

Formation of Breath Figure Arrays in Methanol Vapor Assisted by Surface Active Agents

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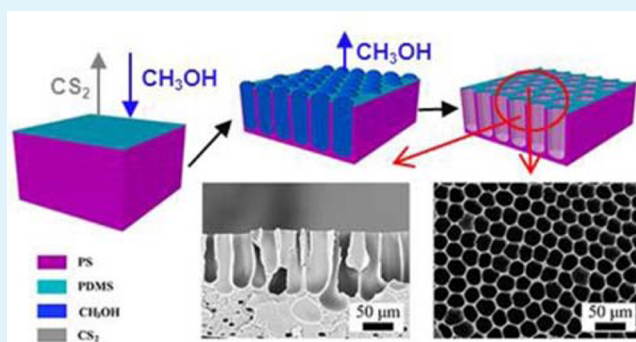
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Supporting Information

ABSTRACT: Breath figure (BF) process is a promising technique for fabricating honeycomb polymer films. It is usually conducted in water vapor. While, in organic vapors only unique polymer can be used to prepare BF arrays as reported in our previous article (Breath Figure in Nonaqueous Vapor. *Soft Matter*, 2013, 506–514), although new structure features are induced in the film. In this paper, a universal modified BF processing is devised for preparing porous films in methanol vapor with conventional polymers, by adding a small amount of surface active agent into the casting solution, such as siloxane- and fluorine-containing block copolymers. The pores in the PS films prepared with this method are of cylindrical shape with large depth-diameter aspect ratio, and the diameter and depth of pores can be well controlled by the experiment conditions. Based on these results, the formation mechanism of honeycomb structure in methanol vapor is discussed.

KEYWORDS: breath figure, surface tension, porous films, methanol vapor



INTRODUCTION

Porous films with highly ordered structures have drawn great attention owing to their unique morphology and broad applications in the fields of templates, biomaterials, optical devices, separation membranes, sensors, and catalysts.^{1,2} Honeycomb films with ordered pore arrays were usually prepared under the guide of hard/soft templates, such as colloidal crystals, emulsions, organisms (bacteria and echinoid, etc.), and so on.³ Recently, breath figure (BF) method, as an alternative way to prepare honeycomb films, was established and developed rapidly, in which in situ generated water droplets acted as soft templates.⁴ In a typical BF process, when polymer solution of organic solvent is cast onto a substrate in moist atmosphere, water vapor condenses into microdroplets on the surface of the solution, due to evaporation cooling effect of the organic solvent. These water droplets can grow, be stabilized by the polymer envelop, and self-assemble into hexagonal shape on the surface of solution, and, finally, produce honeycomb pores on the dry polymer film after the total evaporation of solvent and water.⁵ Compared with other template techniques, BF process has several significant advantages, such as easy operation, low cost, self-removable template, and wide applicability.^{6–9} Therefore, BF process has been employed to fabricate porous films based on various materials, including a wide spectrum of polymers, metal nanoparticles, carbon materials, and small organic molecules.^{10–14}

The BF process has long been carried out in the atmosphere of water vapor, since it was first established by François,

inspired by the formation of fog.^{15,16} Although organic vapors can also form fog under proper condition, they are seldom used to generate droplet templates in BF process. Recently, we reported the successful preparation of BF arrays with a diblock copolymer, polystyrene-*block*-poly(dimethylsiloxane) (PS-*b*-PDMS), by a static BF process in alcohol vapor (A-BF method), such as methanol and ethanol vapor.¹⁷ The pores formed in methanol and ethanol vapor are cylindrical and ellipsoidal, respectively, dissimilar to the spherical holes prepared in water vapor, which can be attributed to the different physical properties of these vapors, including surface tension and saturated vapor pressure. Therefore, changing atmosphere of BF method provides us an efficient means to fine-tune the pore size and shape of the honey-structured films. Unfortunately, this A-BF method is not applicable to many frequently used polymers, which usually produces films with ultralarge unordered pores or irregular particles.¹⁸ Thus, the application of A-BF is strongly restricted.

First, in this article, we report a modified A-BF procedure as a general method for preparing honeycomb films with conventional polymers in methanol vapor. Assisted by PS-*b*-PDMS or polystyrene-*block*-poly(perfluorooctylethyl methacrylate) (PS-*b*-PFMA), polystyrene (PS), and polystyrene-*block*-polybutadiene-*block*-polystyrene triblock copolymer (SBS) BF

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arrays are successfully formed in methanol vapor. Second, the obtained ordered pores have large depth-diameter ratio. The depth and diameter can be well controlled through concentration of polymers, vapor pressure of methanol, and temperature. Most importantly, based on the experiment results, the formation mechanism of the porous structure by A-BF is through elucidated. The surface active agents of siloxane- and fluorine-containing copolymers play an important role of prohibiting the spread of methanol droplets by reducing the surface tension of polymer solution. With the entrapment of the polymer precipitation, methanol droplets are stabilized. Eventually, honeycomb structures form after evaporation of methanol droplets.

EXPERIMENTAL SECTION

Materials. PS (M_n : 119 k, PDI: 1.75) was prepared via thermal polymerization of styrene.¹⁹ PS-*b*-PDMS diblock copolymer was synthesized via atom-transfer radical polymerization (ATRP) according to previous literature.²⁰ The molecular weight of PDMS block is 4670 g/mol, as provided by the manufacturer. The relative number-average molecular weight (M_n) and molecular weight distribution (MWD) of the PS-*b*-PDMS are listed in Table 1. PS-*b*-PFMA was

Table 1. M_n and MWD of PS-*b*-PDMS and PDMS

	PS block (g/mol)	PDMS block (g/mol)	PS- <i>b</i> -PDMS (g/mol)	MWD
PS ₂₀₅ - <i>b</i> -PDMS ₆₃	21 330	4670	26 000	1.22
PS ₇₀ - <i>b</i> -PDMS ₆₃	7230	4670	11 900	1.10
PS ₂₆ - <i>b</i> -PDMS ₆₃	2730	4670	7400	1.29
PDMS	0	4670		

synthesized by ATRP.²¹ The relative number-average molecular weights (M_n) of the PS block and PFMA block are 14 k and 3.5 k, respectively, with a MWD of 1.10. All the molecular weights and MWD were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF). SBS (Aldrich, 21 wt % styrene), carbon disulfide (CS₂) (chromatographically pure, China), and methanol (AR, China) were used as received. The glass substrates (1.0 × 1.0 cm²) were cleaned by detergent and acetone successively and air-dried before use.

Preparation of Honeycomb Films in Methanol Vapor. The saturated methanol vapor was obtained by adding 5 mL of methanol in a 25 mL glass wild-mouth bottle with a silicone stopper (Supporting Information (SI) Figure S1), and it was kept sealed for an hour before use. To remove the water in the sealed system, 1.0 g anhydrous sodium sulfate (Na₂SO₄) was added in methanol and on a supporting stand in the bottle without contacting with methanol liquid, respectively. The temperature of the system was controlled by placing the glass bottle in a water bath and measured with a thermistor in the glass bottle. In a typical A-BF process, the polymer solution was first prepared by dissolving PS and PS-*b*-PDMS in CS₂ with desired concentration. Then, onto a glass substrate placed on the stand in the bottle, 10 μL of the polymer solution was cast. The substrate was taken out after complete evaporation of solvent. All the operation was carried out at 28 °C unless otherwise stated.

Characterization. The morphology of honeycomb films were observed by scanning electron microscopy (SEM) (TM3000, Hitachi, Japan) under an electron beam with an accelerating voltage of 15 kV and a working distance of 2 mm. The cross-section was obtained by fracturing the films at liquid nitrogen temperature. All the samples for SEM observation were coated with a thin layer of gold for better conductivity. The surface tension measurements were carried out on a tensiometer (K100, Krüss GmbH) by Wilhelmy Plate Method. X-ray photoelectron spectroscopy (XPS) spectra were acquired with a PHI Quantum 2000 spectrometer using monochromatic X-rays from an Al K α source with a takeoff angle of 45° from the surface plane. The

atomic fractions of silicon were calculated using the attenuation factors provided by the supplier and the sum of these atomic fractions was normalized to unity.

RESULTS AND DISCUSSION

Preparation of PS Honeycomb Films in Methanol Vapor. The formation of ordered BF arrays in methanol vapor is difficult and seldom reported. Up to now, only block copolymer PS-*b*-PDMS is reported to be able to form BF arrays in methanol vapor.¹⁷ For PS, without exception, shallow and disordered holes with diameter much larger than 50 μm were observed when drying its solution of CS₂ in methanol vapor, as shown in Figure 1a. However, we found that when a small

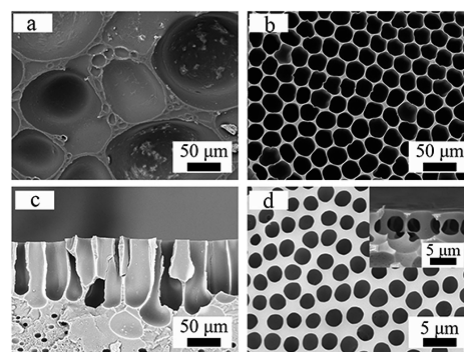


Figure 1. SEM images of PS films prepared in methanol vapor (a–c) and water vapor (d). (a, b, d) Top view, (c, inset in d), cross-sectional view. Casting solution: (a) PS, 120 mg/mL; (b, c) PS, 120 mg/mL, PS₂₀₅-*b*-PDMS₆₃, 0.3 mg/mL; (d) PS, 40 mg/mL, PS₂₀₅-*b*-PDMS₆₃, 0.3 mg/mL.

amount of PS₂₀₅-*b*-PDMS₆₃ (0.3 mg/mL) was added into PS solution, honeycomb film was successfully prepared. The top and cross-sectional views are shown in Figure 1b (SI Figure S2, an image of a large area) and Figure 1c, respectively. For the convenience of comparison, the images of BF array prepared with the same system in water vapor are shown in Figure 1d. Evidently, the BF array morphology formed in methanol is different from that prepared in water vapor. First, the pores on the film prepared in methanol vapor (24 μm) are much larger than those in water vapor (2.5 μm), although the concentration of the casting solutions are identical. Second, the pore openings on the film prepared in methanol vapor are polygonal, while those in water vapor are circular. Occasionally, pores with irregular opening shape are found. Finally, the pores in the film prepared in methanol are cylindrical with large depth-diameter aspect ratio, while those in water vapor are spherical (the inset in Figure 1d). These differences agree with our previous report and again confirm that changing atmosphere of BF process can efficiently alter the morphology of produced honeycomb film.

The influence of several experimental conditions on the morphology of BF arrays was systematically investigated. Figure 2 depicts the dependence of pore diameter on PS and PS-*b*-PDMS concentration. Taking the system of 120 mg/mL PS solution as an example, the pore diameter decreases from 45 to 15 μm as the concentration of PS₂₀₅-*b*-PDMS₆₃ is increased from 0.24 mg/mL to 0.6 mg/mL, as shown in Figure 2a–c. Further increasing the concentration of PS₂₀₅-*b*-PDMS₆₃ does not give smaller pores. The total polymer concentration in the experimental scale has no obvious effect on the pore diameter, as the plots in Figure 2d. While in water vapor, it usually has significant influence on the pore size.^{22–24} Note that the bars

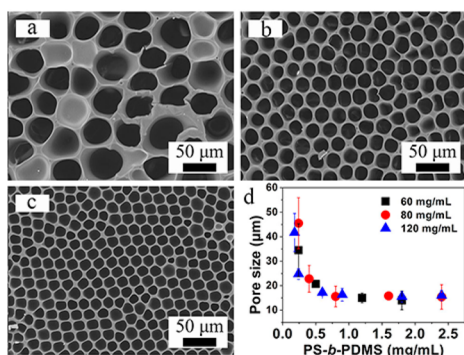


Figure 2. (a–c) SEM images of honeycomb films prepared from the PS/PS₂₀₅-*b*-PDMS₆₃/CS₂ system in methanol vapor (PS: 120 mg/mL). The concentration of PS₂₀₅-*b*-PDMS₆₃ was 0.18 mg/mL (a), 0.24 mg/mL (b), 0.6 mg/mL (c), respectively. (d) Plots of pore diameter versus concentration of PS₂₀₅-*b*-PDMS₆₃.

do not represent the experimental errors but primarily the distribution of pore diameter, indicating that the pores become uniform with the increase of copolymer concentration.

The correlation between the depth of the pores and the concentration of PS and copolymer was investigated by observing the cryo-fractured cross-section. The representative images are demonstrated in Figure 3 and more detailed

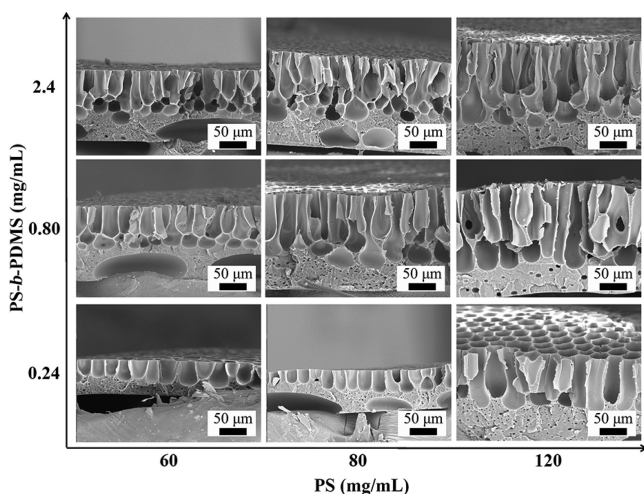


Figure 3. Cross-section view of honeycomb film prepared at various concentration of PS and PS₂₀₅-*b*-PDMS₆₃.

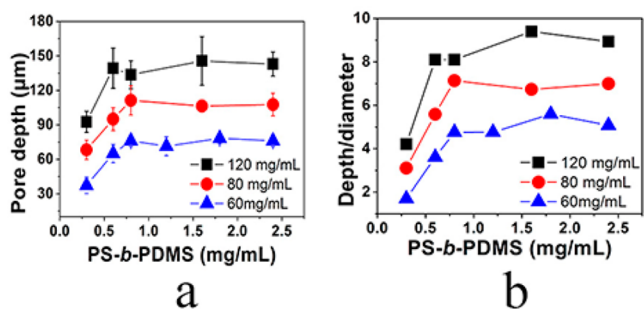


Figure 4. Plots of pore depth (a) and depth-diameter aspect ratio (b) versus concentration of PS and PS₂₀₅-*b*-PDMS₆₃.

information is summarized and plotted in Figure 4a. It is evident that the concentration increase of either PS or PS-*b*-PDMS facilitates the formation of deep holes. The depth of pore increased from 37 to 143 μm when the concentrations of the PS and PS₂₀₅-*b*-PDMS₆₃ were changed from 60 mg/mL to 120 mg/mL and from 0.3 mg/mL to 2.4 mg/mL, respectively. As mentioned above, increasing the concentration of PS₂₀₅-*b*-PDMS₆₃ will reduce the pore diameter to a minimum of 15 μm and the PS concentration has little influence on the pore diameter. Accordingly, depth-diameter aspect ratio ($r_{D/D}$) increases with the concentration of PS and PS₂₀₅-*b*-PDMS₆₃. The $r_{D/D}$ values at different concentration of PS and PS₂₀₅-*b*-PDMS₆₃ are calculated and plotted in Figure 4b. A maximum $r_{D/D}$ of 9.4 is achieved when the concentration of PS is 120 mg/mL and the concentration of PS₂₀₅-*b*-PDMS₆₃ is higher than 0.6 mg/mL. Such a large $r_{D/D}$ value indicates that the pores in PS films actually become channels. To the best of our knowledge, this is the first report that channel structures are prepared with BF method. With the unique structures, the ordered porous films can potentially be a new kind of molding template to produce surface features with ordered cylindrical embossment for electronic and optic devices.²⁵ Also, they may be used as the filtration membranes.²⁶

PS₇₀-*b*-PDMS₆₃ and PS₂₆-*b*-PDMS₆₃ were also used to assist the formation of honeycomb films, and pores with large $r_{D/D}$ were all successfully obtained (SI Figure S3). However, pore size distribution became wider with decreasing the chain length of PS block, and the porous structure became disordered. When homo-PDMS was used, only disordered pores with very large size were found (SI Figure S4), which was very similar to those obtained from pure PS. These results demonstrated the importance of PS block in the copolymer. Therefore, a suitable ratio of PS in PS-*b*-PDMS, such as PS₂₀₅-*b*-PDMS₆₃, is necessary for the formation of ordered honeycomb structure.

The dependence of the morphology on the casting conditions reveals the importance of surface active block copolymer and significant distinction between BF processes in methanol and water vapors, and also demonstrates the advantage of A-BF method when designing and fabricating novel microstructures.

Formation Mechanism of BF Arrays in Methanol Vapor. To gain a better understanding of the role of PS-*b*-PDMS, we first investigate its effect on the formation of methanol droplet array on the surface of polymer solution. It is well-accepted that in the beginning of the BF process, vapor condenses onto the cold surface of the polymer solution due to the solvent evaporation cooling. In order to produce pores, the liquid condensed on the polymer solution must form droplets, but not spread into a thin film or dissolve into the polymer solution. The spread behavior of a droplet on a solution surface can be predicated through its spreading coefficient (S), which is defined as following:²⁷

$$S = \gamma_s - (\gamma_l + \gamma_{ls}) \quad (1)$$

where γ_s and γ_l are surface tension of the solution and condensed liquid, respectively, and γ_{ls} is the interfacial tension between the liquid and the solution. For nonspread behavior, $S < 0$, and for spread, $S \geq 0$. Hence, spread of droplet can be prevented by decreasing γ_s and increasing γ_l .

Methanol has quite low surface tension of 22.0 mN/m (25 °C),²⁸ so that it can spread on most of organic solvents. In our case, the casting solvent is CS₂, with a surface tension of 31.6 mN/m. The dissolving PS hardly changes the surface tension of

the polymer solution (Figure 5a). Therefore, we indeed observed that methanol droplets spread into a thin film on

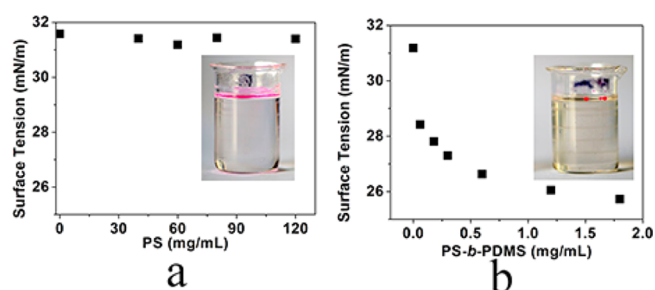


Figure 5. Surface tension of polymer solution against concentration of PS (a) and PS₂₀₅-*b*-PDMS₆₃ (PS: 80 mg/mL) (b). Inserts are digital photographs of methanol droplets (dyed with Rhodamine B for easy observation) on PS solution (a) and PS/PS₂₀₅-*b*-PDMS₆₃ solution (b) (PS: 80 mg/mL, PS₂₀₅-*b*-PDMS₆₃: 0.8 mg/mL).

PS/CS₂ solution surface (Figure 5a and movie 1 in SI). Undoubtedly, honeycomb structures cannot be prepared in methanol vapor with neat PS/CS₂ system.

As shown in Figure 5b, the surface tension of polymer solution (γ_s) decreases sharply by adding a small amount of PS₂₀₅-*b*-PDMS₆₃. The value is decreased from 31.7 to 26.6 mN/m when the concentration of PS-*b*-PDMS is increased from 0 to 0.6 mg/mL. Further increase of PS-*b*-PDMS induces only slightly decrease of the surface tension of solution. The decrease in γ_s is attributed to the preferential aggregation of low-surface-energy siloxane composition at the air/solution interface. After the interface is saturated by molecules of PS-*b*-PDMS, the surface tension of solution is decreased slightly with the further increase of PS-*b*-PDMS concentration. In the dry film, XPS results suggest that the content of silicon atom (3.5%) on the top surface is more than 110 times the average value (0.03%) in bulk (SI Figure S5), indicating that the preferential aggregation of siloxane composition persists the whole BF process. Owing to fact of honeycomb film is covered by hydrophobic PDMS segments, the water contact angle of the film is increased to 136°, while that of the pure PS film is 123° (SI Figure S6).²⁹ The porous films prepared by the BF technique in methanol vapor may have potential applications as superhydrophobic/self-cleaning materials.³⁰ In addition, the methanol droplets floating on the solution surface can be saturated by CS₂ because of its solubility into methanol.³¹ The surface tension of methanol saturated by CS₂ is increased to 24.1 mN/m determined by the tensiometer, indicating the increase of γ_1 in BF process. Therefore, owing to the synergetic effect of the surface activity of PS-*b*-PDMS and the dissolving of CS₂ in methanol, S decreases from 8.0 mN/m to 0.4–1.3 mN/m (γ_1 : 1.2 mN/m). These values are quite small, although still positive. Noticing that the measured value of γ_s may contain considerable error due to fast evaporation of CS₂ during the measurement process,³² we believe that such small S values can reasonably explain the formation of BF arrays in methanol vapor with the assistance of PS-*b*-PDMS.

Nonspread behavior of methanol on PS-*b*-PDMS/PS solution was further confirmed by direct observation. When 3 μ L of methanol was dropped onto PS solution containing 0.8 mg/mL of PS₂₀₅-*b*-PDMS₆₃, methanol spread on the surface at first but quickly shrank into a stable droplet (Figure 5b and movie 2 in SI). The transient spread process at the initial stage reveals that even with the help of PS-*b*-PDMS, the pure

methanol still cannot form droplets on CS₂ surface. However, after CS₂ dissolved into methanol gradually, the surface tension of methanol droplet increased, leading to dewetting process. To further prove the effect of dissolved CS₂, a methanol droplet saturated with CS₂ was added on the surface of polymer solution. A stable droplet was obtained directly, without the spreading process (movie 3 in SI). Therefore, although methanol spreads on PS solution of CS₂, it can form stable droplets on the CS₂ solution with the assistance of PS-*b*-PDMS.

Although PS-*b*-PDMS with short PS block can effectively decrease the surface tension of PS solution (SI Figure S7), they are inefficient for the formation of the honeycomb structure. This can be contributed to the very large Flory–Huggins interaction parameter (χ) between PS and PDMS.³³ In the BF process, stabilization of the formed methanol droplets is also crucial for the formation of ordered honeycomb structure. Once the methanol droplets are formed, the adsorption layer of PS-*b*-PDMS/PS molecule around these droplets can prevent their coalescence, and stabilize them during the entire BF process.³⁴ Poor compatibility between PS and PS-*b*-PDMS with short PS block will lower their ability to stabilize the methanol droplets,³⁵ resulting in the coalescence of the droplets and consequently the disordered pore structure with broad size distribution. As PDMS is totally incompatible with PS, no BF arrays are formed when homo-PDMS is used.

The dependence of pore size on the concentration of PS-*b*-PDMS can be further explained by the surface tension variation. The pore diameter in the resultant honeycomb film is decided by the size of methanol droplets. For a tiny methanol droplet floating on PS-*b*-PDMS/PS solution, its shape is related to the surface and interfacial tensions.³⁶ With the decrease of γ_s , the droplet will evolve from lenticular shape to sphere, leading to decrease in the projected diameter of the droplet in vertical direction (r_d). Noticing the relationship between the concentration of PS-*b*-PDMS and γ_s (Figure 5b), the downward tendency of pore diameter with the increasing concentration of PS-*b*-PDMS can be well explained (Figure 2d). With a small concentration of PS-*b*-PDMS, the γ_s is relatively high, thus methanol droplets will have large r_d and consequently leave large pores after they evaporated. When the concentration of PS-*b*-PDMS is more than 0.6 mg/mL, the preferential adsorption is saturated and γ_s reaches the plateau. As a result, the pore size remained the same with increasing concentration of PS-*b*-PDMS. The concentration of PS has no effect on γ_s , hence it does not alter the pore diameter in the resultant honeycomb structures.

The most striking feature of the porous films produced in methanol vapor is their channel structures. We believe that this is related to the low surface tension and high partial pressure of methanol, and absolutely low interfacial tension between methanol droplet and polymer solution. By reducing the interfacial tension, the obtained pores by BF technique in water vapor have evolved from spherical to ellipsoidal.^{37,38} The methanol droplets should be ellipsoidal at the initial BF process. Depending on the high vapor pressure of methanol, methanol droplets can grow fast. However, during BF process, when the droplets fully cover the entire surface of solution, their growth is restricted by each other and the evolution of r_d comes to a halt unless coalescence occurs. Thus, further supplement of methanol will lead to growth in the z axis direction, producing elongated methanol droplets. This process is energetic unfavorable to water droplets, because the surface tension of water is so large that water droplets tend to maintain

the spherical shape to reduce their surface area. The deformation is feasible for methanol droplets with smaller surface tension, which also can explain the irregular shape of the pore openings. The depth of the pores is proportional to the total amount of condensed methanol during the BF process, which mainly depends on the evaporation time of polymer solution and the partial pressure of methanol vapor (P_m).^{39,40} High polymer concentration can prolong the evaporation time,⁴¹ thus more methanol condenses, yielding deeper pores. High P_m will result in fast condensation rate; thus, it can also increase the total amount of condensed methanol, as well as depth of the pores. To confirm this hypothesis, we carried out two experiments at low P_m , which was achieved by lowering the temperature to 4 °C and dissolving CaCl₂ into methanol,⁴² respectively. As expected, at low P_m the pore depth was decreased obviously, as shown in Figure 6.

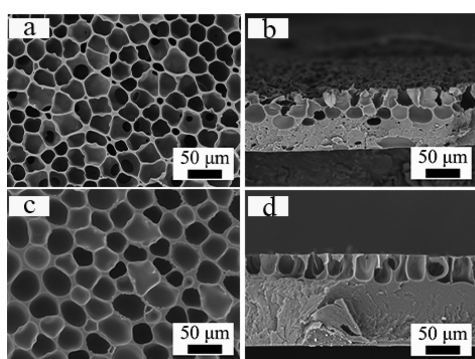


Figure 6. SEM images of honeycomb films prepared at 4 °C (a, b) and in the methanol vapor with a pressure of 3.2 kPa at 28 °C (c, d). (a, c) top view and (b, d) cross-section view. Casting solution: PS, 120 mg/mL; PS₂₀₅-*b*-PDMS₆₃, 2.4 mg/mL.

In summary, the formation process of BF arrays in methanol vapor arrays is illustrated in Figure 7. Upon casting, low-surface-energy siloxane composition preferentially aggregates to the air/solution interface (a and a'). With the evaporation of CS₂, the solution surface cools down and methanol vapor condenses on it (b). Owing to the synergetic effect of the surface activity of PS-*b*-PDMS and the dissolving of CS₂ in methanol, the condensed methanol forms droplets without spreading. These droplets are stabilized by the entrapment of PS and PS-*b*-PDMS (b'). With further evaporation of solvent, the methanol droplets grow, deform along the vertical direction depending on the low surface tension and high vapor pressure of methanol, and self-assemble into dense pores by Marangoni effect simultaneously (c and c'). After completed evaporation of

organic solvent and methanol, ordered pores with cylindrical shape are left in the film (d).

Preparation of Honeycomb Films in Methanol Vapor with Other Polymer and Surface Active Agent. To verify the applicability of the A-BF method, we used it to prepare SBS honeycomb films. As shown in Figure 8a,b, honeycomb

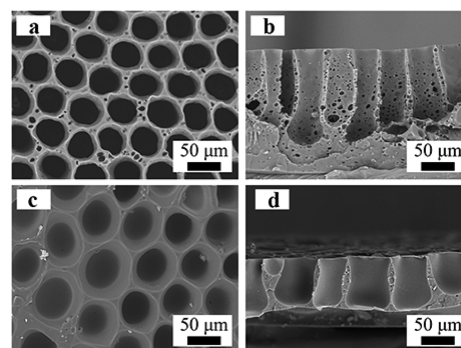


Figure 8. SEM images of SBS (a, b) and PS (c, d) honeycomb film prepared with the assistance of PS-*b*-PDMS and PS-*b*-PFMA, respectively. (a, c) top view and (b, d) cross-section view. Casting solution: (a, b) SBS, 80 mg/mL; PS-*b*-PDMS, 0.4 mg/mL; (c, d) PS, 120 mg/mL; PS-*b*-PFMA, 1.2 mg/mL.

structure with cylindrical pores is obtained, with pore diameter and depth of 47 and 147 μm, respectively. This proves that A-BF method is applicable to different polymers. Besides, according to the proposed formation mechanism of BF arrays in methanol, the PS-*b*-PDMS actually plays a role of surface active agent, to absorb on the surface of polymer solution and decrease the surface tension. Thus, other molecules with similar function can also assist the formation of honeycomb films in methanol vapor. To confirm this hypothesis, another kind of block copolymer with low surface free energy, PS-*b*-PFMA, was employed as the surface active agent and introduced into the solution of PS. As shown in Figure 8c,d, the honeycomb structure was obtained with this solution in methanol vapor. The shape of the pore is also cylindrical in this film. However, compared with BF arrays prepared aided by PS-*b*-PDMS, these BF arrays have much larger pores with diameter of 45 μm. This can be explained by the slow nucleation rate induced by PS-*b*-PFMA because of its oleophobicity. Saunders et al. have proved from both experiment and theory that increased polymer hydrophobicity reduces the water wettability of the air/solution interface, which in turn decreases water droplet nucleation and the final pore size.⁴³ Due to the large diameter and slow condensation rate, the pore depth is small, just 70 μm. Despite all these differences, the above two experiments clearly demonstrate that introducing a small amount of surface active

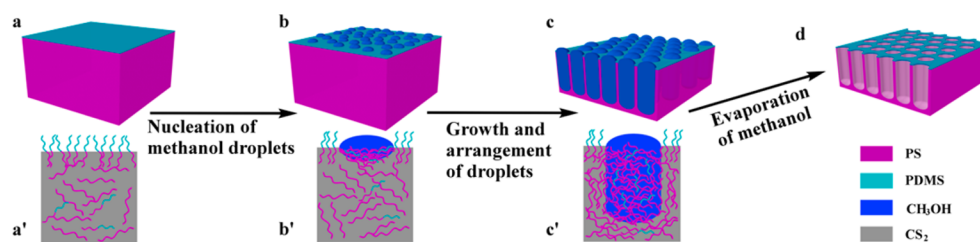


Figure 7. Illustrations of the formation of honeycomb structure in methanol vapor. (a–d) Formation, arrangement, and evaporation of methanol droplets. (a'–c'), distribution of polymer molecular chains in the corresponding process of a–c.

agent is a universal method to prepare honeycomb polymer film in methanol vapor.

CONCLUSION

In conclusion, a general BF method in methanol vapor has been established for the preparation of honeycomb polymer films. With the assistance of a small amount of surface active agent PS-*b*-PDMS, PS honeycomb films were successfully prepared in methanol vapor. The shape of obtained pores is cylindrical with large depth-diameter aspect ratio, indicating a new strategy of changing vapor to control the morphology of honeycomb films. The diameter of the pores is dependent mainly on the concentration of PS-*b*-PDMS, while the pore depth is decided by the concentration of both PS-*b*-PDMS and PS. The formation mechanism of the honeycomb film was discussed. PS-*b*-PDMS was found to be able to significantly lower the surface tension of PS solution of CS₂, thus prevented the spread of methanol droplets saturated with CS₂, which acted as the soft templates during BF process for the formation of pores. The surface tension of the PS-*b*-PDMS/PS solution also decides the shape of the methanol droplets and, consequently, the diameter of the pores. The total amount of the condensed methanol, which is related to the concentration of PS and the partial pressure of methanol, was found to decide the depth of the pores. Totally, the pore shape of large depth-diameter aspect ratio can attribute to the low surface tension and high vapor pressure of methanol. We also confirmed the universality of this method, by using it to prepare SBS honeycomb films, and replacing PS-*b*-PDMS with another surface active agent, PS-*b*-PFMA. With the channel feature and high surface composition of PDMS, the ordered porous films can be potentially used as molding templates for electronic and optic devices, superhydrophobic/self-cleaning materials, and separation membranes.

ASSOCIATED CONTENT

Supporting Information

Experimental equipment image, additional SEM images of honeycomb films assisted by PS₇₀-*b*-PDMS₆₃, PS₂₆-*b*-PDMS₆₃, and homo-PDMS, surface tension of polymer solution against concentration of PS₇₀-*b*-PDMS₆₃, PS₂₆-*b*-PDMS₆₃, and homo-PDMS, water contact angle of honeycomb films, XPS spectrum of films prepared from PS and PS/PS-*b*-PDMS, wetting behavior of methanol droplets on the surface of PS and PS/PS-*b*-PDMS solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

All authors contributed to the experimental design and data analyses. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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