JOURNAL OF MATERIALS SCIENCE **39** (2004) 2243–2247

One-step fabrication of polymer thin films with lithographic bas-relief micro-pattern and self-organized micro-porous structure

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Lithography, which is recognized as a top-down approach, has been the most successful technique for the fabrication of fine micro scale textures. The technique allows us to fabricate very complex structures such as electronic circuits on the computer chip. On the other hand various kinds of self-organization processes have also been investigated extensively as alternative methods. For example, it was reported that micro textures can be formed using the self-organization of polymers as follows. Phase separation in thin films of block copolymers is a thermodynamically driven process [1]. The dewetting process of liquid polymer films can produce complicated patterns like network structures [2]. Polymer films having a honeycomb structure are produced by simple solution casting of various materials [3–10] and the structure can be used as a template for further material patterning [11]. Such mesoscopic patterns formed by self-organization of polymers are becoming increasingly important, because the procedure is more cost-saving and technologically simpler than those for lithography. However, the resultant structures or patterns formed by the self-organized processes are often uniformly regular over substrate surfaces, e.g., stripes, circular droplets, pores, and their combinations [12]. Under the present status of development the non-lithographic methods are not as suitable for fabrication of complicated structures as the conventional lithography. A combination of lithographic and self-organization methods is expected to lead to a wide variety of three-dimensional and/or hierarchical structures on the order of microns.

Here we consider a combination of those methods as a very simple one-step method for fabrication of a micro patterned polymer thin film with such hierarchical structure, which consists of a lithographic bas-relief pattern and a self-organized array of pores. The film is self-supporting. The effects of bas-relief patterns and polymer concentration on the structure of the patterned film are investigated. Scanning electron microscopy reveals the unique porous structure of the film.

The amphiphilic copolymer (Fig. 1: polymer **1**) used for the fabrication of patterned films was synthesized according to the procedure previously reported [13]. Poly(L-lactic acid) ($M_w = 8.5 \times 10^4$ to 1.6×10^5) was purchased from Sigma. The water was purified by a Mili-Q system (Milipore). Other chemicals were commercially available and used without further purification.

The patterned films were fabricated on poly(dimethyl siloxane) (Sylgard184, Dow-Corning), PDMS, elastomer substrates with bas-relief patterns (Fig. 2). The master patterns were produced by Dai Nippon Printing Co., Ltd., Tokyo, Japan. The pattern fabricated in the area of 10 mm × 10 mm consists of photo resist (BMRC-1000) with 10 μm thickness on a copper substrate. The PDMS was cured on the master pattern at 60 °C for 4 h. The PDMS was removed from the master pattern. We used two different patterns: pit and groove. The pit pattern has line width of 15 μm with spacing of 50 and 100 μm. The groove pattern has line width of 20 μm with spacing of 50 and 100 μm. The surface of the PDMS substrate was treated with oxygen plasma for three minutes at 10 W (PE-2000, South Bay Technology), and then, immediately dip-coated with hydroxyethylcellulose (HEC Daicel, Daicel Chemical Industries) using the 1 wt% aqueous solution with a coating speed of 1–10 mm/s. This coating helped the detachment of the patterned polymer thin films as described below. No topographical difference was observed at the micro-meter scale after hydroxyethylcellulose coating, whose thickness was approximately 0.2 μm. For preparation of the patterned film 30×10^{-9} m^3 of dilute benzene solution of the mixture of polymer **1** (0.2 kg/m^3) and the poly(L-lactic acid) (2.0 kg/m^3) was cast onto the PDMS substrate and humidified air (20 °C and 80% RH) was blown to the solution surface from a glass pipe nozzle (ϕ5 mm) at the flow rate in the range from 1.67 to 5.00×10^{-6} m^3/s. The nozzle was placed 10 mm above the solution surface. The *in-situ* observation of the film formation process was conducted using transmission optical microscopy (BX60, Olympus). Then, the PDMS substrate with the fabricated patterned film was immersed in water at room temperature. During the process, the hydroxyethylcellulose coating was dissolved.

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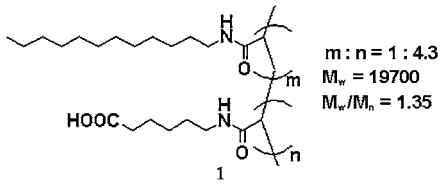

Figure 1 Chemical structure of amphiphilic polymer **1** applied to the fabrication of films.

Therefore, the patterned film was peeled in the water by applying very small force. The patterned films were typically several micrometers thick and 100 mm^2 in extent. The structure of the self-supporting patterned film was observed by scanning electron microscope (S-5200, Hitachi) without any additional conductive coating layer.

The patterned polymer thin film was fabricated under the optical microscope for the *in-situ* observation of the pattern formation process (Fig. 3). At the first stage, a self-organized two-dimensional hexagonal array of the water micro-droplets (ϕ ca. 4 μm) stabilized by polymers was floating on the solution surface (Fig. 3i). The water was originally condensed on the evaporating solution surface from the humid air due to the temperature decrease of the solution [3–10, 13]. As evaporation of the solvent proceeded, the array of droplets touched a plateau of the bas-relief pattern (Fig. 3ii). Then, the parts of the array that were still floating on the solution above the valley of the PDMS substrate started to be pulled in the vertical direction. This was caused by the capillary force between the array and the substrate due to decrease in the amount of solution as the solvent evaporated Fig. 3iii). At this point the monolayer of the water droplets with the polymers in between them was deformed to fit to the bas-relief pattern of the PDMS substrate. Then, the solvent dried up. Finally, the water dried up leaving a porous thin film with the bas-relief pattern. The key point of the present method is that the hierarchical pattern formation process occurred at exquisite timing, at which the transiently-formed self-organized monolayer of the water micro-droplets with polymers in between them was soft enough to be deformed by the capillary force and was not so weak to be torn and be destroyed by the force. Since the polymers contained solvent molecules at this time, the monolayer was pliable. It is important to emphasize that the present method simultaneously involves two processes, the self-organization of water micro-droplets and the bas-relief pattern-imprinting process. These processes result in the hierarchical patterns, an array of the pores and artificially-tailored topography. In analogy with the system of patterned self-assembled monolayer by micro contact printing

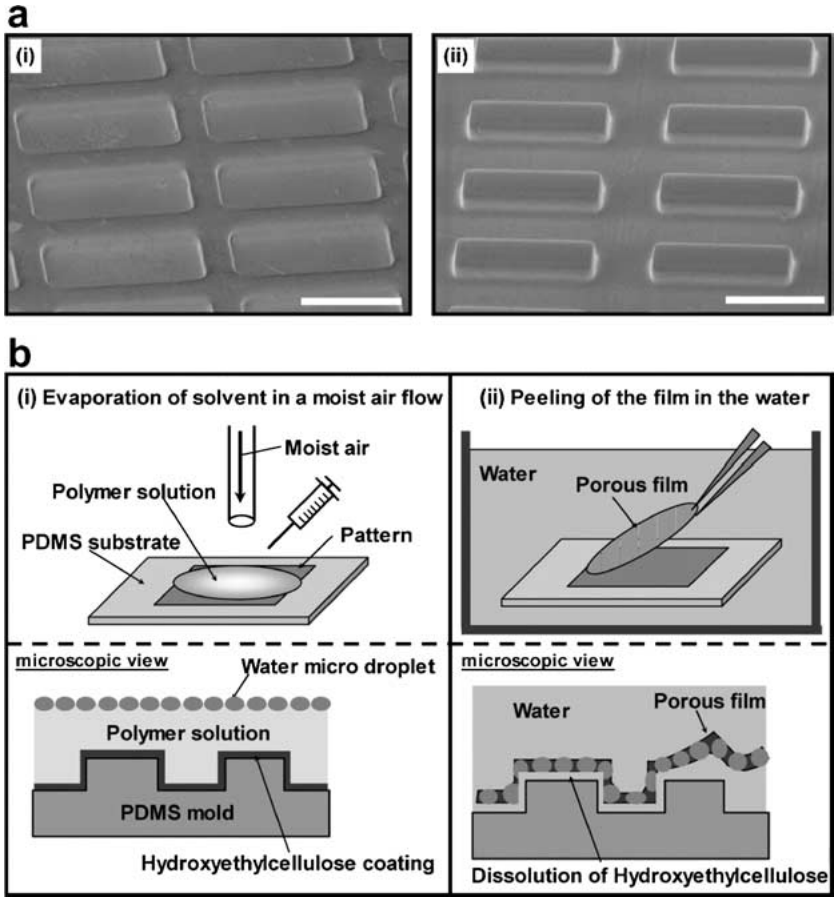

Figure 2 (a) Scanning electron micrographs of the bas-relief patterns of the PDMS substrates (bar: 30 μm). Patterns of (i) pits and of (ii) groove, which have line widths of 15 and 20 μm, respectively, with spacing of 50 and 100 μm. The height of the pits or the depth of the groove is 10 μm. (b) Fabrication process of a patterned polymer thin film with a hierarchical structure. (i) A droplet of the polymer solution was spread onto the PDMS substrate with a bas-relief pattern. Solvent of polymer solution was evaporated in a flow of moist air leaving a patterned polymer porous thin film on the substrate. (ii) Since the hydroxyethylcellulose coating dissolved into the aqueous phase, the porous film was easily peeled with tweezers.

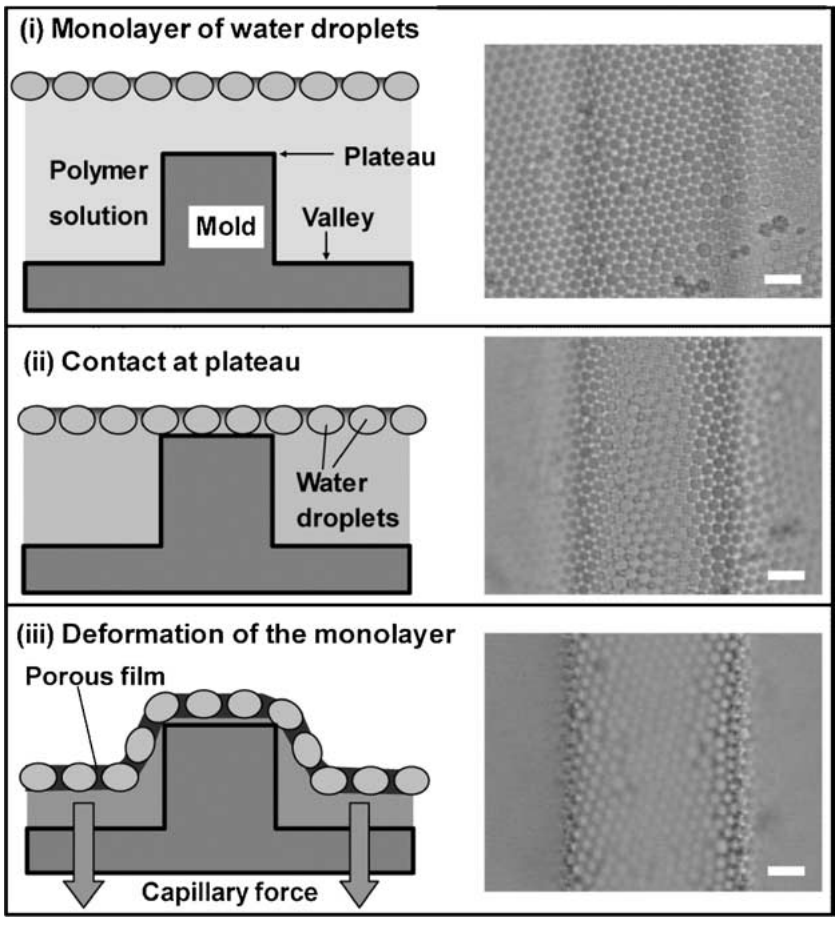

Figure 3 Schematic illustrations (side views) and corresponding snapshots (top views; bar: 10 μm) from the *in-situ* observation for the bas-relief pattern-imprinting process. Note that the array of water droplets at the lower part of the pattern becomes out of focus indicating that the film deforms to fit the bas-relief pattern of the PDMS substrate.

method [14, 15] the printed patterns originate from conventional photolithography and the array of the molecules in the monolayer domains are self-organized at the molecular scale. Therefore, it is possible to say that the difference between such systems and the present one is the length scale of the self-organized structure.

Different self-supporting patterned films were prepared changing the pattern of the mold and the concentration of the solution (Fig. 4). The bas-relief patterns of the PDMS substrate were transferred to the films. The films were self-supporting.

The structure of the reverse side of the films can be controlled by the concentration of the polymer solution. With the higher polymer concentration, 3 kg/m^3, the reverse side of the film was covered by the thin polymer film, which is referred to as the *bottom* (Fig. 4a). On the other hand, the lower polymer concentration, 1 kg/m^3, gave a film without a continuous connecting "*bottom*" (Fig. 4b). The polymers are deposited at the air-solution interface with the water micro-droplets as the template of pores. Therefore, when the amount of the polymer is enough to fill the space between the droplets, the excess polymer is deposited beneath the droplets, resulting in the formation of a continuous *bottom*. In the other case, polymers are deposited only between the droplets resulting in a bottomless porous patterned film.

However, at the middle range of the polymer concentration, unique films were formed. With a concentration in between the above values, 2 kg/m^3, the film showed other morphological patterns of the polymers on the reverse side (Fig. 4c and d). The observation of morphologies of the films prepared using different bas-relief patterns, which are pits and groove, indicates that the *bottoms* are always produced at the valley of the patterns. During the bas-relief pattern-imprinting process, the excess solute polymers in the volume above the valley of the pattern are concentrated and deposited to the valley. This is the reason for the formation of the unique pattern of the *bottom* with a certain value of the total concentration, ca. 2 kg/m^3.

In summary, we developed a simple one-step method, where a solution of a mixture of amphiphilic copolymer and poly(L-lactic acid) is cast at high atmospheric humidity on a substrate that possesses a bas-relief pattern, for fabrication of a patterned polymer thin film with a hierarchical structure. The method is cost-saving because it uses self-organization and the bas-relief pattern-imprinting condensed in one manufacturing process. The hierarchical structures are the bas-relief patterns at tens of micrometer scale, which is originally tailored by lithographic technique, and the ordered array of pores with the diameters of microns, which emerges from a self-organized process. The self-supporting film is obtained by applying the water-soluble polymer

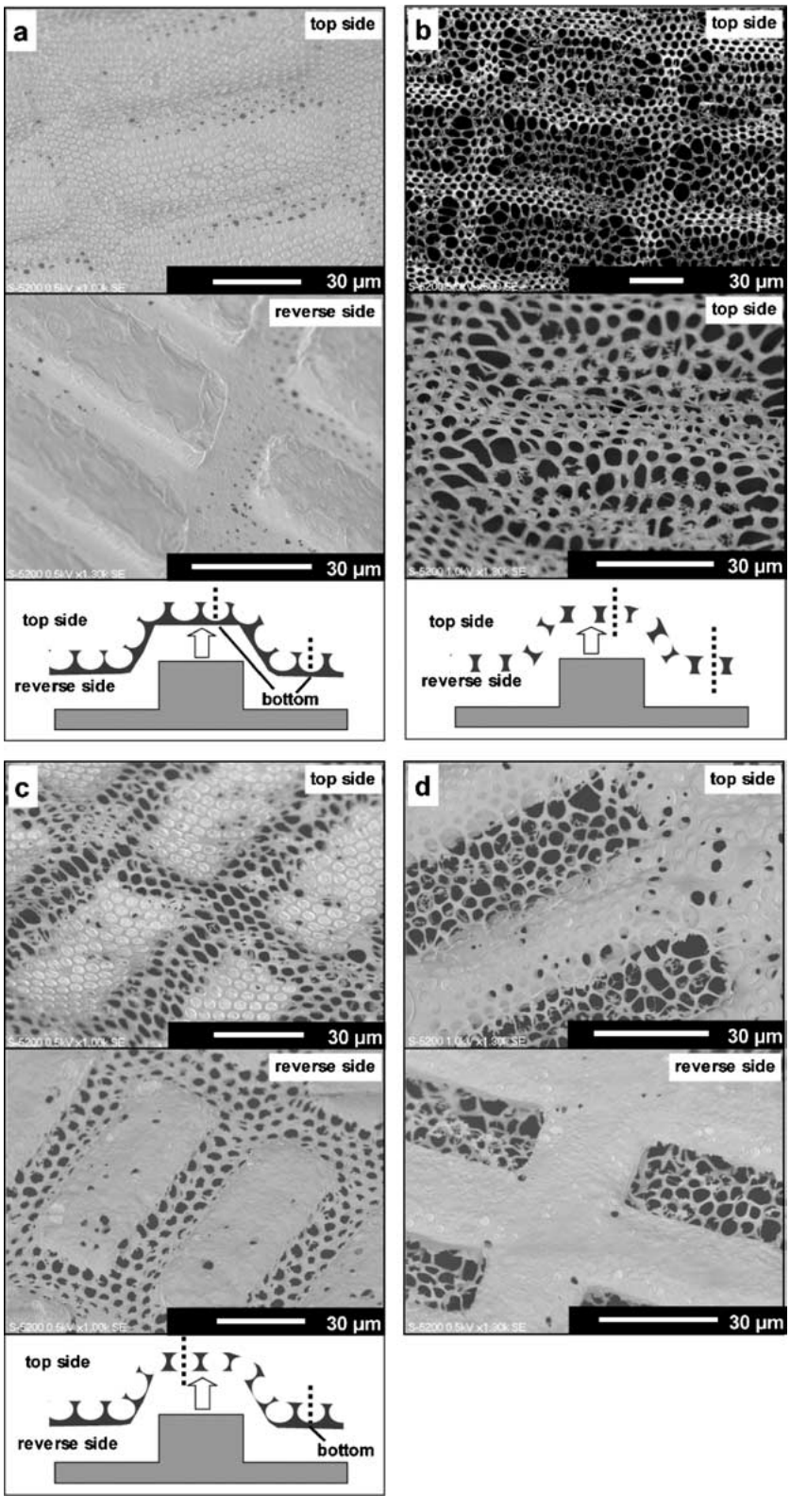

Figure 4 Scanning electron micrographs (bird's-eye view) and schematic illustrations (side view) of patterned porous polymer thin films with bas-relief patterns fabricated from solutions with different total concentrations and on different bas-relief patterns: (a) 3.0 kg/m^3, pit pattern, (b) 1.0 kg/m^3, pit pattern, (c) 2.0 kg/m^3, pit pattern, and (d) 2.0 kg/m^3, groove pattern, respectively. The films, (a), (c), and (d), were imaged from both sides of the self-supporting films. The reverse sides, which show the bottom layers of the films, had contact with the substrate when they were formed. Dotted lines indicate whether *bottoms* existed or not.

coating on the PDMS substrate. The unique bottom morphology at the reverse side of the film can be controlled by the polymer concentration. The present method suggests that hierarchical structures with more complicated lithographic patterns are able to be fabricated for further applications, such as a substrate for micro-electrical-mechanical devices and bio-medical devices.

Acknowledgments

We thank J. Hayashi and M. Hara for information about treatments of the master pattern substrate.

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Received 14 July
and accepted 6 October 2003