Perpendicular Alignment and Selective Swelling-Induced Generation of Homopores of Polystyrene-\textit{b}-poly(2-vinylpyridine)-\textit{b}-poly(ethylene oxide) Triblock Terpolymer

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Supporting Information

ABSTRACT: Arrays of perpendicularly ordered nanopores with pore walls decorated by two or more functional polymer chains are of great importance in various applications. However, such porous structures have been rarely reported so far. Herein, lamellar-forming triblock terpolymer of polystyrene-\textit{b}-poly(2-vinylpyridine)-\textit{b}-poly(ethylene oxide) (PS-\textit{b}-P2VP-\textit{b}-PEO) is blended with PS homopolymers to fabricate a PS matrix embedded with perpendicular PEO@P2VP cylinders via solvent annealing. By further adjusting the annealing humidity and temperature, the perpendicular PEO@P2VP cylinders are capable of running through the entire films. The hydrophilic PEO@P2VP domains could be converted into cylindrical homopores by ethanol swelling, where the functional P2VP and PEO chains are distributed on the pore walls. Moreover, water is able to swell PEO and also produces homopores in such films. The pore sizes of the films are readily tuned in a relatively large range depending on the swelling temperatures and durations. The developed ordered nanostructures are expected to find important applications in the range from template synthesis to membrane separation and to nanofluidics.

INTRODUCTION

Well-ordered nanostructures endowed with abundant functions have aroused tremendous attention over past decades.\textsuperscript{1,2} As a consequence of microphase separation, block copolymers (BCPs) composed of thermodynamically incompatible segments have much potential to acquire a series of ordered morphologies such as spheres, cylinders, and gyroids.\textsuperscript{3} As a typical type of BCPs, diblock copolymers consisting of two segments are extensively employed to manufacture well-defined structures.\textsuperscript{4,5} Compared to diblock copolymers, however, triblock terpolymers containing three chemically different blocks present increased structural diversity as their enormous parameter space provides larger possibility of creating more morphologies.\textsuperscript{6,11}

Perpendicularly ordered pores derived from BCPs are very much desired in ample applications including membrane separation and template synthesis, etc.\textsuperscript{12–15} The hydrophilic blocks of amphiphilic BCPs, for instance, poly(ethylene oxide) (PEO), poly(2-vinylpyridine) (P2VP), and poly(4-vinylpyridine) (P4VP), are capable of acting as the functional sites to bind molecules or salt precursors, leading to functional materials.\textsuperscript{14,16–20} Providing that triblock terpolymers are able to be equipped with two or more hydrophilic chains, it is very interesting to develop perpendicularly ordered pores in triblock terpolymers as the two types of hydrophilic chains involved in one copolymer enable us to prepare multiple functional materials. The two hydrophilic chains may have changing affinities and reactivities, for example, polarity, complexation, hydrogen bonding, etc., and different species can be selectively anchored into the microdomains of one specific hydrophilic block. For instance, gold and iron oxide nanoparticles can be selectively enriched into the P2VP and PEO microdomains in the PS-\textit{b}-P2VP-\textit{b}-PEO films, respectively, by taking advantages of the specific interactions of the precursors to the two blocks.\textsuperscript{21} Thus, obtained composite films are expected to show a catalytic function as well as a magnetical response. Generally, well-ordered porous nanostructures are obtained when the dispersed phases of BCPs are converted into voids. However, controlling the perpendicularly ordered cylinders dispersing in the rigid frameworks of triblock terpolymers are rarely reported since complex parameters will be involved to acquire such ordered morphology. Hence, merely several triblock terpolymers, for instance, poly(styrene)-\textit{b}-poly(isoprene)-\textit{b}-poly(lactide) (PS-\textit{b}-PI-\textit{b}-PLA),\textsuperscript{22} poly(styrene)-\textit{b}-poly(dimethylacrylamide)-\textit{b}-poly(lactide) (PS-\textit{b}-PDMA-\textit{b}-PLA),\textsuperscript{23} and poly(ethylene oxide)-\textit{b}-poly(methyl methacrylate)-\textit{b}-poly(styrene) (PEO-\textit{b}-PMMA-\textit{b}-PS),\textsuperscript{24} have been proposed to prepare the ordered morphologies with cylinders normal to the film surface up to now.

In addition to the perpendicular alignment, how to convert the dispersed phases of BCPs into voids is another concern. So far, several pore generation methodologies have been developed in BCPs.\textsuperscript{25–28} Among them, selective swelling is a facile yet efficient strategy to prepare nanoporous structures.\textsuperscript{28} For example, a P2VP selective solvent, ethanol, is able to swell...
hydrophilic P2VP domains of the diblock copolymer of poly(styrene)-b-poly(2-vinylpyrene) (PS-b-P2VP) while hydrophobic PS chains are plasticized. Then nanoporous structures of BCPs are reserved upon withdrawing ethanol followed by air-drying, where plasticized PS act as the matrix on which P2VP collapse. In our previous studies, PS-b-P2VP and PS-b-P4VP have been employed for fabricating perpendicularly ordered pores by ethanol swelling. The obtained uniform and straight nanopores can also be termed as homopores. Additionally, a number of PS-based BCPs such as poly(styrene)-b-poly(ethylene oxide) (PS-b-P(EO)),30 poly(styrene)-b-poly(N,N-dimethylaminoethyl methacrylate) (PS-b-PDMAEMA),31 poly(styrene)-b-poly(dimethylsiloxane) (PS-b-PDMS),32 and poly(styrene)-b-poly(methyl methacrylate) (PS-b-PMMA)33,34 have been exploited to construct homopores. However, these ordered structures are derived by selectively swelling one block of BCPs, impeding the development of the introduction of multifunctional hydrophilic chains in the swelling-induced nanostructures. Swelling triblock terpolymer with two or more hydrophilic blocks to yield homopores is an interesting alternative but has not been reported yet.

Herein, we report the perpendicular alignment of PEO@P2VP cylinders embedding in the PS matrix by annealing the PS homopolymer-blended triblock terpolymer of PS-b-P2VP-b-PEO (donated as SPO). P2VP and PEO are two commonly used polar homopolymers; however, they have different interactions toward water. Moreover, PS-based block copolymers with either P2VP or PEO as the other block have been widely studied, which gives us much referable information on the phase diagrams and swelling behaviors of terpolymers with a P2VP and a PEO block. Further considering that there are SPO triblock terpolymers available with tunable compositions, we decided to use SPO as a representative to study the annealing behavior and swelling-induced pore generation of terpolymers with double hydrophilic blocks. The perpendicular PEO@P2VP cylinders running through the entire films are well dispersed in the PS matrix by optimizing the humidity and temperature in the course of solvent annealing. As ethanol can swell PEO as well as P2VP domains while water swells only PEO domains, both solvents are subsequently employed to produce homopores in the annealed triblock terpolymer films. The homopores with sizes adjustable by swelling temperatures and durations are therefore realized in the obtained films.

## EXPERIMENTAL SECTION

### Materials

Triblock terpolymer of poly(styrene)-b-poly(2-vinylpyrene)-b-poly(ethylene oxide) (PS-b-P2VP-b-PEO, donated as SPO; \( M_n^{\text{PS}} = 75 \text{ kg/mol}, M_n^{\text{P2VP}} = 21 \text{ kg/mol}, M_n^{\text{PEO}} = 16.5 \text{ kg/mol}, \text{PDI} = 1.04 \)) and PS-OH homopolymer (\( M_n = 6 \text{ kg/mol}, \text{PDI} = 1.07 \)) were purchased from Polymer Source, Inc. (Canada), and were used as received. Chloroform (purity \( \geq 99.9\% \)), ethanol (purity \( \geq 99.8\% \)), and benzene (purity \( \geq 99.9\% \)) were obtained from Sigma-Aldrich and used without further purification. Silicon wafers were cut into the size of 1.5 cm \( \times \) 1.5 cm and then ultrasonicated at least three times in ethanol and dried before use.

### Solvent Annealing of the SPO/PS Films

The fraction of PS is calculated to be 68% (volume fraction, the same as in the following) in SPO as the mass densities of PS, P2VP, and PEO are 1.05,35 1.11,36 and 1.08 g/cm\(^3\), respectively. Different dosages of PS-OH homopolymers were mixed with SPO, forming 3 wt % chloroform solutions of SPO/PS (Table 1). Without other specification, a SPO/PS mixture with 75% PS (including both the PS block in the terpolymer and also the PS homopolymer) was employed in this study. The SPO/PS solutions were filtered 3 times through polytetrafluoroethylene (PTFE) filters with a nominal average pore size of 0.22 \( \mu \)m.

### Preparation of Homopores in the SPO/PS Films

The aligned SPO/PS films were immersed into ethanol at different temperatures for varied durations to generate homopores. To introduce homopores by water swelling, deionized water (pH = 6.9-7.0; conductivity: 8-20 \( \mu \)S/cm) was applied. Further, these homopores can be utilized for the perpendicular alignment of PEO@P2VP cylinders in the SPO/PS nanocomposites.

### RESULTS AND DISCUSSION

#### Morphology Transformation Induced by Solvent Annealing

SPO was dissolved in chloroform at first. Then hydroxyl-terminated PS homopolymers were included in the chloroform solutions of SPO, where the volume fraction of PS was determined to be 75% in the mixture. Thus, spin-coated films with a thickness of ca. 100 nm were annealed by benzene/chloroform (9:1, v/v) for different durations. The annealing solvent was capable of penetrating into the SPO/PS films and...
enhanced the mobility of the polymer chains. The added hydroxyl-terminated PS homopolymer (PS-OH) is expected to segregate to the substrate surface in the process of solvent annealing as the affinity between PS-OH and the native oxide layer is strong.\(^3\) This eliminates preferential interactions and is beneficial to the formation of the neutral layer on the substrate. Therefore, the perpendicular alignment of the triblock terpolymers is expected to be more easily achieved. In addition, some PS-OH molecules may also be localized in the PEO phases due to the interaction of hydrogen bonds between PEO and PS-OH. The thicknesses of the films were then gradually increased in such annealing process.\(^3\) The annealing degree \((D)\) was defined as follows:

\[
D = \frac{T}{T_0}
\]

where \(T\) is the thickness of the swollen films while \(T_0\) is the pristine thickness of the films. Upon withdrawing the annealing solvent at a designated annealing degree from the films, the thicknesses of the swollen films should be recovered to the original value. Meanwhile, the rearranged morphology induced by microphase separation remains in the films.\(^4\) Therefore, the annealing degrees have significant impacts on the final morphologies of the annealed films.\(^4\) As displayed in Figure 1a, the annealing degree of the SPO/PS films is gradually enhanced as a result of the increased film thickness induced by solvent uptake. When the annealing degree was 1.5, perpendicular cylinders surrounded by parallel cylinders appeared in the AFM surface topography (Figure 1b). Ordered structures are not achieved in the films due to the insufficient mobility of polymer chains. Most parallel cylinders then disappeared as the annealing degree came to 2.0, while the perpendicular cylinders with short-range ordering occupied the film surface (Figure 1c). The films endowed with hexagonally packed cylinders normal to the surface were acquired upon improving the

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**Figure 1.** Morphologies of the SPO/PS films annealed with different durations. (a) The dependence of the annealing degree of the films on the time in the course of in situ annealing. The red dots in the curve represent \(D = 1.5, 2.0, 2.1,\) and \(2.2\), respectively. AFM topography images of the annealed films terminated at \(D = 1.5\) (b), \(D = 2.0\) (c), \(D = 2.1\) (d), and \(D = 2.2\) (e) in the solvent annealing process. The inset of (d) is a fast Fourier transformation of the corresponding AFM image. Sizes of the AFM images: 1.5 \(\mu\)m \(\times\) 1.5 \(\mu\)m.
annealing degree to 2.1 (Figure 1d). The fast Fourier transformation image evidences the long-range ordering of the cylinders (the inset of Figure 1d). The diameter of the highly regular cylindrical phases is measured as 31 nm. Further increasing the annealing degree to 2.2 generated a higher solvent concentration in the films, leaving a disordered state in the films behind (Figure 1e).

Without the blending of PS homopolymers in SPO (68% PS), a lamellar morphology was accessible rather than the cylindrical one (Figure S1a), indicative of the lamellar phases of SPO in bulk. When the mass fraction of PS was increased to 72%, the order of the SPO/PS films was lost (Figure S1b). As previously mentioned, 75% PS is suitable to produce perpendicular cylinders in the films. Excessive PS homopolymers possibly lead to a difficulty in phase separation of the SPO/PS, resulting in the transformation of ordered structures into disordered ones (Figure S1c).

**Morphology Optimization by Adjusting the Annealing Humidity and Temperature.** The hydrophilic PEO is largely affected by water moiety in the course of solvent annealing. However, a high humidity of more than 70% should be the prerequisite to fabricate a high degree of lateral ordering in the PEO-based BCP films under solvent annealing as reported previously. To evaluate the order of the annealed films, in our study, perpendicular cylinders are transformed into cylindrical nanopores by ethanol swelling. The resultant perpendicular pores can span ca. 330 nm in the 500 nm thick SPO/PS films when the solvent annealing was conducted under a humidity of 40% (Figure 2a). Notably, the increase of the film thickness from pristine 400 to 500 nm is ascribed to the stretching of the swollen chains along the vertical direction in the process of ethanol swelling. By employing 50% humidity, the length of the perpendicular pores is able to be extended to 370 nm (Figure 2b), suggesting that a high humidity is in favor of the preparation of ordered SPO/PS films by solvent annealing. As the humidity of 60% was adopted, the perpendicular pores seem to run through the entire SPO/PS films as evidenced by SEM observation (Figure 2c), implying that the cylinders were propagated from the top to the bottom surface of the films by solvent annealing previously. We then define the degree of order (DO) as the ratio of the length of the cylindrical pores \( \text{L} \) to the thickness of the entire film \( \text{T} \): \[ \text{DO} = \frac{\text{L}}{\text{T}} \times 100\% \] (2) When the humidity came to 40, 50, and 60%, the values of DO can be up to 66, 74, and 100%, respectively (Figure 2d).
Apparently, the highly regular arrays of perpendicular pores are achieved at humidity lower than 70%. This is because humidity balances the interaction between blocks and the annealing solvent, facilitating the perpendicular alignment of the P2VP and PEO cylinders together with the neutralization effect of the blended hydroxyl-terminated PS homopolymers. However, as a consequence of the negative impact of the excessive water moiety on the selectivity of the annealing solvent, further increasing the humidity destroyed the order of the films (Figure S2).

Apart from humidity, annealing temperature also affects the depth of the ordered pores of the SPO/PS films. The humidity was controlled at 40% in the environment of annealing chamber prior to changing the temperature. A lower temperature, for instance, 20 °C, produces SPO/PS films with ca. 200 nm depth perpendicular pores (Figure 3a). 25 °C is still not enough to obtain the fully aligned cylinders in the films as shown in Figure 2a. In the course of solvent annealing, high temperature can facilitate the mobility of polymer chains and accelerate the self-assembly of SPO/PS. In this case, upon instantly removing the solvent after annealing, fast solvent evaporation along the vertical orientation yields a solvent gradient in the SPO/PS films, producing aligned cylinders normal to the surface in the entire films.42 Thus, homopores were occupied in the 500 nm thick films upon annealed at a slightly higher temperature of 30 °C followed by pore generation (Figure 3b). The values of DO were determined to be 40, 66, and 100% as the swelling temperatures were designated as 20, 25, and 30 °C, respectively (Figure 3c). The small temperature interval makes a big difference in the length of the perpendicular pores. Therefore, the order of the films is much more sensitive to the annealing temperature than the humidity.

**Phase Distribution in the SPO/PS Films.** To make a distinct understanding of the distribution of each phase in the well-registered SPO/PS films, transmission electron microscopy (TEM) images were collected subsequently. The P2VP phases were stained with I2 first.13 The dark and annular P2VP phases with a width of ca. 5.4 nm were unambiguously presented while the unstained PS and PEO domains exhibited gray color (Figure 4a). Because the PS majority domains should construct the matrix in the well-ordered SPO/PS films, the gray cylinders with a diameter of ca. 21.4 nm surrounded by annular P2VP domains are recognized as the PEO phases. Upon exposed to the vapor of OsO4, the PEO43 as well as P2VP44 domains were stained and turned dark in the TEM image (Figure 4b). The diameter of the PEO@P2VP cylinders was determined to be ca. 26.4 nm, which is highly consistent with that of the AFM topography. Therefore, the diameter of the PEO cylinders was calculated to be ca. 21 nm, which is in line with the result determined by the I2-stained samples. The schematic illustration of the distribution of each phase in the SPO/PS films is shown in Figure 4c.

![Figure 4](image1)

*Figure 4.* Phase distribution of the ordered SPO/PS films. TEM images of the SPO/PS films stained with I2 (a) and OsO4 (b). (c) Schematic representation of the phase-separated morphology of the SPO/PS films.

![Figure 5](image2)

*Figure 5.* SEM surface images of the SPO/PS films subjected to ethanol swelling at 50 °C for 30 s (a), 5 min (b), 0.5 h (c), 3 h (d), and 10 h (e). (f) Summary of the pore sizes and surface porosities of the films with different swelling durations.
Tunable Pore Sizes by Ethanol Swelling. The ordered SPO/PS films were initially immersed into ethanol at 50 °C for 30 s merely, leading to the generation of homopores with a diameter of 15.6 nm (Figure 5a). Previously, a swelling duration of several hours is needed in yielding well-ordered pores >10 nm in PS-b-P2VP with an equivalent molecular weight. Therefore, the fast pore generation here is due to the simultaneous swelling of both PEO and P2VP domains by hot ethanol. As the solubility parameters of PEO, P2VP, and ethanol are 22.7, 20.6, and 26.5 MPa$^{1/2}$, respectively, the affinity of ethanol to PEO is stronger than to P2VP, which makes it easier to swell PEO by ethanol compared to swelling P2VP. Hence, the swelling-induced pore generation course should be accelerated in the SPO/PS films. When the swelling duration was prolonged to 5 min, larger pores with a diameter of 19.4 nm were achieved (Figure 5b). The pore sizes are continuously enhanced upon extending the swelling durations. For instance, the pore sizes are determined to be 22.1, 22.8, and 23.4 nm when the swelling durations were designated as 0.5, 3, and 10 h, respectively (Figure 5c–e). With the increase of the pore sizes, the surface porosities of the SPO/PS films are correspondingly enlarged, which were estimated as 12, 15.7, 20.1, 23.7, and 24.1% for the swelling time of 30 s, 5 min, 0.5 h, 3 h, and 10 h, respectively. The pore sizes and surface porosities are summarized in Figure 5f.

In addition to swelling duration, swelling temperature is also a pivotal factor to regulate the pore sizes of the SPO/PS films. Upon immersed into ethanol at a low temperature of 20 °C, the dense SPO/PS films were converted into porous structures with a pore diameter of 11.8 nm (Figure 6a). When the swelling temperature was improved to 30 °C, the pore size was further increased to 16.4 nm (Figure 6b). The pore size has been enlarged to 19.5 nm as the swelling temperature was 40 °C (Figure 6c). A higher temperature, for instance, 60 °C, led to the generation of 22.1 nm homopores in the SPO/PS films.

**Figure 6.** SEM surface images of the SPO/PS films subjected to ethanol swelling at 20 (a), 30 (b), 40 (c), and 60 °C (d) for 0.5 h. (e) Summary of the pore sizes and surface porosities of the films with different swelling temperatures.

**Figure 7.** SEM surface images of the SPO/PS films subjected to water swelling at 50 °C for 0.5 (a), 1 (b), 5 (c), 10 (d), and 15 h (e). (f) Summary of the pore sizes and surface porosities of the films with different swelling durations.
When the swelling temperature was raised from 20 to 30, 40, 50, and 60 °C, the surface porosities of the SPO/PS films were gradually increased from 10.1% to 13.9, 15.1, 20.1, and 21.8%, respectively (Figure 6e). However, the ethanol swelling at 60 °C produced a few surface-blocked pores in the film possibly due to the excessive overflow of the swollen PEO and P2VP chains in the course of the swelling, which also can be observed in our previous work.

**Water-Swelling-Induced Pore Generation.** Providing that water-soluble PEO chains are contained in SPO, the environmentally benign solvent, water, is subsequently selected as the swelling agent to investigate the pore generation process. PEO is a typical type of hydrophilic chains; however, water swelling-induced pore generation was just simply mentioned in the PS-b-PEO films previously, and relevant investigations have rarely been reported. In this study, the PEO chains are surrounded by the hydrophilic P2VP annular domains in the aligned SPO/PS films, providing a great feasibility of the penetration of water into PEO. Swelling the films with aligned perpendicular cylinders in water at 50 °C for 0.5 h produced hexagonally arranged homopores with a diameter of 9.2 nm (Figure 7a). The surface contrast was enhanced as the swelling duration extends to 1 h while the pore size was increased to 11 nm (Figure 7b). As the swelling temperatures were prolonged to 5, 10, and 15 h, the pore sizes were improved to 11.9, 12.3, and 12.6 nm, respectively (Figure 7c–e). Extending the swelling duration to a longer time is not capable of increasing the pore size of the films further. In the course of water swelling, the PEO domains are swollen rather than P2VP. Thus, the water swelling is not able to enlarge pores distinctly compared to ethanol swelling. The surface porosities of these water-swelled films show a similar trend to that of the pore sizes, which were determined to be 7.4, 9.4, 10.8, 11, and 11.1% for the swelling duration of 0.5, 1, 5, 10, and 15 h, respectively (Figure 7f).

Swelling temperature was then adjusted to tune the pore size of the SPO/PS films. For example, the films were subjected to water swelling at 20, 30, and 40 °C for 0.5 h; consequently, the pore sizes were increased from 7.9 to 9.5 and 10.5 nm, respectively (Figure 8a–c). A higher swelling temperature of 70 °C resulted in the production of 12.1 nm pores in the films (Figure 8d), indicative of a stronger swelling capability of water at elevated temperatures. The surface porosity of the SPO/PS films was only 3.2% when the water swelling was performed at 20 °C (Figure 8e). As the swelling temperatures were raised to 30 and 40 °C, the surface porosities were increased to 6.8 and 8.8%, respectively. When the swelling temperature came to 70 °C, a stronger swelling behavior facilitated the improvement of the porosity which is up to 10.3%.

**CONCLUSIONS**

Lamellar-forming triblock terpolymer of PS-b-P2VP-b-PEO (SPO) is employed to construct highly regular phase-separated structures by blending PS homopolymers via solvent annealing. The long-range ordered perpendicularly PEO cylinders surrounded by annular P2VP phases are perfectly embedded into the PS matrix. The perpendicular cylinders running through the films can be accessible by optimizing the annealing humidity and temperature. As the selective solvents for SPO, both ethanol and water are capable of generating homopores in the SPO/PS films, in which pore sizes can be readily adjusted by regulating swelling temperatures or durations. The reported method pave a way to fabricate well-registered perpendicularly nanopores with multifunctional polymer chains for diverse applications.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b01358.

Additional SEM surface images of the SPO/PS films (PDF)

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Notes
The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

Financial support from the National Basic Research Program of China (2015CB655301), Natural Science Foundation of China (21776126), and the Jiangsu Natural Science Foundation (BK20150063) are gratefully acknowledged. We also thank the support from the Program of Excellent Innovation Teams of Jiangsu Higher Education Institutions and the Project of Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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