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# Slow hydrophobic hydration induced polymer ultrafiltration membranes with high water flux

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## ABSTRACT

Polymer ultrafiltration membranes with high water flux have long been pursued to improve filtration efficiency and reduce costs of industrial separation processes such as water treatment and food processing. However, increasing water flux is usually accompanied by decreased rejection property in these membranes. In this paper, we show that by using a polymer functionalized with hydrophobically ionizable groups as additive, polymer ultrafiltration membranes with an increasing concentration of the additive from the active layer to the supporting layer are produced in the membrane casting process due to slow hydration of the additive. The hydrated additive becomes hydrophilic after the membrane formation. The resulting membranes exhibit dramatically enhanced water permeability while maintaining excellent separation property. We demonstrate that polyethersulfone/tris(2,4,6-trimethoxyphenyl)polysulfone-methylene quaternary phosphonium chloride (PES/TPQP-Cl) membrane exhibits a water permeability of up to  $14.6 \text{ l m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$ , which is 35 times that of PES membrane. The membrane also shows excellent anti-biofouling property. The work provides a new methodology for designing high-performance membranes for improving separation efficiency and exploring other novel applications.

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## 1. Introduction

Ultrafiltration (UF) membranes with a pore size range of 2–100 nm are extensively used to remove suspended nanoparticles, bacteria, macromolecules, etc. in various industrial processes [1–7]. Many polymers such as cellulose acetate [8], polyacrylonitrile [2], polysulfone [9], polyethersulfone [10], poly(vinylidene fluoride) [7], and PS-*b*-P4VP diblock-copolymer [11] have been used to produce UF membranes via a non-solvent induced phase inversion method that was first developed more than fifty years ago [12]. These polymer membranes have an asymmetrically porous structure composed of a thin nanoporous selective active layer and a thick macroporous supporting layer. Over the last decades, there have been continuing research efforts in developing UF polymer membranes to achieve antifouling property and high water flux; the main techniques developed thus far include (1) physical coating or chemical grafting of hydrophilic material on the active separation layer, and (2) addition of a hydrophilic

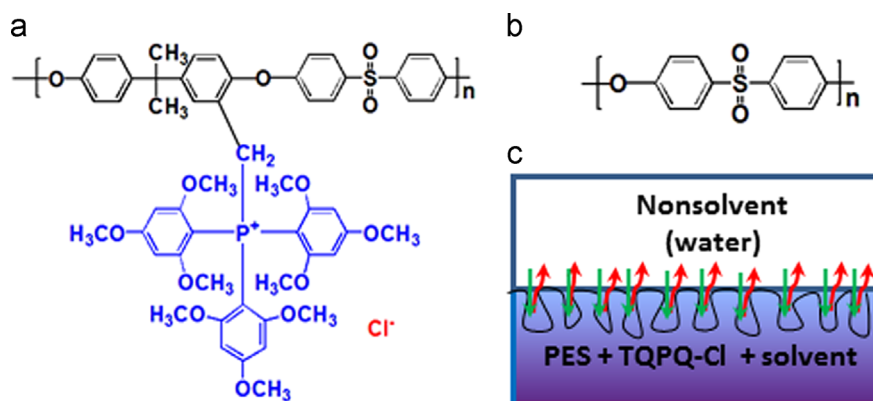
modifier that tends to segregate on the active layer in the membrane formation process [2,3,7,9,10,13,14]. Therefore, in the current UF membranes, the active layer tends to be more hydrophilic than the supporting layer. This membrane configuration has proven effective for improving the fouling resistance of membrane, but it has only resulted in limited improvement in water flux without compromising the rejection property.

In recent years, tremendous research efforts have been made to explore alternative membranes from functional nanoporous materials with extraordinary transport properties such as synthetic carbon nanotubes, but the large-scale fabrication of these membranes for practical applications still remains a huge challenge.

In the present paper, we report a new methodology for tailoring the chemistry and porous structure of polymer UF membranes to dramatically enhance water flux without sacrificing rejection properties. By taking advantage of slow hydration of a polymer additive with hydrophobic and charged groups, and its hydrophilicity after hydration, we have for the first time demonstrated that polymer UF membranes with an opposite concentration gradient of additive and increased porosity can be produced via “oil–water demixing” in the phase inversion process, resulting in favorable pore surface chemistry and microstructure for fast

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**Fig. 1.** (a) Molecular structure of TPQP-Cl, (b) molecular structure of PES, (c) schematic illustration of the formation of polymer UF membranes in the phase inversion process: the solvent (dimethylformamide) diffuses out of the cast polymer solution (indicated by the red arrows) while the nonsolvent (water) diffuses into the polymer solution (indicated by the green arrows); this rapid solvent exchange process leads to precipitation of PES and TPQP-Cl; the color gradient from blue to purple represents an increase in the TPQP-Cl content from the top active surface to the bottom surface of the resulting membrane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

water transport. This methodology can be readily adopted for industrial production of ultrafiltration membranes for practical applications.

As an exemplar system, we synthesized a hydrophobic and charged polymer, tris(2,4,6-trimethoxyphenyl)polysulfone-methylene quaternary phosphonium chloride (TPQP-Cl) by functionalizing polysulfone with hydrophobic quaternary tris(2,4,6-trimethoxyphenyl) phosphonium groups [15,16]. The hydroxide ion exchanged TPQP-Cl was studied as membranes for alkaline fuel cells and desalination [16,17]. The dried TPQP-Cl having a contact angle of  $94^\circ$  (measured from dried dense TPQP-Cl film) was added into polyethersulfone (PES) (its contact angle of  $75^\circ$  measured from dried dense PES film) to prepare PES/TPQP-Cl composite UF membranes. The membranes were prepared by casting polymer solutions with different PES/TPQP-Cl mass ratios. As shown in Fig. 1, due to rapid water (as nonsolvent) exchange with dimethylformamide (as solvent) and slow hydration of its hydrophobic and charged quaternary phosphonium groups, more hydrophobic TPQP-Cl tends to migrate against water penetration. The TPQP-Cl then becomes hydrophilic upon hydration. Therefore, the resulting membrane shows an increase in TPQP-Cl concentration from the top surface to the bottom surface (i.e., additive-rich supporting layer). Note that an additive-rich active layer results from a more hydrophilic additive in the conventional phase inversion process without involving a hydrophobic-to-hydrophilic transition. In this paper, PES/TPQP-Cl membranes are investigated in terms of microstructure, chemical gradient, surface wettability and water permeation and molecular weight cut-off and antibacterial property, and the mechanisms of water permeation enhancement are discussed.

## 2. Experimental

### 2.1. Synthesis of tris(2,4,6-trimethoxyphenyl)polysulfone-methylene quaternary-phosphonium-chloride (TPQP-Cl)

TPQP-Cl was synthesized using the reported method [15,16]. Typically, 5 g of polysulfone (with a mass average molecular weight  $M_w \sim 35,000$  Da and a number average molecular weight  $M_n \sim 16,000$  Da, Sigma-Aldrich Australia) was dissolved in 250 ml of chloroform (anhydrous,  $\geq 99\%$ , Sigma-Aldrich Australia) to form a polysulfone solution. 3.39 g of paraformaldehyde (95%, with a molecular weight of 30.03 g/mol, Sigma-Aldrich Australia) and 12.3 g of trimethylchlorosilane ( $\geq 97\%$ , with a molecular weight of 108.64 g/mol, Sigma-Aldrich Australia) were added to the polysulfone chloroform solution in a flask equipped with a reflux condenser and a magnetic stirrer, and then 0.6 g of stannic chloride (99%, Sigma-Aldrich

Australia) was added dropwise. The reaction mixture was then stirred at  $50^\circ\text{C}$  for 72 h. Subsequently the reaction mixture was poured into absolute ethanol, and white chloromethylated polysulfone (CMPSf) precipitated immediately. The precipitate was filtrated, washed thoroughly with ethanol, and dried in a vacuum oven at room temperature for 12 h. 0.516 g of as-synthesized chloromethylated polysulfone was dissolved in 10 ml of 1-methyl-2-pyrrolidone (NMP, 99.5%, Sigma-Aldrich Australia), and then 0.8 g of tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP, Sigma-Aldrich Australia) was added. The reaction mixture was stirred at  $80^\circ\text{C}$  for 12 h, and then poured into a petri-dish to form a thin membrane and then dried at  $30^\circ\text{C}$  for one week. TPQP-Cl was peeled off in double deionized water and dried at  $30^\circ\text{C}$ . The chemical structure of CMPSf, TTMPP and TPQP-Cl was confirmed by NMR (Supplementary information Figs. S1 and S2). NMR results showed that the degree of chloromethylation was 137% and the degree of quaternary-phosphorization was about 100%. Therefore, the degree of substitution of TPQP-Cl was 1.37.

### 2.2. Membrane preparation

Commercial polyethersulfone (PES, Ultrason<sup>®</sup> E 6020 P from BASF, molecular weight = 51,000 g/mol) was used for membrane casting. Dimethylformamide (DMF,  $\geq 99\%$ , Sigma-Aldrich Australia) was used as a nonsolvent. 200 ml of 15–18 wt% polymer casting solution was prepared by dissolving PES and TPQP-Cl (at a PES/TPQP-Cl ratio of 10/0, 9/1, 8/2 and 7/3) in DMF under stirring for 5 h and then left without stirring until no bubbles were observed. The membranes were prepared by using a Gardco<sup>®</sup> 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  $\mu\text{m}$ . Thereafter, the membrane was solidified in a coagulation bath of double deionized water for several minutes. The resulting membranes were washed and soaked in the double deionized water for 24 h before drying or testing, and denoted  $x\%$  PES/TPQP-Cl  $y$ , where  $x$  stands for the concentration of polymer casting solution, and  $y$  stands of the mass ratio of PES/TPQP-Cl.

### 2.3. Membrane characterization

The scanning electron microscope images were taken with a JEOL JSM 7001F microscope and a FEI Magellan 400 FEG microscope. The contact angle of the membrane was determined using a contact angle goniometer (Dataphysics OCA20, Dataphysics, Germany). A water drop with a volume of 5  $\mu\text{L}$  was dropped onto the membrane with a microsyringe in an air atmosphere. At least

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