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Supporting Information

A facile approach for the fabrication of 2D supermicelle networks

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Methods

1. Preparation of Ultralong micelles

Amphiphilic block copolymer, polystyrene-b-polyethylene oxide (PS-b-PEO), with total molecular weight 23.5 kg mol^{-1} (16.0-7.5 kg mol^{-1}, polydispersity index (PDI=1.09) was purchased from Polymer Source, Inc. and used without any further purification. 1,1'-dioctadecyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate (DiI) was purchased from Sigma-Aldrich and used as the fluorescent dye for copolymer micelles. The detailed preparation of cylindrical micelles by evaporation-induced self-assembly method have been reported elsewhere.[1] By using this method, we can obtain the ultralong cylindrical micelles as shown in Fig. S2. The micelle solutions with a concentration of 0.1 mg/ml were used throughout this study unless specifically noted.

2. Fabrication of PDMS stamp

First, a silicon template was made by the deep reactive ion etching technique. For preparing poly(dimethyl siloxane) (PDMS) stamp, prepolymers and curing agent (Sylgard 184, Dow Corning Co. Ltd.) were mixed with a weight ratio of 10:1. The mixture was degassed under vacuum for 2h to eliminate the air bubbles inside and then poured onto the silicon wafer. Before baking at 68°C for 24h, the mixture with silicon wafer was degassed again for 0.5h to get rid of bubbles formed during pouring process. Then, the prepared PDMS stamp, which has a pattern of square pillars with sizes of 3.5×3.5×3.0μm (length×width×height, i.e. l×w×h) and 2.0μm of gaps (See Fig. S1) was peeled off from silicon wafer and immersed in a bath of ethanol for 16h to remove unreacted compound and dried in the air.

Size and spacing of micropillars may affect the formation of air cushions and liquid bridges between the pillars during the passage of the drop on pillar tops (dewetting) and consequent deposition of aligned micelles. The protocol was tuned by using various pillar sizes and

shapes as depicted in Table S1. Basically, for a fixed concentration of 0.1 mg/ml micelle solution, simply inspection of micelle alignment, branching and coverage of the stamps of various sizes and shapes, indicated which ones were suited for this study.

Original choices for pillars sizes and shapes were, however, made with basis on previous studies that consider two competitive forces on the formation of liquid bridges between two adjacent pillars. [2] One is the capillary force, F_c, and the other one is the structural cohesive force, F_s, of non-Newtonian fluids. Following the previous study,[2] when the sizes of pillars and gaps are appropriate such that these two forces match each other, a good alignment of the micelles can be achieved during dewetting. Furthermore, squared pillars are shown to enhance or direct micelles stretching (Fig. 2) as compared to circular ones (stamp 2).[3]

3. Alignment of ultralong micelles

20μl of micelles solution was deposited on the edge area of the stamp pattern. And then, by using a lens tissue to drag the micelles solution, the wetting process can be controlled resulting in the well-aligned micelles array on top of micro-pillars. After alignment, the stamp is called "inked stamp" in this study. The mechanism of this alignment is similar to Lee's study [4, 5], in which DNA nanowire array was patterned on micropillar-structured surface. Here, we need to notice that the concentration of micelles plays an important role in the formation of micelle array during alignment process. As shown in Fig. S3, with reducing the concentration of cylindrical micelle solution, a decrease in the density of micelles aligned on PDMS stamp was observed.

4. Transfer printing of aligned micelles onto receiver substrate

Following dewetting, visual inspection of the stamp was performed to ensure that no extra water droplet was present on the stamp and the micelles were then immediately transferred to glass without any further drying. The inked stamp was brought into contact with the receiving substrate, such as glass slide, and gently pressed to make sure that stamp was placed in conformal contact with the substrate. And then, the stamp was slowly peeled off to leave the micelle arrays on the receiver substrate. After printing the single layer of micelle arrays, the second layer of micelle arrays will be printed perpendicularly to the first one using the same protocol.

5. Characterization

The patterns of PDMS stamps were investigated by scanning electron microscopy (JEOL, 6010, Japan) at an accelerating voltage of 5.0kV.

Confocal fluorescence imaging was performed using a Laser scanning confocal microscopy (LSM 710, Carl Zeiss Microscopy GmbH, Germany) with a Fluar 40×/1.30 oil M27 objective lens. The dye, Dil, was excited using a HeNe laser operating at 543nm. In order to measure the lengths of these ultralong micelles, a dilute micelle solution (0.01mg/ml) was drop-casted onto a glass slide. After analysis of 500 micelles with software ImageJ, the distribution of micelle lengths can be obtained.

For the observation and analysis of the micelles' thermal fusion, atomic force microscopy (AFM) experiments were performed on an NT-MDT (NTEGRA) microscope with NT-MDT HA_NA tips (resonance frequency around 240kHz). The accessary, heating stage, was used to control the sample temperature during measurements. After printing, samples were left to

dry in the air for at least 24h up to few weeks before heating process. Similar results were found in all cases. All the images were recorded in tapping mode in the air at different temperatures. Before measurements, the samples were equilibrated for 0.5h at each temperature. To obtain the micelle structure by AFM, 50µl micelle solution was placed on a small piece of silicon wafer, which was treated by plasma for 140s, followed by spin coating at 2000rpm. Then, tapping mode was used to measure the micelles in the air.

Differential scanning calorimetry (DSC) analysis of PS-b-PEO was conducted on a PerkinElmer Thermal Analysis instrument. PS-b-PEO copolymer (~11mg) was carefully loaded into a preweighted aluminum pan with cap. A heating rate of 10°C/min was used to obtain DSC thermograms with an empty pan as reference.

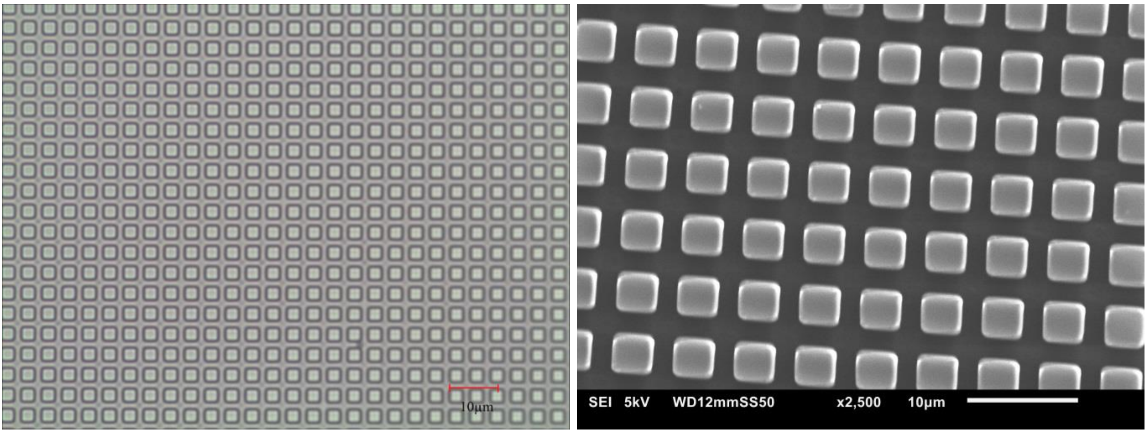
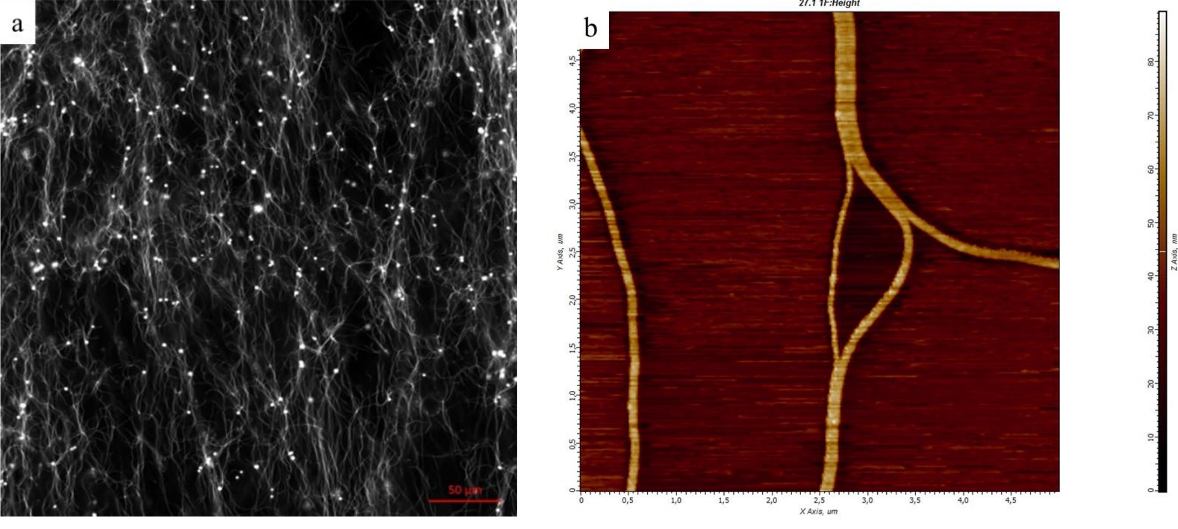


Figure S1. Optical microscopy image and SEM image of PDMS stamp (3.5×3.5×3.0µm, l×w×h).



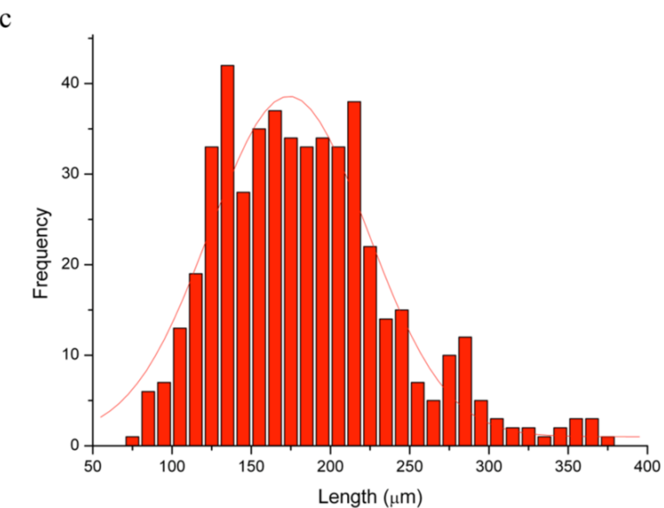


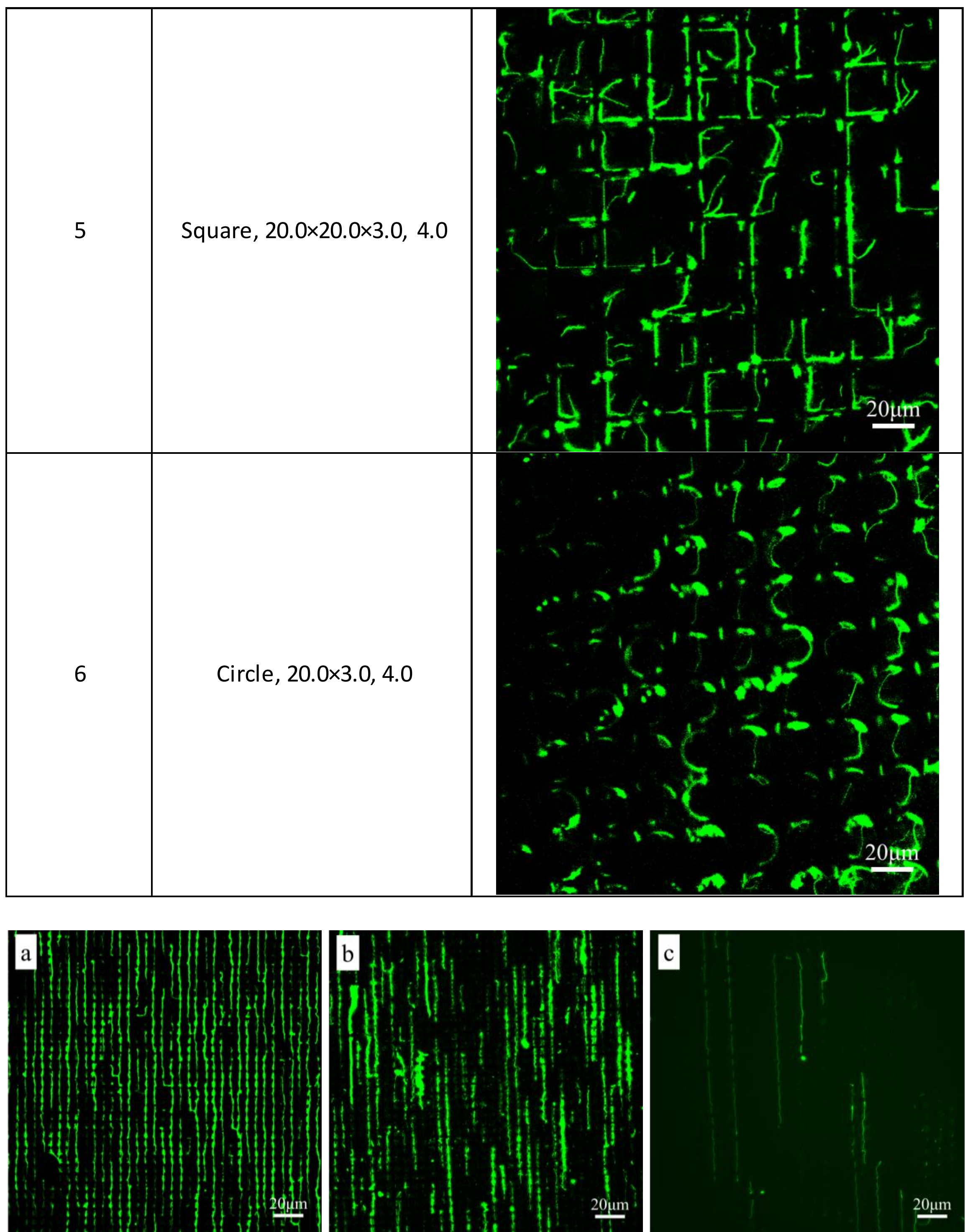
Figure S2. Morphology and length distribution of micelles from a solution of concentration of 0.1mg/mL as used throughout this study (unless specifically noted). (a) Confocal microscopy image of cylindrical micelles in solution; (b) AFM image of cylindrical micelles spin-coated on silicon wafer; (c) Statistical histograms of micelle contour length. Note that some bundling /branching is observed in some cases.

Table S1. list of PDMS stamps with other different shapes and sizes used for alignment of micelles

Note: All the experiments were performed with 0.1mg/ml micelle solution

Stamp No.	Shape and sizes (l×w×h or d×h, gap, μm)	Confocal image of aligned micelles
1	Square, 1.5×1.5×3.0, 1.0	

2	Circle, 5.0×3.0, 3.0	20μm
3	Square, 10.0×10.0×3.0, 3.0	20μm
4	Circle, 10.0×3.0, 3.0	20μm



5	Square, 20.0×20.0×3.0, 4.0	
6	Circle, 20.0×3.0, 4.0	

Figure S3. The effect of micellar concentration on spacing of micelles. Confocal images of micelles aligned on PDMS stamp (l×w×h: 3.5×3.5×3.0μm, gap: 2.0μm). Concentrations used: (a) 0.1mg/ml; (b) 0.05mg/ml; (c) 0.01mg/ml.

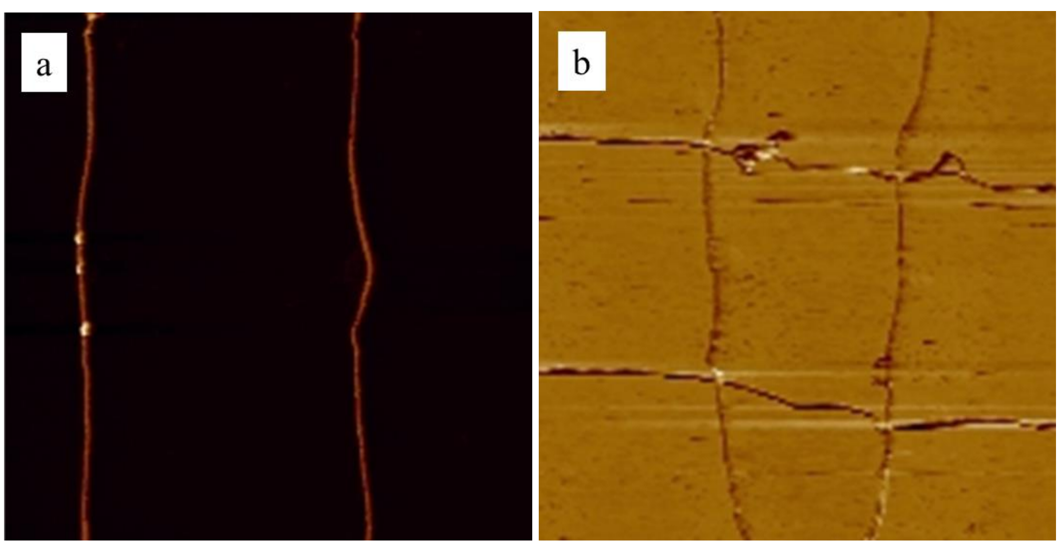


Figure S4. AFM images of transfer printed (a) micelles and (b) micelle network on silicon wafer.

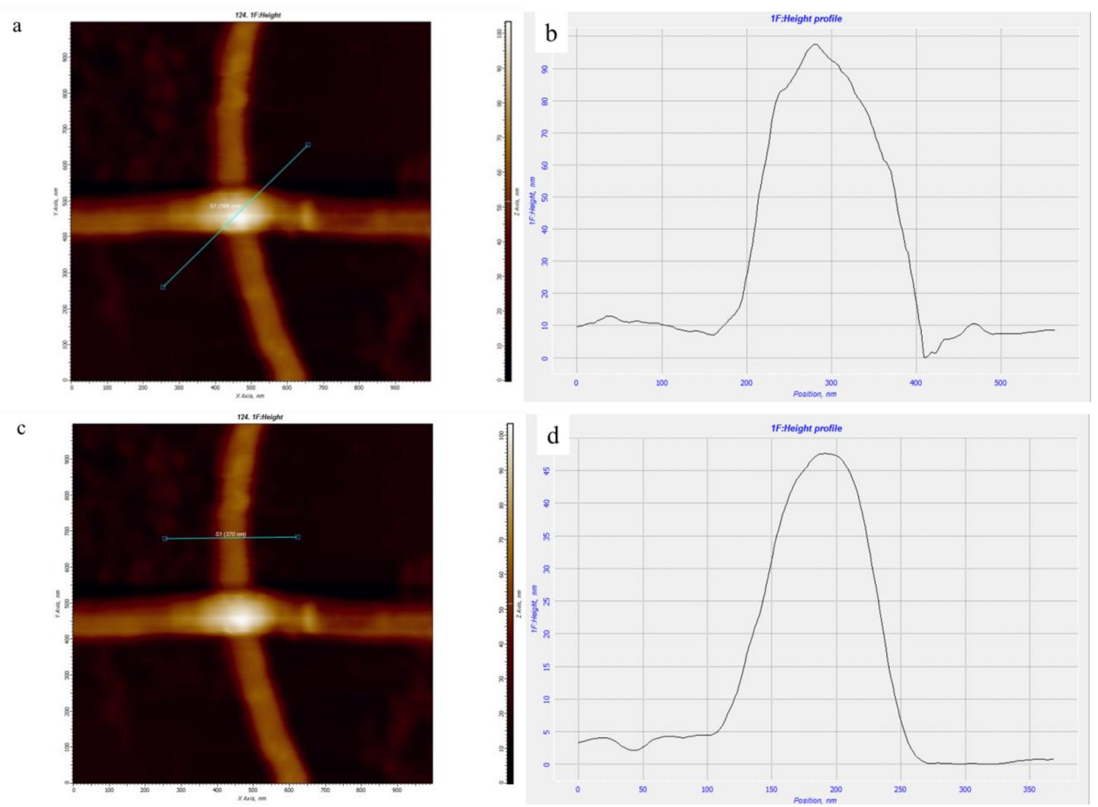


Figure S5. AFM images and corresponding height curves of (a, b) micelles junction measured at 25°C; (c, d) single micelle measure at 25°C.

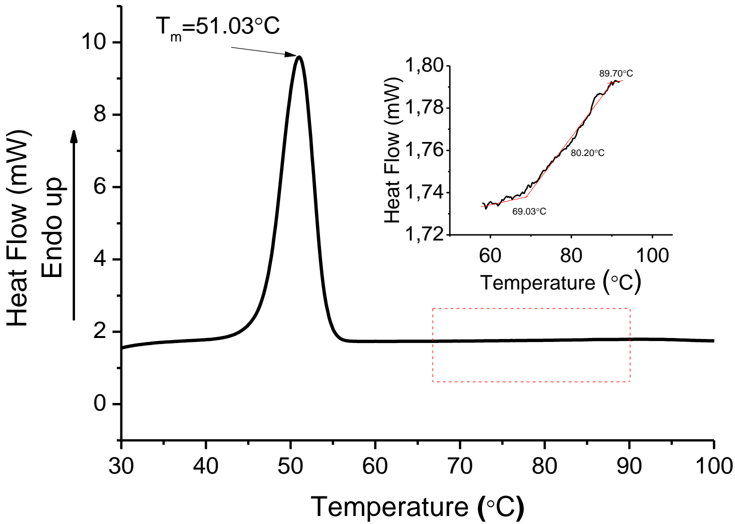


Figure S6. Differential scanning calorimetry thermograms of PS-b-PEO. The heating rate was 10.00°C/min. The inset is the amplification of the marked area in the main curve.

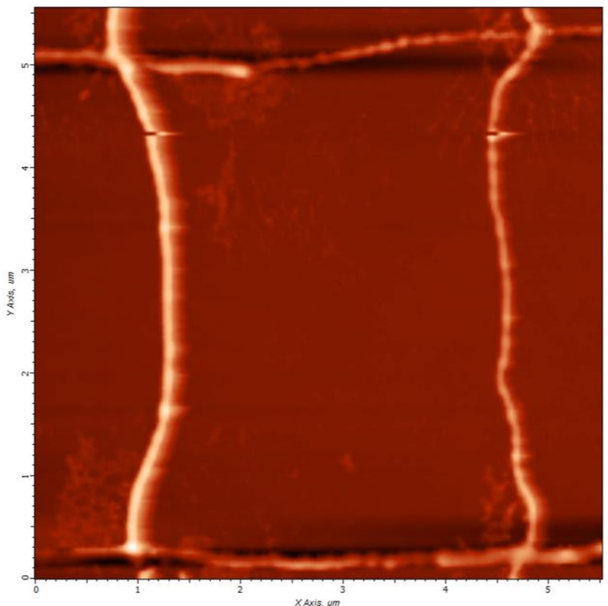


Figure S7. AFM image of 2D micelle network after thermal welding and cooling.

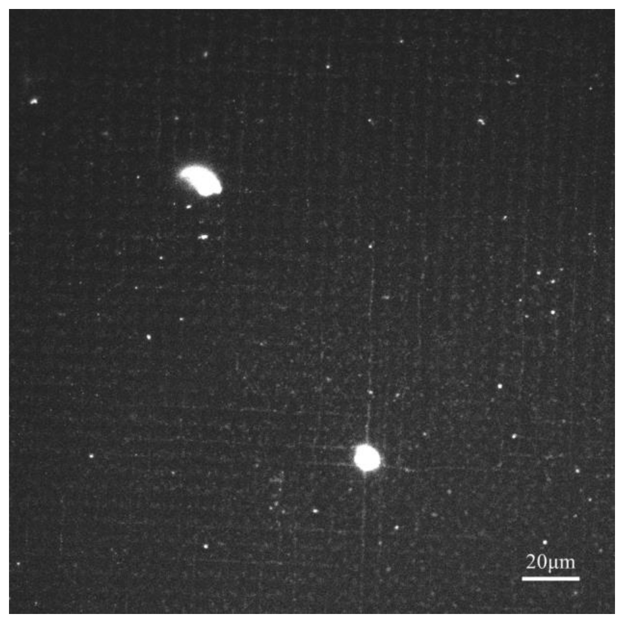


Figure S8. Confocal microscopy image of 2D micelle network after thermal welding and cooling illustrating that after heating process, the fluorescing dye partially leaked out from the micelles leading to a decrease of light intensity of the network.

Interfacial work of adhesion

To estimate the possibility of transferring process, we briefly discussed the interfacial work of adhesion between micelles and stamp (also micelles and substrate) by using the following harmonic-mean equation[6].

$$\boldsymbol{W_{ij}} = \frac{4\gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} + \frac{4\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p}$$

Where $\boldsymbol{W_{ij}}$ is the work of adhesion between two surfaces, $\boldsymbol{i}$ and $\boldsymbol{j}$, $\boldsymbol{\gamma}$ is the surface tension and the subscripts $\boldsymbol{d}$ and $\boldsymbol{p}$ represent the dispersion (nonpolar) and polar components, respectively. The surface free energy data of PDMS, PEO, silicon wafer (with an oxide layer), polytetrafluoroethylene (PTFE) and glass are obtained from literature and listed in Table S1.

Table S1: Surface free energy (mN/m) of PDMS, PEO, silicon wafer(with an oxide layer), polytetrafluoroethylene (PTFE) and glass

	γ	γ^d	γ^p
PDMS[7]	19.8	19.0	0.8
PEO[7]	42.9	30.9	12.0
PTFE[7]	20.0	18.4	1.6
Silicon[6]	46.7	22.1	24.6
Glass[8]	70.5	23.0	47.5

Then, we can calculate the work of adhesion between different materials surface.

$$\boldsymbol{W_{PDMS-PEO} = 50.1\ mN/m}$$

$$\boldsymbol{W_{PTFE-PEO} = 51.8\ mN/m}$$

$$\boldsymbol{W_{Silicon-PEO} = 83.8\ mN/m}$$

$$\boldsymbol{W_{Glass-PEO} = 91.1\ mN/m}$$

$$\boldsymbol{W_{PEO-PEO} = 85.8\ mN/m}$$

It can be seen that the work of adhesion between PDMS and PEO is smaller than that at the silicon-PEO or glass-PEO interface, i.e., $\boldsymbol{W_{PDMS-PEO} < W_{Silicon-PEO}, W_{PDMS-PEO} < W_{Glass-PEO}}$. This suggests that PS-PEO micelles can be transferred from PDMS stamp to glass substrate and silicon wafer. Since the adhesion between PTFE and micelles is similar to that at PDMS-PEO interface, the transfer process from PMDS to PTFE is difficult to succeed.

References

1. L. Jennings, PhD PhD thesis, University of Strasbourg, 2015.
2. B. Su, S. T. Wang, J. Ma, Y. C. Wu, X. Chen, Y. L. Song and L. Jiang, *Advanced Materials*, 2012, **24**, 559-564.
3. J. J. Guan, P. E. Boukany, O. Hemminger, N. R. Chiou, W. B. Zha, M. Cavanaugh and L. J. Lee, *Advanced Materials*, 2010, **22**, 3997-4001.
4. W. C. Liao, X. Hu, W. X. Wang and L. J. Lee, *Biomicrofluidics*, 2013, **7**.
5. J. J. Guan, B. Yu and L. J. Lee, *Advanced Materials*, 2007, **19**, 1212-1217.
6. J. A. Rogers and H. H. Lee, in *Unconventional Nanopatterning Techniques and Applications*, John Wiley & Sons, Inc., 2008, DOI: 10.1002/9780470405789.ch4, pp. 67-94.
7. Solid surface energy data (SFE) for common polymers, http://www.surface-tension.de/solid-surface-energy.htm).
8. R. C. Rowe, *Int J Pharmaceut*, 1989, **53**, 75-78.