Macromolecular
Journals

Formation of Honeycomb Structures and Superhydrophobic Surfaces by Casting a Block Copolymer from Selective Solvent Mixtures

Pao-Hsiang Tung, Shiao-Wei Kuo, Kwang-Un Jeong, Stephen Z. D. Cheng, Chih-Feng Huang, Feng-Chih Chang*

Poly(vinyl phenol)-*block*-polystyrene (PVPh-*b*-PS) diblock copolymers are synthesized by sequential anionic polymerization with *sec*-butyl lithium as the initiator. The PVPh-*b*-PS diblock copolymer is cast (on a substrate) from several solvent mixtures that contain tetrahydrofuran/toluene ratios of 1:0.1, 1:1, and 1:2. After solvent evaporation the resulting films are characterized by SEM, TEM, and contact angle measurements. A honeycomb structure is fabricated from the vesicle structure at relatively low toluene contents. On the contrary, at relatively higher toluene contents, a micelle structure with porous microspheres is formed, which possesses higher surface roughness and results in film surface superhydrophobicity. The simple method described here that uses common/selective mixed solvents may be easily extended to prepare honeycomb structures and superhydrophobic surfaces simultaneously from a wide variety of block copolymers by carefully controlling the weight composition of the block copolymer and the selective solvent content.
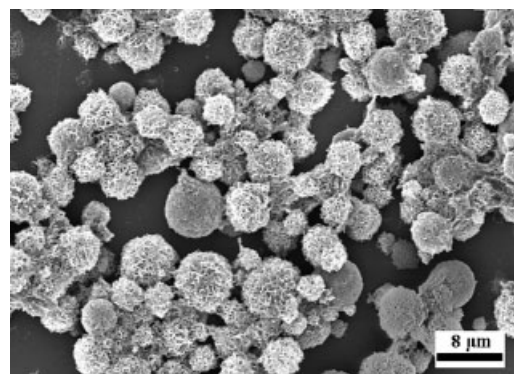
Introduction

Ordered mesoporous materials have been of significant interest in recent years in areas such as photonics, separations, and catalysis, which require organization with a more spatially complex microporous structure on a submicrometer to micrometer order.[1–8] In general, the preparation of microporous materials involves homopolymers, block copolymers,[9] colloidal crystals,[10] and emulsions.[11] When a thin film of a block copolymer is cast from an appropriate solvent on a solid substrate, a highly ordered and microporous honeycomb structure with a characteristic length scale is formed. Such pattern formation has been termed 'breath figures' and has been studied by many previous workers.[12–14]

In addition, superhydrophobic materials with a water contact angle (WCA) higher than 150° have attracted great interest in recent years because of their practical applications in water repellency, self-cleaning, and antifouling properties.[15–19] In general, the WCA is based on the

P.-H. Tung, S.-W. Kuo, C-F. Huang, F.-C. Chang
Institute of Applied Chemistry, National Chiao-Tung University, Hsin-Chu, Taiwan
E-mail: changfc@mail.nctu.edu.tw
K.-U. Jeong, S. Z. D. Cheng
Department of Polymer Science, The University of Akron, Akron, Ohio, USA

WILEY
InterScience®
DISCOVER SOMETHING GREAT

water-repellent behavior of the fractal micro-nanometer scale binary structures of the material. Preparation of the rough surface and subsequent coating of the surface with low surface energy materials is an essential process in fabricating superhydrophobic surface.[20,21] Yabu et al.[22,23] have reported a microporous honeycomb-patterned film prepared by casting a fluorinated copolymer solution under humid conditions which then exhibits a superhydrophobic surface. To the best of our knowledge, the formation of a honeycomb structure in common/selective mixed solvents to form a superhydrophobic surface simply by changing the selective solvent content of the non-fluorinated polymer solution without the need for low-surface energy modification has never been reported.

In this communication, the poly(vinyl phenol)-*block*-polystyrene ($PVPh_{79}$-*b*-PS_{21}) block copolymer is synthesized by combining protecting-group chemistry and anionic polymerization. Either honeycomb structures or block copolymer micelles that exhibit superhydrophobic surfaces can be easily formed by varying the toluene content in the tetrahydrofuran (THF)/toluene mixed solvent.

Experimental Part

The PVPh-*b*-PS copolymer was synthesized by sequential anionic polymerization in THF at $-78\,°C$ with *sec*-butyl lithium as the initiator. Characterization by gel permeation chromatography (GPC) and ^1H NMR spectroscopy revealed a composition with 79 mol-% PVPh and a molecular weight of $13\,000\ g\cdot mol^{-1}$ (PDI = 1.1). A honeycomb structure with a superhydrophobic surface that consisted of PVPh cores and PS coronas was obtained by dissolving the block copolymer in THF at room temperature under stirring overnight and then slowly adding the desired amount of toluene content. The copolymer solution was dropped onto a cleaned glass substrate under humid air (≈60 wt.-% at room temperature). After evaporation of the solvent, the morphology of the film was observed by scanning electron (SEM) and transmission electron microscopy (TEM) analyses. SEM images were observed on a Hitachi S4700I field emission scanning microscope with an acceleration voltage of 5 kV. The specimens were coated with Pt/Pd before SEM observations. TEM images were obtained by using a JEOL JEM-2000EXII instrument operated at 100 kV. TEM samples were deposited from polymer solutions on a carbon-coated copper grid for micelle structure. The contact angle of the polymer sample was measured at $25\,°C$ using a Krüss GH-100 goniometer interfaced with image-capture software by injecting a 5 µL liquid drop.

Results and Discussion

Figure 1 shows various SEM images of cast films of the block copolymer from THF/toluene mixtures that contain different toluene contents after solvent evaporation. It is well known that the formation of block copolymer aggregates in solution may result in various morphologies, such as sphere, rod, vesicle, and large compound micelle, by controlling the copolymer composition and concentration, the nature of the common solvent, the amount of selective solvent, and so on.[24–26] The changing cast-film morphologies obtained by varying the toluene content are shown in Figure 1. For example, only irregular holes are formed in pure THF as shown in Figure 1(a). Figure 1(b) shows the honeycomb structure formed from THF/toluene = 1:0.1 (v/v). On the contrary, Figure 1(c) shows only microspheres in THF/toluene = 1:1 (v/v). By increasing the toluene content to THF/toluene = 1:2 (v/v) (Figure 1(d)), microspheres and nanofibers coexist and exhibit a superhydrophobic surface. The honeycomb structure has been widely observed in homopolymers, star polymers, and block copolymers prepared from single solvent solutions such as CS_2 and CH_2Cl_2.[1–9] Nonetheless, the honeycomb structure of block copolymer prepared from a common/selective solvent system has been rare, based on our knowledge.[27]

Figure 2 shows the detailed honeycomb structure film viewed from different directions, and the corresponding block copolymer solution morphology obtained by dialysis
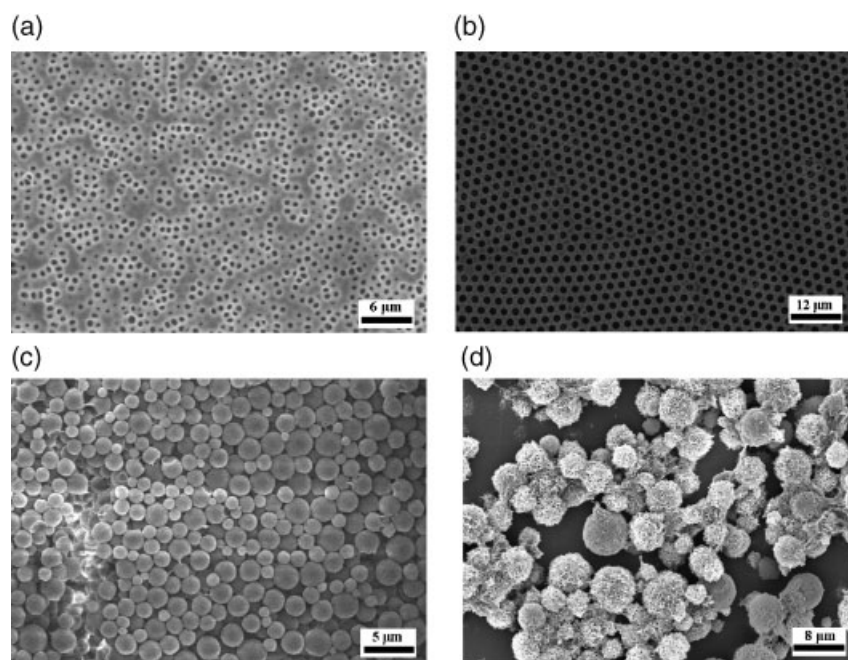

Figure 1. SEM images of solid films prepared by 20 mg of PVPh-*b*-PS in 1 mL of THF and various toluene contents: a) pure THF, b) 0.1 mL toluene, c) 1 mL toluene, d) 2 mL toluene.

methods based on SEM and TEM analyses Clearly, the honeycomb structure can be observed in the SEM (top view) and TEM images (Figure 2(a) and (b)). The fabricated honeycomb structure contains void hexagonal cylinders with a thickness of 40–50 nm as observed from the SEM bottom and side views, and TEM images (Figure 2(b), (c), and (d)). This thickness is close to the microphase separation of the block copolymer in THF solution based on light scattering (40 nm)[28] and small-angle X-ray scattering (38 nm).[29,30] The polymeric micellar morphology after further dilution results in vesicles (Figure 2(e) and 2(f)) and this phenomenon is similar to reported in the literature.[31–33] In a concentrated solution, these vesicles transform into a three dimensionally ordered honeycomb morphology with some intervesicle voids (perforated

bilayer) by the 'breath figures' method.[11–13] The formation of the perforated bilayer structure involves fast adhesive micelle collisions, because of the high concentration, and a subsequent fusion and structural rearrangement of the contacting micelles. In addition, the initial concentrations of the solution have an influence on the wall thickness between the pores and the size of pores (for brevity, data not shown here). The results show that a higher concentration leads to smaller pores, but thicker walls, which is similar to previous work.[2]

Figure 3 shows the micelle structure of the block copolymer in THF/toluene = 1:2 (v/v), which indicates that nanofibers of 40–70 nm length and porous microspheres of 1–5 μm diameter coexist, as observed by SEM and TEM images. The porous microspheres come from the aggrega-
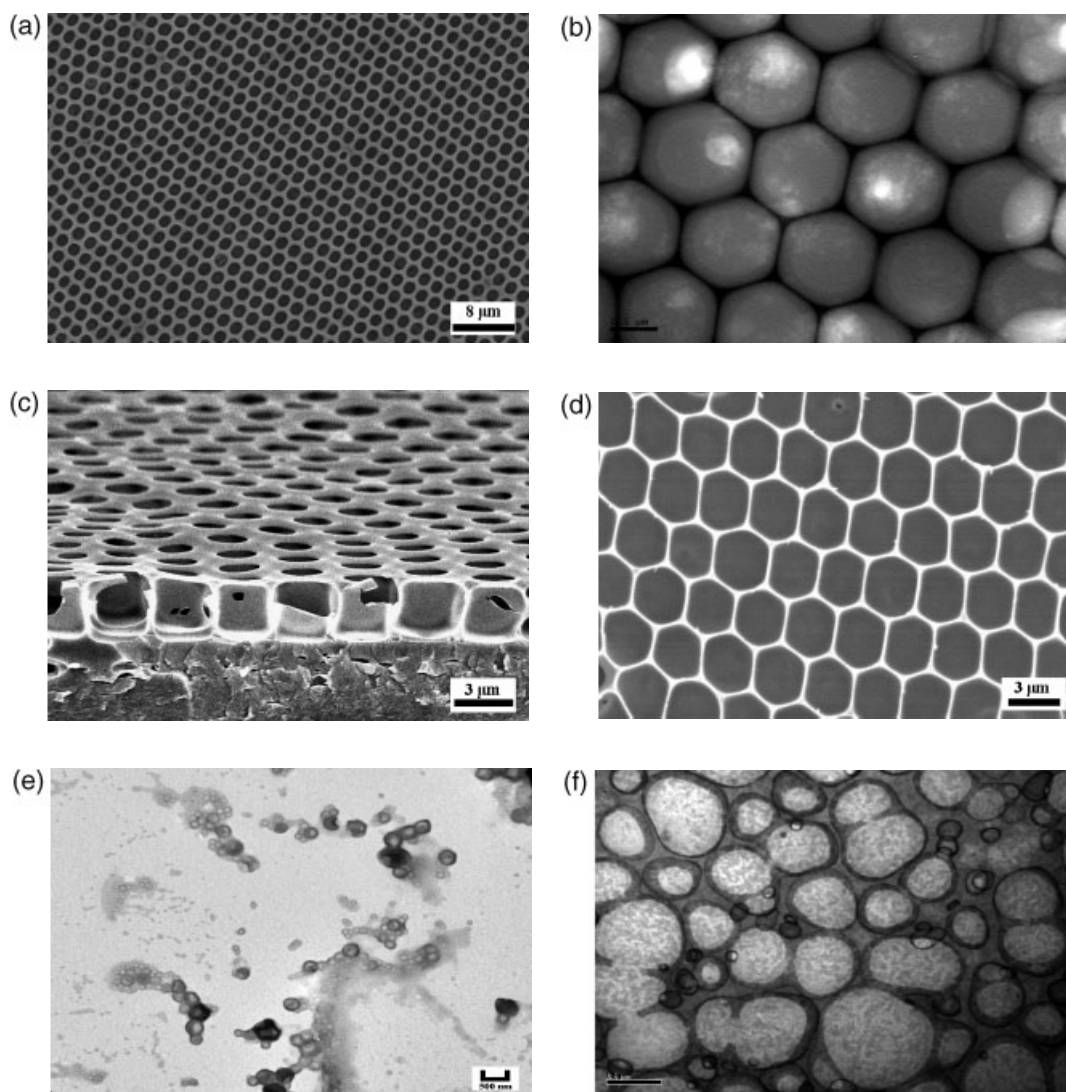

Figure 2. PVPh-*b*-PS copolymer in THF/toluene (1:0.1 v/v, 20 mg · mL⁻¹): a) the SEM top view of a honeycomb structure solid film prepared under moist atmosphere. b) TEM top view, c) SEM side view, and d) SEM bottom view. e) The TEM image of solution micelle morphology of block copolymer by dialysis method and further dilution. f) The TEM image of micellar aggregates without dilution.
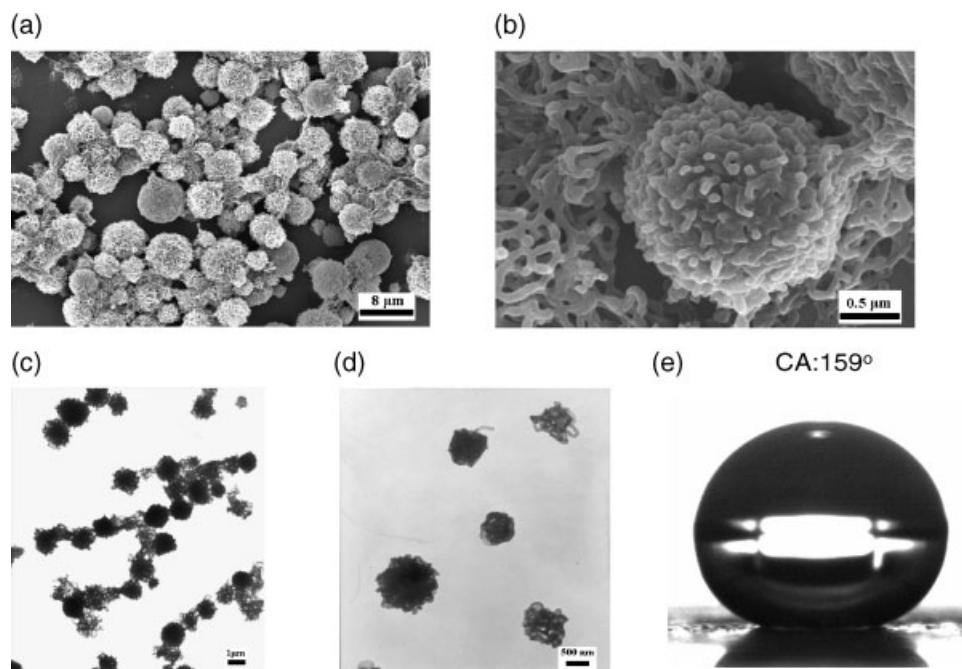
Figure 3. Superhydrophobic surface of PVPh-*b*-PS copolymer in THF/toluene (1:2 v/v, 20 mg · mL⁻¹) content: a) SEM, b) scale-expanded of (a), c) porous microspheres by TEM, d) nanofibers by TEM, and e) contact angle measurement of the superhydrophobic surface.

tion of nanofibers, as shown in Figure 3(a–c). In addition, the corona domain is from the PS phase, which is a result of the superhydrophobic nature of its CH groups. The PVPh is in the core domain (dark image in Figure 3(d)), since RuO_4 preferably stains PVPh. This type of microsphere/nanofiber film is a well known material for creating superhydrophobic surfaces.[34,35] The surface roughness dramatically increases the hydrophobicity of such surfaces, which is similar to the rough surface of a lotus leaf.[36] Air can be trapped in the aperture of the porous microspheres and nanofibers. As a result, the measured WCA of this kind of surface is ca. 159.2° (Figure 3(e)), which is superhydrophobic.

Conclusion

A simple method to prepare honeycomb-structured and superhydrophobic block copolymer films by adjusting the toluene content in THF/toluene mixed solvents is revealed. A honeycomb structure can be fabricated from vesicle structures at a relatively low toluene content. On the contrary, at relatively higher toluene contents, a micelle structure with porous microspheres is formed. These porous microspheres possess greater surface roughness and result in film surface superhydrophobicity. At the same time, these nanofibers interweave to form a network with a PS corona surface. It is believed that the simple method of using common/selective mixed solvents

described here can easily be extended to prepare honeycomb structures and superhydrophobic surfaces simultaneously from a wide variety of block copolymers by carefully controlling the weight composition of the block copolymer and the selective solvent content.

[1] B. deBoer, U. Stalmach, H. Nijland, G. Hadziioannou, *Adv. Mater.* **2000**, *12,* 1581.
[2] P. S. Shah, M. B. Sigman, C. A. Stowell, K. T. Lim, K. P. Johnston, B. A. Korgel, *Adv. Mater.* **2003**, *15,* 971.
[3] C. Barner-Kowollik, H. Dalton, T. P. Davis, M. H. Stenzl, *Angew. Chem. Int. Ed.* **2003**, *42,* 3664.
[4] C. Cheng, Y. Tian, Y. Shi, R. Tang, F. Xi, *Macromol. Rapid Commun.* **2005**, *26,* 1266.
[5] U. Stalmach, B. de Boer, C. Videlot, P. F. van Hutten, G. Hadziioannou, *J. Am. Chem. Soc.* **2000**, *122,* 5464.
[6] H. Duan, M. Kuang, J. Wang, D. Chen, M. Jiang, *J. Phys. Chem. B* **2004**, *108,* 550.
[7] L. Cui, Y. Han, *Langmuir* **2005**, *21,* 11085.
[8] X. Han, J. Xu, H. Liu, Y. Hu, *Macromol. Rapid Commun.* **2005**, *26,* 1810.
[9] S. Jenekhe, X. Chen, *Science* **1999**, *283,* 372.
[10] O. D. Velev, T. A. Jede, R. F. Lobo, A. M. Lenhoff, *Nature* **1997**, *389,* 447.
[11] A. Imhof, D. J. Pine, *Nature* **1997**, *389,* 948.
[12] D. Beysens, C. M. Knobler, *Phys. Rev. Lett.* **1986**, *57,* 1433.

[13] L. Song, R. K. Bly, J. N. Wilson, S. Bakbak, J. O. Park, M. Srinivasarao, U. H. F. Bunz, *Adv. Mater.* **2004**, *16,* 115.

[14] G. Widawski, M. Rawiso, B. Francois, *Nature* **1994**, *369,* 387.

[15] L. Feng, Y. Song, J. Zhai, B. Liu, J. Xu, L. Jiang, B. Zhu, *Angew. Chem. Int. Ed.* **2003**, *42,* 800.

[16] J. Zhang, Y. Lu, W. Huang, Y. Han, *Macromol. Rapid Commun.* **2005**, *26,* 477.

[17] K. Tsujii, T. Yamamoto, T. Onda, S. Shibuichi, *Angew. Chem. Int. Ed.* **1997**, *36,* 1011.

[18] J. P. Youngblood, T. J. McCarthy, *Macromolecules* **1999**, *32,* 6800.

[19] N. Zhao, J. Xu, Q. Xie, L. Weng, X. Guo, X. Zhang, L. Shi, *Macromol. Rapid Commun.* **2005**, *26,* 1075.

[20] L. Feng, S. Li, H. Li, J. Zhai, Y. Song, L. Jiang, D. Zhu, *Angew. Chem. Int. Ed.* **2002**, *41,* 1221.

[21] M. Ma, Y. Mao, M. Gupta, K. K. Gleason, G. C. Rutledge, *Macromolecules* **2005**, *38,* 9742.

[22] H. Yabu, M. Shimomura, *Chem. Mater.* **2005**, *17,* 5231.

[23] H. Yabu, M. Takebayashi, M. Tanaka, M. Shimomura, *Langmuir* **2005**, *21,* 3235.

[24] L. Zhang, A. Eisenberg, *J. Am. Chem. Soc.* **1996**, *118,* 3168.

[25] P. L. Soo, A. Eisenberg, *J. Polym. Sci., Polym. Phys. Ed.* **2004**, *42,* 923.

[26] S. E. Burke, A. Eisenberg, *Langmuir* **2001**, *17,* 16705.

[27] J. Ding, G. Liu, *Macromolecules* **1997**, *30,* 655.

[28] J. Q. Zhao, E. M. Peame, T. E. Kwei, H. S. Jeon, P. E. Kesani, N. P. Balsara, *Macromolecules* **1995**, *28,* 1972.

[29] P. Du, M. Li, K. Douki, X. Li, C. B. W. Garcia, A. Jain, D. M. Smilgies, L. J. Fetters, S. M. Gruner, U. Wiesner, C. K. Ober, *Adv. Mater.* **2004**, *16,* 953.

[30] M. Li, K. Douki, K. Goto, X. Li, C. Coenjarts, D. M. Smilgies, C. K. Ober, *Chem. Mater.* **2004**, *16,* 3800.

[31] M. Mu, F. Ning, M. Jiang, D. Chen, *Langmuir* **2003**, *19,* 9994.

[32] W. Bu, H. Li, H. Sun, S. Yin, L. Wu, *J. Am. Chem. Soc.* **2005**, *127,* 8016.

[33] M. H. Stenzel, *Aust. J. Chem.* **2002**, *55,* 239.

[34] L. Jiang, Y. Zhao, J. Zhai, *Angew. Chem. Int. Ed.* **2004**, *43,* 4338.

[35] Q. Xie, G. Fan, N. Zhao, X. Guo, J. Xu, J. Dong, L. Zhang, Y. Zhang, C. C. Han, *Adv. Mater.* **2004**, *16,* 1830.

[36] L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, *Adv. Mater.* **2002**, *14,* 1857.