CHARACTERIZATION OF NATIVE THIOL-ENE SURFACE CHEMISTRY FOR MICROCHIP ELECTROPHORESIS AND FLUORESCENCE DETECTION

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ABSTRACT
In this work, we report a detailed characterization of two native thiol-ene compositions (no added photoinitiator or other polymer modifiers) in terms of their optical transparency, surface charge and wetting properties. To our knowledge, the effects of thiol-ene curing conditions and ageing on capillary filling and electroosmotic flow (EOF) have not been characterized in detail before. In this work, the main emphasis is put on comparison of stoichiometric thiol-ene compositions with those bearing relatively huge molar excess of “enes” (here 50%) and on their feasibility for microchip electrophoresis (MCE).

KEYWORDS: thiol-ene, microfabrication, microchip capillary electrophoresis, fluorescence detection

INTRODUCTION
The main requirements for a new microfabrication material in chemical analysis include applicability to mass production, good optical transparency and favorable physico-chemical properties such as inert or tunable surface chemistry and easy wetting. Polymer materials offer many advantages including good cost-effectiveness and great variety of starting materials with different properties. However, polymer materials can suffer from ageing effects or unwanted non-specific adsorption, which may greatly affect microchannel wetting and above all, the analytical separation efficiency [1,2]. Recently, thiol-ene based polymers have been introduced as a new fabrication material for microfluidic devices [3-5]. Thiol-enes provide favorable materials properties, such as tunable mechanical strength and wetting, and are cured by very specific and rapid “click” photopolymerization reaction without need for an external initiator [3,4,6].

EXPERIMENTAL
The thiol-ene chips were prepared by mixing trimethylolpropane tris(3-mercaptopropionate) (“thiol”) and 1,3,5-trialyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (“ene”) monomers in molar ratios of 1:1 or 2:3, casting against poly(dimethyl siloxane) PDMS mold, and curing without cover under UV light (225 mW/cm²) for 5-25 min (Fig. 1a). After curing, the inlets (dia 1 mm) were drilled through the crosslinked thiol-ene layer, which was then cleaned with nitrogen gas and placed in the oven at +70°C for 1-2 min. Then, another planar thiol-ene layer was prepared and cured in a similar manner under UV light. The planar cover layer was laminated against the microchannel layer and bonded under UV light for 5 min. The PDMS mold used was prepared by mixing the elastomer and the curing agent in a ratio of 10:1 and cast against a microfabricated SU-8 master (h=20 μm) and cured at +80°C for 3 h. Performance characterization of separation chips was carried out by water contact angle (WCA) measurements and by running a series of MCE experiments in combination with laser induced fluorescence (LIF) detection. A standard MCE layout with effective separation length of 40 mm was used. Sample injection was performed via simple cross or double-T (100 μm length) injectors. The electric field strength used for analysis was 600 Vcm⁻¹ in all the experiments.

RESULTS AND DISCUSSION
No significant differences in the optical transparency at near-UV or visible range was observed between stoichiometric thiol-ene 1:1 and thiol-ene with 2:3 molar excess of “enes” (Fig. 1b). At visible range (ex 488 nm, em 500-700 nm), the detection sensitivities through thiol-ene chips were very similar to that recorded for Borofloat glass.
Figure 1: a) Thiol-ene microchip fabrication process: i) SU-8 master fabrication (cleanroom), ii) casting and curing of PDMS mold and iii-iv) thiol-ene chip fabrication: curing and bonding by UV light. b) Comparison of the fluorescence detection limits between thiol-ene 1:1 and 2:3 compositions and Borofloat glass in the near-UV (ex 355 nm/em 400-700 nm) and visible (ex 488 nm/em 500-700 nm) ranges.

In the UV range (ex 355 nm, em 400-700 nm), some autofluorescence originated from thiol-ene structures, which resulted in an order of magnitude poorer detection limits than that of Borofloat glass.

The effect of UV exposure time (at P=225 mW/cm²) on the hydrophobicity of the thiol-ene surface was studied by monitoring the migration times of selected fluorescein derivatives of different lipophilicity (Fig. 2a). Here, significant changes between the two compositions were observed, indicating that the surface charge and hydrophobicity are greatly dependent on the UV exposure dose. The electroosmotic flow (EOF) was shown to be cathodic and the EOF mobility was the same in thiol-ene 1:1 and 2:3 microchannels cured for 20 and 5 min, respectively. The EOF mobilities varied from +2.5 to +5.8×10⁻⁴ cm² V⁻¹ s⁻¹ depending on the pH and the electrolyte used and were generally slightly lower compared with Borofloat glass microchannels (data not shown).

The UV exposure effects were further studied by monitoring the changes in the migration times as well as in the WCA for a period of 14 days. The WCAs were higher for thiol-ene 1:1 composition (~90º) during the first days, after which the WCAs approached to that of thiol-ene 2:3 composition (70-75º) (Fig. 2b). In MCE experiments, the most lipophilic compound tested, fluorescein dilaurate (LogD=8.48), could not be analyzed in thiol-ene 1:1 channels until the surface reverted to more hydrophilic in about 4 days (Fig. 3a). This suggests that rearrangements take place on the thiol-ene surface unless the surface is fully crosslinked during exposure. Instead, in thiol-ene 2:3 microchannels, no significant (nonspecific) interactions were observed with any of the test compounds (Fig. 3b).
CONCLUSION

In conclusion, our work shows that the bulk polymer composition is reflected to the thiol-ene surface chemistry and the curing conditions have a huge effect on the performance of thiol-ene based separation chips in MCE. Although optical transparency was somewhat independent of the bulk composition, the surface charge and wetting behavior were different between thiol-ene 1:1 and thiol-ene 2:3 compositions.

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REFERENCES


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