Supporting Information

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General remarks

For all moisture and air sensitive compounds Schlenk techniques were used. The solvents (DCM, hexane, DME, toluene, THF and acetonitrile) were taken from the solvent system PureSolv with activated alumina columns. A MB 150B-G glove box from M Braun containing an atmosphere of purified argon was used.

Standard chemicals were ordered by ABCR, Acros, Alfa Aesar, Apollo, Fluka, Merck, Sigma Aldrich, TCI.

TEGO®Rad 2800 (TEGORad or Acrylate PDMS) and TEGOMER 7255 are acrylate polydimethylsiloxane copolymers kindly supplied by Evonik Industries AG (Essen, Germany). Silmer ACR D208, Silmer Acr Di50, Silmer OH ACR Di-10 were supported by Siltech Corporation (Canada). Ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (Irgacure® TPO-L, BASF) was used as comparison. Bench Stable TM RPMI 1640 GlutaMAXTM was purchased from Thermo Fisher; fetal bovine serum (FBS) and penicillin/streptomycin were purchased from Sigma-Aldrich. L-glutamine was purchased from Biowest.

(Bicycloheptenyl)ethyl terminated polydimethylsiloxane (PDMS-NB), 1,300-1,800 cSt, molecular weight (g/mol) 16,000-20,000, and [4-6% (mercaptopropyl)methyl siloxane] - dimethylsiloxane copolymer (PDMS-SH), 120-170 cSt, molecular weight (g/mol) 6,000-8,000 were purchased from Gelest.

Solution-NMR

NMR spectra were recorded with a BRUKER Avance DPX 300 (^{1}H: 300 MHz, ^{13}C: 75.5 MHz, ^{31}P: 121.5 MHz), 200 (^{1}H: 200 MHz, ^{13}C: 50.3 MHz, ^{31}P: 81 MHz) 500 (^{1}H: 500 MHz, ^{13}C: 125.8 MHz, ^{31}P: 202.5 MHz) at 298 K (unless otherwise noted). Chemical shifts are given in ppm (parts per million) relative to TMS (^{1}H NMR and ^{13}C NMR) and 85% H_3PO_4 in D_2O (^{31}P NMR), referenced to the used deuterated solvent ($CDCl_3$: 7.26 ppm (^{1}H), 77.16 ppm (^{13}C); Acetone-d_6: 2.05 ppm (^{1}H); THF-d_8: 1.72 ppm, 3.58 ppm (^{1}H); toluene-d_8: 2.08 ppm (^{1}H), 137.48 ppm (^{13}C); C_6D_6: 7.16 ppm (^{1}H), 128.06 ppm (^{13}C); D_2O: 4.79 ppm (^{1}H).[S1] The NMR spectra were evaluated with MestReNova or Topspin. The coupling constants J are reported in Hz (Hertz), while the abbreviations of the multiplicities are given as follows: s= singlet, d= doublet, t= triplet, q= quartet, p= pentet (quintet), sex= sextet, dd= doublet of doublets, dt= doublet of triplets, dq= doublet of quartets, m= multiplet.

FT-IR

The infrared spectra were recorded on a FT-IR Tensor II spectrometer from BRUKER and on a Vertex 70 from BRUKER and analyzed with the software OPUS. The oscillations are given in cm−1. The following abbreviations were used: st = stretching, as = asymmetric, sy = symmetric.

Mass spectrometry (MS)

All mass spectra were proceeded by the MS service of the Laboratory of Organic Chemistry (LOC) at ETH Zurich. The unity is given in mass per charge (m/z).

Elemental Analysis (EA)

The elemental analyses were performed by the microelemental Analysis service of the Laboratory of Organic Chemistry (LOC) at ETH Zurich. They have been measured on a TruSpec Micro. The results are given in percentage (%).

Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) analysis was performed on a Visotek GPCmax unit. Detection was done with a triple detector array Viscotek TDA 305-040 where the detector concentration (refractive index), the viscosity (4-channel differential viscosity) and light scattering was measured. The solution of a polymer sample is passed through two columns (D5000, org GPC/SEC col, 10 μm particle size) to separate the polymer according to their sizes. The analysis was run at 45 ◦C. The sample concentration was 2 mg/mL in DMF (+0.1 % LiBr), the injection volume 100 μL, with a flow rate of 1 mL/min.

Photo-rheology

Time sweeps were performed using an Anton Paar rheometer (MCR 302); a Hamamatsu LC8 lamp with light emission in the UV-visible range, and a LED (dB instruments) cantered at 405nm, light intensity 2/26 mW/cm2, were used for the irradiation during the tests. The measurements were performed in parallel-plate mode and the gap between the two plates was set to 0.1 mm. The experiments were performed at a constant temperature (25 °C), under a constant shear frequency (1 Hz) and at a strain amplitude of 1%. The irradiating light was turned on 1 min after the beginning of the rheological measurement to stabilize the system before the onset of the photopolymerization process. The changes in the viscoelastic moduli of the material during the polymerization process were measured as a function of exposure time. Photo-rheology curves were collected for TEGOrad 2800 using BAPO-SIL (1 wt% and 0.1 wt%) or TPO-L as photoinitiator. TPO-L was used at twice the molar concentration of BAPO-SIL to ensure that the final formulations contained equimolar amounts of radically cleavable photoactive group.

3D printing

The 3D printing of the TEGORad resin was performed using an Asiga MAX UV DLP printer (380 nm) setting the light intensity at 26mW/cm^2 and an Anycubic Photon Mono SE LCD printer (405nm), light intensity 2mW/cm^2. After the printing process, the structures were soaked in acetone for 20 min at room temperature to remove the unreacted resin. UV post-curing processes were performed on the printed samples using a mercury arc lamp Dymax ECE device in the air (5 min, light intensity 12 mW/cm^2). The samples prepared for the cytocompatibility tests were kept overnight in fresh acetone before post-curing.

The 3D printing of the thiol-norbornene resin was performed using Asiga PICO2 DLP printer equipped with a 405-nm light-emitting diode light source. After the printing process, the structures were washed in acetone by sonication to remove the unreacted resin. UV post-curing processes were performed on the printed samples using CL-100 Ultraviolet Crosslinker (UVP, ThermoFisher Scientific) for 15 min at room temperature.

The 3D printing resins were formulated by mixing PDMS-SH with PDMS-NB (93/7 and 86.5/13.5, w/w) in the presence of BAPO-SIL (1.5 wt% or 0.75 wt%), Sudan I (0.02 wt% or 0.01 wt%), and Vitamin E (0.3 wt%), and sonicated for 1h with no solvent used.

The resolution and dimensional accuracy of the printed structures was assessed using optical microscopy and 3D scanning analysis and compared with the corresponding CAD files. 3D scanning was carried out using a 3D optical scanner (E3, 3Shape). The acquired scans were aligned with the reference digital models prior to comparison. The results were visualized as color-coded 3D deviation maps, highlighting the geometric differences between the printed objects and the reference models, with red regions indicating material excess and blue regions indicating material deficit.

Mechanical test for samples based on thiol-norbornene resin

The tensile behavior of the 3D-printed resin specimens was assessed using dumbbell-shaped samples conforming to ASTM D638 Type IV standards. Testing was carried out with a TA.XT Plus Texture Analyzer (Stable Micro Systems) fitted with a 500-N load cell. The gauge length between grips was set at 11 mm. During testing, force and elongation data were continuously recorded while samples were pulled at a constant speed of 0.01 mm/s until failure. A total of five specimens were tested per group to ensure reproducibility and statistical relevance. The Young's moduli were determined from the stress-strain slope curve from 0 to 2.5% of its linear region. Cyclic tensile loading–unloading tests were conducted for 10 cycles under strain control at 40% maximum strain, with a tensile rate of 5 mm/min.

Cytotoxicity assay for samples based on TEGORad resin

Cell culture

Cellular experiments were performed by using human lung adenocarcinoma epithelial cell line, i.e. A549, and human keratinocytes, i.e. HaCaT. A549, kindly provided by Valentina Monica of the Department of Oncology of the University of Turin, were maintained in BenchStableTM RPMI 1640 GlutaMAXTM supplemented with 10% (v/v) of fetal bovine serum (FBS) and 1% (v/v) of penicillin/streptomycin. HaCaT cells, purchased from Antibody Research Corporation,

were cultured in BenchStableTM DMEM GlutaMAXTM with the addition of 15% (v/v), 1 % (v/v) penicillin/streptomycin, 1 % (v/v) sodium pyruvate and 2 % (v/v) L-glutamine.

Cell proliferation assay

To test the toxicity towards cells, printed samples were washed for 24 h in double-distilled H2O to remove acetone residues, then they were sterilized by UV irradiation for 30 minutes/side and stored in sterile PBS until their used. To prepare the conditioned medium, samples were incubated in the appropriated cell culture medium (i.e. RPMI 1640 or DMEM) for 48 h at 37°C and, after the conditioning, the medium was filtered with 0.22 μm filter and stored at 4°C until its use. Subsequently, A549 and HaCaT cells were seeded into a 96-wells plate at the density of 1x104 and 7x103 cells/well, respectively. Cultured cells were incubated with normal (Ctrl) or conditioned medium (CM) and their viability was assessed after 24 or 72 hours by the colorimetric 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay (Signa-Aldrich). Specifically, MTT was used at the concentration of 0.5 mg/mL and incubated for 2 h at 37°C, then the solution was removed, and the formed salts were dissolved in 200 μL of DMSO (Sigma-Aldrich). At the end, the signal was read with a Synergy-HTX Multi-Mode Microplate Reader (BioTek, Winooski, VM, USA) at 570 nm and 650 nm (reference) wavelengths.

Statistical analysis

In the cytocompatibility assay, data were shown as mean +/- standard deviation and the statistical analyses are carried by two-way Anova were * = p-value < 0.05; ** = p-value < 0.01; *** = p-value < 0.001 and **** = p-value < 0.0001 identified statistically significant differences. On the other hand, n.s. indicates not statistically significant.

Cytotoxicity assay for samples based on thiol-norbornene resin

The cytotoxic potential of two types of 3D-printed materials, containing 7% thiol and13.5% thiols, was evaluated using the MTS assay (CellTiter 96® AQueous One Solution Cell Proliferation Assay, Promega) on Caco-2 cells. Cell viability was expressed as a percentage relative to untreated control cells based on absorbance measurements at 490 nm, obtained via a microplate reader (Infinite M200, Tecan), according to Equation (1):

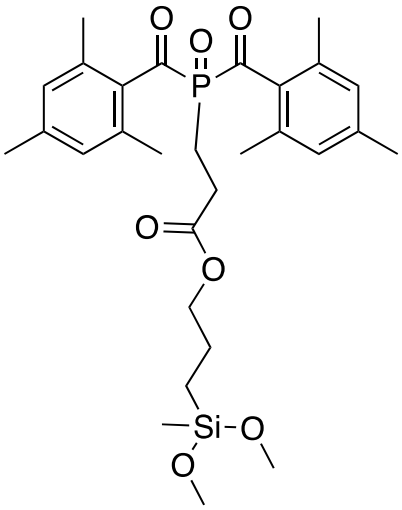
$$\text{Cell viability (\%)} = (OD_{(490)}\ \text{sample}) / (OD_{(490)}\ \text{control}) \times 100\% \quad (1)$$

Caco-2 cells, used between passages 48 and 60, were routinely screened for mycoplasma contamination at both the initial and final passages using the MycoAlert® PLUS Mycoplasma

Detection Kit (Lonza). Cells were seeded in 96-well plates at a density of 10,000 cells per well in 100 µL of growth medium consisting of 87.5% Dulbecco's Modified Eagle Medium (DMEM), 10% fetal bovine serum (FBS), 5% penicillin/streptomycin (50,000 U/mL), and 15 mM HEPES. Cultures were incubated at 37 °C with 5% CO_2 and 95% relative humidity for 24 ± 1 hours to allow cell attachment and reach ~50% confluency. Following this initial incubation, the medium was aspirated and replaced with extracts of the samples. These extracts were prepared from 3D-printed samples cut from the tensile specimens. They were UV-cured for 15 minutes (Asiga Pico Flash), then soaked in 20 mL PBS and incubated in growth media and sonication for 2 hours, at room temperature. The resulting extracts were sterile-filtered through 0.2 µm PTFE syringe filters. Positive control wells were treated with 10 mM hydrogen peroxide in growth medium, while the negative control consisted of untreated medium. All conditions were incubated under the same environmental settings (37 °C, 5% CO_2, 95% humidity) for an additional 24 ± 1 h. Afterward, wells were washed twice with sterile phosphate-buffered saline (PBS), and 120 µL of MTS working solution (100 µL phenol red-free DMEM + 20 µL MTS reagent) was added to each well. Following a 4-hour incubation, absorbance at 490 nm was recorded. Cell viability was calculated relative to untreated control wells.

Syntheses

BAPO-SIL 2a

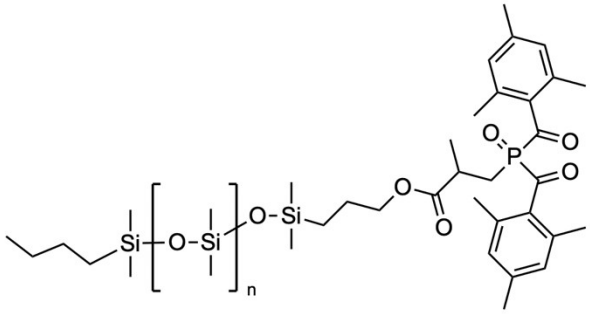


3 g BAPH (1 eq.) is dissolved in dry DME. 2.01 mL 3-(Dimethoxy(methyl)silyl) propyl acrylate (1 eq.) and 0.12 mL degassed TMF (0.1 eq.) are added and the mixture is stirred for 4 h. The solvent was removed under reduced pressure and the residue is dissolved again in dry toluene. 1.84 mL tert-butyl hydrogen peroxide (1.1 eq., 5.5 M in decane) is added dropwise at 0 °C under vigorous stirring while protecting the reaction vessel from light. The mixture is stirred overnight. The solvent is removed under reduced pressure and the product is dissolved in DCM and washed twice with a concentrated sodium hydrogen carbonate solution and twice with brine. The organic phase is combined, dried over Na_2SO_4, filtered and the volatiles are removed in vacuo to yield 4.99 g of a yellow oil. (yield= 96.8%)

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ [ppm] = 0.10 (s, 3H, Si-CH_3), 0.43-0.65 (m, 2H, Si-*CH_2*-CH_2), 1.54-1.75 (m, 2H, Si-CH_2-*CH_2*), 2.23 (s, 12H, CH_3 Mes-o), 2.27 (s, 6H, CH_3 Mes-p), 2.46-2.58 (m, 2H, P-*CH_2*-CH_2), 2.58-2.72 (m, 2H, P-CH_2-*CH_2*), 3.42-3.53 (m, 0.5H, O-CH_3) 3.94-4.11 (m, 2H, Si-CH_2-CH_2-*CH_2*-O), 6.84 (s, 4H, CH_{ar} Mes). ^{31}P{^{1}H}-NMR (202.46 MHz, $CDCl_3$) δ [ppm] = 25.08 (s).

GPC: M_n= 1840 g/mol, PDI= 1.33.

BAPO -SIL (2b)



20 g BAPH (1.1 eq.) are dissolved in 120 mL dry DME in a 500 mL Schlenk flask. 1.4 mL degassed TMG (0.2 eq.) are added before 34.8 mL (1 eq.) monomethacryloxypropyl terminated polydimethylsiloxane (from ABCR, M_n~600 g/mol) are added. The mixture is then heated to 60 °C and is kept at this temperature overnight (16h). Subsequently, the solvent is evaporated and the mixture is dissolved again in 120 mL dry toluene. The reaction mixture must be protected from light for the next step. The resulting crude bis(acyl)phosphane (BAP) is then oxidized by slow addition of 6.12 mL (1.1 eq.) 35% H_2O_2 at 0 °C under vigorous stirring. After about 1h, 5.57 mL of a 2 M HCl solution in diethylether (0.2 eq.) is added to neutralize the mixture. The mixture is then filtered through an alumina plaque (neutral) and the solvent is evaporated using a rotary evaporator to yield 46 g of a yellow product (yield= 87.62%).

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ [ppm] = 0.03-0.11 (m, ~40H, Si-CH_3), 0.47-0.59 (m, 2H, Si-*CH_2*-CH_2), 1.30 (d, 3H, CH-*CH_3*, $^{3}J_{HH}$ = 7.2 Hz), 1.56-1.62 (m, 2H, Si-CH_2-*CH_2*), 2.245, 2.255 (2x s, 12H, CH_3 Mes-o), 2.27 (s, 6H, CH_3 Mes-p), 2.21-2.31 (m, 1H, P-*CH_2*-CH), 2.78 (ddd, 1H, P-*CH_2*-CH, $^{3}J_{HH}$ = 15.4, 6.8 Hz, $^{2}J_{HP}$ = 9.7 Hz), 2.78 (dsex, 1H, P-CH_2-*CH*, $^{3}J_{HH}$ = 6.9 Hz, $^{3}J_{HP}$ = 10.6 Hz), 4.0 (qt, 2H, Si-CH_2-CH_2-*CH_2*-O, $^{3}J_{HH}$ = 7.0 Hz, J_{HH} = 10.6 Hz), 6.84 (s, 4H, CH_{ar} Mes). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$) δ [ppm] = 0.19, 0.30, 1.18, 1.28 (s, Si-CH_3), 14.06 (s, Si-*CH_2*-CH_2), 19.44 (d, P CH_2CH*CH_3*, $^{3}J_{PC}$ = 7.4 Hz), 19.92 (s, *CH_3* o-Mes), 21.33 (s, *CH_3* p-Mes), 22.58 (s, Si-CH_2-*CH_2*), 29.07 (d, P*CH_2*, $^{1}J_{PC}$ = 54.2 Hz), 33.89 (d, PCH_2*CH*, $^{2}J_{PC}$ = 3.5 Hz), 67.70 (s, Si-CH_2-CH_2-*CH_2*-O), 129.39 (s, m-Mes), 136.05 (d, o-Mes, $^{3}J_{PC}$ = 13.5 Hz), 135.90 (d, ipso-Ph', $^{2}J_{PC}$ = 41.7 Hz), 135.93 (d, ipso-Ph, $^{2}J_{PC}$ = 40.9 Hz), 141.47 (s, p-Mes), 174.96 (d, C=O (*CO*-CH-CH_2-P), $^{3}J_{PC}$ = 8.6 Hz) , 215.23 (d, PCO, $^{1}J_{PC}$ = 33.3 Hz), 215.94 (d, PC'O, $^{1}J_{PC}$ = 32.5 Hz). ^{31}P{^{1}H}-NMR (202.46 MHz, $CDCl_3$) δ [ppm] = 24.80 (s). ^{31}P-NMR (202.46 MHz, $CDCl_3$) δ [ppm] = 24.80 (q, $^{3}J_{PH}$= 10.4 Hz). ^{29}Si-NMR (99.36 MHz, $CDCl_3$) δ [ppm] = -21.82, -21.24, -19.18 (Si-O chain), 7.27 (Si-linker-BAPO).

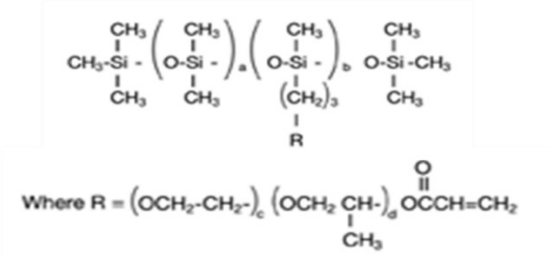
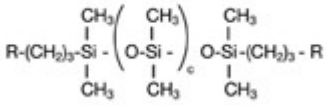
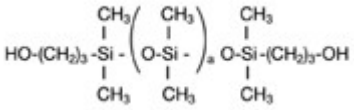
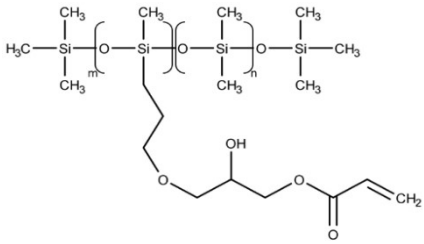
Elemental analysis: C: 52.44%, calc: 52.59%; H: 8.07%, calc: 8.06%.

References

[S1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* 2010, *29*, 2176-2179.

Miscibility

BAPO Sil 1wt% in different silicone acrylates

Silmer ACR D208 Transparent		
Silmer Acr Di50 Slightly opaque		Linear di-functional acrylate-terminated silicone 
Silmer OH ACR Di-10 Transparent		Acrylate Functional with Secondary Hydroxyl Groups Linear-difunctional 
TEGORAD 2800 Transparent		
TEGOMER 7255 transparent		Silicon Acrilate

Photorheology tests

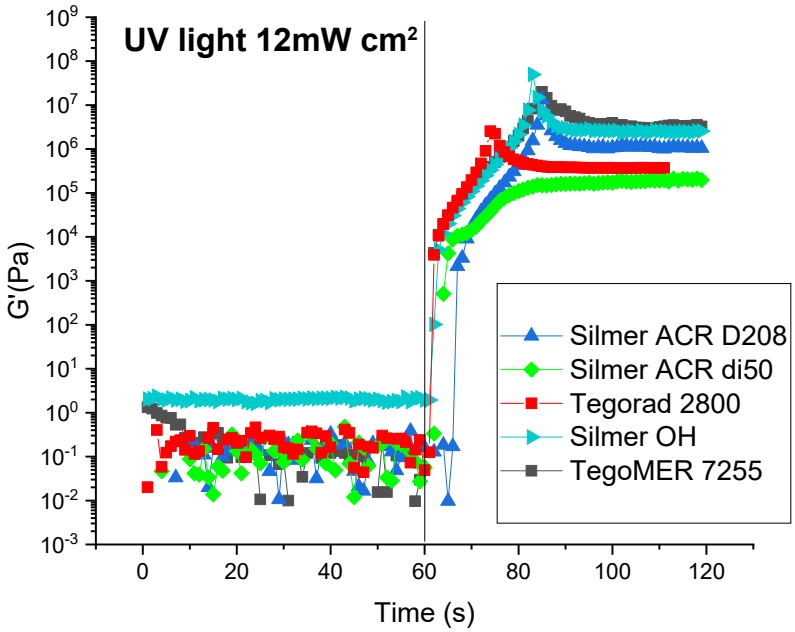


Figure S1 Photorheology plots for the different silicone acrylate monomers tested in presence of 1 of BAPO-SIL performed using a mercury lamp with emission in the UV, light intensity 26 mW/cm^2 (frequency 1HZ, amplitude 1%, light turned on after 60s)

Cyclic tensile loading–unloading tests

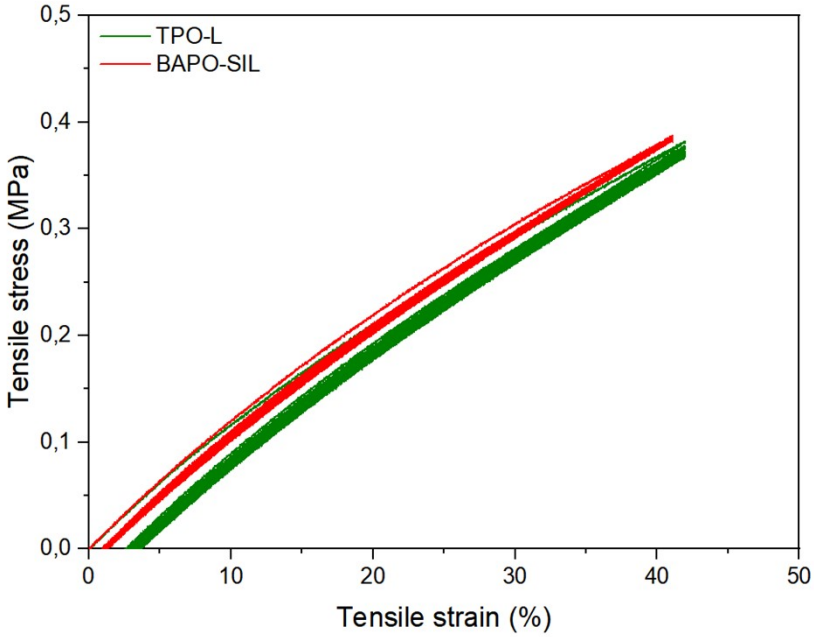


Figure S2 Cyclic tensile loading–unloading tests were conducted for 10 cycles under strain control at 40% maximum strain, with a tensile rate of 5 mm/min. Two TEGORAD 2800-based formulations were tested: one with 1% w/w BAPO-SIL and the other with TPO-L at twice the molar concentration of BAPO-SIL, ensuring that both formulations contained equimolar amounts of radically cleavable photoactive groups.