

Change of Chemical Composition and Hydrogen Bonding Behavior due to Chlorination of Crosslinked Polyamide Membranes

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ABSTRACT: The effect of membrane exposure to hypochlorite oxidant on property changes (chemical composition and hydrogen bonding behavior) of four FilmTec[®] thin film composite crosslinked polyamide membranes has been investigated. Crosslinking densities of the membranes were about 25–35%, with about 3–4 chlorines bound to the repeating unit of the polyamide membranes. This was equivalent to $\sim 39\%$ of all nitrogens being chlorinated in the polyamide membranes assuming the amide nitrogen is the dominant reaction site with chlorine. FTIR spectra showed the amide I band (C=O stretching peak at 1663 cm^{-1}) of polyamide membranes shifted to higher wave-numbers and the peak intensity of

the amide II band (N–H bending peak at 1541 cm^{-1}) decreased after chlorination. The peak shift and decrease of peak intensity resulted from breakage of hydrogen bonds between C=O and N–H groups within the polymers. The XPS and FTIR analytical analysis showed that there is no difference in the chlorine attack of polyamide membranes of higher or lower crosslinking density, and that the chlorination breaks and weakens hydrogen bonding. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2061–2066, 2008

Key words: polyamides; membranes; crosslinking; chlorine; hydrogen bonding

INTRODUCTION

Use of membrane technology to treat water or wastewater is limited by the gradual deterioration of performance due to membrane fouling. Fouling results from accumulation of substances on the membrane surface or within membrane pores and is manifested by a decline in product water flux.¹ Controlling membrane fouling has always been a major challenge in the membrane processes. Reducing fouling would increase membrane life, increase run times between cleanings, and thus decrease operation/maintenance costs. Among techniques used to reduce fouling, disinfection and chemical cleaning are most prevalent and a large number of chemical agents are available.^{2–6} The methods use chemicals to reduce active microorganisms and remove chemically or physically absorbed foulants such as sparingly soluble inorganics, dissolved organics, colloids, and microorganisms.^{7,1} Although these chemicals are effective for reducing scales and deposits, they are chemically

aggressive to many commercial membrane polymers, eventually resulting in performance change.

Several studies have investigated the cause of performance decline and the degradation mechanism of linear polyamide membranes caused by chlorination.^{8–11} The reason for performance decline has been identified as likely due to loss of structural integrity of constituent polymers. Previous studies of polyamide membrane chlorination focused primarily on investigation of linear polyamide membranes because of the difficulties of isolating the crosslinked polyamide layer for instrumental analysis. To the best of our knowledge, chlorination of crosslinked polyamide membranes has not been systematically investigated.

In this article, the effect of crosslinking density on the chlorination of four FilmTec[®] crosslinked polyamide membranes was evaluated by estimating the degree of chlorine bound to the repeating unit of the membranes. In addition, the change of hydrogen bonding behavior of the crosslinked polyamide membranes caused by chlorination was investigated by FTIR analysis.

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EXPERIMENTAL

Polyamide membrane

We have used four commercially available FilmTec[®] membranes (BW30, NF90, LE, and XLE) as

representative polyamide membranes. The membranes are thin film composite crosslinked aromatic polyamide membranes produced by interfacial polymerization of 1,3-phenylenediamine and 1,3,5-benzotriazin-4(3H)-one, having amide bonds (—CONH—) and crosslinked/noncrosslinked portions of the structures. Each virgin membrane sample was prepared by thorough rinsing with flowing deionized (DI) water for 6 h, sonicating in a Milli-Q water bath for 30 min, and then drying at room temperature. Membrane chlorination experiments were carried out using soaking baths. The membranes were exposed to 2000 ppm chlorine solutions for 1 h at pH 4. The total amount of polyamide exposure to chlorine was expressed as ppm h. The soaking tests were performed in Pyrex glass bottles covered with PTFE (polytetrafluoroethylene) caps, and the contents were mixed on a shaker. A chlorine standard was prepared from commercial ~ 6% NaOCl solution. Exact concentrations were determined by titration with a sodium thiosulfate standard. Final pH of the soaking solutions, which were prepared by spiking specific amounts of sodium hypochlorite into the buffer solution, was adjusted with concentrated HCl or 10N NaOH.

X-ray photoelectron spectroscopy

All XPS analyses were performed using an SSI S-Probe Monochromatized XPS Spectrometer, using aluminum K α X-ray source ($h\nu = 1486.6$ eV). The electron flood gun was operated with an energy setting of 3 eV to compensate for membrane surface charging. Wide survey spectra were scanned five sweeps in the range of 0–1000 eV with a resolution of 1 eV.

ATR-FTIR spectroscopy

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra were recorded on a Nicolet Nexus 470 spectrometer. As an internal reflection element, a flat plate Ge crystal at an incident angle of 45° was used to get a higher contribution of the polyamide skin top layer of the membrane. A minimum of 200 scans at a resolution of 1.0 cm⁻¹ were signal-averaged. The membranes were placed on the ATR crystal and pressed onto the surface with a plate press. The instrument was covered and continuously purged with dry air to prevent interference of atmospheric moisture with the spectra.

RESULTS AND DISCUSSION

XPS

The chemical compositions (atomic concentration percentages of oxygen, nitrogen, and carbon) of vir-

TABLE I
Element by Atomic Percent of Virgin Polyamide Membranes

Type	O (%)	N (%)	C (%)
BW30	31.41 ± 0.59	2.09 ± 0.96	66.50 ± 0.69
LE	16.15 ± 2.75	11.76 ± 0.91	72.10 ± 2.17
XLE	15.84 ± 2.30	11.54 ± 0.73	72.62 ± 2.47
NF90	17.39 ± 0.77	11.22 ± 0.67	71.39 ± 0.69

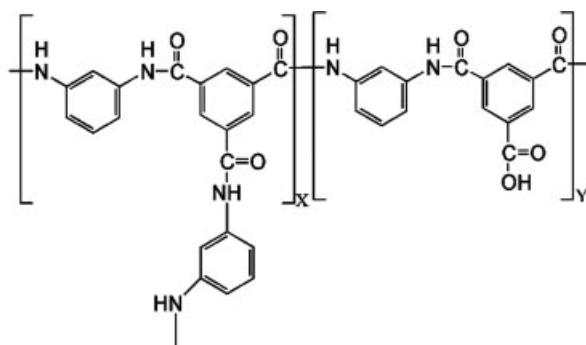
Hydrogen atom is excluded because hydrogen cannot be measured by XPS.

gin crosslinked polyamide membranes were examined by XPS and the results are shown in Table I.

All of the polyamide skin top layers of the virgin FilmTec membranes were composed of carbon, nitrogen, oxygen, and hydrogen. The membranes could be categorized into two groups according to the nitrogen content. The atomic percent of nitrogen on the BW30 membranes was about 2.09. On the other hand, LE, XLE, and NF90 contained about 11–12% nitrogen content. The nitrogen percent of totally linear polyamide material, based on the chemical structure of typical polyamides (Fig. 1), would be about 10%, and the nitrogen percent of totally crosslinked polyamide material would be about 15%. The nitrogen content of LE, XLE, and NF90 membranes were within the range of 10–15%; however, the nitrogen content of BW30 was much less than 10%. Furthermore, the atomic percent of oxygen on BW30 was much larger than other polyamide membranes. The gaps of nitrogen content and oxygen content among the membranes suggest that the BW30 membrane may have an additional source of carbon and oxygen on the surface of the membrane.

Using the atomic percent of oxygen, nitrogen, and carbon in Table I, ratios between the composing atoms were calculated (Table II). As discussed by Koo et al.,¹² the ratios and chemical formula of the polyamide membrane made it possible to roughly estimate crosslinking density (degree of crosslinking, Fig. 1). The crosslinking density, in this study, was defined as the ratio of crosslinked amide form (X) to total amide form (X + Y) in the polymer, and was calculated by solving X and Y values of the LE, XLE, and NF90 membranes. LE and XLE had a crosslinking density of 34.11% and NF90 had a crosslinking density of 25.60% in the polymer chains. The crosslinking density of BW30 could not be calculated because the membrane had another unknown source of carbon and oxygen on the surface of the membrane.

Table III shows the atomic percent of oxygen, nitrogen, carbon, and chlorine after chlorination at 2000 ppm h Cl and pH 4. LE, XLE, and NF90 membranes had about 10% chlorine content after chlorination, but the BW30 membrane had 2.57%. The



Calculation of X and Y value

X formula: $C_{21}O_3N_4$ Y formula: $C_{15}O_4N_2$

i) LE and XLE

$$\frac{O}{N} = \frac{3X + 4Y}{4X + 2Y} = 1.37, X + Y = 1 \rightarrow X = 33.68\%, Y = 66.31$$

$$\frac{O}{C} = \frac{3X + 4Y}{21X + 15Y} = 0.22, X + Y = 1 \rightarrow X = 30.17\%, Y = 69.82$$

$$\frac{N}{C} = \frac{4X + 2Y}{21X + 15Y} = 0.16, X + Y = 1 \rightarrow X = 38.46\%, Y = 61.54$$

∴ X = 34.1%, Y = 65.9%

ii) NF90

$$\frac{O}{N} = \frac{3X + 4Y}{4X + 2Y} = 1.55, X + Y = 1 \rightarrow X = 21.95\%, Y = 78.05$$

$$\frac{O}{C} = \frac{3X + 4Y}{21X + 15Y} = 0.24, X + Y = 1 \rightarrow X = 16.39\%, Y = 83.61$$

$$\frac{N}{C} = \frac{4X + 2Y}{21X + 15Y} = 0.16, X + Y = 1 \rightarrow X = 38.46\%, Y = 61.54$$

∴ X = 25.6%, Y = 74.4%

iii) BW30

No calculation due to another source of carbon and oxygen on the membrane surface

Figure 1 Calculation of crosslinking density of the polyamide membranes.

membranes having higher nitrogen content had more atomic percent of chlorine attached to the membrane (Fig. 2). Crosslinking densities of LE, XLE, and NF90 were calculated using the atomic

TABLE II
Ratio between Atomic Percent of Oxygen, Nitrogen, and Carbon on the Polyamide Membranes

	LE	XLE	NF90	BW30
O/N	1.37	1.37	1.55	15.03
O/C	0.22	0.22	0.24	0.47
N/C	0.16	0.16	0.16	0.03

TABLE III
Element by Atomic Percent of Polyamide Membranes Chlorinated under the Condition of 2000 ppm h Cl and pH 4

	O (%)	N (%)	C (%)	Cl (%)
BW30	30.55 ± 0.79	2.25 ± 1.05	64.63 ± 1.07	2.57 ± 0.75
LE	16.01 ± 1.19	10.03 ± 0.64	62.99 ± 1.35	10.98 ± 0.26
XLE	15.46 ± 0.46	10.23 ± 0.49	63.51 ± 1.11	10.80 ± 0.39
NF90	15.61 ± 0.83	10.08 ± 0.58	63.71 ± 0.78	10.59 ± 0.33

percent of the virgin membranes (Table I and Fig. 1). Similarly, the amount of chlorine bound to the repeating units of the polymeric membranes could be estimated using the crosslinking density and atomic percent of chlorinated membranes (Table III). The repeating unit of LE and XLE membranes was assumed to be $-(C_{21}O_3N_4)_1 + (C_{15}O_4N_2)_{1.93})_n-$ based on the crosslinking density (ratio of 34.11% crosslinked form to 65.89% noncrosslinked forms is the same as 1–1.93). The 10.98% of chlorine content on the LE membrane is equivalent to 3.07 chlorines for each repeating unit, and 10.80% of chlorine content on the XLE membrane is equivalent to 3.01 chlorines per repeating unit. On the other hand, the repeating unit for NF90 was assumed to be $-(C_{21}O_3N_4)_1 + (C_{15}O_4N_2)_{2.91})_n-$, and, thus, the repeating unit of the NF90 had 3.84 chlorines bound per unit. NF90 membranes, with about 20% more nitrogen per repeating unit, had about 20% more chlorines bound to each repeating unit compared to LE and XLE, and this result shows that nitrogen in the polyamide membrane is the important reaction site for chlorine. When amide nitrogen is assumed as the dominant reaction site with chlorine, it is interesting to note that regardless of crosslinking density almost the same percent of nitrogens in their repeating units are chlorinated: 38% for XLE and 39% for LE and NF90.

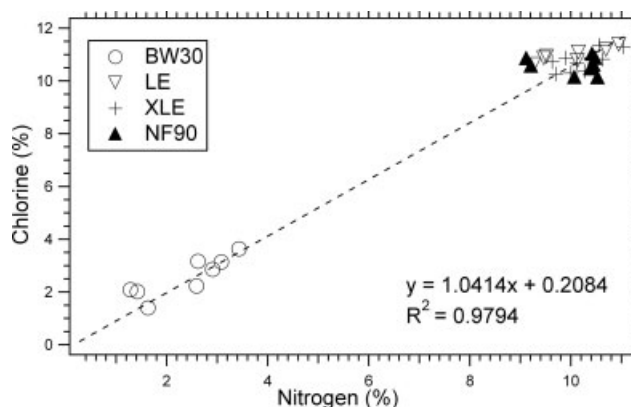


Figure 2 Atomic percent of chlorine and nitrogen of degraded PA membrane surfaces after chlorination at 2000 ppm h and pH 4.

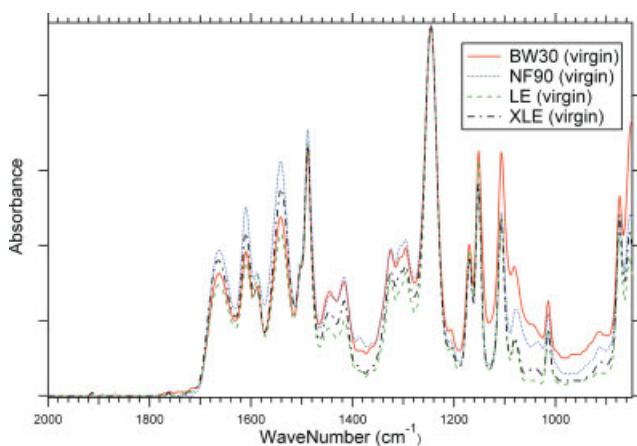


Figure 3 ATR-FTIR absorption spectra of FilmTec polyamide membranes (BW30, NF90, LE, and XLE). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ATR-FTIR spectroscopy

The FTIR of FilmTec membranes showed very similar spectra across all membrane types (Fig. 3). This

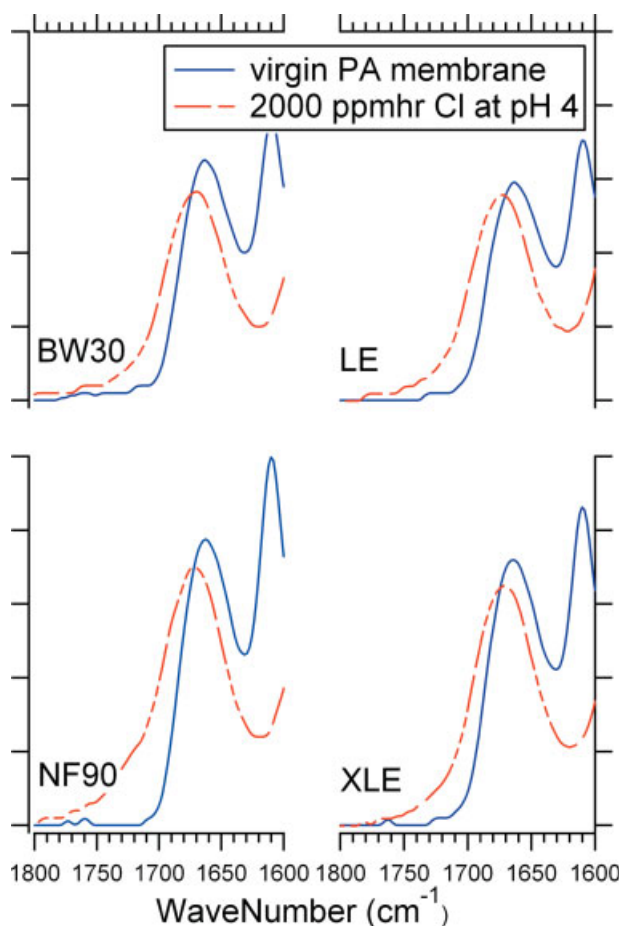


Figure 4 ATR-FTIR absorption spectra of amide I band for virgin and degraded polyamide membranes at 2000 ppm h chlorine and pH 4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was because the FilmTec membranes started from the same monomers (1,3-phenylenediamine and 1,3,5-benzentricarbonyl chloride).

Figures 4 and 5 show the FTIR spectra of amide I and amide II bands of virgin FilmTec membranes and the membranes chlorinated at 2000 ppm h Cl at pH 4, respectively.

All the virgin membranes showed amide I bands near 1663 cm^{-1} , and the peak shift slightly to higher wave-number after chlorination (Fig. 4). Since the amide I band has contributions from several motions, including C=O stretching, C–N stretching, and C–C–N deformation vibration,¹³ the change of

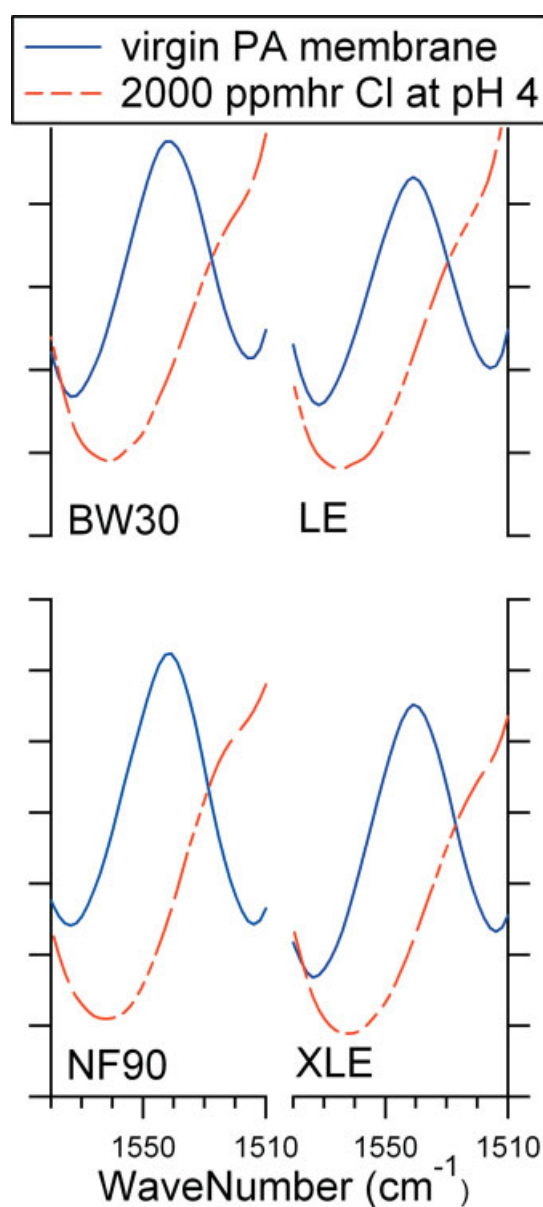


Figure 5 ATR-FTIR absorption spectra of amide II band for virgin and degraded polyamide membranes at 2000 ppm h chlorine and pH 4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

band intensity and the peak shift may be explained by the change of subpeaks composing the amide I band. The amide I band is mainly due to the C=O stretching motion and, on the surface of the polyamide membranes, there are two types of C=O stretching motions due to the stretching of hydrogen bonded carbonyl groups and the stretching of nonhydrogen bonded carbonyl groups [Fig. 6(A)]. The intensity change and peak shift of the amide I band caused by chlorination was likely due to the intensity changes of the two subcarbonyl peaks resulting from the change of concentration of the hydrogen bonded and nonhydrogen bonded carbonyl groups on the membrane. When the amide I band was deconvoluted into two symmetric Gaussian peaks, the peak at lower wave-number was assigned to hydrogen bonded carbonyl groups, since the hydrogen bonded C=O group has a decreased double-bond character of the C=O moiety, shifting the absorption band to lower frequency.¹⁴ Chlorination

breaks hydrogen bonds between C=O and N—H groups, and thus increases the number of nonhydrogen bonded carbonyl groups. Combinations of the decreased peak intensity of lower wave-number (hydrogen bonded) carbonyl groups and increased peak intensity of higher wave-number (nonhydrogen bonded) carbonyl groups shifted the amide I band to higher wave-number.

All the virgin FilmTec membranes showed amide II bands (N—H bending) near 1541 cm^{-1} ,¹⁴ and the peak intensity decreased after chlorination (Fig. 5). This was due to the decline of the number of N—H group and thus breakage of hydrogen bonds in the membrane caused by chlorination [Fig. 6(B)].

According to the performance experiments in our other work,¹⁵ the change of hydrogen bonding behavior due to the chlorination of crosslinked polyamide membranes caused flux changes depending on pH and concentration of chlorine in the soaking bath.

CONCLUSIONS

Analytical analysis using XPS and FTIR provided valuable information about the chemical composition of crosslinked polyamide membranes and the change of hydrogen bonding behavior due to chlorination of the membranes. All of the polyamide skin top layers of the FilmTec membranes investigated were composed of carbon, nitrogen, oxygen, and hydrogen. The BW30 membrane likely has another source of carbon and oxygen on the surface of the membrane. Nitrogen in the polyamide membrane was an important reaction site for chlorine. The crosslinking densities of the membranes, with the exception of the BW30 membrane having another source of carbon and nitrogen, were estimated based on the ratios of the composing atoms (carbon, oxygen, and nitrogen). The repeating units of the membranes and the number of chlorines bound to the repeating units were also calculated with the information on crosslinking densities and the atomic percent of chlorinated membranes. Crosslinking densities of the membranes were about 25–35%, with about 3–4 chlorines bound to the repeating unit of the polyamide. This was equivalent to $\sim 39\%$ of all nitrogens being chlorinated in the polyamide membranes, assuming that the amide nitrogen is the dominant reaction site with chlorine. FTIR spectra showed that the amide I band (C=O stretching peak at 1663 cm^{-1}) of polyamide membranes shifted to a higher wave-number and the peak intensity of amide II band (N—H bending at 1541 cm^{-1}) decreased after chlorination. The changes of the peaks resulted from breakage of hydrogen bonds between C=O and N—H groups of the membranes.

Membranes used for this study were generously donated by FilmTec[®].

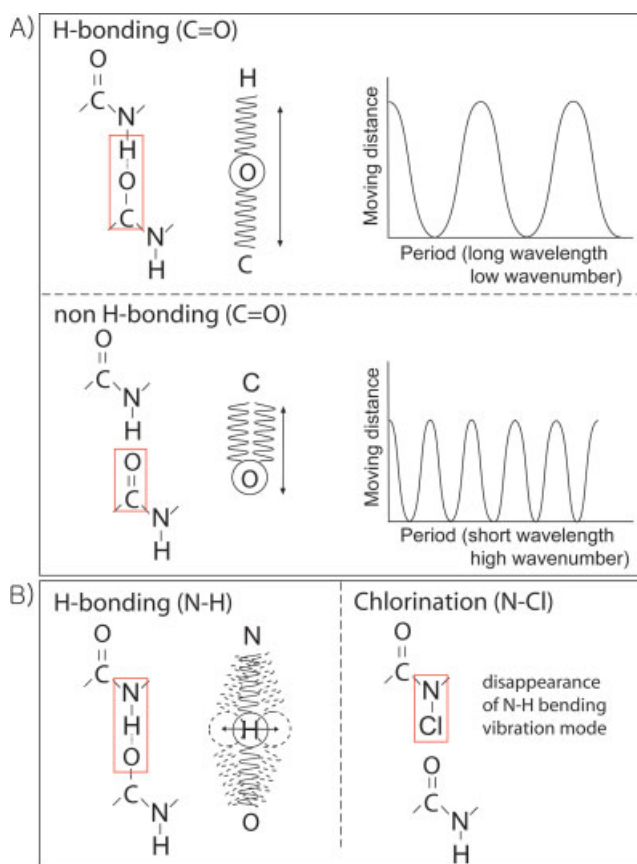


Figure 6 Stretching vibration modes for the carbonyl (C=O) group of the hydrogen bonded amide bond and nonhydrogen bonded amide bond (A). Bending vibration modes for the (N—H) group of hydrogen bonded amide bond and the disappearance of the N—H bending mode after chlorination (B). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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