

SUPPORTING INFORMATION

UV-Induced Cationic Ring-Opening Polymerization of 2-Oxazolines for Hot Lithography

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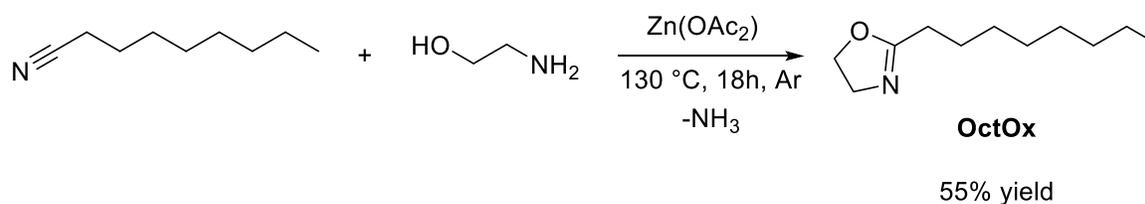
MATERIALS AND EXPERIMENTAL METHODS

Materials. All reagents were purchased from Acros, Fluka and Merck and were used without further purification. Solvents were purchased and distilled prior to usage. 2-Phenyl-2-oxazoline (PhOx), 1,4-butanediol dimethacrylate (BDDMA), hexyl methacrylate (HexMA) and benzyl methacrylate (BMA) were purchased from Sigma-Aldrich and used as received. Thin Layer Chromatography (TLC) was carried out on silica gel 60 F254 aluminum foils from Merck. The photoacid generator tris(4-((4-acetylphenyl)thio)phenyl)sulfonium tetrakis(perfluorophenyl)borate (Irgacure PAG290[®], S-B) was kindly donated by BASF. The photoacid generator consisting of a mixture of triarylsulfonium hexafluoroantimonate salts (S-Sb) in a solution of propylene carbonate (50 wt%) was kindly donated by Tronly. The free radical photoinitiator bis(4-methoxybenzoyl)diethylgermanium (BMDG, Ivocerin[®]) was kindly gifted from Ivoclar Vivadent AG.

Synthetic procedures

Syntheses of 2-oxazoline model compounds 2-octyl-2-oxazoline (OctOx) and 1,6-bis(4,5-dihydrooxazol-2-yl)hexane (BisOx) were conducted according to literature.¹

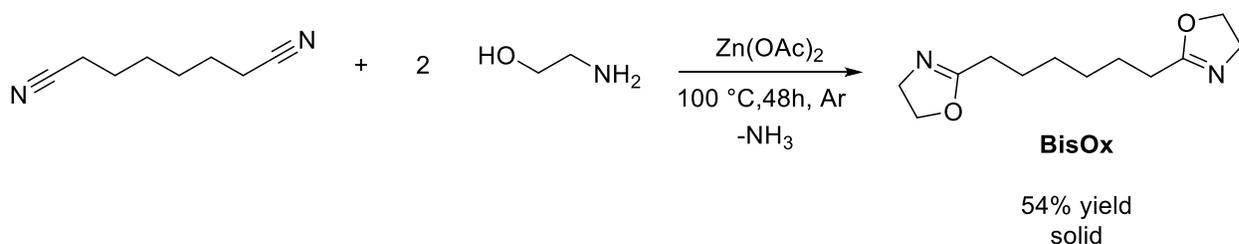
2-Octyl-4,5-dihydrooxazole (OctOx).



The synthesis was conducted under argon atmosphere. In a 100 mL 3-necked round bottom flask with a reflux condenser, a septum, an inert gas inlet and a magnetic stirring bar, 1.37 g (6.3 mmol, 0.025 eq) of zinc acetate dihydrate were dispersed in 34.8 g (250 mmol, 1.0 eq) of nonanenitrile. 18.0 mL of ethanolamine (300 mmol, 1.2 eq) were added dropwise under vigorous stirring at 130 °C. The solution was stirred at 130 °C overnight and the conversion controlled via TLC. After cooling to room temperature, 200 mL of deionized water was added to the reaction mixture and extracted three-times with 200 mL dichloromethane. The combined organic phases were dried over Na₂SO₄

and the solvent evaporated *in vacuo*. The crude product was purified by distillation (b.p. 110 °C/7.5 Torr) yielding 25.2 g of colourless liquid (138 mmol, 55 %). TLC (PE/EA 2:1) $R_f = 0.27$. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 4.21 (t, 2H, $J=9.54$), 3.81 (t, 2H, $J=9.54$), 2.26 (t, 2H, $J=7.80$), 1.62 (q, 2H, $J=7.51$), 1.16-1.39 (m, 10H), 0.87 (t, 3H, $J=6.82$). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ (ppm): 168.8, 67.2, 54.5, 31.9, 29.4, 29.3, 29.2, 28.1, 26.1, 22.7, 14.2. GC-MS rt 9.78 min, > 99 %.

1,6-Bis(4,5-dihydrooxazol-2-yl)hexane (BisOx).



The synthesis was conducted under argon atmosphere. In a 250 mL 3-necked round bottom flask with a reflux condenser, a septum, an inert gas inlet and a magnetic stirring bar, 3.52 g (16 mmol, 0.05 eq) of zinc acetate dihydrate were dispersed in 43.6 g (320 mmol, 1.0 eq) of 1,6-dicyanohexane. 58 mL of ethanolamine (1.20 mol, 3.0 eq) were added dropwise under vigorous stirring at 100 °C. The solution was stirred at 100 °C for

48 hours and the conversion controlled via $^1\text{H-NMR}$. After cooling to room temperature, 200 mL of deionized water was added to the reaction mixture and extracted three-times with 250 mL dichloromethane. The combined organic phases were dried over Na_2SO_4 and the solvent evaporated *in vacuo*. The crude product was purified by distillation (b.p. $132\text{ }^\circ\text{C}/0.03\text{ Torr}$) yielding 38.5 g of colourless solid (172 mmol, 54 %). mp $64\text{-}66\text{ }^\circ\text{C}$. TLC ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 9:1) $R_f = 0.59$. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 4.18 (t, 2H, $J=9.36$), 3.78 (t, 2H, $J=9.56$), 2.23 (t, 2H, $J=7.61$), 1.60 (m, 4H), 1.34 (m, 4H). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ (ppm): 168.6, 67.2, 54.5, 28.9, 28.0, 25.9. GC-MS rt 14.99 min, > 99 %.

Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz FT-NMR spectrometer. Deuterated chloroform (CDCl_3) and dimethylsulfoxide (DMSO-d_6) was used as solvent. Melting points were determined with an OptiMelt automated melting point system from SRS Stanford Research Systems.

Photo-DSC. Photo-DSC studies were conducted using a photo-DSC 204 F1 Phoenix from Netzsch. Filtered UV-Vis light (320-500 nm) was applied using an Exfo OmniCure 2000 with a glassfiber filled double-core lightguide (3 mm fiber diameter). The light

intensity was calibrated by an Omnicure R2000 radiometer and set to 3 W/cm² at the tip of the light guide, corresponding to 130 mW/cm² irradiation intensity at the sample position, measured by an Ocean Optics USB 2000+ spectrometer. All measurements were conducted under inert atmosphere (Nitrogen flow of 20 mL min⁻¹). A 4 min conditioning time at the respective measurement temperature was run before two-fold irradiation (2x 900 s) of the samples. The heat flow of the reaction was recorded as a function of time. Formulations of the respective monomer and 0.5 mol% of S-B per reactive group of 2-oxazoline were prepared. The formulations were weighed into 3 mL brown glass vials and subsequently stirred magnetically for 30 min at room temperature, or above the melting point of the monomer BisOx, respectively. After this time the initiator has been dissolved completely. The triarylsulfonium photoacid generator S-B could not be dissolved in the 2-n-octyl-2-oxazoline, thus propylene carbonate was added to the mixture (PAG/propylene carbonate 50:50 wt%). The sample mass in the aluminium crucibles was 14 ± 0.5 mg. All measurements were conducted in triplicates. The evaluated results represented the overall polymerization enthalpy by the peak area (ΔH_p [J/g]), the time to reach the peak maximum (t_{max} [s]), the time to reach 95 % of conversion by the

peak are (t_{95} [s]), and the peak height (h [W/g]). The calculation of conversion (C [%]) and rate of polymerization (R_p [mol·L⁻¹·s⁻¹]) from photo-DSC analyses were accessible after determination of the theoretical functional group enthalpy (ΔH_{OP}) of the 2-oxazoline reactive moiety.

Theoretical functional group enthalpy by photo-DSC. The theoretical functional group enthalpy was determined using the monofunctional monomer 2-octyl-2-oxazoline (OctOx) in photopolymerizations at 120 °C by photo-DSC and subsequent ¹H-NMR analysis according to Equation S1. For most accurate results in the determination of theoretical functional group enthalpy, the PAG concentration within these measurements was increased to 1 mol% S-B per reactive group to reach enhanced conversions in the photopolymerizations. Hence, the formulation consisted of the monomer OctOx, 1 mol% S-B and propylene carbonate (PAG/propylene carbonate 50:50 wt%). The sample mass in the aluminium crucibles was 14 ± 0.5 mg. After one irradiation period (900 s), the polymer samples were quenched with a drop of pyridine and dissolved in 0.7 mL of deuterated chloroform. After dissolution of the polymer samples, ¹H-NMR measurements gave the conversion by the amount of residual monomer from the integrals of 2-

oxazoline's 4- and 5-positioned proton signals in relation to the octyl substituent's methyl protons as internal standard. The overall enthalpy detected in photo-DSC analysis ΔH_P was set in relation to the conversion determined from $^1\text{H-NMR}$ analysis of the soluble linear-chained polymer (C_{NMR}).

The calculation according to Equation S1 considers the ratio of monomer mass in the total formulation mass ($\frac{m}{m_{tot}}$), as well as the molecular weight MW of the monomer. The results arising from averaged triplicate photo-DSC measurements are summarized in Table S1.

Equation S1 Calculation of theoretical functional group enthalpy ΔH_{OP}

$$\Delta H_{OP} = \frac{\Delta H_P * MW}{\frac{m}{m_{tot}} * C_{NMR}}$$

Table S1. Determination of theoretical functional group enthalpy of 2-octyl-2-oxazoline (OctOx) by photo-DSC and $^1\text{H-NMR}$

T [°C]	C_{NMR} [%]	ΔH_P [J/g]	ΔH_{OP} [kJ/mol]	Mass loss [%]	$\Delta H_{OP,corr}$ [kJ/mol]
120	88.7 ± 0.4	305.0 ± 2.4	68.3 ± 0.4	7.0 ± 0.7	73.1 ± 0.9

The results in Table S1 show the detected polymerization heat ΔH_P from which ΔH_{0P} is derived for OctOx via C_{NMR} . The results for 120 °C show good reproducibility and low standard deviation within the triplicate measurement. The overall mass loss by evaporation deviates the specific enthalpy and was therefore corrected by calculation of $\Delta H_{0P,corr} = 73.1 \pm 0.9 \text{ kJ mol}^{-1}$.

Structural analysis of poly(OctOx) by GPC and ¹H-NMR. Samples of poly(OctOx) from separately conducted photopolymerization experiments by photo-DSC at temperatures of 100, 120 and 140 °C were analyzed by gel permeation chromatography (GPC). Formulations of 2-octyl-2-oxazoline (OctOx) containing 1.0 mol% S-B and propylene carbonate (PAG/propylene carbonate 50:50 wt%) were used for these measurements. Figure S2 shows the ¹H-NMR analysis of OctOx formulation (1 mol% S-B) before and after photopolymerization at 140 °C.

Additionally, GPC analysis of poly(OctOx) photopolymerized at 120 °C with 0.5, 1.0 and 1.5 mol% of S-B and propylene carbonate (PAG/propylene carbonate 50:50 wt%) were conducted to evaluate the impact of PAG concentration on the resulting polymer.

The photopolymerizations by photo-DSC were conducted using equal conditions as in prior photo-DSC studies, namely 130 mW/cm² irradiation intensity, 2 x 900 s irradiation time and 14 ± 0.5 mg sample mass.

The polymer samples were analyzed by GPC on a Viscotek GPCmax VE2001 instrument equipped with three columns (Styragel HR 0.5 THF, Styragel HR 3 THF, Styragel HR 4 THF) and a Viscotek VE3580 RI detector. Dry THF was used as the mobile phase (1.0 mL min⁻¹ flow rate) at 40 °C. Polystyrene standards (in the range between $M_n = 0.370$ and 177 kDa) were used for standard calibration. The photopolymers were dissolved in dry THF, and these solutions were filtered with a 200 nm poly(tetrafluoroethylene) syringe filter. Portions of 100 µL of the samples were injected. Empower Pro software was used for the evaluation of the elugrams and to calculate the number- and weight-average molecular weight (M_n and M_w) and the polydispersity \bar{D} (M_w/M_n) of the polymers. The results from GPC analysis are depicted in Table S2.

Table S2. Results of GPC of poly(OctOx) photopolymerized at temperatures of 100, 120 and 140 °C, and with 0.5, 1.0 and 1.5 mol% S-B at 120 °C

c(PAG) [mol%]	T [°C]	M _n [Da]	M _w [Da]	Đ
1.0	100	7700	16800	2.2
	120	8500	16800	2.0
	140	9200	19100	2.1

T [°C]	c(PAG) [mol%]	M _n [Da]	M _w [Da]	Đ
120	0.5	9600	21100	2.2
	1.0	8500	16800	2.0
	1.5	8000	14300	1.8

From the GPC results of poly(OctOx) in Table S2 the influence of temperature and PAG concentration during photopolymerization is seen. Using a formulation of OctOx containing 1 mol% S-B, the molecular weights increase with higher temperatures in photopolymerization. This is reasoned by the enhanced propagation which is strongly influenced by thermal energy input to the photopolymerization. By the increase of PAG concentration in photopolymerizations at 120 °C the expected reduction of molecular weights is observed. The increase of initiating species in the cationic photopolymerization of OctOx generates shorter polymer chains in the resulting poly(OctOx).

STA (Simultaneous thermal analysis). For STA measurements an STA 449 F1 Jupiter from Netzsch was used. About 14 ± 0.5 mg of the respective formulations (equal to formulations for photo-DSC analysis above; 0.5 mol% S-B per reactive group) were weighed into standard aluminium DSC crucibles and closed with appropriate pierced aluminium lids. Thermal stabilities of photoreactive formulations were determined with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from $25 \text{ }^\circ\text{C}$ to $300 \text{ }^\circ\text{C}$ under nitrogen atmosphere. Thermal stabilities of photopolymer samples were determined with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from $25 \text{ }^\circ\text{C}$ to $500 \text{ }^\circ\text{C}$ under nitrogen atmosphere (Figure S5).

(Thermo)mechanical testing of photopolymers

Formulations and sample preparation of (thermo)mechanical testing specimens.

For mechanical testing specimens, formulations of the monomers with the respective cationic or free radical photoinitiator, S-B or BMDG (Figure S3 and S4), were prepared. In order to reach full conversion in the bulky photopolymer specimen, an increased photoinitiator concentration of 1 mol% per reactive group of respective monomers was

used. The formulations were weighed into 3 mL brown glass vials and treated in an ultrasonic bath for 30 min to dissolve the photoinitiator.

The specimens for mechanical testing were prepared by photopolymerization of the formulations in silicon molds (for DMTA: $5 \times 2 \times 40 \text{ mm}^3$; for Dynstat impact test: $4 \times 10 \times 15 \text{ mm}^3$; for tensile tests: dumbbell-shaped according ISO527-2:2012 geometry 5B, total length of 35 mm, thickness 2 mm). The 2-oxazoline formulations were preheated to $100 \text{ }^\circ\text{C}$ and filled into a preheated silicon-mold ($140 \text{ }^\circ\text{C}$). The mold was attached to a custom-made heating plate ($140 \text{ }^\circ\text{C}$) and the set-up was placed in an Uvitron UV 1080 Flood Curing System with Uvitron Intelliray 600 halide lamps (600 W, 120 mW cm^{-2} , 320-580 nm). The samples were cured for 900 s on both sides of the specimens. Equally heated samples without irradiation confirmed the thermal stability of the formulations in parallel. The specimens of methacrylate formulations were cured using a Lumamat 100 light chamber (Ivoclar Vivadent, $25 \text{ }^\circ\text{C}$, 400–580 nm, 20 mW cm^{-2}) for 420 s on both sides of the specimens. All samples were polished with sandpaper to reach uniform geometries and to remove defects from the photopolymer surface.

DMTA. Dynamic Mechanical Thermal Analysis (DMTA) was performed using an Anton Paar MCR 301 device with a CTD 450 oven and an SRF 12 measuring system. The prepared DMTA samples were tested in torsion mode with a frequency of 1 Hz and a strain of 0.1%. The temperature was increased from -20 to 200 °C with a heating rate of 2 °C min^{-1} . The glass transition temperature was defined as the temperature at the maximum loss factor ($\tan \delta$).

Tensile tests. Tensile tests were performed using a Zwick Z050 equipped with a 1 kN load cell (Zwick Roell, Ulm, Germany) according to ISO 527-1:2012 with a test speed of 5 mm min^{-1} . The dimensions of the specimens were measured with an accuracy of ± 0.02 mm according to ISO 16012:2015. The strain was recorded and analyzed via testXpert II testing software. For each formulation five specimens were tested.

Impact resistance. Dynstat impact resistance testing was conducted using a Karl Frank GmbH Dynstat device (Type 573) with a 1 J hammer tool. The results were determined by conversion to kJ and divided by the respective cross-sectional area. For each formulation four specimens were tested.

Hot Lithography

Comparative Photo-DSC of PAGs for Hot Lithography. In contrast to prior photopolymerization studies, the Hot Lithography 3D-printing was conducted using the commercial PAG mixture S-Sb (solution in propylene carbonate 50 wt%). The structure of the components included in the PAG mixture S-Sb are depicted in Figure S6. Beforehand, the reactivity of S-Sb was compared to the reactivity of S-B in formulations of BisOx via photo-DSC measurements. The formulations contained 0.5 mol% PAG per reactive group in BisOx, respectively. The photo-DSC measurements were conducted at the conditions stated above. The comparative photo-DSC analysis of S-B and S-Sb in BisOx formulations is depicted in Figure S7.

3D printing. 3D printing via Hot Lithography was conducted on a Caligma 200 UV developed by the company Cubicure GmbH, which consists of two UV class 3B diode lasers with an irradiation wavelength of 375 nm and an optical output power of 140 mW. All parts in contact with the formulation, including the vat, the building platform and the coating unit were heated to 120 °C. For printing, a formulation consisting of the monomer

BisOx, 12 wt% of a mixture of triarylsulfonium hexafluoroantimonate salts (S-Sb) in propylene carbonate (50 wt%) was used and 0.05 wt% of the photosensitizer 9,10-dibutoxyanthracene were added to improve the spectral compliance with the 375 nm laser. The specimens were printed with a laser power of 100 %, a scan speed of 50 mm s⁻¹ and a layer thickness of 100 μm, while the contours of each layer were scanned first, followed by scanning of the area within the contours with a hatching distance of 15 μm in x- and y-direction. Figure S8 depicts the Hot Lithography setup in schematic display. Figure S9 depicts a 3D structure of poly(BisOx) printed by Hot Lithography.

Figures



Figure S1. Glassy photopolymer of BisOx + 0.5 mol% S-B per reactive group after photo-DSC measurement at 140 °C

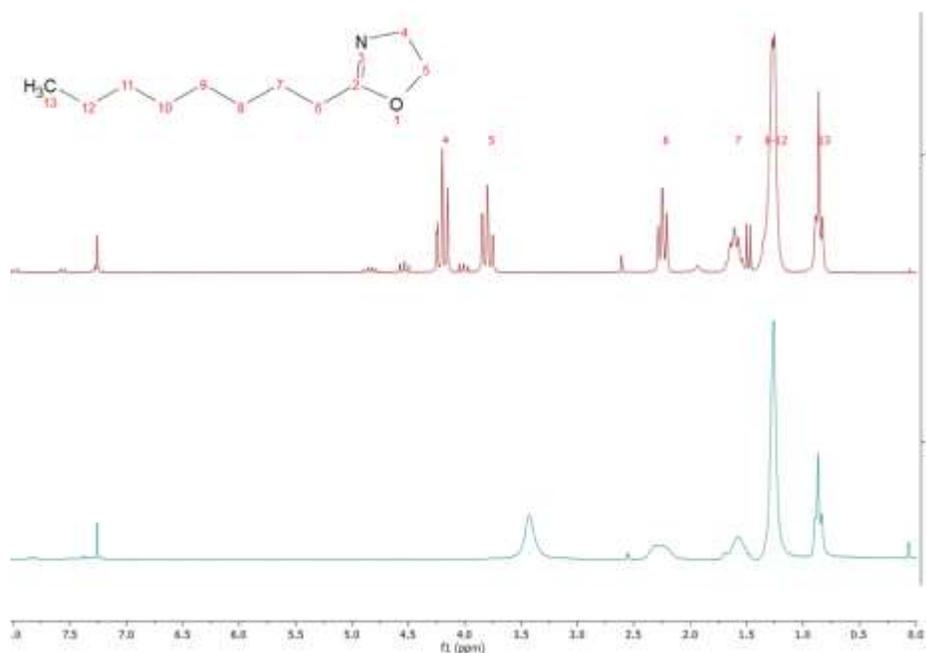


Figure S2. ¹H-NMR of a photoreactive formulation of 2-octyl-2-oxazoline (OctOx, 1 mol% S-B and propylene carbonate (PAG/propylene carbonate 50:50 wt%)) before (red; spectrum 2) and after photopolymerization (blue; spectrum 1) at 140 °C

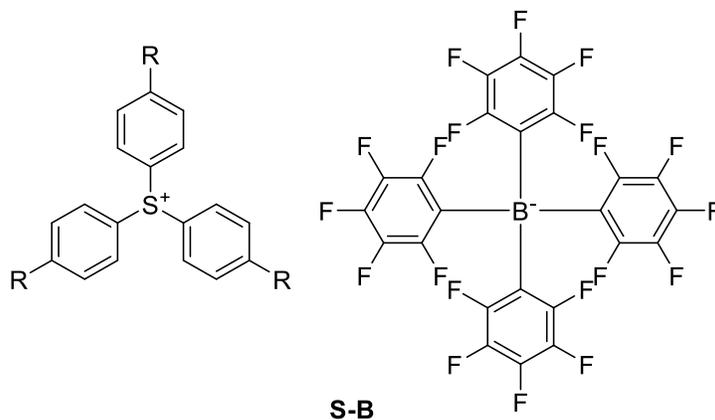


Figure S3 Structure of tris(4-((4-acetylphenyl)thio)phenyl)sulfonium

tetrakis(pentafluorophenyl)borate (S-B) (R = -S-Ph-COCH₃)

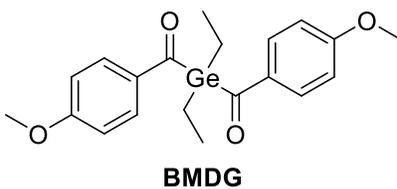


Figure S4. Structure of bis(4-methoxybenzoyl)diethylgermanium (BMDG, Ivocerin[®])

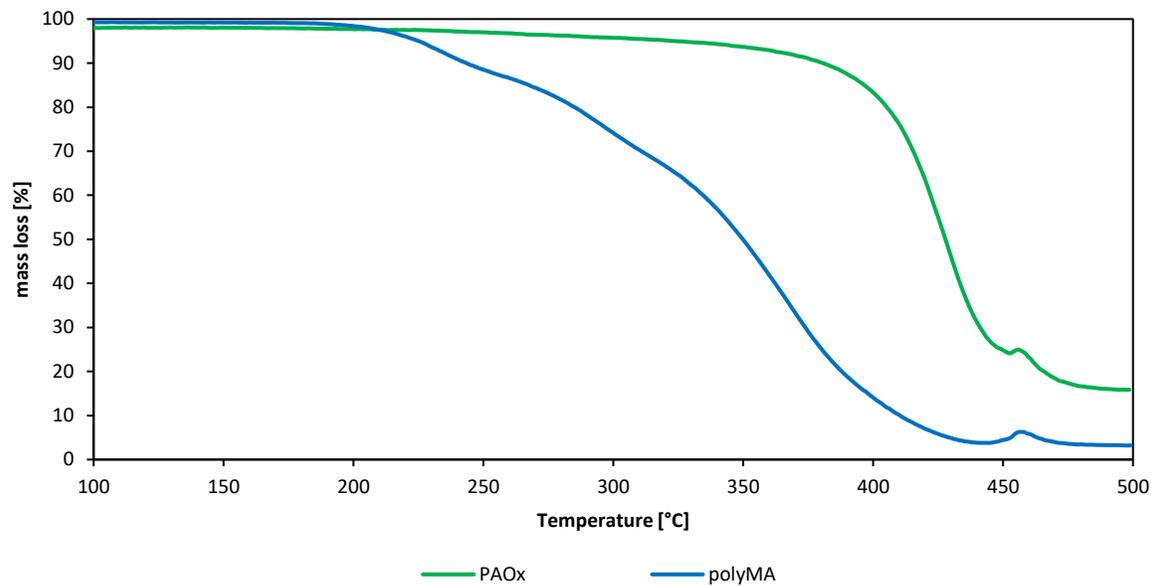


Figure S5. TGA of comparative photopolymers PAOx (BisOx:OctOx:PhOx 20:40:40 + 1 mol% S-B per reactive group of monomers) and polyMA (BDDMA:HexMA:BMA 20:40:40 + 1 mol% BMDG per reactive group of monomers)

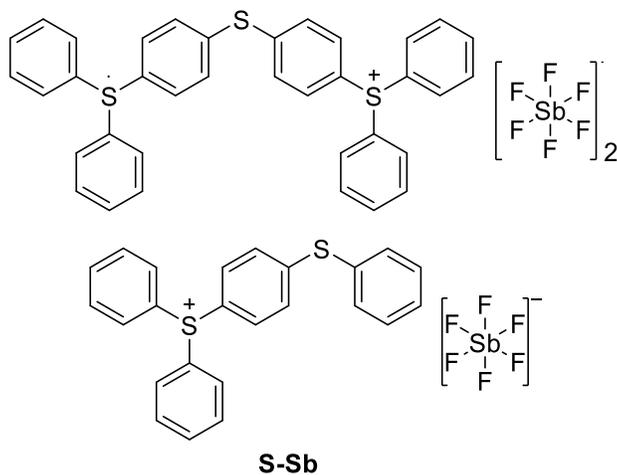


Figure S6. Structure of photoinitiating components in the triarylsulfonium hexafluoroantimonate PAG mixture of S-Sb (50 wt% in propylene carbonate)

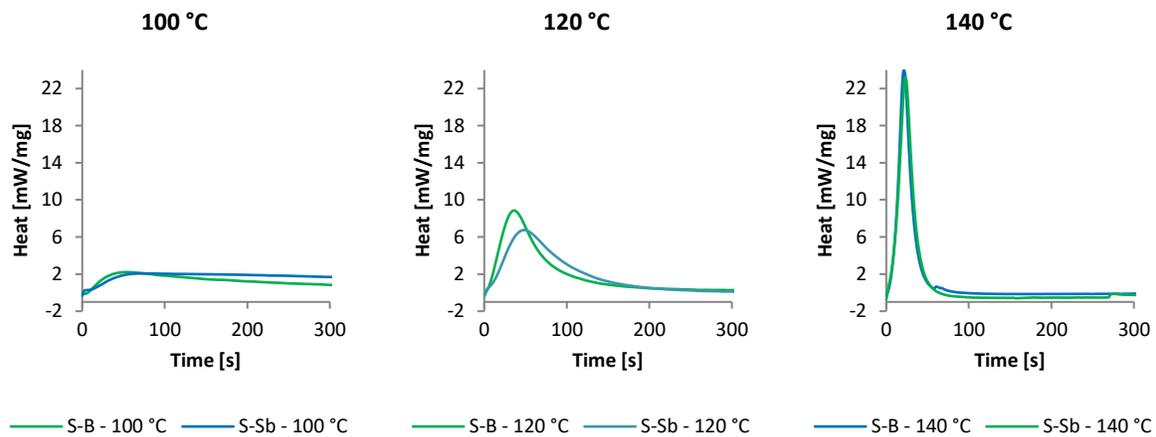


Figure S7. Comparative photo-DSC analysis of BisOx with 1 mol% S-B or S-Sb,

respectively

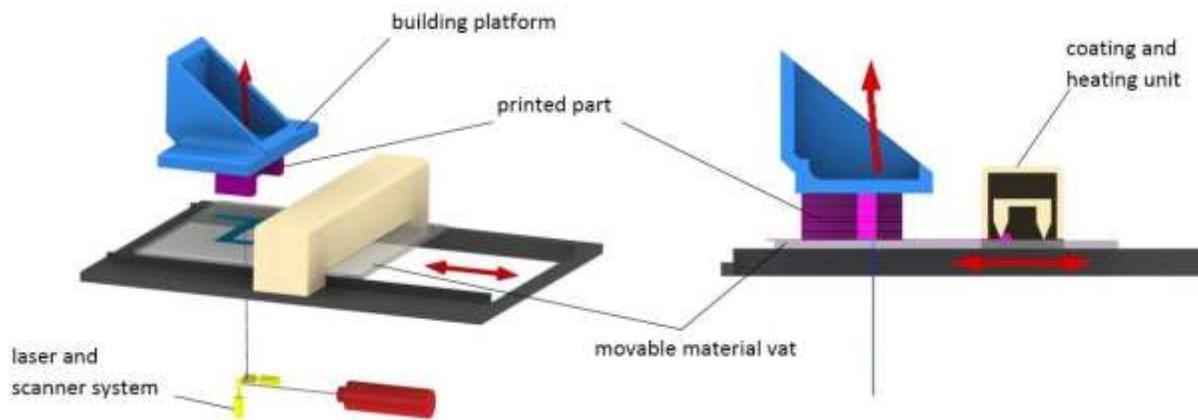


Figure S8. Schematic illustration of the heatable laser-SLA setup in Hot Lithography²

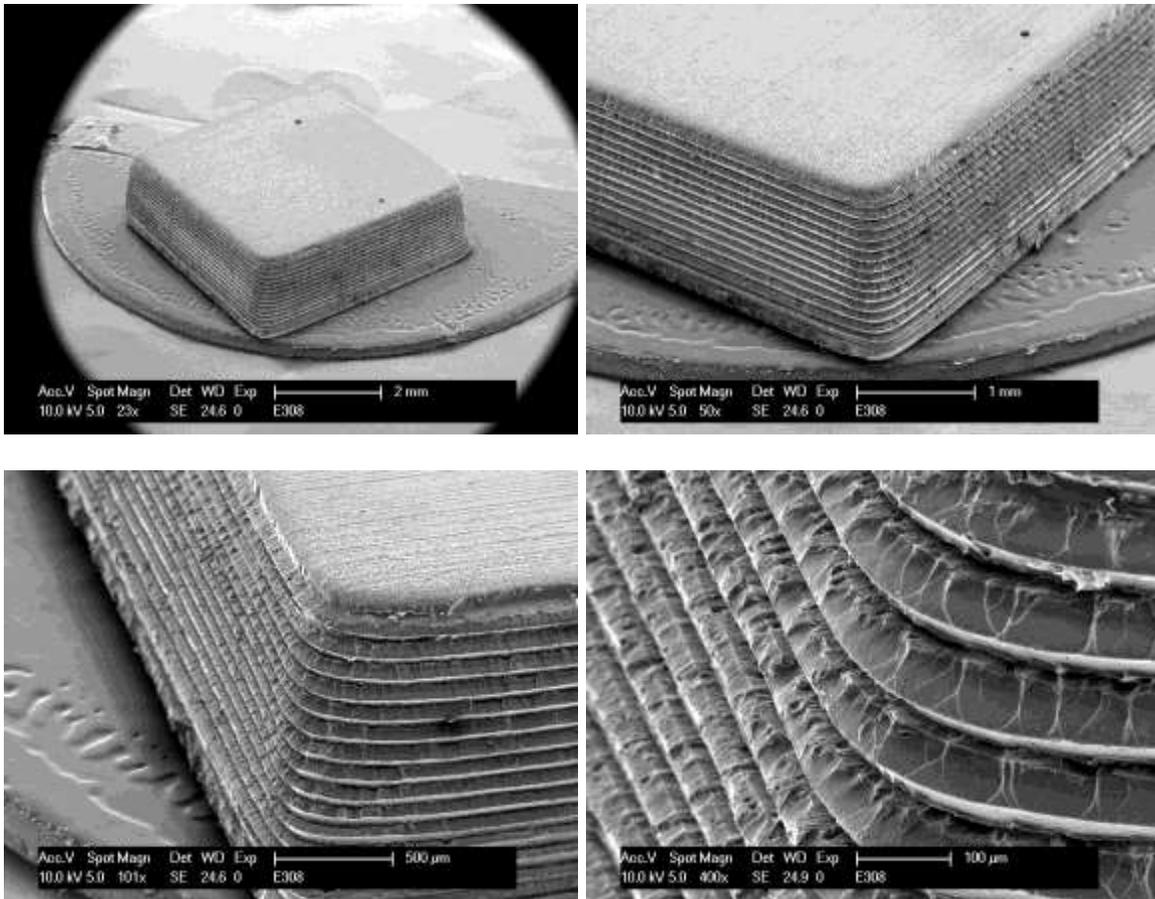


Figure S9. SEM images of poly(BisOx) 3D-printed by Hot Lithography (100 μm layer thickness)

References

1. Witte, H.; Seeliger, W., Cyclische Imidsäureester aus Nitrilen und Aminoalkoholen. *Justus Liebigs Ann. Chem.* **1974**, 1974 (6), 996-1009.
2. Pfaffinger, M., Hot Lithography – New Possibilities in Polymer 3D Printing. *Optik & Photonik* **2018**, 13 (4), 99-101.