

# Selective Swelling Induced Pore Generation of Amphiphilic Block Copolymers: The Role of Swelling Agents

Nina Yan, Yong Wang

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, Jiangsu, People's Republic of China  
Correspondence to: Y. Wang (E-mail: yongwang@njtech.edu.cn)

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**ABSTRACT:** Swelling of block copolymers by selective solvents has emerged as an extremely simple and efficient process to produce nanoporous materials with well-controlled porosities. However, the role of the swelling agents in this pore-making process remains to be elucidated. Here we investigate the evolution of morphology, thickness, and surface chemistry of thin films of polystyrene-*block*-poly(2-vinyl pyridine) (PS-*b*-P2VP) soaked in a series of alcohols with changing carbon atoms and hydroxyl groups in their molecules. It is found that, in addition to a strong affinity to the dispersed P2VP microdomains, the swelling agents should also have a moderate swelling effect to PS to allow appropriate plastic deformation of the PS matrix. Monohydric alcohols with longer aliphatic chains exhibit stronger ability to induce the pore formation and a remarkable

increase in film thickness is associated with the pore formation. High-carbon alcohols including *n*-propanol, *n*-butanol, and *n*-hexanol produce cylindrical micelles upon prolonged exposure for their strong affinity toward the PS matrix. In contrast, methanol and polyhydric alcohols including glycol and glycerol show very limited effect to swell the copolymer films as their affinity to the PS matrix is low; however, they also evidently induce the surface segregation of P2VP blocks. © 2016 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2016**, *54*, 926–933

**KEYWORDS:** block copolymers; nanoporous films; membranes; selective solvents; stimuli-sensitive polymers; surface segregation; swelling

**INTRODUCTION** Nanoporous materials have been widely used in various fields, including separation,<sup>1,2</sup> optoelectronics,<sup>3,4</sup> sensors,<sup>5</sup> biomedicines,<sup>6–8</sup> etc. However, it remains challenging to obtain porous structures with controllable porosities through simple and affordable methods. Materials derived from block copolymers (BCPs) have been considered as one of the promising candidates for ordered structures which can be transformed to periodical, uniform nanopores via chemical or physical methods.

Swelling of BCPs in selective solvents has recently emerged as an extremely simple and efficient way to produce nanoporous materials with highly controllable morphologies and surface chemistries. Compared with selective etching one block of the BCPs through UV, ozone exposure, or hydrolysis and etc.,<sup>9–12</sup> porous structures can be readily obtained by the selective swelling-induced pore generation in which the BCP materials are soaked in a certain swelling agent for periods of time followed by air drying.<sup>13</sup> The advantages of this swelling methodology includes extreme simplicity, broad

suitability, free of chemical reactions, inherent hydrophilic surfaces, reversible pore opening and closing, and etc.<sup>14</sup>

This swelling method is applicable mainly to BCPs with blocks having different solubilities or polarities, particular to amphiphilic BCPs with one hydrophobic block and a more hydrophilic block, for example, polystyrene-*block*-poly(2-vinyl pyridine) (PS-*b*-P2VP). In thin films of cylinder-forming PS-*b*-P2VP produced by spin coating or dip coating, the minority P2VP blocks are randomly distributed in the PS matrix as cylinders. Upon immersion in a solvent selective to P2VP phases, for example, ethanol, ethanol molecules diffuse into the film and are preferentially enriched in the P2VP cylinders as ethanol has a strong affinity toward P2VP but very weak affinity toward PS. With the progressive uptake of ethanol the P2VP chains continue swelling and the osmotic pressure inside the P2VP phase is accumulated on one hand, and the mobility of the PS chains which are composed of the copolymer film matrix is enhanced in the exposure to ethanol at elevated temperatures on the other hand.<sup>13</sup>

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Consequently, plastic deformation of the PS matrix occurs, allowing the volume expansion of the P2VP cylinders. Upon drying in air the spaces previously occupied by the expanding P2VP cylinders are fixed as the PS matrix accommodating these spaces is frozen with the evaporation of ethanol and the temperature lowering down to room temperature. Simultaneously, the P2VP chains collapse, producing pores in these spaces with the collapsed P2VP chains lined along the pore wall. Under stronger swelling conditions the P2VP cylinders expand to a greater extent and consequently neighboring P2VP cylinders are connected and coalesced to form a continuous phase of swelling P2VP chains, correspondingly leading to an interconnected porous phase in the following drying process.

It is obvious that both the compositions of BCPs and the swelling conditions (temperature, durations, etc) play a role in determining the swelling behaviors and consequently the morphologies of the BCPs. Wang and Li found that the swelling temperature played a vital role in the pore generation process and appropriately elevated temperatures were necessary for the formation of pores especially in BCP materials with bulky dimensions.<sup>13,15</sup> A temperature higher than the glass transition temperature of the PS matrix in the swelling solvents will destroy the infrastructure of the materials whereas a too low temperature might be unable to provide sufficient mobility to the PS chains to allow their plastic deformation. Also, it has been reported that prolonged swelling durations led to a stronger swelling degree of BCP and consequently enlarged pores and porosities.<sup>14,16</sup> There have been also some studies revealing that the swelling agents significantly influence the swelling of BCP materials. Li et al. observed changing surface morphologies of polystyrene-*block*-poly (4-vinylpyridine) (PS-*b*-P4VP) films upon a short immersion in several different solvents including acetic acid, propionic acid, isopropanol and dimethylformamide.<sup>17</sup> Chen et al. reported that the pore opening of micellar films of PS-*b*-P2VP was strongly dependent on the nature of the swelling agent. Ethanol easily activated the films within seconds whereas acidic water required hours and neutral or basic water even failed to generate pores in these films with a reasonable timeframe.<sup>18</sup> However, the previous works were not focused on the role of the swelling agents in the pore-forming process, and there is a lack of a systematic and in-depth study on the swelling behaviors and morphology evolutions of BCP materials induced by different swelling agents. Therefore, the swelling effect to the constituent blocks of swelling agents with different affinities remains to be elucidated.

Ethanol has been known to be a good solvent to P2VP and a nonsolvent to PS, and has been demonstrated to be an efficient swelling agent in triggering the pore formation in PS-*b*-P2VP materials with various dimensions.<sup>13</sup> Considering that the hydrophilicity and polarity of alcoholic molecules, and consequently their selectivity toward the constituent blocks of PS-*b*-P2VP, can be readily tuned by changing the chain lengths and numbers of hydroxyl groups in these alcoholic

molecules, in this work we investigate the swelling behavior and also the pore formation process of PS-*b*-P2VP films in a series of linear monohydric alcohols with carbon numbers increasing from one to six and also polyhydric alcohols including glycol and glycerol. Such a focused study is expected to increase our understanding on the role of the swelling agents in the process of selective swelling induced pore generation in amphiphilic BCPs, and also to provide new accessibilities in tuning the morphologies and functionalities of the resulted nanoporous BCP structures.

## EXPERIMENTAL

### Materials

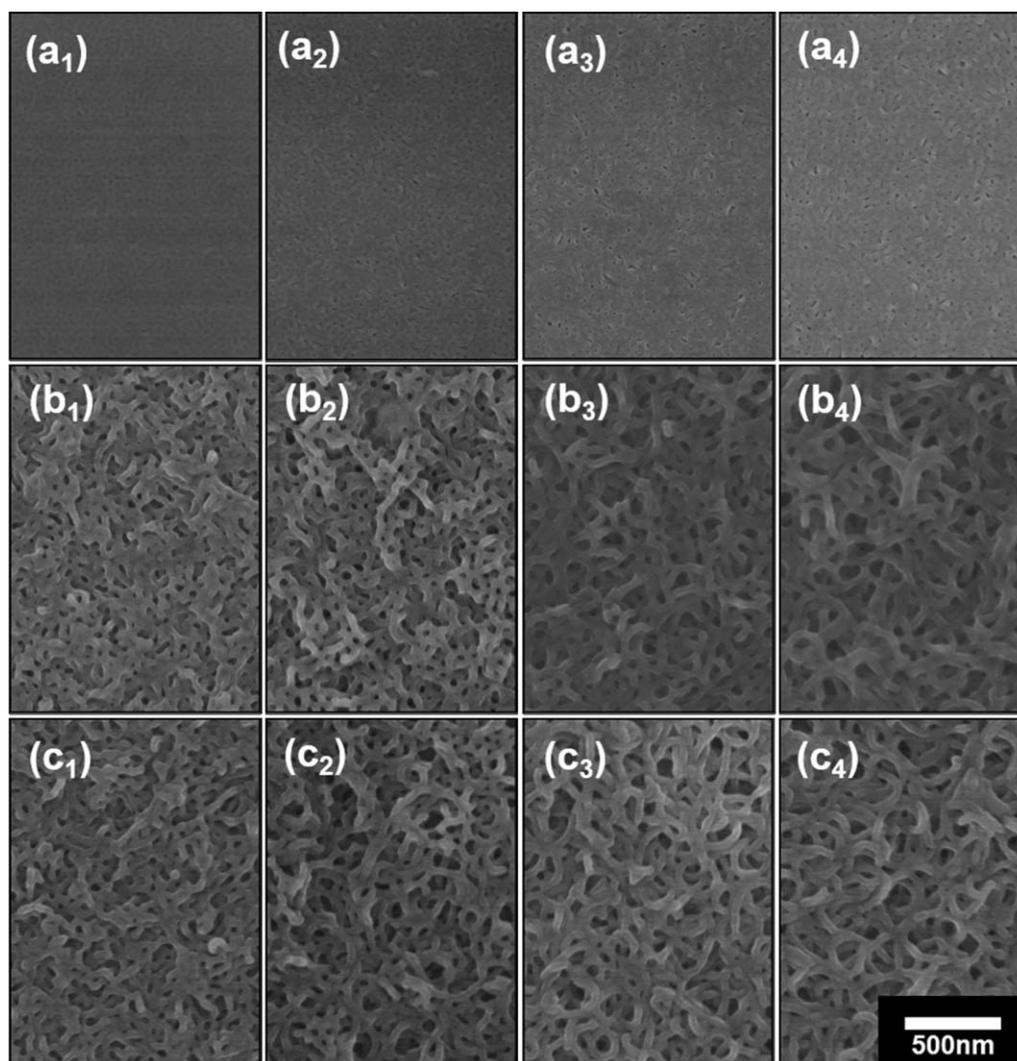
Cylinder-forming diblock copolymers, PS-*b*-P2VP (abbreviated as S2VP below,  $M_n^{PS} = 50,000 \text{ g mol}^{-1}$ ,  $M_n^{P2VP} = 16,500 \text{ g mol}^{-1}$ , PDI = 1.09) was purchased from Polymer Source Inc., Canada and used as received. Chloroform of analytical grade was obtained from local suppliers and used as the solvent to dissolve S2VP. We used alcohols with the highest purity available to us to perform the swelling treatment to avoid any possible interference by impurities. Methanol, ethanol, *n*-propanol, and *n*-butanol with a purity higher than 99.9%, *n*-hexanol ( $\geq 99.0\%$ ), glycol (99.8%), and glycerol ( $\geq 99.5\%$ ) were purchased from Sigma-Aldrich and used as received.

### Swelling Treatment of S2VP Thin Films

S2VP was dissolved in chloroform to obtain a 2 wt % solution, which was then filtrated through a 0.22  $\mu\text{m}$  polytetrafluoroethylene (PTFE) filters three times to remove any big aggregates. The filtered solution was spin-coated on cleaned silicon substrates with the size of 1.5 cm  $\times$  1.5 cm (2000 rpm, 30 s) to produce dense films. The as-coated films were then baked at 70  $^\circ\text{C}$  for at least 2 h to evaporate chloroform remaining in the films. After equilibrium in atmosphere for one day, the films were immersed in 5 mL of different swelling agents preheated to 60  $^\circ\text{C}$  and kept at this temperature in the solvents to perform the swelling treatment. After predetermined durations of time, the films were withdrawn from the solvents and naturally dried in air at room temperature except for the cases of using glycol and glycerol as the swelling agents. In these cases, the films were firstly rinsed with deionized water to replace the solvents and then dried in air as glycol and glycerol have high boiling points and cannot be readily dried at room temperature within reasonable periods of time.

### Characterizations

The thicknesses of the films before and after swelling were measured by a spectroscopic ellipsometer (Complete EASE M-2000U, J. A. Woollam) with the incidence angle of 65 $^\circ$ . Every piece of films was measured at six different positions and the average values were reported. A field emission scanning electron microscope (FESEM, Hitachi S-4800) operated at the accelerating voltage of 5 kV was used to examine the surface and cross-sectional morphologies of the films. The samples were sputter-coated with a thin layer of platinum to



**FIGURE 1** The surface SEM images of S2VP films soaked in (a) methanol, (b) *n*-propanol, and (c) *n*-butanol for (a<sub>1</sub>, b<sub>1</sub>, c<sub>1</sub>) 10 min, (a<sub>2</sub>, b<sub>2</sub>, c<sub>2</sub>) 1 h, (a<sub>3</sub>, b<sub>3</sub>, c<sub>3</sub>) 4 h and (a<sub>4</sub>, b<sub>4</sub>, c<sub>4</sub>) 15 h, respectively. All the images have the same magnification and the scale bar is shown in (c<sub>4</sub>).

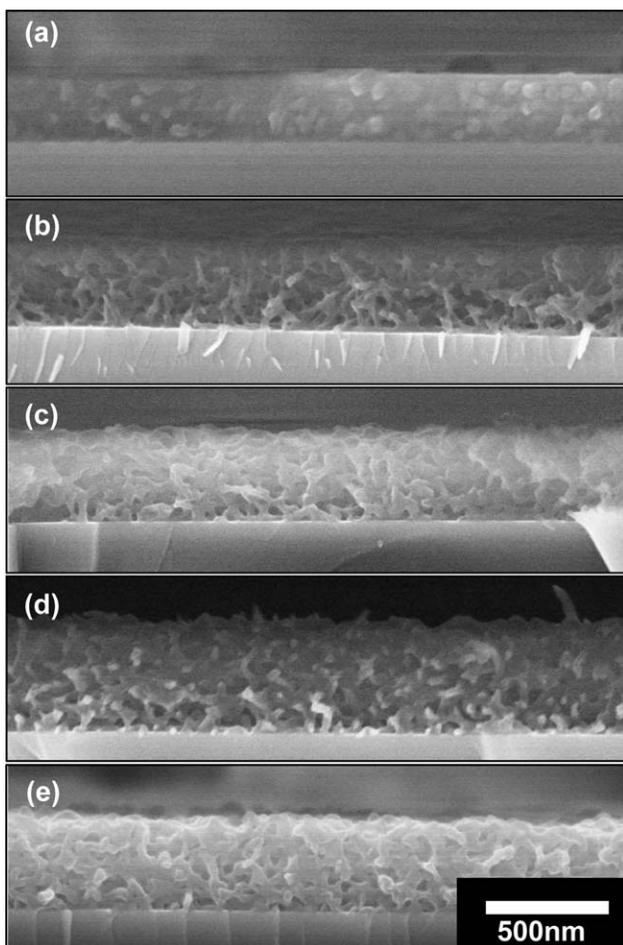
improve electrical conductivity before SEM observations. The static water contact angles (WCAs) of the film surfaces were determined by a contact angle goniometer (Dropmeter A-100, Maist). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 XPS system (Thermo Scientific) equipped with a monochromatic Al K $\alpha$  radiation source. The spectra were calibrated relative to the C 1s binding energy (284.6 eV).

## RESULTS

### Linear Monohydric Alcohols as Swelling Agents

We spin-coated 2 wt % chloroform solutions of S2VP onto silicon substrates followed by baking at 70 °C for 2 h and equilibrating at room temperature for 1 day, producing pristine S2VP films ready for the subsequent swelling treatment. SEM examinations reveal that the pristine S2VP films exhibited a dense morphology with a smooth surface and nonpo-

rous interiors (Supporting Information Fig. S1). The thickness of the pristine S2VP films was  $\sim$ 240 nm as determined both by SEM and ellipsometry. The pristine films deposited on silicon substrates were then subjected to swelling treatment. They were separately soaked in various alcohols at the fixed temperature of 60 °C for set durations followed by withdrawal from the alcoholic baths and air drying at room temperature. We first investigated the swelling behaviors of the S2VP films in linear monohydric alcohols with increasing carbon atoms, including methanol, ethanol, *n*-propanol, *n*-butanol, and *n*-hexanol. The morphologies of the S2VP films swelling treated in these alcohols are presented in Figure 1. There is a general trend for all the alcohols investigated here that the swelling degree of the films deepens with the extending of swelling durations. For the case of methanol as the swelling agent, after a swelling duration for 10 min, round-shaped pores with diameters less than 10 nm appeared on the film surface [Fig. 1(a1)], and

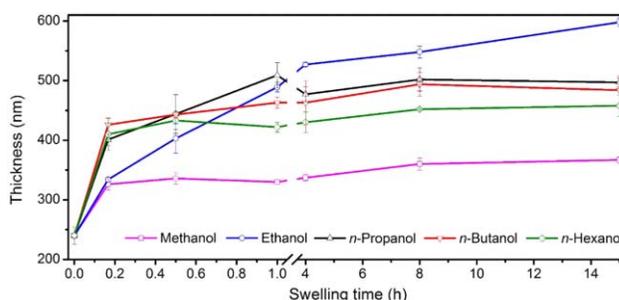


**FIGURE 2** The cross-sectional images of the S2VP films immersed in (a) methanol, (b) ethanol, (c) *n*-propanol, (d) *n*-butanol, and (e) *n*-hexanol for 30 min, respectively. All the images have the same magnification and the scale bar is shown in (e).

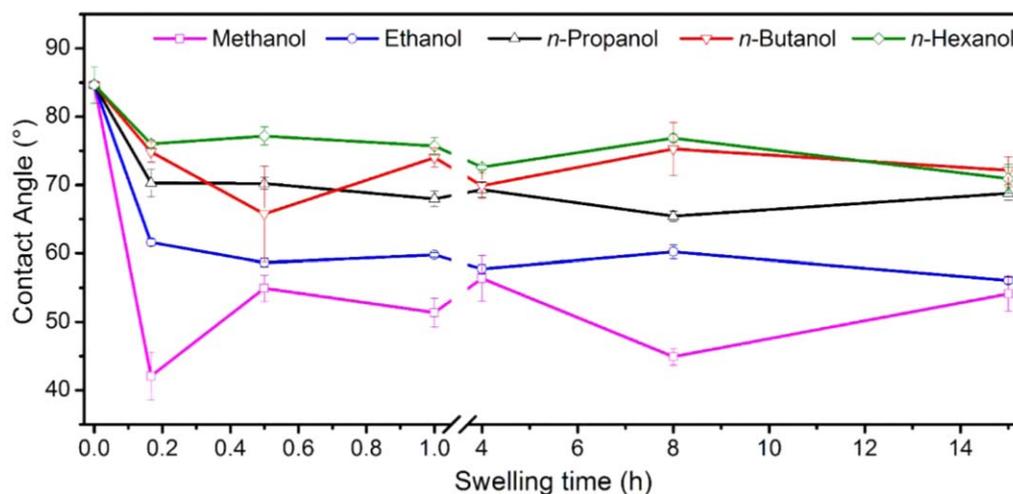
these pores kept no obvious change for a prolonged swelling for 1 h [Fig. 1(a2)]. Further extending swelling to 4 h, some neighboring pores which are originally isolated contacted with each other and were merged, leading to the presence of some elongated pores with larger aspect ratios on the surface [Fig. 1(a3)]. These elongated pores became more evident when the swelling duration was increased to 15 h [Fig. 1(a4)]. Such a mild and progressive pore formation with the prolongation of the methanol immersion can also be observed from the cross sections of these films (Supporting Information Fig. S2). As the swelling agent comes to ethanol, which has one more carbon atom in its molecule than methanol, the swelling of S2VP films also takes place progressively with the soaking duration, but at a faster rate than in methanol. For instance, elongated pores were already shown up after swelling in ethanol for only 10 min, however, it took approximately 4 h to have a clear observation of such elongated pores in the S2VP films soaked in methanol.

When high-carbon alcohols including *n*-propanol, *n*-butanol, and *n*-hexanol are employed as the swelling agents, the S2VP

films experienced a much more drastic swelling compared to that of low-carbon alcohols (methanol and ethanol). Figure 1(b) gives the morphology evolution of the S2VP films swelling-treated in *n*-propanol. The film turned to a highly porous structure with densely packed pores in the form of both elongated and round shapes after a brief swelling for 10 min [Fig. 1(b1)]. Such a porous morphology can never be achieved by swelling in methanol, and is similar to that swelling in ethanol for 15 h. The pores were enlarged in sizes and also in numbers, and the film surface became obviously rough at a swelling duration of 1 h [Fig. 1(b2)]. Interestingly, further extending swelling to 4 h [Fig. 1(b3)], the films were developed to the morphology of interconnected nanofibers and pores with diameter larger than 100 nm appear among the fibers. This fibrous morphology became more evident and the fibers seemed to be less interconnected at a swelling duration of 15 h [Fig. 1(b4)]. Swelling in *n*-butanol and *n*-hexanol also eventually led to fibrous morphologies which appeared to be more pronounced [Fig. 1(c) and Supporting Information Fig. S3]. For instance, the fibers already showed up after swelling in *n*-butanol for only 1 h [Fig. 1(c2)]. We must note that these fibers remained an unchanged diameter regardless of the conditions (swelling agents and durations) under which they were formed. These fibers are actually cylindrical micelles with PS blocks condensed as the cores and P2VP comprising of the coronae, formed through the mechanism of heating-enabled micellization in P2VP-selective solvents.<sup>19</sup> The transitions from S2VP in different dimensions including templated one-dimensional nanostructures, thin films and bulk materials to micelles, either in the shape of spheres or cylinders depending on the subtle interactions between the BCP and the solvent, have been frequently observed in our previous works when strong solvation conditions were applied and the swelling of BCPs was developed to dissolution.<sup>20–22</sup> By applying a gentle ultrasonication oscillation, isolated nanofibers with length up to several  $\mu\text{m}$  can be released from the S2VP films and collected from the swelling bath of *n*-hexanol (Supporting Information Fig. S4), confirming that the fibrous structures observed on the swelling-treated S2VP films are micelles in the form of long cylinders.



**FIGURE 3** The change in thickness of S2VP films after swelling in five linear monohydric alcohols for various durations. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**FIGURE 4** The water contact angles of the S2VP films after swelling in different linear monohydric alcohols for different durations. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

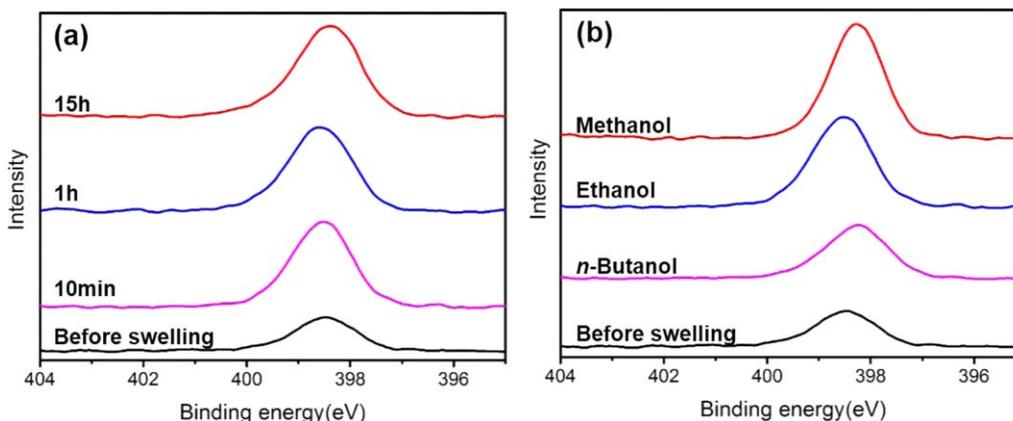
We also note that the films become thicker after swelling, which is clearly revealed by the cross-sectional SEM images. The increase in thickness is a response of the films to the formation of pores as the films are two-dimensionally confined on the silicon substrates and they can only expand their volumes in the direction perpendicular to the film surface. The increase in thicknesses and porosities of the swelling-treated films are greatly dependent on the type of the used alcohols. Figure 2 gives the cross-sectional SEM images of S2VP films subjected to swelling treatment in different alcohols for 30 min. Evidently, soaking in methanol for 30 min leads to a very slight increase in the film thickness and nearly no pores can be observed from the interior of the film [Fig. 2(a)]. In contrast, the cross-sectional SEM images reveal that other alcohols produce a highly porous morphology and notable increase in thicknesses [Fig. 2(b–e)].

We then have a detailed investigation on the change of film thicknesses in different solvents for various durations by ellipsometry. As clearly shown in Figure 3, there is always an evident increase in thicknesses of the S2VP films subjected to swelling treatment in any alcohols investigated here. The increase in thickness shares a similar trend: a fast increase in the initial stage and then leveling off. However, the specific increase profile for each alcohol is significantly different. As shown in Figure 3, methanol results in a moderate increase by 36% in the initial 10 min and later on very slight rise in the following hours. Ethanol leads to a fast and nearly linear increase by 104% in the first hour, and subsequently a lower but continuous increase in the swelling period from 1 to 15 h with a total increase of 149% compared to the initial thickness of the S2VP films. The three high-carbon alcohols produce a very similar change in thicknesses. A considerable increase of  $\sim 70\%$  is obtained in the initial 10 min and the thicknesses then gradually level off with minor undulations. The final thickness increase is slightly reduced in the order of *n*-propanol, *n*-butanol, and *n*-hexanol. We note that in the initial 10 min of swelling the three high-

carbon alcohols induce the largest increase in the film thickness, several times larger than methanol and ethanol. By considering both the change in morphology and thickness of the S2VP films subjected to swelling in different alcohols for identical durations, we can identify that the swelling of S2VP films occurs in different rate in the order of *n*-hexanol  $\approx$  *n*-butanol  $>$  *n*-propanol  $>$  ethanol  $>$  methanol. That is, alcohols with longer carbon chains have a stronger swelling effect to S2VP films, consequently resulting in faster swelling.

We previously demonstrated that there was an obvious increase in surface hydrophilicity as measured by decreasing water contact angles (WCAs) for S2VP films subjected to swelling in ethanol due to the preferential migration of polar P2VP blocks to the surface.<sup>15,23,24</sup> Therefore, WCAs might also serve as a measure to trace the progress of swelling of S2VP films. To this end, we investigated the WCAs change of the S2VP films being swelling treated in each alcohol for various durations. As shown in Figure 4, the WCAs would not keep dropping with the increase of swelling durations for all the cases using different alcohols as swelling agents. All the films have a drastic decrease in WCAs after swelling in each solvent for only 10 min. Subsequently, the WCAs fluctuate in a small range without any substantial change. The WCA of the pristine S2VP films falls within the range of 80° to 90° which is close to that of PS homopolymer,<sup>25</sup> implying that their surfaces are enriched with PS chains.<sup>24</sup> A brief exposure to the five alcohols for 10 min leads to the WCA reduced to approximately 42°, 62°, 70°, 75°, and 76° for methanol, ethanol, *n*-propanol, *n*-butanol, and *n*-hexanol, respectively. That is, under this swelling condition, alcohols with longer carbon chains yield less pronounced increase in the surface hydrophilicity. After extending exposure of 15 h the WCA is stabilized around 55° for both methanol and ethanol, and around 70° for the three high-carbon alcohols.

To have a better understanding on the WCA results, XPS was also employed to analyze the surface compositions of these



**FIGURE 5** The XPS spectra showing the N 1s peaks of the films immersed in (a) ethanol for different durations and (b) different solvents for 10 min, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

films. Figure 5(a) highlights the nitrogen (399 eV for N 1s) contents of S2VP films treated in ethanol for different durations. The nitrogen content is indicative of the relative concentration of P2VP chains on the surface as nitrogen only exists in the pyridyl groups of P2VP blocks. After swelling in ethanol for 10 min, 1 h, and 15 h, the atomic nitrogen ratio of the S2VP films increased from 3.02% for the pristine film to 5.8%, 5.96%, and 6.93%, respectively, confirming the migration of the P2VP blocks to the surface. Therefore, we believe that the significant drop of the WCAs in the first 10 min is due to the migration of the P2VP blocks to the film surface. However, there is still an evident increase of nitrogen content with the swelling duration increasing from 1 h to 15 h, which seems not coincide the nearly unchanged WCA values. As clearly shown in Figure 1, there is a significant change in surface porosity and roughness with the swelling duration, which should also contribute the change of WCAs. According to the Cassie model, the apparent WCA of a porous surface,  $\theta_c$ , can be estimated using the following equation:<sup>26</sup>

$$\cos\theta_c = f_s(\cos\theta + 1) - 1 \quad (1)$$

where  $f_s$  is the area fraction of the solid on the surface and  $\theta$  is the WCA on the corresponding smooth surface. With increasing swelling duration, pores are generally enlarged, leading to decreasing  $f_s$  on one hand; however, as revealed by XPS analysis more P2VP blocks are enriched on the film surface, resulting in decreasing values of  $\theta$  and correspondingly increasing  $\cos\theta$  on the other hand. Therefore, the competing effect of decreasing  $f_s$  and increasing  $\cos\theta$  eventually results in largely unchanged WCAs with the further increase in swelling durations.

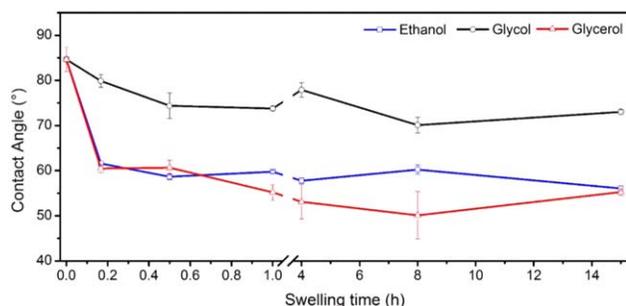
Additionally, XPS were also used to examine the surface compositions of the films immersed in different alcohols for 10 min. As shown in Figure 5(b), the atomic nitrogen ratio of the S2VP film is increased to 6.63%, 5.8%, and 5.19% after swelling treatment for 10 min in methanol, ethanol, and *n*-butanol, respectively, suggesting that alcohols with shorter carbon chains induce more P2VP chain enriched on the film surface. Consequently, the films exhibit correspondingly

decreased surface hydrophilicity, which confirms the WCA analysis.

### Polyhydric Alcohols as Swelling Agents

After the demonstration of that the change in carbon numbers in the alcoholic molecules with one single hydroxyl group significantly influences the swelling behaviors of S2VP films, we then investigate the effect of the number of hydroxyl groups in the alcoholic molecules. To this end, polyhydric alcohols including glycol bearing two hydroxyl groups and glycerol bearing three hydroxyl groups are used to swell the S2VP films. As shown in Supporting Information Figures S5 and S6, SEM examinations on the surfaces and cross sections of the S2VP films soaked in either glycol or glycerol at 60 °C for hours do not reveal the presence of any detectable pores. Moreover, ellipsometry indicates very slight change in the thickness of the films with the swelling duration and an increase in thickness less than 5% is obtained for the films after soaking in both alcohols for 15 h (Supporting Information Fig. S7), which is much lower than the case of any monohydric alcohol we investigated in this work. In addition, we note that the increase in film thickness is larger for films treated in glycerol than in glycol.

However, the change of WCAs of the S2VP films soaked in either glycol or glycerol with the swelling duration is very similar to the case of using ethanol as the swelling agent. As can be seen from Figure 6, there is also a remarkable decrease in WCAs in the initial 10 min of swelling and then the WCAs are stabilized after a prolonged swelling for 15 h. XPS analysis reveal that there is a noticeable increase of N atomic ratio from 3.02% for the pristine S2VP film to 4.08% after immersion in glycerol for 10 min (Supporting Information Fig. S8). Both WCA and XPS characterizations imply that glycol and glycerol are able to force the P2VP blocks to enrich on the film surface. Therefore, we conclude that polyhydric alcohols swell S2VP films to a very limited degree, which is not strong enough to induce the formation of pores at the moderate temperature of 60 °C investigated in this work. Interestingly, it can be clearly seen from Figure 6 that WCAs of the S2VP films subjected to glycol swelling are always 15 to 20° higher than those of the films subjected to



**FIGURE 6** The water contact angles of the S2VP films after swelling in glycol and glycerol for different durations compared with that swelling treated in ethanol. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

glycerol swelling for the same durations, implying a lower surface hydrophilicity of the glycol-treated S2VP films. This should be ascribed to the very low swelling degree of S2VP films in glycol as revealed by the neglectable increase in the film thickness after swelling in glycol (Supporting Information Fig. S7).

## DISCUSSION

In the swelling-induced pore generation of BCPs, the swelling agents penetrate through the PS matrix and are enriched in the P2VP microdomains, which expand their volume with the progressive uptake of the swelling agent. Consequently, the osmotic pressure is accumulated, forcing the plastic deformation of the PS matrix confining the P2VP microdomains. At a critical point, neighboring P2VP domains get contacted and are merged with each other, forming a continuous phase of P2VP chains solvated with the swelling agent. Upon drying the swelling agent evaporates and the P2VP chains collapse, resulting in a continuous porosity in the PS matrix in the position previously occupied by the swelling P2VP chains. In this process, the P2VP chains need to be sufficiently swollen on one hand, and the PS matrix should also be appropriately swollen on the other hand to allow the plastic deformation of the PS matrix. However, the swelling of PS should be controlled low enough to avoid the collapse of the infrastructure of the S2VP films. Therefore, the swelling agents should have swelling effect to both blocks but with a higher degree to P2VP block than to the PS block.

It is well known that monohydric alcohols with larger carbon numbers exhibit weaker polarities (Table 1).<sup>27</sup> Alcohols with reducing polarities have increasing affinity towards PS blocks and weakening affinity toward P2VP blocks which contain pyridyl rings capable of forming hydrogen bonds with alcohols. That is, when the swelling agents changing from methanol to *n*-hexanol their affinity to PS is increased whereas their affinity to P2VP is decreased. The increasing affinity of alcohols with higher carbon numbers to PS can be demonstrated by the decreasing glass transition temperatures ( $T_g$ ) of PS in these alcohols. The  $T_g$  of bulk PS homopolymer in air is around 102 °C.<sup>29</sup> Yaffe et al. found that this

value decreased to 91 °C as the polymer was immersed in methanol and further decreased to 85 °C, 81 °C, and 71 °C when immersed in ethanol, *n*-propanol, and *n*-butanol, respectively.<sup>30</sup> Predictably, the  $T_g$  will be even lower than 71 °C if the solvent changes to *n*-hexanol.

To what degree a polymer can be swollen is dictated by the affinity between the solvent and the polymer, and the difference between their solubility parameter ( $\delta$ ) is a simple but effective measure to assess their affinity. Table 1 also lists the solubility parameter of all the alcohols used in this work. By considering that  $\delta_{PS} = 18.6 \text{ MPa}^{1/2}$  and  $\delta_{P2VP} = 20.6 \text{ MPa}^{1/2}$  (Ref. 28) all these alcohols exhibit a stronger affinity toward P2VP than to PS, that is, they are more selective to P2VP although the selectivity becomes smaller with increasing carbon numbers in the molecules of the alcohols. In addition, we experimentally found that P2VP homopolymers can be quickly dissolved in alcohols like methanol and ethanol whereas PS homopolymers are totally insoluble in either of them, confirming that these alcohols are selective solvents to S2VP block copolymers. Therefore, we can understand that the increased degrees of pore opening of S2VP films with the carbon number in the molecules of the monohydric alcohols is predominantly due to the increasing chain mobility of the PS matrix. With a stronger chain mobility, the PS matrix exhibits a reduced modulus, allowing a pronounced plastic deformation. Consequently, the swelling P2VP microdomains can expand to larger sizes, leading to higher degree of opening.

The swelling-induced pore generation involves first the diffusion of the swelling agent through the PS matrix and then the enrichment of the swelling agent in the P2VP microdomains. Therefore, high-carbon alcohols experience a fast diffusion through the PS matrix as they have higher affinity to PS. As a result, in the initial stage of swelling for the first 10 min, the S2VP films treated in high-carbon alcohols exhibit a much higher increase in the thickness of the films. The following reduced thicknesses for the cases of high-carbon alcohols are because of the collapse of the film infrastructure as the initially integral films are converted to isolated cylindrical micelles, as revealed by the SEM observations [Fig. 1(b,c)]. The very limited increase in thickness for the case of methanol should be attributed to the lowest affinity to PS among all

**TABLE 1** The Solubility Parameters and Relative Polarities of the Alcohols Investigated in this Work<sup>27,28</sup>

Alcohol	$\delta$ (MPa <sup>1/2</sup> )	Polarity (water = 100)
Methanol	29.7	76.2
Ethanol	26.0	65.4
<i>n</i> -Propanol	24.3	61.7
<i>n</i> -Butanol	23.3	60.2
<i>n</i> -Hexanol	21.9	NA
Glycol	29.9	79.0
Glycerol	33.8	NA

these monohydric alcohols investigated in this work and the pores cannot be sufficiently formed because the P2VP microdomains are tightly restrained by the glassy PS matrix. Similarly, for the polyhydric alcohols, both glycol and glycerol have a very strong ability to form hydrogen bonds and therefore, their solubility parameters are much higher than that of PS. That is, they show very low affinity and correspondingly very weak swelling effect to PS matrix. Consequently, they both failed to induce a noticeable pore opening of S2VP films.

By comparing the molecular structures, we found that in the molecules of methanol, glycol, and glycerol, the number of hydroxyl groups is equal to the number of carbon atoms. That is, the ratio between the number of hydroxyl groups and the number of carbon atoms in these three alcohols is one, which is the highest among all the alcohols we investigated here. Therefore, the concentration of hydroxyl groups in the three alcohols is the highest, indicating the highest chances to form hydrogen bonds with nitrogen atoms in the pyridyl rings of the P2VP blocks. Consequently, these three alcohols evidently induced the surface enrichment of P2VP blocks through the surface reconstruction of the S2VP films while the film bulk is mainly kept unchanged because of their very limited swelling effect to the PS matrix.

## CONCLUSION

In the swelling-induced pore generation of amphiphilic block copolymers, the swelling agent is playing a critical role in determining the swelling thermodynamics and kinetics. A suitable swelling agent needs to swell both PS and P2VP blocks, but to different degrees. Alcohols generally show better affinity to P2VP than to PS, and therefore, are selective solvents for S2VP. We investigate the swelling behavior of S2VP films in alcohols with various number of carbon atoms and hydroxyl groups in their molecules at the fixed swelling temperature of 60 °C. Monohydric alcohols exhibit progressively growing ability to induce the pore formation with increasing carbon atoms in their molecules (methanol < ethanol < *n*-propanol < *n*-butanol  $\approx$  *n*-hexanol) as longer aliphatic chains in the alcohols have stronger affinity to PS blocks. Polyhydric alcohols including glycol and glycerol show very limited ability to swell the S2VP films because of their low affinity to PS blocks. The process of pore generation is associated with increase in film thickness and the surface segregation of P2VP chains. For all the monohydric alcohols, there is a general trend that the thickness and wettability increase fast in the initial stage, e. g. 10 min and then level off. Although the swelling effect of methanol and polyhydric alcohols to S2VP films is very weak, they also induce an evident surface segregation of P2VP chains due to their highest possibility to form hydrogen bonds with P2VP.

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