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Biomolecular Embossing

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This communication describes a process utilizing soft lithography, replica molding, and hot and cold embossing in the transfer of DNA texture into poly(ethylene terephthalate) (PET). The imprinting of biological structures may have useful properties in clinical platforms and microfluidics.[1−3] Replica molding has been principally developed by the groups at IBM[4] and Harvard,[5−7] with an imprinted height of <1 nm[8] being reported. Rogers and coworkers recently imprinted a single-walled carbon nanotube.[9] Detailed analysis of the imprinted template showed partial replication at the single nanometer scale. Hammond et al. have also fabricated nanostructures in polyurethane using polyelectrolytes to enhance the adhesion of the carrying substrate in the absence of poly(dimethylsiloxane) (PDMS) using soft lithography.[10] Doubled-stranded DNA has a diameter of 2.4 nm, yet heights measured using scanning probe techniques in ambient conditions are always lower, with even noncontact modes such as transverse dynamic force microscopy yielding values no greater than 1.6 nm.[11]

In this work, we replica-molded DNA immobilized on amino-silanized SiO_2/Si surface in PDMS and polyurethane (PU) and then embossed the biological imprint into PET. The procedure started with a PDMS mold composed of a 10-μm layer of *h*-PDMS spin coated on a 1-mm pre-set S-PDMS support. The composite elastomer was precured at 22 °C for 16 h against a silicon oxide plate and then placed upon a DNA template submerged in an evaporating water bath at 37 °C for 12 h. After evaporation, the mold was postcured for an additional 12 h at the stated temperature. Complete filling of the template was achieved by lateral diffusion of the prepolymer and conformal contact at the final stages of the molding cycle. The maximum resolution of 1−3 nm[9] was achieved at the very end of the curing process. The PDMS mold was washed for 12 h in a solution of 0.1% sodium dodecyl sulfate isopropyl alcohol and further dried for 24 h at 40 °C in a vacuum oven before use.

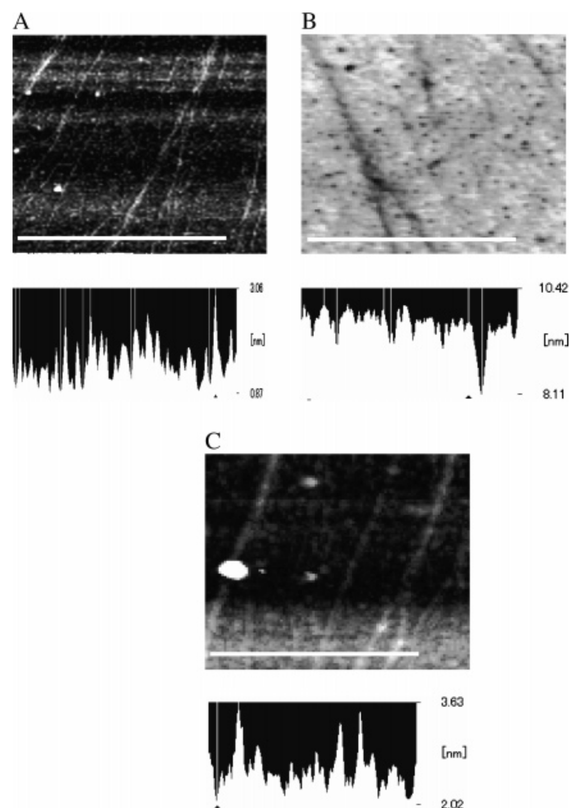

Figure 2. (A) Immobilization of λ DNA on a SiO_2/APS-coated substrate. Height range 0.88−1.83 nm. (B) Negative imprint in *h*-PDMS (0.61−1.51 nm). (C) Aged PU (150 °C) positive imprint (0.5−1.42 nm). Larger scanned images are available in the Supporting Information. Scale bar 2 μm.

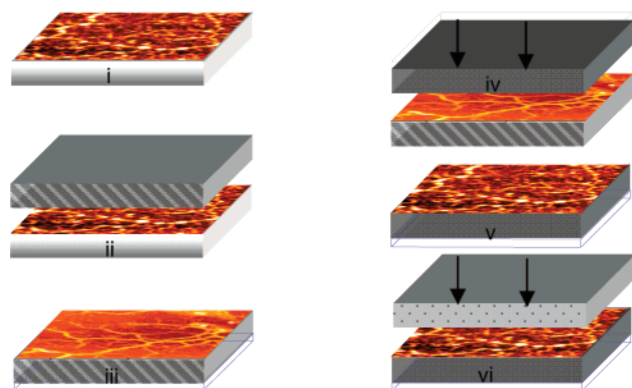

Figure 1. Schematic representation of the fabrication procedure. (i) Immobilization of λ DNA on APS-coated SiO_2. (ii) Replica molding of DNA in precast *h*-PDMS. (iii) Setting of the PDMS composite on a glass support. (iv) Dispensing of PU prepolymer on the PDMS replica, pressing, and UV curing through a quartz plate. (v) Removal of the PDMS, leaving a PU copy on a quartz substrate. (vi) Hot embossing of the PU replica into PET. The dimensions of the plates were 1 mm × 1 cm × 1 cm ($h \times w \times l$).

Figure 1 shows the procedures used in the transfer of the PDMS imprint, polyurethane replica, and PET copy. In short, a 10 μL drop of commercially available UV curable polyurethane (Norland 81) was placed on the hard PDMS set upon a glass support. A quartz plate was pressed on the PU for 15 min at 0.1 mPa, 40 °C. The viscosity of the PU prepolymer is significantly lower at the stated temperature, improving the filling characteristics of the prepolymer to the mold. The PU was then exposed to a UV source for 1 min through the quartz plate. The PDMS replica was carefully removed from the glass support using a technique reported previously.[12] Figure 2A shows the negative and positive imprints of λ DNA in PDMS and PU. The stability of the imprint was tested at 65, 120, and 150 °C for a total of 12 h.

Every 4 h, the mold was cooled to 22 °C and exposed to a UV source for an additional minute before being heated to the next temperature in an effort to prematurely age the polymer.

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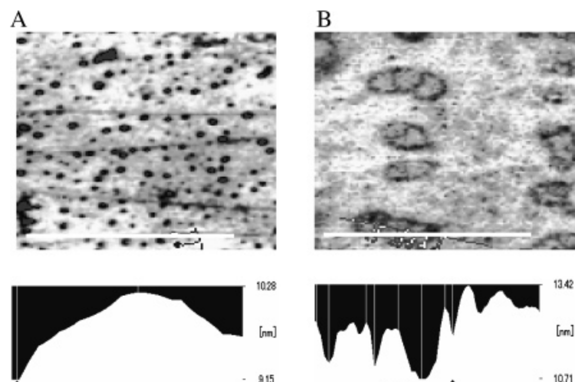

Figure 3. (A) Negative imprint of λ DNA in PET (0.3−1.30 nm). (B) Negative imprint of CT DNA embossed at 0.2 mPa for 10 min at 22 °C in PET (a low-density print was used). Scale bar 2 μm.

No significant change in the vertical height range of the DNA imprint was recorded. However, further exposure of the mold at 220 °C for 5 h resulted in a complete loss in the imprint morphology at the single nanometer scale, due in part to the dissociation of physical cross-links between the polyurethane chains at the surface of the mold.

The starting roughness (RA) of the PET was 1.83 nm with an RMS of 2.49 nm at 22 °C. Embossing was performed in two steps. A polyurethane replica set on a quartz support, cast from a fluorinated silicon master, was hot-embossed into a sheet of PET at 78 °C, 50 Pa, for 5 min and then cooled to room temperature.

After embossing, PET was separated from the PU replica by injecting isopropyl alcohol (IPA) between the two substrates. The preformed PET blanks were embossed again under the same conditions, reducing the surface roughness to 0.22 nm. Given that, a two-stage embossing cycle was adopted during the imprinting of the DNA replica. The injection of IPA between the stamp and replica minimizes distortion of the PU and PET.[12]

Figure 2 shows the negative and positive forms of the DNA imprinted in *h*-PDMS and PU. The vertical height range from all three scans is approximately 1 nm. The linear form of DNA is partially embossed in PET (Figure 3A). An embossing cycle using the intermediate glass transition temperature (78 °C) resulted in significant translocation via lateral diffusion and nonspecific chain−chain association, producing pockets of low (black spots) and high chain density (high resolution) with a peak-to-valley ratio (P−V) of 5.1 nm on the PET surface. In an effort to reduce this value, a polyurethane replica of a silicon surface was embossed again into another PET blank with the second stage of the cycle performed at temperature and pressure of 61 °C, 200 Pa for 5 min, well below the glass transition of the polymer. The resulting blank produced an RA value of 0.17 nm with a peak valley ratio (P−V) of 2.1 nm. The properties of PET are such that embossing of small structures such as DNA can be achieved at room temperature using pressures <1 mPa. This is demonstrated in Figure 3B in which the vertical impression of trapped calf thymus (CT) DNA texture is shown.

The surface stability of the polyurethane at temperatures <150 °C and the pressures utilized in this embossing process significantly extend the lifetime of the mold compared to conventional hot-embossing processes, realizing a replica volume >200 for PET from a polyurethane mold.

This work has indicated the potential of replicating a variety of DNA lengths and configurations into a polyurethane mold and the subsequent embossing of these structures into PET.

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Supporting Information Available: AFM images of immobilized imprinted templates of DNA, *h*-PDMS, PU, and PET. An additional schematic of the fabrication procedure. This material is available free of charge via the Internet at http://pubs.acs.org. The glass transitions of Norland (81) are available through the commercial Web site.

References

(1) Manz, Y.; Graber, N.; Widmer, H. M. *Sens. Actuators* **1990**, *B1*, 244−248.
(2) Chiem, N.; Harrison, D. J. *Anal. Chem*. **1997**, *69*, 373−378.
(3) Ramsey, J. M.; Jacobsen, S. C.; Knapp, M. R. *Nat. Med*. **1995**, *1*, 1093−1096.
(4) Schmid, H.; Michel, B. *Macromolecules* **2000**, *33*, 3042−3049.
(5) Xia, Y. N.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem Rev*. **1999**, *99*, 1823−1848.
(6) Odom, T. W.; Love, J. C.; Wolfe, D. B.; Paul, K. E.; Whitesides, G. M. *Langmuir* **2002**, *18*, 5314−5320.
(7) Thalladi, V. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 3520−3521.
(8) Qiaobing, X.; Mayers, B. T.; Lahav, M.; Vezenov, D. V.; Whitesides, G. M. *J. Am. Chem.* Soc. **2005**, *127*, 854−855.
(9) Hua, F.; Sun, Y.; Gaur, A.; Meitl, M.; Bilaut, L.; Rotkina, L.; Wang, J. F.; Geil, P.; Shim, M.; Rogers, J. A.; Shim, A. *Nano Lett*. **2004**, *4*, 2467−2471.
(10) Kim, Y. S.; Lee, H. H.; Hammond, P. T. *Nanotechnology* **2003**, *14*, 1140−1144.
(11) Round, A. N.; Miles, M. J. *Nanotechnology* **2004**, *15*, 176−183.
(12) Gates, B. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003**, *125*, 14986−14987.

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