



Sulfonated hyperbranched polyglycerol grafted membranes with antifouling properties for sustainable osmotic power generation using municipal wastewater



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ABSTRACT

In recent years, pressure retarded osmosis (PRO) has drawn considerable attention due to its feasibility of harvesting clean and sustainable osmotic power through a membrane process. When municipal wastewater is fed into this process, fouling in the porous substrate of the PRO membrane is the major concern since it can hinder the membrane performance tremendously and lower the power generation. In this work, sulfonated hyperbranched polyglycerol (SHPG) polymers with a dendritic architecture have been molecularly designed and then grafted onto the surface of polydopamine (PDA) coated poly(ethersulfone) (PES) hollow fiber membranes. Comparing to the pristine PES membranes, the SHPG modified PRO membranes show significantly improved resistance to protein adhesion and bacterial attachment due to the high wettability of their ionic polymer brushes. In PRO tests under different hydraulic pressures, the SHPG-grafted membranes show a lower flux reduction and a higher flux recovery rate of 94% vs. 87% in comparison with the pristine PES membranes. Therefore, the osmotic power generation can be significantly sustained by modifying the PRO membranes with SHPG polymers. This work may provide a versatile approach and useful insights for the design of membranes with antifouling properties in the molecular level.

1. Introduction

Osmotic energy generated from salinity gradients is a renewable energy alternative to conventional energy sources. Pressure retarded osmosis (PRO) allows the harvest of osmotic energy through the mixing of solutions with different chemical potentials [1–6]. In this process, water transports from a low salinity solution across a semi-permeable membrane to a high salinity solution against a hydraulic pressure [7–11]. Early PRO processes focused on the mixing of seawater and river water [1,7–9,12]. However, the power density from this feed pair was low due to their small difference in osmotic pressure. Besides, extensive pre-treatments of river water and seawater must be conducted to reduce membrane fouling [13,14], which made the whole process less economically feasible. In Singapore, low value wastewater re-tentate (WWRé) generated from municipal water plants has a low salinity similar to the river water. Thus, it may serve as a potential feed solution for osmotic power generation from an economic perspective [3,15–17]. Since the seawater brine (SWBr) produced from seawater reverse osmosis (SWRO) desalination plants has a higher salinity than seawater, more osmotic energy can be harvested if the SWBr and WWRé

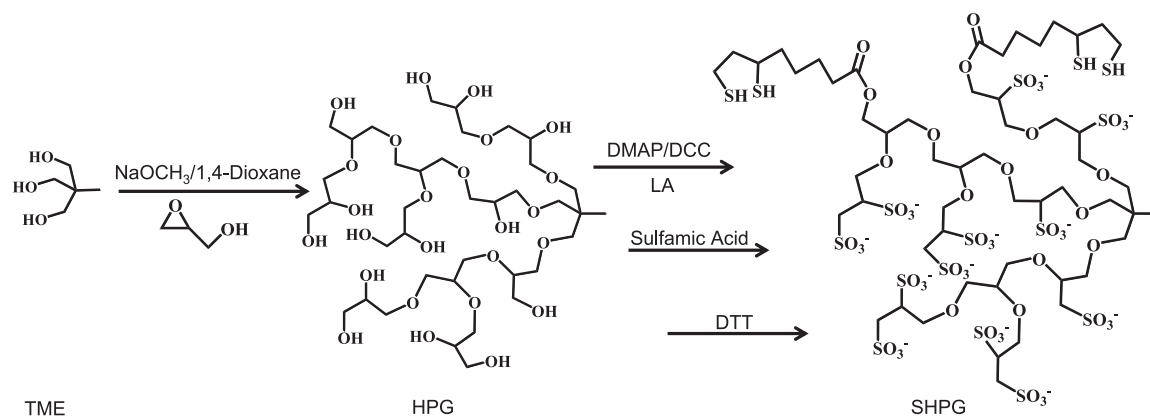
pair is fed into the PRO process [3,15,18,19].

Even though high performance PRO membranes have been developed [3,20,21], previous experiments using SWBr/WWRé as the feed pair showed that the power density could drop tremendously even to near 0 W/m² after a short period of operation due to significant membrane fouling [18,22]. The fouling induced by SWBr on the selective layer was negligible due to the back permeation of water flux [3,23]. However, the permeate water could carry solutes, particles and other compounds in WWRé into the porous support. The accumulation of foulants within the porous substrate may result in severe internal concentration polarization (ICP) and flux reduction [3,13–15,22–28]. Thus, it is essential to develop effective anti-fouling strategies to minimize the fouling tendency of the porous substrate layer.

Several strategies have been proposed to mitigate the fouling phenomena in the PRO process. For example, one could pre-treat WWRé by ultrafiltration, nano-filtration and pH manipulation to remove certain foulants prior to feeding it into the PRO process [18,25,26]. However, the additional pre-treatments may increase energy consumption, footprint and operational cost to run the whole process. The other approach was to design dual-layer PRO membranes consisting of a dense-selective

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Scheme 1. Synthetic Route for the Sulfonated Hyperbranched Polyglycerol (SHPG) Polymers.

layer for power generation and a protect layer for prevention of foulants accumulation inside the porous layer [29]. Nevertheless, some small foulants might inevitably slip through the protection layer and be trapped inside the porous substrate. The preferred strategy is to enhance the antifouling properties of the PRO membranes [29–39]. Since an increase in surface hydrophilicity may result in membranes with enhanced antifouling properties due to the formation of a hydration layer, this layer can serve as a steric and energetic barrier against the bonding between organic foulants and membranes. Thus, grafting hydrophilic materials on porous substrate surfaces is a simple and facile modification method while maintaining the structural properties of the substrates [31–33,35–40]. In addition, this type of post-modifications can be implemented easily on large-scale modifications of commercial membranes.

Li *et al.* has developed a novel architected dendritic hyperbranched polyglycerol (HPG) grafted membrane with enhanced resistance to protein and bacterial compared with a linear polyethylene glycol polymer [31]. The dendritic structure exhibited anti-adsorption behavior without increasing mass transport resistance for water transport. However, it lacked strong repulsive forces to ions, and thus its anti-fouling properties could be easily shielded by inorganic scaling in long-term operations. Therefore, it is essential to explore new and effective surface modification strategies with superior and sustainable antifouling performance.

In this work, we aim to design and graft a negatively charged sulfonated HPG (SHPG) on the substrate surface of PRO membranes for sustainable osmotic power generation using WWRE as the feed solution. To do so, a state-of-the-art thin film composite (TFC) PRO hollow fiber membrane with superior performance was used for the surface modification. The SHPG was synthesized by the ring-opening polymerization of glycidol and then functionalized with α -lipoic acid (LA) and sulfamic acid. Afterwards, the polymer was grafted on the polydopamine (PDA) treated PRO membrane surface via Michael addition. It is worth noting that the mild grafting conditions would not damage the membrane structure [41]. With the enhanced hydration effect and extra electrostatic repulsion, the negatively charged SHPG may provide the current PRO membrane with enhanced antifouling properties. In addition, 10 h PRO tests under different operating pressures were carried out to verify the effect of the antifouling coating and quantify the fouling behavior on the feed side of the membrane. This work may provide useful insights for the design of antifouling PRO membranes and accelerate the commercialization of PRO processes.

2. Experimental section

2.1. Materials

1,1,1-Tris(hydroxymethyl)ethane (TME, 99%), sodium methoxide

(NaOCH₃, 95%), 4-(*N,N*-dimethylamino)pyridine (DMAP, $\geq 99\%$), *N,N'*-dicyclohexylcarbodiimide (DCC, $\geq 99\%$), (\pm)- α -lipoic acid (LA, $\geq 99\%$), sulfamic acid (SA, $\geq 99\%$), DL-dithiothreitol (DTT, 99%), dimethyl sulfoxide (DMSO, $\geq 99.5\%$) and triethylamine (TEA, $\geq 99\%$) were all purchased from Sigma-Aldrich and used as received. Prior to use, 1,4-dioxane (99.8%, Sigma-Aldrich) and glycidol (GLY, 96%, Sigma-Aldrich) were freshly distilled from CaH₂ under a reduced pressure. *N*-Methyl-2-pyrrolidone (NMP, Analytical grade, Merck) and *N,N*-dimethylformamide (DMF, HPLC grade, Fisher Scientific) were employed to dissolve the synthesized polymers. Polyethersulfone (PES, Solvay Advanced Polymers) was used to fabricate the hollow fiber substrate. 1,3-Phenylenediamine ($> 98\%$, TCI, Japan), sodium dodecyl sulfate ($\geq 99\%$, Sigma-Aldrich), trimesoyl chloride ($\geq 98\%$, Alfa-Aesar) and hexane (99.9%, Fisher Chemicals) were utilized to form the TFC layer on the lumen of the PES hollow fiber substrate. Dopamine hydrochloride ($\geq 98\%$, TCI, Japan) and tris(hydroxymethyl)aminomethane (Tris, $\geq 99.8\%$, Sigma-Aldrich) were used to treat the outer surface of the membrane. Gram-positive *Staphylococcus epidermidis* (*S. epidermidis*, ATCC 35984) and Gram-negative *Escherichia coli* (*E. coli*, ATCC DH5 α) were obtained from American Type Culture Collection (Manassas, VA, USA) for the tests of bacterial adhesion.

All nuclear magnetic resonance (NMR) spectra were acquired on a Bruker ARX 300 MHz NMR spectrometer. The chemical shifts were given in ppm and internally referenced to the residual proton signals of $\delta = 2.50$ for DMSO-*d*₆. Gel permeation chromatography measurements (GPC) were performed with an Agilent 1260 system using water as the eluent at a flow rate of 1.0 mL/min. A refractive index detector, a 5 μ m guard column, three PL gel columns (two Agilent Mixed-C 5 μ m columns and one Agilent Mixed-D 5 μ m column) and narrow molecular weight poly(ethylene glycol) standards were used.

2.2. Synthesis of sulfonated hyperbranched polyglycerol (SHPG) polymers

The hyperbranched polyglycerol (HPG) homopolymers were synthesized by a previously reported anionic ring-opening multibranching polymerization (AROMP) of GLY monomers with TME as the initiator and NaOCH₃ as the catalyst (Scheme 1) [31,42–44]. Briefly, TME (181 mg, 1.51 mmol) and NaOCH₃ (24.3 mg, 0.45 mmol) were sequentially dissolved in anhydrous methanol (2 mL) to deprotonate 10% of the hydroxyl groups. The mixture was then stirred at 60 °C for 2 h and evacuated at 80 °C overnight to yield a white salt of sodium alkoxide. The initiator salt was dispersed in the anhydrous 1,4-dioxane (40 mL) by sonication and flushed with argon flow to remove the dissolved oxygen. The reaction flask was sealed with a rubber stopper and heated to 100 °C under continuous stirring. A mixture of freshly distilled, argon-purged GLY (10 mL, 151 mmol) and anhydrous 1,4-dioxane (10 mL) was added dropwise to the reaction flask within 24 h via a syringe pump. Afterwards, the polymerization was continued for

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