

A Simple Technique To Grow Polymer Brushes Using in Situ Surface Ligation of an Organometallic Initiator

Krishna D. Dronavajjala,[#] Ramakrishnan Rajagopalan,[‡] Sundararajan Uppili,[†] Ayusman Sen,[†] David L. Allara,^{*,†,‡} and Henry C. Foley^{*,†,‡}

Department of Chemistry, Department of Chemical Engineering, and Materials Research Institute,
The Pennsylvania State University, University Park, Pennsylvania 16802

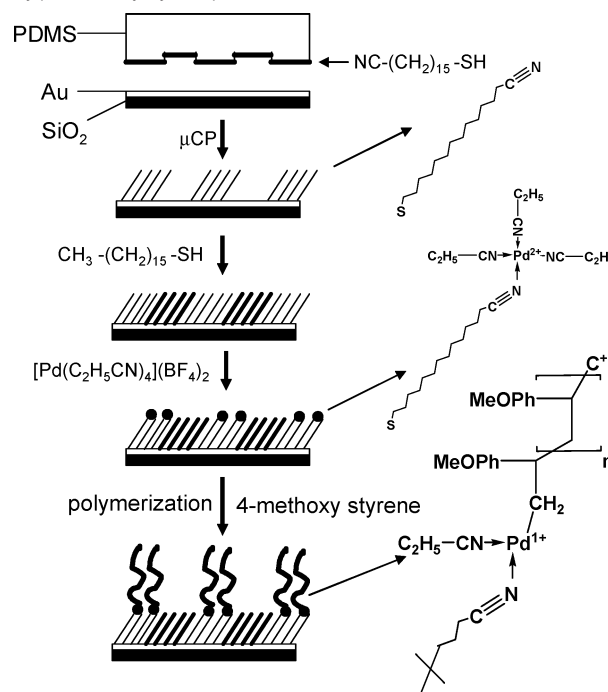
Received June 27, 2006; E-mail: hcf2@psu.edu; dla3@psu.edu

In recent years, research on grafted polymer brushes has resulted in important technological applications in coatings, microelectronics, colloid stabilization, sensors, and biomolecular adhesion.¹ A very useful way of preparing polymer brushes on surfaces is by direct surface-initiated polymerization (SIP). In this technique, initiator groups are bound to the substrate, and polymer chains of controlled thickness, density, and desired functional groups are grown from the substrate with introduction of a monomer. There are numerous reports of SIP on substrates such as Au and SiO₂ in which free radical,² atom transfer radical³ (ATRP), anionic,⁴ cationic,⁵ and ring-opening metathesis⁶ (ROMP) mechanisms were used for the polymerizations. Of these methods, living and controlled polymerization mechanisms give polymer chains of low polydispersity, a prerequisite for the growth of smooth and uniform polymer brushes. However, in the current state of the art, ROMP requires the synthesis of complex initiator molecules to form a SAM on the surface. ATRP involves a multicomponent initiator system, and anionic mechanisms require low temperatures and long reaction times (often many days). In our search to find the simplest and reliable conditions for growing *in-place, just-in-time* highly uniform polymer brush patterns, we have developed a new cationic SIP method. In this report we describe a very simple method in which a highly active cationic Pd organometallic complex is readily ligated to specific sites on a simple SAM which allows efficient, highly controlled growth of patterned polymer brushes at room temperature in a period of hours.

Cationic Pd organometallic complexes have been shown to initiate polymerization of various monomers, for example styrene and its derivatives, and to copolymerize carbon monoxide and ethylene.⁷ These initiators offer another route to the synthesis of polymeric brushes if they can be properly anchored to a surface. For this purpose we sought to anchor a Pd(II) complex⁸ ([Pd(C₂H₅CN)₄](BF₄)₂) on a self-assembled monolayer (SAM) by a simple ligand-exchange method. We formed a SAM of a cyano-terminated alkanethiol (16-mercaptohexadecanenitrile (MHN), see Supporting Information) on a gold surface with the idea of binding the initiator to the SAM surface. The tail group of the SAM displaced one of the propanenitrile ligands on the Pd(II) catalyst, thereby anchoring it to the substrate. This very simple ligand-exchange reaction proceeds at room temperature, and hence it offers a new and simple synthetic route for anchoring a catalyst on a substrate.

Our first step was to form the SAM of MHN on the gold surface (see Scheme 1). A layer of gold 200 nm thick was grown via thermal evaporation on a Si(100) wafer that had been precoated with 15 nm of chromium as an adlayer. The SAM of MHN was

Scheme 1. Steps Involved in the Synthesis of Patterned Poly(4-methoxystyrene) Brushes



formed on the Au substrate by using a method described elsewhere.⁹ Ellipsometry on the substrate indicated a SAM thickness of 2.1 ± 0.1 nm. The chemical structure of the SAM substrate was verified by reflection absorption infrared spectroscopy (see Supporting Information). The presence of the methylene groups in hydrocarbon chains making up the monolayer was made evident by the peaks at 2920, 2850, 1470, and 1430 cm⁻¹, which correspond to CH₂ asymmetric and symmetric stretches and the CH₂ scissors modes, respectively. We also detected the presence of the CN tail group by the peak at 2250 cm⁻¹, which corresponds to a CN stretch.

The next step was to anchor the Pd(II) complex on the SAM substrate. This was done by immersing the SAM substrate in a solution containing 10 mM Pd(II) complex in nitromethane (ACS Reagent Grade) for 12 h under an inert atmosphere. The surface was then rinsed thoroughly with anhydrous dichloromethane to ensure the removal of any physisorbed catalyst from the surface. Successful immobilization of the Pd(II) complex on the surface was confirmed by X-ray photoelectron spectroscopy (XPS). The substrate showed a Pd 3d_{3/2} peak at a binding energy of 343.3 eV. Using XPS, the number of catalytic sites on the surface was calculated to be 0.34 ± 0.06 /nm² (number of sites per unit area; see Supporting Information).

[†] Department of Chemistry.

[#] Department of Chemical Engineering.

[‡] Materials Research Institute.

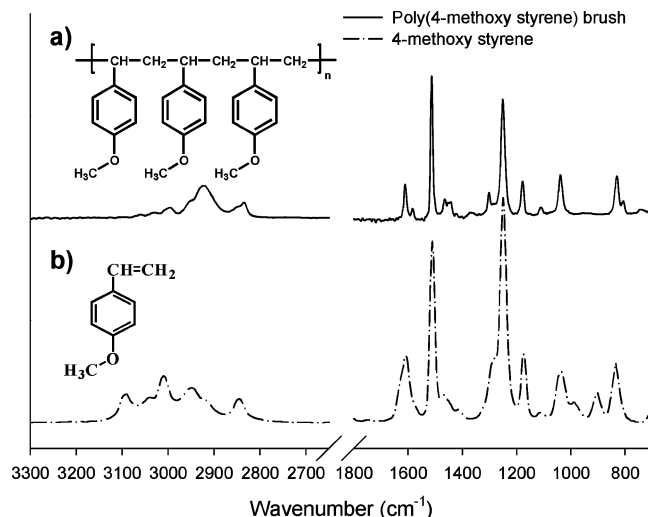


Figure 1. Infrared reflection spectroscopy of (a) polymer brush and (b) monomer 4-methoxystyrene.

The last step was to grow polymer brushes using the anchored initiator on the substrate by placing it in a reaction flask and subjecting it to flowing argon saturated with monomer at room temperature for 24 h. Ellipsometry (632.8 nm laser) of the sample showed a change in the ellipsometric parameters consistent with growth of a 24 ± 1 nm film with a refractive index of 1.6 (bulk poly(4-methoxystyrene) film). Infrared reflection spectroscopy showed the signature of poly(4-methoxystyrene) characterized by the presence of peaks at $1600\text{--}1500\text{ cm}^{-1}$ (benzene ring), $1200\text{--}1100\text{ cm}^{-1}$ (methoxy group), and $3000\text{--}2800\text{ cm}^{-1}$ (methylene stretches in the polymer backbone). The polymerization was further confirmed by the absence of peaks at 988 and 900 cm^{-1} , which correspond to the out-of-plane bending mode of the α -C atom in the vinyl group, which is present in the monomer (see Figure 1) but not in the polymer. Atomic force microscopy images (see Supporting Information) demonstrated that the polymer film was very smooth, with a root-mean-square roughness of about 0.3 nm . These results were completely reproducible.

In-place growth of polymer brushes was illustrated by synthesizing patterned polymer brushes (Scheme 1). A polydimethylsiloxane stamp was coated with the MHN molecule and stamped on a bare gold surface. The stamped substrate was then backfilled by hexadecanethiol solution in ethanol to obtain a patterned nitrile-terminated alkanethiol substrate. The procedure of anchoring the Pd catalyst and conducting the polymerization reaction was the same as that used for the initial experiments. The resulting patterned polymer brushes were characterized by atomic force microscopy (AFM; Figure 2). The profile in the AFM image indicates that ridges of polymer brush developed having a width of just less than $1\text{ }\mu\text{m}$ and a thickness of approximately 29 nm , consistent, within experimental error, with the ellipsometric thickness.

In conclusion, we have demonstrated that a highly active cationic Pd(II) organometallic catalyst can be anchored to a surface by means of ligand exchange with a SAM. We believe that this approach is general and can be extended in order to anchor a whole class of Pd and Rh organometallic catalysts^{7,10} with nitrile ligands on

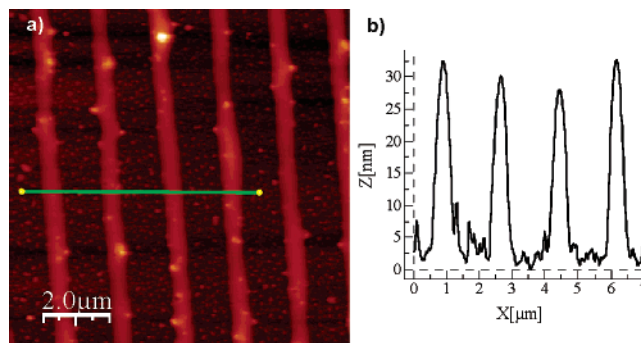


Figure 2. (a) Atomic force microscopy image of a patterned poly(4-methoxystyrene) brush and (b) line profile across the image in (a).

surfaces to perform cationic polymerizations leading to new types of nanoscale materials and controlled formation of precision thickness brushes in nanoscale geometries such as gaps, pores, and channels for a range of applications, and such work is underway in our laboratories at this time.

Acknowledgment. We thank the National Science Foundation for the financial support of this research (NIRT contract no. DMI02-10229) and DARPA.

Supporting Information Available: MHN synthesis, reflection absorption infrared spectroscopy of MHN SAM on gold surface, calculation of Pd coverage on the surface, and AFM of polymer brush. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Caster, K. C. *Polymer Brushes* **2004**, 331–370. (b) Senaratne, W.; Andruzzi, L.; Ober, C. K. *Biomacromolecules* **2005**, *6*, 2427–2448.
- (2) (a) Prucker, O.; Ruhe, J. *Langmuir* **1998**, *14*, 6893–6898. (b) Huang, W.; Skanth, G.; Baker, Gregory L.; Bruening, M. L. *Langmuir* **2001**, *17*, 1731–1736. (c) Hyun, J.; Chilkoti, A. *Macromolecules* **2001**, *34*, 5644–5652.
- (3) (a) Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **1998**, *31*, 5934–5936. (b) Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclován, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716–8724.
- (4) (a) Jordan, R.; Ulman, A.; Kang, J. F.; Rafailovich, M. H.; Sokolov, J. J. *Am. Chem. Soc.* **1999**, *121*, 1016–1022. (b) Advincula, R.; Zjou, Q.; Park, M.; Wang, S.; Mays, J.; Sakellariou, G.; Pispas, S.; Hadjichristidis, N. *Langmuir* **2002**, *18*, 8672–8684.
- (5) (a) Jordan, R.; Ulman, A. J. *Am. Chem. Soc.* **1998**, *120*, 243–247. (b) Zhao, B.; Brittain, W. J. *Prog. Polym. Sci.* **2000**, *25*, 677–710. (c) Kim, I.-J.; Faust, R. J. *Macromol. Sci., Pure Appl. Chem.* **2003**, *A40*, 991–1008.
- (6) (a) Weck, M.; Jackiw, J. J.; Rossi, R. R.; Weiss, P. S.; Grubbs, R. H. J. *Am. Chem. Soc.* **1999**, *121*, 4088–4089. (b) Kim, N. Y.; Jeon, N. L.; Choi, I. S.; Takami, S.; Harada, Y.; Finnie, K. R.; Girolami, G. S.; Nuzzo, R. G.; Whitesides, G. M.; Laibinis, P. E. *Macromolecules* **2000**, *33*, 2793–2795. (c) Buchmeiser, M. R.; Sinner, F.; Mupa, M.; Wurst, K. *Macromolecules* **2000**, *33*, 32–39.
- (7) (a) Sen, A.; Lai, T.-W. *Organometallics* **1982**, *1*, 415–417. (b) Lai, T.-W.; Sen, A. *Organometallics* **1984**, *3*, 866–870.
- (8) $[\text{Pd}(\text{C}_2\text{H}_5\text{CN})_4](\text{BF}_4)_2$ was prepared by dissolving $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (bought from Strem Chemicals and used as received) in an excess of propanenitrile, followed by evacuation. Acetonitrile (displaced by propanenitrile) and excess propanenitrile were both removed by evaporation. To ensure that this occurred, the sample was dried under dynamic vacuum for several hours.
- (9) Frey, S.; Shaporenko, A.; Zharnikov, M.; Harder, P.; Allara, D. L. *J. Phys. Chem. B* **2003**, *107*, 7716–7725.
- (10) Connelly, N. G.; Draggett, P. T.; Green, M. J. *Organomet. Chem.* **1977**, *140*, C10–C11.

JA064549V