

Supporting Information

Non-close-packed Breath Figures via Ion Partitioning Mediated Self-Assembly

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Experimental

Materials and preparation

Linear polystyrene (Molecular mass = 192,000 g/mol) (Sigma-Aldrich), chloroform (TEDIA), toluene (Fisher Scientific), hydrogen bromide (HBr) solution (33 wt. % of HBr in acetic acid, Sigma-Aldrich) and glacial acetic acid (AcOH) (J. T. Baker) were used as received. Glass substrates (Deckgläser Cover Glasses, 22 mm × 22 mm, thickness = 0.13 - 0.16 mm) were used as received. For surface potential imaging of the film, a Bruker SCM-PIT probe was used as received.

Polystyrene was dissolved according to the composition stated in Table S1 in a mixture of chloroform and toluene (volumetric ratio is 9:1) to obtain solution **Y**. Solution **Y_{AcOH}** and **Y_{HBr/AcOH}** were made by adding AcOH and HBr solution into solution **Y** respectively. Concentrations of acid components in the final polymer solutions are listed in Table S1.

Table S1. Composition of solution **Y**, **Y_{AcOH}** and **Y_{HBr/AcOH}**.

	Polystyrene[M]	HBr[M]	AcOH[M]
Solution Y	3.0×10^{-4}	-	-
Solution Y_{AcOH}	3.0×10^{-4}	-	3.2×10^{-3} ^{a)}
Solution Y_{HBr/AcOH}	3.0×10^{-4}	8.6×10^{-4}	2.3×10^{-3}

^{a)}[AcOH] used in solution **Y_{AcOH}** is equivalent to the summation of [HBr] and [AcOH] in solution **Y_{HBr/AcOH}**.

Chemicals listed above are dissolved in a solvent mixture of chloroform and toluene whereby the volume ratio is 9:1.

Experimental Methods

The setup was kept in a controlled environment chamber equipped with a humidity controller (ETS dual control 5200). Ambient conditions were monitored using a hygrometer (Traceable, Fisherbrand Scientific, America) during casting at stable relative humidity ($90.0 \pm 1.0\%$) and room temperature (24 ± 1 °C). Static casting was performed for solution $Y_{\text{HBr/AcOH}}$, Y_{AcOH} and Y onto a glass substrate (Deckgläser Cover Glasses, thickness= 0.13 – 0.16 mm) floating on a water bath surface. Polymer solution (30.0 μl) was drop cast onto the glass substrate and left to dry. Care was taken to minimize external disturbance to the setup during drying of the film.

Note: Ambient relative humidity (RH) should stay within $\pm 1.0\%$ range even though casting is performed close to the water surface. Our experimental results are in line with other reports on breath figures, pointing out the sensitivity of BF patterning towards RH.¹⁻⁴ We found that for $> 91\%$ ambient RH close-packed pores begin to appear, and for $< 89\%$ ambient RH only sparse population of pores can be found.

Infrared Imaging

Solution $Y_{\text{HBr/AcOH}}$ was cast at the same time onto two floating glass substrates of different thickness: Deckgläser Cover Glasses (thickness = 0.13 mm – 0.16mm) and Sail Brand Microscopic Slide (thickness = 1.0 mm – 1.2 mm). Thermal profile of the casting solutions were taken at 3 second intervals using an IR thermal camera (Fluke TI-55). IR emissivity of the casting solutions were taken to be 0.98 (approximated to that of water).

Microscopy

Images of the porous films were obtained using an optical microscope (polarizing metallurgical microscope Olympus BX51 and Olympus SC30 digital camera), and scanning electron microscope (JEOL LV 6360LA).

The casting experiment was performed on the stage of the microscope (Olympus BX51). We observed in the casting of $Y_{\text{HBr/AcOH}}$ that the initial inter-droplet distance was greater than the equilibrium inter-droplet distance D , by at least 1.5 times with no ordered distribution pattern (droplets nucleated randomly).

Analysis

The images were analyzed using ImageJ (Fiji) software to obtain the sizes, separations and radial distribution function plot of the pores. Assuming perfect circles, pore diameters were approximated from pore area measurements. Pore pairs were determined through the Delaunay function in ImageJ (Fiji) before deriving the separation distances. Voronoi analysis was done with the aid of Wolfram Mathematica 9 software and ImageJ (Fiji) software.

Characterization

For atomic force microscopy (AFM) characterization of the pore arrays, polystyrene films were peeled off the glass cover slips and electrically grounded using conductive copper adhesive tape. Under ambient conditions, the film surface was scanned via tapping mode AFM to obtain the film topography. Surface potential (SP) imaging was performed in LiftMode at a tip height of 10.0 nm above the film surface. Both tapping mode AFM and SP imaging were performed using a Dimension ICON Atomic Force Microscope (Bruker).

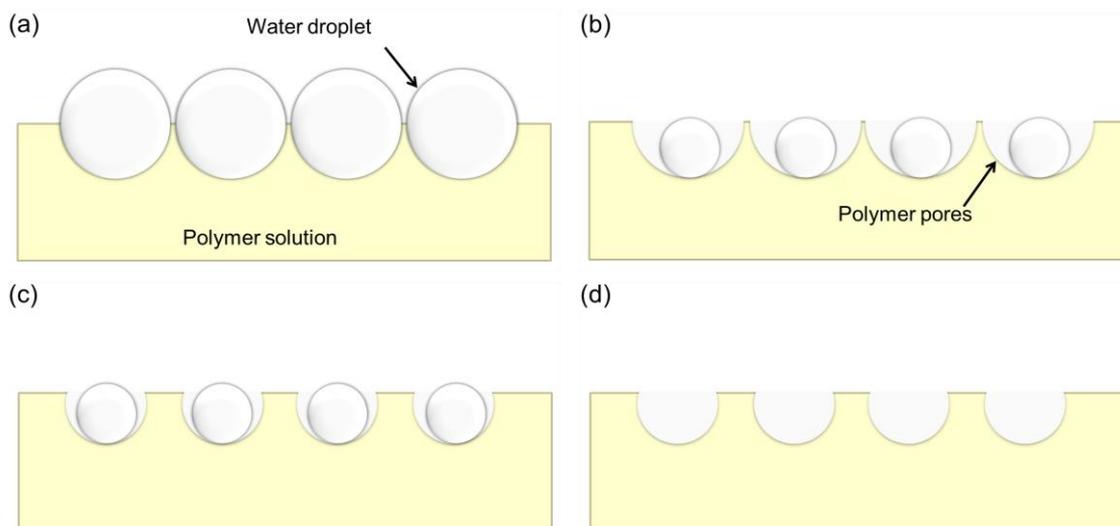


Figure S1. Formation of NCP pore patterns via thermal reversal of BFs requires: evaporation and shrinkage of water droplets (a–b) and shrinkage of pores along with these droplets (b–c) before the solidification of polymer solution (d).

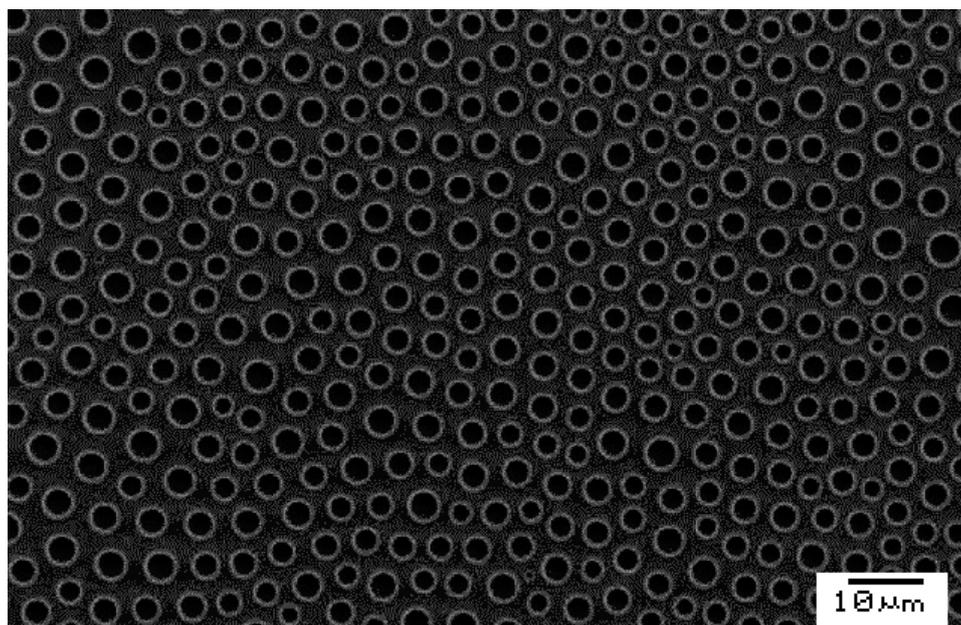


Figure S2. SEM image of pores formed from solution with polystyrene dissolved in only chloroform (i.e. without toluene).

References

- (1) Maruyama, N.; Koito, T.; Nishida, J.; Sawadaishi, T.; Cieren, X.; Ijio, K.; Karthaus, O.; Shimomura, M. Mesoscopic patterns of molecular aggregates on solid substrates. *Thin Solid Films* **1998**, *327*, 854-856.
- (2) Böker, A.; Lin, Y.; Chiapperini, K.; Horowitz, R.; Thompson, M.; Carreon, V.; Xu, Ting.; Abetz, C.; Skaff, H.; Dinsmore, A. D.; Emrick, T.; Russell, T. P. Hierarchical nanoparticle assemblies formed by decorating breath figures. *Nature Materials* **2004**, *3*, 302-306.
- (3) Peng, J.; Han, Y.; Yang, Y.; Li, B. The influencing factors on the macroporous formation in polymer films by water droplet templating. *Polymer* **2004**, *45*, 447-452.
- (4) Cui, L.; Peng, J.; Ding, Y.; Li, X.; Han, Y. Ordered porous polymer films via phase separation in humidity environment. *Polymer* **2005**, *46*, 5334-5340.