

A highly efficient waterborne photoinitiator for visible-light-induced 3D printing of hydrogels

Jieping Wang,^a Sascha Stanic,^b Altan Alpay Altun,^c Martin Schwentenwein,^c Kurt Dietliker,^a Lu Jin,^a Jürgen Stampfl,^d Stefan Baudis^{*b}, Robert Liska,^b and Hansjörg Grützmacher^{*a,e}

^a Department of Chemistry and Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland.

^b Institute of Applied Synthetic Chemistry, Technische Universität Wien, 1060 Vienna, Austria.

^c Lithoz GmbH, 1060 Vienna, Austria.

^d Institute of Materials Science and Technology, Technische Universität Wien, 1060 Vienna, Austria.

^e Lehn Institute of Functional Materials (LIFM), Sun Yat-Sen University, 510275 Guangzhou, China.

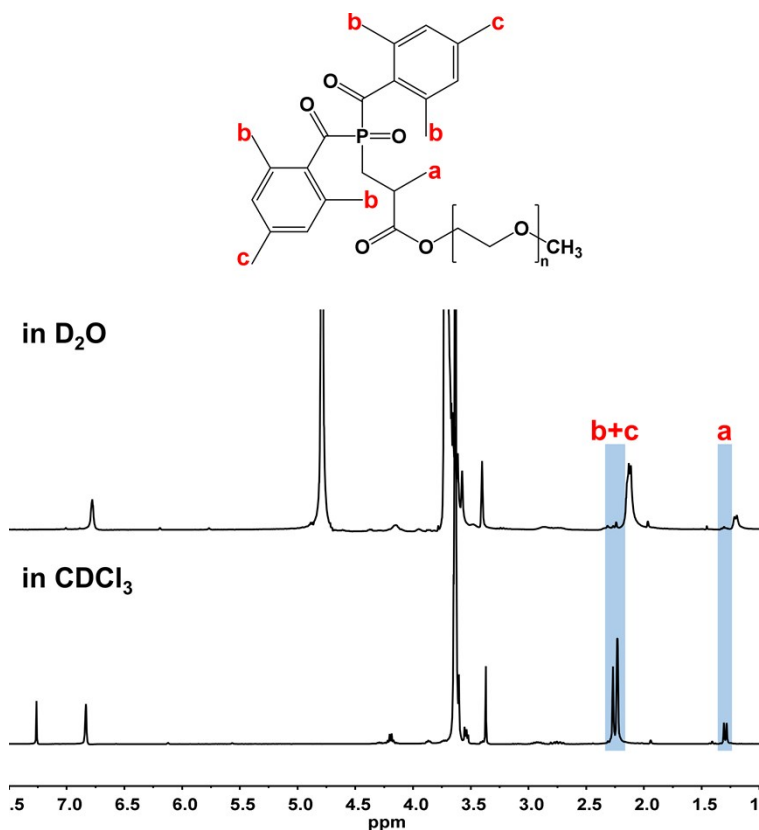


Fig. S1 Comparison of ¹H NMR spectra of PEG-BAPO in D₂O and CDCl₃ with the same concentration (20 mg/mL). The ratio of BAPO group and polyether group is 1:28 in CDCl₃ and 1:33 in D₂O. The peak positions of methyl groups (a-c) of PEG-BAPO in D₂O are moved to up-field in comparison to the spectrum in CDCl₃.

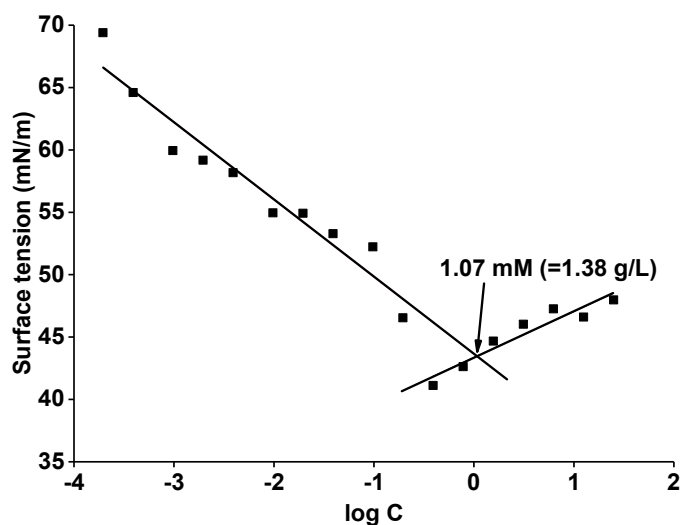


Fig. S2 Determination of critical micelle concentration (CMC) of PEG-BAPO with a tensiometer in H₂O at 25°C. The point of intersection of two lines indicates the CMC value (1.07 mM = 1.38 g/L).

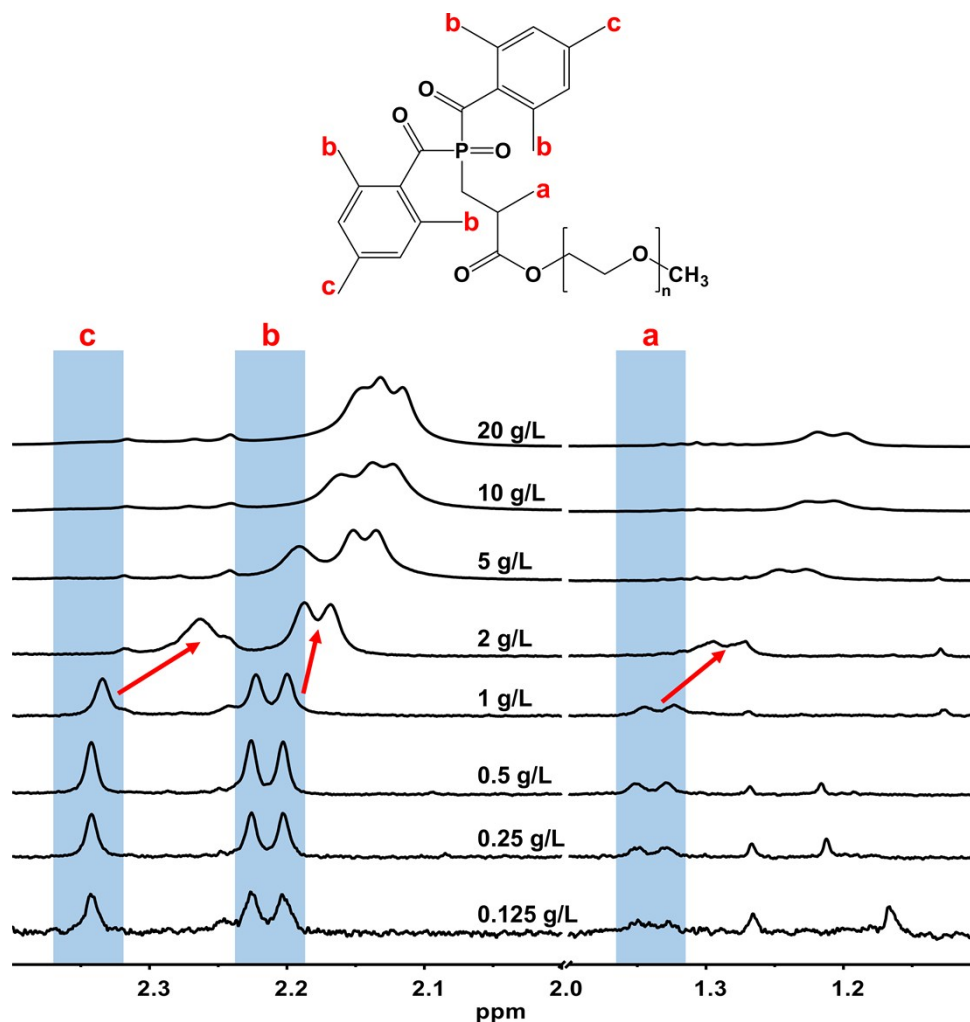


Fig. S3 Selected regions of ^1H NMR spectra of PEG-BAPO at various concentrations in D_2O at $25\text{ }^\circ\text{C}$. An obvious up-field shift of methyl groups (a-c) is observed when the concentration of PEG-BAPO in aqueous solutions increased from 1 g/L to 2 g/L , this suggests the CMC is between these two concentrations.¹

Table S1 DLS measurement of PEG-BAPO in H_2O at different concentrations.

Conc. [g/L]	Z_{ave} [nm]	PDI
5	12.1	0.28
10	8.4	0.24
15	7.1	0.12
20	7.1	0.11

Z_{ave} = Z-average particle size; PDI = polydispersity index

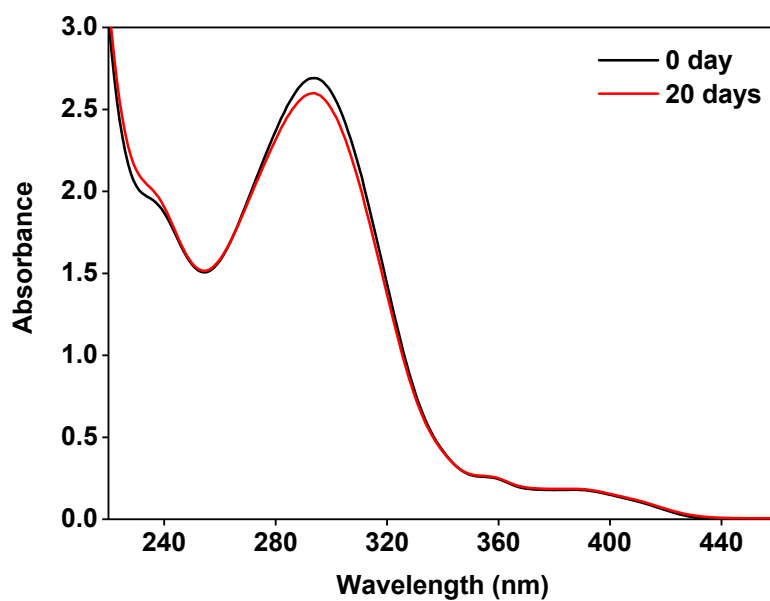


Fig. S4a Storage stability test of PEG-BAPO in a neutral solution (MeCN/H₂O = 50/50 v/v). The remaining concentration is 97% after storing for 20 days in the dark at room temperature.

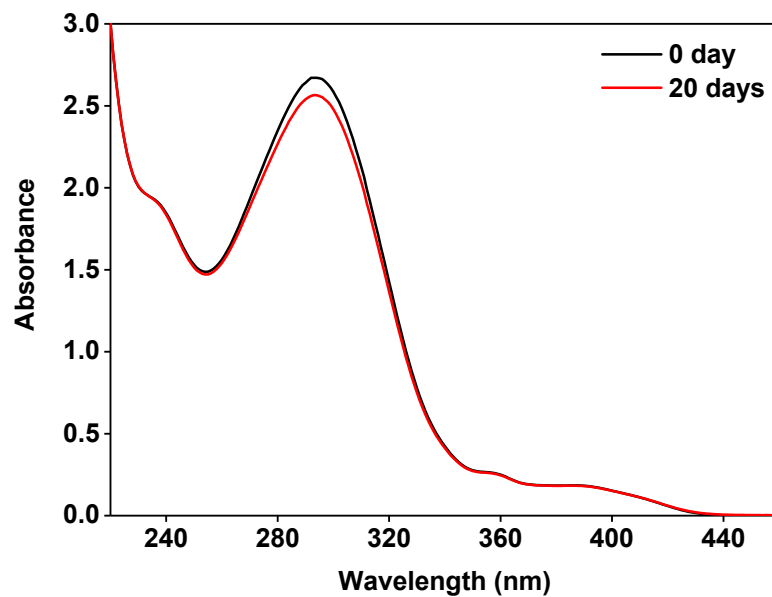


Fig. S4b Storage stability test of PEG-BAPO in an acidic solution (MeCN/H₂O = 50/50 v/v with a few drops of HCl, pH = 2). The remaining concentration is 96% after storing for 20 days in the dark at room temperature.

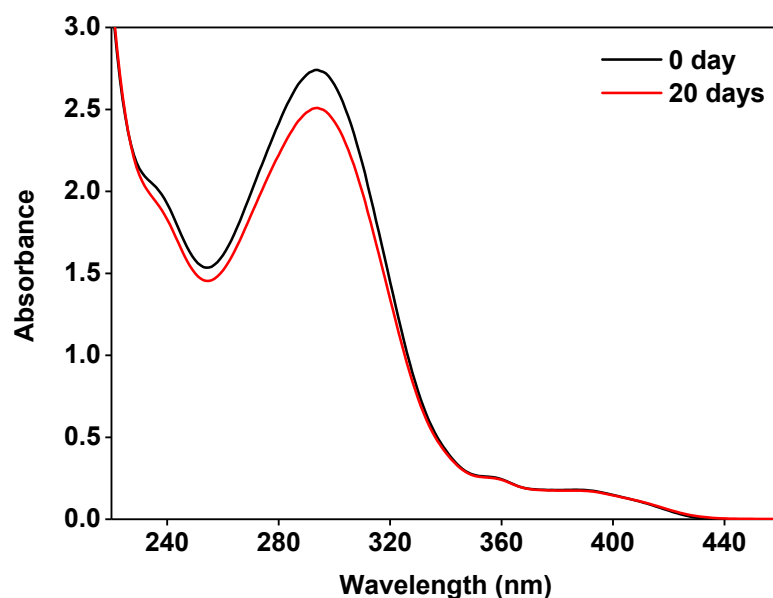
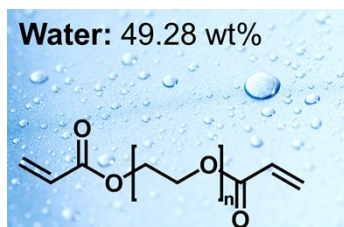
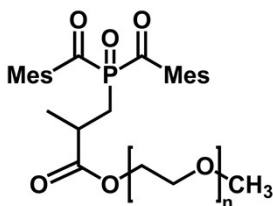


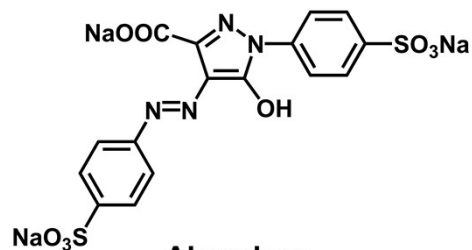
Fig. S4c Storage stability test of PEG-BAPO in an alkaline solution (MeCN/H₂O = 50/50 v/v with a few drops of NaOH, pH = 11). The remaining concentration is 92% after storing for 20 days in the dark at room temperature.



Monomer:
PEGDA, $M_n = 700$ Da,
50 wt%



Photoinitiator:
PEG-BAPO,
0.7 wt%



Absorber:
Tartrazine,
0.02 wt%

Fig. S5 The aqueous formulation for 3D printing of hydrogels.

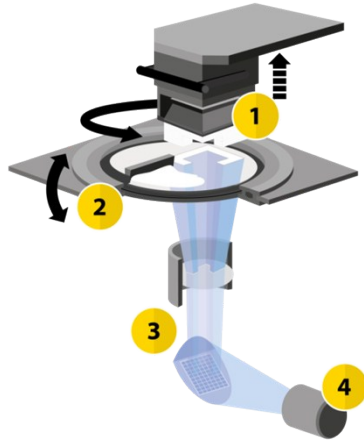


Fig. S6 Schematic setup of CeraFab 7500 printer: 1 – building platform; 2 – vat; 3 – optical system; 4 – LED

The assembly of CeraFab 7500-system comprises a rotating vat filled with the feed material. The light source illuminates the bottom side of the vat via a digital micro-mirror device. The building platform is above the vat and moves upwards the z-axis during the fabrication process.

Table S2 Light penetration tests of aqueous formulations.

Tartrazine conc.	Exposure time	Penetration depth
[wt%]	[s]	[μm]
0	5	0
0	10	230
0	15	250
0.01	10	150
0.01	15	260
0.01	20	278
0.02	5	0
0.02	10	56

Table S3 Printing parameters for the gyroid hydrogel structure.

Parameter [units]	Value
Layer thickness [μm]	25
Light intensity [mW/cm^2]	64.2
Exposure time [s]	10
Waiting time [s]	4
Tilt up speed [steps/s]	20
Tilt down speed [steps/s]	20
Time per layer [s]	36

The waiting time corresponds to the time period before each curing sequence and the tilting parameters correspond to the speed for approaching the part towards the vat before curing or separating the part from the vat after curing respectively. The total time per layer corresponds to a printing speed of approximately 2.4 mm/h in z-direction.

A layer thickness of 25 μm (about half of the penetration depth) was chosen intentionally in order to produce overlapping curing zones to ensure the layer-layer connectivity.

Experimental Section

General considerations

All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in an M Braun dry-box containing an atmosphere of purified argon. Poly(ethylene glycol) methyl ether methacrylate (PEGMEM, $M_n = 950$ Da) and poly(ethylene glycol) diacrylate (PEGDA, $M_n = 700$ Da) were purchased from Sigma-Aldrich and were used as received without further purification. Irgacure 2959 was obtained from BASF Schweiz AG. BAPO-ONa² and BAPO-OLi³ were synthesized according to published procedures. Triethylamine, ethanol, and hydrogen peroxide (35%) were bought from Acros. Deionized water was used in all experiments.

Synthesis of PEG-BAPO

A suspension of bis(mesityl)phosphane (3.59 g, 11 mmol, 1.1 eq.) and triethylamine (0.15 mL, 1.1 mmol, 10 mol%) in ethanol (100 mL) was prepared in a 250 mL Schlenk flask. Poly(ethylene glycol) methyl ether methacrylate ($M_n = 950$ g/mol, 9.50 g, 10 mmol, 1 eq.) was added to the suspension. After stirring for 24 h at 60°C, aqueous hydrogen peroxide (1.9 mL, 22 mmol, 2.2 eq., 35%) was added dropwise at 0 °C, and the solution was vigorously stirred at r.t. for another 6 h. The solvent was removed under reduced pressure and the residual was three times recrystallized from diethyl ether/pentane (40 mL/10 mL, -20 °C), providing a yellow solid after removing the solvent under high vacuum for 14 h (9.31 g, 72.1%).

¹H-NMR (300.13 MHz, CDCl₃, 298 K): δ [ppm] = 1.27 (d, 3 H, CHCH₃, $^3J_{\text{HH}} = 7.2$ Hz), 2.21 (s, 6 H, *o*-CH₃ Mes), 2.21 (s, 6 H, *o*-CH₃ Mes), 2.25 (s, 6 H, *p*-CH₃ Mes), 2.36-2.50, 2.65-2.99 (m, 3 H, PCH₂CHCO), 3.33-3.40 (OCH₃), 3.48-3.87, 4.10-4.22 (CH₂O), 6.81 (s, 4 H, *H*_{ar} Mes);

¹³C NMR (75.47 MHz, CDCl₃, 298 K): δ [ppm] = 19.4 (d, $^3J_{\text{PC}} = 7.6$ Hz, CHCH₃), 19.9 (s, *o*-CH₃ Mes), 21.3 (s, *p*-CH₃ Mes), 29.0 (d, $^1J_{\text{PC}} = 54.3$ Hz, CH₂P), 33.8 (d, $^2J_{\text{PC}} = 3.5$ Hz, CHCO), 59.1 (s, OCH₃), 64.1, 69.0, 70.6, 72.0 (CH₂O), 129.3 (s, C^{3,5} Mes), 135.8 (d, $^2J_{\text{PC}} = 41.1$ Hz, C¹ Mes), 135.9 (d, $^2J_{\text{PC}} = 41.0$ Hz, C^{1'} Mes), 136.0 (d, $^3J_{\text{PC}} = 15.6$ Hz, C^{2,6} Mes), 141.4 (d, $^5J_{\text{PC}} = 1.9$ Hz, C⁴ Mes), 174.8 (d, $^3J_{\text{PC}} = 8.2$ Hz, COCH), 215.5 (d, $^1J_{\text{PC}} = 53.9$ Hz, COMes), 215.8 (d, $^1J_{\text{PC}} = 53.1$ Hz, C²OMes);

³¹P{¹H} NMR (121.49 MHz, CDCl₃, 298 K): δ [ppm] = 24.7 ppm;

IR (ATR [cm⁻¹]): 2879 (s), 1730 (w), 1552(w), 1466 (w), 1444 (w), 1344 (s), 1278 (m), 1242 (m), 1146 (s), 1105 (s), 1032 (s), 957 (s), 842 (s), 728 (m).

Solution NMR spectroscopy

¹H, ¹³C, ³¹P NMR spectra were recorded on Bruker 300 spectrometer operating at 300.13 MHz, 75.47 MHz and 121.49 MHz, respectively. Chemical shifts δ were measured according to IUPAC and are given in parts per million (ppm) relative to TMS and H₃PO₄ for ¹H, ¹³C and ³¹P respectively.

Infrared Spectroscopy (FTIR-ATR)

FT-IR spectra of the dried samples were recorded using a Tensor 27 FT-IR spectrometer (Bruker, Switzerland). For each sample, the diamond crystal of an Attenuated Total Reflectance (ATR) accessory was brought into contact with the area to be analyzed. The contact area was a circle of about 1.5 mm in diameter. All spectra were recorded between 4000 and 600 cm⁻¹ with a resolution of 4 cm⁻¹ and 32 scans per sample.

Ultraviolet–visible spectroscopy

UV/vis spectra were recorded on a UV/vis/NIR lambda-19-spectrometer (range 200 - 600 nm) in 10 mm Quartz cells.

Critical micelle concentration (CMC) determination

The critical micellar concentration (CMC) of PEG-BAPO was determined by surface tension measurements via Wilhelm plate method⁴ in aqueous solutions at various concentrations, using a tensiometer DCAT 21 (Dataphysics, Germany) with a PT11 Wilhelmy plate (L: 10mm, W: 19.9mm, T: 0.2mm) at 25.0 ± 0.2 °C.

Dynamic light scattering (DLS) measurement

The sizes of micelles under different concentrations were characterized by DLS. The particle dispersions were measured at 25 °C in disposable plastic sizing cuvettes. All measurements were performed at an angle of 173° in backscattering mode and each sample was measured 3 times.

Storage Stability

The storage stability test was performed in three different solvents. MeCN/H₂O = 50/50 v/v for stability in neutral solutions, MeCN/H₂O = 50/50 v/v with a few drops of HCl (pH = 2) for stability in acidic solutions and MeCN/H₂O = 50/50 v/v with a few drops of NaOH (pH = 11) for stability in alkaline solutions. PEG-BAPO was dissolved in each solvent in a concentration of 1 × 10⁻³ mol/L

and at $t = 0$ day UV-Vis spectra were measured. Afterward, the solutions were stored in the dark for 20 days at room temperature. At $t = 20$ days UV-Vis spectra were measured again. The concentration was diluted to 2×10^{-4} mol/L for all UV-Vis measurements to ensure that the absorbance stays in the detection range of the UV-Vis spectrometer. The percentage of decline in absorbance at the maximum $\pi \rightarrow \pi^*$ transition of the C=O group ($\lambda_{\max} = 294$ nm) is directly proportional to the percentage in concentration decline, therefore directly providing the remaining concentration of PEG-BAPO.

Photo-Differential Scanning Calorimetry (DSC)

Photo-DSC measurements were performed on a Netzsch DSC 204 F 1 at 25 °C under nitrogen atmosphere (20 mL/min) using a LED-lamp (Omniculture LX, 460 nm) at 8 mW/cm². Photoinitiators (PEG-BAPO, BAPO-ONa, BAPO-OLi and Irgacure 2959) were used in a concentration of 5 mM in an aqueous solution containing 50wt% of PEGDA. 10 ± 0.5 mg of the samples were weighed into the aluminum crucibles that were closed by a glass lid. At the beginning of the measurements, an isothermal period of 240 s was scheduled before the irradiation was activated for 300 s. Subsequently, another isothermal period of 60 s was observed before the second irradiation period of another 300 s was started. The DSC curve from the second irradiation period was subtracted from the first in order to provide a DSC curve, which excludes all thermal effects due to light dissipation. From the resulting DSC curves, t_{\max} , the time to reach the maximum of heat flux, $t_{95\%}$, the time to reach 95% of double bond conversion (DBC, Equation 1), and the DBC itself were extracted from the data obtained.

$$DBC = \frac{\Delta H_P \times M_W}{\Delta H_{0,P}} \quad (1)$$

ΔH_P Heat of polymerization [J/g] (area of the peak)

M_W Molecular weight of the monomer [g/mol]

$\Delta H_{0,P}$ Theoretical heat of polymerization of the monomer [J/mol] (for PEGDA 700, 155 kJ/mol was used)

Photorheological characterization

Rheometric measurements⁵ were performed using an Anton Paar Modular Compact Rheometer MCR 302 WESP with a plate-to-plate measuring system consisting of a 25 mm steel stamp, a glass plate and a gap size of 50 μ m in oscillation mode with 1 Hz and amplitude of 0.1 % strain at 25 °C. Samples were irradiated with a LED-lamp (Omniculture LX, 460 nm) bottom-up through the glass plate with light intensity (8 mW/cm²) as measured at the top of the glass plate with an

Oceanoptics USB200+ radiometer. Storage modulus G' was measured every second; the light was automatically turned on after 120 seconds and the measurement was continued for different, predefined periods. All measurements were done at least in triplicate.

The maximum storage modulus (G'_{\max}) is a measure of the mechanical integrity and the crosslink density, respectively. The slope $\Delta G'/\Delta t$ of this linear fit was taken as a measure for the reactivity of the hydrogel formulation while the delay (or induction) time t_d (at the intersection of the linear fit with the abscissa) was defined as an indicator for the affinity of the formulation to gel. The gel point t_g , the intersection of the curves G' and G'' , was found to be equivalent to t_d , as no substantial increase of G' is observable before t_g is attained.

Penetration tests

A microscope slide was coated with a thin layer of formulation and subsequently exposed to a circular light spot with a diameter of 10 mm. This light exposure (460 nm) was performed for different durations at a light intensity of 64.2 mW/cm². The light exposure initiated local photopolymerization in the exposed area and selectively cured the aqueous formulation. The non-solidified formulation was afterwards removed and the thickness of the cured hydrogel was measured using a micrometer screw. The thickness of the solidified hydrogel is equal to the light-penetration depth for the corresponding energy dose, which equals to the product of irradiance value and light exposure time. Due to the low stiffness of the hydrogel, the obtained values are of course subject to a substantial measurement uncertainty; nonetheless, it is possible to deduce trends and determine basic parameters for the actual printing process.

3D-printing

3D structuring was done using a Lithoz CeraFab 7500 printer. The assembly of the CeraFab 7500-system comprises a rotating vat filled with the feed material. The light source illuminates the bottom side of the vat via a digital micro-mirror device. The building platform is above the vat and moves upwards the z-axis during the fabrication process.

The building envelope of the CeraFab-system is 76 x 43 x 150 mm. The resolution in the x/y-plane is 40 x 40 μm and for the structuring of the photocurable aqueous formulation, the layer thickness was set to 25 μm . The 3D-printing process relies on the concept of photopolymerization. A thin layer of resin is automatically coated onto the vat, the building platform approaches the vat, only leaving a small gap of a couple of 25 μm which remains filled with resin, this gap corresponds to the thickness of an individual layer in the printed object. Approximately 15 mL of the freshly prepared aqueous formulation comprising PEGDA (50 wt%), PEG-BAPO (5 mM, 0.7 wt%) and

tartrazine (0.02 wt%) were poured into the vat before starting the printing process. The photosensitive compounds in the formulation are then cured by selective exposure with light of 460 nm wavelength - where the light hits the formulation the diacrylate compound photopolymerizes into a 3-dimensional network. After completing the layer, including a waiting time of 4 s, the building platform is elevated and the whole sequence is repeated all over again. The waiting time corresponds to the period before each curing sequence and the tilting parameters (tilt up and tilt down speed of 20 steps per second) correspond to the speed for approaching the part towards the vat before curing or separating the part from the vat after curing, respectively. The total time per layer corresponds to a printing speed of approximately 2.4 mm/h in the z-direction. After the layer-by-layer structuring, the cured structures are removed from the building platform using a razorblade. Subsequently, they were carefully cleaned from the excess formulation by immersing the part in water.

References

1. X. Cui, S. Mao, M. Liu, H. Yuan and Y. Du, *Langmuir*, 2008, **24**, 10771-10775.
2. G. Müller, M. Zalibera, G. Gescheidt, A. Rosenthal, G. Santiso-Quinones, K. Dietliker and H. Grützmacher, *Macromol. Rapid Commun.*, 2015, **36**, 553-557.
3. S. Benedikt, J. Wang, M. Markovic, N. Moszner, K. Dietliker, A. Ovsianikov, H. Grützmacher and R. Liska, *J. Polym. Sci. A Polym. Chem.*, 2016, **54**, 473-479.
4. A. Patist, S. S. Bhagwat, K. W. Penfield, P. Aikens and D. O. Shah, *Journal of Surfactants and Detergents*, 2000, **3**, 53-58.
5. C. Gorsche, R. Harikrishna, S. Baudis, P. Knaack, B. Husar, J. Laeuger, H. Hoffmann and R. Liska, *Anal. Chem.*, 2017, **89**, 4958-4968.