

Polymerizable Ionic Liquid Copolymer P(MMA-co-BVIm-Br) and Its Effect on the Surface Wettability of PVDF Blend Membranes^{*}

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Abstract Polymerizable ionic liquid copolymer P(MMA-co-BVIm-Br) was synthesized by radical polymerization technique, and characterized by Fourier transform infrared spectrometry (FTIR), ¹H Nuclear magnetic resonance (¹H-NMR) and gel permeation chromatography (GPC). The resulting copolymer was used to prepare poly(vinylidene fluoride) (PVDF) blend membranes *via* a phase inversion method. The effects of the copolymer on the polymorphism, surface wettability and zeta potential (ζ) of the blend membranes were investigated by ATR-FTIR, contact angle instrument and zeta potential analyzer. Scanning electron microscopy (SEM and SEM-EDS) was also applied to investigate the morphology and the surface element changes of the fabricated membranes. The results indicated that P(MMA-co-BVIm-Br) copolymer existed on the surface of the membrane which made the blend membrane have a positive surface during the experimental pH range. The copolymer was also in favor of the formation of β crystal phase in PVDF membranes. The contact angle experiment indicated that P(MMA-co-BVIm-Br) copolymer could switch the wettability of the blend membranes from hydrophilic to hydrophobic by exchanging Br[−] anion with PF₆[−]. Compared with pure PVDF membranes, the water flux and water recovery flux of the blend membranes were enhanced obviously. The results from the flux recovery ratio (FR) and total fouling ratio (R_t) all suggested that the blend membranes had good anti-fouling properties.

Keywords: PVDF membrane; Polymerized ionic liquid; Surface wettability; Anti-fouling performance.

INTRODUCTION

Polymerizable ionic liquids (PILs) as a new kind of polymeric material, have attracted significant research interest because of their characteristics of changing the surface charges and wettability of the solid surfaces^[1, 2]. The charged properties of PILs would make them have a wide application in polymer electrolytes, or fabricating the charged surface in favor of the ion transfer^[3, 4]. The wettability control is also an important characteristic of the solid surface, which makes PILs have a potential application in fabricating smart materials^[5–7].

Recent findings revealed that the solid surfaces modified by poly(ionic liquid) brushes had a tunable wettability between hydrophilicity and hydrophobicity^[8, 9]. And the wettability surface of the solids could be obtained by simply grafting polymerized ionic liquid brushes on a flat silicon substrate *via* surface-initiated atom transfer radical polymerization (ATRP) or by self-assembled monolayers (SAMs). The tunable wettability of the ionic liquid brushes can be achieved by exchanging their counteranions in the aqueous solutions, such as changing Cl[−] with PF₆[−]^[9]. The obtained switchable surfaces might have a wide application in functional materials and intelligent microfluidic switching. Other studies also showed that the solution properties of the

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copolymers with PIL blocks would be changed from hydrophilic to hydrophobic by exchanging the bromide (Br^-) counteranion of IL blocks with $-\text{N}(\text{SO}_2\text{CF}_3)_2$ anion^[1]. Despite PILs with controllable wettability and charged properties have been considered a promising candidate in membrane separation field, further application of PILs and their copolymers does not appear to be progressing robustly.

Membrane separation materials are a class of special materials with complex three-dimensional pore structure, which have played a critical role in the separation fields, such as chemical industry, water treatment and seawater desalination. With the development of superhydrophilic and superhydrophobic interface, surface wettability control, affecting the separation and anti-fouling properties of the membranes, has become a matter of growing concern in membrane research area. Recently, environmental sensitive membranes with tunable wettability surface were fabricated, and their wettability could be controlled by changing the environmental temperature or pH. Such practice is, therefore, drawing increased attention from the public and researchers on surface modification. By so far, the number of researchers willing to adopt membrane modification to get a hydrophilic or hydrophobic surface continues to grow.

Promising methods for controlling the surface wettability of the membranes are surface modification and physical blending. Surface modification was usually achieved by coating or grafting a functional layer on the prepared membrane surface, the functional grafted layers were usually composed of poly(acrylic acid) or other hydrophilic polymer brushes^[10, 11]. Physical blending acted as a powerful and simple method to fabricate the porous membranes, and thus making them achieve an industrial scale production. First, the polymer and the modifiers were blended in the casting solution. When forming the membrane, the hydrophilic modifier then would migrate onto the membrane surface, improving the surface properties of the membranes. Physical blending has long been considered an applicable method in membrane production that offers many advantages in simultaneous completion of membrane formation and hydrophilic modification. To date, the modifier usually included hydrophilic polymers and amphiphilic copolymers^[12, 13].

Hydrophilic modification is a key point to improve the wettability of the membrane surface by surface modification and physical blending. Nevertheless, using conventional hydrophilic polymer brushes or functional layers to modify the membrane was the most common method. Recently, an encouraging result reported by researchers was that pH- or temperature-sensitive copolymers could be used to control the surface wettability of the membranes by physical blending method. Thus, amphiphilic copolymers, such as PVDF-g-poly(methacrylic acid)^[13] and PVDF-g-poly(*N*-isopropyl acrylamide)^[14] which had pH- and thermo-sensitive properties, have drawn public attention. Especially, amphiphilic ionic liquid copolymers, as a new kind of positively charged and anion-sensitive material, were the favorable choice. These copolymers were usually synthesized from methyl methacrylate (MMA) or styrene (St) as the nonionic monomer and IL as the ionic monomer *via* controlled/living radical polymerization technique, and have exhibited their advantages in self-assembly, anion-material and solid-state ion transport^[1, 3–5]. However, the studies on PIL copolymers in membrane separation field, including the surface wettability control and anti-fouling properties of the porous membranes, remain relatively unexplored.

In this study, poly(methyl methacrylate-*co*-1-butyl-3-vinylimidazolium bromide) (P(MMA-*co*-BVIm-Br)) copolymer synthesized by free radical polymerization was investigated as a modifier to improve the hydrophilicity of PVDF membranes by blending *via* an immersion precipitation process. The advantages of this copolymer are that PMMA segments have a good compatibility with PVDF^[15], and the PBVIm-Br segments contribute to fabricating the hydrophilicity surface of the blend membranes. So in this study the effects of P(MMA-*co*-BVIm-Br) copolymer on the surface wettability of the blend membranes were studied in detail. Besides, the effects of the copolymer on the polymorphism and charged properties of the membranes were also investigated.

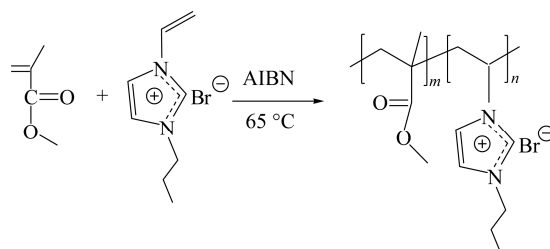
EXPERIMENTAL

Materials

Commercial PVDF (FR904) was obtained from Shanghai 3F company (China). Methyl methacrylate (MMA, A.R.) was purchased from Aladdin Chemical Co. (Shanghai, China). MMA was washed with 5% NaOH solution followed by distilled water, and then distilled under vacuum. 2,2'-Azobis(isobutyronitrile) (AIBN, Aladdin Chemical, 97%) was purified by recrystallization from ethanol. 1-Butyl-3-vinylimidazolium bromide (BVIm-Br, 99%) was purchased from Shanghai Chengjie Chemical Co., and used as received. Solidum hexafluorophosphate (NaPF_6 , A.R.), polyethylene glycol 2000 (PEG2000, A.R.), *N,N*-dimethyl acetamide (DMAc) were all purchased from Aladdin Chemical Reagent Co. (Shanghai, China). Bovine serum albumin (BSA, $M_w = 67$ kDa) and PBS buffer solution (pH = 7.4) were all purchased from Huipu Chemical Co. (Hangzhou, China).

Synthesis of P(MMA-co-BVIm-Br) Copolymer

The copolymer was synthesized *via* radical polymerization process, the reaction is shown in Scheme 1. MMA and IL were the reactive monomers, DMAc was the solvent and AIBN as the initiator. The reaction was taken under nitrogen (N_2) atmosphere. All the reaction reagents were put into a three-neck flask and bubbled with N_2 for 30 min. The mole ratios of $[\text{MMA}]:[\text{IL}]:[\text{AIBN}]$ were controlled as 2:1:0.015. Then the flask was put into an oil bath, and the reaction was controlled at 65 °C for 30 h before quenching in an ice/water bath. The raw product was obtained by precipitating the reaction mixture into diethyl ether. The obtained polymer was repeatedly dissolving and precipitating for three times and then dried in a vacuum oven at 40 °C for 24 h.



Scheme 1 Synthesis route of P(MMA-co-BVIm-Br) copolymer

Preparation of PVDF/P(MMA-co-BVIm-Br) Blend Membranes

PVDF/P(MMA-co-BVIm-Br) blend membranes were prepared *via* an immersion precipitation process. During this process, PVDF and P(MMA-co-BVIm-Br) copolymer with different weight ratios were dissolved in DMAc and stirred at 65 °C for about 12 h. The compositions of the casting solution are shown in Table 1.

Table 1. Compositions of casting solution for PVDF/P(MMA-co-BVIm-Br) blend membranes

Membrane type	M0	M1	M2	M3	M4	M5
PVDF (g)	15	15	15	15	15	15
P(MMA-co-BVIm-Br) (g)	0	1	2	3	4	6
PEG2000 (g)	2	2	2	2	2	2
DMAc (g)	83	82	81	80	79	77
P(MMA-co-BVIm-Br)/PVDF (wt%)	0	6.67	13.30	20	26.60	40

Anion Exchange Experiment

Some researchers had demonstrated that the wettability of charged organic membranes could be tuned by choosing the proper counteranions^[9, 16]. Commonly the PILs containing Br^- anions as counteranions showed a rather hydrophilic behavior, and PF_6^- anions exhibited a hydrophobic behavior^[10]. In this study, the counteranions exchange simply by immersing the membrane into 0.06 mol/L NaPF_6 aqueous solution at room temperature for 12 h, and then the membrane is washed with deionized water.

Characterization

^1H -NMR spectra of the copolymer were recorded on an Avance DMX 500 spectrometer (Bruker, Switzerland) operated at 500 MHz. DMSO- d_6 and tetramethylsilane (TMS) were used as solvent and internal standard, respectively. The molecular weights and molecular weight distributions of the copolymer 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 (DMF) was used as the eluent with a flow rate of 1.0 mL/min at 35 °C.

The chemical composition of the polymers and the membranes were characterized by infrared spectroscopy (FTIR) (Tenson 37, Bruker, Germany) at a 4 cm^{-1} resolution and in the $400\text{--}4000\text{ cm}^{-1}$ wavenumber range. The surface hydrophilicity of the blend membranes was characterized by a water contact angle system (OCA20, Dataphysics, Germany) equipped with video capture at room temperature.

The surface charged properties of the blend membranes were examined using a SurPASS zeta potential analyzer (Anton Paar, Austria). Membranes were cut into $6\text{ cm} \times 3\text{ cm}$ size plates and were placed in the cell. The measurement was carried out at 25 °C by circulating KCl (0.001 mol/L). Zeta potentials were obtained at different pH values and the pH was adjusted using HCl and NaOH solutions.

The surface and interior morphologies of the membranes were investigated by SEM (JSM-5610, JEOL, Japan). The samples were fractured in liquid nitrogen to obtain tidy cross-sections and then sputter-coated with gold layer before SEM observation. The elemental changes of element Br and P on the membrane surface were investigated by the scanning electron microscope equipped with an energy dispersive spectrometer (SEM-EDS, JSM-5610, JEOL, Japan).

The water flux measurements 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, the detailed process could be found from the previous literature^[12]. The water flux J_w ($\text{L}/(\text{m}^2\cdot\text{h})$) was calculated by the following equation:

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

where J_w is the pure water flux ($\text{L}/(\text{m}^2\cdot\text{h})$), V is the permeate volume (L), A is the membrane area (m^2) and Δt is the time length (h).

After that, the flux of BSA solution (1 g/L, pH 7.4) was also measured at 0.1 MPa and recorded as J_p . Subsequently, the membrane was washed with deionized water for 30 min, and then the pure water flux was reevaluated and expressed as J_R . The flux recovery ratio (FR) was calculated as follow^[17]:

$$\text{FR}(\%) = \left(\frac{J_R}{J_w} \right) \times 100\% \quad (2)$$

To analyze the fouling process, the total fouling ratio (R_t) of the blend membrane was defined and calculated as following^[18].

$$R_t(\%) = \left(1 - \frac{J_p}{J_w} \right) \times 100\% \quad (3)$$

RESULTS AND DISCUSSION

Characterization of P(MMA-co-BVIm-Br) Copolymer

The P(MMA-co-BVIm-Br) copolymer was synthesized by conventional free radical polymerization^[3]. The chemical structures of PMMA and P(MMA-co-BVIm-Br) were investigated by FTIR as shown in Fig. 1. Compared with PMMA, several new absorption peaks appeared around 1547, 2875 and 3126 cm^{-1} . The absorption peaks around 1547 and 3126 cm^{-1} were attributed to the absorption peaks of $-\text{C}=\text{N}$ and $-\text{C}-\text{H}$ groups for imidazole, respectively^[19]. The absorption peak around 2875 cm^{-1} was attributed to the $-\text{C}-\text{H}$

vibration absorption peak of alkyl substituent on the imidazole ring^[20]. These phenomena suggested that P(MMA-co-BVIm-Br) copolymers were synthesized.

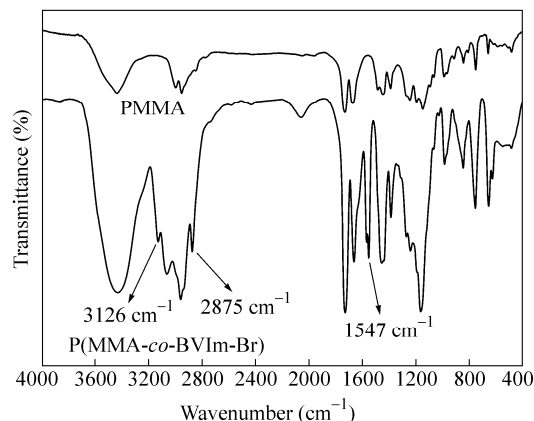


Fig. 1 ATR-FTIR spectra of PMMA and P(MMA-co-BVIm-Br) copolymer

¹H-NMR was also used to investigate the structure of the copolymer as shown in Fig. 2. The results indicated that the chemical shifts appearing around 1.78 (signal a) and 0.94, 0.72 (signal b) were attributed to the methylene protons and methyl protons on the backbone of PMMA, respectively. The chemical shifts appearing around 3.55 (signal c) were attributed to the protons on the ester of PMMA (—OCH₃). The chemical shifts appearing around 9.41–9.85 (signal d) and 7.85–7.96 were attributed to the protons on the imidazole ring of N—CH=N and N—CH=CH—N (Fig. 2), respectively. The chemical shifts appearing around 4.15 (signal g), 1.32 (signal j) and 0.92 (signal i) were attributed to the protons of N—CH₂—CH₂—CH₃, N—CH₂—CH₂—CH₃ and N—CH₂—CH₂—CH₃, respectively^[3, 4]. The mole ratio of [MMA]:[IL] in the copolymer was about 1.12:1 as calculated from the ¹H-NMR spectrum. FTIR and ¹H-NMR results all indicated that P(MMA-co-BVIm-Br) copolymers were synthesized successfully.

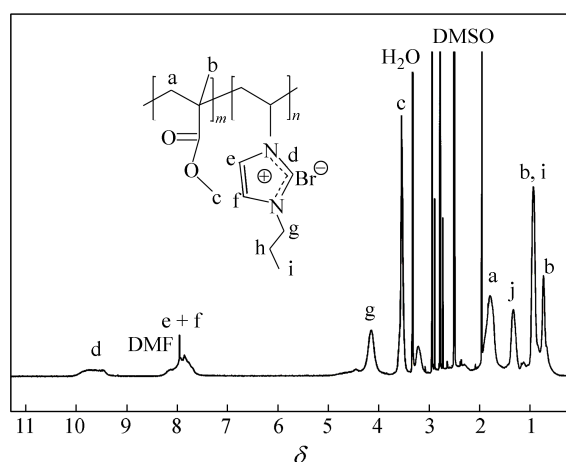


Fig. 2 ¹H-NMR spectrum of P(MMA-co-BVIm-Br) copolymer

The molecular weight of P(MMA-co-BVIm-Br) was characterized by GPC, and the result is shown in Fig. 3. The molecular weights of the P(MMA-co-BVIm-Br) copolymer were about 3.22×10^4 (number-average molar mass, M_n) and 5.08×10^4 (weight-average molar mass, M_w), respectively.

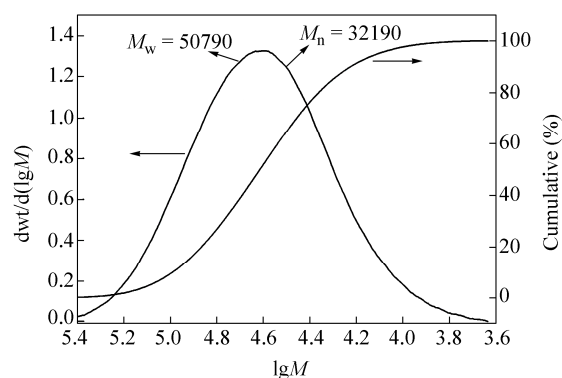


Fig. 3 Molecular weights and molecular weight distribution of P(MMA-co-BVIm-Br) copolymer

FTIR Analysis of PVDF/P(MMA-co-BVIm-Br) Blend Membranes

The chemical composition and polymorphism of the blend membranes were analyzed by FTIR as presented in Fig. 4. Compared with pure PVDF membranes (M0), the typical absorption peaks of —C=O and —C=N groups for the copolymer appeared around 1727 cm^{-1} (M2, M4) and 1564 cm^{-1} (M4), respectively. And with the increase of P(MMA-co-BVIm-Br) in the blend membranes, the absorption intensity of these groups became stronger. These results suggested that P(MMA-co-BVIm-Br) copolymer remained in the surface of the membranes during the coagulation process. The same conclusion was also provided by SEM-EDS, which was used to investigate the element changes on the membrane surface as shown in Table 2.

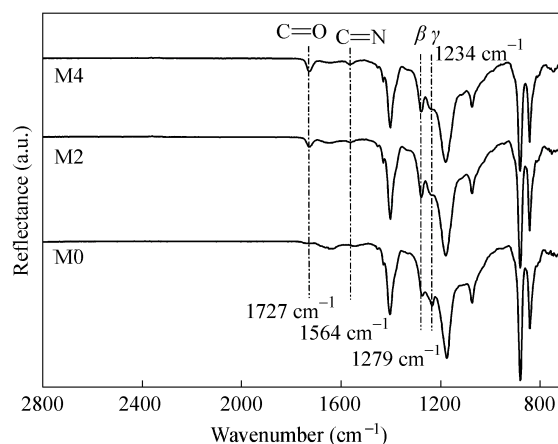


Fig. 4 ATR-FTIR spectra of PVDF/P(MMA-co-BVIm-Br) blend membranes

Table 2. Element content changes on the surface of the blend membranes after ion exchange (BIE: Before Ion Exchange, AIE: After Ion Exchange)

Membrane ID.	Br element weight (%)		P element weight (%)	
	BIE	AIE	BIE	AIE
M1	0.14	0.02	0.01	0.06
M2	0.21	0.03	0.03	0.10
M3	0.34	0.02	0.02	0.20
M4	0.56	0.04	0.02	0.40
M5	0.82	0.06	0.03	0.97

PVDF is a polycrystalline polymer, which has at least four different crystalline forms including α , β , γ and δ forms^[12]. In this study, the polymorphism of PVDF membranes was also investigated (Fig. 4), the results

indicated that the typical absorption peaks of γ and β crystal phases of PVDF appeared around 1234 cm^{-1} and 1279 cm^{-1} , respectively^[21]. And with the addition of the copolymer in the membranes, the absorption intensity of β crystal phase increased, and that of the γ crystal phase decreased. These results suggested that P(MMA-co-BVIm-Br) was in favor of the formation of β crystal phase in PVDF membrane.

Zeta Potential Analysis

The zeta potential can exhibit the surface charged properties of the membranes, and its value is related to pH, concentration and types of metal ions in the aqueous solution. The effects of pH on the zeta potential of the membranes are shown in Fig. 5. It was indicated that the zeta potential of the blend membranes decreased with the increase of pH value, and they were almost positive during the experimental pH range (except M1). As for pure PVDF membrane, its zeta potential changed from positive to negative with the increase of pH value, this phenomenon might be related to the adsorption of charged groups on the surface of PVDF membrane^[22]. The positive potentials of the blend membrane suggested that P(MMA-co-BVIm-Br) copolymer existed in the surface of the membrane and the imidazole group was responsible for the positively charged surface of the membrane.

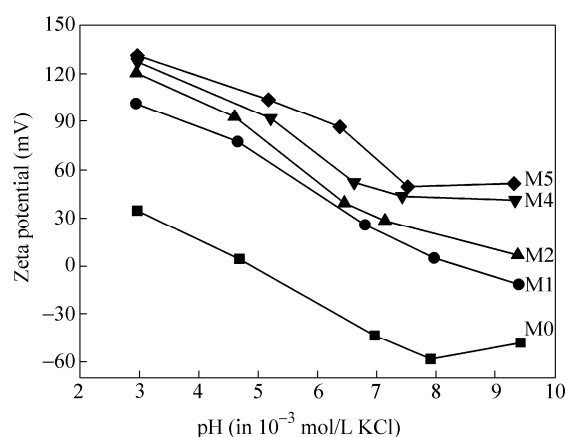


Fig. 5 Zeta potentials of PVDF/P(MMA-co-BVIm-Br) blend membranes at different pH values

SEM Photographs

The surface and cross-section morphology of the membranes was studied using SEM, as shown in Fig. 6. As for the top surface of the membranes from M0 to M5, it was seen that some little granular structure appeared and increased with the increase of P(MMA-co-BVIm-Br) in the membranes. The reason might be that PVDF is a hydrophobic and crystalline polymer, the thermodynamic incompatibility between PVDF and the hydrophilic copolymer would induce the formation of PVDF crystalline structure on the top surface of the membrane. With the increase of the copolymer in the membrane, the interaction between the copolymer and PVDF would increase, thus more and more granular structure formed during the immersion precipitation process^[23, 24], and these structures promoted a higher degree of surface roughness, which would affect the contact angle of the membranes^[25].

The bottom surface of the membranes revealed morphologies different from those of the top surface as exhibited in Fig. 6. There were little pore structure on the bottom surface, and the number of the pore structure first increased (M2 and M4), and then decreased (M5) with the increase of the copolymer in the membrane. The reason might be that during the coagulation process the copolymer migrated onto the surface of the membrane and formed a more dense structure with the increase of the copolymer in the membrane^[13].

As for the cross-section, the membrane M0 exhibited a typical asymmetric morphology with finger-like structure on the top and sponge-like structure on the bottom, which was much different from that of the blend membranes. With the addition of P(MMA-co-BVIm-Br) copolymer in the membranes, a finger-like and large

pore structure appeared in the cross section of the blend membranes, and with the increase of the copolymer, the large pore structure on the bottom surface of the membrane became more and more obvious. These results might be expected based on ternary diffusion models, which related pore formation to instantaneous liquid-liquid demixing during coagulation process. P(MMA-co-BVIm-Br) was a kind of random copolymer with PBVIm-Br as the hydrophilic segments and PMMA as the hydrophobic segments, so the phase inversion was more complicated than that of the hydrophilic polymers. The large pore structure indicated that the copolymer was expected to enhance the exchange rate of solvent-nonsolvent during the phase separation process, which would be in favor of the instantaneous liquid-liquid demixing between PVDF and the solvent^[26].

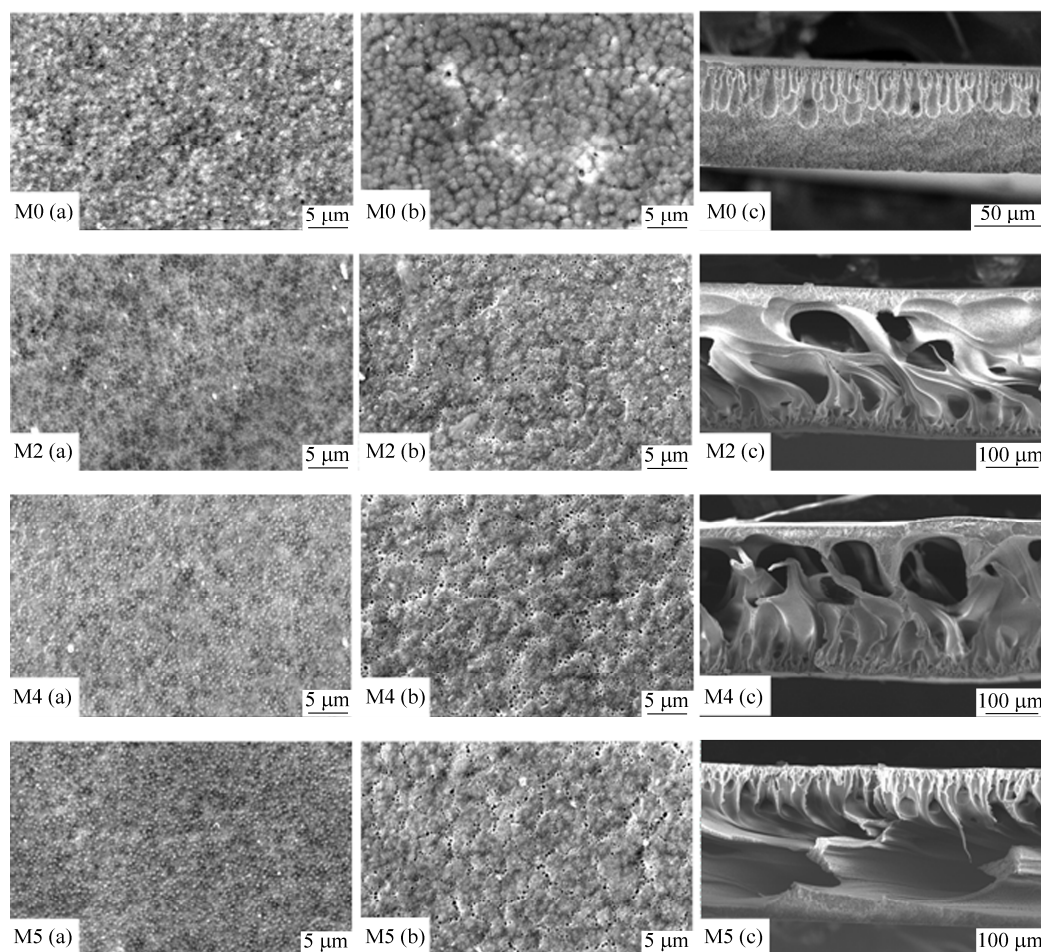


Fig. 6 SEM images of PVDF/P(MMA-co-BVIm-Br) blend membranes: (a) top surface, (b) bottom surface and (c) cross section

Wettability Control of the Membranes

According to the previous literatures^[10, 11], it was known that the wettability of PIL or its copolymers can be controlled by the anion exchange. In this study, P(MMA-co-BVIm-Br) copolymer contains Br⁻ anions in the molecular chains, and the wettability of the copolymer can be changed by anion exchange. In order to make clear the effects of anion exchange on the wettability of the membrane, the blend membrane was immersed in NaPF₆ aqueous solution to exchange Br⁻ with PF₆⁻ in the copolymer.

The element changes on the surface of the membranes were investigated by an SEM-EDS instrument, the results are given in Table 2. It was indicated that the weight percent of bromine (Br) element increased with the addition of the copolymer in the blend membranes. After anion exchange, the weight percent of element Br

decreased obviously. At the same time, P element weight increased, these results kindly suggested that Br^- could be easily substituted by PF_6^- via simple anion exchange. These phenomena also indicated that the copolymer remained in the surface of the membrane during the preparation process, and this conclusion was the same as that by FTIR exhibited in Fig. 4.

In order to further study the effect of the element changes on the wettability of the membranes, the contact angles of the membrane were investigated as exhibited in Fig. 7 and Fig. 8. As for PVDF membrane with PEG as the additives (M0), it had an initial contact angle of 91° as shown in Fig. 7. Compared with the M0 membrane, the initial contact angles of the blend membranes (M2 and M4) were 81° and 75° , respectively. And after 130 seconds, their dynamic contact angles decreased to 74° and 67° , respectively. These results also suggested that P(MMA-co-BVIm-Br) was helpful to improve the hydrophilicity of PVDF membranes, so the initial contact angles of the blend membranes became lower.

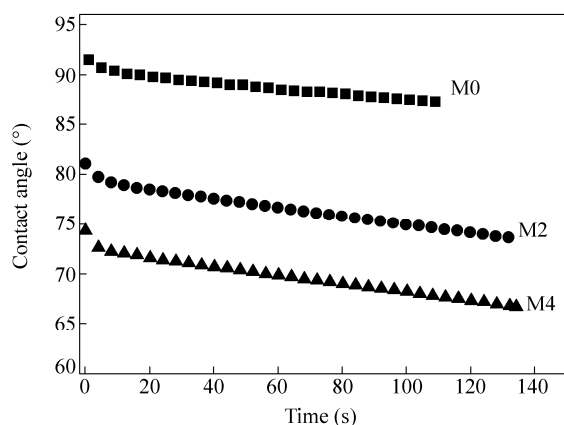


Fig. 7 The dynamic contact angle changes of pure PVDF and the blend membranes

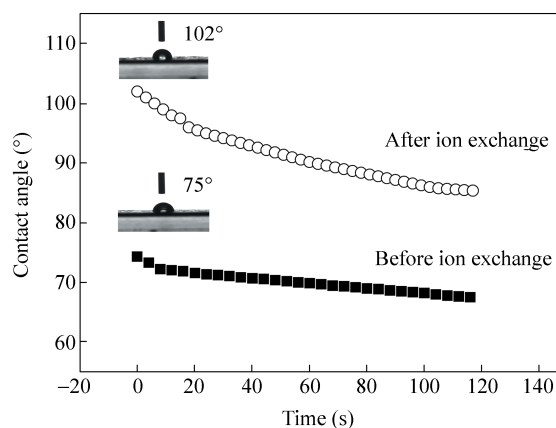


Fig. 8 The contact angle changes of M4 membrane after anion exchange

Figure 8 shows the contact angle changes of M4 membrane before and after the counteranions exchange. It was indicated that the initial contact angle of the membrane was varied from 75° to 102° after Br^- was exchanged with its counteranion PF_6^- . The dynamic contact angle results also showed that the contact angle of M4 membrane decreased from 75° to 67° within 117 s. After anion exchange, the initial contact angle of the membrane increased about 27° , and its dynamic contact angles decreased from 102° to 85° during the measurement time, and the values were all higher than those of the M4 membrane. These phenomena suggested that the wettability of the membranes was changed from hydrophilic to hydrophobic by anion exchange.

The changes of the contact angle clearly showed that water wettability of the blend membranes was controlled by changing the counteranions in PILs. The reason might be that the small Br^- with a high charge density was more strongly solvated through hydrogen bonding than a large anion (PF_6^-) in protic solvent^[9]. So the Br^- in imidazole group might have a better hydrophilic property than PF_6^- .

The surface wettability also affected the water flux of the blend membranes exhibited in Fig. 9. The results indicated that the water flux increased with the increase of copolymer in the blend membranes. The water flux of M0 was $48.5 \text{ L/m}^2\cdot\text{h}$, and that of M4 was about $432.8 \text{ L/m}^2\cdot\text{h}$ which was 9 times higher than that of M0. However, with further increase of the copolymer, the water flux of the blend membrane decreased to $212.5 \text{ L/m}^2\cdot\text{h}$ (M5). And after Br^- was exchanged with PF_6^- , the water flux decreased greatly, as shown in Fig. 9. The most obviously decreased sample was M2, its water flux decreased by 48.6% after anion exchange, which suggested that the wettability of the membranes changed from hydrophilic to hydrophobic via the anion exchange of Br^- and PF_6^- . The water flux of M3 and M4 membranes also decreased obviously after anion exchange. As for M5, it had only a little decrease, the reason might be due to the more dense structure on the membrane surface, and this structure would hinder the anion exchange, so the water flux was not decreased obviously.

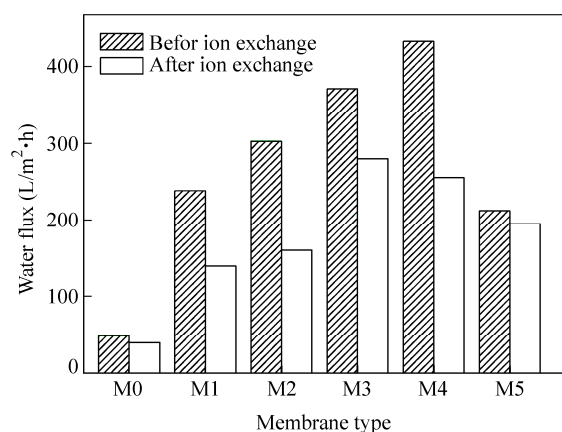


Fig. 9 Water flux changes of the blend membranes before and after anion exchange

Filtration and Anti-fouling Performance

The filtration and anti-fouling performance of the blend membranes were also evaluated, the results are exhibited in Fig. 10. During the experiment, BSA was used as a fouling model, and the membrane investigated in this experiment was virgin PVDF blend membranes and was not exchanged with PF_6^- . It should be explained that in order to make a comparison with BSA flux, the water flux data (J_w) in Fig. 10 were from Fig. 9. From Fig. 10, it was indicated that the filtration flux of BSA (J_p) had the same variation tendency as the water flux (J_w). The water and BSA flux (J_w and J_p) all increased with the increase of the copolymer in the membranes and reached their highest flux value for M4 membrane, and then they exhibited an obvious decrease for M5 membrane. The results from the water recovery flux (J_R) also showed that the water flux was mostly recovered after the membranes were washed with deionized water. These results might find its explanation from the surface pore structure, charged and hydrophilic properties of the blend membranes, and among them, hydrophilicity was the main factor influencing the membrane properties.

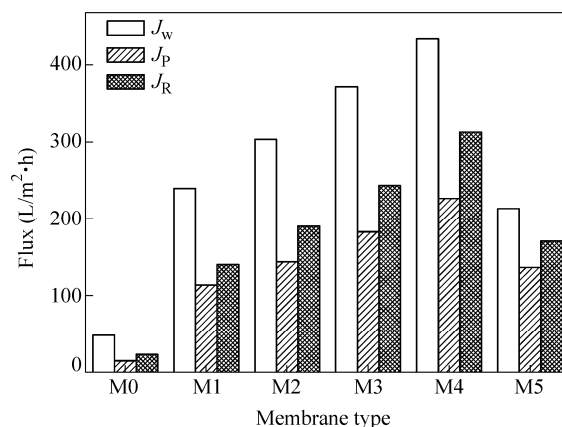


Fig. 10 BSA solution and pure water recovery fluxes of the blend membranes

In order to further study the filtration and anti-fouling performance of the membrane, the water flux recovery ratio (FR) and the total fouling ratio (R_t) of the membranes were all calculated by equation (1) and (2), and the results are shown in Fig. 11. It was indicated that FR increased from 50% to 80% with the addition of the copolymer in the blend membranes, and at the same time R_t decreased from 68% to 40%. These results clearly showed that the anti-fouling properties of the blend membranes were improved by the addition of P(MMA-co-BVIm-Br) copolymer in the membranes. As for M5 membrane, it had the highest water flux recovery ratio and

the lowest total fouling ratio, which suggested that the more dense structure and increasing hydrophilic properties on the membrane surface were in favor of enhancing the filtration and anti-fouling properties of the blend membranes.

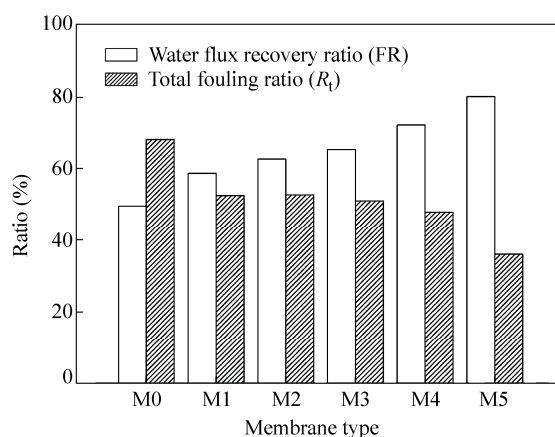


Fig. 11 The water flux recovery (FR) and total fouling ratio (R_f) of PVDF blend membranes

CONCLUSIONS

Polymerizable ionic liquid copolymer P(MMA-*co*-BVIm-Br) was synthesized by radical polymerization method, and its number-average molar mass (M_n) was about 3.2×10^4 . P(MMA-*co*-BVIm-Br) copolymer could change the surface structure and charged properties of its blend membranes with PVDF. ATR-FTIR results indicated that both the imidazole and C=O groups appeared on the membrane surface which affected the charged properties of the membrane. As a result, the zeta potentials of the blend membranes increased with the increase of pH value, and they were almost positive during the experimental pH range. P(MMA-*co*-BVIm-Br) copolymer also enhanced the hydrophilicity and water flux of the blend membranes, which made the membrane have a better hydrophilicity than that of pure PVDF membrane. The wettability of the blend membrane also changed from hydrophilic to hydrophobic by counteranions exchange, as a result, the initial contact angle of M4 membrane increased from 75° to 102° , and at same time the water flux decreased greatly. SEM morphology and SEM-EDS results also supported the above results. Filtration experiment indicated that PVDF/P(MMA-*co*-BVIm-Br) blend membranes had good anti-fouling properties.

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