Novel Regenerable N-Halamine Polymeric Biocides. III. Grafting Hydantoin-Containing Monomers onto Synthetic Fabrics

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ABSTRACT: A novel cyclic-amine monomer, 3-allyl-5,5-dimethylhydantoin (ADMH) was synthesized and characterized. ADMH alone could not be grafted onto ordinary polymers. However, the presence of triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATAT) remarkably enhanced the ADMH grafting yield onto synthetic fabrics. The influences of reaction conditions on the grafting copolymerization were investigated. After chlorine bleach treatment, hydantoin units in the grafted copolymers were transformed into N-halamine structures. Treated 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: 1517–1525, 2001

Key words: synthetic fabrics; grafting; N-halamines; antimicrobial; durable

INTRODUCTION

Micro-organisms can grow and survive on textile materials, particularly on medical use textiles such as hospital gowns, patient drapes, carpeting, and bedding materials, for a lengthy period of time. Such survival ability might contribute to spreading of pathogens inside and from hospitals to outside communities. For example, a recent research report revealed that more than 60% of investigated health care workers' uniforms and gowns have been contaminated by pathogens in hospitals.[1] Survival of micro-organisms on contaminated textile materials is confirmed by several studies,[2–5] with the most recent results indicating that some antibiotic-resistant bacteria could survive on medical textiles for more than 3 months.[6] A surprising finding of the study was that most of the tested bacteria not only survived on all of the textiles and polymers at least for days, but also stayed alive longer on synthetic fabrics than on cotton.[6]

These results suggest that antibacterial properties should be a necessary function on medical and healthcare use textiles and polymers to prevent crosstransmissions of diseases. Antibacterial polymeric materials have been investigated for years with many novel technologies developed. Among the currently investigated biocidal materials, N-halamines were proven to be the suitable biocides that could provide desired antibacterial functions without causing much environmental concerns.[7–10] Recently, N-halamine structures were incorporated into cellulose-containing fabrics by using a conventional pad-dry-cure method.[11–13] The results revealed 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. In addition, the

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biocidal properties of the treated cellulosic samples were both durable and regenerable.

However, many synthetic textile materials and polymers, such as sheets, films, curtains, bags, and gloves, are widely used in medical applications today[6]; thus, these materials could still be potential sources of crosstransmissions of diseases. The purpose of this study was to develop a method that could chemically impart biocidal properties to most synthetic polymers, particularly the ones that have been wide employed in healthcare arena. In the previous study, hydantoin-containing monomers were synthesized, characterized,[14] and grafted onto cellulosic materials.[17] It was found that, due to the allylic structure of the monomers, they seldom 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 several widely used synthetic fabrics in the presence of a multifunctional monomer, triallyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (TATAT), and the antibacterial properties of the grafted fabrics against *Escherichia coli* were investigated.

EXPERIMENTAL

Materials

Synthetic fabrics of polyester #755H (PET), nylon-66 #306A, polypropylene #976 (PP), and acrylic (Orlon #864) were purchased from Testfabrics Inc. Fabrics made from polyester/polyamide (PET/PA) blend microfiber (70% polyester, 30% polyamide) were generously provided by HaloSource Corporation (Seattle, WA). Polyethylene fabric was cut from a highly cut-resistant glove, provided by Ansell Golden Needles Wilkesboro. 5,5-Dimethylhydantoin (DMH, Aldrich), and triallyl-1,3,5-triazine-2,4,6(AH,3H,5H)-trione (TATAT) (Aldrich) were used without further purification. Benzoyl peroxide (BPO, Acros) and potassium persulfate (PPS, Acros) were recrystallized twice from chloroform/methanol and distilled water, respectively. Other chemicals were purchased from either Aldrich or Fisher Scientific, and used without further purification.

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 fulfilled. ^{1}H-NMR spectra were recorded on a GE NMR QE-300 spectrometer. DSC study of the samples was performed using a Shimadzu DSC-50 instrument at a heating rate of 20°C/min under N_2 atmosphere.

Synthesis of ADMH

A solution of 6.4 g (0.05 mol) of DMH in 25 mL H_2O 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. ^{1}H-NMR (DMSO-d6, δ): 1.29(6H, s, CH_3), 3.94(2H, d, N—CH_2), 4.99–5.12(1H, m, ═CH), 5.73–5.86(2H, m, ═CH_2), 8.33(1H, s, NH).

Grafting Copolymerization

Reaction conditions of the chemical modification of different polymers are listed in Table I. A piece of synthetic fabric (about 1 g) was immersed in 20 mL of distilled water containing 0.05% of a nonionic wetting agent (Triton X-100), and the system was heated to an elevated temperature. A known amount (Table I) of ADMH/TATAT mixture dissolved in 10 mL of distilled water was then added and the solution was stirred for several minutes. A known amount of the initiator (see Table I) dissolved in a few milliliters of acetic acid (for BPO) or distilled water (for PPS) was finally added, and the solution was stirred for a certain period of time at the required temperature. After the grafting copolymerization, the grafted sample was taken out and extracted three times with 100 mL of hot acetone at 50°C for 2 h to remove any ungrafted polymers. The fabric was then washed with a large amount of distilled water, dried at 60°C for 24 h, and stored in a desiccator for 72 h to reach a constant weight.

Measurements

Percentage of grafting yield was calculated from the eq. (1):

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

where W_1 and W_2 were the weights of the original and the grafted fabric, respectively.

Table I Grafting of ADMH/TATAT Mixtures onto Synthetic Fabrics and Antibacterial Properties of the Grafted Fabrics against *E. coli*[a]

	PP	PE	Acrylic	PET/PA Blends	Nylon 66	Nylon 66
TATAT/ADMH (mol/mol)	1/5	1/5	1/5	1/8	1/3	1/5
Initiator[c]	BPO	BPO	BPO	BPO	PPS	BPO
Initiator concentration (wt %)	0.3%	0.5%	0.2%	0.3%	0.3%	0.2%
Reaction temperature (°C)	85	80	95	90	90	90
Reaction time (min)	45	90	60	60	60	60
Graft %	11.5	3.6	8.9	17.2	3.4	8.6
$M_{Cl} \times 10^5$ (mol/g)	2.4	0.83	1.7	5.2	0.94	2.1
Contact time (min)[b]	20	30	15	5	25	15

[a] Antibacterial properties were tested according to AATCC Test Method 100. *E. coli* concentration: 10^6–10^7 CFU/mL.
[b] Minimum contact time for a total kill of the micro-organism.
[c] Benzoyl peroxide (BPO) and potassium persulfate (PPS).

To transform the hydantoin structures in the grafted samples to N-halamines, about 1 g of the grafted fabric was bleached by immersing it in 30 mL of 1 wt % regular chlorine bleach solution at 80°C for 30 min, washed thoroughly with excess amount of distilled water, and then air dried. About 0.3 g of the above treated fabric was then cut into small pieces, treated with 30 mL of 0.001 *N* sodium thiosulfate solution containing 0.05 wt % of the wetting agent (Triton X-100) at 80°C for 30 min, and cooled to room temperature. The excess amount of sodium thiosulfate was titrated by a 0.001 *N* iodine solution. The sodium thiosulfate solution was found stable below 80°C. Thus, a high temperature-treated sodium thiosulfate solution was used as a control, and available active chlorine of the bleached grafted fabric was then calculated from eq. (2).

$$M_{Cl} = 10^{-6} \times (V_2 - V_1)/W \quad (2)$$

where V_1 and V_2 represent the volumes (mL) of iodine solution used in the titration of the control sodium thiosulfate solution (V_2), and the sodium thiosulfate solution treated with fabrics (V_1), respectively; and W was the weight (g) of the grafted fabric.

Antibacterial Assessment

Antibacterial properties of the bleached samples were evaluated against *Escherichia coli* according to American Association of Textile Chemists and Colorists (AATCC) Test Method 100. Durability and regeneration of the biocidal properties were tested with machine washing following AATCC Test Method 124. AATCC standard reference detergent WOB was used in all machine-washing tests.

RESULTS AND DISCUSSION

Determination of M_{Cl}

In a previous study,[14] ADMH was copolymerized with several acrylic, substituted acrylic, and vinyl monomers. Due to an effect of "autoinhibition" of allylic structures in radical reactions,[15,16] homopolymerization of ADMH hardly occurs in radical processes. Grafting ADMH onto cellulose was successful only when other comonomers, such as acrylonitrile, were added. Again, ADMH alone cannot be grafted onto synthetic fibers, and it needs other comonomers to work on polyester fabrics. Shown in Figure 1 are the FTIR spectra of PET(A), ADMH/TATAT grafted PET(B), and a spectrum (C) resulting from subtracting spectrum A from spectrum B. Due to a strong absorption band of PET centered at 1708 cm^{-1}, little difference could be directly detected between the grafted and ungrafted samples. After subtracting spectrum A from spectrum B, two new bands at 1770 and 1687 cm^{-1} become prominent in the spectrum (C). The 1770 cm^{-1} band can be attributed to the amide structure of ADMH,[11–13] and the 1687 cm^{-1} band is most likely due to the overlapping of the carbonyl bands of the imide groups of ADMH and TATAT. Similar results could also be observed in other ADMH/TATAT-grafted synthetic fabrics. As an example, Figure 2 shows that in the FTIR spectra of pure and grafted polypropylene (PP), 1687 and 1768 cm^{-1} bands could be observed in the grafted PP. These

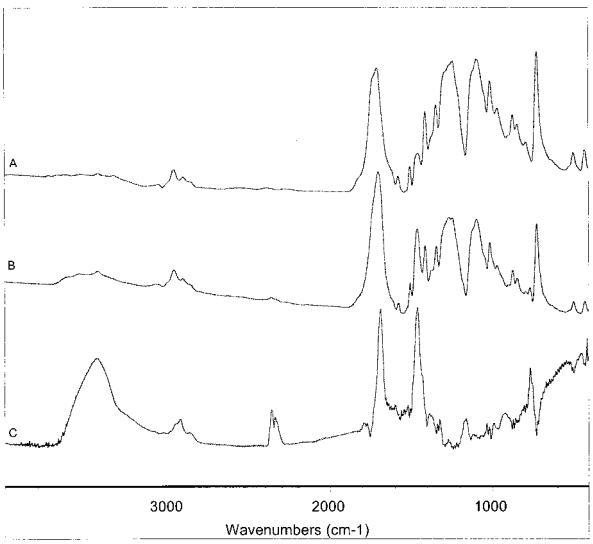

Figure 1 FTIR spectra of (A) PET, (B), ADMH/TATAT-grafted PET, and (C), difference spectra, subtract (A) from (B) (Graft % = 25.3, $M_{Cl} = 7.2 \times 10^{-5}$ mol/g).

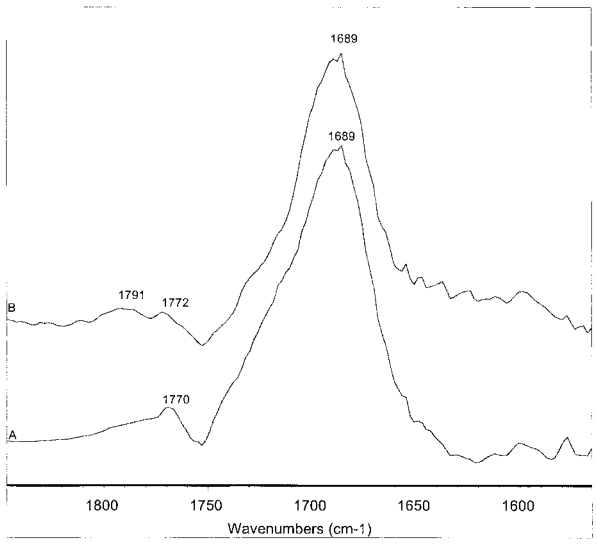

Figure 3 FTIR spectra in the region of 1595–1845 cm^{-1} of: (A), ADMH/TATAT-grafted PET (Graft % = 25.3, $M_{Cl} = 7.2 \times 10^{-5}$ mol/g), and (B), sample (A) after bleach treatment.

findings confirmed that the grafting of ADMH/TATAT mixtures onto synthetic fabrics was successful.

As reported previously,[11–14] hydantoin structures, after exposure to free chlorine, could be transformed into N-halamines. The amide groups in the ADMH grafted polyester (PET), after chlorine bleach treatment, should be converted to halamines. Indeed, such a conversion can be observed from FTIR spectra of the PET samples. In Figure 3, besides the 1770 cm^{-1} band, a broad band centered at about 1791 cm^{-1} was detectable in spectrum B, which could be attributed to the N-halamine structure. This is in accord with our previous findings in the study of ADMH-grafted cotton fabrics.[17] It should be pointed out that, unlike grafted cotton samples, in which the "hydantoin → N-halamine" transformation can be completely achieved at room temperature, the hydantoin structure in grafted PET fabric can only be transferred into N-halamine at higher temperatures (higher than 60°C). Furthermore, even after extended periods of reaction time, only part of the N—H bonds in the hydantoin structures were converted to halamines [see Fig. 3(B)].

These results are probably related to the hydrophobic property of PET and the rigid morphology of the polymeric molecules under their glass transition temperatures (T_g), which prevent a full contact of chlorine with internal hydantoin rings. When temperature was raised to near their T_gs, the swellability and mobility of PET molecules increased, resulting in more internally grafted hydantoin units making contact with a chlorine solution, and thus more halamine structures being produced. However, due to the rigid conformation of the grafts (note that TATAT is a crosslinker), not all of the hydantoins could make full contact with chlorine, and thus only part of them could be transformed.

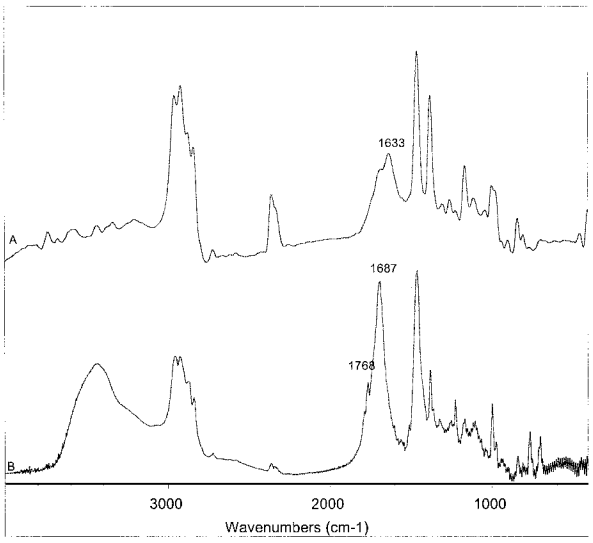

Figure 2 FTIR spectra of (A) PP, and (B) ADMH/TATAT grafted PP (Graft % = 11.5, $M_{Cl} = 2.4 \times 10^{-5}$ mol/g).

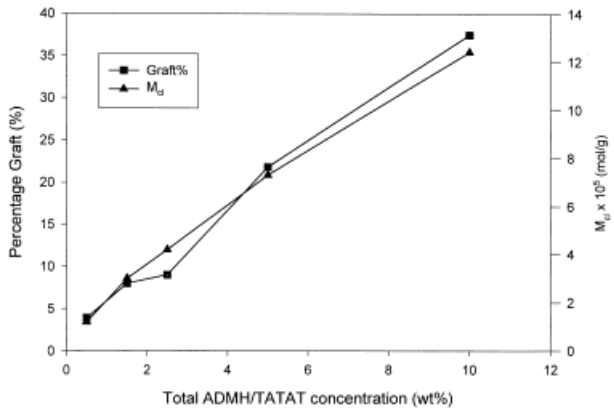

Figure 4 Effect of total monomer concentration on Graft % and M_{Cl} (TATAT molar ratio: 0.2/1 BPO concentration: 0.02 mol/L, $T = 90°C$ and $t = 60$ min).

Because it is the N-halamine structure that provides the antibacterial properties, the available combined chlorine content in the grafted fabric is of interest. The grafting copolymerization process on polymers is rather complicated, the grafted copolymer is not well defined. Thus, the value (M_{Cl}) is an "average" of the total available combined chlorine of the grafted fabrics treated under the present conditions. Nevertheless, this parameter provides valuable information regarding the influence of grafting conditions on the antibacterial properties of the grafted samples, as can be seen in the next section.

Grafting ADMH onto PET Fabrics

Effect of Total Monomer Mixture Concentration

The influence of the concentration of the monomer mixture on grafting copolymerization is shown in Figure 4. Increasing the total monomer concentration, the graft yield and M_{Cl} gradually increased. In a heterogeneous reaction system containing polyester fabrics and a monomer solution, rates of grafting reactions largely depend on the diffusion of monomers from polyester fiber surfaces into the fibers. As monomer concentration goes up, more and more monomers can reach the reactive sites inside PET molecules. Furthermore, increasing monomer concentration may increase the amount of TATAT homopolymer and/or ADMH/TATAT copolymer in the solution, resulting in increased viscosity. This effect hinders termination, particularly through the coupling of growing polymer chains. As a result, the graft yield and M_{Cl} increased.

Effect of Initiator Concentration

The effect of varying the initiator concentration on grafting yield and M_{Cl} is presented in Figure 5. It can be seen that grafting yield and M_{Cl} rapidly increase initially, and then gradually decrease after an optimum value of 0.02 mol/L, as the concentration of the initiator is increased. This "increase-decrease" trend of the grafting reaction has been reported by many authors in free radical grafting reactions on PET.[18,19] As the concentration of the initiator (BPO) increases, a large number of PET macroradicals will be formed, which will initiate the grafting copolymerization, thereby increasing the graft yield and M_{Cl}. However, when the concentration of BPO is higher than 0.02 mol/L, too many free radicals as well as macroradicals are produced, preventing chain growth and formation of macromolecules. Furthermore, the grafting reaction, homopolymerization of TATAT, and the copolymerization of ADMH/TATAT are competing with each other in the system, whichever is favorable depending on direct attack of free radicals onto PET or monomers. The net result is that, a higher concentration of the initiator results in the production of more free radicals, and thus more homopolymer/copolymer macroradicals, therefore reducing the grafting yield, as well as the ADMH unit content in the grafted samples. Consequently, this reduces the available combined chlorine.

The optimum BPO concentration was several times higher than that reported by other authors in BPO-initiated grafting polymerizations of acrylic monomers onto PET,[18] which is still due to

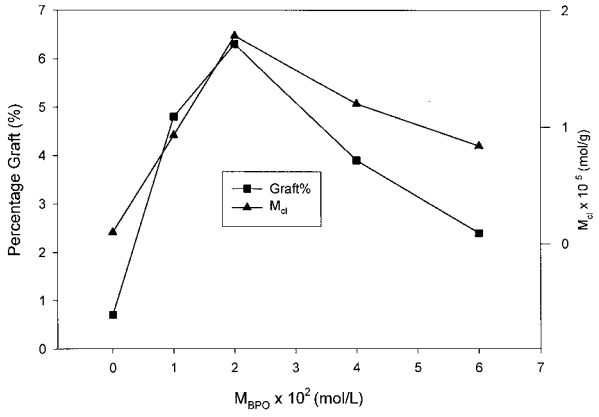

Figure 5 Effect of BPO concentration (M_{BPO}) on Graft % and M_{Cl} (Total monomer concentration: 0.625 wt %; TATAT molar ration: 0.2/1; $T = 90°C$ and $t = 60$ min).

the "autoinhibition" of the allylic structure of ADMH, i.e., some of the initiators are actually consumed by ADMH without forming polymers; this interpretation is in accord with our previous report,[17] as well as with results involving copolymerization of allylic monomers.[15,16]

Effect of TATAT Molar Ratio in Monomer Mixtures

The grafting copolymerization of ADMH/TATAT monomer mixtures onto PET was investigated by varying the TATAT molar fraction in the mixtures, as shown in Figure 6. In a previous study[17] on grafting ADMH/acrylonitrile (ADMH/AN) mixtures onto cotton cellulose, it was found that the molar ratio of ADMH must be less than 50% to achieve a proper grafting yield. When the molar content of ADMH was higher than 50%, the ADMH/AN mixtures acted like pure ADMH, i.e., little grafting reaction. Although ADMH alone cannot be grafted onto PET, the addition of a small amount of TATAT (less than 20% molar ratio of TATAT to ADMH) enhances the ADMH graft yield significantly. The different performance between ADMH/TATAT and ADMH/AN monomer mixtures in the grafting reactions may be attributed to the poly-allylic structures of TATAT, i.e., one TATAT molecule can provide three allylic unsaturated bonds, and thus greatly increases the chance of grafting copolymerization of ADMH/TATAT mixtures onto PET.

The decreasing trend of grafting yield and M_{Cl} at higher TATAT molar ratios shown in Figure 6 could be caused by the formation of more copolymers in the solution rather than on PET fabrics.

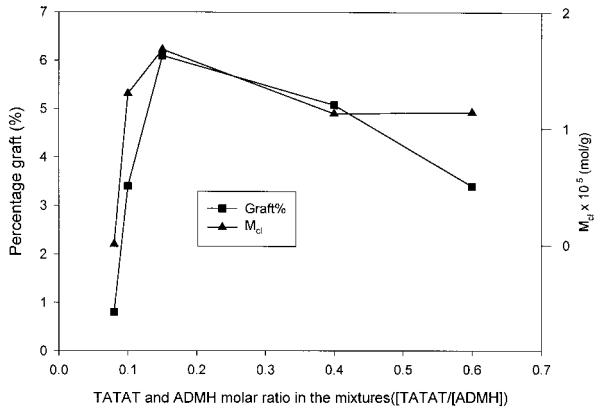

Figure 6 Effect of TATAT molar ratio ([TATAT]/[ADMH]) on Graft % and M_{Cl} (Total monomer concentration: 0.625 wt %; BPO concentration: 0.02 mol/L, T = 90°C and t = 60 min).

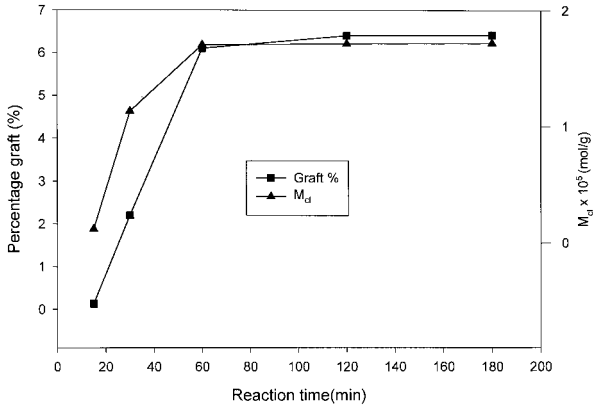

Figure 7 Effect of reaction time (t) on Graft % and M_{Cl} (Total monomer concentration: 0.625 wt %; TATAT molar ratio: 0.2/1, BPO concentration: 0.02 mol/L, and T = 90°C).

In other words, when the molar fraction of TATAT was higher than 0.2/1 to ADMH, instead of being grafted onto PET, a significant amount of ADMH was consumed in the ADMH/TATAT copolymerization. Thus, at a certain TATAT molar content, maximum values of grafting yield and M_{Cl} could be observed.

Effect of Reaction Time and Temperature

The influence of reaction time on grafting copolymerization is presented in Figure 7. An induction period of 15 min was observed. After that, grafting yield and M_{Cl} gradually increased, with extended reaction time to saturated values. Practically, a reaction time of 1 h is enough to obtain optimal grafting results.

The effect of temperature on grafting copolymerization was investigated in the range of 60–100°C, with results presented in Figure 8. Below 80°C, both grafting yield and M_{Cl} are very low. After that, the values of the two parameters increased rapidly. As discussed previously,[17] higher temperature increased the dissociation rate of the initiator (BPO), and rates of the initiation and propagation, resulting in higher grafting yield. More importantly, increasing of the reaction temperature above the T_g of PET (80°C), the swellability and mobility of PET as well as the diffusion rate of monomer mixtures into the PET amorphous region increase significantly. All these factors promote the higher grafting yields and M_{Cl} on PET. However, further increase in temperature will raise the rate of termination reactions, thus initiate the decreasing trend of grafting yields and M_{Cl}.

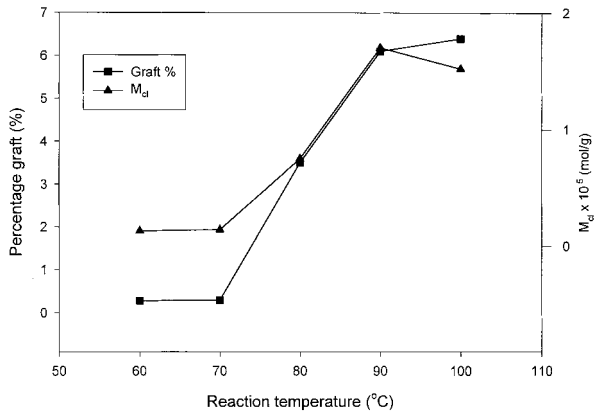

Figure 8 Effect of reaction temperature (T) on Graft % and M_{Cl} (Total monomer concentration: 0.625 wt %; TATAT molar ratio: 0.2/1; BPO concentration: 0.02 mol/L, and t = 60 min).

Grafting ADMH onto Other Synthetic Fabrics

The addition of TATAT into the monomer mixtures greatly enhanced grafting of ADMH onto PET fabrics and other fabrics. In grafting ADMH (5 wt %) alone onto these synthetic fabrics, extended period of times (12 h) only resulted in a grafting yield of less than 0.5 wt %. However, the presence of TATAT greatly improved the grafting yield. Typical examples are shown in Table I. In the reaction of ADMH/TATAT onto hydrophobic nylon fabrics, a water-soluble initiator, PPS, could be employed to initiate the grafting copolymerization, while attempts to use this initiator in reactions with other synthetic fabrics were not successful. This could be attributed to the relatively more "hydrophilic" characteristic of the nylon comparing to other hydrophobic synthetic fabrics such as polyesters.

Antibacterial Properties of Halogenated Grafted Copolymers

As discussed above, after treatment with a chlorine bleach solution, some of the amide groups of the grafted copolymers were converted into N-halamine structures. To find out the stability of the halamine structures the halogenated polymers were stored in a conditioning room. After 2 months of storage at 21°C and 65% relative humidity, little change was detected in the FTIR spectra, and the amount of available combined chlorine was almost unchanged. As the antibacterial properties are provided by the N-halamine structures,[8–14] we anticipate that the antibacterial properties are durable.

The results of biocidal efficacy of the grafted products are shown in Table I and Table II. For the same fabric, increasing the M_{Cl} in the grafted samples, the minimum contact time for a total kill of 10^6–10^7 CFU/mL *E. coli* decreased, indicating that it is the N-halamine structures in the grafted samples that provide the antibacterial properties (see Table II). Compared to our previous studies, the grafted PET needed a much longer contact time for a total bacterial kill of *E. coli* than some previously reported materials do.[11–13] In those cases, at a less than 2 wt % add-on rate of hydantoin rings on the fabrics, 2 min contact time was sufficient for a total kill of 10^6–10^7 CFU/mL *E. coli,* while in the present study of the grafted PET, even at a grafting yield of 25.3 wt %, a minimum contact time of 10 min is needed for a total kill. This difference is most likely caused by the hydrophobic property of the synthetic fabrics, i.e., the hydrophobic feature of the synthetic fabrics prevents the entries of aqueous based bacteria into the inner part of the polymers. Therefore, it is mainly the combined chlorine in the surface area of the materials that makes contact with bacteria and provides the antibacterial properties. The active chlorine inside of the materials does not directly contact the bacteria; instead, it could slowly migrate to the surface. This hypothesis is supported by the antibacterial data for PET/PA microfiber blend

Table II Antibacterial Properties of Halogenated-Grafted PET Samples Against *E. coli*[a]

Sample No.	Graft %	Wash Times[b]	M_{Cl} (mol/g)	Contact Time (min)[c]
1	25.3	0	7.2×10^{-5}	10
2	25.3	5	4.2×10^{-5}	10
3	11.6	0	2.5×10^{-5}	25
4	11.6	10	1.8×10^{-5}	30
5	11.6	15	1.03×10^{-5}	120
6	11.6	25	0.82×10^{-5}	480
7	11.6	40	0.77×10^{-5}	1080
8	11.6	50	0.68×10^{-5}	N/A[d]

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

[b] Machine washing, 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 of the micro-organism.

[d] After 24 h of contact, only one log reduction was observed.

fabric, which has a much larger surface area, and thus can provide much more surface contact with chlorine bleach and the aqueous bacteria suspensions than ordinary PET fabrics. At a percentage graft of 17.2 wt %, a contact time of about 5 min is enough for a total kill (see Table I), indicating that the surface contact and hydrophilic/hydrophobic property are important in determining antimicrobial performance of biocidal materials.

The hydrophobic characteristic of synthetic fabrics is not necessarily a disadvantage; it could ensure excellent durability of the antibacterial properties of the grafted samples, as shown in Table II. After five washes, the contact time necessary for a total kill of *E. coli* was unchanged because the washing could not remove chlorine from internal halamines. Further washes reduced the content of available active chlorine, and the minimum contact time for a total kill went up as the antibacterial properties decreased (see Table II, samples 3 through 8). However, even after 25 washes, the grafted samples still provided a total kill after a contact time of 480 min. In cotton samples, it was previously reported that after several washes,[11–13] the antibacterial properties was completely lost, and rebleaching treatment was necessary to regenerate biocidal properties for the same halamine structure.

Another parallel test showed that in the continuous washing of the fabrics the active chlorine on the fabric decreased only less than 10% of the original content from 25 washes to 40 washes, but the minimum contact time for a total kill became nine times longer. After 50 washes, although there was still as much as 0.68×10^{-5} mol/g available active chlorine left, the sample provided only one log reduction after 24 h of contact. These results suggest that in the grafted synthetic fabrics, some portion of the active chlorine is actually unavailable to bacteria due to the hydrophobic property, and/or the rigid structure of the treated samples. The observed "kill" is resulted from direct contact of surface chlorine or the migrated active chlorine from the unavailable inner part with micro-organisms.

However, after rebleaching, the sample again provided total kill at a contact time of less than 30 min. After 10 of these "bleach → wash 25 times → re-bleach" cycles, the antibacterial property of the sample was unchanged, indicating that the antibacterial property was regenerable.

CONCLUSION

Our results showed that single ADMH grafting onto synthetic polymers resulted in very low graft yields. However, the presence of TATAT enhanced the ADMH graft yield onto commercially available synthetic fabrics significantly. Optimum reaction conditions for the graft copolymerization were investigated. Upon exposure to chlorine bleach at a temperature higher than 60°C, part of the grafted hydantoin structures could be transformed into N-halamines, which provided the treated samples with powerful, durable, and regenerable antibacterial properties against *E. coli.*

It was also found that the hydrophobic characteristic of synthetic fabrics had a great influence on their antibacterial properties. Because the aqueous bacterial suspension could not make sufficient surface contact with the fabrics, a longer contact time was necessary for satisfactory antibacterial results. On the other hand, this property makes the N-halamine structure very stable to repeated laundering, with the results showing that even after 50 washes, the grafted samples still possessed proper antibacterial efficacy.

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REFERENCES

1. Boyce, J. M.; Potter-Byone, G.; Chenevert, C.; King, T. Infect Control Hosp Epidemiol 1997, 18, 622.
2. Lidwell, O. M.; Towers, A. G.; Ballard, J.; Gladstone, B. J Appl Bact 1974, 37, 649.
3. Rubbo, S. D.; Saunders, J. J Hyg Camb 1963, 61, 507.
4. Ransjo, U. J Hyg Camb 1979, 82, 369.
5. Hambraeus, A. J Hyg Camb 1973, 71, 799.
6. Neely, A. N.; Maley, M. P. J Clin Microbiol 2000, 38, 724.
7. Worley, S. D.; Sun, G. Trends Polym Sci 1996, 11, 364.
8. Sun, G.; Chen, T. Y.; Worley, S. D. Polymer 1996, 37, 3753.
9. Worley, S. D.; Sun, G. The Polymeric Materials Encyclopedia; CRC Press: New York, 1996, 1, A-B, p. 550.

10. Sun, G.; Chen, T. Y.; Habercom, M. S.; Wheatley, W. B.; Worley, S. D. Water Res Bull 1996, 32, 793.
11. Bickert, J. R.; Xu, X.; Sun, G.; Williams, J. F. International Conference on Safety & Protective fabric '98, 1998, p. 1.
12. Sun, G.; Xu, X. Textile Chem Colorist 1998, 6, 26.
13. Sun, G.; Xu, X. Textile Chem Colorist 1999, 31, 21.
14. Sun, Y.; Sun, G. J Appl Polym Sci 2001, 80, 2460.
15. Bartlett, P. D.; Tate, F. A. J Am Chem Soc 1953, 75, 91.
16. Schildknecht, C. E. Allyl Compounds and Their Polymers; John Wiley & Sons: New York, 1973, p. 30.
17. Sun, Y.; Sun, G. J Appl Polym Sci, to appear.
18. Lokhande, H. T.; Tell, M. D.; Rao, K. N.; Rao, M. H. J Appl Polym Sci 1984, 29, 1843.
19. Celik, M.; Sacak, M. J Appl Polym Sci 1996, 59, 609.