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Synthesis and surface antimicrobial activity of a novel perfluorooctylated quaternary ammonium silane coupling agent

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Abstract

A novel perfluorooctyl-containing quaternary ammonium salt was designed and synthesized, which was applied as a surface modification agent to provide the treated cotton fabrics with antimicrobial activity and low critical surface energy.

Keywords: Perfluorooctyl-containing quaternary ammonium salt; Surface modification agent; Antimicrobial activity; Low critical surface energy

1. Introduction

As the ever-growing demand for healthy living, there is a keen interest in materials capable of killing harmful microorganisms [1]. The conventional way of making materials bactericidal is to impregnate them with antibacterial agents, such as antibiotics, silver ions, iodine, and quaternary ammonium compounds, which are gradually released over the time. This approach, while certainly useful, is quite limited because the leaching of antibacterial agent is eventually exhausted rendering the material ineffective and poses a potential environmental risk [2,3]. Recently, intensive studies have been focused on the non-release strategy for creating bactericidal surfaces that involves covalent coating. The antimicrobial materials, however, do not necessarily mean that they can ensure the safety of us. For example, hospital materials such as theater drapes, gowns and masks are known to be major sources of cross-infection. In the operating room, liquids such as blood, sweat, and saline solutions can carry bacteria with them, and once they penetrate surgical gown material and possibly contaminate the surgeon's skin if not well protected. Several blood-born pathogens have the potential to be spread in this manner, so do the human immunodeficiency virus (HIV) and the hepatitis B virus (HBV) [4]. Therefore, in order to protect patients and the surgical team from infectious blood and other body fluids, some medical materials should have not only antimicrobial properties but also blood repellency properties [5]. Moreover, in our daily life since talking, coughing, sneezing, and even breathing generate aerosolized droplets of moisture containing, it would be very beneficial to have surfaces capable of killing bacteria and possessing the low critical surface energy. To provide the treated surface with a low critical surface tension, fluorochemicals are most abundantly used for their ability to lower the critical surface tension of the treated surface well below that of most fluid other than a fluorocarbon [6].

In the light of the facts above mentioned, we envisaged that a novel quaternary ammonium silane coupling agent, which contains both perfluoroalkyl group and 3-(trimethoxysilyl)propyl group that can bind to many material surfaces, should be a suitable surface modification agent for providing the treated surface with durable barriers against microorganisms, water, oil, soil, and blood. Recently, fluoroalkyl endcapped cooligomers containing dimethyl(octyl)ammonium segments have been reported to possess not only the surface antibacterial activity but also the surface active property [7]. We describe herein the synthesis and surface antimicrobial activity of the perfluorooctyl-containing quaternary ammonium silane coupling agent.

2. Results and discussion

The synthesis of the perfluorooctylated-containing quaternary ammonium salt **5** was outlined in Scheme 1. The first

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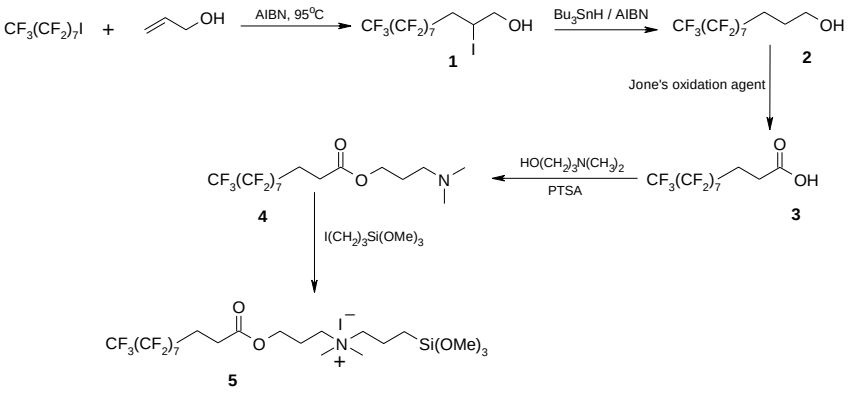


Scheme 1.

step proceeded by a free radical addition of a perfluorooctyl iodide ($CF_3(CF_2)_7I$) to allyl alcohol that was initiated with AIBN to provide the perfluoroalkylated iodohydrin **1** in 75% yield. Compound **1** was then reduced to the perfluoroalkyl alcohol **2** in 75% yield by using tributyltin hydride [8]. Oxidation of **2** with Jone's oxidation agent gave acid **3** in 90% yield. Treatment of **3** with 3-dimethylamino-1-propanol in the presence of *p*-toluenesulfonic acid (PTSA) in toluene provided the ester **4** in 57% yield. Finally, the quaternary ammonium salt **5** was obtained in 96% yield from the reaction of **4** with (3-iodopropyl)-trimethoxysilane in anhydrous CH_3CN. The perfluorooctylated-containing quaternary ammonium salt **5** is soluble in water.

As textile materials are excellent media for growing microorganisms, with compound **5** in hand, we applied it as surface modification agent on the cotton fabrics. Usually, the acidic condition is necessary for the surface modification with silane coupling agents. Because the tensile and tear strength of cotton fabrics would be greatly damaged in the acidic condition, we adopted the pad-dry-cure method to treat cotton fabrics with **5**. To test durability, the treated specimens were washed in a Haier automatic washing machine with soap flake in a normal washing cycle and tumble dried according to AATCC 135-1989 for testing the dimensional changes of woven and knit fabrics after automatic home laundering [9].

The antimicrobial activities of specimens were evaluated quantitatively. The shake flask method [10], a standard test method, was used to measure the reduction rate in the number of colonies formed. *Staphylococcus aureus* (ATCC 6358), a Gram-positive bacterium, was the testing bacterium. In this procedure, a 0.75 ± 0.05 g fabric was dipped into a test tube containing a *S. aureus* culture solution in which the bacteria concentration was $1.5-2.5 \times 10^5$ cfu/ml. The test tube was shaken at 35 °C for 6 h on a rotary shaker at 100 rpm, and 1:100 dilutions of the test solution were made. One milliliter of the dilute test solution was poured onto TGE agar broth, and when this had been incubated at 35 °C for 24 h, the number of colonies in the agar broth was counted. The reduction rate in the number of colonies was calculated using the following equation:

$$\text{Reduction rate in number of colonies}\,(\%) = \frac{A-B}{A} \times 100$$

where, A is the number of colonies before shaking and B, number of colonies after 6 h shaking.

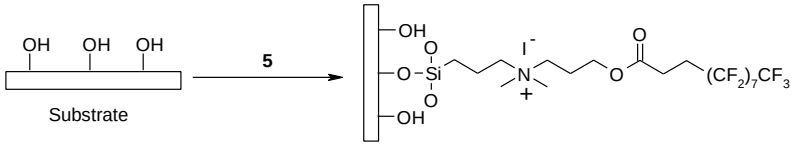
As shown in Table 1, the specimens treated with compound **5** showed a 97.3% reduction in the number of colonies: higher reduction rates indicate better antimicrobial activities. Even after 10 laundering cycles, the antimicrobial activities of treated specimens still remained at a high level. The good durability demonstrated that compound **5** was linked to the substrate by developing permanent covalent bonds (Scheme 2).

The surface properties of treated specimens were investigated by measuring contact angles by means of the pendant drop method at a constant temperature of 20 ± 0.1 °C. The drop was allowed to equilibrate for about 15 s before

Table 1
Reduction rates in number of colonies of the treated specimens[a]

Bacterium	Reduction rates in number of colonies (%)	
	1[b]	10[b]
S. aureus (ATCC6358)	97.3	95.6

[a] All experiments were performed at least in triplicate, the arithmetical average of every experimental result was given.
[b] The times of laundering cycles before testing.



Scheme 2.

Table 2
Contact angles treated specimens measure by pendant drop technique for different test liquids

	C14[a]	C12[b]	C10[c]	Distilled water
Specimen[d]	88.3	79.5	63.3	120.2

[a] Tetradecane, $\Upsilon = 26.7$ mN/m.
[b] Dodecane, $\Upsilon = 25.4$ mN/m.
[c] Decane, $\Upsilon = 23.9$ mN/m.
[d] Treated with compound **5**.

measurement. A homologous series of *n*-alkanes (decane, dodecane, tetradecane) and water were used as wetting liquid. Corresponding contact angles (θ) are depicted in Table 2.

It can be seen from Table 2 that the treated fabrics showed excellent both water and oil repellency. Considering the critical surface energy of human blood is about 42 ± 2 mN/m, the substrate treated by compound **5** should possess the blood repellency. As shown in Fig. 1, the modified specimen showed excellent repellency to selected liquid (coffee, tea, synthetic blood, *n*-dodecane and 30 vol.% isopropanol in distilled water). According to Zisman [11], the homologous series of *n*-alkanes can be used to reckon the critical surface energy of solid. When $\cos\theta$ is plotted as a function of Υ_l (the surface tension of the *n*-alkanes), the critical surface energy of solid can be obtained by extrapolation to $\cos\theta = 1$. The treated specimen showed the critical surface energy $\Upsilon_s = 20 \pm 1$ mN/m, which is markedly lower than water and most oil.

In summary, we designed and synthesized a novel perfluorooctyl-containing quaternary ammonium silane coupling agent, and applied it as a multi-functional surface modification agent on cotton fabrics. The treated substrate showed good durable antimicrobial activity and possessed the ultra low critical surface energy. Studies are currently underway to apply the quaternary ammonium **5** on surface modification of some other materials (glass, plastic etc.), which will be reported in due course.

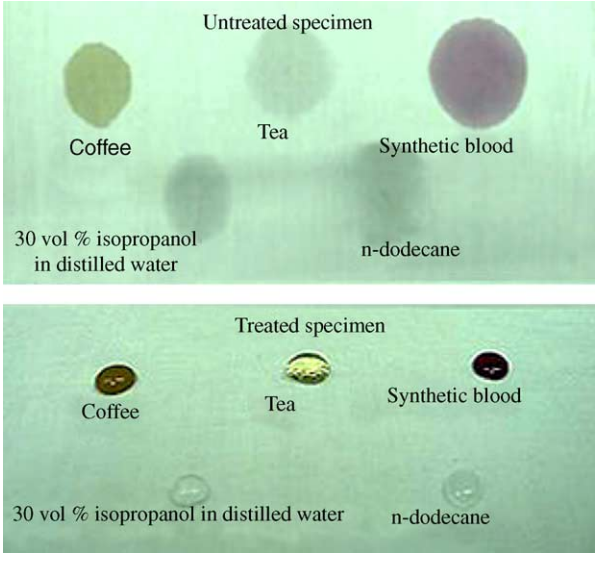


Fig. 1. Photographs of the liquid repellency of the treated and untreated specimen, synthetic blood was prepared according to ASTM method [12].

3. Experimental

Melting points were determined on a Pai-ke melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM 300 (300 MHz) spectrometer with Me_4Si as internal standard. ^{19}F NMR spectra were obtained on Bruker AM 300 (282 MHz) spectrometer in $CDCl_3$ with $CFCl_3$ as external standard, downfield shifts being designated as negative. All chemical shifts (δ) are expressed in ppm, coupling constants (J) are given in Hz. Mass spectra were recorded on a Finnigan-MAT-8430 instrument using EI ionization at 70 eV. IR spectra were recorded on a Shimadzu IR-440 spectrometer.

3.1. 1H,1H,2H,2H,3H,3H-Perfluoro-1-undecanol (2)

Allyl alcohol (14.8 g, 255 mmol) was added dropwise slowly to a mixture of perfluorooctyl iodide (99.6 g, 183 mmol) and AIBN (0.711 g, 4.3 mmol) at 95 °C. The reaction mixture was stirred for 24 h at 95 °C. Then the excessive allyl alcohol was removed in vacuo. Purification of the yellow residue by column chromatography on silica gel (petroleum ether:ethyl acetate = 10 : 1) gave compound **1** (83.2 g, 75% yield) as a white solid. Then to a mixture of **1** (67.1 g, 111 mmol) and AIBN (0.411 g, 2.5 mmol) was added dropwise tributyltin hydride (36.8 g, 127 mmol) at 100 °C for 4 h under nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 24 h. The phase separation phenomenon occurred. The lower liquid phase was collected and chromatographed on silica gel (petroleum ether:ethyl acetate = 10 : 3) to afford compound **2** as a white solid (39.8 g, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70 (t, $J = 6.0$ Hz, 2H), 2.20 (m, 2H), 1.88 (m, 2H), 1.50 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ −80.72 (t, $J = 9.9$ Hz, 3F), −114.24 (m, 2F), −121.66 to −121.87 (m, 6F), −122.65 (s, 2F), −123.46 (s, 2F), −126.06 (s, 2F).

3.2. 1H,1H,2H,2H,3H,3H-Perfluoro-1-undecyl acid (3)

Compound **2** (37.1 g, 77.8 mmol), acetone (150 ml) and ether (50 ml) were placed in a round-bottomed flask equipped with an addition funnel. The Jone's oxidation reagent was added dropwise until a persistent red–brown solution appeared. The solution was extracted with ether (3×50 ml) and the organic phase was washed three times with water (50 ml), dried over anhydrous Na_2SO_4 and filtration. The solvent was removed in vacuo. Recrystallization of the residue from CCl_4gave compound **3** (34.5 g, 90% yield) as a white crystal. ^{1}H NMR (300 MHz, DMSO) δ 2.2–2.5 (m, 4H), 12.50 (s, 1H). ^{19}F NMR (282 MHz, DMSO) δ −80.80 (t, $J = 9.9$ Hz, 3F), −114.05 (m, 2F), −122.06 to

−122.60 (m, 6F), −122.90 (s, 2F), −123.52 (s, 2F), −126.41 (s, 2F).

3.3. Ester **4**

A 500-ml flask was equipped with an automatic water separator carrying an efficient reflux condenser at its upper end. Then acid **3** (31.1 g, 63.1 mmol), 3-dimethylamino-1-propanol (7.5 g, 75.1 mmol), *p*-toluenesulfonic acid (0.05 g, 0.263 mmol) and toluene (200 ml) were added. The reaction mixture was refluxed until no water was collected in the water separator. The solvent was removed in vacuo. The residue was dissolved in 100 ml ether, then washed three times with water (50 ml), brine, dried over anhydrous $MgSO_4$. After the removal of solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2:MeOH acetate = 10 : 1) to give compound **4** (20.8 g, 57% yield) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85 (m, 2H), 2.26 (s, 6H), 2.38 (t, $J = 7.2$ Hz, 2H), 2.40–2.56 (m, 2H), 2.64 (t, $J = 7.8$ Hz, 2H), 4.20 (t, $J = 7.2$ Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ −80.81 (t, $J = 9.9$ Hz, 3F), −114.79 (m, 2F), −121.79 to −122.00 (m, 6F), −122.85 (s, 2F), −123.59 (s, 2F), −126.21 (s, 2F). IR (thin film): 2955, 2823, 2773, 1774, 1465, 1336, 1243, 1208, 1152, 1114, 1043, 984, 705, 658, 529. MS *m/z*: 577(19), 558(5), 475(21), 457(2), 86(8), 84(8), 58(100). Anal. Calc. for $C_{16}H_{16}F_{17}NO_2$: C, 33.29; H, 2.79; N, 2.43. Found: C, 32.89; H, 2.75; N, 2.60%.

3.4. Quaternary ammonium silane coupling agent **5**

A mixture of ester **4** (9.04 g, 15.66 mmol), (3-iodopropyl)trimethoxysilane (6.62 g, 22.8 mmol) and anhydrous CH_3CN (15 ml) was stirred at 50 °C for 24 h. The solvent was removed in vacuo. The residue was washed with anhydrous ether (5 × 20 ml) to give quaternary ammonium salt **5** (13.1 g, 96%) as a pale yellow viscous solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.61 (t, $J = 7.8$ Hz, 2H), 1.81–1.94 (m, 4H), 2.40–2.50 (m, 2H), 2.54–2.62 (m, 2H), 3.04 (s, 6H), 3.66 (m, 2H), 3.30 (s, 9H), 3.36 (m, 2H), 3.62(t, $J = 5.7$ Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ −80.50 (t, $J = 9.9$ Hz, 3F), −114.04 (m, 2F), −120.87 to −121.05 (m, 6F), −121.95 (s, 2F), −122.78 (s, 2F), −125.50 (s, 2F). MS *m/z*: 576(15), 533(7), 475(13), 127(6), 121(18), 91(13), 58(100), 42(24), 41(19). Anal. Calc. for $C_{22}H_{31}F_{17}INO_5Si$: C, 30.46; H, 3.60; N, 1.61. Found: C, 29.27; H, 3.24; N, 1.20%.

3.5. Surface modification of cotton fabrics with compound **5**

The fabrics were padded with the 3% (w/w) compound **5** in MeOH and water (95/5, v/v), the impregnated specimens were dried at 80 °C for 3 min and cured at 160 °C for 3 min.

Acknowledgements

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