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Formation of complex polymeric microstructures through physical self-organization and capillary dynamics

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Abstract
We present a generic way of forming various complex polymeric microstructures using physical self-organization and capillary dynamics. A simple lithographic tool called capillary force lithography is utilized for this purpose, in which the pattern formation is driven by capillary force, not involving any external force or modification. In this method, a patterned polydimethylsiloxane mold is placed on a spin-coated polymer film on a substrate and then the temperature is raised above the polymer's glass transition temperature, allowing for a surface tension-driven flow. One-step and two-step applications of the mold lead to various microstructures in which wetting and dewetting as influenced by the mold channel width and the film thickness gives rise to the self-organization of the structures. The method can also be utilized to produce a polymer sheet with both sides patterned and these sheets can be laminated to generate multi-level structures. An intriguing aspect of patterning microsphere surfaces is also presented. The complex microstructures are not easily accessible by other methods, thus providing a simple and economic way of generating potentially useful templates for biomedical, microfluidic, and optical applications.

1. Introduction

Structures with micrometer length scale (1–50 μm) or 'microstructures' have become an active area of research in physics, materials science, and increasingly in chemistry and biology because of their broad applications ranging from microfluidics to cell adhesion [1, 2]. The fabrication and study of microstructures have drawn considerable interest in the last decade and a number of lithographic and other techniques have been reported, such as microcontact printing [3], metal deposition [4], and photolithography [5, 6]. Of these, physical self-organization involving wetting/dewetting [7, 8] or phase separation [9–12] has emerged as a simple and yet potentially promising way of forming ordered two-dimensional or three-dimensional microstructures.

An example of achieving physical self-organization is to utilize hydrophilic–hydrophobic patterns on a substrate. Gau *et al* [4] investigated the wetting of water on a stripe pattern with a high wettability contrast by thermally evaporating MgF_2 onto a hydrophobic substrate. They observed that water selectively wets the MgF_2 surface, which enables forming of a variety of shapes from microchannels to microchips. An alternative way to induce selective wetting is to use self-assembled monolayers (SAMs) to generate chemically patterned substrates [3]. It has also been found that the wetting could be controlled by properly applying light [5, 6] or electricity [13].

Dewetting is also a convenient way of creating ordered micro- and nanostructures. Higgins and Jones [8] investigated the effects of surface topography on polymer dewetting by casting poly(methyl methacrylate) films on glass substrates that are roughened directionally by rubbing. They observed an anisotropic dewetting, the period of which is in accord with that of the directional rubbing. Furthermore, Sehgal *et al* [14] studied pattern-directed dewetting on a chemically patterned substrate using hydrophilic and hydrophobic SAMs as surface modifiers. They showed that the dewetting pattern follows the substrate pattern period, leading to the formation of droplet arrays. The interplay between the characteristic wavelength of the instability and the size of the template pattern has become an active topic of research both theoretically [15, 16] and experimentally [14, 17].

Thus, wetting and dewetting (or physical self-organization in general) when combined properly would provide a convenient route to fabricate ordered polymeric microstructures. To achieve this goal, most techniques have employed SAMs, photolithography, or metal deposition to modify the surface properties of the substrate. Since such modifications require additional effort and are difficult to make for some systems, a technique that does not involve a surface modification would be valuable.

Recently, we presented a simple lithographic tool called capillary force lithography (CFL) for patterning a polymer film [18, 19]. When a patterned polydimethylsiloxane (PDMS) mold is placed on a spin-coated polymer film and then heated above the glass transition temperature (T_g) of the polymer, the capillarity forces the polymer to melt into the void space of the mold, thus yielding a negative replica when the mold is removed. In forming polymer micro-to-nanostructures by CFL, we observed dewetting of polymer films when the void space of the mold was not completely filled with the films [20–23]. It turned out that the onset of dewetting and the resulting morphology of polymer microstructures highly depended on the molecular weight and thickness of the polymer and the geometry of the mold. In such a one-step application of the mold, polymer blocks or ripples form depending on the channel width and film thickness, for which physical self-organization is responsible.

Interestingly, one can observe a similar ordering of a polymer film when the mold is placed on a pre-existing polymer pattern. In such a two-step application, various multi-level microstructures result such as lattices, ripples, or holes, some of which were reported previously [24]. Since the film thickness is much larger than 100 nm, dewetting has less to do with this ordering, for which capillary dynamics is more likely to be responsible. The term, capillary dynamics, implies that the wetting properties of the polymer could be different in three dimensions within the PDMS cavity, resulting in an unexpected complex microstructure.

Combining these earlier findings and recognizing that, in principle, the PDMS mold can be applied many times to fabricate a certain desired structure, we present herein a generic way of forming polymeric microstructures using physical self-organization and capillary dynamics. The concept is equally applied to freestanding polymer sheets and polymer microspheres as described below. While some of the microstructures have been reported [20, 24], they are included here for completeness and for the conditions under which various structures result.

2. Experimental section

2.1. One-step method

We fabricated a PDMS (Sylgard 184, Dow Corning) mold that has a planar surface with recessed patterns by casting PDMS against a complementary relief structure prepared by the photolithographic method. The mold has equally spaced line-and-space patterns (1, 2, and 3 μm) with a step height of 550 nm. The mold with the patterns was placed on the surface of a polymer layer spin-coated (Model CB 15, Headaway Research, Inc., USA) onto a silicon or silicon dioxide substrate ($SiO_2 \sim 1$ μm) and then heated well above the glass transition temperature of the polymer (typically 130–150 °C). We did not observe any difference between the silicon and silicon dioxide substrates, presumably due to the presence of the native oxide layer on silicon. For the polymer, we used polystyrene (PS) ($M_w = 2.3 \times 10^5$, $T_g = 101$ °C). The substrate was cleaned by ultrasonic treatment in trichloroethylene and methanol for 5 min each and dried in nitrogen. The film thickness was measured by elipsometry (Gaertner L116A, Gaertner Scientific Corp, USA). Scanning electron microscopy (SEM, XL30FEG, Philips Electron Co., Netherlands) was carried out for the cross-sectional images. Atomic force microscopy (AFM, Dimension 3100, Digital Instrument, USA) measurements were made for the planar and three-dimensional images, operated in the contact mode. Details on the experimental procedure can be found elsewhere [18].

2.2. Two-step method

We used two kinds of mold for the two-step method; one is a line-and-space pattern that has a line width of 700 nm with a step height of 100 nm. The other is another line-and-space pattern that has lines varying in width from 1 to 10 μm and a step height of 220 nm. After forming an underlying polymer structure at 150 °C for 1h using the first mold, the second mold is placed on the underlying pattern, rotated by a certain angle with respect to the first mold and the sample is heated above the glass transition temperature, typically 130 °C, for various annealing times. The structures thus obtained were examined by AFM in the contact mode. We used PS ($M_w = 2.3 \times 10^5$, $T_g = 101$ °C) for the polymer and silicon wafer as the substrate. Polymer films were spin coated onto the substrate to a thickness of 350 nm to remove substrate effects. Details on the two-step method can be found elsewhere [24].

2.3. Applications to freestanding polymer sheets

A few drops of a 10 wt% PS solution in toluene ($M_w = 2.3 \times 10^5$) were dispensed onto a patterned PDMS mold. A film ($\sim$11 μm thickness) formed immediately by spin coating the solution at 3000 rpm for 20 s. Then, another patterned PDMS was placed on the polymer film with a certain rotation angle and the temperature was raised above the glass transition temperature, typically 110 °C, for 5 min. To ensure conformal contact, a pressure of $\sim$10 N cm^{-2} was applied on top of the sandwiched PDMS molds. After annealing, the film was easily detached from the molds, forming a freestanding PS sheet with both sides patterned. For a stack of PS sheets, the same step was repeated several times and the sheets thus obtained were laminated through manual alignment under the same conditions as for forming the freestanding sheet. After detachment, a laminated stack of patterned sheets resulted and was analyzed using an optical microscope and SEM.

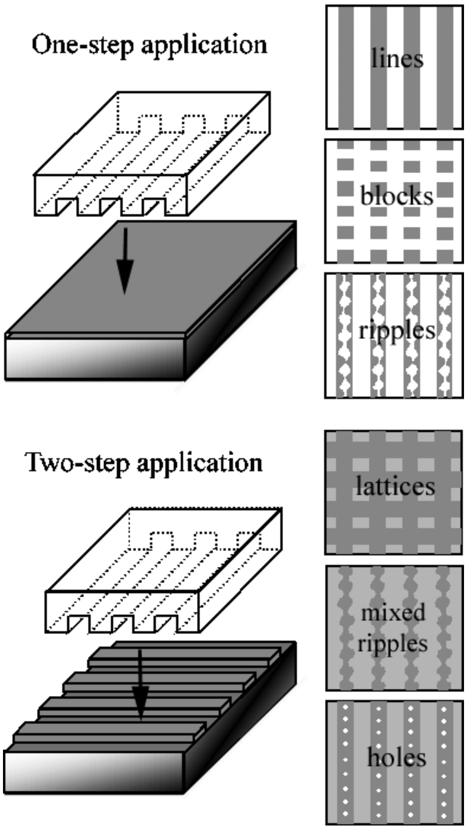

Figure 1. Schematic diagrams of the one-step and two-step methods and the corresponding possible polymeric microstructures. The white background in the one-step method indicates that the substrate surface could be exposed, which is not the case for the two-step method. The gray background in the lower part reflects the non-exposure.

2.4. Applications to polymer microbeads

Monodisperse PS microspheres (3.0 μm in diameter, purchased from Aldrich) were suspended in distilled water at a volume fraction of 10%. To obtain a relatively uniform distribution of particles on the substrate, the latex suspension was spin coated onto a hydrophilic substrate such as glass or silicon dioxide at 1000 rpm for 20 s. The samples were dried overnight at room temperature to ensure complete water evaporation. As the initial rough morphology does not allow for conformal contact between the mold and the substrate, a pressure of $\sim$10 N cm^{-2} was applied on top of the PDMS mold. To allow for the pattern formation on the surface of PS microspheres, the temperature was raised to 120 °C for 15 min. After removal of the mold, the samples were analyzed using an optical microscope and SEM.

3. Results and discussion

3.1. Polymer lines, blocks, or ripples in the one-step method

A schematic diagram for the one- or two-step method is shown in figure 1 with the corresponding possible shapes of polymer microstructures. As shown in the figure, in the case of the one-step method, three kinds of structures are observed by using a line pattern: polymer lines, blocks, or ripples. A prerequisite to block or ripple formation is that the polymer film should be thin enough so as not to fill up the void space of the mold. If the void space is completely filled, there is no room for movement of the polymer melt and simple line patterns result (figure 2(*a*), 1 μm lines and 350 nm thick film). In a previous study of ours [20], we showed that regularly spaced holes initially nucleate on the polymer surface when the void is partially filled and then grown with the aid of the confining PDMS walls, resulting in the formation of distinctly observable, regularly spaced blocks along the channel direction (figure 2(*b*), 1 μm lines, 67 nm

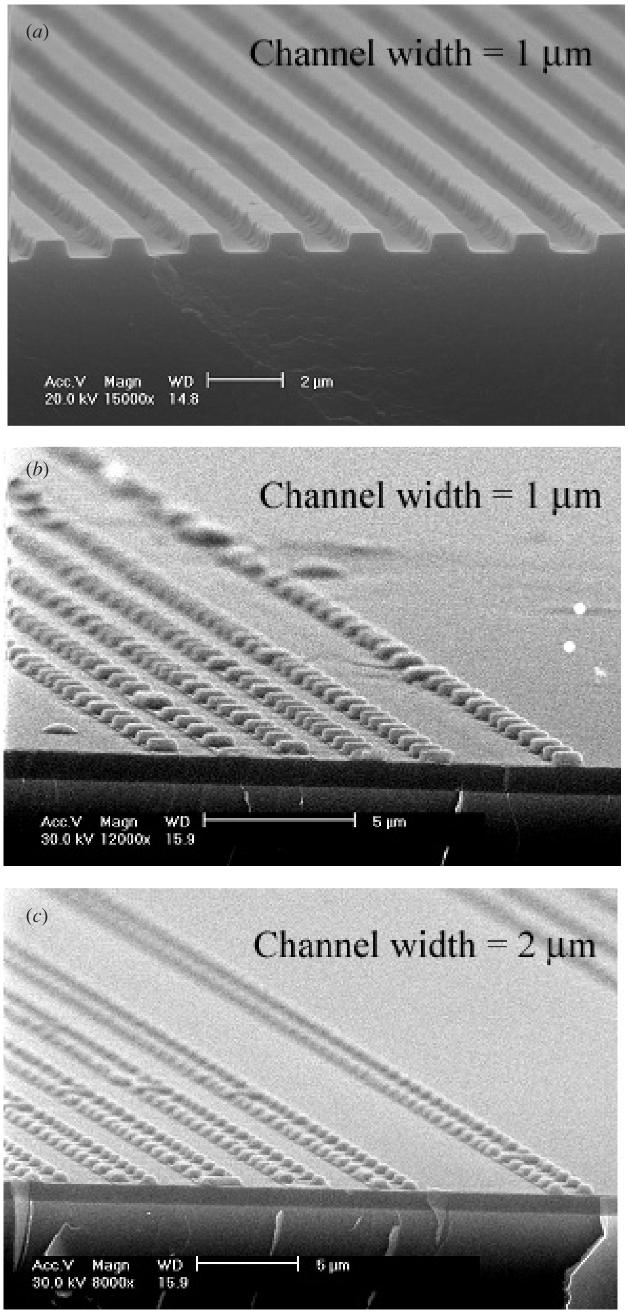

Figure 2. Cross-sectional SEM images of the three kinds of microstructure that result with the one-step method: (*a*) polymer lines, (*b*) blocks, and (*c*) ripples. The channel widths are shown in the figure.

thick film). At present, the underlying mechanism and the period of the blocks are not completely understood, and are currently under investigation. Apparently, the van der Waals intermolecular interactions have less to do with the instability because of thick films inside the channel (>100 nm), for which the capillary instability of a liquid thread is likely to be responsible [25].

Interestingly, when the channel width is relatively large compared with the film thickness, polymer ripples rather than blocks form along the channel direction. In this case, the polymer stripes split along the centerline of the channel (figure 2(*c*), 2 μm lines, 67 nm thick film). Although a detailed explanation is not available for this phenomenon, the meniscus developed within the channel or cavity appears to play an important role in the two kinds of morphology. When the meniscus is fully developed (which requires enough mass) such that a uniform curvature forms, the polymer starts rising until the mass becomes nearly depleted. After a certain incubation time, holes nucleate on the top surface of the polymer and then grow laterally, leading to the regularly separated polymer blocks. This process resembles the conventional dewetting of polymer films [7]. On the other hand, when the meniscus breaks down due to the lack of mass, the polymer stripes split and are localized at both confining PDMS walls of the cavity to minimize the surface-to-volume ratio, which gives rise to the ripple formation. This ripple structure could be potentially useful for templates of microfluidic channels.

To gain an understanding of the polymer block or ripple formation, we consider the film thickness that is needed to form a stable meniscus. A simple geometric consideration gives the contact angle θ at the PS/PDMS interface as follows [26]:

$$\cos\theta = \frac{2(\Delta/L)}{1+(\Delta/L)^2} \tag{1}$$

where Δ is the height difference between the highest and lowest points of the meniscus and L is the half width of the meniscus. If we use 20, 6, and 40 mJ m^{-2} for the interfacial tensions at PDMS–air, PDMS–PS, and PS–air interfaces, respectively [27], a contact angle of 70° results. Our experimental results based on the cross-sectional profile of the meniscus yielded an equilibrium contact angle of 73°, which is slightly larger than the value predicted from Young's law. If we use 73° as the contact angle in equation (1) and solve the equation for Δ, there results

$$\Delta = L\frac{1-\sin\theta}{\cos\theta} \cong 150 \text{ nm} \tag{2}$$

where L is 1 μm. Since the film thickness, 67 nm, is much smaller than 150 nm, a uniformly curved meniscus cannot form whereas a stable meniscus forms in the case of a 1 μm channel ($l = 0.5$ μm, for which $\Delta = 75$ nm), considering mass movement from the adjacent regions. Thus, one can observe a morphological transition from uniform lines to blocks to ripples as the thickness decreases for a given channel width.

In general, uniform lines result when the polymer fills up the void space of the mold. If it partially fills up the void space, two different morphologies emerge, given sufficient time for the system to reach its equilibrium, depending on the relative magnitude of Δ with respect to the film thickness t. For the equal line and space mold pattern under consideration, the maximum height the polymer can reach is $2t$ if all the polymer is used up in filling the void space. Therefore, the block morphology would result if $2t > \Delta$ whereas the ripple structure would if $2t < \Delta$ since a uniformly curved meniscus cannot form if $2t < \Delta$.

3.2. Polymer lattices, mixed ripples, or holes in the two-step method

Since CFL utilizes a natural force of capillarity without any external modification, this natural force could lead to the self-organization of polymers into an ordered structure if it is properly manipulated. In a previous study of ours [24], we have shown that various microstructures can be obtained for different purposes including regular arrays of holes and twisted microstructures, simply by changing the rotation angle of the second mold with respect to the first, the shape and pattern of the second mold, and those of the underlying polymer structure. Also we have shown that the periodicity of the microstructure is entirely determined by that of the underlying polymer structure over which one has control.

While the one-step method utilizes dewetting in a confined geometry, these results suggest how capillary dynamics (or simply wetting) can be used to obtain complex ordered structures without modifying the wetting properties of the substrate. Several microstructures that result when the rotation angle is 90° are shown in figure 3. When the pattern periods of the two molds are the same, a lattice structure is generated as shown in figures 3(*a*) and (*b*) for which 700 nm pattern molds were used. When the pattern periods are different, a hole or mixed ripple structure results depending on the wetting uniformity of the second mold. A symmetric structure results if the wetting is uniform; otherwise, an asymmetric structure forms. The symmetric structures [24] are shown in figure 3(*e*) for two rows of holes and in figure 3(*f*) for one row of holes for which the pattern period of the first mold is 700 nm and that of the second mold is 5 μm in figure 3(*e*) and 1 μm in figure 3(*f*). The asymmetric structure is shown in figures 3(*c*) and (*d*) where holes are on one side and ripples on the other. The pattern period of the first mold is 700 nm and that of the second mold is 5 μm, for which the symmetric structure of figure 4(*e*) should have resulted but for the nonuniform wetting. This asymmetric structure is not easily accessible by other methods. Furthermore, a close examination of the sectional AFM images of the figures revealed that each microstructure is multi-leveled, having three to four different pattern heights that would potentially be useful as templates for optical and microfluidic applications.

The criterion to determine which structure results is related to a number of parameters such as the step heights of the underlying and second mold pattern, the periods of the first and the second molds, the wetting conditions of the second mold, and the temperature [24]. In general, when the step height of the underlying pattern is equal to or larger than that of the second mold, no hole or ripple formation occurs. Instead, an isolated line or lattice pattern results with different pattern heights (figures 3(*a*) and (*b*)). When the step height of the underlying pattern is smaller than that of the second mold (100 nm and 220 nm, respectively for figures 3(*c*)–(*f*)), one can observe hole or ripple formation depending on the channel

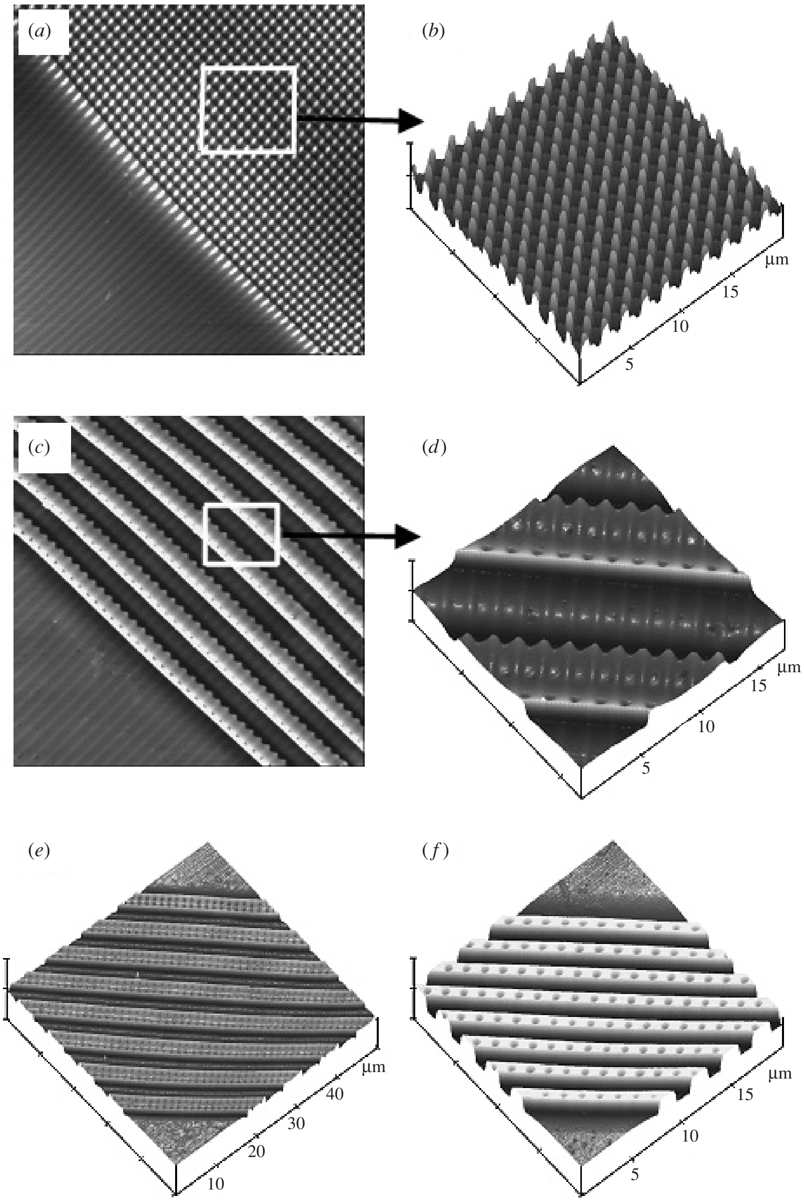

Figure 3. Two-dimensional and three-dimensional AFM images of the several possible microstructures that result with the two-step method (the rotation angle is 90°): (*a*), (*b*) polymer lattices with four different levels of height, (*c*), (*d*) mixed ripples consisting of holes and ripples, (*e*) two rows of holes, and (*f*) one row of holes. The scan size for the planar view is $50 \times 50\ \mu m^2$.

width of the second mold. In particular, the formation of one or two rows of holes depends on the presence of a stable meniscus within the second mold. As described in our previous study [24], the half width of the meniscus within the second mold or the distance to which half of the meniscus extends across the channel is given by

$$L = \Delta \frac{\cos\theta}{1 - \sin\theta} = 220\ \text{nm} \frac{\cos 73^\circ}{1 - \sin 73^\circ} \cong 1.5\ \mu\text{m} \qquad (3)$$

where 220 nm is the step height of the second mold used in the experiment. This result indicates that two separate menisci can form, one each near each of the two PDMS walls, when the channel width of the second mold is larger than two times the half-width or in this case about 3 μm. Then, one can observe two rows of holes as a result of the competition between wetting velocities in upper and lateral directions (figure 3(*e*)). When the channel width is smaller than 3 μm, one row of holes forms due to the stable meniscus as shown in figure 3(*f*). In addition, a uniformly curved surface can be realized even in the channel width larger than 3 μm if the mobility of the polymer is sufficiently high. We have shown this result by simply increasing the annealing temperature from 130 °C to 150 °C for the same annealing time [24].

If the wetting of the second mold is not uniform, one can observe an asymmetric structure as shown in figures 3(*b*) and (*c*). In this case, the wetting on one side progresses faster than that on the other, rendering an asymmetric nature. It is noted in this regard that the ripple structure is a prior step to the hole structure. Although we do not mention the case when the rotation angle is 45° or acute (isolated or twisted microstructures), the wetting dynamics can be explained in a similar manner.

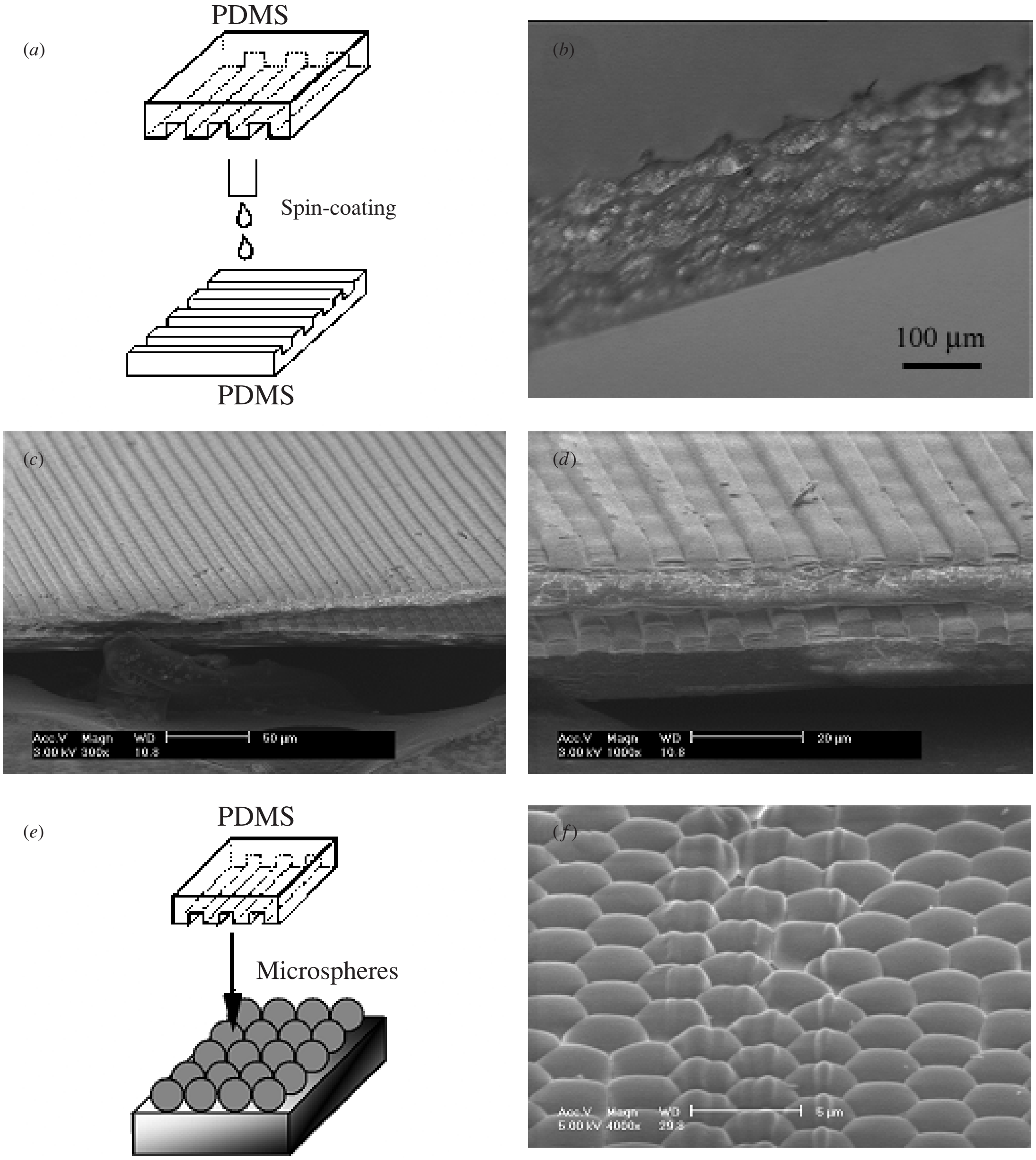

Figure 4. A structured single or stacked polymer sheet fabricated by applying capillary dynamics to freestanding polymer sheets: (*a*) schematic procedure for forming a freestanding sheet, (*b*) an example of five-layer stacked polymer sheet with a groove pattern, (*c*) laminated two polymer sheets having 5 μm lines on both sides (the rotation angle is 90°). Patterning of the polymer microsphere surface using capillary dynamics: (*e*) schematic procedure and (*f*) patterned 3 μm diameter PS microspheres.

3.3. Stacking of freestanding patterned polymer sheets using capillary dynamics

So far CFL has been utilized for the purpose of fabricating various polymeric microstructures for the thin films that are confined to the substrate. It can also be utilized to have freestanding polymer sheets patterned and even stacked to form a multilayer using capillary dynamics. A schematic diagram for the experimental procedure is shown in figure 4(*a*) where two PDMS molds are sandwiched to generate a freestanding sheet in-between. In the course of spin coating and drying, the solution fills the cavity of the underlying PDMS mold (the substrate in this case), forming a film patterned on one side with a flat opposite surface. Carrying out CFL with a second mold that is placed on the flat top side of the film at an angle with respect to the underlying mold pattern and then removing the molds produces a freestanding polymer sheet that is patterned on both sides of the film. It is noted in this regard that the interactions between the PS film and the PDMS mold are minimal such that no sophisticated effort is necessary for the mold detachment. The same step can be repeated many times to produce the patterned sheets. To laminate the sheets after stacking them, the temperature has to be raised above T_g for at least a few minutes under an applied pressure ($\sim$10 N cm^{-2}).

Shown in figure 4(*b*) is an optical image of five stacked layers with a groove pattern. While the alignment was not successful, this result indicates how freestanding polymer sheets can be patterned and stacked into a multilayer structure. Shown in figures 4(*c*) and (*d*) are two 10 μm polymer sheets with 5 μm lines of which each are bonded with apparent good alignment. The gap between the sheets in the figure was generated during sample cutting and was not present in the original laminated sheets. It is noted that each sheet is patterned on both sides, the top pattern being perpendicular to the bottom pattern of the sheet (see the ripple-like structure crossing the top line pattern in figure 4(*d*)). In the experiment, the alignment was performed manually, and thus a slight mismatch is typically observed between the adjoining layers.

3.4. Shaping the surface of polymer microspheres using capillary dynamics

Finally, we demonstrate the use of capillary dynamics to pattern the surface of polymer microspheres. Recently, we found that PS beads can be ordered inside the PDMS channels when a pressure is applied to the colloidal particles between a solid substrate and a patterned PDMS mold [28]. For the ordering to take place, the channel size and height of the mold should be larger than the diameter of the PS microsphere, which is readily understood from geometric consideration. When the microsphere diameter is larger than the channel width, on the other hand, the ordering is highly suppressed. Instead, the microsphere surface is patterned as in CFL.

Shown in figure 4(*f*) is a typical example of patterning the microsphere surface. A PDMS mold with 1 μm wide channels was placed on 3 μm diameter PS beads so that parts of the bead surface could be patterned. It can be seen in figure 4(*f*) that parts of the beads have protruding features due to CFL on the beads. Although precise control over pattern fidelity and uniformity appears to be an obstacle for this purpose at this time, the method presented here would pave the way to tailoring the surface morphology of polymer microspheres.

4. Summary

It has been shown that various complex polymeric microstructures can be fabricated by controlling the wetting and dewetting properties of polymer melt in capillary force lithography. The method is versatile and can be expanded to a variety of substrates since it does not involve any modifications of the substrate surface. A number of intriguing structures have been observed. With the one-step method, lines, blocks, or ripples were generated depending on the film thickness and the channel width. Although PS films were tested throughout the paper, the method is equally applicable to other polymers. With the two-step method, lattices, mixed ripples, or holes were generated when the rotation angle of the second mold was 90°. When the angle was 45° or acute, twisted or discontinuous microstructures formed depending on the film thickness and channel width of the second mold. In addition to applications to polymer films, the method has also been applied to freestanding polymer sheets and polymer microspheres, leading to tailored surface microstructures. Although capillary force lithography has been created as a lithographic tool to replace photolithography for the sub-100 nm regime, we envision that the technique could also be a new genre for forming complex polymeric microstructures through physical self-organization and capillary dynamics.

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