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Polymer brushes

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Nanostructured Polymer Brushes

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Nanopatterned polymer brushes with sub-50-nm resolution were prepared by a combination of electron-beam chemical lithography (EBCL) of self-assembled monolayers (SAMs) and surface-initiated photopolymerization (SIPP). As a further development of our previous work, selective EBCL was performed with a highly focused electron beam and not via a mask, to region-selectively convert a SAM of 4′-nitro-1,1′-biphenyl-4-thiol to defined areas of crosslinked 4′-amino-1,1′-biphenyl-4-thiol. These "written" structures were then used to prepare surface-bonded, asymmetric, azo initiator sites of 4′-azomethylmalonodinitrile-1,1′-biphenyl-4-thiol. In the presence of bulk styrene, SIPP amplified the primary structures of line widths from 500 to 10 nm to polystyrene structures of line widths 530 nm down to approximately 45 nm at a brush height of 10 or 7 nm, respectively, as measured by scanning electron microscopy and atomic force microscopy (AFM). The relative position of individual structures was within a tolerance of a few nanometers, as verified by AFM. At line-to-line spacings down to 50–70 nm, individual polymer brush structures are still observable. Below this threshold, neighboring structures merge due to chain overlap.

Keywords:
- nanolithography
- patterning
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- polymerization

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★ *Dedicated to Prof. Dr.-Ing., Dr.h.c.multipl Klaus K. Unger on the occasion of his 70th birthday.*

1. Introduction

The fabrication of structured polymer layers on solids at the micrometer and nanometer scales is one of the major challenges in micro- and nanotechnology.[1] This is because of the poly- and multifunctionality of polymers that can be directly used in micro- and nanotechnological applications, in which precise control of physical and chemical surface properties is needed.[2] Furthermore, the flexible polymer layer is stimulus-responsive and reacts immediately to environmental changes, such as solvent quality, pH, ionic strength, or temperature, by significant changes in surface properties and layer thickness.[3] Homogeneous and well-defined polymer brushes of high grafting density, prepared by living polymerization techniques,[4–7] render effectively the entire surface, whereas coatings of defined heterogeneities, such as structured polymer brushes or brush gradients,[8] can be used as sensors and actuators in micro- and nanotechnology. It has further been demonstrated that polymer brush layers effectively suppress/control protein or cell adhesion

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and allow the use of otherwise incompatible solids in biological or medical applications.[9,10] Structured polymer coatings with defined features become especially interesting when the structure dimensions are close to the molecular dimensions of the grafted macromolecules.

Various approaches, for example, the use of templating techniques, such as dip-pen nanolithography (DPN),[11] nanoimprinting,[12] or "molecular rulers",[13] to fabricate defined micro- and nanostructured polymer coatings, were recently reported. Especially, surface-initiated polymerization (SIP)[1] on predefined areas of self-assembled monolayers (SAMs) as two-dimensional initiator systems has recently been demonstrated to be a versatile approach to realize complex spatial structures on solids.[14]

We demonstrated the fabrication of structured polymer brushes by a combination of electron-beam chemical lithography (EBCL) of SAMs of ω-functionalized biphenylthiols on gold and the amplification of the primary structures by SIP.[15–19] The regioselective chemical conversion by EBCL of the SAMs on the micrometer *and* nanometer length scales was realized by irradiation trough-structured masks with openings from 1.6 μm down to 50 nm. The resulting polymer structures on the surface after the SIP of styrene on the irradiated areas were found to be from ≈1.6 μm to ≈70 nm with a layer height of about 8 nm.[15]

This combination of a lithography technique to define areas of consecutive chemical conversions (top-down) and self-assembly (bottom-up) was soon adopted by other groups to develop methods for the fabrication of grafted micro- and nanostructured polymer layers. Zauscher et al.[20] patterned a silicon surface with gold by lift-off electron-beam (e-beam) lithography using a poly(methyl methacrylate) (PMMA) resist layer, and immobilized a SAM of initiators for surface-initiated atom-transfer radical polymerization (SI-ATRP) or surface-initiated photopolymerization (SIPP). Structure sizes of the stimulus-responsive poly(*N*-isopropylacrylamide) (PNIPAM) layers down to a line width of 300 nm could be realized. Park et al.[21] used e-beam lithography (EBL) or soft X-ray irradiation to convert 4-nitrobenzaldimine monolayers coupled through an aminosilane or thiol SAM onto gold or silicon dioxide substrates to perform locally restricted consecutive SI-ATRP or other reactions. The smallest structures obtained were just below 100 nm.

Although the combination of EBCL and SIP was immediately successful, some limitations of this process are inherent. First, the fabrication of a single mask with nanometer-sized slits is technologically demanding and expensive, and only this very structure can be reproduced on the surface. For any alteration/optimization of structural parameters, a new mask has to be fabricated and the entire process repeated. Furthermore, for many complex and dense structures a stencil mask is not easily obtainable due to the limitations in the structural integrity of the mask.

Analogous to DPN that creates complex spatial structures in a serial fashion, a highly focused e-beam can be used for the creation of very small areas of defined chemistry. Since DPN is based on the selective adsorption/desorption of molecules, the technique is limited to a spatial resolution of ≈5–10 nm and a line width of ≈15 nm.[22] Direct writing with a focused e-beam allows the fabrication of sub-10-nm structures in SAMs.[23] However, in alkane-based SAMs, electrons locally decompose the monolayer[24] and the consecutive area-selective conversion of surface-bonded moieties is only possible by a second adsorption process of other surface-active molecules into the vacant areas. In contrast, SAMs with biphenyl mesogens stay morphologically intact and the electron irradiation further stabilizes the monolayer via a crosslinking reaction.[25] Such crosslinked biphenyl monolayers can be removed as a freestanding "nanosheet" from the substrate,[26] or can be used as an etch resist to prepare islands as small as ≈10 nm in width and periodic structures with a resolution of ≈20 nm.[27] Irradiation of ω-functionalized biphenyl SAMs results in intralayer crosslinking and, most important, selective conversion (hence the name electron-beam chemical lithography) of, for example, a 4′-nitro group to a 4′-amino group of the bonded SAM.[28] The latter can be used for consecutive coupling reactions of small molecules or selective chemical conversion to an initiator for free-radical SIP.[15–19] Here, we report on EBCL performed by direct writing with a focused e-beam, and the fabrication of polymer nanostructures by SIPP.

2. Results and Discussion

The fabrication of structured polymer brushes by EBCL and consecutive SIP was performed as previously described.[15] A homogeneous SAM of 4′-nitro-1,1′-biphenyl-4-thiol (NBT) was prepared on a silicon wafer covered with a 3-nm-thick CrNi coating for adhesion promotion and a final 10-nm-thick layer of a Au/Pd alloy by self-assembly. The NBT monolayer was then irradiated with a focused beam of a field-emission scanning electron microscope (3 kV, area dosage 40 mC cm^{-2}) to locally convert the terminal 4′-nitro group to the 4′-amino function. The conversion of the crosslinked 4′-amino-1,1′-biphenyl-4-thiol (cABT) to the final surface-bonded, asymmetric, azo initiator (4′-azomethylmalonodinitrile)-1,1′-biphenyl-4-thiol (cAMBT) was performed by diazotization and coupling of methylmalonodinitrile as previously described.[15] Scheme 1 outlines the reaction steps.

Due to the limited stability of thiol-based SAMs at elevated temperatures,[29] the SIP of styrene was not initiated by thermal decomposition of the 4′-azo function but by photolysis of the asymmetric azo function of cAMBT. In contrast to the symmetric, aliphatic azobisisobutyronitrile (AIBN) derivatives that are immobilized on the surface via one or two thiol groups, as normally used for free-radical SIP,[30–33] the SAM of cAMBT features an azo function with a biphenyl moiety in direct conjugation. Its significantly higher extinction coefficient renders this type of initiator more suitable for use in SIPP.[19,34,35] Furthermore, photolysis of cAMBT generates two radicals of very different reactivity. Especially, the detached radical might directly interfere with the growing polymer chain at the interface in free-radical SIP. While Dyer et al.[33] tried to circumvent the problem

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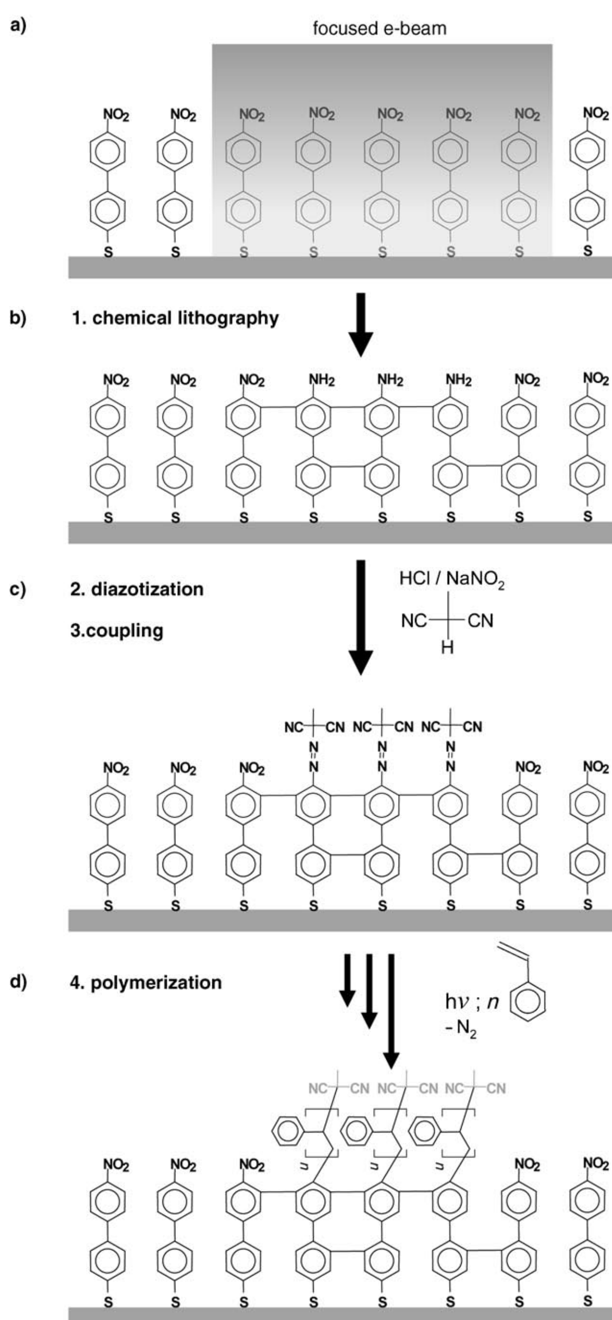

Scheme 1. Preparation of the polymer nanostructures. a) Irradiation of a NBT SAM by EBCL for b) selective local conversion to cAMBT. c) Diazotization and coupling of methylmalonodinitrile yields surfaces with defined areas of crosslinked initiator sites (cAMBT). d) SIPP of styrene at $\lambda_{max}=300$ nm (time of polymerization/irradiation $t_P=3$ h) yields region-selective formation of polymer brushes on the electron-irradiated areas.

of the liberation of a reactive radical by using a dithiol-azo compound, the asymmetric cAMBT reacts upon UV irradiation to give a reactive and surface-bonded radical for SIPP and a free but resonance-stabilized methylmalonodinitrile radical of low reactivity, which cannot initiate a radical chain reaction with vinyl monomers but only (reversibly) terminates the radical polymerization in the bulk phase.

Figure 1 shows a scanning electron microscopy (SEM) image of a test pattern created by direct-writing EBCL and SIPP of bulk styrene at a wavelength of 300 nm and after an

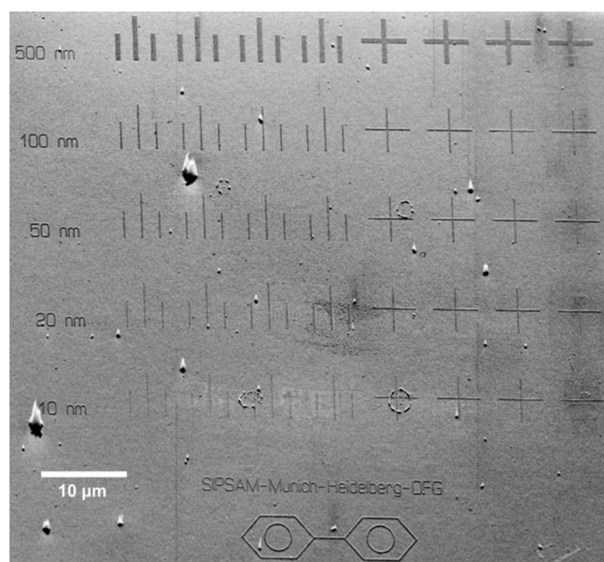

Figure 1. SEM image of a test pattern prepared by direct-writing EBCL and SIPP of styrene. On the left, line widths of 500 to 10 nm of the primary patterns were written directly onto the substrate by the e-beam. Below, some text and the biphenyl structure were inscribed to demonstrate that complex structures can easily be realized by this technique. The defects observable are due to adsorption of impurities after the process was completed.

irradiation time of 3 h. The image contrast results from the difference in secondary-electron yield of the bare surface and areas covered by the polystyrene (PS) brush (dark). The lateral dimensions of the primary features (lines and crosses) created by chemical lithography ranged from 500 to 10 nm. The line sizes are directly "written" into the NBT SAM next to the respective rows. Finally, some text and the chemical structure of a biphenyl molecule (primary line width of 100 nm) are added at the bottom of the writing field. Please note that the individual features are not only very small, but also created at defined spots several micrometers apart. In the micrograph only a few defects arising from postproduction handling of the samples are noticeable. Otherwise, all areas that were irradiated are completely converted into a PS brush. No structural defects that are assignable to the principal procedure could be detected.[36]

The PS structures were analyzed by atomic force microscopy (AFM). The heights of all lines were uniformly 10 nm for lines and crosses with lateral dimensions of 500 to 30 nm and, with approximately 7 nm, slightly lower for lines written with initial widths of 10 nm. The line widths of the respective structures were determined by SEM using the material contrast in the secondary-electron emission of modified (dark) and unmodified (bright) areas.

In Figure 2, individual crosses (from 500 to 10 nm) of the test pattern are displayed along with the analysis of the respective PS lines. As can be seen, the sizes of the final polymer structures (x_{SIPP}) are almost constantly 30 nm wider than the sizes of the initial structures created by EBCL

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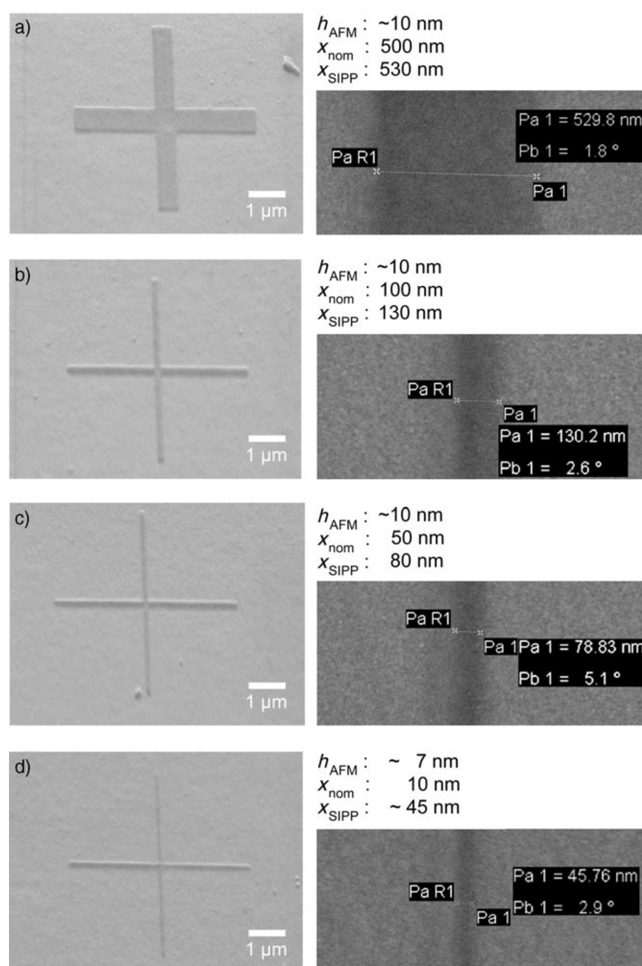

Figure 2. SEM images from details of Figure 1. Left: Individual crosses with initial (EBCL) line width (x_{nom}) of a) 500, b) 100, c) 50, and d) 10 nm (image voltage: 20 kV). Right: SEM analysis of the line width of the resulting PS structures created by SIPP (x_{SIPP}) along with the height of the PS structures determined by AFM (h_{AFM}) in the tapping mode (image voltage: 2 kV).

(x_{nom}). For example, a 500-nm primary structure resulted in a polymer brush 530 nm in width; a 100-nm line, in a 130-nm structure, etc. The smallest feature, a 10-nm written line, resulted in polymer structures with a width of approximately 40–45 nm. A detailed inspection of the edges of all structured brushes revealed that the SEM contrast is gradual and not sharp. This finding can be qualitatively explained by a gradual decrease of the brush layer thickness towards the rims of the structures. One can easily rationalize that polymer chains grafted at the periphery of the structures extend away from the original grafting points towards the polymer-free substrate surface. The abrupt decrease of the local grafting density to zero allows the conformational relaxation of the polymer chains at the edge of the structure, and results in a thinning of the polymer film. Furthermore, the PS is likely to adsorb onto the bare substrate, either gold or a NBT monolayer, in an extended or train-loop fashion, which explains the lateral widening. Interestingly, the lines with an initial width of 10 nm also display a lower height of 7 nm throughout the sample.

Recently, Patra and Linse[37] performed computer simulations of polymer conformations and density profiles in nanopatterned polymer brushes with respect to the height/width ratio, and discussed this effect as well as the reorganization of the softer nanopatterned polymer brushes in detail. Here, it is noteworthy that in the EBCL of a NBT monolayer with a line width of 10 nm, about 25–30 neighboring NBT molecules in the layer are modified to cABT assuming the $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure of the SAM on Au(111)[38,39] or incommensurate structures, as determined by scanning tunneling microscopy of SAMs of other 4′-substituted biphenylthiols.[40] Assuming the idealized case that all cABT in the 10-nm-wide structure is qualitatively converted to the initiator cAMBT, and the photopolymerization yields maximum grafting densities with distances of $\approx$3 nm between each grafting point as reported by Rühe et al.,[32] then a maximum of only about two polymer chains can be neighbored in such a line. In view of the fact that the pattern-generating e-beam has a Gaussian profile, it is more likely that the 10-nm line is mostly formed by rows of single grafted PS macromolecules. With these simple estimations

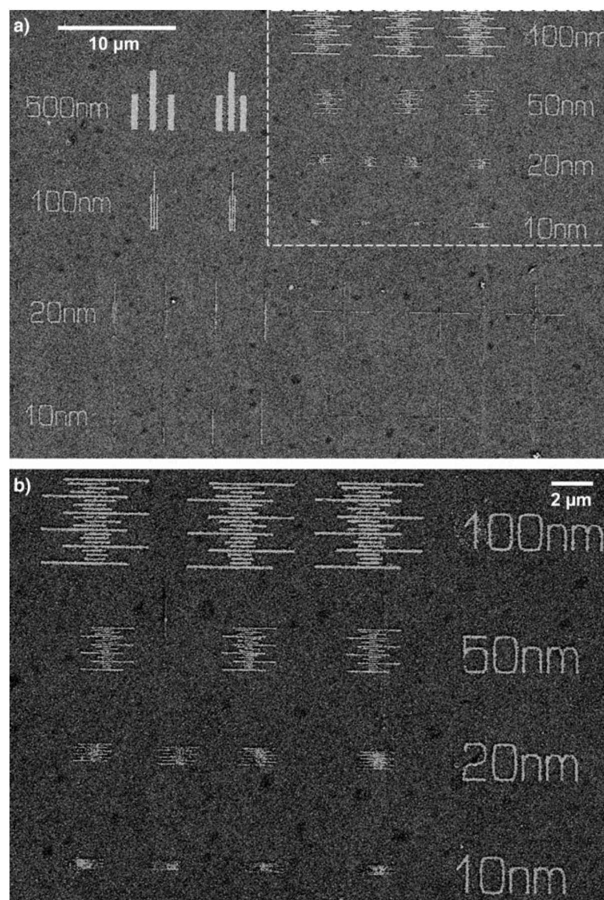

Figure 3. SEM images (3 kV) of PS structures prepared by direct-writing EBCL and SIPP of styrene. a) Overview of complete field with "written" dimensions of the triple lines and interdigitating combs. b) Detailed SEM scan of the upper right-hand corner section of (a) showing lines 100 to 10 nm in width. The structure was chosen such that in the middle of the combs, the line width equals the line-to-line spacing (100 to 10 nm).

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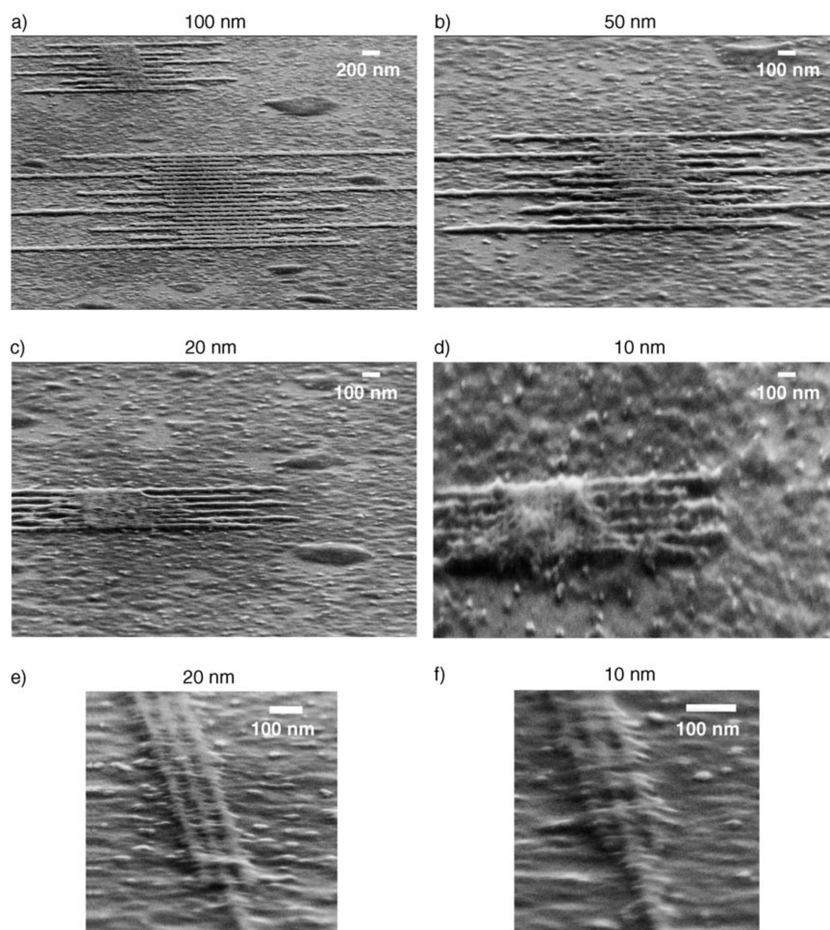

Figure 4. Details from the structures displayed in Figure 3, imaged at 10 kV at an angle of 75°; a–d) interdigitating lines with decreasing line spacings. For example, in (d) the spacing (middle-to-middle) of the longest lines at the line ends was 160 nm. The lines in the center of the structure had a distance of 10 nm. e,f) Details of triple lines from Figure 3 with spacings equaling a line width of 20 and 10 nm, respectively.

in mind, the structural integrity of the smallest structures is surprisingly good.

In a second set of experiments, the structural resolution of the EBCL/SIPP approach was investigated. Figures 3 and 4 show a series of SEM images of PS brush structures prepared as described above. This time, interdigitating lines from 500 to 10 nm were written close to each other with decreasing line-to-line spacings. Analysis of the test patterns by AFM and SEM revealed line broadening after SIPP, as observed before. It is apparent from the details of the neighboring lines (Figure 4) that the resolution of the EBCL/SIPP technique is limited by the molecular dimensions of the grafted polymer chains. Lines 100-nm apart are clearly resolved (Figure 4a), whereas in the 50- and 20-nm structures the features start to merge at the same line-to-line spacings in the structural center. From the SEM measurements we found that for line spacings between 50 and 70 nm, individual lines can still be observed. Below 50 nm the polymer chains from neighboring structures start to overlap and the structures merge.

AFM scans of the final PS brush structures revealed that the projected line distances in the outer periphery, as planned by the EBL writing process of, for example, 160 nm, are in good agreement with the values of 159–160.5 nm found for the peak-to-peak distance in the section analysis (Figure 5). Hence, a structuring in width and relative position of otherwise independent polymer structures can be realized with nanometer precision.

3. Conclusions

The combination of mask-free high-resolution EBCL using a focused e-beam instead of a mask with SIPP allows the preparation of polymer layers with structural features from about 500 nm down to sub-50-nm widths at brush heights of ≈10 nm on a single substrate. Thus, this technique spans the important gap between the available patterning techniques on the micro- and nanoscopic scales. Since neither a complex resist technology other

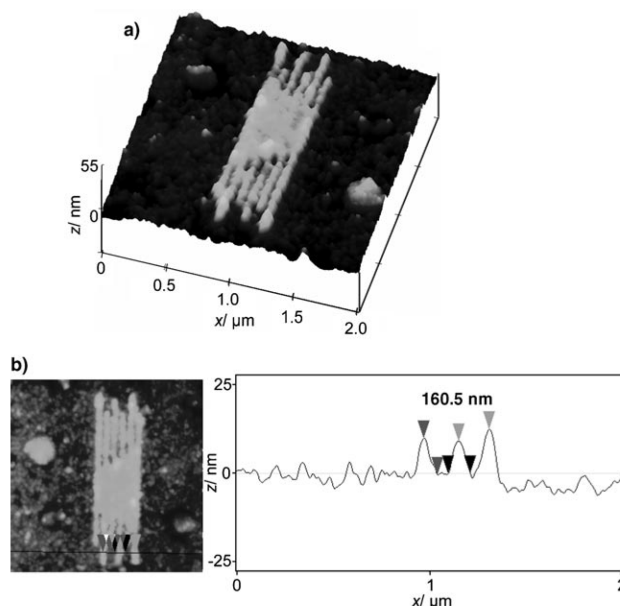

Figure 5. AFM images in the tapping mode of the 10-nm line structure (compare with Figure 4d). a) Three-dimensional plot of a $2 \times 2\ \mu m^2$ scan area. b) Line scan at the periphery of the structure (see solid line in top view). The peak-to-peak distance was found to be 159–160.5 nm, in good agreement with the projected line spacing for EBCL writing of 160 nm.

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than the formation of an e-beam-sensitive SAM nor a mask is needed, and the SIPP can readily be performed with standard laboratory equipment, this approach is versatile for the preparation of complex polymer structures on substrates at the nanometer scale for future applications in micro- and nanotechnology.

4. Experimental Section

The substrates used for EBCL were obtained from the Physikalisch-Technische Bundesanstalt Braunschweig (PTB; Braunschweig, Germany). In brief, a 3-nm-thick CrNi layer was placed on a Si(100) substrate to promote adhesion of a final 10-nm-thick layer of Au/Pd alloy. The formation of monolayers of NBT on the Au/Pd surfaces was performed as previously reported.[15,19,28]

EBCL to convert NBT to areas of crosslinked cABT was performed with a LEO 1530 scanning electron microscope equipped with a Raith Elphy Plus pattern generator. The e-beam energy during the writing process was 3 kV in order to minimize proximity effects but allow sufficient focusing of the beam, thus applying an area dosage of 40 $mC\,cm^{-2}$. The step size of the pattern generator was 3 nm.

SEM was performed with the same instrument; material contrast was achieved by detection of backscattered electrons using an Everhart–Thornley detector, or for angle-dependent measurements ($>40^\circ$) with a secondary-electron detector. The scanning parameters for the presented images are mentioned in the main text. AFM was performed under ambient conditions in the tapping mode on a Multimode apparatus from Veeco Instruments. Scan sizes ranged from $10\times10\ \mu m^2$ to $1\times1\ \mu m^2$.

Chemical conversion of cABT to the crosslinked cAMBT initiator was carried out as previously reported.[15,19] SIPP of the cAMBT initiator patterns was performed as previously reported[19] using a Rayonet photochemical chamber reactor model RPR-100 equipped with an RPR-3000A lamp. The substrate was placed in a quartz glass reactor and submerged in approximately 1 mL of freshly distilled and degassed styrene (Sigma–Aldrich). The polymerization/irradiation time was 3 h at a wavelength of $\lambda_{max}=300$ nm. After SIPP the substrates were washed with an excess of fresh toluene and additional ultrasound treatment was carried out for about 10 s to remove physisorbed polymer from the substrate.

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