

RAPID PERMANENT HYDROPHILIC AND HYDROPHOBIC PATTERNING OF POLYMER SURFACES VIA OFF-STOICHIOMETRY THIOL-ENE (OSTE) PHOTOGRAFTING

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ABSTRACT

In this work we have developed a simple and robust method to permanently pattern alternating hydrophobic and hydrophilic surfaces in off-stoichiometry thiol-ene (OSTE) polymer microchannels. By being able to tune the number of unreacted thiol surface groups of the OSTE Thiol polymers and by taking advantage of spatially photo-controlled surface grafting of methacrylate monomers we achieve defined areas with contact angles from 20° to 115° within one single channel. The surface modification remains stable after storage in air (>2 months) or water (>24h).

KEYWORDS

Rapid prototyping, surface modification, off-stoichiometry thiol-enes, OSTE, contact angles

INTRODUCTION

The precise control of surface wetting properties is essential in microfluidics to manipulate and control liquid flow [1-2]. All microfluidic materials used today suffer from cumbersome surface modification protocols that involve: 1) *surface activation* (often via plasma treatment and/or silanization); and 2) *chemical reactions* between activated surface groups and a modifying functional molecule. Surface wetting modifications through plasma treatment of PDMS [3], or using localized deposition of a thin layer of fluorocarbon based polymer [4], are known to be short-lived and vary several tens of degrees in contact angle during storage or when in prolonged contact with water. Furthermore, many activation protocols are diffusion controlled, leading to uneven surface coatings in high aspect ratio features, such as deep microchannels [5]. Therefore, simplifying and improving surface modification protocols is imperative for both rapid prototyping and for mass fabrication of advanced microfluidic devices while simultaneously allowing for a long shelf life.

We previously demonstrated the use of off-stoichiometry thiol-ene (OSTE) polymers in microfluidics, a family of polymers specifically designed for lab-on-chip applications [6,7]. Contrary to all other microfluidic materials, the OSTE polymers exhibit surfaces with a high density of active surface groups without resorting to either plasma or silane treatment, which greatly simplifies surface modification while simultaneously enabling superior coating homogeneity. We previously showed a surface wetting modification protocol [6] for OSTE, but it required lengthy washing steps, poor predictability and contact angle variations were limited between 35° and 95°.

In this work we introduce a *robust, uncomplicated* and *precise* method for surface wetting *control* on OSTE polymers by: 1) tuning the number of available active groups on the surface via control of the off-stoichiometry; 2) using the rapid radical mediated reaction of thiols with methacrylate monomers, better stability and surface coverage than previously used chemistries is obtained.

EXPERIMENTAL

Substrate material and microfluidic channels

The OSTE polymers are rapidly micromolded by UV-curing on standard Teflon treated SU-8 or untreated PDMS masters. Depending on the prepolymer blend, the OSTE polymers exhibit varying amounts of unreacted surface groups after curing [6]. For the OSTE (off-stoichiometry thiol-ene) polymer substrates and microfluidic channels, we used commercial OSTEMER™ prepolymers (Mercene Labs AB, Sweden) provided with varying amounts of thiol excess (0%, 10%, 25%, 50% and 90% off-stoichiometry). The OSTEMER™ prepolymers were casted on PDMS masters and cured for 20 sec using a UV-lamp (12 mW/cm², unfiltered NUV light, LS307 1000W NUV light source, OAI, Milpitas, USA) (Fig 1, A). The microfluidic chips were produced by “click” bonding a flat lid of another blend of OSTE polymer exposing an excess of allyl groups after curing (30% excess of allyl instead of thiol). This dry, low temperature bonding process is described in details elsewhere [6,7,8].

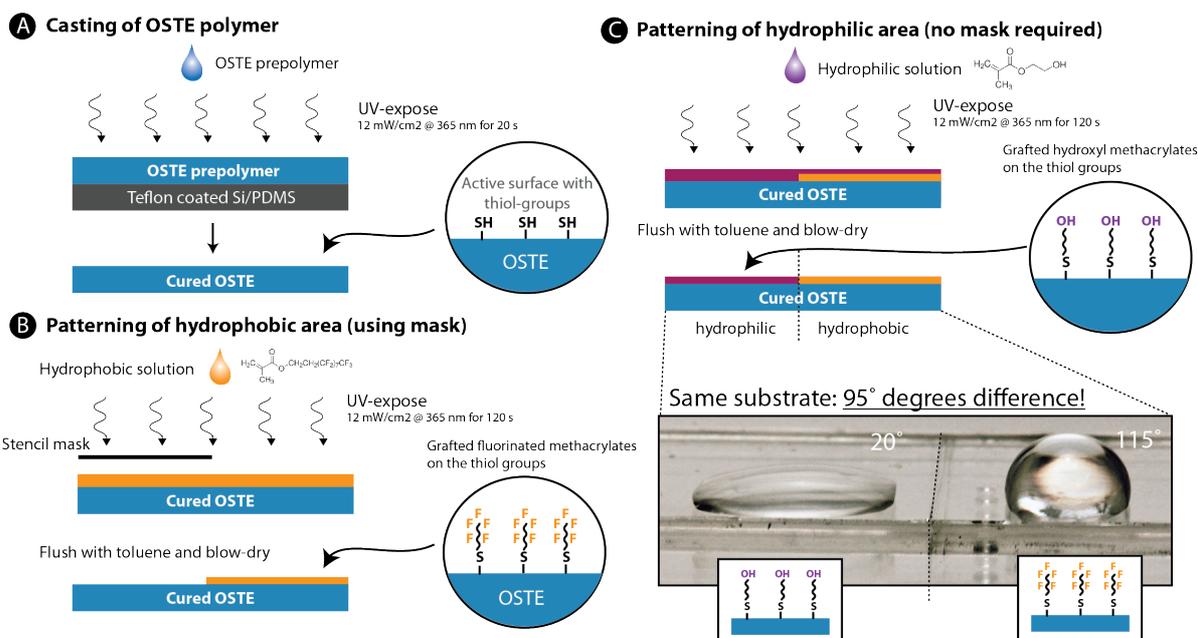


Figure 1: A) An OSTE-polymer with 90% thiol excess is UV-cast on a substrate and peeled off. Large number of unreactive thiol groups are available on the surface that are subsequently used to B) pattern part of the surface hydrophobic by applying a toluene solution of fluorinated methacrylate and expose through an UV-mask. After washing with toluene C) the surface is rendered hydrophilic by immersion in a toluene solution of hydroxy methacrylate and flood exposed. After washing and drying, water droplets are applied on both the hydrophilic part ($CA = 20^\circ$) and hydrophobic ($CA = 115^\circ$) shows a CA difference of 95° on the same surface.

Surface modification method

Fluorinated or hydroxylated methacrylate monomers render the surface hydrophobic or hydrophilic, respectively. Here, solutions of 5% w/w of either of heptadecafluorodecyl methacrylate or 2-hydroxyethyl methacrylate monomers (Sigma Aldrich AB, Sweden) dissolved in toluene with 2% w/w benzophenone (BP) initiator were applied on the OSTE substrates (Fig 1, B, C). The surfaces were subsequently exposed to UV through a stencil mask defining the areas to be modified (120s @ 12 mW/cm^2), rinsed thoroughly in toluene and blow dried in a stream of nitrogen.

Briefly, the surface modification process is initiated in unmasked UV exposed areas by conversion of the thiol into an active thiyl radical through hydrogen abstraction by benzophenone (BP). The thiyl quickly adds methacrylate monomers in a chain-wise polymerization process until the polymer chain is terminated, either via radical-radical coupling to: a) an adjacent growing polymer chain; or b) to the reaction product between BP and the thiol (a diphenyl ketyl radical). As the BP can only abstract hydrogen from the -SH group attached to the surface, the methacrylate will only graft from the surface resulting in a dense layer composed of linear methacrylate polymer chains.

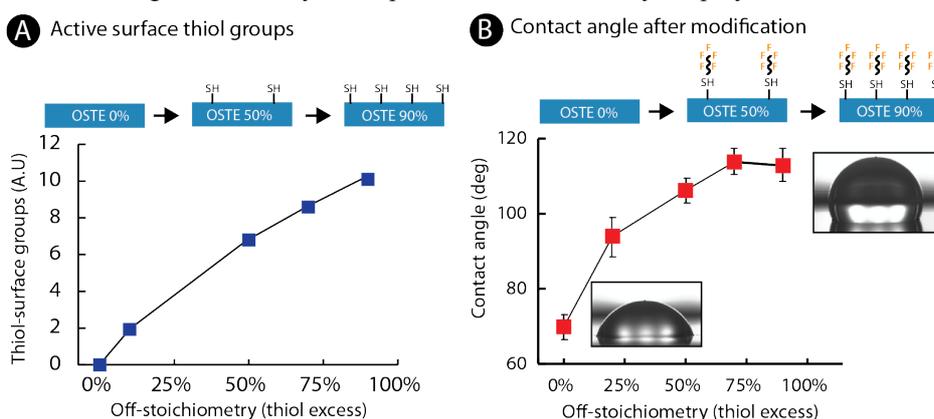


Figure 2: (A) An increasing off-stoichiometry leads to a higher number of active thiol anchors on the surface as verified by XPS analysis. (B) After hydrophobic surface modification (see below) the OSTE samples with more thiol anchors have proportionally higher contact angles, from 68° (OSTE 0% - no thiol groups) to 115° (OSTE 75% and OSTE 90%) (right).

Contact angle and XPS measurements

The density of active surface thiol groups after curing was determined by first modifying the surface with allyltrifluoroacetate, a tri-fluorinated non-homopolymerizing monofunctional allyl molecule (to ensure only one molecule can attach per thiol) and subsequently measuring the fluorine signal with XPS. The signal was shown to be linear as a function of off-stoichiometry, i.e. the excess of thiol functionality in the prepolymer mix (Fig 2, left). Furthermore, the macroscopic contact angles of water droplets after the modification process was measured using a goniometer. The contact angle varied from 65° to 115° using the fluorinated methacrylate on OSTE with 0% to 90% thiol

excess and down to 20° using the hydroxylated methacrylate on OSTE with 90% thiol excess (Fig 2, right). The samples showed little or no apparent change in contact angle after submersion in water and toluene for 24h or accelerated thermal aging (85 °C for 24h) corresponding to ~3 months under ambient conditions (Fig 3: A,B).

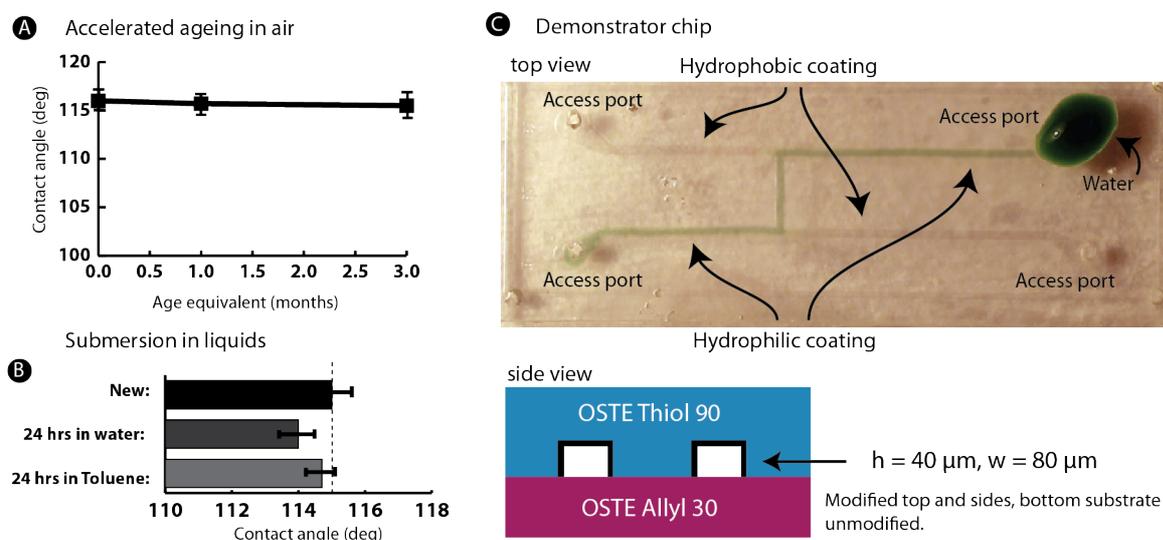


Figure 3: (A) The modified contact angle remained largely unchanged after preliminary accelerated aging test (85 °C for 24h = 3 months) as well as after (B) immersion in water (24h) or toluene (24h). This demonstrate the robustness of the thiol methacrylate coupling as well as the stability of the OSTE polymers. (C) A H-channel demonstrating two areas of different wetting. The green colored water preferentially fills the channels modified with hydroxy methacrylate (hydrophilic) and do not want to enter the channels that are modified with the fluorinated methacrylate (hydrophobic). The rubbery mechanical properties of the modified top layer (OSTEMER™ Thiol 90, $E = 250$ MPa) allows it to adhere leak tight to a harder OSTEMER™ Allyl 30 substrate.

Application: modified microfluidic channels

As a microfluidic demonstrator we patterned hydrophobic and hydrophilic zones in a branched microchannel in OSTEMER™ Thiol 90, fabricated using the soft lithography-like process described previously [6]. In the last step the channel layer was “click” bonded to a flat OSTE layer with allyl excess (OSTEMER™ Allyl 30) using an additional dose of UV [8]. The channels thus had three out of four walls modified. Water with a green water based colouring agent applied at the inlet filled the hydrophilic modified channels while avoiding the hydrophobic sections (Fig 3: C).

CONCLUSION

In this work we have shown that the surface wetting of OSTE polymers can be precisely controlled by modifying the off-stoichiometry, i.e. density of active surface thiol groups, and presented a powerful (95° tuning range), patternable (different wetting zones on one surface) and robust (stable for >24h in water and >3 month equivalents in air) surface modification method. We believe that this method, in combination with the attractive material and manufacturing properties of the OSTE polymers, will enable the research community to rapidly produce permanent surface modifications for flow control not currently possible.

REFERENCES

- [1] D.L. Allara, *A perspective on surfaces and interfaces*, Nature, 437, 638-639 (2005)
- [2] Tan et al., *Design of microfluidic channel geometries for the control of droplet*, Lab Chip, 2004, 4, 292-298
- [3] Datta et al., J. MEMS, 14, 3, 590-597 (2005)
- [4] Andersson et al., *Passive valves based on hydrophobic ...*, Sensors and Actuators B, 75, 1, 136-141, (2001)
- [5] Zhou et al., *Recent developments in PDMS surface modification for microfluidic...*, Electrophoresis, 31, 2-16 (2010)
- [6] Carlborg et al., *Beyond PDMS: Off-stoichiometry thiol-ene polymers ...*, Lab Chip, 2011, 11, 3136-3147
- [7] Saharil et al. *Dry transfer bonding of porous silicon membranes to OSTE(+)*., Proc. of IEEE MEMS 2011, 232-234
- [8] Karlsson et al. *High-resolution micropatterning of off-stoichiometric thiol-enes (OSTE) via a novel lithography mechanism*, Proc. of muTAS 2012, in press

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