

## Micron-Scale Patterning of Hyperbranched Polymer Films by Micro-Contact Printing

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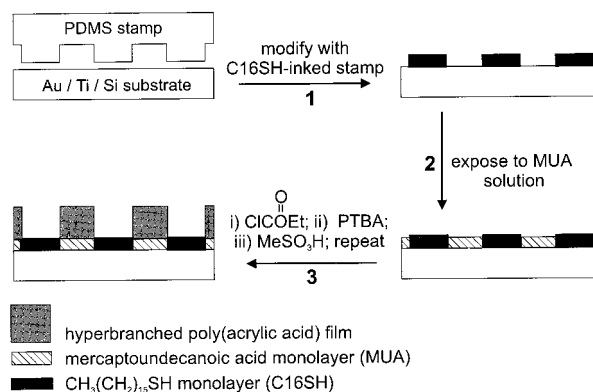
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In this paper we describe micron-scale patterning of covalently grafted, hyperbranched poly(acrylic acid) (PAA) and poly(*tert*-butyl acrylate) (PTBA) organic thin films.<sup>1,2</sup> Scheme 1 outlines the micro-contact printing ( $\mu$ -CP)-based lithography<sup>3</sup> and polymer-grafting steps<sup>1,2</sup> used to prepare these materials. Importantly, polymer growth only occurs in regions of the surface originally modified with monolayers having reactive terminal groups. Ellipsometry, reflectance FTIR, tapping-mode atomic force microscopy (TM-AFM), and optical profilometry indicate that it is possible to prepare patterned films up to 25 nm thick that have critical lateral dimensions on the order of 2  $\mu$ m. Previously we have shown that hyperbranched polymer films can be highly impermeable,<sup>4,5</sup> and thus they hold promise as both wet and dry etch resists.<sup>6</sup> Such films are also highly functionalized and therefore amenable to further elaboration.<sup>1,7</sup>

Whitesides<sup>3</sup> and others<sup>8,9</sup> have described a variety of applications of  $\mu$ -CP, which is a soft lithographic method wherein an elastomeric stamp is used to transfer monolayer-thick patterns onto surfaces.<sup>10–12</sup> This method has been used to prepare metallic,<sup>13,14</sup> protein-modified,<sup>15–17</sup> and novel three-dimensional structures.<sup>18,19</sup> Patterned polymer films have been fabricated by

Scheme 1



using  $\mu$ -CP to define a functional group pattern and then any of several subsequent strategies to selectively modify the stamped surface with a polymeric material. These strategies include spin-coating,<sup>20</sup> selective, sequential deposition of polyionic multilayers,<sup>21,22</sup> and electrodeposition.<sup>23,24</sup> Additionally, Husemann et al. recently used  $\mu$ -CP followed by surface initiated ring-opening polymerization to generate patterned polymer films.<sup>25</sup> In this report, we present the novel use of  $\mu$ -CP to pattern relatively thick, covalently linked polymer films, which have substantial benefits in terms of their stability,<sup>2</sup> level of synthetic flexibility,<sup>1,7,26</sup> and surface passivation characteristics.<sup>4,5</sup>

Either a TEM grid (300 mesh, Electron Microscopy Sciences) or an optical test mask (USAF resolution test target, Melles Griot) was used as the master from which the poly(dimethylsiloxane) (PDMS) stamps were prepared by using a slight modification of a literature procedure.<sup>10</sup> Scheme 1 shows the method used to pattern the substrates with PAA. First, CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>SH (C16SH) was applied to the PDMS stamp and then the Au substrates were patterned by manual application of the stamp to the surface for 30 s. We have found it much easier to stamp methyl-terminated thiols than those having reactive endgroups. Second, the C16SH-patterned substrates were exposed to a 1 mM ethanolic solution of HOOC(CH<sub>2</sub>)<sub>15</sub>SH (MUA) for 1 min.<sup>27</sup> Third, activation of the carboxylic acid terminal groups of the MUA-patterned portions of the mixed-monolayer was achieved via a mixed anhydride followed by reaction with  $\alpha,\omega$ -diamino-terminated poly(*tert*-butyl acrylate) (H<sub>2</sub>NR–PTBA–RNH<sub>2</sub>) to yield a grafted polymer layer. The PTBA was hydrolyzed with MeSO<sub>3</sub>H to yield the first layer of PAA (1-PAA), and then two more cycles of activation, grafting, and hydrolysis were repeated to yield a hyperbranched 3-PAA film. The details of this synthesis and the properties of the resulting films have been reported previously.<sup>1,2,4,5,26</sup> A consequence of this approach is that the resulting polymeric pattern is a negative image of the stamp. FTIR-external reflectance spectroscopic (FTIR-ERS) (Bio-Rad model FTS6000 FTIR equipped with a Harrick Seagull reflection accessory) and ellipsometric

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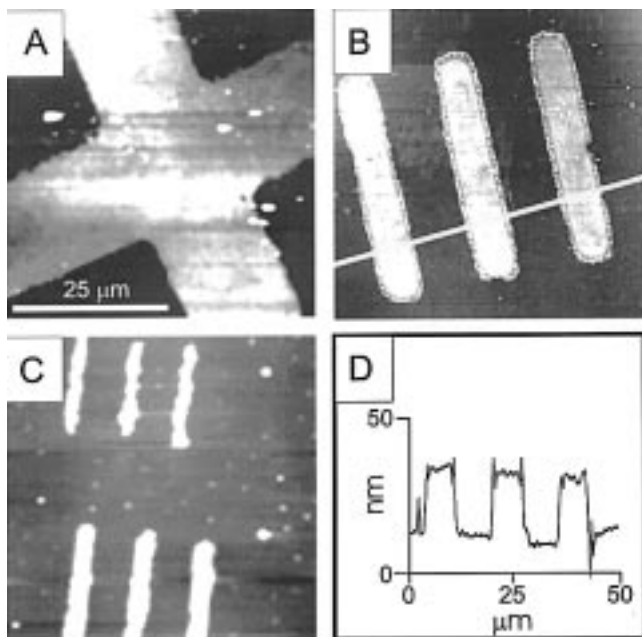
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(27) If the sample is exposed to MUA for >30 min exchange between the C16SH and MUA occurs leading to polymer growth on both patterned and unpatterned portions of the sample.

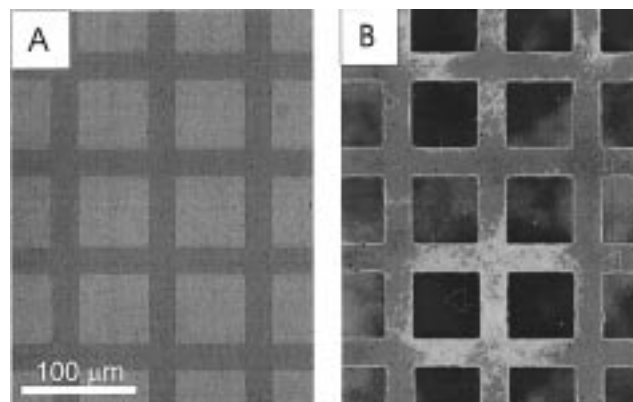


**Figure 1.** (A–C)  $50 \times 50 \mu\text{m}$  tapping-mode AFM (TM-AFM) images of patterned 3-PAA hyperbranched films. Images were acquired with a Digital Instruments Nanoscope III fitted with a “J” scanner. Images were collected at 0.4 Hz, and were flattened and filtered with use of Digital Instruments software to remove high-frequency noise. (A) A TEM-grid patterned region, (B–C) images patterned using a test-grid pattern, and (D) cross-section of the features identified by the white line in (B).

measurements (Gaertner model L2W26D, 632 nm,  $70^\circ$  angle of incidence) were made after each stage of the synthesis to monitor polymer growth. The absence of PAA in macroscopic (i.e., larger than the laser spot size used for the ellipsometric measurements), C16SH-stamped regions of the substrate was confirmed by the 1.8 nm thickness measured before, during, and after the multiple-stage synthesis. In contrast, regions modified with MUA underwent stepwise thickness increases similar in magnitude to those we have reported previously.<sup>2</sup>

We used TM-AFM to confirm pattern transfer of the 3-PAA film. Part A of Figure 1 shows a small region of a 3-PAA grid fabricated with use of the TEM-grid master. The critical lateral dimension of the 3-PAA region is  $20 \mu\text{m}$ . The height difference between the top of the 3-PAA film and the top of the C16SH monolayer is 25.0 nm. Taking into account the 1.8 nm-thickness of the C16SH monolayer, the overall height of the 3-PAA regions of the pattern is 26.8 nm. The ellipsometric thickness of this patterned 3-PAA surface is 11.0 nm. In this case, however, the laser spot size is sufficiently large that it probes both the 3-PAA- and C16SH-modified regions of the surface. Using the ellipsometric thickness measured from homogeneous 3-PAA- (25.5 nm) and C16SH- (1.8 nm) modified surfaces, and taking into account the respective fractional coverages of 3-PAA and C16SH on the patterned surface, we calculate an average thickness of 11.2 nm, which is in excellent agreement with the TM-AFM data.<sup>28</sup> This confirms that growth of 3-PAA on the patterned surface is identical with that on much larger, unpatterned surfaces.<sup>1</sup>

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**Figure 2.** (A)  $250 \times 350 \mu\text{m}$  optical micrograph of 3-PTBA TEM-grid-patterned substrate and (B) an optical profilometer image of the same region. Both images reveal the absence of polymer growth in C16SH-patterned regions and a high degree of geometric uniformity in the 3-PTBA regions.

Parts B and C of Figure 1 are TM-AFM images of 3-PAA films patterned by using the test mask-derived stamp. Critical lateral dimensions of these features range from  $8 \mu\text{m}$  in part B to  $2 \mu\text{m}$  in the upper half of part C. Part D of Figure 1 shows a cross section taken from the image in part B. The interfacial region between 3-PAA and C16SH is on the order of 500 nm wide.

Part A of Figure 2 shows an optical micrograph of a 3-PTBA film patterned by using the TEM-grid-derived stamp. This sample was not hydrolyzed to 3-PAA after the third grafting step, which results in better optical contrast in the images: 3-PTBA is typically twice as thick as 3-PAA.<sup>2</sup> The network of intersecting  $20\text{-}\mu\text{m}$ -wide lines separating the  $63\text{-}\mu\text{m}$ -square areas correspond to regions of the substrate modified with 3-PTBA. Part B of Figure 2 is an image of this same patterned surface obtained by using optical interferometric profilometry (NewView 200, Zygo Instruments). It is evident in these images that the interface between C16SH and polymer is  $<1 \mu\text{m}$ .

In summary, we have shown that 25-nm-thick polymer layers having critical lateral dimensions on the order of  $1 \mu\text{m}$  can be patterned by using a combination of  $\mu\text{-CP}$  and polymer grafting. The remarkable structural and chemical properties of the highly functionalized PAA films,<sup>1,2,4,5,26</sup> coupled with the three-dimensionality of the patterned films, are ideally suited for a range of technological applications including etch resists, spatially segregated, chemically sensitive interfaces,<sup>29</sup> and corrals for isolating cells.<sup>7</sup>

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