Electronic Supplementary Material (ESI) for Soft Matter.

Evaporation-induced formation of self-organized sub-micro gradient concentric rings on pre-cast PMMA films

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Supporting Information.

Video S1. Formation process of the concentric rings on a precast PMMA film via the evaporation of a toluene droplet with a SiC particle in the drop (film thickness: 135 nm; average particle diameter: 360 ± 35μm). The video was recorded by a digital camera (Dino-Lite Pro, Torrance, CA).

The split of the droplet in the video (at about 2 s in the video, which was 67 s after the droplet was deposited on the PMMA film) is due to the pinning effect of the particle. The particle size determines the onset of the split. With continuous evaporation, the morphology of the toluene droplet gradually changed and finally split into two "sub-droplets". Here, we mainly focus on the evaporation behavior of the "sub-droplet" pinned by the particle and the patterns formed after the evaporation of this "sub-droplet". Note that the split of a large droplet into two "sub-droplets" occurred in all the experiments in this study. The arrow points to the SiC particle, which corresponds to the slip direction of a sub-droplet.

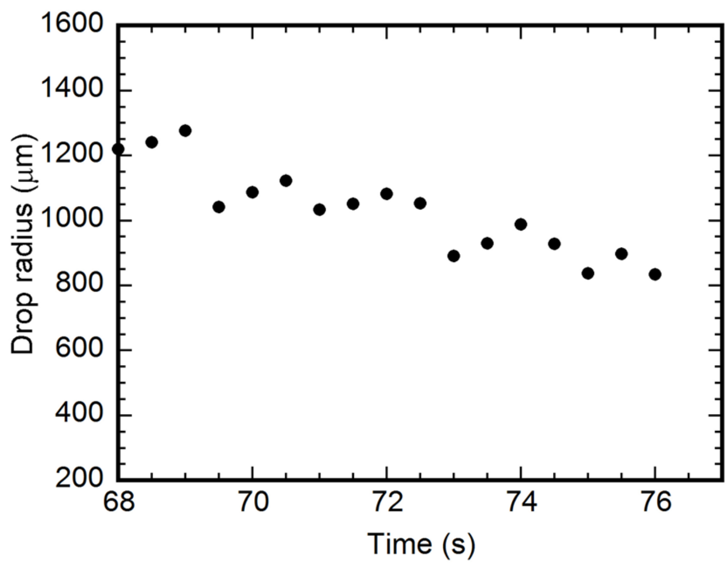

Figure S1. Variation of the drop radius with the evaporation time during the evaporation of a toluene drop on a PMMA film with a SiC particle in the drop (film thickness: 135 nm; average particle diameter: 160 ± 29μm). The particle center was set as the drop center. This plot describes the "advancing-receding" motion of the contact line in the direction indicated by the arrow in Video 1.

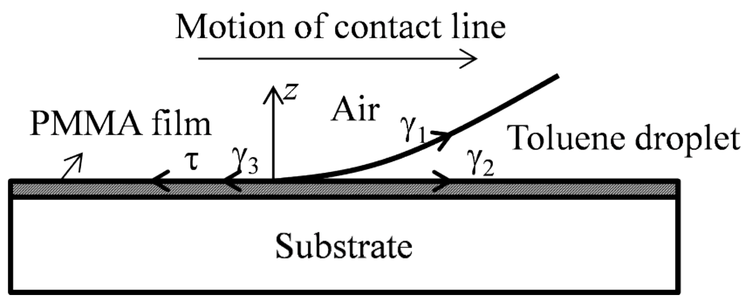

Figure S2. Schematic of the external forces exerted on contact line during stick-slip motion

It is known that the stick-slip motion of the contact line is determined by the tangential components of surface tensions at the contact line. [1] The penetration of toluene into the PMMA film results in the formation of a soft, flowable PMMA layer near the interface between the toluene and the PMMA film. During the motion of the contact line, the soft, flowable PMMA layer experiences local deformation and flow which affect the stick-slip behavior of the contact line. Figure S2 shows a schematic of a contact line under the action of external forces during the stick-slip motion of a toluene droplet on a PMMA film. Accordingly, the equation of motion of a contact line can be expressed as

$$\rho \frac{d^2 x}{dt^2} = \gamma_1 \cos\theta + \gamma_2 - \gamma_3 - \tau$$ * MERGEFORMAT (1)

where ρ is the line density of mass for the contact line, t is time, γ_1 is the surface tension between toluene and air, γ_2 is the surface tension between toluene and the PMMA, γ_3 is the surface tension between air and PMMA, θ is the nominal contact angle of the droplet, and τ is the line force (force per unit length) exerted on the contact line due to the deformation and flow of the soft, flowable PMMA layer near the interface between the toluene and the PMMA film. x

is the displacement of the contact line, which is equal to $R - R_0$ with R being the radius of the droplet and R_0 being the radius of the droplet at the pinning (stick) state.

It is known that most polymer melts and polymer solutions exhibit viscoelastic behavior due to the entanglement of polymer chains.[2-4] If the convection and diffusion of the polymer chains in the vertical direction is small, the concentration of the polymer is high nearly saturated near the interface.[5] It is reasonable to assume that the soft, flowable layer is viscoelastic due to the high concentration and the chain entanglement. The Voigt-Kelvin model, a two-element viscoelastic model, has been widely-used to describe viscoelastic deformation, [6-9] and is used here to describe the rheological behavior of the soft, flowable PMMA layer. The tangential force per unit length as a function of the displacement can be expressed as

$$\tau = 1 \cdot \left(\eta \frac{\partial \mathrm{v}}{\partial z} + \mu \frac{\partial u}{\partial z} \right)_{\text{interface}} \approx \frac{\eta}{\alpha h} \frac{dx}{dt} + \mu \frac{x}{\alpha h}$$ * MERGEFORMAT (2)

where 1 represents the unit length of the contact line, η is viscosity, μ is shear modulus, v is tangential velocity, u is tangential displacement, h is the thickness of the PMMA film, and α is the ratio of the thickness of the soft, flowable PMMA layer to the thickness of the PMMA film. Note that the reference state is referred to the quasi-stationary (stick) state of the droplet before the onset of the slip motion of the contact line. Substituting Eq. * MERGEFORMAT (2) into Eq. * MERGEFORMAT (1) yields

$$\rho \frac{d^2 x}{dt^2} + \frac{\eta}{\alpha h} \frac{dx}{dt} + \mu \frac{x}{\alpha h} = \gamma_1 \cos\theta + \gamma_2 - \gamma_3$$ * MERGEFORMAT (3)

for the motion of the contact line.

To the first order of approximation, there is $\cos\theta \approx \cos\theta_0$ (θ_0 is the nominal contact angle of the droplet at the onset of the slip motion). Using the initial conditions of $x = 0$ and $dx/dt = 0$ at t=0, the variation of the droplet size with time is found as

$$R = R_0 - x$$

* MERGEFORMAT (4)

$$= R_0 - \frac{\alpha h(\gamma_1 \cos\theta_0 + \gamma_2 - \gamma_3)}{\mu}\left[1 - \left(\cosh\frac{\sqrt{\eta^2 - 4\alpha h\mu\rho}}{2\alpha h\rho}t + \frac{\eta}{\sqrt{\eta^2 - 4\alpha h\mu\rho}}\sinh\frac{\sqrt{\eta^2 - 4\alpha h\mu\rho}}{2\alpha h\rho}t\right)e^{-\frac{\eta}{2\alpha h\rho}t}\right]$$

The droplet size during the slip is an exponential decay function of time before reaching next quasi-stationary state, qualitatively in accord with the experimental observation. From Eq. * MERGEFORMAT (4), one can define the characteristic time as $2\alpha h\rho/\eta$. It is clear that the characteristic time increases with increasing the film thickness. Generally, the slip distance (wavelength) can be approximately calculated by the multiplication of the characteristic time and the slip speed, which suggests that the slip motion of a contact line over a thick PMMA film has large slip distance, i.e. wavelength, as supported by the experimental results shown in Fig. 7.

According to Eq. * MERGEFORMAT (4), oscillatory solution is obtained for $\eta^2 < 4\alpha h\mu\rho$, which indicates the presence of local receding-advancing-receding motion of the contact line. Such behavior has been observed experimentally at the “stick” state (Video S1). However it needs to point out that the underlying mechanism is more complicated; it likely involves the fluid-structure interaction between the droplet and the soft, flowable PMMA layer and the evaporation-induced fluid flow in the droplet. One needs to consider the effect of the outward flow near the contact line at the “stick” state on the motion of the contact line since the flow inside the droplet may introduce outflow component of the flow velocity and lead to the soft, flowable PMMA towards to the contact line.

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