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Poly[(mercaptopropyl)methylsiloxane] (PMMS)-based antibacterial polymer coatings prepared by a two-step sequential thiol–ene click chemistry

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ABSTRACT

Poly[(mercaptopropyl)methylsiloxane] (PMMS)-based antibacterial polymer coatings have been prepared through a two-step sequential thiol–ene click chemistry utilizing 1-allyl-3-decylimidazolium bromide (ADIm) as antibacterial monomer and triallyl cyanurate (TAC) as the crosslinker. These films with different content of ADIm were characterized by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and pencil hardness. It was found that the mechanical and thermal properties of these films were largely influenced by the content of ADIm in the films. Films with imidazolium bromide groups displayed excellent antimicrobial activity against *Staphylococcus aureus* with 100% killing efficiency.

1. Introduction

Microorganisms are prevalent on surfaces that we touch everyday. Infections caused by these small organisms result in significant morbidity and, in some cases, mortality [1]. Recently, there has been much effort to overcome such infections by preparing bactericidal materials based on antibiotics [2,3], silver nanoparticles [4], phenols [5] and peptides [6]. However, such approach has some fundamental flaws such as loss of antibacterial chemicals and possibility of drug resistance in pathogens through mutation [7]. Therefore, it is desirable to design new antibacterial materials and methods to eliminate the issues associated with uncontrolled release of biocides. Chemical binding of antibacterial monomers to polymer chains has been carried out to prevent antimicrobial ingredients from leaching [8–13]. However, the preparation of these polymers require complicated design and cumbersome procedures. There is an urgent need for a more convenient method to prepare antibacterial polymers.

UV photopolymerization is a feasible industrial process with applications ranging widely from polymeric coatings to inks and adhesives [14,15]. Recently, thiol–ene photopolymerizable systems are gaining popularity in both academic research and industrial applications, because they possess all the desirable traits of a "click" reaction with short reaction times, wide functional group and solvent tolerance, few to no byproducts [16]. The thiol–ene UV curable coatings are based on a mixture of multifunctional thiols and multifunctional enes. This polymerization process occurs through well-known radical intermediates that involve a free-radical addition followed by a chain transfer reaction [17]. Furthermore, these cross-linked networks are characterized by advantages such as lower film stress, relatively narrow glass transitions, low shrinkage, reduced oxygen inhibition and relatively high functional group conversion compared with those made by acrylic cross-linkers [18].

Poly[(mercaptopropyl)methylsiloxane] (PMMS) with multifunctional enes is suitable for the thiol–ene systems [19]. As for antibacterial agents, some imidazolium salts with long alkyl chains are known to have high antimicrobial properties and are widely used as disinfectants [20]. In this work, we present a facile protocol to prepare PMMS-based antibacterial polymer coatings *via* a two-step sequential thiol–ene click chemistry. As shown in Scheme 1,

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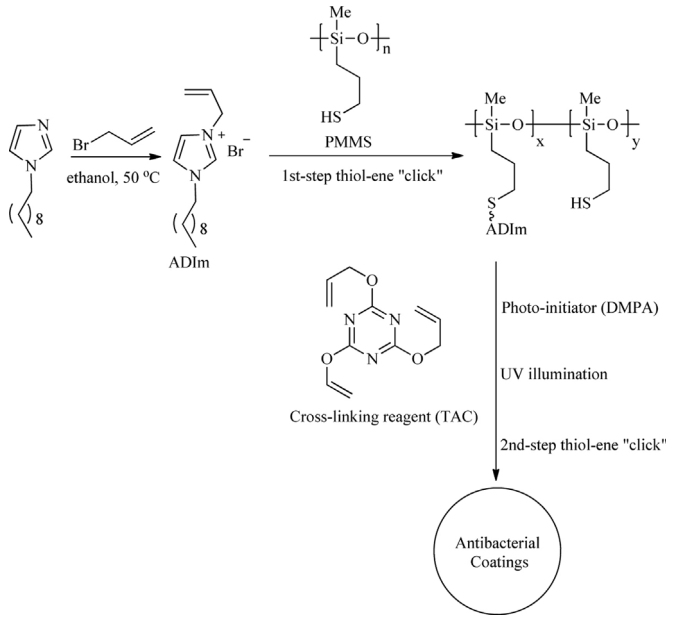

Scheme 1. Polysiloxane-based antibacterial polymer coatings prepared by a two-step sequential thiol–ene click chemistry protocol.

by controlling the molar ratio of PMMS and antibacterial monomer, PMMS-based antibacterial polymers can be partially functionalized in the first-step thiol–ene click process. After then the leaving spare mercapto groups were used as cross-linking sites to form networks in the second-step thiol–ene click process.

2. Experimental

Unless otherwise noted, ACS reagent grade chemicals and solvents were purchased from commercial vendors and used without further purification. Poly(mercaptomethyl)siloxane (PMMS, SMS-992) was purchased from Gelest Inc. Triallyl cyanurate (TAC, 99%), deuterated solvents for NMR and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%) were purchased from (J&K). ^{1}H NMR spectra were recorded in DMSO-d_6 (J&K) using TMS as internal standard on a Agilent 400 MHz. The NMR spectra were analyzed and processed using MestReNova-6.1.1-6384 software. Thermogravimetric analysis (TGA) was performed under a controlled atmosphere of N_2 with a Mettler TGA/DSC 1 instrument between 25 °C and 600 °C at a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) was performed using a TA Instruments Q800 dynamic mechanical analyzer in tension film mode equipped with a gas cooling accessory. Samples were heated from −80 °C to 140 °C for the samples at a ramp rate of 3 °C/min. Pencil hardness was evaluated on photocured films according to the standard test method GB/T 6739-2006. Contact angles (θ) were obtained with a VCA Optima contact angle measuring instrument (AST Products, Inc.) with a drop size of 1.0 μL of deionized water. The θ values were determined five times for a reliable average value.

2.1. Synthesis of 1-allyl-3-decylimidazolium bromide

1-Decylimidazole was synthesized according to previous literature [21]. 1-Decylimidazole (5.49 g, 26.3 mmol) and 3-bromopropene (3.1 g, 26.3 mmol) were added to a 100 mL round-bottom flask containing 30 mL ethanol with condenser. The reaction mixture was stirred for 24 h. Solvent was then removed under reduced pressure. The crude product was washed three times with ether and dried in a vacuum oven at 50 °C for 24 h to give the 1-allyl-3-decylimidazolium bromide (ADIm).

1-Allyl-3-decylimidazolium bromide: This compound was obtained in 97% as a yellow viscous oil. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.30 (s, 1H, –N–CH–N–), 7.87 (s, 1H, –N–CH–CH–N–), 7.78 (s, 1H, –N–CH–CH–N–), 6.07 (m, 1H, –CH=CH$_2$), 5.32 (dd, 2H, =CH$_2$), 4.87 (d, 2H, –CH$_2$–CH=CH$_2$), 4.19 (t, 2H, –N–CH$_2$–), 1.79 (m, 2H, –CH$_2$–CH$_2$–), 1.24 (broad, 14H, –CH$_2$–CH$_3$), 0.85 (t, 3H, –CH$_3$).

2.2. Synthesis of polymers

Typical procedure was used to prepare PMMS$_x$-*g*-ADIm: ADIm (613 mg, 1.86 mmol), PMMS (500 mg, 3.72 mmol-SH) and DMPA (0.05 equiv. to each-ene moiety, 24 mg, 0.094 mmol) dissolving in DMF (50 μL) were added into a Schlenk-type flask. The flask was purged with dry argon for about 3 min and then exposed to the hand-held UV-lamp (λ_{exc} = 365 nm) for 30 min. These reactions were monitored by ^{1}H NMR spectroscopy and were used without further purification for the preparation of crosslinked films. Relative content of PMMS and ADIm were listed in Table 1.

PMMS$_{10}$-*g*-ADIm: ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.30 (s, 1H, –N–CH–N–), 7.80 (s, 2H, –N–CH–CH–N–), 4.23 (d, 2H, –N–CH$_2$–), 4.14 (d, 2H, –N–CH$_2$–CH$_2$), 2.44 (m, 22H, –CH$_2$–S–CH$_2$–, HS–CH$_2$–), 2.13 (s, 8H, –SH), 2.04 (m, 2H, –N–CH$_2$–), 1.76 (m, 2H, –N–CH$_2$–CH$_2$–), 1.55 (s, 20H, ≡Si–CH$_2$–CH$_2$–), 1.20 (s, 14H, –CH$_2$–CH$_3$), 0.82 (t, 3H, –CH$_3$), 0.58 (s, 20H, ≡Si–CH$_2$–), 0.05 (s, 30H, ≡Si–CH$_3$).

PMMS$_{25}$-*g*-ADIm: ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.28 (s, 1H, –N–CH–N–), 7.80 (s, 2H, –N–CH–CH–N–), 4.22 (d, 2H, –N–CH$_2$–), 4.13 (d, 2H, –N–CH$_2$–CH$_2$), 2.45 (m, 10H, –CH$_2$–S–CH$_2$–, HS–CH$_2$–), 2.17 (s, 3H, –SH), 2.03 (m, 2H, –N–CH$_2$–), 1.76 (m, 2H, –N–CH$_2$–CH$_2$–), 1.55 (s, 8H, ≡Si–CH$_2$–CH$_2$–), 1.20 (s, 14H, –CH$_2$–CH$_3$), 0.82 (t, 3H, –CH$_3$), 0.57 (s, 8H, ≡Si–CH$_2$–), 0.05 (s, 12H, ≡Si–CH$_3$).

PMMS$_{50}$-*g*-ADIm: ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.31 (s, 1H, –N–CH–N–), 7.81 (s, 2H, –N–CH–CH–N–), 4.23 (d, 2H, –N–CH$_2$–), 4.15 (d, 2H, –N–CH$_2$–CH$_2$), 2.45 (m, 6H, –CH$_2$–S–CH$_2$–, HS–CH$_2$–), 2.19 (s, 1H, –SH), 2.03 (m, 2H, –N–CH$_2$–), 1.76 (m, 2H, –N–CH$_2$–CH$_2$–), 1.52 (s, 4H, ≡Si–CH$_2$–CH$_2$–), 1.20 (s, 14H, –CH$_2$–CH$_3$), 0.82 (t, 3H, –CH$_3$), 0.57 (s, 4H, ≡Si–CH$_2$–), 0.04 (s, 6H, ≡Si–CH$_3$).

2.3. Preparation of antibacterial polymer coatings via thiol–ene click photopolymerization

For practical photocuring, triallyl cyanurate (TAC) was added to the above PMMS$_x$-*g*-ADIm while maintaining a one-to-one ratio of thiol to alkene. Relative content of PMMS$_x$-*g*-ADIm and TAC were listed in Table 1. DMPA was incorporated at 0.1 wt% as a photoinitiator. DMPA was dissolved using a small amount (no more than 200 μL) of *N*,*N*′-dimethyl formamide (DMF) and then added into the thiol–ene formulations. After mixing thoroughly, the resins were coated onto a round glass pane by means of a film applicator and then irradiated under a 365 nm lamp (intensity, 160 mW/cm^2) for 3 min in ambient conditions to get transparent photocured films with a usual size of 22 mm in diameter and ~100 μm in thickness. The cross-linked samples were soaked in deionized water for 24 h to remove residual DMF and dried in vacuum at 50 °C for 24 h.

Table 1
Antibacterial films prepared from different proportion of components.

Film	PMMS (mg)	ADIm (mg)	PMMS$_x$-*g*-ADIm[a]	TAC (μL)
Film-1	500	0	PMMS$_0$-*g*-ADIm	279
Film-2	500	123	PMMS$_{10}$-*g*-ADIm	251
Film-3	500	307	PMMS$_{25}$-*g*-ADIm	209
Film-4	500	613	PMMS$_{50}$-*g*-ADIm	139

[a] PMMS$_x$-*g*-ADIm represents a polymer with *x*% of mercapto groups of PMMS having been grafted with ADIm.