Electronic Supplementary Material (ESI) for Soft Matter

The Dominant role of the Solvent/Water Interface in Water Droplet Templating of Polymers

Supplementary Methods Part 1: Experimental apparatus

A detailed description of the apparatus and procedure used to induce droplet condensation, control and monitor the flow rate and relative humidity of a nitrogen-rich stream to the flow chamber while also monitoring the contact angles of the condensed droplets was provided in the supporting information of a previous publication [21].

Modifications to this equipment for the work involved in this publication include a fitting to allow temperature recording of the solvent or polymer solution during evaporation and incorporation of a mass balance to record the rate of evaporation. Fine gauge type K thermocouples from Omega were fitted when monitoring the evaporating solution temperature. Data acquisition was achieved using a National Instruments junction box and Labview. Calibration was carried out for each thermocouple prior to use. Incorporation of a mass balance is shown in Figure S1. A new flow chamber was designed for this work and constructed with the Eden250 3D printer from Objet. This was partially inserted into an Adventurer Pro mass balance from Ohaus as indicated in Figure S1. A separate sample holder was placed on the pan of the balance that protruded into the flow chamber without contacting the sides. The sample is dosed through a port in the chamber lid and the mass is recorded through a direct RS232 connection to a laptop. Separate timings are recorded to allow correlation to the humidity and temperature readings. The dashed lines in Figure S1 indicate a large plastic covering to shield the balance while in the fume hood. This ensured the local extraction did not affect the measurements. Prior to an experiment, a test was carried out at the targeted flow rate to ensure there was no effect on the mass reading.

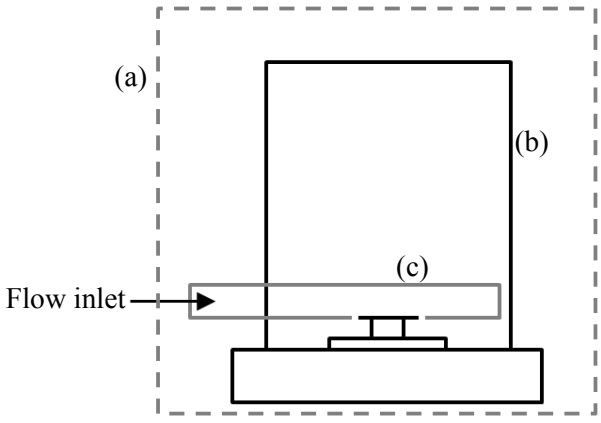

Figure S1: A flow chamber was designed to fit within a mass balance and allow the recording of the solvent mass loss during polymer film formation. The flow inlet is indicated into the chamber. (a) shows the covering to protect the balance from air flows and allow accurate measurement, (b) shows the mass balance, (c) shows the flow chamber designed to allow a sample to protrude into the base without contacting the chamber walls.

Supplementary Methods Part 2: Focused ion beam (FIB) milling

The following is a summary of the preparation technique developed for the scanning electron microscopy (SEM) and focused ion beam (FIB) milling work on the porous polymer films.

The polymer film delaminates from its glass substrate very cleanly using a sharp blade wet with clean water. This ensures minimal mechanical damage to the material. An initial, manual cross-section is carried out by snapping the sample rather than tearing. These small sections are prepared for SEM by attaching to a conductive carbon tab that is in turn fixed to a metal disc and adhered with a conductive paste to an SEM pin-stub. A Cressington Sputter Coater, Model 208HR, was use to deposit palladium onto the polymer samples to improve imaging and cross-sectioning. Normally approximately 25 nm of metal were deposited.

Supplementary Methods Part 3: Reduction in relative humidity during film formation

The following sequence of microscope images shows the video evidence of water droplets evaporating upon a reduction in the relative humidity of the local nitrogen stream, leaving no final structure imprinted in the polymer. This was carried out with a solution of dicarboxy-terminated polystyrene at approximately 3.8%w/w in toluene. One of the droplets is marked with a red arrow to allow ease of comparison across the images.

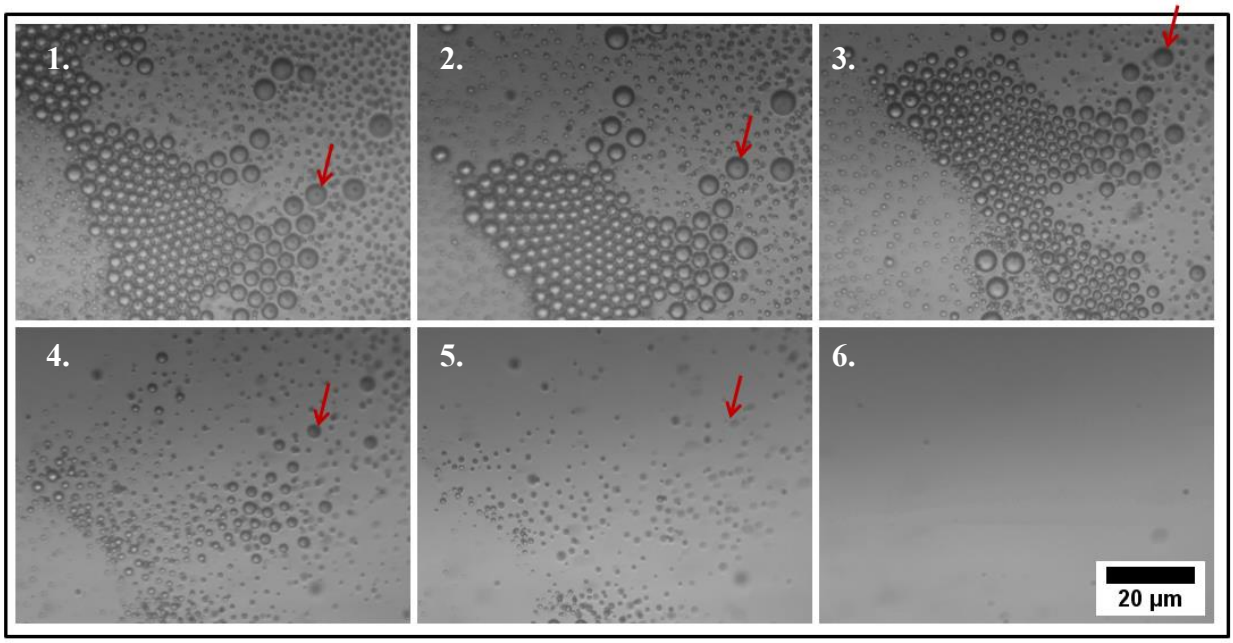

Figure S2: The sequence of images 1-6 shows the evaporation of a raft of water droplets from the surface of a toluene-polymer solution upon reduction in the environmental relative humidity. The red arrow in images 1-5 indicates the same droplet over time, allowing the evaporation to be visualized. The final image, 6, shows that the surface recovers and no structure is imprinted.

Supplementary Methods Part 4: Dilation of pore openings

The sequence of microscope images shown in Figure S3 shows the video evidence of dilation of pore openings. They are taken in the final seconds of the droplet trapping and pore drying. The image in Figure S3 (4) has a white border around the pore openings. This optical effect occurs only after the water has evaporate from the pore, leaving behind the imprinted shapes. This experiment was carried out with a solution of dicarboxy-terminated polystyrene at approximately 3.8%w/w in toluene and a section of the video is also provided in the supporting information.

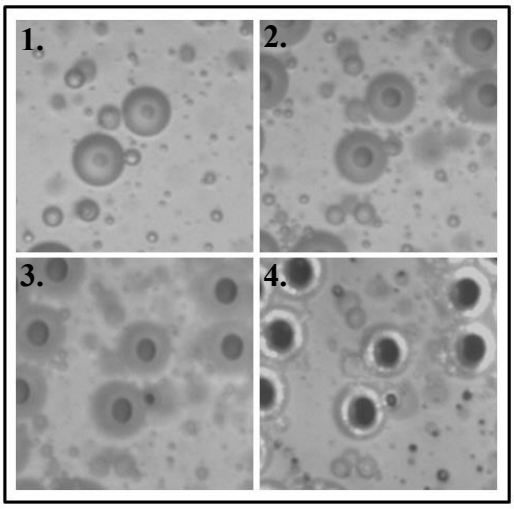

Figure S3: The sequence of images 1-4 shows the dilation of pore openings during the final seconds of pore formation and drying when using a toluene-polymer solution.

Supplementary References

21. Daly, R.; Sader, J.E.; Boland J.J. Langmuir 2012, 28, 13218.