Mesoscale Patterns Formed by Evaporation of a Polymer Solution in the Proximity of a Sphere on a Smooth Substrate: Molecular Weight and Curvature Effects

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ABSTRACT: A drop of polymer solution was constrained in a sphere-on-flat geometry, resulting in a liquid capillary bridge. As solvent evaporated, intriguing surface patterns of polymer formed, which were strongly dependent on the molecular weight (MW) of polymer. Dotted arrays were formed at low MW; concentric rings were produced at intermediate MW; concentric rings, rings with fingers, and punch-hole-like structures, however, were yielded at high MW. Rings with fingers as well as punch-hole-like structures were manifestations of simultaneous occurrence of the "stick-slip" motion of the contact line and the fingering instabilities of rings. In addition, the curvature of the sphere in the sphere-on-flat geometry was found to affect the pattern formation. A decrease in the curvature of the sphere led to an earlier onset of the formation of punch-hole-like structures when high-MW polymer was employed as the nonvolatile solute.

Introduction

Dissipative structures, such as convection patterns1-4 and fingering instabilities,5-7 are formed when a droplet containing nonvolatile solutes (e.g., polymers, nanoparticles, colloids, or DNA) is allowed to evaporate on a solid surface.8,9 However, these self-organized structures are, in general, irregular. The evaporation is, in principle, a nonequilibrium process.9 Therefore, to fully exploit the dynamic self-assembly via irreversible solvent evaporation as a simple, lithography- and external-field-free route to well-ordered mesoscale structures that may have potential technological applications, it requires delicate control over the evaporation process and the associated capillary flow. To this end, several elegant methods have emerged.8,10,11 Recently, regular polymer pattern have been produced continuously from a receding meniscus, formed between two parallel plates, by controlling the speed of the upper sliding plate at a constant velocity while keeping the lower plate stationary.8 In our previous work, we reported that concentric rings of electrically conducting polymer and organometallic polymer of high regularity were formed naturally and spontaneously via controlled, repetitive "stick-slip" motion of the three-phase contact line when a drop of polymer solution was confined either between two crossed cylindrical mounts covered with single crystals of mica sheets10 or between a spherical lens made of silica and a Si substrate (sphere-on-flat geometry), resulting in a capillary-held polymer solution (i.e., capillary bridge).11-17 The evaporation in this geometry was restricted to the edge of the droplet, and the "stick-slip" cycles resulted in hundreds of concentric rings with regular spacing, very much resembling a miniature archery target. Each ring was nanometers high and several microns wide.10-12 By tuning the interfacial interaction between the polymer and the substrate that governed the stability of thin films, intriguing, ordered dissipative structures can be produced as a result of synergy of controlled self-assemblies of the polymer and its destabilization mediated by the interfacial interaction.15

We have reported that the use of solutions with different concentrations and different solvents effectively mediated the pattern formation in an evaporating droplet containing nonvolatile solutes.11 In this paper, we extend our previous work to investigate the molecular weight (MW) effect on the mesoscale polymer patterns formed by drying a drop of polymer solution in a sphere-on-flat geometry (i.e., a spherical lens (or a push-pin) on a Si substrate), as depicted in Figure 1. The patterns, ranging from dotted arrays at low MW to concentric rings at intermediate MW to concentric rings and punch-hole-like structures at high MW, were observed. A qualitative explanation was given to understand the pattern formation. Moreover, the curvature effect of the sphere was also studied by replacing the spherical lens (radius of curvature, R ~ 2.0 cm) with the push-pin (R ~ 2.5 cm). As the curvature decreased (i.e., from 1/R ~ 1/2.0 cm⁻¹ to 1/2.5 cm⁻¹), represented as a decrease in the distance between the sphere and Si, an earlier onset of fingering instabilities of polymer was observed owing to a reduction in the velocity of the displacement of the meniscus (i.e., the liquid-vapor interface) in the capillary bridge.

Experimental Section

Materials. Four polystyrene homopolymers (PS) (Polymer Source, Inc.) with different molecular weight were used in the studies. The number-average MW, Mₙ (and weight-average MW, Mₙ), of PS were 60K (62.5K), 112K (118K), 420K (483K), and 876K (1050K). These four PS are denoted PS-60K, PS-112K, PS-420K, and PS-876K, respectively. All PS were dissolved in toluene to prepare the PS toluene solutions at the concentration of 0.25 mg/mL. Subsequently, the solutions were purified with 0.2 μm hydrophobic membrane filter.

The spherical lens made of fused silica with a radius of curvature, R ~ 2.0 cm, the push-pin made from stainless steel with R ~ 2.5 cm, and silicon wafers were cleaned by the mixture of sulfuric acid and Nochromix. Subsequently, they were rinsed with DI water extensively and blow-dried with N₂.

Sample Preparation. To construct a confined geometry, a spherical lens (or a push-pin) and a Si wafer were used. The sphere...
(i.e., the spherical lens or the push-pin) and Si were firmly fixed at the top and bottom of sample holders inside a sealed chamber, respectively. To implement a confined geometry, an inchworm motor with a step motion of a few micrometers was used to place the upper sphere into contact with the lower stationary Si substrate. Before they contacted (i.e., separated by approximately a few hundred micrometers apart), a drop of ~23 μL PS toluene solutions was loaded and trapped within the gap between the sphere and Si due to the capillary force. The sphere was finally brought into contact with Si substrate by the inchworm motor such that a capillary-held PS solution formed with evaporation rate highest at the extremity (Figure 1). It is noteworthy that the use of a sealed chamber ensured a stable solvent evaporation against possible external influences such as the air convection and the humidity in an open space.

The evaporation took about half an hour to complete. Afterward, the sphere and Si were separated. The intriguing structures were produced on both the sphere and Si surfaces. Because of the curving effect of the sphere, only the patterns formed on Si were evaluated by optical microscopy (OM; Olympus BX51 in the reflection mode) and atomic force microscopy (AFM; Dimension 3100 scanning force microscope in the tapping mode (Digital Instruments)). BS-tap300 tips (Budget Sensors) with spring constants ranging from 20 to 75 N/m were used as scanning probes.

**Results and Discussion**

1. **Molecular Weight Effect.** The structures shown in Figures 2–4 were obtained by drying the four PS toluene solutions placed between the spherical lens (R = 2 cm) and Si substrate. The evaporation took place under controlled conditions (i.e., constant temperature (room temperature) and the same initial polymer concentration, c = 0.25 mg/mL). For the PS with the MW of 60K, irregular dotted arrays were formed exclusively on Si substrate by drying the PS-60K toluene solution in the sphere-on-flat geometry (Figure 1). A typical optical micrograph of randomly distributed PS-60K aggregates is shown in Figure 2a. The average height of PS-60K aggregates was 204 and 126 nm for bigger and smaller PS dots, respectively (Figure 2b). It is important to note that similar patterns were observed for other PS-60K samples at different concentrations (from 0.125 to 5 mg/mL), suggesting that (a) the formation of isolated, randomly dispersed PS-60K aggregates was governed by the dewetting and (b) the force exerted by the deposition of PS-60K was not strong enough to pin the three-phase contact line (i.e., form a “coffee ring”). Thus, the thin liquid film ruptured on the surfaces into randomly distributed PS dots to minimize the surface energy.

When a higher MW PS was used (i.e., PS-112K), microscopic concentric rings of PS-112K were obtained as shown in Figure 3a. The formation of concentric rings was a direct consequence of repetitive “stick—slip” motion of the contact line (i.e., the competition between the pinning force (“stick”) and the de-pinning force (“slip”)) toward the center of sphere/Si contact center.

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**Figure 1.** Schematic illustration of a drop of polymer solution placed between sphere and Si substrate (i.e., sphere-on-flat geometry), forming a capillary-held liquid bridge. The radius of curvature of upper sphere is R. The absolute position of the ring away from the sphere/Si contact center is X.

**Figure 2.** (a) Optical micrograph of randomly dispersed PS-60K aggregates on Si substrate after the evaporation of toluene in the sphere-on-flat geometry. The initial concentration of the PS-60K toluene solution, c, is 0.25 mg/mL. Scale bar = 25 μm. (b) AFM image of PS-60K aggregates, showing the details of dewetted patterns. The image size is 80 μm × 80 μm.

A set of intriguing surface patterns emerged when the PS with the MW of 420K (i.e., PS-420K) was employed. Figure 4a shows an optical micrograph of the pattern of PS-420K produced at different stages of “stick—slip” motion of the contact line as toluene evaporated from the capillary edge. The local viscosity of the contact line was then increased with time. This led to the vitrification of a PS-112K ring before the solution front jumped to next position where it was arrested again. The average jumping distance (i.e., the center-to-center distance between adjacent rings), λc, and the average height of the ring, h, are 30.2 μm and 228 nm, respectively, as determined by AFM (Figure 3b). Locally, the rings appeared as parallel stripes, and the shape of each ring was, however, nonuniform.

The solution front was arrested at the capillary edge as toluene evaporated (Figure 1). The local viscosity of the contact line was then increased with time. This led to the vitrification of a PS-112K ring before the solution front jumped to next position where it was arrested again. The average jumping distance (i.e., the center-to-center distance between adjacent rings), λc, and the average height of the ring, h, are 30.2 μm and 228 nm, respectively, as determined by AFM (Figure 3b). Locally, the rings appeared as parallel stripes, and the shape of each ring was, however, nonuniform.

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We now turn our attention to further address qualitatively the molecular weight effect on the structure formation based on the overlap concentration argument. de Gennes et al. presented three concentration regimes for polymer random coils in solution; they are dilute, semidilute, and concentrated solutions, corresponding to separated chains, overlapping chains, and entangled chains, respectively.24,25 The overlap concentration, \( C^* \), from dilute to semidilute solution is defined as the concentration at which the polymer coils touch each other.24,26

\[
C^* = \frac{3M}{4\pi R g^3 N_A}
\]  

(1)

where \( M, R_g, \) and \( N_A \) are the molecular weight of polymer, radius of gyration, and Avogadro’s number, respectively. \( R_g \) is inversely proportional to the distance from the contact line. This facilitated the fingers from the center of sphere/Si contact (low right of the optical micrograph). The initial concentration of the PS-112K toluene solution, \( c \), is 0.25 mg/mL. Scale bar = 50 \( \mu \)m. The arrow on the upper left marks the direction of the movement of the solution front. (a) A typical 2D AFM height image of PS-112K rings. The image size is 80 \( \mu \)m \( \times \) 80 \( \mu \)m.

25.35 \( \mu \)m and 379 nm at \( X = 3190 \mu \)m (Figure 4b). 25.26 \( \mu \)m and 335 nm at \( X = 3090 \mu \)m (Figure 4c), and 24.90 \( \mu \)m and 327 nm at \( X = 2950 \mu \)m (Figure 4d). The average width and height of fingers at the center connecting two adjacent rings were 3.74 \( \mu \)m and 195 nm (Figure 4d,e).

The emergence of PS-420K surface patterns from rings to rings having fingering instabilities to punch-hole-like structures has been qualitatively understood on the basis of the fact that the velocity of the displacement of the meniscus at the capillary edge, \( v \), was inversely proportional to the distance from the capillary entrance to the meniscus.15,22 A faster \( v \) stabilized the front, while a slower \( v \) led to the development of fingering instabilities at a propagating front.23 As the solution front progressed toward the center of the sphere/Si contact, \( v \) decreased owing to a decrease in the evaporation rate of toluene. As a result, fewer PS-420K were available to transport and pin the contact line. This caused the formation of fingering instabilities. The center-to-center distance between two adjacent rings, \( L_{C-C} \), decreased gradually as the solution front approached the center of sphere/Si contact. This facilitated the fingers from adjacent rings to connect each other. As a result, the sequence of microscopic holes was produced with increasing proximity to the center of sphere/Si contact (low right of the optical micrograph in Figure 4a and 4d–e). Similar surface patterns were observed from the drying of 0.25 mg/mL PS-876K toluene solution, i.e., forming rings, rings with fingers, and a periodic array of punch-holes progressively with a decrease in \( X \) (Figure 1).
on-Si geometry resulted in the formation of concentric rings of PS-112K, as shown in Figure 3.11 It is easy to understand that the speed of the solution front decreased more significant when the higher MW PS was used (i.e., PS-420K and PS-876K). The formation of concentric rings is clearly evident (Figure 4). The polymer coils of PS-420K and PS-876K overlapped significantly since \( C^* \) was only 6.8 and 3.6 mg/mL, respectively. The viscosity increased dramatically during the solvent evaporation as compared to that of PS-112K. The higher the molecular weight of the polymer, the faster is the rate of increase in viscosity due to the increase in concentration as a result of the solvent evaporation.28 This caused a reduction in the speed of solution front, \( \nu \), thereby leading to the development of fingering instabilities at a propagating front.23 Rings with fingers as well as punch-hole-like structures were manifestations of simultaneous occurrence of the “stick–slip” motion of the contact line and the fingering instabilities of rings.

2. Curvature Effect. The mesoscale surface patterns formed by drying the PS toluene solution in the sphere-on-Si geometry can be dynamically tuned by proper choice of the curvature of the sphere. The optical micrograph of the surface pattern produced by drying the 0.25 mg/mL PS-420K toluene solution is shown in Figure 5a. In this study, the spherical lens with
The curvature of 1/2 cm⁻¹ was replaced with a push-pin with curvature of 1/2.5 cm⁻¹. Compared to the patterns in Figure 4, an important piece of information was readily gained from Figure 5: more fingers and punch-holes were obtained under the same range of $\Delta X$ (i.e., the same image size in Figures 4 and 5) as the curvature of the sphere decreased. This is simply because the evaporation rate of toluene in the sphere-on-Si geometry slowed down with a large $R$ of the upper sphere. As a result, the displacement of the meniscus at the capillary edge, $v$, reduced. A slower $v$ triggered the earlier onset of fingering instabilities and thus the punch-hole-like structures subsequently (e.g., the punch-hole-like structures formed at $X = 3250 \mu m$ (Figure 5d,e) as compared to those at $X = 2950 \mu m$ (Figure 4d,e)). The uniform zone of the punch-hole-like structure increased. This suggested the possibility of obtaining well-ordered punch-holes structures over larger surface area by manipulating the curvature of the sphere.

The 2D AFM height images, representing the patterns formed at the different stages of the dying process (i.e., progressed from fingering instabilities on the rings to punch-hole-like structures), are shown in Figure 5b–e. The characteristic distance between adjacent PS fingers on a ring, $\lambda F$, and the height of the ring, $h$, were 24.36 $\mu m$, 339 nm at $X = 4100 \mu m$ (Figure 5b), 20.60 $\mu m$, 303 nm at $X = 3450 \mu m$ (Figure 5c), and 18.99 $\mu m$, 289 nm at $X = 3250 \mu m$ (Figure 5d,e). Further scrutiny of the rings having fingers at their edges in Figure 5b,c revealed the formation of isolated dots, residing (Figure 5b,c) or connecting (Figure 5c) between two adjacent fingers, driven by the Rayleigh instability. As the solution front neared the center of the push-pin/Si contact, the mass transportation was facilitated owing to

Figure 5. Curvature effect. (a) Optical micrograph of surface patterns of PS-420K produced by the evaporation induced self-assembly of the PS-420K toluene solution confined between the push-pin and Si substrate. The radius of curvature of the push-pin is 2.5 cm. The fingers and the punch-hole-like structures (colorful patterns on light gray Si substrate) are clearly evident. The initial concentration, $c$, is 0.25 mg/mL. Scale bar = 70 $\mu m$. The arrow on the upper right denotes the direction of the motion of the solution front. (b–d) 2D AFM height images of surface patterns, roughly corresponding to the locations in the upper left, middle, and lower right of the optical micrograph in (a). (e) A corresponding 3D AFM height image of (d). The image size is $80 \times 80 \mu m^2$. 

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a closer distance between two adjacent rings. This led to the formation of more punch-hole-like structures. The average width and height of fingers at the center connecting two adjacent rings are 5.9 μm and 228 nm as measured by AFM (Figure 5d,e).

Conclusion

Mesoscale polymer patterns were formed by evaporation of a polymer solution in the capillary formed by a sphere resting on a plate (i.e., sphere-on-flat geometry). The change in the polymer molecular weight (MW) led to very pronounced morphological change in the resulting structures. At low MW, the dewetting process occurred, leaving behind randomly distributed dots at the surface. At intermediate MW, the self-assembled concentric rings were formed by repetition of the deposition and recession cycle of the contact lines. At high MW, concentric rings, rings with fingers, and punch-hole-like structures were produced. Furthermore, the change in the radius of curvature of the upper sphere was found to affect the pattern formation. A smaller curvature caused an earlier onset of the formation of fingers and punch-hole-like structures when the high MW PS was utilized as a nonvolatile solute. The present studies provide valuable insights into the rationale of creating intriguing polymer patterns by varying the molecular weight and tuning the radius of curvature of the sphere in the sphere-on-flat geometry, which in turn render the control over the solvent evaporation and associated capillary flow.

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References and Notes

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