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Comparison of antimicrobial activities of polyacrylonitrile fibers modified with quaternary phosphonium salts having different alkyl chain lengths

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ABSTRACT: A series of polyacrylonitrile fibers (PANF) modified with quaternary phosphonium salts having various alkyl chain lengths (C_1, C_2, C_6, C_8, C_{12}) were synthesized and compared for their antimicrobial activities by the improved shake flask method. The as-prepared fibers were named MTPB-PANF, ETPB-PANF, HTPB-PANF, OTPB-PANF, and DTPB-PANF, respectively. The representative microorganisms employed were *Escherichia coli* (*E. coli*), *Staphylococcus aureus* (*S. aureus*), *Pseudomonas aeruginosa* (*P. aeruginosa*), and *Candida albicans* (*C. albicans*). Results from the current study showed that the alkyl chain length of quaternary phosphonium salts not only affected the synthesis of the fibers, but also impacted their antimicrobial activities. There was a rule that the longer the alkyl chain length, the more easily the quaternary phosphonium salts modify the fibers and the better the antimicrobial activities of the modified fibers. All the modified fibers exhibited good broad-spectrum antimicrobial activities. Specifically, DTPB-PANF exhibited an outstandingly high antimicrobial activity, which was nearly unaffected by the environmental pH (3–10). It can kill all the four pathogens in 15 min and had an excellent wash-resistant property. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43689.

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INTRODUCTION

In recent years, the demand for antimicrobial fabrics in domestic and abroad markets has grown significantly because of more awareness of the potential threat of spreading diseases. Some microorganisms are harmful; they can make people, fauna and flora sick, and thus directly or indirectly endanger human health and life. For example, *Escherichia coli* (*E. coli*) can cause a variety of diseases including gastroenteritis, dysentery, hemolytic uremic syndrome, urinary tract infection, septicemia, pneumonia, meningitis,[1–6] etc. *Staphylococcus aureus* (*S. aureus*) is a common bacteria causing food poisoning, and also the most common human pyogenic infection pathogens that can cause local or systemic purulent, such as furuncle and carbuncle, cellulitis, epneumonia, endocarditis, even bacteremia,[7–12] etc. The U.S. Centers for Disease Control report that infections caused by *S. aureus* rank second only to *E. coli*. *Pseudomonas aeruginosa* (*P. aeruginosa*) may cause acute pneumonia or may be a chronic colonizer of the lungs. It occurs in association with malignancy, AIDS, burn wound sepsis, and diabetes.[13–17] However, it is resistant to many antibiotics and disinfectants,[18–20] which makes it a difficult pathogen to treat. *Candida albicans* (*C. albicans*) can cause diseases such as cutaneous candidiasis, mucosal candidiasis, visceral and central nervous system candidiasis, pneumonia, gastroenteritis, endocarditis, osteomyelitis, and septicemia,[21–25] so it has been recognized as an increasingly important human pathogen.[26]

Considering the detrimental effects of the above-mentioned pathogenic microorganisms, it is of important practical significance to develop efficient antimicrobial materials to inhibit the growth and reproduction of the harmful microorganisms. Previously, we synthesized two novel antimicrobial fibers with organophosphorus groups to inhibit or kill pathogens. Results showed that the as-prepared fibers (i.e., MTPB-PANF and ETPB-PANF) demonstrated good antimicrobial activities against *E. coli* and *S. aureus* in 24 h.[27,28] However, their antimicrobial effect was not very ideal, especially for *C. albicans*. And the disinfection process always required a fairly long contact time, which was disadvantageous for their practical applications. So

in the current study, we further prepared a series of antimicrobial fibers using the similarly structured quaternary phosphonium salts except with different alkyl chain lengths for comparison of their antimicrobial activities. Results showed that the alkyl chain length exhibited a significant influence on the antimicrobial activities of the as-prepared fibers. Higher antimicrobial ratio and shorter contact time were achieved by the quaternary phosphonium salt with a longer alkyl chain length. Among the several fibers, the modified fiber named DTPB-PANF displayed amazingly high antimicrobial activities against all the four pathogens in a very short time (i.e., 15 min), and it can be used in a wide pH range without affecting its antimicrobial activities at all.

EXPERIMENTAL

Materials

Na-PANF with -COONa groups and a cationic exchange capacity of 5.0 mmol/g was used as the matrix fiber. Quaternary phosphonium salts having different alkyl chain lengths (i.e., methyltriphenylphosphonium bromide, MTPB, C_1; ethyltriphenylphosphonium bromide, ETPB, C_2; (1-hexyl) triphenylphosphonium bromide, HTPB, C_6; (1-octyl) triphenylphosphonium bromide, OTPB, C_8; and (1-dodecyl) triphenylphosphonium bromide, DTPB, C_{12}) were purchased from Alfa Aesar China (Tianjin), and their purity were all 97+ %. Peptone, beef extract and sodium chloride were purchased from Beijing Aoboxing Biotechnology. Pathogenic *E. coli* and *S. aureus* were supplied by Henan Academy of Institute of Biology, Limited Liability Company, Zhengzhou, China. *C. albicans* (ATCC10231) and *P. aeruginosa* (CMCC10104) were purchased from Nanjing bianzhen biological technology.

Synthesis of Quaternary Phosphonium Salts-Modified Fibers

Quaternary phosphonium salts-modified fibers were synthesized according to our previously reported procedure.[27,28] In a typical test, 0.002 mol quaternary phosphonium salts were separately dispersed in 100 mL deionized water, to which 0.5 g Na-PANF was added. The mixture was shaken in a shaker (100 rpm) at 50 °C for 8 h. Then, the fiber was washed with deionized water until the washing liquor with 1% $AgNO_3$ solution was negative. The obtained fibers were dried at 40 °C to constant weight. The weight gain was determined gravimetrically using the following equation, where W_0 and W_f are initial mass of Na-PANF and final mass of quaternary phosphonium salts-modified fibers, respectively:

$$W_g, \% = \frac{W_f - W_0}{W_0} \times 100 \quad (1)$$

Characterization by FTIR-ATR

FTIR spectra between 400 and 4000 cm^{-1} were collected on a Thermo Electron spectrometer (Nicolet 6700). Samples were prepared by attenuated total reflectance (ATR) method.

Stability of Organophosphorus Groups on Fibers

The concentration of phosphor was used to estimate the stability of organophosphorus groups on the modified fibers. 20 mg fibers were separately immersed into 20 mL distilled water and shaken at 30 °C with 180 rpm in a shaker. After different time intervals, the concentration of phosphor from each sample was measured using inductive coupled plasma atomic emission spectrometer (ICP-AES). The released ratio was calculated from the mass proportion of released phosphor and modified fibers.

Antimicrobial Activity Assay

The media for *E. coli* and *S. aureus* were a mixture of 10 g/L peptone, 5 g/L beef extract and 5 g/L sodium chloride (pH 7.2). The PDA medium for *C. albicans* includes potato juice and glucose. The china blue medium was used for *P. aeruginosa*. After bacteria activation, 1 mL bacterial culture was centrifuged at 12000 rpm in two minutes. The thallus was cleaned with sterile saline, and then dispersed in 20 mL sterile saline uniformly. After that, the modified fibers (phosphorus concentration 25 μmol/L) were immersed into the above-prepared bacterial suspension, and the mixture was incubated at 30 °C with 180 rpm in a shaking incubator. After 24 h, 1 mL bacterial suspension was removed to make different dilutions of bacterial suspension (from 10^{-1} to 10^{-6}). Finally, 100 μL bacterial suspensions of 10^{-4}, 10^{-5}, and 10^{-6} were seeded on a sterile nutrient broth agar. The plates were put into an incubator at culture temperature 37 °C for 24 h. The initial bacterial suspension (without fibers) was used as a negative control group. The number of living colonies was counted and three repeats were conducted for each sample. The antimicrobial ratio was quantified as follows:

$$\text{Antimicrobial ratio } (\%) = (A - B)/A \times 100 \quad (2)$$

where A and B are the number of the colonies detected from the negative control group and the testing group after antimicrobial treatment, respectively.

RESULTS AND DISCUSSION

Synthesis of Quaternary Phosphonium Salts-Modified Fibers

In the same condition that reaction temperature was 50 °C, reaction time was 8 h, pH was close to neutral and the concentration of phosphonium salts was 0.02 mol/L, quaternary phosphonium cations with different alkyl chain lengths (C_1, C_2, C_6, C_8, and C_{12}) were exchanged with Na^+ from -COONa of Na-PANF. Finally we got a series of quaternary phosphonium salts-modified polyacrylonitrile fibers namely MTPB-PANF, ETPB-PANF, HTPB-PANF, OTPB-PANF, and DTPB-PANF. The reaction mechanism was shown in our previous studies.[27,28] In this study, we found that the longer the alkyl chain length, the more intense the interaction between fibers and quaternary phosphonium salts, causing weight gain and phosphor concentration of the modified fibers increased significantly. As shown in Table I, the weight gain were 12.47% (MTPB-PANF), 15.70% (ETPB-PANF), 23.42% (HTPB-PANF), 48.83% (OTPB-PANF), and 70.45% (DTPB-PANF), respectively, meaning 0.349, 0.423, 0.548, 1.072, and 1.377 μmol/g of phosphor were successfully grafted onto the PANF by using the different quaternary phosphonium salts. We suggested that the enhanced phosphor grafting with the increment of alkyl chain lengths can be explained by the surfactant mechanism.[29] In the process of reaction, quaternary phosphonium salt is similar to the surface active agent, at the same concentration, the greater the non polar component of the surface active agent, the stronger the activity is, namely in the homologue, the surface activity of quaternary phosphonium salt can be enhanced with the increase of its alkyl chain

Table I. Effects of Alkyl Chain Lengths on the Synthesis of Modified Fibers

	MTPB-PANF	ETPB-PANF	HTPB-PANF	OTPB-PANF	DTPB-PANF
Molecular weight of quaternary phosphonium salt (g/mol)	357.24	371.26	427.37	455.42	511.54
Weight gain (%)	12.47	15.70	23.42	48.83	70.45
Molar concentration of phosphor on fibers (μmol/g)	0.349	0.423	0.548	1.072	1.377

length. When some functional groups of quaternary phosphonium salt were grafted on the fiber, their alkyl chains form micelles together around fiber, and this will help to enhance the fiber surface reactions. It is easier to form micelles for the longer alkyl chain, therefore, the longer the alkyl chain length, the reaction between quaternary phosphonium salts and fibers become more easily. So we draw the conclusion that quaternary phosphonium salts with longer alkyl chain can be more easily grafted on the Na-PANF structure.

Characterization by FTIR-ATR

The FTIR spectra of Na-PANF and modified fibers were shown in Figure 1. It can be seen that before and after modification, the fibers showed basically the similar trend in 4000–1350 cm^{-1} range, indicating they had the same backbone of PANF. However, there still existed several significant differences. First, the peak at 2924 cm^{-1} and 2853 cm^{-1} (antisymmetric and symmetric stretching vibration of CH_2) became more and more intense with the alkyl chain length increasing. Second, compared with Na-PANF, some new peaks emerged in fingerprint region from 1350 to 650 cm^{-1}, and became more intense with the increase of alkyl chain length. 1116–1114 cm^{-1} was C-P bending vibration absorption peak, 996–997 cm^{-1} was vibration absorption peak of P-Ph, 749–690 cm^{-1} was the characteristic peaks of C=C bending vibration of the benzene ring. The above change of FTIR spectra suggested that organophorsphur groups have been successfully grafted onto Na-PANF.

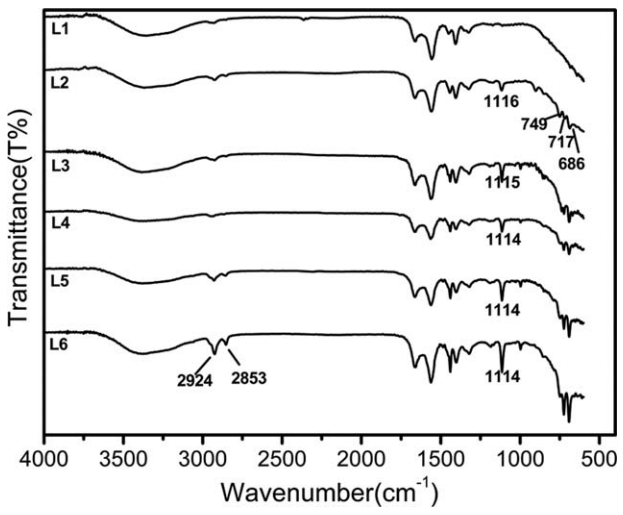

Figure 1. FTIR spectra of Na-PANF and modified fibers (L1: Na-PANF; L2: MTPB-PANF; L3: ETPB-PANF; L4: HTPB-PANF; L5: OTPB-PANF; L6: DTPB-PANF).

Stability of Organophosphorus Groups on Modified Fibers

Released phosphor was measured by ICP-AES after immersing modified fibers in distilled water for 6, 12, 24, 48, 60, and 72 h. As shown in Figure 2, a negligible amount of phosphor was released during the immersion, and the amount decreased obviously with the increment of the alkyl chain length. More specifically, after immersing the modified fibers in distilled water for 72 h, only 0.71% for MTPB-PANF, 0.66% for ETPB-PANF, 0.46% for HTPB-PANF, 0.25% for OTPB-PANF, and 0.03% for DTPB-PANF of phosphor were released from the fibers. This demonstrated that the organophosphorus groups are stable on the modified fibers in water. And the longer the alkyl chain length of quaternary phosphonium salts, the more stable they bind with the matrix fibers.

Antimicrobial Activities

In this work, the improved shake flask method was applied to evaluate the antimicrobial activities of fibers against *E. coli*, *S. aureus*, *C. albicans*, and *P. aeruginosa*. According to the national standard GB/T 20944.3, the fiber had the antimicrobial activity when the antimicrobial ratio $\geq$ 70% against gram bacteria and $\geq$ 60% against *C. albicans*. Figure 3 shows the antimicrobial images before and after antimicrobial test. It can be seen that the number of colonies were substantially reduced on the plate after exposure to quaternary phosphonium salts-modified fibers for 8 h, and the reduction extent was correlated well with the alkyl chain lengths. Specifically, complete sterilization against

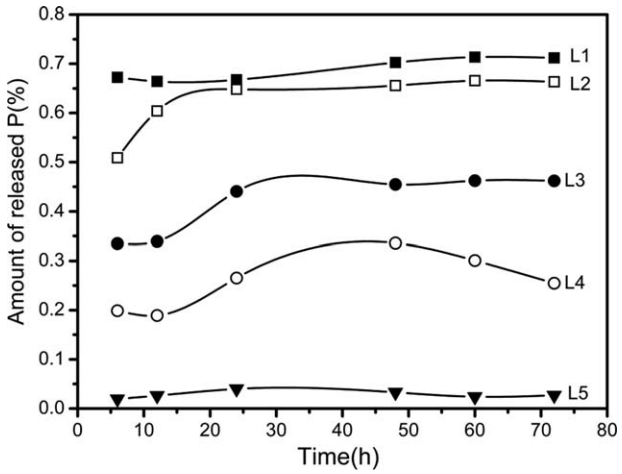

Figure 2. Amount of released P from modified fibers (L1: MTPB-PANF; L2: ETPB-PANF; L3: HTPB-PANF; L4: OTPB-PANF; L5: DTPB-PANF).

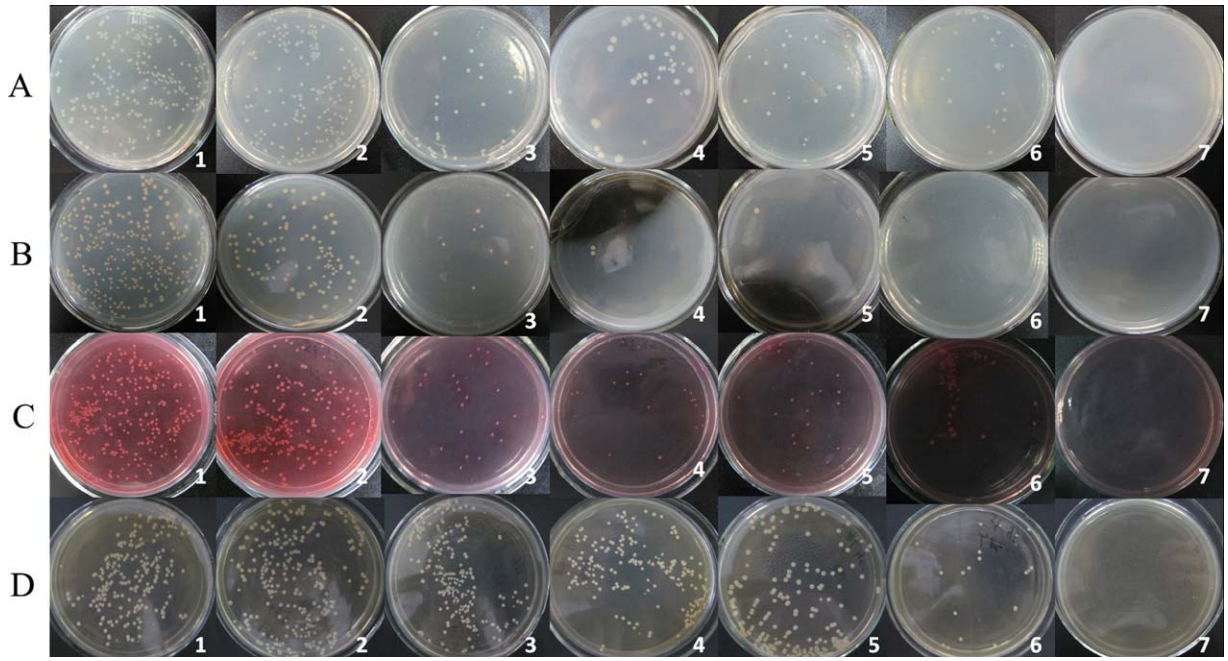

Figure 3. The images before and after antimicrobial test against *E. coli* (A), *S.aureus* (B), *P.aeruginosa* (C) and *C. albicans* (D) (1: control; 2: Na-PANF; 3: MTPB-PANF; 4: ETPB-PANF; 5: HTPB-PANF; 6: OTPB-PANF; 7: DTPB-PANF). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the four pathogens were achieved on DTPB-PANF. To quantitatively assess the antimicrobial effects, the respective antimicrobial ratios were calculated and plotted versus contact time in Figure 4. It showed that the raw Na-PANF exhibited no significant antimicrobial activities for all the studied pathogens even after a contact time of 8 h. After modification of quaternary phosphonium salts, however, the antimicrobial activities increased substantially depending on the pathogens, alkyl chain lengths and contact time. Among the several modified fibers, DTPB-PANF exhibited the best antimicrobial activities after exposing to all pathogens in 2 h, and the antimicrobial ratio was 100%. When the contact time increased to 4 h [Figure 4(A)], OTPB-PANF began to show the antimicrobial activity for *E. coli* with an antimicrobial ratio of 73.17%. As the contact time increased to 6 h, ETPB-PANF and HTPB-PANF also showed the antimicrobial activities and the ratios were 79.16% and 70.59%, respectively. After 8 h, all modified fibers gained good antimicrobial activities, and their antimicrobial ratios were all near or above 80%. For *S. aureus* [Figure 4(B)], MTPB-PANF, ETPB-PANF and HTPB-PANF obtained antimicrobial activities in 6 h, 4 h and 2 h, correspondingly. OTPB-PANF exhibited the same excellent antimicrobial activities as DTPB-PANF throughout the studied contact time. After 8 h, the antimicrobial ratios of all modified fibers against *S. aureus* reached above 99%. Figure 4(C) illustrates the antimicrobial activities against *P. aeruginosa*. Compared to *S. aureus* and *E.coli*, a different phenomenon appeared that the short alkyl chain (MTPB and ETPB) modified fibers displayed better antimicrobial effects than the long alkyl chains (HTPB, OTPB). The former can reach more than 83% of the antimicrobial ratio after 4 h; however the latter was only 60%. Up to 6 h, all modified fibers obtained antimicrobial activities, and the antimicrobial ratios were 89.35% for MTPB-PANF, 88.17% for ETPB-PANF, 84.76% for HTPB-PANF and 81.74% for OTPB-PANF. As can be seen from Figure 4(D), MTPB-PANF, ETPB-PANF and HTPB-PANF were not active against *C. albicans* at all. After 6 h, OTPB-PANF can kill 78.78% of *C. albicans*. The above results demonstrated that some modified fibers appeared antimicrobial activities earlier, others later or inactive. Amazingly, DTPB-PANF showed the strongest antimicrobial activities against all pathogens and the antimicrobial ratios were 100% within 2 h.

To further study the antimicrobial activities of DTPB-PANF, an extra experiment was conducted within a shortened contact time of 15 min. Figure 5 presents plots of $\log_{10}$(number of survivors, the vertical axis) versus contact time (the horizontal axis) of DTPB-PANF against the four pathogens. After 5 min, all *S. aureus* and *C. albicans* were killed, and only 60 colonies ($\log_{10}^{60} = 1.77$) of *E. coli* and 202 colonies ($\log_{10}^{202} = 2.30$) of *P. aeruginosa* survived, corresponding to antimicrobial ratios of 99.99% and 98.97%, respectively. After 10 min, all *E.coli* can be killed; meanwhile the number of viable colonies of *P. aeruginosa* was reduced to 140 ($\log_{10}^{140} = 2.14$) and the antimicrobial ratio reached 99.99%. When the exposure time was prolonged to 15 min, DTPB-PANF killed all the four pathogens.

As compared with the previously reported antimicrobial materials, DTPB-PANF prepared in the current study was more efficient in inhibiting or killing pathogens. For example, the nano-SiO_2 modified wool fibers prepared by Wang *et al.*[30] exhibited the antimicrobial ratios of 90% against *E. coli* and 96% against *S. aureus* after 22 h. The PAN-NH_2-GDGE-PHGH and PAN-NH_2-PEGDGE-PHGH nanofibrous membranes prepared by Mei *et al.*[31] exhibited the antimicrobial ratios of above 99% against *E. coli* and *S. aureus* after 3 h. The polyallylamine-coated glass

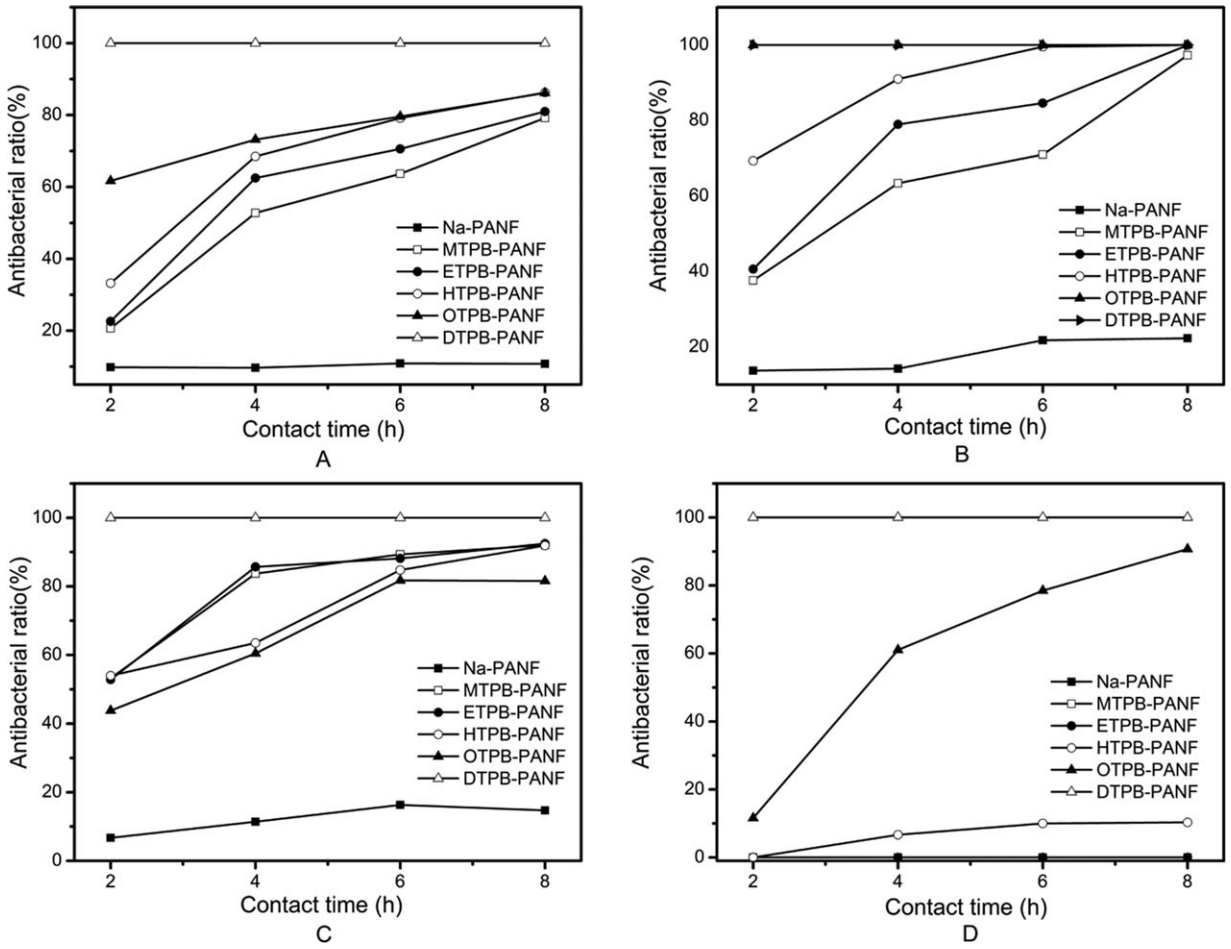

Figure 4. Antimicrobial activities of Na-PANF and modified fibers against *E. coli* (A), *S. aureus* (B), *P. aeruginosa* (C) and *C. albicans* (D) for 2–8 h.

prepared by Iarikov *et al.*[32] exhibited the antimicrobial ratio of 88% against *P. aeruginosa*, which is worse than *S. epidermidis* and *S. aureus* (97%) after 1 h. Elzatahry *et al.*[33] prepared the nanofibers produced by electrospinning containing N-heterocyclic carbene complexes were tested against two Gram-positive bacteria (*S. aureus and B. subtilis*), six Gram-negative bacteria (*S. typhi, E. coli, P. auroginosa, E. faecalis, P. vulgaris,* and *M. leuteus*), and two fungal strains(*S. cervisiae* and *C. albicans*) use the inhibition zone. The results was found to be inactive against *E. coli, P. auroginosa,* and *C. albicans.* Comparatively, DTPB-PANF prepared in this study showed an antimicrobial ratio of 100% for *E. coli*, *S. aureus*, *P. auroginosa,* and *C. albicans* within an extremely short time.

The excellent antimicrobial activities of the as-prepared modified fibers were suggested to be due to both the electrostatic interaction and the hydrophobic effect. As we know, bacterial cell surfaces are usually negatively charged because of acidic phospholipids and membrane proteins in cytoplasmic membranes.[34] On the contrary, organophorsphur groups on the fibers possess positive charges. So the bacterial cells can be adsorbed on the modified fibers through a relatively strong electrostatic interaction. Besides, the adsorption can be further strengthened by the hydrophobic effect as indicated from the fact that the antimicrobial activity increased as the hydrophobic alkyl chain length increased. With increasing the hydrophobic alkyl chain length, they become more active to interact with cytoplasmic membranes.[35] It is expected that the organophorsphur groups may induce a phase separation in the bacterial membrane on binding and disrupt it, leading to the release of cytoplasmic constituents such as K^+, DNA, and RNA and the

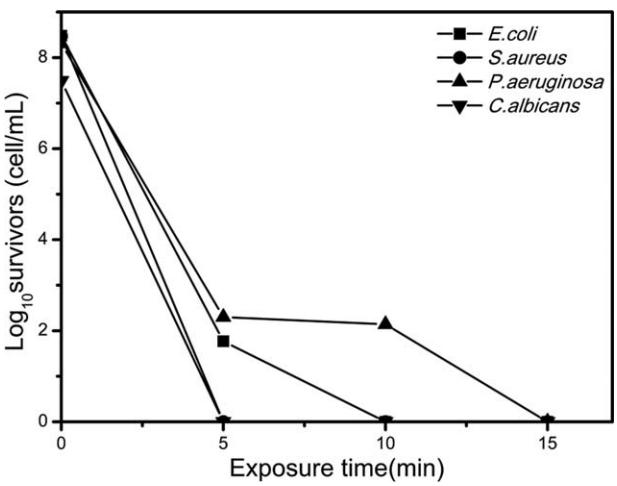

Figure 5. Antimicrobial activities of DTPB-PANF in 15 min.

Table II. Effects of Washing Times on DTPB-PANF's Antimicrobial Activities

	Antimicrobial ratio (%)			
Washing times	*E. coli*	*S. aureus*	*P. aeruginosa*	*C. albicans*
0	100	100	100	100
10	99.99	99.99	99.97	99.93
30	98.84	99.08	98.37	97.95
50	95.33	96.67	93.84	92.11

eventual death of bacterial cells. Moreover, the modified fibers are more advantageous for disinfection of Gram-positive strains (e.g., *S. aureus*) than Gram-negative strains (e.g., *E. coli* and *P. aeruginosa*); because Gram-negative bacteria have the outer cell membrane (composed mainly of lipopolysaccharides and phospholipids) which protects bacteria cells against foreign compounds.[36] *C. albicans* belongs to eukaryotes, and it is 10 times larger than bacteria belonging to prokaryotes. More importantly, it is easy to form biofilm that is a layer of protective film, so commonly used antibiotics and fungicides are difficult to penetrate the biofilm surface to play a role.[37] In our case, only fibers with long alkyl chain (C_8 and C_{12}) put their antimicrobial activities to good use. It was speculated that maybe the long alkyl chain can destroy the biological biofilm of *C. albicans*.

Wash-Resistant Property of DTPB-PANF

To evaluate the wash-resistant property of the modified fibers, DTPB-PANF was washed in 0.1% aqueous solution of laundry detergent for 10 times, 30 times, and 50 times, respectively. After being dried, DTPB-PANF was reused for the antimicrobial activity tests. The results showed (Table II) that the DTPB-PANF had good resistance to water washing. After washing 50 times, the antimicrobial ratios in 24 h declined slightly and stayed above 90% for all the four pathogens, indicating that the antimicrobial properties of DTPB-PANF are very stable. Wang *et al.*[30] have done the similar research using nano-SiO_2 grafted wool fibers as the antimicrobial material. It was reported that after water washing for 35 times, the graft content of nano-SiO_2 dropped to 2.8% and the antimicrobial ratios in 22 h dropped to 69% against *E. coli* and 71% against *S. aureus*, respectively. Therefore, our polyacrylonitrile fibers modified with quaternary phosphonium salts "DTPB-PANF" had more excellent water-resisting property.

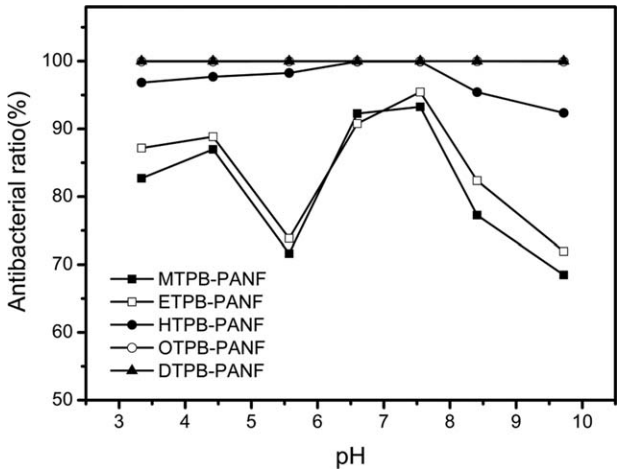

Figure 6. pH effects on the antimicrobial activity of modified fibers against *E. coli*.

pH Effects on Antimicrobial Activities

Since environmental pH may have a certain effect on the physiochemical properties of the modified fibers (e.g., surface charge), a further test was conducted to estimate whether pH affects the antimicrobial activities or not. A pH range of 3–10 was chosen in this current study. Results (shown in Figure 6) showed that the antimicrobial activities of DTPB-PANF and OTPB-PANF with longer alkyl chain were basically unchanged in any pH, and their antimicrobial ratios were 100% and 99.9%. The antimicrobial ratios of HTPB-PANF were slightly decreased in both acidic and alkaline environments, but still kept above 90%. Comparatively, the antimicrobial activities of MTPB-PANF and ETPB-PANF were significantly varied with pH, and the lowest antimicrobial ratio (ca. 70%) was achieved at pH 5.5. It is speculated that this point may be the isoelectric point of *E. coli*,[38] and the cell surface is uncharged at this point which resulted in the decrease of the adsorption ability between *E.coli* and fibers and the consequent decrease of antimicrobial ratios. The optimal pH for MTPB-PANF and ETPB-PANF to inhibit or kill *E. coli* was around 7.0, which was more usual in practical applications. It should be mentioned that throughout the studied pH range, all modified fibers exhibited good antimicrobial activities (i.e., ratio above 70%) against *E. coli*, demonstrating that these antimicrobial fibers will find a wide application in practice.

CONCLUSIONS

Polyacrylonitrile fibers modified with quaternary phosphonium salts containing various alkyl chain lengths possessed high antimicrobial activities against Gram-negative bacteria, Gram-positive bacteria and fungi. And their activities were strongly affected by the alkyl chain length of substituents of the quaternary phosphonium salts. The antimicrobial activities of MTPB-PANF and ETPB-PANF became stronger in the order: *C. albicans* < *E. coli* < *P. aeruginosa* < *S. aureus*. For HTPB-PANF and OTPB-PANF, the order is *P. aeruginosa* < *C. albicans* < *E. coli* < *S. aureus*. DTPB-PANF was the most active among the five modified fibers, and it can kill 100% of the four pathogens in 15 min. Even after washing 50 times, its antimicrobial ratios for the four pathogens still maintained more than 90%. Moreover, pH had little effect on the antimicrobial activities of these modified fibers. So they will act as self-sterilizing materials or be used in many application areas especially textiles, health care products and hygienic applications.

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