

## Contact Line Motion in Dewetted Polymer Droplets on Anisotropic Nanopatterned Surfaces

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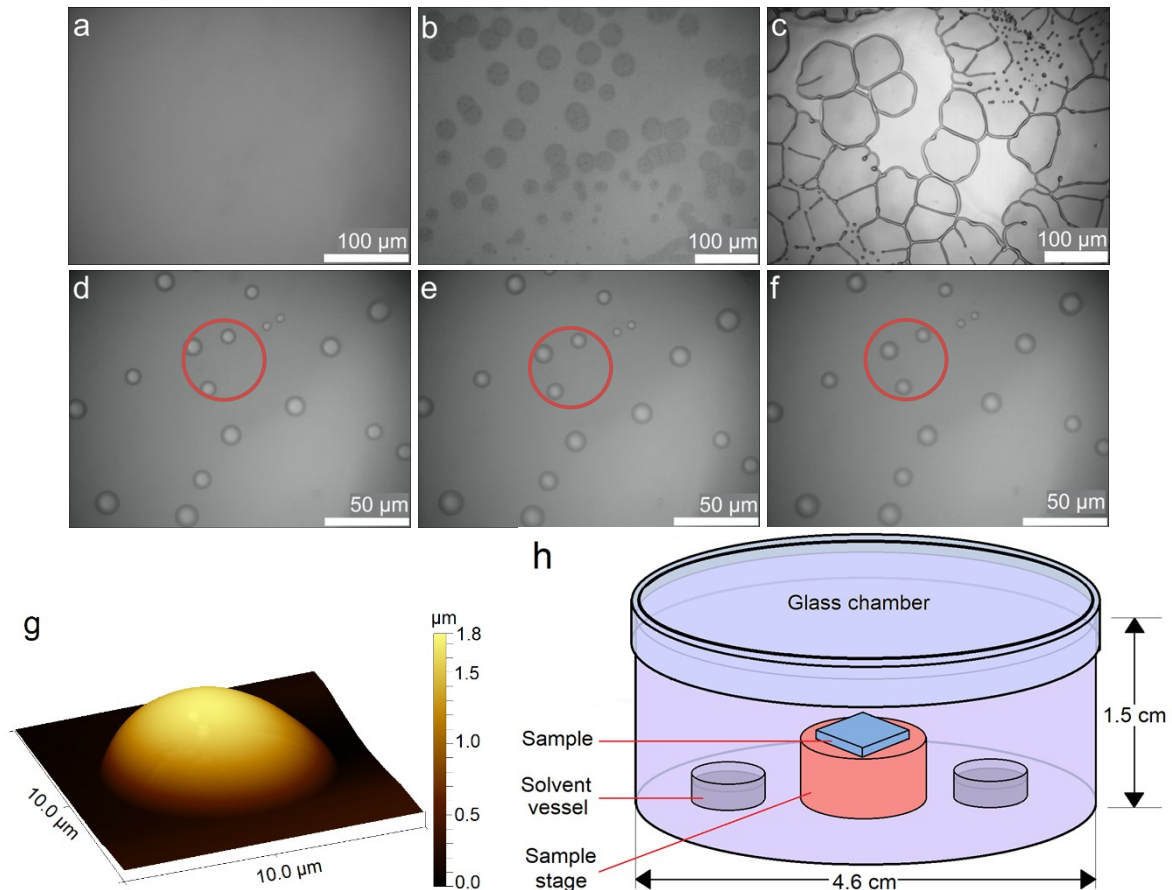
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### Supporting Information

#### S1. Dewetting of PS film by SVE on PDMS Substrate:

Figure S1 shows the optical microscope images of a PS film coated on a flat PDMS substrate with  $C_n = 1.5\%$ . The film was dewetted by solvent vapor exposure (SVE) in the presence of toluene vapors and monitored for different time intervals. The thickness of the PS film on a flat crosslinked PDMS substrate,  $h_F$ , was  $\sim 80$  nm. The standard stages of nucleated dewetting were observed upon continuous exposure to solvent vapors in the case of flat substrates. The dewetting process started with the formation of random holes (Figure S1b), which grew in size and coalesced with the neighboring holes to form an array of threads (Figure S1c). The threads show undulations similar to Rayleigh-Plateau instability and rupture to create an array of droplets after the dewetting duration,  $t_D \sim 20$  min of continuous SVE (Figure S1d). After 20 min, we kept the sample exposed to solvent vapor and tried to observe one location for  $t_D \sim 24$  h. Some smaller droplets coalesce with the neighboring drops to form larger drops, showing the late-stage coarsening process (Ostwald ripening/dynamic coalescence coarsening) up to  $t_D = 1$  h. We observed that after the final coalescence stage, the drops remained intact, and no significant dynamics were observed even after 24 h and 34 h of SVE (Figure S1e and S1f). Hence it can be noted that drop coalescence was the final stage of solvent vapor induced dewetting on flat substrates, after which the morphology remains unchanged. The periodicity of the drops ( $\lambda_D$ ) was  $\sim 39.2$   $\mu\text{m}$ .

The drop shape can be assumed to be hemispherical (Figure S1g) with an equilibrium contact angle,  $\theta_{PS} \sim 39.4^\circ \pm 1.2^\circ$  in all directions, giving it an isotropic shape. Figure S1h shows the schematic of the experimental setup used to perform SVE experiments under the optical microscope.



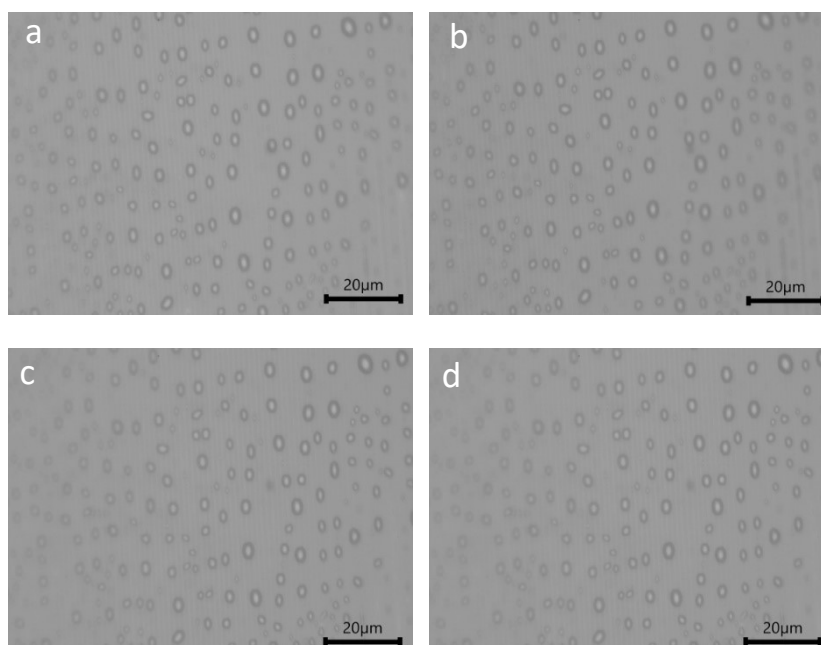
**Figure S1:** Optical microscope images showing the different stages of dewetting of a PS thin film upon SVE: (a) Flat film with the initiation of hole formation. (b) Hole growth and coalescence between neighboring holes. (c) Formation of threads and rupture into droplets. (d) Drops formed after late-stage coalescence after 1 h of dewetting. The exact location is imaged after (e) 24 h and (f) 34 h of continuous SVE. Drop locations and sizes remain the same. (g) The AFM image of a dewetted PS drop with isotropic shape. (h) Schematic of the experimental setup used to perform SVE dewetting experiments.

**Table S1:** Data for variation in average drop diameter in the parallel direction ( $d_y$ ), perpendicular direction ( $d_x$ ) and drop distortion ratio ( $D_r$ ) as a function of  $t_D$  for large PS drops obtained after dewetting on grating substrate.

$t_D$ (h)	$d_x$ ( $\mu\text{m}$ )	$d_y$ ( $\mu\text{m}$ )	$D_r$
0.58	25.5	45.5	1.78
2	27.3	39.1	1.43
8	28.8	31.0	1.08
14	32.4	30.2	0.93
14.3	25.9	40.9	1.58

14.75	24.5	56.8	2.32
15.83	26.3	52.8	2.01
17.3	26.7	49.8	1.86
20.67	30.4	38.6	1.27
21	25.8	50.8	1.97
22	31.8	45.5	1.43
28	35.9	34.1	1.11
29	29.9	28.4	0.95
29.5	27.0	43.8	1.62
30.5	21.0	60.8	2.89
33	24.5	56.2	2.29
34	23.8	52.4	2.27
38	33.6	49.4	1.47
40	34.5	36.3	1.05
41.5	26.7	40.8	1.53
42	25.9	44.3	1.71
43	26.9	48.5	1.8
44	22.8	51.9	2.28
52	26.9	40.9	1.52
55	37.0	34.0	0.92
56	28.5	37.1	1.3
56.5	24.6	43.7	1.78
58	24.3	49.6	2.04

**S2. Thermal dewetting of PS film on patterned PDMS substrate:**



**Figure S2:** OM images showing the same location of a PS film on patterned PDMS substrate dewetted by thermal annealing at 170 °C after (a) 5 h, (b) 16 h, (c) 30 h, and (d) 40 h.

### S3. Calculation of $T_g$ of solvent vapor exposed PS film:

The reduced  $T_g$  of solvent vapor exposed polymer film can be calculated using the Flory -Fox

equation<sup>1</sup>: 
$$\frac{1}{T_g} = \frac{w}{T_g^P} + \frac{1-w}{T_g^S} \quad (1)$$

Where  $T_g^P$  the glass transition temperature of the polymer film (for PS  $\sim 378$  K),  $T_g^S$  is the glass transition temperature of solvent (for toluene  $\sim 117.2$  K), and  $w$  is the weight fraction of the polymer in the swollen film. Based on the weight difference,  $w$  for the swollen PS film was determined to be 0.58. Based on equation 1, the value of effective  $T_g$  of the solvent vapor exposed PS films was obtained to be 195.4 K ( $-77.76$  °C) which shows that the PS films were in the liquid (low viscosity) state at room temperature.

### S4. Calculation of viscosity of PS film

Now, in the low viscosity state, the extent of viscosity reduction due to SVE can be quantified using the Martin equation<sup>2</sup>:

$$\ln \frac{\eta - 1}{\eta_0 C} = \ln [\eta] + k' [\eta] C \quad (2)$$

where  $\eta$  is the solution viscosity,  $\eta_0$  is the solvent viscosity (0.56 cP for toluene),  $k'$  is Huggin's constant  $\approx 0.33$ , and  $C$  is the polymer concentration  $\sim 580$  mg/ml. The value of  $[\eta]$ , the intrinsic viscosity of the polymer, can be calculated using the Mark–Houwink–Sakurada equation<sup>3</sup>:

$$[\eta] = KM^a \quad (3)$$

where  $K = 7.16 \times 10^{-3}$  mL/g,  $M$  is the polymer molecular weight (g/mol) which is 280,000 g/mol for PS, and  $a = 0.7601$  (for  $M$  in the range of 11500 to  $2.8 \times 10^6$  g/mol). From Equations (2) and (3), we can calculate  $[\eta] = 98.9$  ml/g, and the viscosity of the solvent vapor

exposed PS film,  $\eta$ , is found to be  $\sim 5.34 \times 10^6$  Pa·s. On the other hand, pure PS melt viscosity at 170 °C for  $M = 280,000$  Da is calculated to be  $\approx 9.28 \times 10^6$  Pa·s.

### S5. Calculation of solvent diffusion time in PS film

The time ( $t_m$ ) by which the solvent concentration on the substrate would become maximum is based on the relation<sup>4</sup>

$$t_m = \frac{h_f^2}{2D} \quad (4)$$

where  $D$  is the diffusivity of solvent through polymer film, and  $h_f$  is the film thickness. The value of the diffusion coefficient of toluene at its vapor pressure is  $D \approx 0.013 \times 10^{-9}$  cm<sup>2</sup>/s. Vapor pressure of toluene at 25 °C is 28.35 mmHg.<sup>5,6</sup> Equation 4 comes with certain assumptions, such as the system should obey Fickian diffusion, solvent-polymer interaction is not considered, and continuous change in polymer properties is not considered. As these assumptions do not create any major deviation for our PS film system, we used equation 4 to calculate  $t_m$  for different  $h_f$ .  $t_m$  was found to vary between 0.04 s and 1.9 s (for film thickness ranges from 10 nm to 70 nm). Thus, it is clear from the above result that upon SVE, the solvent diffuses through the film much faster than the time required for the film to rupture.

### S6. Drop dynamics studied on patterned silica substrates:

We fabricated grating patterned silica substrates by sol-gel method following the protocol developed by Roy et al.<sup>7</sup> The post patterning thermal annealing step ensures the formation of oxide phase from the gel films. Figure S3 shows the drop shape change due to variation in  $r_s$  for two cycles.

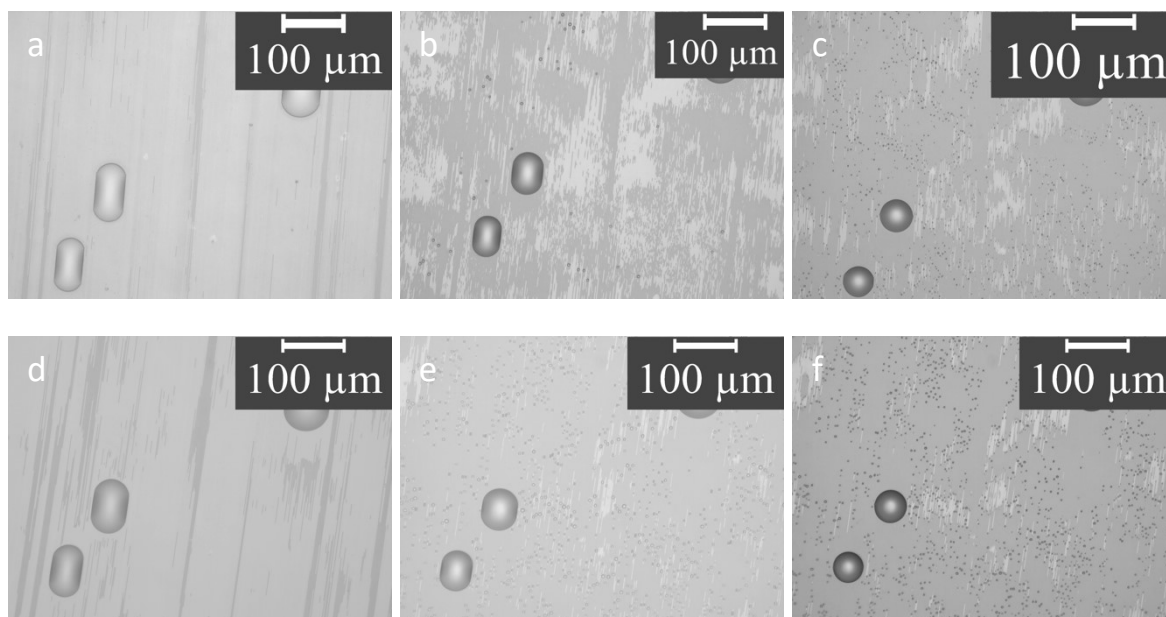


Figure S3: *OM images of a particular location on the dewetted PS film on grating patterned silica substrate. The rate of solvent evaporation is reducing from frames a to c as the larger drops are becoming isotropic. From c to d, fresh solvent was added to the dewetting chamber causing drop anisotropy. The solve evaporation rate again reduces from frames d to f.*

#### References:

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