Selective Swelling Blends of Block Copolymers for Nanoporous Membranes with Enhanced Permeability and Robustness

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ABSTRACT: Block copolymers (BCPs) are important precursors to produce membranes with well-defined porosities. However, it remains challenging to prepare robust and affordable BCP-based membranes. In this work, cheap commodity styrene-butadiene-styrene (SBS) elastic triblock copolymers are mixed with polystyrene-block-poly (2-vinylpyridine) (SV) block copolymers in solutions, leading to macroscopically stable blend films upon casting because of the compatibilizer effect of PS existing in both copolymers. By soaking the blend films in ethanol, the microdomains of poly(2-vinylpyridine) are selectively swollen and cavitated upon drying, resulting in a hierarchical structure with perforated SV phases interwoven with the SBS phases. The blend membranes with 30% SBS exhibit improved water permeability and mechanical robustness due to the presence of elastic SBS compared to neat SV membranes; meanwhile, the rejections of the blend membranes remain largely unchanged. Moreover, the blend membranes exhibit a pH-responsive function, and homoporous SV regions are obtained by pre-aligning the SV phases. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part B: Polym. Phys. 2017, 55, 1617–1625

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INTRODUCTION Microphase separation of block copolymers (BCPs) composed of two or more incompatible homopolymer chains leads to ordered nanostructures with uniform feature sizes tunable in the range of ~10–100 nm.1–3 By leveraging their microphase separation BCPs have emerged as very promising precursors to produce nanoporous membranes with well-defined porosities.4,5 Cavitation of the dispersed phases (composed of the minority blocks) embedded in the microphase-separated BCPs produces scaffolds with nanopores in the positions where the minority blocks are initially occupied. The pore sizes are typically in the range of ~10–100 nm. However, by controlling the conformation of the chains tethered to the pore walls, the pores can be pushed down to ~2 nm.6,7 Usually, nanoporosities are generated in microphase-separated BCPs by selectively degrading the minority phases composed of labile blocks8,9 or by selectively extracting the additives previously incorporated into the minority blocks.10,11 These methods are enabled by the selective removal of the entire or part of the dispersed phases, which are based on chemical reactions or intramolecular interactions (e.g., hydrogen bonding) specific to the chemistry of the BCPs. They are advantageous in faithfully coining the precise geometry of the dispersed phases although their operations are often tedious and frequently require troublesome etching conditions. Alternatively, we recently developed a nondestructive swelling-based strategy, namely, selective swelling-induced pore generation, to produce nanoporous polymers including membranes.12–14 This method is distinguished for its extreme ease and high efficiency as nanoporous membranes can be obtained simply by soaking amphiphilic BCP films in polar solvents. Furthermore, if the swelling is carried out on pre-aligned BCP films with the perpendicular or in-plane orientation homoporous membranes with perfectly ordered cylindrical pores or slit-shaped pores can be prepared, respectively.15–17 Moreover, in contrast to cavitate preformed dense BCP films for both the selective removal and selective swelling approaches, a group of researchers developed a more direct method to produce nanoporous BCP membranes by integrating the self assembly of BCPs into the nonsolvent-induced phase separation (NIPS), and obtained asymmetric porous membranes with thin layers of uniform nanopores sitting on macroporous

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spongy layers. However, most BCP membranes rely on BCPs with polystyrene (PS) [6–20] or its derivatives as the majority blocks. PS-based BCPs are suffering from poor mechanical robustness and thermal stability as PS is an amorphous thermoplastic with a glass transition temperature ($T_g$) of ~100 °C. As a solution to this issue, researchers incorporated a rubbery third block to the PS-based copolymers and obtained membranes with improved mechanical properties via the NIPS method. Recently, we demonstrated that the strategy of selective swelling-induced pore generation was also able to cavitate triblock terpolymers with a rubbery block, and found that the rubbery blocks enhanced the mechanical robustness of the nanoporous membranes on one hand, and evidently accelerated the swelling process, on the other, thus leading to 2–3 folds improved permeability.

Inspired by works developing robust membranes from copolymers containing rubbery moieties, we anticipate that, instead of covalently incorporating the rubbery chains into the backbone of the copolymers, physically blending a rubbery polymer into the pore-forming BCP may also have a similar effect in improving the mechanical stability of the resulted BCP membranes. The most critical point of this blending strategy lies in that the rubbery polymer and the pore-forming BCP should be sufficiently compatible to avoid significant macrophase separation. One solution is to ensure that the rubbery polymer and the pore-forming BCP have one same polymer block which would serve as compatibilizers to minimize macrophase separation. Specific to the selective swelling method, PS-block-poly(x-vinyl pyridine) (PS-b-PxVP, $x = 2$ or 4; abbreviated as SV hereafter) is typically used.

The PxVP blocks comprise the dispersed phases to be cavitated whereas the PS blocks form the scaffolds holding the PxVP phases and the pores after swelling. Therefore, the PS blocks should be used as the compatibilizers, implying that the rubbery polymer should also contain a PS block. Considering that styrene-butadiene-styrene (SBS) triblock copolymers are commodity elastic polymers available in large scale at very low cost we expect that SBS might be a good choice to be blended with SV for the preparation of robust nanoporous BCP membranes. The strategy of blending SBS with SV possesses one additional merit which is highly desired from the aspect of upscalability and practical applications: it reduces the consumption of the very costly pore-forming SV BCPs, which are currently thousands of times expensive than SBS. In addition, the swelling and cavitation behavior of SV with the presence of SBS are expected to be influenced by the confinement effect of the SBS phases, and it may lead to interesting structures not available for the case without SBS, thus providing new possibility to tune the morphologies and performances of BCP membranes.

In this work, we blend SBS and SV at various ratios and explore the selective swelling behavior of the blended films. We investigate the morphologies, phase distributions, and the separation performances of the resulted nanoporous BCP membranes. As expected, the blend membranes show enhanced mechanical properties. Interestingly, because of the SBS framework in the membrane structures, the blend membranes exhibit increased water permeability than neat SV membranes while the selectivity defined by the SV regions remains largely unchanged. In addition, this work suggests a convenient strategy to prepare hierarchical nanoporous nanostructures with tunable morphology and pore sizes, which may find interesting applications in other fields such as biomedical scaffolds and functional coatings.

**EXPERIMENTAL**

**Membrane Preparation**

A certain quality of PS-block-poly (2-vinyl pyridine) [SV, $M_n$ (PS) = 50,000 g mol$^{-1}$; $M_n$ (P2VP) = 16,500 g mol$^{-1}$; $M_w$/$M_n$ = 1.09; purchased from Polymer Source, Canada] and SBS triblock copolymers (YH-792, S/B ratio is 40/60, purchased from SINOPEC, China) were dissolved in chloroform with a total concentration of 2 wt %. The SV/SBS blend solutions were then ultrasonic treated and filtrated with disposable polytetrafluoroethylene strainers (nominal pore size: ~0.22 μm) to remove any big aggregates. The blend films were prepared by spin-coating (at a revolving speed of 2,000 rpm for 30 s) the solution on cleaned silicon wafers. The blend films were then immersed in ethanol at 60 °C for different durations, followed by air drying at room temperature, to cavitate the SV phases by the mechanism of selective swelling-induced pore generation. To prepare homoporous structure in the SV phases, the blend films were first annealed in the vapor of chloroform to perpendicularly align the P2VP cylinders. The prealigned films were then soaked in ethanol at 50 °C for 5 h to convert the P2VP cylinders into perpendicularly pore channels. For the preparation of composite membranes, we followed our previous fabrication procedures. Briefly, a minimum of 20 μL blend solution was directly coated on water-filled macroporous polyvinylidene fluoride (PVDF) membranes (Millipore, nominal pore diameter ~0.22 μm). Heating at 130 °C for 20 min was then performed to evaporate the solvent and more importantly, to enhance the adhesion between the BCP layer and PVDF layer. The BCP-coated PVDF membranes were then subjected to ethanol swelling to cavitate the SV phases at 60 °C for different durations. Thus composite membranes with the BCP blend layers (1–3 μm thickness) as the selective layers and macroporous substrates the supporting layers were obtained. Water permeabilities of the PVDF membranes were much larger than those of the composite membranes. So the resistance of the PVDF supports was considered negligible.

**Characterization**

A field emission scanning electron microscope (S4800, Hitachi) was used to observe the surface and cross-sectional morphologies of different samples, which were sputtering-coated with a thin layer of gold prior to SEM examination to enhance their conductivity. Atomic force microscope (AFM, Park Systems XE-100) at tapping mode was used to characterize the surface morphologies of the blend films.
Spectroscopic ellipsometry (M-2000, J.A. Woollam) was used to determine the thickness of BCP layers at an incidence angle of 65° in the wavelength range from 400 to 999.8 nm. Tensile properties of the composite membranes as well as the PVDF substrates were tested with an electronic universal testing system (CMT6023, Shenzhen SANS). A rotational viscometer (DV-III, Brookfield) was used to test the viscosity of polymer solutions.

**Filtration Tests**

Filtration tests were performed at 0.05 MPa on a stirred cell module (Amicon 8010, Millipore) at room temperature. The composite membranes were pre-pressed at 0.05 MPa for 10 min for both the flux and separation measurements. Deionized water was used to measure the pure water permeabilities (PWP). Bovine serum albumin (BSA, purity >97%, purchased from General Material) and polyethylene glycol (PEG, PDI < 1.2, purchased from Polymer Source, Canada) with a molecular weight of 150 KDa served as the media to probe the separation performances of the membranes. BSA and PEG were dissolved in phosphate buffered solution and in water, respectively, at a concentration of 0.5 g/L. Fast stirring at 900 rpm and small sampling were carried out to avoid the potential concentration polarization. The concentrations of BSA solutions were measured via the UV absorbance at 280 nm with a UV–Vis absorption spectrometer (NanoDrop 2000c, Thermo). The concentrations of PEG solutions were analyzed by gel permeation chromatography (Waters 1515). The permeabilities of the composite membrane after swelling for 5 h versus pH were tested to illustrate its pH-responsive characteristic. HCl or NaOH was used to adjust the pH values of water.

**RESULTS AND DISCUSSION**

SV/SBS blends with arbitrary blending ratios dissolved in chloroform with 2 wt % concentration produced clear solutions maintaining macroscopically stable for months at room temperature. Thin films were obtained by spincoating the SV/SBS blend solutions on silicon substrates. SEM examinations revealed that the as-coated films exhibited dense and relatively smooth surfaces. However, for the films with SBS percentage > 30%, patchy morphologies can be observed. For instance, as shown in Supporting Information Figure S1, isolated patches in irregular shapes with the size of ~1–2 μm appear on the surface of the as-coated blend film with 30% SBS, implying the phase separation of SV and SBS in the blend films takes place in relatively local regions. To discriminate the phases of the blend films we used acetone to selectively extract the SV component, leaving the intact SBS phase in the film. Supporting Information Figure S2 shows the morphology of the acetone-extracted blend films with various SBS percentages ranging from 30 to 90%. Clearly, acetone extraction produces mesh-like structures in the blend films and the mesh sizes become smaller with increasing SBS percentages. Because acetone only dissolves away SV and leaves SBS behind we understand that the patches on the surface of the as-coated blend films (Supporting Information Figure S1) are composed by SV. For the blend film with 30% SBS percentage, acetone extraction produces meshes with the size of ~1–2 μm (Supporting Information Figure S2), which is in good consistence to the size of the patches found on the film before extraction (Supporting Information Figure S1).

For the blend films with SBS percentages lower than 50%, SV is the majority component; however, if we only consider the surface morphology it seems that SV forms the minority phases in the blend films as indicated by the isolated meshes in Supporting Information Figure S2. This observation is very interesting as it seems to be against the well-established phase separation behavior of polymer blends. To confirm
the identification of different phases in the blend films by acetone extraction is reliable, we treated the blend films by ethanol swelling to cavitate the SV phases. Figure 1 shows the SEM images of the SV/SBS membranes with 30% SBS prepared by swelling in ethanol at 60 °C for 5 h. Interestingly, the original nonporous patches on the blend film before swelling turn to be nanoporous regions [Fig. 1(a)], and a closer examination reveals that the nanoporous regions exhibit an interconnected porous morphology similar to that of the neat SV membrane prepared under the same swelling condition [Fig. 1(b) vs. Supporting Information Figure S3]. In the swelling process, the polar solvent, ethanol, selectively swells the P2VP chains in the SV regions. After taken out from ethanol, the swelling P2VP chains collapse while the spaces initially occupied by P2VP are fixed by PS, thus pores are created. During selective swelling, the hot ethanol not only strongly swells the P2VP domains, but also moderately swells the PS domains, thus enhancing segmental mobility of the PS matrix and making the pore formation easier. By contrast, only few pores on the surface are generated when SV films are swelled in acidic water due to the poor interaction between water and PS matrix. We note that for the ultrathin micellar SV films, partial cavitation can occur by swelling in water. Because only the SV phases in the blend films can be cavitated by ethanol swelling, we confirm that the nanoporous regions are the SV phase and the nonporous parts are the SBS phase, which is in accordance with the tests of acetone extraction. Merely from the surface morphology, one may conclude that the SV phases are isolated in the SBS matrix as the dispersed phases.

However, SEM examinations of the cross section [Fig. 1(c,d)] as well as the bottom surface (Supporting Information Figure S4) of the sample reveal that the side of the film directly adhering to the surface of the substrate is mostly porous, implying that it is the SV phase. Therefore, we understand that the SV phases form a continuous phase with isolated protrusions extending to the film surface. That is, in such a blend ratio, the blend film is in a bicontinuous morphology with both SV and SBS segregating as continuous phases interweaving with each other. Such a bicontinuous phase is due to the selective enrichment of the SV and SBS phase to the substrate and air side, respectively. The silicon substrate has a native oxide surface with a high surface energy (60–75 mN/m). In the film coating process, P2VP blocks in SV preferentially wet the substrate surface because P2VP has the highest surface energy (52 mN/m) among all the three blocks composed of both SV and SBS. Because P2VP blocks are covalently linked to the PS blocks in SV, the SV phase is forced to form the underlayer predominantly attaching the substrate surface. In contrast, polybutadiene has the lowest surface energy (32 mN/m) and consequently the strongest tendency to be enriched on the top surface to contact the air side. As a result, SBS forms a continuous phase predominantly covering the top surface and SV is allowed to limit-edly contact the top surface as isolated regions.

We then investigate the morphology of blend membranes with various SBS percentages. Compared to the neat SV membrane without blending SBS (Supporting Information Figure S3), the blend membrane with 10% SBS basically maintains the bicontinuous porous structure while some nonporous areas with sizes smaller than 200 nm scatter on the surface [highlighted by circles, Fig. 2(a)]. With increase of SBS percentage up to 70%, the blend membranes show a composite structure with SBS as the framework and SV as the perforated regions [Fig. 1 and 2(b,c)]. The sizes of the perforated regions decrease with the increase of SBS percentage. For instance, the size is reduced to mainly around 1 μm with the SBS percentage of 50%, and further reduced to less than ~0.5 μm with the SBS of 70%. Such a shrinkage in the size of the perforated regions is reasonable as it is the response of the reduction in the content of SV in the blend.
Such a hierarchical structure of cavitated phases interwoven with the nonporous scaffold is a result of two levels of phase separation occurring in the blend films. One is the macroscopic phase separation between the SV components and the SBS components because they are not completely compatible. The other is the microphase separation between PS blocks and P2VP blocks in the SV phase because of the strong repulsion between the two covalently linked blocks.28 The SV phase is identified after ethanol swelling, as it is cavitated while the SBS phase remains intact through the swelling process. However, it should be noted that as both copolymers have PS blocks, which may serve as compatibilizers the macrophase separation between SV and SBS takes place to a limited degree. Consequently, the blend films maintain macroscopically stable before and after cavitation by ethanol swelling.

Such a hierarchical nanoporous structure with macroscopic stability allows these blend membranes to be used for pressure-driven separations. We then investigate the separation performances of these blend membranes with various SBS percentages as well as the neat SV membrane prepared under identical cavitation conditions (ethanol swelling at 60°C for 5 h). Here, we note that the addition of SBS increases the viscosity of the polymer coating solutions. For instance, the viscosity of the blend solution with 30% SBS at 20°C is evidently increased to 2.46 cP from 1.86 cP for the neat SV solution with the same concentration of 2 wt% (Supporting Information Table S1). The increased viscosity is very much desired as higher viscosities help the solution to be more uniformly coated along the water-filled porous substrates to secure defect-free BCP coating layers. As shown in Figure 3, the blend membrane with 10% SBS prepared by ethanol swelling at 60°C for 5 h displays a water permeability of $596 \pm 34$ L/(m² h·bar) and BSA rejection of $\sim 27\%$. When 30% SBS is blended, the permeability is slightly changed to $569 \pm 64$ L/(m² h·bar) and the BSA rejection is changed to $\sim 26\%$. When the SBS percentage is increased to 50%, the water permeability is sharply decreased to $196 \pm 15$ L/(m² h·bar) and the BSA rejection is increased to $\sim 43\%$. Here, we note that the rejection properties of the neat SV membranes and SV/SBS blend membranes with 30% SBS are similar, as the impermeable SBS regions do not affect the rejections. However, for the blend membranes with 50% SBS, some SBS regions are present at the bottom surface (Supporting Information Figure S5). The dense SBS regions running throughout the membranes can then serve as some kind of containers and retain BSA in the membranes. The drastic decrease of permeability from 30 to 50% SBS is also ascribed to the SBS regions present at the bottom surface. Increasing the SBS percentage to 70 and 90% leads to further reduced permeability and increased rejections. As for the neat SBS film, no water permeates can be collected because of its nonporous nature. The decreased permeability and increased rejection of the blend membranes with rising SBS percentages can be easily understood as higher SBS percentages reduce the ratio of nanoporous regions on the membrane surface, and consequently the surface porosity of the blend membranes.

Considering that the blend membrane with 30% SBS exhibits a similar permeability and rejection to the membrane with 10% SBS while blend with 50% SBS cuts down the permeability more than one half without proportionate improvement in rejection, we choose 30% SBS blending as the optimal condition to balance the membrane performances and the consumption of the costly SV copolymer. In the following sections, all the blend membranes are prepared from SV/SBS blend films with 30% SBS. We prepared SV/SBS blend membranes by swelling in ethanol at 60°C for different times to tune the performances, and make a detailed comparison with that of neat SV membrane. We ex situ monitor the change of the membrane thickness with swelling time by ellipsometry. As shown in Figure 4, the SV/SBS membrane experiences a rapid increase in thickness upon swelling treatment in the initial 1 h and then continues to slightly increase with further prolongation of the swelling time. The thickness of the blend membrane before swelling is $\sim 255$ nm, and is rapidly increased to $\sim 399$ nm after...
swelling for 1 h, and reaches to ~447 nm with a swelling time of 15 h. In comparison, the thickness of the neat SV membrane is increased to a higher degree within the same swelling time. The increase in thickness is due to the volume expansion as a result of pore formation in the membrane during the swelling process.

As the membrane is supported on substrates, the volume expansion of the membrane can only occur in the perpendicular direction. Therefore, the porosity of the membranes (namely the pore volume throughout the membranes) can be easily estimated by comparing the thickness of the membrane before and after swelling treatment. That is, the percentages of thickness increase can be directly regarded as porosity.27 As shown in Figure 4, a swelling time of only 10 min can give a porosity of 28%, and the porosity keeps steadily increasing to 36% with a swelling duration of 1 h. The porosity is then slowly increased to 39 and 43% with a swelling duration of 5 and 15 h, respectively. The increase of porosities with swelling duration is ascribed to the higher cavitation degree of the SV phases. As the swelling approaches saturation eventually, the increase in porosity slows down. In comparison, the neat SV membrane obtains higher porosities within same swelling durations. For instance, the porosity of the neat SV membrane with the swelling duration of 1 and 15 h is 46, and 59%, respectively. This indicates that the blend membrane is cavitated to a lower degree with respect to the neat SV membrane. This is because in the blend membrane the SV phases are three-dimensionally interwoven with the SBS phases, which have a confinement effect to depress the swelling of the SV phases. However, because SBS is an elastomer easy to deform under external forces it cannot completely suppress the swelling of SV phases. Therefore, the SV phases in the blend membranes still can be cavitated, but to a somewhat limited degree.

The surface morphologies of the blend membranes subjected to different swelling time are investigated by SEM. The as-coated blend film is nonporous although some patches exist on the surface (Supporting Information Figure S1). After swelling for 10 min, the SV phases are clearly cavitated, and nanopores in the form of narrow channels or circular openings with an average pore size of ~13 nm appear while the SBS regions keep a nonporous morphology like that before swelling [Fig. 5(a)]. With extending swelling time, the degree of cavitation in the SV regions develops and the pores are progressively enlarged [Fig. 5(b–d)]. The pore size is increased from ~15 nm for a swelling time of 1 h to ~20 and ~23 nm for a swelling time of 5 and 15 h, respectively. The continuous tuning of the pore sizes of the SV regions in the SV/SBS blend membranes corresponds to our previous work on neat SV membranes28 and consequently, tunable separation performances of the blend membranes with swelling time are expected. Importantly, there are nanoscale gaps with the width of ~30–80 nm between the cavitated SV regions and the SBS phases in all the membrane with various swelling times. Moreover, some short SV struts (indicated by arrows in Fig. 5) crossing the gaps connect the SV and SBS phases, implying the merging of the edges of the two phases which remains to some degree even after swelling as a result of their relatively good miscibility of SV and SBS. These gaps are larger than the pores in the SV regions, allowing fast permeation. Moreover, there is a continuous nanoporous SV layer at the bottom of the blend membrane, as shown in Figure 1(c,d). This bottom layer continues working as the selective layer to reject larger species penetrating through the top SV layers.
into the gap, thus guarantee the high selectivity of the blend membranes. Therefore, such a hierarchical structure with nano-gaps between the two phases may contribute to improve water permeability at no expense of separation selectivity.

Figure 6 gives the permeability and retention performances of SV/SBS blend membranes subjected to different swelling durations. The performances of the neat SV membranes are also included for comparison. No water permeates through the blend membrane prior to swelling treatment, confirming a dense and defect-free nature of the coated film before swelling. The blend membrane shows a water flux of 175 ± 6 L/(m²·h·bar) after swelling for 10 min. After swelling for 1, 5, 15, and 24 h, the flux is increased to 257 ± 6, 348 ± 34, 548 ± 55, and 1004 ± 67 L/(m²·h·bar), respectively. The increase of water fluxes with the lengthening of the swelling time is due to the continuous enlargement of the pores in the SV regions as we discussed above.

Correspondingly, the rejections to the PEG molecules with a molecular weight of ~150 KDa exhibit an exactly reversed trend to that of the permeability. That is, the PEG rejections is decreased from ~90%, to ~81%, ~60%, ~48%, and ~29%, respectively, as the swelling duration changes from 10 min, to 1, 5, 15, and 24 h. Moreover, the SV/SBS blend membranes display higher permeability than the neat SV membranes prepared under identical swelling conditions. Specifically, the water flux of the neat SV membranes swelling for 10 min, 1 h, 5 h, 15 h, and 24 h is 125 ± 12, 232 ± 18, 361 ± 42, 650 ± 52, and 785 ± 45 L/(m²·h·bar), respectively, which are all evidently smaller than those of the corresponding blend membranes with a reduction of ~10–34%. The higher permeability of the blend membranes than the neat SV membrane is due to the “nano-gaps” between the SV and SBS phases in the blend membranes as we discussed above. Interestingly, the PEG rejections of the blend membranes change little to those of the neat SV membranes. The largely unchanged rejections are attributed to the fact that the porous SV regions of the blend membranes share the same pore structures with the neat SV membranes prepared under the identical swelling conditions.

The tensile properties of the blend membrane and the neat SV membrane are tested to analyze their mechanical stability, and the results are shown in Figure 7. Because the membranes are in a composite form with the BCP selective layers deposited on the PVDF substrates, the tensile property of the PVDF substrate is also tested as contrast. The PVDF substrate displays a tensile strength of 5.3 ± 0.3 MPa and an elongation at rupture of 48 ± 2%. The tensile strength and elongation at rupture for the neat SV membrane are reduced to 4.5 ± 0.2 MPa and 30 ± 4%, respectively. For the blend membrane, the tensile strength and elongation at rupture are 4.9 ± 0.2 MPa and 40 ± 4%, respectively. Although the tensile properties of composite membranes are mainly determined by the PVDF substrates, the higher tensile strength and elongation at rupture of the blend membrane still indicate its better robustness than the neat SV membrane because of the presence of elastic SBS component in the BCP layers.
Because the nanoporous SV phases deliver the filtration and separation function, the blend membranes keep the functional characteristics of the neat SV membranes. For example, like the neat SV membrane, because of the enrichment of weak-polyelectrolyte-natured P2VP chains on the pore walls in the nanoporous SV regions the blend membranes exhibit a gating effect leading to pH sensitive water permeabilities (Fig. 8). Moreover, as shown in Figure 9, the pore orientation in the SV regions on the membrane surface can be perpendicularly aligned to prepare homoporous structures hosted in the SBS scaffold. A solvent annealing process was first performed on the blend films to pre-align the P2VP cylinders in the perpendicular orientation, and then ethanol swelling is carried out to produce highly ordered homopores in the SV regions. Here we note that the uniform pores in Figure 9 were obtained on Si wafers. SV/SBS blend membranes with homoporous structures on macroporous supports can also be obtained by direct coating or post-transferring. Such a homoporous structure is expected to significantly increase the selectivity of the blend membrane, which is currently under investigation.

CONCLUSIONS

Elastic SBS BCPs and pore-forming SV BCPs are mixed in solution to prepare blend films. Selective swelling induced pore generation is performed on the blend films, and we obtain hierarchical bi-continuous structures with nanoporous SV phases interwoven with the dense SBS phases. We coat the blend solutions on macroporous PVDF substrates to produce composite membranes. The blend membrane with 30% SBS shows best balanced separation performances and consumption of costly SV polymers, and we make a detailed investigation on the morphology and performance of this blend membrane with the neat SV membrane as a control. Due to the presence of “nano-gaps” between the SV and SBS phases the blend membranes show increased water fluxes than the neat SV membranes while the selectivity defined by the SV regions remains largely unchanged. Tensile tests indicate that the blend membrane shows stronger tensile strength and larger elongation at rupture than the neat SV membrane because of the presence of elastic SBS in the blend membranes. Like the neat SV membranes, the blend membranes also exhibit an inherent pH-responsive functionality. Moreover, by pre-aligning the blend film before swelling the cavitated SV regions in the blend membrane can be tailored to possess a highly ordered homoporous structure. We expect that blending with commodity BCPs provides new chances for the upscaling of BCP membranes and also to tune their separation properties. Moreover, such a hierarchical structure with localized nanoporous phases interwoven with solid scaffold may find interesting applications in other fields such as biomedical engineering, and functional coating.

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REFERENCES AND NOTES