



Enhanced membrane antifouling and separation performance by manipulating phase separation and surface segregation behaviors through incorporating versatile modifier

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ARTICLE INFO

Article history:

Received 19 August 2015

Received in revised form

23 October 2015

Accepted 24 October 2015

Available online 28 October 2015

Keywords:

Versatile modifier

Phase separation

Surface segregation

Antifouling membrane

Ultrafiltration

ABSTRACT

In this study, the copolymers (PS_n-co-PEGMA_m) with crosslinked structure were synthesized and blended into polythierylsulfone (PES) matrix to fabricate membranes via surface segregation method. The incorporation of copolymers affected both the phase separation and surface segregation behaviors during membrane fabrication process. On one hand, the copolymers could affect the formation of nodular structure of the as-prepared membranes for increasing the size of polymeric spheres and generating a loose skin layer, which was testified by atomic force microscope (AFM) surface measurement. As a result, the water permeation flux of membranes increased from 166.9 L m⁻² h⁻¹ for the PES control membrane to 333.0 L m⁻² h⁻¹ for the PES/PS₃-co-PEGMA₂ membrane (with 0.80 wt% of copolymer content). On the other hand, the hydrophilic PEO segments in the copolymers could spontaneously migrate to and enrich on the membrane surface, which were demonstrated by X-ray photoelectron spectroscopy (XPS) analysis, as a result, the antifouling properties of the membranes were considerably improved. The separation performance of the membranes was evaluated by bovine serum albumin (BSA) aqueous solution as model system. With incorporation of copolymer as versatile modifier, the permeation flux of BSA aqueous solution increased and the rejection efficiency of all the membranes was 100%.

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1. Introduction

Membrane technology plays an indispensable role on sea water desalination and waste water treatment because of unique advantages including low energy consumption, low operation temperature and high efficiency [1–6]. However, there are a variety of bacteria, organics and particles in water, which generate non-specific interactions with the membrane, leading to serious membrane fouling [7–10]. Pretreatment of feed solution, optimization of module structure and operation conditions can control membrane fouling to some extent, whereas development of antifouling membrane seems more active [8]. Presently, surface grafting and surface segregation are the two dominant methods to construct antifouling membrane. Comparatively, surface segregation method has the inherent advantages such as *in situ*

modification of membrane during the phase inversion process, simultaneous modification of both membrane internal pores and membrane outer surface [11,12].

With respect to surface segregation, numerous researches have been devoted to the design and synthesis of surface segregation additives/modifiers, the evaluation of long-term residence of the surface segregation modifiers in the membrane, and the exploitation of antifouling strategies for membranes. In the pioneering work, Mayes and coworkers synthesized an amphiphilic copolymer containing poly(methyl methacrylate)(PMMA) hydrophobic segment and poly(ethylene oxide)(PEO) hydrophilic segment, to blend with polyvinylidene fluoride (PVDF) to improve the antifouling properties [13], a variety of surface segregation modifiers were subsequently designed to fabricate antifouling membranes, such as PEG-base materials with high hydrophilicity, large excluded volume and unique coordination with surrounding water in an aqueous environment [11,14,15], zwitterionic materials which can form “free water” hydration layers with ionic solvation [16–19] and low surface energy materials referring to organic fluorine and silicone resin with self-cleaning property [20–24]. The

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stable residence of surface segregation modifiers in the membrane, as one major concern for surface segregation method, has attracted considerable research interest [25–27]. In our previous study, polyvinyl chloride (PVC) and polyvinyl formal (PVF) blend ultrafiltration membranes were fabricated by non-solvent induced phase separation (NIPS) method with different casting solution composition. The robust residence of PVF on the membrane surface was demonstrated [26]. With regard to the antifouling mechanism of the surface segregation modifiers, poly(ethylene glycol)-based materials and zwitterionic materials are frequently utilized to engineer hydrophilic or superhydrophilic surface to establish fouling resistant mechanism, and the low surface energy materials are utilized to engineer hydrophobic surface to establish fouling release mechanism [8,12,22,23, 28–30]. In our previous study, novel amphiphilic copolymers which consisted of cellulose acetate (CA) rigid backbone and side chains comprising non-polar hydrophobic polyhexafluorobutyl methacrylate (PHFBM) segments were designed and utilized to construct amphiphilic porous membrane surface via a “forced surface segregation” approach [31]. Due to the existence of hydrophilic fouling resistant domains and hydrophobic fouling release microdomains, the resulting membranes displayed superior antifouling properties for both oil and protein foulants.

Surface segregation method used to prepare antifouling membrane encompasses two key processes: surface segregation process and phase separation process. In the surface segregation process, the surface segregation modifiers which composed of hydrophobic backbones and hydrophilic side chains are blended into bulk polymer in the membrane casting solution, and the hydrophilic segments segregate onto the membrane surface and pore surface during the subsequent phase separation process, meanwhile, the hydrophobic segments will entangle with the polymer matrix. The phase separation process occurs when a thin film of the casting solution immerses into coagulation bath, followed by the exchange of solvent and nonsolvent across the interface, leading to diverse membrane structures. Simultaneous manipulation of the phase separation and the surface segregation behavior is essential to synergistic tuning of membrane surface structure and membrane pore structure [26,32,33]. Particularly, since the skin layer is crucial to membrane separation performance, synergistic tuning of chemical feature and physical morphology of the skin layer is an impending research task and should be further explored.

In the present study, copolymers (PS_n -co-PEGMA $_m$) with crosslinked hydrophobic segments were synthesized by surfactant-free emulsion polymerization, and blended into PES matrix to fabricate membranes via surface segregation method. The incorporation of PS_n -co-PEGMA $_m$ copolymers not only manipulated the phase separation process which led to a loose skin layer but also manipulated surface segregation behaviors which led to a hydrophilic membrane surface. The chemical structure of PS_n -co-PEGMA $_m$ copolymers was confirmed by Fourier transform infrared spectroscopy (FTIR) and ^{13}C solid-state nuclear magnetic resonance spectra (^{13}C NMR). And the thermodynamic properties of PS_n -co-PEGMA $_m$ copolymers were measured using differential scanning calorimetry (DSC). The morphology of membranes and the associated phase separation behavior were analyzed and elucidated with the assistance of scanning electron microscope (SEM) and atomic force microscope (AFM). Furthermore, the surface segregation behavior of the hydrophilic PEO segments in copolymers was investigated with the assistance of X-ray photoelectron spectroscopy (XPS). And the interaction force between foulants and membrane surface was probed by AFM. Finally, ultrafiltration experiments were performed to evaluate the water permeation flux, antifouling properties and separation performance of the resulting membranes.

2. Experimental

2.1. Materials

PES (6020p, Mn = 59,000, flake form) was purchased from BASF Co. (Germany) and dried at 110 °C for 12 h before use. Two monomers, polyethylene glycol methyl acrylate (PEGMA, Mn = 475) was purchased from Sigma-Aldrich Co. (USA), and styrene (St) provided by Damao chemical reagent corporation (Tianjin, China) was washed with 5 wt% NaOH solution, and washed to neutral by deionized water, then vacuum-distilled to remove polymerization inhibitor in it before use. The initiator, potassium peroxydisulfate (KPS) and crosslinking agent, divinyl benzene (DVB) were also purchased from Sigma-Aldrich Co. (USA). N,N-Dimethylformamide (DMF), polyethylene glycol with average molecular weight of 2000 (PEG2000) and bovine serum albumin (BSA) were all purchased from the local reagent corporation and were of commercially analytical grade.

2.2. Synthesis of PS_n -co-PEGMA $_m$ copolymers

The PS_n -co-PEGMA $_m$ copolymers were synthesized using surfactant-free emulsion polymerization as described previously [34–36]. One representative synthesis of the PS_3 -co-PEGMA $_2$ copolymers was shown as follows: 3.00 g St, 0.15 g DVB (5 wt% St), and 2.00 g PEGMA were dissolved into 30 mL of deionized water in a 100 mL three-necked reaction round bottom flask equipped with a stirrer, followed by bubbling nitrogen gas at room temperature for 30 min to release the oxygen in the flask. And then the temperature increased to 80 °C and 0.03 g KPS was added into the flask. Polymerization was conducted at 80 °C for 6 h under nitrogen atmosphere, then the product was under vacuum rotary evaporation at 65 °C, and washed with water to remove the homopolymer of poly (polyethylene glycol methacrylate), then was dried completely at 65 °C for over 72 h. The products were simplified as PS_n -co-PEGMA $_m$, where n represented the mass of St and m represented the mass of PEGMA. Fourier-transform infrared spectrometer (FTIR, VERTEX70) and ^{13}C solid-state nuclear magnetic resonance spectra (NMR, Infinityplus 300) were used to characterize the chemical structure of the products and the thermal properties of them were measured using a differential scanning calorimetry (DSC, 200F3, NETZSCH Co.) at a heating and cooling rate of 10 °C/min under a nitrogen (N_2) atmosphere.

2.3. Membrane preparation and characterization

The blended membranes of PES and PS_n -co-PEGMA $_m$ copolymers were fabricated by surface segregation method, using DMF as the solvent and water as the nonsolvent coagulation bath. The compositions of casting solutions containing PES, PS_n -co-PEGMA $_m$ copolymers, pore-forming agent PEG2000 and solvent DMF are shown in Table 1. PS_n -co-PEGMA $_m$ copolymers were firstly dissolved in DMF and well dispersed by ultrasonication, then PES and pore-forming agent PEG2000 was added to formulate the casting solutions. The casting solutions were stirred for 4 h at 60 °C and degassed at the same temperature for another 6 h to ensure complete release of bubbles. Then, the casting solutions were cooled to room temperature. Afterwards, the casting solutions were cast on glass plates with a steel knife and immersed into water coagulation bath. The resulting membranes were designated as PES/ PS_n -co-PEGMA $_m$ (w) membranes, where n and m indicated the masses of St and PEGMA as synthesis process of PS_n -co-PEGMA $_m$ copolymers, representatively and w indicated the addition amount of PS_n -co-PEGMA $_m$ copolymers during the membrane preparation process. All the membranes prepared for this work were stored in deionized water before use. And the PES control

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