

## Ring-Opening Metathesis Polymerization from Surfaces

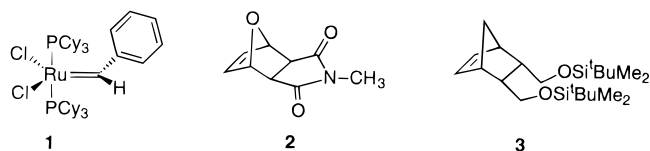
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Polymer brushes, polymers that are confined to a small volume of a surface and, due to steric requirements, stretch away from their grafting point toward the polymer edges, are significant for numerous applications in a variety of technologies.<sup>1,2</sup> Several possible strategies to obtain polymer brushes, such as adsorption of functionalized polymers onto surfaces<sup>3</sup> and surface-initiated polymerization are imaginable.<sup>4–6</sup> The latter has been employed for a variety of monomers utilizing radical,<sup>4</sup> cationic,<sup>5</sup> and anionic polymerization methods.<sup>6</sup> Several requirements to obtain polymer brushes have to be met including low polydispersity, uniform surface grafting density, and linear polymer chains. These requirements are easily achieved with living polymerizations. However, as a result of side reactions and impurities on a surface, most attempts to accomplish living polymerizations on surfaces have failed to date.<sup>5b–7</sup>

In the past decade, ring-opening metathesis polymerization (ROMP) catalyzed by well-defined metal–alkylidines has proven to be an efficient method to control a polymer's molecular structure, size, and bulk properties.<sup>8</sup> Ruthenium-based ROMP initiators, and **1** in particular, have been shown to polymerize a large variety of monomers such as **2** and **3** in a living fashion in



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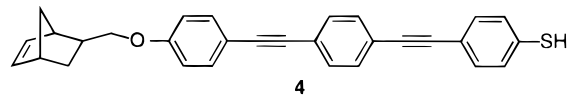
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a number of solvents, ranging from benzene to water.<sup>9</sup> With these recent advances in catalyst design, ROMP is capable of overcoming the obstacles mentioned above for surface polymerization. Herein we describe the first universal method for obtaining a large variety of chemically diverse polymer brushes on surfaces *via* ROMP.

For the purpose of anchoring an initiating unit to the surface, a difunctional “molecular wire”-type molecule **4** has been



synthesized. This molecule can both self-assemble on a gold surface and initiate ROMP after addition of a ruthenium initiator.

To obtain a well-defined polymerization from the surface, all molecules of **4** must be separated from each other to prevent polymerization between initiating units. To accomplish this, a two-step self-assembly procedure recently introduced by Weiss, Allara, and Tour was employed in this study.<sup>10</sup> The gold surface was initially functionalized using dodecanethiol (**5**).<sup>1a</sup> In a second self-assembly step the **5**-functionalized surface was exposed to a 0.3 mM tetrahydrofuran solution of **4** for 30 min. Molecule **4** was found to insert into the structural domain boundaries of the alkanethiolate self-assembled monolayer (SAM).<sup>10</sup> The alkanethiolate matrix supports and separates the single molecules of **4**.

After characterization of the surface, the wafers were immersed in a dilute dichloromethane solution of **1** for 5 min. The surface was then rinsed several times with clean solvent to remove excess catalyst. Finally, exposure of the initiated wafers to a monomer solution of **2** or **3**, with concentrations ranging from 1 mM to 1 M, for a period of 2–60 min resulted in polymerization (for a general synthetic scheme, see Supporting Information).<sup>11</sup>

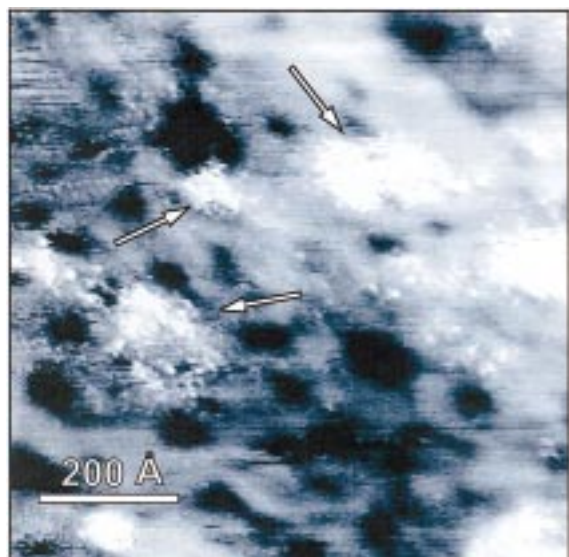
The functionalized surfaces were characterized both before and after polymerization by scanning tunneling microscopy (STM), atomic force microscopy (AFM) and scanning electron microscopy (SEM). A representative 1000 × 1000 Å STM topographic image of an Au{1 1 1} surface covered by an alkylthiolate SAM with inserted **4** (see Supporting Information) showed protruding several angstroms (6–7 Å) from the SAM features (displayed as bright spots) which are absent in pure alkylthiolate SAMs and therefore were assigned as **4**. Analysis of the image shows that single inserted molecules of **4** are, on average, separated by several hundred angstroms.

Figure 1 is a STM image of a polymer-functionalized surface after polymerizing for 2 min in which several polymer brushes inserted into the SAM are clearly visible. The polymerizations were carried out in very dilute monomer solutions to yield only oligomers instead of long-chain polymers, as it was anticipated that longer polymer chains would greatly reduce tunneling through the polymer. The image shows some streaking of the polymer brushes in the scan direction, which can be explained by the polymers' significant protrusion from the SAM and interaction with the tip.

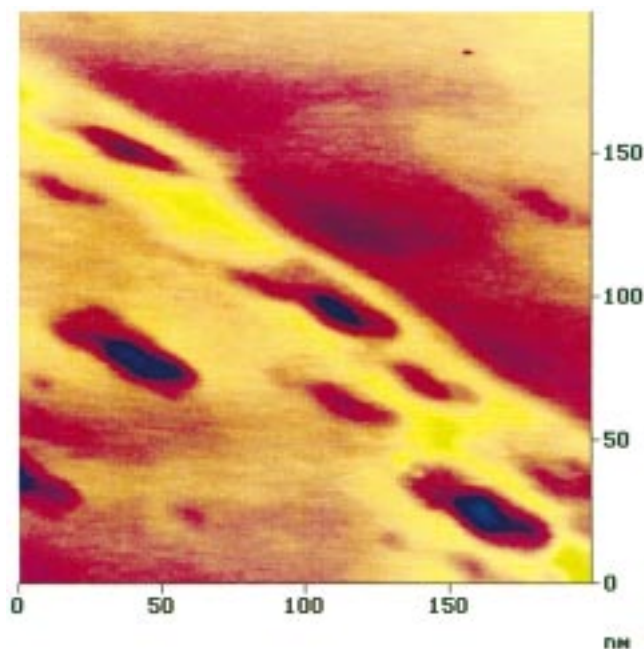
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(11) Immersion of the wafer into the monomer solution for longer periods resulted in continued polymer growth. For the STM characterization the wafers were immersed for only a short period of time (2–20 min) to yield only oligomerization (due to the greatly reduced electron tunneling properties of large polymer brushes), while for the AFM and SEM characterization the wafers were immersed in the monomer solution for longer periods to obtain longer polymer brushes on the surface.

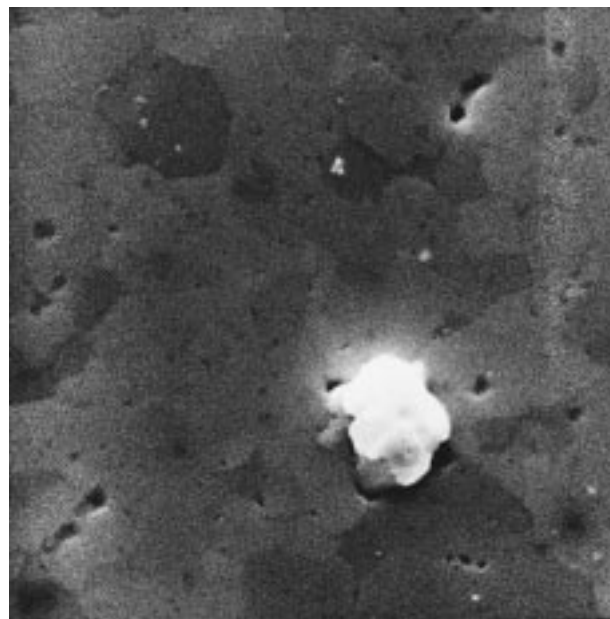


**Figure 1.** A constant-current STM topograph showing a  $800 \times 800 \text{ \AA}$  area on an Au{1 1 1} surface displaying multiple terraces covered by a dodecanethiol monolayer with inserted polymers after polymerization using **2** (tip bias = +1.0 V, tunneling current = 10 pA). Polymer brushes appear as nonuniform bright peaks in the topography. The polymers may be pushed on the surface by the microscope tip making it impossible to determine their actual sizes.



**Figure 2.** A  $200 \times 200 \text{ nm}$  (height of the polymer brushes are between 5 and 7 nm) TMAFM image after polymerization using **2** of polymer brushes on gold. The image was obtained at a  $60^\circ$  scan angle, a scan rate of 0.803 Hz, and a set point of 2.08 V (number of samples 512, integral gain = 0.131, proportional gain 2.74). A first-order plane fit was applied to the image and several noisy scan lines were erased.

To image longer polymer chains on the surface, AFM was employed. AFM can be used, in contrast to STM, for the morphological characterization of nonconducting films, thus making the imaging of longer polymer chains on the surface possible. Figure 2 is a representative  $200 \times 200 \text{ nm}$  tapping mode AFM (TMAFM) scan of a polymer-functionalized surface. The clearly visible protrusions were assigned as polymer brushes on the surface. These features, between 100 and  $400 \text{ \AA}$  in size, are located primarily along the step edges of the surface or in the boundary domains of the terraces. Other AFM images also show very irregular polymer brushes of much larger sizes (several



**Figure 3.** SEM picture of a polymer-functionalized surface after polymerization using **3** (magnification  $3 \times 10^4$ ). The picture was taken at a  $90^\circ$  angle.

thousand angstroms) which were located in very large defect areas on the surface. This is consistent with the two-step self-assembly described in ref 12.

To support the results obtained with STM and AFM, SEM pictures of the monolayer films were taken before and after the polymerization. Although no protrusions were visible on the surface before polymerization, large polymer brushes were visible after polymerization. Figure 3 is a SEM picture of a polymer-functionalized surface. A large polymer brush of several thousand angstroms is visible on the surface. This protrusion is similar in size to the larger polymer brushes seen by AFM. Furthermore, visible on the surface are several smaller protrusions (displayed as white) which we assigned to the smaller, more regular polymer brushes identified by STM and AFM.

Results from all three microscopy techniques prove that a ring-opening metathesis polymerization occurred after treatment of the mixed monolayer-functionalized surfaces with catalyst **1** and the addition of monomers **2** and **3**. Although STM results show small polymer brushes up to approximately  $100 \text{ \AA}$  in diameter, AFM and SEM results show that more highly polymerized features exist on the surface.<sup>13</sup>

In conclusion, we have demonstrated that ROMP can produce single polymer chains from a solid surface. By varying the concentrations of the thiol-containing solutions (dodecanethiol and molecular wire) as well as the insertion times of the thiols, the defect type and density in the surrounding matrix can be controlled.<sup>12</sup> These parameters can be used to fine-tune the overall density at which single polymer molecules are grown and their spacing on the surface.<sup>17</sup> Experiments that determine the living character of these polymerizations as well as the use of this method to obtain both block copolymers and single highly conjugated polymers for electronic applications are currently under way.

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**Supporting Information Available:** A scheme describing the general synthetic strategy, STM and AFM images of the functionalized surface prior to polymerization, and a SEM picture taken from a  $60^\circ$  angle (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>. JA983297Y

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