

Chlorination and Oxidation of Aromatic Polyamides. II. Chlorination of Some Aromatic Polyamides

SHAoyu WU,^{1,*} JING XING,¹ GUODONG ZHENG,¹ HUIQIN LIAN,¹ and LIANFANG SHEN²

¹Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, and ²State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan 430071, People's Republic of China

SYNOPSIS

The effects of chlorine on three kinds of aromatic polyamides: those not containing a substituent, those containing substituents, and those containing heterocyclic aromatic rings, were studied. The correlations between the chemical structures of polyamides and the reactivity to hypochlorous acid were examined by IR and ¹³C solid-state NMR spectra before and after chlorination. It was found that the chlorination of polyamides depends not only on their chemical structures but also on chlorination conditions such as pH value and reaction time. Their response to chlorination corresponds to four types: ring-chlorination, no reaction, *N*-chlorination, and chain cleavage. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In the first article of this series,¹ the synthesis and characterization of some polyamides, which contained or did not contain special groups, were described for a study on their chlorination and oxidation. As described in the first article, the aromatic polyamides are very important reverse osmosis membrane materials for seawater desalination because of their high performance, but they are sensitive to free chlorine and other oxidants which exist in seawater, thus limiting their application.² Many studies on them have been carried out, focusing on the chlorination mechanism and improvement of chlorine resistance, in order to use them directly for seawater desalination and preparation of ultrapure water without removal of chlorine and other oxidants by adding some reductants such as sodium bisulfite.³

Glaser and co-workers^{4,5} studied the mechanism of attack of halogen on aromatic polyamide and found that aromatic ring halogenation was the dominant process by examining the IR and NMR spectra of model compounds and the DuPont Aramid B-9 membrane before and after chlorination.

Avlonitis et al.⁶ also examined the effect of chlorine on a polyamide membrane and confirmed the presence of ring-chlorination, but it depended on the conditions of chlorination. Only in acid conditions did the membrane performance deteriorate due to transformation of the crystalline structure to amorphous in the polyamide during chlorination. In basic conditions, chlorination did not cause any change to the repeat unit in the polyamide backbone within the time scale tested.

Kawaguchi and Tamura⁷ classified the chlorination of polyamides into three categories: no reaction of polyamide derived from secondary amines, ring-substitution of aromatic polyamide, and reversible *N*-substitution of aliphatic polyamide. In this study, we report on the effects of chlorine on various polyamides in different conditions by examining the change of their chemical structures, be-

* To whom correspondence should be addressed.

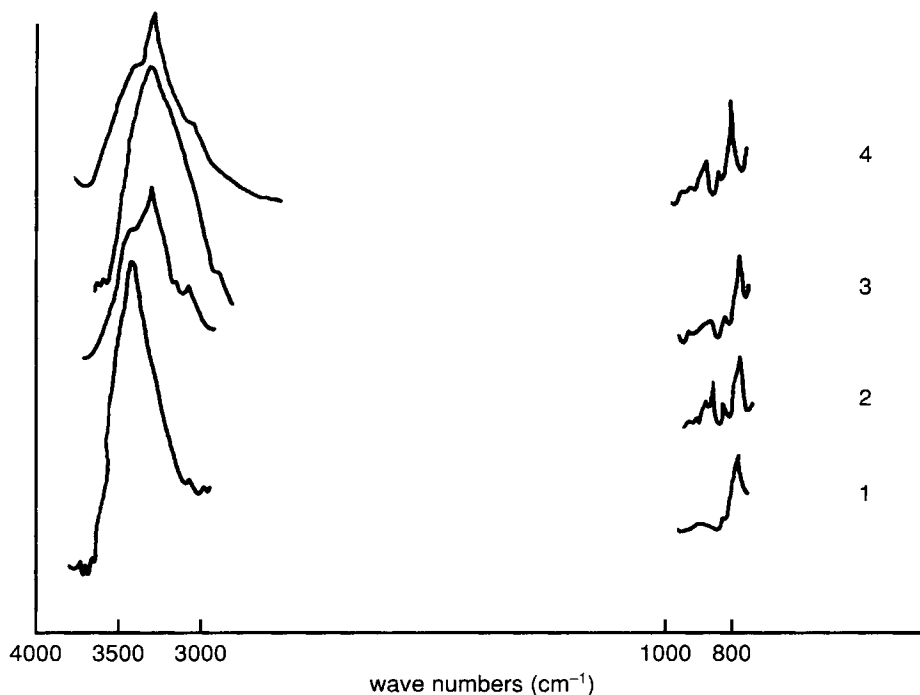


Figure 1 IR spectra of PA1 before and after chlorination under different conditions: (1) before chlorination; (2) pH 2; (3) pH 7; (4) pH 11.

fore and after chlorination, by analysis of their IR and ^{13}C solid-state NMR spectral data.

EXPERIMENTAL

Materials

All polyamides concerned were synthesized as described in the first article of this series.

Chlorination Test

Polyamide powders were soaked in aqueous solution with 1000 ppm active chlorine for 500 h, unless otherwise indicated. pH values of solutions were 2, 7 and 11 adjusted with HCl and NaOH. The total amount of polyamide exposure to chlorine was expressed as ppm h. After chlorination, the polyamides were filtered, washed with water and acetone, and dried carefully under vacuum at 50°C for 24 h.

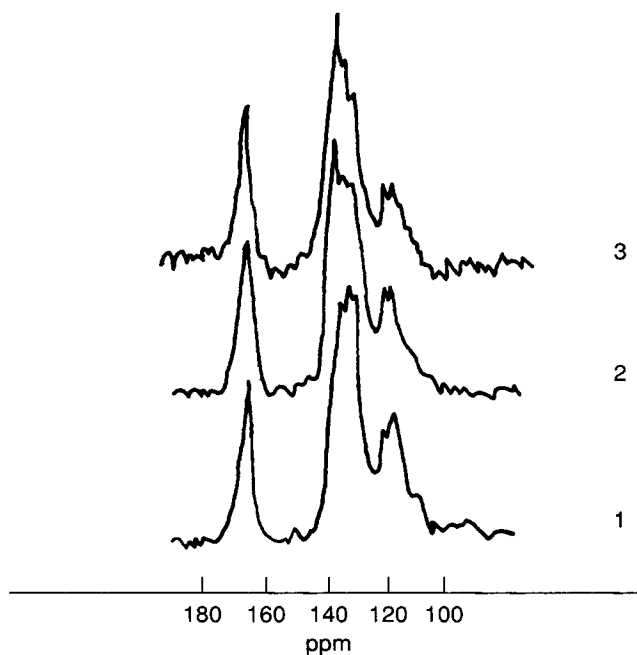


Figure 2 ^{13}C solid-state NMR spectra of PA1 before and after chlorination under different conditions: (1) before chlorination; (2) pH 2; (3) pH 11.

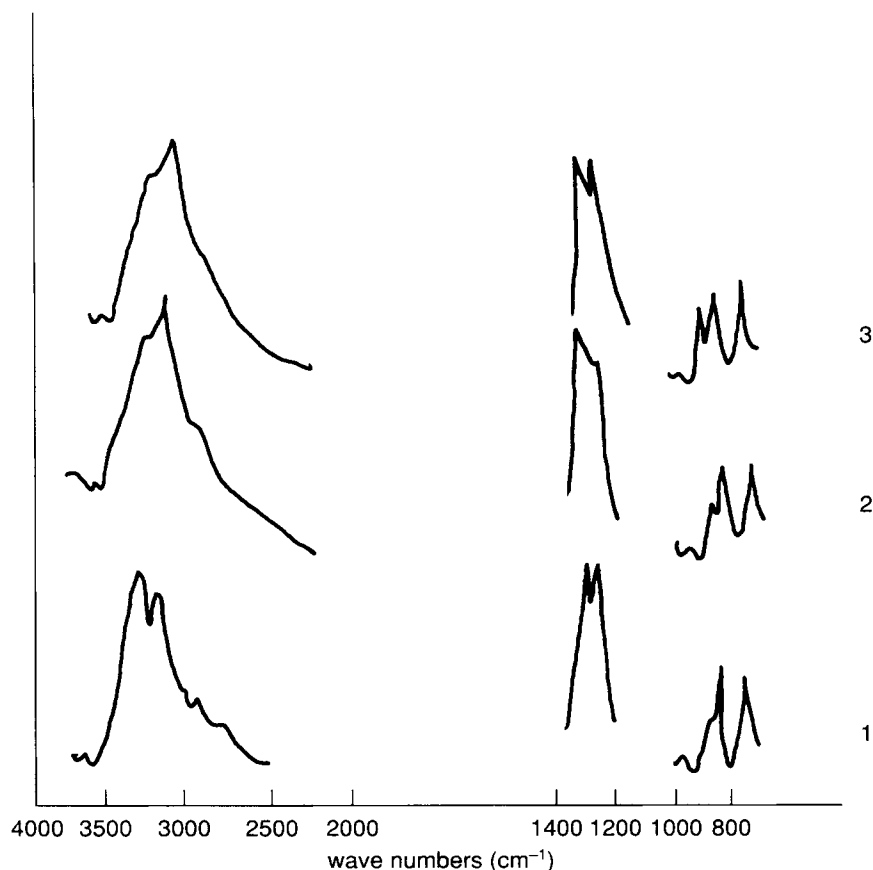


Figure 3 IR spectra of PA2 before and after chlorination under different conditions: (1) before chlorination; (2) pH 11; (3) pH 2.

IR Spectroscopy

The IR spectra of polyamides before and after chlorination were recorded using KBr pellets on a Digilab FTS-20E IR spectrometer.

^{13}C Solid-state NMR

The ^{13}C solid-state NMR spectra of polyamides before and after chlorination were recorded on a Bruker MSL-400-PFT-NMR spectrometer.

RESULTS AND DISCUSSION

Chlorination of Aromatic Polyamides Which Do Not Contain Substituents on Benzenamine

The IR and ^{13}C solid-state spectra of PA1 before and after chlorination at different pH values are

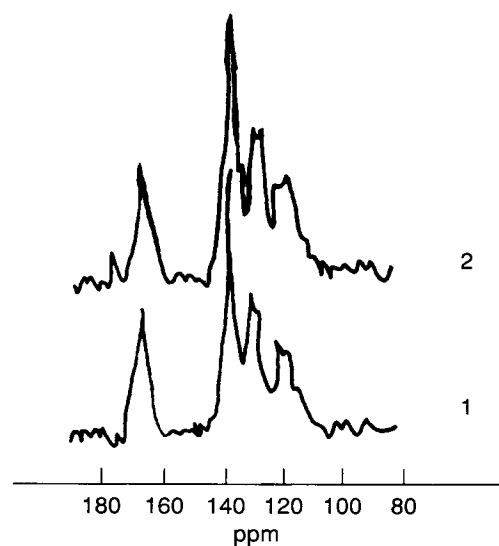


Figure 4 ^{13}C solid-state NMR spectra of PA2 before and after chlorination under basic condition: (1) before chlorination; (2) pH 11.

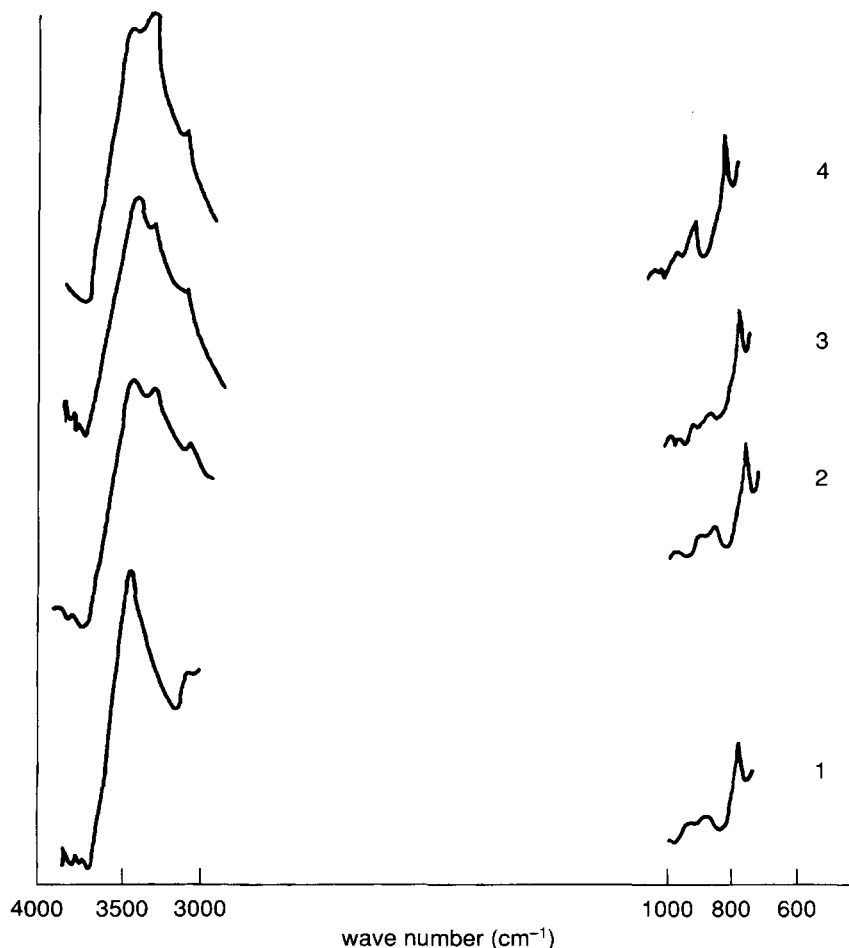
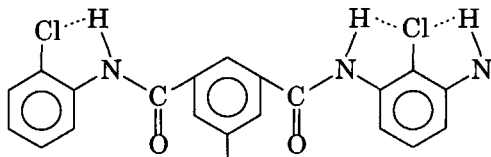


Figure 5 IR spectra of PA3 before and after chlorination under different conditions: (1) before chlorination; (2) pH 2; (3) pH 7; (4) pH 11.

presented in Figures 1 and 2. From Figure 1, we find that the N—H (free) stretching vibration (3430 cm^{-1}) disappeared and it was instead replaced by the N—H (H-bonded) stretching vibration (3315 cm^{-1}) after chlorination. Meanwhile, a new absorption band near 860 cm^{-1} appeared. This means that ring-chlorination occurred. According to the report by Glater and co-workers, the *ortho* ring-chlorination occurs as follows⁴:



The intramolecular H bond forms and makes the N—H free stretching vibration absorption band disappear. The new absorption band near 860 cm^{-1} was assigned to 1,2,4-substitution in benzene.⁴ We can also find from Figure 2 that a peak at 119 ppm appears and makes the peak resolve with 116 ppm after chlorination, which means that the *ortho* C of amine was substituted by Cl and makes the corresponding chemical shift increase.⁸

Comparing the IR spectra of PA1 after chlorination in different pH conditions, we find that the degree of chlorination is different. When pH = 2 or 11, ring-chlorination dominates, and when pH = 7, no obvious chlorination occurs. Figures 3 and 4 are the IR and ^{13}C solid-state NMR spectra of PA2. We suggest that ring-chlorination occurs in acid con-

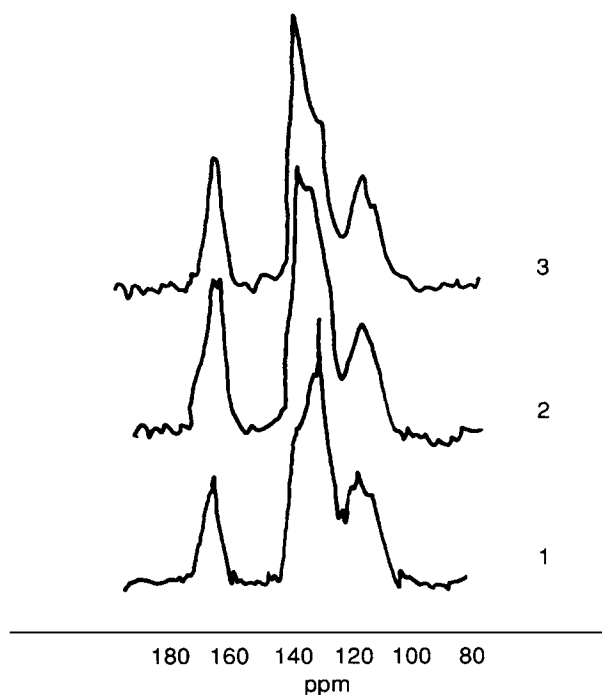
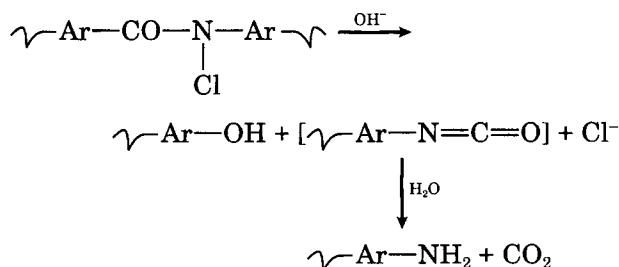


Figure 6 ^{13}C solid-state NMR spectra of PA3 before and after chlorination under different conditions: (1) before chlorination; (2) pH 2; (3) pH 11.

ditions, but in a basic system of chlorination, the chain of the PA2 partially cleaves.

In Figure 3, the C—N stretching vibration absorption band at 1280 cm^{-1} becomes weak after chlorination at pH 11, which means that the CO—N bond cleaves partially. In Figure 4, the new peak near 173 ppm appears which is attributed to COOH after chlorination, thus indicating that an oxidation product forms after chlorination in basic conditions. The possible cleavage mechanism is as follows⁶:



Figures 5 and 6 are the IR and ^{13}C solid-state NMR spectra of PA3 in which trimesoyl chloride, as a crosslinking reagent, was introduced into its structure. Although the degree obviously decreases, ring-chlorination still exists.

Chlorination of Aromatic Polyamides Containing Substituents in Benzenamine

Nita and co-workers⁹ assumed that deactivation of the amide bond and the benzene nucleus of polyamide should improve chlorine resistance and inhibit *N*-chlorination and subsequent Orton rearrangement and they proposed the following methods to improve the chlorine resistance of polyamide:

1. The introduction of a CH_3 substituent at the amide nitrogen inhibits *N*-chlorination.
2. The introduction of CH_3 substituents at all the *ortho* positions of an aromatic compound, inhibiting *N*-chlorination and Orton rearrangement by steric hindrance.
3. The introduction of an electron-withdrawing group at the nucleus which inhibits *N*-chlorination and Orton rearrangement, since such a substituent decreases the electron density of the amide bond and the benzene nucleus.

Kawaguchi and Tamura⁷ reported that polyamides derived from secondary amines possessed a high tolerance to chlorine. In this work, we chose three polyamides which contain $-\text{SO}_3\text{H}$, $-\text{COOH}$, and $-\text{CH}_3$ in benzene amines. Figures 7-9 are their relevant spectra.

By comparison of the spectra before and after chlorination under different conditions, we could not find any changes. This meant that introduction of groups as described above can improve the chlorine tolerance of polyamides.

Chlorination of Polyamides Containing Heterocyclic Aromatic Rings

The IR and NMR spectra of PA7 are given in Figures 10 and 11. From analysis of these spectra, we suggest that *N*-substitution occurs after chlorination

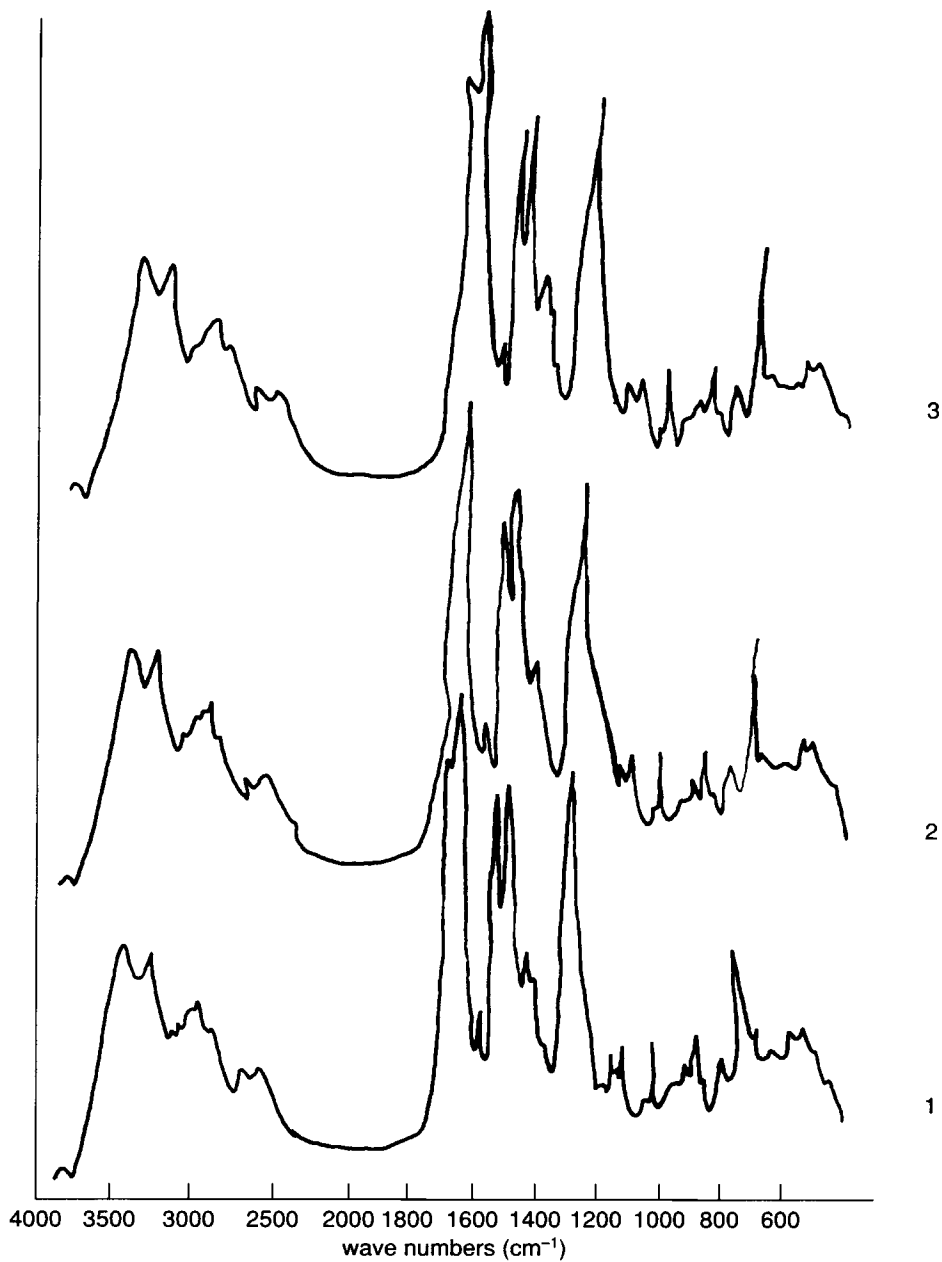


Figure 7 IR spectra of PA4 before and after chlorination under different conditions: (1) before chlorination; (2) pH 4; (3) pH 11.

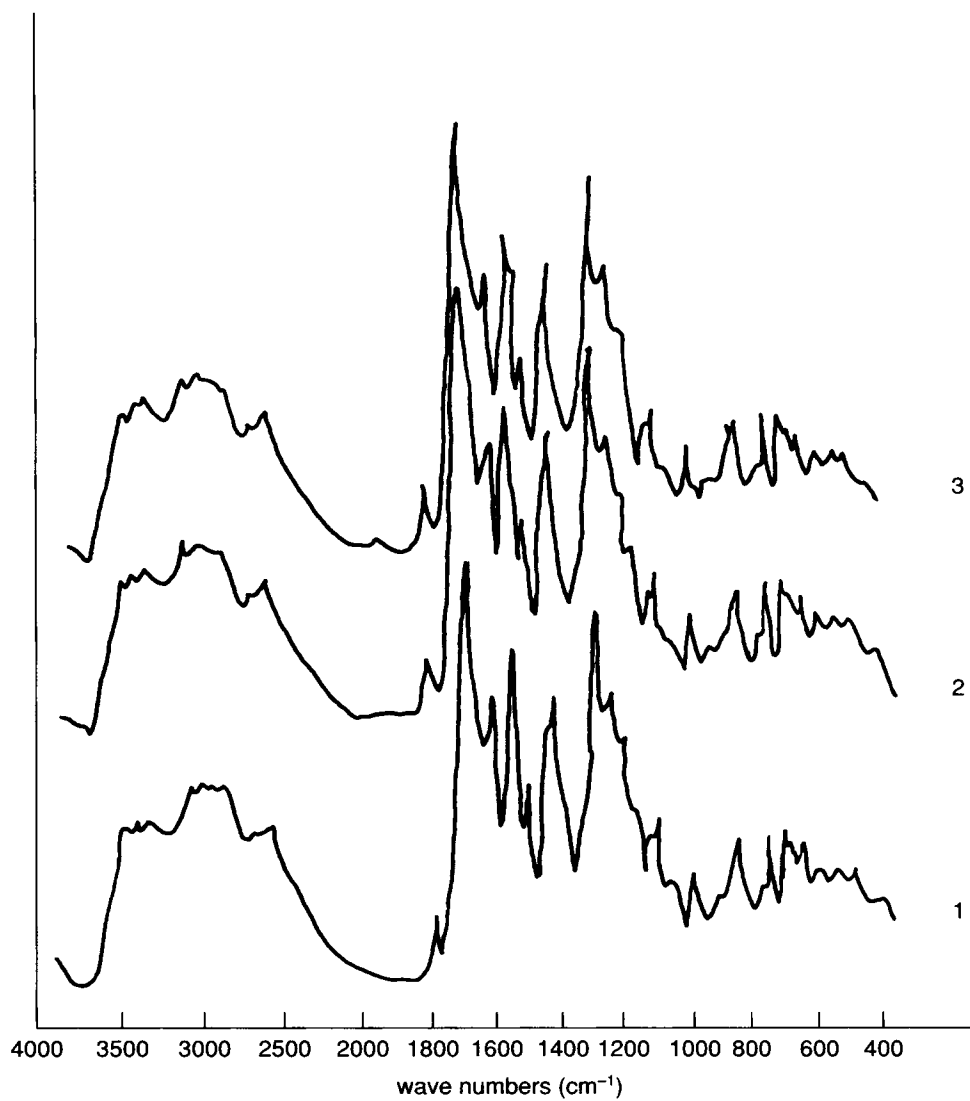


Figure 8 IR spectra of PA5 before and after chlorination under different conditions: (1) before chlorination; (2) pH 2; (3) pH 11.

at pH 2 and no change is caused at pH 11. When pH = 2, the N—H stretching vibration absorption band near 3423 cm^{-1} becomes weak and corresponding N—H vibrations such as the out-of-plane N—H stretching vibration (near 732 cm^{-1}) and the deformation mode of N—H (near 699 cm^{-1}) also becomes weak after chlorination. Meanwhile, some typical bands split into two, e.g., C=O stretching splits into 1690 and 1723 cm^{-1} , amide II into 1508 and 1534 cm^{-1} , and C—N stretching into 1424 and 1445 cm^{-1} , and the higher-frequency peaks are enhanced with the increasing of amount of chlorination. The *N*-chlorination made the absorption frequency of C=O, etc., higher¹⁰ and the peaks split due to the partial chlorination, which means the degree of *N*-substitution increased with the increase of the amount of chlorination. The ^{13}C solid-state NMR spectra of PA7 supports the occurrence of *N*-chlorination. Some of the peaks of carbon become broad after *N*-substitution because the *N*-substitution makes the relevant peak of C overlap.

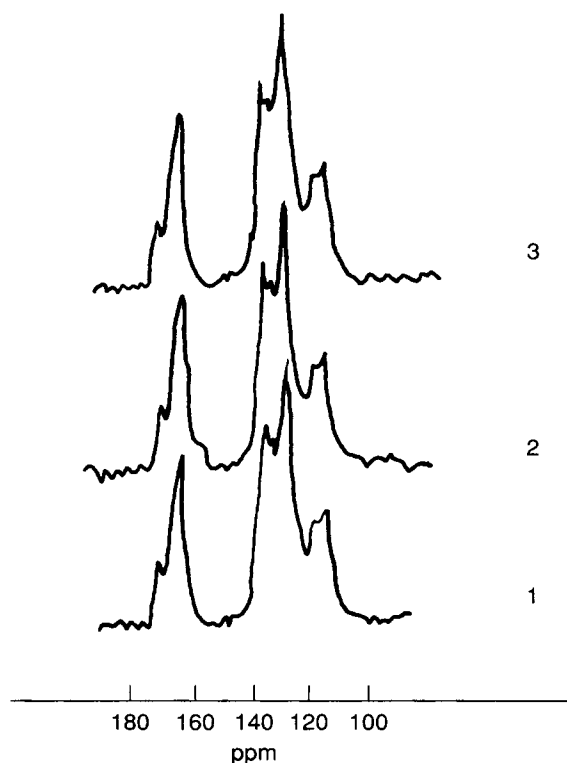


Figure 9 ^{13}C solid-state NMR spectra of PA5 before and after chlorination under different conditions: (1) before chlorination; (2) pH 2; (3) pH 11.

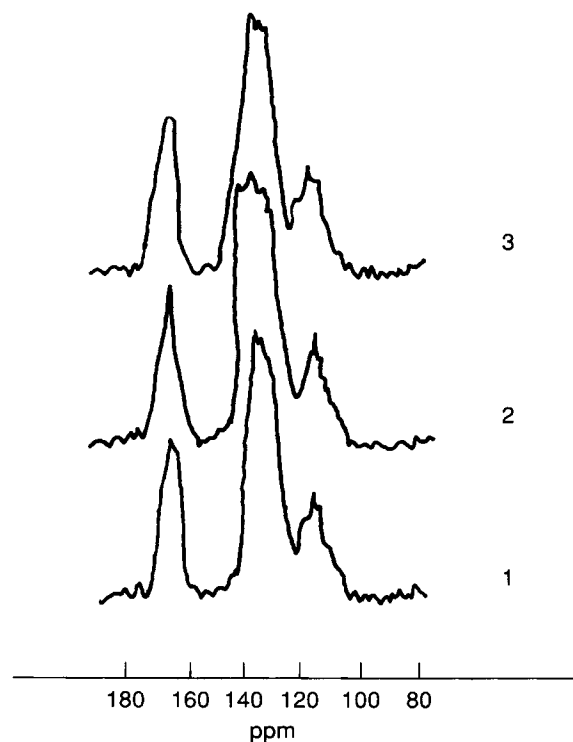


Figure 10 ^{13}C solid-state NMR spectra of PA7 before and after chlorination under different conditions: (1) before chlorination; (2) pH 2; (3) pH 11.

CONCLUSION

The chlorination of polyamides depends on their chemical structures as well as on the pH value of chlorination. The polyamides that do not contain substituents result in ring-chlorination, but the poly(-1,3-phenylene terephthalamide) undergoes partial cleavage of the chain under basic conditions. *N*-chlorination takes place in polyamides which contain heterocyclic aromatic rings under acid conditions.

The polyamides containing certain substituents, either electron-withdrawing groups or sterically hindering groups, show high tolerance to oxidant chlorine. This means that those types of polyamides could be potential materials for reverse osmosis membranes.

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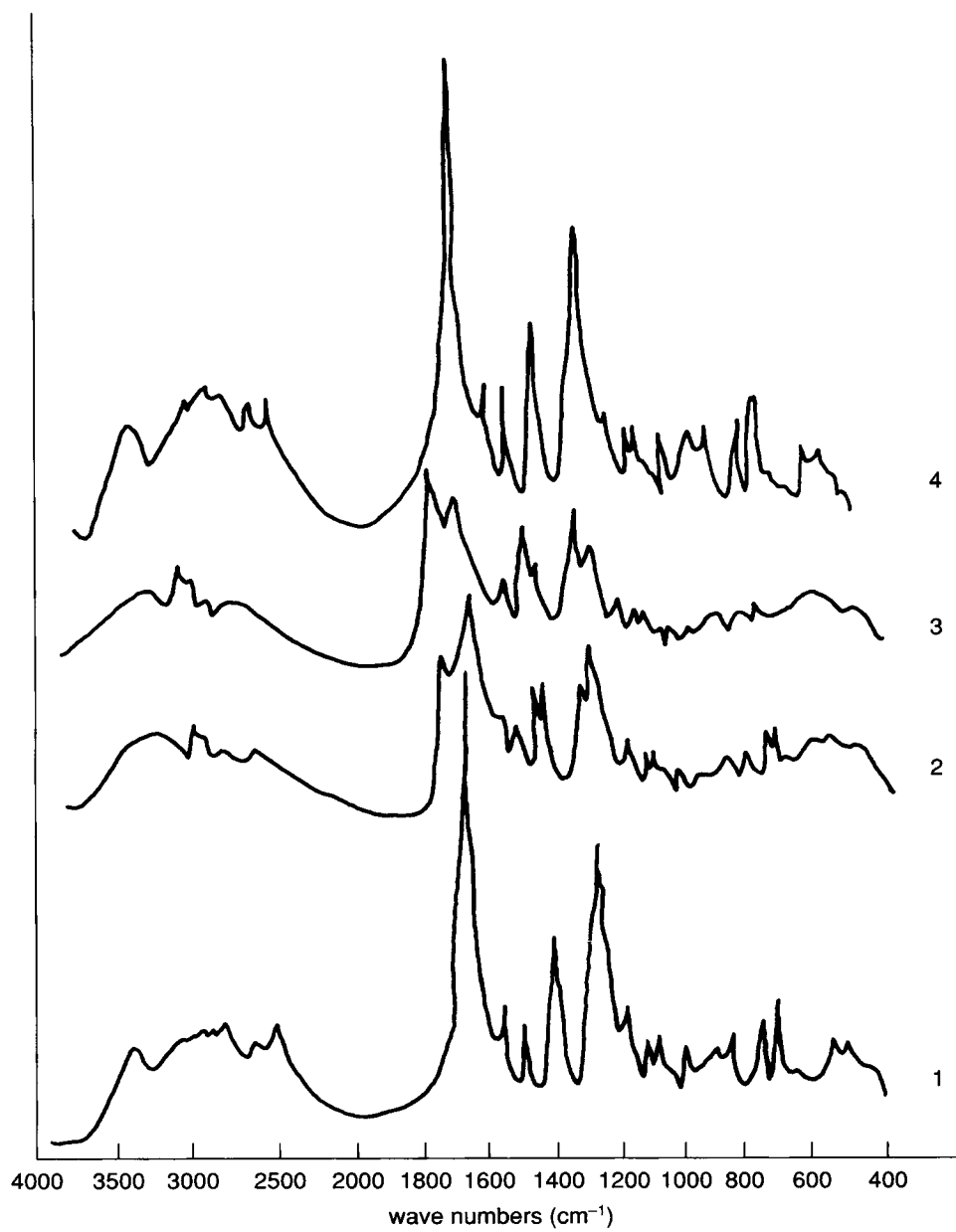


Figure 11 IR spectra of PA7 before and after chlorination under different conditions: (1) before chlorination; (2) pH 2, 500 h; (3) pH 2, 1000 h; (4) pH 11.

REFERENCES

1. S. Wu, G. Zheng, H. Lian, J. Xing, and L. Shen, *J. Appl. Polym. Sci.*, to appear.
2. J. Petersen, *J. Membr. Sci.*, **83**, 81 (1993).
3. J. E. Cadotte and R. J. Petersen, in *Synthetic Membranes*, Vol. I, *Desalination*, A. F. Turbak, Ed., ACS Symposium Series 153, American Chemical Society, Washington, DC, 1981, p. 305.
4. J. Glater, J. McCutchan, S. B. McCray, and M. R. Zachariah, in *Synthetic Membranes*, Vol. I, *Desalination*, A. F. Turbak, Ed., ACS Symposium Series 153, American Chemical Society, Washington, DC, 1981, p. 171.
5. J. Glater, M. R. Zachariah, S. B. McCray, and J. W. McCutchan, *Desalination*, **48**, 1 (1983).
6. S. Avlonitis, W. T. Hanbury, and T. Hodgkiess, *Desalination*, **85**, 321 (1992).
7. T. Kawaguchi and H. Tamura, *J. Appl. Polym. Sci.*, **28**, 3359 (1984).
8. F. W. Wehrli and T. Wirthlin, *Interpretation of C-13 NMR Spectra*, Heyden, London, 1976.
9. K. Nita, Y. Matsui, S. Konagaya, and M. Miyagi, in *ICOM'90*, Chicago, 1990.
10. W. J. de Klein and A. R. Plesman, *Spectrochim. Acta A*, **28**, 673 (1972).

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