Chemical Micropatterning

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A Self-Assembly Approach to Chemical Micropatterning of Poly(dimethylsiloxane)**

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Dedicated to Professor David N. Reinhoudt on the occasion of his 65th birthday

Polydimethylsiloxane (PDMS) elastomers are widely used in biomedical devices, such as medical implants, catheters, and contact lenses, because of their biocompatibility and physical properties.[1–3] PDMS elastomers can be easily molded into (sub)micrometer features and are optically transparent and relatively chemically inert, which are ideal properties for applications in soft-lithographic techniques. In many soft-lithographic applications, the low-energy surface of PDMS can be used advantageously, for example, in microcontact printing of nonpolar species[4] and the transfer-printing technique pioneered by Rogers and co-workers.[5,6] However, the unmodified PDMS surface is hydrophobic, and surface modification is required to print polar inks or proteins,[7–9] to facilitate cell growth,[10] to improve compatibility,[11,12] and for use in microfluidics.[13] A range of methods have been developed to alter the surface chemistry of PDMS; most involve UV/ozone treatment[14] or an oxygen plasma,[15] and subsequent functionalization by forming alkylsilane monolayers. Yet, there is to date no single-step procedure that allows the introduction of a wide range of functional groups on the PDMS surface in a spatially controlled way. Herein, we demonstrate a novel way to selectively modify the surface of a silicone elastomer through minimization of interfacial free energy and the self-assembly of functional molecules at the surface by mirroring the distribution of surface energies on a template. Chaudhury and co-workers[16] have exploited surface energy to drive allyl-functionalized perfluorinated polyethers to the surface of PDMS. Our approach generalizes the principle of surface free energy minimization to drive both hydrophilic and hydrophobic molecules to a surface, thus replicating the pattern on the template surface.

This surface-induced self-assembly-based method of chemically micropatterning of PDMS is shown schematically in Figure 1. A micropatterned alkylthiolate self-assembled monolayer (SAM) on gold is used as a topographically flat, chemical master. Subsequently, a mixture of Sylgard 184 PDMS and a small amount (<5 wt %) of vinyl-terminated small molecules with different head groups is cured against this master. The small molecules preferentially accumulate near the surface areas with complementary surface energy to minimize the unfavorable interactions of the PDMS polymers with the SAMs. During the hydrosilylation (curing) reaction, the silicon hydride groups present in the cross-linking agent of the Sylgard 184 react with the vinyl groups of both the cross-linking dimethylsiloxane oligomers as well as the added functional molecules, thereby "freezing" the chemical pattern into the PDMS elastomer (Figure 1 e). After careful removal of the PDMS, facilitated by water to weaken the interfacial bonds on the hydrophilic areas, flat PMDS surfaces patterned with sub-micrometer features of different chemical functionalities are obtained.

To verify the migration of molecules to the PDMS surface, we studied the cross-linking of PDMS mixed with small amounts of hydrophobic and hydrophilic alkenes against hydrophobic and hydrophilic surfaces, respectively. A perfluorinated silane monolayer on a Si surface was used to force the surface migration of 3 wt % 1*H*,1*H*,2*H*-perfluorodecene added to the PDMS prepolymer, resulting in increasing water contact angles ($\theta_{adv} \approx 124°$, $\theta_{stat} \approx 120°$) relative to "native" PDMS Sylgard 184 ($\theta_{adv} \approx 112°$, $\theta_{stat} \approx 110°$). In contrast, curing undec-11-enyl hexaethylene glycol monomethyl ether (PEG_6) "doped" PDMS against a hydroxy-terminated mercaptoundecanol SAM on gold resulted in significantly more hydrophilic contact angles ($\theta_{adv} \approx 100°$, $\theta_{stat} \approx 90°$), and the pinning of water droplets ($\theta_{rec} < 5°$). The XPS spectra of PDMS treated with perfluorinated molecules show peaks in the F 1s region and an extra peak in the C 1s region, shifted by roughly 7 eV from the main CH peak, indicating the presence of fluorine and carbon atoms bound to fluorine. From the atomic percentages it was estimated that 35 % of the surface layer was covered with 1*H*,1*H*,2*H*-perfluorodecene; more accurate calculations are not possible because the error in XPS measurements generally amounts to about 10 %. The XPS spectrum of PDMS functionalized with the long vinyl-bearing PEG chain also exhibited an extra peak in the C 1s area, roughly 2 eV higher than the main C 1s peak (CH). This peak originates from carbon bound to PEG oxygen atoms. A 30 % coverage of the long PEG chains at the surface after addition of 3 wt % undec-11-enyl hexaethylene glycol was estimated from the atomic ratios. These results are summarized in Table 1.

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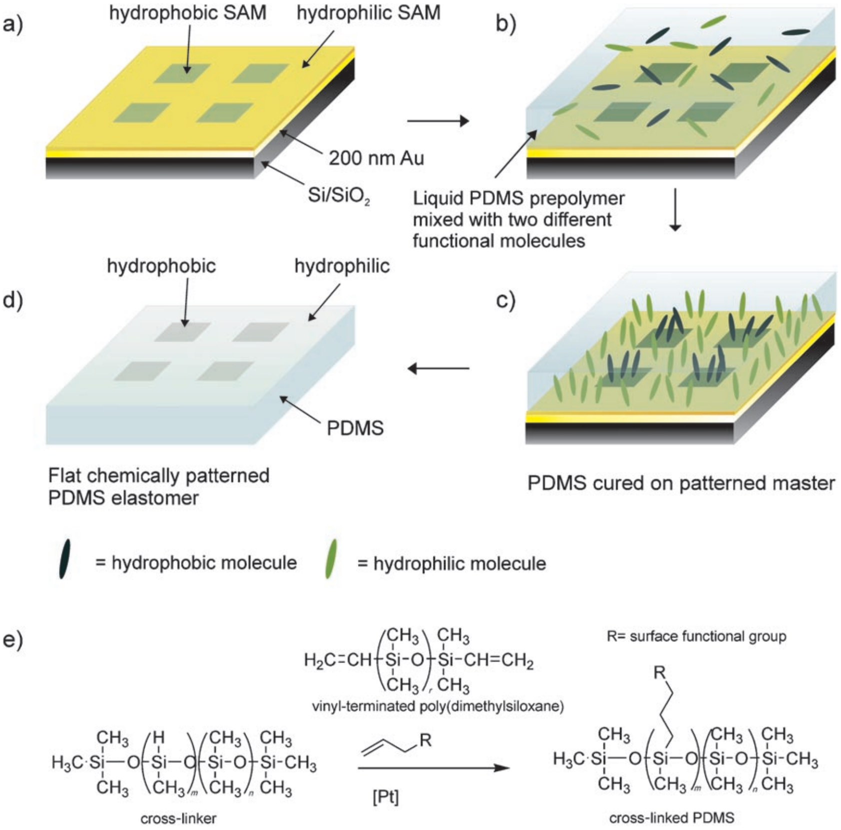

Figure 1. a) A microcontact printed SAM on Au, with strong surface-energy contrast between the two components, is used as a chemical master; b) PDMS prepolymer is mixed with two different functional molecules (a polar and less polar alkene) and poured over the master; c) alkenes self-assemble on the functionalized monolayer and react with the PDMS backbone by a hydrosilylation reaction during curing; d) upon lift-off, a flat PDMS stamp with two different chemical functionalities at the surface is obtained; e) hydrosilylation reaction. The alkene reacts with the silicon hydride under the influence of a platinum catalyst ([Pt]).

Table 1: XPS and contact-angle data for modified PDMS elastomer surfaces.[a]

Sample	C [%]			O [%]	Si [%]	F [%]	θ_{adv} [°]	Coverage [%]
	C–H	C–F	C–O					
PDMS–Sylgard 184 (blank)	44	–	–	26	30	–	113	–
3 wt% 1*H*,1*H*,2*H*-perfluorodecene	26	9	–	21	21	23	124	35
3 wt% undec-11-enyl hexaethylene glycol	34	–	13	27	26	–	95	30

[a] A general ratio between the elements is shown, the carbon percentage is subdivided into percentages of carbon bound to hydrogen, fluorine, or oxygen.

These initial results provide a strong indication that surface energies of the master surfaces can be exploited to guide the preferential migration of small molecules to the PDMS surface. More importantly, by mixing in a combination of vinyl-group-bearing compounds into the PDMS prepolymer and curing against a suitably patterned monolayer, which was formed by microcontact printing and backfilling, chemically patterned PDMS surfaces can be obtained. Initial experiments concentrated on the formation of binary patterns consisting of perfluorinated alkenes and either oligo(ethylene glycol) methacrylate (OEGMA) or the PEG$_6$ derivative described above. The resulting PDMS surfaces contained hydrophilic and hydrophobic patches, as can be inferred from the condensation patterns in Figure 2. These optical images demonstrate clearly that patterns as small as 200 × 500 nm lines can be chemically replicated (Figure 2 b–d).

The AFM friction image in Figure 3 a shows that the 200 × 500 nm lines are clearly replicated into the PDMS surface (topographical image not shown, but only minimal (< 5 nm) height differences exist between the two areas). The friction image in Figure 3 b shows a clear difference between the dark areas with perfluorinated molecules (rounded squares), corresponding to low friction, and the OEGMA chains (surrounding area). Importantly, the changes in surface chemistry seem complete and abrupt at the pattern interfaces, without any evidence of islands or other signs of incomplete "phase separation" at the surface. This result indicates very reliable replication of the master pattern. The pattern appears to be stable to the eye for at least one to two days (typical duration of the experiments). Detailed experiments regarding stability are in progress.

It should be noted that the OEGMA used in these experiments will give rise to some side products during the hydrosilylation reaction. The hydroxy end groups could react in a hydrocondensation instead of hydrosilylation reaction. Furthermore, platinum-catalyzed hydrosilylations can take place across the C=C bond, as well as in a 1,2 or 1,4 addition involving the C=O bond.[17] However, the net result is the covalent incorporation of the oligo(ethylene glycol) chains into the cross-linked PDMS, and a modification of the surface energy.

On the basis of these promising results, we decided to exploit the chemical patterning of PDMS surfaces further by introducing alkenes with other functional groups, for example, initiator molecules for surface-initiated polymerizations. The formation of thin polymer films on PDMS allows a robust route to surface modification and enables a range of applications in microfluidic devices, but the current methods do not allow the introduction of such polymer brushes with controlled spatial resolution. By substituting the perfluoroalkenes used before with 0.5 wt% allyl 2-bromo-2-methylpropionate, an ATRP initiator (ATRP = atom-transfer radical polymerization), and curing against a master patterned with squares of octadecanethiol (ODT) SAM surrounded by a SAM of the hydrophilic 11-hydroxyundecane-1-thiol (HUT),

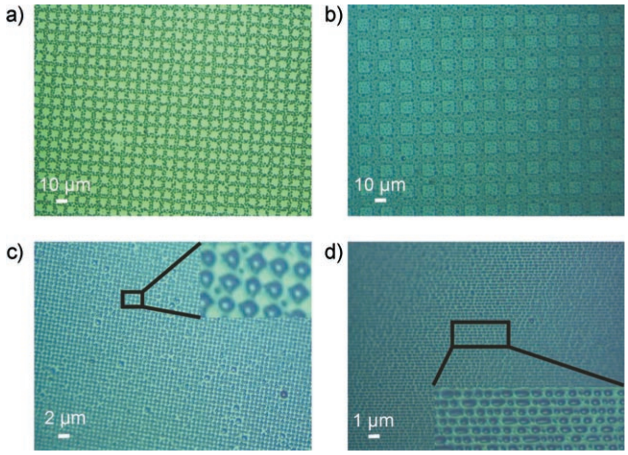

Figure 2. a) Optical micrographs of water vapor deposited on a template functionalized with a square pattern (10×10 µm^2) of hydrophobic octadecylthiol (ODT) and hydrophilic hydroxyundecylthiol (HUT) self-assembled monolayer on gold; b) condensation pattern on PDMS stamp replicated from corresponding (10×10 µm^2) patterned monolayer template; water condensed on the hydrophilic areas with OEGMA; c) condensation pattern on PDMS stamp with a pattern of 1×1 µm^2 dots; d) condensation pattern on PDMS stamp with 200×500 nm line pattern. The PDMS samples shown in (b–d) contain conventional Sylgard 184 PDMS plus a total 2 wt% of hydrophobic and hydrophilic materials (1*H*,1*H*,2*H*-perfluorodecene and OEGMA (MW 360) in a 1:1 molar ratio).

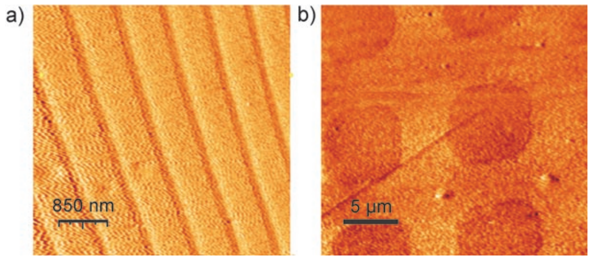

Figure 3. a) Contact-mode AFM friction image of 200×500 nm line pattern of 1*H*,1*H*,2*H*-perfluorodecene (narrow lines) and OEGMA (wide lines) in PDMS, *Z*-scale = 2.0 V; b) contact-mode AFM friction image of 5×5 µm^2 pattern of 1*H*,1*H*,2*H*-perfluorodecene (squares) and OEGMA (surroundings) in PDMS, Z scale = 0.9 V. The dark areas correspond to low friction.

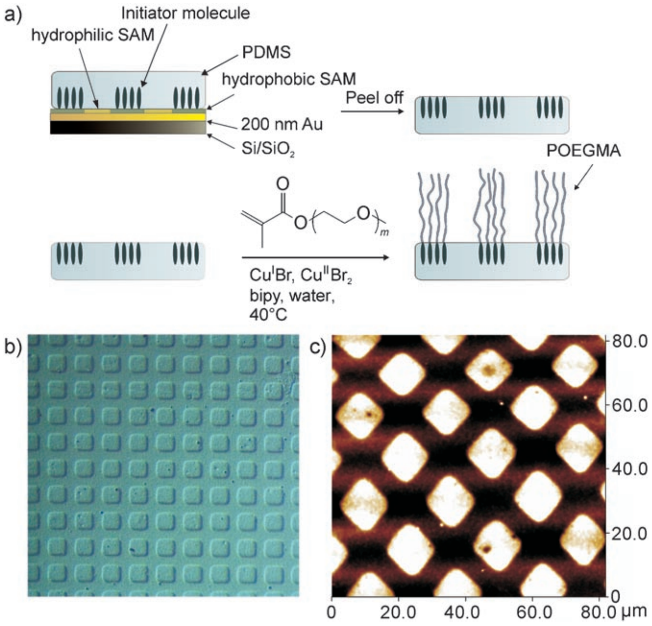

Figure 4. a) Schematic diagram of the polymerization process (bipy = 2,2′-bipyridyl); b) optical micrograph of 10×10 µm^2 square pillars of POEGMA on PDMS; c) AFM topography image of 10×10 µm^2 square pillars of POEGMA on PDMS, *Z* scale = 200 nm.

we can selectively activate areas on the surface of PDMS for surface-initiated ATRP (Figure 4). Polymerization of OEGMA under normal ATRP conditions[18] yielded hydrophilic POEGMA brushes. The optical micrograph (Figure 4b) shows the regular array of 10 × 10 µm^2 squares, and the AFM image (Figure 4c) indicates that approximately 150-nm-thick POEGMA films were produced. This AFM image also very clearly shows the absence of any POEGMA growing in the noninitiator-modified areas, again showing the remarkable degree of selectivity that can be achieved with this surface-driven self-assembly approach. Further analysis was carried out on homogeneously grown POEGMA brushes on PDMS. The advancing water contact angle decreased from 110° for standard PDMS to 58° after polymerization of POEGMA. ATR-FTIR analysis (ATR = attenuated total reflecta) showed a distinctive peak at 1727 cm^{-1}, indicating the presence of the ester group of the polymethacrylate brushes. The signal intensity for the C–H functionalities (broad peaks around 2900 cm^{-1}) also increased after the polymerization. Importantly, we found that the initiator density, and hence thickness of the brushes grown in a fixed time period, can be controlled by changing the weight percentage of alkene initiator added. The addition of 1 wt% allyl 2-bromo-2-methylpropionate resulted in roughly 300-nm-thick POEGMA brush areas.

In conclusion, "doping" with small molecule alkenes can be used to modify the surface of PDMS by forcing these molecules to the surface through curing against a master with a suitably matching surface energy. The chemically patterned PDMS surfaces can then be further amplified by surface-initiated polymerizations. The method described herein allows a straightforward modification of PDMS with a wide range of functional groups into patterns with dimensions at least as small as 200 nm (but probably smaller). The density of these functional groups can be controlled by using different concentrations of alkene "dopants", which, in combination with the ability to pattern, opens up a wide range of potential applications in microfluidics and soft lithography, in which chemically patterned flat stamps have been used for microcontact printing.[19]

Experimental Section

Monofunctional PDMS stamps were made by mixing the two parts of the PDMS kit (Sylgard 184, VWR) in a 10:1 ratio by weight, and adding different weight percentages of the functional molecules prior to curing. The PDMS mixture was poured over a monofunctional SAM on a gold substrate, degassed, left for 24 h at room temperature, and then cured at 70°C. Undec-11-enyl hexaethylene glycol monomethyl ether was synthesized by following the procedure of Prime and Whitesides.[20] A chemically patterned flat stamp was formed by mixing the two parts of the PDMS kit in a 10:1 ratio by weight to a total mass of 4.0 g. Equimolar amounts of 1*H*,1*H*,2*H*-perfluorodecene (Fluorochem) and OEGMA (Aldrich) with a total mass of 0.08 g were added to the prepolymer mixture. The mixture was poured over the patterned monolayer-functionalized substrate, degassed, left for 24 h at room temperature, and then cured at 70°C. After curing and soaking in water for 2 h, the modified PDMS was peeled off the master. A PDMS elastomer functionalized with ATRP initiator was made by mixing the two parts of the PDMS kit in a 10:1 ratio by weight to a total mass of 4.0 g, and 2-bromo-2-methyl propionic acid allyl ester (15 μL, 94.3 mmol) (Aldrich) and Pt catalyst (platinum(0)–1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex; 0.5 μL 0.10 M solution in xylene; Gelest) (to ensure complete cross-linking) were stirred into the mixture after mixing of the base polymer. The mixture was cast against a gold surface functionalized with either an octadecanethiol (ODT) SAM, 11-hydroxy-undecane-1-thiol (HUT) SAM, or mixed patterned SAM of ODT and HUT. The PDMS was left for 24 h at room temperature, then cured at 70°C, soaked in water, and peeled off.

Methoxy-terminated OEGMA (MW 400, 11 g, 23 mmol) was dissolved in water (11 cm^3) at 40°C and degassed by passing a continuous stream of dry N_2 through the solution with stirring (15 min). 2,2′-Bipyridyl (183 mg, 1.2 mmol), $Cu^{I}Cl$ (46 mg, 469 μmol), and $Cu^{II}Br_2$ (10 mg, 47 μmol) were added to this solution. The mixture was then further stirred and degassed with a stream of dry N_2 (15 min). Initiator-functionalized PDMS samples were sealed in Schlenk tubes, degassed (four high-vacuum pump/N_2 refill cycles), and heated to 40°C. The polymerization solution was then transferred by syringe into each Schlenk tube; enough solution was added to submerge each sample completely. After 4 h (or 16 h for the patterned surfaces) the samples were removed, washed with water, then ethanol, and dried under a stream of N_2.

Analysis: Contact-angle goniometry was performed by using a homemade stage with a computer-controlled microsyringe and digital camera. ATR-FTIR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer. Tapping mode atomic force microscopy (AFM) images were obtained by using a Digital Instruments Nanoscope III. Contact-mode AFM images were obtained by using a Molecular Imaging AFM, Agilent. Optical micrographs were obtained by using a Nikon Eclipse ME600L microscope with the DN100 capture system.

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