

A simple route to micropatterned polymer surfaces†

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Polymer surfaces with uniform microscale concave arrays were fabricated by spreading polymer solution on the nonsolvent surface, and the concave-patterned surface could further be used as a template to structure convex-patterned polymer surfaces.

In recent years, increasing attention has been paid to patterning surfaces with micro- and nanometer resolution.^{1–4} Thin polymer films with patterned surfaces have attracted enormous interest for their use in manufacturing advanced electronic, optical and mechanical devices,^{5,6} biotechnology,^{7,8} etc. A variety of techniques have been developed to fabricate specifically patterned polymer films, including photolithography,^{4,9} soft lithography,¹⁰ inverted opals,^{11–13} microphase separation in diblock polymers,¹⁴ Langmuir–Blodgett technique.^{15,16} Water-vapor induced honeycomb-patterned porous polymer films were also prepared by casting a polymer solution in a water immiscible solvent under high humidity.^{17–19} Each of these techniques has its own advantages. However, to some extent, they are very complicated, and involve some elaborate and cumbersome processing steps, or require aggressive chemistry, e.g. a specially designed device and a starting polymer with a special structure are required.²⁰ Herein, we present a very simple and general route to structure a concave patterned polymer film. In this method we spread a polymer solution on the surface of a liquid. The solvent was extracted into the liquid sublayer and a solid thin polymer film with uniform concave arrays was formed. The concave-patterned polymer films were further used as templates to mould convex-patterned polymer films.

We first discuss the preparation of polystyrene (PS) films. In a typical experiment, about 50 μl of PS in tetrahydrofuran (THF) solution was dropped on the surface of ethylene glycol (EG) in a 35 mm diameter petri dish. The polymer solution droplet spread quickly on the EG surface and solidified within a few seconds, resulting in an opaque or semi-transparent film. The film was then taken out and washed thoroughly with ethanol and dried in air. The sample was sputter-coated with 10 nm thick platinum and observed under a Hitachi S4300F scanning electron microscope (SEM) operated at 15 kV.

Fig. 1 shows SEM images of a concave-patterned PS film prepared by spreading 50 μl of 10wt% PS/THF solution on the EG

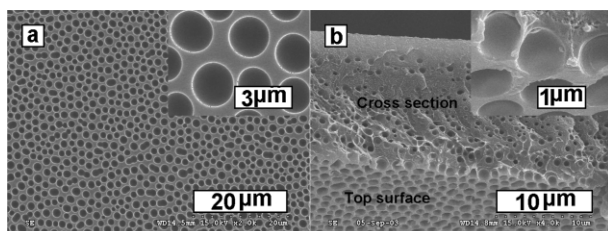


Fig. 1 SEM images of the top surface (a) and cross section (b) of the patterned PS film prepared by spreading 50 μl of 10 wt% PS/THF solution on the EG surface at ambient conditions. Insets show the same samples at larger magnification.

† Electronic Supplementary Information (ESI) available: SEM images of other concave-patterned polymer surfaces. See <http://www.rsc.org/supp-data/cc/b3/b314970f/>

surface under ambient conditions. Fig. 1(a) indicates that the top surface (the side contacting the air during the film-forming process) was patterned with fairly uniform cavities, whose diameters are about 1.5 to 2 μm , and it has a high number density of up to 10^9 features/ cm^2 . Furthermore, from Fig. 1(b) we can see that the thickness of the film was about 15 μm and it has a cross section consisting of closed cells, and the surface cavities are hemispherical cavities with radii of about 0.8–1.0 μm , which is also revealed by atomic force microscopy observation. In addition, the bottom surface of the film (the side contacting the EG surface during the film-forming process) is smooth (image not shown).

Such an asymmetric film with cellular structure originated from the phase separation induced by nucleation and growth when the polymer solution contacted the nonsolvent, EG. A possible mechanism may be as follows: the polymer solution droplet spreads on the EG surface. The THF at the solution/EG interface diffuses into the EG phase quickly because THF is soluble in EG, and a dense skin layer is formed at the bottom of the polymer solution film because EG is a nonsolvent for PS. The THF in the solution above the dense skin can also diffuse into the EG phase through the skin. However, the exchange rate is significantly reduced. The concentration of the solution changes slowly, which results in phase separation by nucleation and growth, and forms a polymer-rich phase and a polymer-lean phase in the spreading polymer solution. The successive solidification of the phase-separated solution leads to a porous, asymmetric structure, in which the polymer-lean phase gives rise to the pores. When the phase separation proceeds at the top surface of the polymer solution, i.e., the air/solution interface, the surface tension results in the specific concave patterned surface.

It was reported that a highly humid atmosphere could cause phase separation of a polymer solution and lead to porous films.^{17–19} However, in the present study, the patterned films were prepared under ambient conditions (25 $^{\circ}\text{C}$, 30–40% relative humidity) and the patterned films could also be fabricated in a dry N_2 atmosphere. Moreover, we cast the same PS solution on a glass substrate and allowed the solvent to evaporate in the air. The obtained film was transparent and non-patterned. Therefore, the environmental humidity did not play an important role in the formation of the patterned films in this work.

The size, shape and density of the cavities on the patterned PS films can be tuned by adjusting the film-forming parameters, such as the concentration of the polymer solution and coagulation temperature. Fig. 2(a) and (b) give the SEM images of the patterned surface of the PS film prepared from 10 wt% and 15 wt% PS concentration. Evidently, the cavity size decreases and the density increases with increasing PS concentration, which can be attributed to the larger viscosity of the polymer solution at higher concentration. The cavities on the surface and the cellular pores in the films originated from the nucleation and growth of the polymer-lean phase in the film-forming process. For a more concentrated solution, it is difficult to form a larger polymer-lean phase because the solution is more viscous.

Fig. 2(c), Fig. 1(a) and Fig. 2(d) give the SEM images of the patterned surfaces of the PS film prepared at 8 $^{\circ}\text{C}$, 25 $^{\circ}\text{C}$, 50 $^{\circ}\text{C}$, respectively. Obviously, the size of the cavities increases as the coagulation temperature is increased. This can also be explained from the growth process of the polymer-lean phase. The main

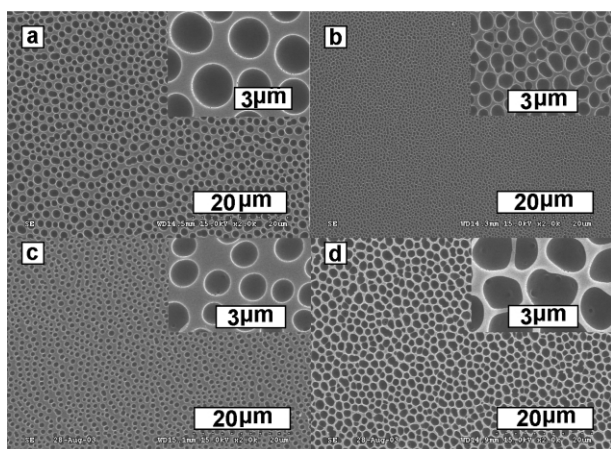


Fig. 2 SEM images of the surface of the PS films prepared under different conditions: (a) 10 wt% PS and (b) 15 wt% PS (coagulation temperature: 25 °C); (c) 8 °C and (d) 50 °C (PS concentration of 10 wt%).

reason may be that increasing temperature reduces the viscosity of the system and therefore reduces the resistance to mass transfer. Furthermore, because of the rapid mass transfer at higher temperature, the cavities on the PS film prepared at 50 °C lose their circular shape and become rough and irregular.

In addition to the above discussed PS–THF–EG system, some other polymer–solvent–nonsolvent combinations can be adopted to fabricate similar concave patterned films. Fig. S1 gives some examples.† However, the cavity density, shape and size of the films as-prepared are different because the interactions between polymer, solvent and nonsolvent are correspondingly different. On one hand, it demonstrates that such a polymer solution spreading on a nonsolvent surface is a versatile route to fabricate concave patterned polymer surfaces. On the other hand, it provides the possibility of altering the features of the surface patterns by selecting polymer–solvent–nonsolvent system.

The as-prepared concave-patterned PS films have been used as templates to fabricate convex-patterned PMMA films. In an experiment, PMMA/acetonitrile solution was cast on the preformed PS concave-patterned film whose patterned surface faces upwards. The acetonitrile was then evaporated in air resulting in a PMMA/PS composite, which was then dipped in cyclohexane at ambient temperature to dissolve the PS template and generated the convex patterned PMMA film. Fig. 3 (a) and (b) shows the convex-patterned surfaces of the PMMA film mould from concave-patterned PS films which were prepared by spreading 10 wt% and 15 wt% PS/THF solution, respectively, on the EG surface at ambient temperature. By comparing with their mother templates (see Fig. 1(a) and Fig. 2(b)), we can see that the size and density of

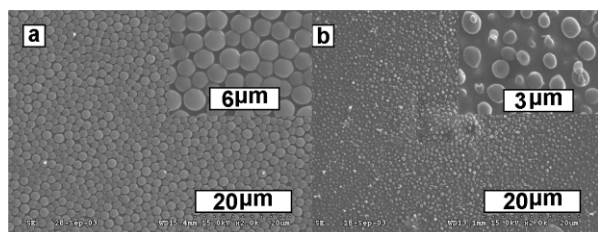


Fig. 3 SEM images of the convex-patterned PMMA films templated from the concave-patterned films prepared from 10 wt% (a) and 15 wt% (b) PS/THF solution.

the structures in the PMMA film are similar to those of the cavities of the PS templates, that is, the interior shape of the dented template cavities was faithfully copied as projected structures. In the casting process, the cavities in the PS films were filled by the PMMA acetonitrile solution completely. After the evaporation of acetonitrile, a PS/PMMA composite was obtained in which cavities and projected structures were exactly matched and occluded. When the composite was immersed in cyclohexane, the PS template layer was gradually dissolved and released the PMMA film with the convex-patterned surface. Obviously, the size, density and array of the structures on the surface completely depend on the corresponding template cavities. We believe convex-patterned surfaces of some other polymer materials can be fabricated using suitable solvents and nonsolvents for the polymers, just as acetonitrile is a solvent for PMMA and a nonsolvent for PS, and cyclohexane is a solvent for PS and a nonsolvent for PMMA.

In summary, a very simple and versatile method was developed to fabricate polymer concave-patterned surfaces by spreading polymer solutions on a nonsolvent surface. Moreover, the as-prepared polymer with the concave-patterned surface can be further used as a template to cast convex-patterned polymer surface. We believe that these patterned polymer materials may find some promising applications in the fields of electronics and photonics. In addition, due to the porous structure through the cross section of the films, they may be also used in biotechnologies, *e.g.* as supports to cultivate cells.

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