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Physical-co-Chemical Multicomponent Micropatterns on Polymer Surfaces by Thermal Pressing Method

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The ability to micropattern materials is of great importance for manufacturing advanced materials and devices. For this purpose a variety of methods have been developed, including X-ray, electron-beam, and photolithography,[1] soft lithography including microcontact printing and replica molding,[2] embossing,[3] cold welding [4], phase separation of polymer blends on patterned surfaces,[5] and deposition onto template sites or self-assembly.[6] Bipolymer features also have been fabricated by microtransfer process.[7] Especially, the ability of patterning biomolecules on solid substrates has become increasingly attractive for the development of molecular and cellular biosensors, biomaterials, and genomic or proteomic arrays.[8] All these applications often require positioning and connecting molecular components with high specificity and precision.[9]

Here we take the advantages of two classical approaches, microcontact printing and hot embossing, to develop a novel thermal pressing method (TPM), which is extremely effective for fabrication of physical-co-chemical patterns on polymer surfaces at a micrometer scale. An inked elastomeric stamp is the key element that transfers the pattern to the substrate. A schematic representation of the multistep TPM is shown in Figure 1. A poly(dimethylsiloxane) (PDMS) stamp with micrometer-scale topographical features of negative circular patterns measuring 30 μm in diameter, 30 μm in space and 4 μm in depth was used in this study.[10] The plasma-treated PDMS stamp was impregnated with a solution of type I macromolecules to form a uniform layer, followed by transfer 3× with an amino-silanized glass slide[11] to fully remove the ink on the ridges.[10,12] Then a glass slide (piranha-treated) covered by type II macromolecules was pressed onto the PDMS stamp to transfer the second component to the ridges. At a temperature a little below T_m but above T_g of semicrystalline polymer, or above T_g of amorphous polymer, the multicomponent stamp was pressed into the polymer film with a nominal pressure of 200 g/cm^2. After the stamp and polymer film cooled to room temperature, the load was released and the film was peeled off. Low adhesive force between PDMS and most kinds of

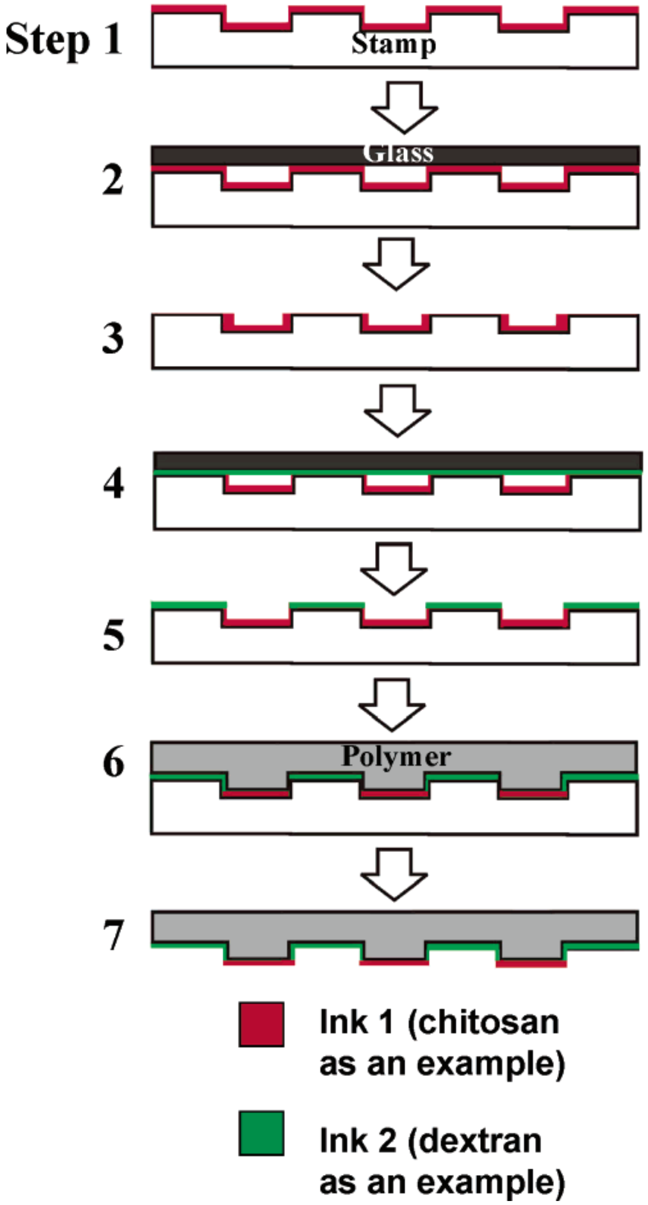

Figure 1. Schematic illustration showing the fabrication process of physical-co-chemical multicomponent micropatterns on polymer film by the multistep thermal pressing method (see text).

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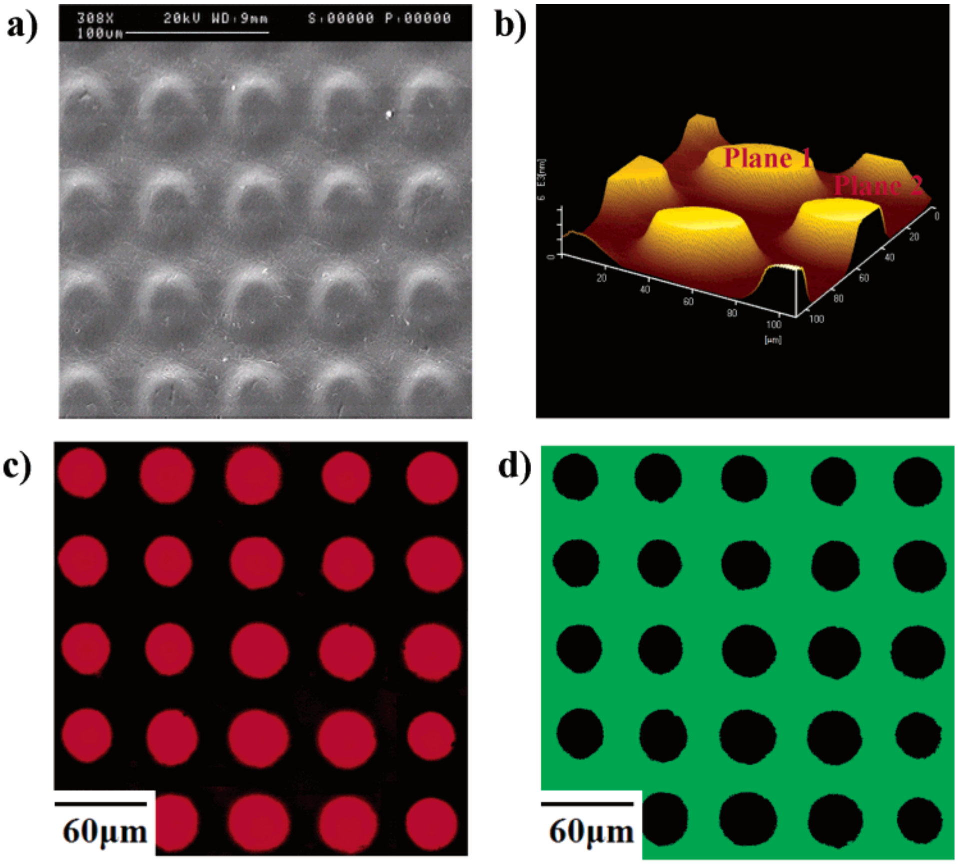

Figure 2. (a) SEM image of physical-co-chemical pattern of Rd-chitosan and FITC-dextran on PCL film created by the thermal pressing method. (b) Dynamic-mode AFM image as a magnification of (a). CLSM images of (c) Rd-chitosan and (d) FITC-dextran patterns obtained when the confocal plane was adjusted to plane 1 and plane 2 in (b), respectively. Concentrations of two kinds of ink were both 2 mg/mL, and the impregnation time for Rd-chitosan was 120 min.

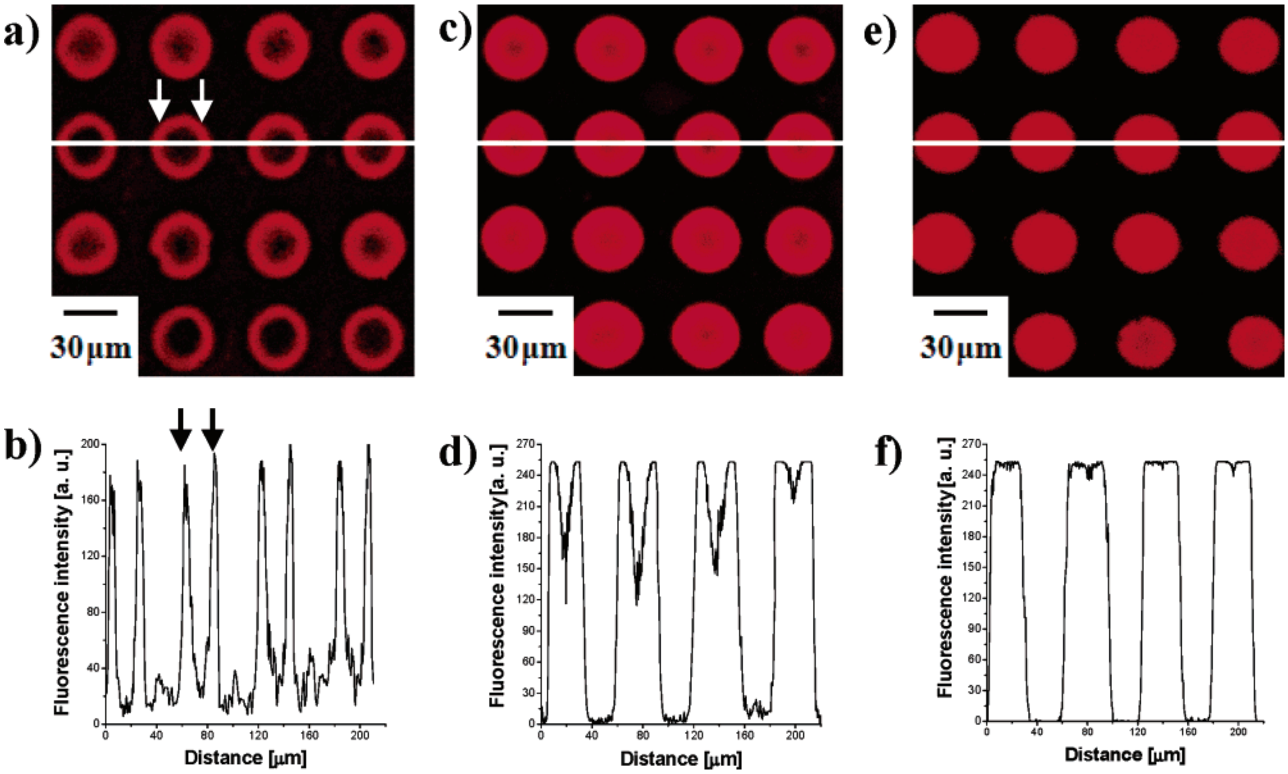

Figure 3. CLSM images ((a), (c), and (e)) and their corresponding line profiles ((b), (d) and (f), respectively) of Rd-chitosan patterns on PCL films created by the thermal pressing method.

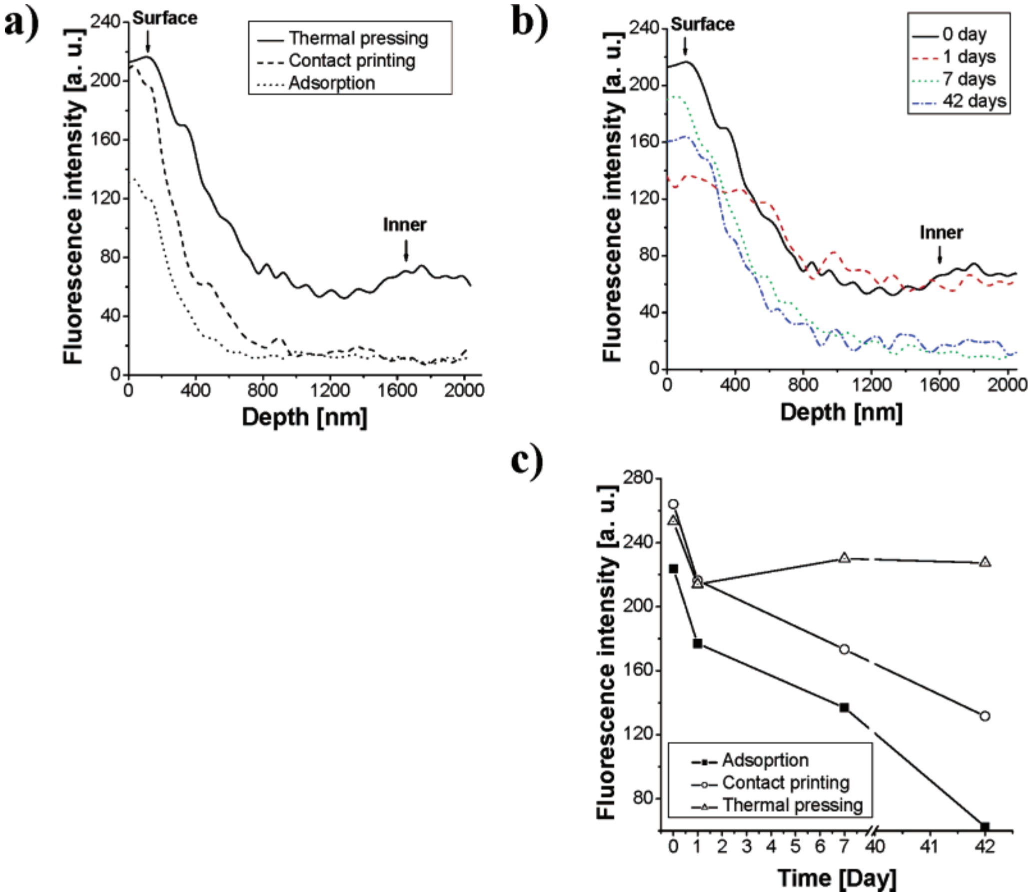

Figure 4. CLSM fluorescence intensity of Rd-chitosan layer on PCL films as a function of the depth in the z-direction collected on (a) samples fabricated with different methods, and (b) samples fabricated by the thermal pressing method after incubated in PBS solution for different time. (c) Fluorescence intensity of Rd-chitosan layer on PCL films fabricated with different methods as a function of incubation time in PBS solution. The intensity was recorded at 571 nm with an excitation wavelength of 550 nm. Concentration of Rd-chitosan solution was 2 mg/mL, and the impregnation and adsorption time were both 120 min.

polymers provides the promise of the success of TPM. Of course, if steps 4 and 5 in Figure 1 are skipped, a patterned surface of a single component can be fabricated.

The amount of substance transferred by glass slides is determined by the distributive coefficient between glass and PDMS. Hydrophobic materials usually behave with stronger binding capacity than hydrophilic surfaces. Specifically, the comparatively high affinity of PDMS stamp to water-soluble macromolecules provides the possibility of introducing a second component, while amino-silanization and piranha pretreatment of the glass slides are adopted to tune the wettability of glass surfaces as well as their distributive coefficients.

The resultant physical-co-chemical multicomponent patterns, exemplified here with co-patterns of rhodamine labeled chitosan (Rd-chitosan) and fluorescein isothiocyanate labeled dextran (FITC-dextran) on polycaprolactone (PCL) film, were characterized with scanning electron microscopy (SEM) (Figure 2a), atomic force microscopy (AFM) (Figure 2b), and confocal laser scanning microscopy (CLSM) (Figure 2c and d). As expected, uniformly periodic physical patterns and spatially localized multicomponent chemical patterns were formed. Figure 2c shows the Rd-chitosan patterns when the confocal plane was adjusted to plane 1, e.g., protuberant parts in Figure 2b, while Figure 2d corresponds to the FITC-dextran patterns at recessed parts (plane 2 in Figure 2b). This demonstrates clearly that the two kinds of biomacromolecules were selectively localized with high-resolution accompanying the formation of physical patterns. Complete transfer of the ink from the stamp to PCL was realized due to the adhesive interface, which is hard to achieve by classical approaches. The different chemical and biological properties as well as functions of these two types of polysaccharides would provide wide potential applications.[13] Moreover, we have successfully applied this method to pattern various macromolecules on different polymer surfaces, for example poly(styrene sulfonate), gelatin, and albumin (which has a comparatively high thermal denature temperature), on poly(L-lactic acid) (PLLA) or poly(methyl methacrylate) (PMMA). Theoretically, any macromolecules that could be used as ink in classical contact printing are suitable for this method. On the other hand, those polymers with hot embossing temperature below flow temperature of PDMS could be all adopted as substrata in TPM.

The shape and quality of the resultant patterns could be easily tuned by the ink concentration and impregnation time in the first step. Due to the effect of the capillary force,[14] the ink tends to agglomerate at the

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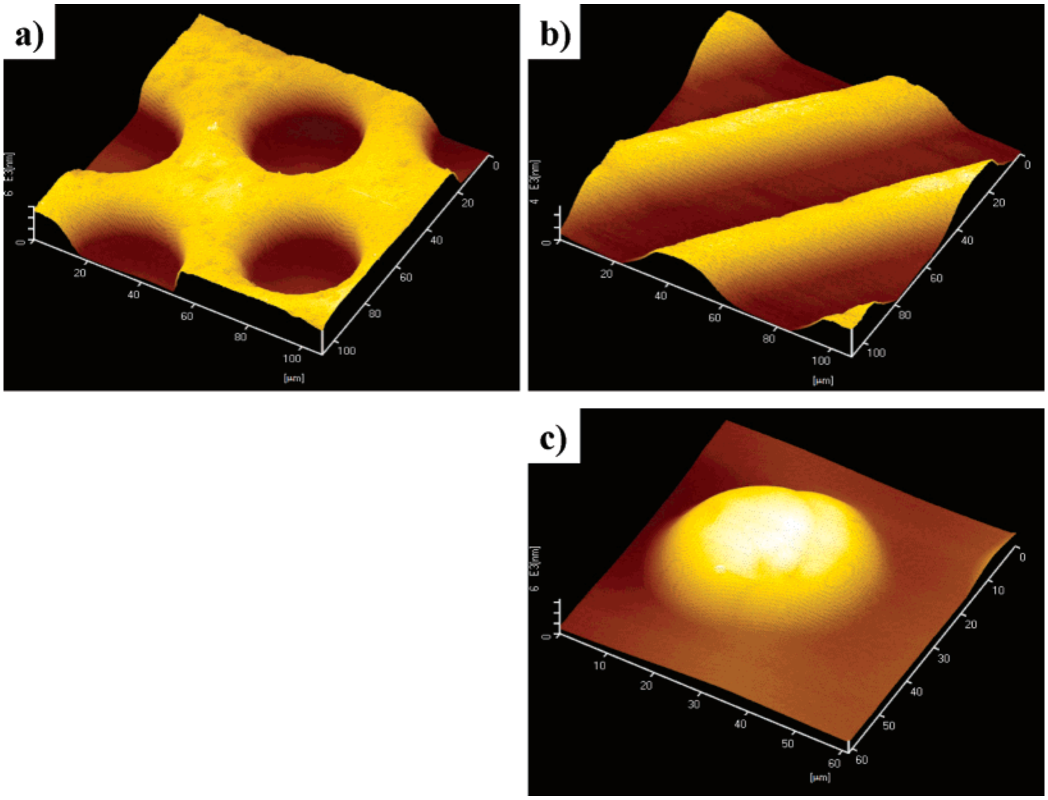

Figure 5. Dynamic-mode AFM images of (a) negative circular, (b) wavelike, and (c) hemispherical patterns on PCL films created by thermal pressing method using corresponding PDMS stamps.

topographical inflection, e.g., the boundary of patterns. We examined this effect with single-component Rd-chitosan patterns for clarity. Low concentration (2 mg/mL) and short impregnation time (20 min) created the ring-shaped patterns on PCL (Figure 3a, and Figure 3b for a fluorescence intensity profile). A higher concentration of 7 mg/mL did improve the fluorescence intensity at the centers of the patterns, yet it was still comparatively lower than that of marginal regions (Figure 3c and d). By prolonging impregnation time to 120 min with ink of 2 mg/mL, uniformly round-shaped patterns were obtained (Figure 3e and f). Our observations hinted that the adsorption process of molecules on the stamp is a kinetics-controlled procedure in which the shape of the patterns depends on the impregnation time much more than on ink concentration. Furthermore, this feature is affected by the nature of the macromolecules. For example, the transition from ring-shaped to round-shaped patterns occurred at a comparatively short period of time when PSS was used. The same phenomenon has been also observed using stamps with positive topographical features. These results show the flexibility of TPM by which different shapes of patterns as well as multi- or single-component patterns can be fabricated. If the ink concentration and impregnation time were discreetly adjusted, nanometer-scale ring-shaped patterns could be obtained using a stamp with micrometer-scale topographical features.

The intrinsic microstructure of the Rd-chitosan surfaces was characterized by the fluorescence intensity measurement at different depths of substrate with CLSM. For comparison, contact printing and solution adsorption of Rd-chitosan on PCL films were also studied. Figure 4a shows that, for TPM and contact printing, intensity at surfaces is similar but much higher than that of adsorption. As the focus plane went deeper, the intensity of the TPM sample deceased slowly and finally to $^{1}/_{3}$ of the surface. For contact printing and adsorption, the decrease was more rapid with the final intensity at $^{1}/_{6}$ of the TPM sample. Though the absolute depth is not accurate, a deeper penetration of the macromolecules for the TPM sample could be inferred. Meanwhile, it should be noted that a larger amount of Rd-chitosan was efficiently transferred by TPM than by pure physical adsorption.

As chitosan is not compatible with PCL thermodynamically, the existing format of chitosan should be thus exclusively caused by physical entrapment, e.g., the interpenetration of molecular chains as partly evidenced by the fluctuation of the fluorescence intensity in the CLSM cross-section (Figure 4a). This was further substantiated by the fact that the TPM sample had a higher stability against incubation in phosphate buffered saline (PBS, pH 7.4) as observed by both CLSM and fluorescence spectroscopy. Figure 4b demonstrates that although the ink at the surface partly desorbed the first day, it recovered again as time progressed in parallel with the decrease of inner amount. Fluorescence spectroscopy reveals a similar alteration tendency (Figure 4c), i.e., the intensity decreased initially and was followed by recovery to a higher and constant level. By contrast, the samples fabricated by contact printing or pure physical adsorption released chitosan continuously as a function of incubation time with remainings of only $^{1}/_{2}$ and $^{1}/_{4}$ after 42 days, respectively. These results would also indicate that the chitosan chains physically entrapped by TPM might gradually migrate to the surface by hydrophilic affinity and the creep of the molecular chains.

The TPM inspires also lower surface wettability compared with pure physical adsorption, as evidenced by water contact angle measurements. Similar values around 85° were found for surfaces with chitosan layers fabricated by TPM and contact printing, which is higher than the value about 65° on adsorbed layer of chitosan on PCL films. The contrast should be attributed to the random conformation of chitosan chains on surfaces fabricated by TPM and contact printing. Orientation of hydrophilic groups of ink macromolecules does not occur easily in these two methods but is in the process of adsorption.

Different dimensions and shapes could be achieved by using stamps with various kinds of topography. Figure 5 shows some examples, e.g., negative circular patterns, wavelike patterns, and hemisphere.[15] These results demonstrate that topography of stamps could be well-replicated on the polymer surfaces, which provides the promise of TPM.

In summary, we have shown here the simultaneous fabrication of physical-co-chemical multicomponent micropatterns on polymer surfaces by a thermal pressing method (TPM). Exemplified with chitosan and dextran, their co-patterns formed on PCL film were verified by SEM, AFM, and CLSM. The pattern shapes could be further tuned by factors such as ink concentration, impregnation time, and molecular nature. Owing to the distinctive microstructure, the created patterns were stable against long-term incubation in PBS solution. Additionally, there is no need of activating the substrate surface, thus this strategy can be extended to patterning inorganic particles, assembled systems of molecules,[16] and small organic or inorganic molecules. The flexibility of the stamp also enables patterning of curved surfaces.

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Supporting Information Available: Experimental section including materials, preparation of films, thermal pressing, characterization, and references (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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