Selective swelling of block copolymer ultrafiltration membranes for enhanced water permeability and fouling resistance

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ABSTRACT

High permeability is one of the most important pursuits of separation membranes. In this work, high-performance ultrafiltration membranes are prepared by synergetically coupling nonsolvent-induced phase separation (NIPS) and selective swelling of a block copolymer, polysulfone-block-poly (ethylene glycol) (PSF-b-PEG). NIPS is used to prepare PSF-b-PEG membranes with a thin skin layer and a fingerlike sublayer. Subsequent selective swelling generates mesopores in the skin layer and enriches PEG blocks on the surface. Compared to the membranes without swelling, the swelling-treated membranes exhibit simultaneously upgraded permeability, hydrophilicity, and fouling resistance. For instance, the permeability of the membrane swollen in 50% acetic acid at 65 °C for 1 h is doubled compared to the pristine one while the rejection is only modestly reduced. Fouling resistance of the swelling-treated membranes is also improved, which is ascribed to the enrichment of PEG on the membrane surface. We demonstrate that the performances of the membranes can be tuned in a relatively wide range by tailoring the swelling conditions, such as swelling reagents, durations and temperatures. Because of the extreme simplicity and high efficiency, this selective swelling strategy is expected to be applicable in tuning the surface properties and improving performances of many other membranes.

1. Introduction

High permeability is always one of the most important pursuits in membrane technology [1–3]. However, most commercial membranes are derived from hydrophobic polymers, e.g. polysulfone (PSF), polyvinyl difluoride (PVDF), and polypropylene (PP), etc., for the sake of adequate mechanical stability. Consequently, they are prone to suffering from low permeability and poor fouling resistance. To address these issues, a number of strategies have been established to develop high-flux membranes by modifying the chemical properties of their surfaces [4,5]. For example, it is generally acknowledged that good permeability can be achieved by providing the surface with high hydrophilicity and porosity [6]. To this end, hydrophilic modifiers, among which poly(ethylene glycol) (PEG) is one of the most popular ones, have been extensively used [7,8].

Specific to PSF, which is a high-performance polymer with a glass transition temperature (Tg) of ~190 °C, is widely used to manufacture separation membranes due to its outstanding thermal resistance, mechanical character, chemical stability, and superior processability [9]. For the sake of improving the hydrophilicity of PSF membranes, lots of physical or chemical methods have been proposed [10], including incorporating inorganic nanofillers into the membrane matrix [11,12], plasma etching to generate polar groups on the surface [13], and directly grafting some hydrophilic groups onto the membrane surface [9,14–16]. Although these methods could improve the hydrophilicity of the PSF membranes, they are typically complicated and tedious, and the permeability does not always show appreciable promotions. Recently, we incorporated PEG chains into PSF membranes by directly precipitating solutions of the block copolymer (BCP) of PSF-b-PEG, in water following the process of nonsolvent-induced phase separation (NIPS) [17]. The produced membranes exhibited evidently enhanced hydrophilicity and permeability several times higher than PSF membranes prepared by other methods [17].

For the preparation of ultrafiltration (UF) membranes from block copolymers, both the traditional NIPS process [18–22] and the emerging selective swelling method [23–26] are used. In the NIPS process, by the exchanging between the solvent inside the casting film and nonsolvent in coagulation bath, the casting film solidifies and transforms into a membrane with a symmetric or an asymmetric structure [27,28]. In contrast, in the selective swelling process, BCP films are immersed in a solvent selective to the minority block for a certain duration. After removal of the films from the solvent followed by
drying, well-defined porosities are generated throughout the BCP films [29]. Moreover, the polar blocks are exclusively relocated on the pore surface of the BCP membranes during the swelling process, rendering enhanced hydrophilicity to the surface. This swelling methodology is featured with unique advantages, such as extreme simplicity, narrow pore size distribution, and inherent hydrophilic surfaces. Selective swelling is predominantly used to prepare polystyrene (PS)-based BCP membranes. However, we recently extended it to produce PSF-b-PEG membranes, which exhibited much better mechanical properties than PS-based membranes, by soaking PSF-b-PEG films in solvent pairs containing both a PSF-selective solvent and a PEG-selective solvent [26].

Considering that PSF-b-PEG UF membranes can be prepared by the NIPS process and mesopores can be created in PSF-b-PEG films by selective swelling, in this work we report on a simple and effective approach to produce PSF-b-PEG membranes with superior performances by synergetically coupling NIPS and selective swelling together. NIPS is first used to prepare PSF-b-PEG membranes with a thin skin layer and a fingerlike sublayer. Subsequent selective swelling generates mesopores in the skin layer and enriches PEG blocks on the surface, endowing the membranes with simultaneously upgraded permeability, hydrophilicity and fouling resistance. Considering that (1) amphiphilic components or additives are frequently included into the polymer dopes for the preparation of ultrafiltration and nanofiltration membranes, and (2) the relocation of either polar or nonpolar moieties in the membrane will occur upon exposure to selective solvents as a result of selective swelling, leading to the tunable microstructures and surface properties, we believe this selective swelling strategy is not limited to block copolymer membranes discussed in the present work, instead it is a rather generic route to upgrade the performances of many different membranes provided an amphiphilic component is included in the membranes.

2. Experimental

2.1. Materials

The PSF-b-PEG block copolymer was obtained from Nanjing Bangding. According to the manufacturer, the polydispersive index (PDI) was ~ 2.00, and the PEG block had a molecular weight of ~20 kDa. The weight ratio of the PEG block in the copolymer was determined to be 25% (Fig. S1) by a thermogravimetry (TG) analyzer (449 F, TA Instruments, USA) at the heating rate of 10 °C/min under nitrogen atmosphere, with the temperature ranging from room temperature to 800 °C. N-methyl-2-pyrrolidone (NMP, 99.5%), Ethanol (Et, ≥99.5%), and Acetic acid (AA, ≥99.5%) were purchased from local suppliers. Bovine serum albumin (BSA, >97%) with a molecular weight of 66 kDa was obtained from Sigma-Aldrich. Phosphate buffer solutions (PBS) tablets (1 tablet dissolved in 100 mL water to give PBS solution with pH 7.4) were purchased from MP Biomedicals, LLC. Humic acid was purchased from Aladdin Industrial Corporation. All reagents were used as received. Deionized (DI) water with a conductivity of ~50 µs/cm was in-house prepared and used throughout the experiments.

2.2. Preparation of PSF-b-PEG membranes

To prepare the casting solutions with a concentration of 15 wt%, 15 g of PSF-b-PEG were dissolved in 85 g of NMP at 60 °C for ample time until the PSF-b-PEG solids were dissolved, followed by mechanical stirring at room temperature for 4 h to make sure the PSF-b-PEG was completely. After degassing in vacuum at room temperature for 12 h, the casting solution (~5 mL) was cast on a clean glass plate with a casting knife preset to the height of 300 µm to produce a casting film. The casting film was allowed to stand in air for 10 s and then plunged into DI water. After 10 min, the membranes were automatically detached from the glass plate, and were thoroughly washed with DI water to remove the residual solvent and stored in DI water for use.

For selective swelling, the PSF-b-PEG membranes were immersed in different swelling reagents, including AA aqueous solutions with varied volume concentrations, Et, and Et + 20%Ac, at preset temperature. After swelling for certain durations, the membranes were removed from the swelling solution, followed by immediately soaking in DI water for 10 min to remove the residual reagents and then kept in DI water for use.

2.3. Characterizations

Scanning electron microscopy (SEM, Hitachi S4800) was performed at the operation voltage of 5 kV to observe the surface and cross-sectional morphologies of the membranes. Membranes were soaked in liquid nitrogen for 30 s and then immediately fractured to expose their cross-sections for SEM observations. All samples were sputter-coated with a thin layer of Au/Pd alloy prior to SEM examination to enhance their conductivity. Atomic Force Microscopy (AFM, Park XE-100) at non-contact mode was performed to view the surface roughness. A contact angle goniometer (DropMeter A100, Maist) was used to analyze the surface hydrophilicity of the membranes before and after swelling, and the measurements were performed on different positions for each sample and the average values were reported. X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi) was conducted to determine the surface compositions of the membranes with 150 W monochromatic Al Kα excitation (hν = 1486.6 eV) on a spot size of 500 µm. High resolution scans were performed by narrow scan (energy step size: 0.05 eV) for chemical analysis of the oxygen element (O, 524.7–539.7 eV).

2.4. Filtration experiments

Pure water permeability (PWP) as well as rejection to BSA was measured with a stirred cell module (Amicon 8010, Millipore) having a working volume of 10 mL and an effective membrane area of 4.1 cm². The operation pressure was 1 bar and the stirring speed was 500 rpm. Filtration tests were conducted for 5 min after pre-pressing the membranes at 1 bar for 20 min to ensure a stable PWP, and a water storage tank was required to continuously supply excessive water flow during filtration tests. BSA dissolved in PBS at a concentration of 0.5 g L⁻¹ was employed to test the rejections of the membranes. The concentrations of BSA solutions were measured at the wavelength of 280 nm with a UV–Vis spectrometer (NanoDrop 2000C, Thermo Scientific).

The PWP (L m⁻² h⁻¹ bar⁻¹) of the membranes was calculated according to the following equation:

\[
PWP = \frac{V}{A \times t \times \Delta P}
\]

where \(V\) is the volume of the water (L) penetrating through the membrane. \(A\) is the effective membrane area (m²), \(t\) is the filtration time (h), \(\Delta P\) is the operation pressure (bar).

The BSA rejection (R, %) of the membranes was calculated by the following equation:

\[
R(\%) = \left( \frac{C_f - C_p}{C_f} \right) \times 100\%
\]

where \(C_p\) and \(C_f\) represent the BSA concentrations (g L⁻¹) in the permeation and the feed.

2.5. Evaluation of static adsorption and antifouling property

The protein adsorption capacity of the membranes was evaluated through BSA static adsorption experiments using BSA solutions with a concentration of 1.0 g L⁻¹. Membrane with an area of 5.3 cm² was placed into a weighing bottle filled with 5 mL of BSA solution. The
weighing bottle was then kept at 25 °C for 12 h to reach the adsorption/desorption equilibrium. The concentrations of the BSA solutions before and after adsorption were determined at the wavelength of 280 nm with a UV–Vis spectrometer.

The adsorption capacity of HA on the membranes was also evaluated by conducting static HA adsorption experiments at pH = 7 [30]. Original solution of HA (1000 ppm) was prepared by dissolving 1 g HA into 100 mL 0.1 M NaOH solution with subsequent addition of 900 mL DI water [30]. The pH of the resulting solution was then immediately adjusted to 7 by adding 4 M HCl solution. This solution was stirred for 4 h at room temperature and filtered through a filter paper. HA solutions (10 ppm) were prepared by diluting original solution of HA with DI water. The membrane with an area of 5.3 cm² were immersed into weighing bottle containing 10 mL HA solution (10 ppm) at pH = 7. After that, the weighing bottle were placed on a shaker at 100 rpm for 24 h. The concentrations of the HA solutions before and after adsorption were determined at the wavelength of 229 nm with a UV–Vis spectrometer.

The static adsorption amount of the membranes was calculated by the following equation:

\[
SA = \frac{C_1 - C_2 \times V}{A}
\]

(3)

where SA represents the static adsorption amount (μg cm⁻²) of the membranes, \(C_1\) and \(C_2\) are the BSA or HA concentrations (μg mL⁻¹) before and after static adsorption tests. \(V\) is the volume of the BSA or HA solution (mL), \(A\) is the effective membrane area (cm²).

In order to intuitively investigate the efficiency of the membrane hydrophilicity on the improvement of fouling resistance, we carried out the flux recovery tests to determine the flux recovery ratio (FRR) of the membranes. In this regard, the PWP of the membranes before BSA or HA static adsorption tests was performed according to the aforementioned procedure and recorded as \(J_0\). After BSA or HA static adsorption tests, the membranes were washed thoroughly with copious DI water. Thereafter, PWP was measured again and recorded as \(J_f\). The FRR (%) was calculated by applying the following equation:

\[
FRR(\%) = \left(\frac{J_f}{J_0}\right) \times 100\%
\]

(4)

To examine the membrane fouling in detail, the irreversible fouling ratio (Rff) were calculated using following equation:

\[
R_{ff} = \frac{J_0 - J_f}{J_0}
\]

(5)

3. Results and discussions

3.1. Morphology and surface properties of PSF-b-PEG membranes

To demonstrate the feasibility of enhancing the water permeability of BCP membranes prepared by NIPS by selective swelling, we used a relatively high BCP concentration (15 wt%) to prepare membranes which can be further modified by selective swelling [17,31,32]. Before performing swelling, we first need to screen out the suitable swelling reagents. In our previous studies, we found that AA, Et, Ac, and their mixtures exhibited swelling effect to PSF-b-PEG dense films to different degrees, which can be tuned by changing the ratios of their mixtures [26]. However, in the present work, the starting PSF-b-PEG materials were highly porous UF membranes, and they may exhibit different swelling behaviors than nonporous, dense films, resulting in structure deformation and/or pore collapse during the swelling treatment. Therefore, we first did preliminary swelling tests on the PSF-b-PEG membranes. The membranes were swollen in different reagents, including AA, 50%AA, Et and Et + 20%Ac, and the swelling temperature and duration were fixed at 65 °C for 2 h, respectively. We found that the PSF-b-PEG membranes swollen in AA, Et and Et + 20%Ac were curled to different extent after the swelling and washing process, whereas the membrane swollen in 50%AA maintained its original size and flat appearance (Fig. 1a-e). The PWP and rejection to BSA of the PSF-b-PEG membranes swollen in different swelling reagents at 65 °C for 1 h.

![Swelling Reagents](Image)

**Fig. 1.** The photograph of membranes (a) before and after swelling in (b) AA, (c) 50%AA, (d) Et, and (e) Et + 20%Ac at 65 °C for 1 h. (f) PWP and rejection to BSA of the PSF-b-PEG membranes swollen in different swelling reagents at 65 °C for 1 h.
membranes prepared by selective swelling only, which were typically larger than 30 nm [26]. This might be because the polymer/solvent/nonsolvent system used in NIPS process influences the distribution of the chain segment on the membrane surface. Additionally, all the membranes displayed an asymmetric morphology with a thin top layer and a highly porous sublayer featured as finger-like matrix. The thickness of the top layer was ~ 300 nm. These results prove that the membrane surface was transferred from dense to mesoporous upon swelling in 50%AA while the cross-sectional structure was well retained. Moreover, the tailoring pore sizes are realized through changing swelling conditions, offering possibilities to adjust membrane separation properties.

The migration of PEG blocks and PSF blocks on the membrane surface during the selective swelling process was revealed by XPS characterizations, as shown in Fig. 3 and S2. Oxygen (O s) was detected in the range of 524.7–539.7 eV by narrow scan. The peak at the binding energy of 533.1 eV (Ph-O-Ph) and 531.6 eV (S-O) are assigned to O 1s in PSF chains, and the peak at 532.3 eV (C-O-C) is formed the O 1s of PEG chains [5,35]. Therefore, we used the area ratio of the deconvolved C-O-C peak from PEG chains over the O 1s peak to indicate the contents of PEG chains on the membrane surface. As shown in Fig. 3, the intensity of the C-O-C peak from PEG chains over the O 1s peak to indicate the contents of PEG chains on the membrane surface. As shown in Fig. 3, the intensity of the C-O-C peak from PEG chains becomes stronger when the original membrane is swollen at 50 °C and 65 °C in 50%AA for 1 h, and the area percentage of the peak increases from 22.5% to 30.7%, and 33.4%, indicating the migration of PEG chains to the membrane surface. Meanwhile, the elemental oxygen content of PEG chains increased from 3.3% to 3.9%, and 4.5% with the increasing swelling degree. Moreover, the ratio of C-O-C/Ph-O-Ph also increased from 0.5 to 0.7, and 0.9 on the membrane surface during swelling process. All the above results suggest that the surface segregation of PEG occurs and can be tailored by changing the degree of swelling.

The enrichment of PEG chains on membrane surface enhances the hydrophilicity of the PSF-b-PEG membranes. We investigated the surface water contact angle of PSF-b-PEG membranes swollen in 50%AA at 65 °C for different durations. As shown in Fig. 4, the water contact angle of the original membrane is measured to be ~ 87°, illustrating that the membrane surface is not very hydrophilic due to the presence of PSF blocks after the NIPS process. With the swelling durations increasing from 0 to 60 min, the water contact angle was gradually decreased from ~ 87° to ~ 62 °, indicating obvious improvement of hydrophilicity as a result of the enrichment of PEG on the membrane surface upon swelling. Further prolonging the swelling duration makes no difference on the water contact angle, illustrating that the swelling of PSF-b-PEG membrane has reached saturation within 60 min and the hydrophilicity can not be further increased by increasing the swelling duration.

### 3.2. Effect of concentrations of swelling reagents

We further investigated the influence of concentrations of AA on membrane filtration performances with the swelling temperature and the swelling duration fixed at 65 °C and 1 h. The maximum concentration of AA was set to 70% as we found that membranes treated in AA solutions with AA concentrations higher than 70% showed seriously shrunk appearance and an extremely low BSA rejection, as discussed in Section 3.1. The PWP and rejection to BSA of the PSF-b-PEG membranes swollen in aqueous AA solutions with various concentrations are shown in Fig. 5. Compared with the original membrane, the membrane swollen in pure water (the AA concentration is 0%) shows an
improved PWP from ~ 354–430 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ and a slightly decreased BSA rejection from 90.7% to 85.0% because water has a strong affinity to PEG chains, and also drives some PEG chains to be enriched on the surface especially at elevated temperature [5]. It should be noted that the temperature of water is an important factor. The PSF-b-PEG membranes are stored in water at room temperature, where the membranes are stable, while selective swelling is carried out in water (the swelling regent) at 65 °C, where the membranes strongly interact with water. There is a general trend that with the AA concentration increasing from 0% to 50% PWP is gradually increased from ~ 430 to 750 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ whereas rejection to BSA is slightly decreased from ~ 85.0% to 77.5%. These adjustable filtration performances of PSF-b-PEG membranes can be explained by the increasing swelling degree of the membranes with the increasing AA concentrations. The swelling reagents exhibit stronger affinity to the block copolymer with higher AA concentrations. That is, AA exhibits stronger affinity to both PEG and PSF than water. Correspondingly, the swelling degree of the membranes is increased, which promotes the cavitation of PEG microdomains and also the enrichment of the PEG blocks to the surface and pore wall. Both the higher porosity and enhanced hydrophilicity contribute to the great improvement of PWP. The slightly decreased rejection to BSA should attribute to the gradually increased pore size of the membranes swollen in AA with growing concentrations (Fig. S3). Nevertheless, when the AA concentration is further increased from 50% to 70%, the PWP of the membrane drops slightly and the rejection to BSA is decreased from 77.5% to 60.8%. This is probably because of the partial collapse of the framework of the membrane structure caused by such a high concentration of AA. To be noted, in any case the level of BSA rejections in the range of 60–85% indicates that the filtration capacities of the produced PSF-b-PEG membranes swollen in AA with different concentrations are all in the UF range.
prove the mobility of PSF blocks, although the PEG blocks (Elevated temperatures can enhance the a blocks and the moderate movement of PSF chains contribute to selec-
markedly increased from ~ 492 to 874 L m⁻² whereas rejection to BSA was decreased from ~ 90.7% to 77.5%. A linear correlation between the degree of swelling and the duration in the fi
edge determined from Fig. S4. Additionally, it should be noted that the improvement of the membrane performance is already pronounced within 10 min upon swelling in 65 °C 50%AA, implying that selective swelling is an efficient and quick strategy in improving the permeability of BCP membranes.

3.5. Fouling resistance of the PSF-b-PEG membranes

As we discussed in Section 3.1 the PEG blocks are selectively en-
riched on the membrane surface and the pore wall after selective swelling, endowing the PSF-b-PEG membranes an improved surface hydrophilicity. Therefore, the membranes are expected to have a good resistance to the adsorption of fouling species including proteins and HA due to the reduced hydrophobic interactions between hydrophilic surface and fouling species. To investigate this effect in improving fouling resistance we conducted the BSA and HA static adsorption tests on the original PSF-b-PEG membrane and the membrane swollen in 50% AA at 65 °C for 1 h. The swelling-treated membrane showed a BSA adsorption of ~ 109 μg cm⁻², which was significantly lower than that of the original membrane (288 μg cm⁻²). Meanwhile the swelling-
treated membrane showed a HA adsorption of ~ 3.8 μg cm⁻², which was lower than that of the original membrane (4.7 μg cm⁻²). One may worry about the durability of the PSF-b-PEG membranes due to the presence of degradable PEG blocks. Our preliminary tests demonstrated that the morphology, permeability and fouling resistance of the membrane swollen in 50% AA remained nearly unchanged after immersion in water for one week, implying that the degradation of PEG chains with a high molecular weight of 20 kDa in our PSF-b-PEG membranes was less pronounced.

For a direct visualization of the improvement in antifouling prop-
erty, we also tested the FRR of the membranes swollen in AA with varied concentrations at 65 °C for 1 h. After BSA adsorption tests, the membranes were washed thoroughly with DI water. By comparing the PWP of membranes before and after BSA adsorption tests, we can obtain the FRR of the membranes. The FRR rises significantly from 57% to 72% and 75%, whereas Rir values decreased from 43% to 28% and 25% when the AA concentration increases from 0% to 30% and 50%, respectively. By comparing the PWP of membranes before and after HA adsorption tests, we can obtain the FRR of the membranes. The FRR

3.3. Effect of swelling temperatures

Section 3.1 shows that the swelling temperature plays a vital role in the process of selective swelling as temperature affects the interaction between the polymer and the swelling solvent as well as the mobility of the polymer chains. In this section, we investigate the filtration performance of PSF-b-PEG membranes swollen in 50% AA at different temperatures for fixed duration of 1 h. The selected temperatures were well below the T_g of PSF (~ 190 °C) to ensure that the PSF chains are still in glassy state otherwise the structure of the membrane will collapse. As shown in Fig. 6, membranes swollen at 25 °C shows a significantly increased PWP from ~ 354 to 492 L m⁻² h⁻¹ bar⁻¹ and a decreased BSA rejection from 90.7% to 82.5% compared to the original membranes, indicating that the improvement in water permeability can be realized by swelling under mild conditions, i.e. at room temperature. As the temperature was increased from 25 to 80 °C, the PWP was markedly increased from ~ 492 to 874 L m⁻² h⁻¹ bar⁻¹ whereas the rejection to BSA was decreased from ~ 82.5% to 52.4%.

As we discussed in our previous study, both the swelling of PEG blocks and the moderate movement of PSF chains contribute to selective swelling-induced pore generation of the PSF-b-PEG membranes. Elevated temperatures can enhance the affinity of AA to PSF and improve the mobility of PSF blocks, although the PEG blocks (T_g ~ 62 °C) are already fully solvated and highly mobilized in 50% AA. As a result, higher temperature will still lead to stronger degree of swelling (including higher porosity and more PEG on the surface) and consequently higher PWP but decreased BSA rejection.

3.4. Effect of swelling durations

Except for the concentration of reagent and temperature, swelling duration is another important parameter in selective swelling process. Based on the above-discussed optimal concentration of AA (50%) and temperature (65 °C), we studied the filtration performance of the PSF-b-PEG membranes swollen for different durations. Fig. 7 shows the PWP and rejection of BSA of these membranes. With the increasing of swelling durations from 0 to 60 min, the PWP presents a rising trend from ~ 354 to 750 L m⁻² h⁻¹ bar⁻¹ whereas rejection to BSA is slowly decreased from ~ 90.7% to 77.5%. A linear correlation between the degree of swelling and the duration in the first 60 min is hence verified. With prolonged swelling durations from 60 to 720 min, the PWP and rejection to BSA remain stable, indicating a maximum swelling degree is realized. These results coincide with the previous water contact angle data, further proving that the degree of swelling reaches the saturation point at the duration of 60 min. The amount of solvent absorbed by PEG is determined by the swelling duration before saturation. More solvent absorption lead to higher swelling degree of the PEG microdomains, and hence stronger deformation of the membrane. Finally, larger pore size and better porosity are obtained at longer swelling durations. The variation trend of pore sizes and porosities of the membranes can be roughly determined from Fig. S4. Additionally, it should be noted that the improvement of the membrane performance is already pronounced within 10 min upon swelling in 65 °C 50%AA, implying that selective swelling is an efficient and quick strategy in improving the permeability of BCP membranes.

Fig. 6. PWP and rejection to BSA of the PSF-b-PEG membranes swollen in 50%AA at different swelling temperature for 1 h.

Fig. 7. PWP and rejection to BSA of the PSF-b-PEG membranes swollen in 50%AA at 65 °C for different swelling durations. The scale style of X axis after break is Log 10.
rises significantly from 78% to 87% and 89% whereas RH values decreased from 22% to 13% and 11% when the AA concentration increases from 0% to 30% and 50%, respectively. Such an improvement of FRRs can be ascribed to the enhanced surface hydrophilicity, which consequently attributes to lower absorption of proteins, demonstrated by SEM, XPS and WCA tests. AA aqueous solutions are generation of mesopores and enrichment of PEG on the surface are blocks on the surface, endowing the membranes with simultaneously ability and fouling resistance of many other membranes as amphiphilic swelling durations, the permeability and filtration properties, J. Membr. Sci. 529 (2017) 201–209.

4. Conclusions

We propose a new strategy to fabricate high-performance PSF-b-PEG membrane by coupling NIPS and selective swelling. NIPS provides the membranes with a thin skin layer and a fingerlike sublayer, while selective swelling generates mesopores in the skin layer and enriches PEG blocks on the surface, endowing the membranes with simultaneously upgraded permeability, hydroporosity and fouling resistance. The generation of mesopores and enrichment of PEG on the surface are demonstrated by SEM, XPS and WCA tests. AA aqueous solutions are found to be efficient and tunable reagents to swell the membranes. By simply changing the concentrations of AA, swelling temperatures and swelling durations, the permeability and filtration performances of the PSF-b-PEG membranes can be adjusted in a relatively wide range. Due to the enrichment of PEG chains on the membrane surface, the swelling-treated PSF-b-PEG membranes exhibit outstanding resistance to protein adsorption as proved by static adsorption and FRR tests. In addition to block copolymer membranes reported in the current work, this selective swelling strategy is expected to be applicable to upgrade the permeability and fouling resistance of many other membranes as amphiphilic components or additives are typically used in the preparation of polymeric membranes by the NIPS process.

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Appendix A. Supporting information

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