



Hydrophilic modification of a PSU membrane with block copolymer of PS-b-SBMA

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Received 26 May 2021; Accepted 22 November 2021

ABSTRACT

Sulfobetaine methacrylate (SBMA) is a well-known zwitterionic molecule that can improve the hydrophilic property of hydrophobic membranes such as polysulfone (PSU). However, SBMA is too hydrophilic to dissolve in organic solvents. Hence, it is difficult to modify the polymer membranes via blending with their casting solution. This paper aims to synthesize an amphiphilic block polymers of polystyrene-block-sulfobetaine methacrylate (PS-b-SBMA) which can be well dissolved in organic solvents for membrane casting. The two PS-b-SBMA copolymers with SBMA content >28% were applied as the additives to cast the PSU ultrafiltration membrane. The PS-b-SBMA copolymer modified membranes showed lower contact angles and 3-folds higher water flux recovery after BSA treatment than the parent PSU membrane. Moreover, SEM images showed that the BSA contaminant on the modified membrane surfaces was much less than that on PSU membrane. Thus, such modified membranes can be applied to prevent protein fouling in the process of ultrafiltration.

Keywords: Polymer; Polysulfone; Membrane; Sulfobetaine methacrylate; Anti-fouling

1. Introduction

Polysulfone (PSU) is one of the most popular material for fabricating ultrafiltration and nanofiltration membrane due to the advantages on good mechanical property, hydrolytic stability and dissolubility in organic solvents [1,2]. But PSU membranes were easy to be contaminated for the intrinsic hydrophobicity. The fouling on the membranes led to the reduction of permeation flux and selectivity [3–5], which limited the application of PSU membranes.

In the last decades, many researchers have focused on the surface modification of PSU membranes via plasma treatment [6,7], photografted polymerization [8], etc. The applied nonfouling molecules for modification can be divided into three generations: 2-hydroxyethyl methacrylate (HEMA)-based polymers, PEGylated-based polymers

and zwitterionic-based polymers [9]. The first generation of polyHEMA-based polymers behave poor antifouling performance in undiluted human blood serum and plasma [10,11], while the second generation of PEGylated-based polymers were chemically unstable because of the decomposed PEG and OEG groups in the presence of oxygen and transition metal ions [12–14]. The third generation of zwitterionic polymers which contain phosphorylcholine (PC), sulfobetaine (SB), or carboxybetaine (CB) groups have been paid increasing attention due to the biocompatibility, long-term stability, and high resistance to nonspecific protein adsorption from complex media [15,16]. Among these zwitterionic monomers, sulfobetaine methacrylate (SBMA) is commercially available and much cheaper than 2-methacryloyloxyethyl phosphorylcholine (MPC) and carboxybetaine methacrylate (CBMA) [9]. The polymers

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containing pSBMA chains exhibit better antifouling performance than PEG [17–19] because of the strong capacity to form a hydration layer via electrostatic interaction between zwitterions and water molecules [20]. In this regard, SBMA has been grafted on surfaces of PVDF [21], polypropylene [22] and PSU membrane [23] by surface-initiated atom transfer radical polymerization (SI-ATRP).

Despite of the easy handling of surface modification, it possibly damages the membrane structure. As an example, surface modification of SBMA largely impaired the rejection ability of PSU membrane [23]. Besides, the surface modification cannot reduce the cross-membrane fouling because of the unmodified porous surfaces inside the membrane [24,25]. In this regard, blending membranes with hydrophilic or amphiphilic polymers were used to improve the anti-fouling property of micropores and microchannels inside [25–27]. But unfortunately, SBMA containing polymers were usually too hydrophilic to be solved with hydrophobic PSU together. The only reported SBMA blended membrane is PVDF-g-SBMA as additive to modify the PVDF membrane [28]. To our knowledge, no SBMA block copolymer blended PSU membrane has been reported.

In this paper, polystyrene-block-sulfobetaine methacrylate (PS-b-SBMA) will be synthesized by successive two-steps ATRP. Then the block copolymers will be blended with PSU to prepare the ultrafiltration membranes. Finally, the performance of the modified membranes is compared with the original PSU membrane by evaluating the water contact angle, water flux recovery and BSA rejection. Such SBMA modified membrane is expected to perform better properties on anti-fouling and show potential value in its application.

2. Experimental

2.1. Materials

Styrene (St) was obtained from Sinopharm Chemical Reagent Co. Ltd and distilled under reduced pressure before use. Sulfobetaine methacrylate (SBMA) was purchased from Sigma Co. Ltd and used as received. The ATRP initiator, ethyl 2-bromopropionate, and 2,2'-bipyridyl (bpy) were purchased from Aladdin Co., Ltd., and used without further purification. Copper(I) bromide (CuBr) was stirred in 2% glacial acetic acid aqueous solution overnight, filtered, and washed with absolute acetone under argon atmosphere [29]. All other chemicals were analytical grade and used as received.

2.2. Synthesis of PS-Br macroinitiator

The macroinitiator was synthesized by ATRP with the molar ratio of [styrene]/[ethyl 2-bromopropionate]/[CuBr]/[bpy] = 120:1:1:2. First, a three-necked flask which equipped with a reflux condenser was placed in an oil bath at 10°C after removing oxygen in the-flask. Then, styrene, bpy, and CuBr were added in turn after 20 min. Finally, the initiator was added into flask under argon atmosphere and the temperature of oil bath was increased to 110°C. After 5 h of reaction, it was ended by expose to air and the solution was diluted with 30 mL of THF. The copper complex was

then removed by passing the solution through a column with activated Al_2O_3 . After the diluted solution was precipitated in ten folds of methanol, the precipitate was collected by vacuum filtration and dried in vacuum oven overnight to obtain the final product.

2.3. Synthesis of PS-b-SBMA block copolymers

Three PS-b-SBMA copolymers with different SBMA chain length were synthesized by using different [SBMA]/[PS-Br] molar ratio as listed in Table 1. First, solvent N-methyl pyrrolidone (NMP, 40 mL), macroinitiator PS-Br (0.7 g), monomer SBMA (0.7 g) and bpy (0.06 g) were added in turn under argon atmosphere at 95°C. Then, CuBr (0.03 g) as catalyst was added to accelerate the reaction after 15 min. The reaction was ended by expose the mixture to air after 6 h of reaction. Then the mixture was precipitated in ten folds of methanol, and the precipitate was collected by filtration. The product was washed with 100 mL of methanol for three times to remove solvent NMP and unreacted monomer SBMA. After that, the product was dried in vacuum oven overnight.

2.4. Polymer characterization

Gel permeation chromatography (GPC; Waters 1525/2414, Waters Instrument, MA) operating at room temperature was used to determine the molecular weight of macroinitiator PS-Br. 1H NMR analysis of PS and block copolymers was performed with deuterated chloroform, using a Bruker DPX 500 spectrometer. The FTIR analysis was performed using a Nicolet I5 FTIR spectrometer with mixture of polymer and KBr crystal at ratio of 1:50. The tablet machine was used to obtain the slice when the mixture was grind. Elemental analysis was made on a Vario MICRO cube (Elementar, Germany) to determine the composition of polymer by compare the content of C, H and N.

2.5. Fabrication of PS-b-SBMA blended PSU membranes

The PS-b-SBMA blended PSU membranes were prepared by immersion precipitation phase transformation. To dissolve the copolymers and PSU in the same cast solution, mixture of DMSO and NMP (3:19, v:v) was set as the solvent. PS-b-SBMA₂ and PS-b-SBMA₃ with SBMA content over 28% were used as additives to fabricate the modified membrane 1 and 2, respectively. The PS-b-SBMA and PSU at 15:85 (wt/wt) were dissolved in NMP/DMSO solution at 18 and 3.6 wt.% of PEG-1000 was added as pore-form agent. After stirring for 12 h to obtain a homogeneous solution, the solution was placed statically for 12 h to release

Table 1
Reactant composition

Sample	PS-Br (g)	SBMA (g)	CuBr (g)	Bpy (g)
PS-b-SBMA ₁	0.7	0.175	0.03	0.06
PS-b-SBMA ₂	0.7	0.35	0.03	0.06
PS-b-SBMA ₃	0.7	0.7	0.03	0.06

the bubble. Then the casting solution was casted onto the glass plate and the plate was immersed in the water at room temperature. The membrane was taken out after peeling off and rinsed with de-ionized water. The pure PSU membrane was prepared as control which was made by the similar way as PS-*b*-SBMA blended PSU membranes.

2.6. Characterization of membranes

The water contact angle of membranes was determined by Spinning drop interfacial tension meter. Scanning electron microscope (SEM, Hitachi, TM-1000) were applied to observe the surface and cross section of membranes.

2.7. Permeation test

In the permeation test, cross-flow was chosen as filtration system and the diameter of membranes was 2.52 cm. When the membranes had been pre-pressured under 0.1 MPa for 30 min, the data can be collected. After balance of the permeation flux, this data was set as original flux (J_{w1}). Then, the pure water was replaced by the BSA solution (pH = 7.4) to conduct protein filtration test for 1 h and the membrane was washed with de-ionized water for 30 min to remove contaminant. Finally, the water was used to determine the final permeate flux (J_{w3}). BSA rejection (*R*) and water flux recovery (*FR*) were used to evaluate the performance of membranes according to Eqs. (1) and (2).

$$R = \left(1 - \frac{C_{BSA}^{permeate}}{C_{BSA}^{feed}} \right) \times 100\% \quad (1)$$

$$FR = \frac{J_{w3}}{J_{w1}} \times 100\% \quad (2)$$

where $C_{BSA}^{permeate}$ and C_{BSA}^{feed} represented BSA concentrations in permeated and feed solutions, respectively. The concentration of BSA in solution was determined by BCA kit at 570 nm (Molecular Device, SpectraMax M3).

2.8. Data analysis

All values were means \pm SD from three independent experiments. Comparisons between multiple groups were performed with the ANOVA test by SPSS. *P*-values less than 0.05 were considered statistically significant.

3. Results and discussion

3.1. Chemical synthesis of PS-*b*-SBMA copolymer

The copolymers of PS-*b*-SBMA were obtained via two-step ATRP. Firstly, the macroinitiator of PS-Br was obtained by the homopolymerization of styrene and ethyl 2-bromopropionate. The GPC result showed that Mn of PS-Br was 7329 g mol⁻¹, and the polymer had narrow molecular weight distribution (PDI = 1.25). For the ¹H NMR spectra of PS-Br in Fig. 2, the characteristic peaks of the aromatic group, methylene proton and benzylic proton linked with Br can be observed at 6.25–7.25, 3.75 and 1.5 ppm

[30], while the peaks at 0.73–2.05 and 3.90 ppm attribute to hydrogen of methylene in ethyl 2-bromopropionate. The molecular weight of PS-Br can be deduced to be 6656 g mol⁻¹ from NMR result, which is close to the data from GPC (Mn = 7329 g mol⁻¹).

Then, the three block copolymers of polystyrene-block-sulfobetaine methacrylate, namely PS-*b*-SBMA₁, PS-*b*-SBMA₂ and PS-*b*-SBMA₃, were synthesized with different SBMA ratio to PS-Br. Compared the spectra of PS-*b*-SBMA₂ and PS-*b*-SBMA₃ with PS-Br (the spectra of PS-*b*-SBMA₁ was not shown), the peak at 3.75 ppm in spectra of PS-Br was disappeared and three new peaks at 3.36 ppm (N⁺(CH₃)₂CH₂CH₂CH₂SO₃⁻), 2.37 ppm (N⁺(CH₃)₂CH₂CH₂CH₂SO₃⁻), 2.84 ppm (–N⁺(CH₃)₂CH₂CH₂CH₂SO₃⁻) appeared in spectra of PS-*b*-SBMA corresponding to three methylene proton of SBMA [31–33].

As the peaks area in the NMR spectra did not present the authentic proportion of polystyrene and sulfobetaine methacrylate in copolymers, Fourier transform infrared spectroscopy and element analysis were further applied for characterizing the copolymer. As shown in Fig. 3A, the peaks at 1,456 and 1,488 cm⁻¹ and peaks at 700 and 1,956–1,740 cm⁻¹ attributed to C–C stretching and curving vibration of benzene ring, while the peak at 539 cm⁻¹ which attributed to C–Br stretching vibration is an evidence of Br existence in the end. In Fig. 3B, new peaks at 1,042; 1,181 and 605 cm⁻¹ appeared which attributed to the symmetric and asymmetric stretching vibration of the sulfonate groups and C–S stretch. When the spectra of block polymer PS-SBMA₁ was treated with software, some peaks belong to SBMA is appear in Fig. 3E, which means success polymerization of the SBMA. The peak intensity at 1,181 and 1,042 cm⁻¹ was stronger in Fig. 3C and D than those in Fig. 3B, indicating the increased SBMA content in the copolymers by the incremental feed ratio of SBMA to PS-Br [32,34].

Element analysis was further used to analyze SBMA content in copolymers according to the different element content in SBMA and PS-Br. In Table 2, the content of nitrogen in the copolymers increased with the feed ratio of SBMA:PS-Br as nitrogen only exists in SBMA, but carbon content decreased with the feed ratio due to the less carbon in SBMA. There is no significant change for hydrogen as its content in SBMA and PS-Br is similar. The content of SBMA in three polymers was calculated to be 11%,

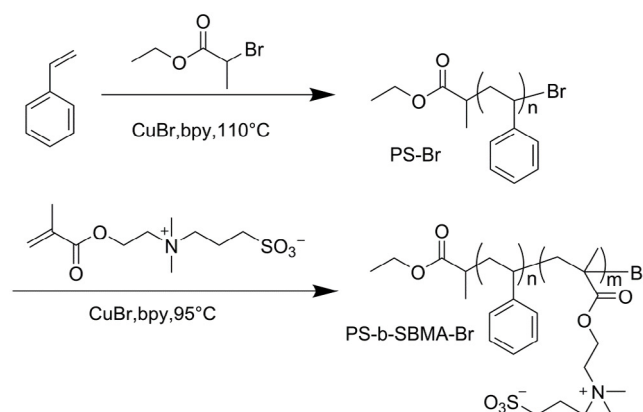


Fig. 1. Synthesis procedure for macroinitiator of PS-*b*-SBMA.

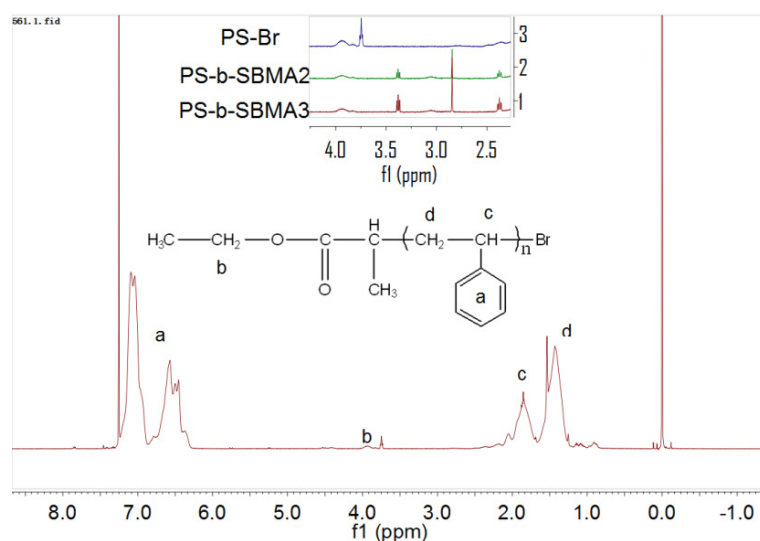


Fig. 2. ¹H NMR spectrum of PS-Br and PS-b-SBMA copolymers.

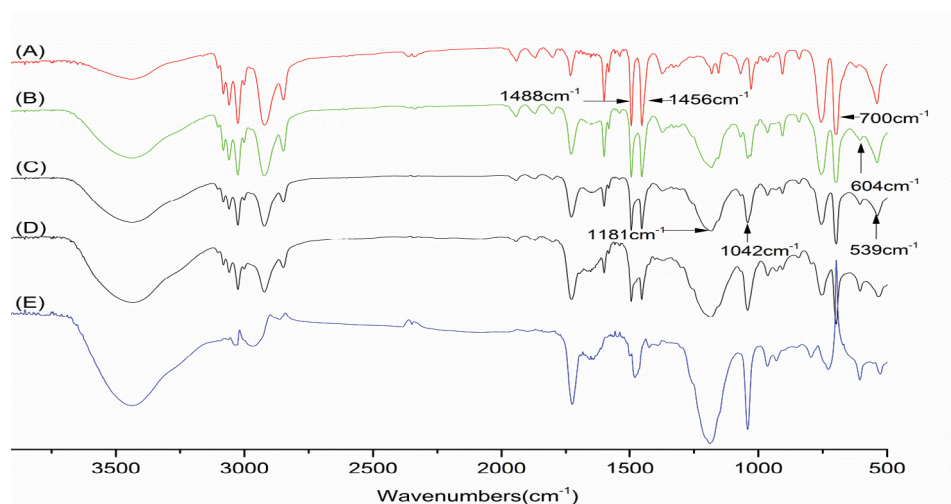


Fig. 3. FTIR spectrum for (A) PS-Br, (B) PS-SBMA₁, (C) PS-SBMA₂, (D) PS-SBMA₃, and (E) subtraction result of B-A.

28.4% and 39.8%. It should be mentioned that N existing in PS-Br may be caused by instrumental error.

3.2. Preparation and characterization of PS-b-SBMA modified PSU membranes

As the PS-b-SBMA would be dissolved with PSU to prepare the casting solution, the solubility of PS-b-SBMA were detected in the commonly used solvents (DMAc, DMF, DMSO and NMP) in membrane fabrication. As shown in Table 3, the SBMA is almost insoluble, while the PS-Br is easy to be dissolved in the four solvents. Hence, the PS-b-SBMA copolymers were soluble in the solvents. Among them, the DMSO with largest polarity could best dissolve the PS-b-SBMA due to the strong hydrophilicity of SBMA.

To prepare the PS-b-SBMA blended PSU membranes, PSU and copolymers were dissolved in the cosolvent of NMP and DMSO, where DMSO was used to attenuate the dissolvability of PS-b-SBMA. The property of membranes

Table 2
Element analysis of polymers

Sample	C (%)	H (%)	N (%)	SBMA percentage (%)
PS-Br	90.94	7.64	0.02	0
SBMA	47.14	7.52	5.01	100.0
PS-b-SBMA ₁	85.05	7.93	0.55	11.0
PS-b-SBMA ₂	79.19	7.59	1.42	28.4
PS-b-SBMA ₃	67.04	7.968	1.99	39.8

was tested via water contact angle and BSA rejection. As shown in Fig. 4A, the contact angle of PSU membrane is 90°, which consisted with other articles [5,6]. By contrast, the contact angles decreased to 68° with the increase of SBMA content in membrane, similar with PSf-g-PEG₇₅₀ modified PSU membranes (70°) [35]. But this contact angle was still higher than other PSU membranes with surface

modification (e.g., HEMA and PEGMA grafted PSU membranes with contact angle at 39° [36]; CO_2 plasma treated PSU membrane at 22° [6]). It was reasonable because of the lower content of hydrophilic chains on surface of blended membranes than surface modified membranes.

From Fig. 4B, it can be seen that BSA rejection of all membranes was over 85%, indicating that all the prepared membranes were ultrafiltration membranes. The membranes showed higher BSA rejection by treatment with 10 g L^{-1} BSA than 1 g L^{-1} BSA solution, which may be due to the higher protein concentration fouling reduced the pore size.

Unlike the damaged membrane structure by surface modification of SBMA, the blended membranes well presented typical ultrafiltration property by accurately controlled parameters in fabrication [23].

3.3. Anti-fouling property of PS-*b*-SBMA modified PSU membrane

Anti-fouling property of membranes was then characterized by the water flux recovery before and after the BSA fouling. From Fig. 5, when the deionized water was

Table 3
Solubility of polymers in different organic solvents

Solubility (g L^{-1})	DMAc	DMF	DMSO	NMP
PS-Br	>100	>100	>100	>100
SBMA	insoluble	insoluble	soluble	slightly soluble
PS- <i>b</i> -SBMA ₁	29	34	55	45
PS- <i>b</i> -SBMA ₂	17	21	52	31
PS- <i>b</i> -SBMA ₃	11	18	48	22

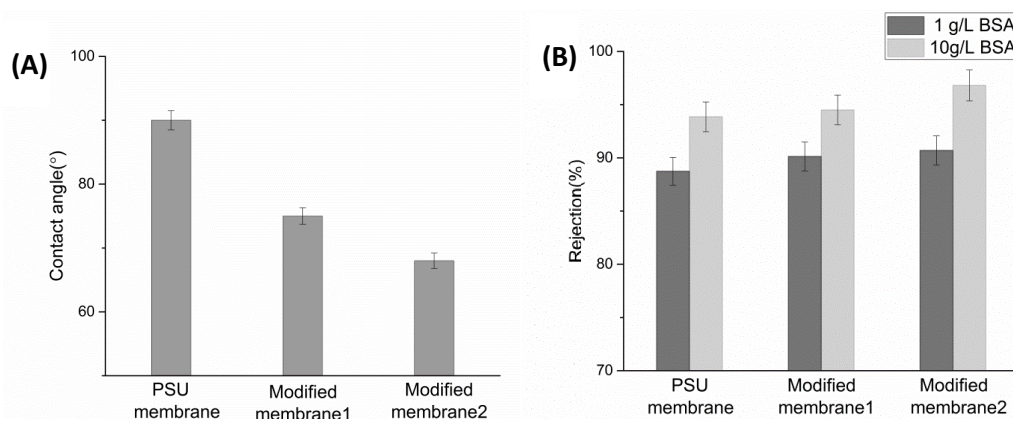


Fig. 4. Water contact angle (A) and BSA rejection (B) of different membranes. Modified membrane 1 and 2 were PSU blended with copolymer of PS-*b*-SBMA₂ and PS-*b*-SBMA₃, respectively.

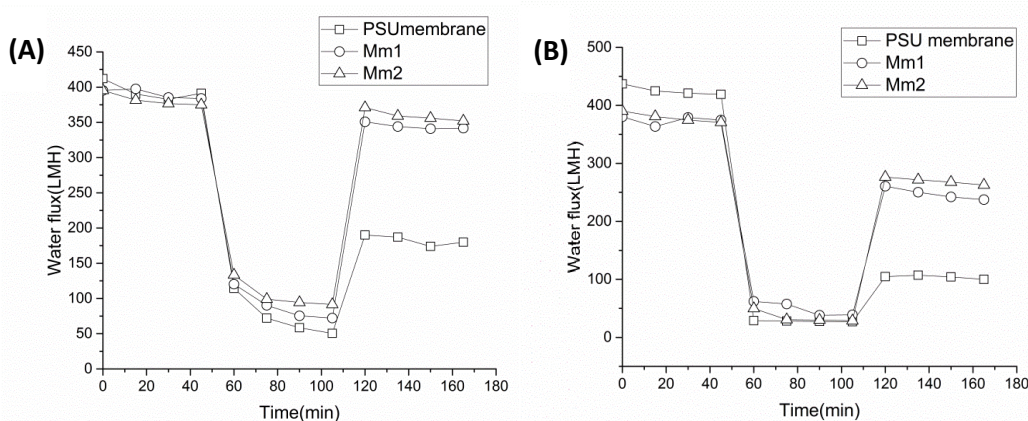


Fig. 5. Flux variation of membranes during ultrafiltration of BSA solutions (A) 1 g L^{-1} BSA and (B) 10 g L^{-1} BSA. Mm1 and Mm2 were PSU membrane blended with copolymer of PS-*b*-SBMA₂ and PS-*b*-SBMA₃, respectively.

replaced with BSA solution, there was a sharp decrease of water flux causing by concentration polarization effect [37] and it often occurred in the early stage of the ultra-filtration process [38]. As the fouling of 1 g L^{-1} BSA solution was slower than 10 g L^{-1} BSA solution, the membrane under treatment of former solution showed higher working flux than that of later solution. When the membranes were washed with deionized water after BSA fouling, the recovery of modified membranes was nearly two folds of parent PSU membrane. It can reach to 94% when treated with 1 g L^{-1} BSA solution, higher than most of surface modified membranes [39]. Besides, the PS-b-SBMA modified membranes also presented excellent anti-fouling property under treatment of 10 g L^{-1} BSA [23], since few

studies used BSA solution with high concentration of 10 g L^{-1} . The improved anti-fouling property of membrane by SBMA may be due to the fact that SBMA can form an hydration shell on the membrane surface and decrease the hydrophobic adsorption between protein and membrane.

To further confirm the anti-fouling property of PS-b-SBMA modified membranes, membrane surfaces before and after fouling were observed by SEM. As shown in Fig. 6a, the surface of PSU membrane was covered by contaminants after treatment of BSA solution at 1 and 10 g L^{-1} , indicating the severe BSA adsorption on unmodified PSU membrane. By contrast, the contamination on PS-b-SBMA modified membranes was slight, though 10 g L^{-1} of BSA solution elicited more surface contamination than 1 g L^{-1} of

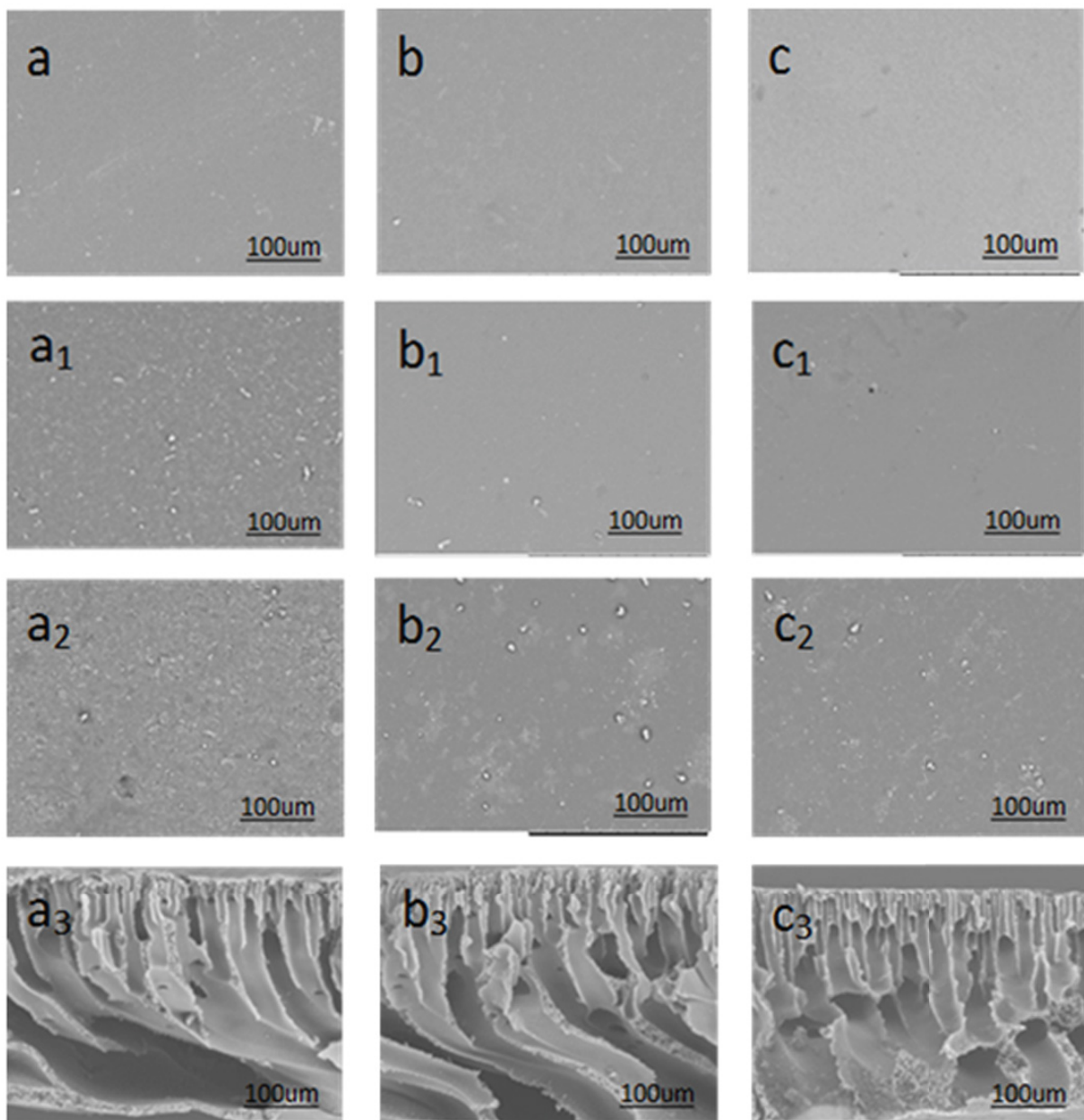


Fig. 6. SEM images of (a) PSU membrane, (b) PSU blended with PS-b-SBMA₂ and (c) PSU blended with PS-b-SBMA₃. (1) and (2) treated with 1 and 10 g L^{-1} BSA and (3) cross-section of membranes.

BSA solution (Fig. 6b and c). Our result was similar with the previous report that PSU-g-DEPAS membrane reduced the surface BSA adsorption compared to PSU membrane [40].

4. Conclusion

Block polymers of PS-*b*-SBMA were synthesized by ATRP with SBMA content exceeding to 28%. Such copolymers were applied to fabricate the SBMA modified PSU membrane via blending the copolymers with PSU. The membrane modification improved the surface hydrophilicity by reducing the water contact angle from 90° to 68°. The modified membranes showed the water flux recovery over 93% and 60% when treated with 1 and 10 g L⁻¹ BSA, which was three folds higher than the parent PSU membrane. Consistently, SEM images confirmed the adsorption of BSA on pure PSU membrane and the suppressed fouling on modified membranes.

Acknowledgement

We gratefully acknowledge the financial support of this study by NSFC (National Natural Science Foundation of China, No 22078287).

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