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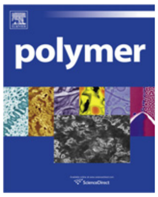

Fouling-resistant polymer brush coatings

Héloïse Thérien-Aubin, Lin Chen, Christopher K. Ober*

Materials Science and Engineering Department, Cornell University, Ithaca, NY 14853, USA

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ABSTRACT

A major problem to be addressed with thin composite films used in processes such as coatings or water purification is the biofouling of the surface. To address this problem in a model system, functionalized polyaramide membranes containing an atom transfer radical polymerization (ATRP) initiator were synthesized as a versatile approach to easily modify the surface properties of the polyaramide. Poly(methacrylic acid) brushes were grown using surface initiated ATRP followed by the functionalization of the poly(methacrylic acid) brushes with different side-chains chosen to reduce adhesion between the membrane and foulant. The relation between membrane fouling and the physicochemical properties of the surface was investigated in detail.

1. Introduction

Aramids have found multiple industrial applications due to their exceptional mechanical properties, good thermal resistance and chemical stability and are widely used as high performance fibers and in the preparation of composite materials. [1] Polyaramides are extensively used as the selective material in the preparation of separation membranes used in ion exchange, [2] gas permeation, [3] nanofiltration [4] and reverse osmosis. [5] One of the main challenges faced with the thin film composite (TFC) polyaramide membranes used in nanofiltration and reverse osmosis is the significant fouling observed on the surface of the membrane restricting the performance of the purification process. [6–9]

Biofouling will occur on almost any surface immersed in water; in the last decade a vast array of highly efficient bio-friendly antifouling coatings was developed for membranes [8,10] and other surfaces. [11,12] These coatings were designed to efficiently inhibit the settlement of the treated surface by algae and bacteria (antifouling coating) and/or provide weak foulant/surface adhesion so that the foulant can be easily washed off (fouling release coating). The traditional antifouling coatings are usually highly hydrophilic and composed of polymers such as PEG [13,14] or zwitterionic polymers. [15–17] In the present work, both antifouling coatings as well as fouling release coatings, which have been largely overlooked until now as reverse osmosis membrane surfaces, [8] are studied. An antifouling coating will inhibit the settlement of the treated surface by protein, algae or bacteria because of their strong interaction with water molecules, while a fouling release coating will have a low surface energy so that the foulant can be easily washed off with the application of a limited shear force.

Polyaramide membranes may be modified by the simple deposition of neutral polymer on the surface, the coating being non-covalently bound to the membrane and also commercially used for the production of PVA coated membranes. [18] Reaction on unreacted amine or acid groups of the polyaramide has also been realized, [19,20] but a high degree of functionalization could be better achieved using grafting from polymerization using redox [21,22] or plasma initiated polymerization. [23] Here, in order to control and modify the surface properties of the membrane to create a fouling-resistant membrane, the same surface-active chemical functionalities, earlier identified in our coating studies are grafted on a thin film composite polyaramide membranes using surface initiated ATRP.

Our previous results have shown that polymer brushes having perfluorinated side-chains are the most efficient at reducing the fouling on the membrane in the presence of a tangential flow, reducing the fouling rate 6-fold more efficiently than a more traditional PEG side-chain. [24] In the present work, the fouling mechanism on a polyaramide membrane is explored in greater detail to obtain a better understanding of this phenomenon and also get new insights to rationally design more efficient fouling-resistant coatings.

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* Corresponding author. Tel.: +607 255 8417; fax: +607 255 2365.
E-mail address: cko3@cornell.edu (C.K. Ober).

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Functional groups were introduced in the polyamide building block used in the fabrication of the polyaramide membrane to act as potential post-polymerization grafting sites for the surface-active polymer brushes, and poly(methacrylic acid) brushes are grown from those sites using SI-ATRP. The brushes are modified with a variety of side-chains to tune the surface properties. The brush-functionalized membranes are used to investigate the relation between surface properties and the adsorption and release of foulants. To better explain the overall fouling mechanism on the polyaramide membrane, the fouling behavior was deconstructed into two sub-phenomena; the colonization of the surface by the foulant and the adhesion between the foulant and the substrate.

2. Experimental

2.1. Material

3,5-Diaminobenzoic acid, 2-bromo-2-methylpropionyl bromide, ethyl-2-bromo-2-methylpropionate, 1,3-dicyclohexylcarbodiimide (DCC), anhydrous triethylamine (TEA), 4-(dimethylamino)pyridine (DMAP), di-tert-butyldicarbonate (Boc_2O), *m*-phenylene diamine (MPD), trimesoyl chloride (TMC), sodium methacrylate, copper (I) bromide, copper (II) bromide, 2,2′-bipyridine (Bipy), polyethylene glycol monomethyl ether (PEG), Zonyl FSO-100^{TM} (a PEGylated fluoroalkyl surfactant), 1H,1H-perfluoro-1-nonanol (C9F17), chlorohydroxypropyltrimethyl ammonium chloride (QA) and polydimethylsiloxane monohydroxy terminated (PDMS) were purchase from Sigma–Aldrich and used as received except for methacrylic acid (purified over an alumina column) and copper (I) bromide (washed with glacial acetic acid). Solvents were purchased from Fisher Chemical and used as received with the exception of THF that was refluxed and distilled over sodium and benzophenone.

2.2. Monomer synthesis

Bromoisobutoxyethyl 3,5-diaminobenzoate or Br-MPD (1) was synthesis as follow (Fig. 1): 10 g of 3,5-diaminobenzoic acid was reacted with 43 g of Boc_2O in 350 mL of THF in presence of 27.5 mL of TEA, the reaction mixture was stirred at 70 °C for 16 h. The solvent was evaporated and the crude product was redissolved in ethyl acetate and extracted with a 0.2 M HCl solution, a 0.2 M $NaHCO_3$ solution and finally with brine. The organic phase was dried over magnesium sulfate and evaporated. The remaining product was then purified with a silica gel column with hexane/ethyl acetate (2:3) as eluent. Yield = 94%. ^{1}H NMR [$CDCl_3$] 1.47 (s, 18H), 7.7 (s, 1H), 8.3 (m, 2H).

10 g of the resulting Boc protected 3,5-diaminobenzoic acid was esterified with ethylene glycol (100 mL) in dry THF (400 mL) in presence of 8.8 g of DCC, 2.1 g of DMAP and 0.8 mL of TEA under reflux for 8 h. After solvent evaporation, the resulting Boc protected 3,5-diaminobenzoate ethylene glycol ester was purified by extraction between dichloromethane and 0.2 M HCl, the organic phase was then washed with brine and dry with $Mg(SO_4)_2$. The crude product obtained was then further purified with a silica gel column with hexane/ethyl acetate (2:3) as eluent. Yield = 87%. ^{1}H NMR [$CDCl_3$] 1.5 (s, 18H), 3.8 (m, 2H), 4.2(m, 2H), 7.6 (m, 1H), 8.0 (m, 2H).

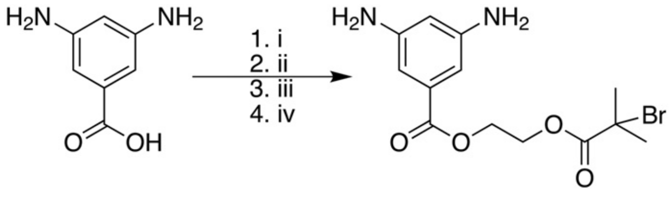

Fig. 1. Preparation of Bromoisobutoxyethyl 3,5-diaminobenzoate (Br-MPD). (i) Boc_2O, TEA, THF. (ii), Ethylene glycol, DCC, DMAP, TEA, THF. (iii) 2-bromo-2-methylpropionyl bromide, pyridine, DMAP, CH_2Cl_2. (iv) TFA, CH_2Cl_2.

The ATRP initiating group was introduced when 6.3 mL of 2-bromo-2-methylpropionyl bromide was added drop-wise to a solution of 10 g of Boc-protected 3,5-diaminobenzoate ethylene glycol ester in 250 mL of anhydrous dichloromethane containing 4.1 mL of pyridine and 0.77 g of DMAP. The solution was then agitated at room temperature for 18 h. The dichloromethane was then washed with a 0.2 M solution of $NaHCO_3$ followed by 0.2 M HCl and finally brine, the organic phase was dry with anhydrous $Mg(SO_4)_2$ and evaporated. The crude product obtained was then further purified with a silica gel column with hexane/ethyl acetate (1:1) as eluent. Yield = 98%. ^{1}H NMR [$CDCl_3$] 1.6–1.8 (m, 24H), 4.4 (m, 4H), 7.7 (m, 1H), 8.1 (m, 2H).

Finally, the deprotection of the amine groups was carried out by dissolving 10 g of Boc-protected bromoisobutoxyethyl 3,5-diaminobenzoate in 200 mL of DCM, 50 mL of trifluoroacetic acid was then added and the solution was agitated at room temperature for 4 h. The bromoisobutoxyethyl 3,5-diaminobenzoate was purified by multiples extractions with $NaHCO_3$ 0.2 M and dried with $Mg(SO_4)_2$ and the solvent evaporated. The product obtained was then purified with an alumina gel column using hexane/ethyl acetate (1:3) as eluent. Yield = 68%. ^{1}H NMR [$CDCl_3$] 1.9 (s, 6H), 4.4 (m, 4H), 7.0 (m, 1H), 7.4 (m, 2H).

2.3. Membrane casting

A polysulfone membrane (PS-20 from Sepro Membrane) was soaked in a 3.4% wt aqueous solution of MPD for 2 min and dried with an air-knife. The membrane was then soaked in a 0.15% wt solution of TMC in hexane for 1 min, and dried for 2 min. After that, the membrane was soaked in a 5% wt solution of **1** in diethyl ether (or in plain diethyl ether for “regular” polyamide standard) for 30 s and dried with an air-knife. The polymerization of the polyamide layer was then promoted by curing the membrane in 95 °C DI water for 2 min. Afterward, the membrane was washed for 2 min with a 200 ppm aqueous solution of sodium hypochlorite, followed by 30 s immersion in a 1000 ppm sodium bisulfite solution. The result is a polyamide layer (Fig. 2) physically tethered to the porous polysulfone support membrane.

2.4. Polymer brush growth

The surface-initiated ATRP polymerization was carried out on a 50 cm^2 membrane; 1 g of sodium methacrylate was dissolved in water (50 mL) the pH of the solution was adjusted to 9.0 with NaOH 0.05 N. The mole ratio of $CuBr/CuBr_2$/Bipy/monomer used during polymerization was 1:0.1:2.2:100. After a polymerization time of 18 h, the membrane was removed from the solution, washed with 0.01 N HCl and cleaned by soxhlet extraction with water for 24 h.

2.5. Brushes functionalization

The esterification of methacrylic acid brushes (Fig. 3) was carried out by immersing a piece of 50 cm^2 of membrane in 50 mL of anhydrous acetonitrile with 17 mg of DCC, 3 mg of DMAP and an excess of alcohol (or a mixture of alcohol in the case of the C9F17/