



## Photo-responsive membrane surface: Switching from bactericidal to bacteria-resistant property

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### ARTICLE INFO

#### Keywords:

Photo-responsive membrane surface  
ATRP  
Click chemistry  
Antibacterial adhesion  
Antifouling

### ABSTRACT

In this paper, a photo-responsive bactericidal and bacteria-resistant membrane was successfully prepared via the integration of atom transfer radical polymerization (ATRP) and click chemistry. *Azide*-functionalized polycationic poly (*N*, *N*-dimethyl-*N*-(2-(methacryloyloxy)ethyl)-*N*-((2-nitrobenzyl)oxy)-2-oxoethanaminium bromide) (PDMAEMA-NBE) was synthesized by ATRP. Then, the PDMAEMA-NBE was clicked on *alkynyl*-functionalized polyethersulfone (PES) membrane surface, and proved by X-ray photoelectron spectrometer (XPS). Upon UV irradiation, the polycationic surface would switch to polyzwitterionic one. Before and after the irradiation, the zeta potentials of the surface altered from +14.7 to −3.8 mV, and the water contact angle decreased from 64.0° to 52.7°. The polycationic surface exhibited excellent bactericidal property and the dead bacteria could detach from the polyzwitterionic surface induced by the subsequent UV irradiation. It demonstrated that the designing of photo-responsive membrane surface could be a new strategy for antibacterial adhesion.

### 1. Introduction

Nowadays, porous membranes are widely applied for many separation technologies such as water purification and hemodialysis [1,2]. However, membrane fouling and the associated decrease of flux result in the operational cost and deteriorate the stable performance of membrane filtration system. Especially, the formation of bacterial biofilms on membrane surface is a major problem to cause adverse effects on membrane application [1,3,4]. The bacterial biofilms are generated by bacterial attachment and the subsequent colonization on membrane surface [5,6]. Therefore, to develop antibacterial membranes has attracted increasing attention. Meanwhile, many studies have focused on two major types of antibacterial surfaces: bactericidal surface (surface for killing attached bacterial) and bacteria-resistant surface (surface for preventing the attachment of bacteria) [7–16]. However, both of them have their own inherent disadvantages. The bactericidal surface would still be fouled by the remained dead bacteria, which may provide nutrients for other colonizers; while the bacteria-resistant surface cannot completely prevent microbial fouling [17]. Therefore, an ideal antibacterial surface should integrate the advantages of these two strategies. It means killing the attached bacteria at the initial bacterial attachment and subsequently removing the dead bacteria. Undoubtedly, building smart surface is an effective route to

achieve the dual-functional surface. Some efforts have been attempted on the integration of dual-functional antibacterial surface via smart surface preparation [18]. Yu et al. designed a kind of switchable bioactivity silicon wafer which combined thermo-responsive poly(*N*-isopropylacrylamide) (PNIPAAm) brushes and surface bioactivity to achieve dual-functional surface [19,20]. In our previous study [21], thermo-responsive polymer was successfully anchored on silicon wafer for killing and detaching bacteria via host-guest self-assembly. These investigations were based on the conformational changes of the PNIPAAm brushes under thermal stimulus. Meanwhile, Jiang et al. have done many works based on the cationic-zwitterionic transformation surface via pH stimulus [22–24].

Recently, photo-responsive materials have been reported and applied to construct smart materials or surface due to their advantages (clean, facile and noninvasive) [25–27]. To prepare a photo-responsive surface, incorporating responsive groups into polymer is a common way. As a photo-responsive moiety, the *O*-nitrobenzyl (ONB) group was initially used as a protecting group to improve the yield in organic reactions [28,29]. Recently, its photo-cleavage behavior has been leveraged as a key component to develop optically responsive smart surfaces [25,30–32]. Gungor and Armani developed a photo-cleavable smart surface via integrating the *O*-nitrobenzyl ester into a copolymer at the junction point between poly(ethylene oxide) (PEO) and

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polystyrene (PS) chains [25]. The smart surface would remove PEO but remain the PS layer once the surface was exposed to UV irradiation. Meanwhile, Kasek and co-workers synthesized poly(*N,N*-dimethyl-*N*-[3-(methacroylamino)propyl]-*N*-[2-[(2-nitrophenyl)methoxy]-2-oxoethyl]ammonium chloride) and the subsequent quaternization with *O*-nitrobenzyl 2-chloroacetate [33]. Under UV-irradiation, the cationic polymer could turn into a zwitterionic form. Unfortunately, no study has been reported on dual-functional membrane surface with anti-bacterial and dead bacteria resistance properties via the photo-response yet. Herein, we attempt to construct a photo-responsive membrane surface which can achieve anti-bacterial and anti-fouling properties before and after UV irradiation, respectively.

Recent years, numerous methods have been applied to improve material surface properties including blending, in situ polymerization/copolymerization, surface coating, ATRP, reversible addition-fragmentation chain transfer polymerization (RAFT), click chemistry, layer-by-layer assembly and so on [18,34–42]. The ATRP technique is widely used in polymer synthesis due to its good control over molecular weight and distribution. Meanwhile, more and more investigations have been focused on integrating the ATRP with click chemistry (especially azide-alkyne cycloaddition) to prepare desired polymeric surfaces, since the ATRP products can be easily post-functionalized with sodium azide. Also, click chemistry is an efficient, good selectivity and high yield reaction [39,43,44]. It has been reported that silica nanoparticles, gold substrate, and polysulfone membrane surface have been successfully modified by combing ATRP and click chemistry [39,45,46].

Herein, a facile method was proposed to click photo-responsive functional polymers onto polyethersulfone (PES) membranes surface. As show in Scheme 1, we firstly prepared epoxy group decorated PES membrane, and then introduced 2-propynylamine via the ring-opening reaction [47,48]. Meanwhile, azido-functionalized polymers were synthesized via ATRP and subsequently post-treated with sodium azide. After that, polycationic were grafted onto the membrane surface through click chemistry to get charged surface. This surface would achieve the alteration of surface hydrophilicity and surface charge under UV irradiation. The protein fouling resistance and anti-bacterial properties of the membrane were investigated. Furthermore, the dead bacteria detaching was investigated. Thus, the aim to develop dual-functional PES membranes was achieved.

## 2. Experimental section

### 2.1. Chemicals

Polyethersulfone (PES, Ultrason E6020P, BASF), 2-propynylamine (99%, Best), glycidyl methacrylate (GMA, 97%, Aladdin), methyl

iodide, ( $\text{CH}_3\text{I}$ , 99%, Aladdin), azoisobutyronitrile (AIBN, 99%, Aladdin), 2-nitrobenzyl alcohol (98%, Best), *N,N*-methylenebisacrylamide (MBA, 97%, Aladdin), 2-(dimethylamino) ethyl methacrylate (DMAEMA, 99%, Best), sodium ascorbate (99%, Aladdin), bromoacetyl bromide (98%, Best), sodium dodecyl sulfate (99%, Aladdin), bovine fibrinogen (BFG, Sigma), bovine serum albumin (BSA, Aladdin), LIVE/DEAD BacLight Bacterial Viability Kit L-7012 (Thermo Co.) and Micro BCA™ protein assay reagent kits (PIERCE) were used as received. Other chemical reagents were purchased from Kelong Chemical Reagent Co., Ltd. (Chengdu, China) Deionized (DI) water was used throughout this study.

### 2.2. Synthesis of PDMAEMA-NBE

#### 2.2.1. Synthesis of *O*-nitrobenzyl 2-bromoacetate

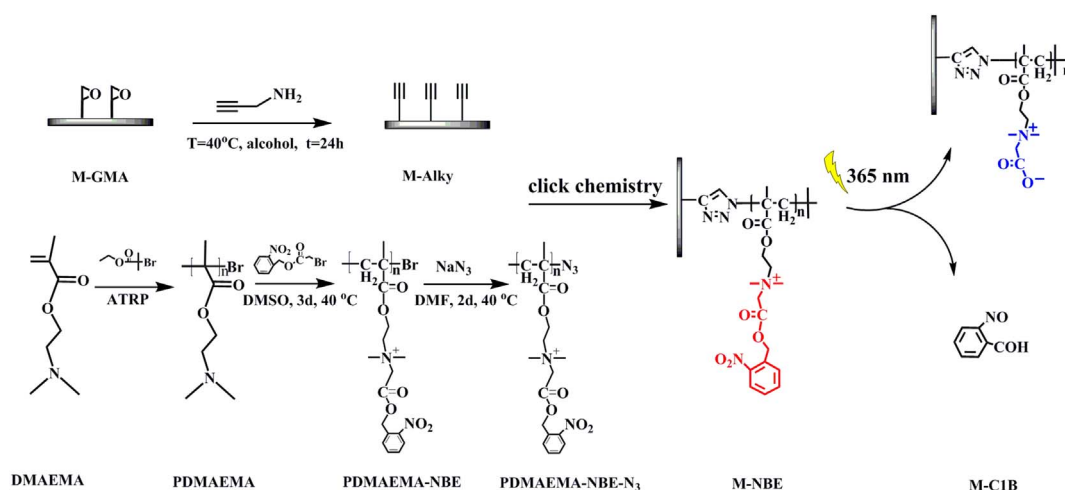
*O*-nitrobenzyl 2-bromoacetate was synthesized by reacting *O*-nitrobenzyl alcohol (4.6 g, 30 mmol) with bromoacetyl bromide (5.2 mL, 60 mmol) in the presence of triethylamine (8.4 mL) in dichloromethane (150 mL) at 0 °C for 24 h [30]. The mixture was filtered and the solvent was evaporated by using a rotating vacuum evaporator. Then, the obtained crude product was purified by silica gel chromatography.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 3.92 (s, 2H), 5.53 (s, 2H), 7.48 (m, 1H), 7.63 (m, 2H), 8.09 (m, 1H).

#### 2.2.2. Preparation of poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA)

Typically, ethyl 2-bromoisobutyrate (64  $\mu\text{L}$ , 0.44 mmol), DMAEMA (4.74 mL, 28 mmol), HMTETA (118  $\mu\text{L}$ , 0.44 mmol), CuBr (63.2 mg, 0.44 mmol) and methanol (20 mL) were separately added into a flask. The polymerization was carried out at 30 °C and terminated after 12 h. The product was purified by dialyzed against water for three days and dried by lyophilization. The product was named as PDMAEMA.

PDMAEMA (1 g) and *O*-nitrobenzyl 2-bromoacetate (2 g) were dissolved in DMSO (20 mL). The reaction was carried out at 40 °C for three days. Then, the mixture was precipitated in acetone and dried in a vacuum oven. The obtained product was named as PDMAEMA-NBE and protected from light to avoid unintentional degradation. Meanwhile, the PDMAEMA was quaternized using  $\text{CH}_3\text{I}$ . In a typical procedure, the PDMAEMA (1 g) was dissolved in DMSO; then,  $\text{CH}_3\text{I}$  (2.72 g) was added into and reacted at 40 °C for 48 h. The mixture was precipitated in acetone and dried in a vacuum oven. The resulting quaternized polymer was named as PDMAEMA-Q.

Excess amount of sodium azide (10–40 fold molar excess compared to bromoterminal) is used for chain end azidation [49–51]. In the study, PDMAEMA-NBE was dissolved in a 1/1 v/v % water/DMF mixed solvent (10 mL) with  $\text{NaN}_3$  in a 20-fold molar excess in a round-bottom



Scheme 1. Illustration of preparing photo-responsive membrane surface.

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