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Composite ultrafiltration membranes from polymer and its quaternary phosphonium-functionalized derivative with enhanced water flux



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ABSTRACT

Novel ultrafiltration (UF) membranes were prepared by blending brominated poly(phenylene oxide) (BPPO) and its quaternary phosphonium derivative (TPPOQP-Br) as additive using a phase inversion method. The chemical structure and microstructure of the membranes were characterized by Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-IR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The XPS results indicated that the BPPO/TPPOQP-Br composite membranes exhibited an increase in the concentration of TPPOQP-Br from the top surface to the bottom surface. In contrast, the composite membranes prepared from BPPO and its quaternary ammonium derivative (TPPOQA-Br) showed an opposite concentration gradient of TPPOQA-Br. This was attributed to the difference in wettability and hydration rate between TPPOQP-Br and TPPOQA-Br, leading to different membrane microstructure and chemical composition distributions. BPPO membrane showed a water flux of $215 \text{ L m}^{-2} \text{ h}^{-1}$ at 100 kPa and its molecular weight cut-off of PEG is 93.8 kDa; the corresponding values of the optimal BPPO/TPPOQP-Br membrane are $873 \text{ L m}^{-2} \text{ h}^{-1}$ and 111.3 kDa, both of which are better than those of BPPO/TPPOQA-Br with the similar additive loading ($381 \text{ L m}^{-2} \text{ h}^{-1}$ and 150.2 kDa). Therefore, the addition of TPPOQP-Br significantly enhances the water permeability while maintaining the excellent rejection properties in the resultant UF membranes. This work extends the choice of the additives in the UF membrane fabrication, and further proves that the addition of hydrophobic and charged polymer with slow hydration property is an effective strategy for improving flux and anti-biofouling properties of UF membranes.

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1. Introduction

Ultrafiltration (UF) membranes have gained considerable attention in the field of waste water treatment [1–3], food processing [4,5], protein separation [6,7], etc. Over the past half century, the non-solvent induced phase inversion technique has been widely used for preparing UF membranes [8]. Typically, the resultant asymmetrical membranes have a very thin, dense skin layer and a thick, macro-porous supporting layer. Until now, many different polymers such as polysulfone (PSf) [9], polyethersulfone (PES) [10], polyacrylonitrile (PAN) [11], celluloses [12] and poly(vinylidene fluoride) (PVDF) [13] are used in the fabrication of UF membranes. To better meet the application needs, these membranes are

required to possess high water permeability, excellent separation properties and good anti-fouling properties. To this end, many techniques have been developed, most of which focus on the surface enrichment of the hydrophilic materials, including: (a) surface modification such as physical coating [14] or chemical [15] and photo-induced [16,17] grafting functional materials especially containing hydrophilic groups onto the top surface of the pre-formed UF membranes, and (2) addition of some hydrophilic modifiers in the casting solution that tend to segregate on the top surface during the phase inversion process [18–22]. Despite the fact that the anti-fouling properties can be improved after modification, it is still challenging to achieve both high water permeability and separation property.

Unlike the common modification via hydrophilization of UF membrane top surface, we have previously developed a new methodology of designing high-performance UF membranes for improving water permeability without losing separation properties [23]. In particular, composite membranes were prepared by blending

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polyethersulfone (PES) and tris(2,4,6-trimethoxyphenyl) polysulfone-methylene quaternary phosphonium chloride (TPQP-Cl). Because of the abundant benzene ring around the charged quaternary phosphonium, TPQP-Cl exhibited higher hydrophobicity and lower hydration than PES, and then it was pushed down to the bottom layer during the phase inversion process. Consequently, the resulting membrane showed an increase in TPQP-Cl concentration from the top surface to the bottom surface along with a unique macro-porous structure at the cross-section, both of which would positively affect the membrane water flux. To further explore this new methodology, it is important to investigate the membrane formation and properties using different polymer backbones; and it is also necessary to understand the effects of quaternary phosphonium functionalized additive in comparison with additives with other charged groups.

In this paper, we synthesized tris(2,4,6-trimethoxyphenyl) poly(phenylene oxide) methylene quaternary phosphonium bromide (TPPOQP-Br) and then prepared the BPPO/TPPOQP-Br composite UF membranes by blending TPPOQP-Br with BPPO. BPPO has good thermal and mechanical properties, and abundant highly reactive $-CH_2Br$ groups [24], and it is commonly available and has been used to prepare UF membranes with good performance [25]. Moreover, we also synthesized triethyl poly(phenylene oxide) methylene quaternary ammonium and then prepared BPPO/TPPOQA-Br UF membranes for comparison. The structures and filtration performance of membranes were investigated in detail.

2. Experimental

2.1. Materials

Brominated poly(phenylene oxide) BPPO (Mw=60,500) with a benzyle substitution ratio of 0.57 was provided by Tianwei Membrane Co. Ltd. China. 1-methyl-2-pyrrolidone (NMP, 99.5%), tris(2,4,6-trimethoxyphenyl)-phosphine (TTMPP), triethylamine and polyethylene oxide (PEG) with different molecular weights (35, 100, 200 kDa) were purchased from Sigma-Aldrich, Australia, and used without further purification.

2.2. Synthesis of tris(2,4,6-trimethoxyphenyl) poly(phenylene oxide)-methylene quaternary-phosphonium-bromide (TPPOQP-Br) [24]

To synthesize TPPOQP-Br, BPPO (1.72 g, an equivalent of 5 mmol $-CH_2Br$ groups) and TTMPP (3.19 g, 6 mmol) were firstly dissolved in 80 mL NMP at room temperature. The mixture was kept stirring at 50 °C for 24 h, and then the resultant solution was cast onto a pre-cleaned glass plate for solvent evaporation at 40 °C. After being washed thoroughly with deionized water and dried under vacuum at 40 °C for 48 h, the final TPPOQP-Br powder was obtained. The molecular structures of BPPO and TPPOQP-Br are shown in Fig. 1.

2.3. Synthesis of triethyl poly(phenylene oxide) methylene quaternary ammonium-bromide (TPPOQA-Br)

TPPOQA-Br was prepared by the reaction of BPPO with triethylamine. 2 g of BPPO was firstly dissolved in 20 mL NMP and then 0.51 g of triethylamine was added. After stirring for 24 h at room temperature, the solution was dried at 40 °C under vacuum for solvent evaporation, followed by washing with deionized water thoroughly and drying under vacuum at 40 °C for 48 h to get the final TPPOQA-Br, whose molecular structure is shown in Fig. 1.

2.4. Preparation of membranes

Commercial BPPO was used as the main component for membrane casting. 50 mL of polymer casting solution was prepared by blending

15 wt% BPPO/NMP solution and 15 wt% TPPOQP-Br/NMP solution (BPPO/TPPOQP-Br weight ratios are: 10/0, 9/1, 8/2 and 7/3, see Table 1). After ultrasonication the blending solution was left to stand overnight until no bubbles were observed. The membranes were prepared by using a Gardco® adjustable micrometer film applicator with a stainless steel blade (Paul N. Gardner Company, Inc., USA). 5 mL of the polymer solution was cast on a clean glass plate with a gap of 200 μ m. Afterwards the membrane was solidified in a coagulation bath of deionized water for several minutes. Finally, the resulting membranes were washed thoroughly and soaked in the double deionized (DDI) water overnight before use. For comparison, the BPPO/TPPOQA-Br 8/2 was also prepared using the same procedures (see Table 1).

2.5. Membrane characterization

The membrane morphologies were observed by scanning electron microscopy (SEM). For the surface morphology observation, the membranes were fixed on a carbon tape and then sputter coated with roughly 0.5 nm iridium (Ir) layer and the images were recorded using a FEI Magellan 400, 450 instrument at an accelerating voltage of 5 kV with different magnifications. For the cross-sectional morphology observation, the membrane samples were firstly immersed in DDI water for 24 h, then water on their surface was removed by filter paper carefully. Afterwards the samples were fractured in liquid nitrogen, followed by drying and coating with Pt for SEM observation. Their images were then recorded using a FEI Nova NanoSEM instrument at an accelerating voltage of 5 kV with different magnifications.

X-ray photoelectron spectroscopy (XPS) was conducted with a Thermo Fisher X-ray photoelectron spectroscopy system (ESCALAB250). The X-ray radiation source was monochromatic Al K α (1486.7 eV) and an incident angle and electron take-off angle of 54° and 90° respectively relative to the sample plane were employed, the elemental analysis from survey scans was used. The content of P or N element was used to determine the amount of quaternary phosphonium or quaternary ammonium groups, which were used to calculate the polymer compositions on the top and bottom surfaces on the basis of TPPOQP-Br and TPPOQA-Br. FTIR spectra of the membranes were measured using an ATR-FTIR (PerkinElmer, USA) spectrometer in the range of 500–4000 cm^{-1} at an average of 32 scans with a resolution of 4 cm^{-1} . The static contact angles of the dried and wet membranes were measured at room temperature using an OCA 15 EC contact angle measuring instrument (Dataphysics, Germany). A water drop with a volume of 5 μ L was dropped onto the membrane with a microsyringe in air. At least 3 contact angles at different locations for each membrane were recorded with time. For wet membrane samples, they were firstly immersed in DDI water for 24 h. Then the membrane was cut into the desired shape and fixed on the glass, after that, the water on the surface of the membrane was removed by the filter carefully. Then the test would be carried out immediately.

2.6. Pure water flux and molecular weight cut off experiments

Pure water flux of the membranes was tested at room temperature using a Sterlitech HP4750 dead-end stirred cell (Sterlitech Corporation, USA) with an inner diameter of 49 mm and an effective membrane area of 14.6 cm^2 . The cell volume capacity is 300 mL and attached to a 5.0 L dispensing vessel. The membrane sample was first pre-compacted at 250 kPa for 1–2 h until it reached a constant flux. Then the water flux was determined at different feed pressures (100, 150 and 200 kPa) by measuring the weight change with the time of the permeate water on a digital balance (PA2102C, Ohaus) interfaced with a computer. The data from the balance was logged to a computer using a program in LabView.

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