

Supporting Information

Visible Light-Induced Controlled Surface Grafting Polymerization of Hydroxyethyl Methacrylate from Isopropylthioxanthone Semipinacol-terminated Organic Monolayers

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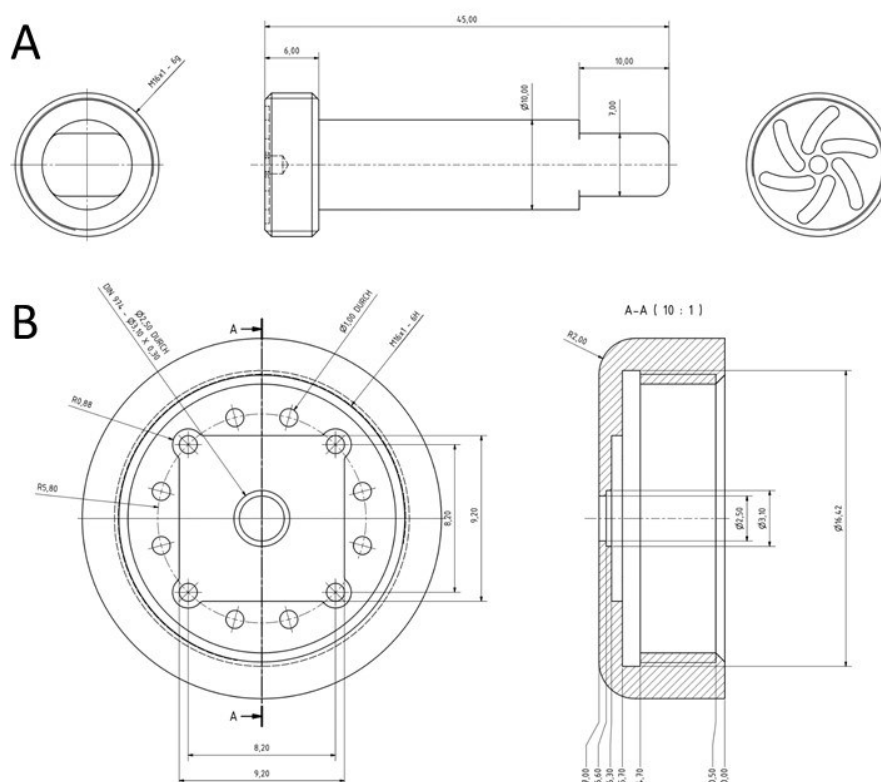


Figure S1: Technical illustration of the holder used to assemble the TEM grid as mask and the piece of silicon for the photopatterning experiment. (A) Assembled holder, (B) the round cavity next to the aperture is used for the TEM grid and the silicon is placed in the rectangular recession above the small holes in the bottom of the holder allowing the polymer solution to completely cover the OTS-ITXSP functionalized silicon. The holder is made of polyether ether ketone with a total size of 45 mm and a thickness of 10 mm (upper part) / 16.42 mm (lower part). The recession for the silicon is 9.2 mm x 9.2 mm and the hole for the TEM grid 3.1 mm with a height of 0.3 mm (B). The little rod has a thread that allows to lock into the lower part and keep both the TEM grid and the silicon in place.

Restart of the living polymerization reaction proven by co-polymerization of HEMA and MD700

To prove the livingness of the polymerization, the end group fidelity was confirmed by further chain extension and restart of the polymerization reaction. First, the hydrophobic methacrylate monomer Fluorolink MD700 (urethane methacrylic modified perfluoro polyether) (100%, Acota, United Kingdom) was polymerized onto the surface. We used the same experimental setups and parameters as in the main article. The Si-OTS-ITXSP surface was placed into a solution of 0.25 w% MD700 in acetone inside a Schlenk tube. The distance of the light source (Nichia NVSU233A-D1 U385 UV LED, $\lambda=385$ nm) and the substrate was fixed to 3 cm and the surface was irradiated for 2 min. After the grafting step, the surface was removed from solution, placed in acetone for 24 h to leach out all uncoupled monomer and analyzed using static water contact angle goniometry as well as spectroscopic ellipsometry (Table S1). After surface characterization, the same surface was immersed into a solution of 0.25 w% HEMA in acetone and irradiated for 30 min. After the polymerization, the sample was again leached for 24 h in acetone and again analyzed by static water contact angle goniometry and spectroscopic ellipsometry (Table S1).

Table S1: Surface analysis of the MD700 brushes and the MD700-HEMA brushes. Water contact angles were determined by static water contact angle goniometry and film thicknesses were determined by spectroscopic ellipsometry. Layer thicknesses are shown as the added layer thickness that arose from the corresponding grafting step (bold compound). Reported values are the average of three independent measurements, the error is the standard deviation.

Surface modification	Add-layer thickness [nm]	Contact angle [°]
Si-OTS-ITX- MD700	12.86 ± 1.27	96.4 ± 2.1
Si-OTS-ITX-MD700- HEMA	34.53 ± 4.09	57.7 ± 2.7

The results in Table 1 show the successful polymerization of MD700 and the possibility to restart the polymerization. After polymerization in a MD700 solution, polymer films with a thickness of 13 nm were obtained and the contact angles were 96°, which corresponds well with the high density of fluorine groups. After retrieval, characterization, and reimmersion, HEMA was polymerized on top of the MD700 layer and an additional film thickness of 35 nm was found on top of the MD700. The increase in layer thickness was connected with a decrease of the static water contact angle from 96° to 58° due to the hydrophilic nature of the HEMA on top of the hydrophobic MD700. As shown in the main article, HEMA directly polymerized onto OTS had contact angles of 48°-56°, indicating that the HEMA overlayer was thick and dense enough to cover the majority of the underlying MD700. These results show, that the ITXSP group is still present at the surface after an initial polymerization and can promote further polymerization reactions after immersion of the surface into a new monomer solution. This possibility of reinitiating the photoinduced polymerization is a strong indication for the living nature of the polymerization mechanism of the reaction. The results are in good agreement with literature where extended kinetic studies were performed to proof the living nature of the polymerization reaction (1,2,3).

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