

Amphiphilic Poly(vinyl chloride)-*g*-Poly[poly(ethylene glycol) methylether methacrylate] Copolymer for the Surface Hydrophilicity Modification of Poly(vinylidene fluoride) Membrane

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ABSTRACT: In this study, a comblike amphiphilic graft copolymer containing poly(vinyl chloride) (PVC) backbones and poly(oxyethylene methacrylate) [poly(ethylene glycol) methylether methacrylate (PEGMA)] side chains was facilely synthesized via an atom transfer radical polymerization method. Secondary chlorines in PVC were used as initial sites to graft a poly[poly(ethylene glycol) methylether methacrylate] [P(PEGMA)] brush. The synthesized PVC-*g*-P(PEGMA) graft copolymer served as an efficient additive for the hydrophilicity modification of the poly(vinylidene fluoride) (PVDF) membrane via a nonsolvent-induced phase-inversion technique. A larger pore size, higher porosity, and better connectivity were obtained for the modified PVDF membrane; this facilitated the permeability compared to the corresponding virgin PVDF membrane. In addition, the modified PVDF membrane showed a distinctively enhanced hydrophilicity and antifouling resistance, as suggested by the contact angle measurement and flux of bovine serum albumin solution tests, respectively. Accordingly, the PVC-*g*-P(PEGMA) graft copolymer was demonstrated as a successful additive for the hydrophilicity modification, and this study will likely open up new possibilities for the development of efficient amphiphilic PVC-based copolymers for the excellent hydrophilicity modification of PVDF membranes. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2472–2478, 2013

KEYWORDS: blends; copolymers; grafting; membranes; poly(vinyl chloride)

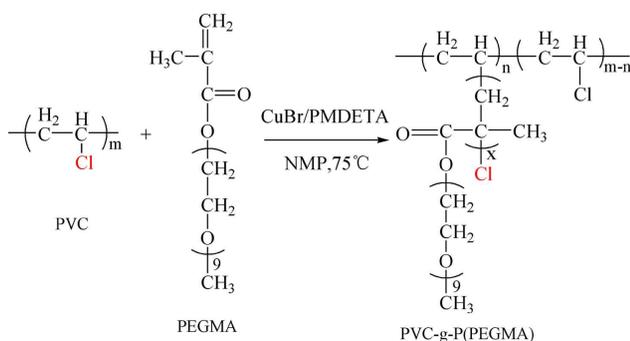
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INTRODUCTION

Poly(vinylidene fluoride) (PVDF) membranes have had many applications in many areas, including microfiltration, ultrafiltration, nanofiltration, distillation, and reverse osmosis systems, because of their excellent chemical resistance, good thermal resistance, and outstanding mechanical properties.^{1–5} However, because of their hydrophobic nature, PVDF membranes are often susceptible to protein fouling when they are applied in wastewater treatment; this is an undesirable phenomenon because frequent membrane cleaning is costly and may result in a short membrane lifetime and low selectivity.⁶ Researchers have made great efforts to improve the hydrophilicity and separation performance of PVDF membranes. Generally, these approaches can be classified into blending,⁷ coating,⁸ surface grafting,⁹ surface physical treatment,¹⁰ and physical adsorption.¹¹ Among these methods, blending with amphiphilic graft copolymers has the great advantages of long-term modification efficiency and facile manipulation.¹² Moreover, amphiphilic graft copolymers

are widely applied to endow membranes with high hydrophilicity and reliable protein fouling resistance.^{13,14} Hashim et al.¹⁵ prepared hydrophilic PVDF membranes from an amphiphilic graft copolymer, PVDF-*g*-poly(ethylene glycol) methylether methacrylate (PEGMA). The PVDF membrane showed excellent antifouling resistance. An amphiphilic PPESK-*g*-poly(ethylene glycol) graft copolymer was applied for the hydrophilic modification of PPESK microporous membranes by Zhu et al.¹⁶ Moreover, Yi et al.¹³ successfully used a polysulfone-based amphiphilic polymer as a modifier to improve the hydrophilicity and antifouling performance of PES membranes. From the aforementioned examples, we deduced that when a graft copolymer shares good compatibility with a corresponding bulk membrane material, excellent effects from membrane modification can be obtained. Hence, in addition to PVDF-based amphiphilic copolymers, the hydrophilicity modification of PVDF membranes can be expanded to poly(vinyl chloride) (PVC)-based amphiphilic polymers because PVC has a structure similar to that of PVDF and exhibits good compatibility with many



Scheme 1. Synthesis of an amphiphilic PVC-g-P(PEGMA) graft copolymer by ATRP. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

polymers.^{17,18} However, published reports on the application of PVC-based copolymers in improving the hydrophilicity and fouling resistance of PVDF membranes have seldom been found.

In this study, we synthesized a well-defined amphiphilic graft copolymer, PVC-g-poly[poly(ethylene glycol) methylether methacrylate] [P(PEGMA)], with direct initiation of the secondary chlorines of PVC via an atom transfer radical polymerization (ATRP) method. Subsequently, PVC-g-P(PEGMA), as an additive, was blended into a PVDF casting solution to prepare PVC-g-P(PEGMA)/PVDF blended membranes. The effects of the introduction of PVC-g-P(PEGMA) on the PVDF membrane hydrophilicity, morphology, and antifouling performance were investigated systematically. Importantly, the blended PVDF membranes displayed improved hydrophilicity and better antifouling performance. To the best of our knowledge, this study may be the first concerning the hydrophilicity modification of PVDF membranes with amphiphilic PVC-based copolymers.

EXPERIMENTAL

Materials

PVDF [FR-904; number-average molecular weight (M_n) = 380,000 g/mol] was obtained from China's Shanghai 3F New Materials Co., Ltd., and was dried at 80°C for 24 h before use. PVC (M_n = 67,774 g/mol), copper(I) bromide (CuBr), N,N,N',N'' -pentamethyldiethylene triamine (PMDETA), and bovine serum albumin (BSA; M_n = 67 kDa) were purchased from Taijing Biological Technology Co., Ltd. (China, Xiamen). PEGMA (97%, M_n = 475 g/mol) was obtained from Aldrich Chemical Co. (Milwaukee, WI) and was passed through an inhibitor-removing column with aluminum oxide before use. 1-Methyl-2-pyrrolidone (NMP) was purchased from Nanjing Houwang Chemical Co., (China) and was distilled under reduced pressure before use. N,N -Dimethylacetamide (DMAc) and other reagents were all chemically pure and were used directly.

Synthesis of the Amphiphilic Graft Copolymer PVC-g-P(PEGMA)

The synthesis route is shown in Scheme 1, and a typical synthesis process was as follows: 20 mL of PEGMA, 0.78 mL of PMDETA, and 2.5 g of PVC were dissolved in 30 mL of NMP in a 100-mL, three-necked flask equipped with a magnetic stirrer. After a homogeneous solution was obtained, N_2 was bubbled for 30 min, and 0.02 g of CuBr was added in the

solution. The reaction solution was kept at 75°C in an oil bath for 10 h under a N_2 atmosphere. After that, the amphiphilic comblike copolymer was gradually precipitated out in deionized water and was purified thrice by redissolution in NMP and reprecipitation in deionized water to completely remove the unreacted reactants and other residual materials. Finally, the graft copolymer PVC-g-P(PEGMA) was obtained and was dried *in vacuo* at room temperature. The structure of PVC-g-P(PEGMA) was characterized by a 500-MHz, high-resolution NMR spectrometer (AVANCE III, 500, Bruker, Germany) in a DMSO solution with TMS as an internal standard.

Membrane Preparation

The membranes were prepared by a classical immersion precipitation inversion process in this study. The compositions for the casting solution are shown in Table 1. The casting solution was stirred in a 65°C oil bath for a predetermined time, and then, a homogeneous solution was obtained. After the bubbles were released absolutely under reduced pressure for several hours, the homogeneous casting solution was spread on nonwoven fabric with a 300 μm thick steel knife. Then, the solution film was immersed immediately in a 50°C coagulation bath of deionized water for 15 min. Subsequently, the formed membranes were washed thoroughly with fresh deionized water to remove any remaining solvent and pore-forming agent and then dried at room temperature before characterization.

Characterization of the Membranes

Attenuated Total Reflectance (ATR)–Fourier Transform Infrared (FTIR) and X-Ray Photoelectron Spectroscopy (XPS)

Analysis. The chemical composition of the membrane surface was analyzed by FTIR–ATR spectroscopy (Thermo Nicolet 360, Nicolet, USA) and XPS (Thermo Scientific ESCALAB 250, USA). The X-ray source was run at a power of 250 W (14.0 kV, 93.9 eV) with an electron takeoff angle of 90° relative to the sample plane.

Scanning Electron Microscopy (SEM). A field emission scanning electronic microscope (Nova, NanoSEM230, FEI Co., USA) was used to observe the surface and cross-sectional morphologies of the membranes. To study the cross-sectional structure, the membranes were fractured into short samples in liquid nitrogen. All of the membrane samples for SEM analysis were sputtered with a thickness of 5 nm of gold before observation.

Water Contact Angle Measurements. The hydrophilicity of the membrane surface was characterized by a contact angle goniometer (OCA20, Data Physics, Germany). A series of magnified images for the water droplets ($\sim 1 \mu\text{L}$) on the top surface of the membranes were obtained with a digital camera at room

Table I. Casting Solution Compositions of the Blend Membranes (wt %)

Membrane ID	PVDF	PVC-g-P (PEGMA)	Poly(ethylene glycol) 2000	DMAc
M1	19	0	3	78
M2	17	2	3	78
M3	15	4	3	78
M4	14	5	3	78

temperature. To minimize experimental error, the contact angles were measured five times for each sample and then averaged.

Static Protein Absorption Experiment

A protein solution (0.4 mg/mL, 0.6 mg/mL) was freshly prepared by the dissolution of BSA (PI = 4.9) into a 0.1M phosphate buffer solution (PBS; pH 7.4). The membrane samples with sizes of $2 \times 2 \text{ cm}^2$ were immersed in ethanol for 10 min and then in 0.1M PBS for 30 min to prewet the membrane surface and were then transferred into vials filled with 15 mL of protein solution. These vials were incubated in a 30°C water bath for 24 h with a shaking speed of 150 rpm to reach protein adsorption and desorption equilibrium. Each sample was washed with 2 mL of PBS three times to remove BSA reversible adsorption on the membrane surface before determination. The concentration change of the protein solution before and after static protein absorption was characterized by an ultraviolet-visible spectrometer (HP 8453, USA) at a wavelength of 280 nm. All of the data were averaged from three samples taken from the same membrane.

Ultrafiltration Experiment

An ultrafiltration experiment was conducted on a dead-end stirred membrane evaluation cell with an effective filtration area of $5.0 \times 10^{-4} \text{ m}^2$. Before measurement, the membrane sample was initially pressurized with deionized water at 0.2 MPa for 30 min. Then, the deionized water flux was recorded as J_{w1} at 0.1 MPa. The permeation flux (J) was calculated by the following equation:

$$J = V/A\Delta t \quad (1)$$

where V , A , and Δt represent the pure water or protein solution permeate volume (L), membrane area (m^2), and permeation time (h), respectively.

After water flux, the flux of the BSA solution (1 g/L, pH 7.4) was measured at 0.1 MPa until a steady flux was obtained as J_p . Subsequently, the membrane was washed with deionized water for 30 min, the deionized water flux was reevaluated, and the steady-state value was defined as J_{w2} . The flux recovery ratio (FRR) was calculated by the following expression:

$$\text{FRR} = (J_{w2}/J_{w1}) \times 100\% \quad (2)$$

RESULTS AND DISCUSSION

Synthesis and Characterization of PVC-g-P(PEGMA)

It was proven that ATRP was a versatile polymerization method for the synthesis of a well-defined graft copolymer.^{19,20} As shown in Scheme 1, PVC served as a macroinitiator to provide the secondary chloride group for initiating the ATRP of PEGMA under the presence of CuBr and PMDETA.^{21,22} The PVC-g-P(PEGMA) graft copolymer was a comblike polymer consisting of a hydrophobic backbone of PVC interwoven with hydrophilic side chains of P(PEGMA).

The successful synthesis of PVC-g-PEGMA was confirmed by $^1\text{H-NMR}$ spectroscopy (Figure 1). Figure 1(1) shows the $^1\text{H-NMR}$ spectrum of PVC. The peaks around 4.4–4.6 ppm were assigned to the proton of the $-\text{CHCl}-$ group in PVC,²² and

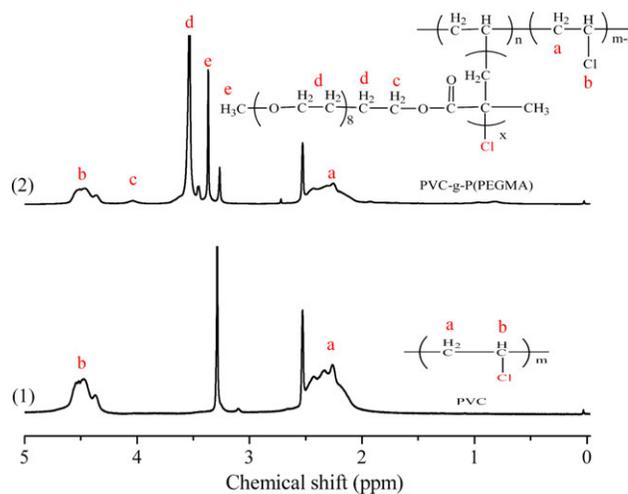


Figure 1. $^1\text{H-NMR}$ spectra for (1) PVC and (2) PVC-g-P(PEGMA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the methylene group in $-\text{CH}_2-$ resonated at approximately 2.3 ppm. Figure 1(2) shows the $^1\text{H-NMR}$ spectrum of the synthesized PVC-g-P(PEGMA), in which several new peaks appeared, except for the peaks ascribed to PVC. The chemical shifts around 4.2, 3.6, and 3.4 ppm were attributed to $-\text{CH}_2\text{CO}_2-$, $-\text{CH}_2-$, and $\text{CH}_3\text{O}-$, respectively. These results were in good agreement with that of the literature.²³ Hence, the appearance of these new peaks demonstrated that PVC-g-P(PEGMA) was successfully synthesized.^{24,25} In addition, the molecular weight of PVC-g-P(PEGMA) could also be determined with the aid of the $^1\text{H-NMR}$ spectrum and was found to be about 67,872 g/mol.

Effect of PVC-g-P(PEGMA) on the Membrane Structure

In this study, the effect of PVC-g-P(PEGMA) on the PVDF membrane structure was investigated via SEM. All of the blended PVDF membranes exhibited a typical asymmetric structure via an immersion precipitation inversion method, which was composed of a porous skin layer and a fingerlike sublayer. The difference among the blended PVDF membranes could be neglected with the increase of PVC-g-P(PEGMA) in the casting solution. However, a great difference existed between the virgin PVDF membrane and the blended PVDF membranes. As shown in Figure 2, the blended PVDF membrane with 2 wt % PVC-g-P(PEGMA) was selected as the representative membrane. The virgin PVDF membrane displayed a dense structure; however, a relatively large pore size, high porosity, and good interconnectivity were obtained for the PVDF membrane after modification with PVC-g-P(PEGMA), which facilitated the membrane permeability. This result confirmed the important effect on the membrane structure imposed by the introduction of PVC-g-P(PEGMA).

Membrane Hydrophilicity

Water contact angle measurement is a regular way to characterize the surface hydrophilicity of membranes. As presented in Figure 3, the contact angle for all of the membranes decreased continuously with increasing drop time, but the blended PVDF

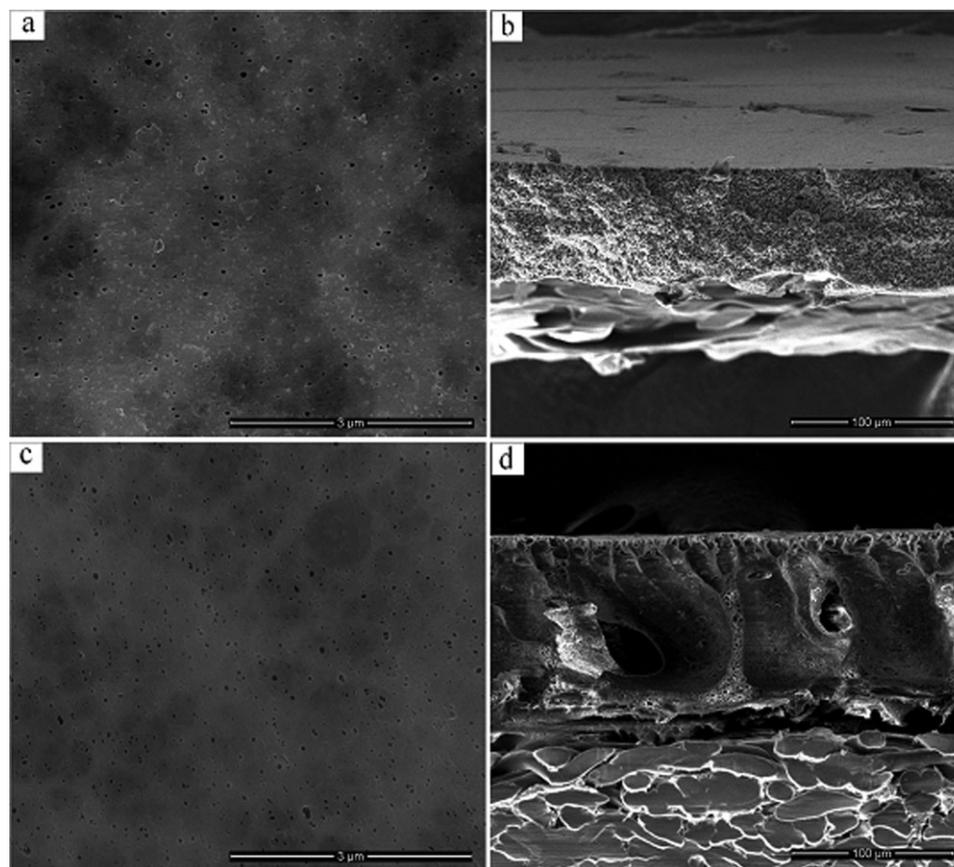


Figure 2. SEM images of the (a,c) top surface and (b,d) cross section for the (a,b) virgin PVDF membrane M1 and (c,d) blended PVDF membrane M2 with 2 wt % PVC-g-P(PEGMA).

membranes exhibited a larger tendency to decline. For example, the contact angle for the blended PVDF membrane M4 declined about 10° during the measured time; this was almost two times that of the corresponding virgin PVDF membrane. Moreover, the initial contact angle was reduced from 87 to 74° when PVC-g-P(PEGMA) was introduced. These results suggested that the synthesized PVC-g-P(PEGMA) could work as effective additive for the improvement of PVDF membrane hydrophilicity.

ATR and XPS Analysis

The chemical composition of the membrane surface played a fundamental role in determining the membrane's surface property and performance. In this study, the surface chemical compositions of the membranes were investigated by ATR/FTIR spectroscopy and XPS. The typical spectra are shown in Figures 4 and 5, respectively. M1 and M4 were selected as representatives to be investigated by ATR/FTIR spectroscopy. In comparison with the virgin PVDF membrane M1, a new peak appeared at about 1728 cm^{-1} ; this was assigned to the stretching vibrations for C=O in the ester group of P(PEGMA) in the case of M4.

The typical XPS wide scans of the membranes are displayed in Figure 5. The relative intensity of O1s was strengthened with increasing content of PVC-g-P(PEGMA) in the PVDF casting solution; this indicated that more P(PEGMA) occupied the membrane surface. The appearance of the O1s peak of the

virgin PVDF membrane was probably from the environment. The combination of ATR/FTIR spectroscopy and XPS suggested that the hydrophilic side chains P(PEGMA) of the synthesized PVC-g-P(PEGMA) successfully immigrated onto the blended PVDF membrane surface.

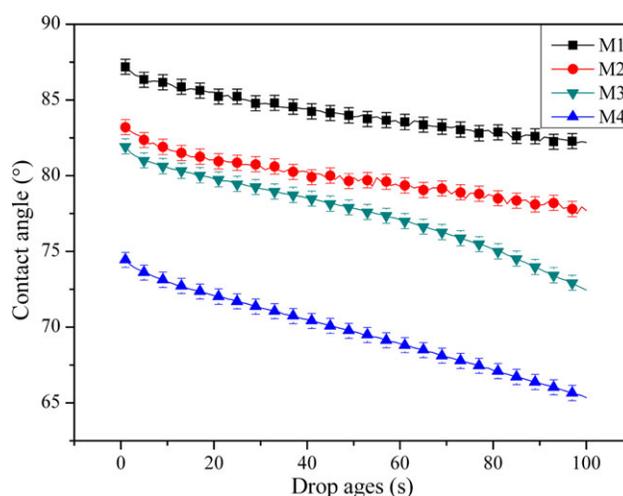


Figure 3. Water contact angles of the PVDF membrane decay as a function of drop ages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

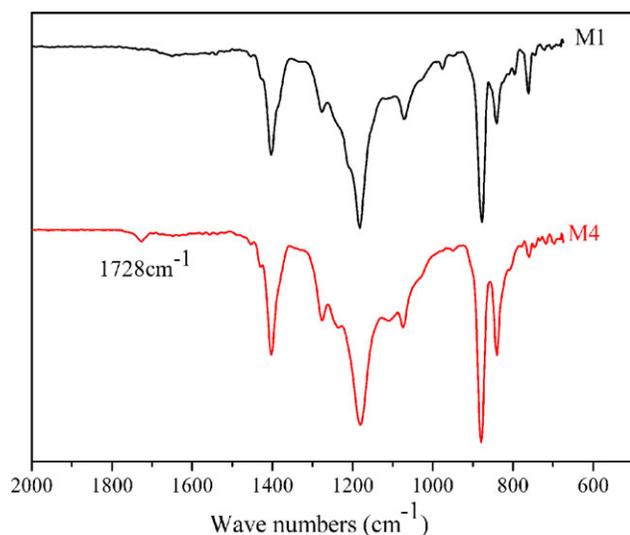


Figure 4. ATR spectra for membranes M1 (virgin PVDF membrane) and M4 [blended PVDF membrane with 5 wt % PVC-g-P(PEGMA)]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Static Protein Adsorption Measurement

The nonspecific adsorption of proteins on membranes are a bad phenomenon in protein filtration, water treatment, and so on. Accordingly, it is necessary to improve the antifouling abilities of membranes with the purpose of their high efficiency in practical applications. In this study, BSA (0.4 and 0.6 mg/mL) was used as a model protein to evaluate the fouling-resistance performance of PVDF membranes. BSA is a negatively charged biomolecule in PBS (pH 7.4), but the negative charge did not work in this study because the PVDF and PVC-g-P(PEGMA) were both neutral under the experimental conditions. Therefore, the hydrophobicity or hydrophilicity was mainly responsible for the adsorption of BSA on membranes in this study. As shown in

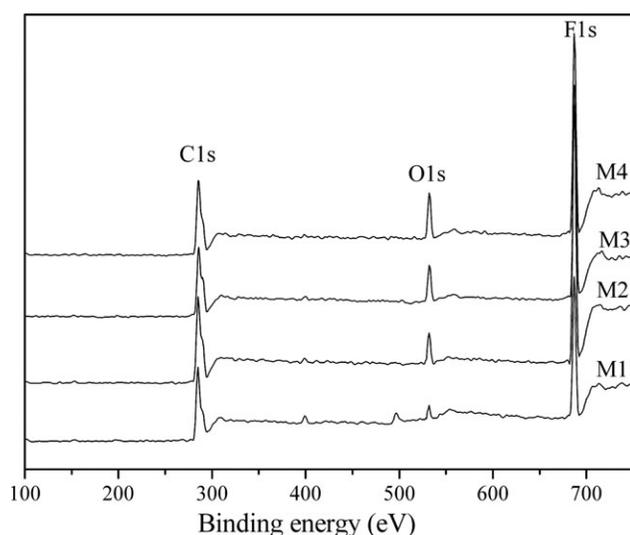


Figure 5. XPS spectra for the virgin PVDF membrane and blended PVDF membranes.

Figure 6, the virgin PVDF membrane (M1) showed the highest amount of protein adsorption because of its hydrophobic nature. It was found that with the increasing hydrophilicity from M1 to M4, the amount of BSA adhering on membranes decreased. The result from the 0.6 mg/mL BSA solution was taken as an example; the BSA deposited on the virgin PVDF membranes (M1) was about $133.9 \mu\text{g}/\text{cm}^2$, whereas the values were reduced to 105.8, 94.4, and $80.4 \mu\text{g}/\text{cm}^2$ for M2, M3, and M4, respectively. The higher the density of P(PEGMA) brushes was on the membrane surface, the lower was the amount of BSA molecules inserting into and contacting the inner PVDF substrate. Judging from previous results, we concluded that the amphiphilic graft copolymer PVC-g-P(PEGMA) had depressed the protein adsorption on the blended PVDF membrane considerably.

Ultrafiltration Performance

To further investigate the antifouling performance of the virgin PVDF membrane and blended PVDF membranes, a series of dynamic filtration measurements were conducted. As depicted in Figure 7, in contrast with the virgin PVDF membrane, the pure water flux of the blended PVDF membrane increased dramatically; this was ascribed to the higher hydrophilicity, larger pore size, and higher porosity. In the case of the BSA solution, the permeate flux of both the virgin and blended PVDF membranes decreased rapidly in the initial stage and then gradually reached a balanced state. However, the value for the blended PVDF membrane remained superior to that of the virgin membrane.

Figure 8 presents the FRR values of the virgin PVDF membrane and blended PVDF membranes. As shown in Figure 7, the protein fouling of the virgin PVDF membrane resulted in a sharp decline in flux after BSA solution permeation; this indicated that a large amount of BSA protein was deposited on the membrane surface and pores. However, the flux loss could be effectively depressed by PVC-g-P(PEGMA). Moreover, FRR increased significantly with increasing content of PVC-g-P(PEGMA) to 97%, especially for membrane M4 with 4 wt % PVC-g-

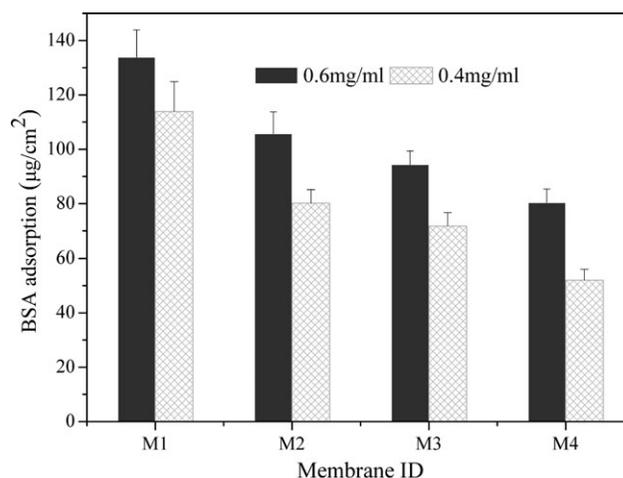


Figure 6. BSA adsorption on the virgin and blended PVDF membranes: M1: 0 wt % PVC-g-P(PEGMA), M2: 2 wt % PVC-g-P(PEGMA), M3: 4 wt % PVC-g-P(PEGMA), and M4: 5 wt % PVC-g-P(PEGMA).

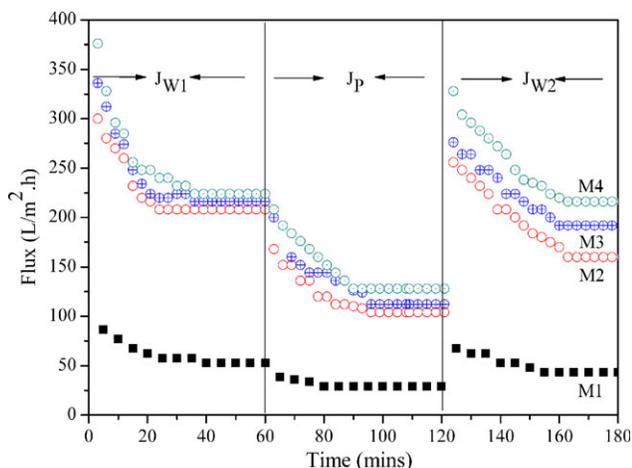


Figure 7. Permeation fluxes of the pure water and BSA solution through the virgin PVDF membrane (M1) and blended PVDF membranes (M2, M3, and M4). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

P(PEGMA), as suggested in Figure 8. This implied that the introduction of PVC-g-P(PEGMA) substantially compressed the irreversible protein fouling on the blended PVDF membrane. This was because the highly hydrophilic P(PEGMA) brush preserved a large quantity of water molecules and formed a water hydration layer, which could prevent the protein molecules from contacting the hydrophobic PVDF directly.^{26,27} In a word, the antifouling ability of the PVDF membrane was enhanced by the addition of PVC-g-P(PEGMA) in the casting solution.

CONCLUSIONS

In this study, a well-defined amphiphilic graft copolymer PVC-g-P(PEGMA) was successfully synthesized by an ATRP method. PVC-g-P(PEGMA) was successful for the modification of the PVDF membrane hydrophilicity. The addition of PVC-g-P(PEGMA) in the PVDF casting solution significantly enhanced

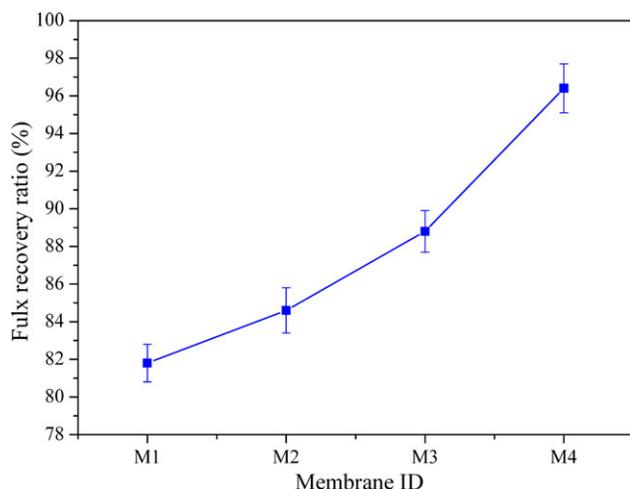


Figure 8. Water FRR values of the membranes (M1, M2, M3, and M4). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the hydrophilicity and antifouling ability of the PVDF membrane. Furthermore, it can be predicted that PVC-based amphiphilic copolymers can be used as good candidates to tune the hydrophilicity and antifouling performance of PVDF membranes.

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