DOI: 10.1002/anie.201103990

VIP Polymerization Catalysts

Polymerization Catalyst Laser-Interference Patterning[**]

*Johannes Huber, Benjamin Scheinhardt, Tobias Geldhauser, Johannes Boneberg, and Stefan Mecking**

The binding of molecular polymerization catalysts to solid supports, in the form of microporous particles or also flat substrates, has been extensively studied.[1,2] The primary aim is to gain control of the morphology of the polymer formed directly during polymerization. This approach can be convenient, for example, in saving additional processing steps if the polymer is formed directly in the desired particle size. For intractable, insoluble polymers not amenable to postpolymerization processing, it is a necessity to directly generate any desirable morphological features during polymerization.

Despite these vast studies, a spatial resolution of catalysts on supports has rarely been achieved.[3–5] Such a spatial resolution could allow for the generation of more complex structures than homogeneously composed polymer particles or films. Such structures are obviously of interest from many different viewpoints, and a multitude of noncatalytic routes for their preparation have been developed.[6–13]

Desirable features of a method generating a spatially resolved catalyst pattern are precision, rapidity, efficiency, and a generic nature. We report herein an approach employing pulsed laser-interference lithography of a coordination polymerization catalyst. Coherent laser light in the UV/Vis range enables utilization of standard laser optics for the patterning process, and the period can be varied over a wide range through the angles of the incident laser beams.[14] We chose the generation of polyacetylene as an example, as it is the prototype of a conjugated, conductive polymer and it is also well known for its notorious postpolymerization unprocessability.[15]

As a catalyst precursor, a mixture of $Pd(OAc)_2$ and 1,3-bis(di-*tert*-butylphosphino)propane was employed.[5,11,16] A methanol solution of this catalyst was spincoated on a silicon substrate. The resulting catalyst film was structured by an interference pattern by means of multiple nanosecond laser pulses, using the second harmonic of a Nd:YAG laser (532 nm). With nanosecond laser pulses, high heating rates and temperatures are realized, thus resulting in a permanent loss of catalyst activity in the areas of constructive interference (see below). Exposure of this patterned catalyst to an acetylene atmosphere at ambient conditions gave polyacetylene paths with variable periods that were determined by the angles of incidence of the laser beams in the preceding structuring step. Paths with a period of 1 and 5 µm, respectively, were prepared in this manner (Figure 1).

Typically, 12 laser pulses with an energy of 550 mJ were applied to obtain polyacetylene paths fully separated from one another, as revealed by AFM and conductivity measurements (see below). The dimensions of the paths slightly depend on the polymerization time. In the polyacetylene patterns of 5 µm period, the uniform paths had a width of 3 to 4.5 µm (depending on polymerization time), and a height of 70–100 nm (for 1 µm period: width 0.8 to 0.9 µm; height 25–30 nm). In the areas of maximum interference most likely a thermal desorption of the catalyst occurs during the patterning process. This desorption possibly accounts for the heightening of the polymer paths at their edges (Figure 1), caused by prior accumulation of intact catalyst from the heated areas by recondensation. Single paths with a length of up to 1 mm could be removed mechanically from the substrate as a whole (Figure 2). This observation demonstrates their internal integrity and continuity, and a remarkable mechanical strength and flexibility of the polyacetylene "wires" generated by this patterning method.

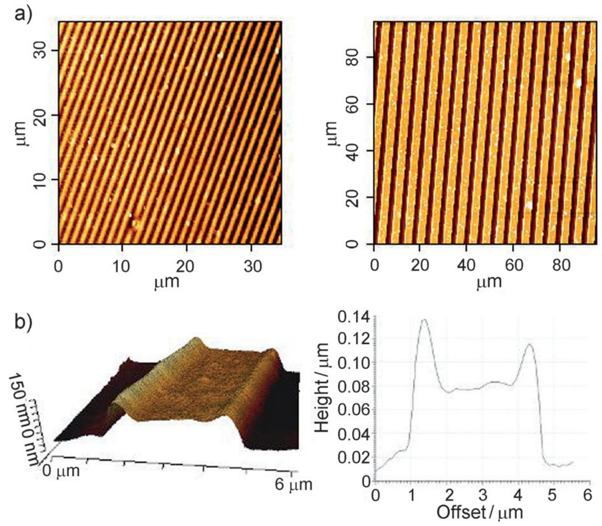

Figure 1. a) AFM images of patterned polyacetylene with a period of 1 µm (left) and 5 µm (right). b) AFM image (left) and cross-sectional topography trace (right) of one single polyacetylene path.

---

[*] Dipl.-Chem. J. Huber, MSc. B. Scheinhardt, Prof. Dr. S. Mecking
University of Konstanz, Chair of Chemical Materials Science
Dept. of Chemistry
Universitätsstrasse 10, 78457 Konstanz (Germany)
E-mail: stefan.mecking@uni-konstanz.de

Dr. T. Geldhauser, Prof. Dr. J. Boneberg
University of Konstanz, Dept. of Physics
Universitätsstrasse 10, 78457 Konstanz (Germany)

[**] Financial support by the DFG (Me1388/7-1 and SFB 767) is gratefully acknowledged. S.M. is indebted to the Fonds der Chemischen Industrie.

Supporting information for this article (patterning procedure; conductivity measurements; piezo apparatus) is available on the WWW under http://dx.doi.org/10.1002/anie.201103990 or from the author.

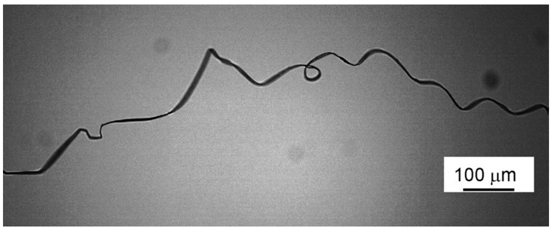

Figure 2. Microscopy image of a single polymer "wire", mechanically removed from the substrate as a whole.

The low intrinsic conductivity of polyacetylene can be enhanced by doping with oxidants.[17] The conductivity of the iodine-doped polyacetylene was probed with a custom-made piezo apparatus, which allows for the precise contacting of a single circuit path under a light microscope (see the Supporting Information). A specific conductivity of 36 S cm^{-1} was determined throughout the sample (5 μm period, 170 h polymerization time).[18] This is at the lower end of conductivities reported for bulk polyacetylene, which vary over a large range from 10^2 to 10^5 S cm^{-1} depending on preparation and postpolymerization treatment procedures.[17,19] Conductivity measurements on adjacent paths showed that they are indeed electrically isolated from one another.

In summary, we have demonstrated the spatial patterning of a polymerization catalyst by means of laser interference. The latter represents a rapid and efficient method, which is also not limited in resolution and the complexity of possible patterns. Polymerization leads to replica of the patterned catalyst, as illustrated by the generation of "wires" of polyacetylene, a polymer not amenable to any postpolymerization processing. The quality and continuity of the polymer paths is not only evident from AFM imaging, but also from the continuous conductivity of the individual lines and their mechanical integrity.

Experimental Section

Catalyst solution: Under an inert atmosphere, a solution of 1,3-bis(di-*tert*-butylphosphino)propane (86.4 mg, 260 μmol) in methanol (20 mL) was added to Pd(OAc)$_2$ (29.2 mg, 130 μmol). After stirring for 10 min, the yellow solution was filtered through a syringe filter (0.24 μm) and methane sulfonic acid (27 mg, 281 μmol) was added to the filtrate to afford a catalyst solution with a concentration of 6.5 μmol Pd mL^{-1}.

General patterning procedure: The entire patterning procedure was performed under an inert atmosphere. In a nitrogen-filled glovebox, a drop of the catalyst solution was spincoated (2500 rpm) on a silicon substrate (1 cm × 1 cm), previously cleaned with acetone. This catalyst film was placed in a custom-made inert gas container and was patterned by 12 pulses with an energy of 550 mJ each of an injection-seeded Nd:YAG laser with its second harmonic (532 nm) and pulse widths of around 13 ns. The delay between the pulses was about 0.5 s. The beam was split in two equally intense beams that are, after travelling the same length, rejoined on the catalyst film under a certain angle. This approach leads to a periodic modulated intensity by interference of the two beams. Patterns with a period of 1 and 5 μm were generated in this fashion. The substrate with the patterned catalyst was placed in a Schlenk tube under an argon flow, and the argon atmosphere was replaced by an acetylene atmosphere (ambient pressure). Exposure times were typically several days at room temperature.

Conductivity measurements: The polyacetylene pattern was doped in an iodine atmosphere by placing the substrate in a vial containing coarse-grained iodine in the back end, subsequently warming the iodine gently with a blow-dryer. At a hundredfold magnification under a light microscope one single polyacetylene path was then contacted by two platinum tips of a piezo apparatus in a certain distance (adjacent paths had been removed previously by scratching with the tips). The resistance of the circuit path was measured by use of a connected commercial multimeter. The specific conductivity was calculated from the resistance measured and the path cross-section area, as estimated from AFM measurements.

Received: June 10, 2011

Keywords: conducting materials · conjugated polymers · laser interference · lithography · patterning

---

[1] *Tailor-made polymers.* (Eds: J. R. Severn, J. C. Chadwick), Wiley, Weinheim, **2008**.
[2] a) G. G. Hlatky, *Chem. Rev.* **2000**, *100*, 1347–1376; b) J. R. Severn, J. C. Chadwick, R. Duchateau, N. Friederichs, *Chem. Rev.* **2005**, *105*, 4073–4147; c) G. Fink, B. Steinmetz, J. Zechlin, C. Przybyla, B. Tesche, *Chem. Rev.* **2000**, *100*, 1377–1390.
[3] T. Diesing, G. Rojas, M. Klapper, G. Fink, K. Müllen, *Angew. Chem.* **2009**, *121*, 6594–6597; *Angew. Chem. Int. Ed.* **2009**, *48*, 6472–6475.
[4] R. F. Harris, M. J. Ricci, R. A. Farrer, J. Praino, S. J. Miller, B. E. A. Saleh, M. C. Teich, J. T. Fourkas, *Adv. Mater.* **2005**, *17*, 39–42.
[5] J. Huber, A. Amgoune, S. Mecking, *Adv. Mater.* **2008**, *20*, 1978–1981.
[6] a) M. Okubo, J. Izumi, T. Hosotani, T. Yamashita, *Colloid Polym. Sci.* **1997**, *275*, 797–801; b) Y. Yun, H. Li, E. Ruckenstein, *J. Colloid Interface Sci.* **2001**, *238*, 414–419; c) L. Jin, Y. Deng, J. Hu, C. Wang, *J. Polym. Sci. A* **2004**, *42*, 6081–6088; d) L. J. Borthakur, T. Jana, S. K. Dolui, *J. Coat. Technol. Res.* **2010**, *7*, 765–772.
[7] S. Holdcroft, *Adv. Mater.* **2001**, *13*, 1753–1765.
[8] a) C. B. Gorman, H. A. Biebuyck, G. M. Whitesides, *Chem. Mater.* **1995**, *7*, 526–529; b) C. N. Sayre, D. M. Collard, *J. Mater. Chem.* **1997**, *7*, 909–912; c) C. Kranz, M. Ludwig, H. E. Gaub, W. Schuhmann, *Adv. Mater.* **1995**, *7*, 38–40.
[9] a) M. L. Renak, G. C. Bazan, D. Roitman, *Adv. Mater.* **1997**, *9*, 392–395; b) F. Shi, B. Dong, D. Qiu, J. Sun, T. Wu, X. Zhang, *Adv. Mater.* **2002**, *14*, 805–809.
[10] M. Xue, Y. Zhang, Y. Yang, T. Cao, *Adv. Mater.* **2008**, *20*, 2145–2150.
[11] J. Huber, S. Mecking, *Angew. Chem.* **2006**, *118*, 6462–6465; *Angew. Chem. Int. Ed.* **2006**, *45*, 6314–6317.
[12] M. Goh, T. Matsushita, H. Satake, M. Kyotani, K. Akagi, *Macromolecules* **2010**, *43*, 5943–5948.
[13] E. Fisslthaler, M. Sezen, H. Plank, A. Blümel, S. Sax, W. Grogger, E. J. W. List, *Macromol. Chem. Phys.* **2010**, *211*, 1402–1407.
[14] T. Geldhauser, P. Leiderer, J. Boneberg, *Langmuir* **2008**, *24*, 13155–13160.
[15] a) A. J. Heeger, *Angew. Chem.* **2001**, *113*, 2660–2682; *Angew. Chem. Int. Ed.* **2001**, *40*, 2591–2611; b) H. Shirakawa, *Angew. Chem.* **2001**, *113*, 2642–2648; *Angew. Chem. Int. Ed.* **2001**, *40*, 2574–2580; c) A. G. MacDiarmid, *Angew. Chem.* **2001**, *113*, 2649–2659; *Angew. Chem. Int. Ed.* **2001**, *40*, 2581–2590.
[16] E. Drent, D. H. L. Pello, Eur. Pat. 576091 (Shell), **1993**.

[17] a) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, A. J. Heeger, *J. Chem. Soc. Chem. Commun.* **1977**, *16*, 578–580; b) C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. MacDiarmid, *Phys. Rev. Lett.* **1977**, *39*, 1098–1101; c) C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, H. Shirakawa, *J. Am. Chem. Soc.* **1978**, *100*, 1013–1015.

[18] At a shorter polymerization time of 17 h, a lower specific conductivity of only 3 $\mathrm{S\,cm^{-1}}$ was observed. Apparently, the longer polymerization time enhances the compactness of the polymer paths.

[19] N. Basescu, Z.-X. Liu, D. Moses, A. J. Heeger, H. Naarmann, N. Theophilou, *Nature* **1987**, *327*, 403–405.