

## Facile Surface Modification of PVDF Microfiltration Membrane by Strong Physical Adsorption of Amphiphilic Copolymers

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**ABSTRACT:** To endow the surface of poly(vinylidene fluoride) (PVDF) microfiltration (MF) membranes with hydrophilicity and anti-fouling property, physical adsorption of amphiphilic random copolymers of poly(ethylene glycol) methacrylate (PEGMA) and poly(-methyl methacrylate) (PMMA) (P(PEGMA-*r*-MMA)) onto the PVDF membrane was performed. Scanning electron microscopy (SEM) images showed that the adsorption process had no influence on the membrane structure. Operation parameters including adsorption time, polymer concentration, and composition were explored in detail through X-ray photoelectron spectroscopy (XPS), static water contact angle (CA), and water flux measurements. The results demonstrated that P(PEGMA-*r*-MMA) copolymers adsorbed successfully onto the membrane surface, and hydrophilicity of the PVDF MF membrane was greatly enhanced. The antifouling performance and adsorption stability were also characterized, respectively. It was notable that PVDF MF membranes modified by facile physical adsorption of P(PEGMA<sub>58</sub>-*r*-MMA<sub>33</sub>) even showed higher water flux and better antifouling property than the commercial hydrophilic PVDF MF membranes. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3112–3121, 2013

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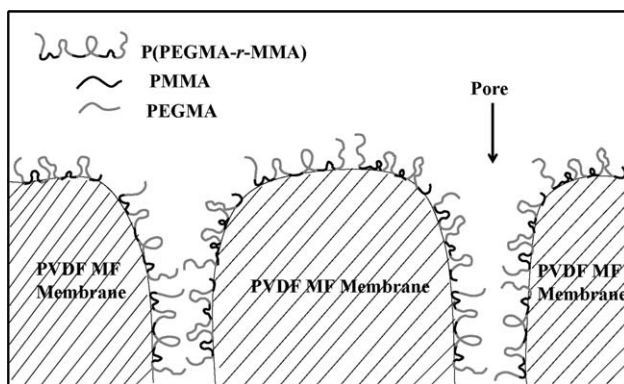
### INTRODUCTION

Because of pollution and inefficient usage of water, the world is heading for a very serious water shortage. Under this situation, water purification has attracted unprecedented attention of science and technology from different areas.<sup>1,2</sup> The filtration process using pressure-driven membranes including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membranes has become a technically and economically competitive technology for water treatment.<sup>3–5</sup> Among these membranes, MF membrane with a pore size of 0.1–10 μm plays an important role in the filtration process to remove the particles and bacteria in water at a relatively low pressure.<sup>6,7</sup> Poly(vinylidene fluoride) (PVDF) is widely used in MF membrane applications because of its excellent chemical resistance, outstanding mechanical property, and good thermal stability. But main limitations of this material are low-flux performance and severe fouling because of its hydrophobicity.<sup>8–10</sup> Although high flux and antifouling MF membranes can be obtained from hydrophilic materials such as cellulose acetate, the poor mechanical and thermal properties, especially chemical sensitivity of these materials shorten the membrane lifespan and limit their widespread commercial application.

In order to improve the water flux and antifouling property, hydrophobic MF membranes have to be modified to increase their hydrophilicity.<sup>11–14</sup> Extensively efforts have been paid to the surface modification of hydrophobic membranes with polymers by surface grafting or blending.<sup>15–26</sup> Surface grafting is an effective way to post-modify the membranes. However, complicated chemical synthesis steps including low-temperature plasma, ultraviolet, and electron beam radiation are necessary to generate reactive groups on the surface for grafting methods, which makes surface grafting not suitable for large-scale industrial production.<sup>17,20,21,27–31</sup> Blending of hydrophilic or amphiphilic polymers during membrane fabrication is another widely applied way to modify the membrane surface. Polyvinylpyrrolidone (PVP) and poly(ethylene glycol) (PEG)-based polymers are the mostly used additives. During the phase-inversion process, macromolecular additives would be enriched to the surface of membranes owing to their hydrophilicity. Unfortunately, to ensure sufficient modification of the membrane, it is necessary to add relatively large amount of macromolecular additives (usually more than 10 wt % of the matrix materials) to the casting solution.<sup>8,15,18,19,22,32</sup> A considerable amount of macromolecular additives remained in the membrane matrix, which has no contribution to the membrane functions and decreases

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**Scheme 1.** Schematic illustration of the PVDF MF membrane modified by physical adsorption of P(PEGMA-*r*-MMA) amphiphilic copolymers.

the mechanical property. It makes the fabrication procedure complicated and increases the production cost.

As an alternative strategy, physical adsorption is also utilized for surface modification of MF membranes. It is a facile way to modify the membrane surfaces by dipping which makes it suitable for large-scale industrial production. And it could also be used to functionalize membranes with complicated structure. Surfactants<sup>33–35</sup> and commercial available block copolymers poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO)<sup>36</sup> have been used as modifying agents to adsorb onto the water treatment membranes. But adsorption of these molecules always faces the concern of limited adsorption stability.<sup>37</sup> To increase the stability of adsorbed layer, post-cross-linking was performed after adsorption of water-soluble polymers.<sup>38–41</sup> However, post-cross-linking added an extra step in the surface modification procedure which would increase the cost of industrial production.

On the other hand, although adsorption mechanism of amphiphilic copolymers onto flat surfaces has been studied for a long time,<sup>42–44</sup> utilization of physical adsorption of amphiphilic copolymers to functionalize water treatment membranes is still far from emphasized.<sup>45</sup> Stability of adsorbed polymer layers is governed by the interaction between the adsorbed segments and substrate. Under certain conditions, they may fuse and entangle with each other, forming a nonleaching surface.<sup>46</sup> However, polymers applied for adsorption modification are normally commercialized products, and thus the polymer–polymer interaction has not been rationally considered. If the adsorbed polymer segments are highly hydrophobic and compatible with the membrane, the interaction between them would be strong enough to make the hydrophilic segments stably tether to the membrane surface. So polymers could not be removed from the surface during application. Herein, adsorption of well-defined synthetic amphiphilic copolymers was performed to modify the PVDF MF membrane surface.

PEG- or PEO-based materials have been extensively applied in the surface modification of water treatment membranes for their excellent hydrophilicity and antifouling characters.<sup>47–50</sup> And it is known that poly(methyl methacrylate) (PMMA) is compatible with PVDF<sup>10</sup> and different methacrylates can be copolymerized by controlled radical polymerization. Herein, the amphiphilic

copolymers of MMA and poly(ethylene glycol) methacrylate (PEGMA) were synthesized by reversible addition–fragmentation chain transfer polymerization (RAFT)-mediated radical copolymerization. In water, they could adsorb onto PVDF surface by strong physical interaction between the PMMA segments and the PVDF surface. And the compatibility of PMMA with PVDF might greatly enhance the stability of adsorbed polymer layers. As a result, the PEO segments were tethered onto the PVDF surface like chemical grafting, endowing the membrane with hydrophilicity and antifouling property. As shown in Scheme 1, a series of well-defined amphiphilic P(PEGMA-*r*-MMA) copolymers has been employed as the agents to modify the PVDF MF membranes by physical adsorption. XPS was applied to confirm the surface chemistry of modified membranes. The performances of modified membranes including hydrophilicity, water flux, antifouling property, and adsorption stability were investigated.

## EXPERIMENTAL

### Materials

Commercial pristine PVDF MF membranes (Beijing Jiuding High-Tech Filtration Company, Beijing, People's Republic of China) with a nominal pore diameter of 0.2  $\mu\text{m}$  were rinsed with isopropanol and *n*-hexane for three times before use. Commercial hydrophilic PVDF MF membranes (GVWP, Millipore) with a nominal pore diameter of 0.2  $\mu\text{m}$  were used after wetting by deionized water. PEGMA ( $M_n = 475$ , Aldrich) was purified by passing through a basic  $\text{Al}_2\text{O}_3$  column to remove inhibitors. Methyl methacrylate (MMA; Beijing Chemical Factory, Beijing, People's Republic of China) and styrene (St; Beijing Chemical Factory, Beijing, People's Republic of China) were distilled under vacuum before use. 2, 2'-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol and stored at 4°C. Tetrahydrofuran (THF, Beijing Chemical Factory, Beijing, People's Republic of China) was dried by purging with nitrogen and passing through alumina columns prior to use. 2-Cyanopropyl-2-(4-fluoro) dithiobenzoate (CPFDB) was synthesized according to a reported procedure.<sup>51</sup> Polystyrene (PS) microspheres of 200 nm in size were synthesized by soap-free emulsion polymerization according to the literature.<sup>52</sup> Deionized water was obtained from a Millipore Milli-Q purification unit. Bovine serum albumin (BSA, 99%, Aldrich), potassium persulfate (KPS, Beijing

**Table I.** Characters of Amphiphilic P(PEGMA-*r*-MMA) Copolymers and PVDF MF Membranes

| Sample   | Characterization of copolymers |         |         | Characterization of PVDF MF Membranes <sup>a</sup> |                    |                           |                                  |   |
|--|--------------------------------|---------|---------|--|--------------------|---------------------------|----------------------------------|---|
|  | PEGMA :<br>MMA <sup>b</sup>    | $M_n^c$ | $M_n^d$ | PDI <sup>c</sup>                                   | Membrane<br>number | $\phi_p$ (%) <sup>e</sup> | $J_{w0}$<br>(L/m <sup>2</sup> h) | Adsorption <sub>BSA</sub> <sup>f</sup><br>( $\mu\text{g}/\text{cm}^2$ ) |
| Unmodified PVDF  | –                              | –       | –       | –  | <b>1</b>           | –                         | –                                | 46.0 ± 3.1  |
| GVWP <sup>g</sup>                                      | –                              | –       | –       | –  | <b>2</b>           | –                         | –                                | 10.6 ± 1.9  |
| P(PEGMA <sub>18</sub> - <i>r</i> -MMA <sub>33</sub> )  | 1 : 1.8                        | 65,300  | 11,900  | 1.14   | <b>3</b>           | 22.2                      | 3060 ± 110                       | 12.2 ± 2.1  |
| P(PEGMA <sub>45</sub> - <i>r</i> -MMA <sub>45</sub> )  | 1 : 1                          | 72,200  | 25,900  | 1.17   | <b>4</b>           | 21.7                      | 5090 ± 146                       | 9.5 ± 1.7   |
| P(PEGMA <sub>58</sub> - <i>r</i> -MMA <sub>33</sub> )  | 1.8 : 1                        | 78,800  | 30,900  | 1.17   | <b>5</b>           | 20.4                      | 5620 ± 155                       | 6.5 ± 1.9   |
| P(PEGMA <sub>50</sub> - <i>r</i> -MMA <sub>102</sub> ) | 1 : 2                          | 87,600  | 34,000  | 1.15   | <b>6</b>           | 15.8                      | 5760 ± 170                       | 11.7 ± 1.8  |

<sup>a</sup> PVDF MF membranes soaked in 5 mg/mL aqueous solution of P(PEGMA-*r*-MMA) amphiphilic copolymers for 1 h.

<sup>b</sup> Copolymer compositions calculated from <sup>1</sup>H NMR spectra in CDCl<sub>3</sub>.

<sup>c</sup> Polydispersion index (PDI) determined by SEC using DMF as eluent at 50°C.

<sup>d</sup>  $M_n$  of the copolymers calculated by conversion of the feeding monomers.

<sup>e</sup> Near-surface mole fractions of the amphiphilic copolymers ( $\phi_p$ ) adsorbed onto the membranes calculated by increase of oxygen in the XPS spectra.

<sup>f</sup> BSA adsorption amounts of different PVDF MF membranes from 1 mg/mL BSA PBS solution (0.1 M; pH = 7.4) for 24 h at 25°C.

<sup>g</sup> Commercial hydrophilic PVDF MF membrane.

MMA, methyl methacrylate; GVWP, Great Valley Writing Project; PEGMA, poly(ethylene glycol) methacrylate; PVDF, poly(vinylidene fluoride).

Chemical Factory, Beijing, People's Republic of China), and other chemicals were used as received.

### Polymerization

As a general procedure, CPFDB (0.72 g; 0.3 mmol), MMA (3 g; 30 mmol), PEGMA (14.25 g; 30 mmol), AIBN (5 mg; 0.03 mmol), and THF (8 mL) were charged into a 20 mL Schlenk flask. The mixture was degassed by three freeze–evacuate–thaw cycles and then the flask was flame-sealed under vacuum. Polymerization was carried out in an oil bath thermostatted at 60°C for 8 h. The reaction was terminated by cooling and exposing the mixture to air. The resulting product dissolved in THF was purified by precipitating into a mixture of diethyl ether and *n*-hexane (1:1 volume ratio) for three times. The composition was determined combining the <sup>1</sup>H NMR spectra with conversion of the feeding monomers.

### Surface Modification of the PVDF MF Membranes

P(PEGMA-*r*-MMA) solutions with different concentration ranged from 0.1 to 5 mg/mL were prepared by dissolving P(PEGMA-*r*-MMA) in water at room temperature under constant stirring. The physical adsorption process was performed through the following steps (i) unmodified PVDF MF membranes were rinsed with deionized water and dried before a certain time immersion in P(PEGMA-*r*-MMA) solutions at 25°C; (ii) then, the membranes were taken out, rinsed with deionized water, and dried again; (iii) the modified membranes were kept in water before characterization.

### Characterization

<sup>1</sup>H NMR spectra were recorded on a Bruker AV400 FT-NMR spectrometer with CDCl<sub>3</sub> as solvent at room temperature. Size-exclusion chromatography (SEC) was performed by a set of a Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT4, and HT5) using DMF as eluent at a flow rate of 1.0 mL/min at 50°C. PS standards were used for the calibration.

Scanning electron microscopy (SEM) sample was placed on carbon tape mounted on an aluminum sample holder and then

sputter coated with platinum for SEM analysis. The SEM characterization was performed using a JEOL 6700 field-emission SEM operating at 5 kV.

X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlK $\alpha$  radiation. The base pressure was about  $3 \times 10^{-9}$  mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. A survey scan spectrum was taken and the surface elemental composition was calculated from the peak area with a correction for atomic sensitivity. Near-surface mole fractions of the amphiphilic copolymers ( $\phi_p$ ) was calculated by

$$\phi_p = \frac{\phi_1 - \phi_2}{\phi_3} \quad (1)$$

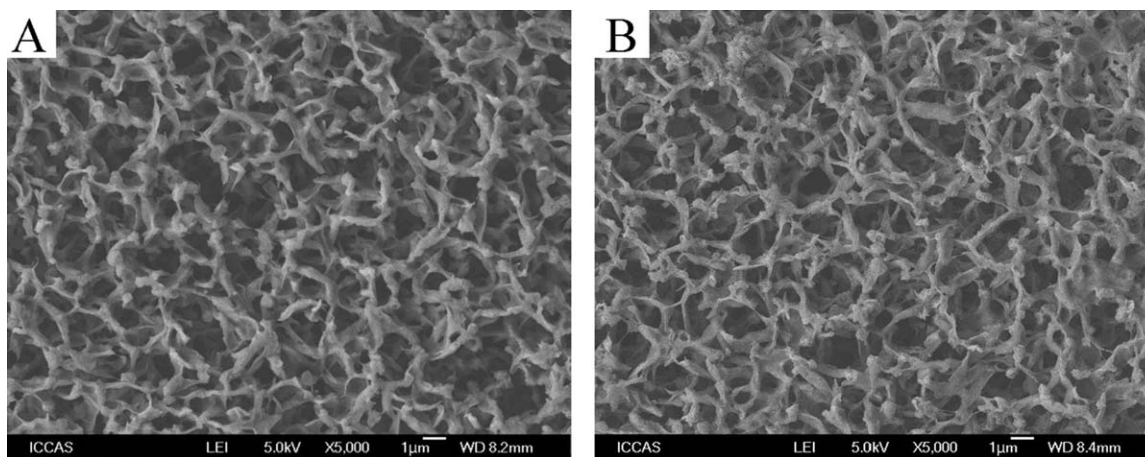
$\phi_1$  given by XPS is number of oxygen atom divided by the number of all atoms (except for hydrogen atoms) on the modified membrane surface.  $\phi_2$  given by XPS is number of oxygen atom divided by the number of all atoms (except for hydrogen atoms) on the unmodified membrane surface.  $\phi_3$  is calculated from the number of oxygen atom divided by the number of all atoms (except for hydrogen atoms) in the amphiphilic copolymers.

Near-surface mole fractions of PEO segments on the membrane surface ( $\phi_{PEO}$ ) was calculated by

$$\phi_{PEO} = \phi_p \phi_4 \quad (2)$$

$\phi_4$  is calculated from the number of all atoms (except for hydrogen atoms) in PEO segments divided by all atoms (except for hydrogen atoms) in the amphiphilic copolymers.

Static water contact angles (CAs) were measured by the sessile drop method on a homemade instrument equipped with a video camera and an image analysis system. Six drops of 5  $\mu\text{L}$  water were injected onto the membrane surface and the obtained values were averaged to acquire the CA of the membrane.



**Figure 1.** SEM images of (A) before and (B) after adsorption of P(PEGMA<sub>18</sub>-*r*-MMA<sub>33</sub>) in 5 mg/mL aqueous solution for 24 h.

Adsorption of BSA onto the membranes was evaluated by the method of Bradford according to the literature.<sup>45</sup> The membranes (4 cm × 5 cm) were rinsed with isopropanol and *n*-hexane for three times, after drying under vacuum for 3 h, they were transferred into a weighing bottle, followed by addition of 20 mL of 0.1 M PBS solution (pH = 7.4). After immersing in the PBS solution for 30 min, the membranes were taken out and further soaked in 10 mL of 1 mg/mL BSA in 0.1 M PBS solution (pH = 7.4) for 24 h at 25°C to reach the BSA adsorption equilibrium. The membranes were incubated for 5 min after addition of dye reagent containing Coomassie Brilliant Blue G-250. The absorbance at 595 nm was determined by a UV-Vis spectrophotometer.

#### Filtration Performance Test

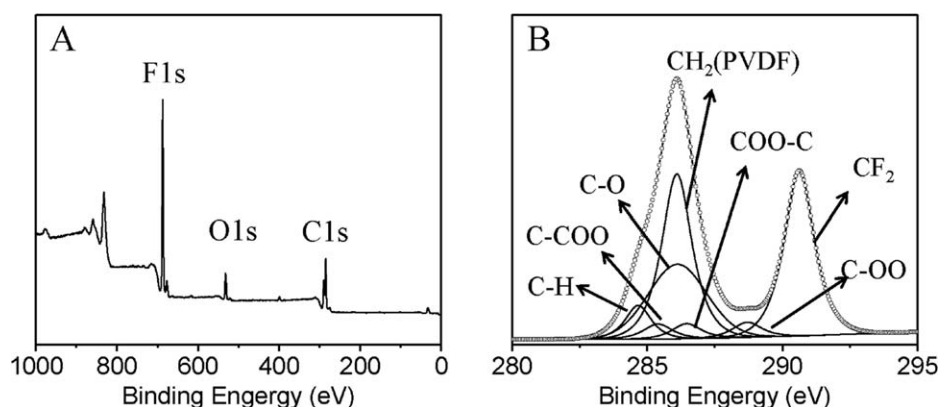
The filtration experiments were performed at room temperature in a dead ended stirred UF cell with a solution reservoir connected to a nitrogen gas tank. The MF membranes were tested at a constant pressure of 0.1 MPa, an effective filtration area of 13.4 cm<sup>2</sup>, a constant temperature of 25°C and a stirring rate of 300 rpm. A 10 min pre-compaction process with deionized water filtration at 0.1 MPa was carried out for each membrane, and then the water flux was recorded as  $J_{W0}$  when it became

stable. For the antifouling test, deionized water was exchanged with 1 mg/mL BSA in 0.1 M PBS solution (pH = 7.4). BSA solution flux was measured as  $J_B$  under the same condition. Afterwards, the recovered water flux was measured as  $J_{W1}$  after simple washing. For the PS microspheres filtration test, the PS microspheres were first diluted in water to prepare 500 ppm solution, and then they were filtrated at 0.1 MPa. Presence of the PS microspheres in filtrate was detected via turbidity measurement.

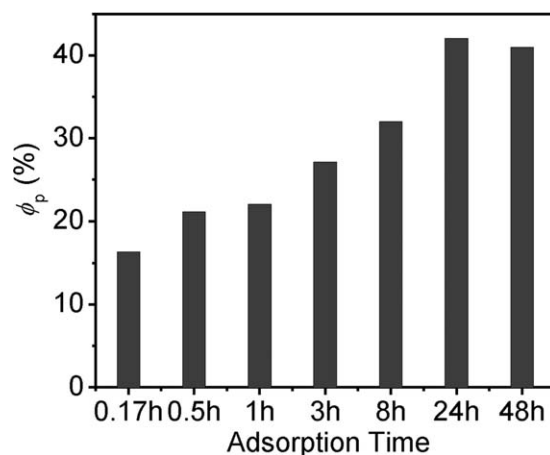
#### RESULT AND DISCUSSION

##### Synthesis of Amphiphilic P(PEGMA-*r*-MMA) Copolymers

Adsorption ability and antifouling property of the amphiphilic copolymers should be greatly related to their structure, composition and molecular weight ( $M_n$ ). Herein, four copolymers with different compositions and  $M_n$  were synthesized by RAFT-mediated radical copolymerization as shown in Table I. Controlled radical copolymerization endowed the copolymers with much improved chain homogeneity relative to the conventional radical copolymerization. Formation of the well-defined copolymers with low polydispersity was revealed in Supporting Information Figure S1, which confirmed that RAFT copolymerization of these two monomers was well-controlled. Supporting Information Figure



**Figure 2.** (A) XPS survey scan spectrum and (B) the C1s core level scan spectra of membrane 3 listed in Table I.



**Figure 3.** Near-surface mole fractions ( $\phi_p$ ) of P(PEGMA<sub>18</sub>-*r*-MMA<sub>33</sub>) adsorbed on the PVDF MF membranes from 5 mg/mL aqueous solution for different time.

S2 depicted the <sup>1</sup>H NMR spectrum of P(PEGMA<sub>58</sub>-*r*-MMA<sub>33</sub>). In this spectrum, peak **a** at 3.4 ppm was assigned to -OCH<sub>3</sub> in PEGMA segments, and peak **e** and **g** at 1.0 and 0.8 ppm were assigned to -CH<sub>3</sub> of main chains.

Because of high  $M_n$  of the copolymers, it was difficult to recognize the signals of CPFDB in the <sup>1</sup>H NMR spectra and thus  $M_n$  could not be calculated from <sup>1</sup>H NMR results.  $M_n$  given by SEC was also inaccurate because it was relative to the PS standards. So the absolute  $M_n$  was determined by conversion of the feeding monomers owing to the living character of RAFT polymerization. Composition of the copolymers could be calculated combining conversion of the feeding monomers with the <sup>1</sup>H NMR results by

$$\frac{N_{\text{MMA}} \frac{S_a}{S_{e+g}-S_e} M_{\text{PEGMA}} + N_{\text{MMA}} M_{\text{MMA}}}{n_{\text{PEGMA}} M_{\text{PEGMA}} + n_{\text{MMA}} M_{\text{MMA}}} = \text{conv} \% \quad (3)$$

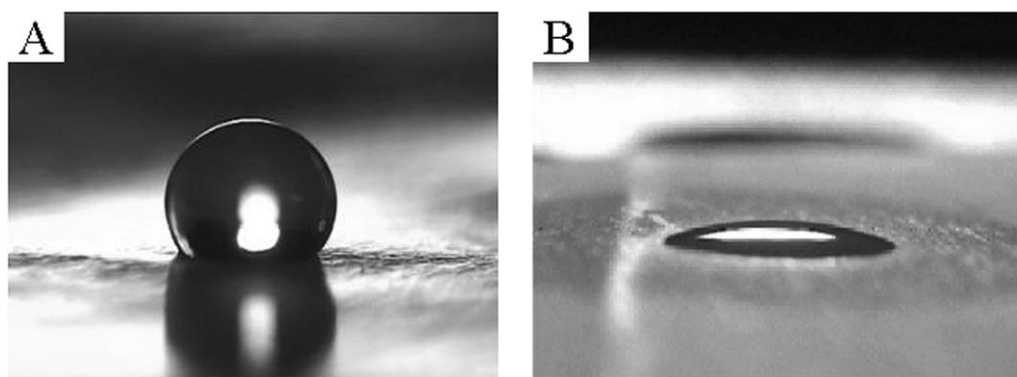
where  $N_{\text{MMA}}$  is the degree of polymerization of MMA.  $n_{\text{PEGMA}}$  and  $n_{\text{MMA}}$  are the feed molar number of PEGMA and MMA.  $S_a$  and  $S_{e+g}$  are the integral area of peak **a** and peaks **e+g** in <sup>1</sup>H NMR spectra, respectively. *conv*% is conversion of the feeding monomers.

DLS measurement showed that the hydrodynamic diameters of all the copolymers in 5 mg/mL aqueous solution were below 10

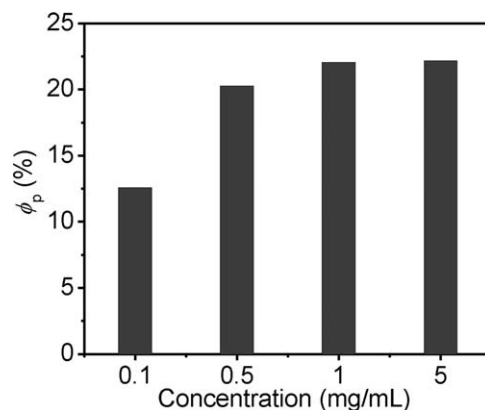
nm, which indicated that the copolymers in water did not form large aggregates.

#### Adsorption of Amphiphilic P(PEGMA-*r*-MMA) Copolymers onto the PVDF MF Membranes

The adsorption process was carried out by soaking the unmodified PVDF MF membranes in aqueous solutions containing different concentration of amphiphilic P(PEGMA-*r*-MMA) copolymers for a certain time. Then the membranes were taken out and rinsed with deionized water for several times to remove the free amphiphilic copolymers before vacuum drying. Influence of the adsorption process on the membrane structure was investigated by SEM. Because the PVDF MF membranes did not swell in water, the adsorption process should have no influence on the bulk property and morphology of the membranes. SEM images shown in Figure 1 confirmed that morphology of the PVDF MF membranes did not change after soaking in 5 mg/mL aqueous solution of P(PEGMA<sub>18</sub>-*r*-MMA<sub>33</sub>) for 24 h. Pore structures of the modified and unmodified membranes were further evaluated by filtrating of 200 nm PS microspheres. PS microspheres were completely rejected by the membrane in both cases, implying that the MF performance was unchanged after surface modification.



**Figure 4.** Profiles of 5  $\mu\text{L}$  water droplets 30 s after application onto (A) original PVDF MF membrane and (B) membrane soaked in 5 mg/mL aqueous solution of P(PEGMA<sub>18</sub>-*r*-MMA<sub>33</sub>) for 10 min.



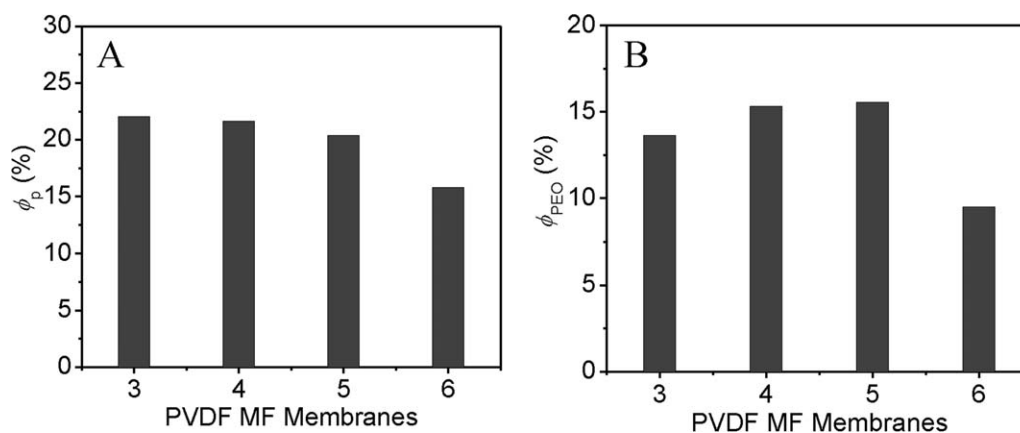
**Figure 5.** Near-surface mole fractions ( $\phi_p$ ) of P(PEGMA<sub>18</sub>-*r*-MMA<sub>33</sub>) adsorbed onto the PVDF MF membranes from aqueous solutions with different concentration for 1 h.

Successful adsorption of amphiphilic P(PEGMA-*r*-MMA) copolymers onto the membrane surface could be proved by both appearance of the O1s peak (binding energy 532.6 eV) in XPS survey scan spectra and analysis of the high-resolution C1s core level scan spectra (shown in Figure 2). C1s could be resolved into seven peaks corresponding to C-H, 284.80 eV; C-COO, 285.52 eV; C-H<sub>2</sub> (PVDF), 286.24 eV; C-O (PEGMA), 286.25 eV; COO-C (MMA), 286.59 eV; C-OO, 288.83 eV; and C-F<sub>2</sub> 290.70 eV.<sup>10</sup> Near-surface mole fractions of the amphiphilic copolymers ( $\phi_p$ ) adsorbed onto the membranes were measured quantitatively by increase of oxygen in the XPS spectra. It should be noted that  $\phi_p$  could not reach 100%, because the X-ray penetrated several nanometers deep into the surface while the adsorbed amphiphilic copolymers only formed a monolayer on the surface.<sup>53</sup> Thus the upmost ultrathin PVDF layer close to the surface could always be detected by XPS. The influence of adsorption time, polymer concentration, and composition in this process were explored separately below.

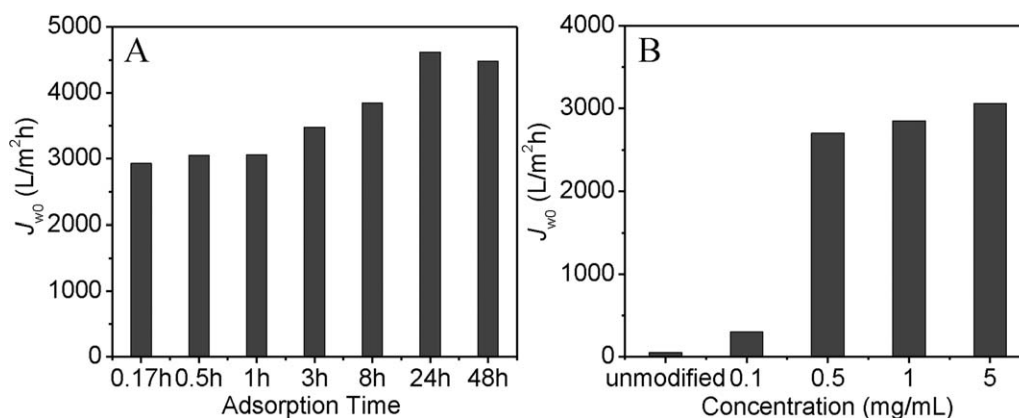
Adsorption time has a great influence on  $\phi_p$ . Although adsorption of the amphiphilic copolymers on flat hydrophobic polymeric surface has been reported to be very fast,<sup>54</sup> the MF membrane is another case. Because of the porous nature and high-surface area of MF membrane, it may take longer time for

the amphiphilic copolymers to diffuse into the pores of membranes. Herein, 5 mg/mL aqueous solution of P(PEGMA<sub>18</sub>-*r*-MMA<sub>33</sub>) was employed to investigate the influence of adsorption time. As depicted in Figure 3, there was only 21% membrane surface covered by the amphiphilic copolymers after 0.5 h of adsorption. After 24 h of adsorption,  $\phi_p$  doubled and it did not further increase with the soaking time, indicating that the adsorption equilibrium was reached. However, hydrophilicity of the membranes increased dramatically with the adsorption time. After only 10 min adsorption, the membrane became totally hydrophilic, and the water droplet could be absorbed into the modified membrane within 1 min and the CA was difficult to test. Figure 4 showed the photos of water droplets on the surface of original and modified membranes (The video of water droplet-absorption process was shown in the Supporting Information.). This result implied that the adsorption not only occurred on the outer surface of membranes but also in the pores. To study the influence of polymer concentration and composition on the adsorption process, the adsorption time was set to 1 h in other experiments.

Influence of the polymer concentration was explored by varying the concentration from 0.1 to 5 mg/mL. The histogram shown in Figure 5 indicated that only a small amount (12.6%) of



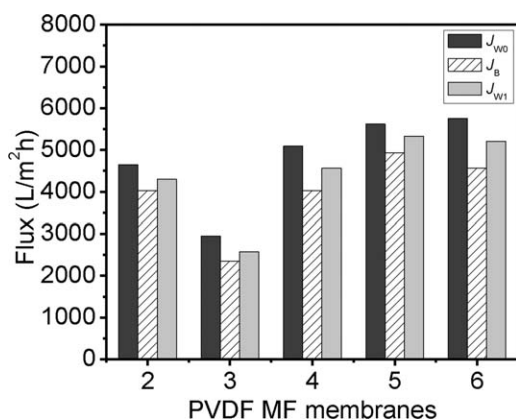
**Figure 6.** Near-surface mole fractions of (A) P(PEGMA-*r*-MMA) copolymers ( $\phi_p$ ) and (B) PEO side chains ( $\phi_{PEO}$ ) adsorbed on the PVDF MF membranes soaked in 5 mg/mL aqueous solutions for 1 h. 3, 4, 5, and 6 indicated the membrane numbers listed in Table I.



**Figure 7.** Water fluxes ( $J_{W0}$ ) of the PVDF MF membranes soaked in (A) 5 mg/mL aqueous solution of P(PEGMA<sub>18-r</sub>-MMA<sub>33</sub>) for different time and (B) aqueous solution of P(PEGMA<sub>18-r</sub>-MMA<sub>33</sub>) with different concentration for 1 h.

amphiphilic copolymers adsorbed onto the membrane surface at very low concentration (0.1 mg/mL). When the concentration increased to 0.5 mg/mL,  $\phi_p$  rose rapidly to 20.3%. It kept constant when the concentration further increased. The CA results also confirmed this conclusion. CA of membrane soaked in 0.1 mg/mL solution of P(PEGMA<sub>18-r</sub>-MMA<sub>33</sub>) only decreased from 126° (CA of the unmodified PVDF MF membrane) to 93°, and other membranes absorbed the water droplets in the CA tests (shown in Supporting Information Figure S3).

Influence of the copolymer composition was also explored using the amphiphilic copolymers listed in Table I. Comparing membrane 3, 4, and 5 which were respectively modified with P(PEGMA<sub>18-r</sub>-MMA<sub>33</sub>), P(PEGMA<sub>45-r</sub>-MMA<sub>45</sub>), and P(PEGMA<sub>58-r</sub>-MMA<sub>33</sub>) in Figure 6(A), it could be observed that  $\phi_p$  decreased with increasing the PEGMA segments content. It indicated that the hydrophilic PEG side chains of PEGMA segments would inhibit the access of more amphiphilic copolymers to the membrane surface.  $\phi_p$  of membrane 3 modified with P(PEGMA<sub>18-r</sub>-MMA<sub>33</sub>) and membrane 6 modified with P(PEGMA<sub>50-r</sub>-MMA<sub>102</sub>) which had the same PEGMA content but different  $M_n$  shown in Figure 6(A) implied that it was



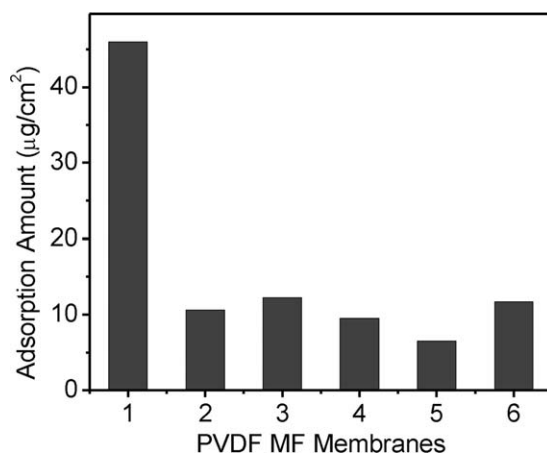
**Figure 8.** Filtration tests of the PVDF MF membranes soaked in 5 mg/mL aqueous solutions of P(PEGMA-*r*-MMA) copolymers with different compositions for 1 h. 2, 3, 4, 5, and 6 indicated the membrane numbers listed in Table I.  $J_{W0}$ ,  $J_B$ , and  $J_{W1}$  were the original water flux, the flux of BSA solution, and the recovered water flux, respectively.

more difficult for high-molecular-weight amphiphilic copolymers to adsorb onto the membranes. The reason was that adsorption of polymers was greatly affected by their diffusion rate. High-molecular-weight polymers had relatively low-diffusion rate in solution, so there was less chance for them to diffuse to the membrane surface and adsorb onto it. Figure 6(B) showed near-surface mole fractions of PEO side chains ( $\phi_{PEO}$ ) on the PVDF MF membranes modified with different copolymers. Although  $\phi_p$  of membranes modified with copolymers with higher PEGMA content was a little lower,  $\phi_{PEO}$  increased with PEGMA content.

#### Filtration Performance

Owing to high hydrophobicity and low-surface energy of PVDF, water flux ( $J_{W0}$ ) of the unmodified MF membrane was only 50  $L/m^2 h$  at 0.1 MPa. After the modification by physical adsorption of P(PEGMA-*r*-MMA) copolymers,  $J_{W0}$  was greatly enhanced, according to the increased hydrophilicity of the modified PVDF MF membranes. Figure 7(A) demonstrated influence of adsorption time on  $J_{W0}$ . After the membrane was soaked in 5 mg/mL aqueous solution of P(PEGMA<sub>18-r</sub>-MMA<sub>33</sub>) for only 10 min,  $J_{W0}$  increased by almost 2 orders of magnitude to nearly 3000  $L/m^2 h$ . It further increased to 4620  $L/m^2 h$  and reached a plateau after soaking for 24 h. For the concentration dependence as shown in Figure 7(B), membrane soaked in 0.1 mg/mL aqueous solution of P(PEGMA<sub>18-r</sub>-MMA<sub>33</sub>) for 1 h showed relatively low  $J_{W0}$  (300  $L/m^2 h$ ). At the concentration of 0.5 mg/mL,  $J_{W0}$  jumped to 2700  $L/m^2 h$ . With further increase of polymer concentration to 1 and 5 mg/mL,  $J_{W0}$  increased slowly to 3000  $L/m^2 h$ . The above observation was in accordance with the variation of  $\phi_p$  shown in Figure 5, confirming that high  $J_{W0}$  of the modified membranes was because of their hydrophilicity enhancement.

It could be observed from Figures 6(B) and 8 that  $J_{W0}$  of the modified membranes demonstrated obvious dependence upon  $\phi_{PEO}$ . Comparing membrane 3, 4, and 5, it could be seen that membranes with higher  $\phi_{PEO}$  showed higher  $J_{W0}$ . However,  $M_n$  seemed to influence  $J_{W0}$  in a different way. Although membrane 6 modified with P(PEGMA<sub>50-r</sub>-MMA<sub>102</sub>) had relatively low  $\phi_{PEO}$  than membrane 3 modified with P(PEGMA<sub>18-r</sub>-MMA<sub>33</sub>), it displayed higher  $J_{W0}$ . It indicated that  $J_{W0}$  was not only



**Figure 9.** BSA adsorption amounts of different PVDF MF membranes soaked in 1 mg/mL BSA PBS solution (0.1 M; pH = 7.4) for 24 h at 25°C. 1, 2, 3, 4, 5, and 6 indicated the membrane numbers listed in Table I.

simply correlated with  $\phi_{PEO}$ , but also affected by the length of poly-PEGMA segments.

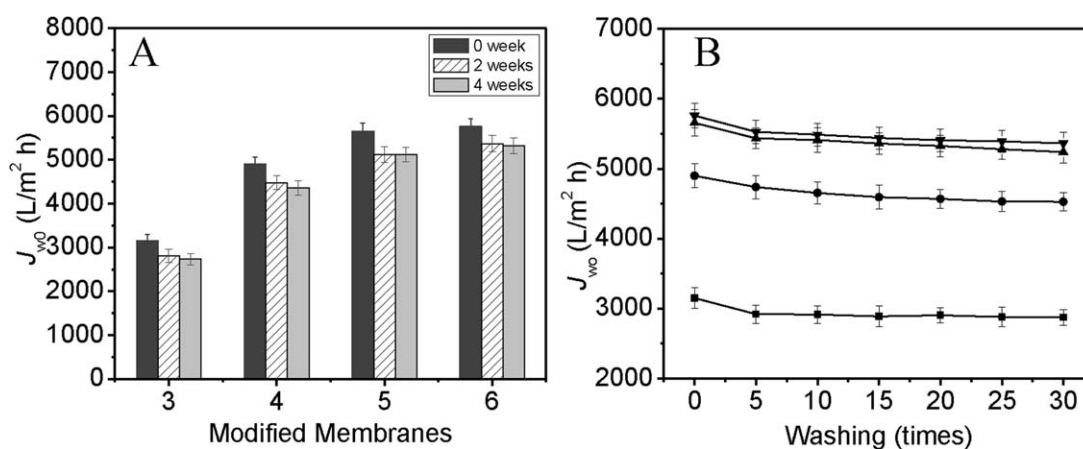
#### Antifouling Property

Decrease of the flux during the MF process caused by protein adsorption is always a great concern. Antifouling property of the membranes is another important parameter to be evaluated. Herein, the protein adsorption was investigated statically and dynamically using BSA as the model protein. The static BSA adsorption was measured by Coomassie Brilliant Blue G-250 according to the literature.<sup>45</sup> As shown in Figure 9, BSA adsorption amounts of the modified membranes were only about 10  $\mu\text{g}/\text{cm}^2$ , while it was 46  $\mu\text{g}/\text{cm}^2$  for the unmodified membrane. Just as expectation, the BSA adsorption amount was also correlated with  $\phi_{PEO}$ . The modified membranes with higher  $\phi_{PEO}$  showed better antifouling property. Membrane 5 modified with P(PEGMA<sub>58</sub>-*r*-MMA<sub>33</sub>) with the highest  $\phi_{PEO}$  showed the best antifouling property (6.5  $\mu\text{g}/\text{cm}^2$ ). It was even better than GVWP, a commercial hydrophilic PVDF MF membrane (10.6  $\mu\text{g}/\text{cm}^2$ ).

MF of BSA PBS solution (1 mg/mL; pH = 7.4) at 0.1 MPa was studied. Although BSA with small hydrodynamic radius could freely pass through the membranes,  $J_B$  was always found to be lower than  $J_{W0}$  in MF process owing to the protein adsorption. As shown in Figure 8, all the modified membranes displayed high ratio of  $J_B/J_{W0}$  (>80%) and  $J_{W1}/J_{W0}$  (>90%), implying that biofouling of membrane caused by BSA adsorption during the MF process was greatly inhibited. It accounted for that successfully antifouling modification has been achieved not only on the outer surface but also in the pores of the membranes.

#### Adsorption Stability

For the surface modification of membranes, physical methods always faces with argument of the stability of adsorbed layers. In this work, adsorption stability of the membranes modified with different copolymers was studied. After soaking in deionized water for 2 and 4 weeks, the modified membranes were taken out in sequence and  $J_{W0}$  was measured at 0.1 MPa. It could be observed in Figure 10(A) that  $J_{W0}$  of all the modified membranes tended to decline slightly with prolonging the soaking time, demonstrating that some amphiphilic copolymers



**Figure 10.** Water flux ( $J_{W0}$ ) variation of membrane 3, 4, 5, and 6 listed in Table I (A) soaked in deionized water at room temperature for different time and (B) washed in deionized water at room temperature for different times. (■), (-), (-▲), and (-▼) presented the membrane 3, 4, 5, and 6 ( $\phi_p$ ) respectively.



leached out from the surface. In addition, this leaching process took place mainly in the first 2 weeks. However, for all the copolymers, more than 85% of  $J_{W0}$  remained even after soaking in water for 4 weeks. The stability of copolymer on the membrane was also evaluated through successively washing by deionized water. For all the membranes, more than 90% of  $J_{W0}$  remained after washing for 30 times [shown in Figure 10(B)]. It proved that P(PEGMA-*r*-MMA) copolymers attached firmly to the PVDF MF membranes surface.

## CONCLUSION

Physical adsorption of amphiphilic random copolymers P(PEGMA-*r*-MMA) as a facile and effective way to modify the PVDF MF membrane surface has been demonstrated in this article. After adsorption, hydrophilicity, water flux, and antifouling property were greatly improved without any influence on the membrane structure. And membrane modified with P(PEGMA<sub>58</sub>-*r*-MMA<sub>33</sub>) (PEGMA : PMMA = 1.8 : 1) even showed better performance than the commercial hydrophilic PVDF MF membrane. The modified membranes were considerably stable after soaking in deionized water for 1 month or washing for 30 times. This research indicates that physical adsorption of tailor-made amphiphilic copolymers is a simple and efficient way to modify the surface of polymer membranes for water filtration application. Furthermore, modification by simple dipping is very useful to functionalize complex structure membranes. This approach could also be expanded to other membrane surface modification.

## SUPPORTING INFORMATION

This material includes the SEC curves and <sup>1</sup>H NMR spectrum of P(PEGMA-*r*-MMA) copolymer. And movie of the water droplet absorbed by the modified membranes is also available.

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