Polymer Brushes

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Site-Selective Surface-Initiated Polymerization by Langmuir–Blodgett Lithography**

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The growth of polymers from surfaces has been conducted to tune surface properties such as wettability, bioadhesion, and surface activity.[1] Polymer brushes can be prepared by covalent attachment of a polymerization initiator onto the surface with subsequent surface-initiated polymerization (SIP) by the "grafting-from" approach.[2] Atom-transfer radical polymerization (ATRP),[3] nitroxide-mediated radical polymerization (NMP),[4] and reversible addition fragmentation transfer polymerization (RAFT)[5] have been used in SIP. Site-specific surface polymerization affords spatially controlled polymer brushes. Nanometer-sized structures are of increasing importance in various fields of nanoscale science. Microcontact printing,[6] photolithography,[7] electron-beam lithography,[8] and other techniques have been used for spatially controlled covalent surface binding of the initiator. These techniques belong to the top-down strategies.

Alternatively, self-assembly offers interesting routes to patterned structures by a bottom-up approach.[9] Block-copolymer lithography[10] and nanosphere lithography[11] are members of this category. Herein we present the use of Langmuir–Blodgett (LB) lithography for the spatially controlled attachment of initiator to form regular stripes of polymer brushes.[12] The width and the periodicity of the stripes can be controlled. Moreover, LB lithography is performed with inexpensive equipment and large areas (several cm^2) can be patterned. We have previously shown that mixed monolayers of L-α-dipalmitoyl-phosphatidylcholine (DPPC) and dyes can be transferred by the LB technique onto a mica surface in regular stripes with sub-micrometer lateral dimensions.[13] The challenge for the present work was to find a polymerization initiator that a) forms LB films, b) is transferred to surfaces periodically from mixed monolayers with DPPC, and c) contains a reactive functional group for covalent attachment of the polymer initiator onto a Si wafer (Figure 1). As the polymerization technique we chose NMP.[3,14] The synthesis of the alkoxy amine initiator **4**, which should fulfill all the requirements mentioned above, is depicted in Scheme 1.

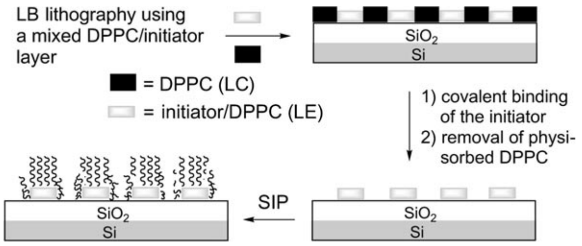
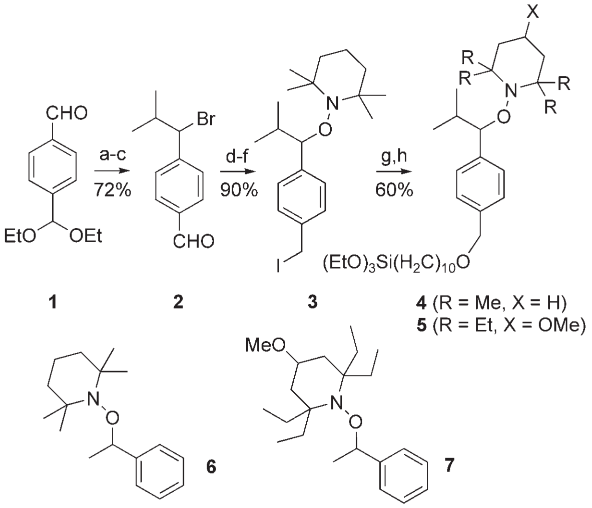


Figure 1. Formation of patterned polymer brushes (LC = liquid condensed phase, LE = liquid expanded phase).



Scheme 1. a) *i*PrMgCl, Et$_2$O; b) aq. HCl; c) HBr (33% in AcOH), CH$_2$Cl$_2$; d) TEMPO, Cu, Cu(OTf)$_2$ (cat.), 4,4′-bis-*tert*-butylpyridine (cat.), benzene; e) LiAlH$_4$, THF; f) TMSCl, NaI, CH$_3$CN; g) NaH, CH$_2$=CH(CH$_2$)$_8$OH, THF; h) HSi(OEt)$_3$, Karstedt cat. OTf = trifluoromethanesulfonate; TMS = trimethylsilyl.

Reaction of **1** with *i*PrMgCl followed by acetal cleavage and subsequent bromination provided bromide **2** (72%). Transformation of **2** into the corresponding alkoxy amine was achieved by using the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) and Cu catalysis.[15] Aldehyde reduction (LiAlH$_4$) and iodination with TMSCl/NaI delivered **3**. Etherification with CH$_2$=CH(CH$_2$)$_8$OH/NaH and hydrosilation

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with Karstedt catalyst and HSi(OEt)$_3$ gave **4**. Alkoxy amine **5**, which has a sterically more demanding nitroxide moiety,[16] was prepared in an analogous manner (see the Supporting Information).

Compound **4** forms stable monolayers in a mixture with DPPC at the air/water interface.[17] The surface pressure/area isotherms of a pure solution of **4**, of DPPC, and of a mixture of **4** and DPPC are given in the Supporting Information. In the LE-phase region, the mixed monolayers (2.5–15 mol% **4** in DPPC) were transferred to an oxidized Si wafer by the LB technique. As an example, Figure 2a shows the AFM image of a covered Si wafer prepared with 10 mol% **4** showing regular stripes of DPPC (width = (0.27 ± 0.01) µm) with channels (width = (0.26 ± 0.02) µm) consisting of DPPC and **4**. The height difference between the LC stripes and the LE channels is approximately 1 nm, which is in agreement with earlier reports.[13] The covered wafer was then dried at 0.01 bar at 80 °C for 2 h to covalently bind **4** onto the wafer. Physisorbed DPPC was eventually removed by washing with CHCl$_3$. SIP was performed in styrene at 125 °C for 24 h with 0.2 mol% **6** as a sacrificial polymerization regulator.[3] To remove physisorbed polystyrene (PS), the brushes were rinsed with CH$_2$Cl$_2$. The AFM image shows the formation of regular stripes of PS brushes. For example, the use of 10 mol% **4** after LB lithography and SIP resulted in PS brushes with channel widths of (0.20 ± 0.02) µm and stripe widths of (0.26 ± 0.03) µm. The height of the stripes increased to (8.0 ± 0.2) nm (Figure 2b). The width of the stripes can be controlled by the concentration of **4** in the mixed phase. The smallest stripes were obtained in the experiments with concentrations of 10 and 12.5 mol%. Lowering as well as increasing the amount of **4** provided wider stripes, while the channel width remained almost constant (Figure 2c).[18]

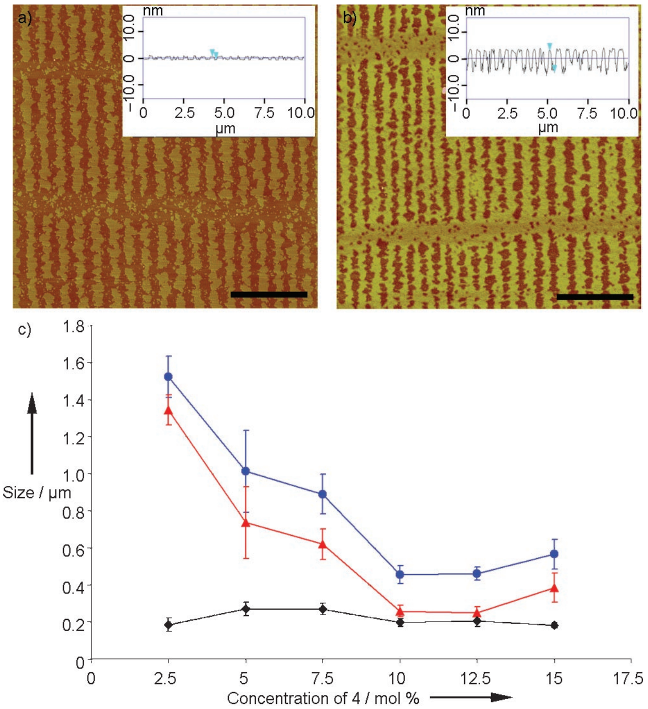

Figure 2. a,b) AFM images of a sample prepared with 10 mol% **4** before (a) and after (b) SIP of styrene (insets show cross sections; scale bars: 2.5 µm). c) Periodicity (sum of stripe and channel size, blue circles), size of stripes (red triangles), and size of channels (black diamonds) as a function of the concentration of **4**.

The density of the chains on the wafer can be determined from the brush height and the number-average molecular weight (M_n) of the surface-bound polymer.[19] The value of M_n is determined from the polymer synthesized in solution with the sacrificial alkoxy amine initiator.[19] Densities ranging from 0.09 to 0.14 chains nm^{-2} were calculated, which proves that the brushes are in the semidiluted regime (see the Supporting Information).[20] The brush heights obtained are typical for dry polymer brushes in the semidiluted regime. Because of the rather low chain density, the brush thickness cannot be further increased by increasing the reaction time.[19]

NMP with TEMPO as a mediator is restricted to styrene derivatives.[3] To extend our methodology to acrylic acid derivatives we conducted the surface modification with **5**. Alkoxy amine **5** bears a nitroxide group, which is able to control acrylate polymerization.[16] LB lithography was performed with a mixed DPPC/**5** monolayer containing 10 mol% **5**. The regularity of stripe pattern improved significantly, indicating better compatibility of **5** with DPPC. Also, the number of vertical stripes appearing with mixtures of **4** at higher concentrations decreased. SIP in styrene with sacrificial **7** for 24 h delivered regular styrene stripes with an average height of (5.3 ± 0.2) nm (Figure 3a). SIP in *n*-butyl acrylate containing **7** at 105 °C for 24 h gave regularly patterned poly(*n*-butyl acrylate) brushes (height = (4.7 ± 0.2) nm, stripe width = 0.18 ± 0.03 µm, channel width = (0.29 ± 0.05) µm; Figure 3b).

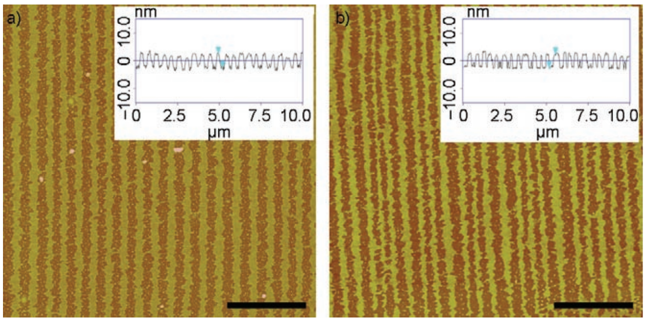

Figure 3. a) AFM image of surface after SIP of styrene with **5**. b) AFM image of surface after SIP of *n*-butyl acrylate with **5**. (Insets show cross sections; scale bars: 2.5 µm).

In conclusion, LB lithography based on dynamic self-assembly can be used for site-specific covalent immobilization of radical initiators onto a Si wafer. Nitroxide-mediated SIP delivers regular stripes of polystyrene and polyacrylate brushes. The polymer stripe width can be adjusted from about 0.2 to 1.3 µm. This technique can be performed with inexpensive equipment, and large surface areas up to square centimeters can readily be patterned (see the Supporting Information).

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