Engineered Polymer Brushes by Carbon Templating

By *Marin Steenackers, Rainer Jordan,* Alexander Küller,* and *Michael Grunze*

Micro- and nanostructured polymer coatings on solids play a key role for many technological applications ranging from molecular electronics to biomedical devices and diverse research fields from biology to physics.[1] Although there are numerous approaches for the preparation of structured polymer surfaces,[1,2] highly defined micro- and nanostructured polymer brushes can be prepared by surface-initiated polymerization (SIP) using structured self-assembled monolayers (SAMs) as initiator templates.[3] The advantage of this approach is the use of an ultrathin self-assembled system as the chemical mediator between the surface chemistry and the needed functionalities for SIP. Furthermore, depending on the structure size, SAMs can be patterned on the micrometer scale, e.g., by microcontact printing [4] or photolithographic techniques, and nanostructured SAM are accessible by SPM-based techniques [5,6] or electron beam lithography.[7] Besides pattern formation, electron irradiation also stabilizes the SAM via lateral cross-linking [8] and induces a chemical contrast (chemical lithography, CL).[9] CL of SAMs and consecutive SIP by free [10–12] or controlled [13,14] radical polymerization results in polymer brushes with controllable shapes on the micro- and nanometer scale.

However, the multi-step procedure of SAM formation, structuring, and functionalization in order to introduce a suitable initiator for the final SIP is too tedious for broader applications. Recently we found that a specific surface-bound initiator is not needed and structured brushes of equal quality can be prepared by direct photografting on aromatic SAMs.[15] Nevertheless, besides the additional step of monolayer preparation, SAM-templating introduces several practical limitations, such as the relative low thermal and chemical stability of commonly used SAM systems. Silane monolayers on oxides are prone to hydrolysis (their poor stability in saline solutions at 37 °C renders them inappropriate for long-term biomedical applications)[16,17] and thiol-based SAMs desorb at elevated temperatures[18] or UV irradiation.[19]

A straightforward and resist-free technique to prepare highly stable micro- and nanopatterned surfaces is the electron-beam-induced carbon deposition (EBCD).[20] Residual hydrocarbons present in the vacuum chamber of an electron microscope are the source for these carbonaceous deposits[21,22] with a composition close to $C_9H_2O_1$ with 90% sp^2 and 10% sp^3 carbon. They are highly cross-linked, thermally and chemically stable, and contain diverse functionalities including C–H, C=O, and OH groups.[23]

In this paper, we present a straightforward method for producing structured polymer brushes of controlled morphology by means of carbon templating. First, a stable ultrathin template layer of carbonaceous material is locally deposited on an inorganic substrate by means of a focused electron beam. Amplification of the template by surface-initiated polymerization results in polymer brush layers of a controlled three-dimensional shape. Taking advantage of the high thermal and chemical stability of the grafting, polymer brushes were further modified by polymer analogue reactions under drastic conditions such as nitration or sulfonation of polystyrene (PS) brushes. By this general approach, stable polymer brushes having all kinds of dimensions, architectures and chemical functionalities can be prepared on various substrates.

As shown in Figure 1a, a carbon template gradient was prepared on a native silicon substrate by EBCD with direct writing with a focused electron beam. In agreement with earlier reports,[23] the atomic force microscopy (AFM) height analysis revealed that the resulting thickness of the carbon deposits followed the locally applied electron dosage. The thickness increase scales linearly with the dose gradient with a maximum thickness of approx. 0.9 nm at the highest electron-beam dosage of 57.7 mC cm^{-2}. The fluctuation in the height profile (Figure 1b) is due to the substrate roughness (rms = 0.41 nm). The structured substrate was immersed in styrene and irradiated with UV light ($\lambda_{max} = 350$ nm) for 16 h. After rigorous cleaning of the substrate with different solvents and ultrasonication to ensure that only chemically grafted polymer remains on the substrate, AFM measurements revealed that the direct photografting occurred selectively on the carbon deposits and the height of resulting polymer brush gradient is determined by the carbon template. As shown in previous studies that describe the use of different substrates such as polyethylene,[24] aromatic SAMs on gold[15] and oxidized diamond,[25] the grafting reaction occurs via the self-initiated photografting and photopolymerization process[15] in which the monomer acts as a photosensitizer that activates a surface functional group by hydrogen abstraction to start a free radical surface-initiated polymerization. The only requirement for the photografting process to occur is the possibility of substituent abstraction (e.g., hydrogen radical) by a radical mechanism.

Selective photografting onto the carbon deposits can be explained by the different bond dissociation energies (BDE) for hydrogen abstraction of the inorganic surface functions (BDE of SiO–H: 119.3 kcal · mol^{-1})[26] and the carbon deposits (BDE of C–H of sp^3 carbon in polycyclic sp^2 hydrocarbons is between

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[*] Prof. R. Jordan, Dr. M. Steenackers
Wacker-Lehrstuhl für Makromolekulare Chemie
Technische Universität München
Lichtenbergstr. 4, 85747 Garching (Germany)
E-mail: Rainer.Jordan@tu-dresden.de

Prof. Dr. R. Jordan
Professur für Makromolekulare Chemie
Department Chemie, TU Dresden
Zellescher Weg 19, 01069 Dresden (Germany)

Dr. A. Küller, Prof. M. Grunze
Lehrstuhl für Angewandte Physikalische Chemie
Universität Heidelberg
Im Neuenheimer Feld 253, 69120 Heidelberg (Germany)

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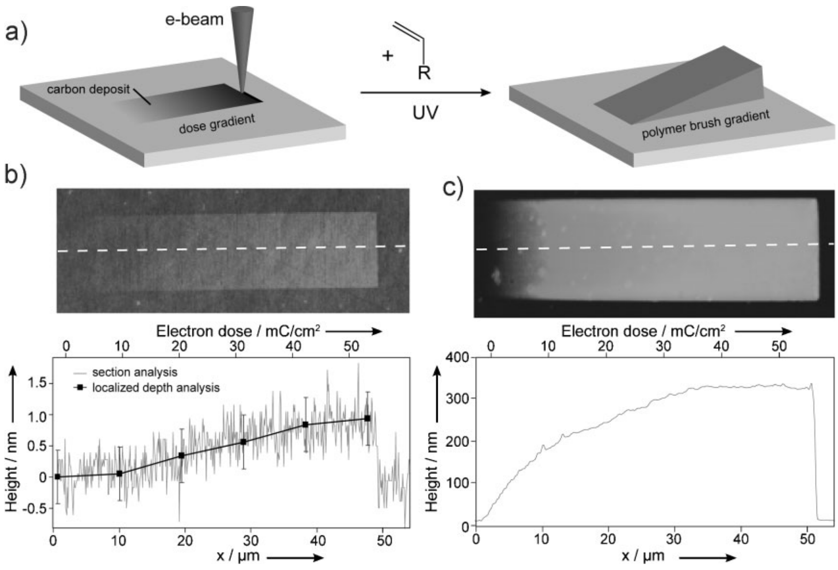

Figure 1. Polymer brushes of programmed morphology by the carbon templating technique. a) Schematic of carbon templating by EBCD on native substrates and template amplification into a polymer brush gradient by direct photografting of vinyl monomers. b) AFM scan and analysis of a carbon template gradient (10 µm × 50 µm) on a silicon substrate prepared by EBCD. c) AFM scan and analysis of the resulting PS brush gradient (10 µm × 50 µm) prepared by direct photografting of styrene.

20 and 72 kcal · mol^{-1}).[27] The gradual increase of the polymer brush thickness is explained by the increase of the polymer grafting density. Recently, we have shown that the polymer brush layer thickness prepared by photografting is proportional to the surface concentration of grafting points.[15] The polymer layer thickness increases from 0 to 35 mC cm^{-2} and remains almost constant above 35 mC cm^{-2} (Figure 1c). For a dose below 35 mC cm^{-2} the carbon deposits only partially cover the silicon substrate; at higher doses they reach full coverage so that the surface concentration of potential grafting points remains constant. Thus, the experiment shows that the locus of polymer brush formation occurs selectively on the carbon deposits. Furthermore, the brush height at a given area is determined by the respective carbon template as defined by the locally applied electron dose. In principle, this two-step procedure is similar to dip-pen lithography[5,6] and consecutive SIP. However, it does not require any specific surface chemistry and readily allows the design of gradients or more complex structures. Furthermore, the direct writing with a focused electron beam allows the fabrication of carbon templates from the macroscopic scale down to 1 nm.[20]

Key for the technological relevance of (structured) polymer coatings is their thermal and chemical stability. As described above, residual physisorbed polymer formed by photopolymerization in bulk was removed by thorough cleaning of the modified substrates using solvents of different polarities and ultrasonication (standard cleaning procedure for PS brushes: ultrasonication in toluene at r.t. for 5 min and repetition in ethyl acetate and ethanol). Neither prolonged ultrasonication of up to 30 min at a variety of solvent polarities nor Soxhlet extraction with mesitylene overnight at 165 °C led to desorption of the polymer brush structures from the silicon dioxide surfaces or changed the polymer structures.

Since the chemical contrast between the carbonaceous material and the bare inorganic substrate leads to selective photografting and EBCD can be performed on a broad variety of substrates, this approach is applicable on almost any (inorganic) substrate. The practical limitations of carbon templating are a reasonable deposition rate of the EBCD and adhesion stability of the deposit. Although most substrates are suitable, we found that no stable carbon deposits could be formed on Au(111) surfaces. So far, we have successfully prepared polymer brush gradients on Si, Si_3N_4, Ge, and Al with a native oxide layer as well as directly on GaAs and GaN (Figure 2). As can be seen from the gradients created on the various substrates, the resulting polymer brush height is not linearly increasing with the applied electron dose gradient. The EBCD characteristics strongly depend on the substrate[21] and, as discussed before,[12,15] prolonged irradiation of deposited material alters the surface chemistry and thus the grafting site density for the photografting. However, Figure 3 shows that a well-defined design of polymer brush shapes can be achieved by using the polymer thickness/electron dose correlation, which can be derived from the gradients for each substrate (panels a–f, Fig. 2).

Furthermore, microstructured polymer brushes were prepared on isolators such as mica and borosilicate glass. The charge accumulation on electrical isolators, which is encountered in direct writing with a focused electron beam, can be circumvented by the use of an electron flood gun in combination with a conductive stencil mask in direct contact with the substrate (see Supporting Information, Figure S1).

The potential of carbon templating for fabricating complex polymer brush structures with defined lateral and normal dimensions is shown in Figure 3. Polymer brush layers of a predefined three-dimensional shape can be designed using the thickness/electron dose dependency found for the gradient structures. For example in Figure 3a, a step-pyramid on Si_3N_4 was created by SIP amplification of a carbon template consisting of four concentric square areas written with different electron doses. "STAIRS" were created by carbon lines of 100 nm width and increasing electron doses for each letter. The SIP amplified the text to structures with heights varying from 6 to 53 nm and line widths from 200 to 350 nm. Because terminally grafted flexible polymer chains now form the three-dimensional object, line/structure broadening is inherent.[11,28,29] In Figure 3c, an array of complex structures of PS brushes such as gradients, cones, pyramids, and cups of lateral dimensions from 8.3 µm down to 1.2 µm is shown. The three-dimensional objects were designed by carbon templating by using the relationship between carbon deposition and local electron irradiation with the consecutive amplification by SIP, as shown for the gradients in Figure 1 and 2 or the single pyramid in Figure 3a. In this case, the structures are formed directly on GaAs as a semiconductor material of high technological relevance but challenging surface chemistry.

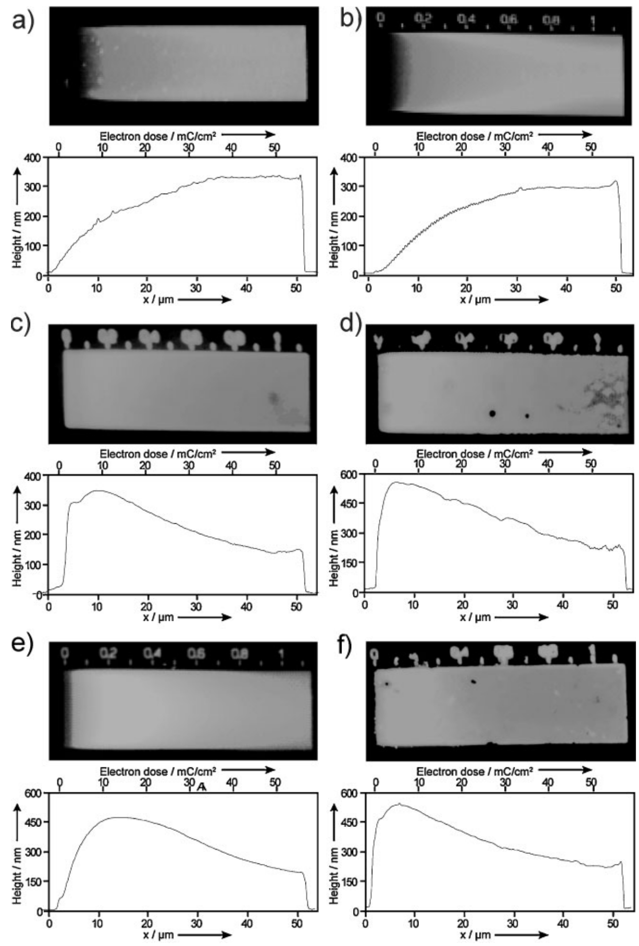

Figure 2. AFM scans (55 µm × 20 µm) and height analysis of PS brush gradients created by reactive carbon templating (EBCD with linear electron dose gradients from 0 to 57.5 mC cm^{-2}) on: a) Si (polymerization time, t_p: 16 h), b) Si_3N_4 (t_p: 19 h), c) Al (t_p: 15.5 h), d) Ge (t_p: 22 h), e) GaAs (t_p: 18 h), f) GaN (t_p: 21 h).

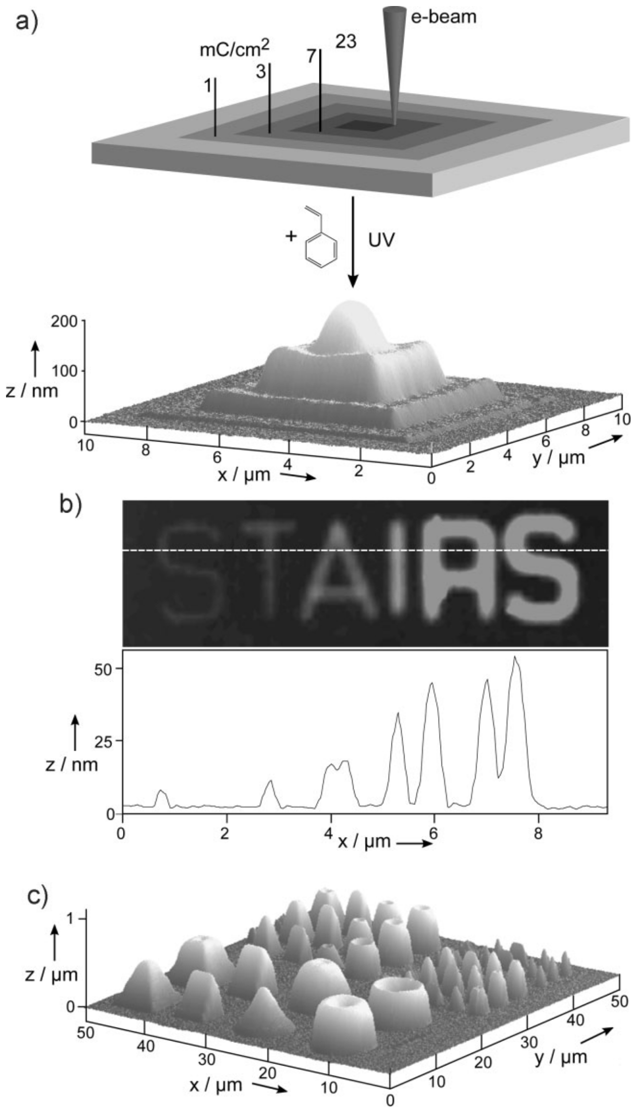

Figure 3. Complex polymer brush structures by carbon templating on various substrates. a) A step pyramid of PS brushes on silicon nitride created from a carbon template of concentric squares written with different electron doses (top: irradiation scheme, below: AFM image). b) AFM and height analysis of 'STAIRS' templated on a silicon substrate with lines of 100 nm width and increasing electron dose for each letter (1, 2, 4, 8, 12, 16 mC cm^{-2}) results in PS brush lines of 6, 10, 16, 35, 44, and 53 nm height and widths between 200 and 350 nm. c) AFM image of PS brush objects of different sizes and shapes on a bare gallium arsenide substrate (maximum structure height: 0.5 µm).

By direct photografting, a broad variety of vinyl monomers can be converted to stable surface-bound functional polymer brushes.[15,24,30] We successfully polymerized the monomers acrylic acid, methyl methacrylate, tert.-butyl methacylate, styrene, 4-vinylpyridine, and 4-vinylbenzylchloride from carbon templates to give polymer brushes of different properties and functionalities (see Supporting Information, Table S1).

An alternative route to more complex polymer brush functionalizations is to employ polymer analogue conversions of the grafted polymers to introduce polymer-pendant functionalities. However, polymer brushes grafted onto surfaces via silane- or thiol-based SAM systems are limited in terms of further wet chemical or photochemical modifications. As mentioned above, the carbon-templated brushes were found to be very stable at elevated temperatures and good solvent conditions, analogous to polymer brushes formed on oxidized diamond.[25] We performed common polymer-analog reactions such as nitration in a mixture of concentrated sulfonic acid and nitric acid at 60 °C for 1 h or sulfonation with sulfonic acid of PS brushes on silicon substrates. The successful conversion of PS to poly(styrene sulfonic acid) (PSSA) and poly(nitrostyrene) (PNS) was confirmed by infrared spectroscopy and wetting experiments. AFM analysis of the resulting structures revealed that the drastic reaction conditions did not desorb the grafted brushes from the carbon templates. The conversion of the PS brushes to PNS or the polyanionic PSSA, however, changes the molar mass of the grafted chains and hence leads to an increase of the polymer brush layer thickness. For example, the layer thickness of a PS brush increases by approx. 140% upon nitration and 170% by sulfonation. This correlates nicely with our earlier findings on the

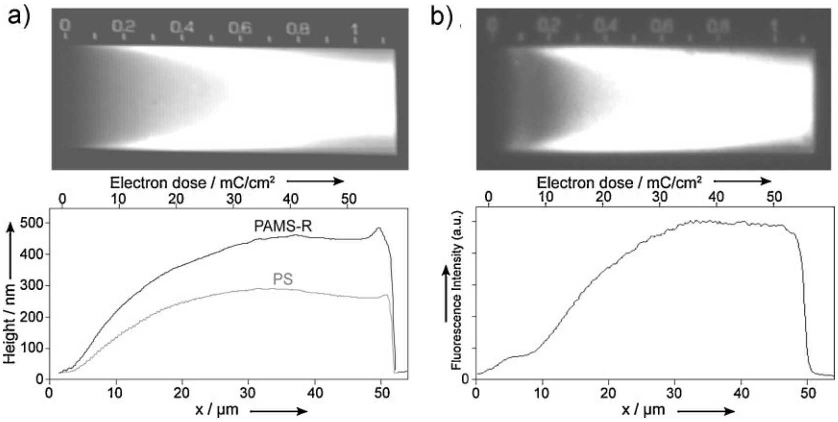

Figure 4. Homogeneous functionalization of structured polymer brushes by surface analogue reactions. a) PS brush gradient (section analysis below) on silicon nitride was first aminoalkylated to PAMS and labled with rhodamine B isothiocyanate to give a PAMS-R gradient (top: AFM image). The introduction of pendant functions results in a homogeneous thickness increase of 155% along the entire gradient. b) Fluorescence micrograph and intensity profile of the same PAMS-R gradient.

conversion efficiency of sulfonation and nitration found for PS brushes on diamond.[25] Furthermore, a multi-step polymer analogue reaction of PS brushes to poly(4-aminomethyl styrene) (PAMS)- a coating that can be used for solid-phase organic peptide synthesis (Merrifield resin) is possible. First, PS brushes were amidoalkylated and hydrazinolysed to give PAMS in a two-step reaction.[25] Secondly, the polymer pendant amino groups were used for the coupling of a fluorescent dye (rhodamine B isothiocyanate) in order to test the conversion as well as analyze the accessibility of the surface amino groups in the entire brush layer by a sterically demanding molecule. Figure 4a shows the height profile of a PS brush on oxidized Si_3N_4 prepared by carbon templating.

Upon conversion to PAMS and reaction with the fluorescence dye to PAMS-R, the brush layer thickness homogenously increased by 155% due to the attachment of the pendant aminomethyl groups and dyes. The AFM inspection of the entire layer did not show noticeable detachment of layer sections or other defects introduced by the reactions (Fig. 4a, top). In Figure 4b, a fluorescence microscopy image of the same structure is shown. All structural features of the carbon templated brush, including the ‘written numbers’ indicating the locally applied electron dose of the EBCD procedure are clearly visible. Furthermore, analysis of the fluorescence image (Figure 4b, below) reveals that the fluorescence intensity directly follows the polymer brush layer thickness. If the fluorescence dye were only coupled to amino groups at the polymer/solvent interface, the resulting fluorescence intensity would have been independent of the polymer layer thickness. The similarity of the height profile and the fluorescence intensity proves that the dye is coupled throughout the entire polymer brush layer.

A general method for the fabrication of stable polymer brush structures on a broad variety of substrates without the need of specific surface chemistry is presented. The mask- and resist-free carbon templating technique allows programmed amplification of the carbonaceous layer by surface-initiated polymerization. This defined placement of polymer brush structures onto a surface allows the specific control of the physical/mechanical properties and the chemical function densities in a predetermined area. In contrast to existing SAM-bonded polymer brush systems, the coupling of the brushes via a stable and highly cross-linked carbonaceous interlayer[20] allows the use of functional and structured polymer brush layers at a broad spectrum of conditions. So far we found that this technique is applicable to metals, semiconductors, and isolators (e.g. Si, Si_3N_4, Ge, GaAs, GaN, mica, glass, Al) and does not require the introduction of specific surface chemistry. Furthermore, the excellent chemical and thermal stability of the polymer brush layers allow consecutive reactions even under drastic conditions. By this general approach, stable polymer brushes with different dimensions, architectures, and chemical functionalities can be prepared on a variety of substrates.

This polymer coating technique can also be used to apply electro-optical devices based on semiconductors in biological systems. The defined morphology of the flexible brushes (locally controlled thickness and chemical function density) will be useful for the specific design of sensors and actuators on the micro- as well as nanometer length scale.

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