Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 5345–5351 **5345**
DOI: 10.1021/ma900329y

Bottle-Brush Brushes: Cylindrical Molecular Brushes of Poly(2-oxazoline) on Glassy Carbon

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Received February 13, 2009; Revised Manuscript Received June 5, 2009

ABSTRACT: We report on the synthesis of brushes of bottle-brushes of poly(2-oxazoline)s on polished glassy carbon (GC) substrates. First, homogeneous and stable poly(2-isopropenyl-2-oxazoline) (PIPOx) brush layers with thicknesses up to 160 nm were created directly onto GC by the self-initiated photografting and photopolymerization (SIPGP) of 2-isopropenyl-2-oxazoline (IPOx). Kinetic studies reveal a linear increase in thickness with the polymerization time. In a second reaction, the pendant 2-oxazoline ring of the PIPOx brushes were used for the living cationic ring-opening polymerization (LCROP) with different substituted 2-oxazoline monomers to form the side chains. Also for the second surface-initiated LCROP from the surface-bound macroinitiator brushes, the thickness increase with the polymerization time was found to be linear and reproducible. Characterization of the resulting bottle-brush brushes by FTIR spectroscopy, contact angle, and AFM indicates a high side chain grafting density and quantitative reactions. Finally, we have demonstrated the possibility of functionalizing the bottle-brush brushes side chain end groups with sterically demanding molecules.

Introduction

Polymer coatings on solids play a key role in diverse research fields from biology to physics.[1] In particular, the covalent modification of semiconductors with functional polymer brushes has received increasing interest due to potential applications in sensor technologies,[2] combinatorial science,[3] and medicine.[4] Polymer brushes are of particular interest in biomedical research, because the grafted polymer chains can extend from the surface into the adjacent liquid phase and mimic real biological environments.[5] For the development of biomedical implants and high-throughput diagnostic sensors, hydrophilic and biocompatible polymers gained much interest. For such applications, poly(ethylene glycol) (PEG) has been the most widely used polymer.[6−8] However, current PEG technology has major limitations for long-term applications. It has been reported that PEG coatings lose their function when placed *in vivo* and can undergo oxidative degradation.[9−11] Recently, poly(2-oxazoline)s (POx) came into focus as a potential alternative to the well studied PEG systems.[12−16] It has been reported that surfaces coated with this type of polymer have quantitatively equal protein-repellent properties as PEG-based coatings and are resistant toward nonspecific protein adsorption.[14,17] In the past decade, we developed different approaches for the preparation of such systems on solids by either the "grafting onto"[18−24] as well as by the "grafting from" method.[25,26] However, the polymer brushes were either bonded to gold substrate by thiols[21,25] or to silica by silane functions.[18,22] As for PEG-based coatings, these systems have a limited chemical and thermal stability which make them inappropriate for long-term applications. E.g., silane-based systems on oxides are prone to hydrolysis and have a poor stability in saline solutions at 37 °C, thus impairing their use for many biomedical applications.[27,28] Thiol-based coatings are mainly limited to coinage metal substrates, and their limited thermal[29] and UV stability[30] are well-known.

Recently, we have reported that defined, stable, and homogeneous polymer brush layers can be prepared directly onto carbonaceous materials by the self-initiated photografting and photopolymerization (SIPGP) of vinyl monomers.[31−33] Hence, the formation of defined reactive interlayers such as self-assembled monolayers (SAMs) is not necessary, and surface-initiated polymerization of vinyl monomers onto carbonaceous surfaces can be performed directly.

Here we report on the preparation of poly(2-isopropenyl-2-oxazoline) (PIPOx) brushes directly onto polished glassy carbon (GC) substrates by the SIPGP approach with 2-isopropenyl-2-oxazoline (IPOx) as the monomer. GC has been widely used as electrode material due to its intriguing electrochemical and mechanical properties.[34,35] Furthermore, it is reported that GC is a suitable material for implants and considered to be "biocompatible".[36]

The monomer, 2-isopropenyl-2-oxazoline (IPOx), has two orthogonal polymerizable groups, namely a vinyl group for living anionic or radical polymerization (here used for the SIPGP) and the 2-oxazoline ring for the living cationic ring-opening polymerization (LCROP). Very recently, we have used the dual-functionality of 2-isopropenyl-2-oxazoline to prepare cylindrical bottle brushes.[37] The PIPOx backbone was converted quantitatively with methyl triflate to a polycationic macroinitiator for the preparation of cylindrical bottle-brushes via the grafting from approach by living cationic polymerization of different 2-oxazolines. With poly(2-ethyl- and 2-isopropyl-2-oxazoline) side chains, the bottle-brushes display a sharp and reversible lower critical solution temperature (LCST) in water.

Here, we have adapted this synthetic route for the preparation of poly(2-oxazoline) bottle-brush structures, covalently grafted onto GC. PIPOx brushes, prepared by the SIPGP of IPOx, were converted in a second reaction to brushes of bottle-brushes by the

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Published on Web 07/02/2009

LCROP of different 2-oxazoline monomers. In the following, these structures are referred to as "bottle-brush brushes".[38]

Until now, only few reports can be found on such bottle-brush brush systems.[38−42] These complex polymer architectures resemble intriguingly to the structure of various polyglycans that can be found on nearly every living cell. It has been shown that carbohydrates in the form of polysaccharides, glycoproteins, glycolipids and other glycoconjugates play essential roles in many biological processes. They serve as recognition sites for the cell and contribute to the steric repulsion which prevent undesirable nonspecific adhesion.[42−44] The highly aggregated surface-tethered carbohydrate ligands, such as the glycocalyx on the cell surface, results in not only the enhancement of binding strength in specific recognition against proteins but also the minimization of nonspecific protein adsorption.[43] Nontoxic bottle-brush brush structures as biomimetic functional soft interfaces between solid semiconductors and biological systems may find direct applications for designing advanced biomedical devices.

Experimental Section

Materials. All substances were from Sigma-Aldrich (Steinheim, Germany) or Acros (Geel, Belgium) and were used as received unless otherwise stated. Methyl triflate (MeOTf), 2-methyl-2-oxazoline (MeOx), 2-ethyl-2-oxazoline (EtOx), acetonitrile (ACN) were dried by refluxing over CaH_2 under a dry nitrogen atmosphere and were subsequently distilled prior to use. Polished glassy carbon (GC) substrates (SIGRADUR G) were purchased from Hochtemperatur-Werkstoffe GmbH (Germany). For structuring during the SIPGP process, square mesh grids with holes of 50×50 μm^2 from Agar Scientific Ltd. (U.K.) were used.

Infrared spectroscopy (IR) was performed using an IFS 55 Bruker instrument equipped with a diffuse reflectance Fourier transform infrared (DRIFT) setup from SpectraTech and a mercury−cadmium-telluride (MCT) detector. For each spectrum, 500 scans were accumulated with a spectral resolution of 4 cm^{-1}. Background spectra were recorded on bare glassy carbon samples.

Atomic force microscopy (AFM) scans were obtained with a Nanoscope IIIa scanning probe microscope from Veeco Instruments (Mannheim, Germany). The microscope was operated in tapping mode using Si cantilevers with a resonance frequency of 320 kHz, a driving amplitude of 1.25 V at a scan rate of 0.5 Hz. The average roughness (rms) was calculated from a 5 μm^2 area.

Microwave (MW). Microwave-assisted synthesis was performed with a CEM Discover LabMate system at a temperature set to 130 °C (150 W). The temperature was monitored by an integrated fiber-optical setup.

Fluorescence microscopy images were obtained with an Axiovert 200 M Zeiss AG microscope equipped with an ORCA-ER camera (Hamamatsu Photonics Japan). The sample was irradiated using a 00 filter set (530−585 nm). The cross section analysis was performed by pixel analysis of the 256 bit black and white fluorescence image using the *Image J* software package.

2-Isopropenyl-2-oxazoline (IPOx), 2-*n*-propyl-2-oxazoline, and 2-butyl-2-oxazoline were synthesized according to a procedure published before.[45,46]

Self-Initiated Photografting and Photopolymerization (SIPGP). Polished glassy carbon (GC) substrates were cleaned by sequential ultrasonification in ethanol, ethyl acetate and toluene before use. The GC substrates were clamped with a square mesh grid (square size: 50×50 μm^2) and subsequently submerged in approximately 2 mL of freshly distilled and degassed IPOx in a glass vial. Polymerization was allowed to complete in 2 to 40 h under constant irradiation with UV light (λ_{max} = 350 nm) at room temperature (RT). After photopolymerization, the samples were immediately cleaned by sequential ultrasonification in ethanol, ethyl acetate and toluene (all HPLC grade) for 5 min each.

Living Cationic Ring-Opening Polymerization (LCROP). The poly(2-isopropenyl-2-oxazoline) (PIPOx) modified GC substrates were submerged in a solution of 2 mL acetonitrile (ACN) with an excess amount of methyl trifluoromethane sulfonate (MeOTf) (0.1 g) at approximately −35 °C under a dry nitrogen atmosphere. After stirring for 6 h at 0 °C, the mixture was allowed to equilibrate to RT and was stirred for another 2 h. Without washing, the GC substrate was taken to a MW reaction vial filled with a solution of 1 g 2-alkyl-2-oxazoline (alkyl = methyl, ethyl, propyl or butyl) and several drops of MeOTf in 3 mL of ACN at 0 °C. Catalytic amounts of MeOTf were added to consume the minor impurities in the liquid phase. The reaction solution was irradiated by microwaves for 20 min with a temperature setting of 130 °C. The solution was cooled to 0 °C, and 150 mg of *N*-*tert*-butoxycarbonylpiperazine (*N*-Boc-piperazine) dissolved in 1 mL of ACN was added. Successively, the solution was stirred for 16 h at room temperature. After this, an excess of potassium carbonate (70 mg) was added to the solution and stirred overnight. The substrate was then removed from the solution and cleaned by sequential ultrasonication in deionized water, ethanol, ethyl acetate, and toluene for 1 min each.

For the kinetic experiments of the second surface-initiated LCROP (SI-LCROP) one GC substrate was modified by SIPGP of IPOx to result in PIPOx brushes of a thickness between 30 and 50 nm. This sample was divided into three pieces and SI-LCROP was performed for 60, 120, and 240 min at 80 °C according to the procedure described above. After a thorough cleaning procedure the resulting layer thickness was determined by AFM. The data are presented in Figure 2b as a relative thickness increase. After 1 h the polymer layer thickness increased by 57% from 30 ± 2 nm to 47 ± 3 nm; after 2 h from 55 ± 3 nm by 142% to 133 ± 4 nm and after 4 h from 44 ± 3 nm by 223% to 142 ± 3 nm.

Deprotection of Poly(2-isopropenyl-2-oxazoline-*g*-2-ethyl-2-oxazoline-Boc) (P(IPOx-*g*-EtOx)). The P(IPOx-*g*-EtOxBoc)-coated GC substrates were submerged in a solution of 1 mL trifluoroacetic acid (TFA) and 1 mL of chloroform. The mixture was stirred at RT for 3 h. Then, the GC substrate was neutralized in a 5% $NaHCO_3$ aqueous solution for 2 h. Finally, the polymer-coated GC substrate was thoroughly cleaned by ultrasonification in water, ethanol, ethyl acetate, and toluene.

Fluorescent Labeling of P(IPOx-*g*-EtOx). A P(IPOx-*g*-EtOx) modified GC substrate was submerged in a 15 mM rhodamine B isothiocyanate solution in methanol for 3 days at RT. Finally, the functionalized GC substrate was cleaned by ultrasonification in ethanol.

Results and Discussion

The preparation of poly(2-oxazoline) based bottle-brush brushes on glassy carbon is schematically outlined in Figure 1. First, structured poly(2-isopropenyl-2-oxazoline) (PIPOx) brushes on glassy carbon (GC) were prepared by self-initiated photografting and photopolymerization (SIPGP) of 2-isopropenyl-2-oxazoline (IPOx) with UV-light of a spectral distribution between 300 and 400 nm (λ_{max} = 350 nm). Structured brushes were realized by irradiation through a stencil mask with rectangular openings of 50×50 μm^2. After the polymerization, the substrate was rigorously cleaned by ultrasound in several solvents with different polarities to ensure that only chemically grafted polymer remains on the substrate. AFM measurements confirmed that polymer was grafted selectively on the irradiated areas and a structured polymer brush was formed. Moreover, the surface roughness of the native GC substrate (rms 4.6 nm) was rendered by the additional polymer layer to a lower value of 3.0 nm (rms). The successful modification of the GC substrate by PIPOx brushes was further confirmed by infrared (IR) spectroscopy (see below). The strong bands at 1648 cm^{-1} and 1128 cm^{-1}

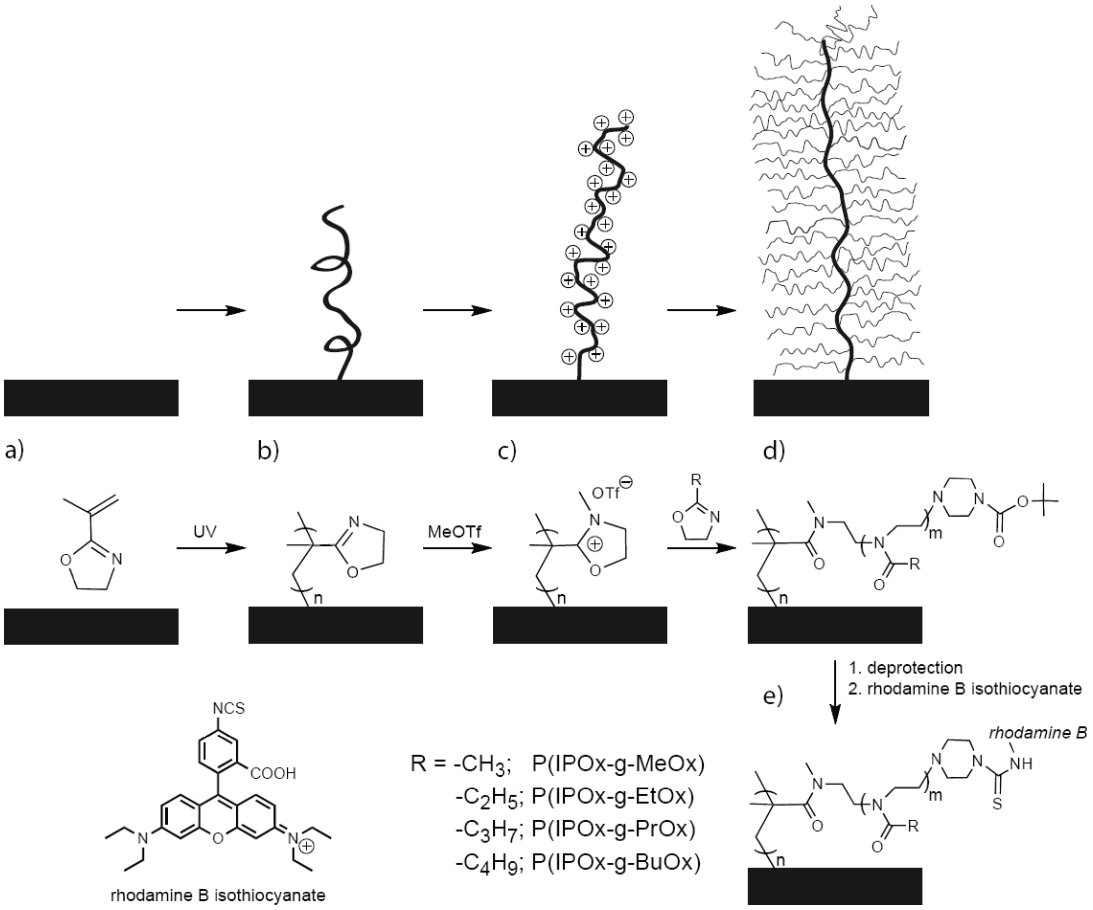

Figure 1. Preparation of PIPOx-*g*-EtOx bottle brushes on GC. (a, b) PIPOx brushes created on GC by the SIPGP of IPOx. (c) Conversion of the PIPOx brush backbone to the macroinitiator salt PIPOxOTf. (d) LCROP of 2-alkyl-2-oxazoline from the PIPOxOTf macroinitiator salt. (e) Termination of the side chain polymerization with *N*-Boc-piperazine and deprotection of the Boc groups allowing the functionalization of the side chain end groups with rhodamine B isothiocyanate.

assigned to the (C═N) and (C−O) stretching modes as well as the two modes at 987 and 951 cm^{-1} originate from the ring skeletal vibration of the 2-oxazoline rings are in agreement with the FTIR spectrum of PIPOx reported earlier.[37]

As shown in previous studies, using different substrates such as polyethylene,[47] aromatic SAMs on gold[33] and oxidized diamond,[31] as well as carbon deposits on various inorganic substrates induced by electron beams,[32] the grafting reaction and the formation of polymer brushes occurs via the SIPGP mechanism in which a vinyl monomer acts as a photosensitizer to activate a surface functional group by hydrogen abstraction to start a free radical surface-initiated polymerization. The only requirement for the photografting reaction is the possibility for hydrogen abstraction by a radical mechanism. Various studies have investigated the surface functionalities of polished GC substrates. Raman spectroscopy has shown that polishing severely disrupts the GC structure.[48] Polishing does not only affect the upper monolayer but changes the GC microstructure within a region of 10−20 nm. Polished GC surfaces are composed of smaller microcrystallites (compared to bulk GC) having many graphitic edges.[48] The formation of PIPOx brushes on polished GC substrates can be explained by the low C−H bond dissociation energy (BDE) on such graphitic edges.[49] Furthermore, polishing causes a partial oxidation of the GC substrate resulting in C−OH and C═O surface functionalities.[50] Collier et al.[51] reported that polished GC substrates are covered with up to 10% of aromatic OH groups. Due to the low BDE of aromatic alcohol groups,[52] it is most likely that hydrogen atoms are also abstracted radically from surface OH functionalities during the SIPGP process.

Ex situ kinetic studies of the SIPGP of IPOx monomer were performed on individual GC samples at different UV irradiation times (2 - 40 h) using the same stencil mask. In Figure 2, the thickness of the polymer brush layer as measured by AFM under ambient conditions is plotted as a function of the UV irradiation time. For polymerization times below 10 h, an almost constant growth rate of 6.1 nm/h is observed. However, the layer thickness growth rate decreases significantly for longer photopolymerization times. We observed that the bulk monomer phase became highly viscous with longer irradiation times due to self-initiated photopolymerization of IPOx in the bulk phase. The limited film growth can therefore be explained by either the monomer concentration decrease and/or the limited mass transport of the remaining monomer molecules. This behavior is in agreement with our previous reports.[53] In this context it should also be noted that the SIPGP results in grafted polymers with a certain degree of branching, since the radical abstraction is also occurring at already grafted polymer chains.[33] Although the grafting density as well as the chain length is not known, the thicknesses of the grown polymer layers as determined by AFM can only be reached if the grafted polymers are in the brush regime.

We have reported recently on the preparation of cylindrical molecular brushes from the dual-functional IPOx monomer.[37] Adapting the synthetic route for the preparation of bottle-brushes in solution for the surface confined bottle-brush brushes, the PIPOx backbone or stem was converted with methyl triflate to a polycationic macroinitiator for the living cationic polymerization of different 2-alkyl-2-oxazolines (Figure 1).

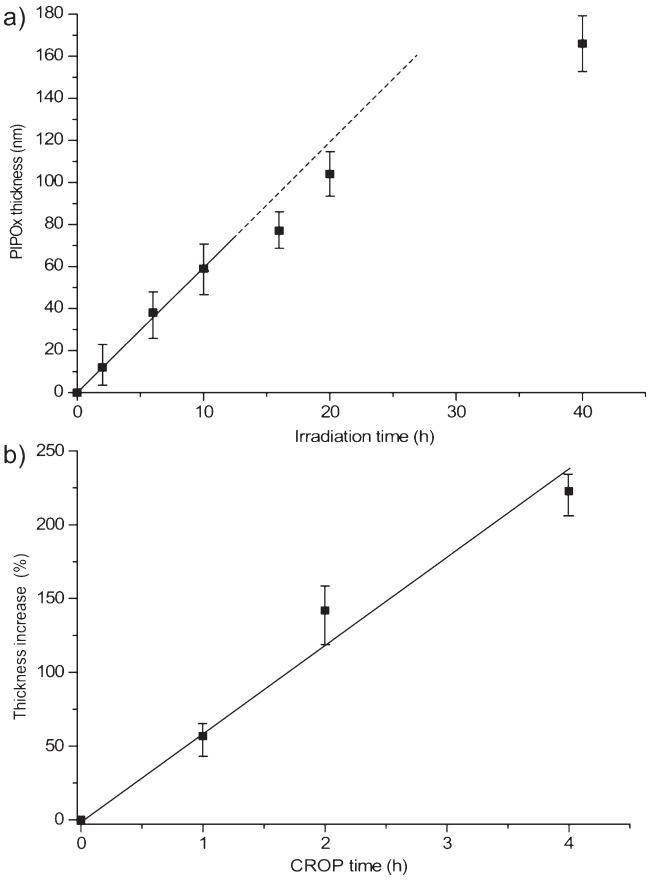

Figure 2. Development of the polymer layer thickness as a function of the polymerization time as measured by AFM on structured polymer grafts ($50 \times 50\ \mu m^2$) for (a) PIPOx brush layer thickness on polished GC prepared by SIPGP (UV-irradiation at max = 350 nm; RT) and (b) relative thickness increase by SI-LCROP using MeOx as the monomer and a PIPOx macroinitiator brush (T = 80 °C).

PIPOx brushes with a thickness of 159 ± 9 nm were converted into the polycationic macroinitiator salt (PIPOxOTf) by submerging the modified GC substrate in a solution of methyl trifluoromethane sulfonate (MeOTf) in acetonitrile and the reaction was allowed to complete within 6 h at 0 °C and 2 h at r.t.. To avoid side reactions of the oxazolinium pendant ring, the substrate was directly transferred in to a solution of a 2-oxazoline monomer in acetonitrile. The LCROP of e.g. 2-ethyl-2-oxazoline (EtOx) was performed for 20 min at 130 °C. Finally, *N*-Boc-piperazine was used to terminate the living polymerization. The terminal piperazine ring allows an additional functionalization of each side chain end after the deprotection of the secondary amine by trifluoroacetic acid (TFA).[37] After the LCROP and deprotection of the Boc-group, the substrate was intensively cleaned by ultrasound in different solvents to remove physisorbed material.

The successful conversion of PIPOx brushes to P(IPOx-*g*-EtOx) bottle-brush brushes was confirmed by FTIR spectroscopy (Figure 3). The (C═N) and (C−O) stretching bands as well as the two ring skeletal vibration bands from the pendant 2-oxazoline ring in PIPOx brushes disappeared and a new intensive band appeared around 1627 cm^{-1} which is characteristic for the carbonyl stretching mode of the amide function. Moreover, the characteristic CH_x deformation modes for EtOx are observed around 1421 cm^{-1}. The complete disappearance of the oxazoline ring IR bands indicates the full conversion of the pendant 2-oxazoline ring. The FTIR spectrum of the surface grafted polymer layer is in good agreement with our recent results on poly(2-oxazoline) bottle-brushes with the analogue composition formed in solution.[37]

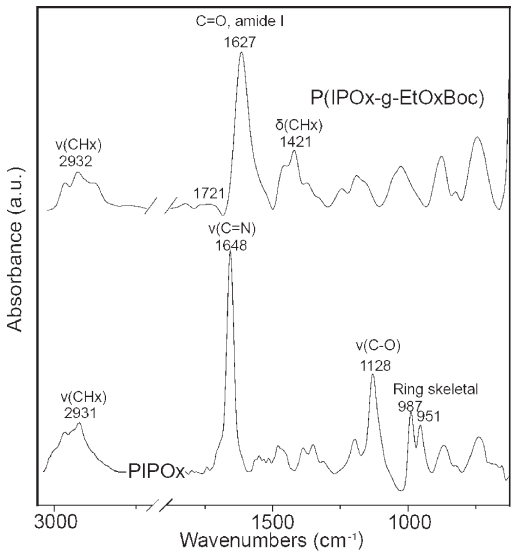

Figure 3. IR spectra of PIPOx and P(IPOx-*g*-EtOxBoc) brushes on GC.

AFM analysis (Figure 4) of the resulting structured polymer layer revealed that the polymer brushes did not desorb during the conversion of PIPOx graft to the polyelectrolyte, the second polymerization forming the pendant chains and the final deprotection reaction. This indicates that beside the ultrasound stability, the polymer grafts created on GC are thermally (the LCROP was performed at 130 °C) as well as chemically stable. Furthermore, AFM measurements showed a significant thickness increase of the polymer layer from 159 ± 9 to 330 ± 10 nm after the LCROP. The layer thickness increase of approximately 108% can be expected due to the stretching of the bottle-brush backbone by the side chain crowding. The deprotection of the Boc group results in a slight thickness decrease of approximately 5% because of the reduction of the molar mass.

Also for the second surface-initiated living cationic ring-opening polymerization (SI-LCROP), the thickness increase as a function of the polymerization time was investigated. For this, one sample with PIPOx brushes was prepared by SIPGP and then divided into three pieces. With each sample, SI-LCROP was performed using MeOx as the monomer for 60, 120, and 240 min at 80 °C. The percentage of the respective thickness increase due to the formation of bottle-brush brushes with PMeOx side chains was found to be linear (Figure 2b). The systematic thickness increase demonstrates that the sensitive SI-LCROP can be performed in reproducible and consistent manner and individual SI-LCROP reactions can be compared. However, these experiments do not give a detailed picture about the grafting efficiency and the resulting polymer architecture. On the other hand, based on our experience with SI-LCROP using initiator functionalized self-assembled monolayers on planar substrates[25] and especially on nanoparticles,[26] the here presented route to coat and functionalize a broad variety of surfaces[32] with the versatile POx has a high potential for the development of functional surfaces for the control of protein adsorption and cell adhesion.[14]

The projected use of polymer brushes in the biomedical field requires a broad choice of functional and biocompatible/bioresponsive surfaces, especially a fine-tuning of the hydrophilic/hydrophobic motifs within the layer to control adhesion and adsorption. Recently, we have reported that for the preparation of cylindrical molecular brushes in solution, the LCROP from the PIPOxOTf macroinitiator can be performed with different 2-alkyl-2-oxazolines. By changing the side chain composition of bottle-brushes, it is possible to change the hydrophobicity of the molecular brushes and to fine-tune the LCST temperature.[37]

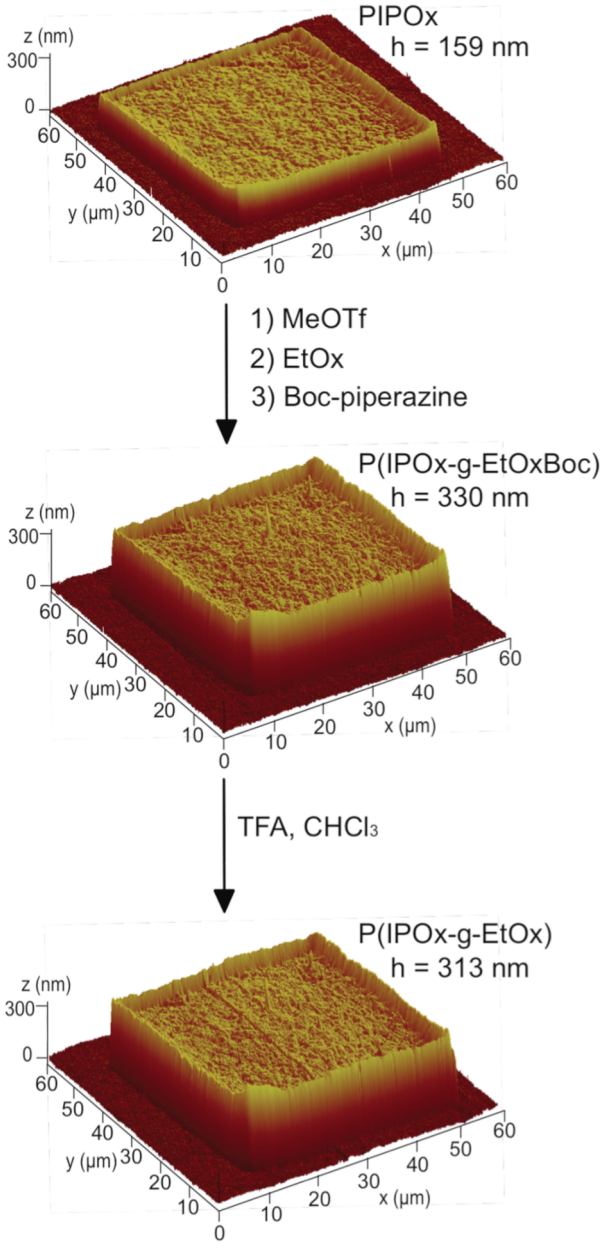

Figure 4. AFM scans of polymer brush structures on GC. (a) SIPGP of IPOx for 40 h through a stencil mask gives structured PIPOx brushes with a thickness of 159 ± 9 nm. (b) LCROP using EtOx and termination with *N*-Boc-piperazine results in 330 ± 10 nm thick P(IPOx-*g*-EtOxBoc) bottle-brush brushes. (c) Same structure after deprotection of the side chain terminal Boc group with a final layer thickness of 313 ± 10 nm.

In order to demonstrate that bottle-brush brushes with a variety of side chains are accessible by this approach in a confined surface layer, we have performed the LCROP from PIPOxOTf brushes with different 2-alkyl-2-oxazolines. Up to now, we have successfully tested 2-methyl-, 2-ethyl-, 2-propyl- and 2-butyl-2-oxazoline (MeOx, EtOx, PrOx and BuOx, respectively). The influence of the bottle-brush brushes side chains on the hydrophilic/hydrophobic character of the polymer layer was investigated by contact angle measurements (Table 1). The LCROP of the different 2-alkyl-2-oxazolines was performed under identical reaction conditions from homogeneous PIPOxOTf brushes on GC prepared by SIPGP of IPOx for approximately 16 h. Table 1 shows unambiguously that the hydrophilicity of the bottle-brush brushes can be adjust by the side chain composition. While side chains of hydrophilic poly(2-methyl-2-oxazoline) resulted in a

Table 1. Static Water Contact Angle of Different Bottle-Brush Brush Coatings on Polished GC Substrates[a]

substrate	static contact angle (deg)
polished GC	85 ± 2
PIPOx	41 ± 3
P(IPOx-*g*-MeOxBoc)	43 ± 2
P(IPOx-*g*-EtOxBoc)	49 ± 2
P(IPOx-*g*-PrOxBoc)	69 ± 3
P(IPOx-*g*-BuOxBoc)	95 ± 2

[a] The PIPOx brushes were obtained by the SIPGP of IPOx overnight (approx. 16 h). The LCROP was performed at 130°C by microwave heating for 20 min.

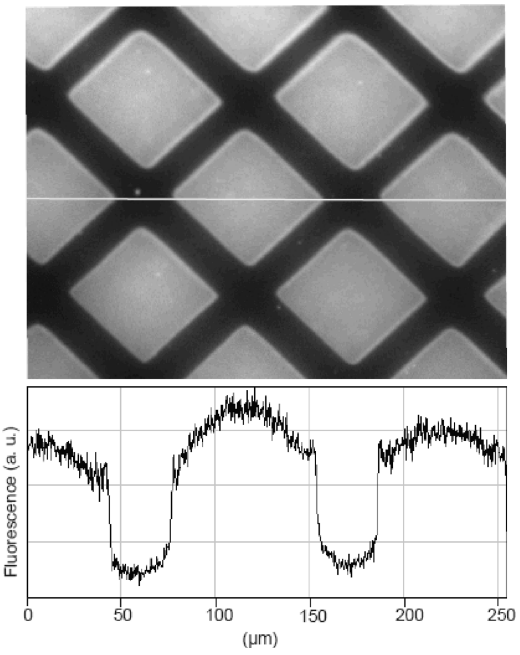

Figure 5. Fluorescence image and section analysis of structured P(IPOx-*g*-EtOx) bottle-brush brushes labeled with rhodamine B isothiocyanate on glassy carbon. The bright regions with high fluorescence intensity coincide with the polymer-modified areas.

static water contact angle of 43°, poly(2-oxazoline)s of increasing hydrophobicity reduced the wettability as expected and e.g. for bottle-brush coatings with poly(2-butyl-2-oxazoline) side chains, the surface was found to be hydrophobic. It is noteworthy that here the Boc end group introduces an additional hydrophobic character into the coating. This observation is in agreement with our findings on the water-solubility and studies of the LCST of poly(2-oxazoline) bottle-brushes in water.[37] For example, after deprotection of a P(IPOx-*g*-EtOxBoc) coating by TFA, the water contact angle decreased significantly and for P(IPOx-*g*-EtOx), a contact angle of 35 ± 2° was measured.

It is noteworthy that all LCROP reactions were performed at 130 °C by microwave heating. This technique is an efficient method for performing the LCROP of 2-oxazoline, overcoming the long reaction times characteristic for that reaction when carried out under conventional heating. Furthermore, the living character of the polymerization is retained under microwave irradiation.[54] In order to estimate the influence of the microwave irradiation, the LCROP of EtOx was performed from structured PIPOxOTf brushes on GC at 130 °C by conventional oil bath heating but in otherwise identical reaction conditions, i.e., a reaction time of 20 min. AFM measurements revealed a thickness increase of approximately 97% (from 150 nm for the PIPOx brushes to 293 nm for the P(IPOx-*g*-EtOxBoc) bottle-brush brushes). Taking the experimental error into account, this result

indicates that the microwave irradiation do not accelerate significantly the surface-initiated LCROP reaction.

In order to demonstrate that the terminal amino groups of the side chains can be further functionalized, P(IPOx-*g*-EtOxBoc) were deprotected and the secondary amine group of the side chain termini of the bottle-brush brushes were labeled with rhodamine B isothiocyanate (Figure 1). After intensive cleaning with ultrasound in ethanol to remove all nonbonded fluorescence dyes, strong fluorescence was detected only at the polymer modified areas (Figure 5). This indicates that the fluorescent dye was selectively and covalently bonded via the thiourea link to the bottle-brush brushes. This experiment also shows that despite the high crowding of polymer chains in such bottle-brush brushes, the side chain terminal amino group is still accessible for further functionalization, even with steric demanding organic molecules. The functionalization of the terminal amino group of bottle-brush brushes with biomolecules (polysaccharides, proteins, etc.) will be the subject of future research.

Conclusions

The self-initiated photografting and photopolymerization (SIPGP) of 2-isopropenyl-2-oxazoline on polished glassy carbon substrates resulted in homogeneous and very stable poly(2-isopropenyl-2-oxazoline) brushes. *Ex situ* kinetic studies revealed an almost linear increase of the polymer brush layer with the polymerization time. The pendant oxazoline ring of the poly(2-isopropenyl-2-oxazoline) brushes was used to perform a second living cationic ring-opening polymerization (LCROP) with different substituted 2-oxazoline monomers to result in bottle-brush brushes. Finally, we have demonstrated the possibility to functionalize the bottle-brush brushes side chain end groups with steric demanding molecules. The ease of chemical modification allows for a precise fabrication of a broad variety of functional surfaces for the design of a soft interlayer between a conductive surface and biological systems.

Acknowledgment. This work was supported by the Elitenetzwerk Bayern in the frame of the international graduate school CompInt ("Materials Science of Complex Interfaces") as part of the IGSSE ('International Graduate School for Science and Engineering') at the Technische Universität München. M.S. is additionally thankful for a postdoc stipend from Wacker-Institute of Silicon Chemistry of the TU München and R.L. for a postdoc stipend from the King Abdullah University of Science and Technology, Saudi Arabia (KAUST).

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