine functionalities could then react with chlorine at high pH to form chloramines and other derivatives that could influence the properties of the polymer film. A representative result of our amine study, based on GC/MS and UV-vis experimental data, is shown in Figure 6. We found that aromatic amines ring chlorinate readily at both pH 7 and 10. Various mono- and dichloramines are produced along with azocompounds formed from the coupling of two aromatic amines. Figure 6 shows that free amines react preferentially at pH 7 and 10 over amide model compounds.

A second model system was used to further explore the chemistry of terminal amino groups. Thus, 3-aminobenzanilide (**9**) was suggested as a model system in a previous investigation[42] whereby the system might generate N—Cl species that would form azocoupling products intermolecularly, modeling additional crosslinking within the membrane active layer. This would be consistent with the observed "tightening" of the membrane observed during aqueous chlorine posttreatment.[41] Our GC/MS experiments using **9** showed chlorination of the aromatic ring at pH 7 and 10 (Table IV). We could not detect any azocoupled products by GC/MS analysis.[43] Our UV-vis experiments show absorbancies in the same region, about 400 to 450 nm, as those found for the oxidation of aniline (see Fig. 7). This leads us to believe that terminal amino groups behave in a chemically similar manner to free amino functionalities.

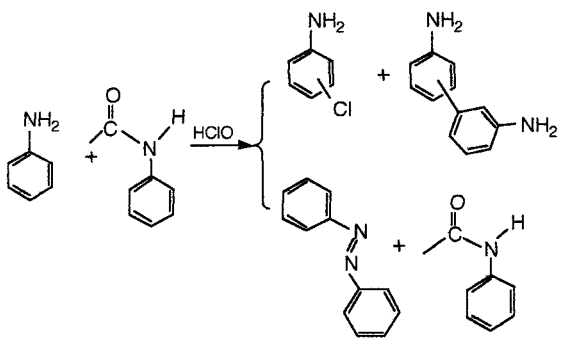


Figure 6 Reaction of aniline and acetanilide with aqueous chlorine.

Overall, these results point to free unreacted diamine and terminal amino groups as participants in the initial polyamide chemical changes that occur upon exposure to chlorine. Our study shows these groups are more reactive than their amide counterparts, which may suggest that amino groups react completely before the amide functionalities are affected. Because the degradation occurs at relatively low chlorine exposures, 500 to 2000 ppm·hr, it is possible that amino groups account for the majority of chemical change that leads to membrane failure.

An important observation from Table IV is that chlorination of the aromatic ring inhibits subsequent chlorine addition. The chlorination of acetanilide leads to the 2- and 4-chloroacetanilide isomers.[44] The reaction of 2-chloroacetanilide leads to the 2,4-dichloroacetanilide and another, uncharacterized, dichloro isomer. Reactions of 2,4-dichloroacetanilide lead to no chlorination at any pH or chlorine concentration. These results are not surprising, given that chlorine is an electron-withdrawing group that deactivates the ring to further electrophilic attack, a well-established

TABLE IV
Reactions of Chlorinated Intermediates

Model compound	[NaOCl]	pH	Degree of chlorination product[a]	Number of isomers	Cleavage products
2-Chloroacetanilide	high	7	major	2	no
2,4-Dichloroacetanilide	high	7	trace, minor	2	yes (trace)
	high	8.5	none	NA[b]	no
	high	10	none	NA	no
	high	12	none	NA	no
3	none	7	major	2	no
	none	8.5	minor	1	no
	none	12	none	NA	yes
4	none	7	major	2	no
	none	12	none	1	no
Aniline	high	7	major	4	NA
	high	10	major	2	NA
9	high	7	major	2	no
	high	8.5	minor	1	no
	high	12	minor	1	no

[a] Chlorination product refers to additional aromatic ring chlorination.
[b] NA, not applicable.

phenomenon.[33] It is also important to note that in no case did we see multiple additions of chlorine to the aromatic ring (i.e., acetanilide going to dichloroacetanilides). This implies that the polyamide layer can reach a "saturation" point where ring chlorination has reached its maximum. This saturation must require continuous exposures much higher than those needed to affect performance loss (i.e., tens of thousands of ppm·hr versus 500 to 2000 ppm·hr).

The majority of the chlorine exposures during this study were done at constant pH, as shown Tables III and IV. However, during the cleaning process, membranes see changes in pH from 2.5 to 11.[45] To understand the effects of these pH changes we evaluated model compound reactivity through a series of pH values starting at pH 7. We also investigated the effect of high pH on N—Cl and ring chlorinated amides, to model the effect changes in pH have on chlorination intermediates.

Most important, we observed the formation of cleavage products from N—Cl containing amides at high pH. Figure 8 shows the formation of amine cleavage oxidation products with time, two species with absorbancies at 350 and 400 nm respectively, upon exposure of **3** to pH 12. At pH 8.5, no significant amine oxidation products are formed during the 2-h duration of the experiment, a result that shows the absence of amide bond hydrolysis. It is important to note from Tables III and IV that the ring chlorinated products, such as 2,4-dichloroacetanilide, do not show the amide bond cleavage behavior at high pH. This suggests that the N—Cl species undergo an accelerated hydrolysis under basic conditions. Our previous experiments show that N—Cl formation does not occur readily at pH 10. Table IV shows that amide bond cleavage of N—Cl species does not occur readily at pH 7 or 8.5. Therefore, to evoke extensive amide bond cleavage upon chlorine exposure, one must generate significant amounts of a N-chlorinated species at a lower pH and then expose that sample to a higher pH. These conditions exist in membrane-cleaning protocols. Residual N—Cl species formed during operation may hydrolyze upon cleaning, leading to a decline in membrane performance.

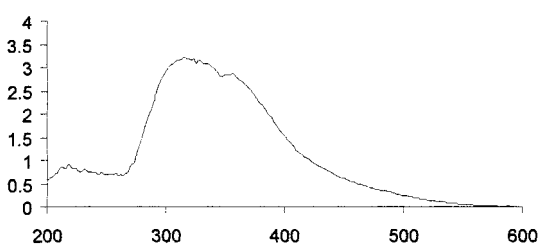


Figure 7 UV-vis spectrum of 3-aminobenzanilide (**9**) after exposure to 40,000 ppm·hr available chlorination.

Another possible degradation mechanism is that at some pH, N—Cl species are generated, and in addition the conditions are basic enough to allow for hydrolysis. Our attempt to determine this pH range can be seen in our studies of **3** and **4** in Tables III and IV. At pH 8.5 no amine–chlorine products are detected in the UV-vis spectrum during the 2-h time scale of our experiment [Fig. 8(a)]. These species are seen only at higher pH values (e.g., 10 and 12). At pH 10, it takes 2 h to generate a detectable amount of amine–chlorine product. At pH 12, these species can be identified after only 3 to 4 min [Fig. 8(b)]. Thus although hydrolysis of the N—Cl amide bond may occur at any basic pH, the lower the pH, the slower the reaction. Thus, there are two important points to consider. First, this experi-

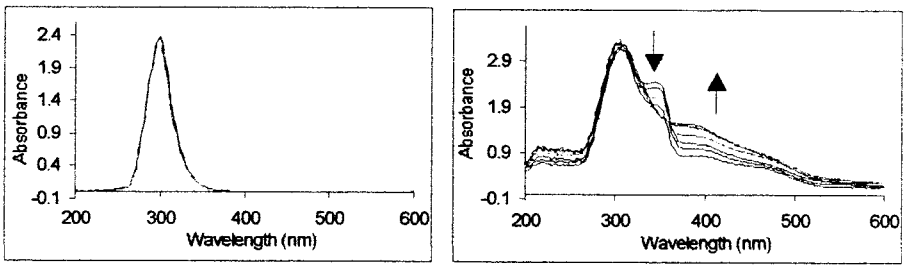


Figure 8 UV-vis spectral data of *N*-chloroacetanilide at: (a) pH 8 for 1 h; (b) pH 12 for 12 h.

ment involves the exposure of a completely N-chlorinated sample to highly basic conditions, pH 12. Our other experiments show that significant amounts of N—Cl species are not generated at this pH. Extensive amide bond cleavage appears to require very specific conditions that cannot be generated at high pH alone. A change in pH from near neutral, where N—Cl species are generated, to a higher pH, where hydrolysis of the amide bond occurs is required. Second, we see no evidence for a pH where the concentrations of N—Cl species and OH^- are simultaneously high enough to cause amide bond hydrolysis (e.g., pH 8.5). We believe that the rates of the two processes are related inversely (as the OH^- concentration increases, the amount of hydrolysis-susceptible N—Cl species decreases). It seems likely that at the pH where sufficient amounts of both species exist, the time scale for amide bond cleavage is slow relative to the known rate of membrane performance loss.

In one final experiment, chlorination of diphenyl sulfone was examined to model the possible chlorination of the polysulfone support. Under conditions that cause ring chlorination in amide model compounds, no chlorination was observed (Table I). These observations are consistent with the reported chlorine tolerance for other polysulfone membrane systems.[46] Thus, it appears that chlorination of the underlying polysulfone support is not a major factor in the degradation of membrane performance.

Our study points to a two-pathway mechanism for the loss of membrane performance. The first occurs at constant pH, especially around pH 7 where hydrolysis is negligible. We find that initially chlorination occurs at free amine and terminal amino functionalities. This occurs at both neutral and basic pH values. This can be followed by amide N—H and aromatic ring chlorination when the pH is below 10; amide bond cleavage does not occur readily under these conditions. We believe the change in membrane performance is caused from a conversion of the polyamide film from a hydrophilic state to a more hydrophobic state. Interfacially polymerized polyamides are swollen with significant amounts of water, in consequence of the film's ability to hydrogen bond using its amide and amino functionalities. Exposure of these films to chlorinating solutions converts the hydrogen-bonding N—H functional groups to the weaker hydrogen-bonding N—Cl groups. We speculate that this change in the polyamide thin film leads to the extrusion of water from the polymer network and then to deswelling of the crosslinked network, a process that becomes irreversible upon "extensive" chlorination. This change leads to membrane failure. Further details of this morphology change and how it leads to membrane failure will be dealt with further in an upcoming study.[47]

However, there is a second pathway for membrane degradation, one that depends on the pH history of the sample. Our data support the conclusion that if chlorine exposure is done at a sufficiently low pH to generate significant amounts of N—Cl species, then subsequent changes to basic pH can lead to hydrolysis of the N-chlorinated amide linkages. This mechanism requires a specific sequence of pH changes during chlorine exposure. The majority of experimentally observed chlorine degradation in polyamide membranes occurs under constant pH conditions. Therefore, we believe this is not the major mechanism of membrane failure.

In this study we used the unit of ppm·hr, the conventional description of chlorine exposure. However, our work demonstrates some of the problems associated with this convention. Aqueous chlorine solutions vary in their chemical composition with pH and available chlorine concentration. Therefore, ppm·hr is a general term that fails to take into account the chemical species active in the degradation. Our research indicates that $[ClO]^-$ may affect only amino groups, remaining inactive in the chlorination of amide and aromatic ring groups in the membrane. We also find that the Orton rearrangement occurs readily in chlorinating solutions where HClO is the major species. Based on these observations, we can suggest that it is HClO that leads to chlorination of aromatic polyamides in RO membranes at standard operating pH values. Above a pH range of 9, where HClO is no longer the major equilibrium species, we find that the

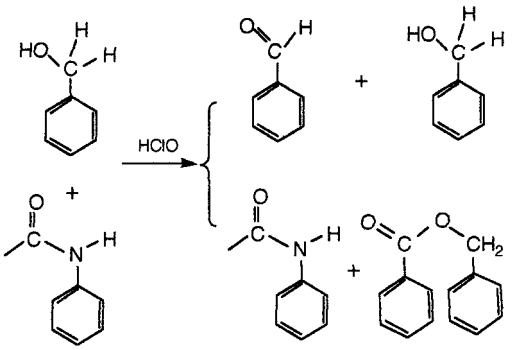


Figure 9 Products of the reaction between aqueous chlorine and a primary alcohol and acetamide mixture.

mechanisms involved in the degradation are different. Therefore, the use of ppm·hr is only the most general of chlorination descriptions. The pH of the feed solution along with the available chlorine concentration will determine the rate and mechanism of the membrane oxidative degradation. One can hope that future investigations will benefit from experiments where the analysis of chlorine exposure is done in terms of the chemical species involved.

Chlorine-resistant model compounds

During the course of experiments in which model compounds were exposed to chlorine in 50 : 50 ethanol : water solutions, we observed the absence of ring chlorination even at high chlorine exposures. In these reaction systems, chlorination was prevented by the competing oxidation of the alcohol, in a reaction known as the Steven's reaction.[48] This result was verified in reactions where benzyl alcohol was added to the amide/chlorinating solution; the products of this reaction are shown in Figure 9. Oxidation of the primary alcohol occurred more readily than amide aromatic ring chlorination.

The fact that alcohol oxidation occurs faster than amide chlorination suggests an alternative strategy for the protection of aromatic polyamides, that is, that of introducing sacrificial reductant groups into the polymer to provide initial and continuing protection from chlorination. This strategy is shown in Figure 10,

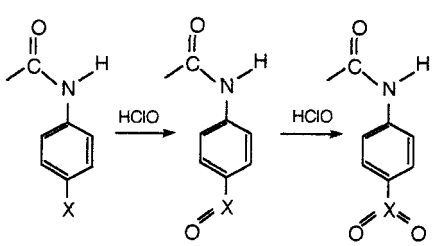


Figure 10 Strategy for using pendant groups as cooperative sacrificial reductant electron-withdrawing groups (X = illustrative element).

which involves placement of a hydrophilic, potentially reducing group on the amine ring of the polyamide. This group is designed to be oxidized by aqueous chlorine species before amide ring chlorination can occur. If this pendant group acted only in a sacrificial manner, it would provide limited chlorine resistance; however, if a pendant group is selected that will oxidize to electron-withdrawing functionalities, this effect should further inhibit ring chlorination by deactivating the aromatic ring to electrophilic substitution.

Table V shows the results of our efforts to develop this technique in a general manner. Three different model compounds were tested at pH 7 and 10 for aromatic ring chlorination. The products of the model compounds' exposure to aqueous chlorine were characterized by GC/MS analysis. Of the compounds examined, the most effective appear to be amides with pendant primary alcohols and hetero-atom–containing pendant groups. *N*-Acetyl-3-aminobenzyl alcohol (**6**) and 4-thiomethylacetanilide (**12**) oxidize readily at the pendant functionality, thus preventing ring chlorination. The secondary alcohol tested, **7**, apparently reacts too slowly, yielding a mixture of ring chlorinated and sacrificially oxidized products.

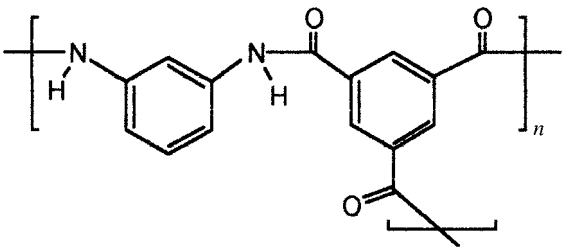
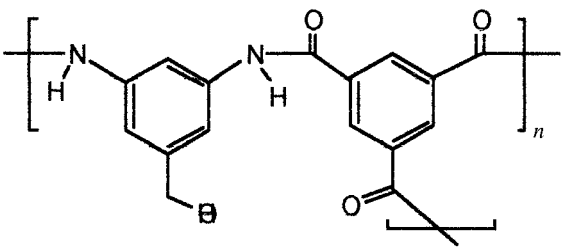
Our strategy might provide some advantages over the addition of electron-withdrawing groups to the amine monomer before interfacial polymerization, an approach that was previously reported. For example, carboxylic acids and sulfonate groups are known to deactivate some commercial RO membranes to oxidation.[22,49,50] This has increased the working lifetime of membranes, but generally they tend to have lower salt rejections than those of their unsubstituted, Cadotte-type analogs. It is possible that the presence of the electron-withdrawing group on the monomer affects the interfacial polymerization reaction, perhaps yielding a polymer with a slightly different morphology. This could be expected because electron-withdrawing groups are known to reduce the basicity of aromatic amines,[33] thereby slowing the rate of polymerization. Also, because interfacial polymerization occurs in the organic phase of the reaction system, it could be important that the substituent affects the amine mono-

TABLE V
Chlorine Resistant Model Compounds

Model compound	[NaOCl]	pH	Degree of chlorinated product	Number of isomers
6	high	7	none	1
	inter[a]	7	none	1
	inter	10	none	0
7	inter	7	major	2
	inter	10	none	0
12	inter	7	none	1

[a] inter, intermediate chlorine concentration.

TABLE VI
Initial Hand-Cast Membrane Studies

RO membrane type	Salt rejection (%)	Flux (gfd)[a]
HR commercial membrane(Koch/Fluid Systems)	99.5	37.5
Hand-cast membranes		
	97.7	8.8
	90.3	3.7

[a] gfd, gallons/sq-ft of membrane/day.

mer's solubility in the organic phase.[51] For example, a carboxyl group on the diamine monomer would likely produce ionic (zwitterions) species, whose solubility and subsequent participation in polymerization characteristics would be affected.

However, there can also be drawbacks to the sacrificial pendant group strategy. Having O—H functionality in the monomer could lead to esterfication by reaction of trimesoyl chloride with the alcohol functionality. Furthermore, certain sacrificial groups might be expected to interfere with the aqueous chlorine posttreatment process. Although the exact role of chlorine during posttreatment is not well understood in the open literature,[40,41] if ring chlorination is the chemical change that occurs, our approach would be counterproductive.

To get preliminary information on the viability of our approach, studies were carried out on the permselectivity properties of one sacrificial reductant model. Hand-cast membranes were prepared from reaction of trimesoyl chloride with the substituted diamine 3,5-diaminobenzyl alcohol and compared with the standard Cadotte, *meta*-phenylene-diamine–based membranes. The membranes examined and the salt rejection and flux data are shown in Table VI. Although salt rejection was low, the flux values for the modified membranes were very low compared to those of the commercial membranes. This could be attributed to the inadvertent aging of the support during the course of the experiment and the absence of any posttreatment. Although the modified membrane suffers from the basic selectivity versus flux trade-off, the results obtained likely represent only the minimal performance of the new membrane material. Further optimization of reaction conditions and/or posttreatment may increase the permselectivity properties to industrially useful specifications. This work is currently under way in our laboratories.

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44. 2-chloroacetanilide was used as a standard for the identification of chlorinated products based on their retention times. Once 2-chloroacetanilide was identified, the second mono-chloro-isomer observed in GC/MS analysis was taken to be 4-chloroacetanilide in agreement with published isomer distributions of the Orton rearrangement.
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