

Preparation of Multi-Level Honeycomb-Structured Porous Films by Control of Spraying Atomized Water Droplets

Pengfei Zhang, Huawei Chen, Deyuan Zhang

School of Mechanical Engineering and Automation, Beihang University, Haidian District, Beijing 100191, People's Republic of China

Correspondence to: H. Chen (E-mail: chenhw75@buaa.edu.cn)

ABSTRACT: Honeycomb-structured porous films have been widely applied in various industrial areas such as chemical sensors, tissue engineering, and micro reactors. In this article, one novel self-assembly approach is proposed to fabricate well-ordered polyphenylene oxide honeycomb films by a facile control of spraying ultrasonic humidifier atomized water droplets. Proper spraying retention time is necessary for porous films formation with highly uniform pore size. The effect of atomized water droplets flux on the pore size and the regularity of the hexagonal arrays were experimentally investigated. The pore size became larger with increasing the solution concentration. Especially, honeycomb films with two-level pores were fabricated by spraying atomized water droplets two times and the influence of interval time on the two-level honeycomb films formation was investigated. Apart from analysis of structural characteristics, self-assembly mechanism was also discussed. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41163.

KEYWORDS: films; porous materials; self-assembly

Received 28 March 2014; accepted 14 June 2014

DOI: 10.1002/app.41163

INTRODUCTION

Honeycomb-structured porous films have received a considerable interest in recent years because of their potential applications in optoelectronic devices,^{1,2} tissue engineering,³ filtration membranes,^{4–6} super-hydrophobic surface,^{7,8} catalysis,⁹ and so forth. In order to fabricate well-defined porous films, a variety of methods, such as lithography^{10,11} and templating,¹² have been developed. However, these methods are still plagued with many disadvantages of cumbersome processes, time-consuming, and high-cost. In contrast, the breath figure method (BFM), a self-assembly technique proposed by Francois and coworkers,¹³ arouse much attention for its high efficiency and low expense to form honeycomb films. In this technique, moist gas flow is blown over a polymer solution, and subsequently micrometer-sized water droplets are condensed onto the solution surface because of the cooling at the air/liquid interface caused by the rapid evaporation of solvent. These condensed water droplets isolatedly float on the solution surface, gradually aggregate and grow together with increasing density under principles of Marangoni convection,¹⁴ resulting in hexagonal arrays driven by repulsive and attractive forces.¹⁵ After complete evaporation of the solvent and water, the porous thin films with regular honeycomb patterns are formed.

Simplicity and versatility enable this honeycomb-structured porous films formation method to become more attractive, and

mono- or multi-layered polymeric thin films with various pore sizes were formed by tuning process variables including humidity, concentration, polymer type, molecular weight, and substrate type.^{16–23} Generally, a moist gas flow or a closed humid environment is necessary, and ambient humidity control is an important factor for formation of porous films with regular pores. The moist airflow was produced by bubbling carrier gas flow through distilled water,^{24,25} and the humid environment in a closed chamber was controlled by saturated aqueous solution.^{8,26} However, the moist airflow must be blown over the solution surface until stable films are formed, and the humid environment in a closed chamber is not prone to dynamically change due to high speed of porous thin film formation. There is little information available in literature about the influence of dynamical change of humidity on the honeycomb films formation. Moreover, the investigations on formation of the porous thin films with regular micro-patterns in literatures are just focused on one-level. The honeycomb films with regular multi-level pores have not been fabricated to our knowledge.

In this article, a novel method to prepare honeycomb-structured films is proposed by spraying atomized water droplets over the polymer solution surface, in which polyphenylene oxide (PPO) and carbon disulfide (CS₂) are used as polymer materials and solvent, respectively. Apart from effect of spraying retention time on formation of well-ordered porous films, the

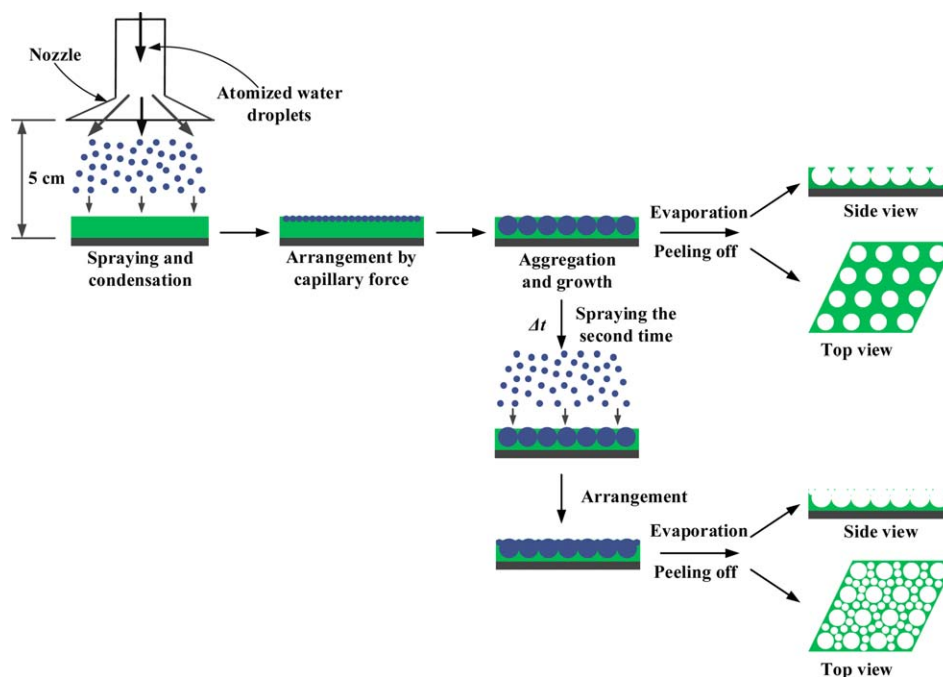


Figure 1. Schematic of honeycomb films formation by control of spraying atomized water droplets. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

effects of other important affecting factors, such as the atomized water droplets flux, ambient humidity, and solution concentration, are also investigated. Especially, the porous thin film with two-level pores is firstly formed by control of spraying water droplets. And its formation mechanism is investigated.

EXPERIMENTAL

Materials

PPO ($M_w = 40,000$) and CS_2 were purchased from Aldrich (America) and Tianjin Chemical Corporation (China), respectively, and were used as received. Water used to produce the atomized water droplets was purified by a Millipore system (Milli-Q, Millipore, America). Atomized water droplets, the size of which is determined by the oscillation frequency,²⁷ with diameter mainly between 1 and 2 μm , were generated by an ultrasonic humidifier (Deerma Humidifier, China) with an oscillation frequency about 1.7 MHz.

Porous Thin Film Formation

PPO solutions were prepared by dissolving PPO in CS_2 . The PPO solutions in CS_2 (about 0.5 mL) were directly casted onto the glass substrate ($20 \times 20 \text{ mm}^2$) at a dry environment (relative humidity < 20%). The atomized water droplets, carried by air, were collected and blown out through a nozzle (20 mm in inner diameter) at a certain flux. The spraying atomized water droplets flux was controlled by the power control button on the humidifier. The height between the nozzle and the substrate was set 5 cm, as shown in Figure 1. The nozzle was moved over the substrate center immediately after casting solutions, kept blowing for a certain time, and finally moved away. In order to form honeycomb films with two-level pores, the nozzle was moved back and kept over the substrate center for a certain time again after it was moved away for an interval time Δt . After complete evaporation

of water and solvent (the total time was about 3 min), a flat porous film was obtained.

Morphology Characterization

Surface morphologies of honeycomb films were characterized using a scanning electron microscope (SEM, Camscan CS-3400, England), operating at a 20 kV accelerating voltage. The samples were sputtered with gold, the thickness of which was about 20 nm. On basis of SEM images, the pore size and distribution were analyzed by Image-pro Plus software (Media Cybernetics, America).

RESULTS AND DISCUSSION

Influence of Spraying Time

Experiments were firstly conducted to investigate the optimum spraying retention time for well-ordered honeycomb films at a spraying flux of 20 mL/s. Figure 2 shows SEM images of films formed from PPO/ CS_2 solutions with a concentration 2 g/L at spraying retention time 5 s, 10 s, 15 s, 20 s, 25 s, and 30 s, respectively. It can be seen that the average pore size increases with the increase of spraying retention time, while porous films with uniform pores in a hexagonal array are only formed in a proper retention time. At the retention time below 15 s, the pores of formed films were randomly distributed and their sizes had no significant regularity [Figure 2(A,B)]. Well-ordered honeycomb films with average pore diameter 3.41 μm and 3.87 μm were fabricated at the spraying time 15 s and 20 s, respectively [Figure 2(C,D)]. However, when the spraying time was increased above 20 s, the regularity of the pore arrangement gradually decreased, and well-ordered porous films with regular patterns became impossible [Figure 2(E,F)].

Using water as a template, honeycomb films were fabricated by directly spraying micro-sized water droplets, different from the

water droplets.

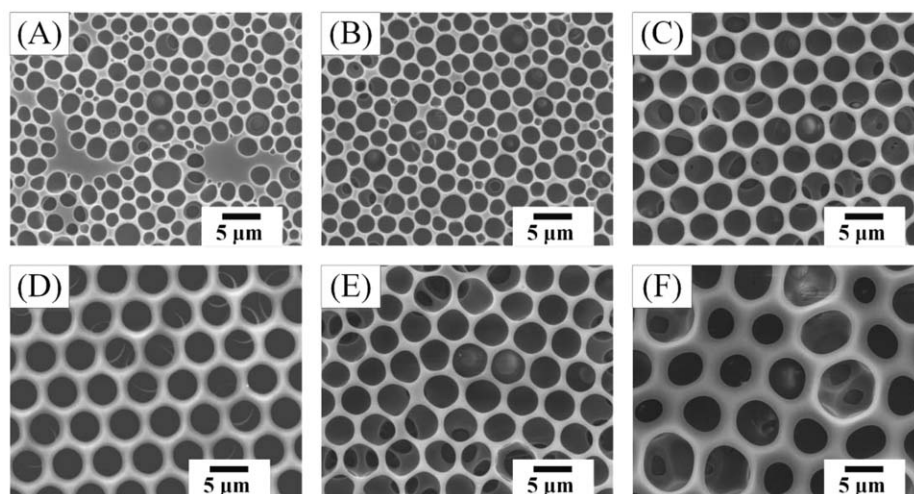


Figure 2. SEM images of PPO honeycomb films formed at different spraying time. (A) 5 s, (B) 10 s, (C) 15 s, (D) 20 s, (E) 25 s, and (F) 30 s. Other conditions: spraying flux 20 mL/s, concentration 2 g/L.

traditional BFM in which all water droplets are nucleated and condensed from water vapor. Water droplets on the solution surface may be formed from the directly spraying or condensed from the atomized water droplets flow. A low supply results in insufficient water to condensation and growth, and excessive water gives rise to too much coalescence.²⁸ Here, fewer water droplets formed on the solution surface at the short spraying time and only sparsely aggregated and grew, resulting in the subsequently formed porous films with randomly distributed pores. Too long spraying time yielded too many water droplets, and resulted in disorder coalescence of water droplets, which caused a decrease in regularity of the pores. Thus, proper spraying retention time is very important for well-ordered honeycomb films formation.

Influence of Spraying Flux

Spraying flux is another important factor in this method. In order to investigate the influence of spraying flux, honeycomb

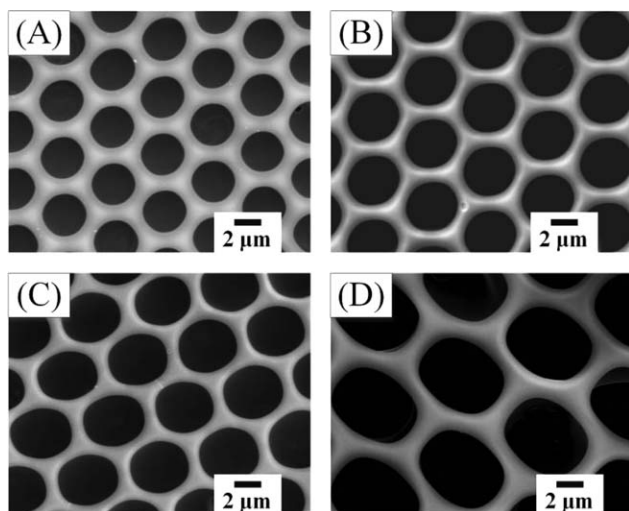


Figure 3. SEM images of PPO honeycomb films formed at different spraying flux: (A) 15 mL/s, (B) 20 mL/s, (C) 25 mL/s, and (D) 30 mL/s. Other conditions: spraying retention time 20 s, concentration 2 g/L.

films were fabricated by change of spraying flux from 10 mL/s to 50 mL/s, with a solution concentration 2 g/L at a spraying retention time 20 s. It was found that the solution could not form regular patterns both at the low spraying flux (<15 mL/s) and the high spraying flux (>30 mL/s). While well-ordered honeycomb films were fabricated at the mediate flux (15 mL/s, 20 mL/s, 25 mL/s, and 30 mL/s), as shown in Figure 3. We can see that the average pore diameter increases approximately from 3.15 to 5.85 μm with increasing the spraying flux from 15 to 30 mL/s (Figure 4). The pore pitch increases as well, while the regularity of the pore slightly decreases.

As a water-assisted method, the array of water droplets was a template for the porous structure of the honeycomb films.^{29,30} The size of the water microsphere and the regularity of the water droplets array directly determine the final porous films. The spraying flux affected water droplets formation on the solution surface, and thus influenced the pores formation of porous films. The quantity of formed water droplets on the solution surface at a low spraying flux was not enough for forming a regular pattern. With the increase of spraying flux, more water droplets

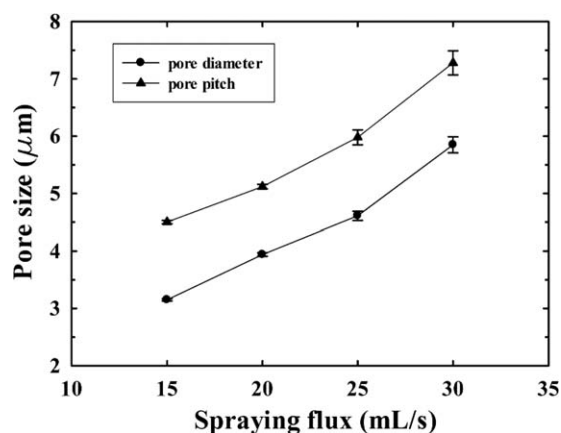


Figure 4. Plots of pore size versus spraying flux.

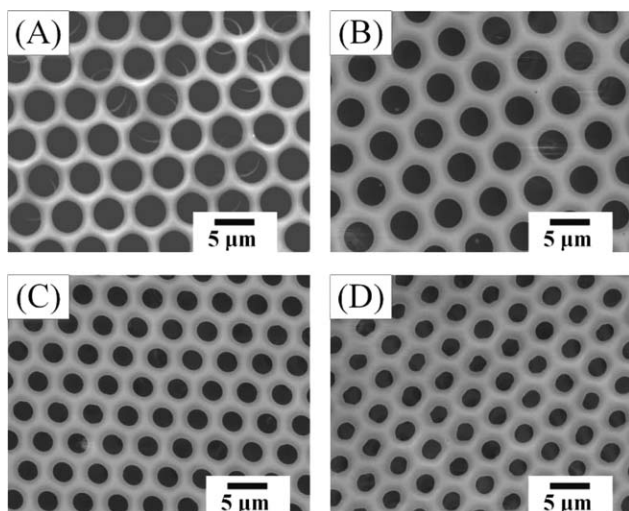


Figure 5. SEM images of PPO honeycomb films formed from various solution concentrations. (A) 2 g/L, (B) 4 g/L, (C) 6 g/L, and (D) 8 g/L. Other conditions: spraying retention time 20 s, spraying flux 20 mL/s.

formed and ensured arrays formation and pores growth. On the other hand, more water droplets increased the probability of coalescence and decreased the regularity of the pore arrangement.

Influence of Concentration

The concentration influence on the porous films formation was investigated by changing the PPO solution concentration at a spraying flux of 20 mL/s, at a spraying retention time 20 s. As shown in Figure 5, well-ordered honeycomb films were fabricated at different concentrations from 2 to 8 g/L. We can see the pore size of the formed films decreases from 3.87 to 2.11 μm with increasing the concentration, indicating the solution concentration greatly impacts the film formation. The concentration influence on the ordered patterns could be explained as follows. The floated water droplets on the solution surface were stabilized by a thin film formed by the congregated poly-

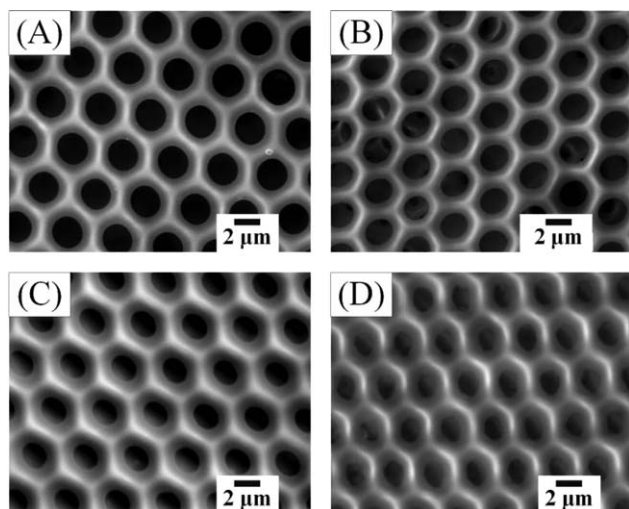


Figure 6. SEM images of PPO honeycomb films formed in a humid environment (relative humidity about 60%) from various concentrations without spraying. (A) 2 g/L, (B) 4 g/L, (C) 6 g/L, and (D) 8 g/L.

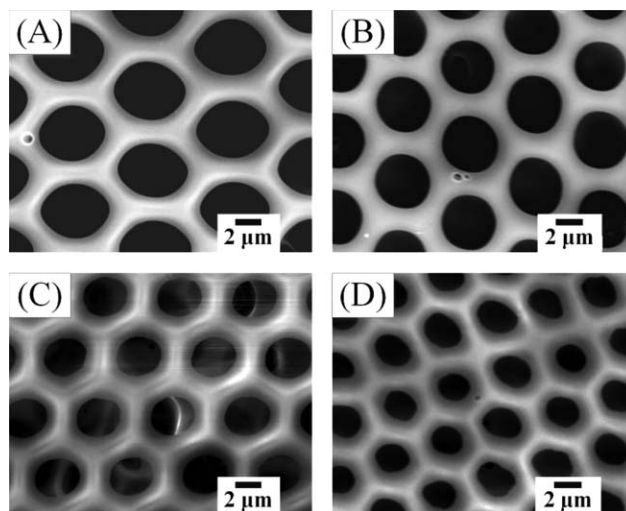


Figure 7. SEM images of PPO honeycomb films formed in a humid environment (relative humidity about 60%) from various concentrations with spraying. (A) 2 g/L, (B) 4 g/L, (C) 6 g/L, and (D) 8 g/L. Other conditions: spraying retention time 20 s, spraying flux 20 mL/s.

mer molecules.^{23,31} When the concentration was low, the strength of the macromolecule thin film was so weak that water droplets could easily aggregate and coalesce, resulting in bigger pores. With increasing solution concentration, more polymer molecules congregated and formed a stronger thin film. So water droplets could be stabilized effectively and their growth capability were decreased, leading to smaller pores.

Honeycomb films formation from a series of concentrations in a humid environment (relative humidity about 60%), in which the humidity was controlled by the method available in the literature,¹⁷ was also investigated. Figure 6 shows the porous films formed without spraying atomized water droplets, just like the traditional BFM, at the concentration 2 g/L, 4 g/L, 6 g/L, and 8 g/L, respectively. Figure 7 shows the corresponding porous films prepared with the spraying atomized water droplets at a spraying flux of 20 mL/s, at a retention time 20 s, in the constant

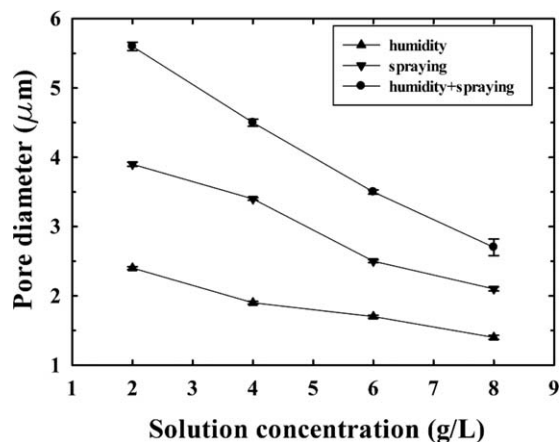


Figure 8. Plots of pore diameter versus concentration under the three conditions: spraying in a dry environment (spraying), no spraying in a humid environment (humidity), and spraying in a humid environment (humidity + spraying).

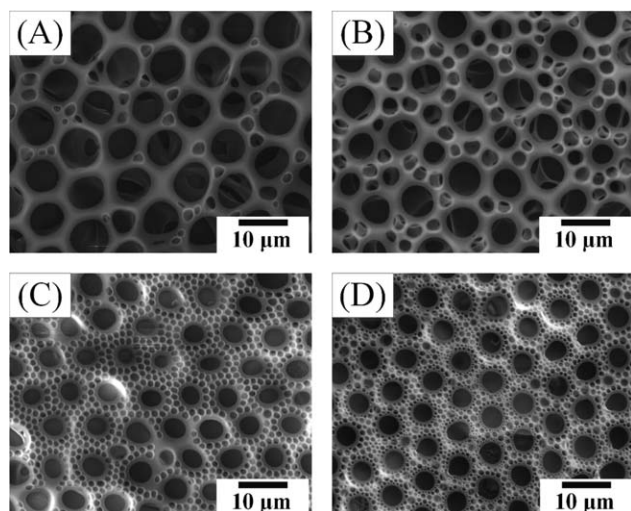


Figure 9. SEM images of PPO honeycomb films formed by spraying atomized water droplets two times at different interval time. (A) 20 s, (B) 40 s, (C) 60 s, and (D) 80 s. Other conditions: spraying retention time 20 s, spraying flux 20 mL/s, concentration 2 g/L.

environment. The results concluded the honeycomb film formation capability of the spraying method in a humid environment. It can be seen that the average pore diameter under the two conditions decreases from 2.36 μm to 1.41 μm and from 5.56 μm to 2.72 μm , respectively, with increasing the concentrations. The pore size with the spraying was significantly enlarged at the corresponding concentration. This should be attributed to the more water droplets formed on the solution surface, owing to the addition of spraying atomized water droplets.

The average pore diameters of the honeycomb films formed under the three conditions, that is, spraying in a dry environ-

ment, no spraying in a humid environment, and spraying in a humid environment, are summarized in Figure 8. It can be noted that the three series of pores have the same changing tendency with changing the concentrations. The pore under the third condition (humidity + spraying) is obviously larger than the other two conditions, while is smaller than the sum of them. Actually, the spraying not only introduced water droplets into the casting system, but also assisted in the evaporation of solvent.^{28,32} A spraying resulted in a fast solvent evaporation, and, therefore, the time for water droplets to grow in the spraying system was shorter than that in the humid environment without spraying. So the effect of spraying in a humid environment on the pore formation was weaker than the sum of spraying in a dry environment and no spraying in a humid environment.

Formation of Honeycomb Films with Two-Level Pores

Considering that solution concentration increases with the solvent evaporation, it is difficult for water droplets to aggregate at the last phase of films formation. We tried to prepare the honeycomb films with two-level pores from solution concentration 2 g/L by spraying atomized water droplets two times at a spraying retention time 20 s, at a spraying flux 20 mL/s. Figure 9 shows SEM images of four kinds of films formed at the interval time 20 s, 40 s, 60 s, and 80 s, respectively. We can see that ill-ordered porous film with nearly no small pores surrounding the big pores was formed at the interval time 20 s. When the interval time was increased to 40 s, the number of the small pores increased but the big pores were still in an irregular array. More small pores began to be formed at the interval time 60 s, and the porous film with well-ordered big pores (pore diameter, 4.09 μm) surrounded by regular small pores (pore diameter, 0.40–0.85 μm) was fabricated when the interval time was 80 s. Porous films formed at a long interval time (>100 s) had no small pores. Moreover, both

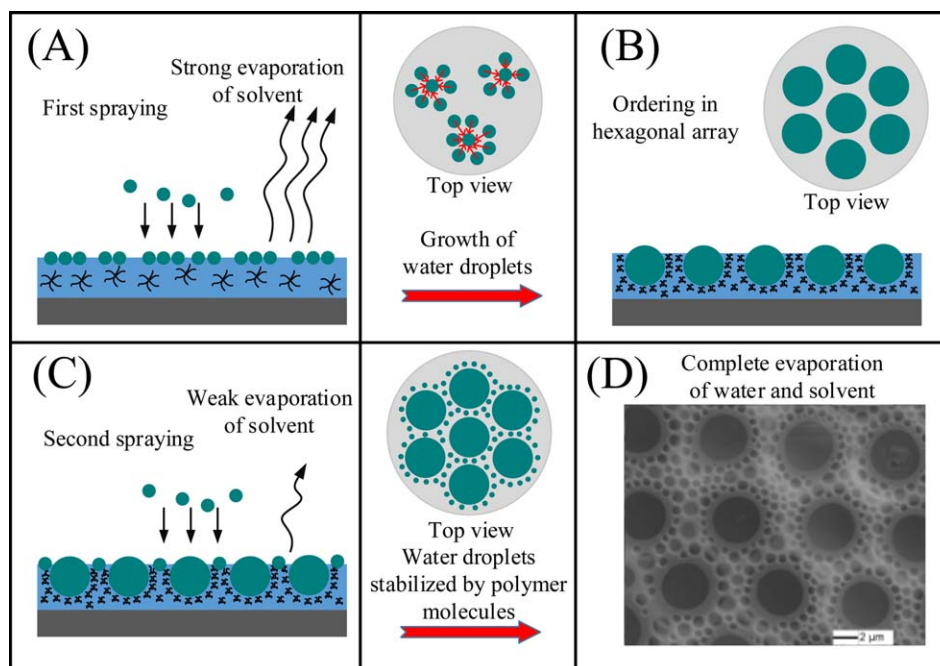


Figure 10. Proposed mechanism of honeycomb-structured porous films with two-level pores. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the size of the big pores and the size of the small pores slightly decrease with the increase of interval time.

The mechanism of the two-level honeycomb films formation may be explained as follows. When spraying atomized water droplets was applied to the casting system, some micro-sized water droplets directly fell onto the solution surface and some condensed onto the solution surface due to the cooling at the air/liquid surface, caused by the strong solvent evaporation [Figure 10(A)]. With the density of water droplets increasing, water droplets aggregated and grew slowly, resulting in a hexagonal array. Meanwhile, the solution concentration increased and polymer molecules congregated around the water droplets [Figure 10(B)]. The resulted polymer molecule thin film was favorable for water droplets stabilization.^{31,33} When the spraying was applied for the second time before the complete solvent evaporation, water droplets from the spraying fell onto the solution surface [Figure 10(C)]. Owing to the stable polymer molecule thin film, it was difficult for water droplets to aggregate and grow. Water droplets formed at the second spraying among the big water droplets were just stabilized at their local position. After complete evaporation of water and solvent, porous films with big pores surrounded by small pores were formed [Figure 10(D)]. Besides, a longer interval time meant less time for water droplets from the second spraying to aggregate and coalesce and stronger polymer molecule thin film from the first spraying to stabilize the water droplets. And thus, smaller pores were formed with a longer interval time due to less time to grow and stronger stabilization.

CONCLUSIONS

A novel approach to prepare well-ordered PPO honeycomb films with various pore sizes has been built by spraying atomized water droplets. The optimum spraying retention time for well-ordered honeycomb films formation was experimentally found ranging from 15 to 20 s. The pore size of formed porous films increased with increase of the spraying flux, while the honeycomb pattern regularity of porous thin film decreased. The solution concentration had a great impact on the microstructure of honeycomb pattern, and honeycomb pattern with smaller pores and thicker walls were formed with improvement of solution concentration. Especially, by spraying atomization two times at an interval time 80 s, we succeeded in fabricating two-level porous films with regular big pores surrounded by small pores.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants 51175020) and NSFC Major Program (Grants 51290292).

REFERENCES

1. Wijnhoven, J. E.; Vos, W. L. *Science* **1998**, *281*, 802.
2. Imada, M.; Noda, S.; Chutinan, A.; Tokuda, T.; Murata, M.; Sasaki, G. *Appl. Phys. Lett.* **1999**, *75*, 316.
3. Shastri, V. P.; Martin, I.; Langer, R. *Proc. Natl. Acad. Sci.* **2000**, *97*, 1970.
4. Santiwong, S. R.; Guan, J.; Waite, T. D.; *J. Colloid Interface Sci.* **2008**, *317*, 214.
5. Wan, L.-S.; Li, J.-W.; Ke, B.-B.; Xu, Z.-K. *J. Am. Chem. Soc.* **2011**, *134*, 95.
6. Cong, H.; Wang, J.; Yu, B.; Tang, J. *Soft Matter* **2012**, *8*, 8835.
7. Yabu, H.; Shimomura, M. *Langmuir* **2006**, *22*, 4992.
8. Brown, P.; Talbot, E.; Wood, T.; Bain, C.; Badyal, J. *Langmuir* **2012**, *28*, 13712.
9. Böker, A.; Lin, Y.; Chiapperini, K.; Horowitz, R.; Thompson, M.; Carreon, V.; Xu, T.; Abetz, C.; Skaff, H.; Dinsmore, A. *Nature Mater.* **2004**, *3*, 302.
10. Campbell, M.; Sharp, D.; Harrison, M.; Denning, R.; Turberfield, A. *Nature* **2000**, *404*, 53.
11. Sun, Z.; Li, Y.; Wang, Y.; Chen, X.; Zhang, J.; Zhang, K.; Wang, Z.; Bao, C.; Zeng, J.; Zhao, B. *Langmuir* **2007**, *23*, 10725.
12. Imhof, A.; Pine, D. *Nature* **1997**, *389*, 948.
13. Widawski, G.; Rawiso, M.; Francois, B. *Nature* **1994**, *369*, 387.
14. Srinivasarao, M.; Collings, D.; Philips, A.; Patel, S. *Science* **2001**, *292*, 79.
15. Stenzel, M. H.; Barner-Kowollik, C.; Davis, T. P. *J. Polym. Sci. A-Polym. Chem.* **2006**, *44*, 2363.
16. Billon, L.; Manguian, M.; Pellerin, V.; Joubert, M.; Eterradosi, O.; Garay, H. *Macromolecules* **2008**, *42*, 345.
17. Chen, H.; Shang, X.; Hagiwara, I.; Zhang, D. *J. Porous Mater.* **2012**, *19*, 511.
18. Bunz, U. H. F. *Adv. Mater.* **2006**, *18*, 973.
19. Escalé, P.; Rubatat, L.; Billon, L.; Save, M. *Eur. Polym. J.* **2012**, *48*, 1001.
20. Hernández-Guerrero, M.; Stenzel, M. H. *Polym. Chem.* **2012**, *3*, 563.
21. Tian, Y.; Ding, H.; Jiao, Q.; Shi, Y. *Macromol. Chem. Phys.* **2006**, *207*, 545.
22. Tian, Y.; Ding, H.; Shi, Y.; Jiao, Q.; Wang, X. *J. Appl. Polym. Sci.* **2006**, *100*, 1013.
23. Zhang, Y.; Tian, Y.; Wang, L. *J. Appl. Polym. Sci.* **2008**, *109*, 1524.
24. Dong, R.; Yan, J.; Ma, H.; Fang, Y.; Hao, J. *Langmuir* **2011**, *27*, 9052.
25. Govor, L.; Bashmakov, I.; Kiebooms, R.; Dyakonov, V.; Parisi, J. *Adv. Mater.* **2001**, *13*, 588.
26. Zhang, R.; Wang, J.; Wang, M.; He, Y. *J. Appl. Polym. Sci.* **2012**, *124*, 495.
27. Barreras, F.; Amaveda, H.; Lozano, A. *Exp. Fluids* **2002**, *33*, 405.
28. Wong, K. H.; Hernández-Guerrero, M.; Granville, A. M.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *J. Porous Mater.* **2006**, *13*, 213.
29. Peng, J.; Han, Y.; Yang, Y.; Li, B. *Polymer* **2004**, *45*, 447.
30. Zhao, B.; Zhang, J.; Wang, X.; Li, C. *J. Mater. Chem.* **2006**, *16*, 509.
31. Dong, W.; Zhou, Y.; Yan, D.; Mai, Y.; He, L.; Jin, C. *Langmuir* **2008**, *25*, 173.
32. Li, J.; Peng, J.; Huang, W.; Wu, Y.; Fu, J.; Cong, Y.; Xue, L.; Han, Y. *Langmuir* **2005**, *21*, 2017.
33. Tian, Y.; Jiao, Q.; Ding, H.; Shi, Y.; Liu, B. *Polymer* **2006**, *47*, 3866.