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Polydimethylsiloxane-polymethacrylate block copolymers tethering quaternary ammonium salt groups for antimicrobial coating

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ABSTRACT

Block copolymers PDMS-*b*-PDMAEMA were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization involving *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) by using poly(dimethylsiloxane) (PDMS) macro-chain transfer agent. And, the tertiary amino groups in PDMAEMA were quaternized with *n*-octyliodide to provide quaternary ammonium salts (QPDMAEMA). The well-defined copolymers generated composition variation and morphology evolvement on film surfaces, which were characterized by X-ray photoelectron spectroscopy, atomic force microscopy, and contact angle measurements. The results indicated that the enrichment of QPDMAEMA brought about lower elemental ratios of Si/N on the film surfaces. The surface morphologies evolved with the variations of QPDMAEMA content, and the variation trend of film roughness was exactly opposite to that of water contact angle hysteresis. With regard to structure-antimicrobial relationships, the copolymer films had more evident antimicrobial activity against Gram-positive, *Bacillus subtilis*, and the surfaces with heterogeneous morphology and higher N^+ content presented better antimicrobial activity. The functionalized copolymers based PDMS and quaternary ammonium salts materials have the potential applications as antimicrobial coatings.

1. Introduction

The growth of bacteria is a particular contamination problem, which can lead to severe infections and diseases [1]. Great efforts have been devoted to develop materials with high antimicrobial performance. Antimicrobial polymers with diverse mechanisms, including quaternary ammonium salts (QAS), polymeric *N*-halamine, and host-defense peptide are of importance. Polymeric *N*-halamines possess the advantages of high efficiency, durability and rechargeability [2]. Host-defense peptides with sequence-specific structure can prevent bacteria from evolving resistance to the membrane-disruption mode [3]. QAS is the most popular antimicrobial polymeric material owing to its simple fabrication process and low cost, though it has relatively lower antimicrobial efficacy compared with polymeric *N*-halamines and antimicrobial peptides [4].

The antimicrobial activity of QAS related polymers was associated with complex factors, such as molecular weight, types of the counter anions, charge density, alkyl chain length and steric hindrance of QAS, hydrophilic–hydrophobic balance, as well as bacteria species [5–9]. Some research groups indicated that QAS containing long alkyl chain substituent of at least 8 carbon atoms showed significant active biocides in water [6,7,10,11]. As well known, poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA) is one of the hydrophilic polymers containing tertiary amino groups, and can be further converted into positively charged polymer with quaternary ammonium salt groups (QPDMAEMA), which has been considered to be a promising polymeric antimicrobial agent [12–14]. A previous study reported antimicrobial polymeric brushes with high density cationic surfaces could effectively kill bacterial cells [15]. Tang's group [16] have studied ammonium containing PDMAEMA with natural rosin as the pendant groups (PDMAEMA-*g*-rosin), and indicated that conformation of hydrophobic group with particularly steric hindrance played an important role for antimicrobial efficacy. Moreover, it was reported that the QAS modification could enhance the mechanical properties of polysiloxane coatings [17].

From the aspect of application, poly(dimethylsiloxane) (PDMS) is one of the versatile candidates to integrate with QPDMAEMA, because of the good fouling-release performance, low surface energy and elastic modulus, as well as biocompatibility, optical transparency, and permeability [18–20]. Actually, there are several approaches utilized to endow PDMS with antimicrobial properties.

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The facile techniques involve blending with various antimicrobial agents [6,21,22], and chemical surface modification of PDMS material with preformed polymers [23–25]. The drawbacks of these manipulations are that they cannot give long-term protection under adverse conditions and the modified surface of PDMS could be transformed into a brittle silica-like layer [26–28]. The available approach is based on constructing copolymers containing antimicrobial functional groups in side chains to tailor brush structures [8,29]. The controlled polymerizations, such as atom transfer radical polymerization (ATRP) [30] and RAFT polymerization [31], are often used to synthesize the target copolymers for antimicrobial purpose. Due to the high flexibility of PDMS chains, the QAS-tethered polysiloxane may readily interact with bacteria, acting not only on the surface but also in bulk, which would prevent the bacteria from colonizing crevices as well as defects of other materials [8].

For the purpose of finding an economic and practical biomedical antibacterial coating, in this study, a series of block copolymers with different content of QPDMAEMA were synthesized via RAFT polymerization and quaternization, taking the effects of charge density and molecular weight on antimicrobial efficiency into account. PDMS was used as macro chain transfer agent (PDMS-CTA) with low surface energy and biocompatibility available, while QPDMAEMA was designated to fulfill the antimicrobial function. The well-defined structure of copolymers endowed greater insight into microphase separation and the resulting antimicrobial activity, which could generate special composition and unique morphology on film surfaces. These block copolymer films were characterized by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and contact angle measurements. With regard to structure-antimicrobial relationships, the antimicrobial activity of the copolymers against Gram-positive and Gram-negative bacteria was preliminarily investigated.

2. Experimental

2.1. Materials

α-Hydride-terminated polydimethylsiloxane (PDMS-H, M_n = 8000 g/mol) was purchased from Hangzhou Silong Material Technology Co., Ltd., China. 2-(Allyloxy)ethanol, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene (Pt ~ 2%), 4-(dimethylamino)pyridine (DMAP, 99%) and *N*,*N*-dicyclohexylcarbodiimide (DCC) were purchased from Sigma-Aldrich. Hydroxyl-terminated polydimethylsiloxane (PDMS-OH) was synthesized from α-hydride-terminated polydimethylsiloxane according to the literature [32]. 4-Cyanopentanoic acid dithiobenzoate (CAD) was synthesized referring to the previous report [33]. PDMS-CTA was obtained according to the literatures [34,35]. *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) (Aldrich, 98%) and hydroxyethyl methacrylate (HEMA) (Tianjin Kemiou Chemical Reagent Co., China) were purified by passing the monomer through basic alumina column. *N*-octyliodide was obtained from Alfa Aesar and used as received. Azobis(isobutyronitrile) (AIBN, Aldrich, 99%) was recrystallized from ethanol and dried. Hexamethylene diisocyanate (HDI) was purchased from Bayer AG., Germany. Gram-positive bacteria (*Bacillus subtilis*) and Gram-negative bacteria (*Escherichia coli*) were supplied from Hebei University of Science & Technology, China, and were incubated at 4 °C on nutrient agar plates.

2.2. Synthesis of PDMS-b-QPDMAEMA block copolymers

The synthesis procedure for PDMS-*b*-QPDMAEMA is described in Scheme 1. RAFT polymerization was conducted in a 50 mL dry three necked flask equipped with a magnetic stirrer. In a typical reaction, DMAEMA (0.942 g, 6 mmol), AIBN (0.0028 g, 0.017 mmol) and PDMS-CTA (1.008 g, 0.12 mmol) were dissolved in toluene (0.95 g). In addition, a certain amount of HEMA was added for crosslinking. The solution was then degassed to remove oxygen, and polymerization was carried out under stirring in water bath at 65 °C for 12 h. The reaction was terminated and quenched to 0 °C, and the crude products were diluted and dialyzed against methanol over 48 h. After dialysis, the solvent was removed by rotary evaporator and the copolymer was dried under high vacuum for 24 h at room temperature to yield a pink product. Block copolymers with different contents were synthesized in the same manner (Table 1). ^{1}H NMR (500 MHz, $CDCl_3$) d (ppm): 0.07 (6nH, m, $C_4H_9(Si(CH_3)_2)_n$), 0.91–1.06 (3H, s, $CH_2C(CH_3)S$), 1.80–1.90 (2H, s, $CH_2C(CH_3)S$), 2.32 (6H, s, $CH_2N(CH_3)_2$), 2.58 (2H, t, $CH_2N(CH_3)_2$), 3.83 (2H, t, CH_2CH_2OH), 4.08 (2H, t, $COOCH_2CH_2N$).

Quaternization reactions were carried out in a 50 mL dry three-necked flask equipped with a magnetic stirrer. In a typical reaction, 0.99 g of PDMS-*b*-PDMAEMA (2.4 mmol of tertiary amine functional groups) was mixed with 0.864 g of *n*-octyliodide (3.6 mmol of iodide ions), then the reactants were dissolved in toluene/acetonitrile (w/w = 1:1) solvents, and the quaternization reaction was proceed at 70 °C for 32 h. A substantial increase in viscosity was observed as a result of the reaction. The product was precipitated by hexane four times. ^{1}H NMR (500 MHz, $CDCl_3$) d (ppm): 0.07 (6nH, m, $C_4H_9(Si(CH_3)_2)_n$), 0.91–1.06 (3H, s, $CH_2C(CH_3)S$), 1.39 (17H, m, $(CH_2)_7CH_3$), 1.80–1.90 (2H, s, $CH_2C(CH_3)S$), 3.47 (6H, s, $CH_2N^+(CH_3)_2$), 3.72 (2H, t, $CH_2N^+(CH_3)_2$), 4.08–4.15 (2H, t, $COOCH_2CH_2N$). It was estimated that all the tertiary amino groups have almost been transformed into QAS groups.

2.3. Preparation of the copolymer films

A certain amount of the obtained block copolymers and HDI were dissolved in acetonitrile to prepare copolymer solution (10 wt%). Then the solution (200 μL) was spin-coating (rotate speed 600 r/s for 6 s and 3000 r/s for 10 s) on clean aluminum sheet (2 cm × 2 cm). The solvent was evaporated at room temperature for 1 h before the samples were cured at 100 °C for 2 h. These films were used for the characterization of surface structure and antimicrobial performance testing.

Table 1
Conversion and relative molecular weight of the prepared block copolymers.

Sample[a]	^{1}H NMR		GPC		
	Conv. (%)	$M_{n,NMR}$ (kDa)	M_n (kDa)	M_w (kDa)	PDI
PDMS	–	8.0	9.3	11.8	1.27
PDMS-*b*-$PDMAEMA_{40}$[b]	80.0	15.2	12.7	16.0	1.25
PDMS-*b*-$PDMAEMA_{60}$	60.0	16.8	15.6	18.7	1.20
PDMS-*b*-$PDMAEMA_{80}$	56.0	20.1	18.9	23.0	1.22
PDMS-*b*-$PDMAEMA_{100}$	72.8	23.5	23.7	28.0	1.18

[a] Each sample of the block copolymers contained approximately 15 repeat units of HEMA estimated by ^{1}H NMR for crosslinking.
[b] Subscripts represented the numbers of repeat units for PDMAEMA estimated by ^{1}H NMR.