

HIGH-RESOLUTION MICROPATTERNING OF OFF-STOICHIOMETRIC THIOL-ENES (OSTE) VIA A NOVEL LITHOGRAPHY MECHANISM

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ABSTRACT

We present an entirely novel, self-limiting photolithography mechanism in off-stoichiometry thiol-ene (OSTE) polymers enabling high-resolution and high-aspect ratio features. The OSTE polymers have previously been shown to be promising materials for fabrication of microfluidic devices with tailored surface modifications and mechanical properties. We here introduce direct lithography for micropatterning of OSTE as an alternative to mechanical machining or casting, resulting in a simple and reliable fabrication method of self-bonding photopatterned multilayer microfluidic devices.

KEYWORDS

lithography, off-stoichiometry thiol-ene, OSTE, micropatterning, microfluidics, microfabrication

BACKGROUND

Hitherto, academia has largely relied on PDMS replica molding for microfluidic device fabrication [1]. However, there are problematic fabrication steps with PDMS such as long curing times, manual punching of through-holes for layer interconnects and non-biocompatible plasma bonding. In addition problems with finished devices, such as absorption of biomolecules into the polymer and non-permanent surface modifications, have created an urgent need for polymer alternatives to PDMS. The epoxy-based negative photoresist SU-8 is an interesting polymer for production of thick micro-structured layers due to its high-aspect ratio and high-resolution features [2]. However, the cured SU-8 is hard and brittle, and is difficult to make hydrophilic at its surface, although some microfluidic devices have been successfully manufactured [3]. Attempts to formulate photosensitive PDMS [4] to form channels and vias have been made, but the utility of the proposed solutions are limited to special cases and not generally applicable for lab-on-chip manufacturing. More promising are attempts to use photosensitive acrylates [5], and more recently thiol-enes for direct photo-patterning [6]. However, no simple direct lithography solution for microfluidic device fabrication is currently available.

With this background, a UV-curable thiol-ene polymer system tailored for lab-on-chip devices was developed [7] and later commercialized by Mercene Labs AB. Based on UV-initiated thiol-ene “click” chemistry and utilising monomers mixed in off-stoichiometric ratios, the novel off-stoichiometry thiol-ene (OSTE) formulations provide mechanical properties controlled by tuning the monomer mixing ratios, where properties range from PDMS-like elastomeric properties to thermoplastic stiffness [7]. Also, controlled surface modification and biocompatible UV initiated “click” bonding is easily achieved through the presence of surface bound thiol and allyl groups, resulting from the off stoichiometric mixing ratios. These properties make OSTE a promising material for microfluidic device fabrication, as previously shown [7]. Vias and 3D-channel interconnects are necessary components in advanced microfluidic devices. However, to this date, no method for batch manufacturing of through holes in OSTE has been described. In this work we investigate the effect of off-stoichiometry on the photolithographic quality and we present here for the first time a novel self-limiting photopatterning mechanism intrinsic to off-stoichiometry thiol-enes (OSTE). Its usefulness is demonstrated in an uncomplicated fabrication procedure for microfluidic chips with vertical interconnects

EXPERIMENTAL

Model systems of on-stoichiometry thiol-ene (tetrathiol:triallyl, 1:1) and OSTE with 60% thiol excess (tetrathiol:triallyl, 1.6:1) were casted on pieces of polished silicon. Plastic foil photomasks and high-resolution glass/chromium masks were used to directly photopattern the OSTE prepolymer using collimated light (300 mJ/cm^2 at 365 nm) from a LS 30/7 1000 W NUV-lightsource (OAI, USA). The patterns were developed using mr-Dev 600 (MicroResist, Germany) for 2 minutes and dried in a stream of nitrogen gas. The fabrication scheme of microfluidic devices using photopatterning of OSTE is described in detail in Figure 1. For these experiments, the commercial OSTE blends OSTEMER™ Thiol 60 and OSTEMER™ Allyl 50 (Mercene Labs AB, Sweden) were casted onto Teflon® AF 1600 (DuPont™, USA) coated flat silicon surfaces and silicon/SU-8 moulds in layer thicknesses varying from 20 to 400 μm . Plastic foil photomasks and a NUV lightsource were used to directly photopattern the OSTE prepolymer (Figure 1.a). Thereafter, heating the stack to 60 °C softened the OSTE polymer and made it easy to peel it from the mask, molds and surfaces (Figure 1.b). The patterns were developed using mr-Dev 600 for 2 minutes (Figure 1.c), whereafter samples were blown dry. To produce closed microfluidic chips, the OSTEMER™ Thiol 60 and OSTEMER™ Allyl 50 layers were pressed in contact. Bonding was achieved via a thiol-ene “click” reaction when exposed to unfiltered UV light (dose: 4000 mJ/cm^2).

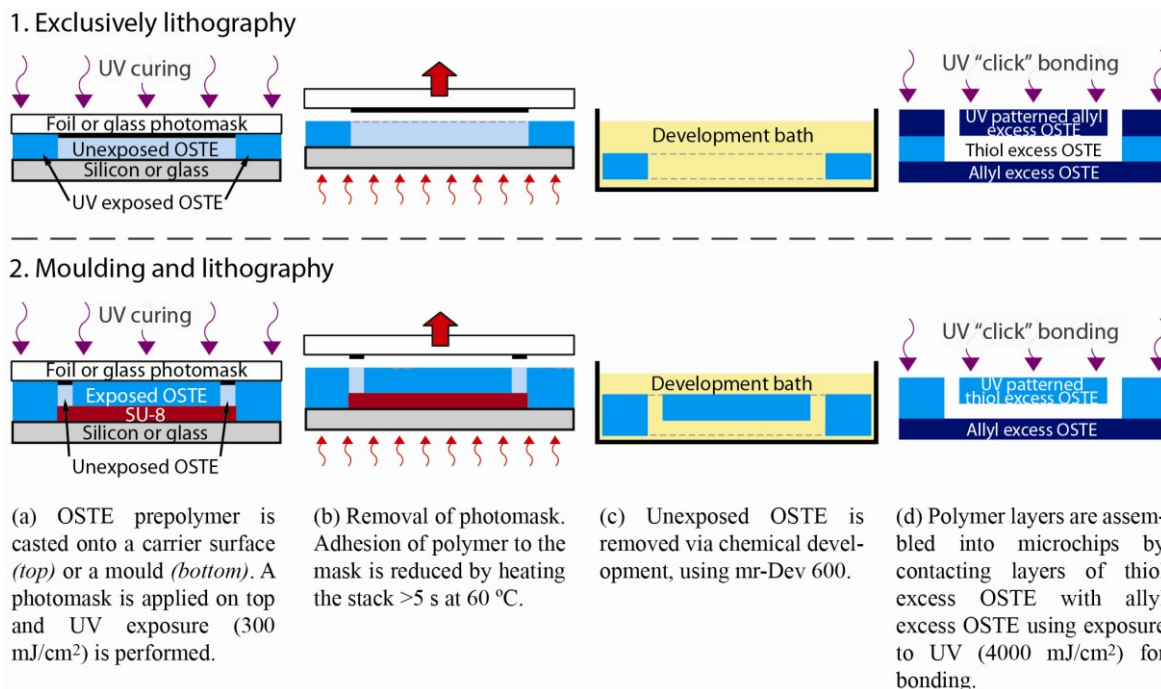


Figure 1: Fabrication of microfluidics chips using lithography for patterning of 1) all chip features (top row) and 2) lithography for patterning of through-holes in combination with a microchannel-defining mould (bottom row).

RESULTS AND DISCUSSION

A distinct difference was observed after UV exposure and development between off- and on-stoichiometric polymer formulations (Figure 2.a-b). The photolithographic pattern fidelity of OSTE is in stark contrast with their stoichiometric counterparts, which appeared more sensitive to over-exposure, resulting in broadening of the pillar structures outside the mask pattern (Figure 2.a-b). A likely cause for this phenomenon is the rapid depletion of the ene-monomer in the region adjacent to the UV exposed polymerising features, as depicted in Figure 2.c. This depletion prevents gelation since the concentration of allyls falls below a critical network formation threshold, which effectively prevents polymer formation outside of the exposed zone.

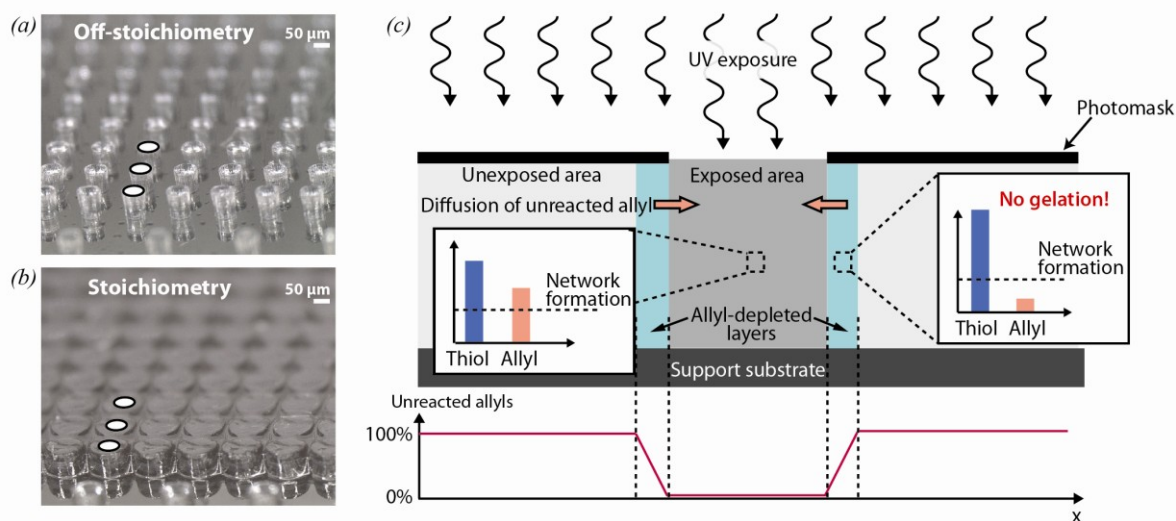


Figure 2: a) Off-stoichiometric thiol-ene polymer is well defined by UV lithography, whereas stoichiometric thiol-ene polymer (b) becomes overexposed. c) Theoretical model of off-stoichiometric thiol-ene lithography. Due to the excess of reactive thiol groups in the exposed area, the region close to the mask edge becomes depleted of allyl groups, thus preventing polymerisation in this region due to over-exposure.

The novel lithography method was used to fabricate structures of high aspect ratio (1:8, Figure 3.a). Also, a very high resolution was observed ($< 2 \mu\text{m}$, Figure 3.b). The lithography process in OSTE was successfully demonstrated for two microchip fabrication approaches: 1) direct lithography to define all microchip structures, including vertical interconnects (Figure 3.c), and 2) casting of OSTE onto a microchannel-defining mould, using lithography and a photomask for definition of vertical interconnects (Figure 3.d). A difference between these two approaches was that the

first method, based on direct lithography, included an alignment step of the UV cured layers. In contrast, the mould casting method required alignment of a mask to the mould prior to the first UV curing. As the last step in both approaches, the patterned layer was bonded to a bottom layer of allyl-excess OSTE, using UV “click” reaction.

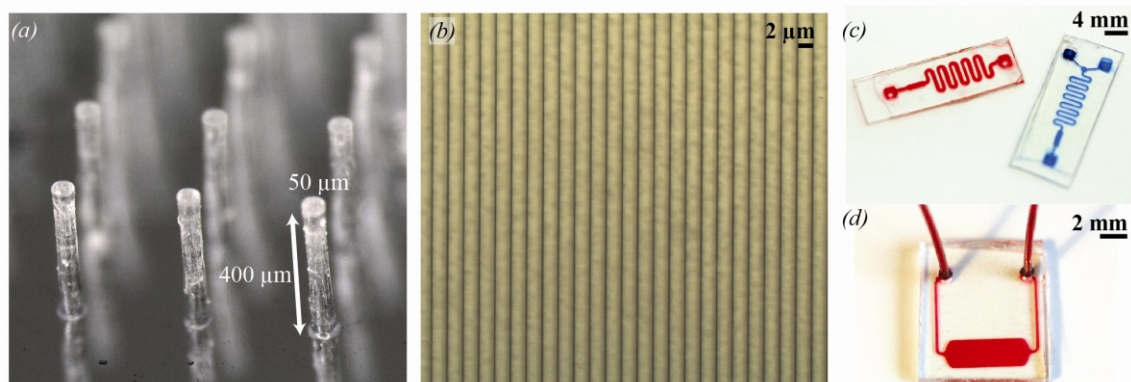


Figure 3: (a) Pillars with an aspect ratio of 1:8 were successfully fabricated. The off-stoichiometric reaction provides high aspect ratio, which limit has not yet been reached. (b) Successful fabrication of 2 μm wide ridges indicates high lateral resolution for OSTE lithography. The resolution limit has not yet been reached. (d-e) Microfluidic chips fabricated using OSTE polymer layers are assembled into microchips by contacting layers of thiol excess OSTE with allyl excess OSTE using exposure to UV (4000 mJ/cm²) for bonding.

CONCLUSION

We show a novel, self-limiting mechanism for lithography in OSTE polymers. The method is used for high-aspect ratio structures and high-resolution patterning, where the limits are yet to be determined. Also, rapid prototyping of lab-on-chips in OSTE through direct lithography was successfully demonstrated and constitutes a promising method. We strongly believe that the excellent lithographic properties of the polymer shown here, combined with the ability for facile surface modifications and bonding, makes OSTE one of the most powerful materials systems for microfluidic applications available today.

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