



# High flux polyethylene glycol based nanofiltration membranes for water environmental remediation



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## ABSTRACT

A hydrophilic thin-film-composite (TFC) nanofiltration (NF) membrane has been developed through the interfacial polymerization (IP) of amino-functional polyethylene glycol (PEG) and trimesoyl chloride. The selective layer is formed on a polyethersulfone (PES) support that is characterized using FTIR, XPS and SEM, and is dependent on monomer immersion duration, and the concentration of monomers and additives. The higher hydrophilicity alongside the larger pore size of the PEG-based selective layer is the key to a high water flux of  $66.0 \text{ L m}^{-2} \text{ h}^{-1}$  at 5.0 bar. With mean pore radius of 0.42 nm and narrow pore size distribution, the  $\text{MgSO}_4$  rejections of the PEG based PA TFC NF membranes can reach up to 80.2%. The rejection rates for different salts of the novel membranes are in the order of  $R(\text{MgCl}_2) > R(\text{MgSO}_4) > R(\text{NaCl}) > R(\text{Na}_2\text{SO}_4)$ ; indicating a membrane with positive surface charges. The pore sizes and water permeability of these membranes are tailored by varying the molecular weight and molecular architecture of amino-functional PEG. These newly developed TFC NF membranes show great potential for water softening, wastewater treatment and separation and purification of active, pharmaceutical molecules.

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## 1. Introduction

Global water issues like fresh water shortage, unbalanced distribution of fresh water, and water pollution require an impending need to address these problems. In recent years, innovative solutions have been devised in attempts to solve these issues for water environmental remediation. For example, polymer membranes are currently deployed for seawater desalination, water softening, treatment of industrial effluents, preparation of pure water, separation of alcohols from water and many other fields [1–10]. An interesting class of advanced membrane separation is nanofiltration (NF). The molecular weight cut-off (MWCO) for a NF membrane with pore diameters varying from 0.5 to 2.0 nm ranges between 200 and  $1000 \text{ g mol}^{-1}$ . Most NF membranes are either positively or negatively charged. Fabrication methods for NF membranes include phase inversion [4,6,11], dip-coating [12,13], graft polymerization [14,15], and interfacial polymerization (IP) [3,16–20]. IP is an advanced technique based on a polymerization reaction that occurs at the interface between two immiscible phases. IP is commonly used to fabricate NF membranes, and recent studies indicate that polymerization

conditions can influence the structural integrity and separation properties of TFC membranes [16–20]. Ahmad et al. showed that the monomer ratio affects the pore structure, surface charge, and thickness of the selective layer in TFC membranes [16]. Ghosh et al. reported that additives like triethyl amine and (+)-10-champor sulfonic acid promote the formation of selective layers of TFC membranes that are integral for their reported higher pure water permeability [17]. Shao et al. developed hollow fiber NF membranes through IP [3], and reported that the pore structures of such NF membranes are tailored by changing the ratio of m-phenylenediamine (MPDA) and piperazine (PIP) in water phase. With an aqueous solution containing 1.75 wt% MPDA and 0.25 wt% PIP, the  $\text{Na}_2\text{SO}_4$  rejection rate of these NF membranes could reach 93.5%, and pure water permeability of  $3.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ . The salt rejection rate and water permeability of these membranes are higher when compared to MPDA membranes with similar mean pore sizes that were fabricated using conventional approaches [3].

The low water permeability, limited fouling and chlorine resistance of NF membranes fabricated from IP limit their widespread applications for desalination and wastewater treatment. Energy requirements of the aforementioned applications can be potentially reduced with high pure water permeability NF membranes, while improvements in membrane fouling and chloride resistance can provide performance longevity. Fang et al. developed TFC NF membranes with positive charges via the IP of

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polyetherimide (PEI) and trimesoyl chloride (TMC) [18], and reported that the rejection rates of  $\text{MgCl}_2$  and  $\text{MgSO}_4$  could reach up to 97.6% and 80.6%, respectively; with a relatively high pure water flux of  $20 \text{ L m}^{-2} \text{ h}^{-1}$  at 2 bar. An et al. synthesized and added zwitterionic monomers into piperazine (PIP) solutions, which were subsequently polymerized using IP with TMC to form TFC NF membranes [19]. With 3.2 mol% of zwitterionic monomers, these membranes displayed little bacterial adsorption and protein fouling whilst possessing a high water flux of  $43.1 \text{ L m}^{-2} \text{ h}^{-1}$  and  $\text{K}_2\text{SO}_4$  rejection of 97.0% at 6 bar [19].

The hydrophilicity of PEG has been utilized to enhance the fouling resistance of polyamide (PA) TFC membranes [21–27]. Freeman et al. coated polydopamine and grafted PEG on PA to fabricate anti-fouling NF membranes [23–26]. The anti-fouling properties of these membranes could be attributed to enhanced membrane wettability through the ether oxygen functional groups (–C–O–C) on the side-chains of the selective layers. Interestingly, the grafted PEGs partially blocked membrane pores; leading to a lower initial water flux which remained unaffected during fouling experiments [23–26]. Ideal NF membranes should possess both anti-fouling properties and high water flux.

In this work, we firstly report that TFC NF membranes with selective layers comprising a new PEG-based polyamide on polyethersulfone (PES) substrates can reject up to 80% of  $\text{MgSO}_4$  with a prominent water flux of  $66.0 \text{ L m}^{-2} \text{ h}^{-1}$  at 5.0 bar. The selective polyamide containing C–O–C in its main chains is fabricated via the interfacial polymerization of amino-functional PEG in an aqueous solution and TMC in n-hexane on the surface of PES substrates. Polymerization conditions were optimized to yield maximal performances of these membranes. We also investigated the effects of branched PEG terminated with amino groups on the tailoring of pore structures. These TFC NF membranes have been physicochemically characterized, alongside their pure water permeability, salt rejections and pore structure.

## 2. Experimental

### 2.1. Chemical and materials

Trimesoyl chloride (TMC), m-phenylenediamine (MPDA) (Sigma-Aldrich), amino-functional PEGs (Jenkem Technology Co., Ltd.), triethanolamine (TEOA),  $\gamma$ -butyrolactone (GBL), N,N'-dimethylacetamide (DMAc), sodium dodecyl benzene sulfonate (SDBS), n-hexane, (Sinopharm Chemical Reagent Co., Ltd.),  $\text{Na}_2\text{SO}_4$ , NaCl,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$  (Shanghai Qiangshun Chemical Reagent Co., Ltd.), ethanol, galactose, maltose, raffinose,  $\alpha$ -cyclodextrin and PEGs (aladdin) were purchased. All reagents were analytical grade and used without further purification. PES 3000p was provided by Solvay cooperation for preparing the support membranes.

### 2.2. Preparation of PES support and TFC (thin-film-composite) membranes

The PES support membrane was fabricated using the wet-phase inversion process [28]. A 15 wt% PES solution was prepared in a mixture containing 60 wt% DMAc and 25 wt% GBL. To remove residual DMAc, the fabricated support membranes were immersed in tap water over 3 days, and soaked in 1.0 wt%  $\text{NaHSO}_3$  solution at room temperature to inhibit bacteria build-up [29].

The TFC NF membranes were prepared via IP on the top surface of the PES support membranes. The detailed polymerization conditions are demonstrated in Table S1 and Table S2. PES membranes were first soaked in pure water over 24 h to remove residual  $\text{NaHSO}_3$  on the surface. Subsequently, the PES supports were immersed in solutions containing amino-functional PEG for a

certain time. Excessive amino functional PEG solutions were evaporated in a fume hood. These PEG-coated PES supports were transferred into a TMC/n-hexane solution at  $40^\circ\text{C}$  in an oven. The resultant NF membranes were post treated in pure water at  $60^\circ\text{C}$  for 1 h. Finally, the thin-film composite membranes were submerged in methanol overnight. The membranes were soaked in a 1.0 wt%  $\text{NaHSO}_3$  solution before characterization. Unless specified, the diamine represents linear amino-functional PEG diamine with the molecular weight of  $600 \text{ g mol}^{-1}$  (PEG600-NH<sub>2</sub>).

### 2.3. Membrane characterizations

FTIR-ATR was performed on a Spectrum One instrument (Perkin-Elmer, USA). ZnSe was used as the crystal plate and the penetration depth was approximately  $50 \text{ \AA}$  with a  $45^\circ$  incident angle. All spectra were recorded over a wave number range from  $4000$  to  $500 \text{ cm}^{-1}$ . XPS measurements were carried out using an AXIS ULTRA DLD spectrometer (SHIMADZU, Japan) with a monochromatized Al K $\alpha$  X-ray source ( $1486.6 \text{ eV}$  photons) at a constant dwell time of  $250 \text{ ms}$  and a pass energy of  $40 \text{ eV}$ . The penetration depth was less than  $10 \text{ nm}$  with a  $90^\circ$  incident angle. DSC was performed on a DSC-Q2000 (TA, USA) from  $-60^\circ\text{C}$  to  $250^\circ\text{C}$  with a heating and cooling rate of  $10^\circ\text{C}/\text{min}$  under dry  $\text{N}_2$  purge ( $50 \text{ mL}/\text{min}$ ). Each membrane was subjected to two heating cycles to remove adsorbed water on PA, and the glass transition temperature ( $T_g$ ) was obtained from the second heating cycle. The morphology of the fabricated membranes was characterized by a scanning electron microscope (SEM, SEM Quanta 200F, FEI Company). The cross-section morphologies of the membranes were prepared by breaking the membranes in liquid nitrogen to avoid destroying the pore structures of the membranes. A contact angle measuring system (G10 Kruss, Germany) was used to measure the static water contact angle of membranes. The deionized water droplet was placed on a dry flat membrane surface and the contact angle was obtained. The reported contact angle value was calculated by averaging over more than five contact angle values at different sites.

### 2.4. Pure water permeability and solute rejection of fabricated hollow fiber membranes

The pure water permeability or the water flux of NF membranes was measured with a self-made cross-flow filtration apparatus. The operating pressure and temperature were kept at 5 bar and  $25^\circ\text{C}$  with condensing apparatus, respectively. To minimize the effects of concentration polarization, the flow rate was set to  $70 \text{ L h}^{-1}$  with current velocity of  $0.71 \text{ m s}^{-1}$ . The water flux and the pure water permeability (PWP) were calculated using the following equations:

$$F = \frac{V}{A \times t} \quad (1)$$

$$\text{PWP} = \frac{F_w}{\Delta P} \quad (2)$$

where  $F$  represents the water flux ( $\text{L m}^{-2} \text{ h}^{-1}$ ),  $V$  (L) is the volume of the pure water (or solution) penetrating through the membrane,  $A$  is the effective membrane area ( $\text{m}^2$ ),  $t$  is the operation time (h);  $F_w$  is the pure water flux ( $\text{L m}^{-2} \text{ h}^{-1}$ ) and  $\Delta P$  is transmembrane pressure (bar).

The solute rejections of NF membranes were calculated by the following equations:

$$R = \left(1 - \frac{C_p}{C_f}\right) 100\% \quad (3)$$

where  $C_p$  and  $C_f$  are the solute concentrations in the permeate and

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