

Shining Light on Poly(ethylene glycol): From Polymer Modification to 3D Laser Printing of Water Erasable Microstructures

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The implementation of stimuli-responsive bonds into 3D network assemblies is a key concept to design adaptive materials that can reshape and degrade. Here, a straightforward but unique photoresist is introduced for the tailored fabrication of poly(ethylene glycol) (PEG) materials that can be readily erased by water, even without the need for acidic or basic additives. Specifically, a new class of photoresist is developed that operates through the backbone crosslinking of PEG when irradiated in the presence of a bivalent triazolinedione. Hence, macroscopic gels are obtained upon visible light-emitting diode irradiation ($\lambda > 515$ nm) that are stable in organic media but rapidly degrade upon the addition of water. Photoinduced curing is also applicable to multiphoton laser lithography ($\lambda > 700$ nm), hence providing access to 3D printed microstructures that vanish when immersed in water at 37 °C. Materials with varying crosslinking densities are accessed by adapting the applied laser writing power, thereby allowing for tunable hydrolytic erasing timescales. A new platform technology is thus presented that enables the crosslinking and 3D laser printing of PEG-based materials, which can be cleaved and erased in water, and additionally holds potential for the facile modification and backbone degradation of polyether-containing materials in general.

responsive materials that exhibit smart and adaptive behavior such as healing, reprocessing, recycling, and degradation.^[2] Merging such a defined control over both morphology and material properties with a tailored 3D structural design that can be adaptive or dynamic in nature over time is believed to be of paramount importance to the field of 3D manufacturing technologies.^[3,4]


A particularly promising additive manufacturing technique that allows for the fabrication of responsive yet arbitrary shaped micro- and nanometer-sized objects is 3D laser lithography, commonly referred to as direct laser writing (DLW).^[5] In brief, DLW relies on nonlinear absorption phenomena whereby a tightly focused laser beam travels through a photoresist in order to create defined 3D geometries with up to sub-100 nm resolution.^[6] As a result of its superior detail, the 3D laser printing technique has hence evolved into a versatile and indispensable tool to

Changes made on a molecular level are rapidly translated into a material response.^[1] Thus, the ability to regulate chemical processes on-demand through external stimuli has been a crucial milestone for the construction of programmable and

access sophisticated structures that find applications in microfluidics,^[7] photonics,^[8] metamaterials,^[9] and cell biology.^[10] Yet, many more opportunities of laser printing remain to be unlocked and several key challenges are to be tackled in order

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DOI: 10.1002/adma.202003060

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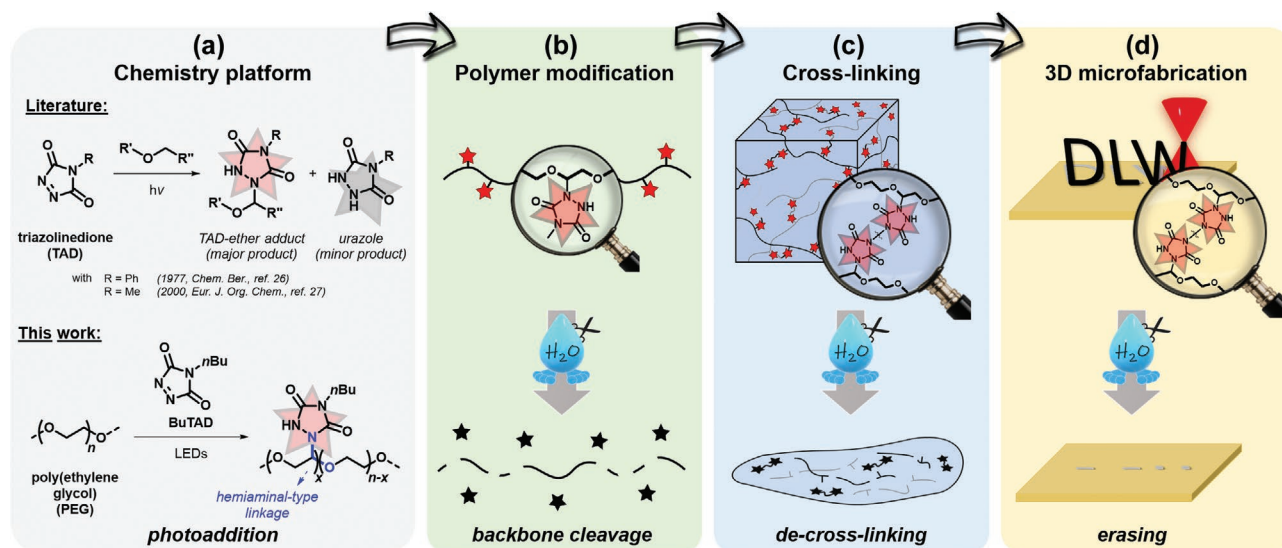


Figure 1. Schematic overview of the applied research strategy to design a novel PEG-based photoresist. a) The photoinduced reaction of triazolinediones (TADs) with ether compounds is exploited in this work for the addition of TADs to polymeric ether substrates. b) The TAD-PEG conjugation platform enables the covalent backbone-modification of polyethers that are susceptible toward hydrolytic cleavage, c) the visible light-induced crosslinking and subsequent de-crosslinking of PEG-based gels through hydrolysis, as well as d) the 3D direct laser writing of microstructures that can be erased by water.

to transform today's science fiction materials into tomorrow's science facts.^[11]

One of the emerging challenges in 3D laser lithography is that direct laser writing techniques are often restricted to the sole fabrication of permanent, unalterable 3D objects as they typically employ negative-tone photoresists that are irreversibly crosslinked.^[4b] A first step toward 4D adaptivity is the ability to erase 3D printed microstructures on demand in an efficient and controllable manner.^[11] Such post-DLW erasing is for instance a highly enabling feature for the repair of structural defects, for the selective removal of support structures (e.g., to construct hanging objects) and for the degradation of biomimetic cell culturing scaffolds, once these become redundant.^[12] Hereto, it is essential to design advanced photoresists, applicable to laser lithography, that can introduce the desired programmed cleavage into the finally printed materials. Thus far, only a few examples have been reported in which the controlled erasing of laser written microstructures can be achieved through the use of labile linkers that can be cleaved upon heating,^[13] in the presence of reducing agents,^[14] under basic conditions,^[15] or by using light of a wavelength, which differs from that in the writing process.^[16]

In order to fully expand the potential of erasable direct laser written microstructures to the realm of bioengineering applications, however, the development of photoresists that are susceptible to much milder cleavage conditions is a prerequisite.^[12,17] Indeed, elevated temperatures, chemical additives, and organic solvents all generally suffer from biocompatibility issues and should thus ideally be avoided. In pursuit of more viable methods to effect a sustained hydrogel degradation, enzyme-labile DLW photoresists have been developed which, although in its infancy, are receiving rapidly increasing attention.^[18] Nonetheless, enzymatic cleavable microstructures are limited to specifically tailored peptide-containing materials and the integration

of these responsive elements into synthetic hydrogels is often cumbersome.^[4b,12,19] An alternative biocompatible trigger to cleave 3D microscopic hydrogels can be found in hydrolysis.^[20] In particular, acrylate-terminated poly(ethylene glycol) (PEG) photoresists have attracted interest because of their susceptibility toward 3D laser printing in the presence of an appropriate photoinitiator, whereas the introduced ester linkages can render the fabricated microstructures prone to hydrolytic cleavage.^[21] Thus far, the sole report to claim mild hydrolysis of direct laser written objects under neutral physiological conditions is on the degradation of PEG-based helical swimmers, although ester cleavage of the actually 3D printed microstructures was only demonstrated under much harsher basic conditions.^[22] While a myriad of strategies have been reported to effect mild hydrolytic cleavage of PEG-based macroscopic structures, e.g., by inserting degradable linkages within the polymer backbone,^[23] applying such biocompatible responsiveness to microfabricated hydrogels thus remains to be addressed.

Guided by the need to expand the toolbox of accessible triggers to erase laser printed structures, we herein present a novel PEG-based photoresist that allows for the fabrication of macro- as well as microsized structures that can be readily erased in water, even at neutral pH. Whereas the process behind 3D printing is thus far mostly dominated by either cationic or free radically induced photopolymerizations of (macro)monomers,^[24] our approach introduced here relies on the straightforward photochemistry of a low molecular weight crosslinker that adds directly onto the backbone of a linear polymer. Specifically, we report the visible light-induced reactivity of 1,2,4-triazoline-3,5-dione (TAD, cf. **Figure 1a**) reagents toward polyether substrates as a straightforward method to synthesize backbone-modified PEG (**Figure 1b**). The observed instability of the resulting TAD-PEG conjugates toward water led us to identify their potential to construct covalently crosslinked macroscopic

PEG-materials upon green light impact ($\lambda \geq 515$ nm), which subsequently can be cleaved through hydrolysis (Figure 1c). Importantly, the possibility to cure the photoresist by multiphoton absorption ($\lambda \geq 700$ nm) was demonstrated by the fabrication of 3D microstructures via DLW at different laser powers, whereby the resulting objects could be completely erased in water at 37 °C (Figure 1d).

Our continued interest in the photochemical reactivity of triazolinediones (TADs)—powerful coupling reagents in organic synthesis, bioconjugation, and polymer science^[25]—formed the starting point of the PEG-photoresist development. TADs namely exhibit good hydrogen abstraction reactivity in ether-containing solvents upon exposure to light with the formation of a covalent addition product (see Figure 1a).^[26] While initially reported in the 1970s as merely an undesired side reaction, Risi et al. exploited this photoaddition for the modification of crown ethers under irradiation,^[27] yet no useful transformations have been reported since. Intrigued by the originally observed side reaction, we initially sought to exploit the photoinduced TAD-ether conjugation in a polymer context as a more straightforward synthesis route toward backbone-functionalized polyethers (cf. Figure 1b), as opposed to the conventionally adopted ring-opening (co)polymerization of tailored monomers.^[28] Hence, we reinvestigated the photochemistry of 4-*n*-butyl-TAD (BuTAD, cf. Figure 1), both toward acyclic and cyclic ether compounds. While no reaction is observed when purple BuTAD solutions (5 mg mL⁻¹) in di-*n*-butyl ether and tetrahydrofuran were kept in the dark, UV-irradiation ($\lambda_{\text{max}} = 365$ nm, 1 h) readily resulted in photobleaching with the formation of the expected reaction products (see Figure S1, Supporting Information). Next to the desired adducts, substantial traces of 4-*n*-butyl urazole (cf. Figure 1a) were also detected, suggesting that the photoaddition proceeds via a reductive pathway.^[27] Full TAD conversion was also observed for equimolar solutions of BuTAD and ether in acetonitrile, albeit after slightly prolonged irradiation times (i.e., 2 h, cf. Figures S2 and S3, Supporting Information).

With the swift addition of the BuTAD model reagent to small molecular weight ethers (re-)examined, the light-triggered backbone-functionalization of polymeric ethers was targeted next. To this end, PEG with an average number molecular weight of 2000 g mol⁻¹ was selected as a readily available bench-mark polyether substrate. Prior to photoaddition, the PEG hydroxyl end groups were quantitatively end-capped with *tert*-butyl isocyanate in order to exclude any possible side reactions that might occur with the electrophilic TAD reagents (see Figures S4–S6, Supporting Information, for detailed characterization).^[29] Having assessed the photostability of the resulting *t*BuPEG 2000 toward UV-light (Figures S7 and S8, Supporting Information), acetonitrile solutions of the polyether (25 mg mL⁻¹) were irradiated in the presence of different BuTAD ratios, ranging from 1 to 35 equivalents per average polymer chain. Photobleaching was only observed when the solutions were exposed to the light-emitting diodes (LEDs, $\lambda = 370$ – 380 nm, 3×3 W, 24 h), after which the amount of covalently attached BuTAD onto the polyether backbone was determined via ¹H NMR analysis, whereby the incorporated *t*Bu groups served as an internal standard (cf. Figure S9a, Supporting Information). PEG modification with up to ten equivalents of BuTAD was shown to proceed with a similar efficiency

compared to the low molecular weight ethers (i.e., yields above 80%), with up to 17% of repeating units being functionalized (see Table S1, Supporting Information). The successful modification of PEG was further evidenced by the higher molecular weight distributions observed in the size exclusion chromatograms and the covalent connectivity of TAD to the polyether backbone was confirmed by means of mass spectrometry (see Figure S9b,c and Tables S2 and S3, Supporting Information). Although higher degrees of PEG functionalization were also achieved, a significantly increased formation of urazole byproducts was noted, thereby lowering the yields of the photoaddition. Nonetheless the formation of the sacrificial byproduct was found to be inevitable, dialysis was proven to be suitable for their removal from the modified polymers (cf. Figure S10, Supporting Information). Remarkably, the TAD-based PEG modification also readily proceeded when different LED wavelengths were applied, including the far end of the visible spectrum (i.e., up to 600 nm, see Table S4, Supporting Information).

Whereas the TAD-*t*BuPEG conjugates were shown to be stable in anhydrous acetonitrile, the stability of the modified polyether toward hydrolysis raised a particular concern, since the resulting adducts contain hemiaminal-type linkages (cf. Figure 1a depicted in blue). Indeed, when dissolved in water and heated at 60 °C for 24 h, the formation of several hydrolysis products, amongst aldehydes and alcohols, could be observed (refer to Figure S11, Supporting Information, for ¹H NMR spectra), which rather limited the applicability of our established light-induced PEG modification strategy to nonaqueous environments. Yet, the ability to cleave a (generally considered) chemically inert polyether backbone under extremely mild conditions, i.e., plain water, inspired us to design covalently crosslinked PEG materials that can be debonded upon hydrolysis.

Thus, once the successful light-induced modification of PEG was established and the susceptibility of the resulting adducts to hydrolytic cleavage assessed, the TAD-based crosslinking of polyethers was next examined. Given the many research efforts that are devoted nowadays to generate photo-crosslinked materials under more benign visible light irradiation, green LEDs ($\lambda = 515$ – 525 nm) were used as the preferential emission source to effect the TAD-ether crosslinking reaction. Specifically, a higher molecular weight PEG ($M_n = 10$ kg mol⁻¹) was selected as a suitable polyether substrate to carry out the macroscopic gelation experiments as it provides a multitude of plausible TAD-reactive sites along the polymer backbone. Similar to the polymer model studies, the polyether was end-capped with *tert*-butyl isocyanate, albeit now combined with a bisfunctional TAD reagent to create a network. Thus, *t*BuPEG 10 000 was dissolved in anhydrous acetonitrile and subjected to green light in the presence of 10 wt% bisTAD crosslinker (see Figure 2). Within 1 h of irradiation, the initial purple formulation was transformed into a colorless gel, as evidenced upon vial inversion (Figure 2a). No regeneration of the purple TAD color was observed over time and the gel was shown to remain intact when kept in acetonitrile for several days (Figure 2b). Subsequent addition of water, however, caused the network to collapse after standing overnight at ambient temperature, eventually resulting in the retrieval of a clear colorless solution (Figure 2c). The hydrolysis was also effected upon addition of buffered solutions (pH = 5, 7.4, and 9, see Figure S12, Supporting Information) with an

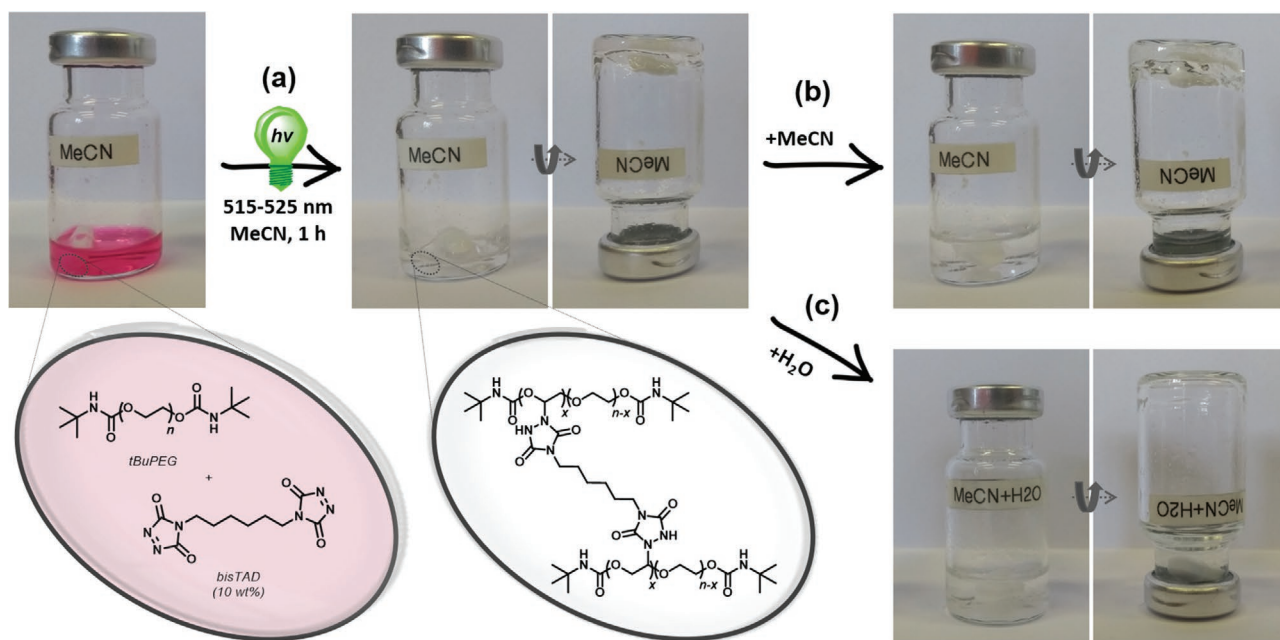


Figure 2. Macroscopic crosslinking investigations. a) Green light irradiation of a PEG solution (*t*BuPEG 10 000) in the presence of a bisfunctional TAD crosslinker (bisTAD) readily transforms the purple solution into a colorless gel. b) Whereas the resulting TAD-PEG network is stable when kept in acetonitrile, c) the addition of water causes the material to collapse and dissolve overnight upon standing at ambient temperature.

accelerated collapse of the TAD-PEG networks observed under both acidic and basic conditions, although several hours were still required to dissolve the network completely.

Following the successful synthesis of PEG-based gels in the presence of a TAD crosslinker and green light, the fabrication of 3D microstructures via DLW was attempted. First, a custom-built laser setup was employed in order to screen some basic writing parameters and assess the performance of the designed TAD-PEG photoresist. Thus, a drop of the resist (0.2 g mL⁻¹ *t*BuPEG 10 000 in MeCN, containing 20 wt% bisTAD) was subjected to different laser wavelengths (ranging from 700 to 1000 nm) and simple 2D lines were patterned onto a glass substrate at different writing powers (see Figure S13, Supporting Information). The most promising writing results for the photoinitiator-free TAD-PEG photoresist were obtained at a writing speed of 100 μm s⁻¹ using 100 fs laser pulses at 700 nm center wavelength, 80 MHz repetition rate, and at an average laser power of 10 mW (i.e., just above the threshold energy of ≈8–9 mW). These conditions are comparable to the writing conditions applied to, for instance, tailored acrylate-based photoresists.^[16c] After development in acetonitrile, the spatially resolved line patterns were observed by optical and scanning electron microscopy (SEM) imaging (cf. Figure S14a, Supporting Information). Further evaluation of the writing threshold for different laser powers revealed the non-linearity of the photoinduced crosslinking and thus the underlying multiphoton absorption process, which is a prerequisite to fabricate high resolution 3D microstructures. It is noteworthy to mention that DLW was also successful at 780 nm center wavelength, thereby enabling lithographic experiments using the TAD-PEG photoresist also on a commercial DLW system (refer to Supporting Information). Furthermore, no writing was observed when blank solutions of either the TAD crosslinker or *t*BuPEG were subjected to the applied DLW conditions.

Having identified appropriate conditions for the use of the TAD-PEG photoresist in 3D laser lithography, more challenging 3D micrometric structures such as boxing rings (15 × 15 × 5 μm³, cf. Figure 3a) and cuboids (8 × 8 × 8 μm³) were written. In contrast to the previously visualized line patterns, SEM inspection showed the 3D blocks and boxing rings to have collapsed upon drying (Figure S14b,c, Supporting Information). Nonetheless, the written structures could be visualized during the development stage by means of laser scanning microscopy (LSM) through the samples' autofluorescence upon 405 nm excitation, thereby enabling a 3D reconstruction of the spatially cured photoresist (see Figure 3b). It should be noted that safeguarding a continuous immersion of the structures in order to prevent their collapse is an important consideration.

Once DLW of the TAD-PEG objects was demonstrated, the possibility to erase the written structures through hydrolysis was evaluated. Hereto, a series of cubes and boxing rings were written into the photoresist and subsequently immersed in deionized water as soon as the residual photoresist was rinsed off. The hydrolysis of the 3D materials was monitored at 37 °C via time-lapse optical microscopy making use of a customized sample holder (Figure S15, Supporting Information) to provide a continuous aqueous environment and also to prevent the structures from collapsing upon drying. Initial attempts failed to differentiate whether the microstructures solely detached and migrated from the glass substrate upon swelling or were actually degraded (see Figure S16, Supporting Information). Further improvements were thus made by incorporating a support structure underneath the pillars of the boxing rings. Moreover, since higher laser writing powers are known to result in more densely crosslinked materials,^[30] different laser powers were utilized to fabricate a series of microstructures in order to investigate whether the effect of the crosslinking density

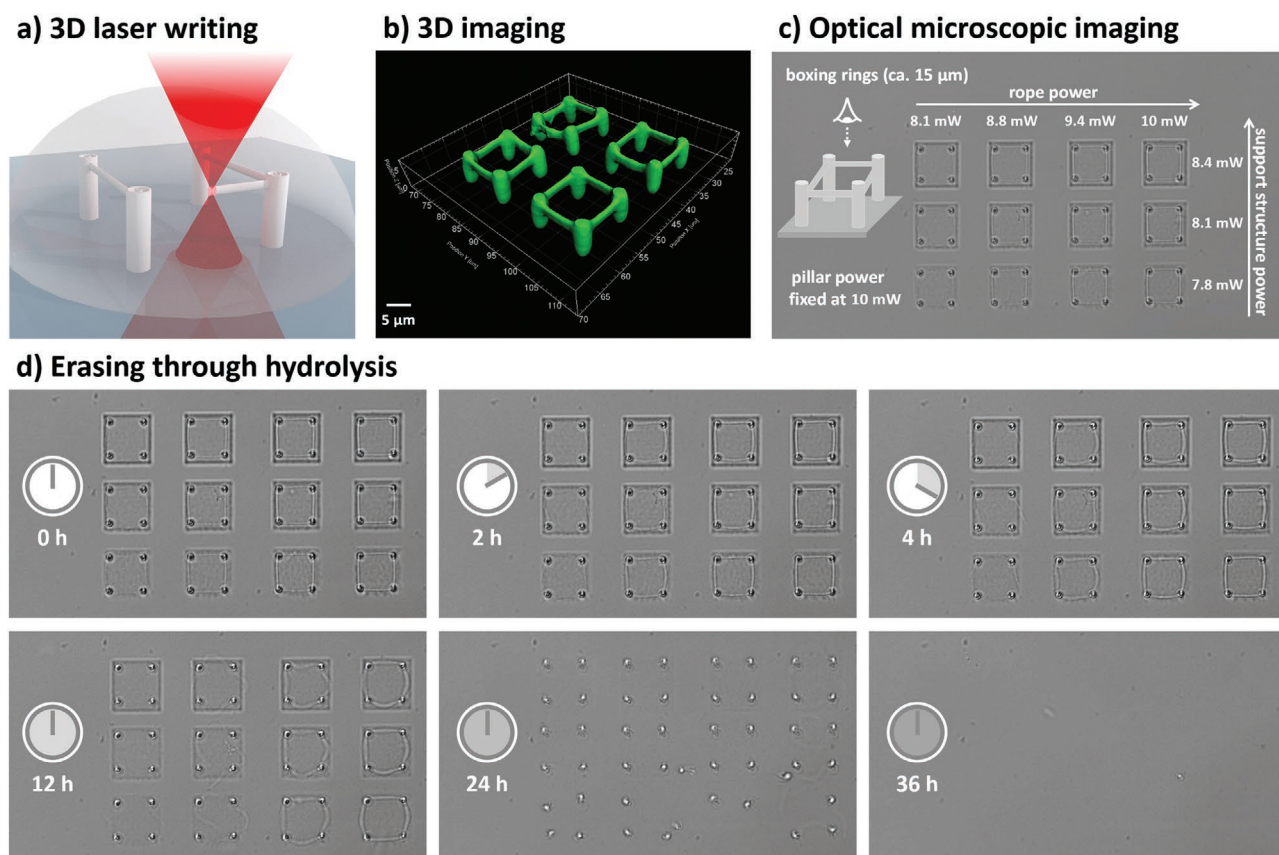


Figure 3. 3D laser lithography demonstration with the TAD-PEG photoresist. a) Visual representation of the micrometric boxing ring structures ($15 \times 15 \times 5 \mu\text{m}^3$), constructed by moving the laser voxel through the resist. b) Laser scanning microscopic 3D reconstruction of the written TAD-PEG boxing ring structures. c) Optical microscopic image of a series of boxing rings, written at varying laser powers (measured at the entrance pupil of the objective lens) in order to investigate the influence of crosslinking density on the rate of hydrolysis. d) Time-lapse optical microscopic imaging of the boxing ring structures being erased upon immersion in water at 37°C .

can modulate the rate of hydrolysis. Specifically, both the support structure and ropes of the boxing rings were written at varying powers (increasing from left to right and bottom to top in Figure 3c), whereas the pillars were fabricated at a constant laser output (i.e., 10 mW, measured at the entrance pupil of the objective lens). The cubic blocks are also written at different powers ranging from 7.5 mW up to 9.1 mW (see Figure S17, Supporting Information). From the latter series, the threshold power required to fabricate well-defined structures is clearly demonstrated, with no writing occurring at laser powers below 8.3 mW, which is in good agreement with the threshold values previously derived for the 2D line patterning experiments.

Time-lapse microscopic imaging allowed for the visualization of the newly written structures when kept in neutral water at 37°C . Shortly after the writing process, all of the TAD-PEG structures were shown to swell and disintegrate after several hours. Specifically, the boxing rings were seen to remain attached to the glass substrate while the ropes disappeared over time and completely vanished within 24 h (refer to Figure 3d and supplementary movie). Eventually, also the pillars—written at higher laser powers—were erased completely after 36 h. As expected, the structures written with the lowest laser powers degraded significantly faster compared to those fabricated at

higher powers, which can be rationalized in terms of their lower crosslinking density. The dense cuboids showcased a better resistance toward hydrolysis, presumably because of a slower diffusion of water, but eventually were also wiped out after 48 h (see Figure S17, Supporting Information). Overall, changing the laser powers during the lithographic writing process allowed for the modulation of the degradation kinetics, thus providing a means to regulate the hydrolytic cleavage timescale of the microstructures without altering the photoresist but by simply changing the DLW parameters.

In summary, we have introduced an alternative one-step approach toward the backbone functionalization of poly(ethylene glycol)s based on the rarely reported side reaction of triazolinediones to ethers upon irradiation. While low degrees of PEG modification were readily obtained, the formed TAD-PEG conjugates were found to be labile in the presence of water. This hydrolytic instability of the photoadducts led us to demonstrate the TAD-PEG system to serve as a promising platform to design adaptive backbone-crosslinked PEG-based materials under mild visible light irradiation ($\lambda > 515 \text{ nm}$). Evaluation of the resulting macroscopic PEG networks demonstrated their stability when kept in acetonitrile, and evidenced their susceptibility to being cleaved when placed in

water, even at neutral pH. Importantly, crosslinking of the unprecedented TAD-PEG photoresist can also be triggered by multiphoton absorption without the need for any photoinitiator, thereby enabling the 3D direct laser writing of erasable PEG-based microstructures with variable crosslinking densities. Our system presents a rare example of a direct laser writable photoresist whereby curing within the confined environment of the laser voxel is performed directly onto the polymer backbone through the addition of a low molecular weight crosslinker. The pioneered PEG-based photoresist excels both in its design simplicity as well as adaptivity of the written microstructures under extremely mild conditions. It is hence believed to constitute an important addition to the realm of existing DLW chemistry platforms that holds potential application in subtractive lithography for the selective postwriting removal of support structures upon submersion in water, as well as in tissue engineering, for instance to target the in vitro degradation of cell scaffolds.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

H.A.H. and F.E.D.P. acknowledge the Research Foundation-Flanders (FWO) and Bijzonder Onderzoeksfonds (BOF)-UGent for financial support. C.B.-K. acknowledges the Australian Research Council (ARC) for funding in the context of a Laureate Fellowship enabling his photochemical research program as well as continued key support by the Queensland University of Technology (QUT). The authors acknowledge support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – 2082/1 – 390761711 and by the Carl Zeiss Foundation. The authors thank Prof. Martin Bastmeyer, Marc Hippler, and Kai Weissenbruch (KIT) for access to LSM and time-lapse microscopy as well as for fruitful discussions with regard to the hydrolysis of the microstructures. H.A.H. acknowledges Matthias Eing for several scientific discussions and Markus Zieger for providing the display image in Figure 3a.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D microstructures, direct laser writing, erasable photoresists, poly(ethylene glycol), triazolinediones

Received: May 6, 2020

Revised: June 5, 2020

Published online:

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