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Formation of well-ordered finger-like structures on pre-cast thin films

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Abstract

In this work, we developed a simple method to construct well-ordered finger-like structures on pre-cast polymer films for the first time. Confining a droplet between a tilt carbon rod and a pre-cast poly(methyl methacrylate) film and limiting the evaporation of the droplet, a gradient finger-like surface structure consisting of multiple arc-segments and line-segments were formed. The wavelength of the arc-segments first decreases, reaches minimum, and then increases with the increase of the distance to the tip of the gradient finger-like structure. The geometric characteristics of the finger-like surface structures are dependent on the droplet volume and the tilt angle. Using this approach and a "four-rod" template, a "cross" surface pattern, which consists of 4 finger-like structures, was constructed. In addition, this method was used to form surface structures on polystyrene (PS) films. The surface structures consisted of slightly undulated lines and disconnected beads in contrast to the continuous ridges formed on PMMA films.

Keywords: self-assembly; evaporation; thin films.

1. Introduction

Evaporation-induced self-assembly has been studied for a long time. The principle of this phenomenon is so-called the "coffee-ring" effect [1], in which the non-volatile solute in a droplet gradually accumulates in the vicinity of the contact line and forms a ridge with the shape conforming to the contact line. If the contact line moves discontinuously in a "stick-slip" mode, multiple ridges covering a larger area can be formed [2-4]. The topology of the evaporation-induced surface patterns, including concentric rings [5], parallel rings [6], parallel straight stripes [7], concentric triangles [8] and etc., are determined by the shape of the corresponding contact line. Various highly-ordered evaporation-induced patterns can be formed if the evaporation of the droplet can be controlled by using some templates. Gradient concentric rings consisting of various materials have been fabricated via a "sphere-on-flat" template [9], and concentric triangles have been formed by replacing the "spherical lens" with a "triangular pyramid" [8]. Surface structure of multi-straight stripes is another typical "coffee-ring" pattern, which have been constructed via a "cylinder-on-flat" template [10] or a "wedge-on-flat" [11] template to maintain a straight contact line. Straight stripes have also been formed in a dip-coating process [12]. To fabricate parallel stripes covering a large area, a "roll-based" system [13, 14], a "computer-controlled" system [7], and an "inkjet printing-based" process [15] have been developed. Recently, Sun and Yang [16-18] developed "particle-on-film", "ring-on-film", and "wire-on-film" templates to produce gradient concentric rings and gradient stripes on pre-cast thin polymer films. They provide a simple method to engineer surface structures on polymer surfaces. Currently, there is no report to demonstrate the formation of well-ordered finger-like structures on polymer surfaces.

In this work, we demonstrate the formation of well-ordered finger-like structures on pre-cast poly(methyl methacrylate) (PMMA) films for the first time. A pure toluene droplet is confined between a tilt carbon rod and a pre-cast PMMA film to limit the evaporation of the droplet and the motion of the contact line. A gradient finger-like structure consisting of multiple arc-segments and line-segments is formed. The geometric characteristics of the gradient finger-like structures are characterized, and the effects of the droplet volume and the tilt angle of the rod are examined. A template consisting of four tilt-perpendicular carbon rods is developed to construct a “cross” pattern of four finger-like structures.

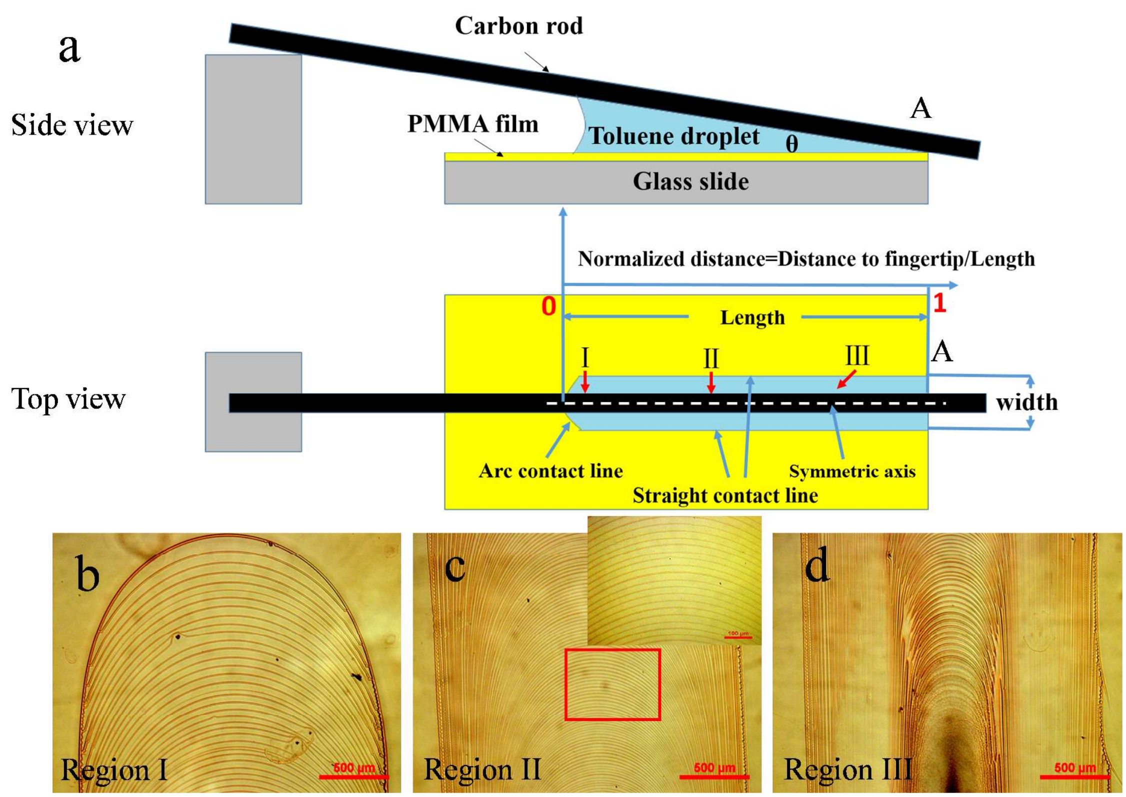


Figure 1. (a) Schematic of the experimental set-up for constructing finger-like surface patterns, and (b-d) the surface patterns formed in the regions of I, II and III indicated in (a). The inset in (c) is an enlarged view of the patterns enclosed in the red box (film thickness: ca. 90 nm; tilt angle: 2.86°; droplet volume: 5 μL)

2. Experimental section

PMMA (Mw=35000) (Fisher Scientific, Pittsburgh, PA) thin films were spin-coated on glass slides (15×20×1 mm^3), using a spin-coater (WS-400B-6NPP/LITE, Laurell Technologies Corp., North Wales, PA). The glass slides were cleaned in an acetone bath ultrasonically for 10 min for three times and dried by condensed air. The solvent for the spin-coating was toluene (Fisher Scientific, Pittsburgh, PA), and the PMMA solution concentration was 1 wt%. The spinning speed was 2000 rpm. The film thickness was 90 nm which was measured by an atomic force microscope (AFM) (Q-scope 250, Agoura Hills, CA). Carbon rods (PENC25HB, 500 μm in diameter, and 10 cm in length) (Pentel of America, Ltd, Torrance, CA) were cleaned ultrasonically in toluene and dried in ambient environment.

Figure 1a shows the schematic of the experimental set-up. One end of a carbon rod was in contact with one edge of a glass slide (1 mm in thickness) at point A and the other end was supported by a glass plate (3 mm in thickness). A droplet of toluene was placed carefully near the point A, and a finger-like droplet was formed between the carbon rod and the PMMA film. The droplet was evaporated at 22 ℃. To examine the effect of tilt angle, a droplet with a volume of 5 μL was used, and the angles between the carbon rod and the glass substrate were 5.71°, 3.81°, 2.86° and 2.29° by varying the horizontal distance between the two contact points from 20 mm to 50 mm. To study the effect of the droplet volume on the characteristics of surface patterns, the tilt angle of 2.86° was used, and the volumes of toluene droplets were 5, 10, 15 and 20 μL.

To construct "cross" surface patterns, four tilt carbon rods were placed on a PMMA film with each rod being perpendicular to adjacent rods and the lower ends of all the four rods being in contact with the polymer film at the same point. Two cases were studied. The first one had a tilt angle of 2.86° for all four rods, and for the other one, the tilt angles of the four rods were 5.71°, 5.71°, 2.86° and 2.29°, respectively. The volume of toluene droplets was 10 μL, which was placed at the "common" contact point on the PMMA film.

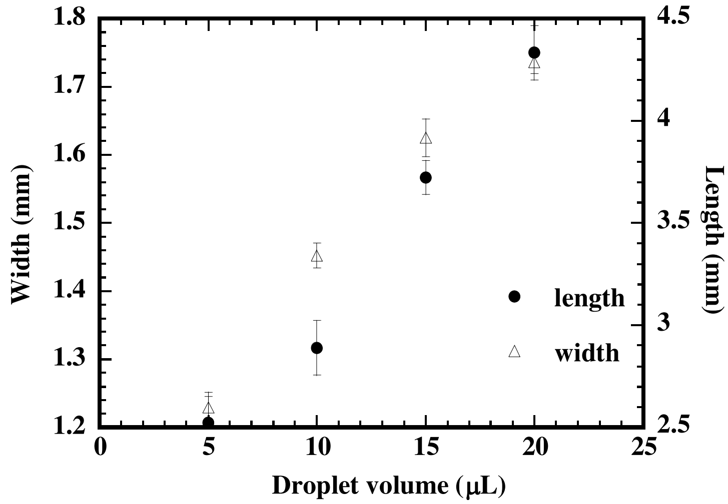
The characteristics of the surface patterns formed after the complete evaporation of a toluene droplet was analyzed, using an optical microscope (Nikon ECLIPSE LV100POL) and a digital camera (Dino-Lite Pro, Torrance, CA).

3. Results and Discussion

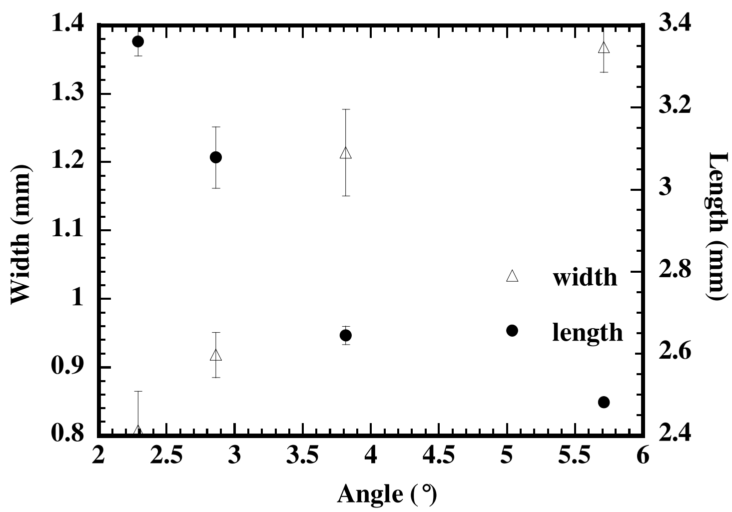
When a droplet was placed near the point A, a liquid bridge between the carbon rod and the PMMA film was formed due to the capillary effect, as shown schematically in Fig. 1a. A contact line on the surface of the PMMA film formed due to the capillary effect. The contact line consisted of an arc segment and two straight segments. The geometric characteristics of the contact line are dependent on the tilt angle and the droplet volume. Receding motion of the contact line towards to the point A occurred due to the evaporation of the droplet, which led to the formation of finger-like patterns on the surface of the PMMA film.

Figures 1b-d show the finger-like surface patterns at three different positions indicated in Fig. 1a. The film thickness was 90 nm, the droplet volume was 5μL, and the tilt angle was 2.86°. Near the tip of the finger-like patterns (Fig. 1b), the patterns consisted of only multiple arc-segments with the two end points of each segment being at the outmost edge of the finger, i.e. the first contact line formed after placing the droplet on the surface of the PMMA film. In the intermediate region (Fig. 1c), the patterns consisted of multiple arc-segments and straight line-segments with each arc-segment smoothly connecting with two straight line-segments (see Fig. S1b and S1c). In the rear region of the finger-like surface structures (Fig. 1d), the widths of the arc-segments (the distance between two endpoints) decreased and approached the diameter of the carbon rod. There is a featureless zone near the point A.

The formation of the finger-like surface pattern is controlled by the motion of the contact line first formed on the PMMA film (the outmost edge of the finger consisting of an arc-segment and two straight line-segments) after placing a toluene droplet. The toluene droplet softened the pre-cast PMMA film, and a softened, flowable PMMA/toluene layer was formed at the interface of the toluene and the PMMA film. As the toluene evaporated, the contact line started to recede which caused the softened PMMA near the contact line to move towards the point A. When the contact line was pinned, i.e. at the stick state, PMMA accumulated near the contact line, resulting in the formation of a polymer ridge. During the evaporation, the contact line experienced a series of stick-slip motion and multiple polymer ridges were formed. The receding stick-slip motion of the contact line of the arc-segment results in the formation of multiple nearly parallel arc-ridges in the middle, and the receding stick-slip motion of the contact line of the line-segments leads to the formation of straight-parallel ridges. The moving rate of the contact line of the arc-segment is higher than that of the line-segments. Thus, several arc-segments converged into the same straight line-segment (Fig. S1a and S1b). Also, local Rayleigh–Taylor instability at the dynamic “stick” state introduced the bead-like shape of the outmost contact line (Fig. S1a-d). With continuous evaporation, less local instability occurred and smooth finger-like ridges were formed. More details of the formation of the evaporation-induced surface patterns on pre-cast films are discussed in our previous work [16].



(a)



(b)

Figure 2. (a) Variation of the dimensions of the outmost finger-like pattern with the droplet volume (tilt angle: 2.86°, film thickness: ca. 90 nm); (b) Variation of the dimensions of the outmost finger-like pattern with tilt angle (droplet volume: 5μL, film thickness: ca. 90 nm)

Figure 2 shows the variation of the dimensions of the outmost finger-like pattern with the droplet volume and the tilt angle of the carbon rod. For a given tilt angle, both the length and width of the outmost finger-like pattern increase with the increase of the droplet volume, since a toluene droplet of a large volume can spread over a large surface area of a PMMA film. For a given droplet volume, the length of the outmost finger-like pattern decreases with the increase of the tilt angle, while the width increases with the increase of the tilt angle. For a small tilt angle, more toluene is confined between the carbon rod and the PMMA film to form a longer liquid bridge, leading to the formation of a thinner and longer finger-like ridge.

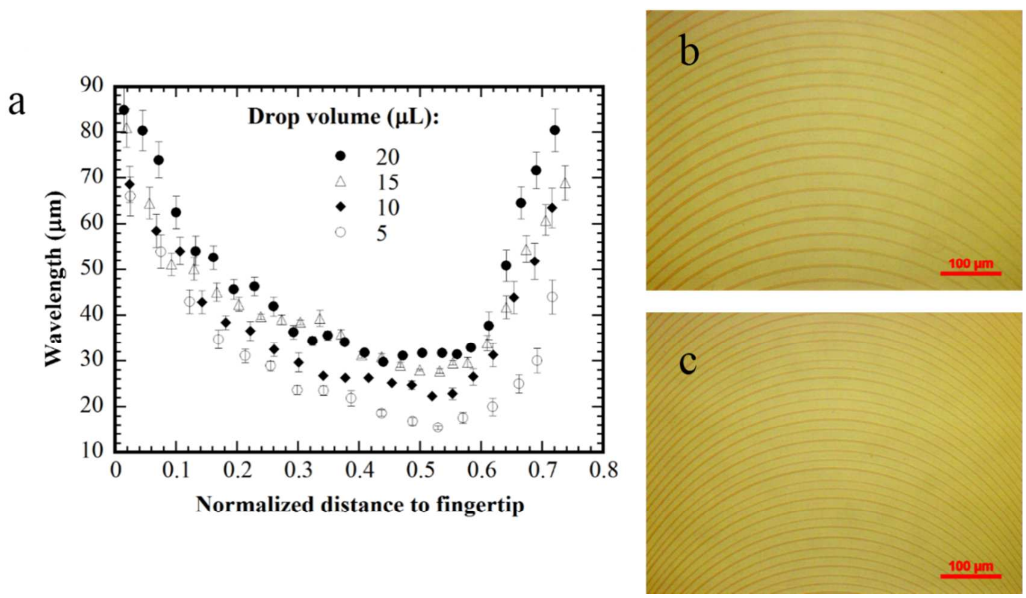


Figure 3. (a) Variation of the wavelength with the normalized distance to the finger tip for different droplet volumes (tilt angle: 2.86°, film thickness: ca. 90 nm); (b and c) Optical images of the typical multiple arc-ridges formed along the symmetric axis for different droplet volumes of (b) 10 μL and (c) 5 μL (tilt angle: 2.86°, normalized distance: 0.5, film thickness: ca. 90 nm)

The distance to the finger tip of the outmost finger-like ridge along the symmetric axis is normalized by the total length of the outmost finger-like ridge. The normalized distance is illustrated schematically in Fig.1 with the normalized distance being 0 at the fingertip and 1 being at the point A. Define wavelength as the distance between two adjacent arc-ridges along the symmetric axis. Figure 3a shows the variation of the wavelength with the normalized distance for different droplet volumes. The variation of the wavelength with the non-normalized distance to fingertip is presented in Fig. S2. As shown in Fig. 3a, the wavelength first decreases with the increase of the normalized distance, reaches minimum when the normalized distance is about 0.52, and then increases with the increase of the normalized distance for all the four different droplet volumes. The increase rate of the wavelength is relatively higher than the decrease rate. Moreover, a larger droplet generally created surface patterns of larger wavelengths than a smaller droplet for the same normalized distance. Such behavior is likely due to less resistance to the motion of the contact line for a droplet of a larger volume. Figures 3b and 3c show the comparison of the multiple arc-ridges of the finger-like patterns formed on the PMMA films of 90 nm thickness with the droplet volumes of 10 and 5 μL, respectively, at a normalized distance of 0.5. The tilt angle was 2.86°. Over the same imaging area, a droplet of 5 μL volume produced more arc-ridges than a droplet of 10 μL volume, indicating that a droplet of a larger volume produced a larger average wavelength for the same normalized distance.

Figure 4a shows the variation of the wavelength with the normalized distance for four tilt angles. The droplet volume was 5 μL. The variation of the wavelength with the non-normalized distance to the finger tip is shown in Fig. S3. The wavelength is relatively independent on the tilt angle for the normalized distance less than or equal to 0.35. The normalized distance, at which the wavelength reaches the minimum, increases with decreasing the tile angle due to the confinement effect of the rod on the evaporation of the toluene droplet. The normalized distances corresponding to the minimum wavelengths are 0.43, 0.49, 0.52, and 0.57 for the tilt angles of 5.71°, 3.81°, 2.86° and 2.29°, respectively. After the wavelength reached minimum, a larger tilt angle led to the formation of the surface patterns with larger wavelengths for the same normalized distances.

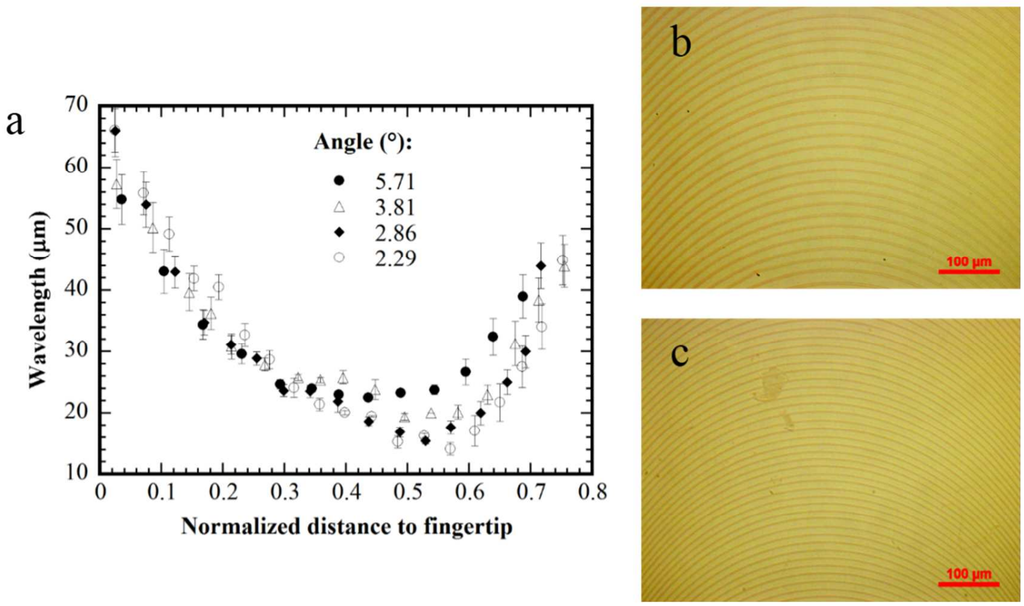


Figure 4. (a) Variation of the wavelength with the normalized distance for four different tilt angles (droplet volume: 5 μL, film thickness: ca. 90 nm); (b) and (c) optical images of the multiple arc-ridges formed along the symmetric axis for two tilt angles of (b) 5.71° and (c) 2.29° (droplet volume: 5 μL, normalized distance: 0.5)

In addition to the droplet volume and the tilt angle, the film thickness and molecule weight of polymer also play important roles in controlling the formation and characteristics of the formed patterns. A PMMA film with larger film thickness tends to form a PMMA/toluene layer with a higher viscosity at the toluene/PMMA interface, which can exert a larger resistance to the motion of contact line. However, there exists the effect of the substrate confinement, which makes thinner films more resistance to the motion of the contact line than thicker films. It is the combining effect of the viscosity of the PMMA/toluene layer and the confinement effect that determines the thickness effect on the geometric characteristics of the surface structures formed on the PMMA films.

A polymer of larger molecule weight in toluene solvent can have a larger viscosity, which will introduce a larger resistance to the motion of contact line. Both the film thickness and the molecular weight can change the slip velocity of the contact line and alter the slip distance, leading to the formation of surface patterns of different dimensional characteristics. In addition, more polymer will accumulate near the contact line at the "stick" state for a thicker film, which forms a polymer ridge of a larger amplitude (height). Systematic study on the effects of the film thickness and the molecule weight will be performed in the future.

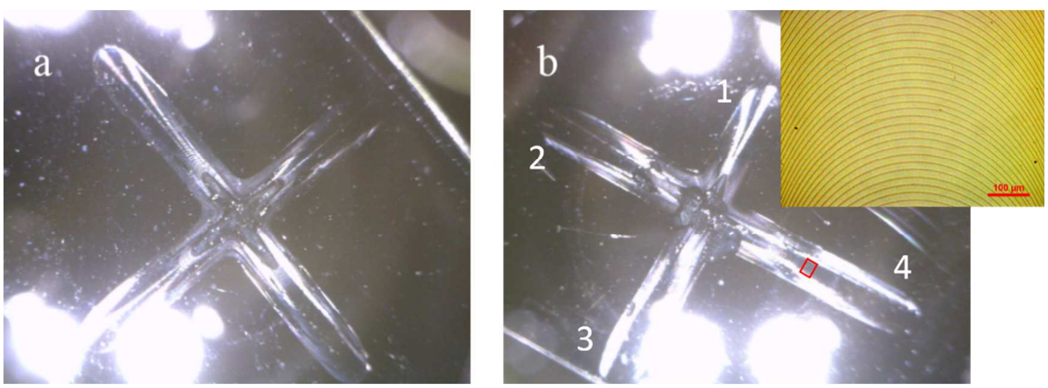


Figure 5. Optical images of the "cross" patterns: (a) the "cross" patterns of the same rod length; (b) the "cross" patterns of different rod lengths. The inset is an enlarged view of the patterns enclosed in the red box in (b)

Figure 5 shows typical "cross" patterns consisting of four single fingers, which were constructed via four carbon rods. The "cross" patterns, as shown in Fig. 5a, were formed, using four carbon rods of the same dimensions at a tilt angle of 2.86°.The carbon rods were perpendicular to adjacent rods. The "cross" patterns have four fold symmetry. Figure 5b shows the “cross” patterns formed, using four carbon rods with different tilt angles. The tilt angle was 5.71° for finger 1, 5.71° for finger 2, 2.86° for finger 3 and 2.29° for finger 4, as indicated in Fig. 5b. As discussed above, the geometrical characteristics of individual finger-like patterns are dependent on the tilt angle between the rod and the PMMA film. The use of different tilt angles led to the formation of the “cross” patterns with different finger lengths and widths. The surface patterns consisting of two fingers and three fingers, which were constructed via templates with two rods and three rods, respectively, are shown in Fig. S4 of supporting information. All of these demonstrated the potential to construct well-ordered surface structures of large area on the surface of polymer films simply through the confinement effect on the evaporation of volatile liquids and the control of geometric configuration of templates.

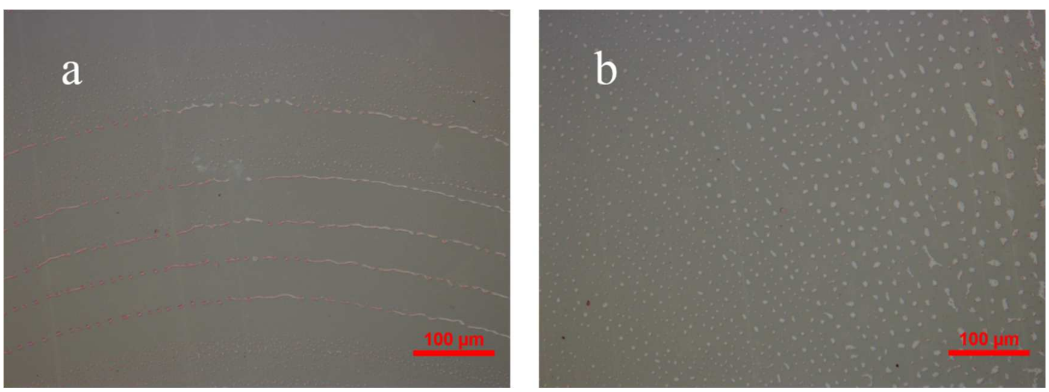


Figure 6. Optical images of the typical surface patterns formed on polystyrene (PS) films (tilt angle: 2.86°, film thickness: ca. 90 nm, normalized distance: 0.25); (a) the region along the symmetric, and (b) the transition region between the arc-segment and the straight line-segment

This method was also used to form surface structures on polystyrene (PS) films. Figure 6 shows the typical surface patterns formed on a pre-cast polystyrene (PS) film via the evaporation of a toluene droplet with the confinement of a tilt carbon rod. The film thickness was about 90 nm, and the tilt angle was 2.86. The surface patterns formed are different from those on the PMMA films. As shown in Fig. 6a, multi-arcs along the symmetric axis were formed, which are not as smooth as the PMMA arcs. The arcs consist of slightly undulated lines and disconnected beads. Beads are also found in some regions between two polymer ridges. As shown in Fig. 6b, only separated beads can be observed in the transition region between the arc-segments and the straight line-segments. Some beads seem to align into arcs, while others align randomly.

Comparing to the continuous surface structures formed on PMMA films, the beads formed on PS films likely can be attributed to the dewetting of the PS/toluene layer at the interface between toluene and the PS film and local instability of the contact line at the dynamic "stick" state. Due to the unfavorable interaction of PS with glass [19] and the local instability at the "stick" state, beads-like structures instead of continuous ridges are more likely to form.

4. Summary

In summary, well-ordered finger-like patterns were fabricated on the surface of a pre-cast PMMA film by forming a toluene-liquid bridge between a carbon rod and the PMMA film and confining the evaporation of the toluene bridge. The finger-like patterns consist of multiple arc-segments and parallel line-segments. The wavelength of the multiple arc-segments along the symmetric axis first decreases, reaches minimum, and then increases with increasing the distance to the fingertip of the finger-like patterns. The dimensions of the finger-like patterns and the wavelength gradient of the multiple arc-segments are dependent on the droplet volume and the tilt angle. Using "four-rods-on-film" templates, the "cross" patterns of four finger-like patterns were also constructed.

In addition, this method was used to form surface structures on polystyrene (PS) films. In contrast the surface patterns formed on PMMA films, the surface patterns formed on the PS films consisted of slightly undulated lines and disconnected beads.

Following similar mechanism, more complex patterns can also be constructed just by setting up templates of various geometrical configurations. The technique developed in this study provides the rationale to construct surface structures over a large area via the control of volatile liquid for the applications in flexible electronics, microfluidics, and biosensory devices.

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