Stamping Oriented Molecular Monolayers Using Liquid Crystal Inks

Robert Thompson, Cory Lund, Steven J. Hickman, Eric Krohn, David L. Patrick

Supplementary Information

Methods. The experimental system consisted of a stamp coated by 8CB (the 'ink') applied to a graphite substrate. 1.5 cm x 1.5 cm stamps were made from mechanically rubbed polyimide (PI) films on glass, grooved Si, or embossed poly(methylmethacrylate) (PMMA) (Figures S1A-C). Polyimide stamps were made by spin coating a polyimide precursor solution (PI 2556, HD Microsystems Inc.) onto clean Indium-Tin-oxide-coated glass, baking to polymerize, followed by rubbing of the cured film with a soft cloth. Biaxial polyimide stamps were made by masking half the film and rubbing the exposed area, then masking the just-rubbed area and rubbing the remaining portion in an orthogonal direction.

PMMA stamps were embossed from Si masters by affixing a PMMA slab with a spring-loaded clamp to the Si master and placing in a 170 °C oven for several minutes (Figure S1D). Embossing produced a replicate on the PMMA surface having the same pitch as the Si masters, but with a sinusoidal profile and shallower groove amplitude of ~20 nm (Figures S1E-H). Si masters were fabricated from <100> oriented single crystals, with a photolithographically defined vertical sidewall groove pattern produced by carbon hexafluoride plasma etching. Grooves were 150 nm deep x 625 nm wide, with a pitch of 2.25 μm (Figures S1E and S1F).

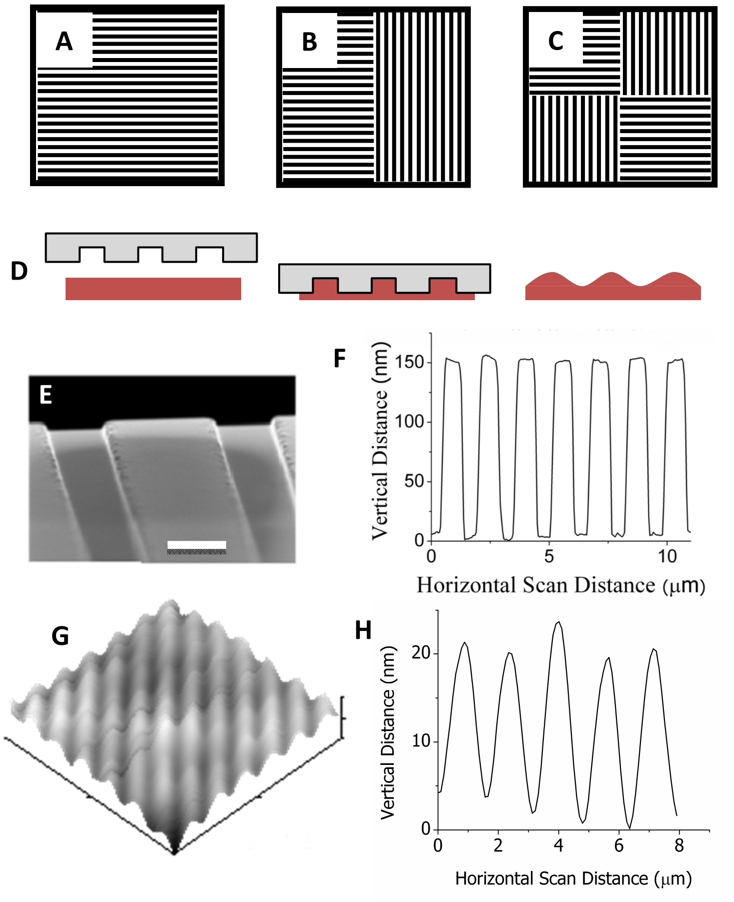

Figure S1. (A-C) Three anchoring patterns were investigated using rubbed PI, embossed PMMA, and Si stamps. Anchoring was planar on all stamps, with lines indicating the orientation of the easy axis. (D) Uniaxial PMMA stamps were made by embossing from a Si master. (E) SEM image of the edge of a Si stamp. Scale bar is 0.625 μm. (F) AFM cross section of a Si stamp. (G) AFM image (15 x 15 x 0.072 μm) of a PMMA stamp with (H) cross-sectional profile.

Films were deposited by gently pressing the inked stamp against a 1.2 x 1.2 cm highly oriented pyrolytic graphite (HOPG) substrate (Advanced Ceramics Inc., ZYB-grade), heating to 100 °C for 2 minutes to erase any memory effects from the initial contact of the stamp, and allowing the assembly to gradually cool to room temperature. Experiments probing the effect of cooling rate between 0.1 – 10 °C sec^{-1} showed it did not significantly affect the results. Although the stamp was nominally in direct contact with the substrate, as a result of surface roughness, the presence of dust particles, and the slow drainage of excess fluid from the gap, we estimate the average separation of the stamp and substrate was 10 – 20 μm, with the gap completely filled by LC. Some additional experiments employing gaskets to maintain a minimum gap size were also performed, but it was found that the best results were obtained with no gasket, using the smallest practical gap size.

Before removing the stamp, selected films were inspected by polarizing optical microscopy, which was used to image the ink layer through transparent PMMA and PI stamps. The ink was observed to align with planar orientation, with the director generally parallel to the local anchoring axis of the stamp. Judging from the observed textures, PI stamps produced the best alignment, with PMMA producing LC layers that were slightly less well ordered. This trend was also mirrored in the measured surface order parameters.

Additional Orientational Data.

Additional results from films deposited using uniaxial Si and embossed PMMA stamps are presented in Fig. S2.

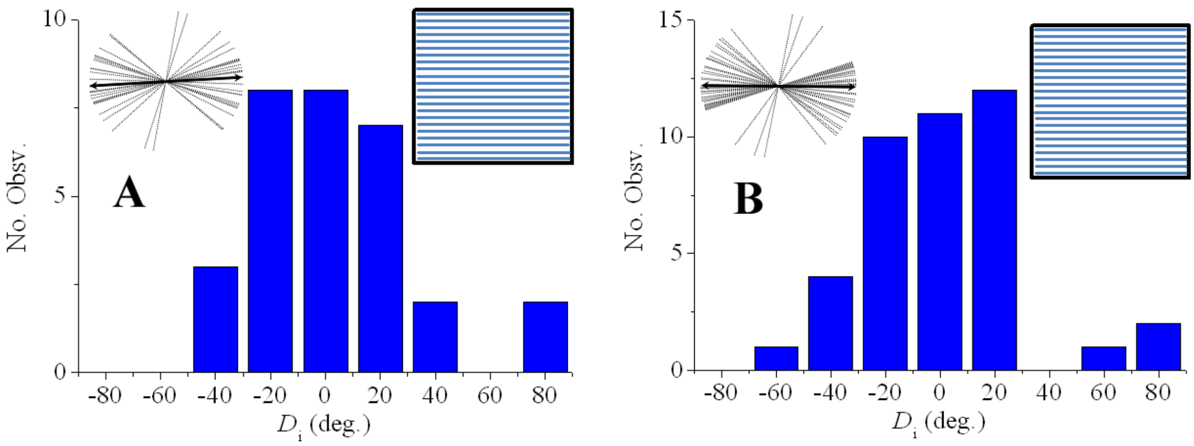

Figure S2. Distributions of the orientations of the highest symmetry axis $\vec{D}_i$ in 8CB monolayers on HOPG deposited with (A) a uniaxial Si stamp, (B) a uniaxial PMMA stamp. Each dotted line in the inset represents a single STM observation, with the thick arrowed line showing the average orientation.