



Anti-biofouling of polyamide reverse osmosis membranes using phosphorylcholine polymer grafted by surface-initiated atom transfer radical polymerization



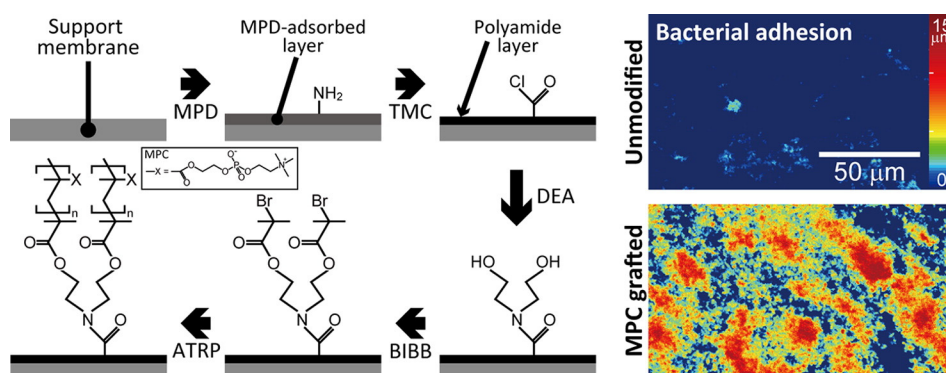
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HIGHLIGHTS

- Phosphorylcholine polymer was grafted onto polyamide reverse osmosis membranes.
- The polymer was grafted by surface-initiated atom transfer radical polymerization.
- The initiator was immobilized onto the surface of the polyamide layer.
- The grafted membrane showed high anti-biofouling activity retaining the water flux.

GRAPHICAL ABSTRACT



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ABSTRACT

The zwitterionic phosphorylcholine polymer was covalently grafted on a polyamide reverse osmosis (RO) membrane for anti-biofouling, using surface-initiated atom transfer radical polymerization (ATRP). Polyamide RO membranes modified with hydroxyl groups of diethanolamine (DEA) were fabricated by interfacial polymerization. The ATRP initiator, 2-bromoisobutryl bromide (BIBB), was immobilized on the fabricated membrane, by condensation between DEA hydroxyl groups and BIBB carboxylic bromide. BIBB immobilization was confirmed by X-ray photoelectron spectroscopy. ATRP was carried out using 2-methacryloyloxyethyl phosphorylcholine (MPC) and immobilized BIBB. Attenuated total reflectance Fourier transform infrared spectra indicated that the MPC polymer was grafted on the membrane surface. The amount of grafted MPC polymer increased with increasing polymerization time. The surface morphology of the MPC polymer-grafted membranes became smoother with increasing polymerization time. The polyamide RO membrane with grafted MPC polymer retained its initial water flux in a crossflow bacterial filtration test, preventing bacterial adhesion on the surface.

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1. Introduction

Water treatment using reverse osmosis (RO) membranes has been widely applied in desalination because of their energy- and space-

saving performance. They can be used to treat seawater containing organic matter including bacteria [1–3], proteins, and polysaccharides [4–7]. However, organic matter decreases membrane performance by adhering to membrane surfaces and blocking pores. Especially, adhered bacteria can grow into biofilms containing extracellular polymeric substances (EPS), such as proteins and polysaccharides [2,8]. This is called biofouling. Adhered organic matter is generally removed by chemical

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treatment, often with chlorine [9]. Typical practical RO membranes are polyamide composites, consisting of a polyamide rejection layer and polysulfone support membrane [10]. Amide bonds in polyamide RO membranes are easily cleaved by chlorine treatment, which decreases membrane performance [11]. Chemical treatment for anti-biofouling is therefore unsuitable for polyamide RO membranes; however, preventing bacterial adhesion is important for their long-term operation.

To prevent adhesion of organic matter on water treatment membranes, immobilization of biocides such as metal nanoparticles [12,13] and enzymes [14] onto membrane surface has been reported. Although the immobilized biocides can effectively kill adhered bacteria, the killed bacteria release various organic matters such as proteins, polysaccharides, and lipids, causing membrane fouling. Therefore the immobilization of biocides is not suitable for long-term operation.

As alternative approaches, surface modification with hydrophilic polymers like polyethylene glycol (PEG) or zwitterionic polymers is commonly undertaken [15]. PEG prevents the adhesion of proteins [16,17], cells [18], and bacteria [19], because of its high hydrophilicity and extruded volume [20]. PEG modification of RO membranes has been used to prevent the adhesion of organic matter [21–25] including bacteria [26]. The zwitterionic polymers such as sulfobetaine polymers and phosphorylcholine polymers reportedly also inhibit the adhesion of organic matter [27–30], and have been applied in the surface modification of RO membranes [31–34]. Zwitterionic polymers have a similar structure to biological membranes, and interact with water molecules via electrostatic interaction more strongly than PEG [35]. Especially, MPC polymers have been widely applied to water treatment membranes to prevent adhesion of organic matters due to their high hydrophilicity and biocompatibility [36,37]. However, the effect of surface modification with hydrophilic polymer on the anti-biofouling, including prevention of the decreased membrane performance in bacterial filtration tests, has not been elucidated.

Modifying the surface of RO membranes with these polymers has generally been carried out by the interfacial reaction of a target surface and a pre-synthesized polymer containing active functionality [21,23,24,26], or by surface-initiated radical polymerization [25,31,38]. The former is a relatively easy modification, but requires polymers with specific functionality. The latter has been more widely applied, because of its compatibility with various monomers, and controllable polymer surface density [39,40]. Atom transfer radical polymerization (ATRP) is often used to accurately control the chain length of synthesized polymers [41,42]. In modifying the surface of RO membranes using ATRP, initiators must be immobilized on the membrane surface, but their direct immobilization on commercial RO membranes remains difficult.

In this study, we developed a prevention technique of biofouling on a RO membrane by covalently grafting a phosphorylcholine polymer using surface-initiated ATRP. A polyamide RO membrane modified with the ATRP initiator, 2-bromoisobutyl bromide (BIBB), was prepared by interfacial polymerization [14,21]. Surface-initiated ATRP was carried out using 2-methacryloyloxyethyl phosphorylcholine (MPC) and immobilized BIBB. The surfaces of the fabricated RO membranes were evaluated by water contact angle measurement, ζ -potential measurement, X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, and field emission scanning electron microscopy (FE-SEM). The water flux and salt rejection were measured to gauge membrane performance. Anti-biofouling properties were evaluated by crossflow bacterial filtration tests.

2. Materials and methods

2.1. Materials

All chemicals, if not otherwise specified, were obtained from Wako Pure Chemical Industries (Osaka, Japan), and were used without further

purification. All aqueous solutions were prepared with deionized water. MPC was kindly provided by NOF (Tokyo, Japan). Polysulfone support membranes were obtained from Nitto Denko (MWCO = 500 kDa; Osaka, Japan). Sodium dodecyl sulfate (SDS), (\pm)-10-camphorsulfonic acid (Tokyo Chemical Industry, Tokyo, Japan), *m*-phenylene diamine (MPD; Tokyo Chemical Industry), and 1,3,5-benzenetricarbonyl trichloride (TMC; Sigma-Aldrich, St. Louis, MO, USA) were used to form the polyamide layer on the RO membranes. Diethanolamine (DEA, Nakarai Tesque, Kyoto, Japan) was used as a spacer molecule to immobilize the ATRP initiator, BIBB (Tokyo Chemical Industry), 2,2'-Bipyridyl (Sigma-Aldrich), copper(II) bromide (Nakarai Tesque), ethyl 2-bromoisobutyrate (Tokyo Chemical Industry), and ascorbic acid (Tokyo Chemical Industry) were used to carry out ATRP.

2.2. Fabrication of polyamide RO membrane and surface modification with ATRP initiator

The polyamide RO membrane modified with DEA was fabricated by interfacial polymerization (Fig. 1) [14,21]. A support membrane was immersed in an aqueous solution containing 2.0 wt.% MPD, 0.25 wt.% SDS, 2.0 wt.% triethylamine, and 4.0 wt.% (\pm)-10-camphorsulfonic acid for 5 min. The membrane was immersed in an *n*-hexane solution of 0.15 wt.% TMC for 1 min, forming the polyamide RO layer. The polyamide RO membrane was immersed in an aqueous solution containing 2.0 wt.% DEA, 2.0 wt.% triethylamine, and 4.0 wt.% (\pm)-10-camphorsulfonic acid for 5 min, to modify the membrane surface with diethanolamine. The membrane was dried at 80 °C for 10 min, rinsed, and stored in deionized water at 5 °C.

2.3. Surface-initiated ATRP

To immobilize BIBB, the DEA-modified membrane was dried with nitrogen, immersed in 20 mL of hexane solution containing 4.2 mmol of dehydrated pyridine and 4.2 mmol of 2-bromoisobutyl bromide (BIBB) for 1 h, and washed with ethanol and deionized water. The BIBB immobilized membrane was immersed in 18 mL of deionized water/methanol (2/8, v/v) containing 10 mmol of MPC, with nitrogen bubbling for 15 min. Two milliliters of deionized water/methanol (2/8, v/v) containing 0.02 mmol of 2,2'-bipyridine, 0.002 mmol of CuBr₂, and 0.02 mmol of ascorbic acid was added. The mixed solution was purged with nitrogen for 15 min, and stirred for a given time in dark. The reacted membrane was washed with deionized water.

2.4. Characterization of surface properties

The water contact angle of the membrane surface was measured using a contact angle meter (DM-300; Kyowa Interface Science, Saitama, Japan). A low contact angle indicates a hydrophilic surface. The ζ -potential of the membrane surface was measured with an electrophoretic light-scattering apparatus (ELSZ-1000ZS; Otsuka Electronics, Osaka, Japan) in aqueous 10 mmol/L NaCl at pH 7.0. The chemical composition of the membrane surface was analyzed using XPS (JPS-9200, JEOL, Tokyo, Japan) and ATR-FTIR spectroscopy (ALPHA FT-IR spectrometer; Bruker Optics, Ettlingen, Germany). The membrane morphology was observed using FE-SEM (JFS-7500F; JEOL). For FE-SEM observations, the membrane samples were freeze dried under vacuum (FDU-1200; Tokyo Rikakikai, Tokyo, Japan), and coated with osmium (Neoc; Meiwafoods, Tokyo, Japan).

2.5. Quantification of grafted MPC polymer

The amount of grafted MPC polymer was quantitated by a colorimetric phosphorus assay [43] (Supplementary data), because MPC contains phosphorus. The weight-average molecular weight of the grafted MPC polymer was estimated from the bulk ATRP, using ethyl-2-bromoisobutyrate (Tokyo Chemical Industry) as an ATRP initiator. The

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