

Triblock Copolymers of Methyl Methacrylate/*N*-Vinyl Pyrrolidone and Their Hydrophilic Effects on Poly(vinylidene fluoride) Porous Membranes

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Received 4 November 2009; accepted 26 June 2010

DOI 10.1002/app.33014

Published online 21 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The new amphiphilic triblock copolymers of poly(*N*-vinyl pyrrolidone-*b*-methyl methacrylate-*b*-*N*-vinyl pyrrolidone) (P(VP-*b*-MMA-*b*-VP)) were synthesized via a reversible addition fragmentation chain transfer polymerization route. Using these copolymers as additives in casting solutions, the porous blend membranes of poly(vinylidene fluoride) and P(VP-*b*-MMA-*b*-VP) were prepared following a typical nonsolvent induced phase separation process. The influences of P(VP-*b*-MMA-*b*-VP) on the morphologies of the blend membranes were observed by scanning electron microscopy. The chemical compositions in membrane surface layers were measured by X-ray photoelectron measurement. Water contact angle

and water flux experiments were used to evaluate the hydrophilicity and permeation properties of the blend membranes. It was found that the P(VP-*b*-MMA-*b*-VP) copolymers could be retained in membrane stably in membrane formation and application process. The copolymers could enrich in surface layer and endowed the blend membrane with efficient hydrophilicity and higher water permeation flux. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2953–2960, 2011

Key words: amphiphilic copolymer; RAFT polymerization; poly(vinylidene fluoride); porous membrane; *N*-vinyl pyrrolidone

INTRODUCTION

The polymers including poly(vinylidene fluoride) (PVDF), poly(ether sulfone) (PES), polysulfone (PSf), poly(vinyl chloride) have been widely used as microfiltration (MF) and ultrafiltration (UF) membranes for water treatments.¹ However, because of the intrinsic hydrophobicity of these polymers, the corresponding membranes are easily fouled by proteins. Meanwhile, such hydrophobicity causes that the higher driven pressure must be applied during filtration process. These problems currently are contributing the mostly considered limits to polymeric UF/MF membranes with high performances.^{2–4}

Ever researches indicated that the fabrication of hydrophilic and biocompatible surface was an ideal route to high-performance UF/MF membranes. Sev-

eral methods, such as surface coating,^{5–8} surface grafting of hydrophilic chains,^{9–13} and blending polar polymer into membrane matrix,^{14–19} etc., have been developed to hydrophilicate porous polymer membranes. Among these methods, the blending method should be the most applicable one because of its relatively simpler process and lower cost.

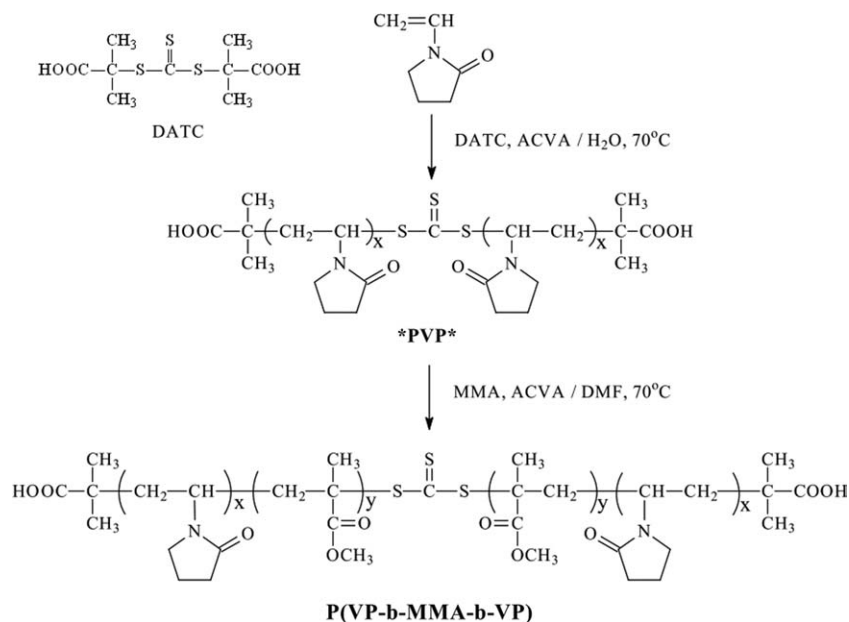
Investigations on blend membrane indicated that the classic hydrophilic polymers of poly(*N*-vinyl pyrrolidone) (PVP) or poly ethylene glycol (PEG) or could not be stably reserved in membrane because they could be dissolved into coagulation bath in membrane formation or into water in filtration process.^{20–22} Consequently, the hydrophilicity, the anti-fouling property, and the reliability could not be realized for corresponding blend membranes. To a certain degree, therefore, PVP or PEG practically were used as the additive for controlling porous structure rather than the effective hydrophilic component for membrane formed via nonsolvent induced phase separation (NIPS) process.^{23,24} Although the amphiphilic polymer was adopted as blend reagent, the strong interaction between its hydrophobic segment and polymer base could improve the stability of amphiphilic polymer in membrane matrix. Using PEG segments as hydrophilic segment, the amphiphilic copolymers with

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Contract grant sponsor: The National 973 Program; contract grant number: 2009CB623402.

Contract grant sponsor: Natural Science Foundation Committee; contract grant number: 20974094.

Contract grant sponsor: Science Foundation of Chinese University; contract grant number: KYJD09011.



Scheme 1 Synthesis and structure of P(VP-*b*-MMA-*b*-VP) copolymer.

triblock,^{25,26} comb-like^{27–29} and branching^{30–32} architectures have been investigated as blended reagents in improving the hydrophilicity and antifouling properties of porous polymeric membranes.

Considering PVP chains having excellent hydrophilicity, biocompatibility and protein resistance,³³ as well as poly (methyl methacrylate) (PMMA) segment having the good compatibility with PVDF,^{34,35} the never reported amphiphilic copolymers of methyl methacrylate and *N*-vinyl pyrrolidone with triblock ABA architecture (P(VP-*b*-MMA-*b*-VP)) were proposed for modification of PVDF porous membranes. Among the reported living radical polymerization (LRP) techniques,³⁶ the advantage of reversible addition fragmentation chain transfer RAFT polymerization lies in that almost all monomers could be used as conventional free radical polymerization.³⁷ So far, RAFT polymerization has been mentioned in the synthesis of amphiphilic block copolymers.^{38–40} In this work, the never reported copolymers P(VP-*b*-MMA-*b*-VP) with different contents of PVP segment were synthesized via RAFT process. Following a typical NIPS process, the P(VP-*b*-MMA-*b*-VP) copolymers were blended into porous PVDF membranes. Considering the hydrophilicity and water absorption property of PVP block, it was expected that the hydrophilicity of PVDF membrane could be improved efficiently by blending P(VP-*b*-MMA-*b*-VP). By investigating the effects of P(VP-*b*-MMA-*b*-VP) on structure, composition, hydrophilicity, and water permeation on membrane, etc., the potential of P(VP-*b*-MMA-*b*-VP) in fabrication of high-performance membranes for water filtration should be revealed.

EXPERIMENTAL

Materials

N-Vinyl Pyrrolidone (NVP) and methyl methacrylate (MMA) were purchased from Aldrich and distilled before use. The initiator of 4, 4'-azobis (4-cyanovaleic acid) (ACVA) was purchased from Qingdao Run Xing Photoelectric Material Company, China. RAFT reagent of *S,S'*-Bis (α,α' -dimethyl- α'' -acetic acid)-trithiocarbonate (DATC) was synthesized following a reported method.⁴¹ PVDF (FR-904, $M_n = 380,000$) was obtained from Shanghai 3F New Materials Company, China. The solvents of *N,N*-dimethyl formamide (DMF) and diethyl ether were of analytical grade and used as accepted.

Synthesis and characterization of P(VP-*b*-MMA-*b*-VP)

The triblock copolymers of P(VP-*b*-MMA-*b*-VP) were synthesized via RAFT polymerization route (Scheme 1). First, NVP, ACVA, and DATC with designed molar ratio were dissolved in deionized water in a round-bottom flask below 20°C. After being bubbled by nitrogen for 20 min, the solution was heated to 70°C and then the polymerization proceeded in nitrogen atmosphere for 5–10 h at same temperature. By precipitating the reaction solution into diethyl ether, the solid of macro-RAFT agent of PVP (*PVP*) was collected and dried in a vacuum oven overnight at 60°C. Second, *PVP*, ACVA, and MMA with designed mass ratio were dissolved in DMF in a flask and the mixture was also bubbled with N₂ for about 20 min below 20°C. By heating the reaction

TABLE I
Membranes Prepared with Different Compositions

Membrane ID	PVDF/P(VP- <i>b</i> -MMA- <i>b</i> -VP)/DMF (wt/wt/wt)	Surface porosity of membrane (%)
M0	12/0/88	0.30
Ma	10.2/1.8 (Copolymer a)/88	4.10
Mb	10.2/1.8 (Copolymer b)/88	5.94
Mc	10.2/1.8 (Copolymer c)/88	9.87

mixture to 70°C, the RAFT polymerization proceeded for 8–10 h in nitrogen. By pouring the reaction mixture into diethyl ether to remove the unpolymerized MMA, the precipitated powder of rough P(VP-*b*-MMA-*b*-VP) was obtained. Ever work primarily indicated the achievement of the like route in RAFT-synthesized polymers.^{42,43}

Before characterization and membrane preparation, the rough P(VP-*b*-MMA-*b*-VP) was carefully washed with distilled water and then dried in a vacuum overnight at 60°C. The chemical composition of P(VP-*b*-MMA-*b*-VP) copolymer was characterized by FTIR (Vecter 22 FT-IR, Bruker Optics) and proton nuclear magnetic resonance spectrometer (¹H-NMR, Bruker, 300 MHz), respectively. The molecular weight was determined by gel permeation chromatograph (GPC, WATERS-515, Waters) using DMF as eluent and polystyrene as calibration standard.

Preparation of PVDF/P(VP-*b*-MMA-*b*-VP) blend membrane

A typical nonsolvent induced phase separation route (NIPS) was adopted to prepare the porous blend membranes. To avoid the influence of the factor on membrane structure and property, no other additives was used as porogenic agents in membrane preparation. PVDF and P(VP-*b*-MMA-*b*-VP) were blended and dissolved in DMF (Table I), and the mixture was stirred at 70°C for 12 h. After being degassed under reduced pressure at 25°C, the thorough homogeneous and transparent casting solution was obtained. This solution was cast into liquid film on a glass plate, and then the supported liquid film was immediately immersed in a coagulation bath of deionized water at 30°C. The solidified membrane was rinsed with water (25°C) for 48 h to remove solvent. Prior to structure and property characterization, the membrane was further dried in a vacuum oven overnight at 30°C.

Characterization of membrane structure and property

The morphology of membrane was imaged on a scanning electron microscopy (SEM, JEOL, JSM-5510LV, Japan) after coating gold (Hitachi E1020). The porosity of membrane was determined by mer-

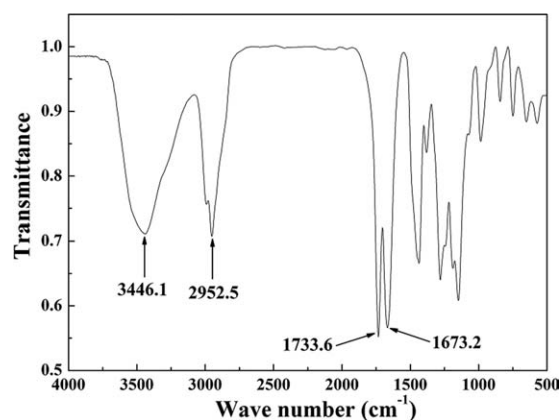


Figure 1 FTIR spectrum of the P(VP-*b*-MMA-*b*-VP) copolymer (copolymer b).

cury porosimetry (Autopore IV9500, Micromeritics). The surface composition of the membrane was characterized using X-ray photoelectron spectroscopy (XPS) (PHI 5000c, Peking-Elmer Instruments). The hydrophilicity was characterized from water contact angle measurement (OCA20, Dataphysics, Germany) at 25°C. The water permeation property was tested on a widely used testing cell using an pressure of 0.1 MPa.^{18,44} The flux (J_w , L/(m² h)) was calculated following eq. (1),

$$J_w = Q/(A \cdot t) \quad (1)$$

Where, Q , t , and A are the volume of permeated water (L), permeation time (h), and filtration area of membrane (20 cm² in this work).

RESULTS AND DISCUSSION

Characterizations of P(VP-*b*-MMA-*b*-VP)

A typical FT-IR spectrum of synthesized P(VP-*b*-MMA-*b*-VP) (Copolymer b) was shown in Figure 1. The strongest absorption at 1733.9 and 1673.2 cm⁻¹ was attributed to the stretching vibration of carbonyl group (C=O) in residue unit of MMA (O-C=O) and NVP (N-C=O), respectively. The absorption at 1450 cm⁻¹ was generated from the stretching vibration of C-O-C group in residue unit of MMA (C-O-C=O). The absorption peak at 2952.5 cm⁻¹ was of the stretching vibration of C-H bonds. The obvious absorption centering at 3446.1 cm⁻¹ was the stretching vibration of hydroxyl group in hydrogen-bond state, which was generated both from the end -COOH group (residue of CTA) and absorbed water.

The GPC curves of synthesized copolymers were given in Figure 2. The calculated molecular weights and polydiversities ($\overline{M}_w/\overline{M}_n$) of copolymers were listed in Table II. The phenomena that the mono

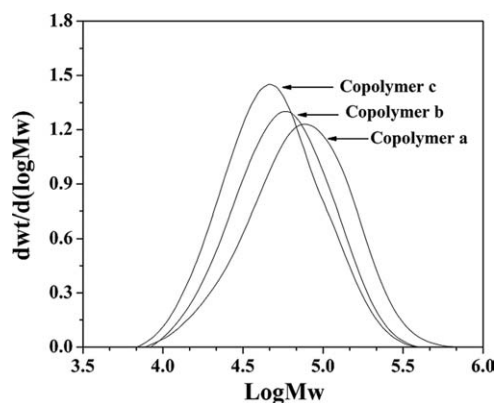


Figure 2 GPC curves of P(VP-*b*-MMA-*b*-VP) triblock copolymers.

peak appeared in GPC curve and the polydispersity was relative small were of the characteristic of RAFT polymerization. For the three copolymers, the number average molecular weight was in comparable range (10^4). In the $^1\text{H-NMR}$ spectrum (Fig. 3), all the characteristic proton peaks from MMA and NVP residue units were found as the indications of chemical structure of copolymer. On the basis of $^1\text{H-NMR}$ spectra, the content of PVP block in each copolymer was calculated as 9.9 wt %, 15.7 wt %, and 46.3 wt %, respectively (Table II).

The results of FTIR, $^1\text{H-NMR}$, and GPC had confirmed the feasible synthesis route of P(VP-*b*-MMA-*b*-VP) via RAFT. In fact, the stronger resonance stabilization by the particular substituent of the radical formed from the vinyl monomer, the higher reactivity for the monomer.⁴⁵ For NVP monomer, there is a pyrrolidone substituent creating p - π resonance from the lone-pair electrons on N atom and the π -bond. For MMA monomer, though there is a strong electron-withdrawing group ($-\text{COOCH}_3$) to enhance the reactivity of MMA, there is also an electron-donating group ($-\text{CH}_3$) acting oppositely. Related work⁴⁶ had showed the reactivity of NVP and MMA were very close ($r_{\text{PVP}} = 0.97$, $r_{\text{PMMA}} = 0.94$). Therefore, it is theoretically reasonable that the preparation of P(VP-*b*-MMA-*b*-VP) begins with the polymerization of NVP monomer.

TABLE II
Characterization Data of P(VP-*b*-MMA-*b*-VP)

Copolymer	a	a	NVP content (wt%)	
			Theory ^b	Experiment ^c
Copolymer a	55,400	1.69	12.2	9.90
Copolymer b	45,400	1.57	20.1	15.7
Copolymer c	35,800	1.40	53.0	46.3

^a Calculated from GPC measurement.

^b The *PVP* content in feed reacting materials.

^c Calculated from $^1\text{H-NMR}$ measurement.

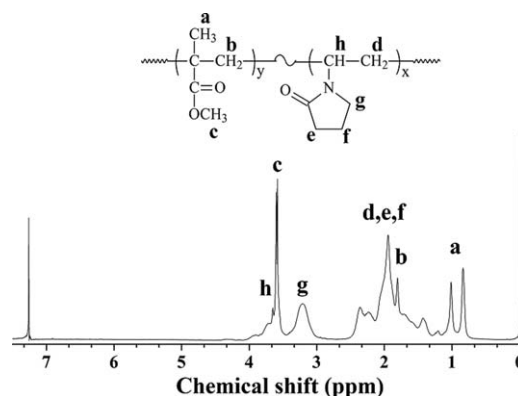


Figure 3 $^1\text{H-NMR}$ spectrum of P(VP-*b*-MMA-*b*-VP) (copolymer b).

Structure and composition of PVDF/ P(VP-*b*-MMA-*b*-VP) of blend membranes

The surface and cross-sectional morphologies of three PVDF/P(VP-*b*-MMA-*b*-VP) blend membranes, as well as the pure PVDF membrane prepared in similar condition were imaged as shown in Figure 4. The surface pore size was about 0.1–0.2 μm , which suggests that these blend membranes are of microfiltration membrane (MF). After P(VP-*b*-MMA-*b*-VP) copolymer was blended, the surface porosity

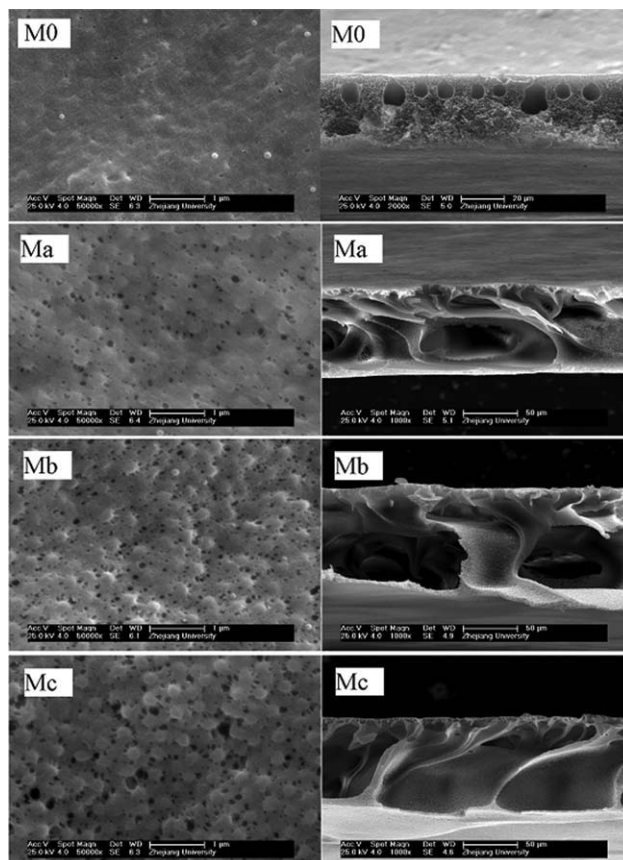


Figure 4 SEM images of surface and cross section of PVDF and blend membranes.

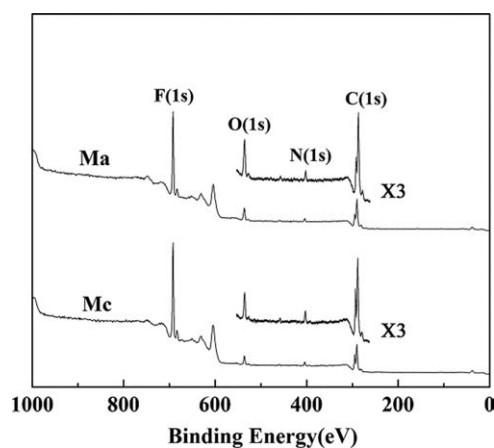


Figure 5 XPS spectra of PVDF/P(VP-*b*-MMA-*b*-VP) blend membrane surfaces.

increased (Table I). At the same time, with the increase of PVP block content in copolymer, the void size in sublayer increased gradually for the blend membranes. As a result, the bulk porosities determined by mercury porosimetry for membrane M0, Ma, Mb, and Mc were about 61, 70, 78, and 85%, respectively. This result can be expected based on ternary diffusion models,⁴⁷ which relates macrovoid formation to instantaneous liquid-liquid de-mixing during coagulation. The presence of the amphiphilic P(VP-*b*-MMA-*b*-VP) component in the casting solution might increase the affinity of the casting solution and precipitant, enhancing the solvent-nonsolvent exchange and leading to instantaneous de-mixing. Macrovoids and thinner skin layers were consequently formed.

To investigate the retaining of P(VP-*b*-MMA-*b*-VP) copolymer in membrane formation, the prepared blend membranes were dissolved in DMSO-*d*₆ for ¹H-NMR measurement to characterized the content of P(VP-*b*-MMA-*b*-VP). It was found that over 90% of P(VP-*b*-MMA-*b*-VP) was reserved in final blend membrane. The loss of P(VP-*b*-MMA-*b*-VP) added into casting solution in blend membrane formation was less than 10%. In comparison, when the water soluble hydrophilic polymers of PEG or PVP were used as blend reagent, these polymers were hardly reserved in PVDF membrane.²⁰⁻²² Thermodynamically, it was the strong hydrophobic interaction

between PVDF chain and PMMA block in copolymer that prohibited the loss of P(VP-*b*-MMA-*b*-VP). Further, this higher reservation ratio of P(VP-*b*-MMA-*b*-VP) should guarantee the controllability of composition and property for the corresponding blend PVDF membranes prepared via NIPS process.

The surface compositions of PVDF/P(VP-*b*-MMA-*b*-VP) blend membranes were analyzed by XPS measurements. From the XPS spectra shown in Figure 5, four major emission peaks at 290.7, 403.5, 535.8, and 692.3 eV were found for C (1s), N (1s), O (1s), and F (1s), respectively. On the basis of the intensity of these peaks, the content of PVP block and P(VP-*b*-MMA-*b*-VP) copolymer in surface layers were calculated as listed in Table III. Concerning the reservation ratio of P(VP-*b*-MMA-*b*-VP) was higher than 90% in membrane preparation, the PVDF/P(VP-*b*-MMA-*b*-VP) ratio adopted in casting solution was used as the composition of bulk membrane to calculate the enriching ratio of PVP block and copolymer in membrane surface layer. As shown in Table III, both the contents of P(VP-*b*-MMA-*b*-VP) and PVP block in surface layer block were much higher than those in whole membrane, suggesting the obvious enrichment of P(VP-*b*-MMA-*b*-VP) and PVP block in surface layer. Such enriching phenomena could be explained from the strong interaction between water in coagulation bath and PVP block in copolymer. During membrane formation, this strong interaction caused PVP block and whole copolymer diffusing to interface between membrane and water coagulation bath. Such diffusion behavior could minimize the interfacial energy in phase inversion.⁴⁸ Simultaneously, the strong hydrophobic-hydrophobic interaction between PVDF chain and PMMA block prohibited the copolymer migrating/dissolving to coagulation bath. Because of the solidification of membrane completed within a few seconds, the diffusing copolymers were fixed in membrane surface layer. Concerning that the water in coagulation bath permeated into the voids inside membrane in solidification of membrane, the enrichment of P(VP-*b*-MMA-*b*-VP) could also occur on the wall of tunnel inside membrane.

The enriching degree of P(VP-*b*-MMA-*b*-VP) in surface layer was 2.69 and 2.22, respectively, for

TABLE III
Compositions in Surface Layers of PVDF/P(VP-*b*-MMA-*b*-VP) Membranes

Membrane ID	P(VP- <i>b</i> -MMA- <i>b</i> -VP) (wt %)			NVP block (wt %)		
	Added ^a	Found ^b	Found/added	Added ^a	Found ^b	Found/added
Ma	15.0	40.3	2.69	1.48	4.00	2.70
Mc	15.0	33.3	2.22	6.94	15.5	2.20

^a Calculated from composition in casting solution.

^b Calculated from XPS measurement.

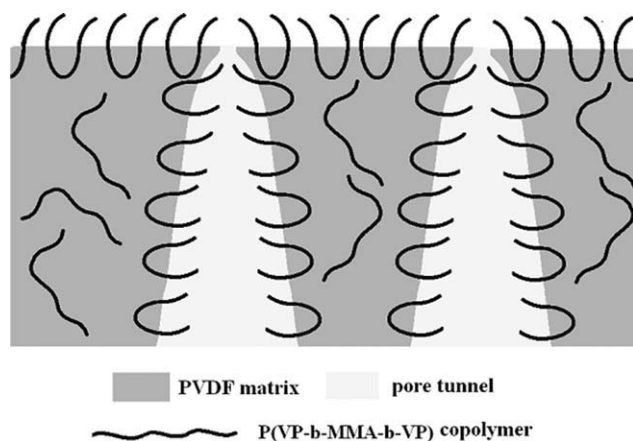


Figure 6 Proposed distribution of P(VP-*b*-MMA-*b*-VP) in blend PVDF membrane.

blend membrane of Ma and Mc. The content and surface enriching degree of PVP blocks in surface layer were also calculated as listed in Table III. The PVP block content in surface of membrane Ma and membrane Mc was 4.00 and 15.5 wt %, respectively. Interestingly, the enrichment degree of PVP block was consistent quite well with the corresponding whole copolymer. Considering the fact that length of all P(VP-*b*-MMA-*b*-VP) chains was smaller than 3.60 nm, and the detected depth XPS measurement was 5–7 nm,⁴⁹ it was still difficult to describe the real distribution state of PVP blocks or P(VP-*b*-MMA-*b*-VP) copolymers in surface layer. Because PVP blocks were connected to end of ABA type amphiphilic copolymer, the faster diffusion of PVP block in membrane formation might yield a state with PVP blocks stretching out of membrane surface (as proposed in Fig. 6). Such distribution should be ideal in endowing the membrane with effect hydrophilicity. Neglecting the size difference among the repeat unit of PVP, PMMA, or PVDF, the coverage ratio of hydrophilic segment of PVP block on the two investigated membrane surfaces might be close to 4.00 and 15.5 wt %, respectively.

Hydrophilicity and water permeation of blend membranes

The hydrophilicity of P(VP-*b*-MMA-*b*-VP) membranes were characterized via water contact angle measurements. The static water contact angles on membrane surface were shown in Figure 7. The pure PVDF membrane had the highest initial water contact angle (98°), while the initial water contact angles of blend membrane were below 80°. The addition of P(VP-*b*-MMA-*b*-VP) increased the hydrophilicity of blend membrane obviously. In mechanism, such improved hydrophilicity was generated from the existence of PVP blocks on membrane surface. The decrease of water angle with water drop

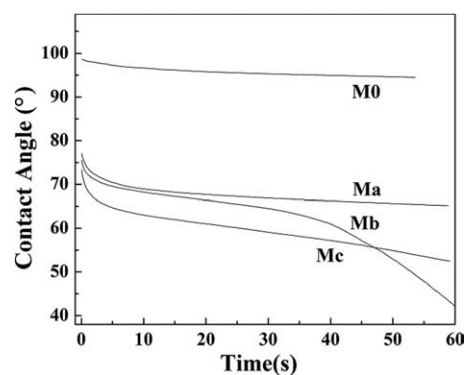


Figure 7 Water contact angles of freshly made PVDF and blend membranes.

age indicated that water could diffuse into the pores in membrane matrix, which suggested the hydrophilicity of the tunnel wall inside membrane matrix.^{50,51} Besides, the evaporation of water in measuring process will reduce the size of water drop and prompt such diffusion. In fact, this water contact angle decrease is usually found for MF or UF membrane, especially those for the membrane having larger pore.

To investigate retaining stability of P(VP-*b*-MMA-*b*-VP) in practical application, the blend membranes were immersed in water (60°C) and continuously shaken for different days. By monitoring the change of water contact angle with shaken time, the reservation stability of P(VP-*b*-MMA-*b*-VP) could be revealed. From Figure 8, it was clearly found that blend membrane containing copolymer with higher VP content had the better hydrophilicity. More importantly, the water contact angles of blend membranes decreased in the beginning day, and then reached a stable value. These observations could be explained from two aspects. First, under the interaction of water, the PVP blocks in surface layer were further rearranged into an ideal distribution structure in which PVP blocks stretched toward the outside of membrane. Such rearrangement would result

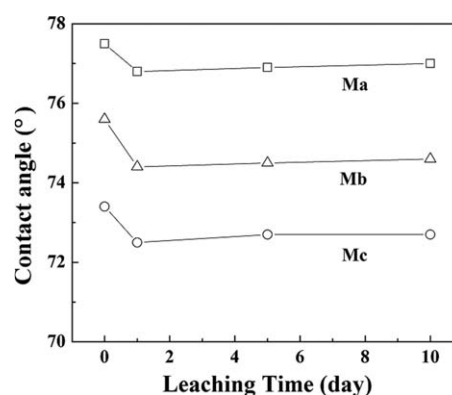


Figure 8 Water contact angles of blend membranes shaken in water at 60°C for different time.

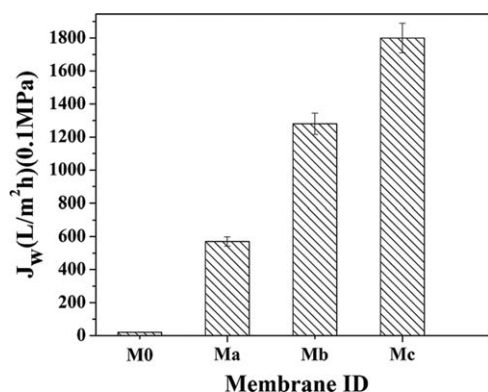


Figure 9 Water fluxes of PVDF and PVDF/P(VP-*b*-MMA-*b*-VP) blend membranes.

in the smaller water contact angle and higher hydrophilicity. Second, the stable water contact angles inferred that the copolymer were not dissolved into water and P(VP-*b*-MMA-*b*-VP) was reserved stably in shaken process, which was attributed to the strong interaction between hydrophobic segment (PMMA) in the copolymer and the hydrophobic membrane matrix (PVDF). Such stability contributed the essence for long-term hydrophilication and reliability of membrane in practical application. In real-water filtration process, the stretching PVP block could absorb water molecules and a hydrated layer be formed on membrane surface. This hydrated layer would prevent the adhesion of foulent on membrane surface.

The water fluxes of prepared membranes were given in Figure 9. Because of the high hydrophobicity of PVDF, no water flux was found for pure PVDF. For the three prepared blend membranes with comparable pore size, the water flux reached 600, 1200, and 1800 L/(m² h), respectively. The water flux increased with PVP block content in copolymer, which was consistent with the increasing trend of hydrophilicity. These results indicated that the blend of PVDF/P(VP-*b*-MMA-*b*-VP) copolymer effectively improved the filtration performance of PVDF membrane. By using other additive to controlling the porous structure in membrane formation, the blend PVDF/P(VP-*b*-MMA-*b*-VP) membrane with proper rejection and higher flux would be realized for water filtration.

CONCLUSIONS

The new amphiphilic triblock copolymers of P(VP-*b*-MMA-*b*-VP) were successfully synthesized via RAFT polymerization. Using these copolymers containing 9.9–46.3 wt % of PVP block, the PVDF/P(VP-*b*-MMA-*b*-VP) blend membranes were prepared through NIPS process. XPS measurement indicated

that the content of P(VP-*b*-MMA-*b*-VP) copolymer in membrane surface layer was over two times of that in the whole membrane. The enrichment of PVP blocks in membrane surface layer endowed the blend membrane with effective hydrophilicity and high water permeation flux. Because of the strong interaction between PMMA block and PVDF chain, the P(VP-*b*-MMA-*b*-VP) copolymer could be retained stably in blend membrane. Such retaining stability of copolymer confirmed that P(VP-*b*-MMA-*b*-VP) should be potential blend reagent in high-performance PVDF membranes for water filtration.

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