

# Synthesis of a Poly(methyl methacrylate)-*b*-Poly[2-(*N,N*-dimethylamino) ethyl methacrylate] Block Copolymer and Its Effects on the Surface Charges and pH-Responsive Properties of Poly(vinylidene fluoride) Blend Membranes

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**ABSTRACT:** A poly(methyl methacrylate) (PMMA)-*b*-poly[2-(*N,N*-dimethylamino) ethyl methacrylate] (PDMAEMA) block copolymer was successfully synthesized by a reversible addition–fragmentation chain-transfer method. The resulting copolymer was used to prepare poly(vinylidene fluoride) blend membranes via a phase-inversion technique. The polymorphism, structure, and properties of the blend membranes were investigated by Fourier transform infrared spectrometry, scanning electron microscopy (SEM),  $\zeta$  potential analysis, and filtration. The results indicate that PMMA-*b*-PDMAEMA could migrate onto the surface of the membrane during the coagulation process, and more of the  $\beta$ -crystal phase appeared with the increase of the block copolymer in the membranes. The surface morphology and cross section of the membranes were also affected by the copolymer, as shown by SEM. The  $\zeta$ -potential results show that the surface charges of the membrane could be changed from positive to negative at an isoelectric point as the pH increased. The blend membrane also exhibited good pH sensitivity, and its water flux showed a great dependence on pH. The filtration experiment also indicated that the blend membrane had good hydrophilicity and antifouling properties. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40685.

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## INTRODUCTION

Amphiphilic block copolymers have attracted more and more attention in recent years because of their applications as stabilizers, emulsifiers, and membrane modifiers.<sup>1–3</sup> Recently, amphiphilic block copolymers have been successfully used in the modification of hydrophobic polymer membranes to improve their hydrophilic, antifouling, and other properties.<sup>4</sup> Poly(vinylidene fluoride) (PVDF) is a widely used, fluoride-containing membrane material because of its very useful combination of processability, good mechanical strength, and thermal and chemical stability. PVDF membranes, as an important product, have been widely used in the industrial separation field. The existing problem is that PVDF has strong hydrophobic properties, which make it easily fouled. So, the antifouling and functional modification of PVDF membranes has attracted more and more attention.

There are usually two methods for modifying PVDF membranes; these are called *surface modification* and *physical blending*. Surface modification is usually achieved by the coating or grafting of a functional layer on the prepared membrane sur-

face; the functional grafted layers are usually composed of poly(acrylic acid), poly(*N*-isopropyl acrylamide) (PNIPAAm), and poly(ethylene glycol) monomethyl ether methacrylate.<sup>5–7</sup> Physical blending is the most practical method for achieving the modification on an industrial scale. When the membrane is prepared, the polymer and modifiers are blended in the casting solution. During the coagulation process, the functional and hydrophilic segments of the copolymer can migrate onto the surface of the membranes, so the properties of the membranes are improved by the copolymers. The modifiers usually include hydrophilic polymers, pore-forming additives, amphiphilic copolymers, and inorganic particles.<sup>8</sup> Among the two modification methods, physical blending may be a good choice, but the main problem is that the hydrophobic segments in the amphiphilic copolymer should have good compatibility with the hydrophobic polymer matrix.

The amphiphilic copolymers used in PVDF membrane modification usually have poly(methyl methacrylate) (PMMA) or PVDF as the hydrophobic segments; this is due to their good compatibility with the PVDF matrix.<sup>9,10</sup> Typical copolymers

used in the modification of PVDF membranes include poly[methyl methacrylate-*r*-poly(oxyethylene methacrylate)] and PVDF-*g*-poly(oxyethylene methacrylate); these were preliminarily reported by Mayes and coworkers.<sup>11,12</sup> Some other amphiphilic copolymers, such as PVDF-*g*-poly(methacrylic acid),<sup>12</sup> PVDF-*g*-PNIPAAm,<sup>13</sup> and PMMA-*b*-PNIPAAm,<sup>14,15</sup> which have pH- and thermally sensitive properties, are usually used to prepare the environmentally sensitive membrane. An environmentally sensitive membrane is a kind of membrane that has a rapid response to the minor stimulus from their surrounding environment, such as temperature,<sup>14–16</sup> pH,<sup>17,18</sup> ionic strength,<sup>19</sup> and others.<sup>20,21</sup>

Poly[2-(*N,N*-dimethylamino) ethyl methacrylate] (PDMAEMA), as a typical pH- and thermally sensitive copolymer, has attracted more and more attention because of its pH, thermal sensitivity, and micellization properties.<sup>22–24</sup> PDMAEMA is a cationic polyelectrolyte; it has a  $pK_a$  of about 7.6 in pure water, and the phase-transition temperature of PDMAEMA in aqueous media is in the wide range 38–50°C.<sup>25</sup> Copolymers bearing PDMAEMA blocks usually exhibit positive charges at low and neutral pHs and show thermal behavior in water and are marked by a lower critical solution temperature (LCST).<sup>26</sup> PMMA-*b*-PDMAEMA also exhibits a specific thermoresponsiveness to selected ions and other factor in aqueous solutions, and its LCST is affected by the pH, ionic strength, and co-anion nature. The LCST of the copolymer changes linearly with pH within the range from 7.7 to 8.1 with a rate of approximately 32°C/pH unit.<sup>27,28</sup>

Amphiphilic copolymers are usually synthesized by radical polymerization, thermal graft copolymerization, and atom transfer radical polymerization.<sup>8</sup> The block copolymers of PDMAEMA, such as PMMA-*b*-PDMAEMA and polystyrene-*b*-PDMAEMA, were usually synthesized by atom transfer radical polymerization,<sup>25,26</sup> oxyanion-initiated polymerization,<sup>29</sup> and reversible addition–fragmentation chain-transfer (RAFT) technique.<sup>24</sup> With these methods, a narrow distribution and well-defined copolymers could be obtained. In the RAFT synthesized process, cumyl dithiobenzoate is usually used as a chain-transfer agent (CTA) and benzoyl peroxide as the initiator. However, former research work has usually focused on chemical characterization, critical micelle concentration study of the copolymer in different pH aqueous solutions, and the thermal sensitivity of the copolymers. PMMA-*b*-PDMAEMA copolymers have seldom been reported in membrane modification.

In this study, the PMMA-*b*-PDMAEMA copolymer was synthesized by a RAFT polymerization process with carboxyl-terminated trithiocarbonates as the CTA and 2,2'-azobisisobutyronitrile (AIBN) as the initiator;<sup>30</sup> this was different from the reported method.<sup>24</sup> The aim of this study was to use the PMMA-*b*-PDMAEMA copolymer as the modifier to improve the pH-sensitive and hydrophilic properties of the PVDF membranes. During the study, the PMMA-*b*-PDMAEMA/PVDF blend membranes were fabricated by a phase-inversion process; the effects of the copolymer on the polymorphism, pH sensitivity, charged properties, and hydrophilicity of the membranes were studied in detail.

## EXPERIMENTAL

### Materials

PVDF (SOLEF 1015), with a melt flow index of 0.2 (230°C, 5 kg), was purchased from Solvay Solexis Co. (Brussels, Belgium). 2-(*N,N*-Dimethylamino) ethyl methacrylate (DMAEMA; 99%) and methyl methacrylate (MMA; analytical reagent) were all purchased from Aladdin Chemical Co. (Shanghai, China). DMAEMA was distilled *in vacuo* before use. MMA was washed with 5% NaOH solution followed by distilled water, and then distilled *in vacuo*. AIBN (Aladdin Chemical, 97%) was purified by recrystallization from ethanol. Other chemical reagents, such as carbon disulfide, chloroform, acetone, sodium hydroxide, methyl trioctyl ammonium chloride, 1,4-dioxane, petroleum ether, *N,N*-dimethyl acetamide (DMAc), poly(ethylene glycol) (PEG2000), bovine serum albumin (BSA), and phosphate-buffered saline buffer solution (pH = 7.4) were all purchased from Huipu Chemical Co. (Hangzhou, China) and were used as received.

### Synthesis of the CTA

In this study, S-1-dodecyl-S'-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic acid) trithiocarbonate was used as the CTA, which was synthesized according to the method reported by Lai et al.<sup>30</sup> Fourier transform infrared (FTIR) was used to investigate the structure; the results indicated that there were strong adsorption peaks at 1714 and 1062  $\text{cm}^{-1}$ , which were attributed to O=C=O and C=S groups. These results are consistent with an earlier article,<sup>30</sup> and this indicated that CTA was synthesized successfully.

### RAFT Polymerization of MMA

PMMA was polymerized with CTA and AIBN as the initiator. The reaction was taken under a nitrogen ( $\text{N}_2$ ) atmosphere. All of the reaction reagents were put into a three-necked flask and bubbled with  $\text{N}_2$  for 40 min. The [MMA]/[CTA]/[AIBN] molar ratios were controlled as 100:1:0.33. Then, the flask was put into an oil bath, and the reaction was controlled at 65°C for 12 h before it was quenched in an ice–water bath. The raw product was obtained by the precipitation of the reaction mixture into cold methanol. The obtained polymer was washed with methanol three times and then dried in a vacuum oven at 40°C for 24 h.

### Synthesis of the PMMA-*b*-PDMAEMA Block Copolymer

PMMA was used as the macro-CTA in the RAFT polymerization of DMAEMA. During the synthesized process, DMAEMA (3.0 g, 20 mmol), PMMA-CTA [0.5 g,  $2.26 \times 10^{-2}$  mmol, number-average molecular weight ( $M_n$ ) =  $2.20 \times 10^4$ , polydispersity index (PDI) = 1.67, as shown later in Table II], AIBN (1.5 mg, 0.009 mmol), and 1,4-dioxane (6.0 g) were added to a 100-mL, round-bottomed flask equipped with a magnetic stirring bar. The reaction mixtures were bubbled with nitrogen for 40 min at room temperature. Then, the flask was immersed in an oil bath, which had preheated to 70°C, and the polymerization was preceded for 6 h before it was quenched in an ice bath. The raw product was obtained by precipitation of the reaction mixture into petroleum ether. The obtained polymer was washed with methanol three times and then dried in a vacuum oven at 40°C for 24 h. The monomer and homopolymer reserved in the product was further removed by the immersion

**Table I.** Compositions of the Casting Solutions for the Preparation of the PVDF/PMMA-*b*-PDMAEMA Blend Membranes

Membrane type	PVDF (g)	PMMA- <i>b</i> -PDMAEMA (g)	PEG2000 (g)	DMAc (g)
M1	12	0	2	86
M2	12	2	2	84
M3	12	4	2	82
M4	12	6	2	80

of the polymer into cool water for 48 h. The resulting polymer was collected and dried in a vacuum oven.

### Preparation of the PVDF/PMMA-*b*-PDMAEMA Blend Membranes

PVDF/PMMA-*b*-PDMAEMA porous membranes were prepared by a phase-inversion method. The formulations of casting solutions are exhibited in Table I. PVDF and PMMA-*b*-PDMAEMA with different weight ratios were dissolved in a DMAc solution and stirred at 60°C for about 12 h to ensure homogeneous mixing. After filtration and degassing, the solution was cast onto a horizontal glass plate at room temperature with a glass blade. After it was exposed to air for 30 s, the nascent membrane was immersed in deionized water for gelation, and the coagulation temperature was 30°C. The resulting membrane was stored in deionized water for at least 2 days before characterization.

### Membrane Characterization

The surface and interior morphologies of the membranes were examined by scanning electron microscopy (SEM; JSM-5610, JEOL, Japan). For this purpose, the samples were fractured in liquid nitrogen to obtain tidy cross sections and sputter-coated with a gold layer before SEM observation. The chemical structure and polymorphism of the membranes were characterized by attenuated total reflection (ATR) infrared spectroscopy (ATR-FTIR; IR200, Nicolet) at a 1-cm<sup>-1</sup> resolution and in the 400–4000-cm<sup>-1</sup> wave-number range. The surface-charged properties of the membranes were examined with a SurPASS ζ potential analyzer (Anton Paar, Austria), the operation pressure is 100 Pa.

The molecular weights and molecular weight distributions of the PMMA macro-CTA and PMMA-*b*-PDMAEMA polymers were measured by a gel permeation chromatography (GPC) system consisting of a Waters 1525 pump, three Waters Styragel columns (Styragel HT2, HT3 and HT4), and a Waters 2414 refractive-index detector. Dimethylformamide was used as the eluent with a flow rate of 1.0 mL/min at 35°C.

<sup>1</sup>H-NMR spectra were recorded on an Avance DMX 500 spectrometer (Bruker, Switzerland) operated at 500 MHz. Hexadeuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) and tetramethylsilane were used as the solvent and internal standard, respectively.

Filtration experiments were conducted on a cross-flow ultrafiltration instrument (SF-SA, Hangzhou Saifei Co., China) with three membrane cells, and the membrane diameter was about 54 mm. Each membrane was initially pressurized at 0.15 MPa

for 30 min, and then, the pressure was lowered to an operating pressure of 0.1 MPa. The pure water flux ( $J_w$ ; L m<sup>-2</sup> h<sup>-1</sup>) was calculated by the following equation:

$$J_w = \frac{V}{A \cdot \Delta t} \quad (1)$$

where  $V$  is the permeate volume (L),  $A$  is the membrane area (m<sup>2</sup>), and  $\Delta t$  is the time (h).

After that, a BSA phosphate-buffered saline solution (1 g/L) was forced to permeate through the membrane at the pressure of 0.1 MPa for 30 min, and the flux was recorded as the filtration flux of BSA ( $J_p$ ). After the filtration of the BSA solution, these membranes were washed with pure water for 30 min at 25°C, and then, the  $J_w$  values were measured again. By comparing the values of  $J_w$ ,  $J_p$ , and the recovered water flux ( $J_R$ ), the cleaning properties of the fouled membranes were investigated. The filtration experiments were measured three times and then averaged.

The water flux of the membrane at different pH values was also conducted on the filtration instrument. The pH value of the pure water was adjusted by 0.1M HCl and 0.1M NaOH aqueous solutions. Before each measurement, the membrane was operated at 0.1 MPa under the measured water for at least 30 min to ensure equilibration between the water and the membranes.

## RESULTS AND DISCUSSION

### Characterization of the PMMA-*b*-PDMAEMA Copolymer

The <sup>1</sup>H-NMR spectrum of the PMMA-*b*-PDMAEMA block copolymer is shown in Figure 1. The chemical shifts appearing at 0.9 ppm (signal a) and 1.8 ppm (signal b) were attributed to the methyl protons and methylene protons on the backbone, respectively. The chemical shifts appearing around 2.2 ppm (signal e) and 4.0 ppm (signal c) were assigned to the methylene protons [–CH<sub>2</sub>–N(CH<sub>3</sub>)<sub>2</sub>] and methyl protons [–CH<sub>2</sub>–N(CH<sub>3</sub>)<sub>2</sub>] on the tertiary amine, respectively. The chemical shifts appearing around 3.4–3.7 ppm (signal f) were attributed to the protons on the ester of PMMA (–OCH<sub>3</sub>).<sup>31</sup>

GPC was used to characterize the molecular weight of the PMMA macro-CTA and PMMA-*b*-PDMAEMA; the results are shown in Table II. Compared with PMMA, the molecular weight of PMMA-*b*-PDMAEMA increased obviously. The <sup>1</sup>H-NMR and GPC results all indicate that the block copolymers were synthesized successfully.

**Table II.** Molecular Weights and Distributions of the PMMA-CTA and PMMA-*b*-PDMAEMA Polymers

Polymer	GPC molecular weight		
	$M_n$	$M_w$	PDI
PMMA-CTA	$2.20 \times 10^4$	$3.68 \times 10^4$	1.67
PMMA- <i>b</i> -PDMAEMA	$3.94 \times 10^4$	$7.91 \times 10^4$	2.00

$M_w$  = weight-average molecular weight.

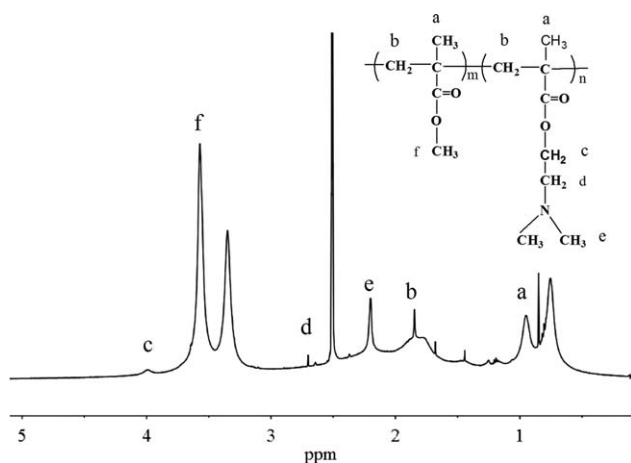


Figure 1.  $^1\text{H}$ -NMR spectrum of PMMA-*b*-PDMAEMA in  $\text{DMSO-}d_6$ .

### Polymorphism of the PVDF/PMMA-*b*-PDMAEMA Blend Membranes

ATR-FTIR is often used to investigate the chemical composition and polymorphism behavior of PVDF blend membranes; our results are presented in Figure 2. Compared with pure PVDF membrane (M1), the blend membranes (M2–M4) all showed C=O adsorption peaks around  $1728\text{ cm}^{-1}$ , and with the increase of PMMA-*b*-PDMAEMA in the membranes, the intensity of adsorption peaks became stronger. At the same time, the adsorption peaks of the C–N and C=S groups appeared around  $1148$  and  $1014\text{ cm}^{-1}$ , respectively. These phenomena indicate that the PMMA-*b*-PDMAEMA copolymer migrated onto the surface of the membranes during the coagulation process. The FTIR results also indicate the adsorption peaks of the  $\alpha$ -crystal phase of PVDF appeared around  $1382$  and  $796\text{ cm}^{-1}$ ; the  $\beta$ -crystal phase appeared around  $1276\text{ cm}^{-1}$ , and its adsorption intensity increased with the increase of the block copolymer in the membranes; this indicated that PMMA-*b*-PDMAEMA was in favor of the formation of the  $\beta$ -crystal phase.

### SEM Photographs

SEM images of the blend membranes are given in Figure 3. As for the top surface of the membranes, the pore size and porosity first increased with the addition of PMMA-*b*-PDMAEMA and then decreased with the increase in the PMMA-*b*-PDMAEMA copolymer in the membranes. As for the cross section of M1, a combined morphology with a fingerlike structure on the top and a spongelike structure on the bottom was found; this was much different from the cross section of the blend membranes. With the addition of the PMMA-*b*-PDMAEMA copolymer in the membranes, a fingerlike and large pore structure appeared in the cross section of the blend membranes, and with the increase of the copolymer, the fingerlike structure on the top surface of the membrane became more and more obvious, and a more spongelike structure appeared on the bottom surface of the membrane (M3 and M4 membranes). These results could be expected on the basis of ternary diffusion models, which relate the pore formation to instantaneous or delayed liquid-liquid demixing during the coagulation process.

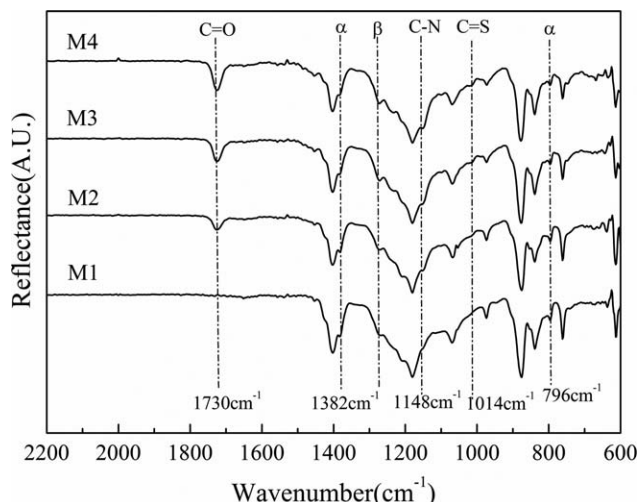


Figure 2. ATR-FTIR spectra of the PVDF/PMMA-*b*-PDMAEMA blend membranes.

Because PMMA-*b*-PDMAEMA is an amphiphilic copolymer, the presence of PMMA-*b*-PDMAEMA in the casting solutions could be expected to increase the affinity of the casting solution and

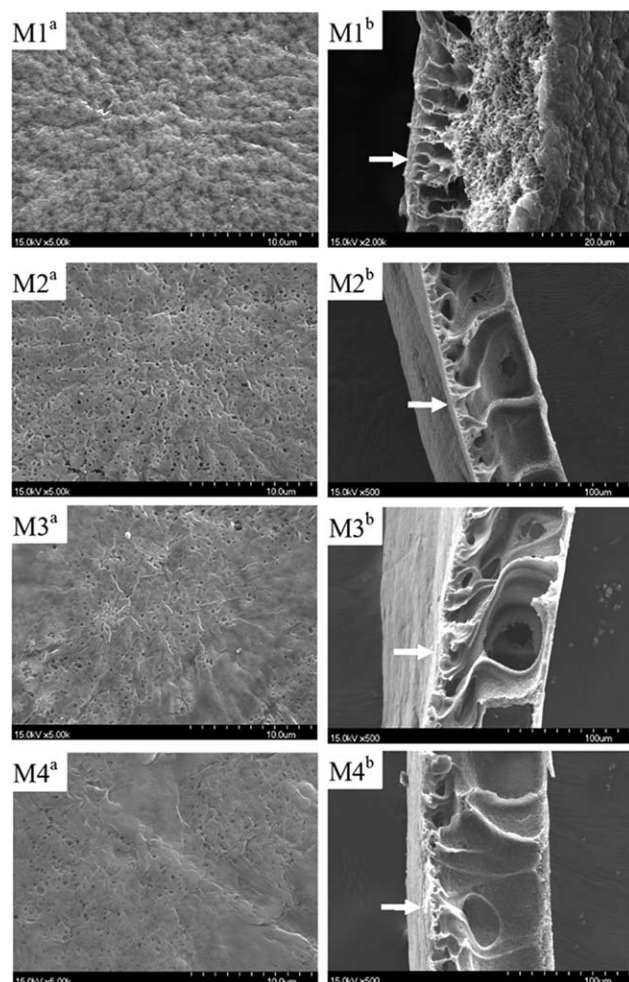
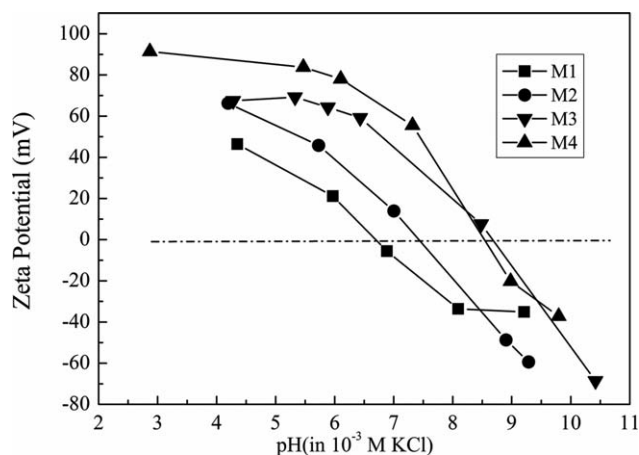


Figure 3. SEM micrographs of the PVDF and PVDF/PMMA-*b*-PDMAEMA blend membranes: (a) top surface and (b) cross section. The arrow direction denotes the top surface of the membranes.



**Figure 4.** pH-dependent  $\zeta$  potential profiles for the pure PVDF and PMMA-*b*-PDMAEMA/PVDF blend membranes. The KCl concentration was  $10^{-3}$  M.

the copolymer; this resulted in a decrease in the solvent–nonsolvent exchange rate. When the content of the copolymer in the casting solution was low, the phase inversion was mainly instantaneous demixing; this was associated with macrovoid formation. However, with the addition of more and more PMMA-*b*-PDMAEMA, the affinity between the solvent and copolymer became stronger; this greatly decreased the diffusion rate of the solvent and nonsolvent during the phase-inversion process, so a delayed phase separation appeared.<sup>32</sup> Therefore, a more sponge-like structure of the sublayer appeared, as shown in the M4 blend membranes. As for the top surface structure of the membrane, the pore size first increased and then decreased with the increase in the amount of the copolymer; these results may have been related to the microphase separation behavior and surface segregation of the copolymer. During the membrane formation process, PMMA was firmly entrapped in the membrane matrix because of the good compatibility with PVDF; the hydrophilic segment of PDMAEMA migrated onto the membrane surface. When the PMMA-*b*-PDMAEMA content was low, the surface segregation was weak. The pore formation was mainly related to instantaneous demixing, and the pore size increased. However, with increasing PMMA-*b*-PDMAEMA in the membrane, more and more PDMAEMA segments migrated onto the membrane surface and formed a dense hydrophilic layer;<sup>11,12</sup> this decreased the pore size on the membrane surface.

#### $\zeta$ Potential Values of the Membranes

To further study the effect of PMMA-*b*-PDMAEMA on the charged properties of the blend membranes, the surface potential ( $\zeta$  potential) of the membrane was investigated. The  $\zeta$  potential of the membranes was related to the pH, concentration, and type of metal ions in the aqueous solution. In this study, the KCl concentration was kept as  $10^{-3}$  M. Figure 4 exhibits the pH-dependent  $\zeta$  potential profiles for the blend membranes. It was indicated that the  $\zeta$  potential of the membranes changed from positive to negative at an isoelectric point (iep) as the pH increased, and the iep value ranged from 6.7 to 8.7. As for the pure PVDF membrane, the changes in the  $\zeta$  potential with the pH value may have been related to the

adsorption of charged groups on the membrane surface. The negative value of the blend membranes above the iep may have been due to the existence of  $\text{OH}^-$  in the solutions because the cationic PDMAEMA was a weak base with a  $\text{p}K_a$  of 7.2, and with increasing pH, the adsorption of  $\text{OH}^-$  increased, so the  $\zeta$  potential of the membranes became negative.<sup>33</sup>

As shown in Figure 4, the different blend membranes had different iep values. The iep value of the pure PVDF membrane was about 6.70, and with increasing PMMA-*b*-PDMAEMA in the membranes, the corresponding iep value increased accordingly. The reason may have been that during the membrane formation process, the PMMA-*b*-PDMAEMA copolymer migrated onto the surface of the membrane, and this improved the charged properties of the blend membranes.

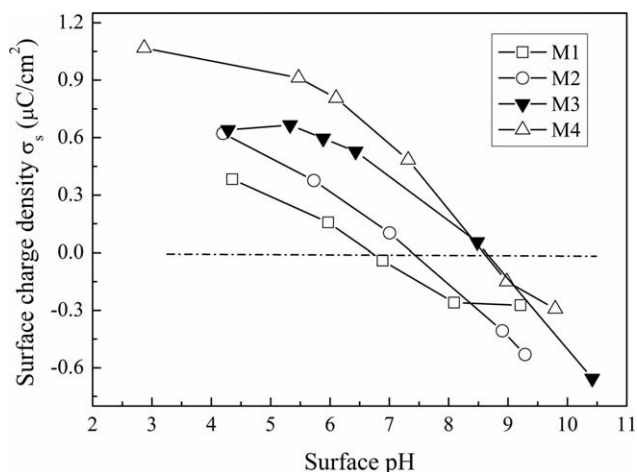
The apparent surface charge density ( $\sigma_s$ ) of the membranes was calculated from the apparent  $\zeta$  potentials with the Gouy–Chapman equation:<sup>34</sup>

$$\sigma_s = \frac{2 \epsilon k T \kappa}{z_+ e} \sinh \left( \frac{z_+ e \zeta}{2 k T} \right) \quad (2)$$

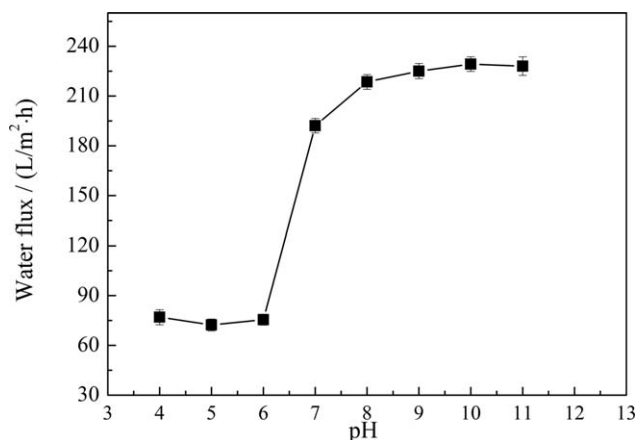
where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\epsilon$  is the solution permittivity ( $\epsilon = \epsilon_0 \epsilon_r$ ,  $\epsilon_0$  is the electric permittivity of the vacuum,  $\epsilon_r$  is the relative permittivity),  $z_+$  is the valency of the counter ions, and  $\kappa$  is the reciprocal of the electrical double-layer thickness. At 25°C, for a 1-1 electrolyte with  $\sigma_s$  ( $\mu\text{C}/\text{cm}^2$ ),  $\zeta$  (V), and  $C_s$  (mol/L), this relation became the following equation:<sup>34</sup>

$$\sigma_s = 11.7 C_s^{1/2} \sinh(19.5 \zeta) \quad (3)$$

where  $\zeta$  is the zeta potential, and  $C_s$  is the salt concentration.  $\sigma_s$  could be calculated from the  $\zeta$  potential with eq. (3) and plotted as a function of the surface pH; the result is presented in Figure 5. It is indicated that the surface-charged density decreased with increasing pH value, and the charges were positive when the pH was lower than the iep value of the membrane. Then, they became negative with increasing pH value. This showed the same variation tendency as the  $\zeta$  potential, as shown in Figure 4. The surface-charged density also reflected



**Figure 5.** Variations in  $\sigma_s$  for the PVDF and PVDF/PMMA-*b*-PDMAEMA blend membranes as a function of the surface pH. The KCl concentration was  $10^{-3}$  M.



**Figure 6.** pH-dependent water flux through the PMMA-*b*-PDMAEMA/PVDF blend membranes (M2).

the surface-charged properties of the membranes. With these properties, the  $\zeta$  potential and  $\sigma_s$  could be used to judge the charged properties of the membrane, and they could also have wide applications in antifouling control in membrane separation.<sup>33</sup>

#### pH-Responsive Properties

PDMAEMA is a typical weak polybase (weak cationic polyelectrolyte) and has the characteristics pH and temperature sensitivity.<sup>35,36</sup> PDMAEMA can obtain a hydrogen proton when it is in a neutral or acidic aqueous solution; this makes it more hydrophilic, but in a basic aqueous solution, the amino in PDMAEMA is easy to deprotonate; this makes it have a certain hydrophobicity.<sup>37,38</sup>

Figure 6 shows the effect of the pH on the water flux of the PMMA-*b*-PDMAEMA/PVDF blend membranes. The results indicate that the water flux of the blend membranes changed greatly with the pH value. When the pH values were adjusted to 5 and 6, the water flux decreased to a low level, but when the pH was 10, the water flux reached the highest value. The water flux of the blend membranes had a great dependence on the pH value. The reason may have been that PDMAEMA is a typical polybase, which is affected greatly by the protonation of H<sup>+</sup>. So, in acidic aqueous solution, the PDMAEMA segments were extended; this decreased the pore size of the membrane; as a result, the water flux decreased accordingly. However, in the basic aqueous solution, the deprotonation of PDMAEMA made the molecular chains shrink greatly; this increased the pore size of the membrane. Thus, the water flux of the blend membrane increased accordingly. These phenomena could be explained by the typical through pore mechanism.<sup>39</sup>

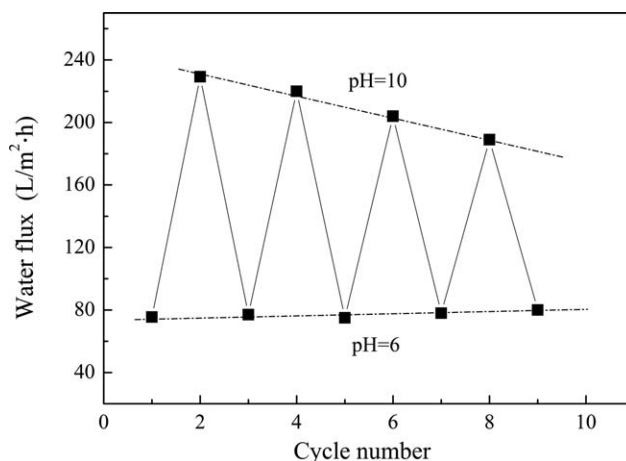
The response to pH changes is a very important property to pH-sensitive membranes. In this study, the response time of the blend membrane to pH changes were not determined quantitatively because of the washing and equilibration steps before the next half-cycle. Figure 7 shows the changes in the water flux of the blend membrane (M2) as the pH of the feed deionized water was varied between pH values of 6 and 10. The results indicate that the water flux of the blend membrane (M2) changed with the pH; it was higher at pH 10 and lower at pH

4. Moreover, the water flux was reversible after four repeated cycles; this suggested that the blend membrane had a good pH response. Compared with the previous cycle, the water flux had some changes; its value decreased at pH 10 and increased at pH 4, although the changes were not very obvious. The reason may have been that PDMAEMA was a polybase, which had a certain pH sensitivity, but it was not a typical pH-responsive material compared with the polymers having carboxyl or sulfonic acid groups. So, it did not have a fast response to adjust the chain extension and shrinkage under different pH conditions at a certain time; this resulted in some little difference in the water flux in the next cycle.

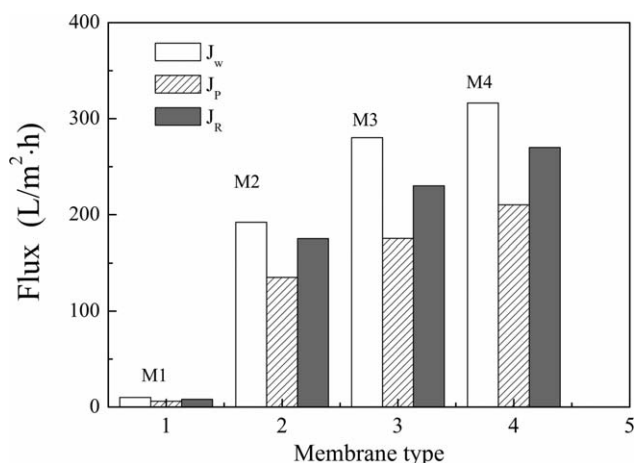
#### Filtration Properties

To investigate the hydrophilic and antifouling resistance of the prepared membranes, the  $J_w$  and protein solution permeation process were conducted first in this study, and BSA was used as a model protein. After that, the membranes were cleaned, and the  $J_w$  values were tested again. The results are shown in Figure 8. It is indicated that the pure PVDF membrane (M1) had a low water flux, and its value was about 10 L/m<sup>2</sup>·h; this was due to the more dense structure of the membranes. When the content of PMMA-*b*-PDMAEMA in the casting solution changed from 0 to 6 wt % (Table I), the water flux of the blend membranes increased from 10 to 316 L m<sup>-2</sup>·h<sup>-1</sup>. These phenomena suggest that the block copolymer could improve the hydrophilicity, so the water flux increased rapidly.

The BSA filtration properties of the membranes are presented in Figure 8. The results indicate that  $J_p$  increased with increasing block copolymer in the membranes, and the highest BSA solution flux value reached 210 L m<sup>-2</sup>·h<sup>-1</sup>. These results were ascribed to the combined effects of the pore size and charged and hydrophilic properties of the blend membranes. As for  $J_R$ , the water flux of the membranes were mostly recovered after the membranes were cleaned by deionized water. The value of  $J_R$  increased with the addition of the block copolymer in the blend membranes. In this study, the enrichment of PMMA-*b*-PDMAEMA on the membrane surface were expected to improve the hydrophilic properties of the membranes. On the other



**Figure 7.** Reversible changes in the water flux of the PMMA-*b*-PDMAEMA/PVDF blend membranes (M2) as the pH of the feed was alternated between 6 and 10.



**Figure 8.** Pure water and BSA solution fluxes of the PMMA-*b*-PDMAEMA/PVDF blend membranes.

hand, the positively charged properties of the blend membrane (as shown in Figures 4 and 5) improved the BSA permeation of the membrane; this was due to the negatively charged properties of BSA under the experimental conditions (pH 7.4). Under these conditions, BSA could increase the fouling of the membrane, but the recovered water flux ( $J_R$ ) was mostly not affected by the higher BSA solution permeation. This might have explained from the surface pore size and increasing hydrophilic properties of the blend membranes. This result also suggested that the blend membranes had good antifouling properties.

## CONCLUSIONS

The PMMA-*b*-PDMAEMA block copolymer was synthesized by the RAFT method. The  $M_n$  was about  $3.94 \times 10^4$ . The PMMA-*b*-PDMAEMA copolymer changed the polymorphism, structure, and charged properties of its blend membranes with PVDF. The FTIR results indicate that the  $\alpha$ -crystal phase was the main existing form in PVDF, but with the addition of the copolymer, the adsorption intensity of the  $\beta$ -crystal phase increased. As for the cross section of the membranes, a more spongelike structure appeared at the bottom surface of the membrane; this was due to the delayed liquid-liquid demixing during the coagulation process. The  $\zeta$ -potential results indicate that the surface charges of the membrane changed from positive to negative at an iep as the pH increased, and the iep value ranged from 6.7 to 8.7. The blend membrane also exhibited good hydrophilicity and antifouling and pH-responsive properties. The water flux of the membranes increased from 10 to  $316 \text{ L m}^{-2}\cdot\text{h}^{-1}$  when the copolymer content increased from 0 to 6 wt % in the casting solution.  $J_R$  increased with increasing PMMA-PDMAEMA; this indicated improvement in the antifouling properties of the membranes. The blend membrane also exhibited a good pH sensitivity. Its water flux was lower under acidic conditions (pH 6) but higher in basic conditions (pH 10), and the water flux of the membrane was reversible when the pH was changed between 6 and 10.

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