Supporting information

1. Micro-imprinting lithography

The spin-coated P4VP/PS bilayer was topographically patterned with the micro-imprinting apparatus developed in our laboratory. The schematic of the imprinting equipment is shown in Figure S-1. The heater is located beneath a metallic sample stage with the temperature range from room temperature to 300 °C. The bilayer on a substrate fixed on the sample holder moves upward by the moving stage connected to a micro-motor. **We used elastomeric PDMS molds fabricated by casting a PDMS precursor (Sylgard 184, Dow Corning Corp) on a photoresist master. We used a 10:1 (by weight) mixture of PDMS precursor and curing agent that had been degassed under vacuum. The photoresist master was patterned by standard photolithography, and we fluorinated the surface before casting the PDMS precursor on the master. After the PDMS precursor was cured at 40□ for 24 h, the mold was separated from the master.** When the conformal contact is formed with a poly(dimethylsiloxane) (PDMS) master pattern, the temperature is raised above the glass transition temperatures of both polymers (150°C). The load cell (maximum load: 2 kg) located above the master pattern holder controls the pressure applied during micro-imprinting. The pressure applied depends on both the load and the contact area of the micropattern on the bilayer. The pressure used is approximately 156800 Pa.

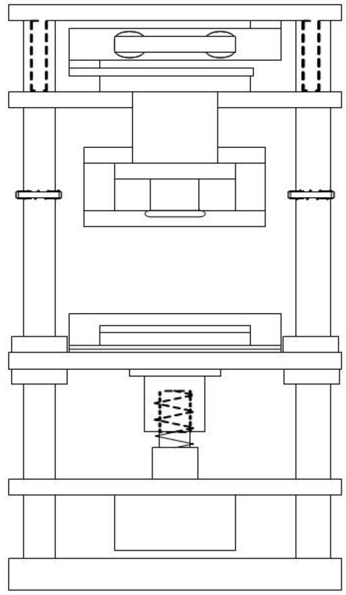

Figure S-1

2. Capillary flow at the edge of the micropattern

Punched bilayer film was examined by AFM in height contrast. As shown in Figure S-2a, the surface profile of the inset of Figure 2a shows that height difference between the elevated regions and the punched ones is approximately 250 nm and the surface of the punched regions looks flat. When P4VP layer was selectively removed by ethanol (Figure S-2b) the punched regions clearly exhibit the parabolic surface profile where punched pattern boundary is thinner than center. It confirms **the local capillary flow at the vicinity of pattern boundary** during micro-imprinting.

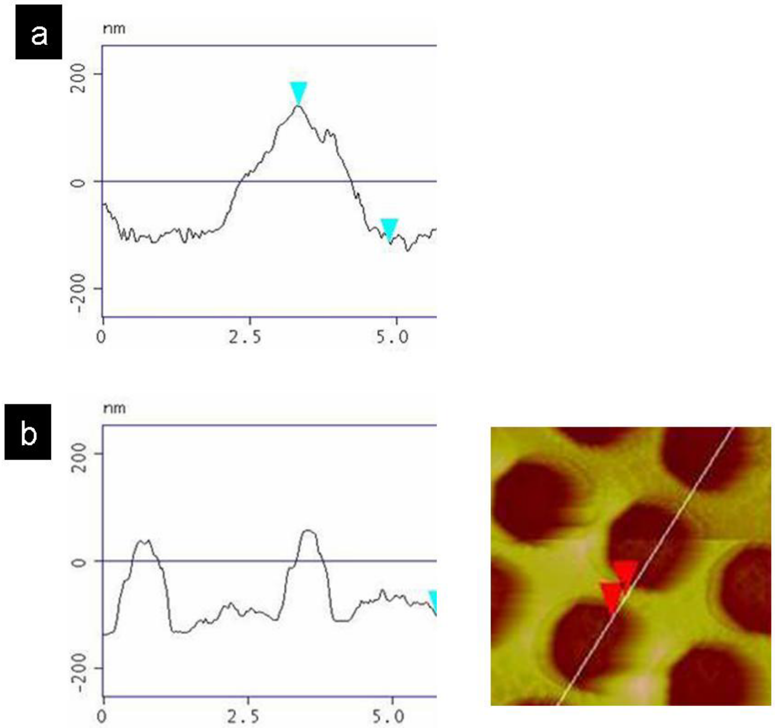

Figure S-2

3. Partial layer inversion

We confirmed the partial layer inversion by examining pattern structures after selective etching of P4VP layer with ethanol as a function of heat treatment time. Within a few minutes of heat treatment at 250°C dewetting of P4VP layer began and micropattern structure shown in Figure 2c was obtained. We took out the sample and dissolved P4VP selectively with ethanol. As expected in Figure 1 (selective dewetting step), the top P4VP layer in the thicker regions and hemi-spherical P4VP domains were all removed (S-3a). The microstructure of a sample treated with ethanol is shown in Figure S-3b after prolonged heat treatment at 250°C to have partial layer inversion occur. As expected in Figure 1 (selective inversion step), only top P4VP layer in the thicker regions was removed while hemi-spherical structure was preserved, which indicates that the partial layer inversion occurred selectively in the thinner regions.

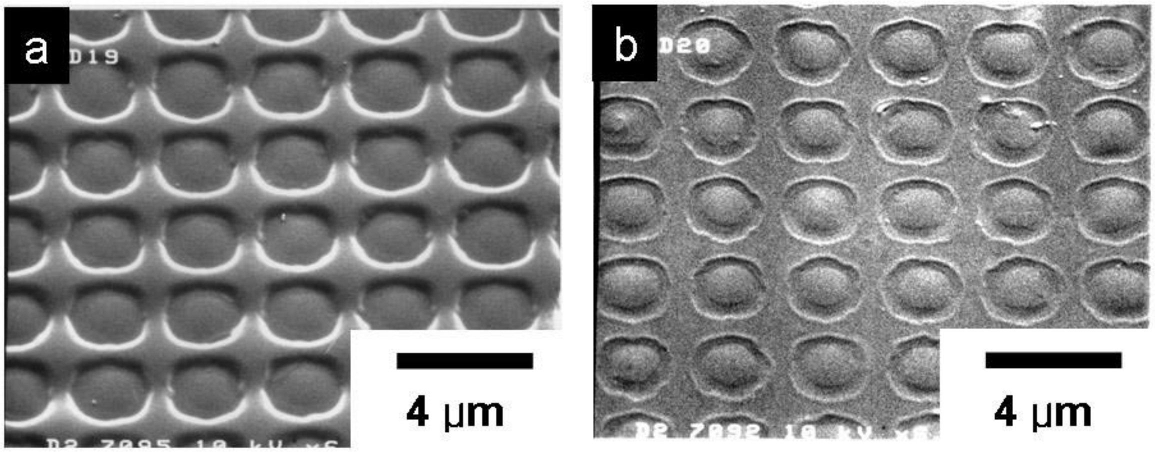

Figure S-3

4. Dynamics of dewetting

We have performed three sets of experiments: (1) change of top P4VP film thickness on the constant thick PS layer, (2) variation of the relative film thickness with the total bilayer thickness fixed and (3) change of the total bilayer film thickness with the thickness of the two individual layers kept same.

Figure S-4 shows the dewetting speed of P4VP layers on PS surfaces as a function of P4VP film thickness. We used the same thickness of PS for three different thicknesses of P4VP. Dewetting speed (hole growth) increases with decreasing film thickness, which is consistent with theoretical prediction and experimental results of previous works. [1,2] Consequently, in our case, the dewetting is initiated at the boundary of micropatterns where film thickness is thinner than other area and develops intermediate patterns during the whole dewetting process. We also prepared a thin P4VP film whose thickness is comparable with that of the elevated regions in our micro-imprinted bilayer (~ 250 nm). Under the conditions used for controlled bilayer dewetting and partial layer inversion (at 250 °C for 100 h) the film did not show any changes, which implies that only thinner parts of the imprinted pattern undergoes the dewetting and partial layer inversion in our experimental conditions.

We also performed another set of dewetting experiments where the relative film thickness was varied with the total bilayer thickness fixed. We fixed the total bilayer thickness of 250 nm similar to that of the elevated regions in the micropatterns and changed the relative thickness from 50 to 200 nm. The dewetting of P4VP layer mainly depended on the thickness of the top P4VP layer. The dewetting occurred when the thickness of the P4VP was below approximately 100 nm under the same experimental conditions used in the current manuscript. In addition we changed the total bilayer film thickness with the thickness of the two individual layers kept same. Again, the dewetting was kinetically governed, which implies that our controlled micropatterns are kinetically driven and vitrified at temperature below T_g of the two polymers.

1. F. B. Wyart, P. Matin, C. Redon, Langmuir, 9, 3682 (1993)

2. S. Qu, C.J. Clarke, Y. Liu, M. H. Rafailovich, S. Sokolov, K. C. phelan, G. Krausch, Macromolecules, 30, 3640 (1997)

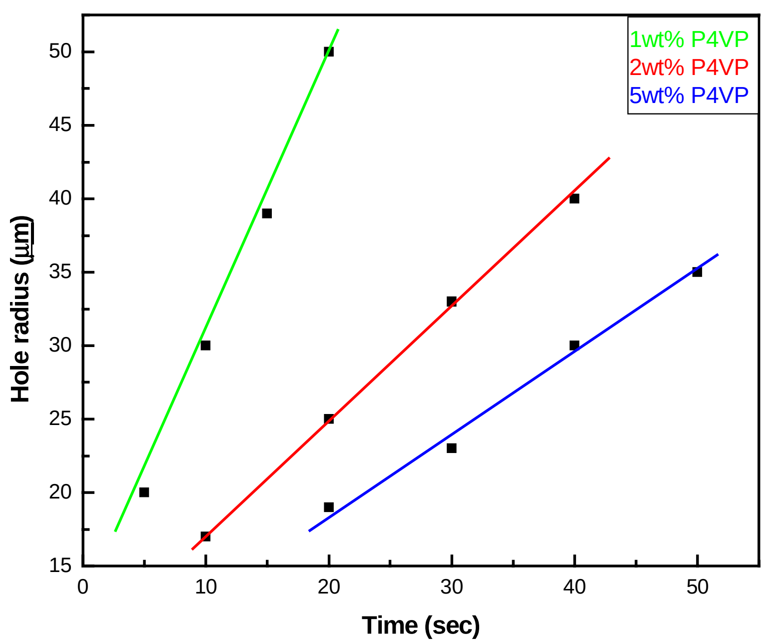

Figure S-4