

Hydrophilic Elastomers for Microcontact Printing of Polar Inks

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A moderately hydrophilic, thermoplastic elastomer (poly(ether-ester)) was investigated as a stamp material for microcontact printing of a polar ink: pentaerythritol-tetrakis-(3-mercaptopropionate). Stamps with a relief structure were produced from this polymer by hot embossing, and a comparison was made with conventional poly(dimethylsiloxane) (PDMS) and oxygen-plasma-treated PDMS. It is shown that the hydrophilic stamps can be used for the repetitive printing (without re-inking) of at least 10 consecutive patterns, which preserve their etch resistance, and this in rather sharp contrast to conventional and oxygen plasma-treated PDMS stamps. It is argued that these enhanced printing characteristics of the hydrophilic stamps originate from an improved wetting and solubility of polar inks in the hydrophilic stamp.

Introduction

In recent years, soft lithography has become a widespread technique to chemically pattern various substrates.¹ As such, microcontact printing (μ CP), has attracted significant attention, primarily because of its processing advantages in comparison to conventional lithographic techniques. In μ CP, the relief structure of a stamp is used to locally transfer ink from the stamp to a substrate. There the ink forms a self-assembled monolayer (SAM), which can then be used for instance, as a resist against etching (Figure 1). A wide variety of inks, including alkanethiols,² alkyltrichlorosilanes,³ proteins,⁴ and polymers,⁵ have been printed on various inorganic substrates, such as gold, silver, silicon, aluminum oxide and glass.

Currently the most common stamp material is poly(dimethylsiloxane) (PDMS). PDMS is a very soft, chemically cross-linked rubber, which easily establishes conformal contact with a substrate and exhibits excellent printing characteristics with apolar inks, such as alkanethiols. One of the drawbacks of PDMS is its very low modulus (~ 2 MPa), which makes it unsuitable for high-resolution μ CP due to pairing, sagging and collapse of the relief structure.⁶ A variety of methods were proposed to

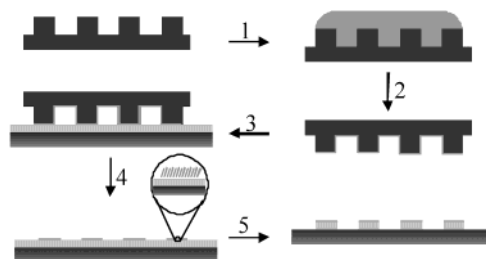


Figure 1. Schematic representation of the microcontact printing process. The inking solution is applied to a structured stamp (1), and the solvent is evaporated (2). The stamp is then brought into contact with the gold-coated substrate (3), and a monolayer is self-assembled (4). This monolayer acts as a resist against etching (5).

overcome this problem, based on the modification of PDMS and/or the use of thermoplastic elastomers.^{7,8,9} Another drawback of PDMS is related to its hydrophobicity, which is a limitation in the μ CP of more polar inks. Such polar inks often exhibit poor wetting characteristics in combination with the hydrophobic PDMS. More importantly, these polar inks also exhibit poor solubility in PDMS and consequently, repetitive printing (without re-inking) of such inks is problematic.

Several methods have been developed to render the PDMS surfaces more hydrophilic, most of them based on an oxygen-plasma treatment. Donzel and co-workers demonstrated that the temporarily hydrophilizing effect of the plasma treatment, which in itself was effective for no longer than 1 h, can be stabilized by grafting poly(ethylene glycol) to the surface.¹⁰ However, this is a surface

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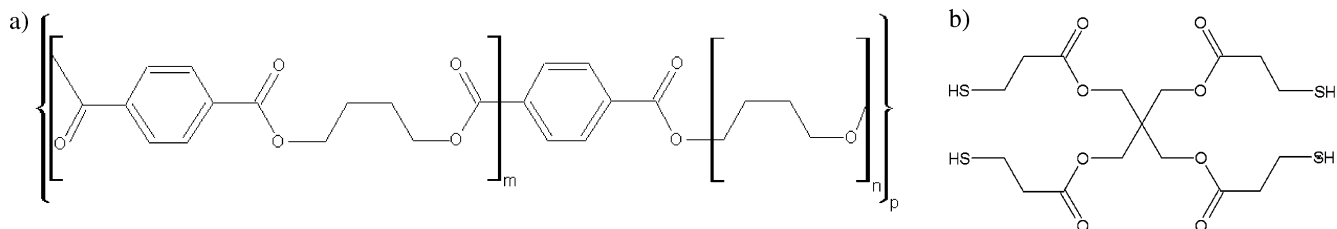


Figure 2. (a) The molecular structure of the poly(ether-block-ester) (PEE). The multiblock copolymer is comprised of hard poly(butyl terephthalate) (PBT) segments and soft poly(tetramethylene glycol) (PTMG) segments. (b) Molecular structure of the ink, pentaerythritol-tetrakis(3-mercaptopropionate) (PTMP).

effect only. Although the surface of such treated stamps wets polar inks, uptake of these inks into the stamp is unlikely which probably makes repeated printing without re-inking difficult. In fact, the barrier properties of the plasma-etched top layer prohibit diffusion of the ink in and out of the bulk of the stamp.¹¹

Here, the printing behavior of a hydrophilic thermoplastic elastomer in combination with polar ink is investigated. A special emphasis is placed on the repetitive printing of self-assembled monolayers and on the etch resistance of these printed patterns.

Experimental Section

Materials.

Poly(tetrafluoroethylene-co-hexafluoropropylene) (Teflon FEP 100, Dupont, Luxembourg, Luxembourg), poly(dimethylsiloxane) (Sylgard 184, Dow Corning, Midland, MI), pentaerythritol-tetrakis(3-mercaptopropionate) (96%, Sigma-Aldrich, Zwijndrecht, The Netherlands), NaCN (97%, Sigma-Aldrich), $K_3Fe(CN)_6$ (98%, Sigma-Aldrich), KOH (85%, Sigma-Aldrich), and ethanol (99.9%, Biosolve, Valkenswaard, The Netherlands) were employed. These materials were used as received, without further modification. Tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane (ABCR, Karlsruhe, Germany) was also used as received, but stored under argon. Poly(ether-ester) multiblock copolymer granules (Arnitel EM400, DSM, Geleen, The Netherlands) were dried for 1 h in a vacuum oven, at 70 °C, prior to use.

Masters.

A calibration grating (TGZ03, Mikromasch, Tallinn, Estonia) for scanning probe microscopy (SPM) was used to prepare grating stamps. To prepare flat stamps, polished silicon (Topsil, Frederikssund, Denmark) was used. To promote release of the polymer from the silicon after replication, the silicon surface was fluorinated using a vapor phase reaction. For this purpose the surface was first oxidized for 5 min by an oxygen plasma at a pressure of 1 mbar and 75 W, using a plasma asher (Emitech K1050X, Ashford, England). The vapor phase reaction was carried out by placing the activated silicon for 1 h in a desiccator containing a drop of tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane at a pressure of 100 mbar. Finally, the silicon was taken out of the desiccator and dried for 1 h at 80 °C in a vacuum.

Preparation of Stamps.

For the preparation of flat (unpatterned) stamps, the fluorinated polished silicon wafer was used as a master; for the preparation of patterned stamps, a fluorinated SPM calibration grating (TGZ03) was used. Poly(ether-ester) stamps were prepared using an intermediate poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) inverse replica of the silicon master. This FEP inverse replica was hot embossed by compression molding in a special machine in which a load and temperature could accurately be applied (Tribotrack, Dacia Instruments, Goleta, CA). This was done at 330 °C, while applying a load of 200 g for 5 min.¹² This intermediate was then used for the hot embossing of the PEE in the Tribotrack, at 230 °C (bottom heater). The PEE

was embossed by placing a granule on the FEP and gently pushing it down until it begins to melt at the bottom. To make identical PDMS stamps, these FEP intermediates were used as masters for cast molding. This was done by mixing the base and curing agent in a 10:1 ratio, degassing this mixture, pouring it onto the master and curing for 24 h at 70 °C. To prepare PDMS stamps with a hydrophilic surface (*ox*-PDMS), normal PDMS stamps were given an oxygen-plasma treatment (1 mbar, 50W) for 15 s.

Microcontact Printing Procedure.

Glass substrates were first cleaned in an UV ozone chamber (UVP PR-100, Upland, CA). On these glass substrates a titanium primer layer (± 5 nm, 8×10^{-8} mbar, 10 kV) was vapor deposited, followed by a gold top layer (± 20 nm, 1×10^{-7} mbar, 10 kV) in an evaporator (Balzers BAK 550, Balzers, Liechtenstein). Microcontact printing was performed using a 1 mM pentaerythritol-tetrakis(3-mercaptopropionate) (PTMP) in ethanol solution, which was sonicated and filtered prior to use. The stamps were cleaned by sonicating in ethanol for 5 min, then soaked in the PTMP solution for 30 s, and dried in a nitrogen flow. Next, the stamp was brought into contact with the gold substrate for 30 s and then removed. Subsequently the gold substrate was rinsed with ethanol. Etching of the patterned gold was performed using an aqueous cyanide etch (1 M KOH, 0.1 M NaCN and 0.01 M $K_3Fe(CN)_6$ solution in demineralized water).¹³ The etching process was terminated after exactly five seconds by rinsing the sample with demineralized water.

Characterization.

Contact angles were measured on a Krüss drop shape analysis system (DSA10, Hamburg, Germany), using the advancing drop method, with ultrapure water. Scanning probe microscopy images were made using a Nanoscope Dimension 5000 with a Nanoscope III controller (Digital Instruments, Santa Barbara, CA), with scan rates between 0.5 and 2 Hz. The monolayer thicknesses were measured by X-ray reflectivity.¹⁴ Copper $K\alpha$ 1-radiation ($\lambda = 0.154$ nm) from a rotating anode X-ray generator (Rigaku RU-300H) was used. The beam was collimated using a parabolic graded multilayer mirror and a pre-sample slit of dimensions (0.1×6) mm² as described elsewhere.¹⁵ The reflected X-ray intensity was corrected for sample-size effects (footprint) at small incident angles as well as for background scattering. The density profile was determined by comparing calculated and experimental reflectivities. Calculations were based on a parameterized slab model. The best-fit curve to the data was determined by a minimization procedure; each set of data was fitted independently.¹⁴ The sample with the monolayer printed using the PEE stamp has a different titanium and gold layer thickness as compared to the other samples. This is because it was evaporated in a different batch.

Results and Discussion

We selected a multiblock copolymer consisting of poly(tetramethylene glycol) (PTMG) and poly(butylene terephthalate) (PBT) segments (Figure 2a) as the material for our hydrophilic rubber stamps.¹⁶ This poly(ether-ester) (PEE) multiblock copolymer derives its thermoplastic

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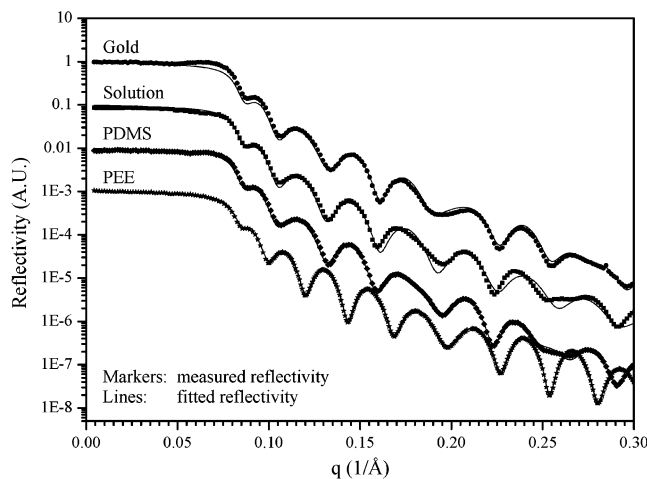


Figure 3. X-ray reflectivity curves of the bare gold substrate, the gold substrate with SAM applied via solution, the SAM printed on gold with a flat PDMS stamp, and the SAM printed on gold with a flat PEE stamp. The symbols correspond to the measured data and the line to the fitted curve. For clarity, each curve has been scaled down by a factor of 10, with respect to the curve above.

elastomeric character from its two-phase nanostructure comprising hard PBT domains, which act as physical, thermo-reversible cross-links in a soft, rubbery PTMG phase. The hydrophilic character of this polymer originates predominantly from the PTMG phase. The advancing contact angle of water on PEE is 77° , as compared to 113° for PDMS (sylgard 184). This demonstrates that PEE is substantially more hydrophilic than PDMS. For this particular study, we selected pentaerythritol-tetrakis-(3-mercaptopropionate) (PTMP) as a representative polar ink. This ink derives its polar nature from its four ester groups (Figure 2b) and was used previously by Delamar and co-workers for positive microcontact printing.¹⁷

In a first set of experiments, a PTMP monolayer was applied to a gold substrate from solution, and a comparison was made with monolayers applied by printing PTMP with flat PDMS and PEE stamps (without a relief structure). The advancing contact angle of water on the solution formed monolayer is $59^\circ \pm 1^\circ$. The SAM printed with PDMS has a significantly higher advancing contact angle, $66^\circ \pm 1^\circ$, and the monolayer printed with PEE has an advancing contact angle of $62^\circ \pm 1^\circ$. If we assume that the solution formed SAM acquires the most dense packing of a conformation that besides the thiol groups that have reacted with the gold also has thiol entities that stick out to the interface, the higher contact angles of the printed thiol point to a less dense occupation of the gold surface with a higher concentration of thiol groups reacted with the gold surface. On the basis of the same argument, the PEE printed thiol layers have a denser packing than the PDMS printed ones. We evaluated these monolayers in more detail using X-ray reflectivity measurements. The X-ray reflectivity (XRR) curves are shown in Figure 3, and the normal (perpendicular to the surface) electron density profiles belonging to these fits are shown in Figure 4. The electron density of glass, titanium, gold and PTMP are invariable for the different samples. These electron densities were used for the fitting procedure and the derivation of the SAM layer thicknesses (Table 1). The SAM applied from solution has an average thickness of

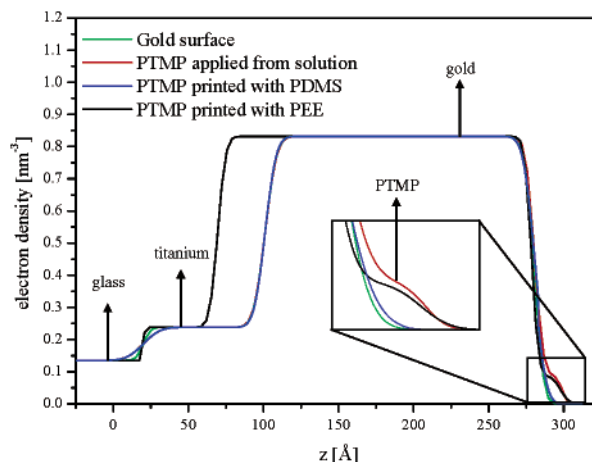


Figure 4. Electron density profiles obtained by fitting of the XRR-data. The box shows a magnification of the PTMP region of the profile. The sample printed with the PEE stamp has different titanium and gold layer thicknesses, because it was evaporated in a different batch.

Table 1. Layer Thicknesses Fitted to the XRR Curves

	layer thickness (Å)		
	Ti	Au	PTMP
gold substrate	81	179	-
SAM from solution	81	179	18 (1.8)
SAM via mCP with PDMS	81	179	2.5 (0.3)
SAM via mCP with PEE	50	209	19 (1.9)

Table 2. Dimensions of the Master, Inverse Replica and Stamps

	spacing (mm)	height (nm)
silicon master	3	515
FEP inverse replica	3	457
PEE stamp	3	454
PDMS stamp	3	453

$18 \pm 1.8 \text{ \AA}$. This agrees very well with a calculated thickness of 19 \AA for a monolayer with two branches of the PTMP molecule attached to the gold substrate and branches sticking out to the surface. A monolayer printed with a flat PDMS stamp has a much lower average thickness ($2.5 \pm 0.25 \text{ \AA}$). For this thickness, the PTMP molecule would have to be spread out over the surface, rather than being packed together. The monolayer printed using a flat PEE stamp, has approximately the same thickness as the SAM applied from solution ($19 \pm 1.9 \text{ \AA}$), which indicates that, similar to the sample prepared by solution dipping, a well-defined, closely packed monolayer is formed.

To test the SAMs with respect to their resistance to etching, we manufactured patterned stamps. Hot embossing of PEE with a fluorinated silicon line grating (Figure 5a) caused adhesion problems. Therefore, we used an intermediate FEP inverse replica (Figure 5b), which is subsequently used for the hot embossing of PEE stamps (Figure 5c). To make identical stamps, the FEP intermediate was also used as a master for the PDMS stamps (Figure 5d). The spacing and height of these stamps, listed in Table 2, show that some height loss occurs during the replication of the silicon master in the FEP. However, accurate replicas are obtained from this FEP inverse replica by both hot embossing (PEE) and cast curing (PDMS). The fast replication process using PEE, minutes rather than hours in case of PDMS, makes this

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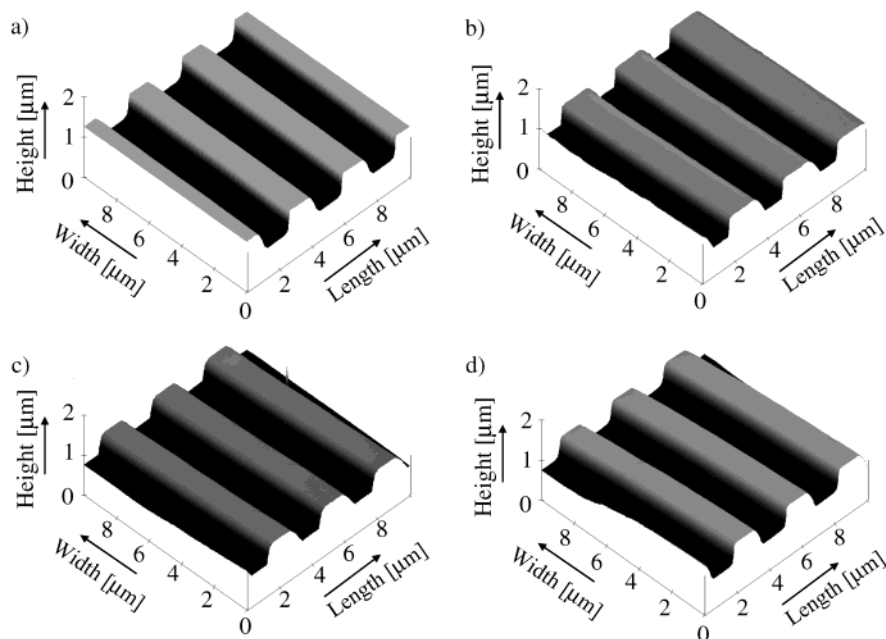


Figure 5. Scanning probe micrographs of (a) the line grating used as master for hot embossing, (b) the FEP inverse replica, (c) the PEE stamp hot embossed using the FEP inverse replica, and (d) the PDMS stamp.

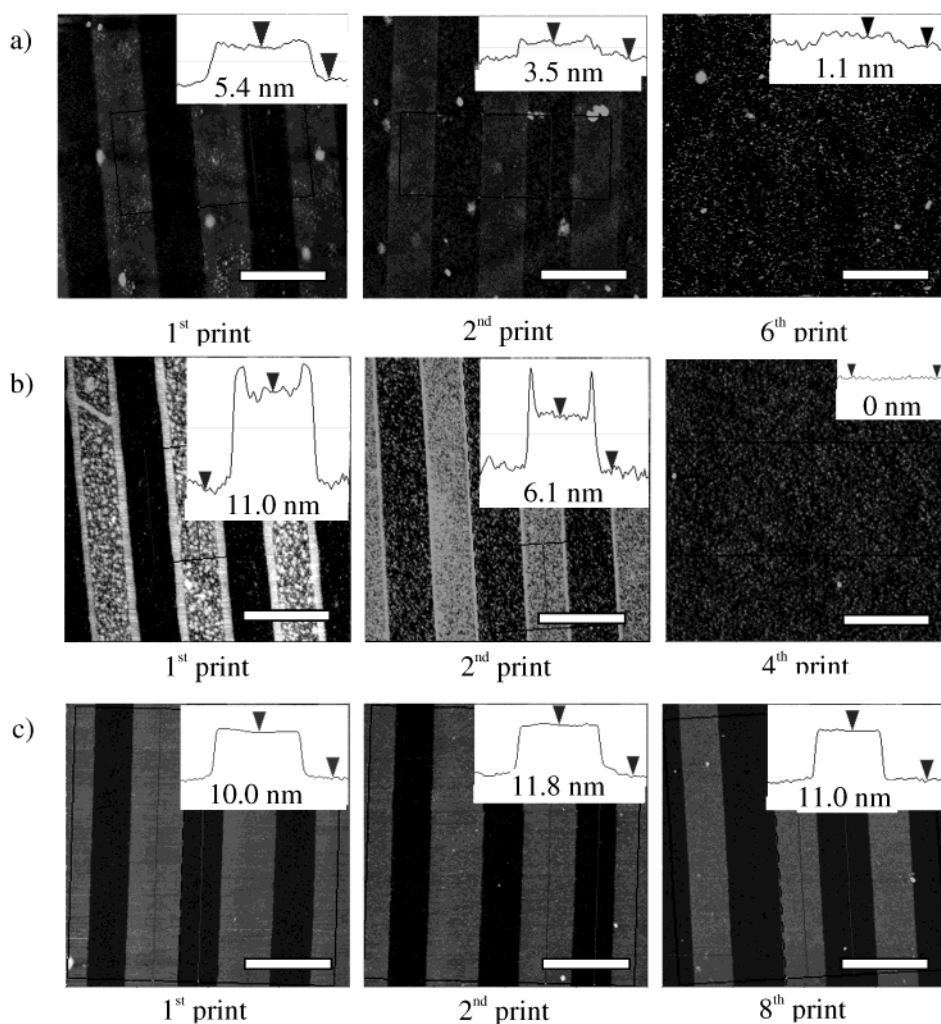


Figure 6. Scanning probe micrographs of etched gold samples, printed with PTMP using (a) PDMS, (b) plasma-treated PDMS, and (c) PEE stamps. Stamps were inked once and then used to print multiple patterns. The scale bar is $3 \mu\text{m}$ in each image.

material a favorable alternative for the currently used PDMS.

We microcontact printed patterned PTMP SAMs on gold using the patterned stamps of PDMS, oxygen plasma-

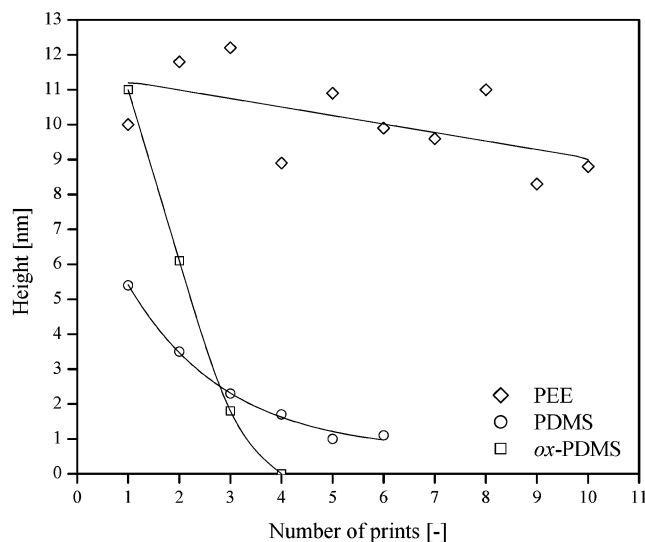


Figure 7. Height of the etched structures, after repetitive μ CP with PEE, PDMS, and ox-PDMS stamps.

treated PDMS (ox-PDMS) and PEE. In all cases a virgin stamp was inked and subsequently used in repetitive printing operations, without reapplying ink to the stamp. The time between each consecutive print was kept as short as was experimentally possible, which is about 10 s. After printing, the patterned gold samples were etched using an aqueous cyanide etch. The height of the etched structures was compared using scanning probe microscopy (SPM) measurements. In Figure 6a we demonstrate that the quality of the etched patterns rapidly deteriorates with the number of prints for the samples printed with PDMS, which indicates a fast depletion of the ink on the stamp. The samples printed with ox-PDMS (Figure 6b) exhibit rather unusual characteristics. Line patterns are observed with elevated edges, suggesting that the resistance to etching is higher there. The center of the printed lines has a patchy appearance, with a lower etching resistance. Moreover, a fast deterioration of the quality of repetitively printed patterns is observed. The samples printed with a PEE stamp (Figure 6c) were remarkably better than the PDMS printed ones, both in the quality of the etched patterns and in the preservation of etch resistance upon repetitive printing. First, the etched structures are much higher than the samples printed with PDMS and comparable with the first print of the ox-PDMS stamp. A well-defined monolayer with an increased resistivity toward etching is formed. Also, only a slight decrease is observed in the height of these structures even after 10 consecutive prints, which indicates that the

quality of the SAM hardly decreases upon repetitive printing. Usually, such printing behavior is attributed to a certain degree of solubility of the ink in the stamp, to diffusion of the ink to the surface of the stamp after printing and to re-formation of a new monolayer after each print.¹⁸ The excellent printing characteristics of PEE stamps, as compared to PDMS and ox-PDMS, are further illustrated in Figure 7. Here the height of etched patterns is plotted as a function of the number of prints. While the PDMS stamp transfers a decreased amount of ink to the surface after each print, and fails after 6 prints and the printing behavior of the ox-PDMS stamp deteriorates even faster, the PEE stamp is able to print at least 10 patterns, with hardly any degradation of the pattern.

A few critical remarks concerning these experiments are appropriate. We used PTMP as a model material for polar inks, not to demonstrate its usefulness as an etch resist. The fabrication of PEE stamps is fast and straightforward, with a simple hot embossing procedure. The PEE multiblock copolymer has an increased stiffness in comparison with PDMS and consequently a slight pressure is required to establish conformal contact. The appearance of PEE is rather opaque which might hinder alignment of stamps using optical markers, a problem which can be overcome to some extent by reducing the stamp thickness. We expect that hydrophilic elastomers can be extremely useful in other soft lithographic techniques such as microfluidics and micro-molding. A careful material selection with respect to properties such as swelling in solvents, chemical resistance and conformal sealing can result in suitable stamp materials for these soft lithographic techniques.

Conclusions

We demonstrated that the use of a hydrophilic, thermoplastic elastomer as stamp material is extremely useful in the microcontact printing of a polar ink. On the basis of contact angle and X-ray reflection measurements, it was shown that printing with these hydrophilic stamps results in well-defined SAMs. These monolayers exhibit a superior resistance toward etching, as compared to SAMs printed with PDMS and oxygen-plasma-treated PDMS. More importantly, repetitive printing of monolayers can be performed without a significant decrease in pattern quality after etching. The improved printing characteristics of thermoplastic elastomers are attributed to the enhanced wetting behavior of this polymer and to (a partial) solubility of the polar ink in the stamp material.

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