Accepted Manuscript

Negatively Charged Hyperbranched Polyglycerol Grafted Membranes for Osmotic Power Generation from Municipal Wastewater

Xue Li, Tao Cai, Chunyan Chen, Tai-Shung Chung

PII: S0043-1354(15)30359-6

DOI: [10.1016/j.watres.2015.11.032](https://doi.org/10.1016/j.watres.2015.11.032)

Reference: WR 11659

To appear in: *Water Research*

Received Date: 16 October 2015

Revised Date: 13 November 2015

Accepted Date: 14 November 2015

Please cite this article as: Li, X., Cai, T., Chen, C., Chung, T.-S., Negatively Charged Hyperbranched Polyglycerol Grafted Membranes for Osmotic Power Generation from Municipal Wastewater, *Water Research* (2015), doi: 10.1016/j.watres.2015.11.032.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**Negatively Charged Hyperbranched Polyglycerol Grafted Membranes for Osmotic
Power Generation from Municipal Wastewater**

Xue Li ^a, Tao Cai ^{a,b}, Chunyan Chen ^a, Tai-Shung Chung ^{a,c*}

^a Department of Chemical & Biomolecular Engineering,
National University of Singapore,
Kent Ridge, Singapore 117585

^b Key Laboratory of Biomedical Polymers of Ministry of Education, Department of Chemistry,
Wuhan University, Wuhan, China 430072

^c Water Desalination & Reuse (WDR) Center, King Abdullah University of Science and Technology,
Thuwal 23955-6900, Saudi Arabia

*To whom correspondence should be addressed
Tel.: +65-65166645; Fax: +65-67791936.
Email address: chencts@nus.edu.sg

Abstract

Osmotic power holds great promise as a clean, sustainable and largely unexploited energy resource. Recent membrane development for pressure-retarded osmosis (PRO) is making the osmotic power generation more and more realistic. However, severe performance declines have been observed because the porous layer of PRO membranes is fouled by the feed stream. To overcome it, a negatively charged antifouling PRO hollow fiber membrane has been designed and studied in this work. An antifouling polymer, derived from hyperbranched polyglycerol and functionalized by α -lipoic acid and succinic anhydride, was synthesized and grafted onto the polydopamine (PDA) modified poly(ether sulfone) (PES) hollow fiber membranes. In comparison to unmodified membranes, the charged hyperbranched polyglycerol (CHPG) grafted membrane is much less affected by organic deposition, such as bovine serum albumin (BSA) adsorption, and highly resistant to microbial growths, demonstrated by *E. coli* adhesion and *S. aureus* attachment. CHPG-g-TFC was also examined in PRO tests using a concentrated wastewater as the feed. Comparing to the plain PES-TFC and non-charged HPG-g-TFC, the newly developed membrane exhibits not only the smallest decline in water flux but also the highest recovery rate. When using 0.81 M NaCl and wastewater as the feed pair in PRO tests at 15 bar, the average power density remains at 5.6 W/m² in comparison to an average value of 3.6 W/m² for unmodified membranes after four PRO runs. In summary, osmotic power generation may be sustained by properly designing and anchoring the functional polymers to PRO membranes.

Keywords: Poly(ether sulfone), pressure-retarded osmosis, thin-film composite membranes, fouling, municipal wastewater, osmotic power

1. Introduction

As the price of fossil fuels fluctuates and global climate changes rapidly, increasing attention has been drawn to find clean, renewable energy sources worldwide. Among them, osmotic power, known as salinity gradient energy, holds great promise due to the readily available resources from freshwater, wastewater, and seawater sources (Gerstandt et al. 2008, Logan and Elimelech 2012, Sivertsen et al. 2013, Skihagen et al. 2011, Ramon et al. 2011). The estimated annual global osmotic power from the feed pair of oceans and river is about 2000 TWh (Wick and Schmitt 1977). The figure could be even higher if the feed pair for the pressure retarded osmosis (PRO) consists of the concentrated brine from reverse osmosis (RO) plants and wastewater. The use of retentates from RO and municipal wastewater plants as the feed pair has also been proposed and demonstrated (Achilli et al. 2009, Achilli and Childress 2010, Chung et al. 2012, Wan and Chung 2015). Not only can it eliminate the expensive pre-treatment process for seawater, but also dilute the seawater RO brine to ecologically-friendly levels for easy disposal. In addition, it also draws extra values from the rejected wastewater. The osmotic power can also serve as a form of energy recovery for RO processes, so that seawater desalination might become a less energy-intensive process (Achilli et al. 2009, Achilli and Childress 2010, Chung et al. 2012).

The development of robust and high performance PRO hollow fiber membranes has advanced rapidly (Chou et al. 2012, Fu et al. 2014, Li and Chung 2014, Wan and Chung 2015, Zhang et al. 2014b). A maximum power density up to ~ 27 W/m² has been achieved by using a synthetic seawater brine of 1 M NaCl as the draw solution and de-ionized water as the feed (Wan and Chung 2015). However, if retentates from RO and municipal

wastewater plants were used as the feed pair, the power density dropped tremendously due to fouling (Wan and Chung 2015). Although pretreatment processes on feed solutions are able to offer some improvements, fouling on membranes, especially biofilm growth, is inevitable in long term operations (Celik et al. 2011, Escobar and Van der Bruggen 2011, Gu et al. 2013, Kim et al. 2015, Kim et al. 2014, Lau et al. 2012a, Li et al. 2012b, Li et al. 2014b, Nunes and Peinemann 2006, Nunes et al. 1995, She et al. 2012, Van der Bruggen and Vandecasteele 2003, Xie et al. 2013, Zhang et al. 2014a). In addition, as fouling occurs in the porous layer underneath the selective layer of membranes in PRO processes, it is more difficult to be cleaned up than that in conventional pressure-driven membrane processes (Chen et al. 2015, Wan and Chung 2015). Therefore, how to mitigate fouling is gradually becoming as the major obstacle to commercialize the PRO technology.

Development of antifouling PRO membranes is an essential way to control fouling. Although many anti-fouling methods have been proposed (Escobar and Van der Bruggen 2011, Liu et al. 2013, Mi and Elimelech 2010, Saeki et al. 2014, Sotto et al. 2011), it is still difficult to design antifouling PRO membranes with the best balanced characteristics because one must take the following counterbalanced factors into consideration such as high hydrophilicity vs. robust mechanical strength, high repulsion to foulants vs. low resistance to water, and multi-functionality vs. easy processing. Among many approaches, surface modification via molecular design appears to be a preferred method because it not only enhances antifouling properties but also maintains membrane bulk properties in terms of cost and productivity (Kang and Cao 2012). We have developed a dendritic

hyperbranched polyglycerol (HPG) anchored PRO membrane with antifouling resistances against protein and bacteria (Li et al. 2014a). However, it lacks of strong repulsive forces to ions and might be fouled by inorganic scaling. If scaling takes place on the membrane surface, the HPG branches would be shielded and no longer effective to prevent the membrane from organic compounds and bacteria. Therefore, new strategies to design antifouling PRO membranes with charged characteristics are of high priority.

Therefore, the objectives of this study are to design a new type of hyperbranched polyglycerol polymer with negatively charged functional branches, as shown in Scheme 1, and to graft it on PRO membranes for osmotic power generation. The polymer is firstly constructed by ring-opening polymerization (ROP) of glycidol, and then functionalized by reacting with α -lipoic acid (LA) and succinic anhydride (SA). The former provides potential grafting sites and the latter offers charged groups. The grafting sites are opened by reductive scission of the disulfide bonds, and covalently attached to the polydopamine treated membrane surface (Figure S1). In this synthesis route, a post-polymerization reaction with LA, instead of initiation with bis(2-hydroxyethyl)disulfide (BHEDS) in the previous study (Li et al. 2014a), is used to introduce multiple grafting sites. The new approach aims to reduce the steric hindrance during grafting without sacrificing the number of antifouling branches protecting the membrane surface. With a combination of hydration effect and electrostatic repulsion, the charged hyperbranched polyglycerol (CHPG) may modify the existing PRO membrane with enhanced anti-fouling resistance using real wastewater as the feed in PRO operations. This work may provide useful insights to molecularly design novel PRO membranes for osmotic power generation using

different feed streams.

2. Materials and Methods

2.1 Synthesis of the Charged Hyperbranched Polyglycerol (CHPG) Polymer

Hyperbranched polyglycerol was synthesized in 1,4-dioxane from self-polymerization of glycidol, using NaOCH_3 as the catalyst and 1,1,1-tris(hydroxymethyl)ethane (THE) as the initiator (Scheme 1). Briefly, THE (362.3 mg, 3.02 mmol), NaOCH_3 (48.9 mg, 0.91 mmol) and anhydrous methanol (4 mL) were introduced into a 250 mL double-necked round bottom flask. The solution was stirred at room temperature for 2 h and evacuated at 80 °C for 6 h to remove methanol. Then 40 mL of anhydrous 1,4-dioxane was transferred into a round bottom flask. Argon was purged into the mixture for 20 min to remove dissolved oxygen. Then the flask was protected under an argon atmosphere, and the reaction was conducted at 100 °C with stirring. On the other hand, Argon was purged for 30 min into a mixture of Glycidol (20 mL, 302 mmol) and 1,4-dioxane (40 mL). Then a glycidol mixture was added slowly into the reaction flask over a period of approximately 12 h with a syringe. After that, the reaction mixture was stirred for an additional 12 h to complete the reaction. The reaction flask was consequently quenched in cold water and diluted with methanol. One liter acetone was used to precipitate the adduct. It was purified twice by re-dissolving in methanol and re-precipitating in acetone. The HPG polymer was dried under vacuum at 80 °C to give a highly viscous liquid (yield ~76%). $[\text{M}]_0/[\text{I}]_0 = 100:1$; $M_{n,\text{NMR}} = 5,700$ g/mol. ^1H NMR ($\text{DMSO}-d_6$, δ , ppm, TMS): 1.38 (3H, - CH_3), 3.25-3.85 ($\text{H} \times (5m+6)$, - OCH -, - OCH_2 -), 4.35-4.84 ($\text{H} \times (m+3)$, - OH), where the number m denotes the degree of polymerization of glycidol monomers in HPG homopolymers.

The HPG ($M_{n,NMR} = 5,700 \text{ g mol}^{-1}$, 11.4 g, 2 mmol) polymer was dissolved in 100 mL DMF. ($\pm$)- α -Lipoic acid (LA, 1.03 g, 5 mmol), dicyclohexylcarbodiimide (DCC, 1.03 g, 5 mmol) and 4-(*N,N*-dimethylamino)pyridine (DMAP, 0.12 g, 1 mmol) were then introduced into the flask. Upon completion of the addition, the solution was stirred at room temperature for 24 h. After that, the reaction flask was quenched in cold water and diluted with methanol. Five hundred miniliter acetone was used to precipitate the crude product. The crude product was redissolved in de-ionized water and dialyzed using a dialysis membrane (Sigma-Aldrich, MWCO 1,000 g mol^{-1}) against de-ionized water for 3 days, with the de-ionized water changed twice a day. Finally, the HPG-LA polymer was isolated via lyophilization and gotten a pale yellow liquid (yield ~98%).

In a typical reaction, HPG-LA (12.2 g, 2 mmol), succinic anhydride (SA, 15.0 g, 150 mmol), triethylamine (TEA, 8.4 mL, 60 mmol) and 120 mL DMF were introduced into a round bottom flask. The reaction was carried out under continuous stirring at 70 °C for 24 h. Excess acetone was used to precipitate the reaction mixture. The crude polymer was redissolved in de-ionized water and dialyzed using a dialysis membrane (Sigma-Aldrich, MWCO 1,000 g mol^{-1}) against de-ionized water for 3 days, with the de-ionized water changed twice a day. Finally, the HPG-LA-SA polymer was isolated via lyophilization (yield ~96%). $M_{n,NMR} = 13,700 \text{ g/mol}$. ^1H NMR ($\text{DMSO-}d_6$, δ , ppm, TMS): 1.38 (3H, - CH_3), 1.7-2.1 (5H $\times n$, - $\text{CH}_2\text{CH}_2\text{C(=O)O-}$, - $\text{CH}_2\text{CHSS-}$, - $\text{CH}_2\text{CH}_2\text{SS-}$), 2.45-2.55 (H $\times n$, - $\text{CH}_2\text{CH}_2\text{SS-}$), 2.7-2.8 (H $\times(m+6)$, - CHC(=O)O- , - $\text{CH}_2\text{C(=O)O-}$), 3.25-3.85 (H $\times(4m+3n)$, - OCH- , - OCH_2- , - $\text{CH}_2\text{CHSS-}$, - $\text{CH}_2\text{SS-}$), 4.1-4.4 (4H $\times(m-n+3)$, - C(=O)OCH_2-), where the numbers m and n denote the degree of polymerization of glycidol monomers in HPG homopolymers and the number of hydroxyl groups in HPG is substituted by LA.

The HPG-LA-SA polymer, or designated as CHPG, ($M_{n,NMR} = 13,700 \text{ g mol}^{-1}$, 13.7 g, 1 mmol) was dissolved in 100 mL of de-ionized water. Argon was used to purge the reaction mixture for 30 min. DL-1,4-dithiothreitol (DTT, 770 mg, 5 mmol) was introduced into the flask. With the protection of argon purging, the mixture was stirred for 24 h for 50 °C. The crude product was dialyzed using a dialysis membrane (Sigma-Aldrich, MWCO 1,000 g mol^{-1}) against de-ionized water for 3 days, with the de-ionized water changed twice a day. Finally, the CHPG polymer was isolated via lyophilization (yield ~95%).

2.2 Preparation of the Modified Hollow Fiber Membranes

Hollow fiber membrane supports were spun from poly(ether sulfone) (PES) as reported (Zhang et al. 2014b). The nascent hollow fibers were soaked in water for two days to remove residual solvents and additives, and subsequently treated with a glycerol/water mixture (50/50 wt%) for another two days before drying in the ambient condition. Then the polyamide layer was synthesized on top of the inner surface of hollow fibers by interfacial polymerization (Lau et al. 2012b, Petersen 1993), and the CHPG polymers were grafted on the outer surface with the aid of polydopamine (Faure et al. 2013, Lee et al. 2007, Liu et al. 2014). The procedures were (Figure S1): (1) A *m*-phenylenediamine (MPD) solution of 2 wt% was pumped into the inner channel of hollow fiber supports at a flow rate of 2.2 mL min^{-1} for 3 min; (2) The excess MPD aqueous solution was purged away with compressed air for 5 min; (3) A hexane solution containing 0.15 wt% TMC at a flow rate of 2.2 mL min^{-1} was brought into the inner channel of the fibers for 5 min; (4) The resultant thin-film composite (TFC) membrane was washed thoroughly with de-

ionized water; (5) A tris buffer solution (0.01 mol/L, pH 8.5) containing 2 mg/mL dopamine-HCl was used to coat the outer surface of TFC membranes for 3 h; (6) Polydopamine-coated membranes were soaked in a 10 g/L CHPG aqueous solution with triethylamine (TEA) of 1% (v/v) at room temperature for 12 h to complete the reaction. Hollow fiber membranes were stored in de-ionized water for further tests.

2.3 Characterizations of Hollow Fiber Membranes

X-ray photoelectron spectroscopy (XPS) analyses were made on a Kratos AXIS Ultra DLD spectrometer with a monochomatized Al K α X-ray source (1486.71 eV photons). The core-level signals were measured at the photoelectron take-off angle (α , with respect to the sample surface) of 90°. All binding energies (BEs) were referenced to that of the neutral C 1s hydrocarbon peak at 284.6 eV. The morphology of hollow fiber membranes was studied by a field emission scanning electronic microscope (FESEM, JEOL JSM-6700F) and a scanning electron microscope (SEM, JEOL JSM-5600LV). Before SEM/FESEM tests, membrane samples were coated using a Jeol JFC-1100E ion sputtering device. The cytotoxic studies were performed on membranes by determining the viability of mouse 3T3 fibroblasts after incubation. Prior to use, membranes were sterilized with 75% ethanol and dried in vacuum conditions. Control experiments were conducted in the absence of membranes.

2.4 Antifouling Assays

To determine the antifouling efficacy of the modified hollow fiber membranes, protein adsorption was demonstrated by fluorescein isothiocyanate conjugated bovine serum albumin (BSA-FITC). The membranes were rinsed with phosphate buffered saline (PBS,

10 mM, pH 7.4), and then immersed in the BSA-FITC solution (0.5 mg/mL BSA-FITC in PBS) at 37 °C for 2 h. The membranes were then gently rinsed three times with PBS. A Leica DMLM fluorescence microscope (Leica Microsystems, Wetzlar, Germany) was employed to detect the adsorption of BSA-FITC on the membrane surfaces, equipped with an excitation filter of 495 nm and an emission filter of 525 nm.

Gram-positive *Staphylococcus aureus* (*S. aureus*, ATCC 25923) and Gram-negative *Escherichia coli* (*E. coli*, ATCC DH5α) were cultured to determine the antibacterial adhesion characteristics and bactericidal efficiency of the unmodified and modified hollow fiber membranes. Both *S. aureus* and *E. coli* were cultured in the tryptic soy broth and suspended in PBS at a concentration of 5×10^7 cells/mL. Individual membrane was immersed in the bacterial suspension at 37 °C for 4 h. After incubation, the membranes were washed at least three times with PBS to remove the loosely and non-adhered bacterial cells. To qualitatively measure the bacteria adhesion, the adhered bacteria were fixed with 3% (v/v) aqueous glutaraldehyde at 4 °C overnight. Then serial dehydration in 20, 40, 60, 80 and 100% of ethanol was performed for 10 min each. After subsequent drying under a reduced pressure, the membranes were sputter-coated with a thin platinum layer, and imaged by SEM. Quantification of bacteria attachment and viability on unmodified and modified membranes was carried out by the spread plate method. After rinsing with PBS, the bacterial-adhered membranes were washed in 2 mL of sterile PBS under mild ultrasonication for 7 min. Then a rapid vortex mixing for 20 s was conducted to release the adhered bacteria cells from the membrane surface. After 10-fold serial dilution of this bacterial solution with PBS, a 100 µL aliquot was spread onto the solid agar plate containing the culture medium. The bacteria were incubated overnight at 37 °C

and the grown cell colonies were counted. The assay was carried out in triplicate with three samples for each surface. The results were presented as the relative viability of bacteria on the unmodified PES hollow fiber membrane surface.

2.5 Membrane Fouling Protocol in PRO Processes

The PRO fouling tests were conducted as reported in literatures (Chen et al. 2015, Li et al. 2014a, Mi and Elimelech 2010, She et al. 2012). The polyamide layer of the TFC membrane faces the draw solution in all tests. Synthetic seawater brine (0.81 mol/L NaCl) and concentrated wastewater (i.e., a retentate from a municipal water recycling plant with an equivalent NaCl concentration of ~0.01 mol/L) were fed to the lumen side and shell side of the membrane module, respectively, with the same flow rate of 0.1 L/min at 24 ± 1 °C. The wastewater retentate has a BOD value (biochemical oxygen demand) of 7.3 ppm, COD value (chemical oxygen demand) of 190 ppm, and TDS value (total dissolved solids) of 1100 ppm. The major cations and anions have been reported in our previous work (Wan and Chung, 2015). Humic substances dominate in the organic foulants, and are of fulvic acids type. Besides, sub-units of humic substances, and low molecular weight matters (i.e., alcohols, aldehydes, ketones, and amino acids) are also found. Prior to tests, membranes were stabilized at 15.0 ± 1.0 bar for 0.5 h. For comparison, an initial water flux was measured under the same conditions in the absence of foulants. In between PRO tests, back washing was performed by feeding de-ionized water into the lumen side of hollow fibers at a particular pressure while rinsing the shell side of the hollow fibers with de-ionized water or acid solution (HCl, pH 2.8) at 0 bar.

3. Results and Discussion

3.1 Synthesis of CHPG Polymers

In the present work, the synthetic process for the preparation of CHPG with pendant thiol groups involves three steps (Calderon et al. 2010, Lee et al. 2013, Wilms et al. 2010): ring-opening polymerization (ROP) of glycidol, using 1,1,1-tris(hydroxymethyl)ethane (THE) as the initiator and NaOCH_3 (a strong base) as the catalyst, esterification reactions of the hydroxyl groups of hyperbranched polyglycerols (HPG) with α -lipoic acid (LA) and succinic anhydride (SA), and reduction of the disulfide groups in the LA components to give thiol groups, as shown in Scheme 1. The molar feed ratio of glycidol to THE was set at 100 and the number average molecular weight (M_n , NMR) of the HPG homopolymers was 5,700 g/mol. Post-polymerization reaction of HPG with LA should be possible to allow the preparation of HPG with multiple grafting sites for the subsequent membrane modification, even though the whole synthetic process suffers from additional reaction step, in contrast to the direct ROP of glycidol from the disulfide containing initiators. The esterification reactions with a [LA] to [HPG] molar feed ratio of 2.5 and [SA] to [HPG] molar ratio of 75 were chosen for subsequent membrane surface coatings as a compromise for well-preserved water solubility and sufficient grafting sites. Reductive scission of the disulfide bonds in LA component was conducted using excess DL-1,4-dithiothreitol (DTT). The use of a DTT/LA molar ratio of 5:1 led to almost 100% cleavage within 24 h at 50 °C. The resultant CHPG polymer was then introduced to the outer surface of TFC membranes as an antifouling grafting layer.

3.2 Membrane Properties

Figure 1 illustrates the morphology of both inner surface and outer surface of TFC membranes. A selective polyamide layer was successfully formed on the inner surface of

PES hollow fiber membrane supports via interfacial polymerization. PES-TFC has a polyamide layer fully covered by worm-like and flake-like curls. The rough curls are a result of rapid MPD migration from large surface pores existing on the support toward interfacial polymerization with TMC (Li et al. 2012a). The morphology of the polyamide layer did not apparently alter after the polydopamine (PDA) modification, but some of the rough curls clearly shrank in the subsequent CHPG grafting reaction. Normally, a crosslinked polyamide is highly resistant to alkaline conditions in CHPG grafting. However, some short polyamide chains or non-reacted functional groups are fairly readily attacked by alkaline, possibly leading to the morphology change. On the outer surface, all membranes exhibit similar porous morphology, giving little evidence of the PDA or CHPG modification. The successful modification of PDA or CHPG can be verified by XPS, which is one of the most powerful analytical techniques available for detecting polymer surfaces. Figure 2 shows wide scan spectra of the outer surfaces of PES-TFC, PDA-TFC, and CHPG-g-TFC. PES-TFC contains C 1s, O 1s, with a small contribution from sulfur (S 2s and S 2p). The high energy resolution spectrum of C 1s splits into three peak components, due to $\underline{\text{C}}\text{-H}/\underline{\text{C}}\text{-C}$, $\underline{\text{C}}\text{-O}/\underline{\text{C}}\text{-SO}_2$ and $\pi\text{-}\pi^*$ groups. The $[\underline{\text{C}}\text{-H}/\underline{\text{C}}\text{-C}]/[\underline{\text{C}}\text{-O}/\underline{\text{C}}\text{-SO}_2]$ peak area ratio of 2:1 remains constant with the ratio of the corresponding functional groups in PES polymers. After the PDA treatment, a nitrogen peak in the wide scan spectrum is evident and the sulfur peaks disappear. The intensity of peaks, where $[\text{N}]/[\text{C}]$ is 0.11, is comparable to the theoretical value for PDA molecules. The C 1s core-level spectrum of PDA-TFC has a series of overlapping bands at about 284.6, 285.6, 286.2, 287.4 and 288.9 eV due to C–N, C–H, C–O, C=O, and O–C=O functional groups which are components of PDA. In the case of CHPG-g-TFC, the

absence of N 1s signal and presence of S 2p signal confirm the complete covering of CHPG on the membrane surface as expected from the chemical structure of CHPG. Although both PES-TFC and CHPG-g-TFC contain carbon and sulfur signals, one can clearly distinguish their differences in chemical bonds from their core-level spectra, indicating the successful grafting of CHPG on the outer surface of hollow fiber membranes.

To warrant safety of surface modified membranes, cytotoxicity tests were assessed on PES-TFC, PDA-TFC, and CHPG-g-TFC membranes by *in vitro* experiments of the cell-viability assay. The membranes were incubated in the 3T3 fibroblasts culture medium for 24 h prior to testing. Figure 3 illustrates the experimental results and shows no statistically significant differences among these testing membranes. Cell viability of CHPG-g-TFC is as high as the pristine PES-TFC membrane, followed by PDA-TFC. In summary, the chemical grafting of CHPG onto the TFC membrane is not harmful to viable cells.

3.3 Protein Adsorption and Bacterial Attachment Behaviors

Protein adsorption is investigated by measuring the relative fluorescence intensity and fluorescence microscopy image of the membranes treated by a 0.5 mg mL⁻¹ phosphate buffered saline (PBS) containing fluorescein isothiocyanate-conjugated BSA (BSA-FITC). Because of the hydrophobic-hydrophobic interaction between PES and protein, the outer surface of PES-TFC is readily susceptible to protein adsorption. Figure 4 illustrates that the PDA deposition has made negligible changes in protein adsorption on the membrane surface, while the grafting of CHPG has introduced the membrane with strong resistances

to proteins. Protein adsorption is drastically inhibited on the CHPG-g-TFC surface. The fluorescence intensity is only 12.7% of that on the PES-TFC surface. We attribute this difference between the PDA deposition and CHPG grafting to the fact that the former possesses benzene rings and possible π - π stacking structure to attract proteins, while the latter has strong repulsive forces from the charged branches.

Microbial attachment is critical to membrane applications due to its tendency to adhere to surfaces in aggregate. Bacterial adhesion on membrane surfaces, demonstrated by Gram-positive *S. aureus* and Gram-negative *E. coli*, has been investigated and shown in Figure 5. The attachments of cells to PES-TFC and PDA-TFC are noticeably high: Bacterial adhesion grows rapidly and stacks in clusters in 4 h. PDA-TFC also has high propensity to bacterial attachments, probably due to the rougher surface provided by the PDA layer and larger area exposed to bacteria. A significant lower number of bacterial cells is evident in the SEM image of CHPG-g-TFC as compared to the unmodified surface. The quantitative changes in viable bacterial colonies are summarized in Figure 5(B). The data suggest that *S. aureus* and *E. coli* form thick biofilms on the PES and PDA modified membrane surfaces, which are coincident with the previous report (Cai et al. 2016). CHPG grafting on the membrane surface is very effective in reducing the number of viable cells. In comparison with the unmodified PES-TFC membrane, the CHPG-g-TFC surfaces reduce ~90% in *S. aureus* adhesion, and 93% in *E. coli* adhesion, respectively.

3.4 Fouling in PRO Processes

Scaling, organic fouling, biofilm growths and their combination inevitably occur in membrane processes using wastewater. In this study, a retentate from a municipal water

recycling plant was used as the feed solution. The PRO experiments were conducted at 15.0 ± 1.0 bar for the PES-TFC, HPG-g-TFC, and CHPG-g-TFC membranes. HPG-g-TFC, prepared following the previous protocol (Li et al. 2014a), was studied as a reference to represent the non-charged grafting. Figure 6 displays fouling and recovering behaviors of TFC membranes. When the PES-TFC membrane (rectangular dots) was subjected to a wastewater feed solution, a fast flux decline was observed immediately. At higher normalized accumulative permeate volumes of 20~50 L/m², PES-TFC fouled less rapidly. This behavior suggests that PES-TFC has little resistance to the wastewater fouling. When the normalized accumulative permeate volume reached 50 L/m², back washing at 15.0 ± 1.0 bar by de-ionized water was carried out. Thus, the flux could be restored to more than 90%. In the second run of PRO testing, water flux substantially declined till the normalized accumulative permeate volume reached 100 L/m², and covered to >90% after back washing, indicating that severe fouling had occurred in the first run, and irreversibly blocked some permeation channels. Figure 7(a) presents changes on the outer surface of PES-TFC. The virgin membrane had a fully porous outer surface. PRO testing in wastewater introduced serious deposition of foulants on the membrane, in which silica fouling may dominate according to our previous study (Chen et al. In press). De-ionized water washing opened some permeation channels and restored the flux to >90%. However, this restoring was fairly vulnerable as a massive amount of foulants still stuck to the membrane as shown in Figure 7(a), and pores blocked even faster in the second run than that in the first run. The third run of PRO testing had a similar performance of the second run, and the flux reduced to about 50% of the initial flux at a normalized accumulative permeate volume of ~140 L/m². After three runs, back

washing by an acid solution (HCl, pH 2.8) was carried out, and then PES-TFC showed a comparable decline in water flux with that of the third run. Effects of polymer grafting were investigated by studying HPG-*g*-TFC and CHPG-*g*-TFC in wastewater PRO tests. Performance of the non-charged HPG-*g*-TFC is illustrated in Figure S2. In the first run, water flux gradually decreased to ~65% at a normalized accumulative permeate volume of 50 L/m², which had been improved in comparison to that of PES-TFC. As shown in Figure 7 (c), no serious fouling was found on HPG-*g*-TFC after the first cleaning. Only a few foulant nodules and films stuck to the outer surface. However, in Run 2 and Run 3, water flux near-linearly dropped, getting closer and closer to that of PES-TFC. From these measurements it appears that the non-charged modification has limited resistances to the real wastewater fouling.

Table 1 lists transport properties of PES-TFC and CHPG-*g*-TFC membranes, in terms of pure water permeability, *A*, salt permeability, *B*, and salt rejection. Both TFC membranes have comparable water permeabilities and salt permeabilities. In the case of the PES-TFC membrane, it has a water permeability of 0.78 L m⁻² h⁻¹ bar⁻¹ and a salt permeability of 0.58 L m⁻² h⁻¹. The membrane grafted by CHPG has slightly amplified resistance to water and salt, reducing permeability to 0.74 L m⁻² h⁻¹ bar⁻¹ and 0.55 L m⁻² h⁻¹, respectively. Figure 6 also compares water fluxes of CHPG-*g*-TFC to PES-TFC in the real wastewater testing. Although the intrinsic properties of these two membranes are comparable, their PRO performances in wastewater are different. At the very beginning of operation on CHPG-*g*-TFC, an immediate decrease of water flux to ~85% was observed. Over the subsequent testing period, water flux slowly reduced to an average value of 75% of the

initial value. De-ionized water washing recovered the flux to >90%, which is almost the same as that of PES-TFC. Figure 7 (b) compares the outer surfaces of CHPG-g-TFC before testing and after cleaning. No salt crystals, particles, and nodules were evident on the cleaned membrane except few sticky films covering parts of the membrane surface. When CHPG-g-TFC was further exposed to wastewater, its water flux underwent slowly declining to an average value of 65% at a normalized accumulative permeate volume of 150 L/m². The acid cleaning at the end of Run 3 recovered the water flux to ~94%, and stabilized the flux in Run 4. Eventually, an average value of ~70% was obtained.

Table 1 also lists changes in power density of PES-TFC and CHPG-g-TFC. The initial power densities of two membranes were kept comparably to be 8.2~8.3 W/m² at 15 bar. After the first run, the power density of PES-TFC dropped to 4.3 W/m², consistent with other PES-TFC membranes in real wastewater PRO tests (4~5 W/m²) (Wan and Chung 2015). The value fluctuated from 3.6 to 4.1 W/m² in the subsequent tests. In comparison, the power density of CHPG-g-TFC only decreased to 6.0 W/m² after the first run, and slowly declined to 5.3 W/m² in the following two runs. The acid cleaning before Run 4 restored the membrane performance and maintained the power density at 5.6 W/m² after Run 4. These results confirm that CHPG-g-TFC exhibits much enhanced membrane performance in power generation tests than PES-TFC. In other words, the efficacy of CHPG-g-TFC antifouling properties is confirmed and grafting this charged polymer onto PRO membranes is promising to reduce fouling for osmotic power generation. The enhancement is probably due to the fact that the charged hyperbranched polymer grafted membrane may form a surface hydration layer in water against foulants. However, one

434 has to realize that the current cleaning method does not effectively remove sticky foulants
435 and a systematic study of cleaning methods is necessary in the future work.

436

ACCEPTED MANUSCRIPT

4. Conclusions

We have designed an antifouling PRO hollow fiber membrane by synthesizing negatively charged hyperbranched polyglycerol and chemically grafting it onto the outer surface of PES hollow fibers. XPS measurements have verified the success of planting such CHPG brushes to membrane surface. The modification does not alter the morphology of membrane's outer surface, but imparts good resistances to protein adsorption and bacterial attachments. In PRO tests under 15 bar, the CHPG-g-TFC membrane achieves the best performance in terms of water flux in comparison to the plain PES-TFC membrane and non-charged HPG-g-TFC membrane. The reduction in water flux is ~30% of the initial value at normalized accumulative permeate volumes of 140~150 L/m² after four runs of testing for CHPG-g-TFC, in comparison to ~50% for the plain PES-TFC. This work may provide useful strategies to design antifouling PRO membranes when using municipal wastewater as the feed for osmotic power generation.

Acknowledgements

This research study is supported by the National Research Foundation, Prime Minister's Office, Republic of Singapore, under its Environmental & Water Technologies Strategic Research Programme and administered by the Environment & Water Industry Programme Office (EWI) of the PUB. It is funded under the project entitled "Membrane Development for Osmotic Power Generation, Part 1. Materials Development and Membrane Fabrication" (1102-IRIS-11-01) and NUS Grant No. R-279-000-381-279. Special thanks are due to Prof. Y.P. Ting, Dr. G.L. Qiu, Mr. C.F. Wan, Mr. Z.L. Cheng, Mr. M. Soon, and Ms. S.C. Chen for their useful comments and assistance.

References

- Achilli, A.; Cath, T.Y.; Childress, A.E. Power generation with pressure retarded osmosis: an experimental and theoretical investigation. *J. Membr. Sci.* **2009**, *343*, 42-52.
- Achilli, A.; Childress, A.E. Pressure retarded osmosis: from the vision of Sidney Loeb to the first prototype installation – review. *Desalination* **2010**, *261*, 205-211.
- Cai, T.; Li, X.; Wan, C.F.; Chung T. S. Zwitterionic polymers grafted poly(ethersulfone) hollow fiber membranes and their antifouling behaviors for osmotic power generation. *J. Membr. Sci.* **2016**, *497*, 142-152.
- Calderon, M.; Quadir, M. A.; Sharma, S. K.; Haag, R. Dendritic polyglycerols for biomedical applications. *Adv. Mater.* **2010**, *22*, 190-218.
- Celik, Evrim.; Liu, L.; Choi, H. Protein fouling behavior of carbon nanotube/polyethersulfone composite membranes during water filtration. *Water Res.* **2011**, *45*, 5287-5294.
- Chen, S.C.; Wan, C.F.; Chung, T. S. Enhanced fouling by inorganic and organic foulants on pressure retarded osmosis (PRO) hollow fiber membranes under high pressures. *J. Membr. Sci.* **2015**, *479*, 190-203.
- Chen, S.C.; Amy, G.L.; Chung, T. S. Membrane fouling and anti-fouling strategies using wastewater retentate as the feed for osmotic power generation. *Water Res.* In press.
- Chou, S.; Wang, R.; Shi, L.; She, Q.; Tang, C.Y.; Fane, A.G. Thin-film composite hollow fiber membranes for pressure retarded osmosis (PRO) process with high power density. *J. Membr. Sci.* **2012**, *389*, 25–33.
- Chung, T. S.; Li, X.; Ong, R. C.; Ge, Q. C.; Wang, H. L.; Han, G. Emerging forward osmosis (FO) technologies and challenges ahead for clean water and clean energy applications. *Curr. Opin. Chem. Eng.* **2012**, *1*, 246-257.

- Escobar, I.C.; Van der Bruggen, B. Modern applications in membrane science and technology. USA: American Chemical Society, **2011**.
- Faure, E.; Falentin-Daudre, C.; Jerome, C.; Lyskawa, J.; Fournier, D.; Woisel, P.; Detrembleur, C. Catechols as versatile platforms in polymer chemistry. *Prog. Polym. Sci.* **2013**, *38*, 236-70.
- Fu, F.J.; Sun, S.P.; Zhang, S.; Chung, T.S. Pressure retarded osmosis dual-layer hollow fiber membranes developed by co-casting method and ammonium persulfate (APS) treatment. *J. Membr. Sci.* **2014**, *469*, 488–498.
- Gerstandt, K.; Peinemann, K. -V.; Skihagen, S. E.; Thorsen, T.; Holt, T. Membrane processes in energy supply for an osmotic power plant. *Desalination* **2008**, *224*, 64-70.
- Gu, Y.; Wang, Y.N.; Wei, J.; Tang, C.Y. Organic fouling of thin-film composite polyamide and cellulose triacetate forward osmosis membranes by oppositely charged macromolecules. *Water Res.* **2013**, *47*, 1867-1874.
- Kang, G.D.; Cao, Y.M. Development of antifouling reverse osmosis membranes for water treatment: A review. *Water Res.* **2012**, *46*, 584-600.
- Kim, Y.; Elimelech, M.; Shon, H.K.; Hong, S. Combined organic and colloidal fouling in forward osmosis: Fouling reversibility and the role of applied pressure. *J. Membr. Sci.* **2014**, *460*, 206-212.
- Kim, D.I.; Kim, J.W.; Shon, H.K.; Hong, S. Pressure retarded osmosis (PRO) for integrating seawater desalination and wastewater reclamation: Energy consumption and fouling. *J. Membr. Sci.* **2015**, *483*, 34-41.
- Lau, W.J.; Gray, S.; Matsuura, T.; Emadzadeh, D.; Chen, J.P.; Ismail, A.F. A review on polyamide thin film nanocomposite (TFN) membranes: History, applications, challenges and approaches. *Water Res.* **2012**, *46*, 584-600.

- 510 Lau, W.J.; Ismail, A.F.; Misdan, N.; Kassim, M.A. A recent progress in thin film
511 composite membrane: A review. *Desalination* **2012**, 287, 190-199.
- 512 Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. Mussel-inspired surface
513 chemistry for multifunctional coatings. *Science* **2007**, 318, 426-430.
- 514 Lee, M.H.; Yang, Z.; Lim, C.W.; Lee, Y.H.; Sun, D.; Kang, C.; Kim, J.S. Disulfide-
515 cleavage-triggered chemosensors and their biological applications. *Chem. Rev.* **2013**,
516 113, 5071-109.
- 517 Li, X.; Wang, K.Y.; Helmer, B.; Chung, T.S. Thin-film composite membranes and
518 formation mechanism of thin-film layers on hydrophilic cellulose acetate propionate
519 substrates for forward osmosis processes. *Ind. Eng. Chem. Res.* **2012**, 51, 10039–
520 10050.
- 521 Li, X.; Cai, T.; Chung T.S. Antifouling behavior of hyperbranched polyglycerol-grafted
522 poly(ether sulfone) hollow fiber membranes for osmotic power generation. *Environ.*
523 *Sci. Technol.* **2014**, 48, 9898-9907.
- 524 Li, X.; Chung, T.S. Thin-film composite P84 co-polyimide hollow fiber membranes for
525 osmotic power generation. *Appl. Energy* **2014**, 114, 600–610.
- 526 Li, Z.Y.; Yangali-Quintanilla, V.; Valladares-Linares, R.; Li, Q.Y.; Zhan, T.; Amy, G.L.
527 Flux patterns and membrane fouling propensity during desalination of seawater by
528 forward osmosis. *Water Res.* **2012**, 46, 195–204.
- 529 Li, Z.Y.; Linares, R.V.; Abu-Ghdaib, M.; Zhan, T.; Yangali-Quintanilla, V.; Amy, G.L.
530 Osmotically driven membrane process for the management of urban runoff in
531 coastal regions. *Water Res.* **2014**, 48, 200–209.

- Liu, Y.; Rosenfield, E.; Hu, M.; Mi, B.X. Direct observation of bacterial deposition on and detachment from nanocomposite membranes embedded with silver nanoparticles. *Water Res.* **2013**, *47*, 2949-2958.
- Liu, Y.; Ai, K.; Lu, L. Polydopamine and its derivative materials: synthesis and promising applications in energy, environmental, and biomedical fields. *Chem. Rev.* **2014**, *114*, 5057-115.
- Logan, B. E.; Elimelech, M. Membrane-based processes for sustainable power generation using water. *Nature* **2012**, *488*, 313-319.
- Mi, B. X.; Elimelech, M. Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents. *J. Membr. Sci.* **2010**, *348*, 337-345.
- Nunes, S.P.; Sforça, M.L.; Peinemann, K.-V. Dense hydrophilic composite membranes for ultrafiltration. *J. Membr. Sci.* **1995**, *106*, 49-56.
- Nunes, S.P.; Peinemann, K.-V. Membrane technology in the chemical industry. Second, revised and extended edition. Germany: Wiley-VCH Verlag GmbH, **2006**.
- Petersen, R.J. Composite reverse-osmosis and nanofiltration membranes. *J. Membr. Sci.* **1993**, *83*, 81-150.
- Ramon, G. Z.; Feinberg, B. J.; Hoek, E. M. V. Membrane-based production of salinity-gradient power. *Energy Environ. Sci.* **2011**, *4*, 4423-4434.
- Saeki, D.; Tanimoto, T.; Matsuyama, H. Anti-biofouling of polyamide reverse osmosis membranes using phosphorylcholine polymer grafted by surface-initiated atom transfer radical polymerization. *Desalination* **2014**, *350*, 21-27.

- 554 She, Q.; Jin, X.; Li, Q.; Tang, C.Y. Relating reverse and forward solute diffusion to
555 membrane fouling in osmotically driven membrane processes. *Water Res.* **2012**, *46*,
556 2478-2486.
- 557 Sivertsen, E.; Holt, T.; Thelin, W.; Brekke, G. Pressure retarded osmosis efficiency for
558 different hollow fibre membrane module flow configurations. *Desalination* **2013**,
559 *312*, 107-123.
- 560 Skihagen, S. E.; Dugstad, J. E.; Aaberg, R. J. Osmotic power – power production based
561 on the osmotic pressure difference between waters with varying salt gradients.
562 *Environ. Sci. Technol.* **2011**, *45*, 4360-4369.
- 563 Sotto, A.; Boromand, A.; Balta, S.; Kim, A.; Van der Bruggen, B. Doping of
564 polyethersulfone nanofiltration membranes: antifouling effect observed at ultralow
565 concentrations of TiO₂ nanoparticles. *J. Mater. Chem.* **2011**, *21*, 10311-10320.
- 566 Van der Bruggen, B. Vandecasteele, C. Removal of pollutants from surface water and
567 groundwater by nanofiltration: overview of possible applications in the drinking
568 water industry. *Environ. Pollut.* **2003**, *122*, 435-445.
- 569 Wan, C.F.; Chung, T.S. Osmotic power generation by pressure retarded osmosis using
570 seawater brine as the draw solution and wastewater brine as the feed. *J. Membr. Sci.*
571 **2015**, *479*, 148-158.
- 572 Wick, G.L.; Schmitt, W.R. Prospects for renewable energy from the sea. *Mar. Technol.*
573 *Soc. J.* **1977**, *11*, 16-21.
- 574 Wilms, D.; Stiriba, S. E.; Frey, H. Hyperbranched polyglycerols: from the controlled
575 synthesis of biocompatible polyether polyols to multipurpose applications. *Acc.*
576 *Chem. Res.* **2010**, *43*, 129-141.

- 577 Xie, M.; Nghiem, L.D.; Price, W.E.; Elimelech, M. Impact of humic acid fouling on
578 membrane performance and transport of pharmaceutically active compounds in
579 forward osmosis. *Water Res.* **2013**, *47*, 4567-4575.
- 580 Zhang, M.M.; Hou, D.X.; She, Q.H.; Tang, C.Y. Gypsum scaling in pressure retarded
581 osmosis: Experiments, mechanisms and implications. *Water Res.* **2014**, *48*, 387-395.
- 582 Zhang, S.; Sukitpaneenit, P.; Chung, T. S. Design of robust hollow fiber membranes with
583 high power density for osmotic energy production. *Chem. Eng. J.* **2014**, *241*, 457-
584 465.

Graphic Abstract

Scheme 1. Synthetic route for the CHPG polymer.

PES-TFC **PDA-TFC** **CHPG-g-TFC**

Figure 1. Comparison of membrane morphology of PES-TFC, PDA-TFC, and CHPG-g-TFC hollow fiber membranes .

Figure 2. XPS wide scan, C 1s, N 1s and S 2p core-level spectra of outer surface of (a) PES-TFC, (b) PDA-TFC and (c) CHPG-g-TFC hollow fibers.

Figure 3. Cytotoxicity assays of (a) PES-TFC, (b) PDA-TFC, (c) CHPG-g-TFC hollow fibers in 3T3 fibroblasts culture medium after 24 h of incubation. Error bars represent the standard deviation of four measurements.

Figure 4. Relative fluorescence intensities and respective fluorescence microscopy images of outer surface of (a) PES-TFC, (b) PDA-TFC, (c) CHPG-g-TFC hollow fibers after exposure to 0.5 mg/mL BSA-FITC solution for 1 h. Scale bar: 100 μm.

Figure 5. SEM images of outer surfaces (A) and viable adherent fractions (B) of (a) PES-TFC, (b) PDA-TFC, (c) CHPG-g-TFC hollow fibers after exposure to *S. aureus* (top) and *E. coli* (below) at an initial cell concentration of 5×10^7 cells/mL for 4 h at 37 °C. The cell number was determined by the spread plate method.

Figure 6. Membrane fouling behaviors by using municipal wastewater as the feed. The normalized water flux decline is plotted against normalized accumulative permeate volume. The draw solution initially contained 0.81 M NaCl, and a wastewater was used as the feed solution. The hydraulic pressure difference between feed and draw solutions was 15.0 ± 1.0 bar. De-ionized water: DI water.

Figure 7. SEM detection on outer surfaces of (a) PES-TFC, (b) PDA-TFC, (c) CHPG-g-TFC hollow fibers before PRO tests and after 1st de-ionized water cleaning. The draw solution initially contained 0.81 M NaCl, and wastewater was used as the feed solution. Hydraulic pressure difference between feed and draw solutions was 15.0 ± 1.0 bar. Back washing was performed to clean the fouled membrane by de-ionized water at 15.0 ± 1.0 bar.

Table 1. Transport properties and power densities of the PES-TFC and CHPG-g-TFC membranes.

Membrane	Water permeability, A (L m ⁻² h ⁻¹ bar ⁻¹)	Salt permeability, B (L m ⁻² h ⁻¹)	Salt rejection (%)	Power density (W/m ²)				
				Initial	After Run 1	After Run 2	After Run 3	After Run 4
PES-TFC	0.78 ± 0.08	0.58 ± 0.06	95.1 ± 5.5	8.3	4.3	3.6	4.1	3.6
CHPG-g-TFC	0.74 ± 0.15	0.55 ± 0.11	94.9 ± 5.8	8.2	6.0	5.9	5.3	5.6

A. 1000 ppm NaCl as the feed solution in the RO test under an applied pressure of 15 bar for transport properties.

B. 0.81 M NaCl and wastewater were used as the feed pair in PRO tests. The hydraulic pressure difference between feed and draw solutions was 15.0 ± 1.0 bar.

1. A method to fabricate antifouling pressure retarded osmosis (PRO) membranes.
2. Real municipal wastewater retentate was employed as the feed.
3. The modified membrane has low fouling propensity and high recovery.
4. The modified membrane has improved power density.