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Negatively charged hyperbranched polyglycerol grafted membranes for osmotic power generation from municipal wastewater

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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 *Escherichia coli* adhesion and *Staphylococcus 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/m^2 in comparison to an average value of 3.6 W/m^2 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.

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; Skilhagen et al., 2008; 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/m^2 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,

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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, 2014; Lau et al., 2015; 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; Chen et al., 2016; Wan and Chung, 2015). Therefore, how to mitigate fouling is gradually becoming as the major obstacle to commercialize the PRO technology.

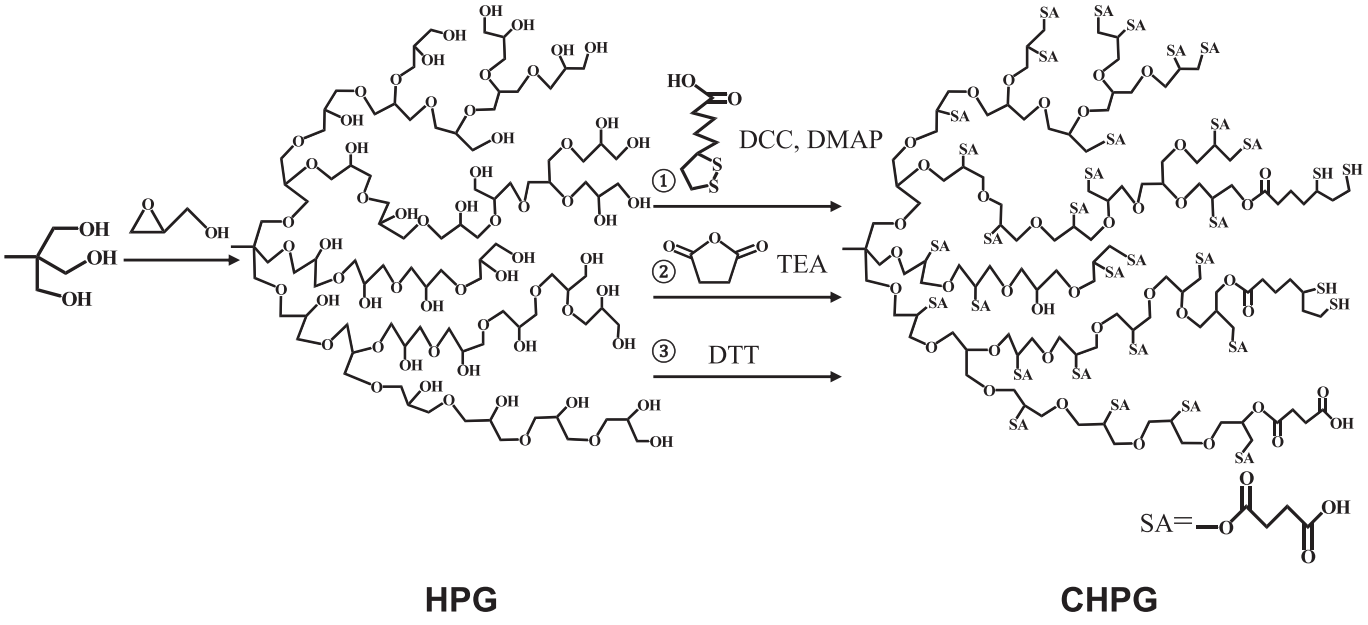
Development of antifouling PRO membranes is an essential way to control fouling. Although many anti-fouling methods have been proposed (Escobar and Van der Bruggen, 2011; Liu et al., 2013; Mi and Elimelech, 2010; Saeki et al., 2014; Sotto et al., 2011), it is still difficult to design antifouling PRO 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 (Fig. 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



Scheme 1. Synthetic route for the CHPG polymer.