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Amphiphilic ABA copolymers used for surface modification of polysulfone membranes, Part 1: Molecular design, synthesis, and characterization

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ABSTRACT

Two kinds of novel amphiphilic ABA copolymers, which are suitable for surface modification of polysulfone membranes, were successfully synthesized via the atom transfer radical polymerization (ATRP) technique, using a bromo-terminated difunctional polysulfone as macroinitiator. Firstly, the difunctional polysulfone macroinitiator was prepared by esterifying the phenolic end groups of polysulfone to α-haloesters. Secondly, the macroinitiator was used to initiate the polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA) and 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (MAIpG), resulting in two kinds of ABA copolymers, i.e., P(PEGMA)-*b*-PSF-*b*-P(PEGMA) and PMAIpG-*b*-PSF-*b*-PMAIpG, respectively. In the case of PMAIpG-*b*-PSF-*b*-PMAIpG, the isopropylidenyl groups of the protected sugar residues were removed by acidolysis treatment, thus the amphiphilic ABA copolymer, PMAG-*b*-PSF-*b*-PMAG, was obtained. The resultant copolymers were characterized by FT-IR, ^{1}H NMR, GPC, and TGA. Semipermeable polysulfone membranes prepared via the standard immersion precipitation phase inversion process, using the synthesized amphiphilic ABA copolymers as additives, display enhanced hydrophilicity and protein resistance compared to unmodified polysulfone membranes.

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1. Introduction

Polysulfone (PSF) is one of the most popular synthetic polymer materials used for fabrication of membranes because of its excellent properties such as chemical inertness, thermal stability, and mechanical strength. To date, PSF membrane has been applied to micro-/ultra-filtration, gas separation, pervaporation, hemodialysis, plasma separators, membrane oxygenators, cell culture, bioartificial organs, and so on [1–8]. However, the hydrophobic nature of PSF is undesirable in the filtration of protein containing solutions and blood-contacting applications. The adsorption of protein onto PSF membrane leads to irreversible fouling on membrane surface as well as the internal pore, and thus reduces the permeation flux and selectivity [9,10]. In blood-contacting applications, the adsorption of serum protein onto PSF membrane can cause life-threatening complications [2]. The irreversible fouling on hydrophobic membrane can be explained by the specific hydrophobic–hydrophilic interaction between membrane surface and the organics in feed solutions [11]. In the past decades, many investigations have demonstrated that hydrophilic modification of hydrophobic membrane was an efficient strategy to abate membrane fouling. By this reason, a variety of methods including coating, adsorption, plasma treatment, and surface grafting polymerization have been explored to fabricate hydrophilic PSF membrane [12–15]. Despite these methods are successful in preparation of hydrophilic PSF membrane, they suffer from the shortcomings such as the hydrophilic coated or grafted surface layers have limited long-term stability, the changes of pore sizes and pore size distributions after coating and grafting, and the required additional processing steps during membrane fabrication.

An alternative approach to prepare hydrophilic membranes is blending hydrophilic polymer with the hydrophobic membrane materials. The commonly used hydrophilic polymers are poly(vinyl pyrrolidone) (PVP) and poly(ethylene glycol) (PEG). To date, blend of PSF with PVP or PEG has been extensively studied for preparation of semipermeable membranes via the standard immersion precipitation phase inversion process [16–18]. Immersion precipitation phase inversion process is a classical method for fabrication of semipermeable polymer membranes, which is that polymer solution is firstly cast on a substrate, and then the polymer film on the substrate is immersed and precipitated in water bath. Because PVP and PEG are water soluble, most of PVP or PEG is leached out from membrane matrix during the membrane formation process, thus, there is only a small portion of PVP or PEG is retained in membrane matrix and surface. In recent years, surface modification of polymer membrane via self-organizing of amphiphilic copolymers has

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received considerable attention because it has been demonstrated to be a facile and versatile strategy to fabricate membranes with enhanced and tailored surface properties [19–22]. The typical characteristic of this method is that the amphiphilic copolymer additives can preferentially segregate to the separation surface of 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. One advantage of this method is that fabrication and surface modification of membrane can be accomplished in one step, avoiding extra processing steps. 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.

The key for surface modification of membrane using amphiphilic copolymer as additives is that the hydrophobic compositions of the additives should be miscible with membrane materials. With this in mind, Hancock et al. [23] prepared amphiphilic linear multiblock and ABA triblock copolymers having hydrophobic PSF blocks and hydrophilic PEO segments (i.e., PSF-*b*-PEO) and used these copolymers as additives to prepare hydrophilic PSF membranes. Another example is Park et al.'s [24] synthesis of amphiphilic comb copolymers having PSF backbone and PEO side chains (i.e., PSF-*g*-PEO) and blended it with PSF to fabricate hydrophilic PSF membranes. These studies demonstrated that amphiphilic PSF copolymer was a class of promising membrane additives. From the synthesis methodology point of view, PSF-*b*-PEO was synthesized via polycondensation and PSF-*g*-PEO was synthesized via Williamson coupling reaction. It is difficult to tune the chemical composition and the hydrophilic/hydrophobic component ratio of amphiphilic PSF copolymers through these methods because of the reaction mechanisms. Fortunately, Gaynor and Matyjaszewski [25] developed a novel strategy to prepare ABA block copolymers having PSF segment via the atom transfer radical polymerization (ATRP) technique, using a difunctional PSF as macroinitiator. In the light of this study, various amphiphilic copolymers having PSF block and structurally well-defined hydrophilic segments can be synthesized conveniently by using this method due to the versatile and "living"/controlled nature of ATRP [26–28].

Aiming at preparation of the novel amphiphilic copolymers which are suitable for surface modification of PSF membrane, we designed and synthesized two kinds of ABA copolymers, in which PSF was selected to act as the hydrophobic **B** block, whereas poly[poly(ethylene glycol) methyl ether methacrylate] and poly(3-*O*-methacryloyl-D-glucofuranose) were selected to form the hydrophilic **A** segments. Due to the biocompatibility of PEG and carbohydrates as well as their specific interaction with protein molecules [29–35], we believe that the amphiphilic copolymers which contain hydrophobic PSF block and structurally well-defined hydrophilic PEG or glycopolymer segments will be an interesting biomaterials. The semipermeable membranes prepared from these materials could be used in various applications such as water filtrations and biotechnology. Moreover, the reactive hydroxyl groups in the glycopolymer segments make it possible to further functionalize this material. On the other hand, the surface segregation of amphiphilic additives depends to a large extent on their ability to migrate through the membrane matrix to the surface. An important determinant of the rate of migration is how entangled the additives is with the matrix, and this in turn is dependent on the molecular structure and molecular weight of the additives. For this reason, it will be very interesting to investigate how these amphiphilic ABA additives affect the morphology and performance of the modified PSF membranes. In the current paper, we mainly focus on the synthesis and characterization of the amphiphilic ABA copolymers. The hydrophilicity and protein resistance of the PSF membrane modified by these amphiphilic ABA copolymers were also preliminarily investigated. The details of using these novel amphiphilic ABA copolymers as additives to fabricate functional PSF membrane will be presented in the forthcoming reports.

2. Experimental

2.1. Materials

Poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n = 475$ g/mol), methacrylic anhydride (MA, 98%), 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (IpG) (98%), anhydrous pyridine, CuCl (99%), 4,4′-dimethyl-2,2′-dipyridyl (DMDP) (99%), and 2-bromoisobutyryl bromide (98%) were purchased from Aldrich Chemical Company and were used as-received. Bisphenol A, 4,4′-dichlorophenyl sulfone, 1-methyl-2-pyrrolidinone (NMP), toluene, potassium bicarbonate (K_2CO_3), sodium hydroxide (NaOH), anhydrous sodium sulfate (Na_2SO_4), methylene dichloride (CH_2Cl_2), triethylamine (TEA), anisole, tetrahydrofuran (THF), petroleum ether (boiling point range 30–60 °C), hydrochloric acid (HCl), *N*,*N*-dimethylformamide (DMF), methanol, formic acid (88%), and anhydrous ethyl ether were commercial analytical reagents. 4,4′-Dichlorophenyl sulfone, bisphenol A, DMF, and anisole were purified according to the standard procedures [36]. All other reagents and solvents were used without further purification. Polysulfone P3500 was purchased from Solvay Advanced Polymers Co. and was dried under vacuum at 135 °C for 3.5 h before use. Bovine serum albumin (BSA) and phosphate buffered saline salt were purchased from Shanghai Chemical Regent Company (Shanghai, China) and were used as-received. Deionized water with a resistivity of 18.0 MΩcm was friendly offered by Institute of Microelectronics Technology of Zhejiang University (China).

2.2. Synthesis of 3-O-methacryloyl-1,2:5,6-di-O-isopropylidene-D-glucofuranose (MAIpG)

MAIpG monomer was synthesized via a slight modification of the strategy published previously [37]. Briefly, to a stirred solution of IpG (15.0 g, 57.6 mmol) in 80.0 ml of anhydrous pyridine, 15.0 ml (100.5 mmol) of methacrylic anhydride was added dropwise at room temperature. The mixture was then heated at 65 °C for 8 h and for another 4 h after the addition of 60 ml deionized water. After stirring overnight at ambient temperature, the reaction mixture was extracted three times with petroleum ether (boiling point range 30–60 °C, 3×80 ml). The combined extracts were washed with 5 wt% aqueous NaOH solution (4×80 ml) and deionized water (3×100 ml) and dried over anhydrous sodium sulfate. After the solvent was evacuated off, the crude product was purified twice by recrystallizing from ultra-saturated petroleum ether solutions to yield MAIpG monomer as colorless transparent crystals. The obtained MAIpG crystals were further dried under vacuum at room temperature for 24 h prior to use.

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.31 (s, 6H, $2CH_3$), 1.41 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 4.05, 4.08, 4.25, 4.54, 5.30, 5.89 (7H, sugar moiety), 5.63, 6.13 (s, 2H, CH_2=C<). Elemental analysis: calculated for $C_{16}H_{24}O_7$: C 58.51, H 7.38. Found: C 58.64, H 7.36.

2.3. Synthesis of dihydroxy-terminated polysulfone (HO–PSF–OH) and bromo-terminated difunctional polysulfone macroinitiator (Br–PSF–Br)

HO–PSF–OH was synthesized via a slight modification of the method reported elsewhere [25]. In a typical experiment, bisphenol A (13.4 g, 58.5 mmol), 4,4′-dichlorophenyl sulfone (14.1 g, 49.0 mmol), NMP (125 ml) and toluene (100 ml) were introduced to a 500 ml three-neck round bottom flask equipped with a Dean–Stark trap, reflux-condenser, mechanical stirrer, and thermometer. After the homogeneous solution was obtained, K_2CO_3 (20.5 g,

Table 1
Compositions of membrane casting solutions

Chemicals	g/100 g of casting solution										
	M0	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5
Polysulfone (P3500)	22	22	22	22	22	22	22	22	22	22	22
P(PEGMA)-*b*-PSF-*b*-P(PEGMA)	0	0.45	0.92	1.41	1.92	2.45	0	0	0	0	0
PMAG-*b*-PSF-*b*-PMAG	0	0	0	0	0	0	0.45	0.92	1.41	1.92	2.45
NMP	78	77.6	77.1	76.6	76.1	75.6	77.6	77.1	76.6	76.1	75.6

147 mmol) was then added. The reaction mixture was stirred at 155 °C for 4.5 h under nitrogen atmosphere, and then was heated to 190 °C for 12 h. Water was removed from the reaction mixture as a water/toluene azeotrope and collected in the Dean–Stark trap. The viscous polymer solution was then cooled to room temperature and precipitated into an excess of water/methanol (v/v = 1:1) with sufficient HCl to neutralize residual K_2CO_3. The precipitates were recovered by filtration. The obtained polymer was further purified by precipitating twice from THF into water/methanol, and then dried under vacuum overnight at 40 °C.

Br–PSF–Br macroinitiator was prepared by esterifying the dihydroxyl terminal polysulfone with 2-bromoisobutyryl bromide at room temperature in the presence of TEA, using CH_2Cl_2 as solvent.

2.4. Synthesis of *P(PEGMA)*-b-*PSF*-b-*P(PEGMA) and PMAIpG*-b-*PSF*-b-*PMAIpG*

Br–PSF–Br (5.0 g) was firstly dissolved in NMP (15 ml) in a single-neck round bottom flask (50 ml) at room temperature and then transferred to a 100 ml nitrogen-filled Schlenk flask, after which PEGMA monomer (6.0 g), CuCl (90 mg, 0.90 mmol) and DMDP (378.6 mg, 2.05 mmol) were added, the flask was sealed with rubber septum, and argon gas was bubbled through the reaction mixture for 30 min while magnetic stirring. Three circles of freeze–pump–thaw were used to degas the system. The reaction flask was charged with argon at room temperature and then placed into an oil bath preheated to 90 °C, and the reaction was allowed to proceed for 20 h. The resultant copolymer was precipitated into a mixture of methanol and deionized water (v/v = 1:1) and then recovered by filtration. The copolymer was further purified by thrice redissolving in NMP and reprecipitaing in methanol/water. Finally, the copolymer was dried under vacuum at 35 °C for 48 h.

To synthesize PMAIpG-*b*-PSF-*b*-PMAIpG, the reaction mixture, containing Br–PSF–Br (6.0 g), MAIpG (12.8 g), anisole (40 ml), CuCl (0.15 g), and DMDP (0.828 g), was charged to an argon-filled Schlenk flask (100 ml). The reaction mixture was bubbled with argon gas for about 30 min and then the flask was sealed with a rubber septum. Polymerization was carried out at 90 °C while stirring. After 28 h, the reaction mixture was cooled to ambient temperature, diluted with 30 ml of THF, passed through Al_2O_3 column, and precipitated into the methanol/petroleum ether mixture (v/v = 1:1). After being reprecipitated thrice from THF into methanol/petroleum ether mixture, the copolymer was recovered by filtration and dried under vacuum at 35 °C for 24 h, and 14.1 g of copolymer was finally obtained.

2.5. Preparation of *PMAG*-b-*PSF*-b-*PMAG*

PMAIpG-*b*-PSF-*b*-PMAIpG (10 g) was introduced to formic acid (88%, 800 ml) and stirred for 48 h at ambient temperature. After 400 ml of deionized water was added, the mixture was stirred for another 3.5 h. The mixture was concentrated under reduced pressure and then was precipitated in an excess of anhydrous ethyl ether. The precipitates were recovered by filtration and were further purified by thrice reprecipitating from DMF into water/methanol (v/v = 1:1) mixture, and then dried under vacuum at room temperature for 48 h.

2.6. Preparation of PSF membranes, using the amphiphilic ABA copolymers as additives

PSF membranes were fabricated via immersion precipitation process. Firstly, casting solutions were prepared by dissolving polysulfone P3500 in NMP, using P(PEGMA)-*b*-PSF-*b*-P(PEGMA) or PMAG-*b*-PSF-*b*-PMAG as additive. The compositions of casting solutions are listed in Table 1. After the homogeneous solutions were obtained, the casting solutions were left for 6 h to allow complete release of bubbles. Secondly, the casting solutions were cast on glass plates using a 150 μm gate-size stainless steel knife. The glass plates were then left in air for 45 s and immersed in a coagulation bath of 90 °C deionized water. The obtained membranes were washed thoroughly with deionized water, and then were dried in air at ambient temperature.

2.7. Characterization

After dispersion in KBr, FT-IR spectra of the copolymer samples were measured on a Bruker Vector 22 FT-IR Spectrometer. ^{1}H NMR spectra were recorded on an Avance DMX 500 spectrometer (Bruker, Germany) operated at 500 MHz. $CDCl_3$, DMSO-d_6 and tetramethylsilane (TMS) were used as solvents and internal standard, respectively. Molecular weights and molecular weight distributions (i.e., polydispersity index, PDI) were measured by Waters gel permeation chromatography (GPC) system consisting of a Waters 1525 pump, three Waters Styragel columns (Styragels 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. The calibration curve was made with PS standards. Thermogravimetric analysis (TGA) characterization was carried out in dry nitrogen atmosphere using a Perkin–Elmer Pyris 1 calorimeter (Germany) and the TGA thermograms were recorded while heating from 50 °C to 800 °C at 10 °C/min.

The separation surface and cross-sectional morphologies of the neat PSF membrane and the PSF membranes modified by ABA copolymer were observed by scanning electron microscopy (SEM) via using a Sirion-100 FEI electron microscopy. The membranes were fractured in liquid nitrogen and were fixed on the sample plates by double-sided adhesive tape. A thin layer of gold was sputtered on the membranes before SEM analysis.

The static water contact angles on modified and unmodified PSF membranes were measured at room temperature and 65% relative humidity using a contact angle goniometer (OCA20, Dataphysics Instruments with GmbH, Germany). Each contact angle presented is the average of at least 10 separate measurements from different surface locations.

To evaluate the protein resistance of the modified and unmodified PSF membranes, BSA was selected as model protein. Membrane samples were cut into a round shape with 25 cm^2 of area and were washed with phosphate buffered saline salt solution (PBS,

0.1 M, pH = 7.3) for five times. The washed membranes were immersed in 10 ml of 1.5 mg/ml BSA solution. The pH of BSA solution was adjusted to 7.3 with 0.1 M PBS. The BSA solutions containing PSF membranes were incubated at room temperature for 24 h to establish adsorption equilibrium. The concentration of BSA in the solution before and after contact with PSF membranes was determined by a UV–vis spectrophotometer (UV-1601, Shimadzu, Japan), and the appearance of adsorbed BSA value on membrane was calculated.

3. Results and discussion

An ongoing challenge in membrane science is the preparation of membranes with specific surface properties of hydrophilic materials such as hydrophilicity, wettability, and biocompatibility, while retaining the advantageous mechanical properties of the hydrophobic materials. Blending amphiphilic polymer with hydrophobic membrane materials is a simple and efficient method to obtain new membranes with designed properties [19–24]. Herein, we report the synthesis of two amphiphilic ABA copolymers which have PSF as hydrophobic **B** block and P(PEGMA) or PMAG as hydrophilic **A** segment. The synthesis routes of MAIpG monomer, bromo-terminated difunctional PSF macroinitiator, and amphiphilic ABA copolymers are schematically illustrated in Fig. 1. In summary, the amphiphilic copolymers were prepared via two steps: (1) synthesis of Br–PSF–Br macroinitiator. To obtain Br–PSF–Br, a dihydroxy-terminated PSF was firstly prepared by the condensation polymerization of 4,4′-dichlorophenyl sulfone and bisphenol A, with bisphenol A in slight excess to synthesis a polymer with phenolic end groups. The HO–PSF–OH obtained was then reacted with 2-bromoisobutyryl bromide to transform the phenolic end groups of PSF to α-haloesters. (2) Synthesis of amphiphilic copolymers, P(PEGMA)-*b*-PSF-*b*-P(PEGMA) and PMAG-*b*-PSF-*b*-PMAG, by ATRP technique, using Br–PSF–Br as macroinitiator and CuCl/DMDP as catalyst system.

3.1. Synthesis of Br–PSF–Br macroinitiator

Up to now, commercial polysulfone is basically synthesized through the polycondensation between bisphenol A and 4,4′-dichlorophenyl sulfone or 4,4′-difluorophenyl sulfone. To prepare the dihydroxyl-terminated polysulfone, HO–PSF–OH, bisphenol A was added in slight excess over the amount of 4,4′-dichlorophenyl sulfone. The FT-IR spectra for HO–PSF–OH and Br–PSF–Br are presented in Fig. 2. The absorption peak at 3440 cm^{-1} in spectrum (a) is assignable to the phenolic end groups of HO–PSF–OH. After esterified with 2-bromoisobutyryl bromide, the absorption peak of phenolic end groups (3440 cm^{-1}) in spectrum (a) disappeared, while a new absorption peak at 1740 cm^{-1} which was ascribed to C═O stretching vibration of the ester groups appeared [see spectrum (b)].

The ^{1}H NMR spectra for HO–PSF–OH and Br–PSF–Br are shown in Fig. 3. From Fig. 3, it can be seen that after the esterification reaction between 2-bromoisobutyryl bromide and HO–PSF–OH, the peak at the chemical shifts of 6.79 ppm which can be assigned to the hydroxyl (–*OH*) protons of the phenolic end groups of HO–PSF–OH was completely disappeared [spectrum (1)], while a new peak at the chemical shifts of 2.05 ppm which can be assigned to methyl protons (–CH_3) of 2-bromopropionyloxy groups of Br–PSF–Br appeared [spectrum (2)], these results suggest that the phenolic end groups of HO–PSF–OH have been actually converted to 2-bromopropionyloxy groups [25].

3.2. Synthesis of P(PEGMA)-b-PSF-b-P(PEGMA) and PMAG-b-PSF-b-PMAG

The ATRP synthesis of P(PEGMA)-*b*-PSF-*b*-P(PEGMA) and PMAG-*b*-PSF-*b*-PMAG was carried out by using Br–PSF–Br as initiator and CuCl/DMDP as catalyst. After repeated purification, the resultant copolymers were characterized by FT-IR, ^{1}H NMR, GPC, and TGA. The FT-IR spectrum for P(PEGMA)-*b*-PSF-*b*-P(PEGMA) is shown in Fig. 2 [spectrum (c)]. Compared to the spectrum for Br–PSF–Br [spectrum (b)], two new adsorption bands at ~2917 cm^{-1} and ~3505 cm^{-1} are appeared in the spectrum for P(PEGMA)-*b*-PSF-*b*-P(PEGMA). The adsorption band at ~2917 cm^{-1} can be assigned to the C–H stretching vibration of –CH_2– group in P(PEGMA) combs, while the broad adsorption band at ~3505 cm^{-1} can be ascribed to the H_2O molecules adsorbed on the PEG segments of P(PEGMA). It is very difficult to completely remove H_2O from P(PEGMA)-*b*-PSF-*b*-P(PEGMA) since PEG is extremely hydrophilic. Moreover, the hydrophilic nature of PEG makes P(PEGMA)-*b*-PSF-*b*-P(PEGMA) susceptible to moisture when it is exposed to air.

The FT-IR spectra for Br–PSF–Br, PMAIpG-*b*-PSF-*b*-PMAIpG, and PMAG-*b*-PSF-*b*-PMAG are shown in Fig. 4. Fig. 4 shows that the spectrum for PMAIpG–PSF–PMAIpG [spectrum (b)] is very similar to that for Br–PSF–Br [spectrum (a)] since the C–H adsorption bands of isopropylidenyl group on the pendent sugar moiety were overlapped with the adsorption bands of methyl group on PSF backbone. After acidolysis treatment, a new broad absorption peak appears at around 3440 cm^{-1}, which is corresponding to the hydroxyl group formed by the deprotection of the isopropylidenyl groups [spectrum (c)], suggesting the formation of the amphiphilic PMAG–PSF–PMAG copolymer.

Besides FT-IR spectroscopic measurements, the chemical composition of the resultant polymers was further confirmed by ^{1}H NMR analysis. As shown in Fig. 5, the ^{1}H NMR spectrum for P(PEGMA)-*b*-PSF-*b*-P(PEGMA) showed peaks with chemical shift as follows [25,38]: the H of Ar–H in PSF backbone showed a chemical shift of 6.9–7.9 ppm; the H of the methyl group in the bisphenol A unit showed a chemical shift of 1.69 ppm; the H of methylene group connected to the oxygen atom of the ester group in the methacrylate (i.e., the H labeled as "b" in Fig. 5) showed a chemical shift of 4.1 ppm; the H of methylene group connected to the oxygen atom of ether group in the PEG segment (i.e., the H labeled as "c" in Fig. 5) showed a chemical shift of 3.64 ppm; the chemical shift of the methyl group at the end of PEG chain (i.e., the H labeled as "d" in Fig. 5) is 3.37 ppm. The ^{1}H NMR analysis for P(PEGMA)-*b*-PSF-*b*-P(PEGMA) indicated that PEGMA moiety existed in the synthesized ABA copolymer.

The ^{1}H NMR spectra for PMAIpG-*b*-PSF-*b*-PMAIpG and PMAG-*b*-PSF-*b*-PMAG with the assignment of the peaks are shown in Fig. 6. From Fig. 6, it can be seen that polymerization of MAIpG monomer initiated by Br–PSF–Br macroinitiator resulted in the appearance of peaks in the regions of chemical shifts at 1.25–1.44 ppm and 3.9–6.0 ppm due to the isopropylidene protons and sugar moiety protons of MAIpG [37], respectively [spectrum (1)]. After acidolysis treatment, the signals ascribed to the isopropylidene protons (i.e., the H labeled as "i" in Fig. 6) completely disappear, while the free –*OH* protons of sugar moiety (i.e., the H labeled as "j" in Fig. 6) appear at ~8.2 ppm [39] [spectrum (2)].

The molecular weights and polydispersity index (PDI) for HO–PSF–OH and ABA copolymers, obtained from GPC analysis, are presented in Table 2. Polymerization of PEGMA and MAIpG monomer with bromo-terminated PSF has resulted in a significant increase in molecular weights relative to the HO–PSF–OH. The GPC traces for HO–PSF–OH, P(PEGMA)-*b*-PSF-*b*-P(PEGMA), and PMAIpG-*b*-PSF-*b*-PMAIpG are shown in Fig. 7. Fig. 7 indicates that the ABA copolymer peaks have shorter retention times than the HO–PSF–OH and therefore have higher molecular weights. The number average molecular weights (M_n) of the HO–PSF–OH and ABA copolymers were also estimated from ^{1}H NMR spectra (Figs. 3, 5 and 6) and the results are listed in Table 2. The M_n and polymerization degree (DP) of HO–PSF–OH were determined from

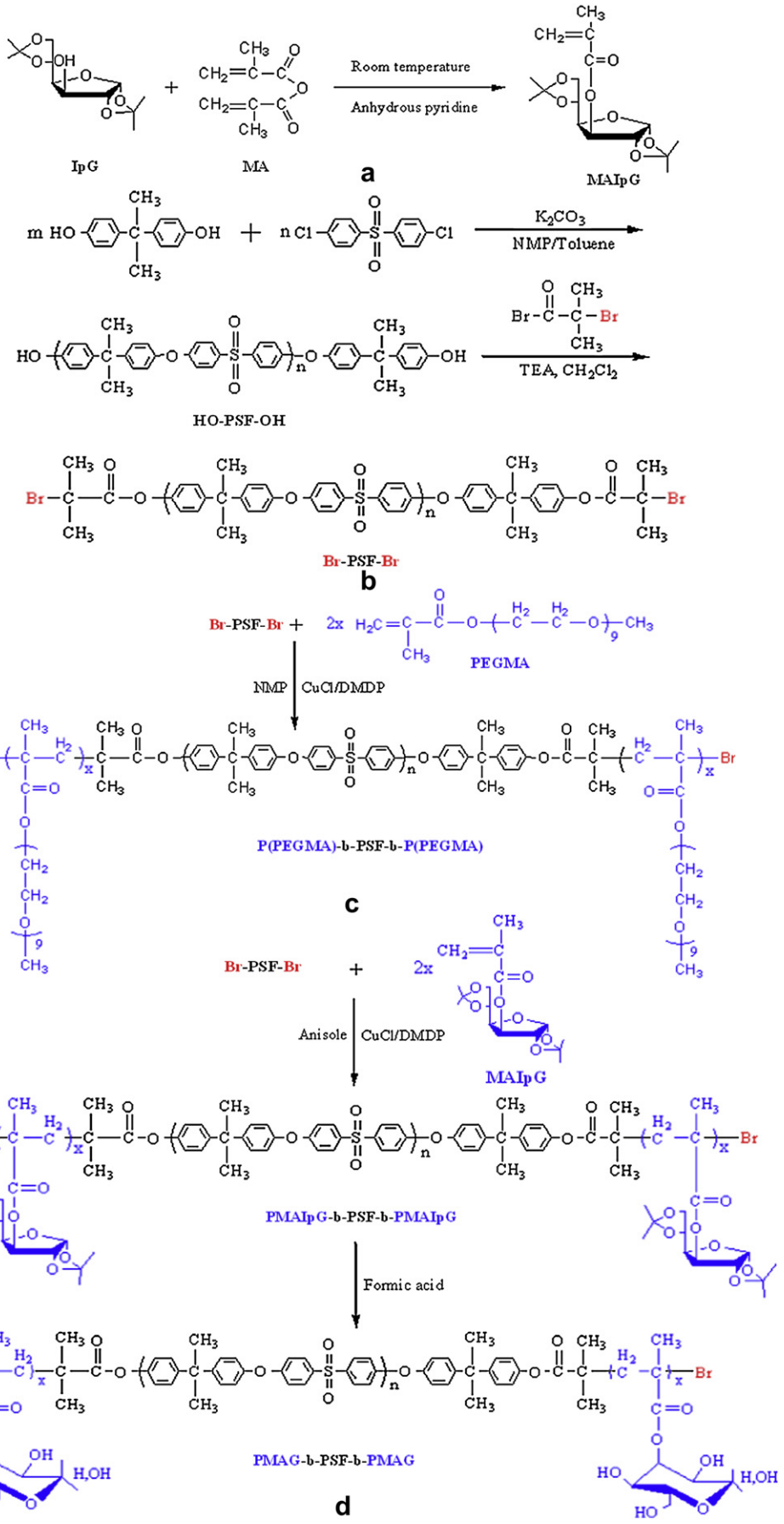

Fig. 1. Schematic illustrating the synthesis of (a) MAIpG monomer, (b) difunctional PSF macroinitiator, (c) P(PEGMA)-*b*-PSF-*b*-P(PEGMA), and (d) PMAG-*b*-PSF-*b*-PMAG.

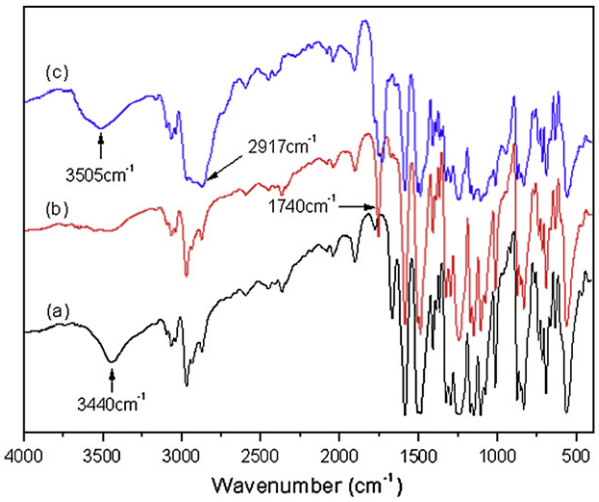

Fig. 2. FT-IR spectra for (a) HO–PSF–OH, (b) Br–PSF–Br, and (c) P(PEGMA)-*b*-PSF-*b*-P(PEGMA).

^{1}H NMR through analysis of the end groups. For P(PEGMA)-*b*-PSF-*b*-P(PEGMA), the M_n was obtained from the product of the DP of PSF and the molar ratio of the $-CH_2-$O of PEG pendent to the aromatic protons of PSF. In the case of PMAIpG-*b*-PSF-*b*-PMAIpG, the M_n was obtained from the product of the DP of PSF and the molar ratio of the protons of sugar moiety to the aromatic protons of PSF.

The thermal stability of the HO–PSF–OH and ABA copolymers was investigated by thermogravimetric analysis (TGA). TGA curves for HO–PSF–OH and P(PEGMA)-*b*-PSF-*b*-P(PEGMA) are shown in Fig. 8. From curve (2) in Fig. 8, it can be seen that while the temperature increased from ~200 °C to ~465 °C, the weight loss of P(PEGMA) [40] segments was about 38.2 wt%, suggesting that the relative molecular weight ratio of P(PEGMA) in P(PEGMA)-*b*-PSF-*b*-P(PEGMA) was approximately 38.2 wt%. In the case of PMAIpG-*b*-PSF-*b*-PMAIpG, a distinct three-region of mass loss was discernible [see curve (3) in Fig. 8]. Firstly, elimination of the sugar pendants commenced at around 210 °C and the weight loss is about 34.9 wt%. The second major weight loss of about 20.5 wt% begun at around 317 °C due to the loss of poly(methacrylate) segments. The third major weight loss commenced at around 380 °C, corresponding to the decomposition of polysulfone block. It is worth to note that while the temperature increased from 100 °C to 380 °C, the weight loss of PMAIpG was about 55.4 wt%, suggesting that the molecular weight ratio of PMAIpG in PMAIpG-*b*-PSF-*b*-PMAIpG copolymer was approximately 55.4 wt%. It seems that curve (2) shows different decomposition temperature for polysulfone compared with (1). However, curve (1) displayed that the decomposition of polysulfone commenced at ~380 °C and finished at ~700 °C. So, the early stage of the decomposition of polysulfone (from ~380 °C to ~465 °C) was overlapped with the decomposition of P(PEGMA). While the decomposition of P(PEGMA) was finished at ~465 °C, the decomposition of polysulfone was continued. This may be the reason for the appearance of curve (2) which shows different decomposition temperature of polysulfone.

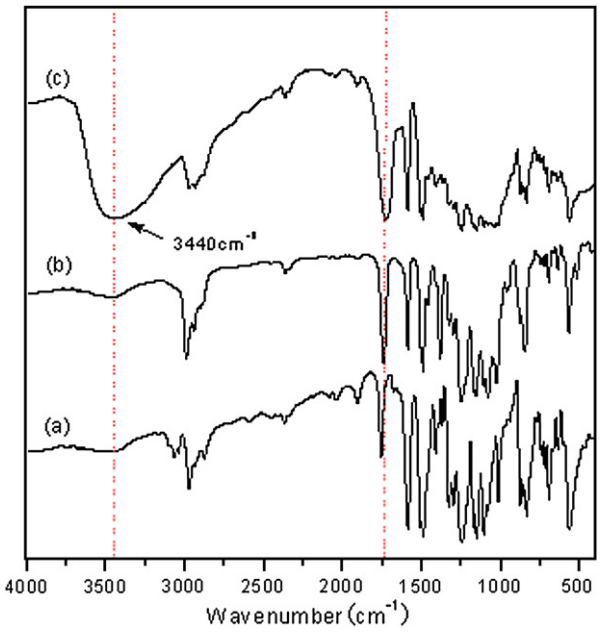

Fig. 4. FT-IR spectra for (a) Br–PSF–Br, (b) PMAIpG-*b*-PSF-*b*-PMAIpG, and (c) PMAG-*b*-PSF-*b*-PMAG.

From the combined FT-IR, ^{1}H NMR, GPC, and TGA analysis results presented hereinbefore, it can be confirmed that P(PEGMA)-*b*-PSF-*b*-P(PEGMA) and PMAIpG-*b*-PSF-*b*-PMAIpG have been successfully

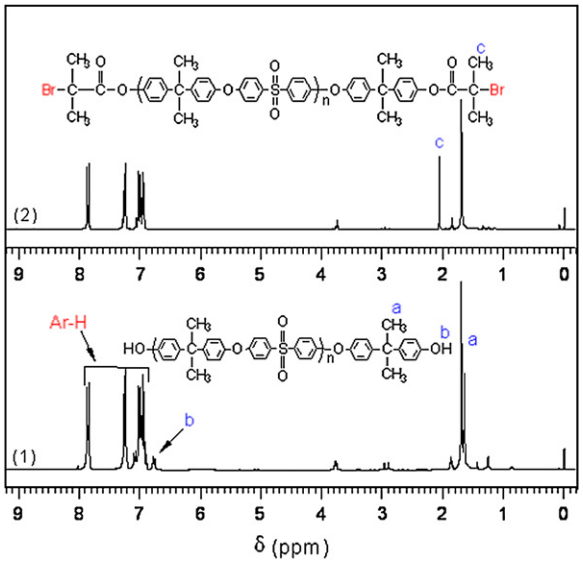

Fig. 3. ^{1}H NMR spectra for (1) HO–PSF–OH and (2) Br–PSF–Br.

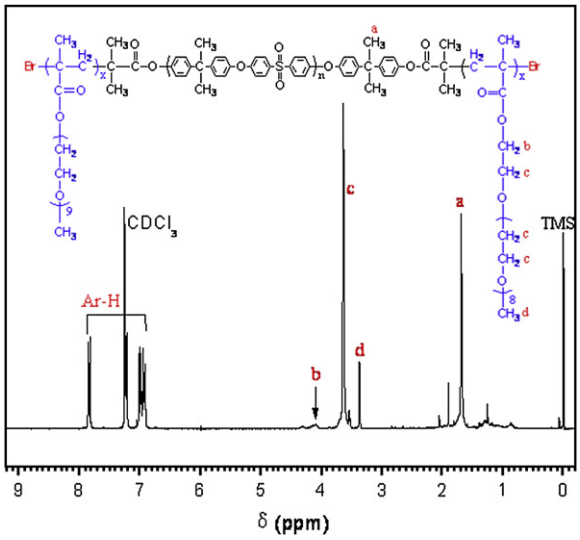

Fig. 5. ^{1}H NMR spectrum for P(PEGMA)-*b*-PSF-*b*-P(PEGMA).

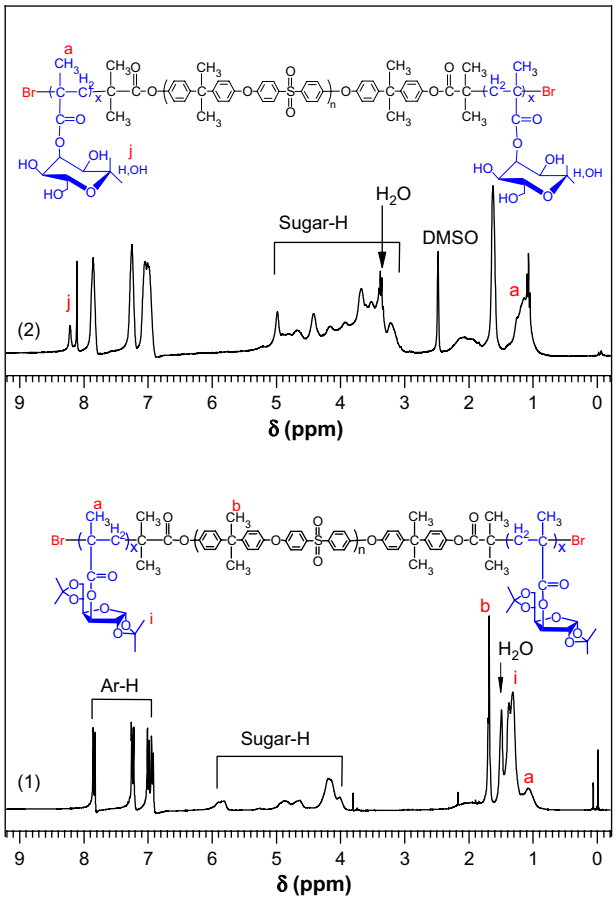

Fig. 6. ^{1}H NMR spectra for (1) PMAIpG-*b*-PSF-*b*-PMAIpG and (2) PMAG-*b*-PSF-*b*-PMAG.

prepared by ATRP, using the difunctional Br–PSF–Br as macroinitiator, under the experimental conditions described in this paper. Moreover, the deprotection of isopropylidenyl groups has been carried out under the presented experimental conditions.

3.3. Membrane morphology

The neat PSF membrane and the PSF membranes modified by P(PEGMA)-*b*-PSF-*b*-P(PEGMA) or PMAIpG-*b*-PSF-*b*-PMAIpG were prepared via the immersion precipitation method. SEM micrographs of the separation surfaces and cross-sections for membranes cast under identical conditions but having different amphiphilic additives are shown in Fig. 9. Both the neat and blend PSF membranes have asymmetric structure, which consist of a dense skin layer and a porous sublayer having a fingerlike structure. However, addition of the amphiphilic ABA copolymer to casting solution results in substantial increase in separation surface

Table 2
Molecular weights and polydispersity index (PDI) for HO–PSF–OH, P(PEGMA)-*b*-PSF-*b*-P(PEGMA), and PMAIpG-*b*-PSF-*b*-PMAIpG

Polymer	GPC molecular weights[a]		Estimated M_n[b] (g/mol)
	M_n (g/mol)	PDI	
HO–PSF–OH	5.6×10^3	1.34	5.18×10^3
P(PEGMA)-*b*-PSF-*b*-P(PEGMA)	8.1×10^3	2.50	7.12×10^3
PMAIpG-*b*-PSF-*b*-PMAIpG	1.25×10^4	1.18	1.16×10^4

[a] Determined by GPC measurements using THF as eluent, calculated based on low polydispersity polystyrene standards.
[b] Estimated from ^{1}H NMR spectra.

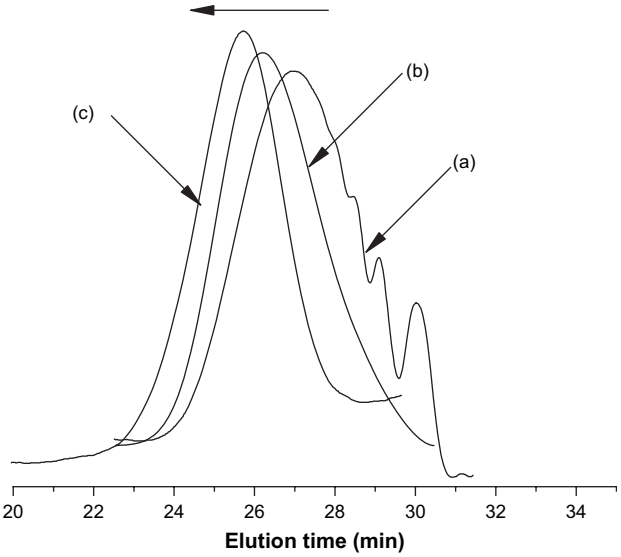

Fig. 7. GPC traces for (a) HO–PSF–OH, (b) P(PEGMA)-*b*-PSF-*b*-P(PEGMA), and (c) PMAIpG-*b*-PSF-*b*-PMAIpG.

porosity, as well as more macrovoid structure in the membrane sublayer. Similar morphological changes have also been observed by the other research groups [19,41]. This enhancement of membrane porosity can provide higher fluxes in the filtration applications.

3.4. Hydrophilicity and protein resistance of PSF membranes modified by the amphiphilic ABA copolymers

The principal objective of this work is to synthesize a series of amphiphilic polymer additives, which when added at low concentrations to the hydrophobic PSF membrane matrix, would spontaneously migrate to membrane surface whereupon the additives would modify the surface properties of the PSF membrane. Contact angle and BSA adsorption measurements are convenient methods for obtaining information about the surface characteristics of membranes. Herein, static water contact angle and static BSA adsorption measurements were performed on PSF membranes containing various concentrations of the amphiphilic ABA

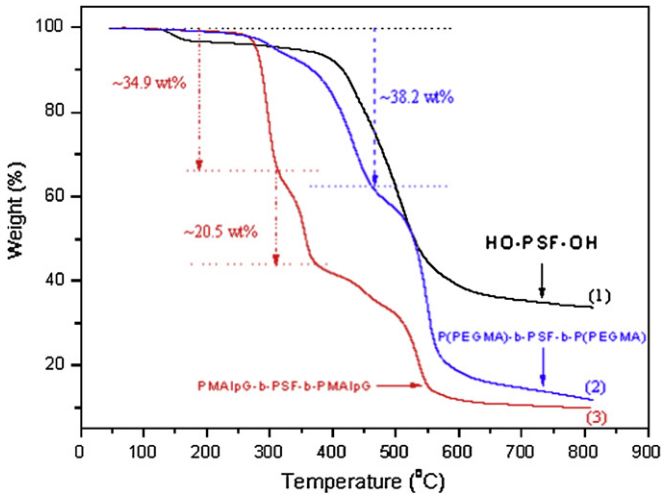

Fig. 8. TGA curves for (1) HO–PSF–OH, (2) P(PEGMA)-*b*-PSF-*b*-P(PEGMA), and (3) PMAIpG-*b*-PSF-*b*-PMAIpG.

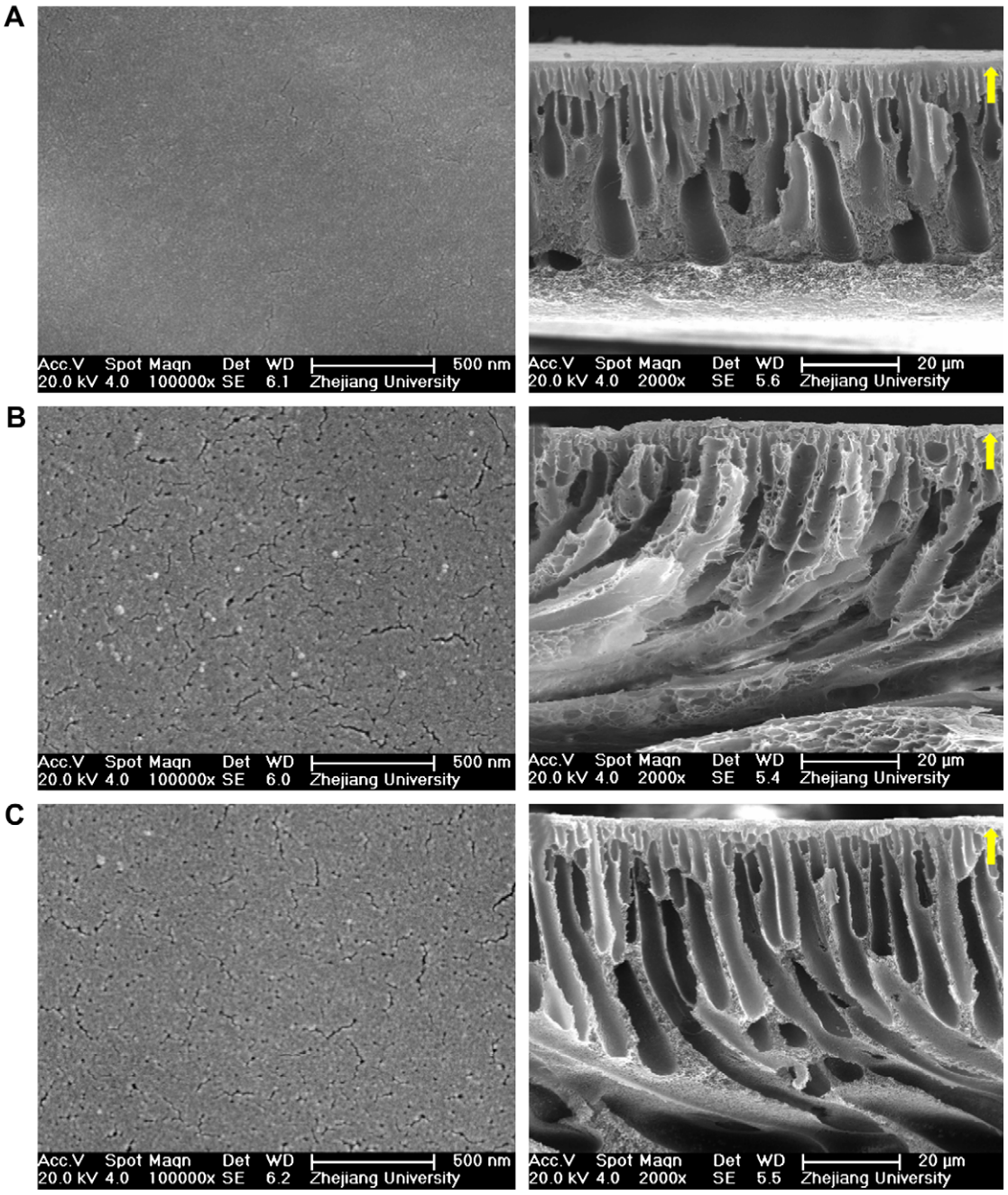

Fig. 9. SEM micrographs of the separation surfaces (left) and cross-sections (right) for (A) the neat PSF membrane and the PSF membranes blended with (B) 4 wt% P(PEGMA)-*b*-PSF-*b*-P(PEGMA) and (C) 4 wt% PMAG-*b*-PSF-*b*-PMAG. Arrows indicate the separation surface.

copolymers synthesized in this paper. By this way we can investigate both the hydrophilicity and the protein resistance of the PSF membrane surface. The water contact angle and BSA adsorption measurement results are shown in Fig. 10. In particular, part (a) of Fig. 10 shows the measurement results for the PSF membrane modified by P(PEGMA)-*b*-PSF-*b*-P(PEGMA), and part (b) of Fig. 10 presents the measurement results for the PSF membrane modified by PMAG-*b*-PSF-*b*-PMAG. The water contact angle and BSA adsorption of unmodified PSF membrane were measured to be ~85° and ~50 μg/cm^2, respectively. It can be seen in Fig. 10 that the addition of even very small amounts (2 wt%) of the amphiphilic copolymers results in a measurable decrease in the water contact angle and BSA adsorption. Moreover, increase in quantities of the amphiphilic copolymer additives results in a steady decrease in the water contact angle and BSA adsorption. These measurement results demonstrate that the PSF membranes modified by P(PEGMA)-*b*-PSF-*b*-P(PEGMA) or PMAG-*b*-PSF-*b*-PMAG display improved surface properties such as hydrophilicity and resistance to BSA adsorption.

4. Conclusion

We have designed and synthesized two kinds of novel amphiphilic ABA copolymers, which contain hydrophobic polysulfone block and hydrophilic poly[poly(ethylene glycol) methyl ether methacrylate] or poly(3-*O*-methacryloyl-D-glucofuranose) segments, by ATRP using a bromo-terminated difunctional PSF as macroinitiator. The difunctional PSF macroinitiator was prepared by conversion of the phenolic end groups of polysulfone to α-haloesters and was used to initiate the polymerization of poly(ethylene

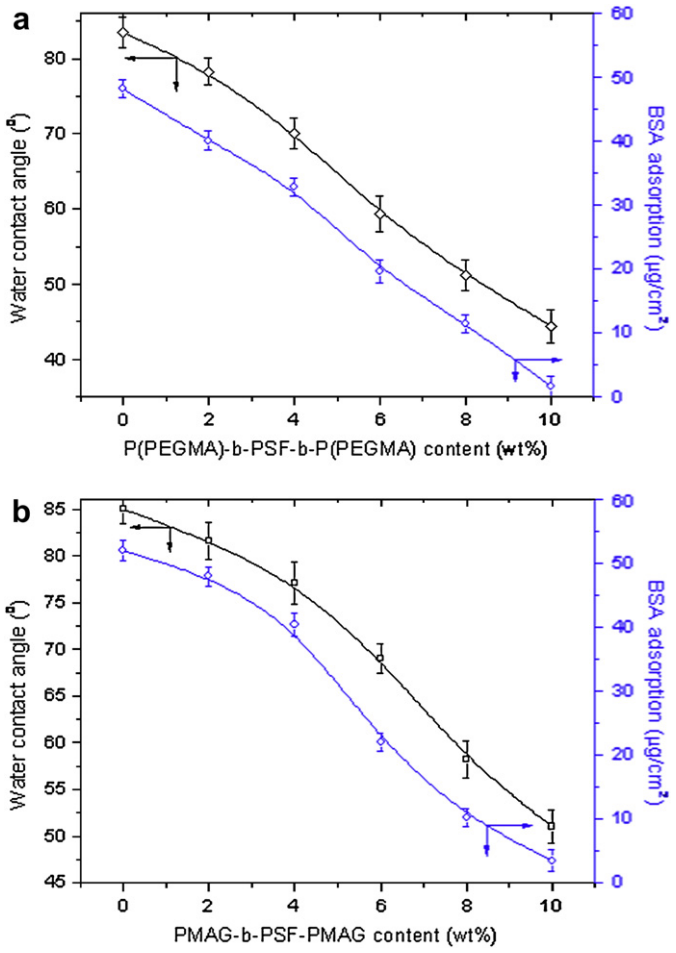

Fig. 10. Static water contact angle and static BSA adsorption measurement results for unmodified and modified PSF membranes: (a) modified by P(PEGMA)-*b*-PSF-*b*-P(PEGMA) and (b) modified by PMAG-*b*-PSF-*b*-PMAG.

glycol) methyl ether methacrylate or 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose monomer. For the copolymer containing protected sugar moiety, after acidolysis treatment, the isopropylidenyl groups of the protected sugar moiety were removed, thus producing the amphiphilic glycopolymer. The chemical composition and molecular structure of the obtained copolymers were confirmed by FT-IR, ^{1}H NMR, GPC and TGA. The use of these amphiphilic ABA copolymers as additives to prepare PSF membranes was also preliminarily explored, the migration of the additives to membrane surface and to modify membrane surface properties was demonstrated by static water contact angle and static BSA adsorption measurements, and experimental results showed that the modified PSF membranes displayed improved surface properties such as hydrophilicity and protein resistance.

Acknowledgements

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References

[1] Haris JE, Johnson RN. In: Mark HF, Bikales NM, Overberger CG, Menges G, editors. Encyclopedia of polymer science and engineering. 2nd ed., vol. 13. NY: John Wiley & Sons; 1988. p. 196–211.
[2] Malchesky PS. Extracorpeal artificial organs. In: Ratner BD, Hoffman AS, Schoen FJ, Lemons JE, editors. Biomaterials science: an introduction to materials in medicine. San Diego: Elsevier Academic Press; 2004. p. 514–26.
[3] Yang YN, Wang P, Zheng QZ. J Polym Sci Part B Polym Phys 2006;44:879.
[4] Lloyd DR. Materials science of synthetic membranes. Washington, DC: ACS; 1985. p. 273–94.
[5] Chrtomir S, Vladimir K, Vojko M, Milan B. J Appl Polym Sci 2005;96:1667.
[6] Bowry SK. Int J Artif Organs 2002;25:447.
[7] Hung MY, Chen SH, Liou RM, Hsu CS, Lai JY. J Appl Polym Sci 2003;90:3374.
[8] Wei YM, Xu ZL, Qusay FA, Wu K. J Appl Polym Sci 2005;98:247.
[9] Ridgway H, Ishida K, Rodriguez G, Safarik J, Knoell T, Bold R. Methods Enzymol 1999;310:463.
[10] Boyd RF, Zydney AL. Biotechnol Bioeng 1998;59:451.
[11] Cornelissen ER, Boomgaard TVD, Strathmann H. J Membr Sci 1998;138:283.
[12] Higuchi A, Sugiyama K, Yoon BO, Sakurai M, Hara M, Sumita M, et al. Biomaterials 2003;24:3235.
[13] Brink LES, Elbers SJG, Robbertsen T, Both P. J Membr Sci 1993;76:281.
[14] Song YQ, Sheng J, Wei M, Yuan XB. J Appl Polym Sci 2000;78:979.
[15] (a) Iwata H, Ivanchenko MI, Miyaki Y. J Appl Polym Sci 1994;54:125;
(b) Kang Guodong, Liu Ming, Lin Bin, Cao Yiming, Yuan Quan. Polymer 2007; 48(5):1165.
[16] Boom RM, Wienk IM, Boomgaard T, Smolders CA. J Membr Sci 1992;73:277.
[17] Marchese J, Ponce M, Ochoa NA, Prádanos P, Palacio L, Hernández A. J Membr Sci 2003;211:1.
[18] Lafreniere LY, Talbot F, Matsuura T, Sourirajan S. Ind Eng Chem Res 1987;26:2385.
[19] Hester JF, Banerjee P, Won YY, Akthakul A, Acar MH, Mayes AM. Macromolecules 2002;35:7652.
[20] Wang YQ, Wang T, Su YL, Peng FB, Wu H, Jiang ZY. Langmuir 2005;21:11856.
[21] Hancock LF. J Appl Polym Sci 1997;66:1353.
[22] Roux SP, Jacobs EP, Reenen AJV, Morkel C, Meincken M. J Membr Sci 2006;276:8.
[23] Hancock LF, Stephen MF, Melissa SZ. Biomaterials 2000;21:725.
[24] Park JY, Acar MH, Akthakul A, Kuhlman W, Mayes AM. Biomaterials 2006;27:856.
[25] Gaynor SG, Matyjaszewski K. Macromolecules 1997;30:4241.
[26] Matyjaszewski K, Xia JH. Chem Rev 2001;101:2921.
[27] Kamigaito Masami, Ando Tsuyoshi, Sawamoto Mitsuo. Chem Rev 2001;101:3689.
[28] Dayananda Kasala, Pi Bong Soo, Kim Bong Sup, Park Tae Gwan, Lee Doo Sung. Polymer 2007;48(3):758.
[29] Halperin A. Langmuir 1999;15:2525.
[30] Prime KL, Whitesides GM. J Am Chem Soc 1993;23:10714.
[31] Besseling NAM. Langmuir 1997;13:2109.
[32] Kobayashi A, Tsuchida A, Usui T, Akaike TA. Macromolecules 1997;30:2016.
[33] Zhu JM, Marchant RE. Biomacromolecules 2006;17:1036.
[34] Okada M. Prog Polym Sci 2001;26:67.
[35] (a) Lee Ren-Shen, Hung Chia-Bin. Polymer 2007;48(9):2605;
(b) Kitajyo Yoshikazu, Imai Tomoko, Sakai Yoko, Tamaki Masaki, Tani Hirofumi, Takahashi Kenji. Polymer 2007;48(5):1237;
(c) Zhen Tian, Meng Wang, Ai-ying Zhang, Zeng-guo Feng. Polymer 2007; 49(2):446.
[36] Armarego Wilfred LE. Purification of laboratory chemicals. 5th ed. Amsterdam: Elsevier; 2003.
[37] Ohno K, Tsui Y, Fukuda T. J Polym Sci Part A Polym Chem 1998;36:2473.
[38] Ting YPR, Lawrence FH. Macromolecules 1996;29:7619.
[39] Gao Chao, Muthukrishnan Sharmila, Li Wenwen, Yuan Jiayin, Xu Youyong, Müller AHE. Macromolecules 2007;40:803.
[40] Wang P, Tan KL, Kang ET, Neoh KG. J Mater Chem 2001;11:783.
[41] (a) Hester JF, Banerjee P, Mayes AM. Macromolecules 1999;32:1643;
(b) Hester JF, Olugebefola SC, Mayes AM. J Membr Sci 2002;208:375.