Preparation, surface properties, and antibacterial activity of a poly(dimethyl siloxane) network containing a quaternary ammonium salt side chain

Qinghua Zhang, Hailong Liu, Xi Chen, Xiaoli Zhan, Fengqiu Chen

Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China

Correspondence to: X. Zhan (E-mail: xlzhan@zju.edu.cn)

ABSTRACT: To obtain a copolymer network with low surface energy and antibacterial properties, a series of hydroxyl-terminated poly(dimethyl siloxane)s (PDMSs) modified by a quaternary ammonium salt (QAS) side chain was synthesized via hydrolytic polycondensation and quaternization. The structures of the intermediate and final products were confirmed by Fourier transform infrared spectroscopy, ^{1}H-NMR, and gel permeation chromatography. The results show that each step was successfully carried out, and objective products were obtained. The modified PDMSs were crosslinked with a commercial polyisocyanate to obtain cured QAS-modified PDMS coatings. The target functional coatings exhibited excellent antibacterial performance with a low surface energy. When the molar content of QAS in PDMS was varied from 10 to 30%, the critical surface energy of the coatings remained in the range 24.05–26.88 mN/m; this indicated that the coatings had minimal adhesion with fouling according to the Baier curve. The bactericidal tests showed that the antibacterial activity was independent of the PDMS molecular weight but was closely correlated with the QAS content in PDMS. The bactericidal rate of the coatings to *Escherichia coli* and *Staphylococcus aureus* was higher than 97% when the molar content of QAS in PDMS was above 20%. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41725.

INTRODUCTION

It is generally known that poly(dimethyl siloxane) (PDMS) materials exhibit many interesting properties; these include an outstanding biocompatibility, good thermal and oxidative stability, good dielectric insulating properties, and excellent fouling-release properties.[1,2] The copolymerization of PDMS and other polymers, such as polyurethane and polyester, can endow new copolymers with the excellent properties of PDMS. Because of their low surface energy and flexibility, PDMS fragments tend to migrate to the air–polymer interface. These physicochemical properties make PDMS an ideal candidate for surface functionalizatio.[3–5] PDMS-modified coatings with excellent stability and biocompatibility could be widely used in biomedical and tissue engineering materials.[6,7] Meanwhile, the antibacterial property of the materials should be considered in these biological application fields.[8–10]

The modification of polymers with antibacterial properties is usually imparted by the addition of a low-molecular-weight biocide, such as organic antibiotics,[11] silver,[12] and nitric oxide,[13] with slow release out of the polymers. However, the duration and effectiveness of the antibacterial performance are limited by loading and releasing kinetics, and the adverse effects that arise from the high toxicity of the released compounds present a concern. A great deal of effort has been devoted to improving the antibacterial durability and reducing the adverse impacts by the introduction of covalently bonded biocidal functions to polymers.[14,15] The antibacterial mechanism of these materials is a contact-killing mechanism. They kill bacteria by direct contact without releasing active biocides.

Quaternary ammonium salts (QAS) with alkyl chain lengths longer than C8 have been widely used as antimicrobial agents to kill microorganisms, including Gram-positive and Gram-negative bacteria, yeasts, and molds.[16] QAS-functionalized surfaces possess biocidal activity through a contact-killing mechanism involving electrostatic and lipophilic interactions with the cell wall of various microorganisms.[17] Kugler et al.[18] reported on the mechanistic aspects of QAS-functional surfaces. According to their findings, for a given microorganism, a threshold QAS charge density must be surpassed to obtain antibacterial activity. QAS groups that have a high polarity tend to migrate inside hydrophobic materials during the curing process; thus,

they will compromise the contact antibacterial activity. In this regard, PDMS modified by pendant QAS groups will facilitate the hydrophobic and contact-killing antibacterial properties of the material surface. Because of the surface migration of the low-surface-energy polysiloxane chain, covalently bonded QAS groups will be carried to the surface.

Majumdar et al.[19,20] reported a crosslinked PDMS matrix with pendant QAS groups based on solution blends of a silanol-terminated PDMS, a QAS-functional alkoxysilane, and the crosslinker methyl triacetoxysilane. According to their findings, the hydrophobicity and high flexibility of the polysiloxane allow for the partial segregation of QAS groups to the coating–water interface. It has been shown that for a given molar concentration of QAS, the antibacterial activities of polymers were better than that of the small-sized compounds. This was probably due to the effect of vicinal QAS groups destabilizing the cell membrane simultaneously over a small area.[21,22] In addition, the high compliance and low surface energy of polysiloxane impart fouling-release characteristics, which will improve the antibacterial efficiency of the surface-functional materials.[23,24]

To prepare the functional copolymers with both a low surface energy and antibacterial properties, a series of hydroxyl-terminated PDMSs grafted with QAS was synthesized via hydrosilylation, alcoholysis, hydrolytic polycondensation, and quaternization, as shown in Scheme 1. Compared to the previous reports,[20,25,26] the method adopted in this study afforded a kind of reactive polysiloxane with dual functionality of hydroxyl and QAS groups; this ensured the controllable structure of products involving molecular weight and QAS content. More importantly, the target products with linear polysiloxanes structure possess a higher flexibility and surface segregation because of its low surface energy properties. On the basis of these reasons, the copolymers show excellent hydrophobic and antibacterial properties.

In this study, well-designed copolymer networks with low surface energies and antibacterial activities were synthesized. The chemical structures of the synthesized PDMS network containing QAS side chains were characterized by Fourier transform infrared (FTIR) spectroscopy, ^{1}H-NMR, and gel permeation chromatography (GPC). The influences of the QAS concentration and polysiloxane structure on the surface wettability properties and antibacterial performances were investigated in detail.

EXPERIMENTAL

Materials

Dimethoxydimethyl silane (DMMS) and γ-chloropropylmethyl-dimethoxysilane (MCPS) were kindly supplied by Zhejiang Feidian Chemical Co. without further purification. The water used here was deionized and then distilled. Allyl glycidyl ether, N,N-dimethyl dodecyl amine, and 1,1,3,3-tetramethyldisiloxane (analytical reagent) were purchased from Hangzhou Mindray Chemical. Ether, methanol, toluene, N,N-dimethylformamide, and tetrahydrofuran (THF; analytical reagent) were products of National Pharmaceutical Group Chemical Reagent Co. All of these chemicals were distilled before use. Anhydrous sodium carbonate, potassium hydroxide, methanol solution of chlorine hydride, trifluoromethane sulfonic acid (TfOH), and Karstedt

catalyst were used as received. Desmodur Z4470 (polyisocyanate, isophorone diisocyanate (IPDI) trimer crosslinking, NCO content = 11.9 ± 0.4%, viscosity at 23°C = 1500 mPa S, Bayer Co.) was used as a curing agent. *Escherichia coli* and *Staphylococcus aureus* were obtained from a the Microorganism Institute of Zhejiang University. The culture medium was commercial.

Synthesis of Hydroxyl-Terminated PDMS Containing a QAS Side Chain

Preparation of 1,3-Bis(glycidoxypropyl)tetramethyldisiloxane (a). The synthesis of **a,** as reported in the literature,[27] was carried out. Allyl glycidyl ether (40.50 g), 15 mL of toluene, and 20 μL of Karstedt catalyst were introduced into a 250-mL, round-bottomed, four-necked flask equipped with a magnetic stirring bar, condenser, and thermometer. Under nitrogen, the flask was heated to 65°C; this was followed by the dropwise addition of 1,1,3,3-tetramethyldisiloxane (20.30 g). Then, the reaction mixture was stirred for 0.5 h. After the flask was heated to 105°C, the reaction mixture was stirred at reflux for 8 h. Then, the final mixture was vacuum-distilled under 5 mmHg, and the distillate was obtained from 198 to 202°C. The target substance (compound **a**) was collected with a yield of 75.6%. The refractive index of the collected distillate was measured as $n25\ D = 1.4495$, which was well consistent with the reported value of $n25\ D = 1.4506$.[28]

IR (KBr, v, cm^{-1}): 1253, 840 (Si—CH$_3$), 1108 (C—O—C), 1058 (Si—O—Si). ^{1}H-NMR (CDCl$_3$, 500 MHz, δ, ppm):0.03 (m, 12 H, Si—CH$_3$), 0.46 (t, 4 H, Si—CH$_2$), 1.55 (m, 4 H, C—CH$_2$—C), 2.55–2.78 (t, 4 H, O—CH$_2$—C), 3.1 (m, 2 H, CH—O), 3.35, 3.64 (m,4 H, C—CH$_2$—O), 3.38–3.43 (m,4 H, O—CH$_2$—C).

Preparation of 1,3-Bis[3-(1-methoxy-2-hydroxypropoxy)propyl]tetramethyldisiloxane (MTS or b). Excess methanol (116 g) and **a** (26 g) were introduced to a 250-mL, round-bottomed, four-necked flask equipped with a magnetic stirring bar, condenser, and thermometer. Under nitrogen, 40 μL of TfOH was added to flask, and the reaction solution was stirred for 8–9 h at 65°C, and then, the pH was moderated via a methanol solution of potassium hydroxide and chlorine hydride. The reaction mixture was stirred for 2 h at 65°C. After filtration, the solvent was removed, and the final mixture was vacuum-distilled under 5 mmHg, and the distillate from 226 to 230°C was obtained. $n25\ D$ was measured as $n25\ D = 1.4496$, which was consistent with reported value of $n25\ D = 1.4512$.[27]

IR (KBr, v, cm^{-1}): 1253, 840 (Si—CH$_3$), 1113 (C—O—C), 1055 (Si—O—Si), 3453 (O—H). ^{1}H-NMR (CDCl$_3$, 500 MHz, δ ppm): 0.01 (m, 12 H, Si—CH$_3$), 0.48 (t, 4 H, Si—CH$_2$), 1.58 (m, 4 H, C—CH$_2$—C), 3.34 (s, 6 H, O—CH$_3$), 3.43 (t, 4 H, O—CH$_2$—C), 3.48 (d, 4 H, O—CH$_2$—C), 3.55 (d,4 H, C—CH$_2$—O), 3.93 (m,2 H, C—CH—C).

Preparation of Hydroxyl-Terminated Poly[(3-chloropropyl)-methyl siloxane]-*random*-PDMS (c). A series of hydroxyl-terminated poly [(3-chloropropyl)-methyl siloxane] (HT-PCPMS)-ran-PDMSs (c) was synthesized via hydrolytic polycondensation between MCPS and DMMS. A representative procedure (HT-PCPMS-ran-PDMS-4) was as follows: a 100-mL, round-bottom flask equipped with a nitrogen inlet, magnetic stirring bar,

Scheme 1. Synthetic illustration of the crosslinked PDMS network modified with QAS.

reflux condenser, and thermometer was charged with 10.98 g (0.06 mol) of MCPS, 16.80 g (0.14 mol) of DMMS, 2.84 g (6.67 mmol) MTS, and 3.6 g (0.20 mol) of deionized water and was heated to 60–70°C. A volume of 6 μL of TfOH was added, and the mixture was heated for 1 h. About 16 mL of methanol was then distilled off from the reaction solution at 80°C. The reaction mixture was refluxed for another 4 h at 80°C. The resulting mixture was neutralized with 1N potassium hydroxide in methanol under stirring at 70 ± 5°C for 10 min. The crude product was dried over anhydrous sodium carbonate and vacuum-distilled to remove low-boiling-point compounds. A slight amount of yellowish viscous liquid was obtained.

IR (cm^{-1}): 790, 1263, 1410, 2961 (Si—CH$_3$), 1023–1092 (Si—O—Si), 1160 (CH$_2$—Cl), 2905 (CH$_2$), 3460 (OH). ^{1}H-NMR (δ, ppm): 0.01 (s, Si—CH$_3$), 0.6–0.68 (m, Si—CH$_2$), 1.77–1.86 (m, Si—CH$_2$—CH$_2$), 3.35–3.41 (m, Si—CH$_2$—CH$_2$—CH$_2$), 3.53–3.76 (m, CH—OH, CH$_2$OCH$_2$, CH$_2$OCH$_3$), 3.92–4.05 (m, OH).

A series of HT-PCPMS-*ran*-PDMS samples with various molecular weights of polysiloxanes and different contents of poly [(3-chloropropyl)-methyl siloxane] (PCPMS) segments was obtained through changes in the ratios of the reactants.

Preparation of Hydroxyl-Terminated Polysiloxanes Modified with QAS hydroxyl-terminated poly [(3-dodecyl-dimethyl-ammonium chloride-propyl)-methyl siloxane] (HT-PQPMS-*ran*-PDMS) (d). Hydroxyl-terminated polysiloxanes modified with QAS (HT-PQPMS-*ran*-PDMS, **d**) were obtained from the quaternization of HT-PCPMS-*ran*-PDMS samples with N,N-dimethyldodecylamine as the quaternizing agent. A representative quaternization procedure (HT-PQPMS-*ran*-PDMS-4) was as follows: 5 g of HT-PCPMS-*ran*-PDMS-4 and 2.99 g of N,N-dimethyldodecylamine were dissolved in 10 mL of N,N-dimethylformamide to a 50-mL, round-bottomed flask. The quaternization reaction was carried out at 120°C for 14 h. A substantial increase in the viscosity was observed. The unreacted and low-boiling-point compounds were removed from the reaction mixture at 1 mmHg and up to 150°C. Finally, a brown viscous liquid was obtained.

IR (cm^{-1}): 1023, 1262, 1464–1469 (C—N). With ^{1}H-NMR (in CDCl$_3$), new peaks appeared at 3.5 ppm (—N$^+$—CH$_2$—) and 3.3 ppm [(—N$^+$—(CH$_3$)$_2$], and a relative decrease in the dimethylamino protons at 2.2 ppm was observed.

Coating (e) Preparation
The cured QAS-modified PDMS coatings were prepared by the mixture of HT-PQPMS-*ran*-PDMS samples with Desmodur Z4470 in THF (5 wt %). The molar ratio of isocyanate to hydroxyl groups (NCO/OH) was controlled in the range of 1.1–1.0. About 0.5 mL of each coating formulation was deposited on the clean substrates by the spin-coating method (2000 rpm, 30 s). The coatings were allowed to cure for 24 h at room temperature; this was done for an additional 24 h in an oven at 50°C.

Measurements
FTIR spectra were recorded on a Nicolet FTIR Tensor 5700 spectrometer (KBr, v, cm^{-1}). The products were dissolved in CDCl$_3$, and ^{1}H-NMR analysis was conducted on this solution with a Bruker 500-MHz NMR spectrometer (Avance DMX500)

at room temperature. The molecular weight and polydispersity index were analyzed on a Waters 1525/2414 gel permeation chromatograph.

The static contact angles reflected the surface wetting properties; these were measured by a CAM200 optical contact angle meter (KSV Co., Ltd.). The static contact angles of water and *n*-hexadecane (each droplet volume was 2 μL) were measured. The surface free energy was calculated from the static contact angles according to Owens and Wendt's equation.[29]

Antibacterial Activity Test
The antibacterial activities of the functional coatings were investigated against *E. coli* and *S. aureus* with the plate count method, as described elsewhere.[30,31] Basically, an aliquot of the 10^8 cfu/mL log phase *E. coli* suspension and *S. aureus* suspension were prepared in Luria–Bertani media and tryptic soy broth media, respectively. The coating samples on coverslips (2 × 2 cm^2) were immersed in 10 mL of *E. coli* suspension or *S. aureus* suspension (10^8 cfu/mL) and incubated in a shaking incubator at 37°C for 2 h. The coating samples were then swabbed with a sterile cotton swab; they were then placed in tubes with 10 mL of Ringer's solution, sonicated for 5 min, and vortexed for 30 s to collect the adherent bacterial cells on the coverslips. Six 10-fold dilutions were prepared, and the surviving bacteria were counted by the spread plate method (100-μL samples of the decimal dilutions were spread on a Petri dish that contained Luria–Bertani agar or tryptic soy broth agar). The Petri dishes were incubated at 37°C overnight. After incubation, the colonies were counted. The percentage reductions in bacterial colonies, as compared to an uncoated coverslip (as a blank control), were reported as the mean value of three replicated samples. Specifically, the bactericidal rate (E_b) was calculated the following equation:

$$E_b = \frac{N_b - N_c}{N_b} \times 100\%$$

where N_b and N_c are the numbers of colonies (which means the surviving bacteria cells) corresponding to the uncoated coverslip and functional coating samples, respectively.

RESULTS AND DISCUSSION

Preparation and Structure of HT-PQPMS-*ran*-PDMS
With the purpose of preparing the PDMS network with biocidal activity, a series of hydroxyl-terminated polysiloxanes grafted QAS side chains (HT-PQPMS-*ran*-PDMS) was synthesized via hydrosilylation, alcoholysis, hydrolytic polycondensation, and quaternization reaction. The expected PDMS network containing QAS was obtained through the crosslinking polymerization of HT-PQPMS-*ran*-PDMS samples and IPDI trimer (Scheme 1). The intermediate product structures of each step were described and characterized in the previous Experimental section.

Figure 1 shows the FTIR spectra of the intermediate and final products. First, **a** was prepared via a hydrosilylation reaction. Figure 1(a) shows that the Si—H vibration peaks at 2134 cm^{-1} from 1,1,3,3-tetramethyldisiloxane and the C=C vibration peaks at 1647 cm^{-1} from allyl glycidyl ether both disappeared. This confirmed the formation of compound **a** through the hydrosilylation reaction. Then, MTS (**b**) was prepared via an alcoholysis
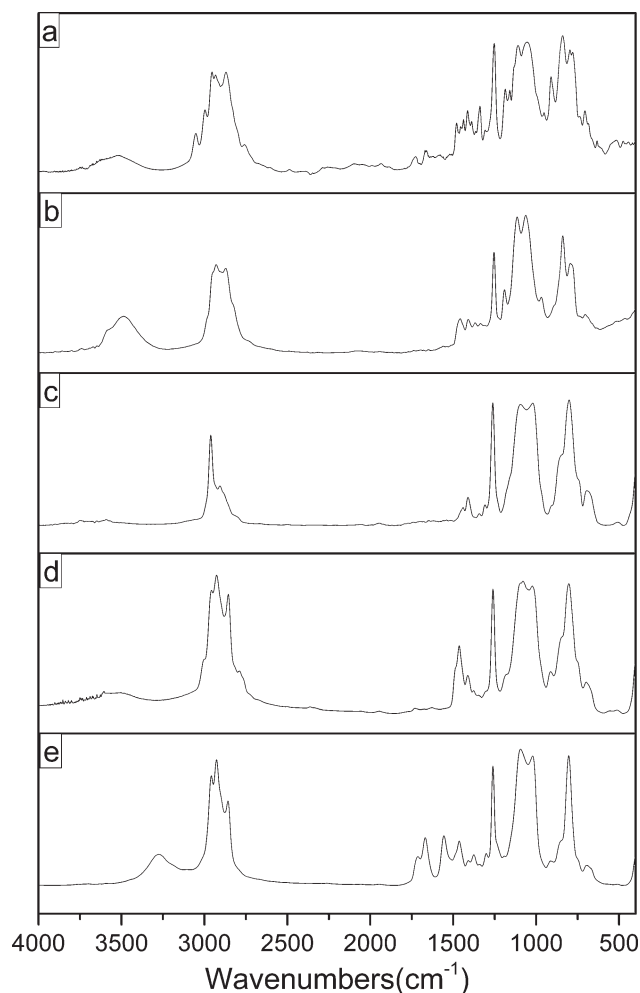
Figure 1. FTIR spectra of the intermediate and final product samples: (a) a, (b) MTS, (c) HT-PCPMS-*ran*-PDMS, (d) HT-PQPMS-*ran*-PDMS, and (e) QAS-modified PDMS network coating.

reaction. As shown in Figure 1(b), a strong hydroxyl vibration peak appeared at 3453 cm^{-1}; this indicated that the epoxy ring opened, and the hydroxyl formed. HT-PCPMS-*ran*-PDMS (**c**) was synthesized via hydrolytic polycondensation between DMMS and MCPS with MTS as a molecular weight modifier. A representative FTIR spectrum of HT-PCPMS-*ran*-PDMS-3 is presented in Figure 1(c). The characteristic absorptions of Si—O—Si near 1023–1092 cm^{-1}, the CH$_2$—Cl vibration peak at 1160 cm^{-1}, and the O—H vibration peak at 3460 cm^{-1} corresponding to the hydroxyl-terminated polysiloxanes chain were clearly visible. This suggested that the hydrolytic polycondensation reaction succeeded. Next, HT-PQPMS-*ran*-PDMS (**d**) was obtained from the quaternization of HT-PCPMS-*ran*-PDMS with *N,N*-dimethyldodecylamine as the quaternizing agent. The representative FTIR spectrum of Figure 1(d) showed that the peaks at 1023 and 1262 cm^{-1} were the typical signals of the C—N group. In addition, the enhancement peak near 1464–1469 cm^{-1} was attributed to C—H bending from the longer alkyl chain (—C$_{12}$H$_{25}$). These signals indicated the formation of QAS. Finally, Figure 1(e) shows the FTIR spectrum of the QAS-modified PDMS network coating prepared by crosslinking

polymerization. The peaks at 3270 cm^{-1} (N—H stretching), 1700 cm^{-1} (C=O stretching), 1540 cm^{-1} (C—N—H bending), and 1260 cm^{-1} (N—C—O stretching) were typical of polyurethane hard segments. As shown in Figure 1, each synthetic step was verified by FTIR spectroscopy.

Among these five steps, the synthesis of the precursor HT-PCPMS-*ran*-PDMS was vital to the chemical modification of polysiloxanes with dual functionality of hydroxyl and QAS groups. A representative result of ^{1}H-NMR spectra (HT-PCPMS-*ran*-PDMS-3) in Figure 2 shows that the hydrogen proportional ratio of Si—CH$_3$ ($\delta = 0.1$ ppm), Si—CH$_2$— ($\delta = 0.6$ ppm) to Si—CH$_2$—CH$_2$— ($\delta = 1.8$ ppm) to Si—CH$_2$—CH$_2$—CH$_2$— ($\delta = 3.5$ ppm) to CH—OH (δ 3.4 ppm) was 11.00:1.00:1.06:1.10:0.14; this was in accordance with the design value (10.87:1.00:1.00:1.00:0.12). Confidently, FTIR spectroscopy and ^{1}H-NMR and analyses indicated that the objective products were obtained successfully.

A series of hydroxyl-terminated polysiloxanes with different molecular weights of polysiloxanes and different contents of PCPMS segments was prepared through the adjustment of the ratio of the raw materials DMMS and MCPS. Table I shows the ratio of raw materials and molecular weight estimated by theoretical calculation and GPC analysis. The molecular weights of hydroxyl-terminated polysiloxanes calculated by the functional group analysis based on hydroxyl were consistent with their theoretical values. The GPC data showed the narrow molecular weight polydispersity index with unimodal distribution throughout the reaction. However, the values from GPC were larger than that designed. This was because in our GPC measurement, polystyrene was used as a standard sample. The refractive index of polysiloxane was greatly different with polystyrene. On the other hand, in the THF solution, hydroxyl-terminated polymers formed hydrogen bonds; this made the hydrodynamic volume of the polymers bigger. So, the molecular weights determined by GPC were higher than the calculated values.

QAS side chains with antibacterial performance were introduced in hydroxyl-terminated polysiloxanes by the reaction of
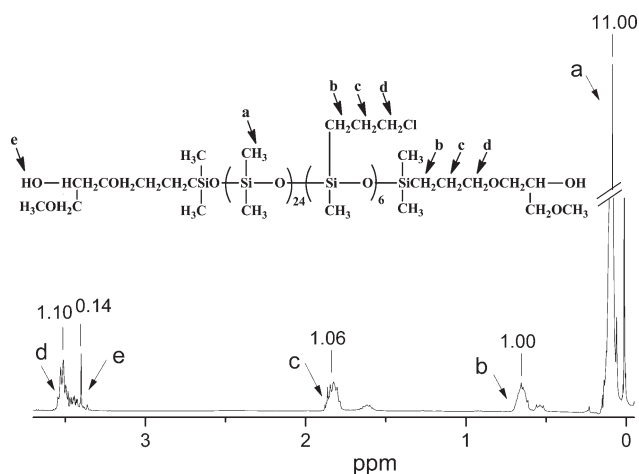

Figure 2. ^{1}H-NMR spectra of the HT-PCPMS-*ran*-PDMS-3 sample in Table I.

Table I. Molecular Weights of the HT-PCPMS-*ran*-PDMS and Ratios of PCPMS and PDMS Segments

Sample	PCPMS in the copolymer (%)	M_n (g/mol): designed	M_n (g/mol): end groups	M_n (g/mol) GPC	M_w/M_n
HT-PCPMS-*ran*-PDMS-1	0	2646	3110	4979	1.50
HT-PCPMS-*ran*-PDMS-2	10	2834	3205	5301	1.52
HT-PCPMS-*ran*-PDMS-3	20	3021	3542	5616	1.52
HT-PCPMS-*ran*-PDMS-4	30	3208	3823	6020	1.58
HT-PCPMS-*ran*-PDMS-5	20	4751	4958	6935	1.61
HT-PCPMS-*ran*-PDMS-6	20	8211	8321	10,347	1.80

M_n, number-average molecular weight; M_w, weight-average molecular weight.

N,N-dimethyldodecylamine with chloropropyl. To define the optimal reaction time, the quaternization reaction kinetics were investigated with polysiloxanes with different molar contents of PCPMS segments (10, 20, and 30%) as reactants. The conversion of the quaternization over time is shown in Figure 3. For all of the samples, the conversion was periodically measured every 2 h. The content of QAS was calculated by a two-phase titration analysis, as described in the literature.[32] The quaternization conversion for the three samples reached 95% after 14 h of reaction at 120°C. As shown in Figure 3, we found that the quaternization reaction of the HT-PCPMS-*ran*-PDMS-4 sample was significantly faster than the others. The reason was that the content of chloropropyl in the polysiloxanes was higher than those in the other two samples, and the higher chance of molecular collisions caused the reaction to be quicker.

Contact Angles and Surface Free Energies
The static contact angle was obtained by a CAM200 optical contact angle meter. Additionally, the measured values of the static contact angles were then used to extract the critical surface energy values of the polymer films according to the so-called Owens–Wendt–Kaelble approach.[29] According to Fowkes, the critical surface energy can be resolved into a dispersion component and a polar component:

$$\gamma = \gamma^d + \gamma^p \tag{1}$$

where γ is the surface tension, γ^d is the dispersion component of the surface tension, and γ^p is the polar component of the surface tension.

Owens and Wendt extended this concept and proposed the following semiempirical equation:

$$\gamma_L(1 + \cos\theta) = 2(\gamma_S^d \gamma_L^d)^{1/2} + 2(\gamma_S^d \gamma_L^d)^{1/2} \tag{2}$$

In this equation, the subscript L refers to the wetting test liquid, the subscript S refers to the solid, and θ is the contact angle.

The critical surface energies of the solid surface (γ_S, γ_S^d, and γ_S^p) were determined with eq. (2), and two different liquids whose surface tension (γ_L), dispersion component (γ_L^d), and polar component (γ_L^p) are known. Water ($\gamma_L^d = 21.6$ mN/m; $\gamma_L^p = 51.0$ mN/m) and hexadecane ($\gamma_L = \gamma_L^d = 26.3$ mN/m) were used in this study as the test liquids to measure the surface energies. These two solvents were of very different polarities and could be used to obtain accurate surface tension data. The contact angles of water and hexadecane measured for the samples of the product and the results of the critical surface energy obtained are shown in Table II.

As shown in Table II, all of the coating samples showed low surface energies with large static water contact angles of more than 90°. The surface energy increased from 24.05 to 26.88 mN/m as the content of QAS increased from 10 to 30%. Although the QAS side chains contained hydrophobic long-chain alkyls, the polar groups in QAS raised the polar component of the surface energy. In generally, a lower surface energy implies less capability for interacting with other compounds. The literature has reported that an empirical relationship between γ_S and the relative amount of bioadhesion known as the Baier curve.[33] As shown in Figure 4, minimal fouling was typically achieved at a critical surface tension of 22–26 mN/m. The surface energy values of all of the samples located in this range were considered to have the lower adhesion with fouling.[33–35]

Evaluation of the Antibacterial Activity
QASs with a long alkyl chain substituent have been widely used as contact antimicrobial agents. This means that the bacteria or microbes could be efficiently killed when they contacted the surface of QAS. The antimicrobial activity can function only if the antibiotic compounds located on the outermost layer of the copolymer network. For our prepared crosslinked copolymer coatings, the antimicrobial QAS group was grafted on the
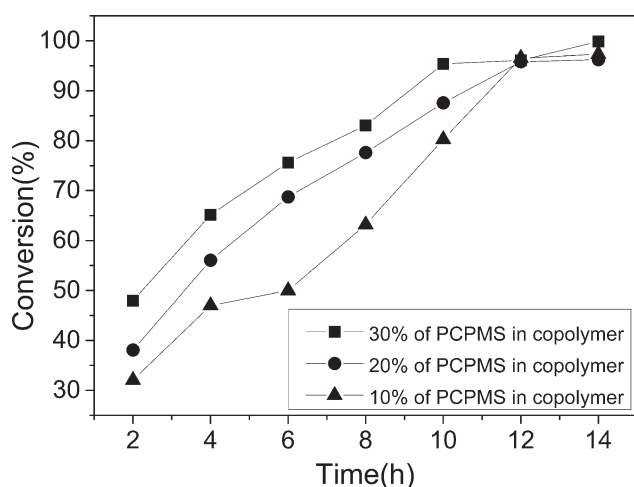

Figure 3. Quaternization reaction conversion versus time at different PCPMS contents.

Table II. Contact Angles and Critical Surface Energy of Hydroxyl-Terminated PDMS Modified with QAS

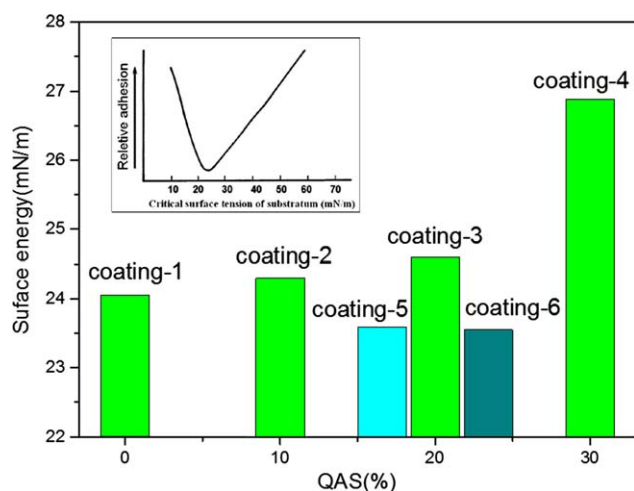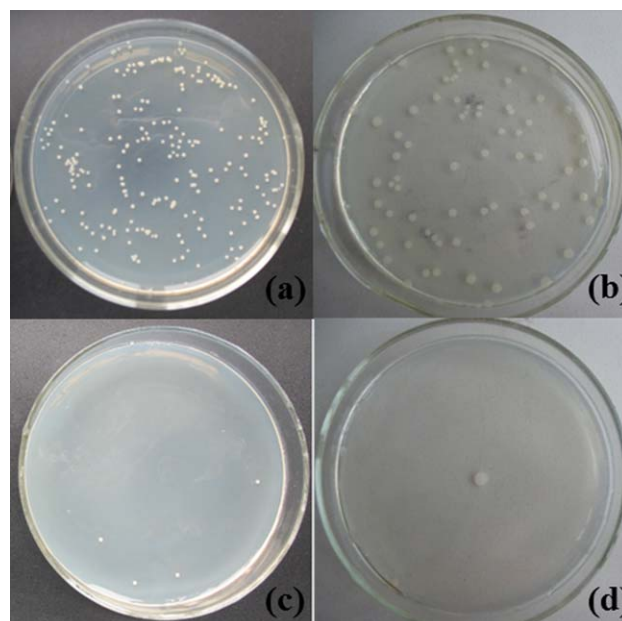| Sample	M_n of HT-PCPMS-ran-PDMS (g/mol)	QAS in HT-PQPMS-ran-PDMS (%)	θ_{water} (°)	$\theta_{hexadecane}$ (°)	γ_S (mN/m)
Coating 1	2646	0	107	29.5	24.05
Coating 2	2834	10	101.1	31.7	24.30
Coating 3	3021	20	99.6	31.5	24.60
Coating 4	3208	30	91	31.2	26.88
Coating 5	4751	20	104.6	32.7	23.59
Coating 6	8211	20	105.4	32.5	23.55

PDMS backbone with a high flexibility and low surface energy. The enrichment of the soft PDMS main chain on the surface promoted the surface concentrations of the QAS side chain. The antibacterial activities of the copolymer film were evaluated according to the literature.[30,31] The bacterial colonies were allowed to grow on the surface of the samples. The antibacterial activity was evaluated according to their bactericidal rate. Table III displays the antibacterial activity of the crosslinked PDMS modified with QAS. An uncoated coverslip was used as a blank control.

Figure 5 shows the antibacterial activities of coating 3 with a 20% content of QAS in HT-PQPMS-ran-PDMS against *S. aureus* and *E. coli* as compared with the blank control sample. We found that the bactericidal rates against Gram-negative bacteria *E. coli* and Gram-positive bacteria *S. aureus* were above 97% when the content of QAS in HT-PQPMS-ran-PDMS was higher than 20%. When the molecular weight of polysiloxanes was similar, the bactericidal rates increased obviously from 53.6/62.8% to 97.3/98.6% with increasing QAS content from 10 to 20%. However, when the QAS content increased from 20 to 30%, a small increase in the bactericidal rates was found. The pure PDMS film with a 0% content of QAS had no antibacterial activity. Meanwhile, the test results show that the antibacterial activity was independent of the molecular weight of polysiloxanes but closely correlated with the total amount of QAS in the

Table III. Antimicrobial Activity of the Crosslinked PDMS Modified with QAS

Sample Uncoated	Blank control	
	Reduction in *E. coli* colony number retention (%)	Reduction in *S. aureus* colony number retention (%)
Coating 1	0[a]	0[a]
Coating 2	53.6	62.8
Coating 3	97.3	98.6
Coating 4	97.4	100
Coating 5	97.7	99.5
Coating 6	99.8	100

[a] There was little change in the bacterial colony number for this coating versus the blank control.

Figure 5. Antibacterial activities against the test microorganisms after 2 h of contact time with the samples: (a) *S. aureus* and blank sample, (b) *E. coli* and blank sample, (c) *S. aureus* and coating 3 with 20% QAS in HT-PQPMS-ran-PDMS, and (d) *E. coli* and coating 3 with 20% QAS in HT-PQPMS-ran-PDMS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. Surface energy of a crosslinked PDMS network modified with QAS and the Baier curve. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copolymers. All of the samples with more than a 20% content of QAS in HT-PQPMS-*ran*-PDMS showed a high broad-spectrum antibacterial activity. This could be explained by the sterilization mechanism of QAS with a C12 alkyl chain length and chlorine as a counter ion, which could provide a good balance of lipophilicity and diffusivity to enable both effective binding to the outer surface of the bacterium cell structure and diffusivity through the cell wall to the cell interior. The surface of the samples provided adequate sterilization groups to kill bacteria when the content of QAS in HT-PQPMS-*ran*-PDMS reached 20%.

CONCLUSIONS

A series of hydroxyl-terminated polysiloxanes modified with QAS with different molecular weights and different contents of QAS was synthesized by the hydrolytic polycondensation of DMMS and MCPS and quaternization with *N,N*-dimethyldodecylamine. On the basis of the analysis of the structure of polysiloxanes coatings with different molar contents of QAS, the surface wetting properties and antibacterial activity were investigated systematically. The copolymer network films exhibited low surface energies of 24.05–26.88 mN/m when the content of QAS in HT-PQPMS-*ran*-PDMS varied from 10 to 30%; this sample had minimal adhesion with fouling according to the Baier curve. As the content of QAS in HT-PQPMS-*ran*-PDMS was above 20%, the bactericidal rates of these modified PDMS coatings against *E. coli* and *S. aureus* were higher than 97%. As a result, the target polymers showed unique surface wetting properties and antibacterial activities and have potential applications as biomedical or tissue engineering materials.

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