

# BEYOND PDMS: OFF-STOICHIOMETRY THIOL-ENE BASED SOFT LITHOGRAPHY FOR RAPID PROTOTYPING OF MICROFLUIDIC DEVICES

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## ABSTRACT

We present an easy to use, rapid fabrication platform for microfluidic systems, based on micro-molding of novel thiol-ene based polymer formulations. The novel fabrication platform addresses major drawbacks of PDMS by allowing large freedom in material and surface properties, including: (photo)patterning of stable surface modifications, bonding without plasma treatment, rapid UV or thermal curing, variable E-modulus, minimized leaching of uncured components [1] and suppressed non-specific binding of biomolecules [2]. This process is potentially suited for both rapid prototyping in the laboratory and medium-scale commercial production, bridging the “development gap”.

**KEYWORDS:** thiol-ene, soft lithography, Click chemistry

## INTRODUCTION

PDMS is used predominantly in prototyped lab-on-a-chip systems because of its attractive mechanical and chemical properties, ease of use, and its wide availability. However, PDMS suffers from many problems: adsorption of proteins, swelling in non-polar solvents and non-permanency of surface modifications, rendering PDMS inadequate for lab-on-a-chip systems that involve biological fluids, e.g. in medical diagnostics.

Two fundamental approaches have been taken to replace PDMS with alternative polymers for the fabrication of microfluidic devices: a) freeform direct photolithography of UV-curable polymer precursors [3]; and b) shaping of thermosets via replica molding [4]. The latter is more versatile because it does not require photolithographic qualities for structuring. Thiol-ene based polymers, further called “thiol-enes”, form an excellent alternative to PDMS since their properties can be widely tuned, provide superior light transparency and excellent resistance to solvents. However, the full potential of thiol-enes for microfluidics has not yet been explored. The most promising approach so far involves a thiol-ene (NOA 61, Norland Products) to fabricate durable microfluidic components (“microfluidic stickers”) via replica molding [5], circumventing well known drawbacks of PDMS and other thermoset polymers but not providing means for efficient surface modification.

## NOVEL CONCEPT

In contrast to previous work (e.g. [5]), we utilize formulations with off-stoichiometry thiol-to-ene ratios as opposed to the previously used 1:1 ratio. This makes excess reactive groups, either allyls or thiols, available on the surface after polymerization, which allow well controlled (patternable) UV-initiated surface modifications and/or covalent layer bonding via so called “Click” chemistry [6], where thiol and allyl groups react to form a thiol-ene bond.

Furthermore, by using different backbones to the thiol-ene prepolymers we have great freedom in tailoring both mechanical and chemical properties of the finished polymer materials, making the process suitable for integrating and combining varying geometrical features, material stiffness and/or surface properties.

## POLYMER FORMULATION

As demonstrators we have developed three off-stoichiometry, photocurable thiol-ene materials (Table 1, Fig 2 A). The first material, material A, consists of PDMS chains with vinyl-siloxane or thiol end. This elastomeric thiol-ene material can have either excess thiol or vinyl groups, depending on mixing ratio, and can be used to replace commercial PDMS, e.g. Sylgard 184. Material B has stiffer tri-azine backbones and is a harder material with excess of allyl groups and material C is a softer thiol-excess material with a mix of tria-azine and pentaerythritol backbones, making it less stiff. The excess groups of material B and C will react with each other and form a covalent bond when the materials are in conformal contact and heated.

We also developed a protocol for patterning surface modifications and for bonding these materials. In the experiments we use a laboratory scale UV-lamp (EFOS Lite, 50W Mercury lamp), to polymerize the materials. To ensure rapid and uniform curing of the materials a photobleaching photoinitiator (TPO-L, BASF, Germany) was added (0,1% w/w) to each of the formulations in Table 1.

Table 1. Photocurable off-stoichiometry thiol-ene based materials developed

	Composition	Properties
Material A	PDMS with vinyl-siloxane or thiol end groups	Elastomeric thiol-ene PDMS material
Material B	tri-allyl-tri-azine : tri-thiol-triacine 4:3 mixture	Hard material with excess of allyl groups
Material C	tri-allyl-tri-azine : tetra-thiol-pentaerythritol 2 : 3	Softer material with excess of thiol groups

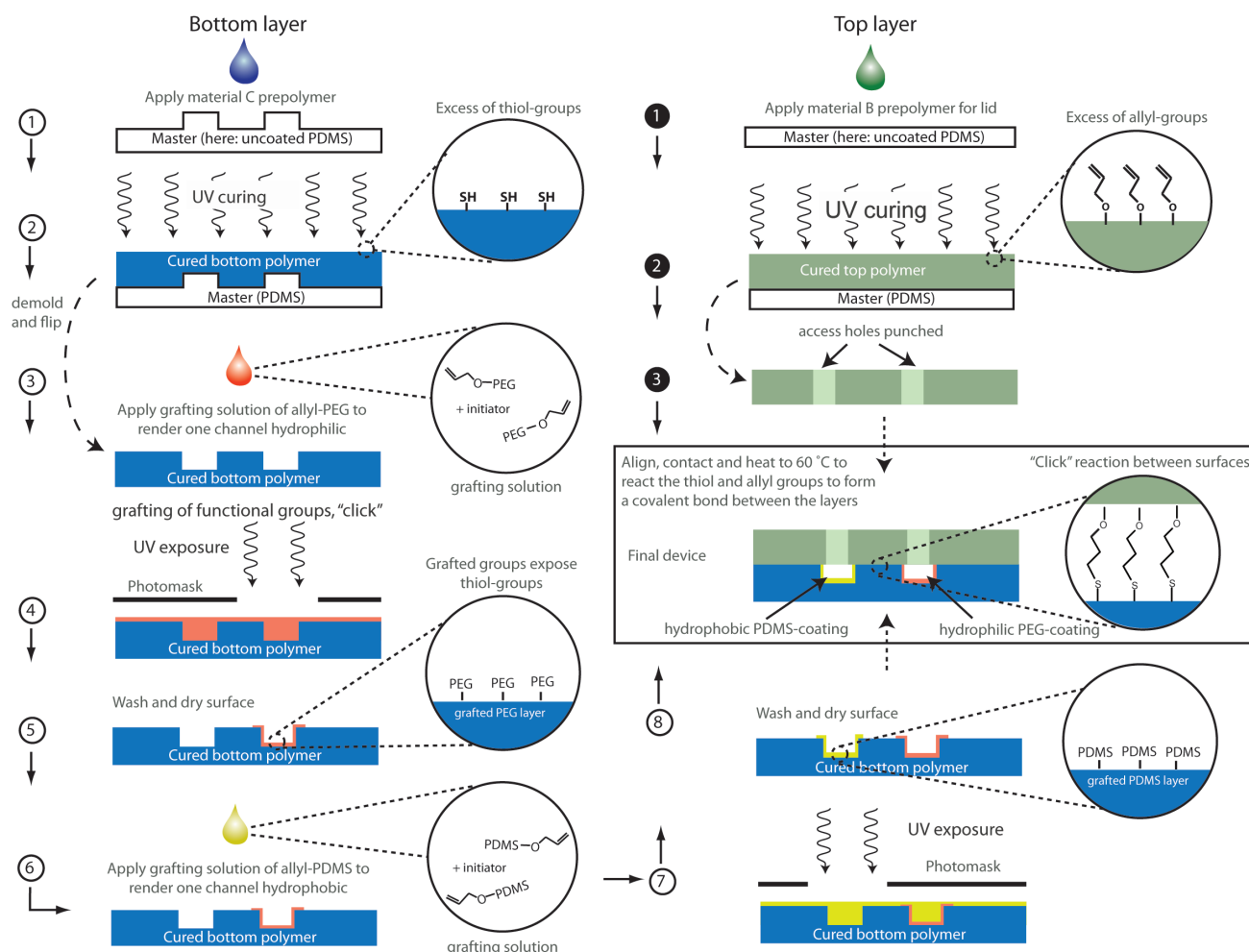


Figure 1: Demonstrator fabrication process developed for a thiolene microfluidic structure with photopatternable tuning of the surface coating (surface energy). Left: Fabrication of the bottom substrate: 1-2) Casting of thiol-ene polymer with excess of allyl-groups (material C) forming two channels. 3-5) Grafting a solution of PEG with two thiol groups. During UV exposure, one of the thiols “Click” reacts with the allyl of the bottom polymer, leaving the rest unreacted. Right: Similar fabrication of the lid (material B) which has an excess of allyl groups. Bottom: Both polymer layers are dry bonded by “click” chemistry by thermally activation @ 60°C.

## SURFACE MODIFICATION AND BONDING

First, we demonstrated the photopatternable surface modification possibilities of the thiol-ene platform. Material C, with excess thiol groups, is casted on a thin PDMS master (which itself was structured on a silicon/SU-8 master) and cured using UV-light. The surface is photopatterned with allyl functionalized red dye (Disperse red) using a photomask. The allyl groups on the dye molecules react with the excess thiol groups on the polymer surface only in the area exposed to UV-light (Fig 2 B).

Second, we demonstrated the modification of the macroscopic wetting properties of the thiol-enes by grafting. For thiol excess surfaces, the graft is initiated by UV exposure of 2-isopropyl thio-xanthone (ITX), which abstracts hydrogen from surface bound thiols, thus providing a radical which can further react with e.g. an allyl. In our experiment, mono(allyl)polyethylene glycol (allylPEG) dissolved in toluene with ITX (1% w/w) changed the water-polymer contact angle from about 70° of the native Material C to 30° in UV-exposed regions (Fig 2 C and D).

Finally we demonstrate a sample soft lithography process flow (Fig 1) and a very simple microfluidic demonstrator device consisting of two channels (Fig 2 E), of which the bottom layer consists of material C and the top layer of mate-

rial B. We changed the wetting properties of the two channels by photopatterning each channel of the bottom layer with a different surface modification using two transparency photomasks. In the left channel we locally grafted poly(allyl)PDMS to make it hydrophobic and in the right channel we locally grafted allylPEG to make it hydrophilic. The layers were dry, low temperature, covalently “click” bonded by softly pressing them in contact and heating at 60 °C for 5 min. The PEG modified microfluidic channel capillary filled with (water based) candy-dyed water, whereas the PDMS modified channel was water repellent and would not fill spontaneously (Fig 2 E).

The whole fabrication process is rapid and utilizes well-known soft-lithography protocols. UV curing and grafting takes less than a minute with a lab scale (50 W) UV-flooding lamp. Using a high power collimated light-source reduces the time further and eliminates the need for a photoinitiator. The process is relatively inexpensive and the monomers are relatively inexpensive and available in commercial quantities. With the demonstrated features, we believe the method has great potential for laboratory scale prototyping and is easily scaled up to medium scale production without major changes to materials and fabrication parameters.

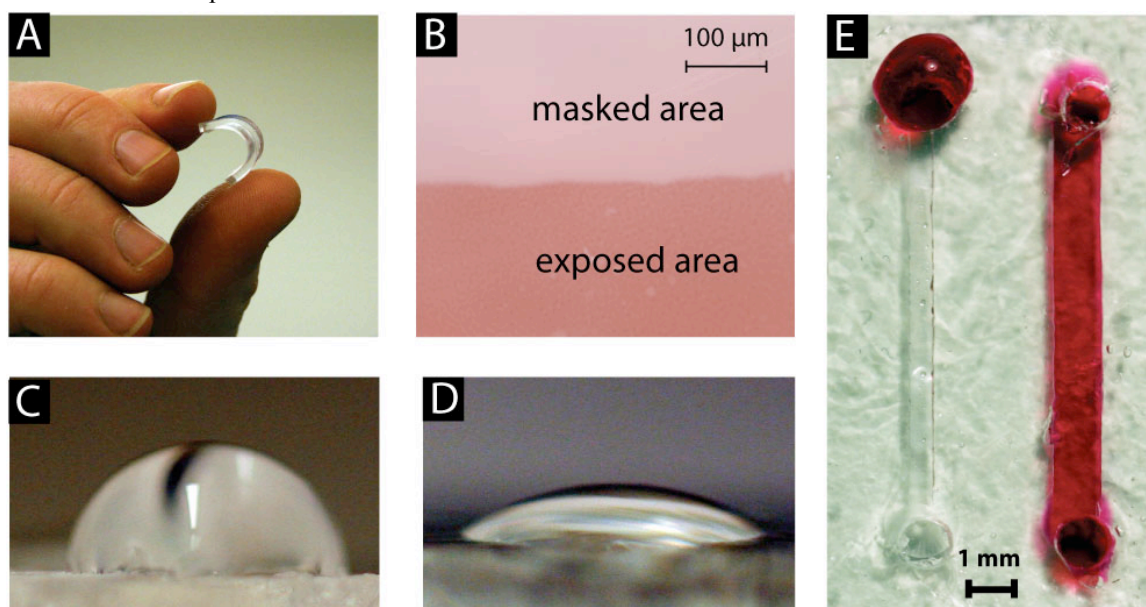


Figure 2: (A) PDMS-like thiol-ene material (material A). (B) Allyl-red photo-patterned with a shadow mask on material C. (C) Contact angle on unmodified material B. (D) Contact angle on material C grafted with allylPEG. (E) Channel modified with thiolPDMS do not fill (left), while channel modified with allylPEG fills capillary (right).

## CONCLUSION

We demonstrated key functional materials, processes and devices for a thiol-ene based polymer soft lithography fabrication platform potentially suited for both uncomplicated rapid prototyping and medium scale production of microfluidic devices.

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