

## **Effective anti-fouling performance of a modified PVDF membrane with a tri-block copolymer of P(St-co-MAA)-g-fPEG as an additive**

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### **ABSTRACT**

In this study, a modified PVDF membrane with excellent hydrophilic and antifouling performance was obtained by the non-solvent induced phase separation method through blending PVDF with an easy prepared amphiphilic tri-block copolymer of P(St-co-MAA)-g-fPEG as an additive. At a proper ratio of PVDF and the additive (e.g., 9:1), the initial water contact angle of the prepared membrane was significantly reduced from about 80° for the PVDF membrane to as low as 48.80° for the modified PVDF membrane. Experimental results indicated that the adsorbed amount for a typically tested protein of BSA (in the concentration range of 0.8 to 2 g/L) by the modified PVDF membranes can be decreased by as much as 93% with comparison to that of the unmodified PVDF membranes. The prepared novel membrane showed a great potential to be used in wastewater treatment applications where protein or organic contamination often present a severe problem to conventional membranes.

### **1. INTRODUCTION**

Polyvinylidene fluoride (PVDF), due to its unique properties, such as excellent chemical stability and engineering processability, and so on, has made it to be one of the ideal polymeric materials for the preparation of membranes used in water and wastewater treatment. However, the strong fouling tendency by proteins or organic matters, resulting from the high intrinsic hydrophobicity of the PVDF material, often

caused a rapid decline of the permeation flux (Zhang and Ma, 2009; Liu et al, 2011; Sun et al, 2013), which has greatly limited the prospect of PVDF membranes in many practical applications (Jim et al, 1992; Belfort et al, 1994; Chan and Chen, 2004). Various researches have shown that blending hydrophilic polymers with PVDF can impart surface hydrophilicity to the conventionally hydrophobic membrane material. The blending method is also considered to be one of the most versatile and valid strategy that can be applied to industrial-scale membrane production. A key issue is to prepare an effective additive that is not only to incur the desired hydrophilicity to the prepared membrane but also to be compatible with the PVDF base membrane material. In the literature, hydrophilic polymers or amphiphilic copolymers, such as PS-*g*-PEGMA, (Venault et al, 2014) PVC-*g*-P(PEGMA) (Shao et al, 2013; Hester et al, 2002; Park et al, 2006), etc. have been reported as the additive to prepare the modified PVDF membranes. In the additives, the hydrophilic chains or segments are expected to migrate to the membrane surface in the membrane formation process while the hydrophobic chains or segments of the additives would stay with PVDF to ensure its good compatibility with the PVDF matrix or base membrane material (Zhu et al, 2013).

In our recent work, we prepared a novel amphiphilic tri-block copolymer of P(St-*co*-MAA)-*g*-fPEG as the additive, used a relatively easier method and cheaper materials. The obtained additive was blended with PVDF to fabricate the modified PVDF membranes through the non-solvent induced phase separation method. The copolymer additive included a strong anchorage group of -PS- that provides hydrophobic interaction with PVDF to ensure the materials' compatibility. The hydrophilic and flexible chains of MAA-*g*-fPEG of the additive can interact with the water molecules, which therefore increases the water wettability of the prepared membrane. Furthermore, the low surface energy group of fPEG can also interact with proteins or organic matters through the anti-adhesion property. A series of experiments were conducted to examine the properties and performance of the various types of prepared membranes.

## **2. EXPERIMENTAL**

### **2.1 Materials**

Polyvinylidene fluoride (PVDF, FR904) was supplied by Shanghai 3F New Material Co. and dried at 100 °C for 12 h before use. Well-defined copolymers of P(St-*co*-MAA)-*g*-fPEG with different PS and MAA ratios were synthesized via the radical polymerization and esterification reactions. Two types of the obtained copolymers were characterized by <sup>1</sup>H-NMR and FT-IR analyses and their ratio (x/y) of the segments St (x) and MAA-*g*-fPEG (y) were determined to be at 1/4 and 1/1, respectively. N-methylpyrrolidone (NMP) and bovine serum albumin (BSA) were purchased from Macklin (China) and used as the polymer solvent and the membrane contaminant,

respectively, in the study. Deionized water (DW, 18.2 MΩ cm ) produced from a millipore water purification system (Millipore ZRXQ015TO) was used to prepare the test solutions in the study.

## 2.2 Preparation of the membranes

PVDF and modified PVDF membranes were prepared by the non-solvent induced phase separation method by using PVDF alone or blending PVDF with the copolymer additive of P(St-co-MAA)-g-fPEG(x/y=4/1 or 1/1) according to procedures described in the previous work of Bai et al. (Zhu et al, 2013). The compositions of the casting solutions for the membranes in this study are given in Table 1. M0 is the unmodified PVDF membrane as a contrast for comparison with the modified PVDF membranes.

Table 1 The compositions of the prepared membranes.

Parameter	Membrane sample name				
	M0	M1	M2	M3	M4
Additive	/	P(St-co-MAA)-g-f PEG(x/y=4/1)	P(St-co-MAA)-g-f PEG(x/y=4/1)	P(St-co-MAA)-g-f PEG(x/y=1/1)	P(St-co-MAA)-g-f PEG(x/y=1/1)
PVDF:Additive (in weight)	/	9:1	7:3	9:1	7:3
Casting solution polymer concentration (wt%)	18	18	18	18	18
Solvent	NMP	NMP	NMP	NMP	NMP

## 2.2 Characterization of the membranes

The water contact angles (CA) of the prepared membranes were measured by a contact angle goniometer (Ramé-hart 500) to evaluate their surface wetting properties. The pendant-drop method was used to obtain the water contact angle readings. For each membrane sample, the contact angle measurement was made at least eight different locations and an average value was reported.

The prepared membranes (square for 3\*3 cm<sup>2</sup>) were also tested for their adsorption to protein molecules. A membrane sample was first rinsed by PBS solution to remove any pollutants or impurities adhered on the surface of the membrane. Then, the membrane was immersed in a BSA solution with different concentrations (in the range of 800-2000 mg/L) at room temperature. The solutions with the membrane samples in the flasks were oscillated in a shaking bath (OLS Grant 200) for 24 h to allow adsorption

successfully reaching the equilibrium. The concentrations of BSA in the solutions before and after the adsorption by the membranes were analyzed with a UV-Vis spectrophotometer (Shimadzu UV3600) at 280 nm. The BSA weight concentrations were determined through a calibration curve of BSA. The adsorbed amounts of BSA on the membrane samples were calculated through a mass balance analysis.

### 3 RESULTS AND DISCUSSION

#### 3.1 Membranes' hydrophilicity

The static water contact angles were used to evaluate the hydrophilicity of the prepared membranes. It is commonly known that a stronger hydrophilicity of the membrane surface would usually have a lower water contact angle. The water contact angle results of all the prepared membranes were shown in Fig. 1. The unmodified PVDF membrane M0 was found to be highly hydrophobic, showed the highest water contact angle of 79.33°. By adding the synthesized amphiphilic copolymer additive into PVDF, the water contact angle of the prepared membranes decreased in all the cases. The results indeed support that the surface hydrophilicity of the modified PVDF membranes was enhanced due to the incorporation of the P(St-co-MAA)-*g*-fPEG additive.

The hydrophilicity of the modified PVDF membranes however appeared also to depend on the ratio of PVDF to the additive. Membrane sample M3 which had a blending ratio of 9:1 with x/y=1:1 showed the lowest water contact angle of 48.8° among all of the prepared membranes, suggesting its strongest surface hydrophilicity. The water contact angle decreased for more than 30° for M3 as compared with M0. The higher hydrophilicity was due to more hydrophilic segments enriched on the surface of

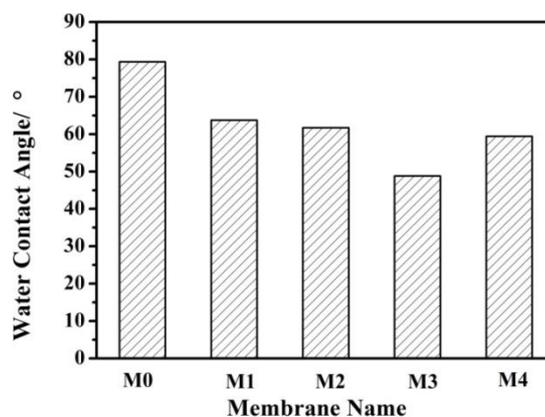


Fig. 1 Static water contact angle for various PVDF membranes prepared.

the modified membrane. A proper ratio of the hydrophilic and hydrophobic segments and their blending ratio would have impact on the hydrophilicity and anti-fouling performance of the prepared membranes, probably due to their impact on the enrichment of the different functional groups on the membrane surfaces.

Different from many previous practice by adding conventional water-soluble polymer, the use of P(St<sub>x</sub>-co-MAA)-g-fPEG<sub>y</sub>, a water-insoluble additive, can retain it with the base membrane material and will not be easily washed away during the phase inversion process for membrane formation. The addition of the prepared amphiphilic polymer -P(St-co-MAA)-g-fPEG, did greatly affect the hydrophilic property of the prepared membranes. The hydrophilicity of the modified PVDF membrane was indeed improved after the addition of the P(St-co-MAA)-g-fPEG additive into the PVDF casting solution.

### 3.2 The static adsorption of BSA

Protein fouling of membranes is often a main challenge in many membrane applications with conventional membranes and it is desirable to eliminate the effect as much as possible. (Shi et al, 2008). The adsorption of protein or organic matters on a polymeric membrane's surface and in the pores is usually caused by the hydrophobic property of the membranes. In the current work, to evaluate the anti-fouling performance of the modified PVDF membranes to protein, BSA as a typical and common protein was used to test its adsorption on the prepared membranes.

Fig. 2 shows the adsorption amounts of BSA on the various prepared membranes under different BSA concentrations. Although the adsorption amount for all the membranes showed an increase with the BSA concentration, the modified PVDF membranes with the amphiphilic copolymer (P(St-co-MAA)-g-fPEG) as the additive can reduce the amount of BSA adsorbed. For instance at the initial BSA concentration of 0.8 g/L, M0 showed the highest BSA adsorption of 122.2 µg/cm<sup>2</sup>. In comparison, the BSA adsorption amount on M3 membrane was the lowest at only 7% of that for M0. The improvement effect appeared to be even more significant at higher BSA concentrations. The anti-fouling performance to BSA may be explained as following. The hydrophilic segments of the MAA-g-fPEG chains in the additive can migrate to the membrane surface during the membrane formation process. The hydrogen bonds can be formed between hydrophilic groups of the additive and the water molecules, which induced the formation of a hydration layer on the membrane surface. The effect of steric exclusion could consequently inhibit the close contact of protein for adsorption to take place (Zheng et al, 2004 and 2005).

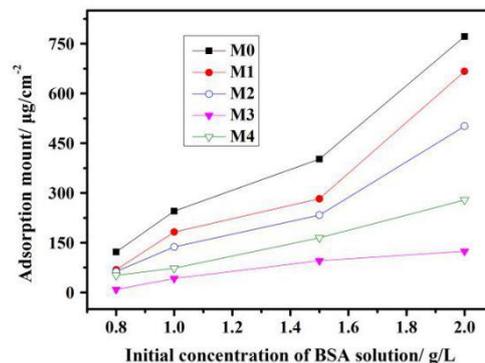


Fig. 2 Adsorption amounts of the various prepared PVDF membranes to BSA under different BSA concentrations in the solutions.

#### 4. CONLIUSIONS

An amphiphilic copolymer of P(St-co-MAA)-*g*-fPEG was successfully synthesized with relatively simple method and cheap materials. The additive can be well blended with PVDF to obtain modified PVDF membranes for anti-fouling performance via the typical non-solvent induced phase inversion method for membrane fabrication. The obtained modified membranes exhibited greatly improved surface hydrophilicity, with water contact angle reduced from about 80° for unmodified PVDF membrane to as low as 48.80° for modified PVDF membrane. The improvement was also depend on the ration of PVDF and the additive as well as the ratio of PS and MAA-*g*-fPEG segments in the prepared additive. The BSA adsorption experiments also demonstrated that the adsorption to BSA to the modified PVDF membrane can be reduced for as high as 93%, as compared to that of the unmodified PVDF membrane.

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