Monolithic Membranes with Designable Pore Geometries and Sizes via Retarded Evaporation of Block Copolymer Supramolecules

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ABSTRACT: We develop a retarded evaporation approach for the alignment of cylinder-forming block copolymer supramolecular monoliths, 3-n-pentadecylphenol (PDP) hydrogen-bonded polystyrene-b-poly(4-vinylpyridine) (PS-b-P4VP). A variety of highly ordered, aligned morphologies are produced by varying the dosages of PDP in the supramolecules. Treatment of the aligned supramolecular monoliths in hot ethanol leads to the dissolution of PDP and the selective swelling of P4VP, yielding enlargeable ordered mesopores along the original P4VP/PDP domains. Particularly, from supramolecular monoliths aligned in the morphology of perpendicular cylinders and gyroids, we obtain highly ordered monolithic membranes containing enlarged straight pores and bicontinuous pores, respectively. The straight and gyroidal pores were filled with phenol-formaldehyde resol and further carbonized to produce well-defined carbon nanostructures including nanofibers and reversed gyroids, demonstrating the pore accessibility and the promising templating functionality of the resulted monolithic membranes.

INTRODUCTION

Pore geometries and size uniformity dictate the performances of porous media in diverse applications, e.g., separation, catalysis, biomedical engineering, and optoelectronics, etc.1–4 There is a constant demand for methodologies to design and manufacture tailor-made pores with sizes down to sub-100 nm at affordable costs. Block copolymers (BCPs) have been proved to be versatile precursors to well-defined mesoporous structures.5–10 Controlled transformation of the dispersed phases embedded in the matrix into voids would yield porosities with the geometries coining the parent structures.

Selective removal of additives previously incorporated into one block of BCPs has been recently demonstrated to be a facile strategy to ordered mesopores.11–21 Straight cylindrical pores and bicontinuous gyroidal pores derived from perpendicular cylinders and gyroids in BCP systems, respectively, are of particular interests in many applications, for instance, membrane separation and photovoltaics.22–27 However, these two well-defined pore geometries are predominantly available in the type of ultrathin films with the thicknesses typically of several tens of nanometers, severely hampering their applications where free-standing, robust materials with pores in large aspect ratios are desired.25,26,28 Moreover, their pore sizes are strictly dictated by the volumes occupied by the additives. Overdosed additives may lead to morphology transition instead of enlarged pores.14 Therefore, it remains challenging for the production of ordered monolithic membranes with designable pore geometries and sizes in the arbitrary thickness.

In this work, by taking advantage of retarded evaporation of supramolecular solutions, we obtain aligned bulk films with tunable morphologies. Uniform mesopores in arbitrary thickness are created by two different effects of one selective solvent. Particularly, we produce 65 μm thick ordered monolithic membranes containing enlarged straight pores or bicontinuous gyroidal pores from corresponding aligned supramolecular monoliths. The obtained monolithic membranes with different pore geometries are further used as templates to synthesize carbon nanofibers and also reversed gyroids.

EXPERIMENTAL SECTION

Materials. Block copolymer of polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP, M_n^PS = 75 kg/mol, M_n^P4VP = 25 kg/mol, and polydispersity = 1.09) and hydroxyl-terminated PS homopolymer (PS-OH, M_n = 6 kg/mol, and polydispersity = 1.07) were purchased from Polymer Source, Inc. (Canada), and used as received. Chloroform (purity ≥99.8%) and ethanol (purity ≥99.8%) were obtained from Sigma-Aldrich and used without further purification. 3-n-Pentadecylphenol (PDP, 90%) was purchased from J&K Scientific Ltd. and recrystallized twice from petroleum ether. Silicon wafers were cut into the size of 1.5 cm × 1.5 cm and then ultrasonicated at least three times in ethanol and dried before use. In most cases, the cleaned silicon
PDP, the experimental temperature should not be lower than 20 °C for at least 12 h for the complete generation of hydrogen bonding between PDP and 4VP. Before use, the supramolecular solutions were filtered three times through polytetrafluoroethylene (PTFE) filters with a nominal average pore size of 0.22 μm to remove any big aggregates. To prepare aligned supramolecular films with different morphologies, the supramolecular solutions were drop-casted onto silicon wafers previously placed on a stand inside a PTFE container with a total volume of ca. 120 mL. Additional chloroform was then filled into the container, and the container was immediately sealed with its lid. There are three holes with the diameter of 2.5 mm drilled on the lid to allow the retarded evaporation of chloroform (Figure S2). The above dropping and filling operations should be performed fast (within 10 s) to minimize the uncontrolled evaporation of highly volatile chloroform as significant loss of chloroform in this stage may lead to the change of the final morphology of the films. We note that during the long evaporation process the container with the sample inside should be kept still and undisplaced otherwise the final morphology maybe be deteriorated or even destroyed because of these disturbances. To prepare supramolecular films with different thickness, the volume of the dropped supramolecular solution and the additional added chloroform as well as the duration of evaporation should be controlled accordingly. Table S1 summarizes the preparation conditions for supramolecular films with different morphologies and thicknesses. Chloroform additionally introduced into the container should be kept in the appropriate amount (Table S1) because overdosed chloroform would lead to the dewetting of the film because of prolonged evaporation. In addition, for the fear of the crystallization of PDP, the experimental temperature should not be lower than 20 °C.

**Alignment of Supramolecular Films.** PS-b-P4VP is dissolved in chloroform with a typical concentration of 0.5 wt %, and then PDP is added into the BCP solution with the mass fractions of P4VP(PDP) ranging from 25 to 70 wt %. The solutions were stirred at room temperature for at least 12 h for the complete generation of hydrogen bonding between PDP and 4VP. Before use, the supramolecular solutions were filtered three times through polytetrafluoroethylene (PTFE) filters with a nominal average pore size of 0.22 μm to remove any big aggregates. To prepare aligned supramolecular films with different morphologies, the supramolecular solutions were drop-casted onto silicon wafers previously placed on a stand inside a PTFE container with a total volume of ca. 120 mL. Additional chloroform was then filled into the container, and the container was immediately sealed with its lid. There are three holes with the diameter of 2.5 mm drilled on the lid to allow the retarded evaporation of chloroform (Figure S2). The above dropping and filling operations should be performed fast (within 10 s) to minimize the uncontrolled evaporation of highly volatile chloroform as significant loss of chloroform in this stage may lead to the change of the final morphology of the films. We note that during the long evaporation process the container with the sample inside should be kept still and undisplaced otherwise the final morphology maybe be deteriorated or even destroyed because of these disturbances. To prepare supramolecular films with different thickness, the volume of the dropped supramolecular solution and the additional added chloroform as well as the duration of evaporation should be controlled accordingly. Table S1 summarizes the preparation conditions for supramolecular films with different morphologies and thicknesses. Chloroform additionally introduced into the container should be kept in the appropriate amount (Table S1) because overdosed chloroform would lead to the dewetting of the film because of prolonged evaporation. In addition, for the fear of the crystallization of PDP, the experimental temperature should not be lower than 20 °C.

**Preparation of Porous Monolithic Membranes.** Upon the complete evaporation of chloroform, the silicon wafers along with the films were taken out of the container and immersed in ethanol at room temperature or elevated temperatures for different periods to generate pores. For thicker films (such as ca. 65 μm) with perpendicular cylinders, they are immersed in ethanol at room temperature for 4 days to completely remove PDP. The complete removal of PDP is verified by FTIR. At the end of ethanol treatment, the samples were taken out and air-dried at room temperature for at least 2 days.

**Template Synthesis of Carbon Nanostructures.** The monolithic films with aligned P4VP(PDP) cylinders or gyroids were treated in ethanol at 60 °C for 1 h to produce ca. 20 μm thick monolithic membranes with cylindrical pores or ca. 7 μm thick monolithic membranes with gyroidal pores. The membranes were immersed into the solution of oligomeric phenol–formaldehyde resin (15 wt %, dissolved by ethanol/water with the weight ratio of 1/1),30 and the solution containing the membranes was maintained in vacuum for ca. 12 h at room temperature to force the carbon precursor to fill the nanopores of the membranes. The membranes were then removed from the solution and dried at room temperature for another 12 h to evaporate the solvent. After that, the filled membranes were kept at 80 °C for ca. 20 h to thermopolymerize the phenolic resin. Finally, the films were calcined at 450 °C under nitrogen for 3 h with a temperature increase rate of 1 °C/min to decompose the BCP template, and then the temperature was increased to 600 °C at the rate of 3 °C/min to carbonize the resin.

**Characterizations.** Field-emission scanning electron microscopy (Hitachi, S4800) was used to view surfaces and cross sections of the films at a voltage of 5 kV. Before SEM examinations the samples were sputter-coated with a thin layer Pd/Pt alloy. The surface topography image of the perpendicularly aligned supramolecular monolith was characterized by atomic force microscopy (XE-100, Park Systems). For the transmission electron microscopy (TEM) observations, the PS-b-P4VP(PDP) monoliths before and after PDP removal were embedded in epoxy resin and microtomed by a diamond knife on a Leica EM UC7 microtoming system at room temperature after curing. Then thin slices with a thickness of ca. 70 nm were retrieved on TEM grids and stained by iodine at 30 °C for 12 h. FTIR spectra were obtained from a
Nicolet 8700 infrared spectrometer in the attenuated total reflection (ATR) mode. Nitrogen adsorption–desorption isotherms of monolithic membranes with the thickness of 65 μm were obtained at 77 K using a Belcorp Mini analyzer. Before the measurements, the membrane was outgassed at 50 °C in vacuum for 12 h. Small-angle X-ray scattering (SAXS, Bruker AXS Co., Germany, λ = 0.154 nm) was used to investigate the structure of supramolecular monolith with a thickness of 65 μm before and after the removal of PDP by ethanol washing at room temperature. The voltage and current were 50 kV and 0.6 mA, respectively. Moreover, the duration of X-ray exposure was 30 min. Sample-to-detector distance is 107 cm. The scattering vector \( q = 2 \pi/(\lambda \sin \theta) \) and \( 2\theta \) is the scattering angle. The center-to-center spacing between adjacent cylinders can be calculated by the equation \( D = 2\pi/(q \sin 60°) \). For the TEM examinations of the carbon replicas, the as-obtained carbon materials were scraped from substrates, dispersed in ethanol followed by sonication, and then deposited on TEM grids. TEM observations were carried out on a JEOL-2100 microscope operated at 200 kV.

## RESULTS AND DISCUSSION

**Fabrication of the Monolithic Membranes with Designable Pore Geometries and Pore Sizes.** Cylinder-forming PS-b-P4VP (M<sub>n</sub><sup>PS</sup> ≈ 75 kg/mol, M<sub>n</sub><sup>P4VP</sup> = 25 kg/mol) was mixed with PDP in chloroform to produce supramolecules (Table S1), PS-b-P4VP(PDP), via the hydrogen bonding between the hydroxyl groups in PDP and the pyridyl groups in P4VP<sup>11–13</sup> (Figure S1). We drop-cast the supramolecular solution on silicon substrates and allowed them to be dried in a partially sealed container at room temperature (rt). The drying process was controllably retarded by introducing additional amount of chloroform into the container to extend the evaporate duration of chloroform in the supramolecular solution (Figure S2). The durations for solutions to be completely dried were tuned by changing the volumes of the additional chloroform. The dried supramolecular monoliths were immersed in ethanol at rt for 12 h to wash away the incorporated PDP, resulting in different morphologies depending on the mass ratios of P4VP(PDP) in the supramolecules, \( f_{P4VP(PDP)} \). Because of the similar density of PS-b-P4VP and PDP, there is a rather small difference between the mass fractions and the volume fractions in our system.\(^{15}\) The structure derived from the neat PS-b-P4VP is featureless except for a few randomly distributed pores (Figure 1a), and ethanol swelling is applied to generate larger pores for a better judge,\(^{31}\) implying a disordered morphology for the dried monolith before ethanol washing. Upon the addition of a small amount of PDP where \( f_{P4VP(PDP)} \) reached 28%, we obtained hollow channels parallel to the surface (Figure 1b), corresponding to a cylindrical morphology in the parallel orientation before ethanol washing. Increasing \( f_{P4VP(PDP)} \) from 28% to 30% induced the morphology transition from parallel cylinders to perpendicular cylinders, as clearly evidenced by the straight cylindrical pores shown in Figure 1c. Moreover, well-defined gyroidal (Figure 1d) and lamellar (Figure 1e) structures were generated with \( f_{P4VP(PDP)} \) continuously increasing to 35% and 50%, respectively. At an even higher \( f_{P4VP(PDP)} \) of 70%, the P4VP(PDP) phase was turned to be the majority, and the supramolecule was segregated into the morphology of parallel PS cylinders embedded into the P4VP(PDP) matrix. After removing PDP by ethanol the matrix collapsed, leading to nanofibers of PS-b-P4VP with a uniform diameter (Figure 1f).

The final morphology of the annealed film before the occurrence of dewetting is strongly dependent on \( f_{P4VP(PDP)} \) and a small change in \( f_{P4VP(PDP)} \) may lead to a noticeable morphology transition. The incorporation of PDP into the P4VP blocks plays two different roles: (1) changing the block ratios of the BCP and (2) tuning the affinity of P4VP blocks to chloroform. With the increase of PDP dosages, the shift of final morphologies can be well explained by the classic phase diagram of BCPS if we consider the component of P4VP(PDP) as an integrated block.\(^{32}\) To compare the affinity of chloroform to PS and P4VP, the polymer–solvent interaction parameter (\( x_{PS} \)) representing the relative affinity of solvent for each block was calculated by the equation

\[
x_{PS} = \frac{V_i}{R} \left( \frac{\delta_i - \delta_p}{\delta_p} \right)^2 + 0.34
\]

where \( V_i \) is the molar volume of the solvent, \( \delta_i \) and \( \delta_p \) are the solubility parameters of the solvent and homopolymers, respectively, \( R \) is the gas constant, and \( T \) is the temperature. At room temperature, solubility parameters are 19.0, 18.6, and 22.2 MPa<sup>1/2</sup> for chloroform,\(^{33}\) PS, and P4VP,\(^{34}\) respectively. The calculated polymer–solvent interaction parameter of chloroform for PS is 0.35 (\( \chi < 0.5 \)) and for P4VP is 0.67 (\( \chi > 0.5 \)). Therefore, chloroform is a slightly selective solvent for PS-b-P4VP with better affinity to PS.\(^{35}\) And in our systems, the presence of PDP enhances the affinity of chloroform to P4VP(PDP) as chloroform has a very good solubility to PDP. In the neat BCP system the mobility of the BCP chains is not sufficiently enhanced, and they cannot reach the ordered state within the time frame defined by the evaporation condition in this study. Upon the incorporation of PDP into the BCP the mobility of the BCP is significantly enhanced as evidenced by the reduced glass transition temperature of P4VP,\(^{14}\) consequently accelerating the achievement of the ordered morphology. The selectivity of chloroform to the supramolecular film is determined by PDP dosages. At small dosages, for example, at \( f_{P4VP(PDP)} = 28% \), chloroform still shows better affinity to PS than to P4VP(PDP). During solvent evaporation, chloroform provides a selective interface for PS, inducing the formation of parallel cylinders in the film surface. Because of the lowest solvent concentration at the surface and a unidirectional gradient in solvent concentration normal to the surface, in-plane parallel structures are frozen at the top surface and then propagate inward into the films with the gradual depletion of chloroform.\(^{35,36}\) At higher \( f_{P4VP(PDP)} \) i.e. 30%, chloroform may become nonselective for the supramolecular system; then the intermediate interface promotes the formation of perpendicular cylinders which propagate inward into monoliths to achieve the ultimately well-organized morphology. The duration of the evaporation process also plays a critical role in determining the final morphology. We observed a transition from cylinders parallel to the surface to cylinders perpendicular to the surface with mixtures of both as intermediates as the evaporation duration increased from 1 to 26 h (Figure 2). Moreover, even longer evaporation duration is required for the propagation of perpendicular cylinders into the entire thickness of the film. For instance, the evaporation duration of 26 h only developed perpendicular cylinders from the monolith surface to the interior at the depth of 1–1.5 μm, and parallel cylinders as well as disordered morphology remained in the deep in the monolith (Figure S4a). In contrast, when the solvent evaporation lasted for 60 h, we obtained perpendicular cylinders traversing the entire supramolecular monolith with a thickness of ca. 6 μm (Figure S4b). Retarded evaporation creates a long-standing gradient solvent field, inducing the

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perpendicular alignment of the supramolecules initiating on the monolith surface and propagating inward into the interior of the monolith until the complete evaporation of the solvent.

Monolithic Membranes with Perpendicular P4VP-(PDP) Cylinders within the PS Matrixes and Arbitrary Thicknesses Swelled for Varied Pore Sizes. We made a detailed investigation on the perpendicularly aligned monolith with $f_{P4VP(PDP)} = 30\%$ before and after the removal of PDP. The atomic force microscopy (AFM) topography image reveals the presence of dark circular dots on the film surface upon the complete evaporation of chloroform (Figure 3a). The dark circular dots correspond to the upper ends of the perpendicular P4VP(PDP) cylinders embedded in the PS matrix (bright regions). The fast Fourier transformation image (inset in Figure 3a) evidence the hexagonally patterned ordering of these cylinders. The domain size and the center-to-center spacing between adjacent P4VP(PDP) cylinders can be determined to be ca. 33 nm and ca. 58 nm, respectively from the profile analysis on the AFM image (Figure 3b). Transmission electron microscopy (TEM) on thin slices of the supramolecule monolith clearly demonstrates the perpendicular orientation of the P4VP(PDP) cylinders (Figure 3c). The dark stripes correspond to the P4VP(PDP) domains as they are selectively stained with iodine. As revealed by TEM, the P4VP(PDP) domains are straight and parallel to each other, and they possess a relatively uniform diameter and center-to-center spacing of ca. 32 and 56 nm, respectively, which are in good consistence with the AFM characterization. SAXS was further used to examine the long-range ordering of the supramolecular monoliths (Figure 3d). The monolith before the removal of PDP gives faint SAXS signals because of the weak contrast in electron density of the PS and P4VP(PDP) phase. However, the primary peak located at $q^* = 0.0125$ Å$^{-1}$ is still discernible, and the center-to-center spacing between adjacent cylinders can thus be determined as ca. 58 nm, which coincides with both the AFM and TEM analysis. After ethanol treatment the SAXS signals become stronger as the removal of PDP enhances the contrast between the two phases. We compared the intensity of the main peak shown in Figure 3d before ($I_{\text{before}}$) and after ($I_{\text{after}}$) ethanol soaking. The $I_{\text{after}}/I_{\text{before}}$ was found to be lower than the theoretical value as reported in Ikkala’s work dealing with a PS-$_b$-P4VP(PDP) supramolecule with a similar composition. However, the strong increase in the measured intensity after ethanol soaking still unambiguously confirms the removal of PDP. Peaks at the position of 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, and $\sqrt{12}$ indicate the long-range ordering of hexagonally packed pores and the corresponding the P4VP(PDP) cylinders before the removal of PDP. Moreover, the primary peak remains at $q^* = 0.0125$ Å$^{-1}$, implying that the removal of PDP by mild ethanol treatment does not change the structural integrity of the PS framework, and the structural correlation...
between the solid cylinders and empty cylindrical pores before and after the removal of PDP is reliable.

Cylindrical pores are typically produced by selectively dissolving away the incorporated additives in the supramolecules with solvents while keeping the PS framework intact. We immersed the as-aligned monoliths in ethanol at rt for different periods. As shown in Figure 4a–c, hexagonally patterned circular pores with uniform diameters appear on the film surface. Cross-sectional TEM examinations reveal that the perpendicular alignment is preserved after the removal of ethanol, and these pores are through pores lined with P4VP chains which appear dark after staining with iodine (Figure 4d). The pore diameter is 10.3 and 15.0 nm after ethanol dissolving for 3 and 5 h, respectively, and further increases to 18.8 nm after dissolving for 12 h. Further prolonged dissolving does not enlarge the pore size any more. Therefore, this is the maximum pore size available by this dissolving method as the incorporated PDP molecules have been completely dissolved away by ethanol at rt for 12 h. We note that ethanol dissolving for durations lower than 3 h does not produce thoroughly opened pores because of the inhomogeneous dissolution of PDP. As confirmed by both SEM and TEM, the center-to-center spacing of adjacent pores does not change with the duration of ethanol dissolving, which remains at ca. 56 nm and is identical to the center-to-center spacing of the P4VP(PDP) cylinders. Therefore, we conclude that the pores are generated at the original positions of P4VP(PDP) cylinders in the supramolecular monoliths with the progressive dissolution of PDP in ethanol at rt. Compared to the original diameter of P4VP(PDP) cylinders which is 32 nm as determined by TEM, the diameters of pores created by the dissolution of PDP are much smaller because the P4VP chains initially hydrogen-
bonded with PDP still occupy a large portion of the space in the original positions of P4VP(PDP) domains after the removal of PDP. The tunable range in pore sizes by ethanol dissolving is regulated by the amount of PDP incorporated in the BCP, and more PDP should be used to obtain larger pore sizes. In the current work, the pore size can be moderately tuned from 10.3 to 18.8 nm by ethanol dissolution at rt. However, as discussed above, there is a sensitive dependence of the morphology on \( f_{P4VP(PDP)} \); for instance, slight increase in \( f_{P4VP(PDP)} \) from 30% to 35% results in the transition of cylinders to gyroids, and extra PDP may induce the change of morphology in stead of enlarged pores.

An alternative approach is therefore desired to tune the pore sizes in a wider range. The mechanism of selective swelling induced pore generation is employed to tune the pore sizes at a more efficient way in terms of both the available range of pore sizes and the time efficiency. This approach is also only involved with ethanol treatment and the only difference compared to ethanol dissolving is that the ethanol treatment is performed at elevated temperatures rather than at rt. As shown in Figure 4e, much larger pores with a diameter of 23.7 nm were produced after ethanol treatment at 55 °C for 1 h, and even larger pores with the diameter of 25.3 nm were obtained upon ethanol immersion at 60 °C for 1 h (Figure 4f). Comparing to the pores produced at ethanol immersion at rt, such large pores obtained at elevated temperatures are ascribed to the dual functions of hot ethanol delivering to different components in the supramolecules. Ethanol dissolves away PDP molecules incorporated in BCP on one hand and simultaneously swells P4VP chains and expands the volume of the space initially occupied by the P4VP/PDP domains, leading to enlarged pores with the evaporation of ethanol in the subsequent drying process.\(^{8,31,37,40-42}\) On the other hand, therefore, besides the removal of PDP, there is an additional contribution in making pores from the swelling of P4VP chains by ethanol. We note that selective swelling in hot ethanol does not destroy the ordering of the pores as the center-to-center spacing between adjacent pores remains unchanged. As pores are enlarged at no expense of pore density in ethanol, swelling the surface porosity increases with pore diameters (Figure S5). The surface porosity considerably increases from 10.3% for the membrane washed in ethanol at rt for 12 h to 18.6% for the one swelling-treated at 60 °C for 1 h. The increase in porosity without the loss the pore uniformity is highly desired for membranes targeted for separation applications.\(^{43}\) The pore sizes and porosities of membranes produced by different ethanol treatments together with the diameter of the original P4VP(PDP) cylinders are summarized in Figure 4g. Apparently, the pore diameters of membranes produced at 55 or 60 °C are still smaller than the domains size of the original P4VP(PDP) cylinders. This is due to the presence of P4VP chains lined along the pore walls as ethanol only swells rather than removes the P4VP blocks covalently bonded to the PS matrix.

It should be noted that the pores in the produced membranes are mainly closed on the ends attaching the silicon substrate (Figure S6a) because of the preferential wetting of P4VP(PDP) to the bare Si surface terminated with hydroxyl groups.\(^{44}\) However, through membranes with pores opened on both ends were prepared by using PS-grafted Si wafers as the substrates (Figure S6b). Hydroxyl-group-terminated PS homopolymers were grafted on the surface of Si wafers, and during the annealing process the substrate surface was preferentially wetted by the PS blocks in the supramolecules. In the following ethanol soaking, this PS layer would be pierced by the expanding P4VP chains, leading to the pore opening on this end.\(^{45}\)

By controllably retarding the evaporation process of the solvent, we are able to prepare perpendicularly aligned supramolecular films and corresponding membranes containing cylindrical straight pores with arbitrary thicknesses (Figure S7). Varied evaporation durations are required for the aligned films...
with different thicknesses, which can be readily controlled by the amount of chloroform additionally introduced into the container. A 250 nm thick film with the perpendicular alignment requires the solvent evaporation to last for 6 h, and thicker films typically require longer evaporation. For instance, the evaporation duration should last for 12, 36, and 96 h for films with the thickness of 600 nm, 2 μm, and 13 μm, respectively. We produced aligned films with different thicknesses and recorded the required durations of evaporation (Figure 5a). By being subjected to ethanol washing to remove PDP, these films are converted to ordered porous membranes. A membrane with a thickness of 13 μm gains reasonably good robustness and is capable of free-standing (Figure S8). In addition, the change from yellowish to colorless of the washed film evidence the removal of PDP. Theoretically, membranes with aligned ordered pores can be developed to be arbitrary in thickness provided a sufficiently retarded evaporation of the solvent. For example, perpendicularly aligned monoliths and corresponding ordered porous monolithic membranes with extremely large thicknesses, i.e., 65 μm, can be prepared by retarding the evaporation for ca. a week. Nitrogen adsorption tests demonstrate that the membrane exhibits a very sharp pore size distribution centering around 18.9 nm (Figure 5b) which is highly consistent with SEM examinations. SEM examinations on the cross sections of the membrane show straight pores running from the top surface to the bottom surface of the membrane. Closer SEM observations at different depths demonstrate that the pores in the positions either near the top, bottom, or middle keep perpendicularly aligned and relatively uniform in diameter (Figure 5c).

**Enlarged Bicontinuous Pores of Gyroidal Structures.** Gyroidal structures are very fascinating in the design of functional materials for their unique bicontinuous structures. However, it is even more difficult to tune the feature size of the gyroids because they appear in a very narrow region in the phase diagram. As already shown above, gyroids can be produced at \( f_{P4VP(PDP)} = 35\% \), and pores appear with the removal of PDP by ethanol dissolving. We demonstrate that these pores embedded in the gyroids can be tuned in a certain range. The circular pores have an initial average diameter of 13.9 nm after dissolving away PDP at rt by ethanol (Figure 6a,b). After ethanol swelling at 55 °C for 1 h the pore is enlarged to 18.7 nm, and the gyroidal structure is well preserved because of the swelling effect of hot ethanol (Figure 6c,d). The pore is further increased to 26.1 nm after ethanol swelling at 60 °C for 1 h, but the gyroidal structure is slightly deformed (Figure 6e,f). Even stronger swelling in ethanol, for instance, swelling at 70 °C for 12 h, leads to the complete collapse of the gyroids and the formation of a disordered fibrous structure (Figure S9).

**Carbon Nanostructures Templated from the Monolithic Membranes.** To demonstrate the pore accessibility as
well as the potential applications of the produced monolithic membranes, we prepared carbon nanostructures in the shape of nanofibers and reversed gyroids. The BCP membranes with cylindrical pores and gyroidal pores were infiltrated with resol solutions followed by thermal polymerization and were then calcinated in inert atmosphere at 600 °C to degrade the BCP components and also to carbonize the resols. Figures 7a−c show that the products templated from membranes with cylindrical pores are bundled carbon nanofibers with uniform diameters. The length of the carbon nanofibers is close to the thickness of the membrane templates as carbonization of resols at low temperatures, for example, 600 °C in this work, leads to minor shrinkage.46 Interestingly, the diameter of the nanofibers (∼38 nm) is noticeably larger than the size (∼25.3 nm) of the straight pores in the membrane templates. This observation can be explained by the penetration of resols in the P4VP layers lining along the membrane pores. As revealed by the AFM analysis discussed earlier, the size of the original P4VP(PDP) micromdomains is ∼33 nm, and the diameter of nanopores is ∼18.8 nm after the removal of PDP by ethanol washing at rt, implying that the P2VP chains lining along the pore walls occupy the remaining thickness of ∼14.2 nm. The oligomeric resol dissolved in the ethanol/water mixture is expected to diffuse into the P2VP lining layer and were converted to carbon together with the resol filling the bulky pores in the subsequent carbonization. Therefore, by considering both the diameter of the original nanopores (∼25.3 nm) in the template and the thickness of the P4VP lining layers (∼14.2 nm), we can roughly estimate that the diameter of carbon nanofibers is 39.5 nm, which is in good consistence with SEM imaging.

Similarly, by using membranes with gyroidal pores as templates, we prepared ordered nanoporous carbons with periodical porosities. The SEM images shown in Figure 7d,e reveal that the obtained carbon exhibits a continuous framework with well-defined pores reversibly replicating the original gyroidal membranes. The highly ordered morphology of the gyroidal carbon replica is further verified by TEM image (Figure 7f). The diameter of carbon skeletons is estimated as ∼28 nm, which is slightly larger than the voids size of the templates, which should also be attributed to the carbonization of resols residing in the P4VP layers lining along the pore walls. Considering their structural uniformity and tunability, the templated carbon nanostructures are expected to find interesting applications, for example, in the fields of energy storages47 and catalysis.48 The successful production of carbon nanofibers and reversed gyroids from the micrometric thick monolithic membranes demonstrates the open and easily accessible nature of the membranes, on the one hand, and suggests their potentials as controllable templates for the synthesis of functional materials with different compositions, on the other.

CONCLUSION

In conclusion, a retarded evaporation approach is reported for the alignment of block copolymer supramolecular films with arbitrary thickness. PDP is hydrogen-bonded to PS-b-P4VP to form the supramolecule of PS-b-P4VP(PDP), and a number of aligned periodic structures have been reproducibly prepared. Ethanol is used to transform the aligned monoliths into ordered porous membranes. We discover that in addition to the dissolution effect to PVP, hot ethanol is able to considerably enlarge the pores through its selective swelling effect to P4VP. Particularly, ordered monolithic membranes featured as uniform straight pores or gyroidal pores are prepared with exceptionally large thicknesses, i.e., 65 μm. By solution infiltration of carbon precursors into the monolithic membranes followed by carbonization, we produce well-defined carbon nanostructures in the form of nanofibers and reversed gyroids, demonstrating the pore accessibility and potentials as controllable templates of the resulted monolithic membranes. This work opens new avenue for the design and production of tailor-made monolithic membranes with flexibly tunable pore geometries, pore sizes, and macroscopic dimensions to fit diverse applications.
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