

## Micron Patterning of Polydiacetylene Supramolecules Using Micro-contact Printing in Conjunction with Langmuir-Blodgett Deposition

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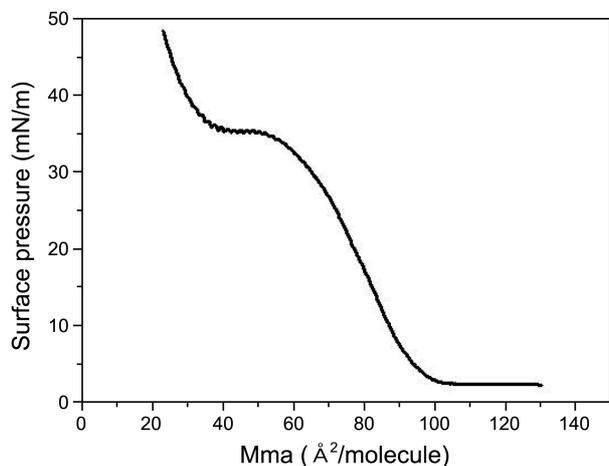
Since the pioneering discovery by Wagner,<sup>1</sup> polydiacetylenes (PDAs) have been extensively investigated as potential materials for sensor systems as well as active components of optical and electrical devices.<sup>2,3</sup> Undoubtedly, the most appealing and promising features of PDAs are their stress induced colorimetric and fluorogenic transitions that have been harvested as a response to thermal, chemical, mechanical and biological recognition events.<sup>4-9</sup> During the last decade, advances in the design, synthesis and application of new PDA derivatives have promoted a demand for methods to reliably fabricate patterned PDA layers on solid substrates. Accordingly, several PDA patterning techniques including macroarray,<sup>10</sup> microcontact printing,<sup>11</sup> replica molding,<sup>12</sup> micromolding in capillaries<sup>13</sup> as well as photolithographic,<sup>14</sup> electrophoretic deposition<sup>15</sup> and probe tip methods<sup>16</sup> have been described.

In this work, we demonstrate a simple and straightforward method to pattern PDA supramolecules using Langmuir-Blodgett (LB) deposition and micro-contact printing ( $\mu$ -CP). The general procedure consists of the following steps. First, a surface-patterned polydimethylsiloxane (PDMS) mold is replicated from a photoresist-patterned silicon substrate.<sup>17</sup> Secondly, LB films of the PDA supramolecules are deposited on the surface of the patterned PDMS.<sup>18</sup> Lastly, the PDA LB films are selectively transferred onto silicon substrates using the  $\mu$ -CP technique. The combination of LB

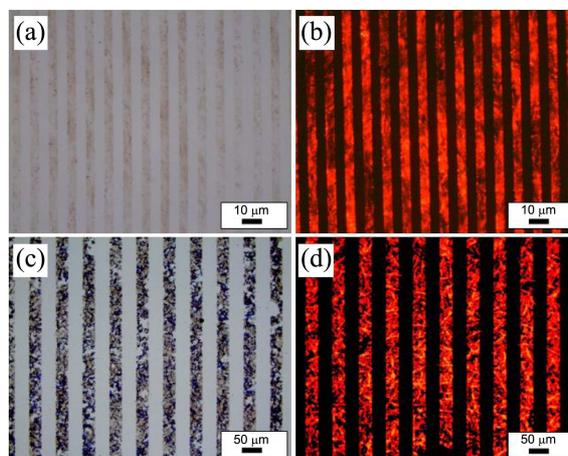
deposition and  $\mu$ -CP can conveniently fabricate micron-sized patterns of PDA supramolecules. Therefore, we believe the patterned PDA supramolecules will find great utility in sensor and optical applications.

Figure 1 shows a surface pressure-molecular area ( $\pi$ -A) isotherm of a diacetylene monolayer derived from 10,12-pentacosadiynoic acid (PCDA) on the water subphase. The surface pressure starts rising at an area of 100 Å<sup>2</sup> and gradually increases upon compression until the onset of a plateau-like region at about 35 mN/m. Upon further compression, the surface pressure rises to nearly 48 mN/m. The LB multilayers were prepared by accumulation of up-strokes and down-strokes at a pressure of 25 mN/m on PDMS substrates. The quality of the deposited monolayer on a substrate can be evaluated by the transfer ratio. For an ideal transfer, the transfer ratio is equal to 1. Transfer ratios for diacetylene supramolecule deposition on PDMS substrates are close to 1 during up-strokes but these are close to zero during down-strokes (data not shown here). This result indicates that diacetylene supramolecules transfer onto the PDMS surface only for up-strokes, which is due to the hydrophobic PDMS surface.

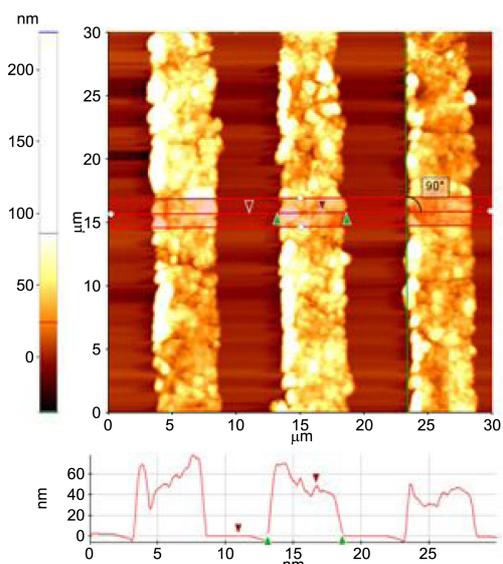
Figure 2(a) and 2(c) shows optical images of diacetylene supramolecule patterns on Si substrates fabricated by transferring a diacetylene supramolecule LB layers using the



**Figure 1.** Surface pressure-molecular area ( $\pi$ -A) isotherm of a diacetylene supramolecule monolayer at the air-water interface.



**Figure 2.** Optical and fluorescence images of 5  $\mu$ m lines, denoted as (a) and (b), and 30  $\mu$ m lines, denoted as (c) and (d), comprised of 10 layers of diacetylene supramolecule on a Si substrate.



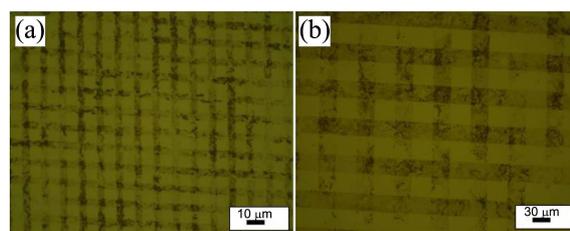
**Figure 3.** AFM images and cross-sections of patterns of 5  $\mu\text{m}$  lines comprised of 10 layers of polydiacetylene supramolecules on a Si substrate.

micro-contact printing ( $\mu\text{-CP}$ ) technique. The masters bearing 5 and 30  $\mu\text{m}$  wide lines (Figure 2(a) and 2(c)) are used for the  $\mu\text{-CP}$  process. The bright parts in the figure are patterned diacetylene supramolecules, and the dark parts are bare Si surfaces. The shape and width of the diacetylene supramolecule patterns are well-matched with PDMS stamps. Since PDAs are known to exhibit blue-to-red transition upon thermal stress and the red-phase PDAs emit fluorescence, the next phase of the current effort focuses on the generation of fluorescent patterns. Accordingly, Si substrates, immobilized with patterned blue-phase PDA supramolecules obtained by using the  $\mu\text{-CP}$  method, were heated at 100  $^{\circ}\text{C}$  for 1 min. As shown in Figure 2(b) and 2(d), the heat-treated Si substrate displays bright red fluorescing pattern images, which confirms successful blue-to-red transition of the patterned polydiacetylene supramolecules upon thermal stress.

Figure 3 displays AFM images and cross-sections of 5  $\mu\text{m}$  line patterns of 10-layered PDA supramolecules on Si substrate. Consistent with the optical and fluorescence results, the width and shape of the patterns are well matched with the geometric features of the master. The measured average height of the transferred patterns of PDA supramolecules is 40 nm.

The methodology described in the present study lends itself well to multistep patterning. To demonstrate this, we have transferred PDA supramolecule lines directly on top of a previously transferred PDA patterns using the  $\mu\text{-CP}$  technique. The procedures used are identical to those described above for a single printing level. Figure 4 shows optical images of the multiply transferred PDA supramolecule patterns on a Si substrate.

This investigation has led to the development of a convenient strategy for the fabrication of densely-packed PDA supramolecule patterns on solid substrates. The red phase PDA supramolecule patterns emitting red fluorescence are



**Figure 4.** Optical images of multiply transferred polydiacetylene supramolecule lines. 5  $\mu\text{m}$  (a) and 30  $\mu\text{m}$  (b) wide line patterns have been used for multi-transfer.

efficiently fabricated on Si substrates by the combination of LB and  $\mu\text{-CP}$  techniques. When this technique is combined with the novel optical properties of polydiacetylenes, we believe this methodology will enhance the versatility of PDA molecules for sensor and optical applications.

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## References

- Wegner, G. Z. *Naturforsch.* **1969**, *24b*, 824.
- Yoon, B.; Lee, S.; Kim, J.-M. *Chem. Soc. Rev.* **2009**, *38*, 1958.
- Peng, H.; Sun, X.; Cai, F.; Chen, X.; Zhu, Y.; Liao, G.; Chen, D.; Li, Q.; Lu, Y.; Zhu, Y.; Jia, Q. *Nat. Nanotechnol.* **2009**, *4*, 738.
- Chen, X.; Kang, S.; Kim, M. J.; Kim, J.; Kim, Y. S.; Kim, H.; Chi, B.; Kim, S.-J.; Lee, J. Y.; Yoon, J. *Angew. Chem. Int. Ed.* **2010**, *49*, 1422.
- Chen, X.; Lee, K. M.; Yoon, J. *Bull. Korean Chem. Soc.* **2011**, *32*, 3775.
- Kim, K. M.; Oh, D. J.; Ahn, K. H. *Chem. Asian J.* **2011**, *6*, 122.
- Jung, Y. K.; Kim, T. W.; Kim, J.; Kim, J.-M.; Park, H. G. *Adv. Funct. Mater.* **2008**, *18*, 701.
- Lee, J.; Jeong, E. J.; Kim, J. *Chem. Commun.* **2011**, *47*, 358.
- Kwon, I. K.; Kim, J. P.; Sim, S. J. *Biosens. Bioelectron.* **2010**, *26*, 1548.
- Ahn, D. J.; Kim, J.-M. *Acc. Chem. Res.* **2008**, *41*, 805.
- Shim, H. Y.; Lee, S. H.; Ahn, D. J.; Ahn, K.-D.; Kim, J.-M. *Mat. Sci. Eng. C* **2004**, *24*, 157.
- Yarimaga, O.; Lee, S.; Kim, J.-M.; Choi, Y.-K. *Macromol. Rapid Comm.* **2010**, *31*, 270.
- Baek, J. H.; Ahn, H.; Yoon, J.; Kim, J.-M. *Macromol. Rapid Comm.* **2008**, *29*, 117.
- Morigaki, K.; Baumgart, T.; Offenhäusser, A.; Knoll, W. *Angew. Chem. Int. Ed.* **2001**, *40*, 172.
- Yarimaga, O.; Yoon, B.; Ham, D.-Y.; Lee, J.; Hara, M.; Choi, Y.-K.; Kim, J.-M. *J. Mater. Chem.* **2011**, *21*, 18605.
- Okawa, Y.; Aono, M. *Nature* **2001**, *409*, 683.
- The PDMS stamps were prepared using a standard method (Xia, Y.; Whitesides, G. M. *Angew. Chem. Int. Edit.* **1998**, *37*, 551).
- Measurement of the surface pressure-area ( $\pi\text{-A}$ ) isotherms and LB films deposition experiment were performed with a computer controlled KSV Minitrough II instrument (KSV instruments Ltd., Finland) at room temperature. Ultra-pure water with a resistivity of ca. 18.2 M $\Omega$  and pH value of 5.8, purified by a Milli-Q ultra-pure water system, was used as the subphase for PDA supramolecule LB film deposition. The chloroform solution of PDA supramolecule ( $5 \times 10^{-4}$  M, 200  $\mu\text{L}$ ) was spread onto the air-water interface using a glass syringe (Hamilton Co., USA). After complete evaporation of the chloroform, the monolayer floating above the water surface was compressed at a speed of 10 mm/min. The LB films were transferred onto surface-patterned PDMS substrates by dipping them at a constant surface pressure of 25 mN/m using a dipping speed of 5 mm/min.