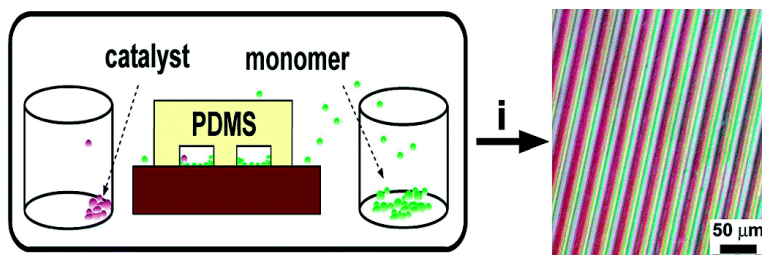


## Solventless Polymerization: Spatial Migration of a Catalyst To Form Polymeric Thin Films in Microchannels

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*J. Am. Chem. Soc.*, **2003**, 125 (31), 9256-9257 • DOI: 10.1021/ja029954a • Publication Date (Web): 09 July 2003

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## Solventless Polymerization: Spatial Migration of a Catalyst To Form Polymeric Thin Films in Microchannels

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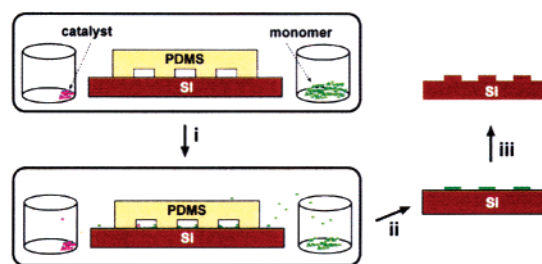
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This paper reports a solventless process, which involves spatial migration of a Grubbs's catalyst<sup>1,2</sup> that polymerizes norbornene, to generate polymeric thin films inside microchannels formed via soft lithography.<sup>3</sup> Conventional photolithography<sup>4</sup> requires the use of solvents during the spin-coating, developing, and photoresist removing steps. Such solvents are costly and create environmental concerns.<sup>5</sup> We aim to develop a process that will reduce or eliminate the use of solvents in microfabrication for cost reduction and pollution minimization. We have previously reported a solventless polymerization process to form patterned thin films on a substrate.<sup>6</sup> In that process, however, the catalyst needed to be dissolved in a solvent for patterning. Here, we report a total solvent-free process for patterning polymeric thin films. This solventless process, taking advantage of the well-known catalytic ring-opening metathesis polymerization (ROMP)<sup>1,2,7</sup> and the thermodynamic differences in adsorption/reaction of monomers inside and outside microchannels, selectively polymerizes volatile monomers inside the microchannels. We also demonstrate that this process, as a complementary alternative to spin-coating, layer-by-layer deposition,<sup>8</sup> or plasma-assisted polymerization,<sup>9</sup> is easily compatible with reactive ion etching (RIE), usually a subsequent step after patterning with polymers in microfabrication.

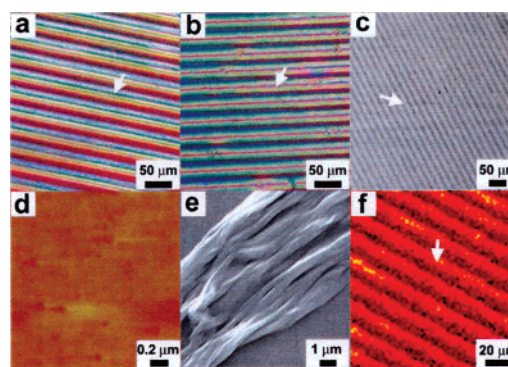
When the catalyst powder<sup>10</sup> and norbornene were stored in separate vials within a closed chamber for 12 h, we found that the norbornene turned into an insoluble and nonvolatile solid, whose infrared (IR) spectrum is identical to that of the poly(norbornene) obtained by solution ROMP.<sup>10</sup> After the reaction time was extended to ~120 h, X-ray fluorescence spectroscopy (XRF) analysis of the formed poly(norbornene) exhibited the signals of Ru and Cl (in the ratio of ~1:2), confirming that the Grubbs's catalyst initiated the polymerization of norbornene.<sup>10</sup> We reasoned that a trace amount of molecules of the highly efficient Grubbs's catalyst migrated into the vials containing norbornene via Brownian motion and catalyzed the polymerization of norbornene in the solid state. We then utilized this phenomenon to generate patterned polymeric thin films on a substrate by polymerizing norbornene inside microchannels.

Figure 1 illustrates the simple experimental procedure: a vial containing the catalyst powder, a vial containing the norbornene solid, and a silicon wafer conformally contacting a premold poly(dimethylsiloxane) (PDMS) stamp with microchannels are located inside a chamber. After briefly reducing the pressure of the chamber, closing the system, and allowing polymerization, we observed that the amount of norbornene reduced significantly after ~12 h due to its sublimation and the polymerization in the microchannels. We then removed the stamp and treated the wafer by etching processes.

Optical microscopy indicates that poly(norbornene) lines selectively form on the surface of the wafer inside the microchannels in



**Figure 1.** An illustration of solventless polymerization and patterning: (i) reducing the pressure and closing the system; (ii) polymerizing and removing the stamp; and (iii) etching.

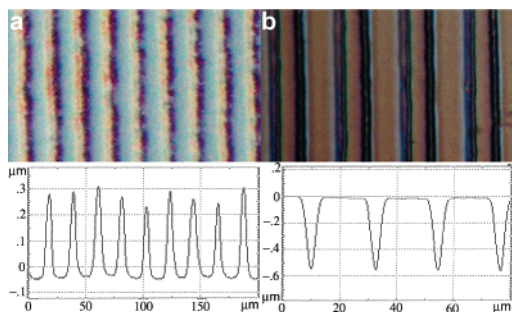


**Figure 2.** Optical images of the polymer lines (indicated by arrows) on different substrates: (a) a silicon wafer, (b) a glass, and (c) a gold surface; (d) an AFM image of one of the polymer lines; (e) an SEM image of detached polymer lines; and (f) a ToF-SIMS image of the polymer lines.

addition to the formation of a thin polymeric film on the remaining catalyst and the insoluble solid in the vial containing the norbornene (if any norbornene remains). No polymer was found outside the microchannels on the open surface of the silicon wafer. As an example, Figure 2a shows the patterned thin films (with gaps of 20  $\mu\text{m}$ ) on a silicon wafer. The same process also works on a glass substrate (Figure 2b). On a glass slide coated with a gold thin film, poly(norbornene) lines also formed on the gold surface inside the microchannels (Figure 2c), which rules out the possibility that the polymerization of norbornene is initiated by Lewis acidic  $\text{SiO}_2$  or  $\text{SiO}_x$  on the surface of the silicon wafer. As a control, we repeated the experiment with only a vial of norbornene in the chamber. We did not observe the polymer formation when the catalyst was absent. This result proves that both the catalyst and the monomer have to be present in the closed chamber for the polymerization. When the Grubbs's catalyst and norbornene were used, this solventless polymerization also proceeded on a silicon wafer coated with a thin layer of a radical inhibitor (e.g., *tert*-butyl-catechol),<sup>10</sup> proving that the solventless polymerization of norbornene in the presence of the Grubbs's catalyst is unlikely via a radical mechanism. Our

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**Figure 3.** Optical images and the height profiles of the silicon wafers that were patterned with poly(norbornene) solventlessly and etched using “wet” etching (a) and RIE (b).

attempt to solventlessly polymerize styrene inside the microchannel using benzoyl peroxide as a radical initiator yielded no poly(styrene) films. This result agrees with the characteristics of radical polymerization; that is, initial propagation demands a high concentration of monomers (which is unavailable under the conditions for solventless polymerization).

The polymer lines are thicker at the edges ( $\sim 190$  nm) than in the middle ( $\sim 130$  nm) when the microchannels are wide ( $\geq 20$   $\mu\text{m}$ , Figure 2a). This observation suggests a higher local concentration of the monomers at the junctions of the two surfaces. Atomic force microscopy (AFM) reveals that the film is quite smooth ( $R_a = 0.3$  nm, Figure 2d) and is composed of polymer fibers  $\sim 30$  nm wide.<sup>10</sup> The smoothness of the polymeric lines suggests a liquidlike phase of the monomers inside the microchannels. These polymeric thin films appear to have very high molecular weight because they are insoluble despite swelling and detaching from the wafers in organic solvents, such as chloroform or dichloromethane. Scanning electron micrographs (SEM) of each detached polymer stripe indicate distinguished fiberlike structures (Figure 2e). These results suggest that the polymerization is initiated at the opening of the microchannels, and the polymer chains grow along the walls of the microchannels. Figure 2f shows the total ion image obtained by time-of-flight secondary ion mass spectrometry (ToF-SIMS) on one sample with gaps of 10  $\mu\text{m}$ . The concentration of Ru in each polymeric line is too low to yield detectable signals of Ru.<sup>10</sup> ToF-SIMS, however, displays the signal of a trace amount of Ru from the sample obtained by combining the detached polymer stripes.<sup>10</sup> These results, again, confirm that the polymerization is initiated by the Grubbs’s catalysts.<sup>2,10</sup>

The polymer lines generated by this solventless process were used as an etching resistant in the standard silicon wet etching process ( $\text{CrO}_3/\text{HF}/\text{H}_2\text{O}$ ) and RIE. Although the susceptibility of the double bonds in poly(norbornene) to  $\text{CrO}_3$  causes the roughness at the edges of the line patterns, the profile of the etched lines, measured by an  $\alpha$ -stepper, indicates that the replica maintains good fidelity with the stamp (Figure 3a). We also tested the compatibility of the polymer films with RIE, in which the environment was less oxidative than  $\text{CrO}_3$ . The optical image and the profile of the etched surface (Figure 3b) display the well-defined trenches and the smooth surfaces of the polymer-covered regions, suggesting that this solventless procedure is quite compatible with RIE. In addition, the RIE-formed patterns correspond exactly to the patterns on the stamp, which further confirms that no polymers formed outside the microchannels.

To understand the reason no polymers formed outside the microchannel, we constructed hydrophilic microchannels.<sup>10</sup> We observed no polymer formation in the hydrophilic microchannels<sup>10</sup> under the conditions used in previous experiments. Therefore, we suggest that the hydrophobicity of PDMS<sup>11</sup> mainly results in the preferable formation of poly(norbornene) inside the microchannels: the PDMS surface absorbs more norbornene than the silicon wafer does and also partially contributes to the capillary condensation of the volatile monomer inside the microchannels. In addition, the high surface-to-volume ratio of the microchannels allows the local concentrations of the monomers and the catalyst to be at least  $\sim 10^4$  times higher inside the microchannels than they are outside.<sup>10</sup>

In conclusion, we demonstrated here a simple additive process evolved from a previously unexplored catalyst migration phenomenon for generating polymeric thin films solventlessly, which should be applicable to other volatile monomers and living polymerization catalysts<sup>12</sup> with high efficiency.

**Acknowledgment.** This work was partially supported by the RGC (Hong Kong), DAG (HKUST), and a DuPont Young Faculty Grant. We thank Prof. Benzhong Tang for the use of their optical microscope.

**Supporting Information Available:** Details of IR, XRF, and ToF-SIMS measurements, a profile of the patterned films, controls in hydrophobic and hydrophilic microchannels, and the analysis of surface/volume ratios (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA029954A