



Advanced ultrafiltration membranes by leveraging microphase separation in macrophase separation of amphiphilic polysulfone block copolymers



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ARTICLE INFO

Keywords:

Block copolymer
Fouling resistance
Polysulfone
Surface segregation
Ultrafiltration membranes

ABSTRACT

Water-soluble polymers are generally required in the process of nonsolvent-induced phase separation (NIPS) as additives or modifiers to enhance the hydrophilicity and permeability of ultrafiltration membranes. In this work, we demonstrate that amphiphilic block copolymers, polysulfone-*block*-poly (ethyleneglycol) (PSf-*b*-PEG), dissolved alone in solvents without any additives lead to highly permeable, fouling-resistant membranes via the NIPS process. PEG blocks deliver dual functions in the membranes. Selective enrichment of PEG blocks on the membrane surface as a result of surface segregation enhances the hydrophilicity and consequently fouling resistance of the membranes. Moreover, microscale phase separation of the block copolymers drives the formation of interconnected PEG microdomains distributed throughout the bulk membrane as confirmed by the transmission electron microscopy analysis on stained membrane slices. PEG microdomains serve as water channels facilitating water transport through the membrane. As a result, thus produced membranes exhibit excellent permeability a few times higher than other PSf-based ultrafiltration membranes with similar retentions. For instance, a membrane having the molecular weight cut-off of 70 kDa gives a water permeability as high as $450 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. Furthermore, the retentions of the PSf-*b*-PEG membranes can be tuned in a relatively wide range simply by adjusting the copolymer concentration in the casting solutions. Using amphiphilic block copolymers alone as the base materials for the preparation of ultrafiltration membranes by NIPS not only simplifies membrane manufacturing process but also opens a new avenue to prepare advanced membranes with upgraded permeability and fouling resistance.

1. Introduction

Membrane-based water treatment requires membranes having good hydrophilicity [1–4] to allow water penetration and to alleviate the deposition of foulants. However, most membranes are prepared from polymers which are highly hydrophobic in nature, for example, polysulfone (PSf), polyvinylidene fluoride (PVDF), polypropylene (PP), etc. To enhance the membrane hydrophilicity and fouling resistance, amphiphilic copolymers which are composed of both hydrophilic and hydrophobic chains are frequently incorporated into casting solutions as additives or modifiers for the preparation of microfiltration or ultrafiltration (UF) membranes via the process of nonsolvent-induced phase separation (NIPS) [5,6]. The principle for the use of the amphiphilic copolymers lies in that the hydrophobic segments are mixed with the membrane skeleton composed of the base polymers by chain entanglement whereas the hydrophilic ones are forced to segregate on the pore walls/membrane surface in the phase inversion process [7]. A long-standing surface hydrophilicity, and consequently

enhanced permeability and fouling resistance are therefore expected as the hydrophilic chains migrated on the surface are not easy to leach out in operations because they are covalently bonded to the hydrophobic parts. Of course, this requires that the hydrophobic parts in the copolymer additives have a good compatibility with the base polymers.

Amphiphilic copolymers with the hydrophilic and hydrophobic chains connected in the random [8], graft [9], and block [10–12] mode have been used for this purpose. For instance, triblock copolymers of hydrophilic polyethylene oxide (PEO) and hydrophobic polypropylene oxide (PPO) connected in the sequence of two end PEO blocks capping one PPO middle block, that is, PEO-*block*-PPO-*block*-PEO, are extensively used and are doped into the casting solutions of many different polymers and enhanced membrane wettability and fouling resistance are generally achieved [13,14]. However, the incorporation of the copolymer additives inevitably complicates the membrane manufacturing process, and even worse, it may unexpectedly change the phase separation process and possibly weaken membrane performances [15]. To minimize these issues, these copo-

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lymers are typically doped into the casting solutions with percentages less than 20% [8–14].

Very recently, we blended amphiphilic block copolymer (BCP), polysulfone-*block*-polyethylene glycol (PSf-*b*-PEG), with PSf base polymer at various percentages up to 70%. We observed no compatible issue between the homopolymer and block copolymer as they were miscible at any blend ratio. Thus-produced blend membranes exhibited greatly improved performances in terms of permeance, hydrophilicity and fouling resistance. In addition to the surface segregation effect of the PSf-*b*-PEG copolymers, such superior performances are believed to be contributed also by the additional water permeability through PEG microdomains [16]. In this previous work, the PSf-*b*-PEG block copolymer was used with percentages up to 70% and they should not be regarded as additives any longer and actually they also served as one of the membrane-forming base polymers [16]. However, the PSf homopolymer was still involved as the other base polymers.

In contrast to the extensive use of amphiphilic copolymers as additives along with membrane-forming base polymers, it is rarely reported for the use of these copolymers alone as the membrane-forming base polymers. Using amphiphilic copolymers alone as the base polymers in the NIPS process makes the recipes of the casting solutions extremely simple which contain only the copolymer and the solvent and other additive is not required anymore. Such a simple recipe strongly benefits the membrane manufacturing and promises stable control in membrane performances, which is strongly desired from the viewpoint of large-scale production. More importantly, in addition to the phase separation at the macroscale in the NIPS process, there is also the possibility of microscale phase separation between the hydrophilic chains and hydrophobic chains in the copolymers [17,18], providing new and additional measures to gear, and to improve the membrane performances. However, the commonly used copolymer additives are not suitable to be used as base polymers to produce membranes because of their poor mechanical stability and membrane-forming property as “materials”. For instance, the PEO-*block*-PPO-*block*-PEO copolymers which typically have a molecular weight lower than 20,000 Da do not have any mechanical strength and even worse, cannot be solidified from the solution through the typical NIPS process [19,20].

Considering that PSf-*b*-PEG block copolymers with various PEG volume fractions can be readily synthesized with good yields at affordable costs [21], the copolymers themselves may serve as a good candidate for the production of separation membranes if we appropriately choose the PEG content in the copolymers. In the present work, we lower down the PEG content in the PSf-*b*-PEG block copolymers to 21 wt% and the copolymers are expected to largely maintain the good mechanical strength and the membrane-forming property of the PSf homopolymer on one hand, and the presence of PEG in the copolymer may enhance the hydrophilicity and permeance of the membrane through the effect of both surface segregation and “water channel” effect of the PEG microdomains on the other. The novelty and significance of the current work are multiple, which include (1) it opens a new avenue to produce hydrophilic PSf membranes, which is highly important and demanded as PSf membranes are extensively used in a diversity of fields and the strong hydrophobicity of PSf is always a problem [22]; (2) it suggests a simplified process to produce advanced UF membranes in which additives are no longer required; (3) it solves the issues of incompatibility between the base polymer and the additives and the leaching out of the additives which frequently plague the traditional NIPS process where foreign additives are involved.

2. Experimental

2.1. Materials

The PSf-*b*-PEG block copolymer was provided by Nanjing

Bangding. According to the manufacturer, the PSf block has a molecular weight comparable to that of Solvay P3500 polysulfone, and the PEG block has a molecular weight of ~20 kDa. The weight ratio of the PEG block in the copolymer was determined to be 21% by thermogravimetry. PSf homopolymer (P3500) and PEG homopolymer (molecular weight=400 Da) were obtained from Solvay and Sigma, respectively. Reagent grade N-methyl-2-pyrrolidone (NMP, purchased from Sinoharm Chemical Reagent Co.) was applied as the solvent to dissolve the copolymer. We selected deionized (DI) water as the only component of the nonsolvent in the coagulation bath. Bovine serum albumin (BSA) was purchased from Sigma-Aldrich and was dissolved in phosphate buffer solutions (PBS) to be used in the rejection and fouling resistance tests.

2.2. Preparation of PSf-*b*-PEG membranes

The casting solutions of five different ratios in weight (ranging from 14% to 18%) were prepared by dissolving varying quantities of PSf-*b*-PEG in NMP at 60 °C. It took several hours to ensure that the PSf-*b*-PEG was visually dissolved and then the solution of BCP was handled under mechanical stirring at room temperature for 4 h so that PSf-*b*-PEG was completely dissolved in NMP. We kept the casting solutions in vacuum oven overnight to remove air bubbles. Subsequently, the copolymer solution was cast onto a nonwoven with a casting knife to obtain a casting film of 220 μm thick. The cast film was allowed to stand in air for 10 s and then coagulated in DI water at room temperature. The prepared membranes were thoroughly washed with DI water and stored in water for use. Water was changed every other day to avoid the growth of microorganisms. To compare the fouling resistance, blend membranes of PSf and PEG homopolymers were also prepared. The two homopolymers were mixed together with 21 wt% PEG and were dissolved in NMP with the total polymer concentration of 15%, and the following process for the membrane preparation is identical to the preparation of PSf-*b*-PEG membranes.

2.3. Characterization

Scanning electron microscopy (SEM) investigations on samples sputter-coated with Au/Pd alloy were performed with a field emission SEM (Hitachi S4800) operated at 5 kV to observe the surface and cross-sectional morphology. Samples were fractured in liquid nitrogen to expose their cross sections for SEM observation. The X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB 250 XPS system (Thermo Scientific) using a monochromatic Al K α X-ray source. To compensate the surface charge effects, all binding energies in the spectra were referenced to the C 1s neutral peak at 285.0 eV. Transmission electron microscopy (TEM) was used to probe the morphology of PEG microdomains in the membrane. The membrane was embedded in epoxy resin and microtomed by a diamond knife on a Leica EM UC7 microtoming system at room temperature after curing. Then thin slices with a thickness of ca. 70 nm were connected on holy carbon grids and stained by osmium tetroxide (OsO $_4$) at 30 °C for 12 h. TEM was conducted with a FEI Tecnai TF20 transmission electron microscope operated at 200 kV. Gel permeation chromatography (GPC, Waters 1515) was applied to measure the molecular weight cut-off (MWCO) of the membrane. A contact angle goniometer (Dropmeter A-100, Maist) was employed to obtain the water contact angles. For each sample, at least 10 sites were tested and the averaged water contact angle was reported.

Cloud points were determined by the titration of the casting solutions with a concentration of 15 wt% different polymers, including polysulfone homopolymer and PSf-*b*-PEG copolymer in NMP, to which non-solvent, DI water, was added. The volume of the polymer solution is 10 ml. The cloud point is defined as the added amount of DI water at which the liquid-liquid phase separation was visually observed and the precipitate did not redissolve at 60 °C within 6 h.

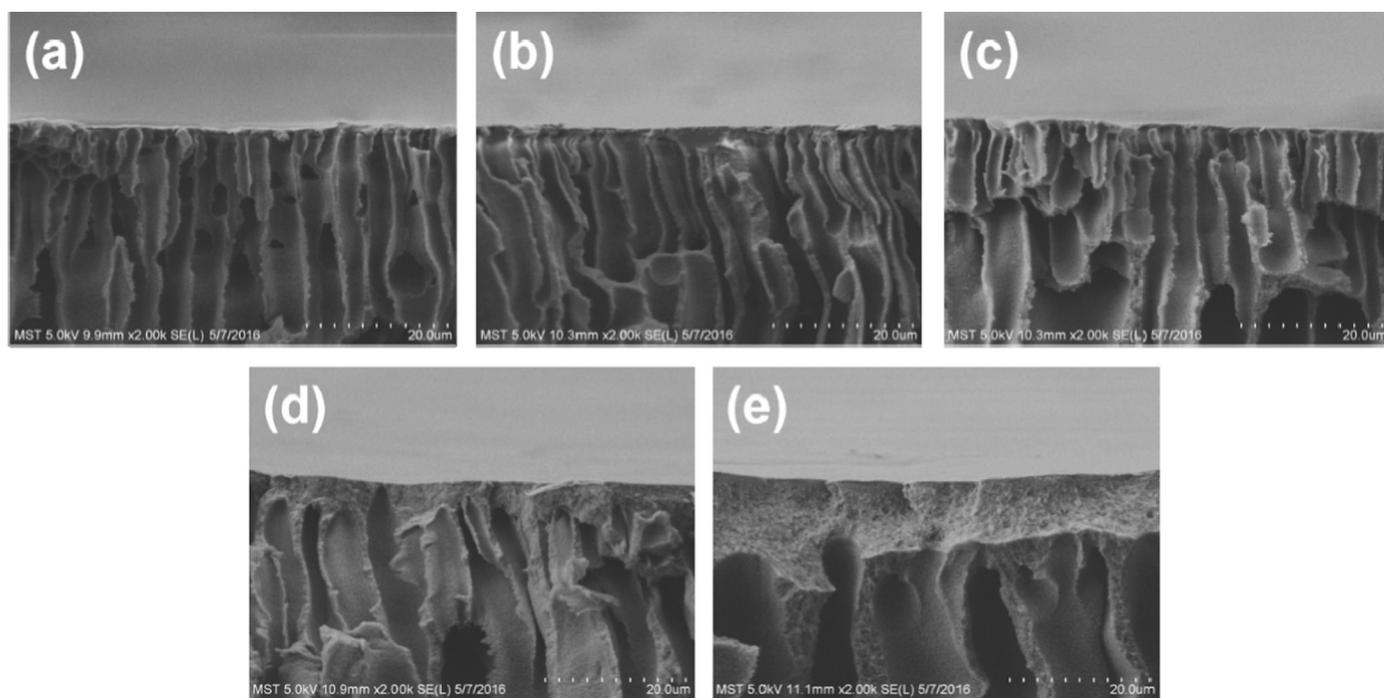


Fig. 1. The cross-sectional SEM images of PSf-*b*-PEG membranes prepared at varied copolymer concentrations: (a) 14%, (b) 15%, (c) 16%, (d) 17%, and (e) 18%.

2.4. Filtration and separation tests

Water flux as well as the retention to BSA was measured with a stirred filtration cell (Amicon Model 8010, Millipore). For retention tests, BSA was dissolved in the PBS buffer solution at the concentration of 0.5 g/L. Retention rates for BSA were tested by measuring the concentrations of BSA both in the feed and permeate solutions using a UV-Vis spectrometer (NanoDROP 2000C, Thermo Scientific). The water flux J_1 ($\text{L m}^{-2} \text{h}^{-1}$) and the pure water permeability (PWP) were calculated using the following equations:

$$J_1 = \frac{V}{A \times t} \quad (1)$$

$$\text{PWP} = \frac{V}{A \times t \times \Delta P} \quad (2)$$

where J_1 represents the water flux ($\text{L m}^{-2} \text{h}^{-1}$), V (L) is the volume of the pure water penetrating through the membrane, A is the effective membrane area (m^2), t is the operation time (h). The BSA rejections of UF membranes were calculated by the following equations:

$$R = \frac{C_f - C_p}{C_f} \quad (3)$$

where C_p and C_f are the BSA concentrations (g/L) in the permeate and the feed solutions, respectively.

Molecular weight cut off (MWCO) of the membrane was determined using aqueous solutions of dextrans with four different molecular weights including 10 kDa, 40 kDa, 70 kDa, and 500 kDa (The concentration was 2.5 g/L, 1.0 g/L, 1.0 g/L, and 2.0 g/L, respectively). The concentrations of the dextran solutions were analyzed by GPC. Rejection values were plotted against the molecular weight of solutes in a curve. The molecular weight corresponding to 90% rejection was defined as MWCO of the membrane.

2.5. Antifouling tests

The antifouling property of the membrane was determined by using the reported procedure [23]. The membrane prepared at 15% copolymer concentration was used to alternatively filtrate DI water and the

BSA solution with a concentration of 0.5 g/L for three cycles. We considered the membrane was fouled after the BSA filtration so we thoroughly washed the membrane with DI water at the end of every filtration with the BSA solution. The blend membrane of the PSf and PEG homopolymer was identically treated for comparison. The pure water flux of the cleaned membrane after three cycles of BSA filtration, J_4 ($\text{L m}^{-2} \text{h}^{-1}$), was tested and compared to the stable water flux in the first filtration of DI water, J_1 ($\text{L m}^{-2} \text{h}^{-1}$), to determine the flux recovery ratio (FRR). FRR can be calculated by the following equation:

$$\text{FRR} = \frac{J_4}{J_1} \times 100\% \quad (4)$$

3. Results and discussions

The PSf-*b*-PEG copolymer having a PEG weight ratio of 49% used in our previous work [16] in the preparation of PSf/PSf-*b*-PEG blend membranes was first explored in the present work to prepare a neat copolymer membrane. This copolymer formed homogenous casting solutions by dissolving in NMP which was readily precipitated in water, leading to solidified “membranes”. However, these membranes exhibited a dense structure and no water permeation at all under the pressures up to 5 bar. This can be explained by the slower phase separation of the casting solution as the high contents of PEG increase the affinity between the casting solution and the nonsolvent (water) which decelerates the precipitation of the copolymer solution. To solve this problem, we accordingly turned to PSf-*b*-PEG copolymers with a PEG content as low as 21 wt% to ensure the formation of a porous membrane via the NIPS process. Moreover, PSf-*b*-PEG copolymers with such a lower PEG content are also desired as they will maintain the mechanical strength and thermal stability of the PSf homopolymer to a greater degree compared to the copolymers with higher PEG contents because PSf is much stable both mechanically and thermally than PEG [24].

3.1. Morphology and surface properties of PSf-*b*-PEG membranes

The NIPS process of the copolymer did not exhibit any noticeable

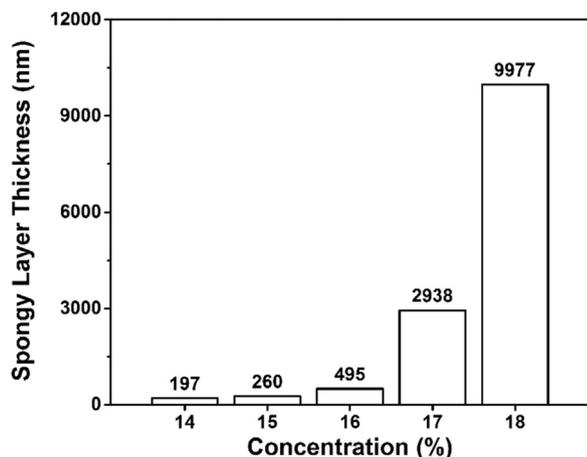


Fig. 2. The thickness of the spongy structures in the sublayer of membranes prepared at various copolymer concentrations.

difference compared to that of the PSf homopolymer. The resulting membranes showed a nontransparent, white-colored appearance and had a thickness of approximately 200 μm . The cross-sectional structures of PSf-*b*-PEG membranes prepared from solutions with varied copolymer concentrations were characterized by SEM. As shown in Fig. 1, the membranes showed an asymmetric structure consisting of a dense top layer and a highly porous sublayer featured as finger-like cavities. Such a structure implies that the membranes were formed through the instantaneous demixing mechanism because the casting solutions containing the PSf-*b*-PEG copolymer and NMP still have high mutual affinity to nonsolvent, water [29]. When we compare the structures of the membranes prepared from different polymer concentrations, it is obvious that the finger-like pores are enlarged with increasing copolymer concentrations. Moreover, higher copolymer concentrations, for example, 16–18%, lead to the development of sponge-like structure on top of finger-like macrovoids and the length of the sponge-like structure is increased with rising copolymer concentrations in the casting solutions. As shown in Fig. 2, the thickness of the sponge-like structure is lower than 300 nm for membranes prepared at the copolymer concentration of 14% and 15%, and is increased to \sim 500 nm at the copolymer concentration of 16%, and is further drastically increased to approximately 3 μm and 10 μm at the concentration of 17% and 18%, respectively. The enlarging finger-like macrovoids and the thickening sponge-like structures in the sublayers with increasing polymer concentrations have been frequently observed in different polymer/solvent/nonsolvent systems [25], and this is explained by the retarded solvent exchange during NIPS as a result of increased viscosity of the casting solutions with rising polymer concentrations [26,27]. This is more or less like the situation of increasing copolymer dosages in the preparation of PSf/PSf-*b*-PEG blend membranes in our previous work [16]. For the casting solutions with higher copolymer concentrations, e.g. 17% and 18%, demixing takes place in a somewhat retarded way, also leading to denser spongy structures in the sublayer [28], and higher copolymer concentrations retard the demixing to larger extents, thus leading to thicker spongy structures. Thicker spongy structures reduce the solvent exchange [23] and allow longer duration for the polymer-lean phases to grow and coalesce, thus forming larger finger-like macrovoids [29,30]. Therefore, higher copolymer concentrations lead to membranes with larger macrovoids in the sublayers.

However, in the specific case of PSf-*b*-PEG block copolymers we discuss here, the change of the affinity between the casting solutions and the nonsolvent is also playing an important role. A higher PSf-*b*-PEG concentration means a higher content of PEG in the solutions which leads to an increased affinity between the solution and the nonsolvent. Introduction of PEG components into the casting solution

increases the affinity of the nonsolvent and the casting solution. We measured the cloud points of PSf homopolymer and PSf-*b*-PEG copolymer in NMP solution. For 10 ml solutions with a total polymer concentration of 15%, the cloud point for the PSf homopolymer solution was 0.71 ml of water whereas the cloud point for the copolymer solution was 1.15 ml of water, clearly indicating the delayed phase separation of the PSf-*b*-PEG copolymer compared to PSf homopolymer.

We also examined the surface morphology of the membranes, and found that the top surfaces of the membranes prepared at different copolymer concentrations similarly took a non-porous, dense structure under SEM characterization (shown in Fig. S1).

The PEG blocks in the copolymer are expected to be preferentially enriched on the membrane surface during the NIPS process because of the effect of surface segregation [7]. XPS analyses were used to investigate the surface composition of the membrane prepared from 15% copolymer concentration. Peaks originated from carbon, oxygen, and sulfur appeared on the XPS curve of the membrane, and the surface O/S ratio was determined to be 11.38 by comparing the peak area of these elements. In contrast, for the bulk PSf-*b*-PEG material the O/S ratio is calculated to be 6.67 by considering that the percentage of PEG blocks in the copolymer is 21 wt% if we assume that both PSf and PEG blocks are homogeneously distributed throughout the membrane. The higher content of oxygen on the surface of the PSf-*b*-PEG membrane suggests the selective enrichment of PEG chains on the membrane surface because S exists only in the PSf block whereas O is present in both blocks. A higher surface O/S ratio than the bulk value implies that more PEG chains are migrated to the membrane surface. The presence of PEG chains on the membrane surface was confirmed by the characterization of WCAs although it does not necessarily imply that there are more PEG chains on the membrane surface than in the membrane interior. The WCA of PSf homopolymer membranes was about 72°; however, the PSf-*b*-PEG membranes prepared from varied copolymer concentrations all exhibited a WCA of approximately 65°. The reduced WCA suggests an enhanced surface hydrophilicity mainly caused by the presence of water-affinitive PEG chains on the surface as all the membranes show a similar surface topography [31]. The enhanced hydrophilicity is very much desired because it promises better water permeability and fouling resistance, which will be discussed later.

3.2. Filtration performances of PSf-*b*-PEG membranes

The pure water permeability (PWP) and retention to BSA of PSf-*b*-PEG membranes prepared from various copolymer concentrations are shown in Fig. 3. There is a general trend that with the copolymer concentration in the casting solutions increased from 14% to 18% PWP is decreased from \sim 420 to 270 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ whereas BSA rejection is increased from \sim 60% to 90%. The decreasing PWPs and increasing rejections with copolymer concentrations can be easily explained by the tightening skin layer of the membrane with increasing polymer solutions, which has been frequently observed in many different polymer/solvent/nonsolvent systems [25,32]. The level of BSA rejections in the range of 60–90% indicates that the produced membranes at various copolymer concentrations are all in the UF range. Compared to other PSf-based UF membranes using different hydrophilic additives including PEG homopolymers, our membranes prepared in this work are outstanding. Our membranes usually exhibit one to two times higher PWP than other membranes with similar rejections. For instance, the PSf-*b*-PEG membrane prepared at 18% copolymer concentration maintains 90% BSA retention while its PWP reaches 255 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$. In contrast, PSf membranes prepared using polymer-grafted TiO_2 nanoparticles [33] and chitosan derivatives [34] as additives exhibited similar BSA retentions but their PWPs were as low as 31 and 115 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$, respectively. Furthermore, PSf membranes prepared using PEG homopolymer as the additive exhib-

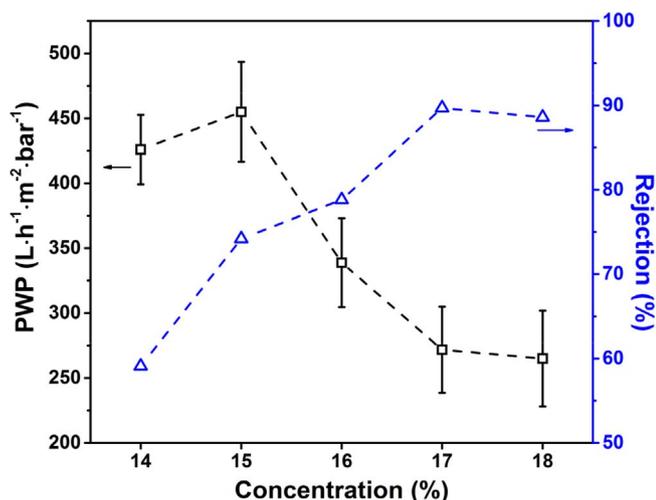


Fig. 3. Pure water flux and BSA retention of PSf-*b*-PEG membranes prepared at varied copolymer concentrations.

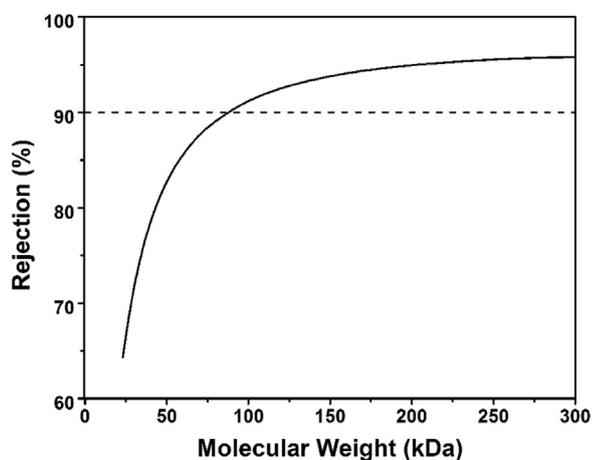


Fig. 4. Rejections of the PSf-*b*-PEG membrane prepared at the copolymer concentration of 15% to dextrans with different molecular weights. The dashed line indicates the determination of the MWCO of the membrane.

ited a slightly lower water flux ($210 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) and a much lower BSA retention (56%) [35]. The BSA rejections of the membranes vary between 60% and 90% depending on the copolymer concentrations while the permeances maintain at relatively high level, which offers us the flexibility to tune the membrane discrimination properties to fit changing application occasions simply by adjusting the copolymer concentrations in the casting solutions. We also tested the MWCO of the membrane prepared from 15% copolymer concentration which exhibited the largest PWP of $455 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ among all the membranes prepared from different copolymer concentrations. As shown in Fig. 4, the membrane recorded a MWCO of 70 kDa which suggests that the membrane can reject 90% of molecules with a molecular weight of 70 kDa. According to the definition of MWCO, the membrane should give a rejection rate higher than 90% to BSA which has a molecular weight of 67 kDa. However, as indicated in Fig. 3, the tested rejection of the membrane is 75%, smaller than the value expected from the MWCO. This inconsistency may be ascribed to the difference in the different conditions as well as in the molecular shape of BSA and dextran. In the tests of BSA rejections and MWCOs the BSA concentration and the total dextran concentration are 0.5 g/L and 6.5 g/L, respectively, and the big difference in the concentration of solutes may influence their penetration through the membrane. In addition, BSA is in the shape of ellipsoids [36], and is therefore, more difficult to penetrate the membrane pores compared to glucose which is in a linear thread-like shape [37].

3.3. The water channels effect of the PEG microdomains in the membrane

The excellent permeability of the PSf-*b*-PEG membranes should of course be ascribed to the enhanced hydrophilicity compared to the PSf homopolymer membranes as we discussed above. However, we do not think that a moderate increase in surface hydrophilicity will lead to such significant upgrade in water permeance. Moreover, similar improved hydrophilicity had also been frequently obtained in other works using different hydrophilic additives [33,34], however, significant enhancement in permeability like the present work is seldom obtained. Importantly, we attribute this superior permeability to the special microstructures originated from the microphase separation of PSf-*b*-PEG block copolymers.

PSf is a strongly hydrophobic polymer whereas PEG is water-soluble and highly hydrophilic, therefore, there is a strong repulsion interaction between the two polymers, driving them to separate from each other. However, in their block copolymers, they two are covalently bonded together, and consequently their phase separation can only occur in the micro scale. The PEG block has a weight percentage of 21% and according to the phase diagram of block copolymers [17] they will form cylinder-like microdomains distributed in the matrix of PSf.

To study the microphase-separated morphology of the copolymer in the membrane, we made TEM analysis on the microtomed membrane prepared at 15% copolymer concentration. To enhance the contrast of PSf and PEG phases under TEM, PEG domains were stained preferentially with OsO_4 . As show in Fig. 5, worm-like PEG domains appearing darker as a result of staining are present in the grey background which is the PSf matrix phase. This figure clearly shows the homogenous distribution of PEG microdomains in the membrane interior and no macroscale phase separation of these two blocks occurs, which is the particular advantage of block copolymer. The PEG microdomains have a diameter of approximately 20–30 nm, and they are randomly oriented and three dimensionally interconnected with each other, forming a continuous phase distributed in the PSf matrix.

These interconnected PEG microdomains serve as water channels in the filtration. PEG is highly water-affinitive and therefore, the PEG microdomains are highly water permeable as water molecules can transport along the solid PEG phases through mechanism, for example,

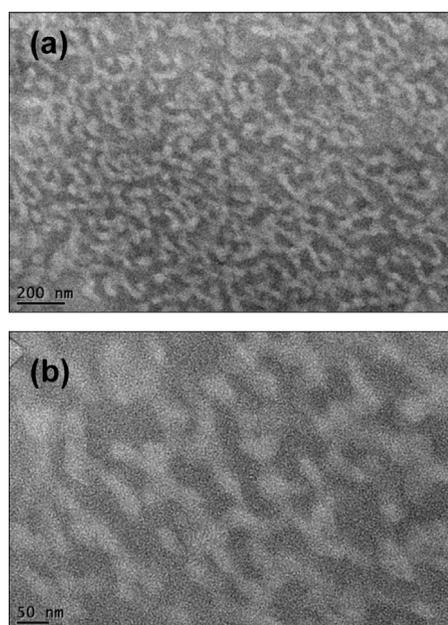


Fig. 5. The TEM images with different low (a) and high (b) magnification of a stained slice of the PSf-*b*-PEG membrane prepared at 15% copolymer concentration. The PEG phases appear darker in the image because of the selective enrichment of OsO_4 .

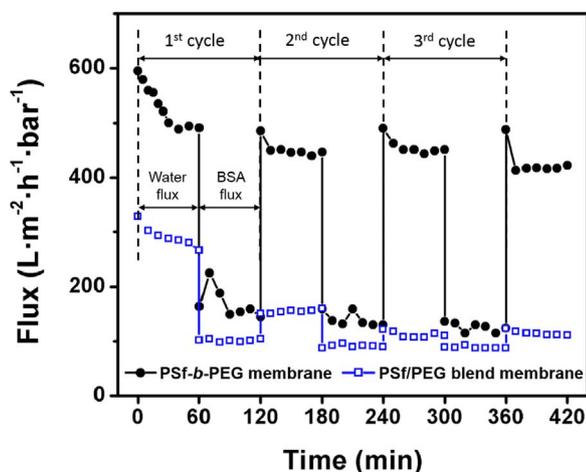


Fig. 6. Changes in the flux of the PSf-*b*-PEG membrane and the PSf/PEG blend membrane in the alternative filtration of pure water and BSA solutions for three cycles.

exchange of hydrogen bonds [38]. As the PEG microdomains are interconnected water molecules can diffuse through the membrane following the pathway of the PEG microdomains. Therefore, the PEG microdomains deliver a function of water channels accelerating the transport of water in the membrane. In addition, the porosity in the membrane originated from the macrophase separation during the NIPS process still exists and allows water transport through the membrane. Due to the additional effect of water channels the PSf-*b*-PEG membranes exhibit much higher water permeance than other membranes which do not contain water channels.

3.4. Fouling resistance of the PSf-*b*-PEG membranes

As we discussed in Section 3.1 the PEG blocks are selectively enriched on the membrane surface as a result of surface segregation, the PSf-*b*-PEG membranes exhibit an improved surface hydrophilicity. Consequently, the membranes are expected to have a good resistance to the adsorption of foulants including proteins because of the reduced hydrophobic interactions of hydrophilic membrane surfaces. To investigate the fouling resistance of the PSf-*b*-PEG membranes we tested the flux recovery ratio (FRR), which is an indicator of the antifouling performance of membranes, of the membrane prepared at 15% copolymer concentration. The membrane was first used to filtrate DI water for 60 min until a stable water flux was achieved. Then the BSA solution was used to foul the membrane for another 60 min. After fouling, we washed membranes thoroughly with DI water. The water flux of the cleaned membrane was tested again. Such alternative filtration of DI water and BSA solutions was repeated for three cycles. As we can see in Fig. 6, the original water flux was stabilized around $490 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. After fouling by the BSA solution, the flux was declined to less than $200 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. The water flux of the cleaned membranes was recovered to $\sim 420 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ after three cycles of alternative filtration of DI water and BSA solutions, which remained unchanged with further filtration with DI water. The FRR is therefore can be determined to be 86%.

It had been reported that the FRRs of other PSf-based membranes prepared using different hydrophilic additives, including chitosan derivatives [33], polymer-modified TiO₂ nanoparticles [34], and polyaniline nanofibers [39], varied in the range from 68% to 78%. Moreover, we also prepared PSf membranes with PEG homopolymer as the additives and compared the fouling resistance of the PSf-*b*-PEG membrane and PSf/PEG blend membrane with the same content (3.15 wt% in the entire casting solutions) of PEG component in the casting solutions. As shown in Fig. 6, the initial pure water flux of PSf/PEG blend membrane was around $270 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. After three cycles of tests, the final flux was about $110 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, and its

FRR could be determined to be 41%, which is less than one half of the PSf-*b*-PEG membranes. Therefore, we conclude that the fouling resistance of the PSf-*b*-PEG membranes is outstanding compared to PSf homopolymer membranes using different additives. Moreover, the fouling resistance of PSf-*b*-PEG membranes is expected to be long standing because the PEG blocks would not leach out as they are covalently bonded to the PSf blocks consisting of the membrane matrix. This long-standing hydrophilicity and fouling resistance is a special advantage of the PSf-*b*-PEG membranes and very much desired because foreign additives physically doped into the membranes frequently suffer from leaching out during operations, leading to fading and loss of the hydrophilicity and fouling resistance with time [6].

4. Conclusions

Block copolymers of PSf and PEG (PSf-*b*-PEG) are used to prepare UF membranes by the NIPS process. The recipe of the membrane casting solutions contains only the copolymer and the solvent and no additive or modifier is involved. Interestingly, the produced membranes exhibit permeability up to several times higher than other PSf-based membranes prepared using various additives while their retentions are similar. The retentions of the copolymer membranes can be tuned in a relative wide range simply by adjusting the copolymer concentrations in the membrane casting solutions. The membranes have enhanced surface hydrophilicity and consequently good fouling resistance as indicated by FRR tests. The excellent performances of the PSf-*b*-PEG membranes are ascribed to the PEG blocks covalently bonded to the PSf blocks consisting of the membrane matrix. The PEG blocks are selectively enriched on the membrane surface as a result of surface segregation in the phase inversion process, leading to the enhanced hydrophilicity. Moreover, as a result of microphase separation of the block copolymer PEG blocks form interconnected cylindrical microdomains distributed throughout the bulk membrane, and the PEG microdomains serve as water channels facilitating water transport along the membranes. This “amphiphilic block copolymer alone” strategy is expected to be expanded to prepare other advanced polymeric membranes with upgraded permeability and fouling resistance.

Acknowledgements

Financial support from the National Basic Research Program of China (2015CB655301), the Natural Science Foundation of Jiangsu Province (BK20150063), and the Project of Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) is gratefully acknowledged.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.memsci.2016.12.009.

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