communications

Patterned Polymer Brushes Grafted from Bromine-Functionalized, Chemically Active Surface Templates**

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The use of selectively activated surfaces to fabricate brush systems has attracted great attention, as these structures can be used to combine topographical properties with the possibility to select the appropriate chemical functionality for applications in both electronic[1] and biological[2] areas. Stable, covalently bonded polymer films provide versatile possibilities to tailor the chemical, mechanical, electrical, and energetic properties of surfaces. There are two main approaches to synthesize polymers attached to the surface, which are classified as "grafting to" and "grafting from" techniques. Since the "grafting to" method has some limitations,[3] for instance, diffusion of the bulky polymer chains to the immobilized functional groups on the surface, the "grafting from" approach is generally preferred to synthesize homopolymer or block-copolymer[4,5] brushes tethered to particles or substrates by use of different polymerization techniques, such as conventional radical, controlled radical, carbocationic, anionic, ring-opening metathesis, and group transfer.[6,7] The development of controlled/living polymerization systems leads to the synthesis of defined-polymer or block-copolymer brushes tethered covalently to the surface from one end. In particular, atom-transfer radical polymerization (ATRP)[8–10] allows well-defined brushes to be grown on the surface under mild conditions. In this latter technique, a lower-oxidation-state metal complex abstracts a halogen from an alkyl halide to generate a radical center. The addition of monomers to this active species continues until the higher-oxidation-state metal complex deactivates the active center and creates the dormant species. One of the main advantages of ATRP for surface-initiated polymerization is the low concentration of active centers during the polymerization because of the high deactivation rate in comparison to the activation rate. This equilibrium allows termination reactions to be suppressed and, thus, the living character of the brushes is protected, which can also be used to create block copolymers on the surface.

The polymerization propagates by starting from suitable halide groups present on the surface. Although tertiary or secondary alkyl halide functions are widely used as an initiator in the literature,[11] it is known that primary alkyl halide functions are also sufficient to initiate the polymerization.[12] The patterning of these initiators offers the possibility to fabricate patterned polymer-brush systems, which are of special interest, for example, in sensors, combinatorial arrays, and micro- and nanofluidic devices. Approaches targeting the patterning of polymer-brush films include the patterning of the initiator by microcontact printing,[13,14] photo[15] and electron-beam lithography,[16] and scanning force microscopy (SFM)-tip mediated nanografting.[17] Suitable templates for the site-selective growth of such systems are also chemically active surface patterns on self-assembled monolayers of silane molecules,[18,19,20] which allow the local modification of surfaces. Different chemical functionalities, tailor-made surface properties, and different adhesion and binding properties of the generated patterns can be used for subsequent modification schemes applied to the templates. This technique is used here to pattern the initiator, which is employed in the "grafting on" process (see Figure 1). The fact that chemically active surface patterns can be used not only to graft materials but also to covalently stabilize them on the surface pattern is a major advantage of chemically active surface templates.

We use a patterning technique that utilizes an electro-chemical-oxidation process to generate local carboxylic acid functions on an *n*-octadecyltrichlorosilane (OTS)-coated silicon wafer.[18] Within this process, surface terminal CH_3 groups of the OTS monolayer are converted into COOH functions by sufficient voltage pulses. This oxidation process is mediated by water and the voltage is applied via a conductive SFM tip,[18,21] a copper transmission electron microscopy (TEM) grid,[22] or hydrophilic stamps.[23] These methods allow the transfer of a pattern structure to the substrate with different dimension ranges. With SFM tips, the fabrication of structures down to 10 nm[21] is possible; the resolution obtained for TEM-grid printed structures has been demonstrated down to ≈ 7 μm, limited up to now by the dimensions of available TEM grids. While the tip inscription of chemically active surface patterns is a relatively slow process, the parallel patterning of the surface is reliably fast (a grid structure of ≈ 7 mm^2 can be oxidized in 10 s) and larger modified areas become accessible. The latter method is used in this approach to obtain chemically structured surface templates to graft polymers to the surface. For this purpose, a suitable initiator has to be assembled on the grid structure. Due to the chemical selectivity of the printed replica of the grid, self-assembly is a suitable method to bind the initiator to the surface template. The COOH-terminated, oxidized areas, resembling the bar structure of the TEM grid, mediate the site-selective binding of an additional trichlorosilane

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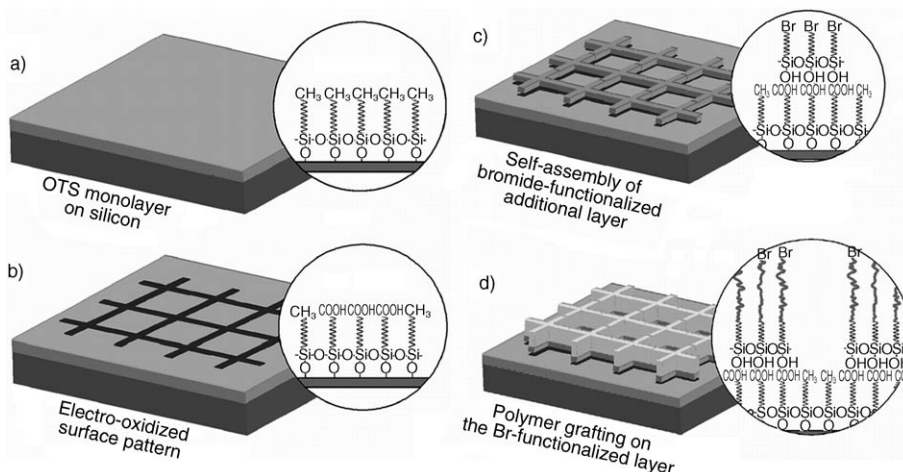WILEY InterScience®
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Figure 1. Schematic outline of the experiment to graft polymer brushes from surface templates. a) Self-assembled monolayers of *n*-octadecyltrichlorosilane on silicon wafers are used as a substrate for the generation of chemically active surface patterns. b) The electrochemical oxidation of the surface terminal CH_3 groups to COOH functions is performed with the aid of a copper TEM grid. The chemical functionalization resembles a replica of the grid structure. c) The COOH groups are transferred onto a bromine-functionalized surface by the site-selective self-assembly of a bromo-undecyltrichlorosilane precursor that attaches to the COOH functions. This precursor provides the necessary initiator function for the subsequent ATRP polymerization of styrene on the surface template (d).

layer.[22] Commercially available bromo-undecyltrichlorosilane is a suitable molecule that can act as an initiator for ATRP polymerization.[8] Bromo-undecyltrichlorosilane was self-assembled onto the oxidized grid structure, forming a ≈ 2 nm high, homogeneous layer, as confirmed by SFM, via hydrogen-bond formation of the hydrolyzed trichloro species of the precursor molecules and the COOH-terminated patterns of the inscribed template structure.[24] Water-vapor condensation on the grid structures[22] can be used to analyze the modification procedure qualitatively.

Water-vapor condensation generates a visible contrast that can be seen in the optical microscope. The COOH-terminated oxide pattern exhibits a strong hydrophilic/hydrophobic contrast to the unmodified OTS background due to a low water contact angle of $<5°$ on such areas, which causes a strong condensation of the water vapor on the bar structures. This contrast is observed to be significantly weaker after the functionalization of the bar structures with bromo-undecyltrichlorosilane, due to the lower hydrophilicity of the bromine-functionalized surface, but is still well observable (Figure 2a) (a water contact angle of 82° is usually found[25]). Nonspecifically absorbed water droplets on the unmodified surface of the OTS layer are sometimes observed[23] but in general a better absorption of small drops on the bar structures of the grid is seen, which appears with significantly darker contrast. Nonetheless, optical images of the same surface spot after the evaporation of the water vapor reveal no detectable optical contrast of the surface (Figure 2b). With this functionalized surface template, a suitable initiator to perform ATRP polymerization is locally attached to the surface and the grafting of the polymer is performed under mild conditions. Tests on the macroscopic

scale of this process on silicon wafers directly coated with bromo-undecyltrichlorosilane show the formation of polymer films. However, no detectable formation of polymers was observed in the reaction vessel, as was checked by gel-permeation chromatography (GPC) investigations of the polymerization solution after the surface-initiated grafting process. The small amount of generated material on the surface is one of the major problems for performing a complete characterization that is usual-
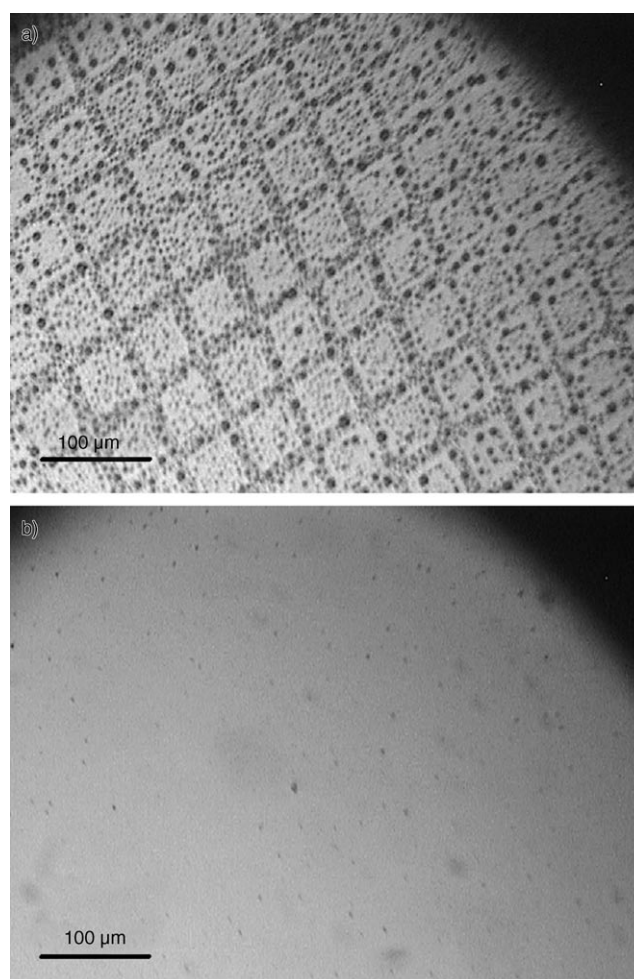

Figure 2. Representative optical microscopy images of a bromine-functionalized surface pattern imprinted with a mesh 400 copper TEM grid. a) Due to the hydrophilic character of the bromine-functionalized surface, water vapor condensates preferentially on the bar structures rather than on the unmodified, hydrophobic OTS substrate. The optical contrast can be observed easily by optical microscopy. b) After the water vapor has evaporated the optical micrograph does not show any surface features any more.

ly applied to polymer systems with classical methods. Only a limited number of characterization tools are available to investigate the grown polymer films. The study of model systems is in this respect only of restricted use, as the growth mechanism of polymer brushes will crucially depend on the quality of the initiator layer. Aspects such as diffusion limitation and steric hindrance create a situation that makes the "grafting from surfaces" approach difficult to compare to polymer brushes synthesized in solution or grafted onto silica nanoparticles.[26] Therefore, the main focus of our investigation is a feasibility study to create patterned polymer brushes. Besides the inspection of the films by SFM and the determination of the film thickness by scratch tests, additional Fourier transform infrared (FTIR) investigations have been performed to prove the chemical structure of the grown polymers.

Attenuated total reflection (ATR)-FTIR spectra of polystyrene (Figure 3a, dashed line), which was polymerized with ethyl α-bromoisobutyrate, Cu(I)Br, and pentamethyl diethylene triamine (*N*-[2-(dimethylamino)ethyl] *N,N',N'*-trimethyl-1,2-ethanediam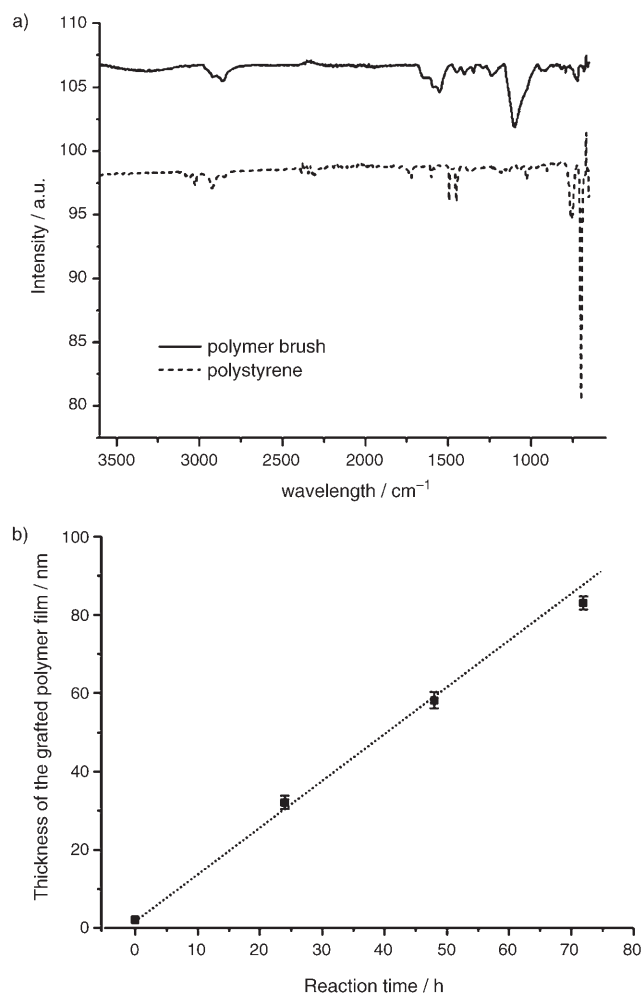ine) (PMDETA), shows characteristic peaks at 3026 and 2923 cm^{-1} (CH$_2$- and CH-), a peak originating from the carbonyl moiety of the initiator at 1726 cm^{-1}, and the characteristic peaks of the aromatic styrene unit at 1601, 1493, and 1453 cm^{-1}. Out-of-plane deformation vibrations at 757 and 698 cm^{-1} are an indication of a monosubstituted aromatic system. An ATR-FTIR investigation of the polymer film grafted from the bromine-terminated surface (Figure 3a, solid line) reveals the presence of the aromatic system on the surface (1644, 1598, and 1553 cm^{-1}) and the CH$_2$ unit (2863 cm^{-1}). Moreover, bands associated with the silicon substrate at 3333 cm^{-1} (OH function) and 1097 cm^{-1} (siloxane and silanol functions) can be identified. The thickness of the macroscopic layers was investigated by additional scratch tests, which locally remove the polymer film down to the silicon substrate, as confirmed by the smooth line within the line profile. This allows the determination of the film thickness. The film thickness scales approximately linearly with the applied grafting time.

This surface-initiated grafting process could also be performed on the previously introduced bromine-functionalized patterned surface templates. Figure 4 depicts optical microscopy images of films that have been grown on the patterned surface.

The grafting process produces a contrast in the optical image that resembles the bar structure of the initial surface pattern (Figure 4). Clear boundaries between the grafted grid replica and the unmodified OTS within the square structures of the pattern are observed, demonstrating the selectivity of the polymerization process on the bromine-functionalized surface areas. The dark contrast of the squares originates from the nonspecifically bound catalyst that is absorbed on the OTS surface. This catalyst and other contaminations that might attach to the surface can be easily removed by cleaning with Scotch tape. This process does not affect the polymer brush or the unmodified OTS area, as hydrophobic surface properties are dominating here, but it significantly reduces the amount of contamination in the monolayer areas. Moreover, this test shows that the film is stable and well grafted to the surface. Alternatively, "classic" cleaning by rinsing with a chloroform/methanol mixture was also applied. After several rinsing steps, comparably clean OTS areas were found surrounded by polymer brushes. Differences in the film height can be identified by the different color of the film in a few areas, whereas the overall film thickness is observed to be rather homogeneous across the sample. Optical micrographs were recorded with a low-magnification CCD camera system on the SFM setup. The bar width is difficult to determine in these images due to the limited resolution of the system. Therefore, SFM investigations were also performed to determine the structure and size of the patterned polymer brushes. The patterning was performed in this case with a fine bar mesh 1000 TEM grid with a patch size of 25 μm.

Tapping-mode images (Figure 5a and b) of bromine-terminated patterns on a templated OTS monolayer were recorded after the ATRP polymerization. The bars of the grid are ≈7 μm wide, which is in good agreement with the dimensions of the copper grid used for the electroprinting of the surface template. The height of the polymer films is in
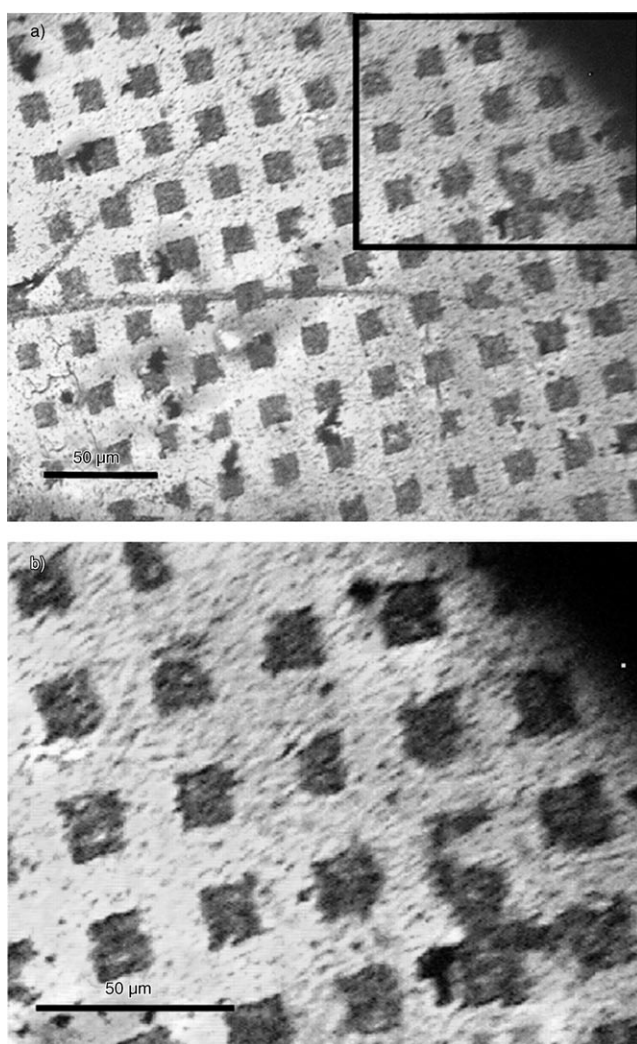
Figure 3. a) ATR-FTIR spectrum of polystyrene (bulk polymerized as well as grafted from the surface). b) Analysis of the thickness of the polystyrene layer grafted from the bromine precursor at different polymerization times.

Figure 4. a, b) Optical micrographs of the surface templates after grafting polymer brushes to the surface. Compared to the bromine-functionalized surface patterns, of which the pattern could not be distinguished after the evaporation of condensed water, a clear optical contrast is produced by the grafted polymer film. A magnified view of (a) as indicated by the square is represented in (b).

sponsible for the reduced activity of the polymer end chains; the effects of the drying step on the accessibility of the bromine functions or the fact that the bromo initiator is oxygen sensitive could also be considered as possible explanations for the reduced activity. More careful experimental conditions during the film preparation and characterization may be helpful to improve the film quality. Nonetheless, these preliminary studies demonstrate the potential to prepare three-dimensional, well-controlled architectures of micropatterned surface structures. To show the versatility of the use of chemically active surface templates fabricated by electro-oxidative lithography, nanostructured patterns inscribed to the surface with a conductive SFM tip[18] have been used to generate smaller surface structures. Also, a good selectivity was achieved here and thin lines less than 100 nm wide were generated. Details of this approach will be discussed in a forthcoming publication.

In conclusion, grafting polymer films from chemically active surface templates fabricated by electro-oxidative lithography provides a convenient and powerful way of patterning a polymer onto the surface in a versatile fashion. It represents the first example of the subsequent chemical modification of TEM-grid electroprinted microstructures. As demonstrated earlier,[22] the combination of different patterning techniques is a promising way to hierarchically create structures with different feature dimensions. As a consequence, the whole dimension range from the millimeter down to the nanometer regime can be covered with the electro-oxidative patterning approach. Moreover, the combination of different modification schemes[28] represents an attractive possibility for the step-by-step assembly of more complex features. The mild reaction conditions required for ATRP polymerization, in combination with the possibility to functionalize the surface patterns with other initiators,[11] opens the possibility to design 3D architectures. This may include the controlled formation of defined block systems, which offer attractive solutions to create not only a chemical contrast but also a topographical contrast, a feature that is certainly interesting for biomedical applications of such surface templates or responsive brush systems.

the range of 40 to 50 nm (see line profile of Figure 5c). It is of interest to check if the chains of the polymer brush are still Br terminated, as this would open the possibility to form patterned structures consisting of two different polymer blocks. For this purpose, the grid structures were used for an additional ATRP polymerization cycle in *tert*-butyl acrylate. Figure 5f reveals the increase in height of the bar structure, measured close to the structures shown in Figure 5a. The height of the bar features increased to 60–80 nm, which suggests that the bromine is still active and can be used for the grafting of additional polymer layers. However, the quality of the film appears to be poor. The structure of the film on the bar patterns before the second polymerization step changed after the grafting of the *tert*-butyl acrylate to be grainy (Figure 5e), which might indicate that not all of the bromine functions are still active after the first inspection with SFM. The cleaning steps might be re-

Experimental section

OTS (Sigma–Aldrich) was self-assembled on clean silicon wafers (Silicon Quest International) as described elsewhere.[28a] Surface patterns where generated by pressing a TEM grid (SPI Supplies) to the OTS surface and applying a bias voltage of −25 V with respect to the TEM grid for a time period of 40 to 60 s. The substrates were subsequently carefully cleaned in aqueous HCl solution and rinsed with clean water (MilliQ) before blow drying in a stream of nitrogen.

Bromo-undecyltrichlorosilane was self-assembled in dry bicyclohexyl (Fluka), which was dried over sodium from a 1 mm solution onto the grid-printed patterns. Self-assembly times of 10 min were sufficient to obtain homogeneous films of ≈2-nm thickness.

Primary bromine-functionalized surfaces were placed in a conical polymerization tube with a magnetic stirrer bar. The styrene
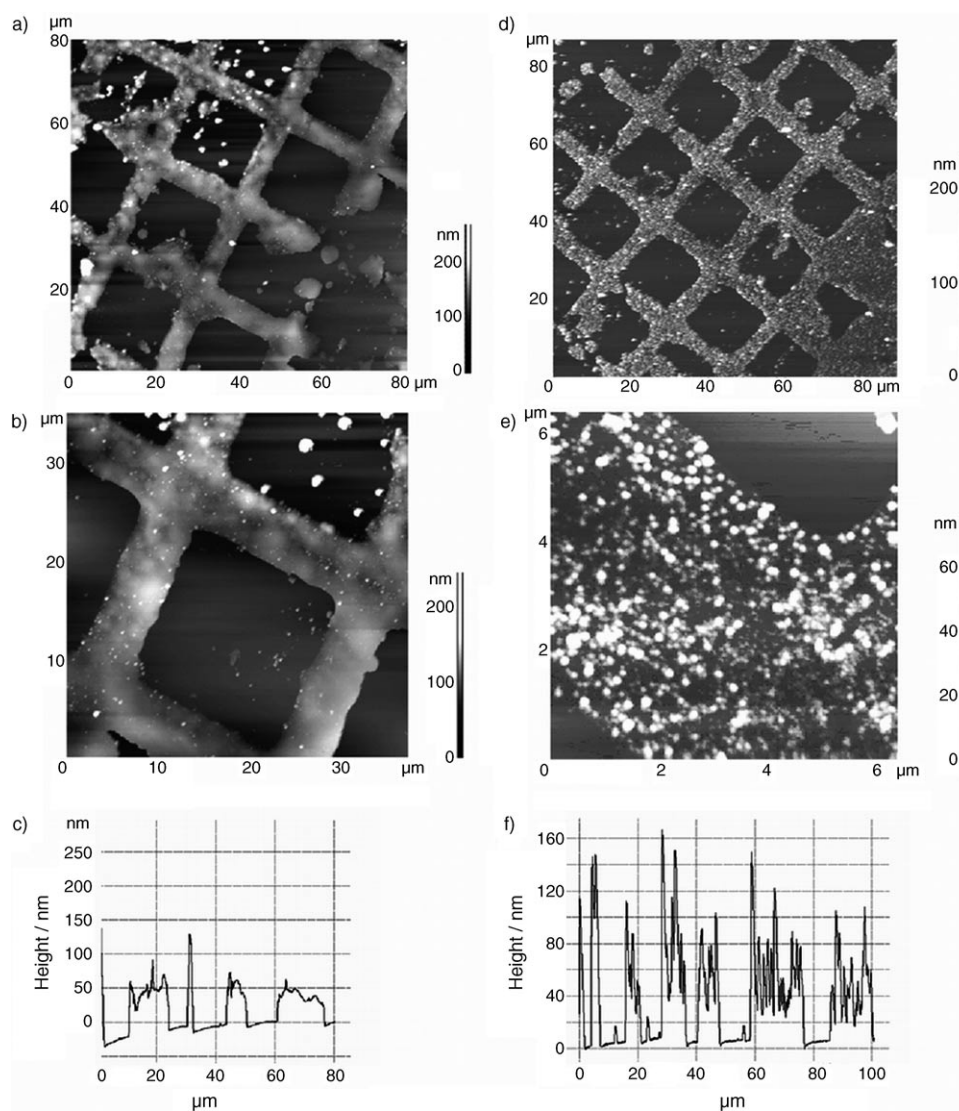
Figure 5. Tapping-mode SFM images of the polymers grafted from the surface template. a, b) Polystyrene was grafted from the bromine-functionalized bars, representing the TEM-grid replica on the surface. c) Line profile of the structure. d, e) Bar structures in the vicinity of the surface area depicted in (a) and (b) after the grafting of the second block *tert*-butyl acrylate. f) Line profile of (d).

(35 mmol) monomer, Cu(I)Br (0.07 mmol) catalyst, and hexaoligoethylene-oxide-substituted triethylenetetramine (HEOTETA) (0.07 mmol) ligand were added into the tube. The reaction mixture was stirred at room temperature for 15 min and the solution turned green as complex formation occurred but remained homogenous. The tube was immersed in an oil bath (60 °C) after bubbling with argon for 10 min and was allowed to react for up to 60 h. The wafer was dipped into methanol twice to remove the residual metal–ligand complex, which attached to the surface during the polymerization, after which it was dried with pressurized air. When necessary, additional cleaning with Scotch tape was applied to remove residuals from the surface.

Investigation of the patterned structures was performed using FTIR spectroscopy on a Perkin–Elmer 1600 FTIR system, and by tapping-mode SFM with an NTegra Aura from NT-MDT. Standard silicon tapping-mode SFM tips from Digital Instruments with a typical force constant of 20 to 80 N m^{-1} were employed for the investigation.

Keywords:

polymerization · electro-oxidative lithography · surface patterning · polymer brushes

[1] R. C. Bailey, J. T. Hupp, *Anal. Chem.* **2003**, *75*, 2392 – 2398.
[2] N. Nath, A. Chilkoti, *Adv. Mater.* **2002**, *14*, 1243 – 1247.
[3] B. Zhao, W. J. Brittain, *Prog. Polym. Sci.* **2000**, *25*, 677 – 710.
[4] S. G. Boyes, W. J. Brittain, X. Weng, S. Z. D. Cheng, *Macromolecules* **2002**, *35*, 4960 – 4967.
[5] X. X. Kong, T. Kawai, J. Abe, T. Iyoda, *Macromolecules* **2001**, *34*, 1837 – 1844.
[6] S. Edmondson, V. L. Osborne, W. T. S. Huck, *Chem. Soc. Rev.* **2004**, *33*, 14 – 22.
[7] M. Husseman, E. E. Malmstrom, M. McNamara, M. Mate, D. Mecerreyes, D. G. Benoit, J. L. Hedrick, P. Mansky, E. Huang, T. P. Russell, C. J. Hawker, *Macromolecules* **1999**, *32*, 1424 – 1431.
[8] J. S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614 – 5615.

[9] J. Pyun, T. Kowalewski, K. Matyjaszewski, *Macromol. Rapid Commun.* **2003**, *24*, 1043–1059.

[10] J. B. Kim, W. X. Huang, M. D. Miller, G. L. Baker, M. L. Bruening, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 386–394.

[11] K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921–2990.

[12] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, *28*, 1721–1723.

[13] Y. N. Xia, G. M. Whitesides, *Angew. Chem.* **1998**, *110*, 568–594; *Angew. Chem. Int. Ed.* **1998**, *37*, 551–575.

[14] R. R. Shah, D. Mecerreyes, M. Husemann, I. Rees, N. L. Abbott, C. J. Hawker, J. L. Hedrick, *Macromolecules* **2000**, *33*, 597–605.

[15] O. Prucker, M. Schimmel, G. Tovar, W. Knoll, J. Rühe, *Adv. Mater.* **1998**, *10*, 1073–1077.

[16] Y. Tsujii, M. Ejaz, A. Yamamoto, T. Fukuda, K. Shigeto, K. Mibu, T. Shinjo, *Polymer* **2002**, *43*, 3837–3841.

[17] M. Kaholek, W.-K. Lee, B. LaMattina, K. C. Caster, S. Zauscher, *Nano Lett.* **2004**, *4*, 373–376.

[18] R. Maoz, E. Frydman, S. R. Cohen, J. Sagiv, *Adv. Mater.* **2000**, *12*, 725–731.

[19] H. Sugimura, *Int. J. Nanotechnol.* **2005**, *2*, 314–347.

[20] a) Y. J. Jung, Y.-H. La, H. J. Kim, T.-H. Kang, K. Ihm, K.-J. Kim, B. Kim, J. W. Park, *Langmuir* **2003**, *19*, 4512; b) U. Schmelmer, R. Jordan, W. Geyer, W. Eck, A. Golzhauser, M. Grunze, A. Ulman, *Angew. Chem.* **2003**, *115*, 577-581; *Angew. Chem. Int. Ed.* **2003**, *42*, 559–563; c) R. Konradi, J. Rühe, *Langmuir* **2006**, *22*, 8571–8575; d) Q. He, Y. Tian, A. Kuller, M. Grunze, A. Golz-hauser, J. Li, *J. Nanosci. Nanotechnol.* **2006**, *6*, 1838–1841; e) A. Ramakrishnan, R. Dhamodharan, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 1758–1769; f) S. J. Ahn, M. Kaholek, W.-K. Lee, B. LaMattina, T. H. LaBean, S. Zauscher, *Adv. Mater.* **2004**, *16*, 2141–2145.

[21] R. Maoz, S. R. Cohen, J. Sagiv, *Adv. Mater.* **1999**, *11*, 55–61.

[22] S. Hoeppener, R. Maoz, J. Sagiv, *Nano Lett.* **2003**, *3*, 761–767.

[23] S. Hoeppener, R. Maoz, J. Sagiv, *Adv. Mater.* **2006**, *18*, 1286–1290.

[24] R. Maoz, J. Sagiv, D. Degenhard, H. Möhwald, P. Quint, *Supramol. Sci.* **1995**, *2*, 9–24.

[25] N. Balachander, C. Sukenik, *Langmuir* **1990**, *6*, 1621–1627.

[26] A. Tsuchida, M. Suda, M. Ohta, R. Zamauchi, N. Tsubokawa, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 2272–2279.

[27] J.-J. Shyue, M. R. De Guire, *Langmuir* **2004**, *20*, 8693–8698.

[28] a) S. Hoeppener, R. Maoz, S. R. Cohen, L. F. Chi, H. Fuchs, J. Sagiv, *Adv. Mater.* **2002**, *14*, 1036–1041; b) S. Liu, R. Maoz, G. Schmid, J. Sagiv, *Nano Lett.* **2004**, *4*, 845–851; c) S. Hoeppener, U. S. Schubert, *Small* **2005**, *1*, 628–632; d) D. Wouters, U. S. Schubert, *J. Mater. Chem.* **2005**, *15*, 2353–2355.

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