

Supporting Information

Ion-modulated flow behavior of layer-by-layer fabricated polymer thin films

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Experimental

Poly(diallyldimethylammonium chloride) (PDAC, Mw 200-350 kDa), and poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSMA, Mw 20 kDa) were obtained from Aldrich and used as received to prepare polymer thin films in 2 mg/mL with a 0.3 M or 0.6 M NaCl or NaBr concentration.

Polymer thin films were fabricated by manual dipping. Polymer deposition time was 10 min. The films were rinsed with water between depositions of polymers with opposite charges. Finally, the as-prepared polymer thin films were rinsed with water to remove the surface adsorbed salt.

Several drops of water were placed on the patterned poly(dimethylsiloxane) (PDMS)

stamp, onto which the silicon wafer with films was placed. The whole sample was turned upside down and maintained for a few hours to allow water evaporation. The stamp was then peeled off gently.

AFM images were collected using a Veeco Dimension AFM in a tapping mode. Silicon tips with a resonance frequency f_0 of 150 kHz and a spring constant of 20N/m were used. The scanning frequency was 0.8 Hz. The contact force between the tip and the samples was kept as low as possible. To measure the elastic modulus of a film, a triangle 100 nm cantilever with a force constant of 0.09 Nm^{-1} and an integrated silicon nitride (Si_3N_4) tip was applied. Then the elastic modulus was measured via using the force-deformation curve during loading and unloading. Water contact angle tests were conducted with a VCA Optima XE system at room temperature using a water droplet with a volume of 2 μL . The thickness of the polymer thin film was measured by a variable-angle spectroscopic ellipsometer (model VASE; J. A. Woollam Inc., Lincoln, NE).

Flow behavior of thin films:

In order to demonstrate the flow behavior of thin films, we measured the thickness of as-prepared thin film and the cross-section profiles of patterned film using AFM. As shown in Fig. S1, the thickness of the as-prepared thin film is about 48 nm which is quite similar to the ellipsometry result.

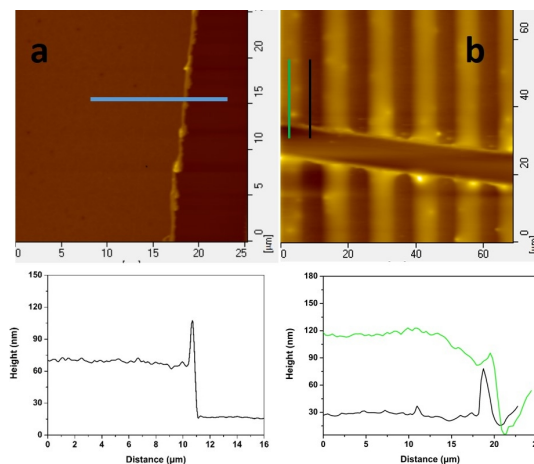


Fig. S1 SFM image of polymer thin films assembled in Cl^- ion solutions. (a) the as-prepared film thickness (b) water induced patterns of polymer thin films. Lower is their corresponding line profiles.

We scratched some films along the perpendicular direction of the linear patterns (Fig. S1b). The total heights of the patterns (difference between non-contact areas of the films and silicon substrate) are about 120 nm (the blue line), which are much larger than the as-prepared thickness of the films (~ 48 nm). The thickness of the films in the contact areas, in other words, the thickness of the polymer thin films that remain after they moved, is about 20 nm (difference between contact areas of the polymer films and silicon substrate) shown by the black line, which is much smaller than the thickness of the as-prepared films. Thus, the decreased height of the multilayers in the contact areas is around 28 nm, while the increased height of the films in the non-contact areas is around 70 nm. This result clearly reveals the wet PDMS stamp causes the films move from contact areas to non-contact areas, and patterns are formed by the flow of the films instead of imprint in the Z direction. If the patterned structures are caused by imprint, the pattern heights should still keep the same as the thickness of as-prepared films. In our case, the films in the contact regions of the stamp are obviously pushed to the non-contact regions under the capillary force. Therefore, the pattern structures are formed clearly by flow of the films from the contact regions to non-contact regions.

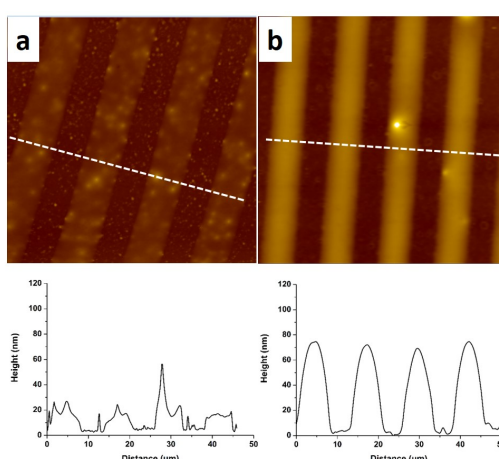


Fig. S2 AFM images of induced patterns by the flow of polymer thin films assembled in Br⁻ ion solutions (a) and (b) in Cl⁻ ion solutions. Below are corresponding line profiles.

In order to investigate the effect of ion concentration on flow behavior of the film,

we carried out experiments of films assembled in a lower ion concentration (0.3 M). Fig. S2 still showed this "high flow" behavior of films assembled in Cl⁻ ion solutions is clear since the ratio of pattern heights to film thickness can reach up to 2.4. While "low flow" behavior of films assembled in Br⁻ ion solutions is revealed by the ratio of pattern heights to film thickness which is only 0.41. Results showed this is really an ion specific effect not an ion concentration effect.