Polymer Nanostructures

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Fabrication of a Full-Coverage Polymer Nanobrush on an Electron-Beam-Activated Template**

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Along with chemistry, morphology is an important tool to control the properties of surfaces and interfaces. Impressive examples from nature are the lotus effect, which leads to the ultimate hydrophobic surface, and the structuring of the skin of marine animals such as sharks, which prevents adhesion of algae and parasites. To mimic such effects and produce surfaces with even more sophisticated properties for industrial applications and scientific research, practical tools must enable the control of surface morphology down to the nanometer scale. One of the most promising approaches in this regard is the fabrication of 3D polymer brush patterns by surface-initiated polymerization (SIP) combined with electron-beam lithography (EBL)[1,2] or electron-beam chemical lithography (EBCL).[3–7] The advantages of EBL and EBCL are high lateral resolution, as far as a focused electron beam or interferometric patterning is used, and the ability to write complex patterns by adjusting the irradiation dose. Both EBL-SIP and EBCL-SIP rely upon the use of self-assembled monolayers (SAMs) and allow preparation of polymer brushes with heights of 100–200 nm and lateral sizes of the individual features in the sub-micrometer range. Whereas EBL-SIP involves the patterning of a photoresist with subsequent fabrication of a metal pattern and its functionalization by SAMs,[1] EBCL-SIP exploits patterning of a SAM template.[3–7] One approach within this framework relies upon aromatic SAMs such as nitro-substituted biphenyl thiols on gold.[3–6] As these films remain mostly intact under electron irradiation, reduction of the tail groups from nitro to amino can be performed,[8] with the amino groups serving as specific nucleation sites for SIP. In another approach, not aromatic but aliphatic SAMs are used, and electron irradiation promotes an exchange reaction between the primary unsubstituted SAM and potential molecular substituents bearing the tail groups (e.g., amino) suitable for SIP.[7] A characteristic feature of polymer brush patterns made by both EBL-SIP and EBCL-SIP is their chemical inhomogeneity. Whereas the polymer brush itself is comprised of a polymer, the areas between the 3D features have a different chemical identity, for example nitro groups in the case of the aromatic template[3–6] or methyl moieties in the case of the aliphatic matrix.[7] As a result, the effects of morphology on the one hand and chemistry and surface energy on the other hand can be entangled when using such patterns as model surfaces, for example in biology-inspired research. Herein, we show that this drawback can be avoided by using a sophisticated primary template comprised of SAMs with mostly deactivated tail groups suitable for SIP. Whereas SIP on such a template gives a thin but homogeneous "background" brush, the regeneration of these groups by electron-beam activation lithography (EBAL) promotes the controlled growth of 3D polymer features on this background, resulting in the formation of chemically homogeneous morphology patterns exclusively comprised of the polymer material.

As primary templates, we used SAMs prepared from commercially available 11-aminoundecanethiol (AUDT) hydrochloride on gold. As a test polymer system, we used poly-*N*-isopropylacrylamide (PNIPAM). It is well known that PNIPAM brushes can be grown on a template containing amino tail groups by surface-initiated atom transfer radical polymerization (SI-ATRP) of its monomer, *N*-isopropylacrylamide (NIPAM).[4,7] To start SI-ATRP, a surface initiator, bromoisobutyryl bromide (BIBB) should be selectively attached to the tail groups (see Figure 1).

Despite the high density of the amino groups, the growth of the PNIPAM brush on the pristine AUDT templates was limited. The C1s and N1s X-ray photoelectron spectra of these templates before and after SI-ATRP are shown in Figure 2. While for the pristine SAMs these spectra exhibit characteristic features related to the aliphatic backbone (C1s) and amino tail group (N1s),[9] a noticeable increase in both C1s and N1s intensity occurs after SI-ATRP under standard conditions (see references [1,4,7]). Furthermore, the main C1s and N1s emissions shift, in accordance with the chemical composition of PNIPAM, and a peak at 288.3 eV characteristic of the C=O group of PNIPAM appears in the C1s spectrum. The thickness of the polymer film was estimated to be approximately 4 nm by both X-ray photoelectron spectroscopy (XPS) and ellipsometry, which is far below the value expected from the density of the primary amino tail groups (100–200 nm). However, as soon as pristine AUDT templates were irradiated by electrons before the SI-ATRP procedure, a progressive increase of the PNIPAM film thickness was observed with increasing irradiation dose. As an example, the C1s and N1s XPS spectra of an AUDT film consecutively exposed to 1 $\mathrm{mC\,cm^{-2}}$ dose (10 eV electrons) and subjected to SI-ATRP are shown in Figure 2. Both of these spectra exhibit significantly higher intensities than the analogous spectra for the non-irradiated films subjected to SI-ATRP. For this

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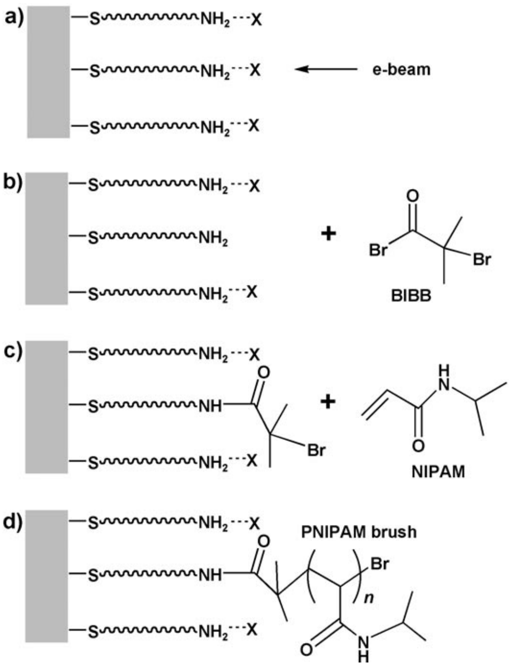

Figure 1. EBAL/SI-ATRP with AUDT template: a) electron-beam-induced activation of amino groups; b) selective anchoring of the surface initiator (BIBB) to the activated sites; c) start of polymerization; d) the resulting PNIPAM brush. Note that brush growth occurs on the non-activated areas as well, but the thickness is significantly smaller.

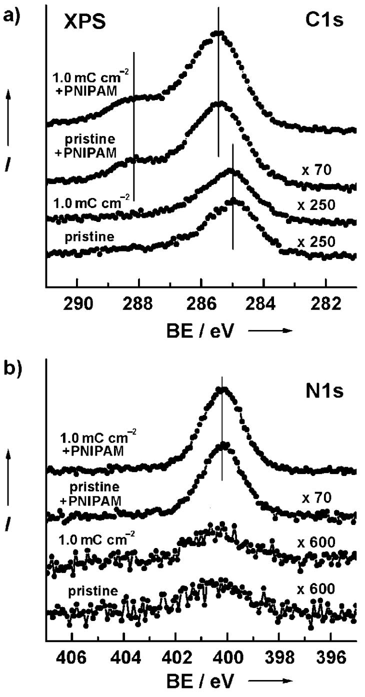

Figure 2. a) C1s and b) N1s XPS spectra of pristine and irradiated (1 mCcm^{-2}) AUDT templates before and after SI-ATRP (PNIPAM brush formation). The spectra are differently scaled and shifted vertically for better comparison. The positions of the characteristic emissions are marked by the thin solid lines. BE = binding energy.

particular dose, the polymer film thickness was estimated at approximately 20 nm by both XPS and ellipsometry. As mentioned above, the increasing dose resulted in further increase of the polymer film thickness, so that no Au4f signal from the substrate could be observed by XPS.

The question is what the reasons are for the repressed reactivity of the primary AUDT template and for the activating effect of electron irradiation. The XPS spectra of pristine and irradiated AUDT films did not show any pronounced difference apart from a somewhat lower intensity (Figure 2). For a dose of 1 mCcm^{-2}, the thicknesses for pristine and irradiated films were estimated to be approximately 20.3 and 17.9 Å, respectively, which suggest a thickness reduction upon irradiation. Considering that 20.3 Å significantly exceeds the expected thickness of the AUDT SAM (ca. 15.0 Å),[10] the presence of some weakly bound species at the SAM–ambient interface can be assumed, which were partly desorbed upon electron irradiation. These species could not be identified as hydrochloride residues, physisorbed AUDT molecules, or oxidized amino groups, as XPS did not show the corresponding signals. At the same time, there was a pronounced O1s emission at 532.6 eV in the XPS spectra of pristine AUDT SAMs, which was progressively reduced upon irradiation (e.g. by a factor of two for 1 mCcm^{-2}). Thus, the weakly bound species might be water molecules coordinated to one or several adjacent amino moieties.

To get further evidence that the activating effect of electron irradiation is not related to the formation of irradiation-induced defects[11] but to the activation of the amino groups of the AUDT template, we performed similar SI-ATRP experiments for SAMs formed from an unsubstituted alkanethiol (dodecanethiol, DDT) on gold substrate.

According to XPS and ellipsometry data, a PNIPAM brush of a noticeable thickness was formed neither on pristine nor on irradiated (up to 3 mCcm^{-2}) DDT templates. The measured average thickness of the PNIPAM film was about 0.5 and 1.0 nm, respectively, which is far below the values observed for the irradiated AUDT template.

The above results allow us to conclude that the majority of the amino groups of the pristine AUDT SAMs are deactivated with respect to SI-ATRP because of binding to an oxygen-containing quencher moiety (note that repressed reactivity of amino tail groups has been reported for other SAM systems).[12] This bond is obviously weaker than the covalent anchoring of the AUDT molecules to the substrate but strong enough to survive the extensive rinsing and SI-ATRP procedure. Even though the identity of this quencher is not clear at the moment, its effect on the SI-ATRP ability of the pristine AUDT template is obvious. However, it is even more important that the quencher can be removed by electron irradiation, with the density of the activated amino groups being controlled by the dose. This phenomenon is the physical basis of EBAL combined with SIP or SI-ATRP (Figure 1). Several examples of PNIPAM brushes fabricated by this technique are presented in Figure 3 as both top and 3D views. To demonstrate the broad versatility of the EBAL approach, we consciously avoided the fabrication of simple dot and stripe (constant height) patterns in favor of more complicated gradient features of various shapes. In Figure 3,

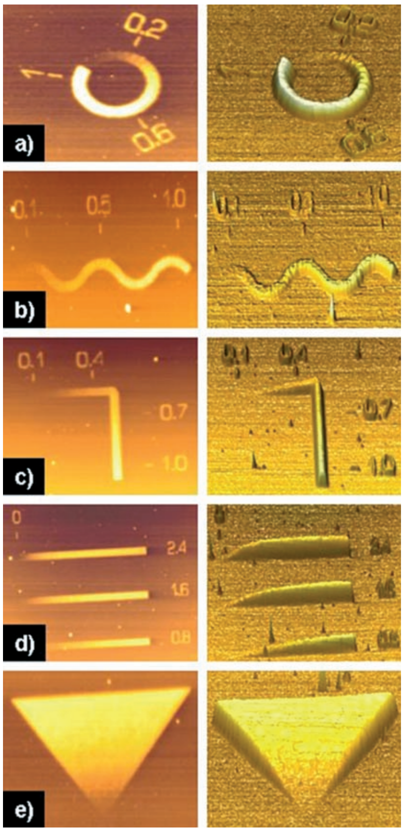

Figure 3. AFM images (left: top view, right: 3D view) of the gradient PNIPAM patterns obtained by EBAL/SI-ATRP with AUDT SAMs as templates: a) snail, b) snake, c) angle, d) stripes, and e) triangle. The irradiation doses were written along with the brushes and can be seen in some of the images. The size of the top-view images (a)–(e) is 15×15, 25×25, 25×25, 30×30, 20×20 μm^2, respectively.

we demonstrate AFM images of gradient "snail", "snake", "angle", "stripes", and "triangle" patterns. The height profiles along the gradient features exhibit a continuous and gradual rise of the brush thickness with increasing irradiation dose up to the saturation thickness, which, for the majority of the brushes, is about 110 nm. The height saturation observed around 0.8 mC cm^{-2} is presumably related to the saturation of the activating effect of the electron beam (i.e., almost complete activation of the amino tail groups) and onset of the extensive irradiation-induced damage,[11] including decomposition of the amino groups. Thus, for 1 keV electrons, the dynamical range of EBAL/SI-ATRP is 0–0.8 mC cm^{-2}.

As demonstrated by the results presented in Figure 3, a polymer brush pattern of any shape with the height varying from 0 to 110 nm can be fabricated within this range. This 3D brush is located on a homogeneous, flat polymer background as additionally demonstrated by the control AFM measurements on a PNIPAM film prepared on the pristine AUDT SAM template (not shown). Note that there is quantitative agreement regarding the saturation dose between the EBAL (1 keV) and homogeneous irradiation (10 eV) results if a scaling factor between the given kinetic energies is taken into account.[6]

In conclusion, we have presented a new technique that enables the fabrication of full-coverage polymer brush patterns of variable shape, including complicated gradients, on a nanometer length scale. This technique untangles chemistry and morphology, enabling us to monitor exclusively morphology effects on chemically homogeneous surfaces and interfaces. The technique relies upon commercially available compounds and requires a low patterning dose (less than 1 mC cm^{-2}).

Experimental Section

The gold substrates were prepared by thermal vapor deposition of 100 nm gold (99.99 % purity) onto polished single-crystal silicon (100) wafers (Silicon Sense) primed with a 5 nm titanium adhesion layer. The resulting films had a grain size of 20–50 nm and predominantly possessed (111) orientation.

Dodecanethiol (DDT), *N*-isopropylacrylamide (NIPAM), bromoisobutyryl bromide (BIBB), triethylamine (NEt$_3$), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), copper(I) bromide (CuBr), ethanol, methanol, and dichloromethane were purchased from Sigma-Aldrich Chemie GmbH, Germany and 11-aminoundecanethiol hydrochloride (AUDT) from Asemblon Inc., USA. The purity of AUDT as measured by NMR spectroscopy and HPLC was better than 99 %. Different batches of this compound gave fully reproducible results. All chemicals were used without further purification.

SAM templates were formed by immersion of fresh gold substrates in a 1 mM solution of AUDT or DDT in ethanol for 24 h at room temperature. In the case of AUDT, 3 vol % NEt$_3$ was added to the solvent to remove HCl.[10] After immersion, the samples were extensively rinsed with pure ethanol and blown dry in an argon stream. No rinsing with acetic acid[10] was performed.

Homogeneous electron irradiation was performed by a flood gun delivering electrons with a kinetic energy of 10 eV; the residual gas pressure was approximately 5×10^{-9} mbar. The gun was mounted at a distance of approximately 11 cm from the sample to assure uniform illumination.

XPS measurements were carried out with an LHS 12 spectrometer and an $Al_{K\alpha}$ X-ray source (290 W) at a base pressure of less than 1.5×10^{-9} mbar. The spectra were measured in the Au4f, C1s, N1s, O1s, and S2p regions. The binding energy (BE) scale was referenced to the Au 4f$_{7/2}$ peak of the DDT/Au sample at a BE of 84.0 eV.

Ellipsometry measurements were carried out using an M-44 ellipsometer from J. A. Woollam Co. Inc., USA. The data were analyzed with the accompanying software. The incident angle was set to 75° and calibrated with a silicon wafer as a reference. A refractive index of 1.45 was assumed for all films in the thickness calculation.

EBAL patterning was performed by a LEO 1530 scanning electron microscope (Carl Zeiss AG, Germany) with a Raith Elphy Plus Pattern Generator System. The electron-beam energy was chosen at 1 keV; the residual gas pressure was approximately 5×10^{-6} mbar.[4]

The SI-ATRP of NIPAM was performed according to the standard procedure (see the Supporting Information).[1,4,7]

AFM images were obtained in the contact mode with an Autoprobe CP scanning probe microscope from Park Scientific Instruments (USA).

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