

SURFACE MODIFICATION OF PVDF POROUS MEMBRANES*

Jian-hua Li^{a,b}, Jing Miao^a, Xi-sheng Shao^a, You-yi Xu^{b**} and Qi-qing Zhang^a

^a *Institute of Biomedical and Pharmaceutical Technology & College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350001, China*

^b *Institute of Polymer Science, Key Laboratory of Macromolecule Synthesis and Functionalization, (Ministry of Education), Zhejiang University, Hangzhou 310027, China*

Abstract A novel method for the surface modification of PVDF porous membranes was introduced. Styrene-(*N*-(4-hydroxyphenyl) maleimide) alternating copolymer SHMI-Br was blended with PVDF to fabricate SHMI-Br/PVDF membranes. The C-Br bond on the SHMI-Br/PVDF membrane was served as initial site of ATRP, and P(PEGMA) brush was grafted on the PVDF membrane. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR/FTIR) was used to prove the P(PEGMA) brushes were successfully grafted onto the SHMI-Br/PVDF membrane surface. Introduction of P(PEGMA) brushes on the PVDF membrane surface enhanced the hydrophilicity effectively. When the PEGMA degree of grafting was 16.7 wt%, the initial contact angle of PVDF membrane decreased from 98° to 42°. The anti-fouling ability of PVDF membrane was improved significantly after P(PEGMA) brush was grafted. Taking the PEGMA degree of grafting 16.7 wt% as an example, the flux of protein solution was about 151.21 L/(m² h) when the pH value of the BSA solution was 4.9. As the pH value was increased to 7.4, the flux was changed to 180.06 L/(m² h). However, the protein solution flux of membrane M3 (PEGMA: 0 wt%) was only 73.84 L/(m² h) and 113.52 L/(m² h) at pH 4.9 and 7.4, respectively.

Keywords: PVDF membrane; SHMI-Br; Surface modification; Hydrophilicity; Anti-fouling ability.

INTRODUCTION

Various polymers, including polysulfone, polypropylene, polyethersulfone *etc.* have been widely used as membrane materials. Poly(vinylidene fluoride) (PVDF) has been received a great deal of attention due to its excellent chemical resistance, good thermal stability, well-controlled porosity and outstanding mechanical properties^[1–4]. However, its low surface energy and high hydrophobicity may cause serious nonspecific protein adsorption, which is unfavorable to the performance and will shorten the life of PVDF membranes.

Apart from the excellent mechanical bulk properties, an ideal antifouling membrane should also preserve the antifouling characteristics of the membrane surface and pores. The antifouling material such as poly(ethylene glycol) (PEG) has been extensively studied and considered as one of the promising materials to synthesis of membranes without fouling in the past decades^[5–10]. It's generally identified that the PEG chain could bind water through hydrogen bond, forming a “barrier” that is the key for the resistance to nonspecific protein adsorption. Additionally, the PEG-based functionalities, such as poly(ethylene glycol) methyl ether methacrylate (PEGMA), have also been broadly used for the surface modification of porous membrane in order to endow the membrane

* This work was financially supported by the Natural Science Foundation of Fujian province (No. 2011J01044), the National Basic Research Program of China (973 Program of China, No. 2009CB623402), Scientific Research Foundation in Fuzhou University (2010-XQ-17, 022284), Opening Research Foundation of Key Laboratory of Biomedical Material in Tianjin City (00801103), the Scientific Major Research Project of Fujian Province (2010NZ0001-1).

** Corresponding author: You-yi Xu (徐又一), E-mail: opl-yyxu@zju.edu.cn

Received July 17, 2012; Revised September 11, 2012; Accepted September 17, 2012

doi: 10.1007/s10118-013-1256-1

with excellent hydrophilicity.

In the past decades, a variety of methods, including coating, adsorption, plasma treatment, blending and surface grafting polymerization, have been explored to fabricate hydrophilic PVDF membranes^[11–14]. In these methods, blending and surface grafting polymerization are more popular than others in preparation of hydrophilic PVDF membranes. However, the surface grafting modification only imparts hydrophilicity to the membrane separation surface. It has some drawbacks for membrane antifouling performance, because foulant accumulation is not only at the separation surface but also within the pore channels of fouled membranes. For the blending method, modification agents enriched on the membrane surface are subject to being removed during the operation and aggressive cleaning process.

In this paper, styrene-*N*-(4-hydroxyphenyl) maleimide) alternating copolymer SHMI-Br was blended with PVDF to fabricate SHMI-Br/PVDF membranes. The C—Br bond on the SHMI-Br/PVDF membrane was served as initial site of ATRP and P(PEGMA) brush was grafted on the PVDF membrane. The influencing factors on the graft density, including monomer concentration, reaction time and temperature, were examined systematically. Fourier transforms infrared spectroscopy (FTIR) confirmed the P(PEGMA) segments were on the PVDF membranes. The surface morphologies and the cross-structures of the modified PVDF membranes were observed by scanning electron microscopy (SEM). This blending/ATRP combined method provided a new way to surface modification of polymer membranes.

EXPERIMENTAL

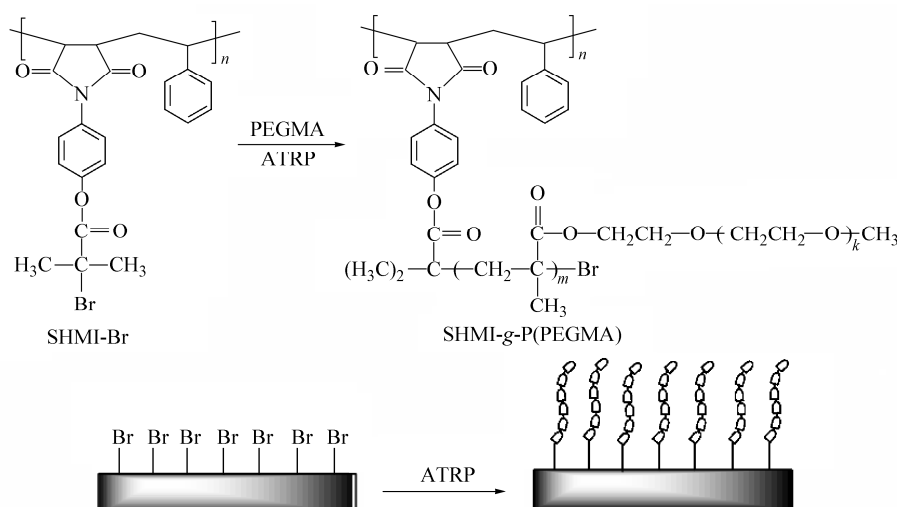
Styrene-*N*-(4-hydroxyphenyl) maleimide] alternating copolymer SHMI-Br was synthesized in our previous work^[15]. Poly(ethylene glycol) methyl ether methacrylate (PEGMA) ($M_n = 475$) was purchased from Aldrich. PVDF (FR-904) ($M_n = 3.8 \times 10^5$) was obtained from Shanghai 3F New Materials Co. Ltd. and it was dried at 110 °C for 12 h before use^[16]. Copper (I) bromide (CuBr, 95%) from Aldrich was purified by subsequent washing with acetic acid and ethanol and then dried in vacuum at the room temperature. 2,2'-Bipyridine (bpy, > 99%) was used as received. Bovine serum albumin (BSA, $M_n = 67$ kDa) was purchased from Aldrich. The phosphate buffered saline (PBS, 0.01 mol/L, pH = 7.4) was prepared by the addition of pre-packaged buffer salts (Aldrich) to deionized water. Other reagents were obtained from Shanghai Chemical Reagent Company, China.

Blending/ATRP Combined Method for Grafting P(PEGMA) Brushes on the PVDF Membrane

The typical mechanism of fabrication of grafted PVDF membranes is given in Scheme 1. SHMI-Br/PVDF blend membranes were prepared by the phase inversion method. The compositions of casting solutions are listed in Table 1. The cast solutions were prepared by dissolving a certain ratio of SHMI-Br and PVDF in 50 mL DMF. After stirring 48 h in 70 °C water bath, bubbles were released under reduced pressure (–50 kPa) for 30 min. The homogeneous solution was spread with a 300 µm casting knife on a clear glass plate and immediately immersed into a 60 °C coagulation bath of water. The membranes were peeled off from the glass plate and washed thoroughly with deionized water to remove residual solvent and then kept in fresh deionized water for further use.

Table 1. Casting solution compositions of SHMI-Br/PVDF blend membranes

Membrane ID	SHMI-Br (g)	PVDF (g)	PEG600 (g)	DMF (mL)
M0	0	9	1.7	50
M1	0.9	8.1	1.7	50
M2	1.8	7.2	1.7	50
M3	2.7	6.3	1.7	50



Scheme 1 The grafting on the SHMI-Br/PVDF blend membrane by ATRP

The SHMI-Br/PVDF blend membranes (4 cm × 4 cm) were immersed into in 60 mL H₂O/MeOH (*V*:*V* = 0:1 to 1:0) mixture solution in a Schlenk flask (100 mL). After PEGMA (2–8 g), CuBr (0.05 g, 0.35 mmol) and bpy (0.4g, 2.56 mmol) were added in under stirring, the reaction mixture was bubbled with argon for about 40 min and the flask was sealed with a rubber septum. Grafting polymerization was carried out at 20–80 °C with stirring. After 6 h, the grafted membranes were taken out and washed with abundant deionized water and methanol under ultrasonic. Then the membranes were dried under vacuum at 25 °C. The degree of grafting (GOD) was calculated according to Eq. (1)

$$\text{GOD} = (W_g - W_0)/W_0 \times 100\% \quad (1)$$

where W_0 is the mass of the nascent membrane and W_g is that of the modified membrane. Each result is an average of at least three parallel experiments.

Equipments

The surface chemical compositions of membranes were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR) (Thermo Nicolet 360, Japan).

The surface and cross-section morphologies of membranes were characterized by field emitting scanning electronic microscopy (FESEM, SIRION-100, FEI Co., Ltd.). The cross-section samples were prepared by membranes fractured in liquid nitrogen. All samples were sputter-coated with gold-palladium alloy to a thickness of 5 nm before microscopic analysis.

The hydrophilicity of membranes was characterized on the basis of an optical angle measurement system (OCA20, Data Physics, Germany) at ambient temperature. Water droplets (*ca.* 1 μL) were dropped carefully onto the surface of membranes with a micro-syringe. A magnified image of the droplet was recorded by a digital camera. Static contact angle was determined from the image with a calculation software. The contact angle of a membrane was averaged from tests at five different points.

Pure water flux as well as BSA solution flux in PBS (pH = 4.9 and pH = 7.4, respectively) of the membrane was assessed using a dead-end filtration system. The system consisted of a reservoir and an air gas cylinder. Before the filtration experiments, the membranes were incubated and pressurized with distilled water for 30 min. In the present study, the trans-membrane pressure was set at 0.1 MPa and data collection was made every 5 min. The permeation flux (J_w or J_p) was checked from time to time until the flux was steady and calculated by Eq. (2):

$$J_w = V_w/A\Delta t \text{ or } J_p = V_p/A\Delta t \quad (2)$$

where the parameters V_w , V_p , A , and Δt denote the pure water and protein solution permeate volume (L), membrane area (m²) and permeation time (h).

RESULTS AND DISCUSSION

Grafting P(PEGMA) Brushes on SHMI-Br/PVDF Membranes

The reaction solvent composition was very important for ATRP process, and it was easy to control the reaction rate by adjusting the reaction solvent composition. Hence, the influence of H₂O/MeOH on the graft density was investigated in this paper, and the results are demonstrated in Fig. 1. With the other conditions unchanged, increasing the H₂O ratio in H₂O/MeOH mixed solvent improved the grafting reaction rate and the DOG of P(PEGMA) brush was grown significantly. It was in accordance with the reaction rule of ATRP^[17, 18]. In this paper, reaction solvent composition $V(\text{MeOH})/V(\text{H}_2\text{O}) = 1:1$ was chosen as the solvent composition for grafting reaction.

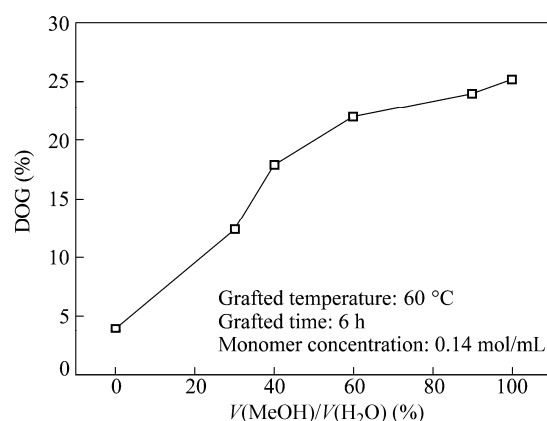


Fig. 1 Influence of $V(\text{MeOH})/V(\text{H}_2\text{O})$ on the PEGMA degree of grafting

Figure 2 displays the DOG as a function of the reaction temperature. The result demonstrated the DOG increased as the temperature rose from 20 °C to 80 °C. But above 60 °C, the reaction solution became viscous because of the self-polymerization of PEGMA monomer. As a result, 60 °C was selected as the temperature of graft polymerization in the present study.

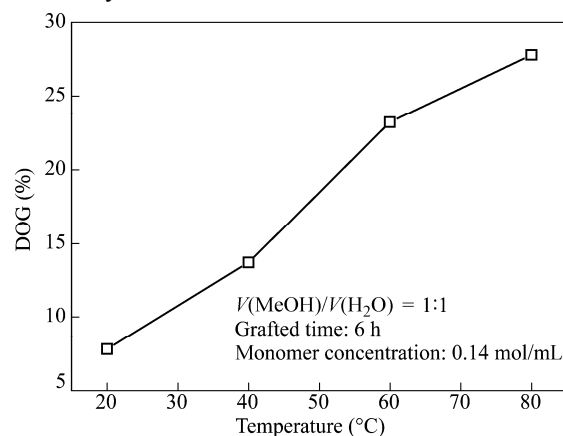


Fig. 2 Effect of reaction temperature on the PEGMA degree of grafting

The effect of monomer concentration on DOG is demonstrated in Fig. 3. The result indicated the DOG increased with the monomer concentration rising. The DOG increase was fast at the beginning and slowed down gradually when the concentration surpassed 0.15 mol/L. This result may be attributed to the super-high viscosity of the reaction medium for the self-polymerization of PEGMA monomer. Hence, 0.15 mol/L was selected as the monomer concentration in this work.

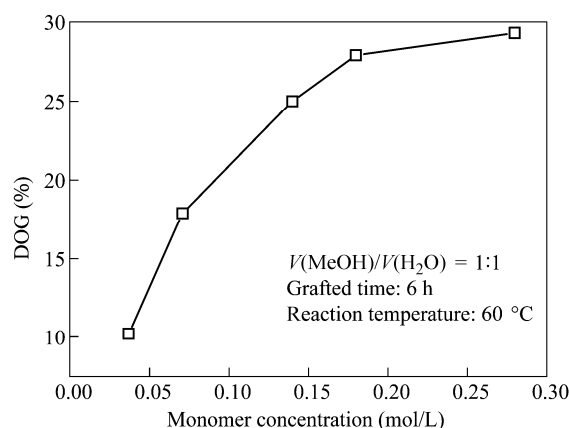


Fig. 3 Effect of PEGMA concentration on the PEGMA degree of grafting

The Surface Chemical Composition Characterization of Membranes

The surface chemical composition of membranes played a fundamental role in enhancing hydrophilicity and reducing nonspecific protein adsorption. In this paper, the surface chemical composition of SHMI-Br/PVDF blend membranes and SHMI-g-PEGMA/PVDF grafted membranes was investigated by ATR/FTIR, and the typical spectra are shown in Fig. 4 and Fig. 5, respectively. From Fig. 4, the band at 1780 cm^{-1} was attributed to $\text{C}=\text{O}$ of $\text{O}=\text{C}-\text{N}-\text{C}=\text{O}$ in SHMI-Br. The peaks at 1714 cm^{-1} and 1665 cm^{-1} were ascribed to $\text{C}=\text{O}$ in $-\text{O}-\text{CO}-(\text{CH}_3)\text{Br}$, which indicated that SHMI-Br had enriched on the surface of PVDF membrane during the fabrication of SHMI-Br/PVDF blend membranes.

After P(PEGMA) brush was grafted on different SHMI-Br/PVDF blend membranes, some new peaks appear in Fig. 5. The peak at 1109 cm^{-1} was ascribed to the $\text{C}-\text{O}-\text{C}$ group in P(PEGMA) brush. The band at 1735 cm^{-1} was attributed to $\text{C}=\text{O}$ stretch of P(PEGMA) brush. The peak at 2877 cm^{-1} was a characteristic absorbance of the $\text{C}-\text{H}$ stretch vibrations of $-\text{CH}_2-\text{CH}_2-$ groups in PEGMA. The appearance of these new bands indicated that the P(PEGMA) brush had been successfully grafted on the SHMI-Br/PVDF blend membrane. From Fig. 5, we can also see that intensity of the three new peaks was increased with the growing of SHMI-Br content in the blend membrane. This was because the increase of $\text{C}-\text{Br}$ on the blend membrane provided more active initial sites for ATRP of PEGMA grafting.

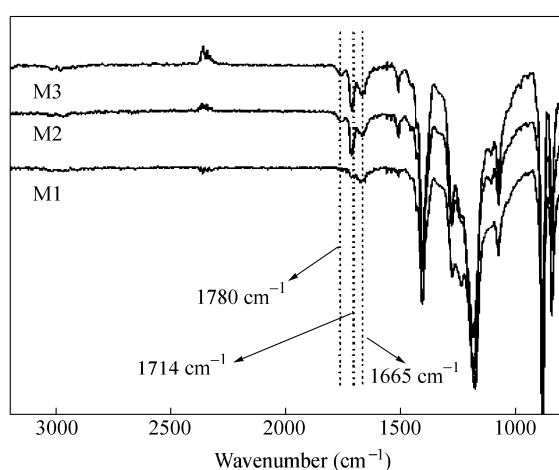


Fig. 4 ATR-FTIR spectra of SHMI-Br/PVDF blend membranes

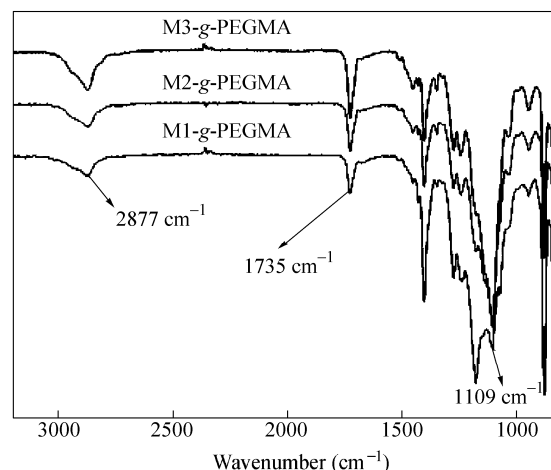


Fig. 5 ATR-FTIR spectra of PEGMA grafted SHMI-Br/PVDF membranes

The Morphology Characterization of Membranes

The SEM micrographs of SHMI-Br/PVDF blend membrane M3 and PEGMA grafted M3 membrane were studied, and the results are shown in Fig. 6. From the Fig. 6, we can see that the pore size and porosity on the top surface of M3 was decreased after P(PEGMA) brush was grafted. Zhu and coworkers^[19] also obtained the similar result for the preparation of PPESK membranes. From the bottom surface (A2, B2) and cross section (A3, B3) micrographs we can see that the PVDF bottom surface became coarse after the P(PEGMA) brush was grafted. We can infer from the SEM result that the P(PEGMA) brush can be grafted not only on the surface but also on the inner surface of pores *via* the method of this paper. The similar phenomenon was observed by other researchers^[20].

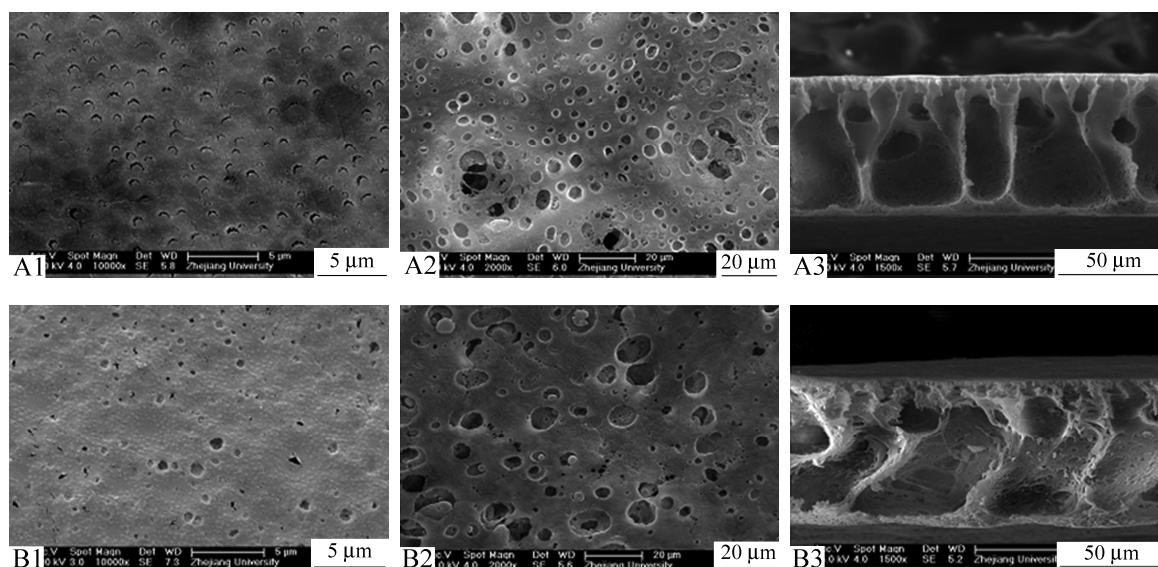


Fig. 6 SEM micrographs of M3 (A1, A2, A3) and 7.5 wt% PEGMA grafted M3 membrane (B1, B2, B3); A1, B1: top surface, A2, B2: bottom surface, A3, B3: cross section

The Hydrophilicity Characterization of Membranes

Surface hydrophilicity was one of the most important factors for the filter membrane performance and much attention has been paid to it^[21, 22]. In this paper, the hydrophilicity of membranes was evaluated by contact angle measurements using the captive bubble method, and the results are shown in Fig. 7. The SHMI-Br/PVDF membrane M3 showed an initial water contact angle of 98°. After the P(PEGMA) brush was grafted on the M3 surface, it's easily observed that the initial contact angle decreased gradually along with the degree of grafting of P(PEGMA) brush. When the degree of grafting of PEGMA was 7.5 wt%, the initial contact angle was 68°, about 30° decrease comparing with M3. And when the PEGMA degree of grafting was grown to 16.7 wt%, the initial contact angle decreased to 42°. At the same time, we can also see that the contact angle on the M3 almost remained stable during the contact time. However, the contact angle on the grafted membranes reduced gradually within the measurement time. With the degree of grafting increase, the decreasing rate of contact angle was enhanced. The results indicated that the P(PEGMA) brush gave these membranes an excellent hydrophilicity.

Antifouling Performance of Membranes

To investigate the fouling resistance of the prepared membranes, after the pure water flux, the protein solution permeation process was conducted and BSA was used as a model protein. As shown in Fig. 8, The pure water flux of M3 was 280.86 L/(m² h). When the degree of grafting of PEGMA was increased, the pure water flux was decreased dramatically. When the degree of grafting was 16.7 wt%, the flux decreased to 248.13 L/(m² h). After filtrating with BSA solution, the flux decreased dramatically for all membranes because of the deposition protein molecules on the membrane surface and inside the membrane pores^[23, 24]. But the grafted membranes had a

lower reducing ratio than membrane M3. And when the BSA solutions of different pH were permeated, the flux of grafted membranes was quite different. Take the membrane with PEGMA degree of grafting 16.7 wt% for example, the flux of protein solution was about 151.21 L/(m² h) when its pH value was 4.9. When the pH increased to 7.4, the flux of protein solution was changed to 180.06 L/(m² h). However, the protein solution flux of M3 was 73.84 L/(m² h) and 113.52 L/(m² h) at pH 4.9 and pH 7.4, respectively. The flux result showed that the grafted PEGMA brush improved the anti-fouling performance of SHMI-Br/PVDF membranes.

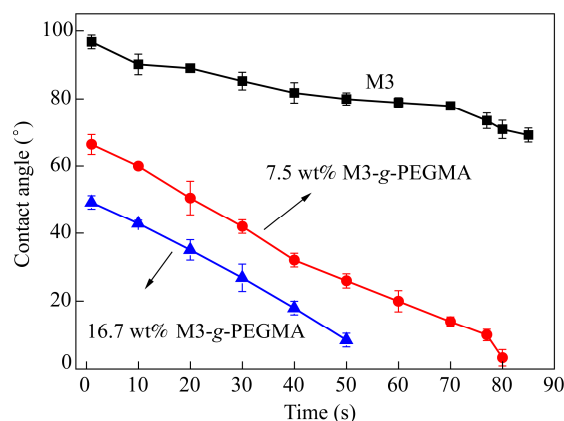


Fig. 7 Contact angle changes with time of PEGMA grafted membranes with different DOG

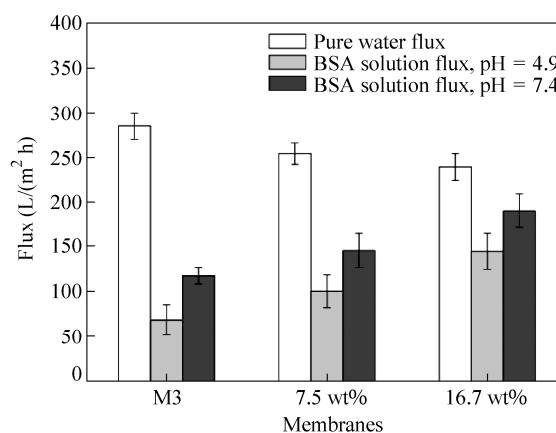


Fig. 8 The water and BSA solution flux of M3 and M3-g-PEGMA membranes with different degrees of grafting

CONCLUSIONS

In this paper, a novel method for the surface modification of PVDF porous membranes was introduced. Styrene-(*N*-(4-hydroxyphenyl) maleimide) alternating copolymer SHMI-Br was blended with PVDF to fabricate SHMI-Br/PVDF membranes. The C—Br bond on the SHMI-Br/PVDF membrane was served as initial site of ATRP, and P(PEGMA) brush was grafted on the PVDF membrane. The P(PEGMA) brushes have been successfully grafted on the SHMI-Br/PVDF membrane surface, which was proved by ATR/FTIR analysis. Introduction of P(PEGMA) brushes on the PVDF membrane surface had enhanced the hydrophilicity and anti-fouling ability of PVDF membranes effectively, which can be inferred from results of contact angle measurements, water flux and protein solution flux.

REFERENCES

- Li, J.H., Xu, Y.Y., Wang, J.H. and Du, C.H., Chinese J. Polym. Sci., 2009, 27(6): 821
- Hester, J.F., Banerjee, P. and Mayes, A.M., Macromolecules, 1999, 32: 1643
- Wang, P., Tan, K.L., Kang, E.T. and Neoh, K.G., J. Mater. Chem., 2001, 11: 783
- Akthakul, A., Salinaro, R.F. and Mayes, A.M., Macromolecules, 2004, 37: 7663
- Harris, J.M., Plenum Press, New York/London, 1992
- Ma, H., J. Hyun, Stiller, P. and Chilkoti, A., Adv. Mater., 2004, 16: 338
- Su, Y.L., Cheng, W., Li, C. and Jiang, Z.Y., J. Membr. Sci., 2009, 329: 246
- Rossi, N.A.A., Mustafa, I., Jackson, J.K., Burt, H.M., Horte, S.A., Scott, M.D. and Kizhakkedathu, J.N., Biomaterials, 2009, 30: 638
- Hatakeyama, E.S., Ju, H., Freeman, B.D. and Gin, D.L., J. Membr. Sci., 2009, 330: 104
- Chang, Y., Cheng, T.Y., Lee, K.R. and Lai, J.Y., J. Membr. Sci., 2008, 323: 77
- Chiang, Y.C., Chang, Y. and Ruaan, R.C., Langmuir, 2012, 28(2): 1399

- 12 Chang, Y., Shih, Y.J. and Wei, T.C., *Langmuir*, 2011, 27(9): 5445
- 13 Chang, Y., Ko, C.Y. and Lai, J.Y., *J. Membr. Sci.*, 2009, 345: 160
- 14 Yi, Z., Zhu, L.P., Xu, Y.Y. and Zhu, B.K., *J. Membr. Sci.*, 2010, 365: 25
- 15 Li, J.H., Xu, Y.Y. and Du, C.H., *Chinese J. Polym. Sci.*, 2009, 27(6): 821
- 16 Liu, F., Tao, M.M. and Xue, L.X., *Desalination*, 2012, 298(16): 99
- 17 Wang, X.S., Lascelles, S.F. and Armes, S.P., *Chem. Commun.*, 1999, 18: 1817
- 18 Wang, X.S. and Armes, S.P., *Macromolecules*, 2000, 33(18): 6640
- 19 Zhu, L.P., Dong, H.B., Wei, X.Z., Yi, Z., Zhu, B.K. and Xu, Y.Y., *J. Membr. Sci.*, 2008, 320: 407
- 20 Qiu, G.M., Zhu, B.K., Wang, X.Q. A and Xu, Y.Y., *Acta Polymerica Sinica (in Chinese)*, 2005, (5): 783
- 21 Park, J.Y., Acar, M.H. and Mayes, A.M., *Biomaterials*, 2006, 27: 856
- 22 Hashim, N.A., Liu, F. and Li, K., *J. Membr. Sci.*, 2009, 345: 134
- 23 Li, M.Z., Li, J.H. and Zhang, Q.Q., *J. Membr. Sci.*, 2012, 405-406: 141
- 24 Li, J.H., Xu, Y.Y. and Zhu, L.P., *J. Membr. Sci.*, 2009, 326: 659