

Supporting Information

Solid-phase Microcontact Printing for Precise Patterning of Rough Surfaces: Using Polymer- Tethered Elastomeric Stamps for the Transfer of Reactive Silanes

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Table S1. Characterization of the polymer (PTrisAAm) brush-modified substrates and the free polymer in 1,4-dioxane:water (1:1) mixture at 70 °C for 14 h.

Sample code	Substrate type	Targeted DP	Mn, Polymer ^a (kg mol ⁻¹)	Đ ^a	Conversion (%) ^b	Brush length [nm], AFM	Brush length [nm], ellipsometry
St 1	Stamp (Flat)	20	4.20	1.30	>99	30	---
St 2	Stamp (Flat)	100	14.48	1.26	>99	67 ± 30	---
St 3	Stamp (*Structured)	200	14.93	1.38	97.6	---	---
St 4	Stamp (Flat)	200	27.54	1.46	>99	70 ± 29	---
St 5	Stamp (Flat)	200	29.70	1.46	>99	70 ± 29	---
St 6	Stamp (Flat)	200	33.94	1.67	90.9	---	---
St 7	Stamp (Structured)	200	43.69	1.26	92.0	---	---
St 8	Stamp (Flat)	500	29.33	1.63	98.8	84 ± 31	---
W 1	Si wafer (**)	200	32.80	1.43	89	11 ± 2	20 ± 4
P 1	Polymer in solution (No grafting)	200	23.11	1.20	76	---	---

^adetermined by SEC (NMP Eluent using PS standards)

^bdetermined by ¹H-NMR, using the intensity of the signal belonging to one hydrogen on PTrisAAm and its ratio to total intensity of one hydrogen on TrisAAm monomer together with one hydrogen on PTrisAAm polymer

*See Figure S1 (B)

** Here, the grafted wafers obtained in the simultaneously performed batches of this polymerization have been used for the brush length analysis.

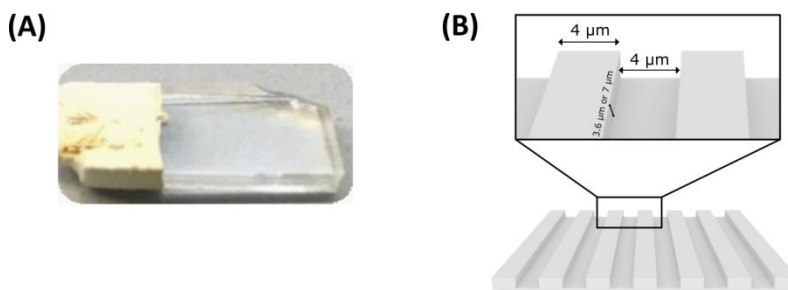


Figure S1. (A) Photo of grafted PDMS stamp covered with PTFE stripe to detect the grafted brush length (B) Illustration of a structured PDMS stamp.

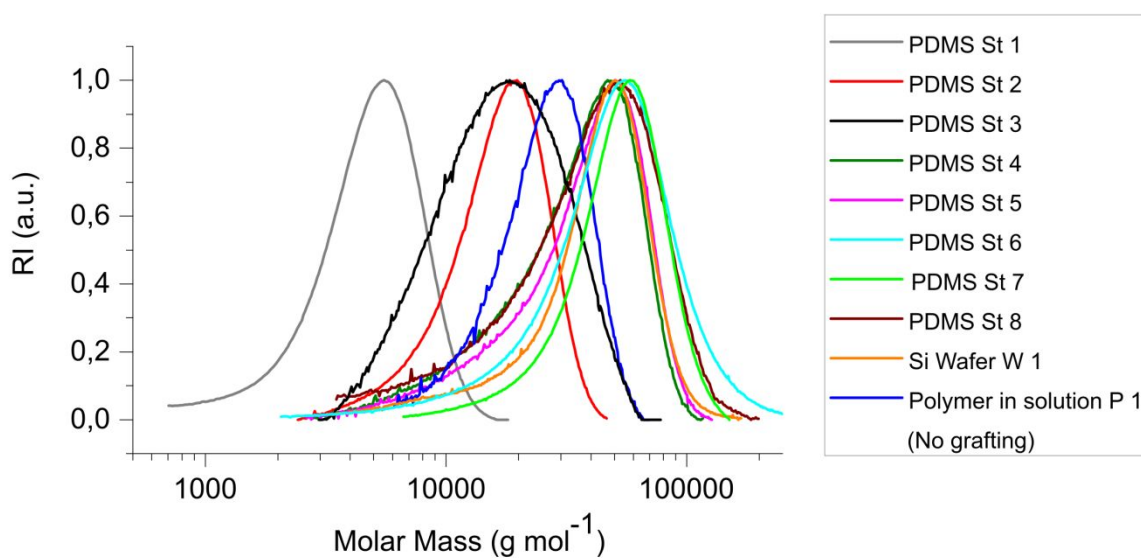


Figure S2. Molecular weight distribution models of polymers shown in Table S1.

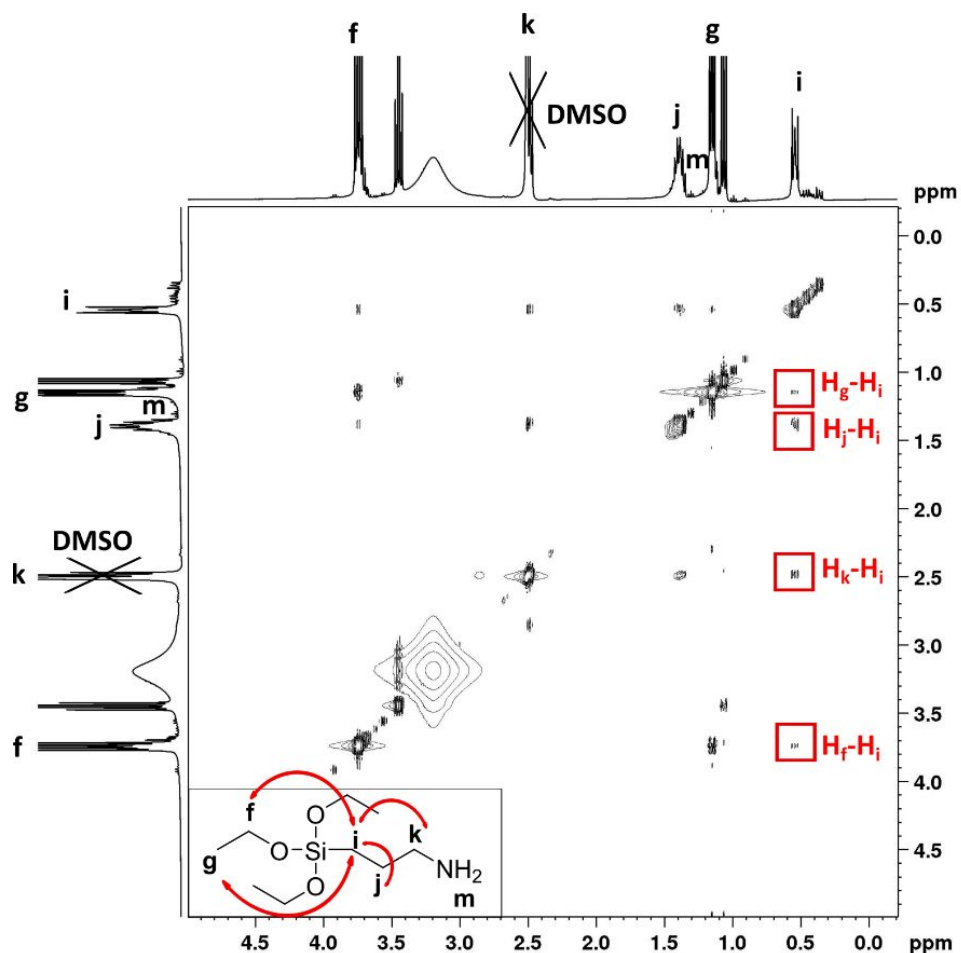


Figure S3. ^1H - ^1H NOESY spectrum (400 MHz, DMSO-d_6) of APTES.

In the comparison of ^1H - ^1H NOESY spectra of APTES conjugated PTrisAAm and APTES mixed PTrisAAm it could be argued that the signal *d* is overlapping with another signal *k* which belongs to APTES proton and cause a sign on the same spot due to the correlation of APTES protons within itself. For this purpose, the analysis of ^1H - ^1H NOESY spectrum of pure APTES is performed (Figure S) and it is proven that there is no sign of correlation of APTES molecule itself (between *k* and *i*) on the aforementioned spot.

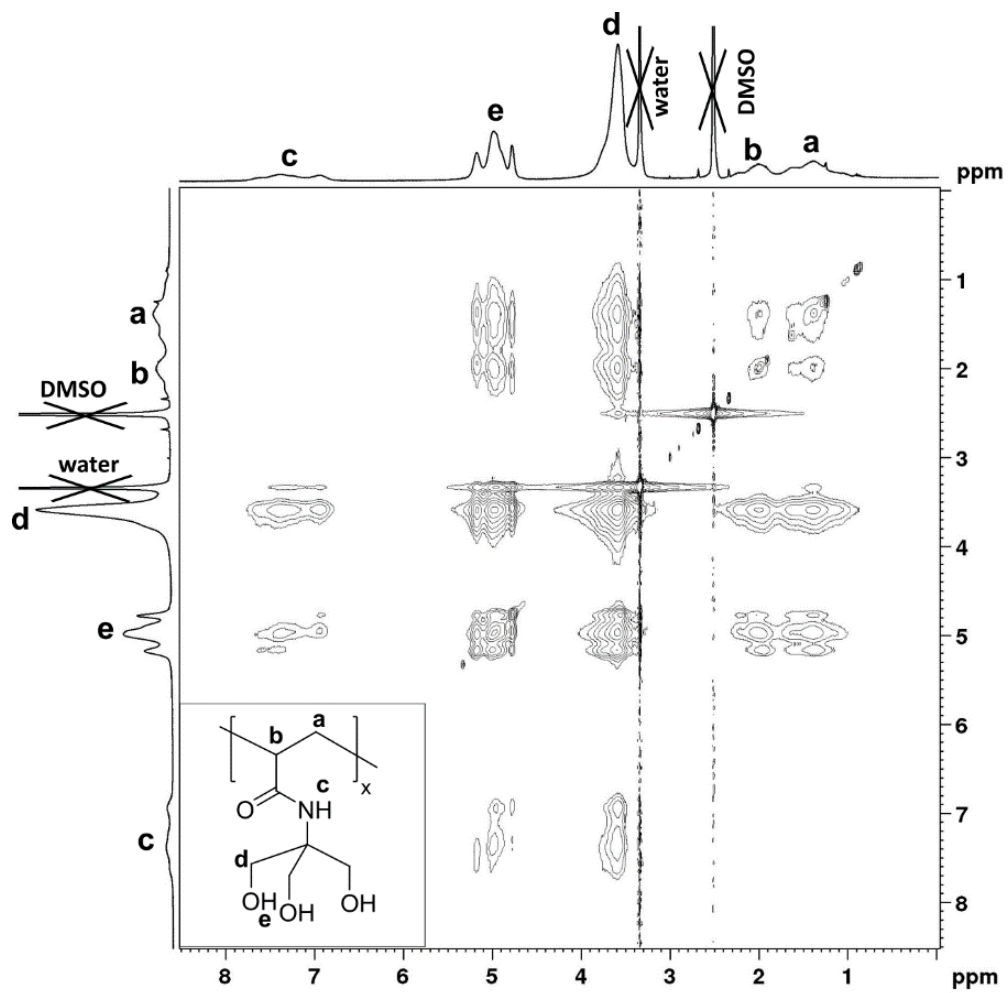


Figure S4: ^1H - ^1H NOESY spectrum (400 MHz, DMSO-d_6) of PTrisAAm.

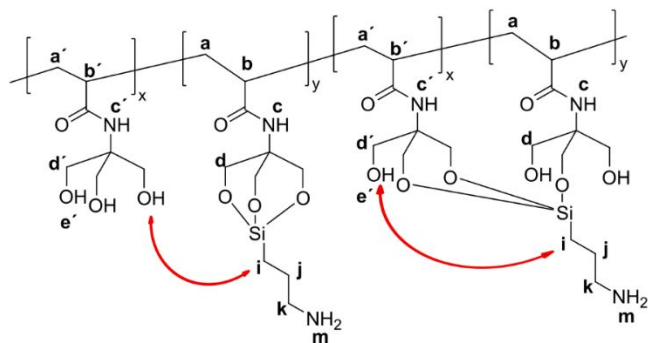
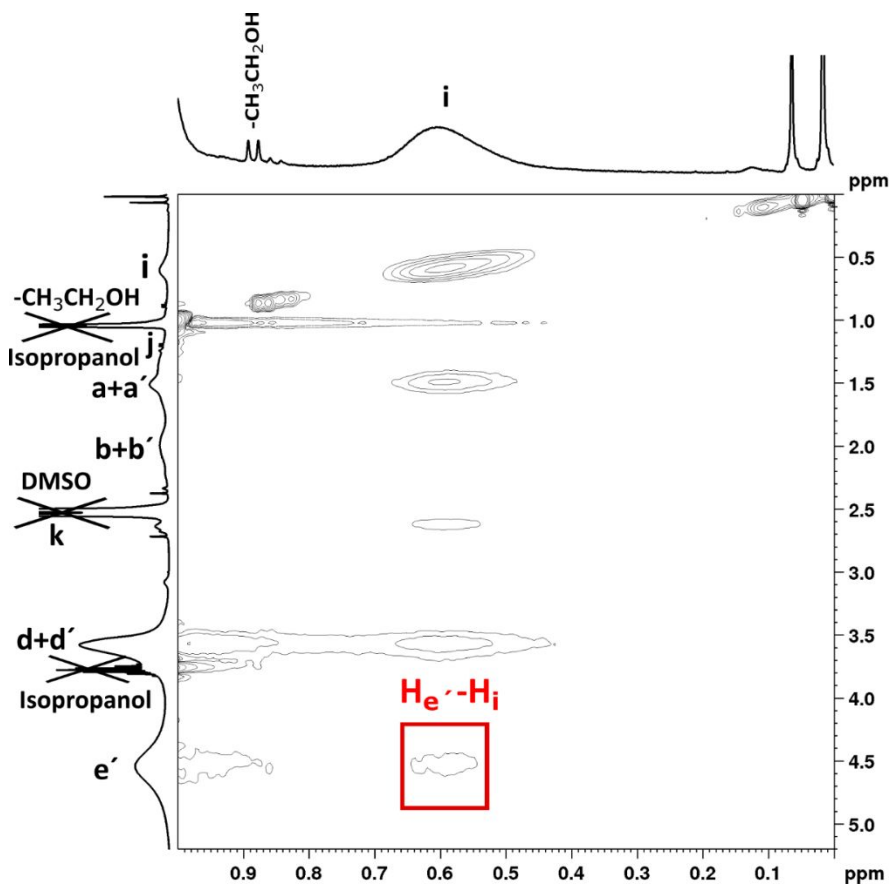


Figure S5: Zoom-in view of the ^1H - ^1H NOESY spectrum (400 MHz, DMSO-d_6) of the PTrisAAm-APTES conjugate (P1 conjugated with APTES). Herein, the presence of faintly pronounced cross-peaks indicating a scalar coupling between the APTES-bound protons (e.g. signal i) and the signals of an unsubstituted hydroxy moiety e' is observable.

As it has been reported, the polymer-bound hydroxy moieties strongly interact with hydroxy functionalities even from adjacent monomeric units as a result of their strong ability to form hydrogen bonds.^[S1] Accordingly, a NOESY cross-correlation can also be observed between the

silane signals and signals emerging from adjacent monomeric units. The occurrence of the faintly pronounced cross-peak H_e-H_i suggests this assumption. In addition, due to this interaction, it seems also plausible that an APTES molecule may be bound to hydroxy functionalities of two adjacent monomeric units, thereby, bridging them.

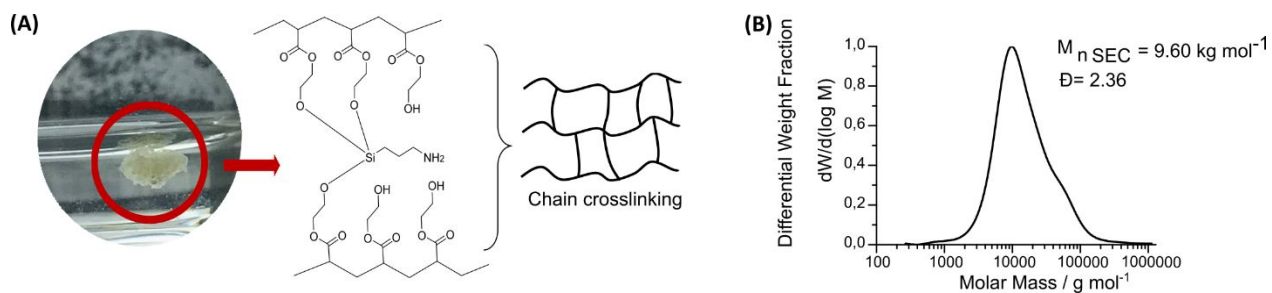


Figure S6. (A) Photo of chain crosslinking occurred after APTES conjugation of PHEA (B) SEC data of corresponding PHEA that is performed by ATRP. Sample measured against Pullulan-Standards in DMSO with 0.1 M LiBr, Oven temperature 80 °C, flow: 1 mL min⁻¹.

Table S2. Ellipsometry results of the PTrisAAm grafted Si wafers - Before and after inking.

Substrate Code	Targeted DP	Average thickness (nm)
W1-Before inking	200	20±4
W1-After inking	200	20±1

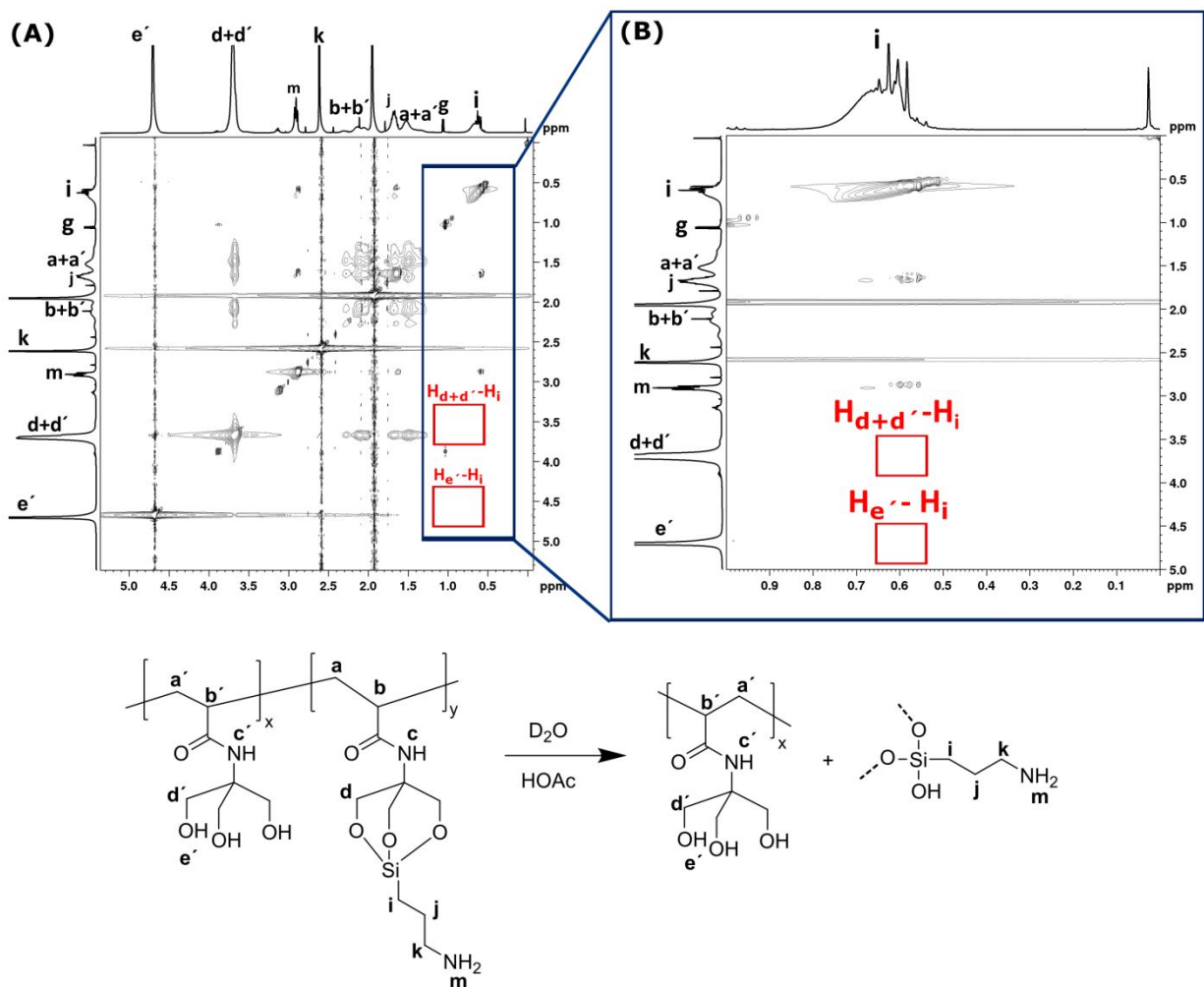


Figure S7. ¹H-¹H NOESY spectrum (400 MHz, D₂O with 1% v/v CH₃COOH) of PTTrisAAM-APTES conjugate. (A) shows a full spectrum, whereas (B) represents a zoom-in view of the correlation of signal *i* with the polymeric backbone. Under acidified aqueous conditions, the ink detaches from the polymer as indicated by the loss of proton couplings between signals originating from the polymer and proton signals that can be assigned to the APTES ink (exemplary indicated by the absence of a coupling signals between H_{e'} and H_i and also between H_{d'} and H_i). Consequently, these conditions, which are applied on the APTES inked stamp during the printing process, induce detachment of the ink from the PTTrisAAM carrier polymer.

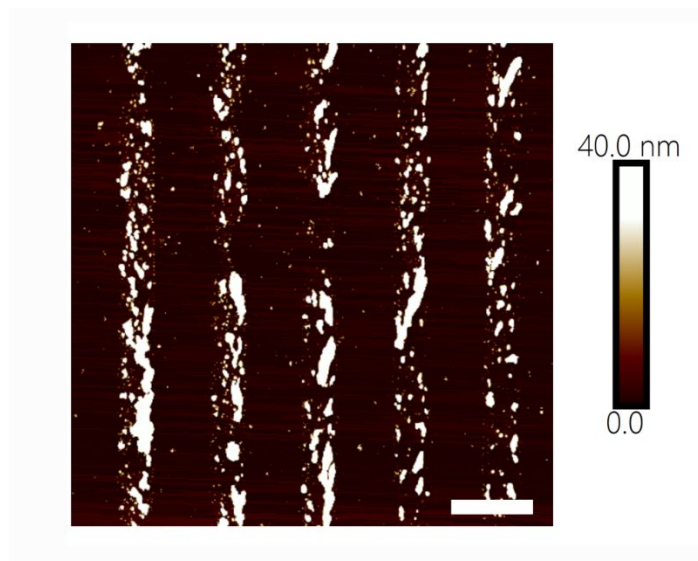


Figure S8: AFM image of the substrate after 1st printing washed by ethanol and MiliQ water. The stripe pattern withstands the washing procedure, which indicates the formation of a printing layer covalently attached to the printing substrate. The scale bar is 10 μm .

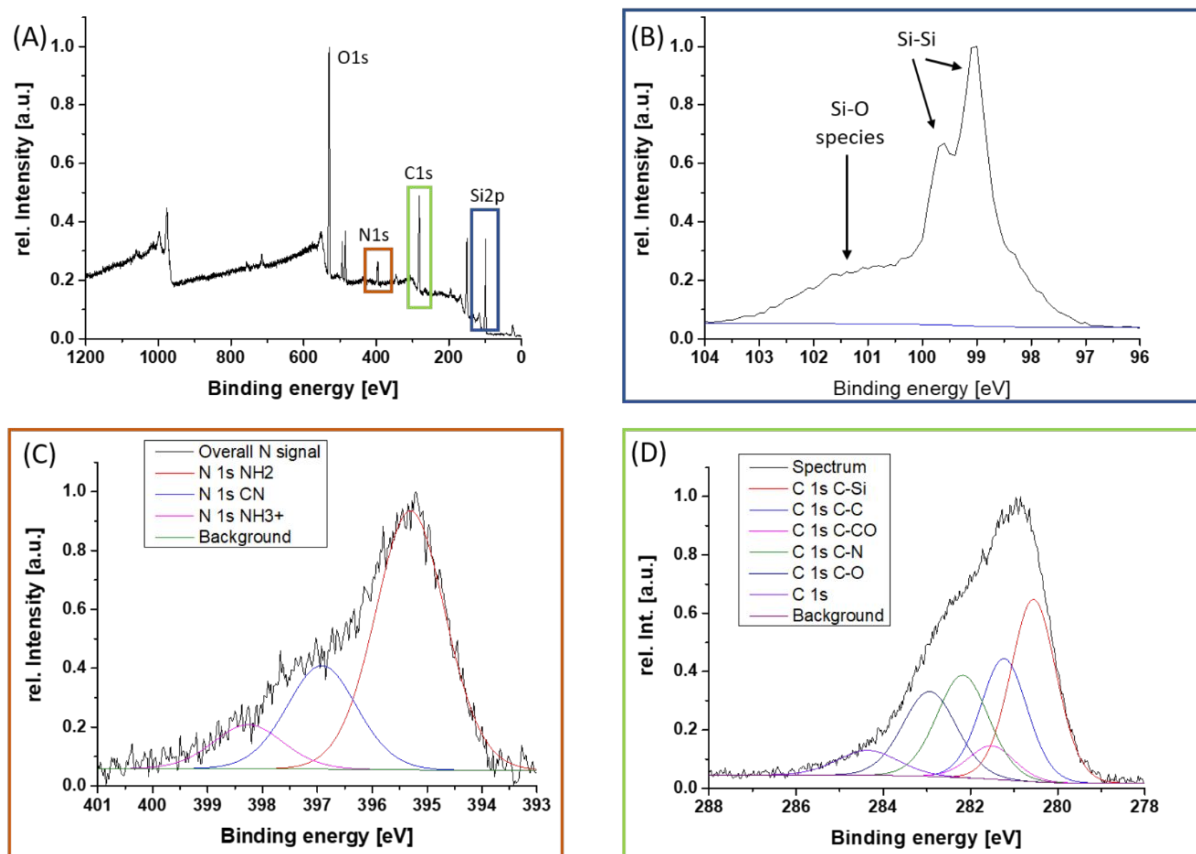


Figure S9. XPS data of a silicon wafer subjected to the solid-phase microcontact printing with a flat stamp. (A) depicts the full signal region. *Zoom in*-views show the characteristic region for silicon Si2p (B), nitrogen N1s (C) and carbon C1s (D). A more profound discussion of the findings is provided in the text below.

To obtain an insight into the chemical nature of the printed areas, X-ray photoelectron spectroscopy (XPS) was conducted. Exhibiting a penetration depth of ~ 10 nm, this method is capable of elucidating the elemental composition of the superficial, imprinted layer. As sample, a Silicon wafer was analyzed, which was addressed *via* a μ CP process using a flat stamp (stamp St 6) and used directly for analysis.

The resulting XPS spectra are depicted in Figure S 9. An overall spectrum in Figure S 9(A) shows a set of signals, corresponding to the binding energies characteristic for Si, C, O and N at the wafer

surface. A closer look into the individual peaks allows for a more profound chemical description of the printing layer.

A *zoom in*-view of the region specific for Si(2p) is depicted in Figure S 9(B). This view reveals an overlay of several signals, of which the doublet at ~ 99 eV can be attributed to elemental Si, whereas the signals at higher binding energies are characteristic for Si-O species. These may originate from a superficial layer of SiO₂ as a result of the wafer surface oxidation, which was applied prior to the printing procedure. Alternatively, the presence of Si-O species is also indicative for condensation products of alkoxy silanes, and can, therefore, already be a first hint for the transfer APTES to the substrate. To conclude more specifically on the APTES transfer, the signal region < 400 eV was investigated as shown in Figure S 9(C). This region, which is indicative for N(1s) shows a broad, asymmetric peak. Note, that a charge neutralizer was applied due to the insulating character of the sample top layer. As a result of a charge overcompensation, a linear peak shift by 3.85 eV has to be considered for the nitrogen signals (which emerge from the substrate's top layer). The shape of this peak can be explained by a sum of three different nitrogen signals characteristic for the un-protonated and quaternized amino functionalities (R-NH₂ and R-NH₃⁺), along with a further signal which shows the presence of an oxidized amino species of unknown origin at the surface. The former two of the underlying species strongly suggest the transfer of APTES. In addition, also the carbon region C1s was investigated in more detail (Figure S9 (D)). The shape of this peak occurring at this region seems more complicated, and can be explained by the sum of signals characteristic for C-C and C-N bonds, being indicative for APTES transfer. To reproduce the measured peak more accurately, we considered also the transfers of other compounds that could be transferred during μ CP, which are PDMS, also in its oligomeric form, along with some residual PTrisAAm polymer. Accordingly, signals characteristic for C-CO

bonds as well as for C-Si bonds were implemented in the model fit. A linear combination of signals characteristic for the aforementioned bonds represented the shape of the measured peak the most accurate. In particular, the shoulder at 284.4 (peak at 280 eV has to be corrected to due to charge neutralization) suggests a pronounced underlying signal characteristic for C-Si. These facts, in sum, indicate the transfer of (oligomeric) PDMS as well as a small fraction of the carrier polymer PTrisAAm, which accompany the transfer of APTES. The APTES transfer is strongly suggested by the nitrogen spectrum as shown in Figure S 9 (C).

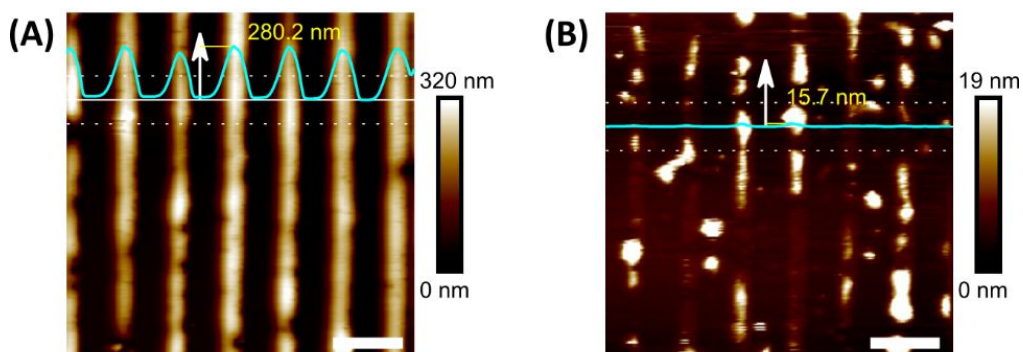


Figure S10. AFM-height images of the printing experiments performed without the sacrificial printing process. Accordingly, unexpected topographies were observed. (A) Before washing the printed substrate (B) After washing the printed substrate. In order to avoid the formation of said stripes, the protocol had to be adapted. The scale bars are 10 μm . These topographies can only be explained by the transfer of remaining oligomers inside the PDMS stamp and the diffused solvents during the grafting from, inking processes.

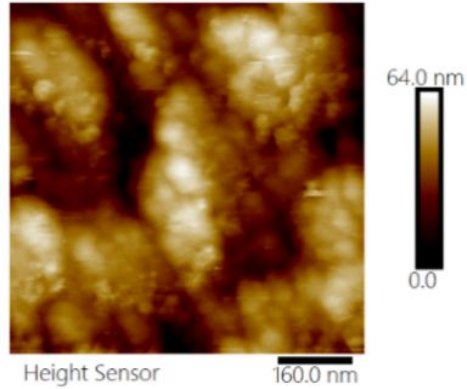


Figure S11. AFM-height image of silica gel modified glass showing 61 nm average roughness. The scale bar is 160 nm.

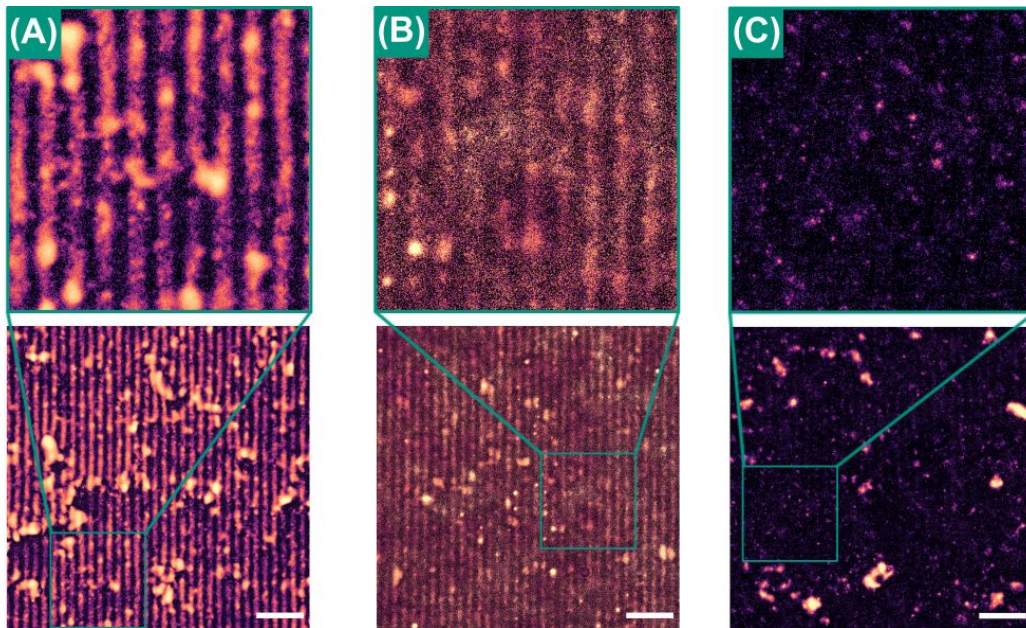


Figure S12. Printing on silica gel modified glass (after washing). Fluorescence microscopy images of the printings performed on silica gel modified glass and its inset: (A) with bare PDMS stamp-without grafted polymer and without covalently attached ink (Rh6G) (B) printing with polymer grafted PDMS stamp-without covalently attached ink (Rh6G) (C) printing with polymer grafted PDMS stamp-with covalently attached ink (APTES). The scale bars are 40 μm .

REFERENCES

[S1] Saito, N.; Sugawara, T.; Matsuda, T. Synthesis and Hydrophilicity of Multifunctionally Hydroxylated Poly(Acrylamides). *Macromolecules* **1996**, *29* (1), 313–319.