

## Surface-Initiated Ring-Opening Metathesis Polymerization on Si/SiO<sub>2</sub>

Namyong Y. Kim,<sup>‡</sup> Noo Li Jeon,<sup>†</sup> Insung S. Choi,<sup>†</sup> Seiichi Takami,<sup>§</sup> Yoshiko Harada,<sup>‡</sup> Krista R. Finnie,<sup>‡</sup> Gregory S. Girolami,<sup>‡</sup> Ralph G. Nuzzo,<sup>\*,‡</sup> George M. Whitesides,<sup>\*,†</sup> and Paul E. Laibinis<sup>\*,§</sup>

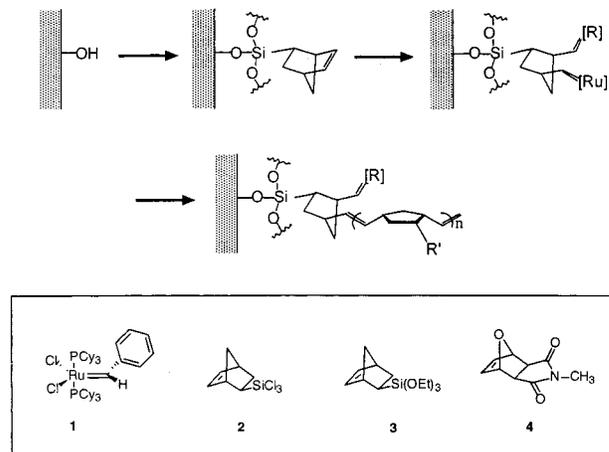
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, Department of Chemistry and the Seitz Materials Research Laboratory, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, and Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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This paper describes a method for growing thin polymer films from the surface of a silicon wafer bearing a native oxide (Si/SiO<sub>2</sub>) by ring-opening metathesis polymerization (ROMP).<sup>1,2</sup> We have prepared norbornene-derived polymer films with a wide range of thicknesses (up to 1 μm) and with a control over the chemical composition of the film perpendicular to the surface. Recently, surface-initiated polymerization has become an area of great interest, and several groups have developed approaches to grow thin polymer films on silicon and gold using cationic, anionic, and radical methods.<sup>3</sup> However, these methods often require rigorous reaction conditions and/or an input of thermal energy and have limited abilities to produce films of controlled thickness and chemical composition. Notably, Weck et al. recently reported the use of ROMP in a surface-initiated polymerization.<sup>1b</sup> In their work, the polymerization was allowed to occur only at defects within a self-assembled monolayer (SAM) and yielded an extremely small amount of a polymeric material on the surface. Characterizations of the polymerization process and the resulting polymer were not possible. In this paper, we present the use of surface-initiated ROMP as a strategy for offering a high degree of control over a surface polymerization process that occurs at room temperature and demonstrate its use in the facile formation of patterned polymer films on silicon when used with the technique of microcontact printing (μCP).

Scheme 1 outlines our three-step procedure: (i) the formation of a self-assembled monolayer (SAM) on silicon that presents norbornenyl groups; (ii) the attachment of a ruthenium catalyst [(Cy<sub>3</sub>P)<sub>2</sub>Cl<sub>2</sub>Ru=CHPh, Cy = cyclohexyl] (**1**) to the surface using the norbornenyl groups; (iii) the polymerization of added monomers to generate the film.<sup>4</sup> In the first step, a SAM of 5-(bicycloheptenyl)trichlorosilane (**2**) was formed on a Si/SiO<sub>2</sub> surface by immersing a UV-ozone cleaned substrate in a toluene solution of **2** (60 mM) for 6–12 h. The presence of the resulting 0.6 nm thick film of **2** was confirmed by attenuated total reflection (ATR) IR spectroscopy (see the Supporting Information) and ellipsometry. We then

Scheme 1. Schematic Outline of the Procedure



attached an immobilized derivative of catalyst **1** to this norbornenyl surface by dipping the substrate into a CH<sub>2</sub>Cl<sub>2</sub> solution of **1** (17 mM) for 30 min. Subsequent exposure of the substrate to norbornene-based monomers such as 5-(bicycloheptenyl)triethoxysilane (**3**) or exo-N-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**4**) (0.01–0.4 M) in CH<sub>2</sub>Cl<sub>2</sub> produced a polymeric film on the surface. Typical polymerization times were 30 min, and the substrate was washed extensively with CH<sub>2</sub>Cl<sub>2</sub> between each step. We characterized the resulting films by transmission IR spectroscopy, ellipsometry, optical microscopy, scanning electron microscopy, and atomic force microscopy (AFM).

Parts a and b of Figure 1 show transmission IR spectra of films of poly-**3** and poly-**4** on silicon, respectively, prepared by the procedure in Scheme 1. In Figure 1a, the strong C–H stretching peaks at 2974 and 2928 cm<sup>-1</sup> are due to the ethoxy groups of poly-**3**. In Figure 1b, the spectrum shows a characteristic C=O stretching peak at 1740 cm<sup>-1</sup> for poly-**4**, indicating the growth of an anchored film from the surface.<sup>5</sup> To confirm that the polymer films formed by a surface-initiated ROMP process, we examined the requirements for the reaction. Specifically, when samples were processed as shown in Scheme 1 but without formation of a SAM from **2**, we observed negligible growth of a polymer film on the surface by IR spectroscopy and ellipsometry. Similarly, samples that had not been exposed to **1** before the addition of a monomer did not produce polymer films. The results suggested that the surface-immobilized [Ru] catalysts as anchored to the surface by the norbornene-terminated SAMs were responsible for the polymerization.

In principle, the polymerization of the norbornenyl monomers by a [Ru] catalyst could proceed by either a ROMP or a cationic polymerization mechanism.<sup>6</sup> The two processes would yield different products as cationically derived polymers would retain the bicyclic ring structure of norbornane with loss of the double bonds, while polymers produced by ROMP would contain a monocyclic ring and retain the double bonds. To eliminate the cationic mechanism, we treated a film of poly-**3** with HBr and characterized the resulting film by X-ray photoelectron spectroscopy (XPS). We observed peaks for bromine in a stoichiometry relative to carbon that would be expected if there was one double bond per

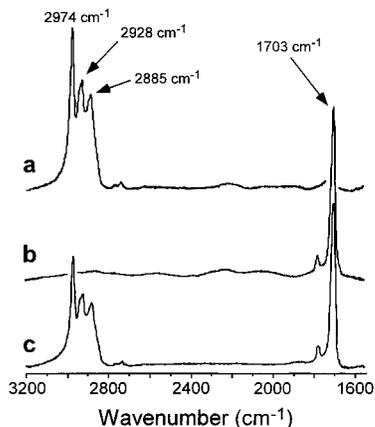
<sup>‡</sup> Department of Chemistry, MIT.

<sup>†</sup> Harvard University.

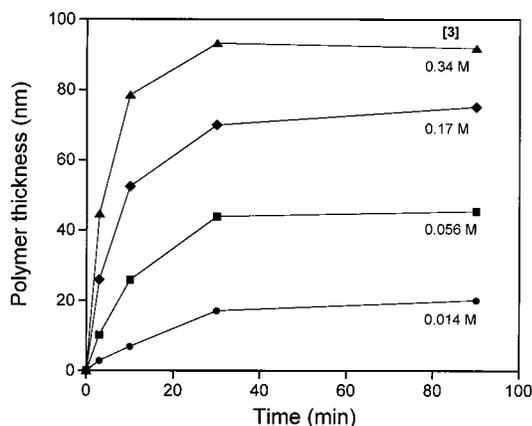
<sup>‡</sup> University of Illinois at Urbana–Champaign.

<sup>§</sup> Department of Chemical Engineering, MIT.

\* To whom correspondence should be addressed.



**Figure 1.** Transmission IR spectra of (a) poly(5-(bicycloheptenyl)triethoxysilane) [poly-3], (b) poly(exo-*N*-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide) [poly-4], and (c) bilayered polymer film, [poly-3/4], on silicon.



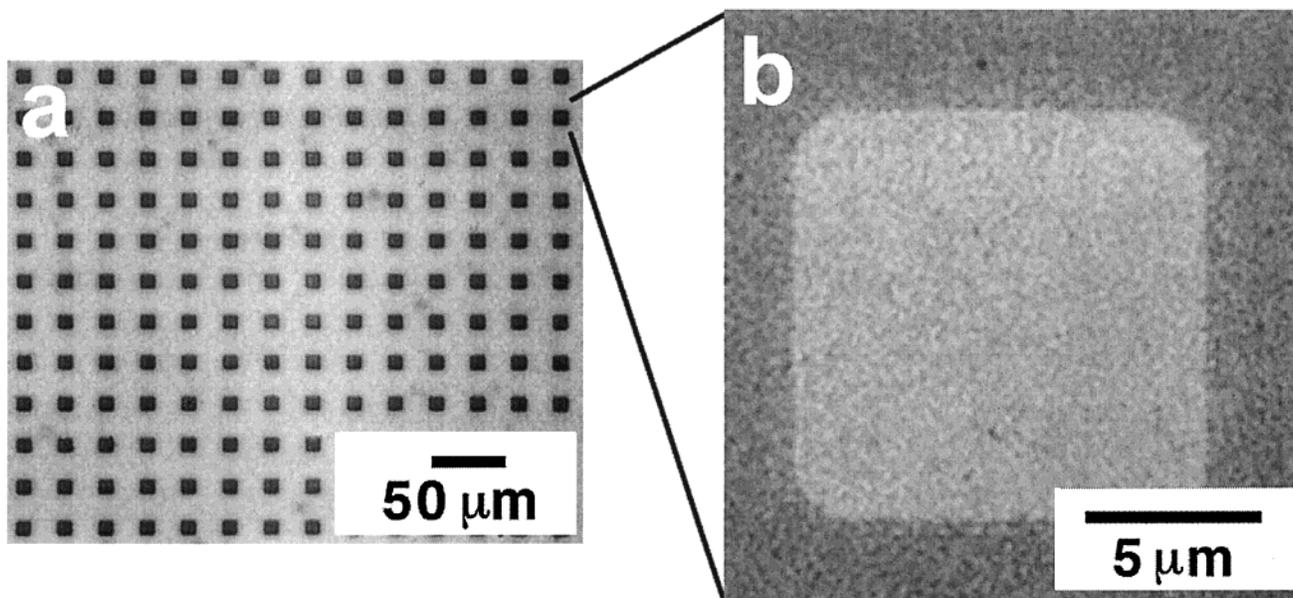
**Figure 2.** Ellipsometric film thickness of poly-3 prepared using various concentrations of **3** in  $\text{CH}_2\text{Cl}_2$  and reaction times of 3, 10, 30, and 90 min. The reproducibility in film thickness was  $\pm 5\%$ .

norbornenyl unit in a ROMP polymer.<sup>7</sup> In addition, we compared the IR spectrum for polynorbornene as prepared on a surface with that formed by ROMP in solution (see Supporting Information for IR spectra).

The IR spectra for both polymers were quite similar and supported formation of the surface polymers by a ROMP mechanism.

Figure 2 summarizes an ability to control the thickness of the polymer films (as measured by ellipsometry) by varying the monomer concentration and polymerization time using **3** as a monomer.<sup>8</sup> The polymer thickness for all concentrations of **3** increased with increasing monomer concentration,<sup>9</sup> and the polymer growth stopped after  $\sim 30$  min, presumably due to deactivation of the immobilized catalyst.<sup>10</sup> During this 30 min period, we were able to use the living nature of the active [Ru] catalyst to form a layered film on the surface. For example, by exposing an active substrate presenting the [Ru] catalyst to a  $\text{CH}_2\text{Cl}_2$  solution of **3** (0.34 M) for 3 min and to a solution of **4** (0.27 M) for 30 min, we formed a grafted bilayer film of poly-**3** and poly-**4**. The total thickness of the copolymer film was 92 nm by ellipsometry. In contrast, exposure only to **3** for 3 min yielded a 45 nm thick film that exhibited only the spectral characteristics for poly-**3** as in Figure 1a. In contrast, the transmission IR spectrum of the copolymer film exhibited both methyl (C–H stretching) peaks from the ethoxy groups of poly-**3** and the C=O stretching peak from poly-**4** (Figure 1c). XPS data for the copolymer film resembled that for a poly-**4** film, suggesting that the poly-**3** film was localized near the substrate and covered by a layer of poly-**4**. The observations are compatible with the formation of a layered copolymer film and suggest a notable strategy for possibly forming grafted multilayered polymer films on substrates.<sup>11</sup>

The requirement of the procedure of presenting an immobilized [Ru] catalyst on the surface provided the basis for producing laterally patterned polymer films on silicon. We employed microcontact printing ( $\mu\text{CP}$ )<sup>12</sup> to produce a pattern of norbornenyl units on a silicon substrate; however, our initial attempts to directly contact-print **2** led to unsatisfactory results due to a slowness for the reaction of **2** with the  $\text{SiO}_2$  surface. Instead, we first patterned the silicon surface by contact-printing octadecyltrichlorosilane onto the  $\text{SiO}_2$  surface and then formed a monolayer of **2** in the underivatized areas by contacting the slide with a 60 mM solution of **2** in toluene for 6–12 h. The resulting chemically



**Figure 3.** Optical (a) and SEM (b) micrographs of patterned poly-**3** films on  $\text{Si}/\text{SiO}_2$ . The thickness of the poly-**3** film is 50 nm.

patterned substrate, when exposed sequentially to **1** and a monomer, yielded a patterned polymer (Figure 3).<sup>13</sup> The polymer film was a negative of the  $\mu$ CP pattern and appeared uniform in thickness across the sample by profilometry and AFM.<sup>14</sup> The edge resolution for the process appeared to be on the order of a micron and depend presently on our ability to pattern the initial norbornenyl monolayer. Efforts to reduce the lateral feature sizes of the patterns and the complexity of the grown polymer films are presently underway.

In conclusion, surface-initiated polymerization using ring-opening metathesis polymerization (ROMP) by **1** can be used to grow covalently attached norbornene-based polymer films from an oxide surface by solution-phase procedures. This reaction offers an ease of use and a control over the thickness and chemical composition of deposited films. The ability of the reaction to generate patterned polymer films on silicon (and likely other substrates)—both in the plane and along the surface normal—offers new possibilities for fabricating a variety of features in current microelectronic and MEMS devices. These possibilities are targets of our current study.

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**Supporting Information Available:** ATR IR spectrum of Si/SiO<sub>2</sub> with a monolayer of Nbn-SiCl<sub>3</sub>, transmission IR spectra of polynorbornene prepared on a surface by an immobilized [Ru] catalyst and in solution by **1**, and transmission IR spectrum of poly-**3** prepared in solution by **1**. The material is available free of charge via the Internet at <http://pubs.ac-s.org>.

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- (4) All reactions used anhydrous solvents and were performed under a nitrogen atmosphere in a glovebox.
- (5) See Supporting Information for an IR spectrum of poly-**4** prepared in solution by **1**.
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- (7) By XPS, the atomic ratio of C to Br was roughly 12:1 and close to the expected empirical ratio of 13:1 based on the polymer structure.
- (8) We obtained polymer films as thick as 1  $\mu$ m using the neat monomer.
- (9) We have not yet determined the grafting density and chain lengths for the polymer chains due to the small amounts of polymer prepared on the employed flat substrates.
- (10) Possible causes for deactivation of the surface catalyst are solvent impurities and decomposition during the polymerization. Samples immersed in CH<sub>2</sub>Cl<sub>2</sub> for 10–30 min before exposure to a monomer solution produced films of diminished thicknesses (by ~50% or more).
- (11) Zhao and Brittain have formed a grafted bilayer of polystyrene-*block*-poly(methyl methacrylate) from a silicate surface by a sequential carbocationic polymerization of styrene followed by a radical polymerization of methyl methacrylate.<sup>3g</sup> An advantage of ROMP may be the possibility of forming a family of layered films by varying the sequence of exposure to a set of different norbornenyl monomers.
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