Surface modification of reverse osmosis membranes with zwitterionic coating for improved resistance to fouling

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HIGHLIGHTS

- Surface modification of commercial RO desalination membranes
- p(4VP-co-EGDA) co-polymerization via initiated chemical vapor deposition
- Functionalization of the co-polymer to carboxybetaine zwitterion surface moieties
- Significant reduction of bacterial cell attachment on modified membrane surface
- Perm selectivity under cross flow conditions comparable to virgin membranes

ARTICLE INFO

ABSTRACT

Copolymer films of poly(4-vinylpyridine-co-ethylene glycol diacrylate) (p(4-VP-co-EGDA)) were synthesized and first deposited on various substrates via initiated chemical vapor deposition (iCVD). As-deposited copolymer films were converted to surface zwitterionic structures containing poly(carboxybetaine acrylic acetate) (pCBAA) units by a quaternization reaction with 3-bromopropionic acid (3-BPA). Conversion to a zwitterionic structure was confirmed by FTIR and high-resolution XPS N1s scans. Biopolymer adsorption of the deposited copolymer coatings was investigated by quartz crystal microbalance with dissipation (QCM-D) using a model foulant-bovin serum albumin (BSA). The optimized copolymer films were then deposited onto commercial RO membranes and with subsequent zwitterionicalization. Inertness to bacterial adhesion of the modified membranes was investigated by counting the number of *Escherichia coli* and *Pseudomonas aeruginosa* cells attached on the membrane surface under static conditions. Bacterial adhesion studies revealed an almost 98% reduction in micro-organism attachment onto the surface of modified membranes compared to bare membranes, which clearly demonstrates the effectiveness and superior performance of the zwitterionic coating against bacterial adhesion. The salt rejection performance of the modified membranes resulted in improved salt rejection (98%); however, permeate flux was slightly compromised compared to virgin membranes. AFM analysis demonstrated that modified membranes showed lower RMS roughness compared to virgin membranes.

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1. Introduction

Membrane fouling is by far the most serious problem found in separation processes such as water desalination, industrial water treatment, juice concentration, and hemodialysis [1–3]. Among the other types of fouling, organic fouling and biofouling are the most severe in nature and pose a serious challenge for membranes based separation processes such as seawater desalination and wastewater reclamation. Organic fouling may be caused by the bio-molecule foulant present in the feed water. These bio-molecule foulants are represented by three important classes, namely, proteins, polysaccharides and natural organic matter (NOM). Proteins and alginate adsorption on RO membrane surfaces are known to play a direct role in membrane-biofouling, with protein providing the food for bacteria and alginate being the major part of the extra cellular polymeric substances (EPS) [4,5] in the biofilm matrix. It has already been reported that surfaces that resist protein adsorption also inhibit the microbial attachment [6–8].

Biofouling is caused by the adhesion and subsequent growth of microorganisms on membrane surfaces. When a biofilm forms on a separation membrane, e.g., reverse osmosis (RO) membranes, the film acts as a secondary membrane, which adversely affects the separation process. Progressive biofilm formation on RO desalination membranes causes a significant decrease in trans-membrane pressure, resulting in a decline in permeate flux with time [9]. To maintain an optimum permeate flux, higher operating pressures are required. Furthermore, the

physical damage to the membrane caused by biofilm activity results in an increase in salt passage, i.e., reduced salt rejection. To minimize the adverse effects of biofouling, frequent chemical cleaning is used, which shortens membrane life. The cumulative effect of these factors causes a significant increase in the operating cost of the desalination process [10].

Among several methodologies used to combat biofouling, the development of anti-biofouling and/or antifouling coatings is a very promising methodology that is being actively pursued by many researchers. These antifouling coatings have been successfully used in applications such as coatings for ship hulls [11], marine equipment, biomedical implants [12], biomedical devices, biomedical biosensors [13], food packaging, and other industrial equipment.

Zwitterionic materials have been extensively explored for their ultra-low protein adsorption [14] and as hydrophilic or fouling-resistant modifiers [15–18]. Bărboiu et al. have prepared macromolecular carboxybetaines by reacting vinyl pyridine polymers with α,β-unsaturated carboxylic acids. They found that reacting 4-VP with alpha, beta unsaturated acids (i.e., the weak acid acrylic acid) resulted in major fractioning of betaine units; however, reacting 4-VP with maleic acid (a strong acid) resulted in betaine and corresponding salts [19].

Several innovative techniques have been developed to synthesize zwitterionic coatings. The most common of these techniques include self-assembled monolayer (SAM) formation [7], solution polymerization with solvent evaporation [20,21] and atom transfer radical polymerization (ATRP) [22–25]. However, these methods have several limitations, e.g., SAMs require specific surface functionality, which limits this method to gold substrates. The use of harsh solvents in ATRP, such as pretreatment with 3,4-dihydroxyphenyl-L-alanine (DOPA) [7] prior to ATRP, are not suitable for delicate RO membranes. Furthermore, the use of solvents in solution polymerization and ATRP not only damage delicate substrates such as RO membranes but may also lead to increased surface roughness, which deteriorates anti-biofouling properties. Therefore, solvent-free deposition of antifouling coatings on RO membranes is the best strategy.

Initiated chemical vapor deposition (iCVD) is an all-dry, solvent-free deposition technique. The iCVD method is capable of retaining functional groups on deposited polymeric surfaces as opposed to other deposition processes such as plasma-enhanced chemical vapor deposition (PECVD) and UV plasma and solution-phase polymerization. For instance, labile functional groups are not well retained and may be easily cleaved from the surface during PECVD. During UV plasma coating, the high-energy excitation from the UV plasma causes a variety of side reactions that affect monomer functionality and therefore compromise the antifouling performance of the gel coating [26].

Li-Ping Zhu's group [27] synthesized amphiphilic precursor poly (vinylidene fluoride)-graft-N,N-dimethyl aminoethyl methacrylate (PVDF-g-PDMAEMA) by ATRP followed by blending with PVDF to prepare flat membranes. Synthesized membranes were then reacted with tetrahydrofuran (THF) solution and a quaternizing agent: either 1,3 propane sultone (PS) or 3-bromopropionic acid (3-BPA), which yielded SBMA or CBAA, respectively. XPS results showed that only 70% of PDMAEMA was quaternized in 48 h with 1,3-propane sultone, while only 62% of PDMAEMA was quaternized in 96 h with 3-bromopropionic acid. Such a lower conversion (quaternization) of PDMAEMA precursor and resulting reduced surface zwitterionic content are not ideal for antifouling action.

R. Yang et al. have recently prepared copolymer films via iCVD and zwitterionicalized to polysulfobetaines (pSBs)) using quaternizing agent 1,3 propane sultone (1,3 PS) [28]. These authors have shown that in contrast to most bulk solution-phase polymerization and solvent evaporation methods, their reaction scheme resulted in the highest concentration of zwitterionic moieties (up to 90%) on the top surface (~10 nm) of a commercial RO membrane. This high concentration of zwitterionic moieties is highly desirable for antifouling applications.

In this article, we report the first synthesis of the copolymer film poly(4-vinylpyridine-co-ethylene glycol diacrylate) (p(4-VP-co-EGDA)) via iCVD followed by gas phase quaternization with 3-BPA to yield zwitterionic copolymer containing poly carboxybetaine acrylic acetates (pCBAAs). Synthesized copolymer coatings were successfully applied to a flat sheet Koch® membrane system, TFC-HR, hereafter referred to as Koch membrane. Thicker films (up to 250 nm) with different compositions of zwitterionic copolymer p(85–25% 4-VP-co-EGDA) chemistries were first deposited onto silicon wafer. Ultra-thin films (38.66 nm, standard deviation ± 3.1 nm) with optimized copolymer chemistry were then deposited on Koch membranes under identical conditions. Compositional analyses of the synthesized coating were performed by employing FTIR and XPS techniques. Furthermore, bacterial adhesion testing was performed utilizing two bacterial strains; *Escherichia coli* and *Pseudomonas aeruginosa* strains, the later being more hydrophobic in nature and abundantly present in seawater. The authors wish to note that this is the first time that the iCVD library of functional groups has been extended to polycarboxybetaine types of zwitterionic moieties and that a new antifouling zwitterionic coating has been successfully deposited onto commercial RO membranes.

2. Experimental

2.1. Synthesis of copolymer film and zwitterionicalization

Different compositions of copolymer p(4-VP-co-EGDA) films were deposited on silicon wafers and commercial RO membranes using an iCVD reactor (Sharon Vacuum) previously described in detail [29,30]. In separate glass jars attached to the reactor, the EGDA monomer (vapor pressure = 0.0939 Torr at 25 °C) and the 4-VP monomer (vapor pressure = 1.68 Torr at 25 °C) were heated and the TBPO (tert-butyl peroxide) initiator was maintained at room temperature, and their vapors were fed into the chamber over heated filament arrays (80% Ni–20% Cr, Good fellow, USA). Copolymer compositions within the deposited films were varied by systematically changing the vapor flow rate of each monomer while keeping the initiator flow rate fixed.

All chemicals were used without further purification. Copolymer p(4-VP-co-EGDA) coatings were deposited on test grade silicon (Si) wafers (Wafer World, USA) without any pretreatment. Prior to deposition, commercial RO membranes TFC-HR (Koch Membrane System, USA) with area approximately 11×7 cm^2 were cleaned with high purity argon and then treated with oxygen plasma for 5 min. According to the manufacturer specifications, the Koch membranes are of polyamide type and do not contain any antifouling coating on their surfaces. During iCVD depositions, 97% tert-butyl peroxide TBPO, (Aldrich), 90% EGDA (Sigma Aldrich), 95% 4-VP (Sigma Aldrich) and argon were fed into the iCVD reactor at room temperature through mass flow controllers (1479 MFC, MKS Instruments, USA). EGDA and 4-VP monomers were heated to 85 °C and 55 °C, respectively, and the flow rates of both monomers were systematically varied to yield varying zwitterionic content on the deposited copolymer films. During thin film synthesis, the filament temperature was maintained at 200 °C while the substrate was fixed at 20 °C. Total pressure in the vacuum chamber was maintained at 0.450 Torr for all depositions. Table 1 describes all parameters adopted during iCVD depositions and provides subsequent compositions obtained for all deposited copolymer films.

Deposited film thicknesses were monitored in situ by interferometry with a 633 nm He–Ne laser source (JDS Uniphase). Thicknesses of deposited Si wafers were more accurately measured by a Woollam M-2000 Spectroscopic Ellipsometer (J. A. Woollam Co., Inc., USA) at three different incident angles (65°, 70°, 75°) using 190 wavelengths from 315 to 718 nm. The data were fit using the Cauchy–Urbach model.

The precursor in the copolymer film (4-VP), which contains tertiary nitrogen, was converted to quaternary pyridinium ion during the post-deposition reaction at the gas–solid interface. EGDA, which is more hydrophilic than ethylene glycol methacrylate (EGDMA), was