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# Surface modification of polypropylene microfiltration membrane by grafting poly(sulfobetaine methacrylate) and poly(ethylene glycol): Oxidative stability and antifouling capability



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## ABSTRACT

PolySBMA and polyOEGMA, which are typical polyzwitterion and polyether with good antifouling capability, have been extensively studied in the surface modification of polymer membranes. It is necessary to evaluate their oxidative stability because aqueous solutions with oxidizing agents are usually used to remove foulants from membrane surfaces in practical applications. PolySBMA and polyOEGMA were grafted on PPMM surface via UV-induced graft polymerization. Protein adsorption and filtration results indicate that both of the polySBMA- and polyOEGMA-grafted membranes have excellent hydrophilicity and antifouling capability. However, their oxidative stability against  $\text{H}_2\text{O}_2/\text{Cu}^{2+}$  and  $\text{NaClO}$  solutions is remarkably different. FT-IR/ATR and TOF-SIMS analyses show that polySBMA degrades faster than polyOEGMA in the oxidation process, mainly due to the ester hydrolysis and elimination of sulfobetaine units. As a result of 72-h oxidation, the polySBMA-grafted membrane has an increased water contact angle from  $36^\circ$  to  $118^\circ$  and deteriorated antifouling capability, whereas the polyOEGMA-grafted membrane almost maintains the surface properties. Our findings indicate that poly(ethylene glycol)-based graft is a suitable choice in the design of antifouling surfaces for separation membranes.

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## 1. Introduction

Separation membranes have been widely applied in water treatment, food production, and protein purification, due to their high efficiency and easiness of implementation as well as low cost [1,2]. However, membrane fouling during the separation process has inevitably hinders their practical applications, which is mainly caused by adsorption of living organisms, particulates or colloids [3,4]. Therefore, it is a significant scientific issue to improve the antifouling capability of polymeric membranes. In general, good resistance to nonspecific protein adsorption is one of the key

parameters for antifouling membranes, which is mainly influenced by the surface chemistry [5,6]. According to the entropic effects of dehydration, hydrophilic materials can form water barriers on the surface, resulting in an energy unfavorable process for expelling water molecules from the hydrophilic layer by proteins [7,8]. Therefore, surface hydrophilization is a common way to improve the antifouling capability of hydrophobic membranes [9].

PEG and polyzwitterion are the most promising antifouling polymers for surface modification. PEG forms surface hydration layer mainly via hydrogen bonding, while polyzwitterion binds water molecules via strong electrostatic interaction [10–12]. PEG is easily available to academic and industrial researchers and has extensive history for reducing nonspecific adsorption of proteins, cells and bacteria [13,14]. On the other hand, it has been widely reported that PEG is susceptible to oxidation, especially in the presence of oxygen and transition metal ions [15–17]. Therefore, it is necessary to find a new generation of antifouling polymers for surface modification. Jiang and coworkers have carried out a series of studies on the antifouling capability of polyzwitterions, such as polySBMA and poly(carboxybetaine methacrylate) [18–20]. They found that polySBMA brushes can reduce nonspecific protein adsorption ( $< 0.3 \text{ ng cm}^{-2}$ ) to a level comparable with that on PEG brushes [21,22]. Chen and coworkers characterized water

**Abbreviations:** SBMA, *N*-(3-sulfopropyl)-*N*-(methacryloxyethyl)-*N,N*-dimethylammonium betaine; polySBMA, poly(sulfobetaine methacrylate); OEGMA, oligo(ethylene glycol) methacrylate; polyOEGMA, poly[oligo(ethylene glycol) methyl ether methacrylate]; PEG, poly(ethylene glycol); PPMM, polypropylene microfiltration membrane; FESEM, field scanning electron microscope; FT-IR/ATR, attenuated total reflectance Fourier transform infrared spectroscopy; TOF-SIMS, time-of-flight secondary ion mass spectroscopy; XPS, X-ray photoelectron spectroscopy; BSA, bovine serum albumin; FL-BSA, fluorescent-labeled BSA; WCA, water contact angle; NMR, nuclear magnetic resonance; *GD*, grafting density; *rm*, the remaining mass ratio of grafting chains; *RFR*, relative flux reduction; *FRR*, flux recovery ratio

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information of polySBMA (or PEG) chains, including the number and molecule structure, via measuring spin–spin relaxation time by LF-NMR [23,24]. They illustrated that eight water molecules are tightly bound with one sulfobetaine unit of polySBMA, which is higher than one water molecule per ethylene glycol unit ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ) of PEG. These high qualities of water molecules may be responsible for the excellent nonspecific protein resistance of polySBMA. As a consequence, polySBMA has been used to modify different membrane surfaces for antifouling, including poly(vinylidene fluoride) [25,26], polyethersulfone/polysulfone [27,28], and polyurethane [29,30]. Our previous work also introduced polySBMA onto PPMs by UV-induced graft polymerization or co-deposition with polydopamine; the modified membranes show excellent hydrophilicity and protein/bacterial resistance for short-term use [31,32]. However, it must be pointed out that practical applications are quite different from model researches. Membrane separation usually works in a very complicated environment, which leads to much attention to long-term stability of the antifouling property [33,34]. Few works have found polySBMA is not stable in some specific environments, for example sea water [35], NaClO solution [36], and high temperature [37], although the mechanism is not yet clear. And more importantly, separation membranes are normally cleaned with oxidative solutions periodically [38,39]. Therefore, the oxidative stability is a crucial criterion for those membranes designed for long-term use.

This study aims at investigating the oxidative stability of two well-known antifouling polymers, polySBMA and polyOEGMA. PPMs were modified with polySBMA and polyOEGMA via UV-induced graft polymerization.  $\text{H}_2\text{O}_2/\text{Cu}^{2+}$  and NaClO solutions were used as the oxidants. A detailed comparison is made by investigating the oxidative stability, hydrophilicity and antifouling performance of the membranes. Moreover, a mechanism is suggested for the oxidative degradation process of polySBMA chains.

## 2. Materials and methods

### 2.1. Materials

PPMM (average pore size  $\sim 0.20 \mu\text{m}$  and porosity  $\sim 75\%$ ) was supplied by Membrana GmbH, Germany. OEGMA ( $M_n = \sim 360$ ) was purchased from Sigma-Aldrich (USA) and used after removing added inhibitors. SBMA (97%) was obtained from Aldrich and used without further purification. BSA (pI 4.8, 67 kDa) and FL-BSA (pI 6.0,  $66 \pm 2$  kDa) were purchased from Sinopharm Chemical Reagent (China) and Shanghai Jiahe Biotechnology Co. Ltd. (China), respectively. Phosphate-buffered saline (PBS, pH 7.4, ionic strength 10 mM) was prepared from analytical-grade chemicals and ultra-pure water (18.2  $M\Omega$ , produced from an ELGA Lab Water system,

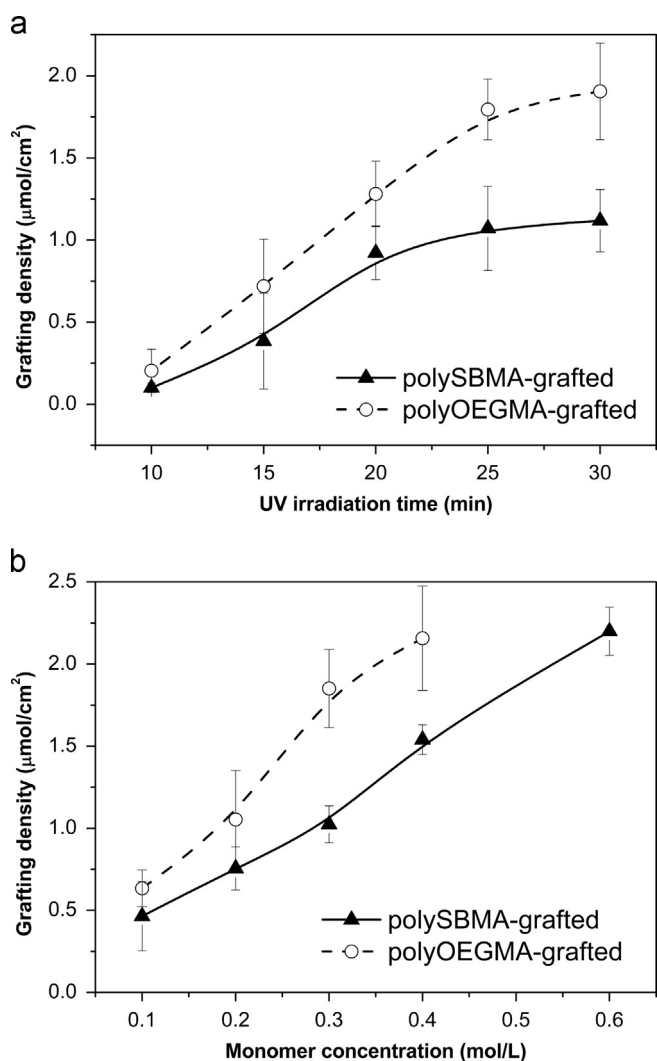


Fig. 1. Effect of (a) UV irradiation time and (b) monomer concentration on the grafting density of polySBMA and polyOEGMA on PPMs.

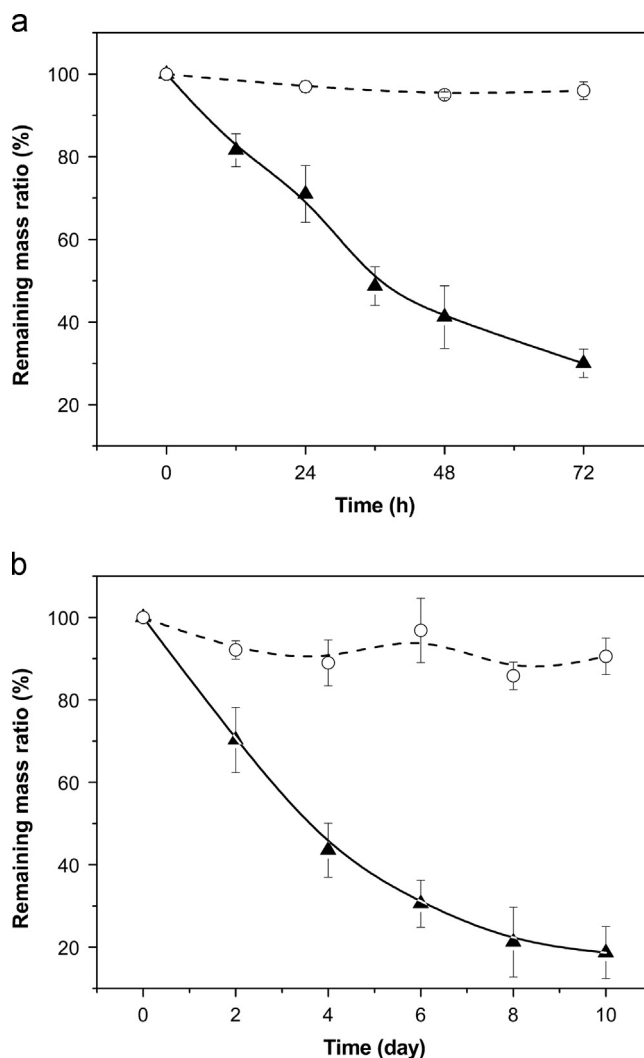


Fig. 2. Remaining mass ratios of polyOEGMA- (hollow circle) and polySBMA-grafted (solid triangle) PPMs after oxidation in (a) 0.1 mM  $\text{Cu}^{2+}$  with 0.01 mM  $\text{H}_2\text{O}_2$  and (b) 6.7 mM NaClO solutions.

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