

SYNTHESIS OF AMPHIPHILIC COMB-SHAPED COPOLYMERS USED FOR SURFACE MODIFICATION OF PVDF MEMBRANES*

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Abstract The synthesis of a novel amphiphilic comb-shaped copolymer consisting of a main chain of styrene-(*N*-(4-hydroxyphenyl) maleimide) (SHMI) copolymer and poly(ethylene glycol) methyl ether methacrylate (PEGMA) side groups was achieved by atom transfer radical polymerization (ATRP). The amphiphilic copolymers were characterized by ¹H-NMR, Fourier transform infrared (FTIR) spectroscopy and gel permeation chromatography (GPC). From thermogravimetric analysis (TGA), the decomposition temperature of SHMI-*g*-PEGMA is lower than that of SHMI, and the graft ratio of PEGMA in the SHMI is 18.6%. The experimental results of solubilities showed that SHMI, SHMI-Br and SHMI-*g*-PEGMA had excellent solubility in polar solvents, such as DMF, DMSO and NMP. SHMI-*g*-PEGMA had higher solubilities in H₂O and methanol, while lower solubility in CHCl₃ than SHMI and SHMI-Br. PVDF blend membranes were prepared via the standard immersion precipitation phase inversion process, using amphiphilic SHMI-*g*-PEGMA copolymer as additives. The morphology and hydrophilicity of the blend membrane surfaces were characterized by SEM and water contact angle. It is demonstrated that the blend membranes display enhanced hydrophilicity compared to unmodified PVDF membranes. Finally, the permeation and anti-fouling properties were investigated. The result shows that amphiphilic SHMI-*g*-PEGMA copolymer increases the permeability and anti-fouling property of PVDF membranes greatly.

Keywords: Comb-shaped copolymer; Amphiphilic; Surface modification; Hydrophilicity; Anti-fouling property.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is one of the most extensively applied membrane material in industry area due to its excellent chemical resistance, thermal stability, low toxicity and low price^[1]. But its hydrophobic nature is also well known, which results in the adsorption and deposition of hydrophobic organics on the membrane surface. In order to solve this problem, the hydrophilic modification of PVDF membranes has been widely explored in recent years. A variety of methods have been explored to fabricate hydrophilic PVDF membranes^[2–5]. The blending of amphiphilic polymers with PVDF is one of the most popular methods for PVDF membrane surface modification^[6–8]. The typical character of this method is that the amphiphilic copolymer additives can preferentially segregate to the separation surface of the membrane and to the internal pore surface during the coagulation process, which results in hydrophilic and anti-fouling surface as well as higher porosity and higher permeability. The other advantage is the long-term stability of hydrophilic and anti-fouling layers on membrane surface since the additives are hydrophilic but water insoluble polymers.

Controlled/"living" radical polymerization has been explored as a means of producing well-defined polymers^[9, 10]. Atom transfer radical polymerization (ATRP), one of the most popular methods of controllable polymerization, has already been widely used for the synthesis of block, graft and star copolymers and polymers

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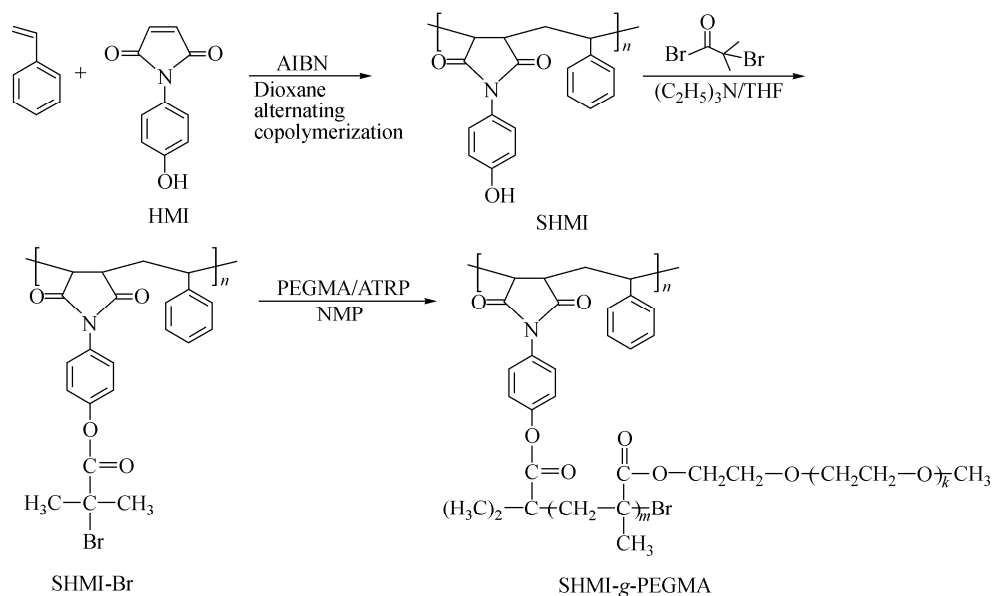
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with more complex structures based on a wide variety of monomers^[11, 12]. Graft copolymers have been prepared by ATRP with various approaches such as grafting to or grafting from^[13–15]. The combination of ATRP and grafting allows the control of the mainchain parameters (degree of polymerization (DP) and weight-average molecular weight (M_w)/number-average molecular weight (M_n)) and the predetermination of side-chain density and side-chain distribution. These strategies have led to graft copolymers with controlled polydispersities, functionalities, copolymer compositions, backbone lengths, branch lengths and branch spacings^[16–18].

In recent years, *N*-substituted maleimide (MI) monomers, such as *N*-phenylmaleimide and *N*-hydroxyphenylmaleimide (HMI) have become important because they contain a rigid planar ring and can effectively enhance the glass-transition temperature (T_g) and degradation temperature of copolymers^[19, 20]. So some groups have studied the alternating copolymerizations of MI monomers with electron-rich monomers^[21–23]. Pu *et al.*^[24] synthesized the styrene/maleimide copolymer with 4-(*N*-ethyl-*N*-(2-hydroxyethyl) amino)-4'-nitroazobenzene as side chain via ATRP. This material can work as an organic second-order nonlinear optical (NLO) polymer. Xu *et al.*^[25] synthesized a kind of pure graft copolymer with PA6 grafts and alternating styrene/maleimide copolymer main chains. The copolymer showed better thermal behavior, better solvent resistance ability and better dimensional stability than those of pure PA6. However, the synthesis of amphiphilic graft copolymers with alternating styrene/maleimide copolymer main chain and poly(ethylene glycol) methyl ether methacrylate (PEGMA) side groups has not been reported so far.

Aiming at preparation of a novel amphiphilic copolymer which is suitable for surface modification of PVDF membranes, we designed and synthesized an amphiphilic comb-shaped copolymer based on styrene/maleimide alternating copolymer, with poly(ethylene glycol) methyl ether methacrylate (PEGMA) as side chains. The synthesis route is shown in Scheme 1. The synthesis of the amphiphilic copolymer begins from the preparation of *N*-(4-hydroxyphenyl) maleimide (HMI). HMI is then copolymerized with styrene to produce styrene-(*N*-(4-hydroxyphenyl) maleimide) alternating copolymer (SHMI). The hydroxyphenyl groups in SHMI can be esterified with 2-bromoisobutyryl bromide to form SHMI-Br, and then used as macroinitiator in the ATRP to yield amphiphilic comb-shaped copolymer SHMI-*g*-PEGMA. The SHMI, SHMI-Br and SHMI-*g*-PEGMA were characterized with ¹H-NMR, Fourier transform infrared (FTIR) spectroscopy and gel permeation chromatography (GPC). Thermal stability and solubility of the copolymers were investigated. Finally, PVDF



Scheme 1 The synthesis route of SHMI-*g*-PEGMA

blend membranes were prepared via the standard immersion precipitation phase inversion process, using the synthesized amphiphilic SHMI-*g*-PEGMA copolymer as additives. The morphology and hydrophilicity of the blend membrane surfaces were characterized by SEM and water contact angle. The permeability and anti-fouling properties of blend PVDF membranes were investigated finally.

EXPERIMENTAL

Materials

2-Bromoisobutyryl bromide (> 97%) and 4-aminophenol from Alfer Aser Co. were used as received. Poly(ethylene glycol) methyl ether methacrylate (PEGMA) ($M_n = 475$) was purchased from Aldrich and used as received. Copper(I) bromide (CuBr, 95%) from Aldrich was purified by subsequent washing with acetic acid and ethanol and then dried in vacuo. PVDF (FR-904) ($M_n = 3.8 \times 10^5$) was obtained from Shanghai 3F New Materials Co. LTD and was dried at 110°C for 12 h before use. Other reagents were obtained from Shanghai Chemical Reagent Company, China. 2,2'-azobisisobutyronitrile (AIBN) was purified by recrystallization in ethanol before use. Tetrahydrofuran (THF) was dried over Na chip and distilled. 1,4-dioxane, styrene (St), *N,N'*-dimethylformamide (DMF) and 1-methyl-2-pyrrolidinone (NMP) were dried by CaH_2 and distilled under reduced pressure. Triethylamide (Et_3N), maleic anhydride, phosphorus pentoxide (P_2O_5), sulfuric acid, isopropanol, methanol, ethanol, copper(II) bromide (CuBr_2), 2,2'-bipyridine (bpy, > 99%) were 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.

Synthesis of *N*-(4-hydroxyphenyl)maleimide (HMI)

HMI was synthesized from 4-aminophenol and maleic anhydride via a reported procedure^[19]. $^1\text{H-NMR}$ (in DMSO-d_6 , δ): 6.87–6.90 (2H, $-\text{CH}=\text{CH}-$), 7.12–7.17 (4H, aromatic protons), 9.2 (1H, phenolic protons). Elemental analysis found % (calcd %) C: 63.54 (63.49), H: 3.68 (3.70), N: 7.44 (7.41).

Synthesis of Styrene/Maleimide Alternating Copolymer (SHMI)

A three-necked flask equipped with a magnetic stir, reflux condenser and N_2 inlet tube was charged with styrene (0.02 mol, 2.3 mL), 4-HPM (0.02 mol, 3.78 g), AIBN (0.2 mmol) and dioxane (30 mL). After degassed with N_2 for 30 min, the reaction flask was sealed and placed in a 60°C oil bath for 8 h. After polymerization, the reaction mixture was diluted by 50 mL dioxane, and the polymer was isolated by precipitating the solution into 800 mL methanol. The precipitated polymer was filtered and was purified by dissolution in dioxane and reprecipitation in methanol three times. Finally, the resultant copolymer was dried at 40°C for 48 h under vacuum (yield 93%).

Synthesis of Macroinitiators (SHMI-Br)

SHMI-Br was synthesized via a modification of a reported method^[20]. SHMI (5 g, hydroxyphenyl groups = 17 mmol) was dissolved into 120 mL THF and then stirred at 0°C 30 min under N_2 . After Et_3N (7 mL, 51 mmol) was introduced as acid acceptor, 2-bromoisobutyryl bromide (6.3 mL, 51 mmol) was dissolved into 30 mL THF and added via a constant-voltage funnels during 30 min. The mixtures were stirred under 0°C for 3 h and room temperature for 18 h. Finally, the resultant mixtures were poured into a large excess of methanol and separated by filtration (degree of esterification 100%, yield 98%).

Synthesis of Alternating Comb-Shaped Copolymer (SHMI-*g*-PEGMA)

Typical polymerization conditions for the synthesis of comb-shaped copolymer SHMI-*g*-PEGMA are as follows. Macroinitiator SHMI-Br (3.0 g, 1.1357×10^{-2} mmol), PEGMA (6.4 g, 13.5432 mmol), CuBr (0.195 g, 1.3543 mmol), CuBr_2 (0.02029 g, 0.09058 mmol) and NMP (60 mL) were charged into an argon-filled Schlenk flask (100 mL). The reaction mixture was bubbled with argon for about 30 min and the flask was sealed with a rubber septum. Polymerization was carried out at 90°C with stirring. After 8 h, the reaction mixture was cooled to ambient temperature and precipitated into methanol. After being reprecipitated thrice from NMP into methanol, the copolymer was recovered by filtration and dried under vacuum at 25°C (yield 87%).

Preparation of Blend Membranes

SHMI-*g*-PEGMA/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-*g*-PEGMA and PVDF in 50 mL DMF. After stirred 48 h in 70°C water bath, casting solutions were released bubbles under reduced pressure (−50 kPa) for 30 min. The homogeneous solution was spread with a 300 μm casting knife onto a clear glass plate and immediately immersed into a 60°C coagulation bath of water. After peeled off from the glass plate, the membranes were washed thoroughly with deionized water to remove residual solvent and kept in fresh deionized water for further use.

Table 1. Compositions of SHMI-*g*-PEGMA /PVDF blend membrane casting solutions

	SHMI- <i>g</i> -PEGMA (g)	PVDF (g)	DMF (mL)
M0	0	9	50
M1	0.9	8.1	50
M2	1.8	7.2	50
M3	2.7	6.3	50

Equipments

¹H-NMR spectra was recorded on an Avance DMX 500 spectrometer (Bruker, Germany) operated at 500 MHz. CDCl₃, DMSO-*d*₆ and tetramethylsilane (TMS) were used as solvents and internal standard, respectively. Molecular weights and molecular weight distributions of styrene/maleimide alternating 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. THF was used as the eluent with a flow rate of 1.0 mL/min at 35°C. Elemental analysis was performed with an elemental analyzer (Vario EL III, Elementar). Thermal gravimetric analysis (TGA) characterization was carried out on a Perkin-Elmer Pyris 1 calorimeter (Germany) in dry nitrogen atmosphere, and the thermograms were recorded while heating from 50°C to 800°C at 10 K/min. Infrared spectra of the copolymer samples was measured on a Bruker Vector 22 FT-IR Spectrometer.

The top surface and cross-section of membranes were observed by means of a Sirion FE scanning electron microscope (SEM, FEI USA). All membrane samples were dried at room temperature and coated with a thin layer of gold before observation.

The top surface hydrophilicity of membranes was characterized on the basis of a water contact angle system (OCA20, Dataphysics, Germany) equipped with video capture at room temperature. To minimized experimental error, the contact angles were measured five times for each sample and then averaged.

Filtration experiments were conducted on the membrane with a diameter of 60 mm using a dead-end stirred filtration cell. Under the pressure of 100 kPa and the feed temperature at (25 ± 0.1)°C, the flux of pure water (J_w) was obtained from the volume of the permeated water within 30 min and calculated as: $J_w = Q/(A \times \Delta t)$ where J_w is the pure water flux (L/(m²h)), Q is the permeate volume (L), A is the membrane area (m²) and Δt is the time (h). After that, a 1 g/L BSA phosphate-buffered saline solution was forced to permeate through membrane at the same pressure for 30 min, and the flux was recorded as J_p . After filtration of BSA solution, these membranes were cleaned via shaking in pure water for 2 h at 25°C and then the pure water fluxes (J_R) were measured again. By comparing the value of J_w , J_p and J_R , the water flux recovery and the cleaning property of the fouled membrane were investigated. The filtration experiments were measured five times and then averaged.

RESULTS AND DISCUSSION

Synthesis of SHMI and Macroinitiator (SHMI-Br)

Styrene and HMI represent a monomer pair with a strong tendency toward radical alternating copolymerization. The copolymerization of these monomers proceeded much faster than their homopolymerization in the presence of AIBN as an initiator. The ¹H-NMR spectrum of the SHMI synthesized in this paper is shown in Fig. 1(B).

The resonances (a–c; $\delta = 2.2$ –3.8) are assigned to protons of succinimide and vinyl group of styrene. The resonances (d–e; $\delta = 6.75$ –7.2) are the aromatic ring protons of styrene and HMI. The resonance (f; $\delta = 9.7$) is the proton of phenolic group in HMI. The integration ratio of phenolic proton (f) and aromatic protons (d–e) is 1:9.3, which shows that SHMI synthesized under the conditions of this paper has alternating structure.

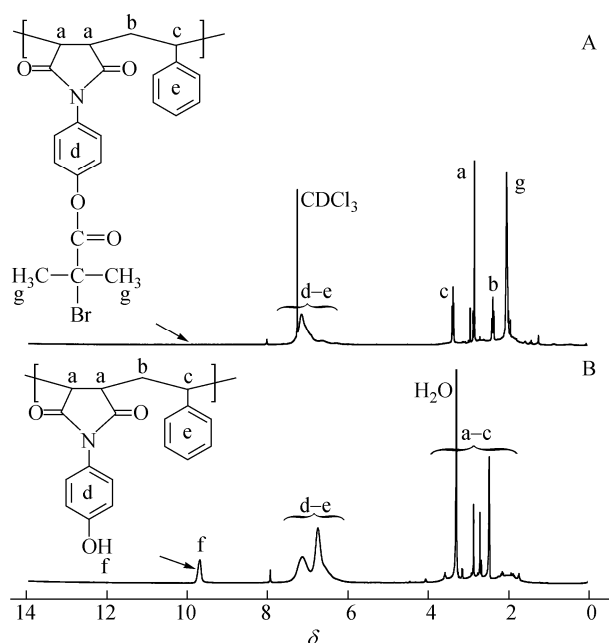


Fig. 1 ¹H-NMR spectra of SHMI and SHMI-Br
A) SHMI-Br, CDCl₃; B) SHMI, DMSO-d₆

The macroinitiator (SHMI-Br) was synthesized by the esterification of hydroxyphenyl groups in SHMI with 2-bromoisobutyryl bromide, and its ¹H-NMR spectrum is shown in Fig. 1(A). The spectrum displays that the resonances for the proton of phenolic group (f; $\delta = 9.7$) in SHMI disappear completely, which indicates that the hydrogen reactive site of phenol proton in SHMI has been totally converted to 2-bromopropionyloxy groups^[26]. The new resonance (g; $\delta = 1.97$) was the methyl proton which indicated the presence of 2-bromoisobutyryl bromide segments in macroinitiator SHMI-Br.

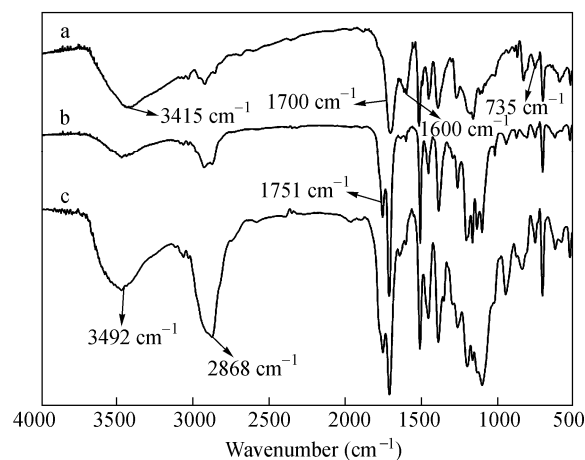


Fig. 2 FT-IR spectra of SHMI (a), SHMI-Br (b) and SHMI-g-PEGMA (c)

The FT-IR spectra of SHMI and SHMI-Br are presented in Fig. 2. The spectrum of SHMI shows the expected absorbance for the aromatic ring (1600 cm^{-1} and 735 cm^{-1}) and characteristic absorbance for carbonyl groups of maleimide at 1700 cm^{-1} . The absorption peak at 3415 cm^{-1} in spectrum (a) is assignable to the phenolic group of SHMI. After esterified with 2-bromoisobutyryl bromide, the absorption peak of phenolic end group (3415 cm^{-1}) in spectrum (a) disappeared (a small peak at 3415 cm^{-1} was assigned to H_2O molecules absorbed on SHMI-Br), while a new absorption peak at 1751 cm^{-1} which was ascribed to $\text{C}=\text{O}$ stretching vibration of the ester groups appeared (see spectrum b). The FT-IR spectrum analysis indicated that hydrogen reactive site of phenolic proton in SHMI has been totally converted to 2-bromopropionyloxy groups.

Synthesis of Alternating Comb-Shaped Copolymer (SHMI-g-PEGMA)

The ATRP synthesis of SHMI-g-PEGMA was carried out by using SHMI-Br as macroinitiator and $\text{CuBr}/\text{CuBr}_2/\text{bpy}$ as catalyst. After repeated purification, the resultant copolymers were characterized by ^1H -NMR and FT-IR. The ^1H -NMR for SHMI-g-PEGMA showed peaks with chemical shift as follows (Fig. 3).

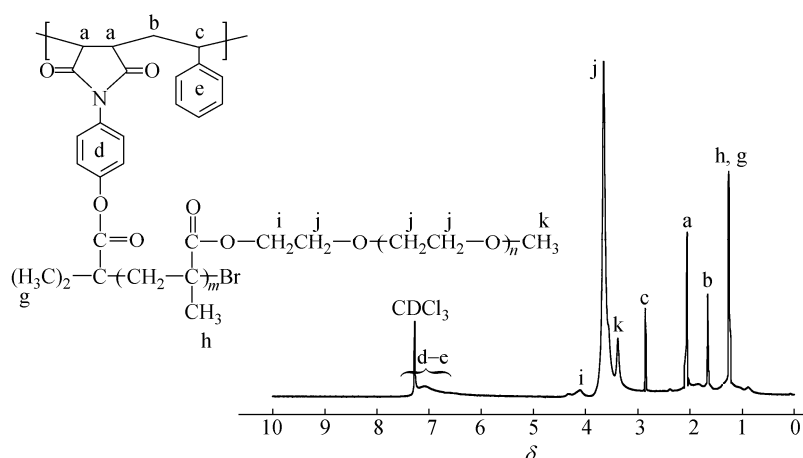


Fig. 3 ^1H -NMR spectrum of SHMI-g-PEGMA (solvent: DMSO-d_6)

The resonances (a–c, $\delta = 1.5\text{--}3.0$) can be assigned to protons of succinimide and vinyl group of styrene (a–c); the resonances (d–e; $\delta = 6.5\text{--}7.5$) are the aromatic ring protons in SHMI backbone. The H of methylene groups connected to the oxygen atom of the ester group in the methacrylate shows a chemical shift of $\delta = 4.1$ (i, $\delta = 4.1$); the H of methylene groups connected to the oxygen atom of ether group in the PEG segment shows a chemical shift of $\delta = 3.68$ (j, $\delta = 3.68$); the chemical shift of the methyl group at the end of PEG chain is $\delta = 3.37$ (k, $\delta = 3.37$); the H of methyl groups connected to the vinyl group in the PEG segment and the methyl proton in 2-bromoisobutyryl bromide segment show chemical shifts (g) of 1.25 (h, g $\delta = 1.25$). The ^1H -NMR analysis for SHMI-g-PEGMA indicates that the PEGMA moieties exist in the synthesized SHMI copolymer.

Besides ^1H -NMR analysis, the chemical composition of the resultant polymers was further confirmed by FT-IR spectroscopy measurements (as shown in Fig. 2c). Compared to the spectrum for SHMI-Br (spectrum b) two new adsorption bands at *ca.* 2868 cm^{-1} and *ca.* 3492 cm^{-1} appeared in the spectrum for SHMI-g-PEGMA spectrum (c). The adsorption band at *ca.* 2868 cm^{-1} can be assigned to the C-H stretching vibration of $-\text{CH}_2$ groups in the PEGMA polymer brush, while the broad adsorption band at *ca.* 3505 cm^{-1} can be ascribed to the H_2O molecules adsorbed on the PEG segments of PEGMA. It is very difficult to completely remove H_2O from SHMI-g-PEGMA because PEG is extremely hydrophilic. Moreover, the hydrophilic nature of PEG makes SHMI-g-PEGMA susceptible to moisture when it is exposure in the air.

GPC Characterization

The molecular weight and polydispersity index (PDI) for SHMI, SHMI-Br and comb-shaped copolymer SHMI-*g*-PEGMA were obtained from GPC analysis. The results are presented in Table 2. In the results, SHMI and SHMI-Br keep almost the same polydispersity, which indicate that the esterification degree of SHMI is 100% with 2-bromoisobutyryl bromide just as shown by $^1\text{H-NMR}$ measurements (Fig. 1B). Graft copolymerization of PEGMA and SHMI-Br macroinitiator has resulted in a significant increase in molecular weight relative to that of SHMI. The molecular weight (M_n) of SHMI-*g*-PEGMA reaches 13100. These results indicated that PEGMA can be successfully grafted on the SHMI by ATRP.

Table 2. Molecular weights and polydispersity index (PDI) for SHM, SHMI-Br and SHMI-*g*-PEGMA

Polymer	GPC molecular weight		
	M_n	M_w	PDI
SHMI	8200	16100	1.96
SHMI-Br	10500	20400	1.94
SHMI- <i>g</i> -PEGMA	13100	27400	2.09

Thermal Stability Analysis

The thermal stabilities of the SHMI and comb-shaped copolymers SHMI-*g*-PEGMA were investigated by thermal gravimetric analysis (TGA), and the results are shown in Fig. 4. It can be seen from the curve of SHMI that the decomposition temperature of SHMI is around 410°C which is coincide with that reported^[17]. However, from the curve of SHMI-*g*-PEGMA, a distinct two-step degradation process is discernible for the SHMI-*g*-PEGMA copolymer sample. The onset of the first major weight loss is at about 210°C and corresponds to the decomposition temperature of the P(PEGMA) component^[27]. The second major weight loss begins at about 410°C, corresponding to the decomposition temperature of the backbone polymer SHMI. The decomposition temperature of SHMI-*g*-PEGMA is lower than that of SHMI due to the decrease of molecular regularity of SHMI-*g*-PEGMA and the destruction of hydrogen bonds^[24]. It is worth to note that while the temperature increased from 100°C to 310°C, the weight loss of P(PEGMA) was about 18.6%, suggesting that the relative weight ratio of P(PEGMA) in SHMI-*g*-PEGMA was approximately 18.6 wt%^[28]. From the result, we can infer that SHMI-*g*-PEGMA has better thermal stability than P(PEGMA)^[27].

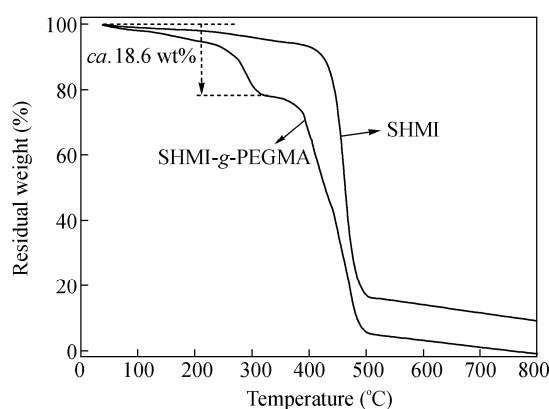


Fig. 4 TGA curves for SHMI and SHMI-*g*-PEGMA

Solubility of SHMI-*g*-PEGMA

The solubilities of SHMI, SHMI-Br and SHMI-*g*-PEGMA in different solvents are listed in Table 3. SHMI and SHMI-Br have the same solubility in these solvents. However, the solubility of the amphiphilic copolymer SHMI-*g*-PEGMA is different to that of SHMI and SHMI-Br, which is caused by the introduction of PEGMA side groups in the main chain. It is shown that SHMI and SHMI-*g*-PEGMA have excellent solubility in polar

solvents, such as DMF, DMSO and NMP, because that these solvents can form H-bonding with phenol OH groups in SHMI and ether groups in the PEG segment of SHMI-*g*-PEGMA^[24, 29]. But SHMI-*g*-PEGMA has better solubility in H₂O and methanol than SHMI and SHMI-Br because of its PEGMA side groups. When the graft degree of PEGMA is increased to a certain degree, the comb-shaped copolymer of SHMI-*g*-PEGMA can be soluble in H₂O and methanol totally. However, the solubility of SHMI-*g*-PEGMA in CHCl₃ is decreased comparing to that of SHM and SHMI-Br.

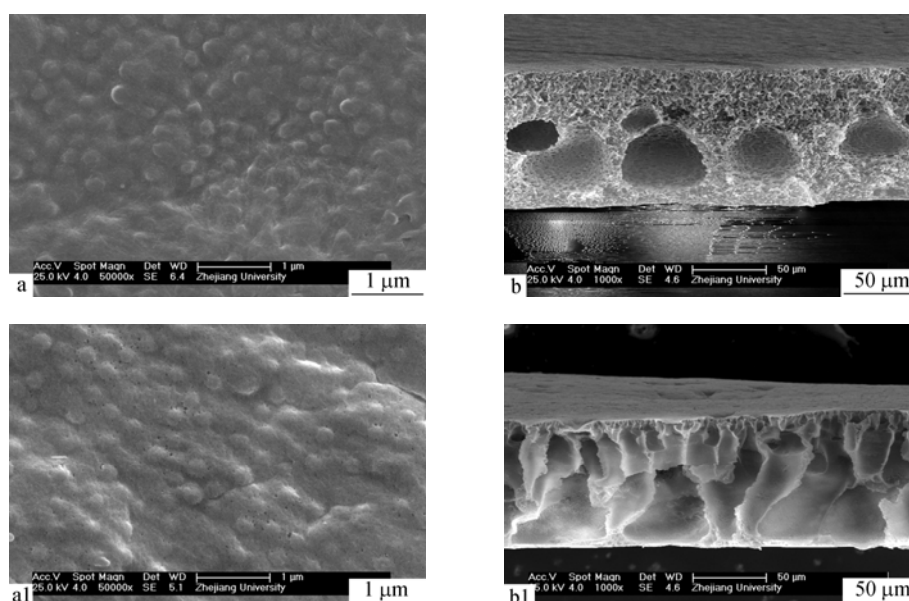
Table 3. Solubilities of SHMI, SHMI-Br and SHMI-*g*-PEGMA

Solvent	SHMI	SHMI-Br	SHMI- <i>g</i> -PEGMA
CHCl ₃	+	+	+/-
THF	+	+	+
H ₂ O	—	—	+/-
DMF	+	+	+
DMSO	+	+	+
NMP	+	+	+
Methanol	—	—	+/-

+ soluble; +/- partially soluble; — insoluble

Morphologies of Pure PVDF and Blend PVDF Membranes

The SEM images of the pure and blend PVDF membranes are given in Fig. 5. For the separation surfaces, a tendency toward larger average pore size and porosity with the addition of amphiphilic comb-shaped copolymer SHMI-*g*-PEGMA was observed, which increased with the content increase of SHMI-*g*-PEGMA in cast solution. On the other hand, since deionized water was used as the coagulation bath, all the membranes exhibited macrovoid formation in the cross-sections, and the macrovoids were larger in the blend membranes than in pure PVDF membrane. This result may be expected based on ternary diffusion models^[30], which relate macrovoid formation to instantaneous liquid-liquid de-mixing during coagulation. The presence of the amphiphilic SHMI-*g*-PEGMA component in the casting solutions might be expected to increase the affinity of the casting solution and precipitant, enhancing solvent-nonsolvent exchange and creating the conditions for instantaneous de-mixing and associated macrovoid formation. As a result, the ability of enhancing solvent-nonsolvent exchange and creating the conditions for instantaneous de-mixing becomes stronger with the content increase of SHMI-*g*-PEGMA in cast solutions, and consequently, the size of the macrovoids becomes larger.



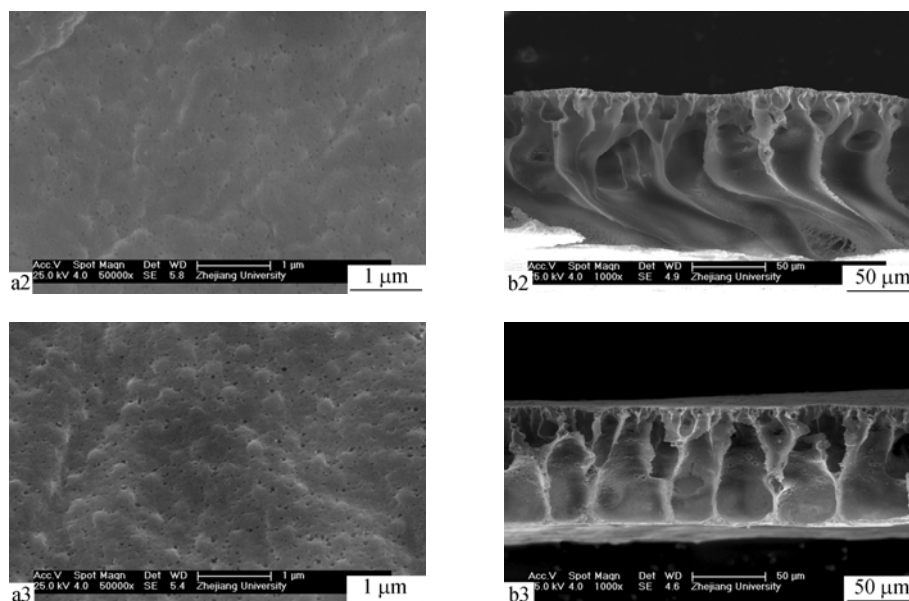


Fig. 5 SEM micrographs of PVDF (a: top surface, b: cross-section) and SHMI-*g*-PEGMA/PVDF blend membranes (a1, a2, a3: top surfaces of M1, M2, M3; b1, b2, b3: cross-sections of M1, M2, M3)

The Hydrophilicity of Pure PVDF and Blend PVDF Membranes

Surface hydrophilicity is one of the most important factors to the filtration membrane, and much attention has been paid to it^[31, 32]. Usually, the most convenient way to obtain the relative hydrophilicity of a polymer membrane surface is the contact angle measurement. The static contact angle of pure PVDF membrane and blend PVDF membranes are shown in Fig. 6. We can infer from the result that the initial contact angles of blend PVDF membranes decreased greatly with the ratio increase of SHMI-*g*-PEGMA in the membrane. The pure PVDF membrane has an initial contact angle of 95°, while the initial contact angle of M3 membrane decreases to 58°. We can also see that the contact angles on the pure PVDF membranes almost remain stable during the contact time. However, the contact angle on the blend PVDF membranes reduces gradually within the measurement time. With the ratio increase of SHMI-*g*-PEGMA in blend membranes, the decreasing rate of contact angle increased. So we can infer that SHMI-*g*-PEGMA can not only increase the hydrophilicity of membrane surface, but also hydrophilicity within pores.

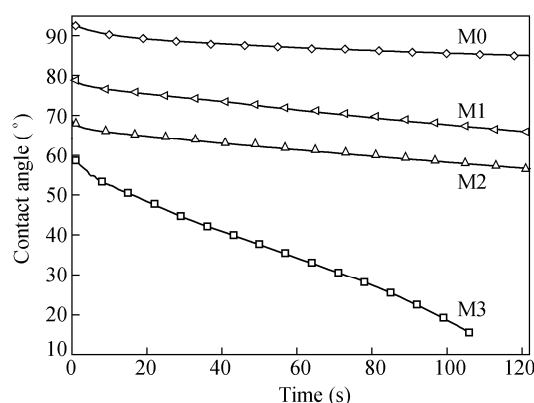


Fig. 6 Time dependence of water contact angle on the membrane surfaces

Filtration Performance

To investigate the fouling resistance of the prepared membranes, after testing the pure water flux, a protein solution permeation process was conducted in this study, and BSA was used as a model protein. After that, the membranes were cleaned, and pure water fluxes were measured again. The results are compared in Fig. 7. Since pure PVDF membrane had a relatively dense surface, very small water flux ($62 \text{ L}/(\text{m}^2\text{h})$) was obtained. At the meantime, the limited number of pores on the surface of pure PVDF membrane results in a dramatic loss of the flux after the foulant solution permeation experiment. The SHMI-*g*-PEGMA/PVDF blend membranes have the higher water fluxes, and the loss of the foulant solution fluxes is not as serious as that of pure PVDF membrane, which might be ascribed to the increase of pore size and porosity on the surface of SHMI-*g*-PEGMA/PVDF blend membranes. Though considerable loss of foulant solution fluxes was also observed for M1, M2 and M3, the water flux can be mostly recovered after the membranes were cleaned by deionized water. And the J_R was increased with the content of SHMI-*g*-PEGMA increasing in blend membranes. Many researches have revealed that if the water state on the surface is similar to an aqueous solution or the free water fraction is high, the protein irreversible adsorption could be reduced effectively^[33, 34]. In this study, the enrichment of the amphiphilic polymer SHMI-*g*-PEGMA might be expected to increase the free water content at membrane surface. Thus, protein molecules have little or no conformational change when they approach the membrane surface. Therefore, irreversible protein adsorption or deposition is decreased greatly, and the water flux can be sufficiently recovered after water washing. As a result, the SHMI-*g*-PEGMA increased the permeation and antifouling properties of PVDF membrane greatly.

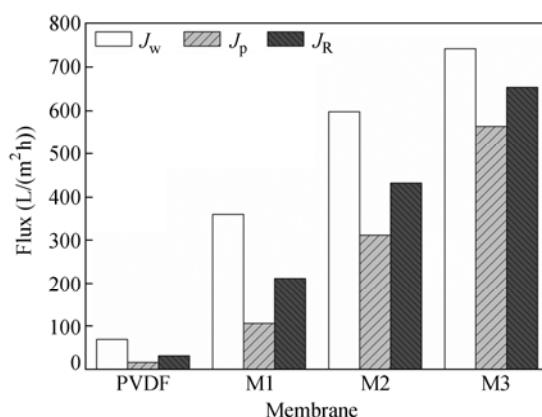


Fig. 7 Pure water and BSA solution fluxes of the membranes

CONCLUSIONS

A novel comb-shaped copolymer SHMI-*g*-PEGMA has been successfully synthesized by atom transfer radical polymerization (ATRP). This amphiphilic copolymer was synthesized by styrene-(*N*-(4-hydroxyphenyl) maleimide) alternating copolymer (SHMI) and PEGMA. The molecular weight of SHMI-*g*-PEGMA (M_n) is 13100. The decomposition temperature of SHMI-*g*-PEGMA is lower than that of SHMI, and the graft ratio of PEGMA in the SHMI-*g*-PEGMA is 18.6 wt%. The solubilities of copolymers in different organic solvents showed that SHMI, SHMI-Br and SHMI-*g*-PEGMA had excellent solubility in polar solvents, such as DMF, DMSO and NMP. However, SHMI-*g*-PEGMA had higher solubilities in H₂O and methanol and lower solubility in CHCl₃ than SHMI and SHMI-Br. The surface and cross-section morphology of pure PVDF and SHMI-*g*-PEGMA/PVDF blend membranes were characterized *via* SEM, and the hydrophilicity of membranes was characterized by water contact angle. The results showed that the content increase of SHMI-*g*-PEGMA in cast solutions can increase the pore size, porosity and the hydrophilicity of blend membranes. The filtration

performance of pure PVDF and SHMI-*g*-PEGMA/PVDF blend membranes shows that the enrichment of amphiphilic polymer SHMI-*g*-PEGMA on the surface of PVDF membranes increases the permeation and antifouling properties of SHMI-*g*-PEGMA/PVDF blend membranes.

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