



## Original article

# Facile preparation of antibacterial polymer coatings via thiol-yne click photopolymerization



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## ARTICLE INFO

## Article history:

Received 6 August 2015

Received in revised form 23 December 2015

Accepted 29 December 2015

Available online 8 January 2016

## Keywords:

Antibacterial polymer

Thiol-yne

Click chemistry

UV-curing

Coatings

## ABSTRACT

Novel antibacterial polymer coatings were prepared by a facile thiol-yne click photopolymerization of 1-propargyl-3-alkyl-1,3-diazanyl-2,4-cyclopentadiene bromide ([PAIM]Br) and tetra(3-mercaptopropionate)pentaerythritol (PETMP) (2:1 molar ratio) using 2,2-dimethoxy-2-phenylacetophenone (DMPA) as initiator. The antibacterial activity of the coatings was tested against *Staphylococcus aureus* (ATCC 292130) and *Escherichia coli* (ATCC 25922) by the dynamic shake method. The evaluation results revealed the antibacterial polymer coatings exhibited excellent inhibitory activity against *S. aureus* and *E. coli*, especially for *S. aureus*.

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## 1. Introduction

Infection caused by pathogenic microorganisms on material surfaces has been a long-term problem for public health. Using antibacterial polymer coatings to protect material surfaces is an effective antibacterial method [1,2]. In recent years, antibacterial polymers with biocidal groups covalently bonded to their chains have attracted a tremendous amount of attention due to their advantages with reduced residual toxicity, increased efficiency and selectivity, and prolonged active lifetime [3]. However, most antibacterial polymers that include quaternary ammonium [4], phosphonium salts [5], *N*-alkylimidazolium [6] or *N*-alkylpyridinium [7] as pendant groups to the polymer chain exist in the form of chain and require complicated design and application procedures. In order to achieve certain potentially practical applications, it is necessary to process the polymers into films [8]. The reaction of thiol-yne belongs to the click reaction family [9,10], which possesses remarkable advantages, such as mild reaction conditions, high reaction rate, functionality tolerance and atom economy [11]. Furthermore, it has also the additional feature that two thiol groups could react with one ethynyl group via a well-known two-step processes [12]. These advantages of thiol-yne

click reaction make it promising to prepare functional polymers with unique properties [13]. In addition, UV-curing is an important technique in the field of coatings for its advantages such as high-speed processing, low energy consumption, and environmental friendliness by avoiding solvent exposure [14,15]. In view of the above mentioned merits and in continuation of our research [16], we report here the novel preparation of antibacterial polymer coatings by utilization of thiol-yne click photopolymerization. Exposure time of UV-curing reaction is determined by FT-IR and FT-ATR spectra. The thermomechanical properties and thermal stability of these films are characterized by DMA and TGA. The glass-transition temperatures ( $T_g$ ) and antibacterial properties are discussed.

## 2. Experimental

All chemicals were purchased from commercial vendors and were used as received without further purification unless otherwise mentioned. <sup>1</sup>H NMR spectra were recorded in DMSO-*d*<sub>6</sub> (J&K) using TMS as internal standard on an Agilent 400 MHz. The NMR spectra were analyzed and processed using MestReNova-6.1.1-6384 software. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer using KBr window and performed at room temperature. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded on a Thermo Nicolet IR 100 spectrometer with

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a diamond ATR crystal. 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. A TA Instruments Q2000 DSC equipped with a liquid nitrogen cooling accessory was used to investigate the glass transition temperature ( $T_g$ ) of film samples between 8 mg and 12 mg. The midpoint value of the glass transition was reported after three heating and cooling cycles at 10 °C/min. Dynamic mechanical properties were evaluated using a TA Instruments Q800 DMA with a frequency of 1 Hz, strain rate of 0.05%, and heating rate of 3 °C/min.  $T_g$  values were taken as the midpoint from DSC scans and as the peak maximum in  $\tan \delta$  plots from DMA.

### 2.1. Synthesis of *N*-alkyl derivatized yne monomers **3a–d**

*N*-alkyl derivatized yne monomers were synthesized via the quaternization reaction represented in Scheme 1. Alkyl imidazoles **2a–d** were prepared following the method in literature with modifications [17]. An example synthesis procedure for **3a** is given as follows. 1-Hexylimidazole **2a** and 3-bromopropyne (mole ratio 1:1) were added to anhydrous ethanol. The synthesis was carried out in a round bottom flask equipped with a stirrer and a condenser at 50 °C for 24 h. Then, solvent was removed using a rotary evaporator. The crude product was washed three times with ether and dried in a vacuum oven at 50 °C for one day to obtain yne monomer **3a**. This same procedure was used to synthesize modified yne monomers **3b–d**.

1-Propargyl-3-hexyl-1,3-diazany-2,4-cyclopentadiene bromide ([PHIM]Br) **3a**: This compound was obtained in 90% as a white solid, m.p. 91–92 °C.  $^1H$ -NMR (DMSO- $d_6$ , 400 MHz, Fig. S1 in Supporting information):  $\delta$  9.41 (s, 1H, –N–CH–N–), 7.91 (s, 1H, –N–CH–CH–N–), 7.87 (s, 1H, –N–CH–CH–N–), 5.26 (d, 2H, –CH<sub>2</sub>–C $\equiv$ ), 4.23 (t, 2H, –CH<sub>2</sub>–N–), 3.88 (s, 1H,  $\equiv$ CH), 1.80 (m, 2H, –CH<sub>2</sub>–CH<sub>2</sub>–), 1.27 (broad, 6H, –CH<sub>2</sub>–CH<sub>3</sub>), 0.86 (t, 3H, –CH<sub>3</sub>).

1-Propargyl-3-octyl-1,3-diazany-2,4-cyclopentadiene bromide ([POIM]Br) **3b**: This compound was obtained in 92% as a yellow viscous oil.  $^1H$ -NMR (DMSO- $d_6$ , 400 MHz, Fig. S2 in Supporting information):  $\delta$  9.41 (s, 1H, –N–CH–N–), 7.91 (s, 1H, –N–CH–CH–N–), 7.87 (s, 1H, –N–CH–CH–N–), 5.26 (d, 2H, –CH<sub>2</sub>–C $\equiv$ ), 4.23 (t, 2H, –CH<sub>2</sub>–N–), 3.88 (s, 1H,  $\equiv$ CH), 1.80 (m, 2H, –CH<sub>2</sub>–CH<sub>2</sub>–), 1.25 (broad, 6H, –CH<sub>2</sub>–CH<sub>3</sub>), 0.86 (t, 3H, –CH<sub>3</sub>).

1-Propargyl-3-decyl-1,3-diazany-2,4-cyclopentadiene bromide ([PDIM]Br) **3c**: This compound was obtained in 88% as a slight yellow solid, m.p. 54–55 °C.  $^1H$ -NMR (DMSO- $d_6$ , 400 MHz, Fig. S3 in Supporting information):  $\delta$  9.40 (s, 1H, –N–CH–N–), 7.90 (s, 1H, –N–CH–CH–N–), 7.86 (s, 1H, –N–CH–CH–N–), 5.25 (d, 2H, –CH<sub>2</sub>–C $\equiv$ ), 4.22 (t, 2H, –CH<sub>2</sub>–N–), 3.87 (s, 1H,  $\equiv$ CH), 1.79 (m, 2H, –CH<sub>2</sub>–CH<sub>2</sub>–), 1.24 (broad, 6H, –CH<sub>2</sub>–CH<sub>3</sub>), 0.86 (t, 3H, –CH<sub>3</sub>).

1-Propargyl-3-dodecyl-1,3-diazany-2,4-cyclopentadiene bromide ([PDODIM]Br) **3d**: This compound was obtained in 86% as a white solid, m.p. 80–81 °C.  $^1H$ -NMR (DMSO- $d_6$ , 400 MHz, Fig. S4 in

Supporting information):  $\delta$  9.37 (s, 1H, –N–CH–N–), 7.89 (s, 1H, –N–CH–CH–N–), 7.85 (s, 1H, –N–CH–CH–N–), 5.24 (d, 2H, –CH<sub>2</sub>–C $\equiv$ ), 4.21 (t, 2H, –CH<sub>2</sub>–N–), 3.87 (s, 1H,  $\equiv$ CH), 1.79 (m, 2H, –CH<sub>2</sub>–CH<sub>2</sub>–), 1.24 (broad, 6H, –CH<sub>2</sub>–CH<sub>3</sub>), 0.86 (t, 3H, –CH<sub>3</sub>).

### 2.2. Preparation of antibacterial polymer coatings via thiol-yne click photopolymerization

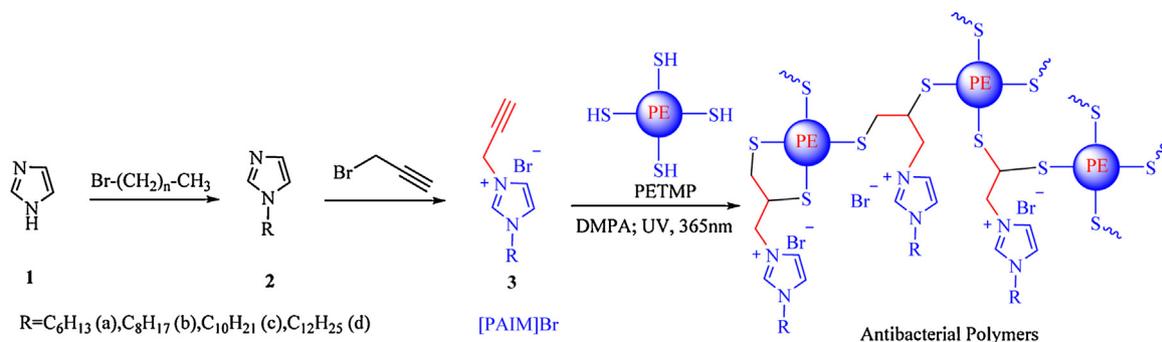
All of the *N*-alkyl derivatized yne monomers were readily miscible in PETMP thiol monomer (2:1 molar ratio) with DMF and mild sonication, resulting in optically clear, homogeneous liquid mixtures. Then 2,2-dimethoxy-2-phenylacetophenone (DMPA) (0.05 eq. to each thiol moiety) as initiator dissolved in DMF was added to the above mixtures, followed by mild sonication. The thiol-yne formulations were coated onto a round glass pane by means of a film applicator and then irradiated on a conveyor exposure to give pale yellow and transparent photocured films with a usual diameter of 22 mm and thickness of 20–35  $\mu$ m. The conveyor UV-curing system employed was an Exposure Model RW-UVAT201-20 (RunWing Co., Ltd., Shenzhen, China) equipped with a 2 kW Hg-lamp, and the applied conveyor speed was 3 m/min for 20 s exposure in one run. The resulting cross-linked samples were soaked in deionized water for 24 h to remove DMF and trace amount of residual monomer from the networks and dried in a vacuum oven at 37 °C.

## 3. Results and discussion

Appropriate exposure time for the UV-curing reaction can be determined by tracking the infrared characteristic absorption peak of sulphur and alkynyl (Fig. S5 in Supporting information). The characteristic peak of thiol and alkynyl appeared in 2557  $cm^{-1}$  and 2125  $cm^{-1}$ , respectively. With increasing exposure time, the characteristic peak of thiol and alkynyl decreases. Photopolymerization is almost finished within 100 s. The Fourier transform attenuated total reflection infrared spectrometry (FT-ATR) characterization of four antimicrobial films also confirm that the characteristic peak of thiol and alkynyl (with a dotted box around it) vanish completely within 100 s of irradiation (Fig. 1).

Thermogravimetric analysis (TGA) was used to characterize the thermal stability of the thiol-yne networks. Fig. 2 shows the TGA thermograms for the thiol-yne networks as a function of alkyl chain length. All four antibacterial films with different alkyl chain lengths showed parallel thermogravimetric curves. These polymers have a small amount of weight loss before 200 °C, which may be caused by the residual water in the polymer. Besides, the initial onset of degradation for the thiol-yne networks was observed around 250 °C, which is higher than antibacterial polymers containing quaternary ammonium [18,19].

Experimental DSC scans are provided in Fig. S6 in Supporting information and experimental DMA  $\tan \delta$  and storage modulus ( $E'$ )



Scheme 1. Synthetic route of antibacterial polymer coatings.

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