Notes

N-Chloro-Hindered Amines as Multifunctional Polymer Additives

Zhaobin Chen and Yuyu Sun*

Department of Human Ecology, The University of Texas at Austin, Austin, Texas 78712

Received April 24, 2005
Revised Manuscript Received June 30, 2005

Introduction

Hindered amine light stabilizers (HALSs) are one of the most important light/thermal stabilizing agents of polymeric materials. They are widely available with low cost and low toxicity, and they have excellent compatibilities with a broad range of commercially significant polymeric materials.[1−7] Most HALSs contain piperidine structures, which can be further chemically modified to achieve different functions. In the presence of chlorinating agents, it is possible to transform HALSs into *N*-chloro-hindered amines (NCHAs). For example, Zakrzewski reported that NCHAs could be prepared in benzene using sodium dichloroisocyanurate as chlorinating agent.[8] Later, Nishimoto and co-workers synthesized NCHAs in toluene with the presence of *tert*-butyl hypochlorite.[9] However, to date, the performances of NCHAs have not been fully investigated.

In our continuing effort in the development of antimicrobial polymers,[10−13] NCHAs were evaluated as potential candidates of antimicrobial agents. We found that piperidine-based HALSs could be readily transformed into NCHAs in diluted sodium hypochlorite bleach, significantly simplifying the preparation processes. NCHAs could simultaneously provide antimicrobial functions as well as photostabilities and thermal stabilities.

Experimental Section

Materials. A hindered amine light stabilizer, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (BTMP), was purchased from Aldrich and recrystallized from petroleum ether. Isotactic polypropylene (PP, Aldrich) was purified by dissolution in hot *o*-xylene followed by precipitation with methanol.[14a] Other chemicals were reagent grade and used as received. *Escherichia coli* (*E. coli*, ATCC 15597) and *Staphylococcus aureus* (*S.* aureus, ATCC 6538) were provided by American Type Culture Collection.

Instruments. FT-IR spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer (Woburn, MA). ^{1}H NMR and ^{13}C NMR studies were carried out using a Varian Unity-300 spectrometer (Palo Alto, CA) at ambient temperature in $CDCl_3$. UV/vis analysis was performed using a Beckman DU-640 spectrophotometer (Fullerton, CA. Sample concentration: 1.0×10^{-3} mol/L in methanol). The photostability was characterized following ASTM D 4329 Cycle A (8 h UV treatment with uninsulated black panel at 60 ± 3 °C; 4 h condensation with uninsulated black panel at 50 ± 3 °C) using a QUA accelerated weathering tester (Q-panel products Inc., Cleveland, OH). The thermal stability of the samples was determined by oven aging at 130 °C.[14b] In the photostability and thermal stability studies, the carbonyl index of the samples was used as a measure to evaluate the stabilizing effects of BTMP or Cl−BTMP following established methods.[14c] Briefly, in the photostability or thermal treatments, at different periods of time, the FT-IR spectra of the samples were collected, and the carbonyl index at 1713 cm^{-1} was calculated according to the following equation:[14c]

$$\text{carbonyl index} = [(\log I_0/I_t)/d] \times 100 \quad (1)$$

where I_0 is the intensity of incident light, I_t is the intensity of transmitted light, and d is film thickness (μm). Because the formation of carbonyl groups (e.g., ketones, carboxylic acids,, and esters) is related to PP degradation, higher carbonyl index values indicate lower stabilizing effects.[14]

Preparation of Bis(*N*-chloro-2,2,6,6-tetramethyl-4-piperidinyl) sebacate (Cl−BTMP). Recrystallized BTMP was crushed into fine powders. A standard sieve was used to collect powders in the range of 60−80 mesh (0.42−0.31 mm). The powders were submerged in 0.6 wt % sodium hypochlorite aqueous solutions containing 0.05 wt % of Triton X-100 at room temperature for 4 h under constant stirring. The bath ratios were kept at 1:30 and the pH values were adjusted to 7.0 using pH buffers. After chlorination, the powders were collected, washed thoroughly with a large amount of distilled water, filtered, and dried at ambient temperature under reduced pressure. After recrystallization from petroleum ether, Cl−BTMP was obtained as colorless needles.

Preparation of Cl−BTMP-Containing Polymers. A predetermined amount of Cl-BTMP was added into 5% PP solutions in hot *o*-xylene under constant stirring. After evaporation of the solvent, polymer films (thickness: 70 ± 5 μm) were obtained by hot pressing at 170 °C for 15 s. Chlorine contents of the resultant samples were determined by iodimetric titration.[13] BTMP-containing PP films were prepared using the same method.

Antimicrobial Properties. The antimicrobial functions of the samples were challenged with *E. coli* (gram-negative) and *S. aureus* (gram-positive). It should be noted the *S. aureus* species used in this study are biosafety level-2 microorganisms, which are of moderate hazard to personnel and instruments.[15] Class II biosafety cabinet and appropriate personal protective equipment including gloves, respirators, gowns, and foot covers were used in the antimicrobial tests. All the microbial studies followed the guidelines provided by the U.S. Department of Health and Human Services.[15]

To determine the antimicrobial functions of Cl−BTMP powders, 1 g of the sample (60−80 mesh) was packed into a glass column (i.d.: 6 mm), which was sealed with sterilized glass fibers on both sides (empty-bed volumes of 0.4−0.6 mL).[10−13] A 10 mL aliquot of an aqueous suspension containing 10^6−10^7 CFU/mL of *E. coli* or *S. aureus* passed through the column. The flow rate of the suspension was controlled by compressed air (0.5−1.6 mL/min). To ensure that no free chlorine was present in the antimicrobial studies, the effluent was tested with chlorine testing strips with an accuracy of 0.05 ppm of chlorine. No detectable free chorine was found in any of the tests. The effluent was collected, serially diluted, and each dilution was placed onto Luria-Bertanil agar plates (for *E. coli*) or tryptic soy agar plates (for *S. aureus*), respectively.

* Corresponding author. E-mail: yysun@mail.utexas.edu.

10.1021/ma050874b CCC: $30.25
Published on Web 08/17/2005

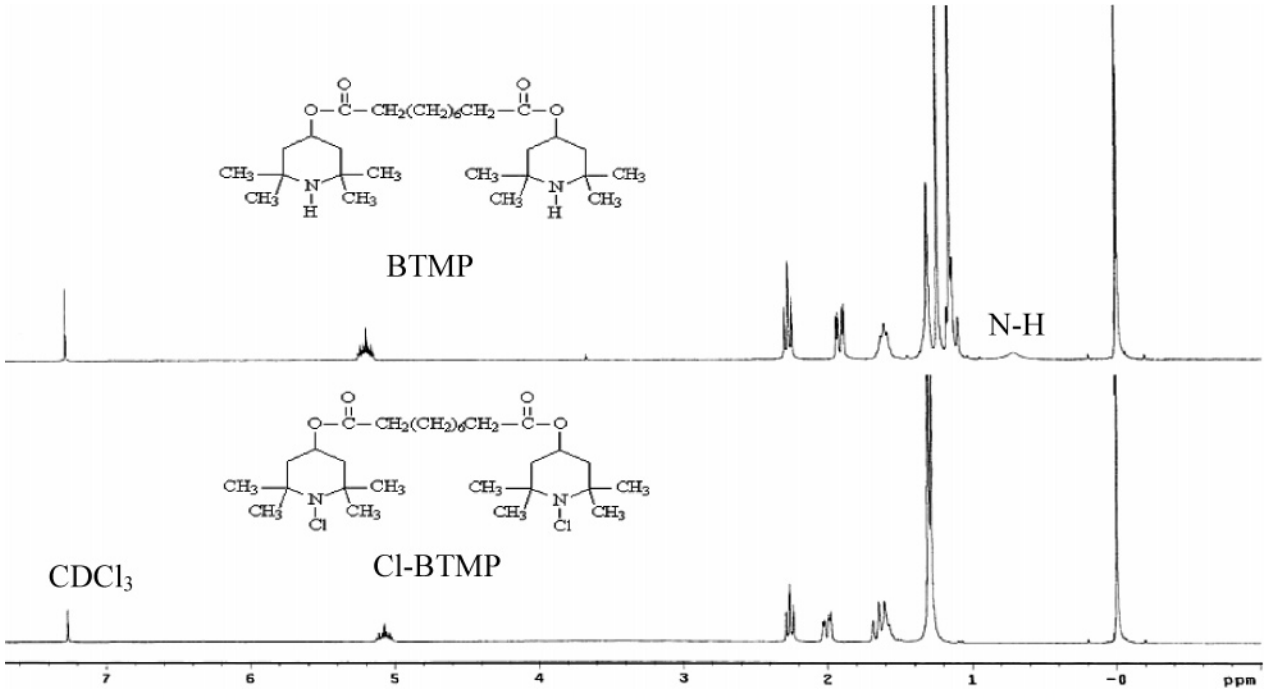

Figure 1. [1]H NMR spectra of BTMP and Cl−BTMP.

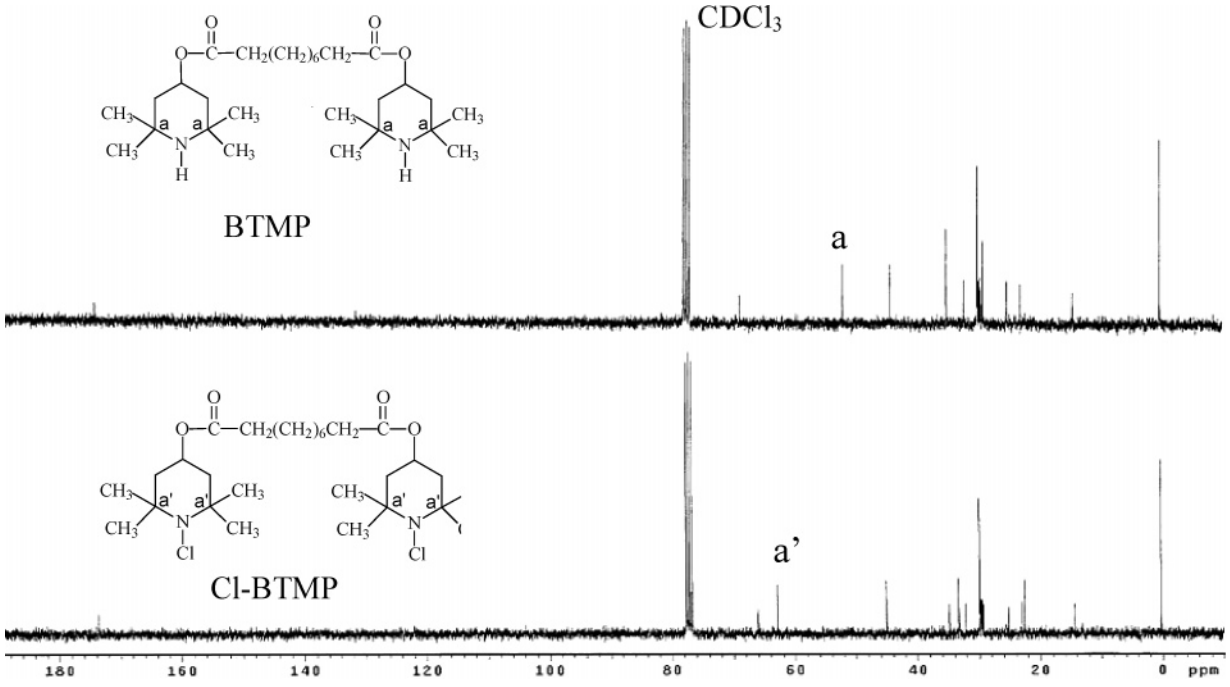

Figure 2. [13]C NMR of BTMP and Cl−BTMP.

The same procedure was also applied to BTMP as controls. Bacterial colonies on the agar plates were counted after incubation at 37 °C for 24h.

In the study of Cl−BTMP-containing PP films, 10 μL of an aqueous suspension containing 10^6−10^7 CFU/mL of *E. coli* or *S. aureus* was placed onto the surface of a film (4 × 4 cm). The film was then "sandwiched" using another identical film. After a certain period of contact time, the entire "sandwich" was transferred into 10 mL of 0.03 wt % sodium thiosulfate aqueous solution. The mixture was vigorously shaken for 5 min. An aliquot of the solution was serially diluted, and 100 μL of each dilution was plated onto agar plates. The same procedure was also applied to the BTMP-containing samples as controls. Bacterial colonies were counted after incubation at 37 °C for 24 h.

Results and Discussion

To confirm the chemical structure of Cl−BTMP, Figure 1 shows the [1]H NMR spectra of the samples. In the spectrum of BTMP, the amino protons showed a weak and broad peak at 0.71 ppm.[16−18] After bleach treatment, the N−H group was transformed into N−Cl structure, and the 0.71 ppm signal disappeared in the spectrum of Cl−BTMP. In the [13]C NMR studies (Figure 2), before chlorination, the two neighboring carbons (C_a) of the N−H group in BTMP showed a peak at 51.4 ppm, which shifted to 62.6 ppm upon bleach treatment ($C_{a'}$). This 11.2 ppm difference could be caused by the replacement of N−H structures with N−Cl groups

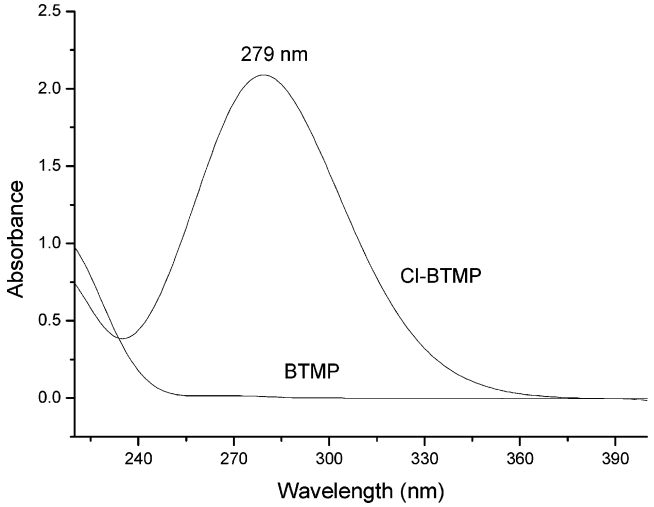

Figure 3. UV/vis spectra of BTMP and Cl−BTMP (sample concentration: 1.0×10^{-3} mol/L in methanol).

because the latter had stronger electron withdrawing effect than N−H groups.

Another evidence of the synthesis of Cl−BTMP was provided by UV/vis studies, as shown in Figure 3. At higher than 250 nm, BTMP did not show any absorption. However, after chlorination, a broad peak centered at 279 nm could be detected in the spectrum of Cl−BTMP. The UV absorption of chloramines have been well established.[19−22] The new peak could be caused by the disruption/disassociating of the N−Cl bond[19] and/or the transition from a bonding to an antibonding orbital.[22]

Cl−BTMP could be readily incorporated into PP films through solution mixing followed by thermal pressing. Iodimetric titrations[13] showed that Cl−BTMP retained 95−100% of its original chlorine content after these treatments, indicating that Cl−BTMP was stable enough for the conventional processing technologies of PP.[23]

The antimicrobial functions of the samples were challenged with 10^6−10^7 CFU/mL of *E. coli* (gram-negative) and *S. aureus* (gram-positive). In the antimicrobial tests of Cl−BTMP (BTMP as controls), the samples were packed into columns, and bacteria suspensions passed through the columns. It was found that although BTMP could not kill bacteria, Cl−BTMP provided total kill of 10^6−10^7 CFU/mL of *E. coli* and *S. aureus* at contact times of 7.8−8.4 min for 10 mL of bacteria suspensions. At even shorter contact times, the flow became unstable. Similarly, with the presence of 0.1−4 wt % of BTMP, PP films did not show any antimicrobial effects. However, in Cl−BTMP-containing PP, at higher than 0.1 wt % of Cl−BTMP, the films provided total kill of the bacteria in less than 15 min.

Durability is an important feature of the antimicrobial functions of the samples. After storage at 25 °C and 80% RH for 6 months, Cl−BTMP or Cl−BTMP-containing PP films retained more than 96% of the original chlorine content, and the antimicrobial activities were unchanged. The excellent stability could be related to the unique hindered piperidine structure. In Cl−BTMP, the neighboring carbons of the N−Cl groups were attached to four electron donating methyl groups, which tended to destabilize any developing negative charge on N as Cl^+ left the molecule.[24−26] As a result, the N−Cl structure was stabilized, and high chlorine stability was observed.

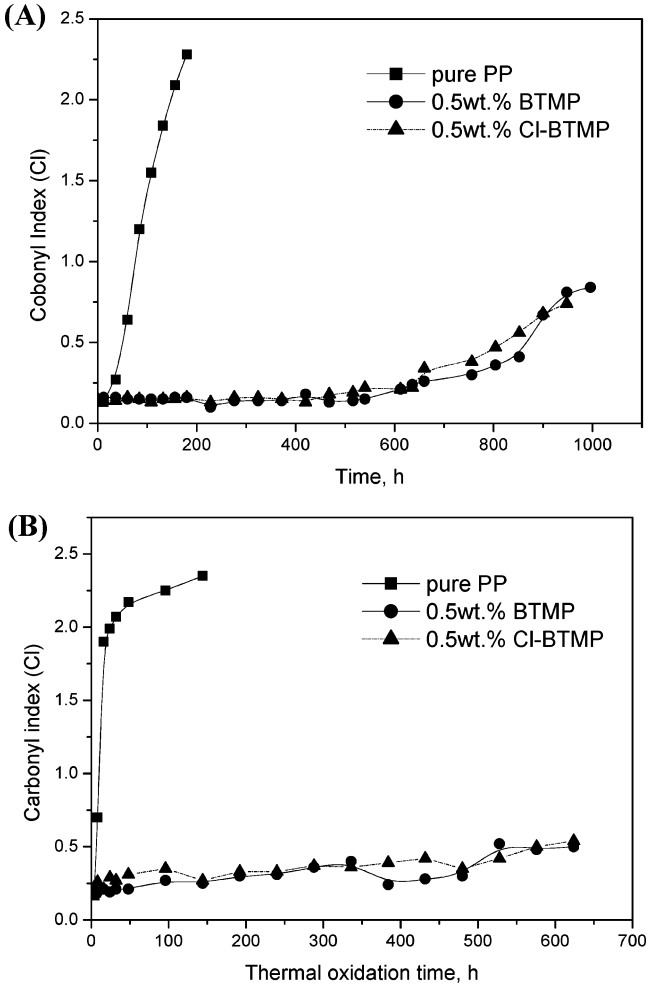

Figure 4. Carbonyl index in (A) photostability studies and (B) thermal stability studies of pure PP, PP films containing 0.5 wt % of BTMP, and PP films containing 0.5 wt % of Cl−BTMP.

To evaluate the rechargeability, Cl−BTMP and Cl−BTMP-containing PP films were first treated with 1.0 wt % sodium thiosulfate solutions at room temperature for 120 min to partially quench the chlorine, and then rechlorinated with 0.6 wt % sodium hypochlorite solutions. After 20 cycles of the rechlorinating treatments, the chlorine contents[27] and antimicrobial activities of the samples were essentially unchanged, indicating that the antimicrobial functions were fully rechargeable.

Figure 4 shows the carbonyl index of the film samples in photostability and thermal stability studies.[14c] Under UV treatments (Figure 4A), the carbonyl index of pure PP increased rapidly, implying fast oxidization of the samples.[5,6] In the presence of BTMP or Cl−BTMP, the carbonyl index of the sample was essentially unchanged up to 600 h of UV irradiation. Similar results were obtained in the thermal stability studies, as shown in Figure 4B. These findings suggest that in addition to antimicrobial functions, Cl−BTMP could also provide effective UV and thermal stabilizing effects.

Conclusions

Our results showed that HALSs could be readily transformed into NCHAs in diluted sodium hypochlorite bleach at room temperature. NCHAs-containing samples demonstrated powerful, durable, and rechargeable antimicrobial functions against both gram-negative and

gram-positive bacteria with excellent photostability and thermal stabilizing effects. The wide availability, low cost, and low toxicity of HALSs, the ease in NCHAs preparations, and the unique properties of the resultant materials suggest that NCHAs have the potentials to be a class of multifunctional additives of polymeric materials.

Acknowledgment. This research is funded by the College of Natural Sciences at the University of Texas at Austin.

Supporting Information Available: Chemical structures of BTMP and Cl−BTMP; FT-IR spectra of the film samples in photostability and thermal stability studies; DSC and TGA curves of BTMP and Cl−BTMP; and chlorine content of Cl−BTMP after different cycles of rechlorination treatments. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Zweifel, H. *Plastics Additives Handbook*, 5th ed.; Hanser: Munich, 2000.
(2) Edenbaum, J. *Plastic additives and Modifiers Handbook*; Van Norstrand Reinhold: New York, 1992.
(3) Pritchard, G. *Plastic Additives*; Chapman & Hall: London, 1998.
(4) Motyakin, M. V.; Schlick, S. *Macromolecules* **2001**, *34*, 2854.
(5) Kruczala, K.; Bokria, J. G.; Schlick, S. *Macromolecules* **2003**, *36*, 1909.
(6) Kruczala, K.; Varghese, B.; Bokria, J. G.; Schlick, S. *Macromolecules* **2003**, *36*, 1899.
(7) Motyakin, M. V.; Schlick, S. *Macromolecules* **2002**, *35*, 3984.
(8) Zakrzewski, J. *Synth. Commun.* **1988**, *18*, 2135.
(9) Nishimoto, S.; Chaisupakitsin, M.; Inui, T. *Radiat. Phys. Chem*. **1992**, *39*, 413.
(10) Sun, Y.; Chen, Z. U.S. Patent application, No. 60/640,985 (pending)
(11) Sun. Y.; Sun. G. *Macromolecules* **2002**, *35*, 8909.
(12) Sun, Y.; Sun, G. *Ind. Eng. Chem. Res.* **2004**, *43*, 5015.
(13) Braun, M.; Sun, Y. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 3818.
(14) (a) Setnescu, R.; Jipa, S.; Osawa, Z. *Polym. Degrad. Stab*. **1998**, *60*, 377. (b) Jansson, A.; Möller, K.; Gevert, T. *Polym. Degrad. Stab*. **2003**, *82*, 37; (c) Rabek, J. F. *Photostabilization of Polymers Principles and Applications*; Elsevier Applied Science: New York, 1990.
(15) Richmond J. Y.; McKinney, R. W. *Biosafety in Microbiological and Biomedical Laboratories*, 4th ed.; U.S. Government Printing Office: Washington, DC, 1999.
(16) Lambert, J. B.; Bailey, D. S.; Michel, B. F. *J. Am. Chem. Soc.* **1972**, *94*, 3812.
(17) Booth, H.; Little, J. H. *J. Chem. Soc., Perkin Trans. 2: Phys. Org. Chem.* **1972**, *12*, 1846.
(18) Lee, C. S.; Lau, W. W. Y.; Lee, S. Y.; Goh, S. H. *J. Polym. Sci. Part A: Polym. Chem.* **1992**, *30*, 983.
(19) Metcalf, W. S. *J. Chem. Soc.* **1942**, 48.
(20) Kleinberg, J.; Tecotzky, M.; Audrieth, L. F. *Anal. Chem.* **1954**, *26*, 1388.
(21) Czech, F. W.; Fuchs, R. J.; Antczak, H. F. *Anal. Chem.* **1961**, *33*, 705.
(22) Price, W. C. *Annu. Rep.* **1939**, *36*, 47.
(23) The DSC and TGA results suggested that Cl−BTMP was thermally stable up to 200 °C. See the Supporting Information for the thermal analysis of the samples.
(24) Kaminski, J. J.; Bodor, N.; Higuchi, T. *J. Pham. Sci.* **1976**, *65*, 553.
(25) Worley, S. D.; Williams, D. E.; Barnela, S. B. *Water Res*. **1987**, *21*, 983.
(26) Worley, S. D.; Williams, D. E. *Crit. Rev. Environ. Control* **1988**, *18*, 133.
(27) See the Supporting Information for the chlorine content of Cl−BTMP after different cycles of rechlorination treatments.

MA050874B