

Novel Regenerable N-Halamine Polymeric Biocides. II. Grafting Hydantoin-Containing Monomers onto Cotton Cellulose

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ABSTRACT: A novel cyclic-amine monomer, 3-allyl-5,5-dimethylhydantoin (ADMH) was synthesized with good yield by the reaction of allyl bromide with 5,5-dimethylhydantoin (DMH), and was characterized by FTIR and $^1\text{H-NMR}$ spectra. ADMH alone cannot be grafted onto other polymers. However, the presence of acrylonitrile markedly enhanced the ADMH graft yield onto cotton cellulose. The influence of reaction conditions on the graft copolymerization was investigated. After chlorine bleach treatment, hydantoin units in the grafted copolymers were easily transformed into N-halamine structures. Grafted samples exhibited potent antibacterial activity against *Escherichia coli*, and the functional properties were shown to be durable and regenerable. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 617–624, 2001

Key words: regenerable antibacterial; grafting; hydantoin containing; cotton

INTRODUCTION

Contamination of textile materials by micro-organisms such as pathogenic bacteria, odor-generating bacteria, molds, fungi, and virus is of great concern in medical, institutional, and apparel products in recent years. Survival of micro-organisms on textile materials and transfer of these micro-organisms between patients and health care workers (HCWs) has been demonstrated, and it has been accepted that hospital gowns, patient drapes, carpeting and bedding materials, etc., can be important elements in crosstransmission of diseases.^{1–4} Medical gowns and uniforms

used currently provide barriers for HCWs, but have proven to be ineffective in studies by numerous researchers.^{5–9} The occurrence of contaminated cleaning cloths in domestic applications has also been investigated. Results from different studies indicated that more than half of the investigated dishcloths and cleaning cloths were contaminated by one or more of the following organisms: *Escherichia coli*, *Staphylococcus aureus*, *Streptococcus faecalis*, and *Clostridium perfringens*.^{10–12} Further studies showed that wiping hard surfaces with contaminated cloths could result in crosscontamination of hands, equipment, and other surfaces.¹³

These findings suggest that biocidal properties should be a necessary feature of medical and related healthcare and hygienic-use textiles. Antimicrobial textiles and polymeric biocides have been reviewed by several researchers recently.^{14–16} Among the currently investigated biocidal materials, N-halamines have shown al-

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most instant and total kill to a wide range of micro-organisms without causing environmental concerns. There are several advantages associated with those N-halamine structures, including the properties that they are stable under a broad range of temperatures, and are regenerable by chlorine bleaching after loss of activity from extensive uses.^{17–19} Recently, N-halamine structures were incorporated into cellulose-containing fabrics by a conventional pad-dry-cure method in the presence of formaldehyde.^{20–22} The results indicated that as little as 1% (wt) add-on of halamine structures provided the materials with powerful biocidal properties (6–7 log reduction) against most common pathogens, after a contact time of 2 min. The biocidal properties of the treated samples were both durable and regenerable.

In the first article, we have reported synthesis and characterization of hydantoin-containing vinyl monomers.²³ It was found that, due to the allylic structure of the monomers, they were difficult to form homopolymers. However, these monomers could be readily copolymerized with most acrylic, substituted acrylic, and vinyl monomers. All the copolymers showed biocidal efficacy after exposure to chlorine, and their antibacterial properties were durable and regenerable. In this study, a hydantoin-containing monomer, 3-allyl-5,5-dimethylhydantoin (ADMH) was grafted onto cotton cellulose in the presence of acrylonitrile (AN), and the antibacterial properties of the grafted fabrics against *Escherichia coli* were investigated.

EXPERIMENTAL

Materials

Bleached, desized cotton print cloth #400 (Testfabrics Inc.) was used throughout the study. 5,5-Dimethylhydantoin (DMH, Aldrich), ammonium cerium (IV) nitrate (Acros, ACN), and allyl bromide (Acros) were used without further purification. Acrylonitrile (AN) (Acros) was distilled twice before use.

Instruments

FTIR spectra were taken on a Nicolet Magana IR-560 spectrometer using KBr pellets. The samples were made thin enough to ensure that the

Beer-Lambert law was obeyed. ¹H-NMR spectra were recorded on a GE NMR QD-300 spectrometer. DSC measurements of the samples were performed with a Shimadzu DSC-50 instrument at a heating rate of 20°C/min under a nitrogen atmosphere.

Synthesis of ADMH

A solution of 6.4 g (0.05 mol) of DMH in 25 mL H₂O containing 2.8 g (0.05 mol) of KOH was combined with a solution of 4.4 mL (0.05 mol) allyl bromide in 10 mL of methanol. The solution was stirred at 60°C for 2 h, cooled, and dried under reduced pressure at room temperature. The solid was recrystallized from petroleum ether, yielding, 7.7 g (92%); m.p., 74–75°C. ¹H-NMR (DMSO-d₆, δ): 1.29(6H, s, CH₃), 3.94(2H, d, N—CH₂), 4.99–5.12(1H, m, =CH), 5.73–5.86(2H, m, =CH₂), 8.33(1H, s, NH).

Graft Copolymerization

About 1 g of cotton were immersed in 30 mL of distilled water containing a known amount of ammonium cerium (IV) nitrate (ACN). The initiator was allowed to interact with cotton for 30 min, and the ADMH/AN mixture of known composition was added to the solution. The solution was stirred for a certain period of time at a known temperature. After the graft copolymerization, the cotton sample was removed from the mixture and extracted three times with 100 mL of hot DMF at 60°C for 2 h to remove any ungrafted polymers. The cotton sample was then washed with excess distilled water, dried at 60°C for 24 h, and then stored in a desiccator for 72 h to reach constant weight.

Measurements

Percentage graft was calculated from the following equation:

$$\% \text{ Grafting} = (W_2 - W_1)/W_1 \times 100 \quad (1)$$

where W_1 and W_2 are the weights of the original and the grafted cotton, respectively.

ADMH content in the grafted samples was calculated according to eq. (2):

$$C_{\text{ADMH}} = 6.0 \times 10^{-3} \times (W_2 - W_1) \times \phi_{\text{ADMH}}/W_1 \quad (2)$$

where C_{ADMH} is the mol content of the ADMH unit in the grafted cotton, 6.0×10^{-3} is the reciprocal of the molecular weight of the ADMH unit in the grafted copolymers, and ϕ_{ADMH} is the weight fraction of ADMH unit in the grafted copolymers (see text below).

Antibacterial Assessment

To transform hydantoin groups into N-halamine structures, the grafted cotton samples were bleached according to a method previously reported.²¹ Antibacterial properties of the bleached samples were evaluated against *Escherichia coli* according to the American Association of Textile Chemists and Colorists (AATCC) Test Method 100. Durability and regeneration of the biocidal properties were tested with laundering following AATCC Test Method 124. AATCC standard reference detergent WOB (anionic) was used in all laundering tests.

RESULTS AND DISCUSSION

Determination of ϕ_{ADMH}

ADMH was copolymerized in a previous study²³ with several acrylic, substituted acrylic, and vinyl monomers. Grafting ADMH alone onto cotton proved to be difficult, and this must be attributed to the "autoinhibition" of the allylic structure of the monomer, i.e., like other allylic monomers, once formed, the allylic radical is very stable. In addition, degradative chain transfer competes exceptionally well with normal propagation, and the polymer chains are terminated by transfer after the addition of only a very few monomer units.^{24,25} However, separate studies showed that ADMH could be readily grafted onto other polymers in the presence of most mono- or polyfunctional acrylic and vinyl monomers.

Figure 1 shows the FTIR spectra of pure cotton and an ADMH/AN grafted cotton. In the grafted sample, the 2243 cm^{-1} band is attributed to $\nu(\text{CN})$,²⁶ and the 1707 and 1770 cm^{-1} bands can be assigned to the imide and amide structures in hydantoin rings, respectively,²⁷ in agreement with the previous article.²³ This confirms that ADMH/AN mixtures can be grafted onto cotton cellulose. The fractional weight of ADMH in the grafted copolymer can be calculated from the corresponding FTIR spectra using a method reported

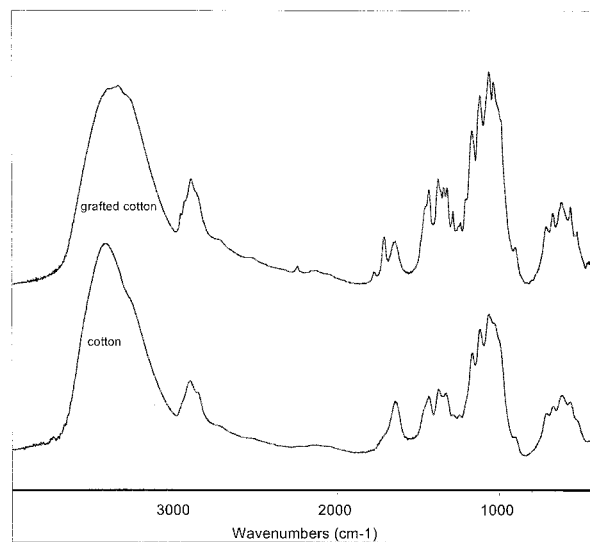


Figure 1 FTIR spectra of cotton and a ADMH/AN grafted cotton (graft % = 15.7, $C_{\text{ADMH}} = 0.043 \text{ mol/g}$).

previously.²³ In the FTIR spectra of ADMH/polyacrylonitrile (PAN) physical blends, as ADMH content increased, the 1770 cm^{-1} band became intensified, while the 2243 cm^{-1} band weakened. In the plot of A_{1770}/A_{2243} vs. $W_{\text{ADMH}}/W_{\text{AN}}$ (A_{1770} and A_{2243} represented the areas of the 1770 , 2243 cm^{-1} bands, and W_{ADMH} and W_{AN} , the weights of ADMH and PAN in the physical blends, respectively), a linear relationship was obtained and the slope was determined to be 0.74. Consequently, ϕ_{ADMH} , the weight content of the ADMH units in the grafted copolymers, could be calculated from eq. (3),

$$\phi_{\text{ADMH}} = 0.74 \times A_{1770} / (0.74 \times A_{1770} + A_{2243}) \quad (3)$$

It should be mentioned that because the graft copolymerization process is complicated, the graft copolymer cannot be accurately defined. Thus, the value of ϕ_{ADMH} is only an average. Nevertheless, this parameter works well in understanding the influence of reaction conditions on ADMH content, and in determining the antibacterial properties of the grafted samples, as can be seen in the next section.

Effect of Initiator Concentration

The effect of varying the concentration of ammonium cerium (IV) nitrate on the percentage graft yield and C_{ADMH} is presented in Figure 2. It can clearly be seen that percentage graft and C_{ADMH}

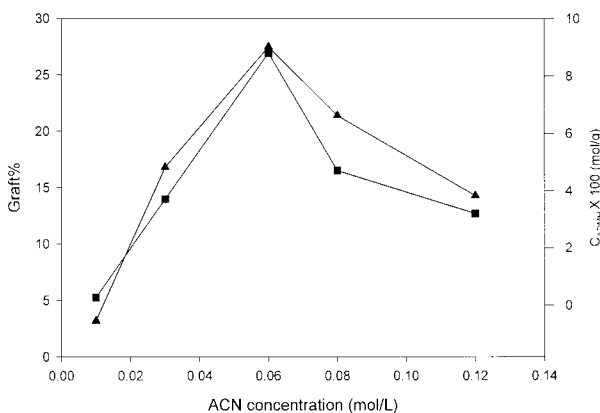


Figure 2 Effect of ACN concentration on: ▲, grafting yield, and ■, C_{ADMH} (total monomer concentration: 5 wt %; ADMH molar fraction: 20 mol %; $T = 45^\circ\text{C}$ and $t = 180$ min).

increase and then decrease around an optimum value of 0.06 mol/L. As the concentration of the initiator increases, a large number of cotton macroradicals can be formed, thus increasing the graft yield and C_{ADMH} . However, when the concentration of the initiator is higher than 0.06 mol/L, further increase in initiator concentration brings in the following effects: (1) abundant free radicals, particularly acrylic homopolymers and/or AN/ADMH copolymer macroradicals could be formed in the solution, which might terminate the growing chains; (2) free radicals formed on the main chain of cotton cellulose could be oxidized, and thus terminate the reactive sites; and (3) the graft copolymerizations and homopolymerizations of acrylonitrile, and copolymerizations of ADMH/AN are in a status of competing with each other in the system, depending on the direct attack of free radicals to cotton or to monomers. The net result is that, a higher concentration of initiator results in the production of more free radicals, and thus more homopolymer/copolymer macroradicals, therefore, reducing the graft yield, as well as the ADMH unit content in the grafted samples.

It is worth noting that in the present study, the optimum initiator concentration is several times higher than that reported by other authors in other ACN-initiated grafting polymerizations of acrylic monomers onto celluloses.^{28–30} We believe that this finding is most likely due to the “autoinhibition” of the allylic radicals resulting from ADMH,²³ i.e., some of the initiators are actually consumed by ADMH without forming polymers;

this interpretation is in accord with published results in other similar systems involving copolymerizations of allylic monomers.^{24,25}

Effect of ADMH Content in the Monomer Mixtures

The graft copolymerization of ADMH/AN monomer mixtures onto cotton was investigated by varying the ADMH molar fractions in the mixtures. The data show that with increases in the ADMH content in the monomer mixtures, graft yield decreases. Grafting acrylonitrile alone onto cotton results in a graft yield of 63.8 wt %; however, keeping other conditions constant, when the molar ratio of ADMH in the mixtures is 50%, the graft yield is only 3.2 wt % (see Fig. 3). Separate studies showed that when the molar content of ADMH was higher than 50%, the monomer mixtures acted as pure ADMH, i.e., extended periods of grafting (12 h) resulted in a graft yield of less than 1 wt %. These findings indicate that the presence of ADMH reduces the graft yield of acrylonitrile component, which can also be explained by the “autoinhibition” effect of the allylic structure in ADMH. However, Acrylonitrile enhances the ADMH graft yield to a considerable extent, showing positive synergism.

The ADMH molar content in the monomer mixtures influences the value of C_{ADMH} in a quite different manner. This value increases with the increase of ADMH molar content up to 20% and then decreases with further increases in the ADMH content, as shown in Figure 3. This “increase–decrease” trend must be the consequence

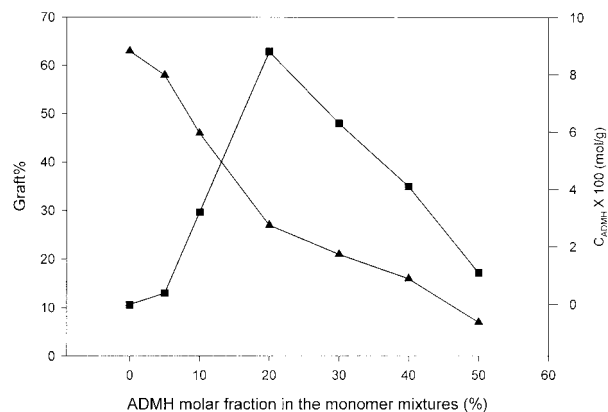


Figure 3 Effect of ADMH mol fraction in the monomer mixtures on: ▲, grafting yield, and ■, C_{ADMH} (total monomer concentration: 5 wt %; ACN concentration: 0.06 mol/L, $T = 45^\circ\text{C}$ and $t = 180$ min).

of an “equilibrium” between graft yield and ϕ_{ADMH} . Continuously increasing the ADMH molar content causes the total graft yield to decrease, while the content of the ADMH units in the grafted copolymers (ϕ_{ADMH}) increases. Thus, at a certain ADMH molar content (20%), a maximum value of C_{ADMH} could be observed. For C_{ADMH} , the synergistic effect was at its highest when an AN/ADMH mixture contains 20 mol % of ADMH.

Effect of Total Monomer Mixture Concentration

Figure 4 shows the influence of the monomer mixture concentration on graft copolymerizations. It can be seen that, as the total monomer concentrations increases, the graft yield and C_{ADMH} gradually improved. In this heterogeneous reaction system, the graft copolymerization largely depends on the diffusion of monomers into cotton samples. As monomer concentrations go up, more and more monomers can reach reactive sites on cotton molecules. Furthermore, increasing monomer concentrations may increase the amount of PAN homopolymer and/or AN/ADMH copolymer in the solution, and consequently, this will result in increased viscosity. This effect hinders termination, particularly through the coupling of growing polymer chains. As a result, the graft yield and C_{ADMH} of the reaction are benefited.

It should be noted that, however, when the total concentration is higher than 5 wt %, the trend of the increase is not very significant. For example, the monomer concentration was raised

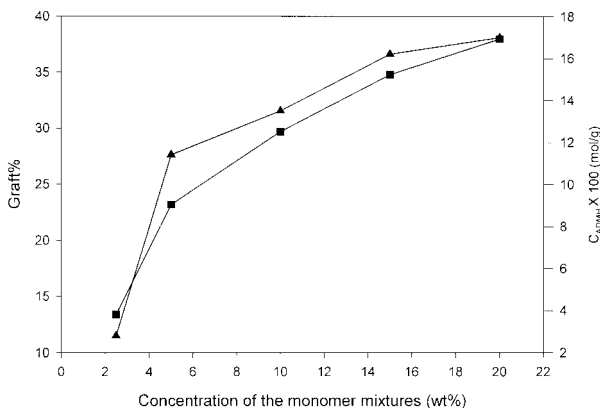


Figure 4 Effect of total monomer concentration on: ▲, grafting yield, and ■, C_{ADMH} (ADMH molar fraction: 20 mol %; ACN concentration: 0.06 mol/L, $T = 45^\circ\text{C}$ and $t = 180$ min).

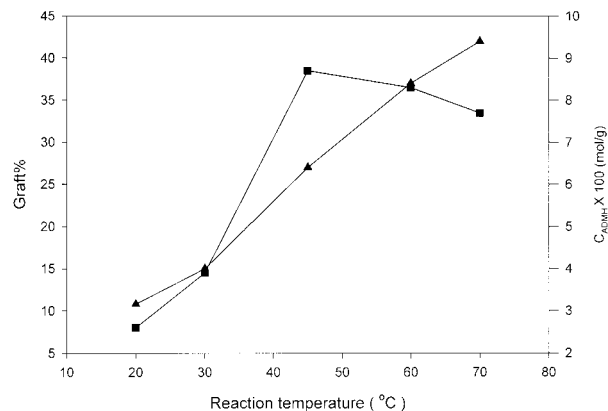


Figure 5 Effect of reaction temperature on: ▲, grafting yield, and ■, C_{ADMH} (total monomer concentration: 5 wt %; ADMH molar fraction: 20 mol %; ACN concentration: 0.06 mol/L, and $t = 180$ min).

from 5% to 20 wt %, a four-time increase, but the graft yield only improved about 1.4 times, and C_{ADMH} , was a little better, about two times.

Effect of Reaction Temperature

The effect of temperature on graft copolymerization was investigated over the range of 20–70°C. The results are presented in Figure 5. It can clearly be seen that grafting reaction favors a high temperature in general. But in the case of C_{ADMH} , the yield first increases in the temperature range of 25–45°C, and beyond this limit it decreases.

Raising temperature increases the following parameters such as the dissociation rate of ACN, initiation, propagation, and termination rates of polymerization, monomer mobility, swellability, and mobility of cotton fibers, as well as the diffusion of monomers into the fiber. All of these factors, except the increase of termination rates, result in the increase of grafting yield.

The “increase–decrease” trend of C_{ADMH} is most likely due to the influence of the temperature on ϕ_{ADMH} . It was found that ϕ_{ADMH} increases with the increase in temperature up to 45°C; and after this, further increases decreased ϕ_{ADMH} . Consequently, under a temperature higher than 45°C, although the grafting yield increases, C_{ADMH} decreases. These findings may suggest that compared to ADMH, polymerization of AN is favored at higher temperatures. Another possible explanation is that under a higher temperature (higher than 45°C), some PAN homopolymer, in-

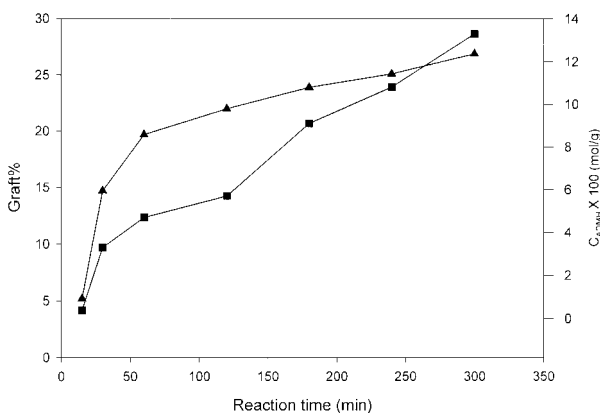


Figure 6 Effect of reaction time on: ▲, grafting yield, and ■, C_{ADMH} (total monomer concentration: 5 wt %; ADMH molar fraction: 20 mol %; ACN concentration: 0.06 mol/L, and $T = 45^\circ\text{C}$).

stead of AN/ADMH copolymer, may be grafted onto cotton fibers.

Effect of Reaction Time

The influence of reaction time on graft copolymerization is presented in Figure 6. With longer reaction time, both grafting yield and C_{ADMH} are higher than with short reaction time, but at different levels. For example, from a reaction time of 30 to 300 min, the percentage of grafting yields increased only 1.7 times, but the C_{ADMH} increased 4.3-fold. This means that with longer reaction times, ϕ_{ADMH} and C_{ADMH} increase more quickly than the grafting yield. This result is not very surprising, because the reactivity of AN is higher than that of ADMH, and thus AN preferentially enters the copolymer. As a result, there is a drift in the comonomer composition toward ADMH as the reaction time is extended, and the grafting yield increases slowly comparing to C_{ADMH} .

Antibacterial Properties of the Halogenated Copolymers

After treatment with a regular chlorine bleach, the amide groups of the grafted copolymers can be readily transformed into N-halamine structures, as demonstrated in Figure 7. Figure 7 shows the FTIR spectra in the region of $1680\text{--}2350\text{ cm}^{-1}$ of a grafted cotton sample before bleaching treatment, after bleaching, and after repeated machine washes, respectively. Before chlorine bleaching [Fig. 7(A)], the grafted sample shows a

band at 1770 cm^{-1} , attributing to the amide group of the hydantoin rings. After the bleaching, the 1770 cm^{-1} band disappears and a new band centered at 1782 cm^{-1} appears [Fig. 7(B)]. The difference of 12 cm^{-1} in wave number between the bleached and unbleached samples strongly suggests that the hydantoin structures have transformed into N-halamine structures.²⁷

The stability of the N-halamine structure was studied by laundering the treated fabrics following the AATCC Test Method 124. In the present study, it was found that the N-halamine structures in the grafted cotton samples could survive 10 washes. After 15 washes, the N-halamine structures were reduced back to hydantoin. As a result, the 1782 cm^{-1} bands changed back to 1770 cm^{-1} [note particularly the difference between Fig. 7(C) and (D)]. However, after another bleaching treatment, the 1770 cm^{-1} band converted into 1782 cm^{-1} again [Fig. 7(E)]. The same “ $1782 \rightarrow 1770 \rightarrow 1782$ ” cycle was repeated at least for 10 times on the fabric samples. Because the antibacterial properties of the modified fabrics are provided by the grafted N-halamine structures,^{16–23} this result demonstrated the durable and regenerable antibacterial properties of the samples.

The biocidal efficacy of the halogenated samples were evaluated by using a bacterium, *Esch-*

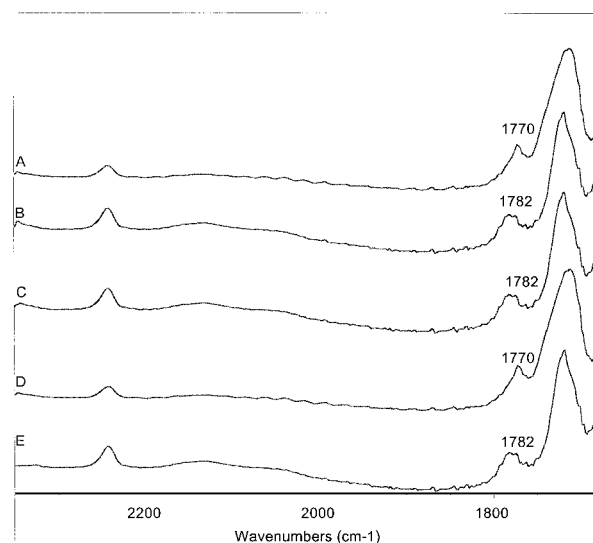


Figure 7 FTIR spectra in the region of $1680\text{--}2350\text{ cm}^{-1}$ of: (A), ADMH/AN grafted cotton (graft % = 15.7, $C_{ADMH} = 0.043\text{ mol/g}$); (B), sample (A) after chlorine bleaching; (C), sample (B) after 10 machine washes; (D), sample (B) after 15 machine washes; and (E), sample (D) after chlorine rebleaching (see text for details).

Table I Antibacterial Properties of Some Halogenated Grafted Samples Against *E. coli*^a

Sample No.	Graft wt %	C _{ADMH} (mol/g)	Wash Times ^b	Contact Time (min) ^c
1	15.2	3.4×10^{-2}	0	20
2	15.2	3.4×10^{-2}	10	30
3	15.2	3.4×10^{-2}	20	180
4	26.4	9.0×10^{-2}	0	10
5	26.4	9.0×10^{-2}	20	60

^a Antibacterial properties were tested according to AATCC Test Method 100. *E. coli* concentration: 10^6 – 10^7 CFU/mL.

^b Laundering, following AATCC Test Method 124, AATCC standard reference detergent WOB was used in all of the machine washing tests.

^c Minimum contact time for a total kill.

erichia coli, at a concentration of 10^6 – 10^7 CFU/mL, following the AATCC Test Method 100. The results are shown in Table I. As the ADMH unit content increased in the grafted samples, the contact time for a total kill of 10^6 – 10^7 CFU/mL *E. coli* reduced (note the difference between sample 1 and sample 4), indicating a fast inactivation of the micro-organism and better biocidal efficacy. After 10 washes, the fabrics demonstrated that the contact time for a total kill of *E. coli* was increased slightly from 10 to 20 min, indicating that the N-halamine structures on the fabrics were very stable under the washing conditions. However, more intensive washes could convert the N-halamine structures back to their precursors (see Fig. 7), which can be seen from the decreased antibacterial properties (see Table I, samples 2, 3, and 5). However, after exposure to the chlorine bleach again, the samples regained a total kill at a contact time of less than 30 min. This “bleach → wash 10 times → rebleach” cycle was repeated for 10 times, but the antibacterial properties of the samples were unchanged, indicating the antibacterial properties were fully regenerable.

CONCLUSION

A novel hydantoin-containing allylic monomer, ADMH, was employed in graft modification of cotton fabrics. Although ADMH alone could not be grafted onto polymers, the presence of acrylonitrile enhanced the ADMH grafting yield on cotton cellulose. The effects of the initiator concen-

tration, ADMH molar ratio in the monomer mixtures, total concentration of the monomer mixtures, reaction temperature, and time of the graft copolymerization were investigated. The ADMH grafting reaction favors a higher concentration of total monomer mixture, higher temperature in the tested temperature range, and a longer reaction time. Hydantoin units in the grafted copolymers were readily converted to N-halamine structures upon exposure to a commercially available chlorine bleach. The N-halamine derivatives of the corresponding grafted samples exhibited potent antibacterial properties against *Escherichia coli*, and these properties were durable and regenerable.

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