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Full Length Article

Hydrophilic and photo-crosslinkable diblock copolymers employed for robust antifouling membrane coatings

Zhang Ganwei, Bai Renbi*, Shen Shusu, Zhou Xiaoji, Guo Yongfu

Center for Separation and Purification Materials & Technologies, Suzhou University of Science and Technology, Suzhou 215009, PR China
Suzhou Key Laboratory of Separation and Purification Materials & Technologies, Suzhou University of Science and Technology, Suzhou 215009, PR China
School of Environmental Science & Engineering, Suzhou University of Science and Technology, Suzhou 215009, PR China

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ABSTRACT

Bifunctional copolymers bearing hydrophilic units and photo-crosslinkable units were prepared and employed to coat PVDF membranes and thus improve their antifouling properties and coating stability. A series of methoxy poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate) (mPEG-*b*-PHEMA) diblock copolymers were prepared via the atom transfer radical polymerization (ATRP) of 2-hydroxyethyl methacrylate (HEMA) using different mPEG macroinitiators, and then reacted with cinnamoyl chloride to obtain methoxy poly(ethylene glycol)-*block*-poly(2-cinnamoyloxyethyl methacrylate) (mPEG-*b*-PCEMA). Coating PVDF microfilter membranes with mPEG-*b*-PCEMA and subsequently photo-crosslinking the PCEMA block yielded crosslinked copolymer coatings. The successful preparation of these coatings was confirmed by SEM, TGA, ATR-FTIR and XPS characterization. The hydrophilicity of the membrane increased along with the amount of diblock copolymer coating on the coated PVDF membrane. Based on the results of BSA adsorption and filtration experiments, the antifouling properties of the coated PVDF membrane remarkably improved. Furthermore, the mPEG block chain length and its content in the diblock copolymer had a significant effect on the surface properties of the coated PVDF membrane. More importantly, the copolymer coatings were very stable thanks to the crosslinking of the PCEMA chains of the diblock copolymer.

1. Introduction

Membrane filtration is widely considered as one of the most efficient ways to treat water and a variety of wastewaters because of its advantages such as low energy consumption, short process times, high efficiency, and simple operation, etc. [1–5]. However, one of the major challenges encountered with membrane technology is the adverse effects arising from membrane fouling [1–7]. Irreversible fouling in particular, resulting from biological and organic foulants, may cause a significant decline in the permeation flux and separation efficiency. In addition, irreversible membrane fouling impedes the effective recovery of these membranes by common cleaning methods, which significantly increases the cost and limits the applicability of membrane separation technology in practice. Therefore, there is still an urgent need for the development of novel approaches to address issues arising from membrane fouling.

Generally, most membranes are hydrophobic and are typically fabricated from materials such as polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyethylene (PE), or polypropylene (PP). Biological or organic foulants can readily adhere to the surfaces or pore walls of those membranes. To facilitate the removal of these foulants, the membranes should be highly hydrophilic. Numerous methods have been developed to fabricate hydrophilic membranes, including a variety of physical and chemical approaches, such as blending hydrophilic components with base membrane materials [8–12], grafting hydrophilic monomers or polymers onto the surfaces of membranes [13–17], directly treating membranes with alkali solvents or via irradiation [18–23], and so on. Unfortunately, these methods inevitably exhibited certain deficiencies. The blending of hydrophilic composites with hydrophobic membrane substrates was hindered by the poor compatibility between these components [9,11,24–27]. In addition, the hydrophilic composite was readily released from the blend membrane during the filtration process, which not only gradually reduced the antifouling performance of the membrane, but also led to secondary contamination of the filtrate. The grafting of hydrophilic components onto the surfaces of membranes has traditionally required a multiple-

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* Corresponding author at: Center for Separation and Purification Materials & Technologies, Suzhou University of Science and Technology, Suzhou 215009, PR China.

E-mail address: brb998@outlook.com (B. Renbi).

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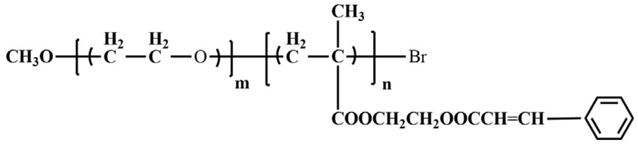
step process, which is both time-consuming and technically challenging. Meanwhile, surface grafting typically suffers from relatively low initiator efficiencies and monomer conversion rates [28,29], which limit the scalability and thus hinders mass production. Meanwhile, directly treating a membrane with an alkali solution or via irradiation can damage the bulk properties and structure of the membrane, thus affecting the membrane's overall performance.

In comparison with the above-mentioned methods, the direct coating method can provide a simple way to improve the hydrophilicity of a membrane and readily accommodate large-scale industrial applications. A layer of hydrophilic polymers can be immobilized on the surface of a membrane due to the adsorption affinity interactions after the coating process. Since hydrophilic polymers can provide better antifouling properties, the coated membrane can become more immune to the foulants. Polymers, such as chitosan or poly(2-methacryloyloxyethyl phosphorylcholine-*co*-n-butyl methacrylate) [poly(MPC-*co*-BMA)], have been used to coat PVDF membranes via an immersion method, a flow through method and combinations of the flow through and surface flow method. The results demonstrated that the modified membranes had much higher hydrophilicity and better antifouling properties than the unmodified membranes [30,31]. Amphiphilic block copolymers, such as polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO), polystyrene-*block*-poly(ethylene glycol) methacrylate (PS-*b*-PEGMA) and poly(propylene oxide)-*block*-poly(sulfobetaine methacrylate) (PPO-*b*-PSBMA), have also been used to coat membranes via self-assembly processes [32–34]. The coated membranes exhibited enhanced antifouling properties because the assembly process positioned the hydrophilic block of these copolymers at the outer surfaces of these membranes.

Although the coating approach is easily performed in practice and provides a dramatic improvement in membrane antifouling performance, we must note that the above-mentioned coating composites are loosely spread on the surfaces or pore walls of the membrane. Consequently, these hydrophilic coatings are not very stable and tend to detach from the membrane and thus contaminate the filtrate during filtration.

To achieve a feasible strategy for preparing a membrane coating, we designed and synthesized a bifunctional diblock copolymer based on methoxy poly(ethylene glycol)-*block*-poly(2-cinnamoyloxyethyl methacrylate) (mPEG-*b*-PCEMA), the structure of which is shown in Scheme 1. The mPEG polymer is a well-known hydrophilic macromolecule, which can endow the membrane with hydrophilicity and thus provide high resistance against membrane fouling. Meanwhile, the PCEMA polymer chain was selected for its demonstrated ability to undergo photo-crosslinking without the need for additives [35]. A similar photo-crosslinkable polymer chain named poly(2-cinnamoyloxyethyl acrylate) (PCEA) has been used previously to lock the structures of poly(dimethylsiloxane)-containing block copolymer coatings on cotton fabrics [36]. Thus, we anticipated that the mPEG-*b*-PCEMA diblock copolymer could be used to coat membranes. With an optimized coating procedure, the mPEG-*b*-PCEMA block copolymer would cover the surface and pore walls of the membrane. More importantly, the block copolymer coatings should be stable and robust.

While we are not aware of any reports on membrane coatings based on bifunctional diblock copolymers containing both hydrophilic and photo-crosslinkable units, a few approaches have been reported describing the preparation of stable hydrophilic membrane coatings via crosslinking methods. For example, dopamine, polydopamine and its derivatives were directly coated onto the surfaces of commercial membranes to obtain stable hydrophilic surfaces [26,37–40]. However, the presence of aromatic rings in polydopamine limited the hydrophilic performance [41]. To enhance the hydrophilicity of the coating, a variety of organic or inorganic components, including amino-terminated PEG (PEG-NH_2), TiO_2, SiO_2 and multiwall carbon nanotubes have been grafted or embedded onto polydopamine-modified membranes [24,38–40,42–45]. In another example, a hydrophilic monomer, initiator and crosslinker were mixed and coated onto the surface of a membrane [46–48]. A hydrophilic coating layer was formed after the monomer underwent polymerization and the crosslinking treatment. Obviously, the above-mentioned approaches suffer from two major shortcomings. First, multi-step manipulations are required, thus hindering the large-scale production of these materials and their applicability in practice. Second, there were inevitably some unreacted monomers that remained in the coating layer. In comparison, our method differs from those reported by other researchers in both the polymers used and the coating strategy, as in our case the crosslinkable diblock copolymer solution flows through the membrane and then undergoes a photo-crosslinking reaction to yield a stable hydrophilic coating. Because of the simplicity of this coating process, the absence of residual monomers, the durability of the coating, and the excellent antifouling properties of the coated membrane, our current strategy has excellent potential for a wide range of applications.



Scheme 1. Structure of the mPEG-*b*-PCEMA diblock copolymer.

2. Experimental section

2.1. Materials

The monomer, 2-hydroxyethyl methacrylate (HEMA, 98%, Sigma-Aldrich) was purified via a previously reported procedure [49]. HEMA-TMS and methoxyethyl 2-bromoisobutyrate (MEBrIB) were synthesized via the methods described in our previous reports and their structures and purity were confirmed by ^{1}H NMR spectroscopy [35,50]. The purified monomer and initiator were kept at 4 °C prior to use. Copper(I) bromide (CuBr, Fluka, 98 + %) was purified via stirring in acetic acid at 80 °C for 12 h and then was washed at least ten times with ethanol before it was dried overnight under vacuum at room temperature [35,50]. Triethylamine (99%, Aladdin), anisole (99%, Aladdin) and dichloromethane (CH_2Cl_2, 99%, Aladdin), were purified via refluxing with sodium for 12 h prior to distillation. mPEG-OH, 2-bromoisobutyryl bromide (98%, Sigma-Aldrich), 2,2′-bipyridine (99%, Aladdin) and tetrahydrofuran (THF, 99%, Aladdin) were used as received. All other reagents and solvents were of analytical grade and used without further purification unless specified otherwise.

2.2. Preparation of mPEG-b-PCEMA

A solution of mPEG-OH (M_n = 5000 g/mol, 10.02 g, 0.002 mol) and triethylamine (2.81 mL, 0.02 mol) in dry CH_2Cl_2 (145.0 mL) was cooled in an ice–water bath. Subsequently, a solution of 2-bromoisobutyryl bromide (1.24 mL, 0.01 mol) in dry CH_2Cl_2 (5.0 mL) was added dropwise under vigorous stirring and this solution was kept stirring in the ice-water bath for 1 h. The reaction mixture was allowed to warm to room temperature and stirred overnight. This mixture was then poured into water and extracted with CH_2Cl_2. The CH_2Cl_2 extracts were subsequently washed once with 0.1 M HCl, once with 0.1 M NaOH, and five times with distilled water. The solution was dried with magnesium sulfate after washing. The product was then precipitated into diethyl ether and this process was repeated three times. The final product was dried under vacuum at room temperature for 24 h. The mPEG macroinitiator was obtained with a yield of 9.49 g (91%) and named as mPEG5K macroinitiator. Meanwhile, mPEG1K macroinitiator and mPEG10K macroinitiator were prepared via the same procedure, using mPEG-OH (M_n = 1000 g/mol) and mPEG-OH (M_n = 10000 g/mol), respectively.