On The Replication of Block Copolymer Templates by Poly(dimethylsiloxane) Elastomers**

By Dong Ha Kim, Zhiqun Lin, Ho-Cheol Kim, Unyong Jeong, and Thomas P. Russell*

Recently, there has been considerable interest in fabricating sub-micrometer and nanometer-scale structures. The ability to pattern surfaces with regularly sized and spaced features on the nanoscopic level is desirable for many potential applications. Block copolymers offer an attractive route to overcome some of the limitations of conventional lithographic techniques, since they self-assemble into a variety of ordered morphologies on the length scale of tens of nanometers.[1-6]

Siloxane-based elastomers, in particular poly(dimethylsiloxane) (PDMS), have found widespread uses as stamps for transferring patterns for optical systems,[7-11] microelectronic devices,[12-14] and sensors.[15] However, pattern transfer has been limited in practice to dimensions greater than ~0.1 μm. More recently, capillary force lithography has emerged as a promising route to generate patterned surfaces on the 0.1 μm length scale using PDMS as an elastomeric mold.[16] Here we describe attempts to replicate block copolymer templates for the preparation of textured PDMS surfaces on the tens of nanometers length scale. Templates with hexagonal arrays of nanopores oriented normal to the surface produced from asymmetric poly(styrene)-block-poly(methyl methacrylate) diblock copolymers, denoted PS-b-PMMA, were used as masters to fabricate PDMS with nanoscopic surface patterns.

Shown in Figure 1A is a height-contrast atomic force microscopy (AFM) image of a 27 nm thick film of PS-b-PMMA with a molecular weight of 7.3 × 10^4 and a PMMA volume fraction of 0.3. The film was prepared on a neutral random copolymer brush.[17] Hexagonally packed arrays of cylindrical

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[1] Prof. T. P. Russell, Dr. D. H. Kim, Dr. Z. Lin[1]
Silvio O. Conte National Center for Polymer Research
Polymer Science and Engineering Department
University of Massachusetts at Amherst
Amherst, MA 01003 (USA)
E-mail: russell@mail.pse.umass.edu
Dr. H.-C. Kim
IBM Almaden Research Center,
650 Harry Road,
San Jose, CA 95120 (USA)
U. Jeong
Department of Chemical Engineering and Polymer Research Institute
Pohang University of Science and Technology
Kyungbuk, 790-784 (Korea)
[2] Current address: Department of Materials Science and Engineering,
University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA.
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Fig. 1. Height-contrast AFM images and schematic diagram for fabrication of the negative PDMS replica. A) Surface of 73 k PS-b-PMMA ordered on the anchored random copolymer brush surface. B) (A) After selective removal of PMMA domains by UV exposure and acetic acid rinsing. C) Surface of PDMS replica released from PS template. Inset: 2D FFT pattern of the same area. The size of all images is 1 μm × 1 μm.
PMMA microdomains oriented normal to the surface are seen. The PMMA microdomains are ~20 nm in diameter with a center-to-center distance ($\lambda_{C-C}$) of ~39 nm. Figure 1B shows a height-contrast AFM image of the arrays of nanopores in a crosslinked PS matrix after PMMA was selectively removed by UV exposure followed by acetic acid rinsing.

A negative replica was produced by placing a PDMS elastomer prepolymer on the top of the porous, crosslinked PS template. Since PDMS does not wet the PS template, air is trapped within the nanopores forming bubbles at the top of each pore. After crosslinking the PDMS under atmospheric conditions, the PDMS was peeled from the template and the AFM height-contrast image in Figure 1C of the PDMS surface in contact with the PS template was obtained. A hexagonal array of hemispherical depressions in the PDMS is seen with the same $\lambda_{C-C}$ as the template. Shown in the inset is a two-dimensional (2D) fast Fourier transform (FFT) of the AFM image showing reflections characteristic of a hexagonally packed system.

At atmospheric pressure, $P_0$, the radius of the bubble, $r$, at the top of each pore is defined by $\gamma_{PDMS}$, the surface tension of PDMS, and $D$, the diameter of the pore. $\theta$, the contact angle, shown schematically in Figure 2A, is given by [18]

$$P_i = \frac{2\gamma_{PDMS}}{r} = \frac{4\gamma_{PDMS} \cos \theta}{D}$$

(1)

With 20 nm diameter pores and $\gamma_{PDMS} = 20$ mJ m$^{-2}$, $\theta$ is calculated to be 88°. From a line scan of the AFM image (Fig. 2B) $\theta \sim 78°$, which is close to the expected value. Assuming a hemispherical shape of the depression, the depth of each hemisphere is

$$h = \frac{D}{2 \cos \theta} (1 - \sin \theta)$$

(2)

Substituting for $D$ and $\theta$, $h = 3$ nm, whereas the depth of each depression is measured to be ~5 nm. Thus, while the depressions are not perfect hemispheres, this simple model describes the observations reasonably well.

PDMS surfaces with a positive pattern can be obtained by filling the template prior to crosslinking. This can be achieved either by removing the air trapped in the nanopores, by dissolving the PDMS in a solvent, or by applying external force. Liquid PDMS was placed on top of the porous, crosslinked PS template under vacuum, then crosslinked. Shown in Figures 3A and 3B are height-contrast AFM images of the PS template after PMMA was selectively removed and that of the PDMS after peeling the elastomer from the copolymer template, respectively. It should be noted that a higher weight-average molecular weight copolymer ($M_w = 1.09 \times 10^5$) was used here where the diameter of the cylindrical domains was 32 nm with $\lambda_{C-C} = 53$ nm. The reduction in the lateral or-

Fig. 2. A) Schematic diagram for negative PDMS replica–PS template interface. B) 2D cross-sectional profile of negative PDMS replica obtained from AFM image.

Fig. 3. Height-contrast AFM image of positive PDMS replica generated by removing the air trapped in the nanopores. A) Surface of 103 K PS-PMA-PMA template after selective removal of PMMA domains by UV exposure and acetic acid rinsing. B) Surface of positive PDMS replica released from PS template. C) Surface of PS template after removal of PDMS replica. The size of image is 2 µm × 2 µm.
dering is a result of the increase in molecular weight of the copolymer.\textsuperscript{[19]} The surface of the PDMS was covered with 4 nm high hemispherical caps with an average diameter of 37 nm. In comparison to the pore depth of 40 nm, it is evident that the PDMS did not fully penetrate into the pore. The inability to completely replicate the porous master may arise from the low elastic modulus of the PDMS (SYLGARD 184) that can give rise to tearing or deformation of the siloxane polymer upon removal from the master.\textsuperscript{[20,21]} The surface of the template after removing the PDMS replica is shown in Figure 3C. As seen, the resolution of the features is poorer than in the original template and some remaining PDMS can be seen on the surface. Other siloxane polymers have been developed by several researchers to produce free-standing features down to 50 nm.\textsuperscript{[22-24]} However, while these harder siloxanes improved the negative replicas of the block copolymer masters, the positive replicas were brittle, causing the nanoscopic replicas to fracture.

To improve the filling of the nanopores, solutions of the PDMS in toluene were used. Toluene, a good solvent for PS, enhances the wetting of the pores. Significant swelling of the crosslinked PS template was avoided by increasing the crosslink density of the PS matrix. After evaporating the toluene, the PDMS was crosslinked, the replica peeled from the copolymer master (Fig. 4A) and, as seen in Figure 4B, 5 nm high, 20 nm diameter discs with an average separation distance of 34 nm were produced. Thus, while the size and separation distance between the pore was replicated with high fidelity, the penetration of the PDMS into the pores, even with the use of the solvent, was limited.

To enhance the filling of the porous template by the PDMS an electric field was applied. The porous, crosslinked PS template was prepared on a silicon wafer. A lower aluminum electrode was placed beneath the wafer. The PDMS prepolymer was placed on the surface of the template and covered with a sheet of aluminized Kapton (Fig. 5A). The Kapton side of the upper electrode was placed in contact with the PDMS to avoid shorting. The separation distance between the two electrodes in this geometry was 500 \textmu m. The applied voltage produces an electric field gradient at the PDMS–air interface, corresponding to an electrostatic pressure that acts to draw the PDMS into the pores. The pressure operating on the interface is given by\textsuperscript{[25-28]}

$$\Delta P = U \varepsilon \varepsilon_0 \varepsilon_{PMOS} \frac{\varepsilon_{PDMS} - 1}{\left[(d - h_0) + \varepsilon_{PDMS} h_0\right]^2} + \frac{2 \varepsilon_{PMOS} \cos \theta}{R} - P_0$$

The first term is the electrostatic pressure, where $U$ is applied voltage, $\varepsilon_{PDMS}$ is the dielectric constant of the PDMS with curing agent, $\varepsilon_0$ is the dielectric permittivity in vacuum, $d$

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Fig. 4. Height-contrast AFM images of the positive PDMS replica prepared by solution spreading method. A) Surface of 69 K PS-b-PDMS template after selective removal of PMMA domains by UV exposure and acetate acid rinsing. B) Surface of positive PDMS replica released from PS template. The size of the images are 2 \textmu m \times 2 \textmu m.

Fig. 5. A) Schematic diagram of experimental set-up for the generation of positive PDMS replica by applying external electric field. B) Height-contrast AFM image of the surfaces of the positive PDMS replica produced by applying electric field under nitrogen atmosphere. The size of the image is 2 \textmu m \times 2 \textmu m.
is distance between the electrodes and $R_0$ is the thickness of the template. The second term is the Laplace pressure, and $P_0$ is atmospheric pressure, with the other variables being previously defined. If $\Delta P > 0$, the PDMS will be drawn into the template. Figure 5B shows the PDMS surface produced with a 1.09 x 10^5 PS-b-PMMMA template (Fig. 3B). As can be seen, the diameter and separation distance of the pores in the template have been replicated with high fidelity. However, even with an applied field of 3.5 kV cm^{-1}, the discs on the PDMS surface are only 6 nm in height, in comparison to the pore depth of 40 nm. Consequently, while the applied field has enhanced the filling of the pores, complete filling of the pores has not occurred.

It should be noted that, if the porous template is removed from the substrate and placed on the surface of liquid PDMS, the pores of the template will fill and the template will sink into the PDMS. Consequently, the failure to completely fill the porous template on the surface of a substrate by the three routes discussed, is a consequence of the difficulty in removing air trapped in the base of the pores. In addition, it is not possible to independently determine whether the nanoscopic cylinders have been torn during removal. Though the uniform height of the cylinders seen would argue against this. All efforts, to date, have been unsuccessful in perfect replication. Thus, while the lateral features of the template can be replicated with high fidelity, the heights of the replicated features, while uniform, did not match those of the master. Nonetheless, the replicas have a well-defined and controllable topography and are being examined for use in nano-contact printing.

Experimental

A hydroxy end-functionalized random copolymer of styrene and m ethyl methacrylate, denoted PS-r-PMMMA, having a styrene fraction of 0.6, was synthesized in bulk via a 2,2,6,6-tetramethylpiperidin-1-yl oxide (TEMPO) “living” free-radical polymerization. The molecular weight was determined to be $M_w=9600$ with $M_w/M_n=1.80$ by size-exclusion chromatography. The random copolymer was anchored to the native oxide surface of silicon substrates by annealing spin coated films under vacuum at 165 °C for 3 days. This allows the alcohol end group to diffuse to and covalently bond to the oxide surface. After rinsing with toluene, a well-defined, thin layer of PS-r-PMMMA having thickness of ~6 nm remained. Asymmetric PS-b-PMMMA was synthesized via anionic polymerization. The molecular weights of PS-b-PMMMA used in this study were 69,000, 73,400, and 109,000 g mol^{-1} with polydispersities of ~1.06. These copolymers are designated as 69 K, 73 K, and 109 K, respectively.

Films with thickness about the bulk period ($L_b$) of the block copolymers were prepared by spin casting solution of the block copolymers onto surfaces to which the random copolymer was grafted. Film thickness was measured with a Rudolph Research AutoES-1 ellipsometer using a helium-neon laser ($\lambda = 632.8$ nm) at a 70° incidence angle. The samples were annealed at 170 °C under vacuum for 2 days and then quenched to room temperature by placing the samples on aluminum plate. Deep UV exposure of the diblock copolymer films, followed by acetic acid rinsing was used to selectively remove PMMA and produce an ordered, nanoporous template.

The PDMS used in this work was made from Sylgard 184 (Dow Corning Corp.). A 10:1 ratio (w/w) of the liquid prepolymers and curing agent were mixed and allowed to cure at room temperature onto block copolymer template.

To apply an electric field the block copolymer template was coated with PDMS prepolymer and sandwiched between two 12.7 µm thick Kapton sheets that were coated on one side with 100 nm aluminum that served as the electrodes. The thickness of PDMS was controlled by Teflon spacer and a voltage of ~1800 V was applied for 3 days under nitrogen atmosphere. All the surfaces of PDMS which were in contact with the block copolymer templates were rinsed with hexane and ethanol several times after separating from the templates.

AFM images were obtained in both height and phase contrast mode using a Digital Instruments Dimension 3000 scanning force microscope in the tapping mode. Etched silicon tips on a cantilever (NanoProbe) with spring constants ranging between 40.0 and 66.0 N m^{-1} (as specified by the manufacturer) were used.

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Low-Temperature Fabrication of Efficient Porous Titania Photoelectrodes by Hydrothermal Crystallization at the Solid/Gas Interface

By Donghye Zhang, Tsukasa Yoshida,* and Hideki Minoura

Nanostructured porous films of titanium dioxide (TiO\textsubscript{2}) currently enjoy a number of important applications, for example, in photocatalysts,\textsuperscript{1,2} sensors,\textsuperscript{3} displays,\textsuperscript{4} batteries,\textsuperscript{5} and

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* Dr. T. Yoshida, Dr. D. Zhang, Prof. H. Minoura
Environmental and Renewable Energy Systems (ERES) Division
Graduate School of Engineering, Gifu University
1-1 Yanagido, Gifu 501-1193 (Japan)
E-mail: yoshida@aphchem.gifu-u.ac.jp