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Introducing a PEGylated diblock copolymer into PVDF hollow-fibers for reducing their fouling propensity

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ABSTRACT

Polyvinylidene fluoride (PVDF) hollow fibers (HF) membranes are widely used in industry but their hydrophobicity makes them prone to biofouling, which in turn limits their lifetime and generates high maintenance costs. Inspired from recent advances on antifouling flat-sheet membranes prepared by *in-situ* modification, we used a copolymer of polystyrene and poly(ethylene glycol) methacrylate (PS-*b*-PEGMA) for the preparation of low-biofouling PVDF-based HF. An SEM analysis evidenced the pore-forming effect of PS-*b*-PEGMA, but no clear difference as the copolymer content increased from 1 to 5 wt%. The amphiphilic copolymer promotes water transfer (proven by diffusion kinetics), but the increase in viscosity has an opposite effect, hence the structures obtained. ATR-FTIR and XPS analyses revealed the presence of the copolymer, which decreased the membrane water contact angle (from 110 ± 6° to 75 ± 2°) and increased their hydration (from $80 \pm 10\,\mathrm{mg/cm^3}$ to $1550 \pm 70\,\mathrm{mg/cm^3}$). Additionally, HFs were stronger with the addition of PS-*b*-PEGMA. Biofouling by *Escherichia coli* was eliminated in static conditions, and flux recovery ratios of 75% (with PS-*b*-PEGMA) *versus* 50% (without copolymer) was measured after 3 water/BSA filtration cycles, demonstrating the improvement of the antifouling capability of the PVDF-based HF membranes.

1. Introduction

Fouling is a major issue in numerous applications of membranes including water treatment [1], food industry [2] or blood contactors [3], regardless of the geometry (flat sheet *versus* hollow-fiber) and structure (dense *versus* porous) of the membrane at play. Common membrane materials in these applications are hydrophobic (polysulfone, PSf; polyvinylidene fluoride, PVDF; *etc.*). So, in order to tackle this challenge, one needs to either surface-modify the membrane with hydrophilic brushes or nanoparticles [4–6], or apply an *in-situ* modification process using an amphiphilic copolymer [7,8]. Indeed, it is widely accepted that in order to reduce biofouling on model interfaces or membranes, one needs to create a hydrophilic protective layer surrounding the polymer matrix, which will prevent the interactions of biofoulants with the hydrophobic matrix via hydrophobic–hydrophobic interactions [9,10].

Surface modification processes can be classified into two major classes: the coating processes [11–14] or the grafting processes [4,15–17]. The main difference between these two classes is the nature of the interactions created between the hydrophobic matrix and the surface-modifier. It is covalently bonded to the matrix polymer after a grafting process while low energy interactions are at play in coating processes, which then questions the stability of the antifouling layer. But whether one uses coating or grafting, there will be at least two unit operations involved in the whole membrane preparation process: (1) formation of the membrane and (2) surface-modification. In this respect, *in-situ* modification may be an ideal alternative. Indeed, membrane is formed and modified all at once, as an amphiphilic copolymer is blended with the matrix polymer in a common solvent, before applying a phase-inversion process [7,8,18–20]. In addition, even though surface segregation can be expected for thermodynamic reasons and leads to heterogeneous distribution from the top (nonsolvent/system interface) to the bottom (system/substrate interface) layers, a fast kinetic of solvent/nonsolvent exchanges as in common wet-immersion process leads to trapping of the copolymer in the whole bulk of the membrane before migration: in other words, the whole membrane and not only the surface, is modified. The downside of *in-situ* modification processes is mostly related to the control of final membrane structure: it is uneasy to foresee the effect of the copolymer on membrane formation, and thus, dedicated study should be performed for a fine tuning of the membrane structure.

Considering more specifically the modifiers, three major classes of polymers are regarded as efficient antifouling materials: (1) the

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PEG-based copolymers [21–23], (2) the zwitterionic-based copolymers [24–26] and (3) the mixed-charge or pseudo-zwitterionic copolymers [27,28]. These three major classes of materials act as anti-biofouling material, very efficient against proteins, bacteria or cells, but other materials can be used to minimize fouling (organic fouling, colloidal fouling) as well as efforts can be oriented toward the shaping of the membrane surface to minimize fouling. Important efforts on material design and surface-modification processes for antifouling RO and NF membranes have been recently reviewed by Choudhury et al. [29]. Coming back to the three major classes of materials, the zwitterionic-based and pseudo-zwitterionic copolymers provide a tighter hydration layer, but face solubility issues when blended with hydrophobic polymers. Actually, it is extremely challenging to solubilize a hydrophobic polymer such as PVDF with a zwitterionic or pseudo-zwitterionic copolymer, often too hydrophilic. A possible way to overcome this issue is to graft a zwitterionic head to the matrix polymer and blend the resulting copolymer to the matrix polymer, as it was done by Li et al. [30]. But this method then questions the versatility of the surface-modifier, which can almost be used with one matrix polymer only. For these reasons, PEG-based copolymers may be more attractive to readily form antifouling membranes. PEG can be grafted to numerous different hydrophobic blocks compatible with most common hydrophobic matrix polymer, which facilitates their widespread application in the design of fouling-resistant membranes. Poly(ethylene glycol) methyl ether methacrylate was recently grafted to methyl methacrylate, and the resulted copolymer blended with PVDF [31]. Another example is the blending of polyethersulfone (PES) with a triblock copolymer containing one block of polyurethane and two blocks of methoxyl poly(ethylene glycol) for improving the hemocompatibility of PES membranes [32]. Similarly, Liu et al. successfully blended a triblock copolymer of poly(butyl methacrylate), poly(poly(ethylene glycol) methyl ether methacrylate) and poly(hexafluorobutyl methacrylate) with PVDF to form antifouling membranes for oil/water separation [33]. Ourselves, we designed a series of diblock and triblock copolymers in which the hydrophobic block was polystyrene (PS) and the hydrophilic block was poly(ethylene glycol) methacrylate (PEGMA), and prepared flat PVDF membranes by vapor-induced phase separation process [34,35]. Given the efficiency of the PS-*b*-PEGMA and PEGMA-*b*-PS-*b*-PEGMA copolymers to provide flat-sheet VIPS PVDF membranes with antifouling properties in versatile situations (contact with bovine serum albumin, lysozyme or plasma proteins such as fibrinogen, contact with bacteria or blood cells, *etc.*) and provided the good compatibility of PS with PVDF ensuring stability of the system, it was decided to test this material design in the preparation of hollow-fibers (HF), much more used in industry, and for which there is also a critical need for efficient and stable surface modification despite the continuous efforts of many research group worldwide [36–39]. Formation of antifouling HF membranes is more challenging to achieve, control and understand as non-solvent diffuses from both the lumen and the outside of the polymeric system during membrane formation, unlike in flat-sheet geometry. Inspired from our knowledge on the design of flat PS-*b*-PEGMA/PVDF membranes, and because similar amphiphilic copolymer has never been tested in HF geometry, we decided to test PS-*b*-PEGMA as a potential antifouling polymer for PVDF HF membranes. The rationale for using the PVDF/PS-*b*-PEGMA couple relies also on previously reported results that highlighted good affinity between the polymer and the copolymer, leading to stable modification. Remarkable stability results obtained in surface coating by Chiag et al. [40] and later on Lin et al. [41], even during filtration of municipal wastewater for several days, proved that the copolymer stayed strongly anchored to the PVDF matrix. Therefore, even stronger anchoring is expected if the copolymer is blended to PVDF before membrane formation. In addition, if large macrovoids can be expected, due to the pore-forming effect of PEGylated copolymers, it should not have any impact on the mechanical stability of the membranes if we control the initial solid content in the casting solution. This study describes first the formation and physico-chemical characterization of PS-*b*-PEGMA/PVDF HF membranes. In particular, we will stress on membrane formation mechanism and on the potential effect of the copolymer on membrane structure. We will also conduct an in-depth physico-chemical analysis of the HF membranes before moving onto the hydrophilicity of the systems, and their resistance to biofouling in static and dynamic conditions. We hope to demonstrate that PS-*b*-PEGMA/PVDF HF membranes are a credible solution for mitigating biofouling in the numerous applications of PVDF-based HF.

2. Materials and methods

2.1. Materials

PVDF polymer (Mw: 150,000 g/mol) was bought from Kynar® Co. (commercial name: HD 4000). Poly(ethylene glycol) methacrylate (PEGMA, Mw: 475 g/mol) and styrene (99%) were bought from Sigma-Aldrich Co., as well as copper bromide (CuBr, 99.99%), 2,2′-bipyridine (bpy) and methyl 2-bromopropionate (MBrP, 98%). Tetrahydrofuran and *N*-Methyl-2-pyrrolidone were purchased from Tedia. Phosphate buffered saline (PBS buffer, pH 7.4) and albumin from bovine serum (BSA protein, 66.5 kDa) were both obtained from Sigma Chemical Co. Beef extract and peptone used in bacterial culture were purchased from Scharlau and Becton, respectively. Glutaraldehyde, 25 wt% in water, was bought from Acros Organics. DI water was produced in the laboratory with a water purification system (Thermo Scientific® Pure Lab).

2.2. Synthesis of the copolymer

The synthesis of the diblock copolymer of polystyrene and poly(ethylene glycol) methacrylate) by atom transfer radical polymerization is briefly reminded here. CuBr and bpy were used as the catalyst while MBrP was the initiator. PS was first synthesized by mixing styrene, MBrP, CuBr and bpy according to the following molar ratios: [styrene]/[MBrP]/[CuBr]/[bpy]: 60/1/1/2. The reaction was performed at 120 °C for 24 h. Afterward, 45 mL of THF was added to dilute the resulting polymeric solution. Then, the solution was passed through an aluminum oxide column, and subsequently precipitated using methanol as non-solvent (The total volume was 300 mL). The precipitation step was repeated 3 times. The synthetized PS polymer contained 60 repeat units of styrene. The second step of the reaction consisted of adding the PEGMA blocks to the PS polymer to form the final copolymer. For this, PEGMA, PS_{60}, CuBr and bpy were mixed in THF solvent, according to the following molar ratios: $[PEGMA]/[PS_{60}]/[CuBr]/[bpy] = 108/1/1/2$. Total solid content was 50 wt%. The reaction was performed for 24 h at 60 °C, at the end of which 30 mL of THF was added to the solution. The solution was passed through an aluminum oxide column, and precipitated using 250 mL of a mixture of ether and hexane (1/1: v/v). The precipitation step was repeated 3 times. Finally, the polymer was dried at room temperature. It yielded a white powder, which was stored at 4 °C until use.

A ^1H NMR analysis, performed on Bruker 500 MHz instrument and using chloroform-D as the solvent permitted to verify the structure of the copolymer. A typical NMR spectrum of the copolymer is presented below in Fig. 1. Gel phase chromatography was performed using a Viscotek chromatograph (Viscotek GPCmax module) and a Jordi Gel CN15073 column. Flow rate was fixed to 1 mL/min and the column temperature was 25 °C. The molecular weight of PS was found to be 5820 g/mol and its polydispersity index was 1.3, while the molecular weight of the