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Durably Antibacterial and Bacterially Antiadhesive Cotton Fabrics Coated by Cationic Fluorinated Polymers

Jing Lin,*[,†] XiaoYu Chen,[†] ChunYan Chen,[†] JieTao Hu,[†] CaiLong Zhou,*[,‡] XianFang Cai,[†] Wei Wang,[†] Cheng Zheng,[†] PeiPei Zhang,*[,§] Jiang Cheng,[‡] ZhanHu Guo,*[,∥] and Hu Liu[#]

[†]School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, P. R. China

[‡]School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China

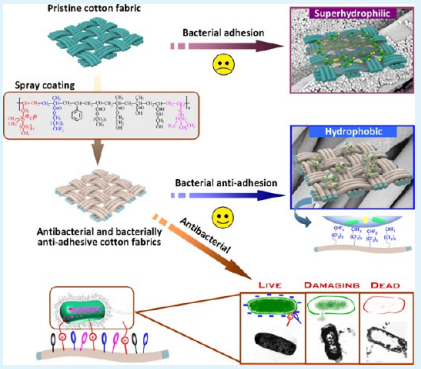
[§]Department of Bioengineering, University of Maryland at College Park, College Park, Maryland 20742, United States

[∥]Integrated Composites Laboratory (ICL), Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States

[#]National Engineering Research Center for Advanced Polymer Processing Technology, Zhengzhou University, Zhengzhou, Henan 450002, P. R. China

Supporting Information

ABSTRACT: Considerable attention has been devoted to producing antibacterial fabrics due to their very wide applications in medicine, hygiene, hospital, etc. However, the poor antibacterial durability and bad bacterial antiadhesion capacity of most existing antibacterial fabrics limit their applications. In this work, a series of antibacterial and polymeric quaternary ammonium monomers with different alkyl chain length were successfully synthesized to copolymerize with fluorine-containing and other acrylic monomers to generate cationic fluorinated polymer emulsions and durably antibacterial and bacterially antiadhesive cotton fabrics. The relation between antibacterial constituent and its antibacterial activity was investigated. The study indicated that the alkyl chain length and contents of the antibacterial monomers, as well as the add-on percentage of polymer greatly influenced the antibacterial activities of the fabrics. In addition, it was found that incorporation of fluorine component into the polymer greatly enhanced the antibacterial activity and bacterial antiadhesion of the treated fabrics due to the low surface energy induced hydrophobicity. Finally, antibacterial and antiadhesive models of action of the obtained fabrics were illustrated.



KEYWORDS: *antibacterial, bacterial antiadhesion, cotton fabric, cationic polymer, hydrophobicity*

INTRODUCTION

Antibacterial fabrics have attracted great attention due to their importance and indispensability for many fields, including medicine, hygiene, hospital, etc. Antibacterial fabrics could inhibit the growth of the bacteria and microbes or even kill them, thus reducing the transmission of infectious diseases. Incorporating some antibacterial moieties into fabrics has been extensively adopted by either chemical or physical treatment, such as metal and oxide nanoparticles (Ag,[1−3] ZnO,[4−6] TiO_2,[7,8] Cu_2O,[9] and SiO_2[10]), nanocomposite particles (TiO_2 (MgO or ZrO_2)/SiO_2,[10] Ag@ZnO,[11] TiO_2/Fe_3O_4/Ag,[12] and MgO/Al_2O_3[13]), hybrid particles (ZnO/chitosan[14] and *N*-chloramine/SiO_2[15]), organic quaternary ammonium salts (QAs),[16−18] guanidine,[19] *N*-chloramines,[20] chitosan,[21] etc.

Despite the fact that considerable recent progress has been made in developing antibacterial fabrics, one challenge in the field is that the antibacterial ability of antibacterial materials on the fabrics may be gradually diminished after a period of use, where the live/dead bacteria could adhere on the fabrics to form biofilm that is difficult to be removed. Therefore, fabrics integrated with antibacterial durability and bacterial antiadhesion need to be urgently improved. One of the most effective ways of gaining antibacterial durability is to design non-dissolution-type antibacterial cationic polymers. For instance, scientists have been trying to design and synthesize different antibacterial cationic polymers with durable properties over the years. One of the most important features of these polymers is their versatile structures, such as quarternary ammonium,[22] phosphonium,[23] pyridinium,[24] and imidazolium.[25] Current studies demonstrated that the incorporation of antibacterial cationic polymers can enhance antibacterial durability of fabrics but bacterial antiadhesion of fabric is usually difficult to achieve because bacterial adhesion is complicated and governed by the interplay among the physicochemical, interfacial, and geometrical characteristics of the fabric surface and bacteria.[26,27] Conventionally, the bacterial antiadhesion could be achieved by either repelling or killing the approaching bacteria. The repelling of bacteria was realized by introducing elements,

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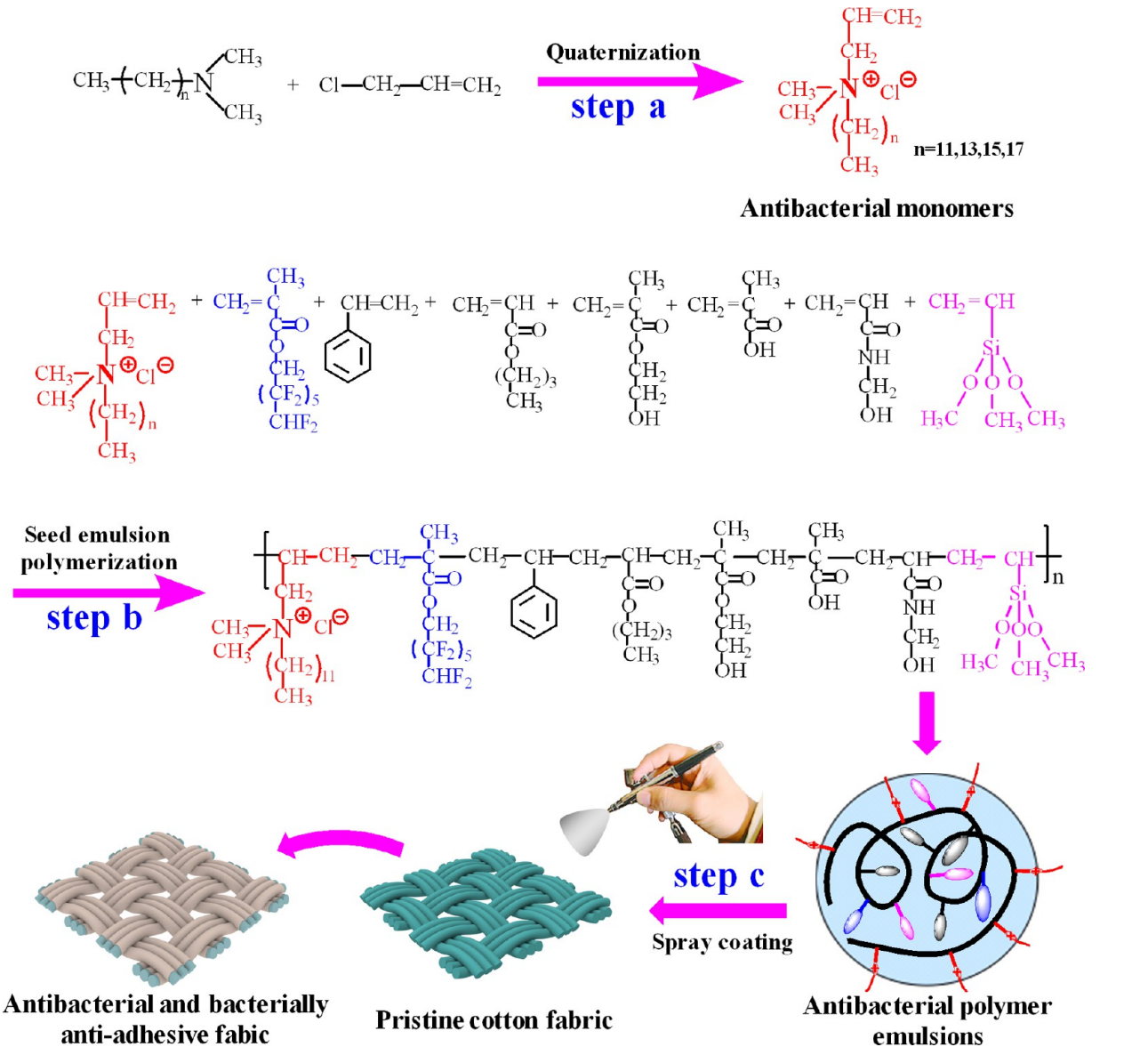

Figure 1. Schematic of the synthesis route for the antibacterial and bacterially antiadhesive cotton fabric.

such as highly negatively charged polymers (electrostatic repulsion), similar hydrogel forming polymers (steric repulsion) mostly based on poly(ethylene glycol), or special polymers with low surface energy (ultrahydrophobic repulsion).[28−30] The killing of bacteria can be achieved by either release-killing of antibacterial moiety from a matrix or contact-killing of antibacterial surfaces.[31−35] Unfortunately, up to now, only a few literatures about antibacterial and bacterially antiadhesive fabrics were reported. For instance, Sivakumar et al. have developed a bacterially antiadhesive cotton cloth coated by chalcones.[36] Spasova et al. reported that novel superhydrophobic nanofibrous mats of poly(vinylidene fluoride-*co*-hexafluoropropylene)/ZnO possessed good antiadhesive and antibacterial properties.[37] Therefore, considerable efforts need be made to design and develop new antibacterial and bacterially antiadhesive fabrics.

The present work aims to develop durably antibacterial and bacterially antiadhesive cotton fabrics coated by antibacterial cationic fluorine-containing polymers. The fabrics were prepared by spray-coating of the polymers that mainly comprised of antibacterial quaternary ammonium monomers with different alkyl chain lengths and fluorine-containing monomers. The relation between the antibacterial constituent and antibacterial activity was investigated. The factors that affect the bacterial antiadhesion of treated fabrics were also studied. Owing to the coexistence of quaternary ammonium and fluorine components, the as-prepared fabrics had remarkably durable antibacterial activity and bacterial antiadhesion. Additionally, antibacterial and bacterially antiadhesive models of the treated fabrics were proposed.

EXPERIMENTAL SECTION

Materials. Alkyl-dimethyl tertiary amines (ADTA-12, ADTA-14, ADTA-16, and ADTA-18; the corresponding chemical formula: $C_nH_{2n+1}N(CH_3)_2$, n = 12, 14, 16, and 18, respectively.) and 3-chloropropene for preparing antibacterial monomers were purchased from Shanghai Macklin Biochemical Co., Ltd. For the synthesis of antibacterial polymer emulsion, dodecafluoroheptyl methacrylate (GO4) was supplied from Harbin Xeogia Fluorine-silicon Material Co. Ltd. Styrene (St), butyl acrylate (BA), 2-hydroxyethyl methacrylate (HEMA), methyl acrylate (MAA), acrylamide (AM),

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Table 1. Summary of the Experimental Description for Antibacterial Polymer Emulsions and Antibacterial Cotton Fabrics

	antibacterial polymers	alkyl chain component	fluorine component	antibacterial film	antibacterial fabrics	add-on of polymer (wt %)
E1	different alkyl chain lengths	6 wt % C_{12}	9 wt % G04	P1	F1	6
E2		6 wt % C_{14}	9 wt % G04	P2	F2	6
E3		6 wt % C_{16}	9 wt % G04	P3	F3	6
E4		6 wt % C_{18}	9 wt % G04	P4	F4	6
E5	different contents of M3(C16)	1 wt % C_{16}	9 wt % G04	P5	F5	6
E6		2 wt % C_{16}	9 wt % G04	P6	F6	6
E7		4 wt % C_{16}	9 wt % G04	P7	F7	6
E3		6 wt % C_{16}	9 wt % G04	P3	F3	6
E8	different contents of G04	6 wt % C_{16}	0 wt % G04	P8	F8	6
E9		6 wt % C_{16}	1 wt % G04	P9	F9	6
E10		6 wt % C_{16}	3 wt % G04	P10	F10	6
E11		6 wt % C_{16}	6 wt % G04	P11	F11	6
E3		6 wt % C_{16}	9 wt % G04	P3	F3	6
E3	different add-ons of polymer	6 wt % C_{16}	9 wt % G04	P3	F12	1
E3		6 wt % C_{16}	9 wt % G04	P3	F13	2
E3		6 wt % C_{16}	9 wt % G04	P3	F14	4
E3		6 wt % C_{16}	9 wt % G04	P3	F3	6
E3		6 wt % C_{16}	9 wt % G04	P3	F15	8

vinyltrimethoxysilane (A-171), and 2,2′-azobis-(2-methylpropionamidine) dihydrochloride (AIBA, V50) as initiators were procured from Sigma-Aldrich. Hydrophilic isocyanate trimer (Bayhydur XP 2487/1) as cross-linker was supplied by Covestro (formerly Bayer Material Science Co. Ltd.). The cotton fabrics in the experiment were procured from the local industry. *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* (ATCC 25922) were purchased from Guangdong Institute of Microbiology. Mueller-Hinton broth (MHB) and Mueller-Hinton agar (MHA) were purchased from Sigma-Aldrich.

Preparation of Antibacterial and Polymeric Monomers. The preparation route of antibacterial and polymeric monomers via a quaternization reaction is illustrated in Figure 1 (step a). Typically, the requisite amounts of alkyl-dimethyl tertiary amines and ethanol were added in a 100 mL round-bottom flask in a water-bath reactor equipped with a thermometer, magnetic stirrer, and reflux condenser. Thereafter, a requisite amount of 3-chloropropene as the quaternization agent (molar ratio of alkyl-dimethyl tertiary amines/3-chloropropene equals to 1:1.05, 50 wt % in ethanol solution) was added dropwise into the above mixture in 1 h under vigorous stirring at 60 °C, followed by heating to 68 °C for another 3 h. Finally, the obtained mixture was cooled, the solvents were then removed by distillation, and the unreacted tertiary amines and 3-chloropropene were further washed away by petroleum ether three times; the final antibacterial and polymeric monomers (M1, M2, M3, and M4, shown in the Figure S1) were obtained from the reaction of ADTA-12, ADTA-14, ADTA-16, and ADTA-18 with the 3-chloropropene.

Preparation of Antibacterial Polymer Emulsions. Antibacterial polymer emulsions were prepared by a seed emulsion polymerization process. The synthesis route is shown in step b of Figure 1. The recipe for the synthesis of the antibacterial polymer emulsions is given in Table 1. In a typical synthesis, appropriate amount of water and 0.2 g of $NaHCO_3$ were added into a three-necked flask equipped with reflux condenser, mechanical stirrer, and dropping funnels. Thirty five grams of acrylic monomer mixture, including 42 wt % St, 50 wt % BA, 2 wt % MAA, 3 wt % HEMA, 1 wt % AM, 2 wt % A-171, and a requisite amount of G04 (1, 3, 6, and 9 wt %, respectively, based on the total acrylic monomers), were pre-emulsified in a wild-mouth bottle using 6 g of water and a requisite amount of antibacterial monomer (1, 2, 4, and 6 wt %, respectively, based on the total acrylic monomers) as emulsifier. Ten percent of the pre-emulsion was added into the above three-necked flask, followed by adding ten percent of AIBA solution (10 g, 1 wt % based on the total monomers). The preparation of seed latex was carried out at 68 °C for 0.5 h, and the rest of monomers and initiator solution were added dropwise in 2.5 h. Thereafter, the reaction temperature was increased to 70 °C and kept for 3 h to finally obtain the antibacterial polymer emulsions. For comparison, 11 kinds of different antibacterial polymer emulsions (E1, E2, E3, E4, E5, E6, E7, E8, E9, E10, and E11) were also prepared by adjusting antibacterial monomers (M1, M2, M3, and M4), contents of M3 (1, 2, 4, and 6 wt %), and contents of GO4 (1, 3, 6, and 9 wt %). A photograph of the synthesized antibacterial polymer emulsions is shown in Figure S2.

Preparation of Antibacterial Cotton Fabrics. Cotton fabrics were first washed with sodium dodecyl sulfate solution (1 wt %) for 1 h and then rinsed with distilled water several times; the fabrics were dried in a vacuum oven at 70 °C for 12 h. The cotton fabrics were cut into square samples with a dimension of 20 cm × 20 cm. The treatment solution was prepared by mixing a requisite amount of antibacterial polymer emulsions and waterborne cross-linker XP 2487/1 (the isocyanate-to-hydroxyl (NCO/OH) ratio was preferably 1.2:1); it was diluted to 10 wt %, then uniformly sprayed onto the pristine cotton fabrics with a spraying pen (see step c of Figure 1). Afterward, the fabric samples were cured at 80 °C for 3 h with a coating of the antibacterial polymer. The add-on percentage (add-on %) of polymers on the treated fabric samples was calculated by the following eq 1

$$\text{add-on } \% = (W_t - W_0)/W_0 \times 100\% \quad (1)$$

where W_0 and W_t are the weights of the fabric samples before and after treatment, respectively. By adjusting the antibacterial polymer emulsions and add-on %, the treated antibacterial fabrics were obtained and coded as F1, F2, F3, F4, F5, F6, F7, F8, F9, F10, F11, F12, F13, F14, and F15, illustrated in detail in Table 1.

Characterization and Measurement. Structures of antibacterial monomers and polymer were characterized by Fourier transform infrared (FTIR), recorded in KBr disks on a Bruker Vector 33 FTIR spectrometer (Bruker Instruments Co., Germany) over the range 4000−400 cm^{-1}. The structures of antibacterial monomers were further characterized by ^1H NMR on a Bruker Avance NMR-500 MHz spectrometer using dimethyl sulfoxide as solvent. The surface morphologies of pristine and treated fabrics and the elemental distribution of polymer on the treated fabrics were observed by field-emission scanning electron microscopy (FESEM) (Merlin system, Zeiss) combined with energy-dispersive X-ray spectroscopy (EDX) (model Inca400, Oxford Instruments). The contact angle (CA) analysis of water and diiodomethane on the fabrics was performed with an optical contact angle meter (OCA40 Micro; Dataphysics, Germany). The total surface free energies (γ_s) of treated fabric could be calculated by combining the Owens−Wendt−Rabel−Kaelble and the Young eqs 2 and 3

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (2)$$

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$$(1 + \cos\theta)\gamma_L = 2(\gamma_s^d\gamma_L^d)^{1/2} + 2(\gamma_s^p\gamma_L^p)^{1/2} \quad (3)$$

where γ_s^d and γ_s^p are the dispersion and polar component of the solid surface and γ_L^d and γ_L^p are the dispersion and polar component of testing liquid,[38] respectively; the fabric surfaces were wetted by specific liquids (deionized water and diiodomethane in this work) with predefined polar and dispersive components (γ^p = 51.0 mN/m and γ^d = 21.8 mN/m, γ^p = 2.3 mN/m, and γ^d = 48.5 mN/m, respectively). Tensile strength and elongation at break of fabrics (the warp and weft direction) were determined by a Tensile Tester (Shimadzu AG-X plus). Fabric softness was measured by an automatic textile stiffness tester (RH-R1000), where a lower value of downward pressure indicated better fabric softness. Air permeability was determined by an air permeability tester (FX3300) with a test pressure difference of 200 Pa. Each reported value represented the means of five measurements. The whiteness of the fabrics was measured by a Datacolor Elrepho photospectrometer (Elrepho 070); each sample was measured at three different positions, with each reported value representing the means of five samples.

Antibacterial Activity Assessment. *Test Microorganisms and Media.* Typical bacterial microorganisms including *S. aureus* and *E. coli* were selected for the antibacterial activity assessment. The bacterial suspensions employed for the tests contained from 10^6 to 10^7 colony forming units (CFUs). MHB was used as the bacterial liquid nutrient growth medium for the determination of minimum inhibitory concentration (MIC) and was freshly prepared (within 1 week) according to the manufacturer directions as follows: 12 g of MHB powder was added into 500 mL of sterile distilled water and heated to dissolve; the medium was transferred to a flask, then sealed and sterilized by autoclaving at 120 °C for 30 min. MHA was used as the bacterial growth medium for determination of minimum bactericidal concentration (MBC). Sterile Petri dishes of MHA were prepared according to the manufacturer's specification as follows: 16 g of agar powder was added into 500 mL of sterile distilled water and heated to dissolve; the medium was then transferred to a flask, sealed, and sterilized by autoclaving at 120 °C for 30 min.

MIC Determination of Antibacterial Monomers. MIC was used as an effective qualitative method of antibacterial ability assessment. MIC of antibacterial monomers were determined against *S. aureus* and *E. coli* by a serial dilution method.[38,39] Serial 2-fold dilutions of antibacterial monomers were prepared in a series of tubes, with concentrations ranging from 7.81 to 2000.00 μg/mL. Each sterile test tube was charged with 4 mL of MHB, 2 mL of bacteria suspension at 1 × 10^6 CFU mL^{-1}, and 2 mL of the above antibacterial monomer dilutions that were adjusted to final concentrations (500.00, 250.00, 125.00, 62.50, 31.25, 15.63, 7.81, 3.91, and 1.95 μg/mL respectively). Controls (without any antibacterial monomer) were also performed with 2 mL of pure distilled water substituting antibacterial monomer. The testing tubes were then incubated with a shaking incubator at 37 °C at 150 rpm for 18 h. The minimum concentration at which there was no visible turbidity was taken as the MIC of antibacterial monomers. The MIC measurement was done in triplicate to confirm the value of MIC for each type of bacteria.

MBC Determination of Antibacterial Monomers. The MBC was defined as the lowest concentration of an antibacterial agent that kills bacteria in the planktonic culture. MBC of antibacterial monomers and control were determined against *S. aureus* and *E. coli* by an extension of the MIC according to the reported literature.[40] The MBC test was initiated by pouring the MHA onto sterilized Petri dishes to be solidified to form MHA plate. Ten milliliters of bacterial culture taken out from the tubes in the MIC test was inoculated uniformly onto the surface of MHA plate and then incubated at 37 °C for 24 h. Triplicate samples were performed for each test concentration.

Zone of Inhibition (ZOI) Determination of Antibacterial Fabrics. ZOI determination is a method for detecting dissolution/non-dissolution type of antibacterial materials.[41] The typical cotton fabric F3 was cut into disk-shaped fabric wafers using a puncher with the diameter and thickness of 10 and 0.3 mm, respectively. A 20 μL bacteria suspension with 1 × 10^6 CFU mL^{-1} was dropped onto the MHA plates in the Petri dishes. The treated fabric wafers were placed on the surface of MHA. After that, the Petri dishes were incubated for 18 h at 37 °C. ZOI formed around disk-shaped fabric wafers was recorded as an indication of dissolution/nondissolution type of the antibacterial agent.

Live/Dead BacLight Bacterial Viability Assay for Antibacterial Polymer Film. Live/dead bacterial viability assays were used to intuitively evaluate antibacterial properties of antibacterial polymer films (P1, P2, P3, and P4 containing bacterial monomers with different alkyl chain lengths C12, C14, C16, and C18, respectively; P5, P6, P7, and P3 with 1, 2, 4, and 6 wt % contents of M3 with C16, respectively) against *S. aureus* and *E. coli*, which is a live/dead bacterial fluorescence stain method using the fluorescent dye mixture of a green SYTO9 and red propidium iodide (PI). In a typical procedure, a uniform thin antibacterial polymer film coated on the slide glass surface was first prepared by spin-coating of a requisite amount of antibacterial polymer emulsions (E1, E2, E3, E4, E5, E6, and E7, separately) and cross-linker; the molar ratio of the two components were preferably 1.2:1. Subsequently, 100 μL of bacteria suspension with *E. coli* and *S. aureus* at 10^8 CFU mL^{-1} each was applied to the obtained antibacterial polymer film and further incubated for 24 h at 37 °C. Thereafter, 25 μL of fresh SYTO9/PI mixture, which was prepared according to the manufacturer's instructions, was added on the surface of bacteria using a microliter syringe and the testing sample was covered with a piece of glass coverslip; the thorough staining of bacteria was allowed to occur at room temperature in darkness for 15 min. Afterward, the bacteria were observed under an Olympus BX51 epifluorescence microscope using green and red filters with excitation/emission 440−480/515−540 nm and 540−560/630−660 nm, respectively.

Bacterial Antiadhesion of the Treated Fabrics. Bacterial antiadhesion of treated fabrics was estimated, as reported by Oh et al.[42] and Sivakumar et al.[36] with slight modifications. The treated fabrics and control (untreated fabrics) were vertically immersed in 25 mL of bacterial suspension (*S. aureus* or *E. coli*) with 10^7 CFU mL^{-1} and incubated under static conditions for 2 h at 37 °C. The testing samples were drawn in a single vertical motion from the bacterial suspension and held vertically for 3 min to allow remaining droplets to slide away and then transferred into a tube with 25 mL of fresh MHB and further incubated for 24 h at 37 °C at an agitation speed of 120 rpm. After the incubation, the samples were removed using sterile forceps and washed twice with 5 mL of sterile water to remove the unadhered bacteria. Afterward, the samples were put into a test tube containing 5 mL of phosphate-buffered saline (PBS) solution; those strongly adhered on the fabric were then removed by 2 min of water-bath ultrasonication. The same operation was performed five times. The above detached bacteria in PBS solution were mixed and then homogenized using a Tissue Tearor homogenizer, and then 100 μL of this solution spread onto the MHA plates and further incubated at 37 °C for 24 h. After counting the number of colonies, the number of adhered bacteria was calculated by multiplying the number of colonies by the dilution factor. The bacterial antiadhesion rate is estimated as in eq 4

$$\text{bacterial antiadhesion rate (\%)} = (\text{CFU}_{\text{control}}\ \text{mL}^{-1} - \text{CFU}_{\text{sample}}\ \text{mL}^{-1})/\text{CFU}_{\text{control}}\ \text{mL}^{-1} \quad (4)$$

where $\text{CFU}_{\text{control}}$ mL^{-1} represents the number of viable bacteria per unit volume of culture for the untreated fabrics and $\text{CFU}_{\text{sample}}$ mL^{-1} represents the number of viable bacteria per unit volume of culture for the treated fabrics.

Morphology of Bacterial Adhesion on the Treated Fabrics. Bacterial adhesion on the treated fabrics was intuitively observed by scanning electron microscopy after the adhesion experiments. The sample treatment before testing was performed according to the following procedure: the samples were washed with sterile PBS three times, followed by fixation with 2.5% glutaraldehyde solution (in 0.1% phosphate buffer at pH = 7.2) for 1 h, and finally washed twice with phosphate buffer and once with distilled water. The fixed bacteria were dehydrated with a series of graded ethanol solutions (50, 75, 90, and 100 wt %, for 15 min each). Afterward, samples were dried overnight

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in a dessicator, then treated with platinum at 30 mA for 1 min and observed by FESEM.

Antibacterial and Bacterial Antiadhesion Durability of the Treated Fabrics. Antibacterial and bacterial antiadhesion durability of the treated fabrics was evaluated by an accelerated laundering test (AATCC test method 61-1996) reported in our previous work.[43] One standard wash in 45 min using a rotating washing fastness tester (SLH-FZ001A) is equivalent to five typical hand or home launderings. The regression of the bacterial reduction rate and bacterial antiadhesion rate of the treated fabrics was measured after 5, 10, 15, 20, and 25 repetitive washing cycles.

RESULTS AND DISCUSSION

Effect of the Alkyl Chain Length. Molecular structures of antibacterial monomers and their polymers were confirmed by FTIR and ^{1}H NMR spectra (Figures S3 and S4, respectively). To investigate the constituent-antibacterial activity relation of synthesized antibacterial monomers (M1, M2, M3, and M4) with different alkyl chain lengths (C12, C14, C16, and C18, respectively), MIC and MBC values were determined, as shown in Figure 2, and the experimental picture of the MIC and MBC

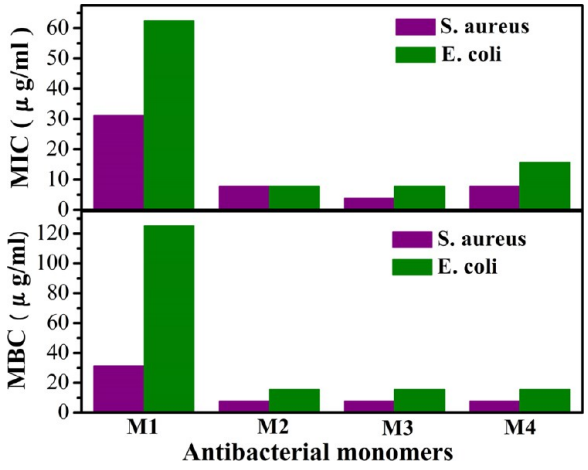

Figure 2. MIC and MBC values of antibacterial monomers (M1, M2, M3, and M4) with different alkyl chain lengths.

determination is shown in Figure S5. It can be clearly seen that all of the antibacterial monomers exhibited good antibacterial activity against both *S. aureus* and *E. coli* and slightly better against *S. aureus*. It was found that individual MIC and MBC values were associated with the alkyl chain length of the antibacterial monomers. The longer alkyl chain (from C12 to C16) resulted in lower MIC and MBC values of antibacterial monomers, but both MIC and MBC values increased when further increasing the alkyl chain length to C18. M3 with C16 shows the best antibacterial activity with the lowest MIC (3.91 and 7.81 μg/mL against *S. aureus* and *E. coli*, respectively) and MBC (7.81 and 15.63 μg/mL against *S. aureus* and *E. coli*, respectively). It was also found that MIC and MBC values of the same antibacterial monomer against *S. aureus* were less than those of *E. coli*. Therefore, the antibacterial properties of the synthesized antibacterial monomers are indeed influenced by their alkyl chain length; this result agrees well with the published literature.[44] This is probably because the higher surface activities favor enhancement of the antibacterial activities with the increase of the alkyl chain length, as reported in the literature.[45] Additional data of surface activities of these monomers was provided in the Supporting Information (Figure S6); surface activities of antibacterial monomers increased in the following order: M1 < M2 < M4 ≈ M3. Therefore, the alkyl chain length of monomers greatly influenced the surface activities, further influencing the antibacterial activities. As Zhang et al.[46] and Qian et al.[47] stated that monomers with higher surface activities could potentially provide a new strategy for developing antimicrobial polymers by endowing them with extremely antibacterial activities owing to the polycationic structures that might facilitate the penetration of polymer chains into cell membranes, thus improving the bacteria deactivation.

Effect of Antibacterial Monomers. To investigate the effect of antibacterial monomers on the antibacterial activity of polymers, the optical live/dead bacterial viability images of polymer films (P1, P2, P3, and P4) with different antibacterial monomers and polymer films (P5, P6, P7, and P3) with different contents of M3 (1, 2, 4, and 6 wt %, respectively) are shown in Figure 3. Live and dead bacteria were stained in green and red, respectively, and the merged image displayed an orange composite color. It was obviously observed that the densities of dead bacteria on the film from P1 to P4 both for *S. aureus* and *E. coli* first increased and then decreased by increasing the alkyl chain length and almost no live *S. aureus* and little *E. coli* existed on the P3 film, exhibiting the best antibacterial activity. It was also found that the densities of dead bacteria increased on the film from P5 to P3 by increasing the antibacterial monomers from 1 to 6 wt %, indicating that antibacterial activity of the polymer film could be enhanced by incorporating more antibacterial monomers.

To further quantitatively assess their influence on the antibacterial properties of the fabrics, the bacterial reduction rate of antibacterial fabrics (F1, F2, F3, and F4) treated by cured antibacterial polymers (E1, E2, E3, and E4) of different antibacterial monomers and antibacterial fabrics (F5, F6, F7, and F3) treated by antibacterial polymers (P5, P6, P7, and P3) with different contents of M3, were determined by the shake flask method (Figure 4). It was found that the bacteria reduction rate of antibacterial fabrics (F1, F2, F3, and F4) with different antibacterial monomers first increased by increasing the alkyl chain length and then slightly decreased afterward. The bacteria reduction rates of F1, F2, F3, and F4 against *S. aureus* were 84.35, 94.64, 99.98, and 97.57%, respectively. The bacteria reduction rate of F1, F2, F3, and F4 against *E. coli* were 81.6, 91.3, 98.36, and 96.43%, respectively. F3 fabric showed the best antibacterial activity well consistent with the results of the MIC, MBC, and live/dead bacterial viability assay.

Influence of Add-on Percentage of Antibacterial Polymer. The above results have demonstrated that the antibacterial properties of antibacterial fabrics were greatly influenced by the amounts of antibacterial monomers. The effects of the add-on percentage (add-on %) of antibacterial polymer (E3) on fabric F3 were also investigated, as shown in Figure 4. It was found that with increasing the add-on % value from 1 to 8 wt %, bacteria reduction rates of *S. aureus* and *E. coli* were greatly improved from 72.72 to 100%, and from 70.52 to 99.99%, respectively. It is indicated that an increased add-on % value, namely, a higher level of antibacterial monomers introduced into the fabric, could improve the antibacterial activity. Therefore, antibacterial properties of antibacterial fabrics were also influenced by the add-on percentage of antibacterial polymer.

Effects of add-on percentage of polymer on the mechanical and physical properties of the fabrics were investigated after treatment. Figure S7 indicated that all of the treated fabrics

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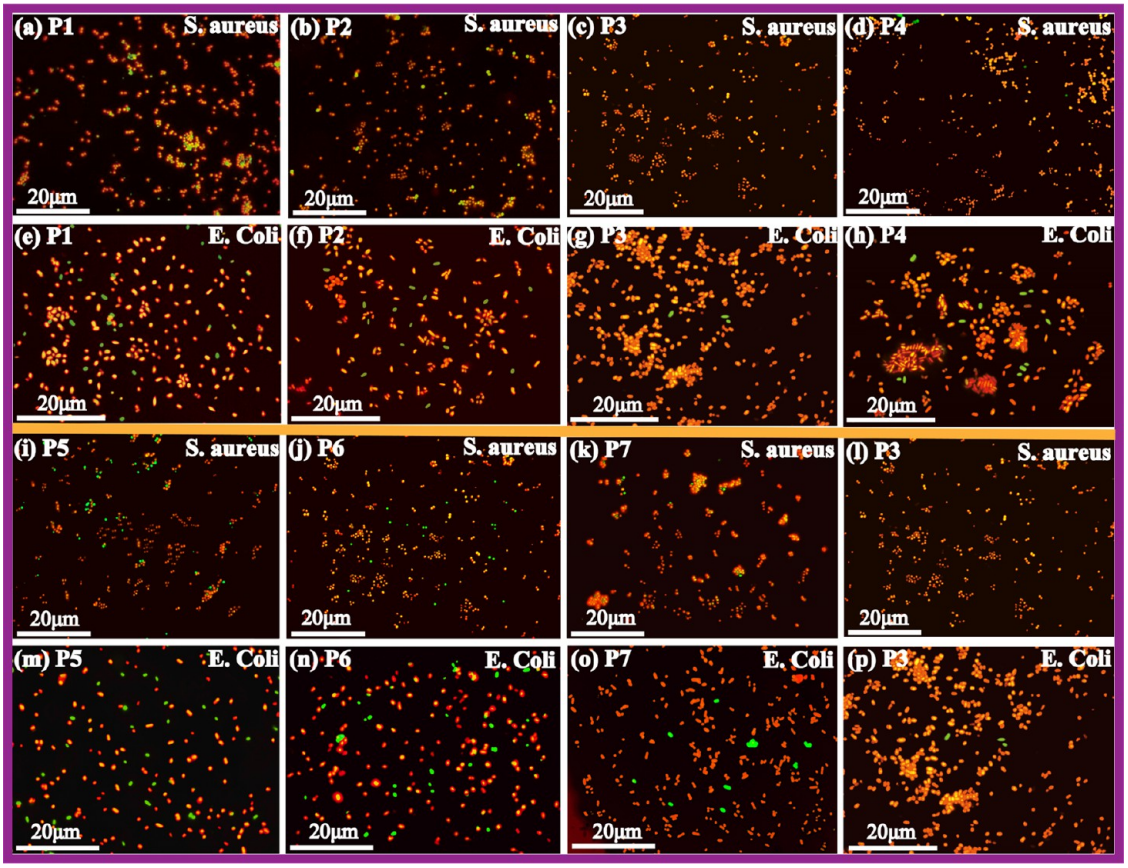

Figure 3. Fluorescence microscope images of polymer films containing different kinds of antibacterial monomers ((a) P1, (b) P2, (c) P3, and (d) P4 against *S. aureus* and (e) P1, (f) P2, (g) P3, and (h) P4 against *E. coli*;) and polymer films containing different contents of antibacterial monomers ((i) P5, (j) P6, (k) P7, and (l) P3 against *S. aureus* and (m) P5, (n) P6, (o) P7, and (p) P3 against *E. coli*;).

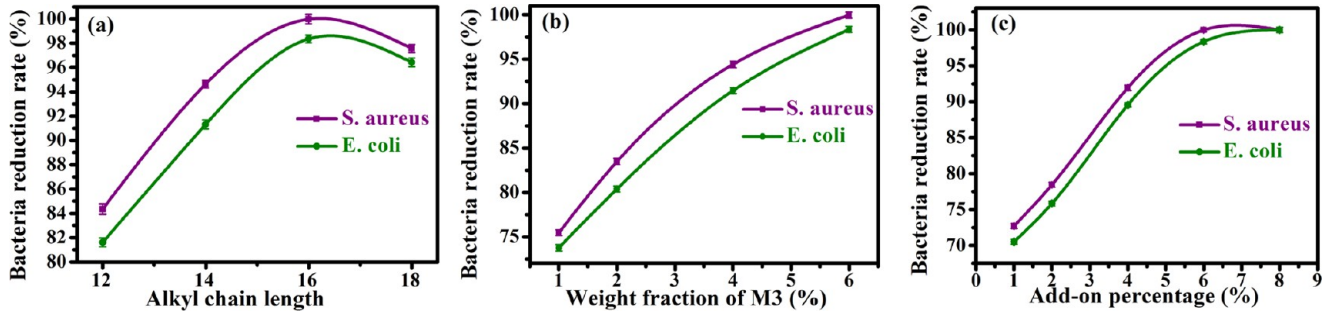

Figure 4. Bacterial reduction rate of antibacterial fabrics (F1, F2, F3, and F4) containing different lengths of alkyl chain (a), antibacterial fabric (F5, F6, F7, and F3) contents of antibacterial monomers (b), and different add-on % values (c).

Table 2. Mechanical and Physical Properties of the Pristine and Treated Fabrics

properties	pristine fabric	fabric F12	fabric F13	fabric F14	fabric F3	fabric F15
tensile strength (MPa)	13.17(warp)	14.94(warp)	15.75(warp)	16.01(warp)	16.52(warp)	17.1(warp)
	8.25(weft)	9.66(weft)	9.98(weft)	10.18(weft)	10.41(weft)	10.77(weft)
elongation at break (%)	129.39(warp)	128.61(warp)	128.22(warp)	118.78(warp)	118.22(warp)	114.55(warp)
	182.78(weft)	182.28(weft)	174.56(weft)	168.78(weft)	165.83(weft)	162.06(weft)
softness (mN)	212 ± 2(warp)	213 ± 1(warp)	215 ± 2(warp)	216 ± 1(warp)	218 ± 2(warp)	220 ± 2(warp)
	225 ± 2(weft)	227 ± 1(weft)	238 ± 2(weft)	231 ± 3(weft)	233 ± 1(weft)	234 ± 2(weft)
air permeability (mm/s)	474 ± 4	473 ± 3	464 ± 5	461 ± 3	457 ± 4	446 ± 5
white index (%)	90.8 ± 0.2	90.8 ± 0.2	90.7 ± 0.2	90.6 ± 0.1	90.5 ± 0.2	90.5 ± 0.1

exhibit no change in appearance, as compared with the pristine fabric. As shown in Table 2, the coated polymer layer did not remarkably affect the mechanical and physical properties of the fabrics. Compared with the pristine fabric, with the increase of add-on percentage of polymer on the fabric, the tensile strength of treated fabrics (F12, F13, F14, F3, and F15) both for warp

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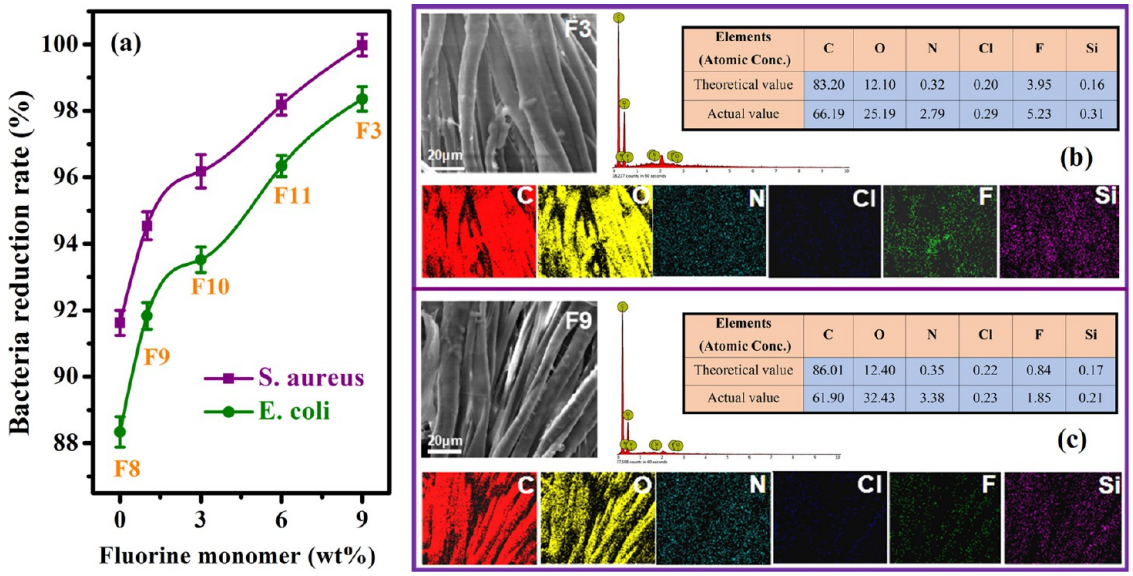

Figure 5. Bacterial reduction rate of antibacterial cotton fabrics with different amounts of fluorine component (a) and SEM-EDX results (including elements mapping) of F3 (b) and F9 (c).

and weft direction slightly increased, whereas elongation at their break slightly decreased. Softness of the treated fabrics (in the warp and weft direction) decreased by 4% less than that of pristine fabric. The air permeability of the fabric slightly decreased by 6% less than that of the pristine fabric, which might be due to the coating slightly blocking the interspace of the fibers, and the white index of the fabrics changed a little. These results indicated the treated fabrics basically preserved the inherent mechanical and physical properties of the pristine fabric.

Influence of Fluorine Component. From Figure 5a, the results of antibacterial testing demonstrated that the bacteria reduction rate of the antibacterial fabrics increased (91.62, 94.54, 96.18, 98.18, and 99.98% for F8, F9, F10, F11, and F3 against *S. aureus*; 88.34, 91.83, 93.52, 96.34, and 98.36% for F8, F9, F10, F11, and F3 against *E. coli*, respectively) by increasing the introduced fluorine component, indicating that the incorporation of fluorine component into the antibacterial polymer coated on cotton fabrics greatly enhanced the antibacterial capability of the treated fabrics. It is deduced that the hydrophobic fluorine component grafted on the polymer chains facilitated deeper penetration of hydrophobic segments of the polymer chain into membrane lipid domains, leading to membranolysis and cell death, thereby preventing the colonization of bacteria and enhancing the antibacterial capability, just as previous studies reported that the incorporation of a higher dose of fluorine component led to the significant improvement of antibacterial and osteogenic activities[48] and fluorine was an effective antibacterial material due to its effect on the bacterial metabolism as an enzyme inhibitor,[49] well supporting our result.

The bacteria adhered on the antibacterial cotton fabrics and control (the pristine fabric) were observed by SEM, as shown in the Figure 6. For the control sample, large amounts of bacteria adhered on the pristine fabric surface; the bacterial adhesive reduction both in *S. aureus* and *E. coli* was obviously displayed in all of the antibacterial fabrics (F8, F9, F10, F11, and F3) as compared to that in the pristine fabric, with an especially great reduction for antibacterial fabrics (F9, F10, F11, and F3) due to the fluorine component. Sivakumar et al.[36] previously reported that hydrophilic surfaces prevent bacterial attachment and hydrophobic organisms have a greater propensity to attach to hydrophobic surfaces than hydrophilic ones in their work. However, a few researchers have found that in in vitro environments, hydrophobic surfaces showed less bacterial adhesion when compared to the hydrophilic ones.[50,51] Herein, further investigation was undertaken by combining the water contact angles (WCAs) on the treated fabrics and bacterial antiadhesion rates (Figure 7). It is interesting that the more hydrophobic the antibacterial fabric (the WCA of F8, F9, F10, F11, and F3 were 87.5, 106.2, 117.2, 120.6, and 122.8°, respectively), the higher is the bacterial antiadhesion rate (F8, F9, F10, F11, and F3 against *S. aureus* were 76.42, 87.54, 93.35, 96.14, and 99.63%, respectively; F8, F9, F10, F11, and F3 against *E. coli* were 71.54, 84.68, 91.36, 94.38, 99.14%, respectively), also with less adhered bacteria on the fabric (see in Figure 6). In fact, bacterial adhesion on a surface is a complex process that has several parameters as determinants (the properties of the bacterial cell surface, the liquid environment, the properties of the material surface, etc.). In this work, the fluorine component on the treated fabric surface in this work seems to play an important role in bacterial antiadhesion. As shown in Figure 5b,c, the results of SEM-EDX mapping demonstrate that the surface elements (C, O, N, Cl, F, and Si) are distributed uniformly on the treated fabric surfaces (F3 and F9) and EDX analysis demonstrates that the actual content of fluorine elements (5.23 mol % for F3 and 1.85 mol % for F9, respectively) is higher than the theoretical contents (3.95 mol % F3 and 0.84 mol % for F9, respectively) in the coating, suggesting the fluorine component can migrate to the surface of coating on the treated fabric and cause a low calculated surface energy (29.1, 27.2, 18.0, 14.5, and 12.8 mN/m for F8, F9, F10, F11, and F3, respectively). Therefore, these data confirmed that the bacterial antiadhesion rate of the treated fabrics increased with decreasing the surface energy contributed by more contents of fluorine; meanwhile, incorporating the fluorine component on the fabric indeed enhanced the bacterial antiadhesive capability, which is similar to the observation from previous literature works.[50,51] Xu et al.[52] also confirmed that fluorine-containing side chains in

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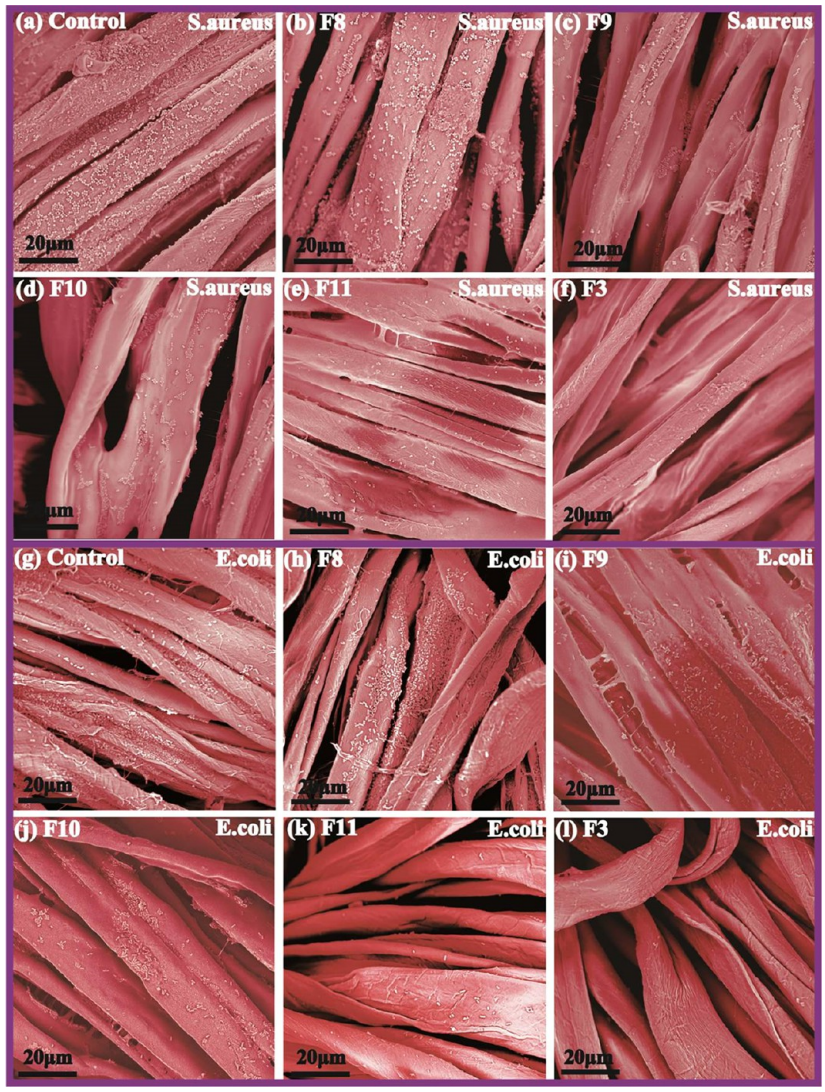

Figure 6. SEM images of the adhered bacteria on the control and treated cotton fabrics, with different amounts of fluorine component. ((a) control, (b) F8, (c) F9, (d) F10, (e) F11, and (f) F3 against *S. aureus*; (g) control, (h) F8, (i) F9, (j) F10, (k) F11, and (l) F3 against *E. coli*).

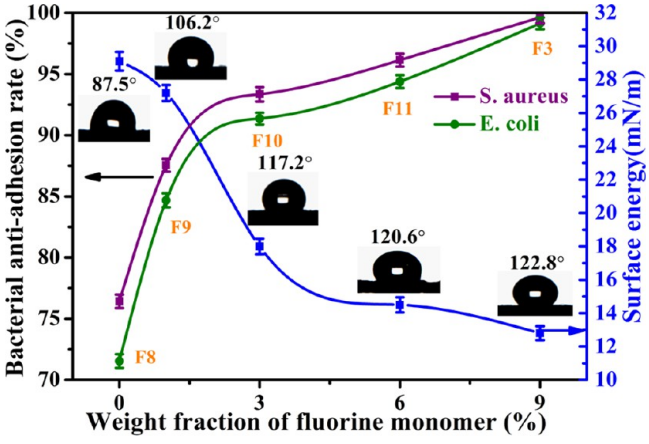

Figure 7. Bacterial antiadhesion rate, WCA, and surface energy of the antibacterial cotton fabrics (F8, F9, F10, F11, and F3), with different amounts of fluorine component.

polymer exhibited good fouling-release functionality because of their low surface energy. This is on the basis of the facts that to the best of our knowledge, on one hand, due to the rough, porous, and naturally hydrophilic properties of the pristine fabric, the bacteria solution could easily wet its surface, penetrate into its cavities, and be locked into it eventually. As a comparison, the treated fabric surface became smoother than that of the pristine fabric, observed from three-dimensional (3D) surface profiles (Figure S8), as well as more hydrophobicity was induced by increasing of the introduced fluorine component, making it harder for the bacteria suspension to wet the surface and penetrate into the fiber interior, thus causing less bacteria to adhere on the fabric surface. On the other hand, the incorporation of fluorine component into the polymer enhanced the antibacterial capability, as mentioned above, preventing the colonization of bacteria and fewer bacteria to contact and adhere on the fabric so as to indirectly enhance the bacterial antiadhesion.

Antibacterial and Bacterially Antiadhesive Durability. Antibacterial and bacterially antiadhesive durability of typical treated cotton fabric (F3) were assessed by determining the change of the bacteria reduction rate and bacterial antiadhesion rate after the washing durability test. From Figure 8a, it was found that the bacteria reduction rate of the treated cotton fabrics against *S. aureus* and *E. coli* did not change much with an

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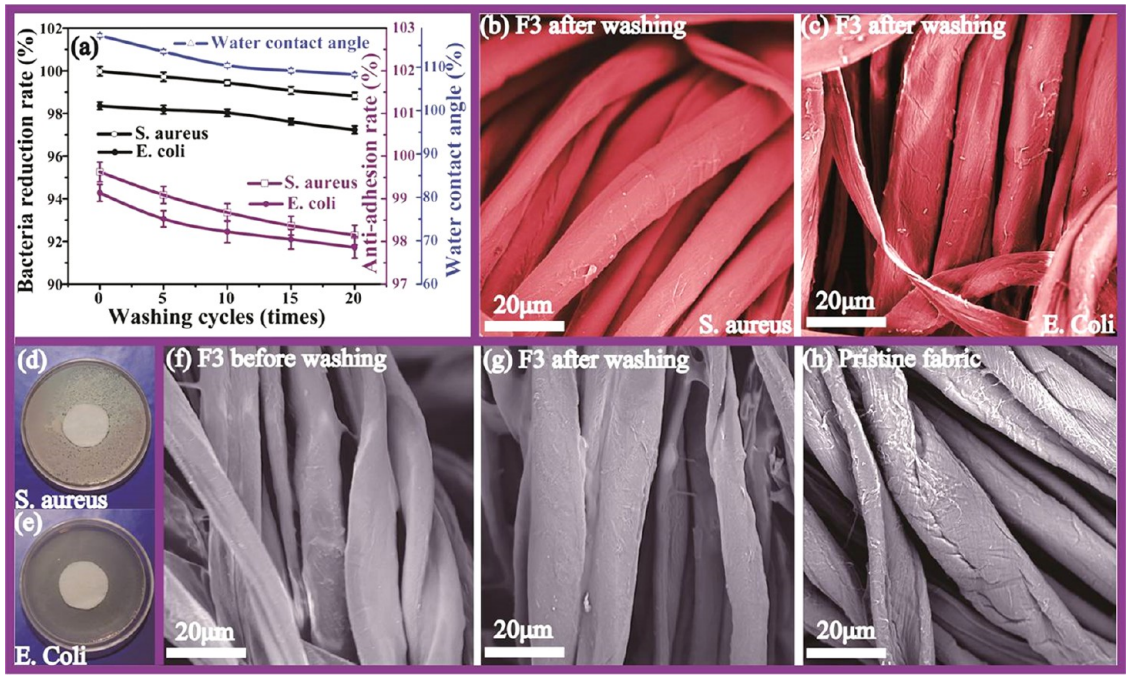

Figure 8. Bacteria reduction rate and the bacterially antiadhesive rate of F3 and CA on F3 (a), SEM images of bacteria (b and c for *S. aureus* and *E. coli*, respectively) on F3 after 20 repetitive washing cycles, ZOI of F3 (d and e for *S. aureus* and *E. coli*, respectively), and surface topography of treated fabrics (f and g for F3 before and after washing, respectively) and the pristine fabric (h).

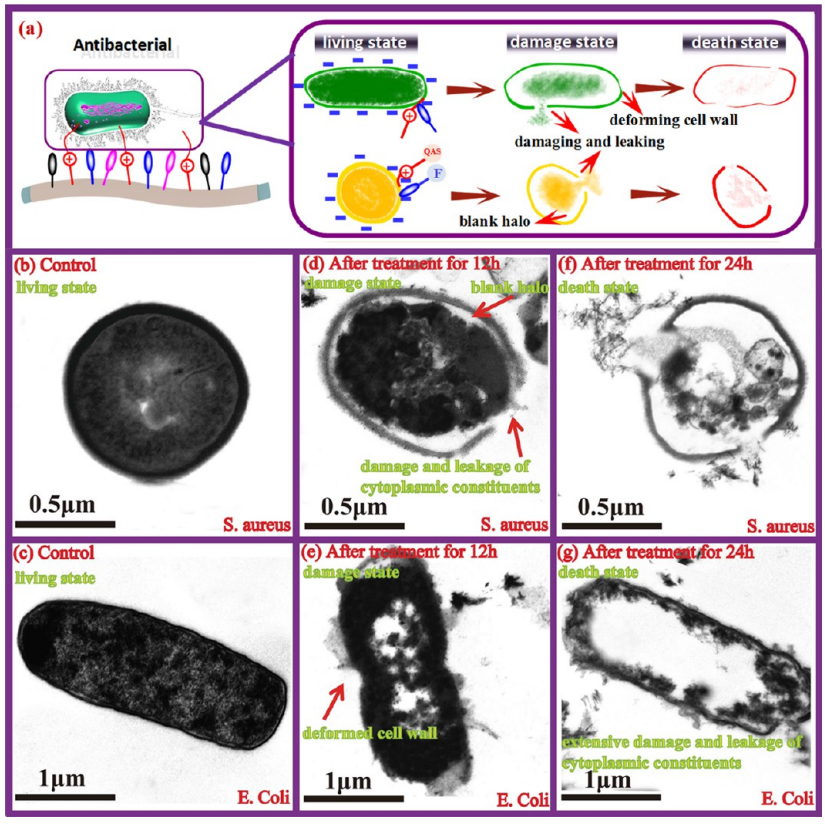

Figure 9. (a) Antibacterial action model of treated fabrics. TEM images of bacteria in different antibacterial processes ((b) and (c) for control of *S. aureus* and *E. coli*, respectively; (d) and (e) for bacteria of *S. aureus* and *E. coli* after treatment for 12 h, respectively; (f) and (g) for bacteria of *S. aureus* and *E. coli* after treatment for 24 h, respectively).

increase of washing cycles from 0 (99.98 and 98.36%, respectively) to 20 (98.83 and 97.23%, respectively); the bacteria reduction rate could maintain a low decrease of 1.15% after 20 repetitive washing cycles, indicating that the treated cotton fabrics could retain the antibacterial capability. In addition, after 20 repetitive washing cycles, the bacterial

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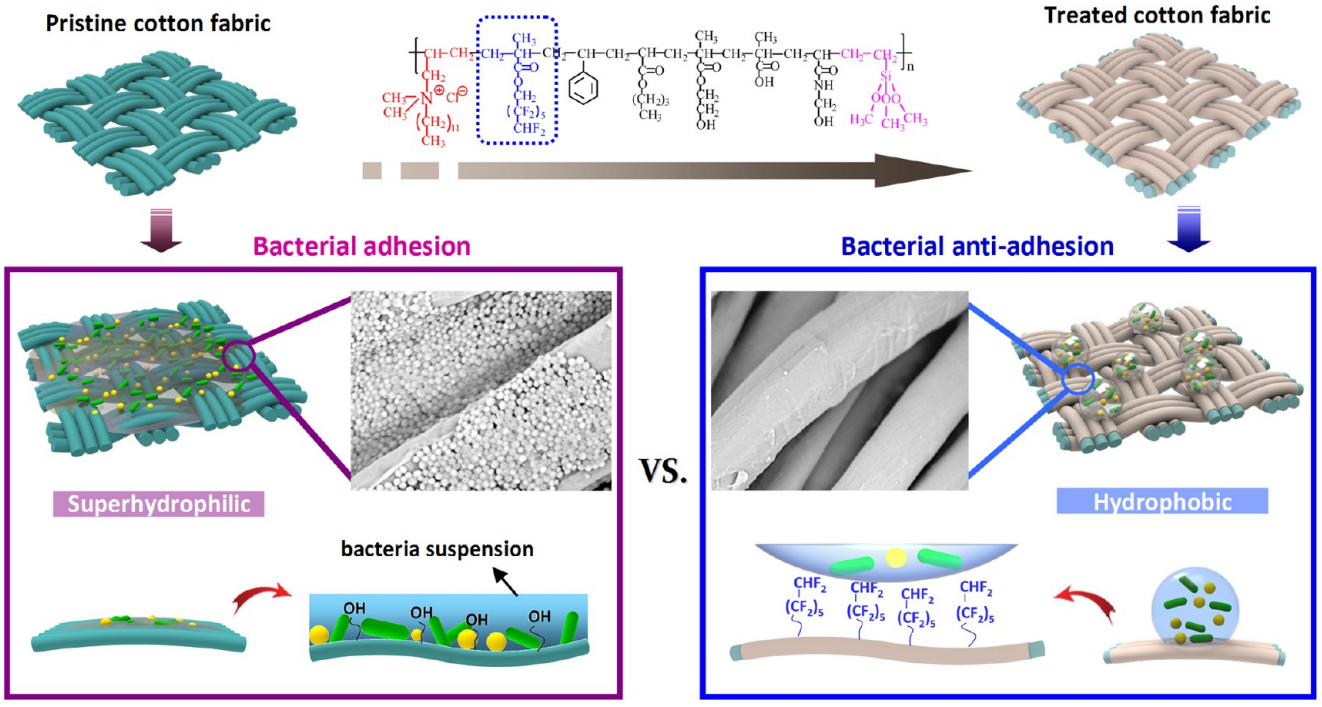

Figure 10. Comparison of the bacterially adhesive and antiadhesive action model of the pristine and treated fabrics.

antiadhesion rate changed little (only a decrease of 1.5% for F3 after 20 times of washing durability testing as compared with the sample before washing) and few *S. aureus* and *E. coli* could be seen on the surface (Figure 8b,c) after washing, further confirming the good bacteria antiadhesive durability of the treated cotton fabrics. The reason why the treated cotton fabric exhibits good antibacterial and bacterially antiadhesive durability is that on one hand, antibacterial monomer can covalently copolymerize with the resin matrix so that antibacterial segments could not dissolve and lose over time, thus providing a durable antibacterial capability; evidence could be found that the ZOIs for the treated fabric (F3) against *S. aureus* (Figure 8d) and *E. coli* (Figure 8e) were both 0 mm. On the other hand, the wetting properties of the fabric surface was retained because of little reduction of CA (<10°) (Figure 8a). Additionally, there is almost no alteration of surface topography for F3 after 20 washing cycles (Figure 8g) as compared to that for F3 before washing (Figure 8f), both with a layer of smooth antibacterial polymer coating on the fiber and by contrast, the pristine fabric exhibiting relatively rough fibers (Figure 8h).

Antibacterial and Bacterially Antiadhesive Action Models. To further investigate the antibacterial and bacterially antiadhesive mechanism, antibacterial and bacterially antiadhesive action models of treated fabrics were proposed to illustrate the antibacterial process. As shown in Figure 9a, the model of antibacterial action of antibacterial fabric is involved in three possible successive processes combined with the following transmission electron microscopy (TEM) observation: (I) living state: initial contact occurred through an electrostatic effect (the negatively charged bacteria and positively charged QA of the incorporated antibacterial polymer) and hydrophobic interaction (hydrophobic interaction of the alkyl and fluorine chains with membrane proteins of bacteria). At this living state, before/just on contact with antibacterial fabric, the control of both *S. aureus* (Figure 9b) and *E. coli* (Figure 9c) displayed a structurally intact cell wall; (II) damage state: passive diffusion of the polymer chains (the alkyl and fluorine chains) through the cell wall proceeded due to their lipophilic property; simultaneously, the bacteria structure was disrupted (including deformation of the cell wall, damage of the cytoplasmic membrane, and leaking cytoplasmic constituents). After action of the antibacterial polymer-coated fabric for 12 h, it can be observed that *S. aureus* (Figure 9d) and *E. coli* (Figure 9e) displayed the structural disintegration and deformation of the cell wall (indicated by a red arrow), with a blank halo at the edge of the cell (introduced by the red arrow) and a blurred cytoplasmic membrane. Moreover, the partially destroyed cytoplasmic membrane was out of protecting the integrity of the interior of the cell, resulting in the leakage of cytoplasmic constituents. Results indicated that the antibacterial polymer was disturbing the cell structure. This is because the synergistic antibacterial action of QA and fluorine chains greatly enhanced the antibacterial activity. Thus, it can be deduced that the polymer chains may interact more effectively with the bacteria due to its nearby fluorine-containing component causing enhancement of lipophilicity so as to facilitate deeper penetration of the polymer chain inside the bacteria to disrupt cytoplasmic constituents; and (III) death state: extensive release of cytoplasmic constituents and the resultant death of cell were in progress.[53−55] After the antibacterial treatment for 24 h (Figure 9f,g), it can be obviously observed that a further disturbance of the antibacterial polymer causes extensive leakage of cytoplasmic constituents, resulting in cell death.

Furthermore, the bacterially antiadhesive model of action is illustrated in Figure 10. Although there is still no consensus in the bacterially antiadhesive mechanism due to its complexity, bacterial antiadhesion is indeed closely related to the properties of the material surface, as previously confirmed. For the pristine fabric surface, water is easily absorbed on its surface and is one of the important nutrient resources for bacterial growth, so that bacteria in a realistic atmosphere in the existing form of complex atmosphere aerosols of humidity are easily attracted

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on the hydrophilic pristine fabric due to the bacterial chemotaxis and bacteria suspension in the water environment could easily wet the pristine cotton fabric surface due to the natural porous, rough, and hydrophilic properties, further penetrating into the surface cavities of the fabric and being locked into it, resulting in a large number of bacteria adhering onto the pristine fabric surface (see corresponding SEM images in Figure 10). By contrast, after treatment of the antibacterial polymer, water is repelled by the treated fabrics with and without the fluorine component, with varying degrees of WCA (Figure 7) and could not be absorbed onto the treated fabric's surface due to its hydrophobic property, where bacterial chemotaxis might be diminished and complex atmosphere aerosols of humidity might also be repelled due to hydrophobicity of the treated fabric surface. Moreover, the treated cotton fabric's surface became smoother, more hydrophobic, and of low surface energy after being coated with antibacterial fluorinated polymer due to fluorine property, making it harder to wet the surface of the bacteria suspension in the aqueous environment in a near spherical droplet state and not penetrate into the fiber interior; therefore, the antibacterial coating plays a significant role in constituting a barrier for bacteria to reach the fabric surface, weakening the interaction of the bacteria with the fabric surface and making the bacteria energetically unfavorable to adhere on the fabric surface, thus resulting in less bacteria to adhere on the fabric surface.

CONCLUSIONS

Antibacterial activity assessment demonstrated that all of the prepared antibacterial monomers, polymers, and fabrics exhibited good antibacterial activities against both *S. aureus* and *E. coli*, and slightly better for *S. aureus* and the antibacterial activity was related to their alkyl chain length and contents of antibacterial monomers, fluorine component, and add-on percentage. Incorporation of the fluorine component into the antibacterial polymer coated on cotton fabrics greatly enhanced the bacterial antiadhesion of the treated fabrics. The antibacterial and bacterially antiadhesive action model illustrated that the synergistic antibacterial action of QA and fluorine chains greatly enhanced the antibacterial activity and the hydrophobicity and low surface energy of the fluorine component contributed to the bacterially antiadhesion. In addition, the treated fabrics maintained good antibacterial and bacterial antiadhesive durability after 20 cycles of washing and the treated fabrics basically preserved the inherent mechanical and physical properties of the pristine fabric.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b16235.

Photograph of the synthesized antibacterial monomers; photograph of the synthesized antibacterial polymer emulsions; FTIR of the antibacterial monomers; ^{1}H NMR spectra of the antibacterial monomers; experimental pictures of the MIC and MBC determination; surface activities of antibacterial monomers; photographs of the pristine and treated fabrics; comparison of 3D surface profiles of the pristine and treated fabrics (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: linjin00112043@126.com. Phone: +86-13798199726 (J.L.).
*E-mail: cebujzz@mail.scut.edu.cn. Phone: +86-20-87112057 (C.L.Z.).
*E-mail: zpp823@gmai.com. Phone: +86-13148944644 (P.P.Z.).
*E-mail: zguo10@utk.edu. Phone: (865) 9742-933 (Z.H.G).

ORCID

Jing Lin: 0000-0003-0486-8280
Jiang Cheng: 0000-0002-9947-6193
ZhanHu Guo: 0000-0003-0134-0210

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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