

**Surface and Site-Specific Ring-Opening
Metathesis Polymerization Initiated by Dip-Pen
Nanolithography****

Xiaogang Liu, Shouwu Guo, and Chad A. Mirkin*

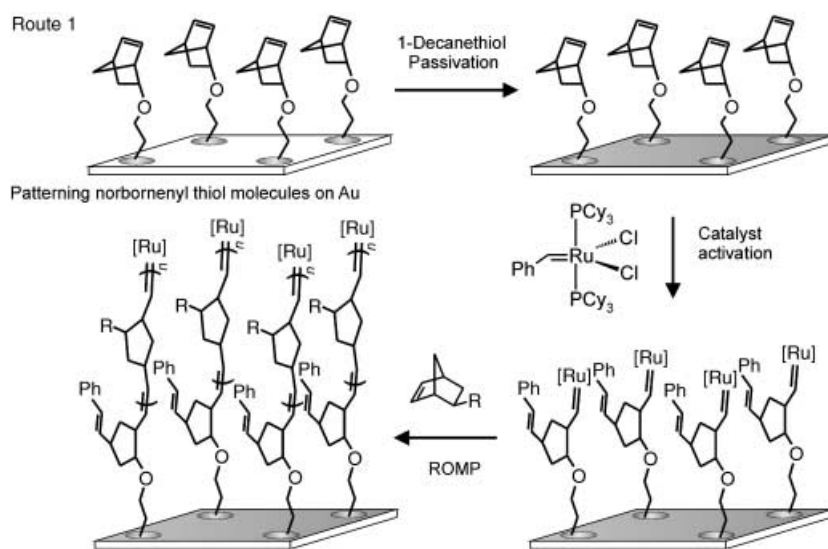
Patterned polymeric structures have attracted significant interest for possible applications in the development of sensors, catalysis, and optical devices.^[1,2] Thus far, several strategies, based upon photolithography, electron beam lithography, and microcontact printing have been developed for generating polymer arrays.^[2] While useful for many applications, these methods do not allow one to control nanostructure composition in a site-specific manner and, therefore, do not allow one to fabricate complex multi-component polymer arrays over the nano- to micrometer length scales. Having the capability to generate multicomponent arrays with nanoscopic features could afford one the opportunity to construct and study high-density combinatorial libraries of novel macromolecular systems.

Herein, we report a novel approach, based upon dip-pen nanolithography (DPN)^[3] and ring-opening metathesis polymerization (ROMP),^[4-6] to the fabrication of polymer brush arrays on the nanometer length scale.^[7] The combined approach utilizes the attributes of DPN and ROMP for synthesizing high-density polymer brush arrays with control over feature size (on the nanometer length scale), shape, and interfeature distance. Furthermore, the capability of directly delivering monomers through a standard AFM microcantilever will allow one to generate small, but diverse, libraries of nanoscale polymer brushes that comprise large numbers of structurally distinct compounds by assembling many possible combinations of small building monomers containing desired active functionalities.

To explore the potential of the combined approach and provide the basis for the studies leading to the design of combinatorial polymer libraries, two complementary routes have been developed for synthesizing arrays of the nanoscale polymer brushes based on DPN and ROMP. Route 1 is an approach based on growing polymers from a DPN-patterned template (Scheme 1). To test the viability of this route, 10-(*exo*-5-norbornen-2-oxy)decane-1-thiol molecules were patterned on a gold substrate by bringing a tip coated with norbornenylthiol in contact with the substrate. The *exo* isomer rather than the corresponding *endo* isomer was used to optimize ROMP reactivity.^[8] Subsequently, the substrate

[*] Prof. C. A. Mirkin, X. Liu, Dr. S. Guo
Department of Chemistry and Institute for Nanotechnology
Northwestern University
2145 Sheridan Road, Evanston, IL 60208-3113 (USA)
Fax: (+1) 847-491-7713
E-mail: camirkin@chem.northwestern.edu

[**] We acknowledge the AFOSR, DARPA through ARO (no. DAAD19-03-1-0065), and NSF for support of this research. We thank P. A. Bertin and J. M. Gibbs for providing the norbornenyl monomers.



Scheme 1. Graphical representation of surface-initiated ROMP by DPN.

was dipped into a solution of 1-decanethiol (0.005 M) in acetonitrile for 1 min to form a passivating layer on the gold surface around the norbornenylthiol nanostructures. After the samples had been rinsed with acetonitrile and dried with compressed difluoroethane, they were further immersed in a solution of Grubbs' first generation catalyst ($[(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}]$ (Cy = cyclohexyl), 0.1 M) in dichloromethane for 20 min. The surface was then rinsed with dry dichloromethane several times to remove excess catalyst. Finally, exposure of the catalyst-initiated wafers to a solution of norbornenyl-functionalized monomers (0.05 M) for a period of 10–240 min resulted in polymer brush arrays.

Line and dot arrays of the polymer brushes comprised of *exo*-5-norbornen-2-ol were constructed according to the method in Scheme 1. Topographic AFM images show the height of the polymer structures and provide insight into the uniformity of the polymer growth process (Figure 1 a–c). For example, the average diameter of each polymer brush dot is $78(\pm 4)$ nm and the average height is $5(\pm 1)$ nm (Figure 1 d).^[9] It should be noted that polymer brush nanostructures with different feature sizes (many micrometer to sub-100 nm-length scale), shapes (dots, lines, and other types of geometries), and compositions could be routinely generated by controlling the feature size and shape of the norbornenylthiol template (by DPN), the polymerization reaction time (10–240 min), and the choice of the norbornenyl-functionalized monomers. In addition, the feature height of the polymer nanostructures can be controlled over the 1–10 nm range by adjusting the polymerization reaction

time (Figure 2). However, under these conditions the polymer growth stopped after about 240 min, presumably because of deactivation of the immobilized catalyst.^[2c] Arrays of nanoscale polymer brush patterns consisting of the electrochemically active monomers *exo*-5-norbornen-2-yl ferrocene-carboxylate (**1**) and *exo*-5-norbornen-2-ylferrocenyl acetate (**2**) were synthesized on gold electrodes by the above-mentioned procedure as a control experiment. Differential pulse voltammetry (DPV) measurements on the patterns that consist of the polymerized monomer **1** show an anodic peak at 185 mV versus the ferrocene/ferrocenium couple (FcH/FcH^+), which is consistent with the solution DPV measurements of the oxidation potential for the norbornenyl ferrocenyl derivative ($E_{\text{pa}} =$

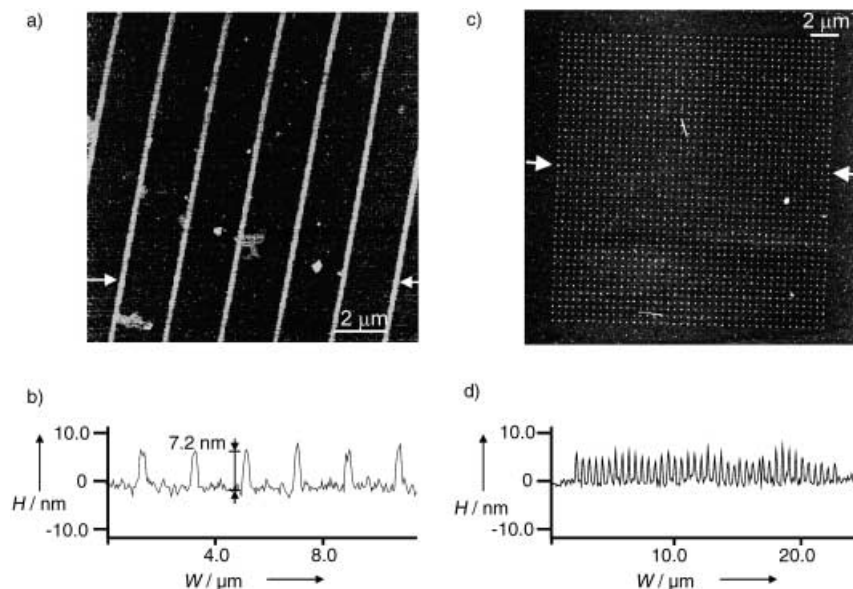


Figure 1. Polymer brush nanostructures prepared according to Scheme 1: a) Topographic AFM image of polymer brush lines. The speed of norbornenylthiol deposition, polymerization time, and measured average full-width at half-maximum (FWHM) values are $0.02 \mu\text{m s}^{-1}$, 60 min, and 480 nm, respectively; b) cross-sectional topography trace for a selected line from Figure 1 a; c) topographic AFM image of a polymer brush dot array. The norbornenylthiol deposition and polymerization times are 1 s and 30 min, respectively; d) cross-sectional topography trace for a selected line from Figure 1 c.

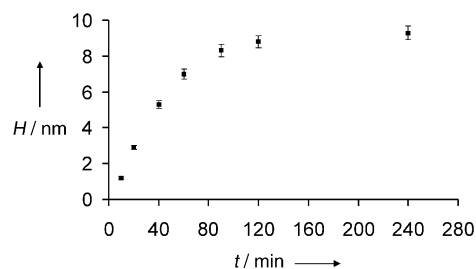


Figure 2. The height of poly-*exo*-5-norbornen-2-ol brush nanostructures plotted as a function of polymerization reaction time.

180 mV versus FcH/FcH^+ , Figure 3a). In contrast, DPV measurements on the diblock copolymer patterns consisting of two blocks of electrochemically distinct ferrocenyl monomers **1** and **2** exhibit two anodic peaks at -50 mV and 190 mV, which correspond to the sequential oxidations of the two different types of ferrocenyl moieties (Figure 3b). Taken together, the data presented here unambiguously confirm that the polymers indeed grow from the catalyst-initiated patterns generated by DPN.

An alternative procedure (Route 2) that involves transporting the norbornenyl monomers to catalyst-activated substrates with an AFM microcantilever was developed (Scheme 2) in an effort to evaluate the potential of generating a polymer brush array where each dot is a different polymer with a different degree of polymerization. These types of arrays could be useful in the generation of combinatorial libraries of nanoscale polymer features. To generate a substrate suitable for catalyst activation, a silicon oxide substrate was modified with 5-(bicycloheptenyl)trichlorosilane and immersed in a solution of Grubbs' first-generation catalyst in dichloromethane for 20 min. After being washed several times with dichloromethane to remove excess catalyst, the catalyst-tethered substrate was immediately used for generating polymer brushes with a monomer-coated AFM tip. Thus, in principle, a wide range of polymers with various numbers of repeating monomer units can be easily

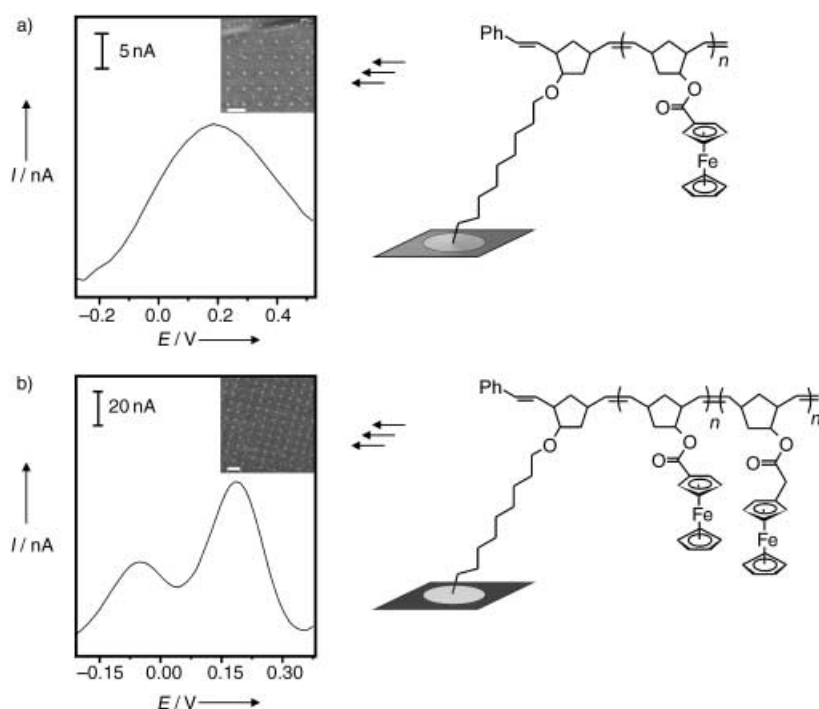
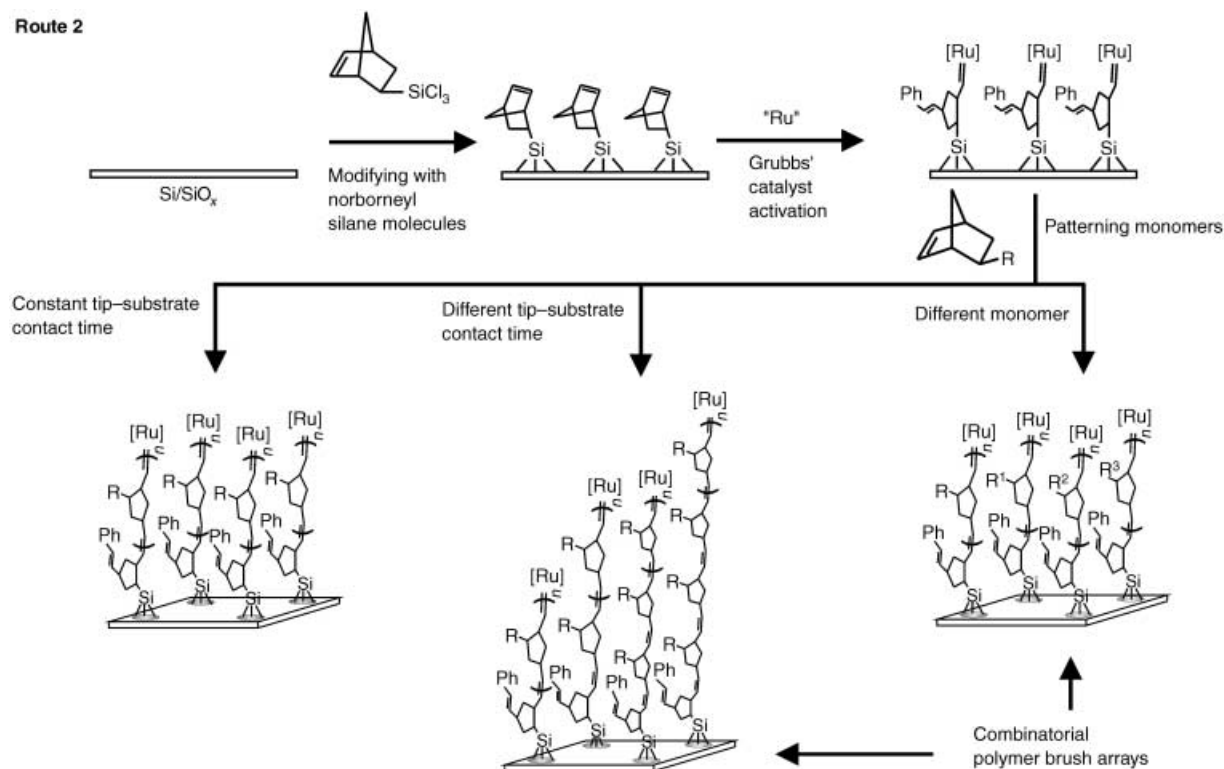


Figure 3. a) DPV of an electrode (0.28 mm^2) patterned with poly-**1** by DPN and ROMP (inset: AFM topography image of the poly-**1** pattern. The scale bar is $2 \mu\text{m}$); b) DPV of an electrode patterned with diblock copolymers consisting of monomer **1** and **2** by DPN and ROMP (inset: AFM topography image of the diblock copolymer brush pattern. The scale bar is $2 \mu\text{m}$). For DPV experiments: scan rate = 50 mVs^{-1} ; pulse period = 200 ms ; pulse amplitude = 50 mVs^{-1} ; and pulse width = 50 ms .

Route 2



Scheme 2. Graphical representation of ROMP initiated by DPN and a monomer-coated tip.

generated by deliberately controlling the tip–substrate contact time. Significantly, a high-density two-dimensional array of polymer brushes that consists of different norbornenyl monomer entities in different spatially defined regions can be generated by this approach (Scheme 2).

As proof-of-concept, the monomer, *exo*-5-norbornen-2-ol, was delivered to a catalyst-activated silicon oxide substrate by an AFM tip and polymerized in situ. In a typical patterning experiment, a conventional silicon nitride AFM microcantilever coated with a solution of the monomer in dichloromethane was brought into contact with the substrate to generate an array of polymers in a glove box (N_2 atmosphere). An AFM topographic image of such an array comprising *exo*-5-norbornen-2-ol as the chain-propagating monomer shows that features of controlled height (22 ± 1 nm) can be reproducibly generated (Figure 4a). An important feature of this

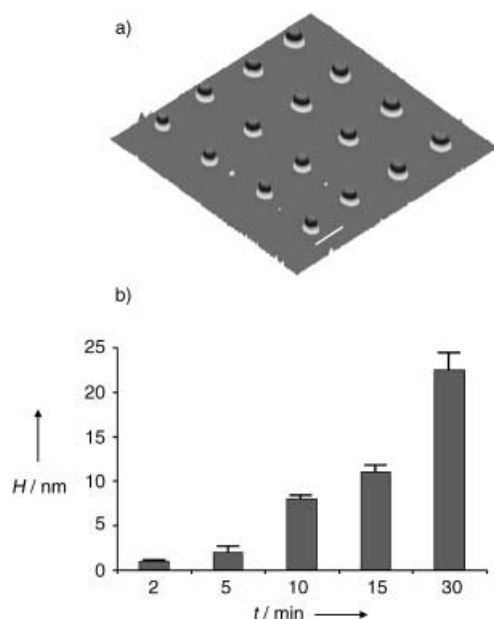


Figure 4. a) Three-dimensional topographic AFM image of an array of polymer brush dots generated according to the method in Scheme 2 (the scale bar is 2 μ m); b) a plot of nanostructure height (poly-*exo*-5-norbornen-2-ol) as a function of tip-induced polymerization reaction time (as measured by tip–substrate contact time). The data points are the averaged measurements, and the vertical bars correspond to the standard deviation.

monomer–DPN approach is the ability to monitor and control the living polymerization process on the catalyst-tethered surface with the monomer-coated microcantilever.^[10] As anticipated, the height of the polymer brush nanostructures increases with tip–substrate contact time (Figure 4b). It is noted that the polymer growth rate in the monomer–DPN approach (Scheme 2) is much faster than that under comparable bulk conditions (Scheme 1). This can be attributed, in part, to the higher local concentration of the monomer accessible to the catalyst-activated sites on the patterned substrate. Indeed, the polymerizable ink is confined to the region near the tip and point of contact with the catalyst.

In conclusion, a novel approach for synthesizing arrays of nanoscale polymer brushes, based upon a combination of

DPN and a surface-initiated ROMP method, has been demonstrated on metallic and insulating substrates. These approaches are important because they point towards a route to combinatorial libraries of functional polymer nanostructures of almost limitless chemical complexity, which can be constructed in situ. The capabilities demonstrated by these single-pen experiments will be dramatically facilitated through the use of multipen arrays that do not require the step-by-step changing of inks and pens during a conventional DPN experiment.^[3c,n]

Experimental Section

Exo-5-norbornen-2-ol, 10-(*exo*-5-norbornen-2-oxy)decane-1-thiol, *exo*-5-norbornen-2-yl ferrocenecarboxylate, and *exo*-5-norbornen-2-ylferrocenyl acetate were synthesized according to literature procedures.^[5b,11] All other reagents were purchased from the Aldrich Chemical Company and used without further purification. All solvents were distilled under nitrogen and saturated with nitrogen prior to use. All reactions were performed in a dry nitrogen atmosphere or in a glove box unless otherwise noted. Silicon oxide wafers were cut into 0.5×0.5 cm² slides and sonicated sequentially in dichloromethane, methanol, and nanopure water for 10 min. The wafers were then immersed in freshly mixed ammonia peroxide solution ($NH_3:H_2O:H_2O_2:H_2O$ (v:v:v) = 1:1:5) for 1 h at about 100 °C, after which time they were rinsed with nanopure water followed by ethanol. The gold substrates were prepared by coating a Si wafer coated with silicon oxide with a Ti adhesion layer (5 nm) followed by 50 nm of gold using an Edwards Auto 306 evaporator. DPN experiments were carried out in a glove box (23 °C, N_2 atmosphere) with a Thermomicroscopes CP AFM driven by customer lithography software (NanoInk, Inc., Chicago, IL) and commercial Si_3N_4 cantilevers (Thermomicroscopes Sharpened Microcantilever A, force constant: 0.05 N m⁻¹). To minimize piezo tube drift problems, a 90- μ m scanner with closed loop scan control was used for all DPN experiments. AFM topography images were acquired using a Digital Instruments Multi-mode Nanoscope IIIa with an extender electronics module in tapping mode. Electrochemical experiments were performed with a Bioanalytical Systems (BAS) Model 100B using Au disk electrodes with a Pt wire counter electrode and a silver wire reference electrode.

Received: July 4, 2003 [Z52309]

Keywords: lithography · nanostructures · polymers · ring-opening polymerization · scanning probe microscopy

- [1] a) J. M. J. Fréchet, E. Eichler, H. Ito, C. G. Willson, *Polymer* **1983**, *24*, 995; b) O. Prucker, J. Rühe, *Macromolecules* **1998**, *31*, 592; c) S. L. Clark, P. T. Hammond, *Adv. Mater.* **1998**, *10*, 1515; d) Y. Xu, J. T. Watson, M. L. Bruening, *Anal. Chem.* **2003**, *75*, 185; e) A. Pogantsch, G. Trattig, G. Langer, W. Kern, U. Scherf, H. Tillmann, H.-H. Hörhold, E. Zojer, *Adv. Mater.* **2002**, *14*, 1722; f) C.-H. Jang, B. D. Stevens, P. R. Carlier, M. A. Calter, W. A. Ducker, *J. Am. Chem. Soc.* **2002**, *124*, 12114.
- [2] a) W. M. Lackowski, P. Ghosh, R. M. Crooks, *J. Am. Chem. Soc.* **1999**, *121*, 1419; b) T. A. von Werne, D. S. Germack, E. C. Hagberg, V. V. Sheares, C. J. Hawker, K. R. Carter, *J. Am. Chem. Soc.* **2003**, *125*, 3831; c) B. Rowan, M. A. Wheeler, R. M. Crooks, *Langmuir* **2002**, *18*, 9914; d) B. Domercq, R. D. Hrehá, Y.-D. Zhang, N. Larribeau, J. N. Haddock, C. Schultz, S. R. Marder, B. Kippelen, *Chem. Mater.* **2003**, *15*, 1491; e) N. Y. Kim, N. L. Jeon, I. S. Choi, S. Takami, Y. Harada, K. R. Finnie, G. S. Girolami, R. G. Nuzzo, G. M. Whitesides, P. E. Laibinis, *Macromolecules* **2000**, *33*, 2793; f) M. Husemann, D. Mecerreyes, C. J.

- Hawker, J. L. Hedrick, R. Shah, N. L. Abbott, *Angew. Chem.* **1999**, *111*, 685; *Angew. Chem. Int. Ed.* **1999**, *38*, 647; g) M. Weck, J. J. Jackiw, R. R. Ross, P. S. Weiss, R. H. Grubbs, *J. Am. Chem. Soc.* **1999**, *121*, 4088; h) U. Schmelmer, R. Jordan, W. Geyer, W. Eck, A. Götzhäuser, M. Grunze, A. Ulman, *Angew. Chem.* **2003**, *115*, 577; *Angew. Chem. Int. Ed.* **2003**, *42*, 559; i) D. M. Jones, W. T. S. Huck, *Adv. Mater.* **2001**, *13*, 1256.
- [3] For selected examples, see a) R. D. Pine, J. Zhu, F. Xu, S. Hong, C. A. Mirkin, *Science* **1999**, *283*, 661; b) S. Hong, J. Zhu, C. A. Mirkin, *Science* **1999**, *286*, 523; c) H. Zhang, S.-w. Chung, C. A. Mirkin, *Nano Lett.* **2003**, *3*, 43; d) L. M. Demers, D. S. Ginger, S.-J. Park, Z. Li, S.-W. Chung, C. A. Mirkin, *Science* **2002**, *296*, 5574; e) M. Zhang, D. Bullen, S.-W. Chung, S. Hong, K. S. Ryu, Z. Fan, C. A. Mirkin, C. Liu, *Nanotechnology* **2002**, *13*, 212; f) Y. Li, B. W. Maynor, J. Liu, *J. Am. Chem. Soc.* **2001**, *123*, 2105; g) B. W. Maynor, Y. Li, J. Liu, *Langmuir* **2001**, *17*, 2575; h) A. Noy, A. E. Miller, J. E. Klare, B. L. Weeks, B. W. Woods, J. J. DeYoreo, *Nano Lett.* **2002**, *2*, 109; i) R. McKendry, W. T. S. Huck, B. Weeks, M. Fiorini, C. Abell, T. Rayment, *Nano Lett.* **2002**, *2*, 713; j) L. A. Porter, Jr., H. C. Choi, J. M. Schmeltzer, A. E. Ribbe, L. C. C. Elliott, J. M. Buriak, *Nano Lett.* **2002**, *2*, 1369; k) P. E. Sheehan, L. J. Whitman, *Phys. Rev. Lett.* **2002**, *88*, 156104; l) G. Agarwal, R. R. Naik, M. O. Stone, *J. Am. Chem. Soc.* **2003**, *125*, 7408; m) P. Manandhar, J. Jang, G. C. Schatz, M. A. Ratner, S. Hong, *Phys. Rev. Lett.* **2003**, *90*, 115505; n) P. Belaubre, M. Guirardel, G. Garcia, J. B. Pourciel, V. Leberre, A. Dagkessamanskaia, E. Trévisiol, J. M. Francois, *Appl. Phys. Lett.* **2003**, *82*, 3122; o) C. L. Cheung, J. A. Camarero, B. W. Woods, T. Lin, J. E. Johnson, J. J. De Yoreo, *J. Am. Chem. Soc.* **2003**, *125*, 6848.
- [4] "Ring Opening Metathesis Polymerisation and Related Chemistry," *NATO Sci. Ser. II* **2002**, 56.
- [5] a) A. G. M. Barrett, B. T. Hopkins, J. Köbberling, *Chem. Rev.* **2002**, *102*, 3301; b) K. J. Watson, J. Zhu, S. T. Nguyen, C. A. Mirkin, *J. Am. Chem. Soc.* **1999**, *121*, 462; c) M. R. Buchmeiser, G. Seeber, M. Mupa, G. K. Bonn, *Chem. Mater.* **1999**, *11*, 1533.
- [6] T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18.
- [7] For other examples of SPM-based lithography, see a) I. W. Lyo, P. Avouris, *Science* **1991**, *253*, 173; b) W. T. Muller, D. L. Klein, T. Lee, J. Clarke, P. L. Mceuen, P. G. Schultz, *Science* **1995**, *268*, 1995; c) S. L. Brandow, W. J. Dressick, C. S. Dulcey, T. S. Koloski, L. M. Shirey, J. Schmidt, J. M. Calvert, *J. Vac. Sci. Technol. B* **1997**, *15*, 1818; d) S. S. Wong, E. Joselevich, A. T. Woolley, C. L. Cheung, C. M. Lieber, *Nature* **1998**, *394*, 52; e) R. Maoz, E. Frydman, S. R. Cohen, J. Sagiv, *Adv. Mater.* **2000**, *12*, 424; f) H. Sugimura, N. Nakagiri, *J. Vac. Sci. Technol. B* **1996**, *14*, 1223; g) G.-Y. Liu, S. Xu, Y. L. Qian, *Acc. Chem. Res.* **2000**, *33*, 457; h) C.-H. Jang, B. D. Stevens, P. R. Carlier, M. A. Calter, W. A. Ducker, *J. Am. Chem. Soc.* **2002**, *124*, 12114; i) A. Bruckbauer, L. Ying, A. M. Rothery, D. Zhou, A. I. Shevchuk, C. Abell, Y. E. Korchey, D. Klenerman, *J. Am. Chem. Soc.* **2002**, *124*, 8810.
- [8] J. D. Rule, J. S. Moore, *Macromolecules* **2002**, *35*, 7878.
- [9] Note that the error was determined by analyzing the highest point of each dot in a 20×20 array and not from the height profile in Figure 1 d.
- [10] Note that in a typical DPN experiment a molecule-coated AFM cantilever can be used not only for transporting molecules onto a substrate, but also for imaging the nanostructures in contact mode to determine whether or not the molecules have been deposited. High scan rates (> 6 Hz) do not lead to appreciable ink deposition. All nanostructures were subsequently imaged separately with a Digital Instruments Multimode Nanoscope in the tapping mode.
- [11] G. H. Posner, J. S. Ting, C. M. Lentz, *Tetrahedron* **1976**, *32*, 2281.