Journal of Membrane Science 497 (2016) 142–152

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Zwitterionic polymers grafted poly(ether sulfone) hollow fiber membranes and their antifouling behaviors for osmotic power generation

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ARTICLE INFO

Article history:
Received 17 July 2015
Received in revised form
14 September 2015
Accepted 15 September 2015
Available online 18 September 2015

Keywords:
Poly(ether sulfone)
Pressure retarded osmosis
Zwitterionic polymer
Thin-film composite membrane
Antifouling

ABSTRACT

Fouling on pressure retarded osmosis (PRO) membranes must be eliminated to maximize the efficiency of osmotic power generation. This is particularly applicable to PRO membranes due to its nature of fouling when wastewater is fed. To improve this, PRO thin-film composite (TFC) membranes for the first time will be redesigned by incorporating well-defined zwitterionic copolymers of [2-(methacryloyloxy) ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (DMAPS) or 2-methacryloyloxyethyl phosphorylcholine (MPC) onto the poly(ether sulfone) (PES) hollow fiber membranes. The introduction of 2-methacryloyloxyethyl lipoate (MEL) components into the zwitterionic copolymers provided sufficient grafting sites for the facile decoration of polydopamine (PDA) pretreated PES membranes via Michael addition. The PDMAPS and PMPC grafted membranes were shown to be effective in reducing protein adsorption and bacterial adhesion, in comparison to the pristine PES membranes and PDA pretreated membranes. The pristine TFC–PES membranes are fouled greatly in high pressure PRO tests with concentrated wastewater, resulting in a flux reduction of 61%. In contrast, the TFC–PES membranes grafted by zwitterionic PDMAPS and PMPC copolymers exhibit substantial improvement of flux recovery up to 98% after backwashing and hydraulic pressure impulsion. In summary, the osmotic power generation may be sustained by grafting the PRO membranes with the properly designed zwitterionic polymers.

1. Introduction

Oceans and water in high concentrations of salt can provide osmotic energy which is more attractive, renewable and green in comparison to conventional fossil fuel. The process of pressure retarded osmosis (PRO) is the most suitable in terms of versatility and cost to effectively convert osmotic energy into electricity [1–5]. Unfortunately, early stages of PRO research discontinued in particularly due to lack of effective membranes [6–9]. In 2009, Statkraft from Norway continued on the research with the construction of the first ever prototype PRO plant. This greatly contributed to the progress on PRO membranes and system modeling [10–15].

A successful PRO process requires PRO membranes with minimal fouling tendency. The separation process tends to clog the membranes by depositing the retained inorganic materials, organic compounds and microorganisms on the membrane surface or even into the membrane pores [12,16–24]. The magnitude of such effects is typically much larger for PRO process, other than conventional pressure driven membrane processes, once a porous support is subjected to fouling from the feed solution. Fouling can be reduced by various methods such as pretreatment of feed solution, periodic cleaning, or surface modification of PRO membranes. In terms of cost and productivity, surface modification of PRO membranes via molecular design will be the preferred method to eliminate fouling without affecting bulk properties.

Tethering of well-defined polymer brushes onto the membrane surfaces can be accomplished by either “grafting from” or “grafting to” approaches [17,25,26]. In “grafting from” a membrane surface, the polymer layer is constructed in situ by chain propagation through successive addition of monomer units from initiating sites on the surface. The “grafting from” approach exhibits a higher grafting efficiency due to less steric hindrance duration diffusion of small monomers. In “grafting to” a membrane surface, a prefabricated polymer with well-defined functionalities is covalently linked to the substrates. Although the achievable grafting density via “grafting to” methods tends to be lower than that of “grafting from” methods, precision engineering of the surface properties is made more controllable due to the fact that the molecular

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http://dx.doi.org/10.1016/j.memsci.2015.09.037
0376-7388/

parameters of the prefabricated polymers applied can be thoroughly characterized in terms of molecular weight, molecular weight distribution and other physicochemical properties prior to conjugation. In addition to direct polymerization of functional monomers, "grafting to" method of prefabricated polymers have attracted much attention due to the possibility of preparing specific functional polymer brushes that are inaccessible by the direct polymerization methods.

Surface grafting of poly(ethylene glycol) (PEG) is the most commonly used method for the generation of ultralow fouling surfaces due to its hydration property via hydrogen bonding. However, long term usage will cause a reduction in their antifouling properties due to the oxidative degradation of PEG chains. Zwitterionic-based materials have been considered as the most suitable alternative for the preparation of ultralow fouling surfaces [27–33]. Water molecules can be bound stronger than PEG chains via electrostatically induced hydration. Nonspecific protein adsorption from single-protein solutions can be reduced greatly with effectiveness better than PEG-modified surfaces. In addition, they have high resistance to bacterial adhesion and biofilm formation.

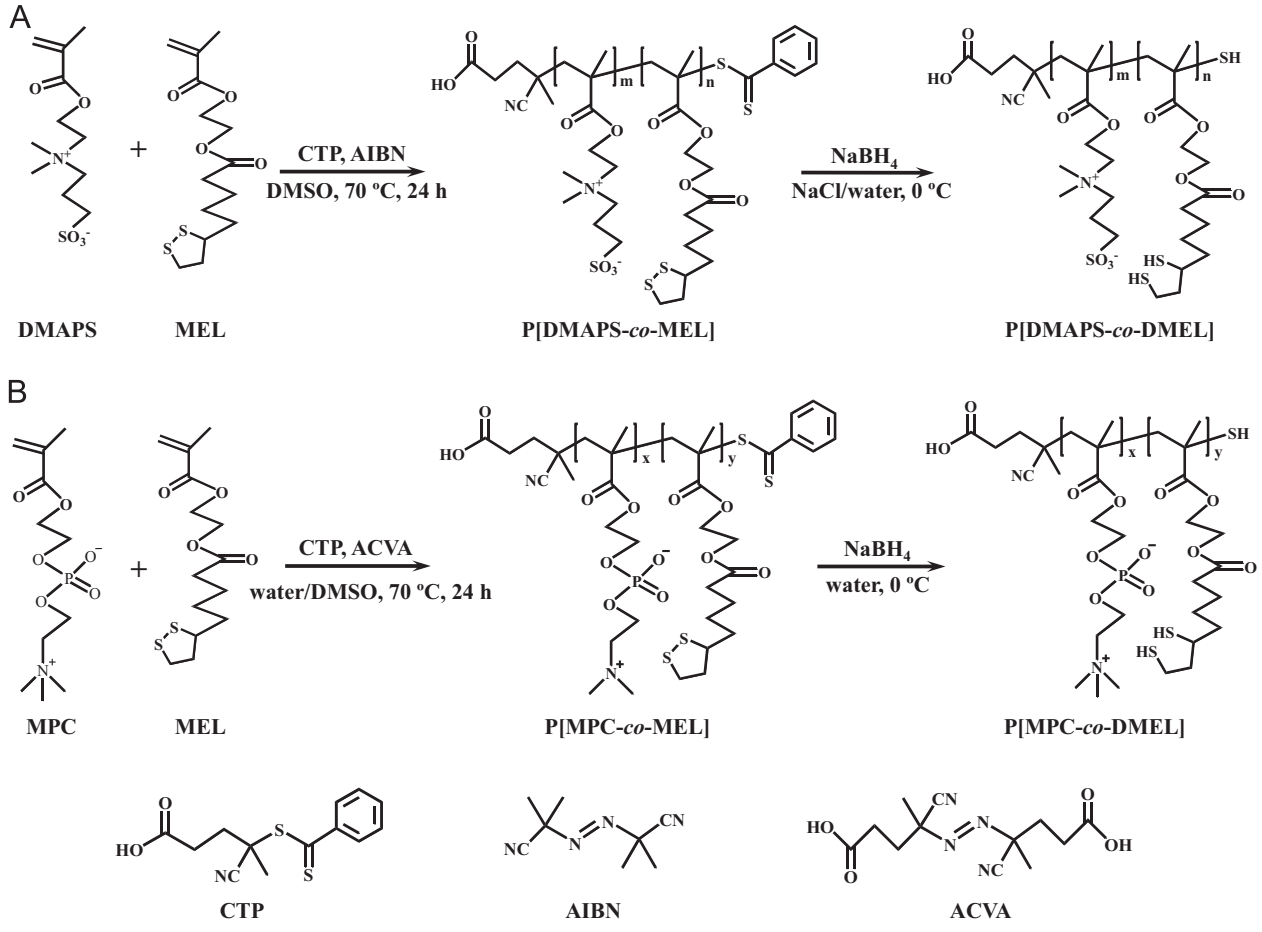
The aim of this study is to demonstrate a simple and versatile mean for the surface modification of PRO membranes via the "grafting to" method and to explore new and effective antifouling strategies by grafting zwitterionic copolymers onto the PRO membrane surfaces. Scheme 1 illustrates the synthetic routes of two zwitterionic copolymers. It involves reversible addition–fragmentation chain transfer (RAFT) polymerization of a zwitterionic monomer, either [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (DMAPS) or 2-methacryloyloxyethyl phosphorylcholine (MPC) and a disulfide-containing monomer, 2-methacryloyloxyethyl lipoate (MEL) in the presence of 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CTP) as the RAFT agent and 2,2′-azobis(2-methylpropionitrile) (AIBN) as the initiator, followed by cleavage of the disulfide groups using excess $NaBH_4$ as the reducing agent.

Scheme 2 illustrates the step-by-step procedure to incorporate the zwitterionic copolymers onto the poly(ether sulfone) (PES) hollow fiber membranes via the "grafting to" approach: (i) modules fabrication from PES hollow fiber membranes; (ii) deposition of an ultrathin polyamide layer on the inner surface of hollow fiber membranes via in situ interfacial polymerization; (iii) polydopamine (PDA) pretreatment of the outer surface of the membranes; (iv) tethering of zwitterionic copolymers with thiol functionalities onto the PDA pretreated PES membranes via Michael addition. To the best of our knowledge, incorporation of zwitterionic polymers onto the PDA pretreated PRO membranes has never been proposed. The current work may provide useful insights on the fabrication of sustainable PRO membranes with ultralow fouling characteristics for osmotic power generation.

2. Experimental section

2.1. Materials

Dimethyl sulfoxide (DMSO, ≥99%), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CTP, >97%), [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (DMAPS, 97%), 2-methacryloyloxyethyl phosphorylcholine (MPC, 97%), sodium borohydride ($NaBH_4$, 98%), dopamine hydrochloride (Dopa,



Scheme 1. Synthetic route for the P[DMAPS-*co*-DMEL] and P[MPC-*co*-DMEL] random copolymers.