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Antibacterial effect of surface-functionalized polypropylene hollow fiber membrane from surface-initiated atom transfer radical polymerization

Fang Yao[a], Guo-Dong Fu[a,*], Junpeng Zhao[b], En-Tang Kang[b,*], Koon Gee Neoh[b]

[a] *School of Chemistry and Chemical Engineering, Southeast University, Jiangning District, Nanjing, Jiangsu 211189, PR China*
[b] *Department of Chemical & Biomolecular Engineering, National University of Singapore, Kent Ridge 119260, Singapore*

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ABSTRACT

Microporous polypropylene (PP) hollow fiber (PPHF) membranes with surface-grafted block copolymer brushes of poly(ethylene glycol) monomethacrylate (PEGMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) (PPHF-*g*-(PPEGMA-*b*-PDMAEMA)) were prepared via consecutive surface-initiated atom transfer radical polymerization (ATRP). The effective pore size of the surface modified PPHF membranes could be adjusted by controlling the graft chain length, or the ATRP time. Quaternization of the tertiary amine groups of the PDMAEMA block with 1-bromododecane gave rise to a high concentration of quaternary amine salt (QAS) on the PPHF membrane surface. The antibacterial effect of the quaternized PPHF-*g*-(PPEGMA-*b*-PDMAEMA) membrane was assayed with *Escherichia coli* (*E. coli*, a Gram-negative bacterium) and *Staphylococcus aureus* (*S. aureus*, a Gram-positive bacterium) cultures. In addition to bactericidal properties, the functionalized membrane surface also exhibited anti-fouling effect for bacteria due to the hydrophilic nature of the P(PEGMA) block on the PPHF-*g*-(PPEGMA-*b*-PDMAEMA) membrane. The permanence of antibacterial effect of the functionalized PPHF membrane was also demonstrated in repeated applications of the quaternized PPHF-*g*-(P(PEGMA)-*b*-PDMAEMA) membrane.

1. Introduction

Microporous polypropylene (PP) hollow fiber (PPHF) membranes have been widely used in microfiltration and ultrafiltration process for water treatment, food processing and separation of pharmaceutical products because of their good mechanical properties, good chemical resistance, good thermal stability, high surface areas and low cost [1,2]. Surface modification is a good approach to functionalize materials without affecting their bulk properties [3–5]. To improve the antifouling properties of PPHF membrane surface, methods including chemical treatment [6,7], plasma deposition [8–12], UV-induced surface graft polymerization [13–15], high energy irradiation [16,17], and ozone-induced surface graft polymerization [18,19] have been employed to reduce the membrane fouling. Surface fouling is a main obstacle for the application of PPHF membranes in bioreactors for wastewater treatment [20–23].

PPHF membranes are potentially useful biomedical devices such as artificial lung (blood oxygenation) and artificial kidney (hemodialysis) [24]. Colonization of bacteria on the surface of biomaterials and subsequent infectious complications are common causes of the failure in many biomedical devices [25]. Cationic polymers with quaternary ammonium or biguanide groups exhibit good antimicrobial activities [26]. Introduction of cationic polymers on the surface of materials can thus confer the materials with antimicrobial properties [25,27,28]. Polymers containing quaternary ammonium groups have been immobilized on various substrates, such as glass beads [29], polymeric beads [30,31] and polymeric fibers [32–35]. An antibacterial surface of PPHF membranes not only makes them potentially useful in biomedical field, but also extend their application in water treatment. The fouling of PPHF can be partially attributed to the adsorption of organic species and adhesion of microbial cells [12]. PPHF membranes with an antibacterial and hydrophilic surface can kill the bacteria, largely restrain the growth of microbe, and reduce the membrane fouling, which makes them very attractive in water treatment.

Recent progress in controlled living radical polymerization, especially in atom transfer radical polymerization (ATRP), has provided a powerful tool for preparing nearly monodispersed polymers with controlled molecular weights [36–38]. Well-defined and multi-functional polymer brushes can also be prepared via ATRP [39,40]. PPHF membrane with surface-grafted polymer brushes of well-defined nature and multi-functionality, will be of interest to academic research and practical applications alike. However, the difficulty in immobilization ATRP initiators on PPHF membrane surfaces, because of the saturated hydrocarbon molec-

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* Corresponding authors. Tel.: +86 25 52090625; fax: +86 25 52090621.
E-mail address: fu7352@seu.edu.cn (G.-D. Fu).

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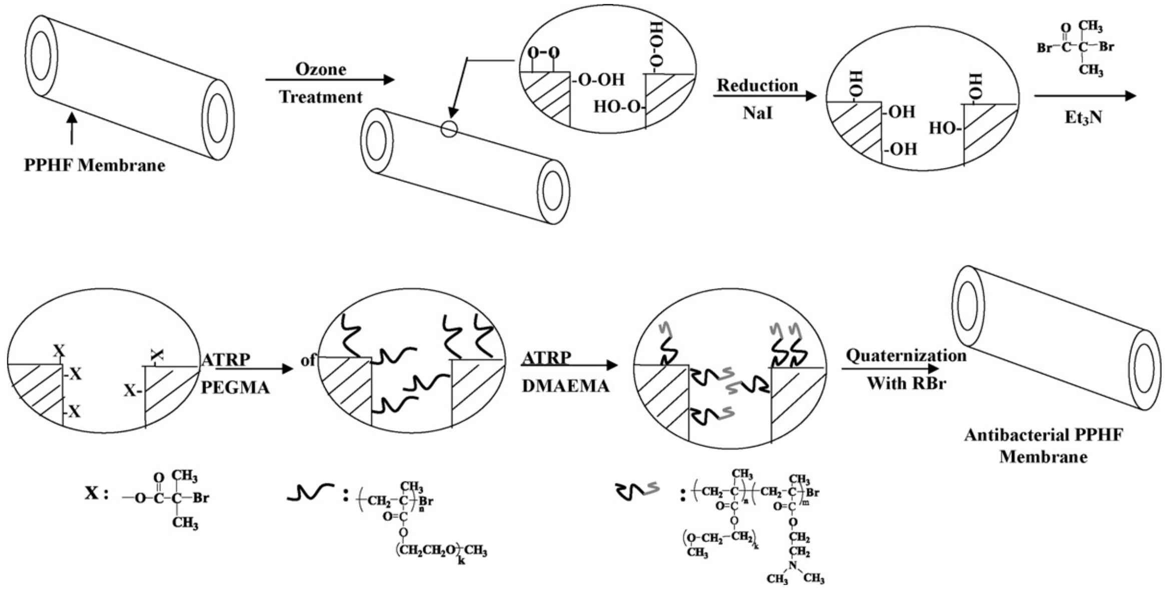

Fig. 1. Schematic illustration of the process of preparing polypropylene hollow fiber membrane with well-defined block copolymer brushes and antibacterial properties.

ular structure of PP, has hindered the preparation of functional PPHF membrane by the ATRP method. In the present work, PPHF membranes with covalently tethered and well-defined block copolymer brushes of poly(ethylene glycol) monomethacrylate (PEGMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) (PPHF-*g*-(PPEGMA-*b*-PDMAEMA)) have been prepared via surface-initiated ATRP. The procedures are shown schematically in Fig. 1. Initially, organic peroxide species were introduced onto the PPHF membrane surface via ozone pretreatment. After conversion of the peroxide groups into hydroxyl groups, ATRP initiators were immobilized onto the PPHF membrane surface via reaction of the hydroxyl groups and acryl bromide. Consecutive surface-initiated ATRPs of PEGMA and DMAEMA, and subsequent quaternization of the tertiary amine groups with alkyl bromide produce the PPHF-*g*-(PPEGMA-*b*-PDMAEMA) membrane with well-defined block copolymer brusher with good antimicrobial properties.

2. Materials and methods

2.1. Materials

Microporous polypropylene (PP) hollow fiber (PPHF) membranes with pore size in the range of 40–200 nm were provided by Kaihong Co., Hangzhou, China. The PPHF membrane has an outer diameter of about 400 μm and a wall thickness of about 40 μm. The monomers, poly(ethylene glycol) monomethacrylate (PEGMA, $n = 6$, $M_n \sim 360$ g/mol, 99%) and (2-dimethylamino)ethyl methacrylate (DMAEMA, 97%), were purchased from Aldrich Chemical Co., of Milwaukee, WI, USA. They were used after removal of inhibitors in a ready-to-use disposable inhibitor-removal column (Aldrich Chemical Co.). Analytical grade tetrahydrofuran (THF) was purchased from Tedia Co., Fairfield, OH, USA. Copper(I) bromide (CuBr, 99%,) and copper(II) bromide ($CuBr_2$, 97%) were obtained from Aldrich chemical Co. Cu Br was purified with acetic acid before use. 2-Bromoisobutyryl bromide (98%), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethlyenetriamine (PMDETA, 99%), triethylamine (99.5%) and hydrochloric acid (37%) were also purchased from Aldrich Chemical Co. and were used as received. *Escherichia coli* (*E. coli*, ATCC DH5a) and *Staphylococcus aureus* (*S. aureus*, Newman), were obtained from the American Type Culture Collection. Purified argon was used in all reactions.

2.2. Initiator-immobilization on the PPHF membrane surface

2.2.1. Preparation of the PPHF membrane with hydroxyl-functionalized surface

About 1 g of the PPHF membranes were exposed to a continuous stream of O_3/O_2 at room temperature (~25 °C) for about 5 min. The O_3/O_2 mixture was generated from an Azocozon RMU 16-04EM ozone generator. The gas flow rate was adjusted to 300 l/h to give rise to an ozone concentration of about 0.045 g/l of the gaseous mixture. Under these conditions, a 5 min pretreatment time would give rise to a peroxide content of about 1.8×10^{-4} mol/m^2 of the membrane surface. The amount of peroxide groups was determined by reaction with (2,2-diphenyl-1-(2,4,6-trimtrophenyl)-hydrazyl), or DPPH, using the procedure described earlier [19]. Conversion of the peroxide group into hydroxyl group was carried out using the method reported earlier [41]. About 1 g of the ozone-treated PPHF membranes were put into a 50 ml round bottom flask containing 25 ml of isopropyl alcohol. Then, 1 ml of glacial acetic acid and 10 ml of saturated isopropyl alcohol solution of NaI were added. The reaction was allowed to proceed at 60 °C for about 1 h. The PPHF membranes were removed from the solution and rinsed thrice with excessive amounts of water and acetone. PPHF membranes with hydroxyl groups on surface (PPHF-OH) were obtained after the membranes have been dried under reduced pressure for about 24 h.

2.2.2. Preparation of the PPHF-i membrane with initiator-immobilized surface

About 0.5 g of the dried PPHF-OH membranes, 10 ml of dry THF and 0.5 ml of triethylamine were introduced into a 50 ml two-neck round-bottom flask equipped with a dropping funnel and an argon inlet/outlet. After cooling to 0 °C, 1.0 ml of 2-bromoisobutyryl bromide (41 mmol) in 10 ml of THF was added slowly, with continuous stirring, to the mixture over a period of 1 h under an argon atmosphere. The temperature was allowed to rise to room temperature and the reaction was carried out under stirring for another 24 h. The PPHF membranes with immobilized atom transfer radical polymerization initiators (PPHF-i) were obtained by washing thrice with ethanol and water to remove the $(C_2H_5)_3N{\cdot}HBr$ salt adsorbed on the membrane surface. The PPHF-i membrane has a bromine content of about 0.2 wt.% as determined by elemental analysis.