Heavyweight Dendritic Inks for Positive Microcontact Printing

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Poly(propylene imine) dendrimers with dialkyl sulfide end groups were prepared and developed as inks for positive microcontact printing $((+)\mu CP)$ on gold. Long $(C_{10}H_{21}-S-C_{10}H_{20}-)$, medium $(C_3H_7-S-C_4H_8-)$, and short (CH_3-S-CH_2-) dialkyl sulfide end groups were attached to second- and third-generation PPI dendrimers to create a family of dendritic sulfides. The dendritic inks flatten upon adsorption and form monolayers on gold. $(+)\mu CP$ was performed on gold using commercially available poly(dimethylsiloxane) as stamp material and *n*-octadecanethiol as etch resist. The gold beneath the dendrimers was selectively etched away with an acidic $Fe(NO_3)_3$/thiourea solution to give the positive copy of the original master pattern. The multivalent sulfide attachment and the relatively high molecular mass of these dendrimers ensured minimal lateral ink spreading and thus optimal feature reproducibility. Contact times were varied to analyze the spreading rates of the dendritic inks. The spreading rates of the dendritic inks were found to be much lower than that of pentaerythritol tetrakis(3-mercaptopropionate). $(+)\mu CP$ with the new inks was extended to submicrometer features. Optical microscopy, scanning electron microscopy, and atomic force microscopy were used to characterize the etched samples. Lines with a width of 100 nm were faithfully replicated with the third-generation dendrimers bearing medium (C_3-S-C_4-) end groups.

Introduction

The transfer of molecules to surfaces by means of microcontact printing (μCP) allows simple and efficient formation of micrometer-sized patterns.[1,2] μCP consists of bringing a "molecularly inked", elastomeric stamp into conformal contact with a substrate in order to form self-assembled monolayers (SAMs) on the surface exclusively in the areas of contact between the stamp and the substrate. The SAM can pack and organize well enough to act as a wet etch resist, as was first shown for *n*-alkanethiols on gold.[1,3] The pattern etched into the gold substrate is the negative replica of the original master [negative microcontact printing, $(-)\mu CP$; see Figure 1]. Although downsizing the features replicated by μCP would be very attractive for nanofabrication, several difficulties have to be overcome to enter in the submicrometer range. The main limiting factors of downsizing the printed patterns are (i) the low mechanical stability of the elastomeric stamp, which is prone to collapse and deformation,[4] and (ii) the lateral spreading of the ink molecules during printing, when conformal contact is achieved between the stamp and the surface.[5] Several ways have been proposed to increase the mechanical stability of the stamp, which range from improving the hardness of the PDMS[6] or the application of alternative stamp materials[7] to introducing new μCP techniques, such as chemically

Figure 1. Schematic representation of $(-)\mu CP$ (A) and $(+)\mu CP$ (B): (1) the PDMS stamp is pealed off from the master and inked with the ink solution, (2) the solvent is evaporated and conformal contact with the substrate is achieved, (3) a monolayer is formed in the contact areas and the stamp is lifted off, and (5) the sample is etched. An additional step in $(+)\mu CP$ is (4) the sample is dipped in an etch-resistant adsorbate solution. In $(-)\mu CP$, the negative replica of the original master is obtained. In $(+)\mu CP$, the positive replica of the master is obtained.

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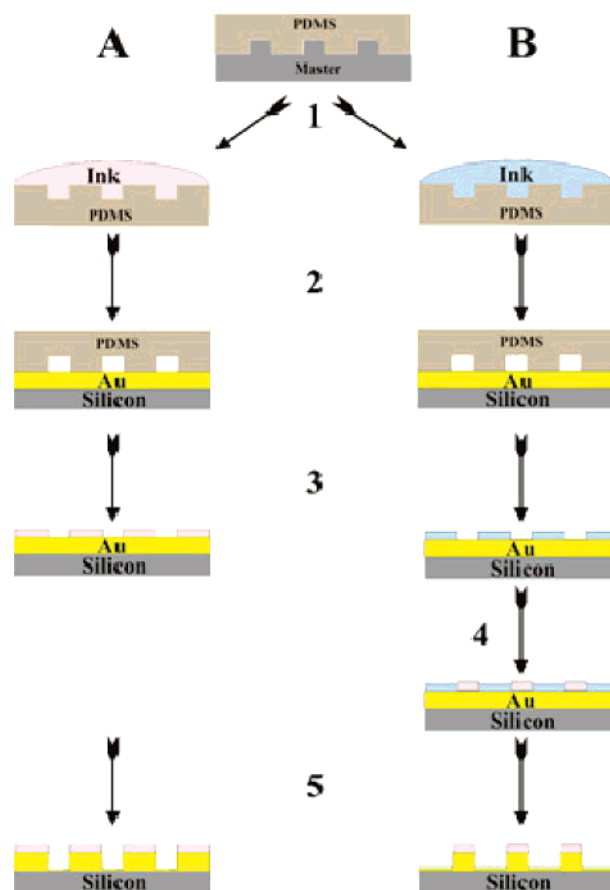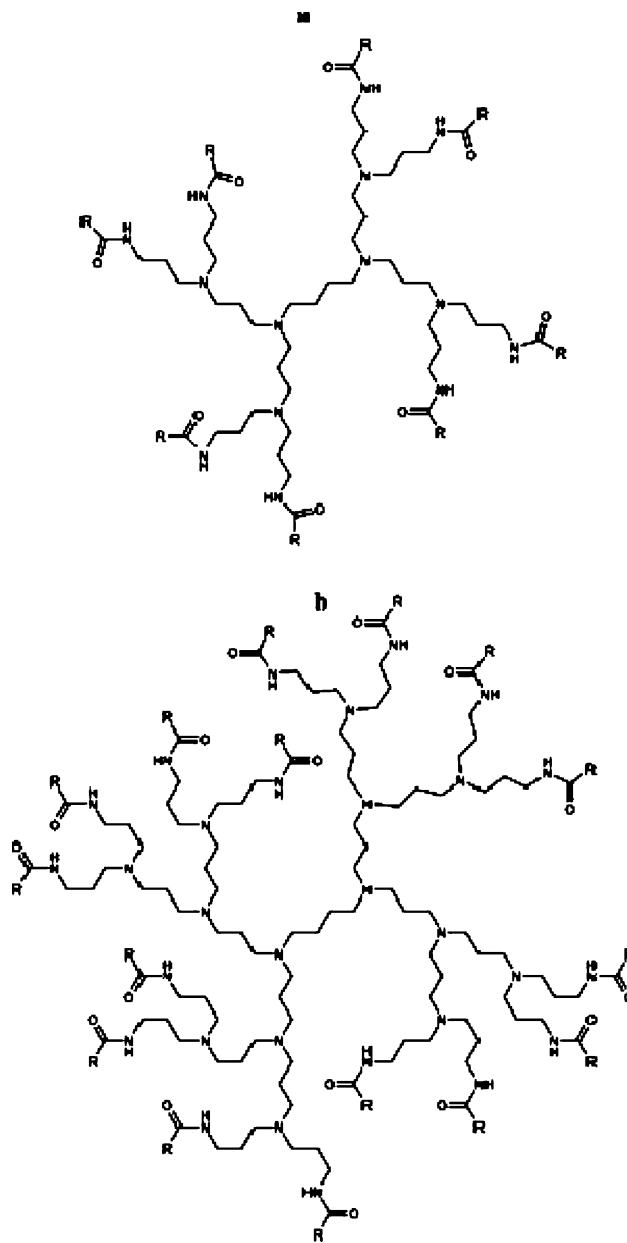
patterned flat stamps.[8] Catalytically active stamps have been developed to prevent ink spreading.[9] Using inks with increased molecular weight or with multiple attachment points could reduce the spreading rate of the molecules, but on the other hand, that would be realized at the expense of order and etch resistance of the formed monolayer.[10]

The extension of the μCP methodology to positive μCP [$(+)\mu$CP; see Figure 1] has resulted in the possibility of pattern replication by printing a poorly etch resistant ink[11,12] followed by immersion of the sample in a second, etch-resistant adsorbate solution, which fills the available areas and acts as a resist in the subsequent etching step. It is an additional advantage of $(+)\mu$CP that one can use stamps with a high filling ratio to replicate master features with a low filling ratio. Originally, pentaerythritol tetrakis(3-mercaptopropionate) (PTMP) was proposed as a positive ink, because it forms a stable SAM on gold and copper, is not replaced by etch resistant *n*-alkanethiols [such as *n*-octadecanethiol (ODT)], and does not provide significant etch resistance.[11,13]

Dendrimers are highly branched, globular macromolecules that represent excellent building block candidates for nanostructured materials since, in contrast to most linear polymers, dendrimers have a well-defined molecular weight rather than a broad distribution of molecular weights.[14] It was shown that amine- and hydroxyl-terminated poly(amidoamine) dendrimers form stable, densely packed SAMs on gold, which are porous for electroactive species.[15] Dendrimers were also used as inks for $(-)\mu$CP when amine-terminated dendrimer SAMs were patterned on silicon, creating 140-nm-wide dendrimer SAM lines with 70-nm interline spacing.[16]

In this study we combine the high molecular weight of dendrimers with the affinity of dialkyl sulfides for gold and introduce a family of poly(propylene imine) (PPI) dendrimer-based dialkyl sulfides as positive inks for μCP on gold. Although the concept of "heavyweight" inks is not entirely new,[10,17] to use them as positive inks is innovative. Dendrimers with tertiary amine and dialkyl sulfide functionalities adsorb to gold with both the sulfur atoms and the amine core.[17] Their high molecular mass and multiple sulfide attachment points to the gold surface should reduce the lateral spreading during printing and limit the exchange with molecules that form an etch-resistant SAM. Hence, in contrast to PTMP, $(+)\mu$CP with dendritic inks tolerates a wide range of printing times and stamp aspect ratios. In addition, the open structure of the dendrimers should allow the access of electroactive species to the surface through the SAM and significantly decrease the etch resistance.

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Scheme 1. Structure of the Second- and Third-Generation Poly(propyleneimine) Dendrimers with Dialkyl Sulfide End Groups

G2-S, G3-S	R: CH₃-S-CH₂-
G2-M, G3-M	R: CH₃-(CH₂)₂-S-(CH₂)₄-
G2-L, G3-L	R: CH₃-(CH₂)₉-S-(CH₂)₁₀-

Results and Discussion

Synthesis and Monolayer Characterization. Dialkyl sulfides with different chain length [L = long ($C_{10}H_{21}-S-C_{10}H_{20}-$), M = medium ($C_3H_7-S-C_4H_8-$) and S = short ($CH_3-S-CH_2-$)] were attached to second- (G2) and third-generation (G3) PPI dendrimers according to a method already published by our group.[17] First, the *n*-alkylthiol was reacted with the ω-bromocarboxylic acid to form the thioether carboxylic acid. Next, the acid was activated with pentafluorophenol and dicyclohexyl-carbodiimide (DCC) and reacted with the amino-terminated PPI by stirring overnight in CHCl₃. Six dendritic dialkyl sulfides were synthesized as shown in Scheme 1. The three second-generation dendrimers (G2) with eight end groups and the three third-generation dendrimers (G3) with 16 end groups have different polarities according to the carbon chain length in the
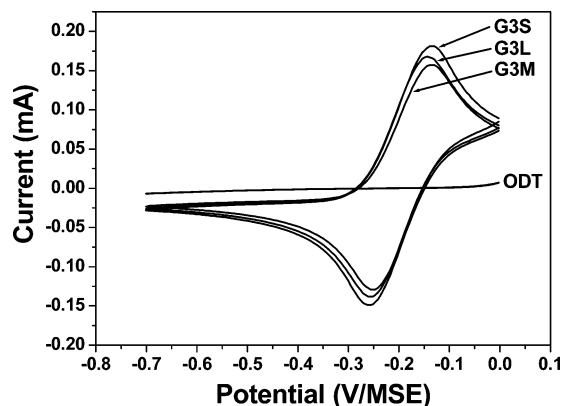
Figure 2. Heterogeneous electron transfer through third-generation dialkyl sulfide dendrimer and ODT SAMs on gold electrodes. [Cyclic voltammetry in 1 mM $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ and 0.1 M K_2SO_4. The scan rate was 100 mV s^{-1}].

Table 1. Advancing (θ_{ADV}) and Receding (θ_{REC}) Water Contact Angles, X-ray Photoelectron Spectroscopy (XPS), and Electrochemical Capacitance (C_{ML}) of Dendritic Dialkyl Sufide SAMs on Gold Substrates

| | θ_{ADV}/θ_{REC} (deg) | | immersion | |
| | | | XPS bound S (%) | C_{ML} (μF cm^{-2}) |
compd	immersion	printing		
G2-S	57/14	82/33	41	28.1
G3-S	52/19	81/30	42	32.5
G2-M	64/24	76/30	25	19.6
G3-M	63/31	79/29	27	17.4
G2-L	58/20	77/32	45	27.0
G3-L	60/19	77/32	51	24.1

dialkyl sulfide end group. ^{1}H NMR, ^{13}C NMR, MALDI-MS, and elemental analysis data (see Experimental Section) are consistent with the expected molecular structures.

SAMs of the dendritic dialkyl sulfides were prepared by two different methods: (i) by immersion of the gold sample for 12 h in a 10^{-5} M dendrimer solution in ethanol and (ii) by printing with an inked ($c \approx 10^{-5}$ M), featureless PDMS stamp for 1 min. In both cases the samples were rinsed with clean solvent after SAM formation to remove the excess of adsorbate. The variation in dialkyl sulfide chain length did not significantly affect the contact angle of the dendrimer SAMs. Dendrimer monolayers formed via printing showed higher contact angles than those formed in solution (Table 1). The higher contact angle of the printed monolayer suggests the transfer of low-molecular-weight PDMS fragments, in particular for the polar dendrimers G2-S and G3-S. The hysteresis between θ_{ADV} and θ_{REC} of about 30–40° for all SAMs indicates a disordered monolayer.

The percentages of sulfur bound to gold have been determined on the basis of the S_{2p} region of the X-ray photoelectron spectrum of the dendritic dialkyl sulfide SAMs (Table 1). The attachment to the gold surface is achieved, for example, with about four sulfur atoms in the case of G3-M, and about six atoms in the case of G3-S. Assuming that more attachment points within one molecule cause a flatter dendrimer conformation, the XPS results are consistent with the ratio of the effective film thickness deduced from the electrochemical capacitance measurements. Higher capacitance values (C_{ML}) generally represent lower monolayer thicknesses.[18]

The dendritic dialkyl sulfide SAMs on gold had much lower blocking ability against electroactive species than an ODT SAM,
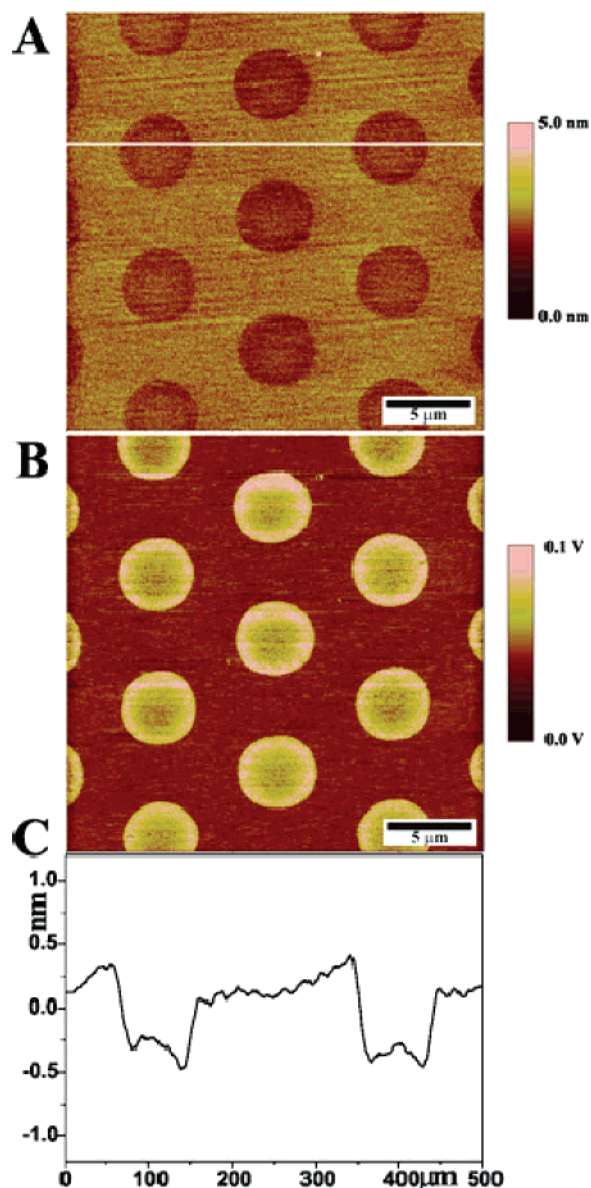
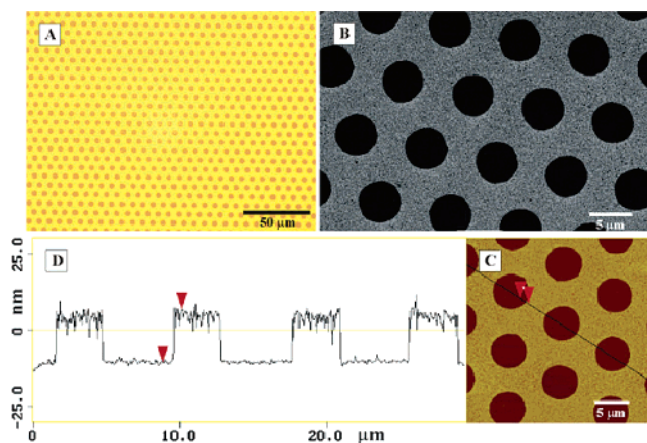(18) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559–3568.

Figure 3. AFM height (A), friction (B), and cross section (C) images of a gold surface patterned by μCP (contact time 60 s) using G3-M ($c = 5 \times 10^{-5}$ M in ethanol) and subsequently immersed in ODT ($c = 10^{-4}$ M in ethanol) for 5 s.

as shown by heterogeneous electron-transfer measurements. Figure 2 shows the cyclic voltammetric current–potential responses for ODT and dendrimer SAMs on gold in 1 mM Fe-$(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ and 0.1 M K_2SO_4. The well-ordered ODT SAM blocked the surface efficiently. The voltammograms of the dendrimer SAMs are distinctly different: the currents were much higher, showing efficient electrochemical reactions between the ferro-/ferricyanide and gold. There were no significant differences between the extent of electron transfer through different dendrimer SAMs. All dendrimers SAMs allowed electrochemical reaction between the electrode and electroactive species in the electrolyte solution.

"Molecular ruler" experiments performed through AFM imaging confirmed that the dendritic dialkyl sulfides absorbed in a flattened conformation on the gold surface. The AFM height and friction images of a patterned gold surface with G3-M and ODT are presented in Figure 3. The G3-M SAM was formed in the dots, where the inked PDMS stamp and the gold surface were contacted during μCP, and the ODT was assembled from solution on the uncovered areas surrounding the dots. The G3-M and the

Figure 4. Images of etched gold patterns produced by $(+)\mu$CP using G3-L (6×10^{-6} M in ethanol) as ink and ODT (10^{-4} M in ethanol) as backfilling, followed by wet etching. The duration of printing was 1 min and the dipping time in ODT was 15 s. The sample was etched in an Fe(III)/thiourea etching bath[2] for 2.5 min at 45 °C. (A) Optical microscopy; (B) scanning electron microscopy (SEM); (C) AFM height; (D) AFM cross-section image.

ODT monolayers can be clearly differentiated in the friction image (Figure 3B). The height image shows that the G3-M SAM is appreciably thinner than the ODT SAM formed during 5 s dipping. The thickness of an *ordered* ODT SAM is about 2 nm,[19] but an ODT SAM assembled in only 5 s may be significantly thinner, which implies a nanometer or even subnanometer dendrimer SAM thickness at most.

The advancing contact angle of the G3-M SAM printed on gold and dipped in ODT solution in ethanol for 5 s increased significantly, from 79° to 103°, approaching the water contact angle of an ODT SAM: 113°.[19] This increase suggests that the voids present in the dendrimer monolayer are filled by ODT molecules and increase the hydrophobicity of the surface. However, the etch resistance of the dendrimer layer remained much lower than that of the ODT SAM.

Positive Microcontact Printing. The high molecular weight of dendrimers, the low etch resistance of their SAMs on gold, and the fact that they are not easily replaced by ODT make the dendrimers excellent inks for $(+)\mu$CP. The SEM and AFM images of a patterned and etched 20 nm thick gold film on a silicon wafer are presented in Figure 4. The dendritic ink was printed on a gold surface for 1 min with a PDMS stamp to form the dot-patterned dendrimer SAM. After that, the sample was immersed in ODT solution for 5−15 s. ODT formed an etch-protective SAM on the remainder of the surface. The dendrimer SAM was not etch-resistant and the gold underneath was etched away to give the positive copy of the original master.

All dendrimers exhibited proper positive ink behavior, resulting in islands where the gold was completely etched away (black dots in Figures 4 and 5). The surrounding matrix was backfilled with ODT for 5−15 s. The packing and quality of the ODT SAM was high enough to act as an etch barrier. An acidic solution of 10 mM Fe(NO$_3$)$_3$, 15 mM thiourea, and 1.2% HCl at 45 °C was found to be optimal for the selective etching of this system.[2] The common alkaline etching solutions [1 M KOH, 0.1 M Na$_2$S$_2$O$_3$, 0.01 M K$_3$Fe(CN)$_6$ and 0.001 M K$_4$Fe(CN)$_6$] did not provide enough selectivity during the etching. The superiority of acidic over alkaline etching baths and the high selectivity of acidic etching system in the case of PPI-based dendrimer SAMs is likely a consequence of the protonation of the amine groups
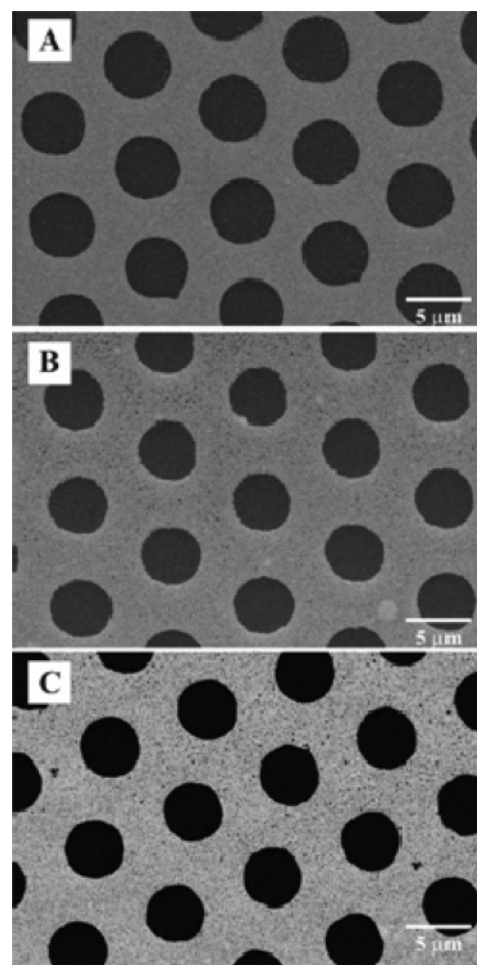

Figure 5. Scanning electron microscopy of etched gold patterns produced by $(+)\mu$CP using as ink (A) G2-M (1.6×10^{-4} M in ethanol), (B) G2-L (10^{-5} M in ethanol), and (C) G2-S (3.3×10^{-5} M in ethanol). The duration of printing in all cases was 1 min, and samples were dipped in ODT for 15 s and etched in an Fe(III)/thiourea etching bath for 2.5 min at 45 °C. G2-S was printed with an oxidized PDMS stamp.

inside the dendrimer: the protonation "swells" the dendrimers and makes the gold surface more accessible for electroactive species.

The $(+)\mu$CP experiments with the second- and third-generation dendrimers with short dialkyl sulfide end groups (G2-S and G3-S) were carried out using oxidized PDMS stamps. These inks are rather polar and therefore assisted the extraction of polar, low molecular weight PDMS impurities from the bulk of the stamps.[20] These impurities obscured the positive pattern formation because of their etch-resistance on the gold surface. It is known that all plasma treatment methods significantly reduced the amount of silicone-related material transferred during printing as compared to untreated PDMS stamps.[21] Indeed, after oxidizing the PDMS stamp surface, G2-S and G3-S were successfully used as positive inks to replicate 5-μm-wide features (Figure 5C).

Dendrimers G2-L and G3-L showed a low solubility in ethanol, while dendrimers G2-S and G3-S were too polar to use conventional PDMS stamps. Therefore, dendrimer G3-M was selected to test the lateral spreading during printing and SAM formation. This dendrimer has optimal solubility, medium polarity, and high molecular weight.

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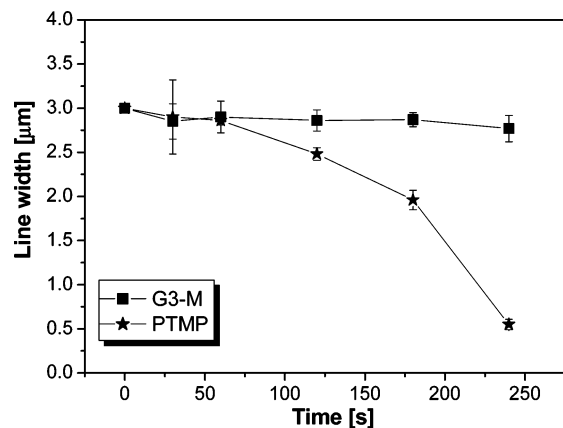(21) Langowski, B. A.; Uhrich, K. E. *Langmuir* **2005**, *21*, 6366−6372.

Figure 6. Plot of the width of the ODT-protected stripe area after $(+)\mu$CP with G3-M and PTMP vs the printing time. After printing the samples were immersed in ODT solution for 10 s, etched in an Fe(III)/thiourea etching bath for 2.5 min at 45 °C, and characterized by means of SEM imaging.

To test the spreading tendency during conformal contact of the stamp with the surface of the dendritic inks, micrometer-sized line patterns of G3-M were printed on gold with increasing printing time. Subsequently, the samples were immersed in ODT solution and etched under identical conditions. SEM was used to characterize the etched surfaces and determine the width of the ODT-protected gold stripes. The results of the printing with G3-M were compared to the results of the same experiments carried out with PTMP as positive ink (Figure 6). Any lateral spreading on the surface during the printing step led to an increase of the ink-covered area and, by necessity, to a decrease of the available bare gold area that would be covered by the ODT SAM. In the case of line patterns, information about the lateral spreading could be obtained by measuring the line width. In Figure 6 the width of the ODT protected stripe area is plotted versus the printing time of G3-M and PTMP. The concentration in weight of the inks was the same in both cases: 0.6 g/L. While the G3-M/ODT system did not show a significant line width decrease with time, the PTMP covered the entire surface within 5-min printing by lateral spreading. Figure 6 indicates that it is not impossible to use PTMP as ink for submicrometer features by carefully controlling the printing time,[22] but this requires a time-consuming optimization of the printing process for each stamp. Faithful submicron feature replication with the dendrimer ink is much more straightforward than with the conventional PTMP.

The spreading of G3-M on the surface was further investigated by $(+)\mu$CP with PDMS stamps made by the combination of capillary force lithography and replica molding.[22] Stamps with 300-nm-wide trenches were prepared by this convenient and inexpensive method. Even for a dendrimer printing time of up to 5 min there was no significant decrease in the width of the ODT-protected areas, which implies a lateral spreading rate of less than 20 nm min^{-1} for G3-M during conformal contact (Figure 7).

To achieve even higher resolution of the replicated patterns, a silicon master with 100-nm-wide gratings (1-μm period) was used to prepare PDMS stamps for $(+)\mu$CP. Because $(+)\mu$CP provides inverse feature replication, a PMMA imprint of the original silicon master was used as a master to prepare PDMS stamps. This feature inversion was necessary to provide the 100-nm-wide gold feature after the $(+)\mu$CP process. Figure 8 shows the result of $(+)\mu$CP experiments performed with G3-M as the

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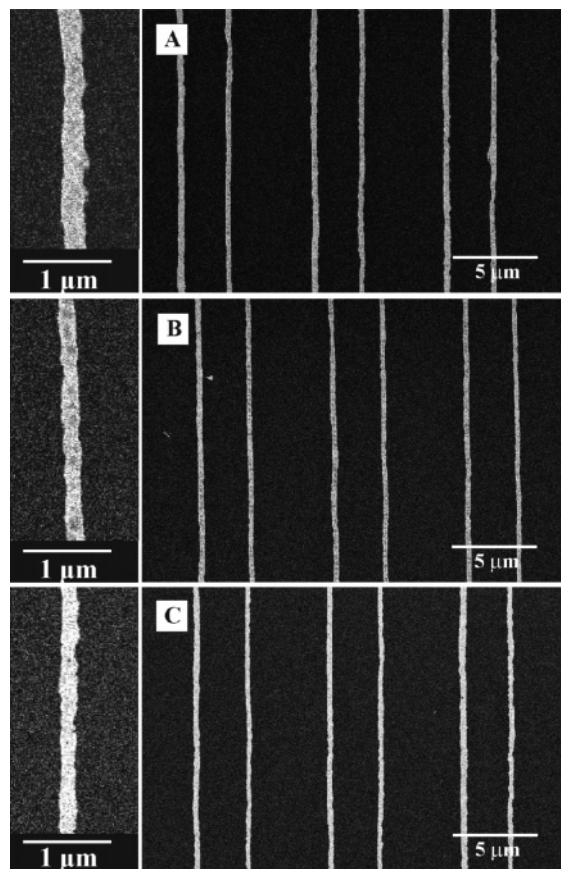

Figure 7. SEM images of etched submicrometer gold lines printed with second-generation stamps prepared by capillary force lithography.[22] The stamp was inked with 5×10^{-5} M G3-M; printed for 1 min (A), 3 min (B), and 5 min (C); subsequently dipped in a 10^{-4} M ODT solution for 5 s; and etched for 2.5 min in an Fe(III)/thiourea etching bath at 45 °C.
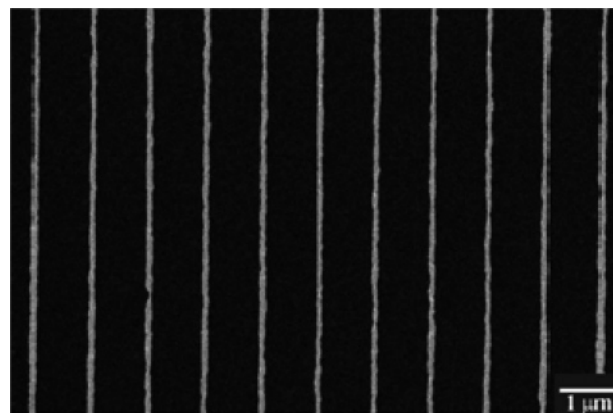

Figure 8. SEM image of 100-nm-wide gold lines made by $(+)\mu$CP [4×10^{-5} M G3-M in ethanol, printing for 2 min, dipping in 10^{-4} M ODT in ethanol 6 s, etching in Fe(III)/thiourea at 45 °C for 2.5 min].

ink and ODT as the etch resist. It is evident from Figure 8 that $(+)\mu$CP with this heavyweight dendritic ink results in faithful replication of features on the order of 100 nm.

Conclusions

We successfully applied PPI dendrimer dialkyl sulfides as inks for positive microcontact printing and demonstrated their low spreading tendency on the surface during conformal contact between the stamp and the gold surface. Well-defined submicrometer gold wires on silicon were fabricated by positive

microcontact printing using stamps made from commercially available PDMS and using acidic $Fe(NO_3)_3$ and thiourea-based etching solutions. The new inks will be useful when sub-100-nm features should be replicated and fabricated by means of microcontact printing.

Experimental Section

Synthesis: All starting materials are commercially available and were used as received. The pentafluorophenylesters of methyl-thioacetic acid and propylthiovaleric acid were prepared in analogy to described procedures.[17] The synthesis of G2-L and G3-L have been described elsewhere.[17] G2-S, G3-S, G2-M, and G3-M were prepared in a similar way. The procedure for G3-M is as follows.

Modification of Third-Generation Poly(propyleneimine) Dendrimer with Medium Dialkyl Sulfide Chain (G3-M). The third-generation amine-terminated poly(propyleneimine) dendrimer (206 mg, 0.15 mmol) was dissolved in dry $CHCl_3$ (4 mL) and a solution of the pentafluorophenyl ester of propylthiovaleric acid (1.05 g, 3 mmol) in 6 mL of $CHCl_3$ was added to it. The solution was stirred at room temperature for 2 days under N_2 atmosphere. After the reaction the brownish mixture was washed twice with K_2CO_3 (0.05 M) and demineralized water (pH = 7). The organic phase was concentrated and was added dropwise to stirred isopropyl ether. The suspension was centrifuged and the solution above the oily and viscous precipitate was removed by decantation. Finally, the collected product was dried in high vacuum. Yield: 561 mg (89%) yellowish viscous liquid.

G3-M. ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.0$ (48H, t, CH_3), 2.5 (64H, t, SCH_2), 2.3 (32H, t, CH_2CH_2CO), 3.3 (32H, m, CONHCH_2), 2.6 (84H, m, NCH_2), 1.8−1.5 (156H, m, −$(CH_2)_n$−), CONH not visible. ^{13}C NMR ($CDCl_3$, ppm): $\delta = 173.5$ (NHCO), 51.9 (NCH$_2$CH$_2$-CH$_2$CH$_2$N), 51.4 (NCH$_2$CH$_2$CH$_2$N), 51.0 (NCH$_2$CH$_2$CH$_2$NH), 37.3 (NHCH$_2$), 35.9 (COCH$_2$), 34.2 (CH$_2$SCH$_2$), 31.7 (CH$_2$), 29.2 (NCH$_2$$CH_2CH_2$N), 25.0 (CO$CH_2CH_2$), 22.9 ($CH_3CH_2$), 13.5 ($CH_3$). $C_{216}H_{432}N_{30}O_{16}S_{16}$ (FW = 4219.0). Elemental analysis found: C = 60.53, H = 11.05, N = 10.07. Calcd: C = 61.49, H = 10.32, N = 9.95. MALDI-TOF-MS: $m/z = 4220$ [M + H$^+$].

G2-M. Yield: 940 mg (91%) as a yellowish viscous liquid. ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.0$ (24H, t, CH_3), 2.5 (32H, t, SCH_2), 2.3 (16H, t, CH_2CH_2CO), 3.3 (16H, m, NHCH_2), 2.8 (36H, m, NCH_2), 1.8−1.6 (76H, m, −$(CH_2)_n$−), CONH not visible. ^{13}C NMR ($CDCl_3$, ppm): $\delta = 173.4$ (NH-CO), 53.6 (NCH$_2$CH$_2$CH$_2$$CH_2$N), 51.9 (N$CH_2$-CH$_2CH_2$N), 51.6 (N$CH_2CH_2CH_2$NH), 37.8 (NH$CH_2$), 36.3 (CO$CH_2$), 34.5 ($CH_2SCH_2$), 32.0 (S$CH_2CH_2$), 29.6 (NCH$_2$$CH_2CH_2$NH), 27.0 (NCH$_2$$CH_2CH_2$N), 25.3 (CH$_2$), 23.2 (CH$_2$), 13.7 ($CH_3$). $C_{104}H_{208}$-$N_{14}O_8S_8$ (FW = 2039.4). Elemental analysis found: C = 59.99, H = 10.07, N = 9.17. Calcd: C = 61.25, H = 10.29, N = 9.61. MALDI-TOF-MS: $m/z = 2040$ [M + H$^+$].

G2-S. Yield: 720 mg (78%) as a yellowish viscous liquid. ^{1}H NMR (D_2O, ppm): $\delta = 2.0$ (24H, s, CH_3), 3.1 (16H, s, SCH_2CO), 3.5 (16H, m, NHCH_2), 2.5−2.3 (36H, m, NCH_2), 1.6−1.4 (28H, m, −$(CH_2)_n$−), CONH not visible. ^{13}C NMR (D_2O, ppm): $\delta = 172.5$ (NHCO), 53.0 (NCH$_2$CH$_2$CH$_2$$CH_2$N), 51.3 (N$CH_2CH_2CH_2$N), 50.6 (N$CH_2CH_2CH_2$NH), 38.0 (NH$CH_2$), 37.1 (CO$CH_2$), 25.3 (NCH$_2$$CH_2$-CH$_2$NH), 23.6 (NCH$_2$$CH_2CH_2$N), 21.7 ($CH_2$), 15.3 ($CH_3$). $C_{64}H_{128}$-$N_{14}O_8S_8$ (FW = 1478.3). Elemental analysis found: C = 51.87, H = 8.62, N = 13.39. Calcd: C = 51.99, H = 8.72, N = 13.26. MALDI-TOF-MS: $m/z = 1479$ [M + H$^+$].

G3-S: Yield: 298 mg (78%) yellowish viscous liquid. ^{1}H NMR (D_2O, ppm): $\delta = 2.0$ (48H, s, CH_3), 3.1 (32H, s, SCH_2CO), 3.4 (32H, m, NHCH_2), 2.8−2.6 (84H, m, NCH_2), 1.7−1.5 (60H, m, −$(CH_2)_n$−), CONH not visible. ^{13}C NMR (D_2O, ppm): $\delta = 172.5$ (NHCO), 53.3 (NCH$_2$CH$_2$CH$_2$$CH_2$N), 51.3 (N$CH_2CH_2CH_2$N), 50.6 (N$CH_2CH_2CH_2$NH), 38.1 (NH$CH_2$), 37.2 (CO$CH_2$), 25.3 (NCH$_2$$CH_2$-CH$_2$NH), 23.5 (NCH$_2$$CH_2CH_2$N), 21.8 (CH$_2$), 15.4 ($CH_3$). $C_{136}H_{272}$-$N_{30}O_{16}S_{16}$ (FW = 3096.9). Elemental analysis found: C = 51.18,

H = 7.77, N = 12.10. Calcd: C = 52.74, H = 8.85, N = 13.57. MALDI-TOF-MS: $m/z = 3098$ [M + H$^+$].

Microcontact Printing. Stamps were prepared from commercially available Sylgard-184 poly(dimethylsiloxane) (Dow Corning). The curing agent and the prepolymer were manually mixed in 1:10 volume ratio and cured overnight at 60 °C against the master. The cured stamp was pealed off from the master at the curing temperature. Silicon masters with micrometer-sized features were fabricated by photolithography. The silicon master with submicrometer lines was obtained from our NaPa partner AMO GmbH.

Gold substrates were obtained from Ssens BV (Hengelo, The Netherlands) as a layer of 20 nm gold on titanium (2 nm) on silicon. Before use, the substrates were treated with oxygen plasma, immersed in ethanol for 1 h, rinsed with water (Millipore) and ethanol, and dried with nitrogen.

All glassware was cleaned with Hellmanex II (Helma GmbH & CoKG) (sonicated in a 2% aqueous solution).

Before printing, the stamps were rinsed with pure ethanol and dried in a filtered steam of nitrogen. The stamps were inked with a few drops of solution of the dendrimer in ethanol ($\approx 10^{-5}$ M). After drying the surface of the stamps with nitrogen, conformal contact was achieved manually. In the case of micrometer-sized features the stamps were weakly pressed against the gold surface at the initial stage of the printing to induce the formation of conformal contact. No external pressure was applied during the printing of submicrometer features.

The etching solution consisted of 10 mM $Fe(NO_3)_3$, 15 mM thiourea, and 1.2% HCl. Before every μCP experiment the freshly prepared etching solution was kept at 45 °C in a warm bath for 10 min before the samples were etched.

Monolayer Characterization. *Contact angles* were measured on a Krüsss G10 contact angle setup equipped with a CCD camera. Advancing and receding contact angles were determined automatically during growth and reduction of a clean water droplet by the droplet shape analysis routine.

XPS measurements were performed on a Quantera scanning X-ray multiprobe instrument from Physical Electronics, equipped with a monochromatic Al Kα X-ray source producing approximatly 25 W of X-ray power. Spectra were referenced to the main C 1s peak set at 284.0 eV. A surface area of $1000\,\mu m \times 300\,\mu m$ was scanned with an X-ray beam about 10-μm-wide.

Electrochemical measurements were performed in a three-electrode setup using the SAM-covered gold plate as working electrode, a platinum disk as counter electrode, and a Hg/HgSO$_4$ (MSE) as reference electrode. [$E°_{Hg/HgSO_4} = 0.62$ V vs normal hydrogen electrode (NHE)]. An AUTOLAB PGSTAT10 equipped with a frequency response analysis (FRA) module for electrochemical impedance spectroscopy was used for the measurements, and 0.1 mM K_2SO_4, 1 mM $K_3Fe(CN)_6$/$K_4Fe(CN)_6$ in water was used for cyclic voltammetry.

AFM analyses were carried out with a NanoScope III (Veeco/Digital Instruments, Santa Barbara, CA) multimode atomic force microscope equipped with a J-scanner, in contact mode by using Si_3N_4 cantilevers (Nanoprobes, Veeco/Digital Instruments) with a nominal spring constant of about 0.32 N m^{-1}. To ensure maximum sensitivity for lateral forces in the friction-force images, the sample was scanned at 90° with respect to the long axis of the cantilever. AFM imaging was performed at ambient conditions.