Novel Refreshable *N*-Halamine Polymeric Biocides: Grafting Hydantoin-Containing Monomers onto High Performance Fibers by a Continuous Process

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ABSTRACT: In this study, a continuous "pad-dry-cure" process was developed for the first time to graft a cycloamine monomer, 3-allyl-5,5-dimethylhydantoin (ADMH), onto several high performance fibers, including Nomex, Kermel, and a PBI/Kevlar blend. The influence of reaction conditions on the grafting copolymerizaiton was studied. It was found that in the presence of a difunctional monomer, poly(ethylene glycol)–diacrylate (PEG–DIA), ADMH could be readily grafted onto these fibers. After exposure to chlorine, the hydantoin structures in the grafted samples could be transformed into *N*-halamines, which provided powerful, durable, and regenerable antibacterial activities against both gram-negative and gram-positive bacteria. The influence of hydrophobic/rigid properties of the fabrics on grafting reactions as well as on their antibacterial activities was discussed, and the importance of full contact was emphasized.
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Key words: high performance polymers; modification; halogenated; graft copolymers

INTRODUCTION

Poly(*m*-phenylene isophthalamide) (Nomex), poly(aromatic imide-amide) (Kermel), polybenzimidazole (PBI), and poly(*p*-phenylene terephthalamide) (Kevlar) are typical examples of high performance fibers that possess superior mechanical properties, fire resistance, and excellent thermal, chemical, and oxidative stabilities. It is for these reasons that they have found wide usage in many demanding areas. For example, fabrics manufactured from these high performance fibers are worn by firemen, military personnel, and race car drivers; fabricated underwear garments are used by astronauts; and gloves made from high performance fibers have replaced those made from asbestos in many regions.[1] Recently, their applications in carpets, upholstery fabrics, and some medical purposes have also attracted increasing attention.[2]

Because of the rapidly growing interest in these high performance fibers, their roles in the transmission of infectious diseases should also be considered, especially in some "high risk" applications. It is widely accepted that textile materials are an excellent medium for cross-infections. Survival of microorganisms on contaminated textile materials and transfer of these microorganisms directly or indirectly from the textiles to new victims have been investigated by numerous researchers for decades.[3–6] The most recent results indicated that some antibiotic-resistant microbes could survive on common textiles for more than 3 months, and it is interesting to note that most of the tested germs survived longer on synthetic materials than on natural fabrics.[7] Although no direct studies were conducted on infectious diseases caused by these high performance fabrics, infection-resistant properties should be necessary functions of these materials used in some demanding areas. Among the currently investigated biocidal materials, *N*-halamines have proved to be the most promising candidates because they can provide fast and total kill against a wide range of microorganisms, without causing environmental concerns, and it is highly unlikely for the microorganisms to establish resistance.[8–11]

In our previous work, a hydantoin-containing monomer, 3-allyl-5,5-dimethylhydantoin (ADMH), was designed and synthesized. It was found that ADMH could be grafted onto natural and synthetic fabrics in the presence of a multifunctional monomer [e.g., triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATAT)] by either an exhaustion or a continuous method.[12] It was further demonstrated in our previous research[12(d)] that the continuous technique was superior to the exhaustion method in the grafting reaction because of the cost, time, and environmental concerns. Besides, given that in the continuous technique very limited aqueous solution was involved in the curing

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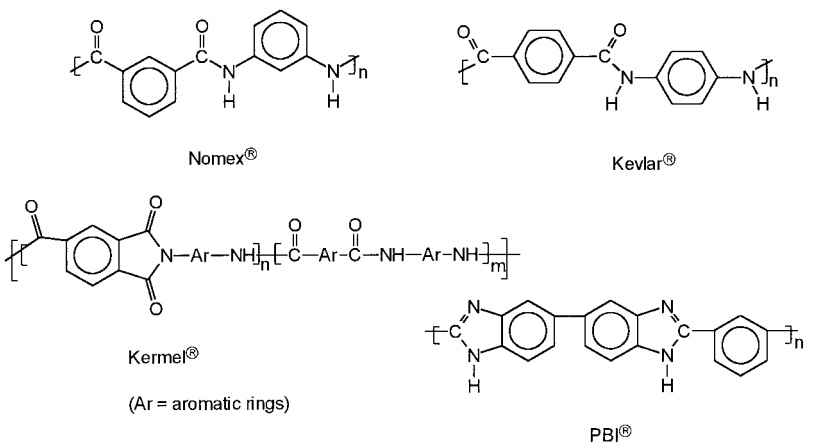


Figure 1 Chemical structures of the synthetic fibers.

process, the grafting efficiency was much higher than that in the exhaustion process. After bleach treatment, the grafted fabrics showed very promising antibacterial abilities against *Escherichia coli* (*E. coli*) and *Staphyloccocus aureus* (*S. aureus*), indicating that ADMH could be a universal candidate for the antimicrobial finishing of textile materials.

However, the use of TATAT in grafting reactions is not ideal for commercial applications. For example, because of its low water solubility, an emulsion was employed in the finishing formulation, whose stability is a concern in real applications. More important, after grafting, the hand of the fabrics became stiff, which could be caused by the rigid structure of TATAT. It was believed that new multifunctional monomers with softer structures and higher water solubility might be able to solve the problems of TATAT. Poly(ethylene glycol)–diacrylate (PEG–DIA), a typical example of such monomers, was employed in this study.

The purpose of this study was to develop a practical continuous process to graft ADMH onto the high performance fabrics in the presence of PEG–DIA. The influence of reaction conditions on the grafting copolymerization was studied, the graft copolymers were characterized, and their antimicrobial activities against gram-negative *E. coli* and gram-positive *S. aureus* were evaluated.

EXPERIMENTAL

Materials

Fabrics manufactured from Nomex IIIa poplin 4.5 oz and a PBI/Kevlar twill (40/60) 4.5 oz were kindly supplied by Southern Mills (Austell, GA). Kermel twill 7.0 oz was made by Amoco Fabrics. Chemical structures of the fibers are shown in Figure 1. ADMH was synthesized in this lab (Pittsburgh, PA), as reported previously.[12] Benzoyl peroxide (BPO; Acros), 2,2′-azobisisobutyronitrile (AIBN; Acros), and potassium persulfate (PPS; Acros) were recrystallized from chloroform/methanol, EtOH, and distilled water, respectively. Ammonium cerium(IV) nitrate (CAN; Acros), 2′2′-azobis(2-methylpropionamidine) dihydrochloride (AMPAD; Aldrich, Milwaukee, WI), 4,4′-azobis(4-cyanopentanoic acid) (ACPA; Acros), PEG–DIA (MW = 258; Aldrich), and a polyethylene softener (Sequa Chemicals, Chester, SC) were used without further purification. Other chemicals were purchased from either Aldrich or Fisher Scientific (Pittsburgh, PA) and were used as received.

Instruments

FT-IR spectra were taken on a Nicolet Magana IR-560 spectrometer (Nicolet Instruments, Madison, WI) using KBr pellets. The samples were made thin enough to ensure that the Beer–Lambert law was fulfilled. DSC and TGA studies of the samples were performed by using Shimadzu DSC-50 (Shimadzu, Kyoto, Japan) and Shimadzu TGA-50 instruments at a heating rate of 10°C/min under N_2 atmosphere.

Grafting copolymerization

Two methods were employed in the preparation of the padding bath. In the case of water-insoluble initiators (BPO and AIBN), required amounts of PEG–DIA, the softener, and the initiator were first mixed together, to which a certain amount of ADMH aqueous solution was slowly added with stirring. For the water-soluble initiators (ACS, PPS, AMPAD, and ACPA), all of the chemicals (ADMH, PEG–DIA, the softener, and the initiator) were dissolved in distilled water. In the padding process, fabrics were dipped in the padding bath and padded at a required expression (100%). This "dip-pad" process was repeated twice. The fabrics were dried at 50°C for 5 min, cured at an elevated temperature for a certain period of time, and then

washed with a large amount of distilled water, dried at 60°C for 24 h, and stored in a conditioning room (25°C, 65% relative humidity) for 48 h to reach constant weight. Percentage graft was calculated from the relation

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

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

Chlorination

To transform the hydantoin structure in the grafted samples to *N*-halamines, the grafted fabric was immersed in a diluted bleach containing 3000 ppm active chlorine (bath ratio = 50 : 1) at room temperature for 30 min, washed thoroughly with a large excess of distilled water, and air dried. The active chlorine content of the fabric was determined by a modified titration method as reported previously.[12(c)] In the present study, about 0.3 g of the treated fabric was cut into small pieces and treated with 30 mL of 0.001*N* sodium thiosulfate solution containing 0.05 wt % of a nonionic wetting agent (Triton X-100) at room temperature under constant stirring overnight. The excess sodium thiosulfate was titrated with a 0.001*N* iodine solution. Nonchlorinated grafted fabrics were also titrated by using the same methods as those for controls. Available active chlorine of the bleached grafted fabric was then calculated from the following equation:

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

where V_1 and V_2 represent the volumes (mL) of iodine solution used in the titration of the sodium thiosulfate solutions treating the samples and the controls, respectively; and W is the weight (g) of the bleached grafted fabric.

Antibacterial assessment

The antibacterial properties of the grafted samples were explored according to a modified AATCC Test Method 100 against *E. coli* (gram-negative) and *S. aureus* (gram-positive). The fabrics were cut into small pieces ($\sim$ 4 cm^2). Two pieces of the fabrics were put together in a sterilized container, and 100 μL of an aqueous suspension containing 10^6–10^7 colony forming units (CFU)/mL of bacteria were placed onto the surfaces of the fabrics. The fabrics were then "sandwiched" using another set of the two identical fabrics. To ensure sufficient contact, a sterilized 50-mL beaker was placed onto the top of the fabrics. After different contact times, the entire "sandwich" was placed into 10 mL of 0.03% sodium thiosulfate aqueous solution to quench the active chlorine on the fabrics. The resultant solution was then vigorously shaken for 5 min. Previous studies have demonstrated that the sodium thiosulfate aqueous solution had no influence on the growth of the bacteria. An aliquot of the solution was then serially diluted, and 100 μL of each dilution was plated onto a nutrient agar plate. The same procedure was also applied to the nonchlorinated samples as controls. Bacterial colonies on the agar plates were counted after incubation at 37°C for 24 h. Durability of the biocidal properties were tested with machine washing according to AATCC Test Method 124. AATCC standard reference detergent 124 was used in all the machine-washing tests.

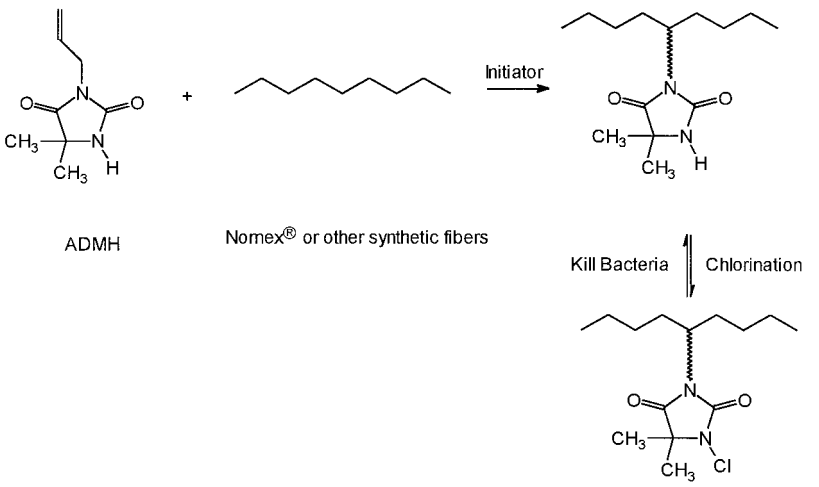
RESULTS AND DISCUSSION

Grafting copolymerization

Influence of initiators

Chemical modifications of the synthetic fibers are shown in **Scheme 1**. The first-step reaction is a radical-initiated grafting copolymerization. Initiators are decisive factors in the copolymerization, typical examples of which are shown in Figure 2. The most striking feature is that the water- insoluble initiators provide higher percentage graft than the soluble ones. In the case of the two inorganic initiators (PPS and ACN), no weight increases could be detected after grafting. Because of their strong hydrophilic characteristics, it is more favorable for the water-soluble initiators (especially the inorganic ones) to dissolve in water than to adsorb onto the fabrics. In the drying process, with the evaporation of water, these initiators could migrate from the inner parts and concentrate on the surfaces of the fabrics. Thus, during curing, the initiators could initiate the grafting copolymerization only on the surfaces, resulting in very low percentage grafts for these inorganic initiators. It is interesting to note that ACPA performs much better than the other three water-soluble initiators in the grafting reactions, although it is also soluble in water. A proposed reason is that possible interactions between the acid groups of ACPA and the $-NH_2$ end groups of the fibers could result in a favorable adsorption of the initiator into the fibers.

In grafting reactions using AIBN and BPO, because they are hydrophobic and insoluble in water, the absorption of these initiators onto the fabrics is preferable. As a result, in the grafting copolymerization using water-insoluble initiators, the grafting reactions could be initiated in both the surface and inner parts of the fabrics, thus resulting in higher percentage grafts than those using water-soluble initiators. The higher efficiency of BPO over that of AIBN in the grafting copolymerization may be caused by the much shorter half-life of BPO than that of AIBN at higher than



Scheme 1 ADMH grafting copolymerization and chlorination on the synthetic fibers.

100°C,[13] and/or the stronger ability of BPO than that of AIBN to form active sites on the polymeric molecules of the fabrics because of its stronger oxidation abilities.

To provide further information regarding the influence of initiators, Figure 3 shows the effect of varying BPO concentrations on percentage grafts on the fabrics. It can be seen clearly that the grafting yields rapidly increase initially, and then gradually reach relatively constant values at 0.4–0.5 wt % of BPO. As the concentration of BPO increases, a large number of textile polymer macroradicals will be formed, which will initiate the grafting copolymerization, thereby increasing the grafting yield. At even higher BPO concentrations, however, the graft yields may gradually reach saturation values.

There are two other things worth noting about these results. First, the grafting reaction on Nomex seems to be easier than that on the other two fabrics, which could be caused by the relatively "softer" structure of Nomex than that of either Kermel or PBI/Kevlar. The reported glass-transition temperature (T_g) of Nomex was around 260°C; Kevlar, around 300°C; and no T_g values were detected in either Kermel or PBI.[1,14] This flexible structure may ensure a better penetration of the monomers and the initiators into the inner parts of the fabrics, resulting in a higher grafting yield. Second, the optimum BPO concentrations for the grafting reactions in the present study are several times higher than that in the grafting onto ordinary synthetic fabrics, such as nylon and polyester.[12(d)] Again, this could be attributable to the stable aromatic structures of the

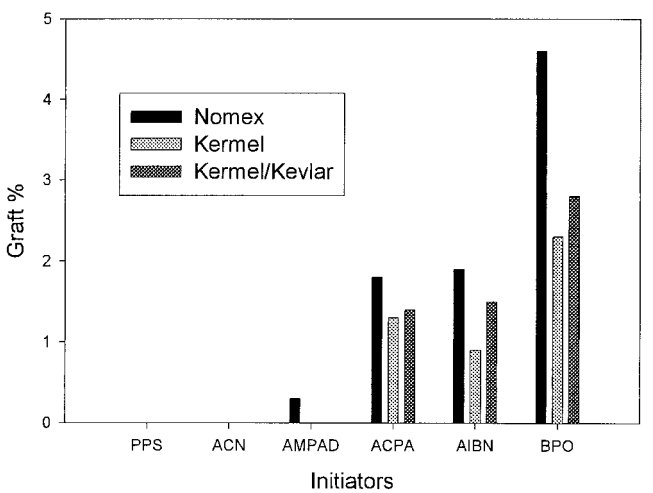


Figure 2 Influence of initiators on Graft%. Padding bath contained: ADMH, 3 wt %; PEG–DIA, 2 wt %; softener, 1.5 wt %; initiators, 0.5 wt %. The fabrics were dipped-padded twice at a 100% expression, dried at 50°C for 5 min, cured at 140°C for 5 min, washed, and dried.

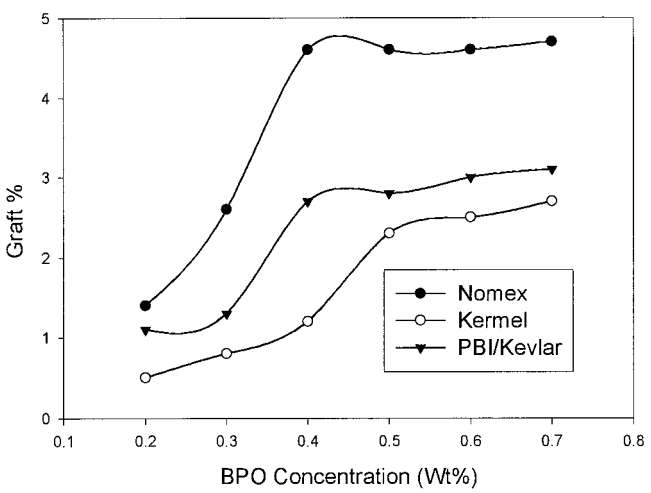


Figure 3 Influence of BPO concentration on Graft%. Padding bath contained: ADMH, 3 wt %; PEG–DIA, 2 wt %; softener, 1.5 wt %. The fabrics were dipped-padded twice at a 100% expression, dried at 50°C for 5 min, cured at 140°C for 5 min, washed, and dried.

fabrics. That is to say, it is more difficult for Nomex, Kermel, and PBI/Kevlar than for nylon and polyester to produce radicals, which might be a reason for few published results of using radical reactions on these polymers. Besides, in the previous study, TATAT was used to enhance the graft copolymerizaiton of ADMH onto nylon and polyester. However, in the present work, PEG–DIA is employed. Because of the obvious lower polymerization activity of PEG–DIA than that of TATAT, a higher BPO concentration may be necessary for an appropriate grafting yield.

Influence of curing temperature and time

The effect of temperature on the graft copolymerizations was investigated over the range of 100–160°C. The results are presented in Figure 4. Below 110°C, the percentage grafts were lower than 1 wt %; above that temperature, the grafting yields increase rapidly until reaching their optimum values, and then gradually decrease. As discussed previously,[12(d)] raising the temperature would increase the dissociation rate of BPO as well as the initiation and propagation rates of the graft copolymerization, resulting in higher graft yields. More importantly, at higher temperatures, the swellability and mobility of the fibers as well as the diffusion rate of monomer mixtures and initiators into the polymer amorphous regions would also increase. All these factors promote the grafting reactions. However, at higher than the optimum temperatures (130–140°C), the increase of the termination rates may become dominant, which will decrease the grafting yields.

The influence of curing time on the grafting copolymerizations is summarized in Figure 5. With the increasing of reaction time, percentage grafts gradually increase to saturated values. Practically, a reaction time of 5 min is enough to obtain optimal grafting results. A similar trend, but at a much longer reaction time (~ 30–60 min), was observed in our previous study in exhaustion grafting systems,[12(b,c)] indicating that the present continuous process is superior to the ordinarily used exhaustion systems in grafting reactions.

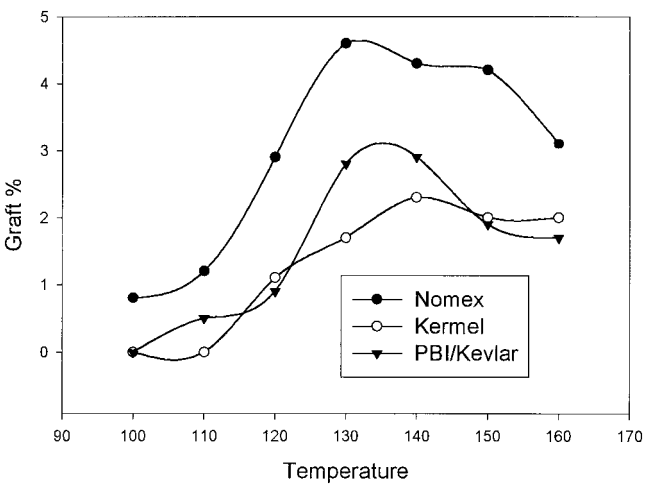


Figure 4 Influence of temperature on Graft%. Padding bath contained: ADMH, 3 wt %; PEG–DIA, 2 wt %; BPO, 0.5 wt %; softener, 1.5 wt %. The fabrics were dipped-padded twice at a 100% expression, dried at 50°C for 5 min, cured at different temperatures for 5 min, washed, and dried.

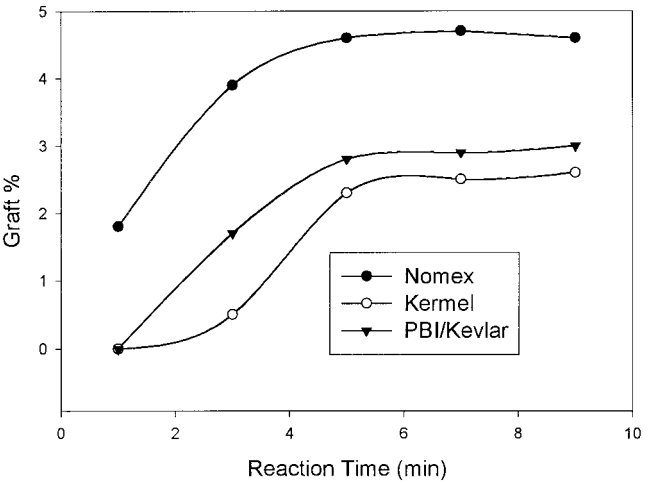


Figure 5 Influence of reaction time on Graft%. Padding bath contained: ADMH, 3 wt %; PEG–DIA, 2 wt %; BPO, 0.5 wt %; softener, 1.5 wt %. The fabrics were dipped-padded twice at a 100% expression, dried at 50°C for 5 min, cured at 140°C for different periods of time, washed, and dried.

FT-IR study

The grafting copolymerization was further characterized by FT-IR study. Figure 6 shows the FT-IR spectra of Nomex (spectrum A), ADMH/PEG–DIA grafted Nomex (spectrum B), and their difference spectrum (spectrum C, subtracting spectrum A from spectrum B) in the region of 1570–2000 cm^{-1}. Because of the strong amide I band of Nomex[15] centered at 1646 cm^{-1}, little difference could be directly detected between the grafted and ungrafted samples. However, after subtracting spectrum A from spectrum B, three new bands at 1764 (as a weak shoulder), 1736, and 1693 cm^{-1} could be observed. The 1764 cm^{-1} band could be attributed to the amide structure of ADMH,[12] and the 1736 and 1693 cm^{-1} bands are most likely attributable to the overlapping of the carbonyl bands of the imide groups of ADMH and the ester groups of PEG–DIA. Similar results could be observed in other ADMH/PEG–DIA-grafted fabrics. As an example, Figure 6 also shows the FT-IR spectra of pure and grafted Kermel, and their difference spectrum (Fig. 6, spectra D–F). After subtracting spectrum D from spectrum E, a 1764 cm^{-1} band could be observed in spec-

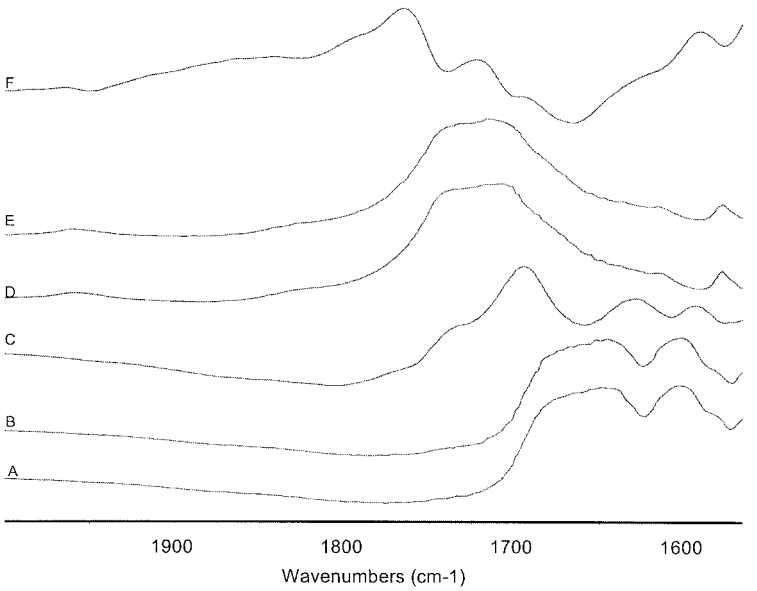


Figure 6 FT-IR spectra of (A) Nomex, (B) ADMH/PEG–DIA grafted Nomex, (C) difference spectrum of A and B (subtracting spectrum A from spectrum B), (D) Kermel, (E) ADMH/PEG–DIA grafted Kermel, and (F) difference spectrum of D and E (subtracting spectrum D from spectrum E), in the region of 1470–1990 cm^{-1}.

trum F. All these findings suggest that ADMH/PEG–DIA mixtures are grafted onto the fibers.

Thermal study

One of the most important characteristics of these high performance fibers is their excellent thermal stability. Consequently, the effect of grafting of ADMH on their thermal properties is of great concern. Figure 7 shows several typical DSC results. Because of melting and decompositions of the fibers,[15] pure Nomex [Fig. 7(A)] exhibits a broad endothermic peak in the range of 360–520°C, which is slightly decreased because of the grafting [see Fig. 7(B)]. In the chlorinated grafted sample [Fig. 7(C)], besides the very similar endothermic peak centered at around 420°C, a weak, broad exothermic peak at about 160°C was detected, which can be attributed to the decomposition of the N—Cl bond under heat treatment, in agreement with our previous results.[16]

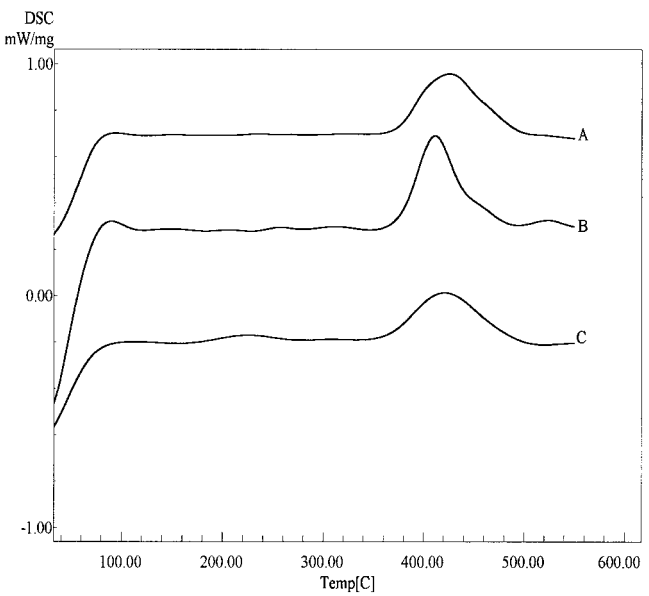


Figure 7 DSC curves of (A) Nomex, (B) ADMH/PEG–DIA grafted Nomex (Graft% is 4.6%), and (C) sample B, after chlorination.

TGA analyses of the same samples are presented in Figure 8. For Nomex [Fig. 8(A)], the initial weight loss from room temperature to 360°C is most likely attributable to the evaporation of the absorbed moisture and the releasing of water from the rupture of hydrogen bonding.[15] Higher than 360°C, the sample gradually decomposes. Very similar results can be obtained in the grafted and chlorinated grafted samples [Fig. 8(B), (C)], which shows slightly lower decomposing temperatures. All these findings suggest that grafting and chlorinating have only slight negative influences on the thermal behaviors of the high performance fibers, indicating that this can be a technically sound approach for the functional modifications of these fibers.

Antibacterial properties of the chlorinated grafted copolymers

We reported previously that after exposure to ordinary chlorine bleach, the hydantoin structures in grafted samples could be transformed into *N*-halamines, which provide powerful, durable, and

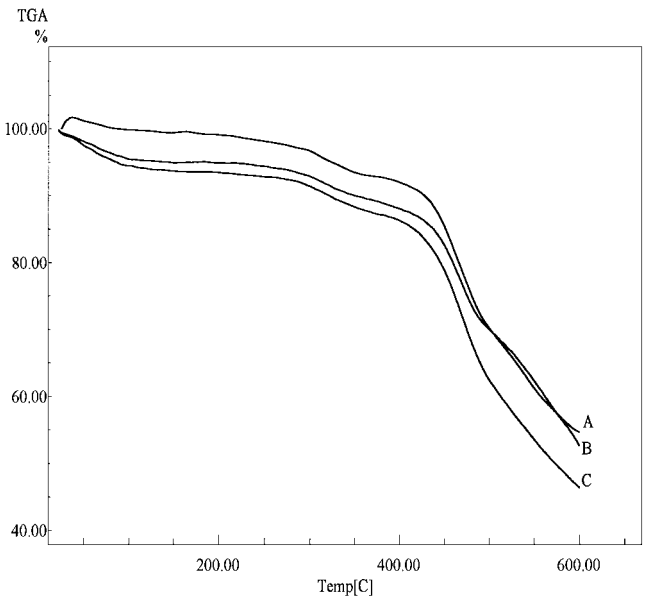


Figure 8 TGA curves of (A) Nomex, (B) ADMH/PEG–DIA grafted Nomex (Graft% is 4.6%), and (C) sample B, after chlorination.

regenerable antibacterial activities.[12] Similarly, in the present study, after chlorination, all the grafted fabrics showed antibacterial activities against *E. coli* and *S. aureus*; typical examples are presented in Table I. It can be seen clearly that all samples showed much stronger antibacterial activity against *S. aureus*, a typical gram-positive species, than against *E. coli*, a gram-negative species. For example, at a 10-min contact time, treated Nomex demonstrated a 99% (2 log) reduction of *S. aureus*, but no kill against *E. coli*; after 30 min of contact, Nomex can provide a 99.9999% (6 log) reduction to *S. aureus*, but only a 99.9% (3 log) reduction to *E. coli*. Similar results can be observed for Kermel and PBI/Kevlar blends (see Table I for details). These findings are most likely caused by the different structures of gram-positive and gram-negative bacteria: The lipid bilayer cell membranes of the gram-positive bacteria are covered by a porous peptidoglycan layer, which does not exclude most antimicrobial agents. On the other hand, gram-negative bacteria are surrounded by two membranes. The outer membrane functions as an efficient permeability barrier because it contains lipopolysaccharides and porins. As a result, gram-negative bacteria are better protected than gram-positive bacteria against antimicrobial agents.[17]

Significant differences were found between Nomex and the other two fabrics regarding their antimicrobial efficacies. The Nomex sample provided a 99.9999% (6 log) reduction to 10^6–10^7 CFU/mL of *E. coli* after 60 min of contact. However, the Kermel and PBI/Kevlar samples demonstrated only a 99.9% (3 log) reduction, even after 120 min of contact. A similar trend is also observed in the antibacterial tests against *S. aureus* (see Table I for details). These differences could be caused by the more available active chlorine on Nomex than on Kermel and PBI/Kevlar.

A good and sufficient contact between the testing fabric and the bacterial inoculum is very essential to demonstrate the antibacterial functions. In this study, a sterilized 50-mL beaker was placed on top of the fabrics in the antibacterial tests to enhance the contact. Separated studies showed that without this beaker, even after 180 min of contact time, the same chlorinated Nomex fabric could provide lower reductions only to *E. coli* and *S. aureus,* respectively. All these results indicate that *N*-halamines (and many other antibacterial agents) kill microorganism by contact, not by releasing biocides. Because of the hydrophobic properties of the fabrics, if the contact is insufficient, a false result might consequently be obtained. Special care should be taken in the design of antibacterial test methods, especially for some hydrophobic materials.

The hydrophobic characteristic of the high performance fabrics is not necessarily a disadvantage. It could ensure excellent durable antibacterial activities. As shown in the washing test, after five washes, little change can be detected in their antibacterial efficacies; and even after 50 washes, although the active chlorine (M_{Cl}) decreased dramatically, some of the samples could still provide 90% (1 log) reduction of the bacteria (Table II).

Another important advantage of these polymeric *N*-halamines is that their antibacterial activities can be regenerated after loss from repeated usage. As can be seen from Table II, upon rebleaching, all the samples

TABLE I
Percentage Reduction of *E. coli* and *S. aureus* after Different Contact Times[a]

			E. coli				*S. aureus*			
Fabric	Graft %	$M_{Cl} \times 10^5$ (mol/g)	10 min	30 min	60 min	120 min	10 min	30 min	60 min	120 min
Nomex	4.6	1.22	UD*[b]	99.9	99.9999	99.9999	99	99.9999	99.9999	99.9999
Kemel	2.3	0.34	UD	90	99.9	99.9	UD	99.9	99.99	99.999
PBI/Kevlar	2.8	0.41	UD	UD	99.9	99.9	UD	99.9999	99.9999	99.9999

[a] Bacteria concentration 10^6–10^7 CFU/mL.
[b] UD, no reduction was detected.

TABLE II
Percentage Reduction of the Bacteria after Washing at a Contact Time of 60 min[a]

Wash times	Nomex			Kermel			PBI/Kevlar		
	$M_{Cl} \times 10^5$ (mol/g)	*E. coli*	*S. aureus*	$M_{Cl} \times 10^5$ (mol/g)	*E. coli*	*S. aureus*	$M_{Cl} \times 10^5$ (mol/g)	*E. coli*	*S. aureus*
0	1.22	99.9999	99.9999	0.33	99.9	99.999	0.41	99.9	99.9999
5	1.20	99.9999	99.9999	0.28	99.9	99.99	0.41	99.9	99.99
15	0.63	99.9999	99.9999	0.23	99.9	99	0.37	99.9	99
30	0.27	99.9	99.99	UD[b]	90	90	0.20	90	99
50	UD[b]	90	90	UD[b]	UD[b]	UD[b]	UD[b]	UD[b]	UD[b]
50[c]	1.14	99.9999	99.9999	0.29	99.9	99.999	0.43	99.9	99.9999

[a] Bacteria concentration 10^6–10^7 CFU/mL. All the samples were tested with machine washing according to AATCC Test Method 124. AATCC standard reference detergent 124 was used in all the machine-washing tests.
[b] UD, no reduction was detected.
[c] Samples were rebleached after 50 times of washing.

show their original "killing powers" again. After 10 rounds of bleach/wash 15 times/rebleach cycles, the antibacterial properties of the samples were essentially unchanged, indicating that the antibacterial properties of the grafted samples were regenerable.

CONCLUSIONS

This is the first study concerning functional modifications of high performance fibers by continuous grafting approaches. We demonstrated that ADMH/PEG–DIA mixtures could be readily grafted onto Nomex, Kermel, and PBI/Kevlar blends. The thermal behaviors of the fibers were essentially unchanged upon grafting. Reaction conditions, especially initiators, have significant influences on the grafting reactions. As a general phenomenon, water-insoluble initiators are more promising candidates. After exposure to chlorine, the hydantoin structures in the grafted samples could be transformed into *N*-halamines, which can provide powerful, durable, and regenerable antibacterial activities against both gram-negative and gram-positive bacteria. For the same sample, different antibacterial test methods could provide different, sometimes completely opposite results. Special care should be taken in the design of antibacterial test methods to ensure sufficient contact of the biocides with the microorganisms, especially for some hydrophobic/rigid materials.

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