Preparation and Characterization of Polymerizable Hindered Amine-Based Antimicrobial Fibrous Materials

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A polymerizable hindered amine-based antimicrobial fibrous material was successfully prepared by grafting 2,2,6,6-tetramethyl-4-piperdyl methacrylate onto cotton fabrics and sequentially chlorinating the grafted materials with diluted sodium hypochlorite solutions. The effects of grafting conditions on the grafting reactions were investigated. The resultant polymeric amine *N*-halamine fibrous material provided a total kill of 10^6-10^7 cfu/mL of *Escherichia coli* (ATCC 15597), *Staphylococcus epidermidis* (ATCC 35984), and *Staphylococcus aureus* (ATCC 6538) within 30 min. Autoclave treatment and TGA study showed that the covalently bound chlorines have excellent thermal and hydrolytic stabilities. The antimicrobial function was both durable and rechargeable. These properties make the new fibrous materials attractive candidates for a broad range of applications.

Introduction

Microorganisms have strong abilities to survive on ordinary materials; some species, including drug-resistant strains, can stay alive for more than 90 days.[1–9] Contaminated materials could serve as important sources for cross-contamination and cross-infection.[9–15] One of the potential methods to reduce such risks is to introduce antimicrobial functions into high-touch, high-risk materials. To achieve this goal, antibiotics,[16–18] phenol derivatives,[19–21] metal particles or ions,[22–25] quaternary ammonium compounds,[26–28] dendrimers,[29] *N*-halamines,[30–44] and others have been incorporated into a wide range of materials to inactivate microorganisms.

An *N*-halamine is a compound containing one or more nitrogen−halogen covalent bonds, which are formed by the halogenation of imide, amide, or amine groups.[45] The antimicrobial action of *N*-halamines is believed to be a manifestation of a chemical reaction involving the transfer of positive halogens from the *N*-halamines to appropriate receptors in the microbial cells. This process can effectively destroy or inhibit the enzymatic or metabolic cell processes, resulting in the expiration of the organisms. Among different *N*-halamine structures, the antimicrobial activities have the following order: imide *N*-halamines > amide *N*-halamines ≫ amine *N*-halamines. On the other hand, the stability of the N−X bond follows this order: imide *N*-halamines < amide *N*-halamines ≪ amine *N*-halamines. These phenomena are believed to be caused by electronic effects.[45] That is to say, in *N*-halamine structures with a general formula of $N(R_1R_2)$–X (X is Cl or Br), the strength of the N−X bond is significantly influenced by R_1 and R_2. If R_1, R_2, or both are electron-donating groups (in the case of amine *N*-halamines), they would tend to destabilize any developing negative charge on N as X^+ leaves the molecule. Therefore, the stability of the molecule would increase. Similarly, electron-withdrawing groups attached to nitrogen (in the case of amide and imide *N*-halamines) would decrease the stability but increase the antimicrobial function.[45]

We have great interest in amine *N*-halamines for their durable antimicrobial activities and good thermal, hydrolytic, and storage stabilities. In our previous investigations,[31,35] we found that structurally hindered amines, one of the most widely used photostabilizers for polymers,[46] could be readily transformed into *N*-chloro hindered amines (*N*-halamine) by a simple hypochlorite bleach treatment. The resultant amine *N*-halamines could be physically mixed with conventional polymers to provide not only durable and rechargeable antimicrobial activities but also excellent light and thermal stabilizing effects.[31] To broaden the application of this class of *N*-halamines, in this study, we report the preparation and characterization of hindered amine-based *N*-halamines that are covalently bound onto conventional fibrous materials. In this approach, a vinyl hindered amine monomer, 2,2,6,6-tetramethyl-4-piperdyl methacrylate (TMPMA), was grafted onto cotton cellulose. After bleach treatment with diluted sodium hypochlorite solution, the grafted TMPMA moiety was transformed into polymeric amine *N*-halamines, providing exceptionally durable and fully rechargeable antimicrobial activities with good hydrolytic and thermal stabilities.

Experimental Section

Materials. Cotton fabrics (purchased from Testfabrics Inc.) were cleaned with acetone to remove impurities before use. TMPMA (Wako chemicals Inc.) was purified by precipitation from acetone solution into water. *Escherichia coli* (ATCC 15597), *Staphylococcus epidermidis* (ATCC 35984), and *Staphylococcus aureus* (ATCC 6538) were provided by American Type Culture Collection. Cerium(IV) ammonium nitrate (Alfa Aesar), nitric acid (Acros), sodium thiosulfate solution (0.0100 M, Ricca Chemical), potassium iodide (Acros), and other chemicals were analytical grade and used as received.

Measurements. Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet 6700 spectrometer with ATR model (Smart performer accessory) at 2-cm^{-1} resolution and 128 scans. ^{1}H NMR spectra were obtained using a Bruker Avance EM500 spectrometer. A 0.5-g sample of PTMPMA-*g*-fabric was pretreated with 10 mL of trifluoacetic acid solution (90%) at 80 °C for 24 h. Trifluoacetic acid was evaporated under vacuum, 5 mL of distilled water was added to the residues, and the insoluble solid was removed by filtration. After the removal of water by rotary evaporation and drying in a vacuum oven for 24 h, the resultant solid was dissolved in D_2O for ^{1}H NMR

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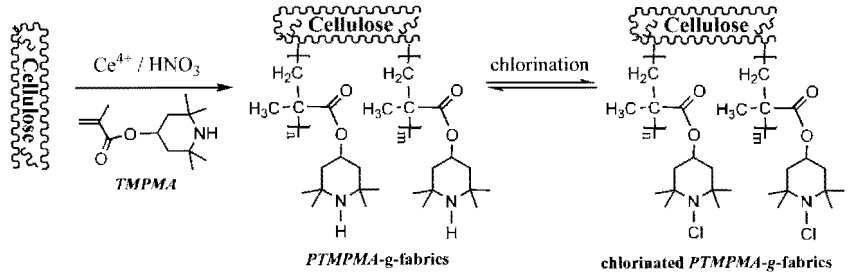
Scheme 1. Preparation and Chlorination of PTMPMA-*g*-Fabrics



analysis. Thermogravimetric analysis (TGA) was carried out on a TA Q50 thermogravimetric analyzer at a heating rate of 20 °C/min under nitrogen gas flow.

Preparation of TMPMA Grafted Fabrics (PTMPMA-*g*-Fabrics). In a typical run, a certain amount of TMPMA was dissolved in distilled water containing the equimolar acetic acid to prepare 100 g/L (0.44 mol/L) TMPMA solution, and the final pH value was adjusted to 5−6 with acetic acid. A predetermined amount of cotton fabric was placed in a 250-mL three-necked flask equipped with a condenser and magnetic stirrer. The 150 mL of TMPMA solution, 0.30 g (0.55 mmol) of cerium(IV) ammonium nitrate, and 0.5 mL of nitric acid were added into the system. After purging with N_2 for 10 min, the reaction system was kept in a water bath (50−55 °C) for 3 h with constant stirring under nitrogen atmosphere. Afterward, the fabrics were washed thoroughly with running hot water, 50% (v/v) of alcohol solution (to remove the homopolymer of TPMPMA that might adherent to the fabric) and distilled water. The fabrics were dried in air overnight and stored in a desiccator to reach constant weights. The graft yield was calculated according to eq 1:

$$\text{graft yield (\%)} = \frac{(W_g - W_0)}{W_0} \times 100 \qquad (1)$$

where W_0 and W_g were the weights of the original and grafted fabrics, respectively.

Chlorination of PTMPMA-*g*-Fabrics. The PTMPMA-*g*-fabrics were immersed in 0.1% sodium hypochlorite solution containing 0.05% (v/v) of a nonionic wetting agent (TX-100) under constant stirring for 30 min at room temperature. The fabrics were then washed thoroughly with running hot water and distilled water and dried in air overnight and stored in a desiccator.

The active chlorine contents of the chlorinated PTMPMA-*g*-fabrics were determined by iodimetric titration with a modified method as reported previously.[30] In the current study, 10−50 mg of chlorinated PTMPMA-*g*-fabrics were cut into fine powders, and treated with 1 g of KI in 40 mL of 50% ethanol solution (the solution contained 0.05% (v/v) of TX-100 and the pH value was adjusted to 4 with acetic acid) at room temperature under constant stirring for 1 h. The formed I_2 was titrated with standardized sodium thiosulfate aqueous solution. The unchlorinated PTMPMA-grafted fabrics were tested under the same conditions to serve as controls. The available active chlorine content on the fabrics was calculated according to eq 2:

$$\text{Cl \%} = \frac{35.5}{2} \times \frac{(V_S - V_0) \times C_{Na_2S_2O_3}}{Ws} \times 100 \qquad (2)$$

where V_S, V_0, $C_{Na_2}S_2O_3$ and W_S were the volumes (mL) of sodium thiosulfate solutions consumed in the titration of the chlorinated and unchlorinated samples, the concentration (mol/L) of the standardized sodium thiosulfate solution, and the weight of the chlorinated sample (mg), respectively.

Antibacterial Function of the Chlorinated PTMPMA-*g*-Fabrics. To ensure laboratory safety, the guidelines provided by the U.S. Department of Health and Human Services[47] were followed in all the microbial studies. *S. aureus* (ATCC 6538, Gram positive), *S. epidermidis* (ATCC 35984, Gram positive) and *E. coli* (ATCC 15597, Gram negative) were used to challenge the antibacterial functions of the chlorinated PTMPMA-*g*-fabrics.

The antibacterial tests were conducted according to a modification of AATCC Test Method 100−1999. In this study, *S. aureus*, *S. epidermidis*, and *E. coli* were grown in broth solutions (tryptic soy broth for *S. aureus* and *S. epidermidis,* and Luria-Bertan, or LB broth, for *E. coli*) for 24 h at 37 °C. The bacteria were harvested with a centrifuge, washed with phosphate-buffered saline (PBS), and then resuspended in PBS to densities of 10^6−10^7 cfu/mL. The freshly prepared bacterial suspensions (100 μL) were placed on the surfaces of four square swatches of the chlorinated PTMPMA grafted cotton cellulose (1 × 1 in. per swatch). After a certain period of contact time, the swatches were transferred into 10 mL of sterilized sodium thiosulfate solution (0.03%), sonificated for 5 min, and vortexed for 60 s. The solution was serially diluted, and 100 μL of each diluent was placed on agar plates (LB agar for *E. coli* and tryptic soy agar for *S. aureus* and *S. epidermidis*). The colony-forming units on the agar plates were counted after incubation at 37 °C for 24 h. Pure cotton fabric and the correspondent unchlorinated PTMPMA grafted cotton fabrics were tested under the same conditions to serve as controls. Each test was repeated three times.

Durability of the antimicrobial properties was tested with machine washing following AATCC Test Method 124−2001. AATCC standard reference detergent 124 was used in all the machine-washing tests. To test the rechargeability of the active chlorines, the chlorinated PTMPMA-*g*-fabrics were first treated with 0.3% sodium thiosulfate solution for 1 h to partially quench the active chlorine and then rechlorinated with the same conditions in the preparation of the first generation of the *N*-halamine fibrous materials. After certain cycles of this "bleaching−quenching−bleaching" treatment, the chlorine content and antimicrobial functions of the samples were retested.

Results and Discussion

Preparation and Chlorination of PTMPMA-*g*-Fabrics. The preparation of the *N*-halamine-based fibrous cellulose comprised two basic steps, grafting and chlorination, as shown in Scheme 1. In grafting, TMPMA monomers (in the form of acetic acid salt) were grafted onto cellulose molecules. After chlorination, the grafted TMPMA moieties were transformed into amine *N*-halamines, providing antimicrobial functions.

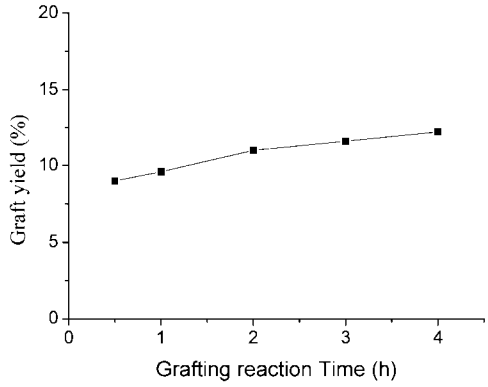


Figure 1. Effects of grafting reaction time on graft yield (6.0 g of fabric in 150-mL solution that contained 0.44 mol/L TMPMA and 3.6 mmol/L ceric salt at 50−55 °C).

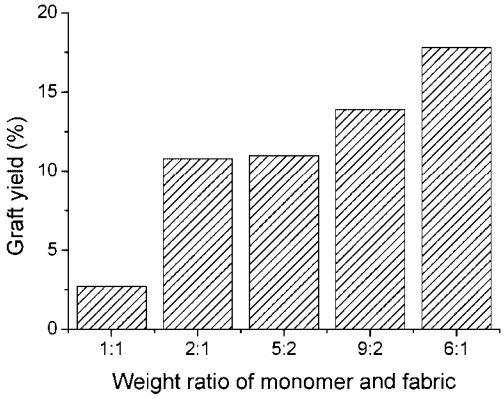


Figure 2. Effects of weight ratio of monomer to fabric on graft yield (in 150-mL solution that contained 0.44 mol/L TMPMA and 3.6 mmol/L ceric salt at 50−55 °C for 3 h).

In grafting, the ceric ion (Ce^{4+}) redox system was employed as the initiator. This system has been widely used as initiators for grafting vinyl monomers (acrylic acid, acrylamide, acrylonirile, styrene, and vinyl acetate.) onto polysaccharides such as starch, cellulose, and chitosan.[48–53] It is believed that Ce^{4+} could oxidize cellulose, creating free-radical grafting sites primarily at C2 and C3 carbons on the polymer backbones to start the grafting polymerization.[54–56]

The influences of grafting conditions on graft yield were investigated. Shown in Figure 1 are the effects of grafting time. It can be seen that the graft yield rapidly increases to 9.0% in the first 30 min. After that, this effect becomes less obvious: after 3 h of grafting, the graft yield reaches 11.6%; when the time is further extended to 4 h, the graft yield slightly increases to 12.2%.

The influences of the weight ratio of TMPMA to the fabric are presented in Figure 2. Keeping other conditions constant, increasing TMPMA content significantly increases graft yield initially. For example, when the weight ratio of TMPMA to fabric is increased from 1:1 to 2:1, the graft yield markedly increases from 2.7 to 10.8%. In this heterogeneous reaction system, the graft polymerization largely depends on the diffusion of the monomers into the inner parts of the cotton cellulose. As monomer concentrations go up, more monomers can reach the reactive sites on cotton molecules, leading to higher graft yield. On the other hand, however, the grafted TMPMA chains on the fabrics carry positive charges (in the salt form), which can repel the diffusion of the positively charged monomers to the fabrics, particularly at high graft yields. The net influence on grafting yield can be the competition of these two effects.

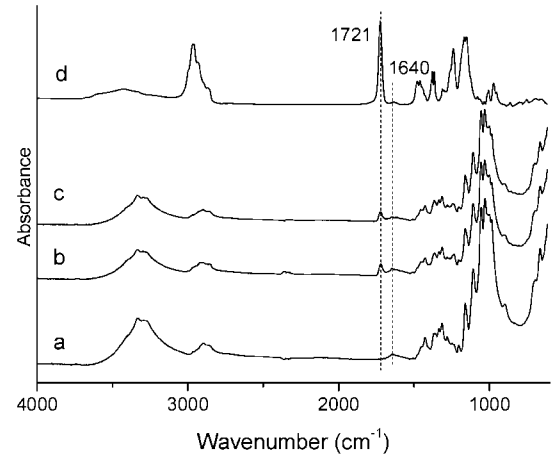


Figure 3. FT-IR spectra of (a) original cotton fabrics, (b) PTMPMA-*g*-fabrics (graft yield 17.8%), (c) chlorinated PTMPMA-*g*-fabrics (graft yield 17.8%), and (d) PTMPMA (prepared in hexane at 70 °C with 0.5% AIBN as initiator).

Besides, at higher than 9/2 weight ratio, gelation of the grafting solution was observed, indicating that too much TMPMA could promote chain transfer reaction to the monomer. Thus, a large amount of TMPMA was consumed in the homopolymerization in the solution, resulting in gel formation.

After grafting, the grafted fabric (PTMPMA-*g*-fabric) was chlorinated by diluted sodium hypochlorite aqueous solution. During chlorination treatment, the N−H bond of the piperidyl structure in PTMPMA-*g*-fabric was transformed into N−Cl bond, leading to the formation of polymeric amine-based *N*-halamine structures.

The reactions were followed with FT-IR and ^{1}H NMR studies. Figure 3 shows the FT-IR spectra of the original fabric, PTMPMA-*g*-fabric before and after chlorination, and the homopolymer of TMPMA (PTMPMA, prepared in hexane with 0.5% AIBN as initiator at 70 °C for 3 h). In the spectrum of the original cotton fabric (Figure 3a), the broad peak above 3000 cm^{-1} is assigned to the hydroxyl group, and the weak band at 1640 cm^{-1} is caused by water of hydration.[29] After grafting, a new peak at 1721 cm^{-1} can be observed in the spectrum of PTMPMA-*g*-fabric (Figure 3b). This peak is attributable to stretching vibration of the ester carbonyl groups of the grafted PTMPMA chains, which is confirmed by the spectrum of pure PTMPMA (Figure 3d),[57] suggesting that PTMPMA has been successfully grafted onto cotton fabrics. After chlorination, the N−H bond of the piperidine structure in PTMPMA-*g*-fabric was transformed into an N−Cl bond. Unfortunately, due to the rather weak IR absorbance of the N−Cl bond and the relatively low content of PTMPMA in the fabric, little difference could be detected between the spectra of the unchlorinated and chlorinated PTMPMA-*g*-fabrics (Figure 3b and c).

After treatment with trifluoacetic acid, PTMPMA-*g*-fabrics were degraded into oligosaccharides grafted with PTMPMA (in the form of trifluoacetate salt), which could be dissolved in D_2O for NMR analysis. As shown in Figure 4, in the ^{1}H NMR spectrum of pure PTMPMA (Figure 4a), the signal at 0.93 ppm is attributed to the proton resonances of the methyl groups in the main chain (H5), and the signals at 1.16−1.29 ppm are caused by the protons of the methyl groups of the piperdyl ring (H1). The protons of methylene of the main chain (H2) and piperdyl ring (H4) show signals at 1.60−2.02 ppm, and the hydrogen atom of methine of the piperdyl ring (H3) displays peaks around 5.06 ppm. Similar peaks can be found in the spectrum of the PTMPMA-*g*-fabrics after trifluoacetic acid

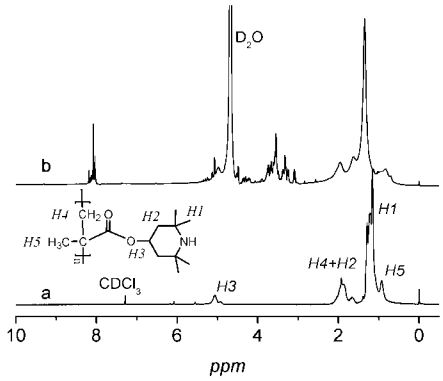


Figure 4. ^{1}H NMR spectra of (a) pure PTMPMA in $CDCl_3$ and (b) PTMPMA-*g*-fabric (graft yield 17.8%) after trifluoacetic acid treatment (in D_2O).

treatment, as shown in Figure 4b. There is slight shift of the characteristic peaks, which can be caused by the difference in NMR solvents ($CDCl_3$ vs D_2O). In addition, proton resonances of oligosaccharides are observed as multipeaks at 3.03−5.34 (the protons in the D-glucose units) and 8.00−8.20 ppm (hydroxyl protons). These findings further suggest that TMPMA has been grafted onto cotton cellulose.

After chlorination, the N−H bond of the hindered piperidyl structure in the grafted fabric could be transformed into amine *N*-halamines.[31] The presence of active chlorines on the resultant fabrics could be confirmed by a potassium iodine test. In this test, a small KI particle was placed onto the surface of PTMPMA-*g*-fabrics before (control) and after chlorination (sample) treatment. The graft yield was 17.8%, and both fabrics were wetted with a drop of distilled water before the test. As shown in Figure 5, the sample fabric shows a yellow color after only 5 s, and the color becomes much darker after 3 min. No color change can be observed on the control fabric. This test strongly suggests the presence of a N−Cl bond on the fabrics that could oxidize I^- to I_2. To quantitatively determine the chlorine content of the fabric samples, an iodometric titration test was performed,[30] and typical results are summarized in Table 1. The active chlorine contents of chlorinated PTMPMA-*g*-fabrics with 17.8, 10.8, and 2.7% of graft yield are 2.56, 1.55, and 0.45%, respectively, which are very close to their corresponding theoretical values.

Antibacterial Activities. The antibacterial functions of the chlorinated PTMPMA-*g*-fabrics were challenged with 10^6-10^7 cfu/mL of *S. aureus*, *S. epidermidis*, and *E. coli*. The results are summarized in Table 2. The most striking finding is that all the samples tested provide a total kill of 10^6-10^7 cfu/mL of the test species within 30 min. Active chlorine content of the samples does not seem to significantly affect the antimicrobial potency. For example, with 0.45% active chlorine, the fabric provides a total kill of *S. aureus* and *E. coli* in 30 min. When the active chlorine content is increased to 1.55%, it still takes the sample 30 min to kill 10^6-10^7 cfu/mL of *E. coli*, and 20 min to kill the same amount of *S. aureus*. On the other hand, our previous studies[36] showed that if cotton fabrics were grafted with amide-based *N*-halamines, with less than 1% active chlorine content, the fabrics provided a total kill of 10^8-10^9 cfu/mL of *E. coli* and *S. aureus* in only 3 min. Since the bactericidal action of *N*-halamines is caused by the transfer of positive halogens from the N-halamines to appropriate receptors in the bacteria cells,[45] these findings imply that the piperidyl-based amine *N*-halamines in the PTMPMA-*g*-fabric are very stable, as will be discussed in the sections below.

Stability, Durability, and Rechargeability of the Active Chlorines and Antimicrobial Activities of the Chlorinated PTMPMA-*g*-Fabrics. Hydrolytic and thermal stability of the N−Cl bonds in the chlorinated PTMPMA-*g*-fabrics was first challenged with autoclave treatment in a pressure steam sterilizer at 124−126 °C for 15 min, according to the manufacturer's recommendation for sterilization. After this treatment, 89.5, 87.1, and 77.8% of the original active chlorines were retained in the chlorinated fabrics with 17.8, 10.8, and 2.7% of graft yield, respectively (Table 3), and the antimicrobial activities of the autoclaved samples were essentially unchanged. Since a wide range of medical/hospital articles are required to be sterilized before they can be used, and the autoclave is still the most widely used sterilization method in general practice, these findings point to significant potentials of the new amine *N*-halamine-based fibrous materials.

Our previous studies showed that polymeric imide and amide *N*-halamines have much lower thermal/hydrolytic stability; e.g., most of the chlorines would be lost after autoclave treatment, and the resultant polymers showed significant color change to black (unpublished results), indicating decomposition of the N−Cl bond. Under the high-temperature/high-moisture conditions, the N−Cl bond could be (1) hydrolyzed to form N^- and Cl^+ or (2) thermally decomposed to form $N^\bullet$ and $Cl^\bullet$ radicals. However, in the chlorinated PTMPMA-*g*-fabrics, the two neighboring carbon atoms of the N−Cl group are attached to four electron-donating methyl groups (see Scheme 1 for structure). As discussed earlier, this electronic effect would destabilize any developing negative charge on N atom as Cl^+ leaves the molecule.[45] Thus, the active chlorines in the chlorinated PTMPMA-*g*-fabrics should have high hydrolytic stability.

The thermal stability of the N−Cl bond in chlorinated PTMPMA-*g*-fabrics was investigated with TGA. As shown in Figure 6, pure cotton fabric does not show any significant weight loss before 300 °C (Figure 6a). Both pure PTMPMA (Figure 6d) and PTMPMA-*g*-fabrics (graft yield 17.8%, Figure 6b) begin to lose weight staring from around 230 °C, which is correspondence to the thermal decomposition of PTMPMA polymer chain.[57] In the TGA curve of the chlorinated PTMPMA-*g*-fabric, the sample displays noticeable weight loss starting from 180 °C (Figure 6c), and this is most likely caused by the thermal decomposition of the samples induced/accelerated by the N−Cl bond breakage.[30,32] Given the fact that the autoclave treatment was conducted at 124−126 °C, these TGA results strongly suggest that the N−Cl bonds in chlorinated PTMPMA-*g*-fabrics are thermally stable enough to survive autoclaves.

Durability and rechargeability are two other important features of the new hindered amine N-halamine-based fibrous materials. At 20−25 °C and 30−90% RH, the samples have been stored for more than 10 months without any significant changes of the active chlorine contents on the fabrics as well as the antimicrobial efficacies against *E. coli* and *S. aureus*. In machine washing test, even after 30 rounds of continuous washing without chlorination treatment, the samples still retained at least 71% of the original active chlorines (see Table 3), further confirming the hydrolytic stability of the N−Cl bonds. To test rechargeability, the chlorinated *PTMPMA-g*-fabrics were first treated with 0.3% of sodium thiosulfate solution to partially quench the active chlorine for 1 h, and then rechlorinated with 0.1% of sodium hypochlorite solution at room temperature for 30 min. After 10 cycles of the quenching-rechlorinating treatment, at least 94% of the original active chlorine was retained (see Table 3), and the antimicrobial activities were unchanged.

Conclusions

A polymerizable hindered amine monomer, 2,2,6,6-tetramethyl-4-piperdyl methacrylate (TMPMA), was successfully

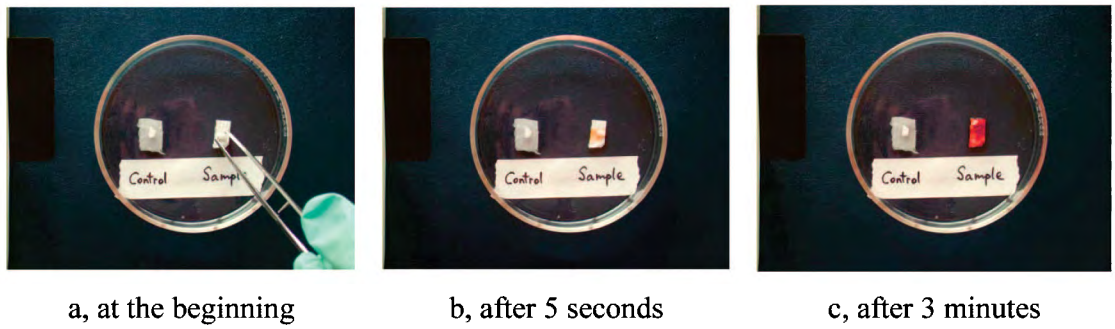


Figure 5. KI test by putting a small KI particle on wetted PTMPMA-*g*-fabrics before (control) and after (sample) chlorination.

Table 1. Active Chlorine Contents of Selected PTMPMA-*g*-Fabric

PTMPMA-*g*-frabics (graft yield, %)	active chlorine content after chlorination (wt%)[a]
17.8	2.56 ± 0.03
10.8	1.55 ± 0.01
2.7	0.45 ± 0.02

[a] Every titration test was repeated five times.

Table 2. Antibacterial Activities of Chlorinated PTMPMA-*g*-Fabrics with Various Active Chlorine Contents

active chlorine content of fabrics (%)	minimum contact time for a total kill (min)		
	S. aureus	*S. epidermidis*	*E. coli*
0.45	30		30
0.78		30	30
1.55	20		30
2.56		20	20

Table 3. Active Chlorine Contents of PTMPMA-*g*-Fabrics after Various Treatments

samples	active chlorine content at different graft yield (wt %)[a]		
	17.8%	10.8%	2.7%
freshly chlorinated	2.56 ± 0.03	1.55 ± 0.01	0.45 ± 0.02
after steam sterilization	2.29 ± 0.10	1.35 ± 0.01	0.35 ± 0.02
after 30-rounds laundry	2.32 ± 0.02	1.45 ± 0.03	0.32 ± 0.01
after 10-rounds recharge	2.41 ± 0.04	1.47 ± 0.05	0.44 ± 0.03

[a] Every titration test was repeated five times.

grafted onto cotton cellulose via free radical polymerization with the initiation of Ceric salt. The grafted fabrics were treated with diluted sodium hypochlorite solution to transform the N−H bond in the grafted TMPMA chains into amine N-halamines. The new polymeric N-halamine fibrous materials demonstrated powerful, durable, and rechargeable antibacterial activities against both gram-positive and gram-negative bacteria. Thanks to the excellent hydrolytic stability and thermal stability, the active chlorines in the new polymeric N-halamine fibrous materials were autoclavable, making the new materials attractive candidates for a broad range of applications such as hospital gowns/uniforms, bedding materials in healthcare/institutional settings, and a wide variety of consumer hygienic products. Additionally, using the strategy demonstrated in this article, TMPMA can be readily grafted onto other cellulose derivatives and natural or synthetic polymers that carry hydroxyl groups, turning the resultant polymers into rechargeable antimicrobial materials. The new materials may find applications in medical devices, dental equipment, water purification and transportation, food packaging and food storage, air filtration, etc.

A series of these TMPMA-based polymeric amine N-halamines are being studied in this laboratory to provide further information about the structure−property relationship and potential applications of this class of exceptionally stable N-halamines.

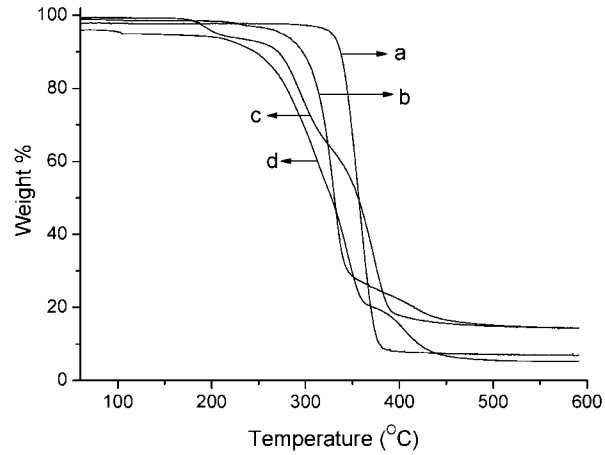


Figure 6. TGA curves of (a), original cotton fabric; (b), PTMPMA-g-fabric (graft yield: 17.8%); (c), chlorinated PTMPMA-g-fabric (graft yield: 17.8%) and (d), pure PTMPMA.

Acknowledgment

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