



Effect of type of poly(ethylene glycol) (PEG) based amphiphilic copolymer on antifouling properties of copolymer/poly(vinylidene fluoride) (PVDF) blend membranes



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ABSTRACT

The antifouling properties of poly(vinylidene fluoride) (PVDF) membranes were investigated by blending several types of synthesized amphiphilic poly(poly(ethylene glycol) methyl ether methacrylate- methyl methacrylate) [P(PEGMA- MMA)] copolymers with different initial PEGMA/MMA monomer ratios and PEG side chain lengths. Many types of membranes were prepared using different copolymer/PVDF blend ratios via nonsolvent induced phase separation. The membranes with similar pure water permeabilities and surface pore sizes were prepared by controlling the dope solution composition. Thus, the bovine serum albumin antifouling properties could be assessed under similar hydrodynamic filtration conditions. The membrane hydrophilicity, surface PEGMA coverage, and antifouling properties of the prepared membranes increased with increasing copolymer/PVDF ratio and PEGMA/MMA monomer ratio of the copolymers and PEG length of the copolymer. A molecular dynamics simulation was performed to assess the surface chemical composition, and the results were compared with those of X-ray photoelectron spectroscopy. The antifouling properties depended more strongly on the membrane surface hydrophilicity when the copolymer chemical structures, that is, the PEGMA/MMA monomer ratio and PEG side chain length, were changed, rather than when the copolymer/PVDF blend ratio was changed.

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1. Introduction

Among membrane materials, poly(vinylidene fluoride) (PVDF), a semi-crystalline polymer with excellent physical and chemical properties and good thermal stability, has attracted much attention [1,2]. Membrane fouling resulting from the attachment of foulants to the PVDF membrane degrades the permeability of a pressure-driven membrane [3]. Therefore, control of foulant adsorption onto the membrane surface is crucial to the preparation of antifouling PVDF membranes [4,5].

Numerous modification methods have been adopted to improve the antifouling properties of PVDF membranes [6]. Surface modification is an effective approach to obtain fouling-resistant membranes. Hydrophilic moieties can be introduced on the membrane surface through covalent bonding via grafting [4,7,8] or through physical interaction via coating [9–11]. In grafting and coating methods, only the membrane's outer surface is treated rather than the membrane bulk. The grafting method requires

caustic chemical treatment or special equipment, which decreases the ease of membrane preparation. In the coating method, the stability of the coated hydrophilic layer on the membrane surface depends strongly on the physical affinity of the coating material with the membrane surface. The coated layer can easily be detached from the membrane surface by changes in the solution pH [12] or by the application of backflushing during the filtration process [6]. As an alternative method, blending modification can avoid the difficulties and shortcomings mentioned above and provides the ease of one-step modification. Although blending conventional hydrophilic homopolymers such as poly(ethylene glycol) (PEG) and poly(vinyl pyrrolidone) with PVDF has been reported [13–15], this approach is not perfect because some homopolymer leakage occurs during membrane preparation. Blending amphiphilic copolymers with the host membrane material to create antifouling PVDF membranes has an advantage in that amphiphilic copolymers leak less than homopolymers. During nonsolvent induced phase separation (NIPS), the hydrophilic chains of the amphiphilic copolymer segregate and are concentrated on the membrane surface to minimize the interface energy, and the entanglement of the hydrophobic segments with PVDF chains can tightly anchor the hydrophilic segments on the

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membrane surface [2,16].

Different types of amphiphilic copolymers, including mainly block [17,18], comb [19], and branched copolymers [20,21], have been used to prepare blend membranes. Some researchers demonstrated that the antifouling properties of the hydrophilic surface were strongly related to the hydration layer near the surface. Thus, the formation of this tightly bound hydration layer produces significant repulsive hydration forces that prevent proteins from making direct contact with the surface [22–24]. Note that the physicochemical properties of the amphiphilic copolymer (i.e., its molecular weight and surface chemistry) and their surface packing (i.e., the thickness of the hydrophilic layer, packing density, and chain conformation) primarily determine the strength of surface hydration [22]. Recent experimental and computational studies have proved that a PEG-based copolymer showed considerable protein adsorption resistance [25,26].

Our previous work illustrated that grafting of poly(ethylene glycol)methyl ether methacrylate (PEGMA) was more efficient in improving the antifouling properties than grafting of other hydrophilic monomers [27]. Liu et al. synthesized the amphiphilic brush-like copolymer poly(methyl methacrylate-poly(ethylene glycol) methyl ether methacrylate) [P(PEGMA-MMA)] by a radical polymerization method and used this copolymer as a macromolecular additive for PVDF hollow fiber membrane preparation [28]. During the NIPS process, the PEGMA side chain would segregate onto the membrane/water interface to reconstruct a hydrogel layer because of its hydration by surrounding water molecules, which resulted in good protein fouling resistance. Zhang et al. confirmed that the hydrophilic segment of an amphiphilic copolymer aggregated onto a membrane surface during phase separation in a PVDF/P(PEGMA-MMA) blend and improved the water flux recovery after back-flushing [29].

Hester et al. synthesized comb-like PVDF-g-poly(oxyethylene methacrylate) side chains (POEM) and poly(methyl methacrylate-polyoxyethylene methacrylate) [19]. POEM and PEGMA have different chain lengths and terminal groups, whereas both have the $-\text{CH}_2-\text{CH}_2-\text{O}-$ unit [30]. This finding showed that PVDF-g-POEM, with a longer POE side chain, rendered the PVDF membrane more hydrophilic and resistant to fouling because of the higher surface coverage of POEM side chains [31].

Although it is well understood that PEG-based amphiphilic copolymers reduce protein adsorption on PVDF membranes, scientific insight into the protein fouling resistance of copolymer structures has still not been systematically obtained. Most published papers considered only the PVDF/hydrophilic homopolymer or copolymer ratio [32,33]. A few papers studied the effect of the monomer ratio or hydrophilic segment length of the copolymer [31,34]. Additionally, the works mentioned above compared the membrane fouling propensities of membranes with different water permeabilities. Because the water permeability can strongly affect the fouling properties [35,36], the blending effect should be evaluated for membranes with similar water permeabilities.

In this study, the effect of the synthesized copolymer chemical structures (PEGMA/MMA monomer ratio and PEG side chain length) and the copolymer/PVDF blend ratio on the hydrophilicity and antifouling properties of the prepared membranes were studied (Fig. 1). By adjusting the dope solution composition, membranes with similar water permeability and pore size were prepared so as to evaluate the bovine serum albumin (BSA) antifouling properties under similar hydrodynamic conditions. The effects of the chemical structures of the synthesized copolymers and the copolymer/PVDF blend ratio on the hydrophilicity and antifouling properties were compared to find an appropriate approach to preparing membranes with high antifouling properties.

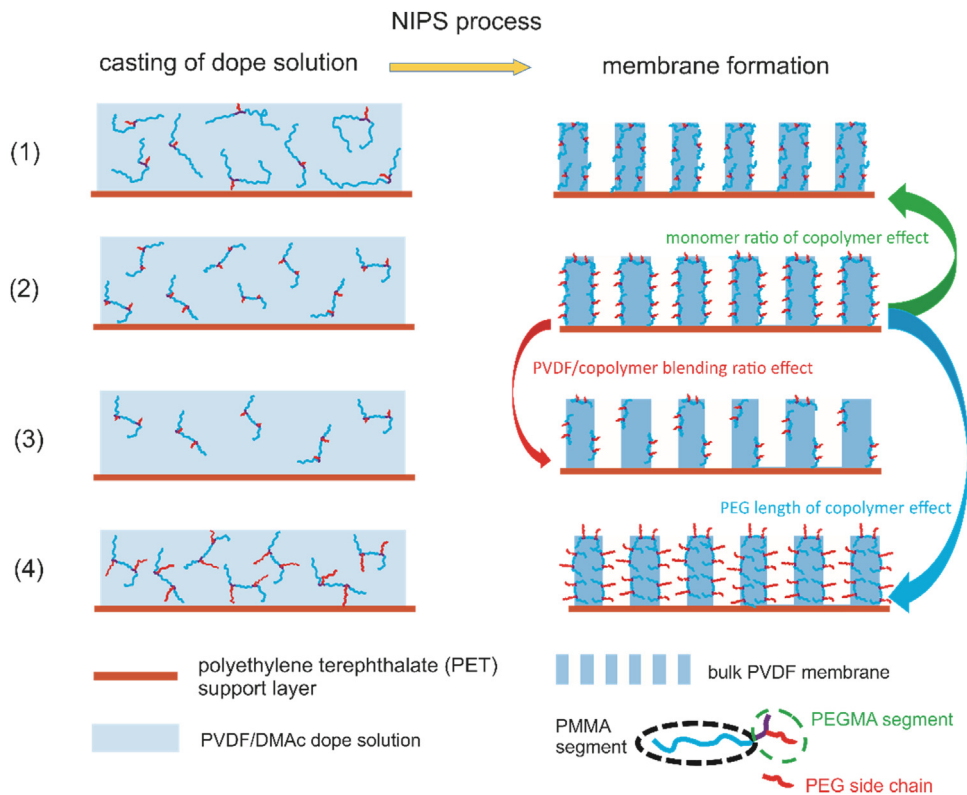


Fig. 1. Schematic of P(PEGMA-MMA)/PVDF blend membrane formation by NIPS. Process (1): PEGMA/MMA monomer ratio (low), PEG side chain length (short), copolymer/PVDF blend ratio (high); process (2): PEGMA/MMA monomer ratio (high), PEG side chain length (short), copolymer/PVDF blend ratio (high); process (3): PEGMA/MMA monomer ratio (high), PEG side chain length (short), copolymer/PVDF blend ratio (low); process (4): PEGMA/MMA monomer ratio (high), PEG side chain length (long), copolymer/PVDF blend ratio (high).

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