

Supplemental Information

**Vertically Oriented Nanoporous Block Copolymer Membranes for  
Separation and Filtration**

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## **1. Experimental**

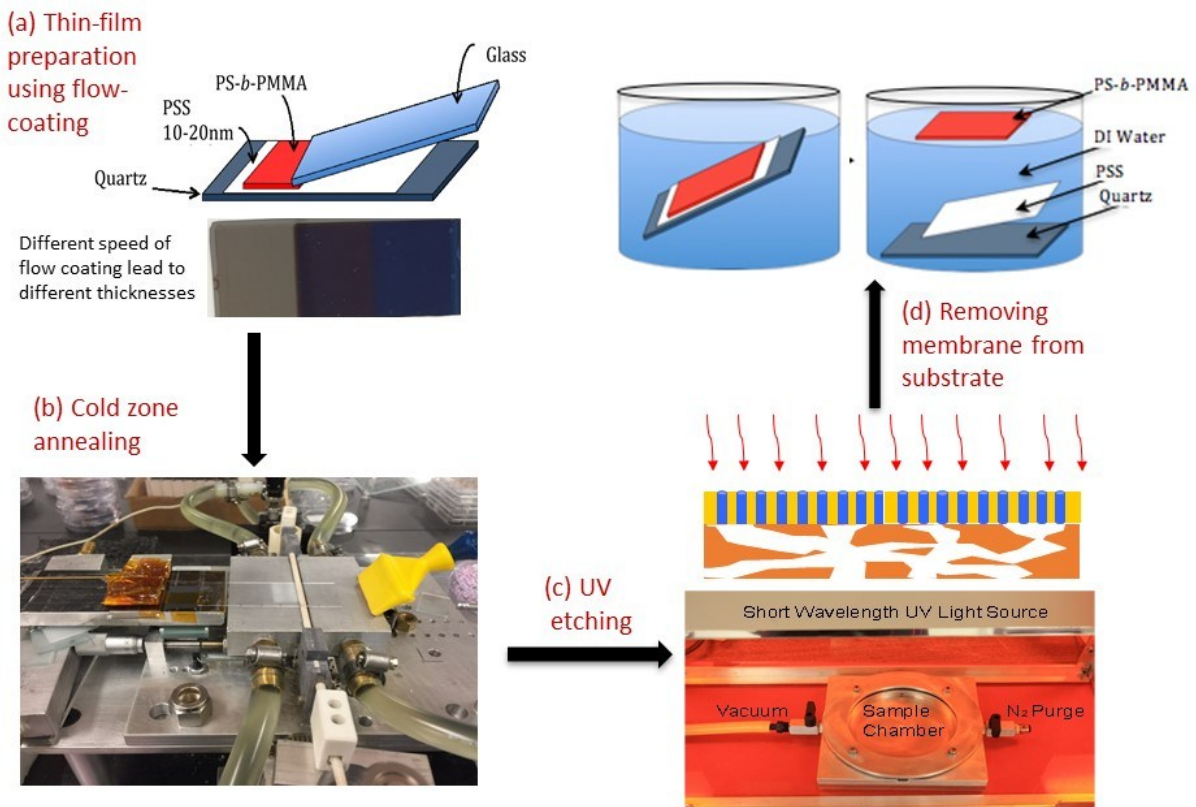
**1.1. BCP Materials.** Poly (styrene-block-methyl methacrylate) (PS-b-PMMA) diblock copolymer ( $M_w=57k-25k$ ,  $M_w/M_n=1.07$ ) was obtained from Polymer Source Inc. and used as received. The PDI of the diblock copolymer is 1.07; the glass transition temperature ( $T_g$ ) for PS block is 106 °C, and for PMMA block is 127 °C. The ratio of polymer chain lengths (volume fraction of the PS block is  $\sim 0.7$ ) corresponds to the formation of cylindrical morphology. The obtained BCP was dissolved in laboratory grade toluene (Sigma-Aldrich, ACS reagent,  $\geq 99.5\%$ ) to prepare 3% solutions for the casting of thin films. The solutions were purified using 0.2  $\mu\text{m}$  PTFE filters (Thermo Scientific, Rochester). Poly (4-styrene sulfonic acid) (PSS) was purchased from Aldrich Chemistry and used as received. Amorphous quartz substrates were obtained from G. M. Associates Inc. and rinsed with toluene followed by 1 hour of ultraviolet-ozone (UVO) treatment in order to modify the surface hydrophilicity. The supporting polyethersulfone (PES) membrane filters (0.2  $\mu\text{m}$ ) were obtained from Sterlitech Corporation and used as received.

**1.2. Fabrication of the membranes.** The multilayer block copolymer thin films were fabricated onto porous PES supporting membranes using the following steps, which are schematically presented shown in Scheme 1.

- a) Thin-film preparation.** PSS thin films were flow coated from a 1 wt% solution onto UVO treated quartz substrates to obtain films of 30 ~ 40 nm thickness. Before casting the BCP thin films, the residual solvent was extracted by drying the prepared thin films at 140 °C for 6 hours under vacuum, followed by 15 min of UVO treatment. The BCP films were flow-coated afterward from toluene solutions onto the prepared substrates under various speeds to provide different film thicknesses, as shown in Scheme 1. Film thicknesses were determined using a thin film interferometer (F-20 UV Thin Film Analyzer, Filmetrics, Inc.) with a resolution of 1 nm. An ellipsometer confirmed the thickness of the thin films on quartz substrates.<sup>1</sup>
- b) Cold Zone Annealing.** The basic set up for a sharp cold zone annealing was based on the design described previously by Lovinger et al.<sup>2</sup> The hot zone is provided by a low resistance nickel-chrome wire, which is powered by an adjustable current source (Digital DC Power Supply, B&K Precision Corp.). The two cold blocks are provided by the circulation of low molecular mass polydimethylsiloxane (PDMS) oil at -5 °C connected to a chiller system (Thermo Scientific). For sharp cold zone annealing, the distance between the cold blocks and the hot wire was adjusted to 1 mm to provide a relatively high-temperature gradient of ~35 °C/mm. The height of the three blocks was adjusted to optimize the temperature gradient. The resulted temperature gradients were determined using a thermal infrared (IR) imaging camera (Testo 875 Thermal Imager Kit) with an accuracy of 0.1 °C. During the CZA process, the BCP thin film samples were swept at various speeds under specific experimental conditions, such as the maximal temperature  $T_{\max}$  of ~210 °C and the temperature gradient  $\nabla T$  of ~ 35 °C/mm. Compared to uniform oven annealing, this method was expected to enhance significantly the ordering speed.<sup>3,4</sup>
- c) Ultraviolet Etching.** After CZA, the thin film samples were exposed to ultraviolet (UV) irradiation in a closed chamber under vacuum for 2 hours, followed by rinsing with acetic acid and distilled water to remove the etched polymer residuals. The UV treatment was expected to decompose the PMMA phase while at the same time, to crosslink the PS matrix,

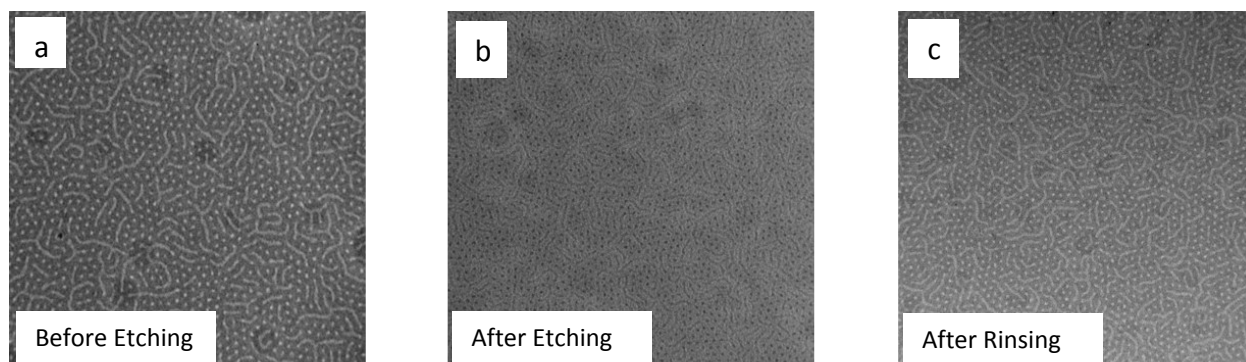
enhancing the mechanical properties, thus making it resistant to different solvents. The samples were then kept under vacuum overnight to remove the residual solvent. The wavelength of the UV light was 254 nm (UVC 2914.957  $\mu\text{w}/\text{cm}^2$ ) provided by XX-15S Shortwave UV Bench Lamp.

**d) Fabrication of membranes.** After CZA, the samples with cylindrical morphology were floated at the water/air interface and transferred onto PES supporting membranes due to the high solubility of PSS in water. These multilayer membranes were exposed then to UV light in the absence of oxygen for about 2 h, followed by rinsing with acetic acid and distilled water in succession for 2 h. The multilayer block copolymer thin films were floated onto the water and transferred on porous PES supporting membranes, as shown in Scheme 1.



**Scheme 1:** Flow chart of block copolymer membrane fabrication procedure.

**1.3. Thin Film Characterization.** The surface morphology of these thin-film samples was characterized using a Dimension Icon Atomic Force Microscope (AFM) (Bruker AXS) under the Peak Force Quantitative Nanomechanical mode. We used the software Nanoscope Analysis (Bruker Corp.) for AFM images and ImageJ (NIH) for the height and the morphology composition (cylinder ratio) analysis reported in text of paper.



**Figure S1.** TEM images of PS-b-PMMA thin films: (a) before etching; (b) after etching and before rinsing; (c) after rinsing. (Image sizes = 1.1  $\mu\text{m}$  width)

## 2 Supporting Results and Discussion

**2.1 Transmission Electron Microscopy:** The TEM images of the PS-b-PMMA thin films at different stages are shown in Figure S1. AFM revealed that the cylinder diameter is  $\sim 23\text{nm}$  before etching. After PMMA degradation, its residuals as the cylinder phase can be observed, a dimension also conformed from AFM studies. This remaining phase turns from a relatively white to a black phase after etching, and it is totally removed by solution rinsing (Fig. S1). Furthermore, the UV exposure provided crosslinking of the polystyrene (PS) block, thus enhancing the mechanical strength and the dimensional stability of the films.<sup>5,6</sup> Additionally, due to the crosslinking of the PS matrix after UV irradiation, the membrane with nanochannels exhibits good resistance to all kinds of organic solvents.<sup>7</sup> The UV etched membranes remained the same after rinsing with toluene and acetone. These characteristics of the membrane would increase its durability at harsh filtration conditions, such as high temperature and strong acid or basic environments.

## References

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