

# Biocidal Acyclic Halamine Polymers: Conversion of Acrylamide-Grafted-Cotton to Acyclic Halamine

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Received 13 August 2007; accepted 11 December 2007

DOI 10.1002/app.27958

Published online 6 March 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Biocidal acyclic halamine materials can be prepared by chlorination of amide structures grafted onto polymers such as cellulose. This approach extended available halamine structures and potential applications in medical textiles and polymers. However, the conversion yield of the amide bonds to acyclic halamine was quite low (~6%) according to the grafted amide bonds. By using instrumental analyses of FTIR, NMR, and LC-MS, imidization reaction on amide bonds during the graft polymeriza-

tion was identified as one of the major side reactions that could lead to the low conversion yield. Potassium persulfate was found accountable for the imidization reaction of amide structures. Potential solutions to this side reaction were proposed and evaluated as well in this study. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3480–3486, 2008

**Key words:** radical polymerization; halogenated; graft copolymers

## INTRODUCTION

Microorganisms such as viruses, bacteria, and fungi have strong ability to survive on the surface of fibrous materials,<sup>1–4</sup> which justifies the need of developing antibacterial textiles. Among many biocides like silver, triclosan, and chitosan, *N*-halamines have shown to be an excellent biocidal agent that can provide almost instantaneous and total kill of a wide range of microorganisms.<sup>5,6</sup> Many efforts have been made to incorporate *N*-halamine structures onto polymeric substrates.<sup>7–9</sup> Cyclic *N*-halamines have been employed in water disinfection, and as a result, the cyclic halamine precursor monomers were synthesized and incorporated onto polymeric substrates via radical graft polymerization.<sup>10–12</sup> The radical graft polymerization mechanism on cotton cellulose using potassium persulfate (PPS) as an initiator was also studied.<sup>13</sup>

As an effort to expand studies on halamine structures that can be employed on textiles, acyclic amine/amide monomers such as acrylamide and methacrylamide were grafted onto cotton cellulose, and the grafted cotton samples were converted to acyclic biocidal *N*-halamine fabrics as well.<sup>14</sup> The

grafting yields of the monomers were pretty high, however, the resulted *N*-halamine contents on the fabrics were unproportionally low, indicating that there might be certain side reactions during the grafting reaction or chlorination of the grafted acyclic amides. Also, the grafted amide structures showed relatively lower stability during acidic and basic chlorination, which may inhibit further application of the acyclic halamines in textile materials.

This study was intended to discover the side reactions in PPS-initiated radical graft polymerization of acrylamide on cotton cellulose, chlorination of the grafted samples, and find proper solutions to reduce the side reactions and improve practicality of applications of the acyclic halamine in textiles. FTIR, NMR, LC/MS, and electron microprobe were employed in the study.

## EXPERIMENTAL

### Materials and reagents

Pure cotton print cloth #400 was purchased from TestFabrics (West Pittston, PA). PPS (Acros) were recrystallized from distilled water. 3-Allyl-5,5-dimethylhydantoin (ADMH) was synthesized according to a method reported previously.<sup>11</sup> Acrylamide (AM), methacrylamide (MAM), *N*-*tert*-butyl acrylamide (BAM), and polyacrylamide (PAM, FW: 1500) (Aldrich, St. Louis, MO) were used as received.

### Instrumentation

FTIR spectra were taken on a Nicolet 6700 spectrometer (Thermo Electron) using KBr pellets. NMR experi-

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Contract grant sponsor: National Science Foundation; contract grant number: CTS 0424716.

Contract grant sponsor: National Textile Center; contract grant number: S06-CD01.

Contract grant sponsor: University of California, Davis (Jastro-Shields Graduate Research Award).

*Journal of Applied Polymer Science*, Vol. 108, 3480–3486 (2008)  
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**TABLE I**  
**Chlorination Degree of Acrylamide-Grafted-Cotton**

Grafting Temp./Time	Add-on (grafting yield) (%)	Chlorine (ppm)	Conversion ratio (%)
135°C/1 min	1.81 (56.0)	602	6.68
120°C/4.7 min	2.01 (62.2)	712	7.13
100°C/46.5 min	1.85 (57.2)	503	5.47
80°C/601.5 min	1.89 (58.5)	542	5.77

Grafting condition: acrylamide 2.486% (0.35M) and potassium persulfate 4.725% (0.175M) solution, wet pick up 130%; chlorination: 300 ppm available chlorine, pH 11, 30 min; conversion ratio equals the moles of loaded chlorine divided by that of nitrogen.

ments were performed on a Bruker DRX-500 spectrometer with a proton frequency of 500 MHz at 298 K.

**Grafting polymerization**

All of the chemicals (monomers and the initiator) were mixed in appropriate ratio in distilled water. Fabrics were dipped in the monomer/initiator solution and padded at a required expression. This “dip-pad” process was repeated twice. Padded fabrics were dried under at 60°C for 10 min in an oven. The samples were cured in an oven at 105°C for 30 min, and then extracted with deionized water in a Soxhlet extractor for 72 h and dried at 60°C. Add-on refers to grafted polymer weight percentage increase based on the original weight of cotton after the reaction. Grafting yields equals actually grafted polymer on cotton divided by the loaded amount of the monomer.

**Characterization and analysis**

The treated cotton was extracted in water to remove any unattached monomer or oligomers. The extraction solution was directly analyzed by using a mass spectrometer (ESI/MS) (AB MDS SciEX Q TRAP) to identify the contents. The treated cotton fabrics after extraction were degraded in 6M HCl at 60°C for selected time durations, and then neutralized with sodium hydroxide solution. The MS spectrum was acquired by syringe infusion of the analyte at 15 μL/min into the ESI source. A good quality spectrum was obtained by averaging the acquired data over a period of 1 min. In collision-induced dissociation (CID) experiments on the mass spectrometer, nitrogen was used as the collision gas, and normalized collision energy of 35% was used to bring about fragmentation.

**RESULTS AND DISCUSSION**

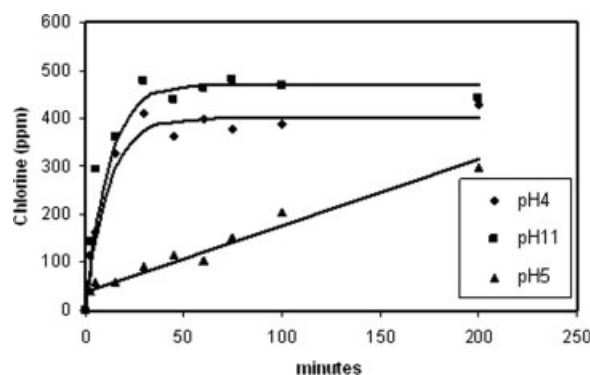
**Formation and hydrolytic stability of acyclic halamine**

AM was easily grafted onto cellulose by using PPS as an initiator and a regular wet fabric treatment

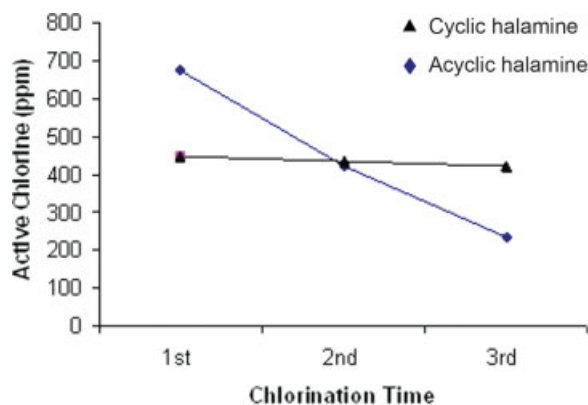
process. Grafting yields were around 60% (Table I). Conversion of the amide N—H into N-halamine (N—Cl) was conducted by immersing the grafted samples in a diluted chlorine bleach solution (pH 11, 300 ppm available chlorine) for 30 min. The chlorinated poly(acrylamide)-g-cotton (PAM-g-cotton) showed active chlorine contents of 500–700 ppm, a very encouraging number in the active chlorine amount. However, the amounts of the active chlorine were only 5–7% of the expected active chlorine content (assuming that each chlorine atom substitutes for one hydrogen atom at amide nitrogen) on the samples (Table I), indicating a very low conversion of the grafted acyclic amide (NH) structures to halamines (N—Cl).

Different chlorination conditions were used to increase the conversion yields. Figure 1 shows the results of chlorination time and active chlorine contents on the grafted samples under three different pH conditions. Under neutral condition, equilibrium was not reached within a duration of 200 min. When the chlorination was carried out under pH 11, the maximum active chlorine content on the grafted cotton could be reached at 30 min. Under acidic condition, the chlorine content of the grafted cotton leveled off after 30 min chlorination as well and the maximum chlorine content, however, was lower than that under pH 11. This result is opposite to the chlorination of Nomex fabrics which was favored under acidic condition.<sup>15</sup> Such a result might be due to the fact that cotton can swell under alkaline condition. Thus, the accessibility of the grafted amides under alkaline condition is greater than that under acidic condition. However, the maximum conversion yields of N—H to N—Cl were still at 7% based on the available NH contents.

More interestingly, it was found that the regenerability of chlorinated PAM-g-cotton was extremely



**Figure 1** Chlorination kinetics of PAM-g-cotton under different pH conditions. Grafting condition: acrylamide 2.486% (0.35M) potassium persulfate 4.725% (0.175M), dry at 60°C 10 min, cure at 105°C 30 min; chlorination: 300 ppm available chlorine, 30 min.



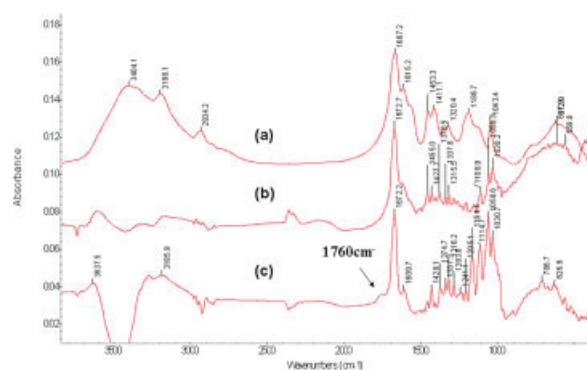
**Figure 2** Comparison of regenerability of acyclic and cyclic halamines. Chlorination: 300 ppm available chlorine, pH 11, 30 min; excess amount of  $\text{Na}_2\text{S}_2\text{O}_3$  was used to quench active chlorine on the samples between 1st, 2nd, and 3rd chlorinations. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

low when compared with that of cyclic halamines (Fig. 2), which may indicate potential hydrolysis of the acyclic halamines during chlorination reaction. These properties of acyclic halamine would possibly affect their applications on textiles.

### Conversion of amide to acyclic halamine

Conversion ratios of cyclic amide to *N*-halamine were in the range of 23–30%, and possible crosslinking reactions of the cyclic amide with cotton during grafting reaction might have contributed to the low conversion rate.<sup>16</sup> But, that reaction is not applicable here. In a study of chlorination of polyacrylamide in NaOCl solution, it was proposed that the electrostatic repulsive forces between chloroamine anion  $-\text{CONCl}^-$  and chlorinating agent  $\text{ClO}^-$  contributed to the low conversion ratio (63% maximum).<sup>17</sup> Considering the above factor, the chlorination efficiency of the acyclic amides on cotton should be lower than 100%, but 7% of conversion ratio was still abnormally low.

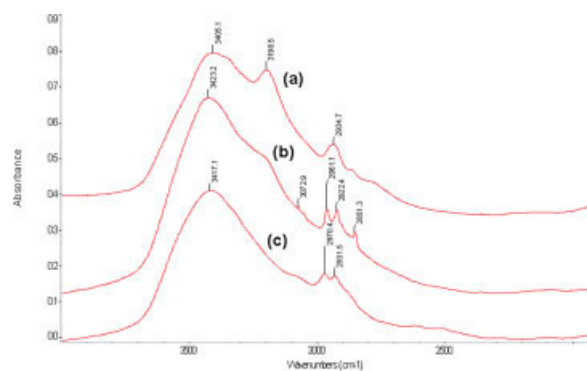
FTIR spectra of polyacrylamide grafted cotton (PAM-g-cotton), pure homo polymacrylamide (PAM), polyacrylamide-coated cotton (PAM-coated cotton), and pure cotton samples were taken. Figure 3 shows spectrum (a), a basic IR spectrum for a polyacrylamide homopolymer (FW: 1500), spectrum (b), result of subtracting FTIR spectrum of pure cotton from that of PAM-coated cotton, and spectrum (c), subtraction result of PAM-g-cotton and untreated cotton. The relative peak height ratio of amide band II (N—H bending) versus amide band I (carbonyl stretching) were used to predict the status of amide hydrogen. In the spectrum of PAM-coated cotton, those two peaks were resolved with the setting of



**Figure 3** FTIR spectra of (a) polyacrylamide FW: 1500, (b) subtracted FTIR spectrum of polyacrylamide-padded-cotton and untreated cotton cellulose, (c) subtracted FTIR spectrum of polyacrylamide-grafted-cotton and untreated cotton cellulose. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

medium sensitivity and full width at half height (FWHM) of 40. The peak height ratio is smaller for PAM-g-cotton ( $H_{1672/1608 \text{ cm}^{-1}} = 0.17$ ) than that of PAM-coated cotton ( $H_{1672/1608 \text{ cm}^{-1}} = 0.38$ ), indicating some loss of hydrogen at the amide nitrogen of PAM-g-cotton. Then, extracts from PAM-g-cotton, which contain homopolyacrylamide produced but not grafted on cotton during grafting reaction, were analyzed by FTIR (Fig. 4). Similarly, it showed the loss of NH bonds in the homopolymer compared with the regular polyacrylamide. IR spectrum of poly(*N*-*tert*-butyl acrylamide)-g-cotton (PBAM-g-cotton) (Fig. 4, spectrum c) further confirmed the loss of hydrogen at the amide nitrogen on PAM-g-cotton, since PBAM-g-cotton only has one N—H. These results support possible formation of secondary or tertiary amide structures on the polyacrylamide chains.

NMR spectra of the extracts were taken to determine the possible formation of secondary or tertiary



**Figure 4** IR spectra of (a) polyacrylamide (PAM, FW: 1500), extracts of (b) polyacrylamide-g-cotton (PAM-g-cotton), and (c) poly(*N*-*tert*-butyl acrylamide)-g-cotton (PBAM-g-cotton). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

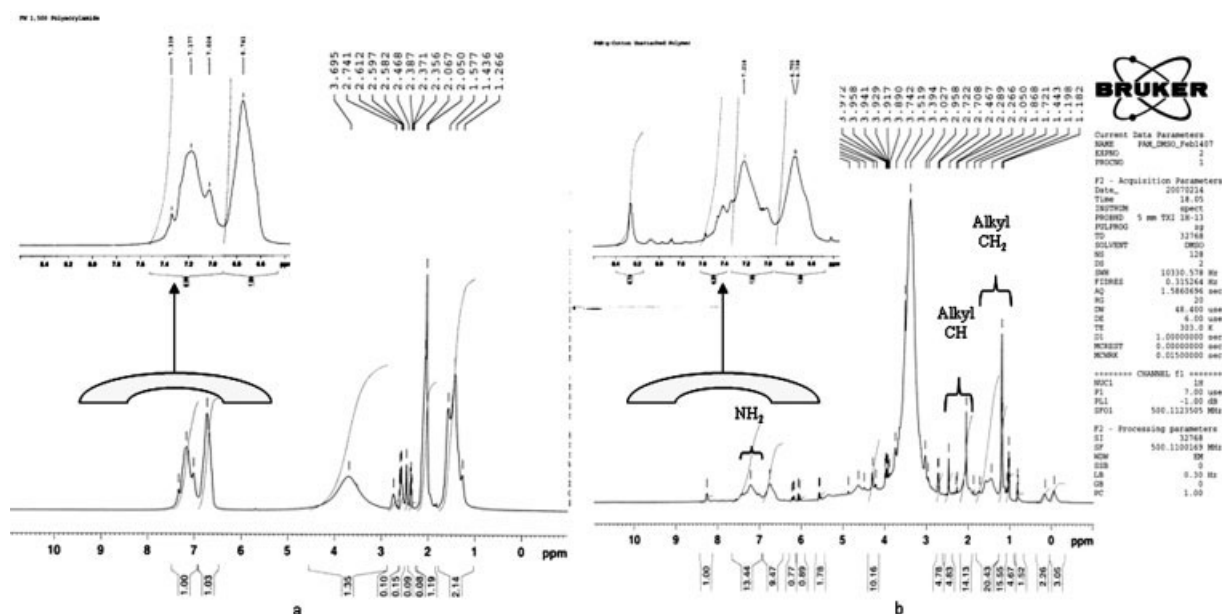


Figure 5  $^1\text{H}$  NMR of (a) standard polyacrylamide (FW 1500) and (b) byproduct extracts of PAM-g-cotton.

amides on PAM-g-cotton, which could be a reason of low conversion yields of N—H to N—Cl. Because of the resonance interaction between the unshared pair of electrons on nitrogen and carbonyl group, two protons attached to the amide nitrogen are not magnetically equivalent. As shown in Figure 5, the relative integral of two amide proton peaks ( $\delta$  7.2 and  $\delta$  6.8) of the regular polyacrylamide (FW 1500) are 1.9 calculated with respect to a value of 3 for the total integral of the  $\alpha$ - and  $\beta$ -methylene proton resonances. There was no observable secondary amide proton, and a 5% loss of hydrogen on nitrogen as calculated in Table II might be due to integration inaccuracy (the ratio of alkyl hydrogen versus nitrogen hydrogen should be 3 : 2 based on the polymer structure  $-\text{CH}_2-\text{CH}(\text{CONH}_2)-$ ). In the NMR spectrum of PAM-g-cotton extract, there was a peak ( $\delta$  7.4) sitting at the shoulder of the primary amide proton peak ( $\delta$  7.2), which is assigned as secondary amide proton ( $-\text{C}(\text{O})-\text{NHR}$ ) according to the work of Glickson and Applequist.<sup>18</sup> One more peak at  $\delta$  8.3 suggests the formation of cyclic imide ( $-\text{C}(\text{O})-\text{NH}-\text{C}(\text{O})-$ ) between neighboring amide groups.<sup>19</sup> The small peak of  $1760\text{ cm}^{-1}$  in Figure 3 (spectrum c) also lends support to the formation of cyclic imide.

As summarized in Table II, NMR spectrum confirmed that the protons attached to the amide nitrogen on the extracts from PAM-g-cotton were around 59.3% of the theoretical value (40.7% loss). Among the remaining 59.3% of amide proton, 50% was still primary amide proton and 9.3% was transformed to secondary amide proton. 40.7% loss of the amide proton may be due to the formation of nitroso or  $N,N$ -disubstituted amide. Although this result was from the extracted products from PAM-g-cotton, it also represents the structures of the grafted polyacrylamide on cotton. This loss of NH groups on the PAM-g-cotton could explain the abnormal low formation of acyclic halamine structures.

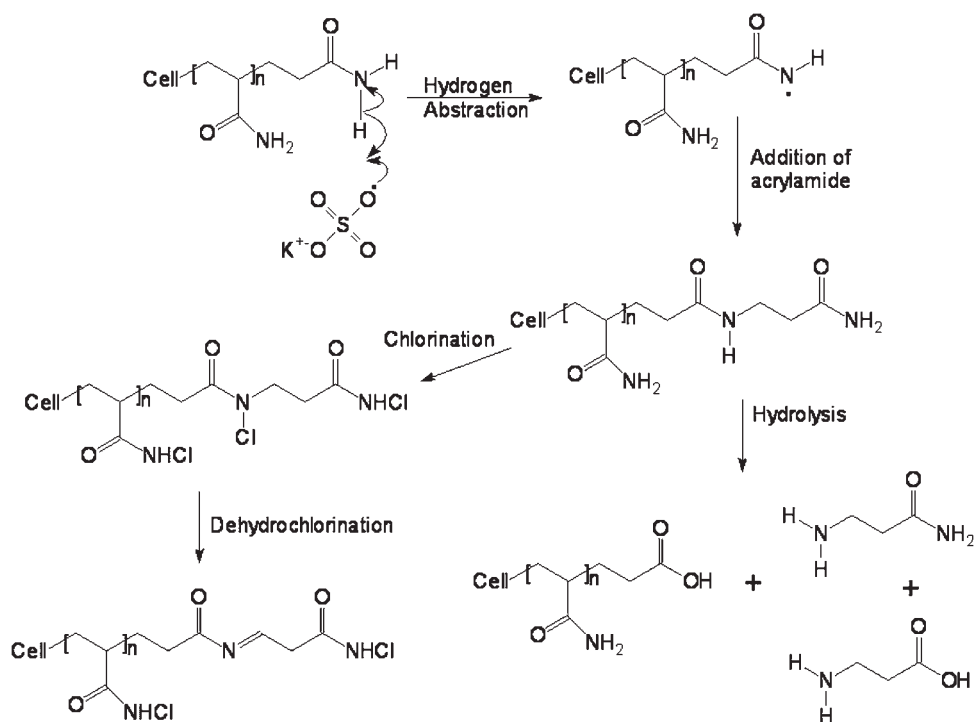
### Imidization

The loss of N—H groups on the amide could be caused by a proposed reaction due to the presence of extra persulfate radicals (Scheme 1). The formed secondary amide could be first chlorinated to acyclic halamine. However, potential formation of imide ( $\text{N}=\text{C}$ ) structures due to an elimination of HCl from acyclic N—Cl and vicinal CH makes regeneration of N—H to N—Cl impossible. In addition, hydrolysis of secondary amide also expedites the loss of amide

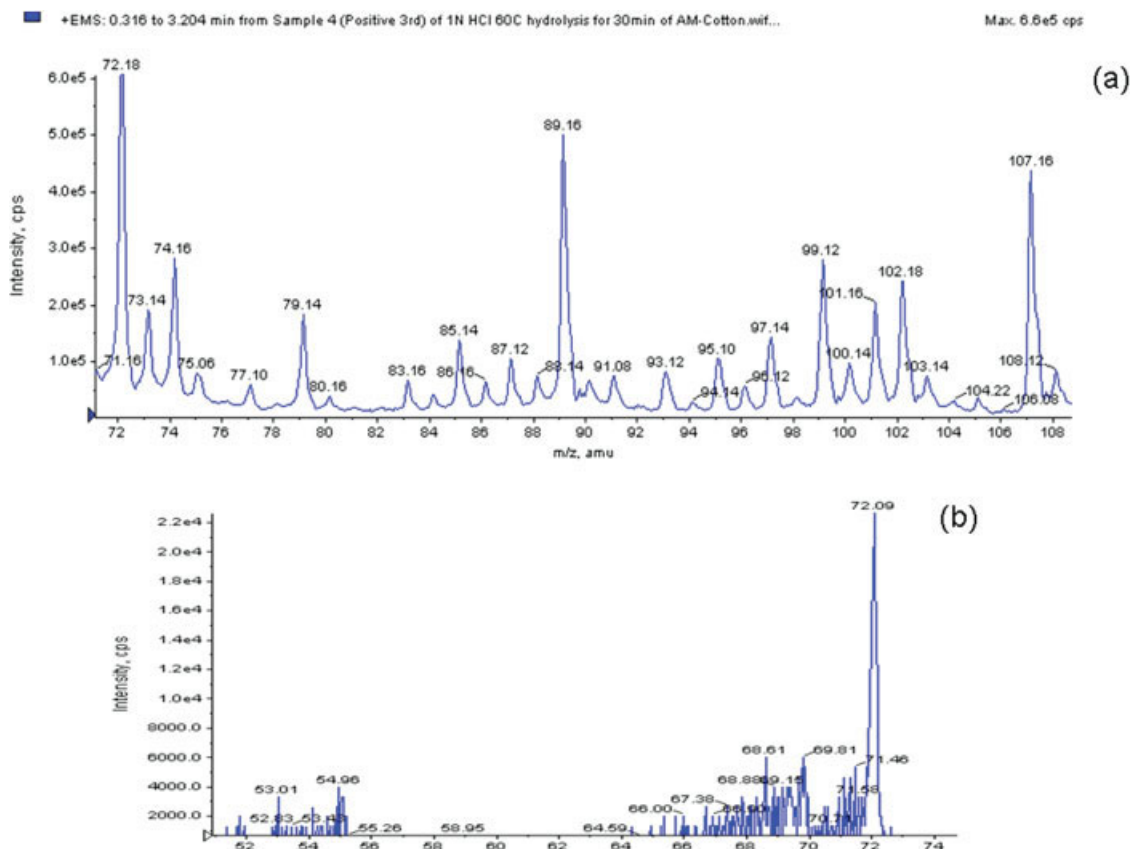
TABLE II  
Relative Integrals of Amide Proton Peaks of the Amide Polymers

Sample	NH ( $2^\circ$ )	NH ( $1^\circ$ )	Calculated total NH	Loss of H at N (%)
Polyacrylamide (FW 1,500)	0	1.9	2.0	5.0
Extract of unattached polymer on PAM-g-cotton	0.185	1.0	2.0	40.7





Scheme 1 Mechanism of imidization.



**Figure 6** Mass spectra of (a) hydrolysates of PAM-g-cotton (1N HCl 60°C, 60 min) and (b) collision-induced dissociation of  $m/z$  89. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE III**  
Impact of Grafting Environment, Initiator, and Monomers on Conversion Ratio of N to N—Cl

	N%	Loss of nitrogen (%)	Chlorine (ppm)	Conversion ratio (%)
PAM-g-cotton #1	0.3140			
After chlorination	0.231	0.264	658	11.3
PAM-g-cotton #2	0.319			
After chlorination	0.248	0.222	539	8.59
PAM-g-cotton #3	0.371			
After chlorination	0.286	0.229	472	6.52

Grafting recipe #1: PPS 22 mM; #2: PPS 44 mM; #3: PPS 88 mM; AM is 350 mM for all trials.

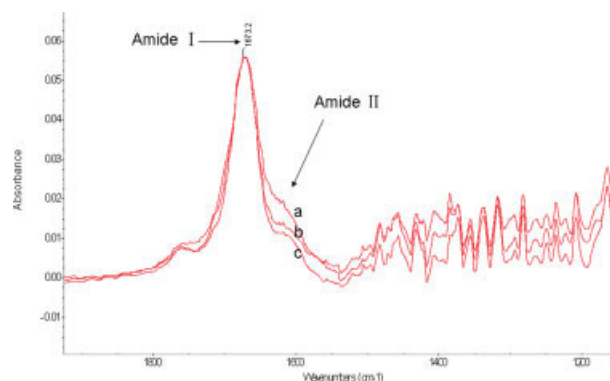
groups grafted on cotton. To confirm the proposed reactions, PAM-g-cotton was hydrolyzed by 6M HCl for 30, 60, 180, and 240 min at 60°C, respectively, for NMR and LC-MS analyses. Since the primary amide is also vulnerable to acid hydrolysis, ammonium chloride is one of the major products in the hydrolysate. Ammonium ion was identified by  $^1\text{H}$  NMR: (500 MHz,  $d_6$ -DMSO) at  $\delta$  7.121 (4H, t,  $J = 50$  Hz). Then, the hydrolysates were subjected to mass spectrometry analysis. Two peaks  $m/z$  89 and  $m/z$  107 were observed [Fig. 6(a)] (200- $\mu\text{M}$  acrylamide was spiked into the hydrolysate to serve as a reference). The CID of  $m/z$  89 gives  $m/z$  72 [Fig. 6(b)] suggested that  $m/z$  89 is a derivative of acrylamide. If the imidization happened as denoted in Scheme 1 after hydrolysis, two peaks  $m/z$  89 (3-amino-propanamide in protonated form) and  $m/z$  107 (ammonium salt of  $\beta$ -aminopropanoic acid in protonated form) should show up in positive mode mass spectrum. Thus, the LC-MS confirmed the imidization of amide nitrogen which is proposed by low conversion ratio of N to N—Cl. Obviously, the elimination of HCl of  $\alpha$ -hydrogen and chlorine on the secondary amide can easily lead to the formation of conjugated double bonds of C=O and N=C, which could turn the chlorinated PAM-g-cotton to light yellow. This was also observed on the treated and chlorinated fabrics. Such an effect could further inhibit applications of acyclic halamines on cellulosic materials.

#### Potential solutions to imidization and hydrolysis

Based on the Scheme 1, to reduce imidization reaction the amount of radical initiators should be reduced. Thus, the amount of the initiator PPS was reduced while the amount of monomer was maintained same. As shown in Table III, the conversion ratios of N—H to N—Cl increased with decreasing PPS amount in the grafting formulations. These results correlated with IR spectra (Fig. 7) very well. With the increase of the PPS dosage, the ratio of amide band II versus band I decreased indicating greater loss of amide hydrogen.

The high tendency of persulfate radical to abstract hydrogen atoms from amide should contribute to the side reaction. Thus, other initiator that has lower tendency to abstract hydrogen from nitrogen, such as cerium ammonium nitrate (CAN), was employed to replace PPS. Cerium ion will form a complex with an anhydroglucose unit, which is followed by an electron transfer within the complex.<sup>20</sup> Subsequently, the C3–C4 bond of the glucopyranoid ring is broken and cellulosic radicals are formed, which could initiate graft polymerization. As shown in Table IV, the conversion ratio of N—H to N—Cl was 11.5% for CAN-initiated PAM-g-cotton, an immediate increase in the formation of acyclic halamine. This result is a clear indication of reduction of imidization reactions. However, CAN is less effective in initiating grafting of acrylamide onto cotton which result in lower amount of grafting yield under the similar condition with PPS-initiated grafting.

Another approach to reduce imidization of amide bonds is to select different monomers that could potentially inhibit the side reaction. When methacrylamide (MAM) was employed in the grafting reaction, the conversion ratio was a little higher (7.58%)



**Figure 7** FTIR spectra showing the impact of PPS dosage on the ratio of amide band II versus band I. PPS dosage: 22 mM (a), 44 mM (b), and 87 mM (c). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE IV  
Impact of Potassium Persulfate Dosage on Conversion Ratio of N to N—Cl

	N%	Chlorine (ppm)	Chlorination conversion rate (%)
PAM-g-cotton; initiator: 18.2 mM CAN	0.067	194	11.5
PAM-g-cotton; initiator: 175 mM PPS	0.275	416	5.99
PMAM-g-cotton; initiator: 175 mM PPS	0.272	521	7.58
PBAM-cotton <sup>a</sup> ; initiator: 175 mM PPS	0.0405	166	15.9

<sup>a</sup> Because of low solubility in water, the concentration of *N-tert*-butyl acrylamide was 87.5 mM, while that of acrylamide (AM) and methacrylamide (AM) was 350 mM.

than that of PAM-g-cotton (5.99%). Since the allyl hydrogen in MAM could provide another competing site in reacting with PPS, the existence of MAM decreased the extent of imidization. Substitution at amide nitrogen should be able to further protect it from imidization. As an attempt, *N-tert*-butyl acrylamide was used in the grafting reaction. The conversion yield from N—H to N—Cl (15.9%) was much higher than that of PAM-g-cotton (Table IV). However, no matter 15.9 or 11.3% (Table III, 22 mM PPS dosage) conversion, it is still far less than the achievable 63%<sup>11</sup> conversion of N—H to N—Cl for polyamide. The bulky steric hindrance in BAM stops the chlorination from going to completion. While in case of acrylamide, the simultaneously formed carboxylic acid (from hydrolysis<sup>14</sup>) along the polymer chain repels the major chlorinating agent ClO<sup>-</sup> at pH 11 and further decreases the conversion ratio.

### CONCLUSIONS

Radical graft polymerization of acrylamide on cotton could have imidization reaction as one of the major side reactions, which is responsible to the low conversion yield of the grafted amide to acyclic halamine on the chlorinated PAM-g-cotton. The use of the radical initiator, PPS, is mostly responsible for the imidization. Reduced amount of the initiator in the graft polymerization could reduce the side reaction. The use of initiators that would not abstract hydrogen from amide group could also reduce the reaction. More interestingly, the use of monomers

that would inhibit the hydrogen abstraction on the amide group could also help.

### References

- Wendt, C.; Wiesenthal, B.; Dietz, E.; Ruden, H. *J Clin Microbiol* 1998, 36, 3734.
- Neely, A. N.; Maley, M. P. *J Clin Microbiol* 2000, 38, 724.
- Asai, N.; Fujiwara, K.; Taguchi, H.; Morigaki, T.; Morita, A.; Furui, S. *Kyoto-fu Hoken Kankyo Kenkyusho Nenpo* 2001, 46, 6.
- Munk, S.; Johansen, C.; Stahnke, L. H.; Adler-Nissen, J. *J Surf Deterg* 2001, 4, 385.
- Worley, S. D.; Williams, D. E. *Crit Rev Environ Control* 1988, 18, 133.
- Worley, S. D.; Sun, G. *Trends Polym Sci* 1996, 4, 364.
- Worley, S. D.; Chen, Y.; Wang, J. W.; Wu, R. *Surf Coat Int Part B: Coat Trans* 2005, 88, 93.
- Liang, J.; Wu, R.; Wang, J. W.; Barnes, K.; Worley, S. D.; Cho, U.; Lee, J.; Broughton, R. M.; Huang, T. S. *J Ind Microbiol Biotechnol* 2007, 34, 157.
- Sun, Y.; Sun, G. *J Appl Polym Sci* 2003, 88, 1032.
- Sun, Y.; Sun, G. *J Appl Polym Sci* 2001, 81, 1517.
- Sun, Y.; Sun, G. *J Appl Polym Sci* 2001, 80, 2460.
- Sun, Y. Y.; Chen, T. Y.; Worley, S. D.; Sun, G. *J Polym Sci Part A: Polym Chem* 2001, 39, 3073.
- Liu, S.; Sun, G. *Carbohydr Polym* 2008, 71, 614.
- Liu, S.; Sun, G. *Ind Eng Chem Res* 2006, 45, 6477.
- Sun, Y.; Sun, G. *Ind Eng Chem Res* 2004, 43, 5015.
- Qian, L.; Sun, G. *J Appl Polym Sci* 2004, 91, 2588.
- Chen, S. P.; Tanaka, H. *Kami Pa Gikyoshi* 1994, 48, 485.
- Glickson, J. D.; Applequist, J. *Macromolecules* 1969, 2, 628.
- Haas, H. C.; MacDonald, R. L. *J Polym Sci Part A: Polym Chem* 1971, 9, 3583.
- Jagur-Grodzinski, J. In *Heterogeneous Modification of Polymers*; Jagur-Grodzinski, J., Ed.; Wiley: Chichester, 1997; Chapter 4.