Homoporous Membranes with Tailored Pores by Soaking Block Copolymer/Homopolymer Blends in Selective Solvents: Dissolution versus Swelling

Mingjie Wei, Wei Sun, Xiansong Shi, Zhaogen Wang, and Yong Wang*

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, Jiangsu, P. R. China

ABSTRACT: Extraction homopolymers premixed in aligned films of block copolymers by rinsing with selective solvents has long been used for the preparation of membranes with uniform straight pores (homoporous membranes). It is frequently assumed that only the dissolution of homopolymers contributes to the pore formation. However, in this work, we demonstrate that the effect of swelling plays a significant role in determining the pore sizes. We prepare blended films of block copolymers of polystyrene-block-poly(2-vinylpyridine) (PS-b-P2VP) and P2VP homopolymers with low molecular weight and anneal the films to perpendicularly align the P2VP microdomains. Rinsing the aligned films in ethanol results in homoporous membranes, and the pore sizes can be tuned by the dosages of P2VP homopolymers. Interestingly, the pore sizes can also be effectively tailored by changing the rinsing temperatures and/or durations because of the significant contribution of the selective swelling of P2VP blocks under strong rinsing conditions in addition to the contribution of the dissolution of P2VP homopolymers. We identify the portion of the contribution from dissolution and from swelling.

1. INTRODUCTION

Porous films with uniform straight nanopores opened at both ends, featured with both homogeneous pore sizes and homogeneous pore geometries, can be termed as homoporous membranes (HOMEs). HOMEs with perpendicularly aligned cylindrical pores have been finding interesting applications in diverse fields such as size-selective separation, drug delivery, photolithography, and template synthesis for one-dimensional nanostructures. There have been a number of strategies for the fabrication of HOMEs with anodization of aluminum, track-etching of polymers, and microfabrication of silicon as the most extensively used ones. Recently, self-assembly based on the microphase separation of block copolymers (BCPs) has emerged as a promising alternative to produce HOMEs because of its flexibility in morphology regulation, ease in operation, and affordable costs. BCPs are hybrid macromolecules containing two or more chemically distinct homopolymers chains covalently linked together. They undergo microphase separation under appropriate thermodynamic conditions, leading to a variety of well-defined periodic nanostructures, including spheres, cylinders, gyroids, lamellae, etc. The preparation of HOMEs from BCPs involves two main steps: (1) perpendicularly aligned orientation of the cylindrical microdomains in BCPs and (2) the transformation of the aligned cylinders into straight pores. There is a constant demand for HOMEs with precisely and continuously tailorably pore sizes to fit dynamic application situations. However, the tunability in the pore sizes of the BCPs-derived HOMEs is specific to the varying pore-generating strategies. The most direct way to create pores is to chemically etch away the blocks comprising of the aligned cylinders given there are labile bonds in these blocks. This method has been extensively used in BCPs containing poly(methyl methacrylate) (PMMA), polylactide (PLA), poly(dimethylsilane) (PDMS), etc., and the pore sizes of thus produced HOMEs are completely determined by the diameters of the aligned cylinders which are fully transformed to through pores. To tune the pore sizes of the resultant HOMEs, one needs to repeat the entire alignment and etching process by using BCPs with correspondingly changed molecular compositions, which not only is cumbersome and tedious but also requires synthesis of BCPs with the exact composition. Alternatively, Russell and others developed a much flexible method to tune the sizes of the cylinders and subsequently the pores in BCPs-derived HOMEs. They mixed homopolymers or small molecules with BCPs which were incorporated into the domains of the minor block by solubilization or noncovalent interactions, e.g., hydrogen bonds, in the alignment step. These additives were then removed simply by rinsing, leading to through pores along
the previously aligned microdomains. The pore sizes in this method are governed by the dosages of the additives, enabling tunable pore sizes from the BCP with a fixed molecular composition. However, the tuning range in pore sizes of this method is still very limited as the additive dosages beyond the saturation will be excluded from the microdomains of the minor block, no longer contributing to enlarge the pore sizes and resulting in phase separation in macroscale. Moreover, they combined the two methods together and produced HOMEs with pore sizes in the range 6−22 nm. They blended the PMMA homopolymer with BCPs of polystyrene (PS) and PMMA (PS-b-PMMA), allowing the PMMA homopolymer to be solubilized in the domains of the PMMA blocks. Perpendicular alignment of the blended films was achieved by thermal annealing under vacuum. Rinsing in acetic acid removed the PMMA homopolymers, and UV irradiation further degraded the PMMA moieties in the BCPs; therefore, HOMEs exhibited pore sizes with larger tunability due to the dual pore-forming mechanisms. However, this method is also tedious and only applicable to the very limited number of BCPs with labile blocks, which are inherent to the pore-making mechanism of chemical etching and selective dissolution. Therefore, it remains demanding and challenging for the preparation of HOMEs with pore sizes tunable within wide ranges through simple and highly controllable methods.

In addition, in the preparation of HOMEs through selective dissolution, a selective solvent is used to extract the premixed homopolymers, and the extraction operation is typically operated with little care as it is frequently assumed that rinsing will not change the pore sizes as long as the incorporated homopolymers are completely extracted. It is no doubt that the selective solvent has a swelling effect to the blocks with the same chemical composition to the homopolymer in the BCPs. The swelling of these blocks will play a role in the formation of pores in the soaking of the blends with the selective solvent as we previously demonstrated that selective swelling of amphiphilic block copolymer led to nanoporous structures.

However, only very few works noticed or implied the contribution of the swelling effect, and no effort has been made to elucidate the swelling effect so far. The role of the block swelling in the pore formation remains to be elucidated, and to what degree the swelling effect contributes to the pore formation needs to be clarified and tuned through easy measures. For instance, Vriezekolk et al. very recently prepared nanoporous films by rinsing PS-b-P4VP/P4VP homopolymer blends with ethanol and demonstrated that the pore sizes can be tuned by varying the compositions of the blends. However, they lost the pore uniformity when the pore size exceeded 30 nm because of macrophase separation. Moreover, they merely showed the pore openings on the top surfaces of the films, and it was unclear whether these pores were through and straight pores. In this work, we identify the contribution from the dissolution effect of the homopolymer and the swelling effect of the corresponding blocks in the soaking of blends of PS-b-P2VP and P2VP homopolymers with ethanol. More importantly, by taking advantage of the dual effects of ethanol soaking in the pore-forming process, the pore sizes of thus-obtained HOMEs are tailored to be as large as 50 nm at no expense of pore ordering and uniformity, which is never achieved previously. The success in the fabrication of such enlargeable, straight, and through pores should be at least attributed to (1) the use of P2VP homopolymer that has a much lower molecular weight than the P2VP block (5 kg/mol vs 72 kg/mol), thus preventing the previously observed macrophase separation between the homopolymer and the BCP, (2) the perpendicular alignment by solvent annealing before the pore-forming step, and (3) the controllable soaking in ethanol at elevated temperatures rather than at room temperature to allow the formation of enlarged pores because of the additional swelling effect.

2. EXPERIMENTAL SECTION

2.1. Materials. Polystyrene-b-poly(2-vinylpyridine) block copolymer (PS-b-P2VP, M

7 = 290 kg/mol, M

p2VP = 72 kg/mol, PDI = 1.10), poly(2-vinylpyridine) homopolymer (abbreviated as hP2VP below, M

7 = 5 kg/mol, PDI = 1.06), and polystyrene homopolymer terminated with hydroxyl groups (abbreviated as PS-OH below, M

7 = 6 kg/mol, PDI = 1.07) were purchased from Polymer Source Inc. and were used without further purification. Organic solvents including chloroform, ethanol, and toluene with the purity in the analytical grade were obtained from local suppliers and were used as received.

2.2. Preparation of HOMEs. PS-b-P2VP block copolymer and P2VP homopolymer were mixed in chloroform, and the total polymer concentrations of the resulting solutions were varied in the range of 1−2.5 wt % depending on the required thicknesses of the blended films. The different dosages of added P2VP homopolymer defined as the weight ratios of hP2VP to PS-b-P2VP, 10% and 30%, were used in this work, and the neat BCP without any additional P2VP homopolymer, corresponding to a dosage of 0%, was also studied as a control. The polymer solutions were filtered through poly(tetrafluoroethylene) (PTFE) membranes with a nominal pore size of 0.22 μm to remove any insoluble aggregates. The solutions were then spin-coated on the substrates of silicon wafers or NaCl crystals at 2000 rpm for 30 s to prepare the films with different hP2VP dosages. To prepare HOMEs with pores opened on both ends, the silicon wafers were subjected to hydrophobic modification by grafting a layer of PS-OH with a thickness of ~4 nm on the surface. The detailed procedure for the modification is given in our previous work. The polymer films were then exposed to saturated chloroform vapor in a sealed glass container for a certain duration followed by quick removal of the container lid. This allowed chloroform in the polymer films to evaporate within a few seconds to perpendicularly align the P2VP phases. Such annealing in chloroform does not cause dewetting, and the uniformity in the film thickness was well preserved. Finally, the annealed films were immersed in ethanol at 50 °C for 3 h or 25 °C for 10 s followed by air drying at room temperature to produce HOMEs with varying pore sizes.

2.3. Characterization. The thicknesses and refractive index of polymer films were investigated by a spectroscopic ellipsometer (Complete EASEM-2000U, J.A. Woollam) at an incidence angle of 65° in the wavelength range from 400 to 999.8 nm. The surface hydrophilicity of polymer films was probed using a contact angle goniometer (DropMeter A100, Maist). For each sample, at least five different positions were measured, and the averaged values of water contact angles (WCAs) were reported. Transmission electron microscopy (TEM, JEM2100, JEOL) was used to analyze the sizes and distances of P2VP domains in the annealed films at an accelerating voltage of 200 kV. The annealed films with the thickness of ~110−120 nm deposited on NaCl crystals were immersed in deionized water, allowing the polymer films to be exfoliated from the NaCl substrates and floated in water. The films were then collected on copper grids. After air drying, the polymer films transferred onto copper grids were exposed to iodine vapor at room temperature for 3 h to selectively stain the P2VP phases. The morphologies of the films after ethanol soaking were examined by scanning electron microscopy (SEM, S4800, Hitachi) operated at 5 kV. To enhance conductivity, the samples were sputter-coated with a thin layer of platinum–palladium alloy prior to SEM observations. For the cross-sectional SEM samples, we first made a precut on the back side of the sample substrate and immersed the sample in liquid nitrogen for approximately half a minute followed by breaking the sample along the precut to expose the cross sections for SEM imaging. To observe the bottom side of the
polymer films, the annealed polymer films coated on silicon substrates with or without the modification of PS-OH were immersed in 5 wt % HF to etch away the sacrificial silicon oxide layer, allowing the complete exfoliation of the films from the substrate. Another silicon substrate was used to collect the film floating in the HF solution with bottom side up. The film was then subjected to ethanol immersion at 50 °C for 3 h to produce pores.

3. RESULTS AND DISCUSSION

We first prepared neat PS-b-P2VP films and blended films with 10% and 30% hP2VP dosages on the substrates of silicon wafers or NaCl crystals by spin-coating. The incorporation of hP2VP into the films was confirmed by the increase of surface hydrophilicity as measured by WCAs. The neat PS-b-P2VP film showed a WCA of 87°, while for the blended films with the addition of 10% and 30% hP2VP, the WCA decreased to 80° and 73°, respectively. The three films before solvent annealing were then subjected to ethanol soaking at 50 °C for 3 h and drying in air at room temperature. Disordered pores were found on the surface of all the films and more pores emerged on films with higher hP2VP dosages (Figure S1), confirming the corresponding dosages of hP2VP incorporated into the blended films. These results also suggest that alignment of the films prior to the pore-making treatment is mandatory to obtain well-defined uniform through pores.

We previously demonstrated that perpendicularly aligned cylindrical phases could be achieved by annealing PS-b-P2VP films in chloroform vapor.34 In this work, we extended this chloroform annealing process to the blended films with the purpose to achieve the perpendicular alignment of P2VP cylinders containing both the P2VP blocks and hP2VP. Interestingly, we found that the annealing duration needed to perpendicularly align the blended films (∼8 and ∼5 min for the films with 10% and 30% hP2VP dosages, respectively) was shorter than that of the neat BCP films (∼10 min). This should be ascribed to the plasticization effect of the P2VP homopolymer which has a low molecular weight (5K Da) and a much higher segmental mobility compared to both the PS and P2VP blocks. We transferred the annealed films on TEM grids and stained the P2VP phases with I2 to obtain a better contrast. TEM micrographs in Figure 1 show hexagonally arranged dark dots, corresponding to the projected P2VP cylinders as P2VP phases appear darker after I2 staining. As will be discussed later on, there is a P2VP layer on the bottom side of the polymer film wetting the Si substrate. However, the P2VP wetting layer is very thin, typically with a thickness of a few nanometers,31 while the P2VP cylinders have a height of ∼110–120 nm. Therefore, much more iodine will be enriched in the P2VP cylinders, and such a thin wetting layer will not obscure the identification of the heavily stained P2VP cylinders under TEM. It is clear that P2VP cylinders are perpendicularly aligned in the PS matrix in the hexagonal pattern, indicating that the chloroform annealing was also applicable to the alignment of block copolymer/homopolymer blended systems. Moreover, as both P2VP blocks and hP2VP can be stained by I2, the P2VP cylinders appearing dark are composed of them both and hP2VP is compatible to and solubilized in the P2VP blocks.35 For the neat PS-b-P2VP film, the mean diameter of the P2VP cylinders was 42 nm. The P2VP domains became larger with the addition of hP2VP. When 10% and 30% hP2VP were added, the mean diameter of the P2VP cylinders was increased to 51 and 56 nm, respectively. As the sizes of P2VP cylinders were determined by the volume fraction of the P2VP phases in the PS-b-P2VP/hP2VP system, we could also

Figure 1. TEM images of the annealed neat PS-b-P2VP film (a, b), the blended films with 10% (c, d) and 30% (e, f) dosages of hP2VP. The insets are the corresponding bar charts of the diameter distribution of P2VP cylinders. The P2VP phases appear dark with the selective enrichment of I2.
theoretically estimate the P2VP diameters of the blended films according to the diameter of P2VP cylinders in the neat PS-b-P2VP film and the dosages of the hP2VP. As the densities of bulk PS and P2VP are 1.05 and 1.11 g/cm³, respectively, and the densities of the P2VP block and hP2VP should be no noticeable difference, the volume fraction of the P2VP phase in neat PS-b-P2VP can be determined to be 19.0% and was increased to 26.1% after 10% dosage of hP2VP. The diameter of the aligned P2VP cylinders with 10% dosage of hP2VP therefore can be estimated to be 49 nm if we neglect the change in thickness and the packing density of polymer chains with the addition of hP2VP. Similarly, we can estimate that the theoretical diameter of P2VP cylinders was 58 nm for the blended film with 30% hP2VP. Clearly, the theoretical values are in excellent consistence with that obtained from TEM observations, which implies that all the P2VP homopolymers are incorporated into the cylinders; otherwise, the calculated diameters should be lower than that of the TEM results.

We also found that the domain distances (nearest edge-to-edge distances) of P2VP cylinders decreased with the addition of hP2VP, which was 46 nm for the neat PS-b-P2VP film and decreased to 33 and 28 nm for the blended films with 10% and 30% dosages of hP2VP, respectively. It was reported that when the molecular weight of the added homopolymer was far smaller than that of the corresponding block in the BCP, the polymer would be uniformly distributed in the phase domains, which is the case of the current work. The uniform distribution of hP2VP in the P2VP cylinders can be confirmed by the change of the nearest center-to-center distance (D), namely, the center distance of the nearest P2VP cylinders. For the block copolymer A-b-B/homopolymer B’ system, the B’ phase with a relatively small weight is dispersed evenly in the B domains, leading to the enlargement of the B domains and shrinkage of the A domains, while D remains unchanged. In contrast, if the molecular weight of B’ is similar to that of the B block and the B phase is restricted in the middle of the B domains, D would increase. Figure 2 represents the diameters of P2VP cylinders (D_{P2VP}) and nearest edge-to-edge distances of P2VP cylinders (this region is composed of PS phases and therefore is defined as D_{PS}) in the films with different hP2VP dosages.

The incorporation of P2VP homopolymer increases the sizes of the P2VP cylinders whereas their numbers remained unchanged, and the sizes of the pores induced by ethanol soaking increased with the incorporation of P2VP homopolymer at no expense of the pore densities. As a result, the surface porosities of the membrane were also increased by adding homopolymers. The surface porosities ε can be estimated using the equation

$$ε = \frac{n_p \pi r^2}{A_m}$$

where n_p is the counted number of the pores in an area A_m of the membrane, and r is the mean pore radius. The calculation was based on SEM images. For the membranes derived from neat BCP and the blends with 10% and 30% hP2VP, the calculated surface porosity was 13.2%, 21.6%, and 27.8%, respectively. The improvement of the porosities is very effective as a dosage of 30% hP2VP leads to a more than doubled porosity compared to the neat BCP without the incorporation of the homopolymer, which is highly desired in applications like separation where higher porosities enable larger permeability.

Table 1 summarizes the structural parameters of the annealed films with varying dosages of hP2VP before and after ethanol soaking. We found that the pore sizes of all the membranes were smaller than the sizes of the corresponding P2VP cylinders before ethanol soaking, implying that the space occupied by the P2VP chains was not completely transformed to empty channels; that is, there were some residual P2VP chains lined on the pore walls after ethanol soaking. By comparing the pore diameters and the corresponding sizes of the P2VP cylinders, we can estimate that the thickness of the lined P2VP layers along the pore wall is around 3–5 nm...

![Figure 2](image-url)

*Figure 2. Diameters of P2VP cylinders, D_{P2VP}, and the nearest edge-to-edge distances of P2VP cylinders (this region is composed of PS phases and therefore is defined as D_{PS}) in the films with different hP2VP dosages.*

DOI: 10.1021/acs.macromol.5b02133

depending on the pore sizes. More importantly, the increased volume of the pores in the ethanol-soaked membranes derived from the blended films compared to the membrane obtained from the neat BCP film are very close to the increased volumes of the P2VP cylinders in the blended films by the addition of hP2VP (Supporting Information). These observations suggest that the added hP2VP was completely removed in the ethanol soaking process, and the simultaneously occurring selective dissolution of hP2VP and selective swelling of P2VP blocks for the pore formation did not suppress each other.

For the films deposited on silicon substrates with a native oxide layer, a dense P2VP layer would form at the bottom of the film during solvent annealing due to the preferential wetting of the P2VP chains on the surface of the hydroxyl-group-terminated silicon substrates, thus hindering the pore formation on the bottom surface of the films and consequently reducing the porosity and ordering of the pores on this surface (Figure S2). Therefore, substrate modification to avoid the dense layer was necessary. After modification with PS-OH, the hydrophobicity of the substrates was enhanced and the enrichment of the P2VP chains at the interface and the consequent formation of dense layer could be avoided. Upon immersion in the HF solution, the intermediate oxide layer is destroyed, allowing the separation of the polymer layer and the silicon substrate. Consequently, the bottom morphologies of the films can then be observed with SEM, and the results are shown in Figure 4. Clearly, by using the modified silicon as substrates, the obtained membranes exhibited bottom surfaces with hexagonally patterned, uniform pores, similar to that on

---

Table 1. Structural Parameters of Polymer Films with Different hP2VP Dosages Treated in Ethanol at 50 °C for 3 h

<table>
<thead>
<tr>
<th>items</th>
<th>0% hP2VP</th>
<th>10% hP2VP</th>
<th>30% hP2VP</th>
</tr>
</thead>
<tbody>
<tr>
<td>vol fraction of hP2VP (%)</td>
<td>0</td>
<td>8.7</td>
<td>22.3</td>
</tr>
<tr>
<td>P2VP domain size (nm)</td>
<td>42</td>
<td>51</td>
<td>56</td>
</tr>
<tr>
<td>surface pore size (nm)</td>
<td>33</td>
<td>44</td>
<td>50</td>
</tr>
<tr>
<td>bottom pore size (nm)</td>
<td>23</td>
<td>43</td>
<td>47</td>
</tr>
<tr>
<td>surface porosity (%)</td>
<td>13.2</td>
<td>21.6</td>
<td>27.8</td>
</tr>
<tr>
<td>bottom porosity</td>
<td>6.4</td>
<td>20.6</td>
<td>24.6</td>
</tr>
<tr>
<td>thickness increase (%)</td>
<td>4.6</td>
<td>6.4</td>
<td>6.0</td>
</tr>
</tbody>
</table>

The deviation in the determination of domain sizes and pore sizes on SEM images are in the range of 3–8%, and the deviation of the film thickness obtained by ellipsometry is <5%. The variation in porosities calculated from Equation 1 are determined by that of the corresponding pore sizes. The bottom porosity was determined from films prepared on PS-modified surfaces.
the top surface. For membranes derived from films with 0%, 10%, and 30% hp2VP dosage, the mean diameter was 23, 43, and 47 nm, respectively. We notice that the pore size on the bottom surface was smaller than that on the top surface (23 nm vs 33 nm) for the membrane derived from the neat BCP film. However, pores on the top and bottom surface were almost equally sized for membranes derived from blended films with both 10% and 30% hp2VP dosages.

For all membranes there was always a minor but noticeable increase in thickness after the ethanol soaking treatment (Table 1). This, once again, confirms the contribution to the pore formation by selective swelling of the P2VP blocks because if the pores were generated exclusively by removal of P2VP homopolymers, the membrane should have an unchanged or a reduced thickness. The thickness increase is caused by the stretching of the PS matrix along the z-axis pushed by the accumulated osmotic pressure with the uptake of ethanol and also the migration of the P2VP blocks on the membrane surface.13 Ethanol has a strong affinity to P2VP but a weak affinity to PS. In addition, PS exhibits a glass transition temperature ($T_g$) of approximately 100 °C;39 therefore, the PS matrix is still remaining in the glassy state in ethanol when the temperature is elevated to 50 °C, thus holding the structural integrity of the polymer films. However, ethanol also exhibits a weak plasticization effect to PS as the $T_g$ of PS was observed to be decreased to ~85 °C when PS was immersed in ethanol;40 as a result, PS matrix has an enhanced mobility to be moderately stretchable in ethanol at elevated temperatures. Ethanol molecules will be progressively enriched in the P2VP domains, and osmotic pressure is consequently accumulated in the P2VP microdomains, forcing the outflow of expanding P2VP chains onto the film surface on one hand and the vertical stretching of the PS matrix on the other hand. The lateral deformation of PS matrix is suppressed because of the confinement effect of the substrate and the counteracting effect of the numerous expanding P2VP cylinders inside the PS matrix. Upon drying, with the loss of the ethanol P2VP chains are frozen and collapsed on the film surface, and the stretched PS matrix cannot return to its initial position because of the loss of driving force (expanding P2VP chains) and chain mobility without the plasticization effect of ethanol. Therefore, the spaces previously occupied by the condensed P2VP chains are partially converted pores with P2VP chains lining along the pore walls.

Creation porosity in solids leads to the change of its refractive index as air filled in the pores has the lowest refractive index down to 1; thus, the porosity of the membranes can be determined by monitoring the change of the refractive index of the BCP films with spectroscopic ellipsometry before and after ethanol soaking using the equation41

$$n_{mem}^2 = n_{matter}^2(1 - \phi_{pore}) + n_{air}^2\phi_{pore}$$

(2)

where $n_{matter}$, $n_{matter}$, and $n_{air}$ are the refractive index of the membrane, bulk material, and air, respectively. Taking the membrane derived from the neat PS-b-P2VP film as an example, the porosity of the membrane obtained from the ellipsometric method was ~12.9%, very close to its surface porosity calculated from SEM results, ~13.2% (Table 1). The ellipsometric porosity represents the bulk porosity of the membrane as an integral material whereas the porosity based on surface SEM images only represents the porosity of the membrane surface. A bulk porosity close to the surface porosity therefore indicates that the pores are opened with uniform diameter throughout the entire thickness of the membrane.

The uniform through pores were confirmed by the cross-sectional morphology of the membranes. As can be seen from Figure 5, hollow channels (pores) running from the top to the bottom surface were densely embedded in all the three membranes with varying hp2VP dosages. These pores were largely perpendicular to the surface although a number of them were tilted to a certain angle. We note that the tilted pores will increase the transport distance and therefore may reduce the permeability in membrane separation. Such slightly tilted orientation of the pores is believed to be inherited from the correspondingly tilted P2VP cylinders before ethanol soaking although the exact mechanism for that is currently unclear. Importantly, these cross-sectional SEM images clearly demonstrate that these through pores possessed uniform diameter at different positions inside the interior of the membranes, which
is in consistence with the porosity analysis discussed above. Especially, we did not observe a clearly tapered pore structure for the neat film although SEM examinations indicated a larger pore size on the top surface than on the bottom surface. In addition, the fact that its bulk porosity is close to the surface porosity also implies a uniform pore diameter along the membrane thickness. Therefore, the smaller pores on the bottom side should be attributed to the residual wetting P2VP layers on the periphery of the initially larger pores, reducing the sizes of the pores viewed from the top direction. Such residual wetting layers are very thin and do not noticeably reduce the bulk porosity of the membrane, and consequently we observed also a close bulk porosity and top surface porosity for this membrane.

As we discussed above, both the dissolution of P2VP homopolymer and the swelling of P2VP blocks contribute to the formation of the through pores. It should be helpful to discriminate these two contributions. As the dissolution of the P2VP homopolymer with low molecular weights in ethanol occurs spontaneously under ubiquitous conditions while the swelling of P2VP blocks with high molecular weights typically requires higher temperatures and/or long durations to reach the same degree of pore opening,29,30,33 we performed the ethanol soaking of the films at low temperature for a very short duration, e.g., 25 °C for 10 s, to largely suppress the selective swelling of the P2VP blocks. As can be seen from Figure S3, hexagonally patterned pores appeared on the surface of the films with varying P2VP dosages subjected to ethanol soaking at 25 °C for 10 s. The pore sizes were 15, 30, and 44 nm for the neat film and the blended films with the P2VP dosage of 10% and 30%, respectively. These pores were formed predominantly because of the dissolution of the P2VP homopolymer. Pores also appeared in the neat BCP film without additional dosing of P2VP homopolymers. The exact reason for this observation is currently unknown, and it might be explained by the following conjecture. There might be some BCP molecules with much shorter PS blocks than the averaged length produced during the synthesis of the BCPs. This portion of BCPs can be easily dissolved in ethanol with the solubilization effect of P2VP blocks, and they were removed by ethanol soaking and led to small pores. According to our previous study,29,30,33 the selective swelling induced pore forming would cause the increase of the membrane thicknesses, as could also be seen from that of ethanol soaking at 50 °C for 3 h (Table 1). However, after being soaked in ethanol at 25 °C for 10 s, the membrane thicknesses decreased rather than increased (Table 2), confirming that the dissolution of the hP2VP was the dominating contribution for the pore forming.

As shown in Table 2, the surface porosities based on SEM imaging are close to the bulk porosities based on ellipsometry for all the three membranes, indicating that the pores observed on the membrane surface were penetrating through the entire thickness of the membranes. Figure S4 gives the cross-sectional SEM image of the membrane derived from the blended film with 30% hP2VP dosage, and uniform and through pores were clearly evidenced. In the ideal case where only does the dissolution of hP2VP occur, the resulted porosities should be identical to the volume fractions of hP2VP in the blended films as all the added hP2VP is removed and the swelling of P2VP blocks does not happen to contribute to the pore formation. As given in Table 1, the volume fractions of the blended films with 10% and 30% dosage of hP2VP are 8.7% and 22.3%, respectively, which are very close to the porosities of the films soaked at 25 °C for 10 s (Table 2). Therefore, we conclude that the added hP2VP was almost completely extracted by ethanol at 25 °C merely for a very short duration as low as 10 s.

By comparing the average pore sizes or the surface porosities of the membranes prepared at different ethanol soaking conditions, we found that soaking in ethanol at high temperature produced much larger pores, especially for the blended films with lower hP2VP dosages, because of the additional contribution for pore formation from the selective swelling of the P2VP blocks which becomes pronounced at elevated temperatures. Taking the membrane derived from the blended film with 10% dosage of hP2VP as an example, the

Table 2. Structural Parameters of the Films with Different hP2VP Dosages Treated in Ethanol at 25 °C for 10 s†

<table>
<thead>
<tr>
<th>items</th>
<th>thickness increase (%)</th>
<th>pore sizes (nm)</th>
<th>surface porosity (%)</th>
<th>bulk porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% hP2VP</td>
<td>−2.5</td>
<td>15</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td>10% hP2VP</td>
<td>−12.6</td>
<td>30</td>
<td>10.0</td>
<td>9.6</td>
</tr>
<tr>
<td>30% hP2VP</td>
<td>−10.6</td>
<td>44</td>
<td>21.5</td>
<td>18.8</td>
</tr>
</tbody>
</table>

†The deviation in the determination of pore sizes on SEM images are in the range of 3–8%, and the deviation of the film thickness obtained by ellipsometry is <5%. The variation in porosities calculated from Equation 1 are determined by that of the corresponding pore sizes.
porosity produced solely by the dissolution of hP2VP; that is, the volume fraction of hP2VP in the blended film before ethanol soaking was estimated to be 8.7%, and such a low porosity was achieved by soaking at 25 °C for 10 s. In contrast, the porosity was significantly increased to 21.6% when the ethanol soaking conditions were changed to 50 °C for 3 h where both dissolution of hP2VP and swelling of P2VP blocks took effect. As discussed above, the exposure to ethanol at 25 °C for 10 s completely extracted all the added hP2VP from the blended film, and thus the contribution for the pore formation remained unchanged when the soaking condition was enhanced to 50 °C for 3 h. Therefore, the selective swelling of P2VP blocks contributed an additional porosity of 12.9%, and the portion of contribution from the dissolution of hP2VP and the swelling of P2VP blocks was 40.3% and 59.7%, respectively. That is, by increasing the soaking temperature to trigger the swelling of P2VP blocks, the porosity can be increased by 2.5-fold compared to the pore formation merely by extraction of hP2VP.

4. CONCLUSIONS

We demonstrate that a simple soaking in ethanol is able to produce homoporous membranes with pore sizes tunable in the range 15−50 nm from the blended films of amphiphilic block copolymer, PS-b-P2VP, and P2VP homopolymer. The P2VP phases can be rapidly aligned by annealing in chloroform to allow the perpendicular orientation of P2VP cylinders. Transmission electron microscopy reveals that the domain sizes of the P2VP blocks are increased with the localization of P2VP homopolymers whereas the phase spacing remains unchanged. Soaking in ethanol of the aligned blended films leads to membranes with uniform, straight pores because of the dual effects of the ethanol: the dissolution of P2VP homopolymers and the selective swelling of the P2VP blocks. Brief soaking at room temperature allows merely the dissolution of P2VP homopolymers, leading to small pores down to 15 nm, while longer immersion in ethanol at 50 °C triggers also the swelling of the P2VP blocks, thus producing pore reaching 50 nm. Therefore, simply by regulating the soaking conditions, we are able to tune the pore sizes in a wide range while maintaining the highly ordered and uniform nature of these pores.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b02133.

Additional SEM characterizations; the estimation of the volume increase caused by the addition of P2VP homopolymers (PDF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: yongwang@njtech.edu.cn (Y.W.).

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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.

REFERENCES


