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Supporting Information

Ordered Microporous Membranes Templated by Breath Figures for Size-Selective Separation

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Experimental

Materials. PS_{247}-*b*-$PDMAEMA_{14}$ (M_n = 27900 g mol^{-1}, M_w/M_n = 1.24),[1] PS_{187}-*b*-$PHEMA_{15}$ (M_n = 20500 g mol^{-1}, M_w/M_n = 1.10),[2] and PS_{141}-*b*-PAA_{14} (M_n = 17700 g mol^{-1}, M_w/M_n = 1.35)[3] were synthesized by atom transfer radical polymerization (ATRP) using a reported procedure. Polystyrene (PS, M_n = 235000 g mol^{-1}, M_w/M_n = 2.89) was provided by Zhenjiang Chiemei Chemicals (China). PS microspheres with diameters of 2.0 and 5.0 μm were purchased from Shanghai Aladdin Chemicals. Water used in all experiments was de-ionized and ultrafiltrated to 18.2 MΩ with an ELGA LabWater system. All other reagents were analytical grade and used without further purification.

Membrane Preparation. The ordered membranes were prepared via the breath figure method.[4] Typically, an aliquot of 100 μL of polymer solution was cast onto the surface of ice or water or other liquids under a 4 L min^{-1} humid airflow. The humidity of the airflow was maintained to be above 70% by bubbling through distilled water and was measured by a hygro-thermograph (DT-321S, CEM Corporation). A stainless steel woven wire mesh was used as the support to fabricate a composite membrane. The mesh was covered with a thin layer of PS nanofibers, which were fabricated by electrospinning according to our reported procedure.[5] The thickness of the mesh can be facilely controlled by varying electrospinning time. For example, electrospinning for 15 seconds leads to sparse nanofiber mesh with irregular and large pores of tens of microns. Then the ordered membrane was transferred onto the pre-treated mesh surface to give a composite membrane.

Filtration Assay. A piece of composite membrane with diameter of 12 mm was mounted in a permeation module. PS microspheres were dispersed in a mixture of water and ethanol (1/1, vol/vol) with a concentration of 2 mg mL^{-1}. The experiments were performed in a dead-end mode and any additional pressure is not necessary. A microinfusion pump (WZ-50C2, Zhejiang University Medical Instrument Co., LTD, China) was used to control the flow rate of the dispersion. The filtrates were collected and analyzed.

Characterization. Field emission scanning electron microscope (FESEM, Hitachi S4800 and Sirion-100, FEI) was used to observe the surface morphology of membranes after being sputtered with gold using ion sputter JFC-1100. Pore diameter was analyzed using ImageJ (v1.42q, by Wayne Rasband). Size distribution of the microspheres was analyzed by a Nano-ZS nanosizer (Malvern Instruments, Worcestershire, UK).

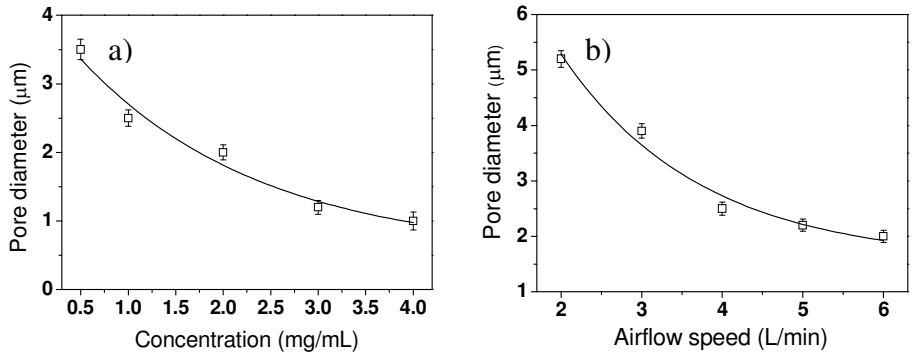

Figure S1. Effects of a) PS-*b*-PDMAEMA solution concentration and b) airflow speed on the pore diameters of the ordered membranes.

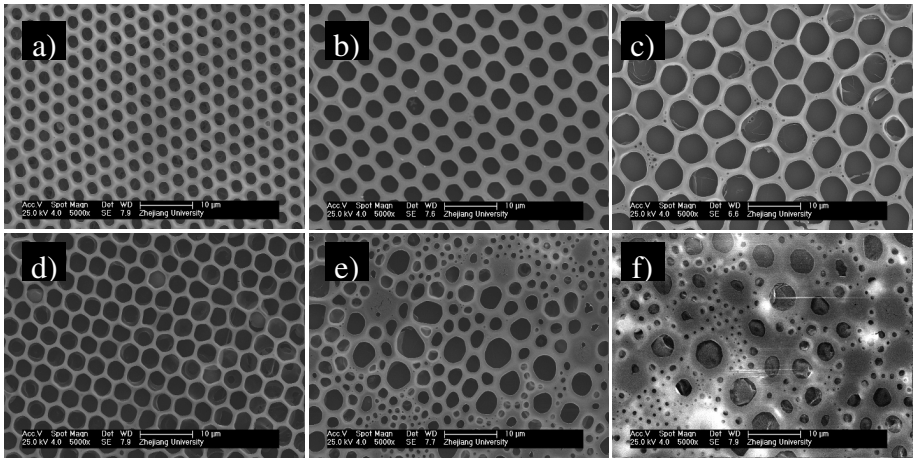

Figure S2. SEM images of membranes prepared from a,d) PS-*b*-PHEMA, b,e) PS-*b*-PDMAEMA, and c,f) PS-*b*-PAA at a-c) an air/ice interface or d-f) an air/water interface.

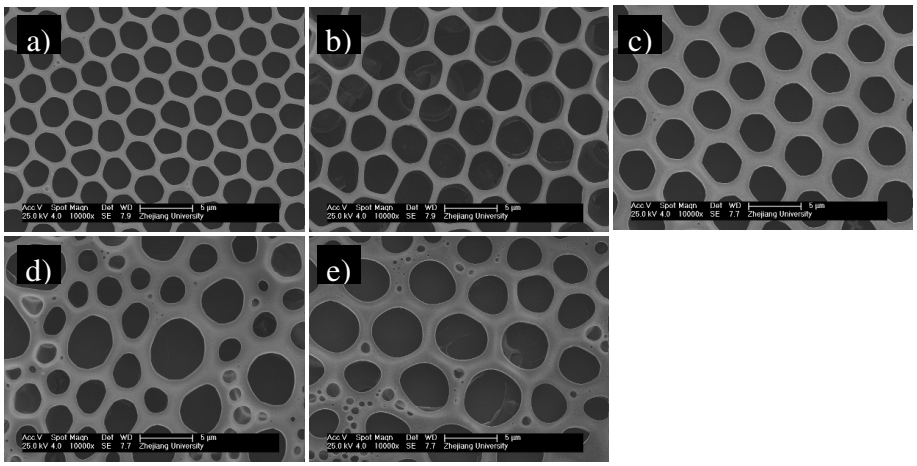

Figure S3. SEM images of PS-*b*-PDMAEMA membranes prepared at air/water interfaces. The temperature of water is a) 0, b) 9, c) 17, d) 26, and e) 35 °C.

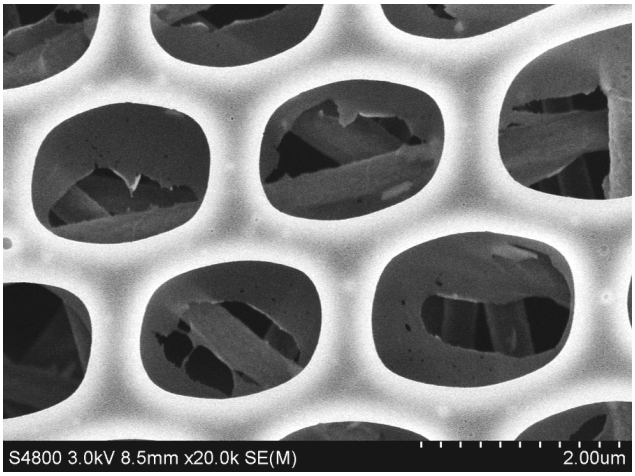

Figure S4. SEM image of a PS-*b*-PDMAEMA membrane prepared from the solution with high polymer concentration. The membrane has been transferred onto a piece of electrospun nanofiber mesh.

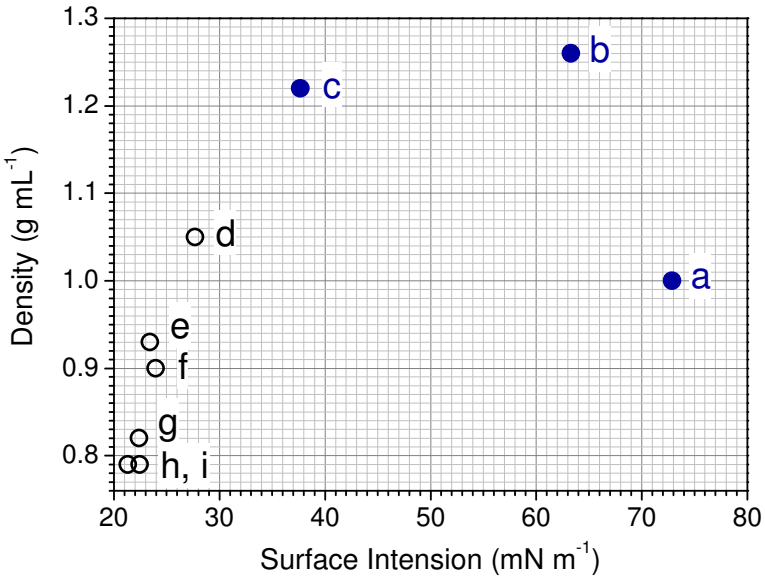

Figure S5. Formation of ordered membranes with through-pores on the interfaces of air and liquids with different surface intensions and density. Filled circle: a) water, b) glycerol, and c) formic acid. Hollow circle: d) acetic acid, e) tetraethyl orthosilicate, f) ethyl acetate, g) ethanol, h) isopropanol, and i) methanol.

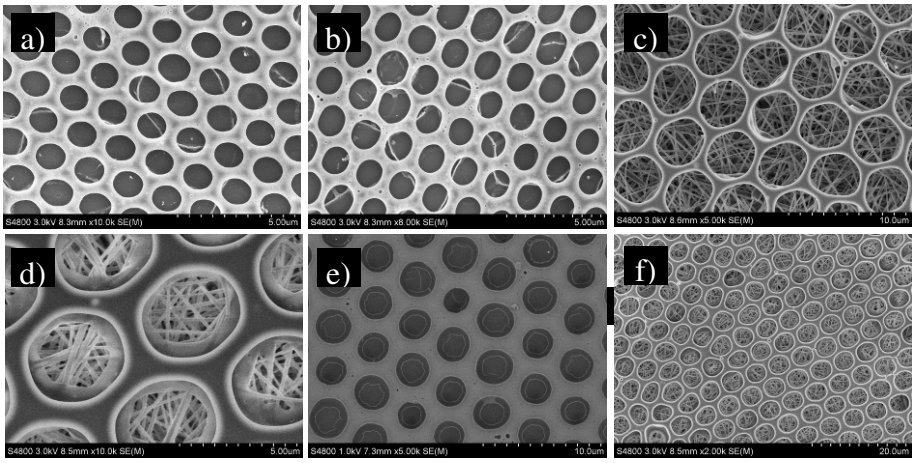

Figure S6. SEM images of ordered membranes prepared from a,d) PS-*b*-PDMAEMA at an air/glycerol interface, b,e) PS-*b*-PDMAEMA at an air/formic acid interface, and c,f) PS at c) an air/ice interface or f) an air/water interface.

References:

(1) Ke, B. B.; Wan, L. S.; Chen, P. C.; Zhang, L. Y.; Xu, Z. K. *Langmuir* **2010,** *26*, 15982.

(2) Ke, B. B.; Wan, L. S.; Xu, Z. K. *Langmuir* **2010,** *26*, 8946.

(3) Chen, P. C.; Wan, L. S.; Ke, B. B.; Xu, Z. K. *Langmuir* **2011,** *27*, 12597.

(4) Wan, L. S.; Lv, J.; Ke, B. B.; Xu, Z. K. *ACS Appl. Mater. Interfaces* **2010,** *2*, 3759.

(5) Wan, L. S.; Ke, B. B.; Wu, J.; Xu, Z. K. *J. Phys. Chem. C* **2007,** *111*, 14091.